**Basalt - fluid interactions at subcritical and supercritical conditions:
An experimental study**

By

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Abstract

To investigate the interaction between fluids and basalt at subcritical, near-supercritical, and supercritical hydrothermal conditions (350-400°C/500 bar), eight experiments have been conducted. These used a continuous-flow, high temperature and pressure hydrothermal apparatus. The basalt was reacted with three fluids: distilled water; geothermal brine; and natural seawater. Two further experiments used only seawater as a control to determine its behaviour without the influence of basalt.

With distilled water, the fluid chemistry results show elevated SiO₂, K, Cl, SO₄, and H₂S in solution for the first 12 days of both experiments. This is due to volcanic glass dissolution. After glass was removed, fluid composition was controlled by the remaining rock minerals. At 400°C, the secondary mineral assemblage at the bottom of the Reactor (fluid entry point) is composed of grossular, wollastonite, anorthite, and chlorite. These results show the effectiveness of distilled water, which lacks any alkali cations, at removing Na and K rapidly from the rock. At the top of the Reactor (fluid exit point) the secondary minerals are anorthite and celadonite. At 350°C, the secondary mineral assemblage at the bottom is anorthite and chlorite, while celadonite is the dominant secondary mineral at the top. In both experiments, celadonite replaces solely olivine. The formation of celadonite through reaction with distilled water shows that it can be formed by the interaction of deuteritic water and basalt without addition of other components.

The geothermal brine contains high concentrations of SiO₂, K, SO₄, Na, Cl and has an acidic pH. At 400°C, fluid chemistry displays elevated SiO₂ concentrations for approximately two weeks due to glass dissolution. At 350°C, SiO₂ concentration is initially high after temperature increase, but decreases gradually over the remainder of the experiment. At 400°C, the secondary mineral assemblage at the bottom of the Reactor is composed of anhydrite and biotite, while at the top of the Reactor, smectite is the only secondary mineral. At 350°C, anhydrite and smectite are found at the bottom, while only smectite is found at the top. The lack of biotite at 350°C suggests this mineral's precipitation kinetics are too slow to outcompete chlorite precipitation.

The seawater-only experiments were conducted as controls to determine its behaviour during heat-up and provide the input solution composition for the seawater-basalt experiments. Both seawater-only experiments (377°C and 342°C) show the precipitation of anhydrite, caminitite and brucite due to their retrograde solubilities. The effluent solutions are greatly depleted in Ca,

Mg and SO₄.

In the seawater-basalt experiments at near-supercritical (400°C) and subcritical conditions (350°C), elevated SiO₂ concentrations due to glass dissolution are not observed. This is attributed to rapid secondary mineral precipitation. Fluid chemistry and mass balance calculations show almost complete removal of SO₄, and in particular, Mg, from the seawater while Ca shows a considerable loss from the rock. Three mineralization fronts were identified: (1) glass dissolution; (2) chloritization; and (3) anhydrite precipitation. In both experiments, there is a switch from chloritization to smectitization. This is accompanied by a decrease in Mg/Fe ratio in smectite. This mineral was also found at the top of both experiments, but its composition was more reflective of the rock.

In terms of reactivity, the order of phases from most to least reactive is glass – olivine – clinopyroxene – plagioclase – Fe-Ti oxide. For the aluminosilicate phases this is attributed their respective Al contents. The seawater-basalt experiments also emphasise the fast rate of reaction at which Mg is fixed by the rock, which is conjectured to take less than a few hours.

Considering all experiments, the distilled water results show a rock control on fluid chemistry while in the remaining basalt experiments, the chemistry is largely controlled by the fluid.

Temperatures calculated using standard Na/K geothermometer did not estimate, in most cases, values close to the experimental temperature. This is due to the inability of the rock to sufficiently adjust the Na/K ratio given the secondary mineral assemblages that form.

Dedication

This thesis is dedicated to my parents and sister. My father, Riccardo, passed away on February 11th 2019 during the last year of my Doctoral studies. He cannot physically enjoy this special moment with us, but I am sure he is rejoicing next to me. My mother, Enrichetta, is the best and strongest woman that I know. She is my example of strength, courage and initiative. And my sister, Martina, one of the most intelligent and thoughtful persons, with whom I grew up.

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Chapter 1: Introduction

1.1. The Submarine Environment at Mid-Ocean Ridges

The hydrothermal systems located in mid-ocean ridge basalts (MORB) at seafloor spreading centres are of global importance. They are not only responsible for the transfer of an enormous amount of heat, but also the exchange of chemical components between the oceanic crust and seawater (Alt, 2013; Edmond et al., 1979; Thompson, 1983). Submarine hydrothermal systems account for about 30% of the heat lost from the oceanic crust (Sclater et al., 1981; Stein and Stein, 1994; Williams, 1976). Their thermal potential is much larger than that of onshore geothermal resources and they could provide a significant part of the global future energy demand in an environmentally sustainable manner (Owusu and Asumadu-Sarkodie, 2016). Much of this potential is a result of the hydrothermal fluids being present at supercritical conditions ($>374^{\circ}\text{C}$ for pure water) and can therefore transfer a much larger amount of heat when compared to subcritical fluids.

Submarine hydrothermal systems develop where two oceanic plates diverge and up flowing basaltic magmatism forms a ridge. These can be identified as “fast” ridges having a narrow and shallow axial valley where the hydrothermal circulation is present near a well-defined heat source; or “slow” ridges which are defined as those with a deep and enclosed rift valley where there is frequently an absence of a well-defined heat source (Babcock et al., 1998; Detrick et al., 1987; Kent et al., 1990; Sinha and Evans, 2013; Sinton and Detrick, 1992). Figure 1.1 shows a typical section of a submarine hydrothermal system. It is composed of three main zones: the recharge zone; the reaction zone; and the discharge zone (Cann, 1971; Cann, 1969; Cann and Funnell, 1967; Chernysheva, 1971; Melson et al., 1968; Melson and van Andel, 1966; Miyashiro et al., 1971; Quon, 1963; Shido et al., 1974). The recharge zone is hosted by volcanic sediments, basalt, pillow-lava and breccia while the reaction zone is hosted by sheeted basaltic dikes and gabbros.

Changes in the mineral composition of oceanic crust and of seawater chemistry are regulated by the alteration processes occurring during fluid circulation. Cold seawater descends in the recharge zone through fractures away from the ridge. It becomes heated to subcritical and then supercritical conditions in reaction zone (4-5 km depth) by heat from uprising magma. The fluid then rises buoyantly to the seafloor through the discharge environment comprising

“focussed” out-flow venting zones at high-temperatures (300-400°C) where fluids create polymetallic mounds and steep-sided chimneys from a few meters to tens of meters in height at the seafloor; or “diffuse” out-flow venting zones at low-temperature (<50°C) which typically take place through low mounds and cracks that are often occupied by biological communities (Cann and Strens, 1989; Scheirer et al., 2006). The distribution, morphology, rheology, lithology and thermal structure of MORB have been also described in detail by various authors (Atwater and Mudie, 1968; Ballard, 1977; Bott, 1996; Crawford and Webb, 2002; Karson et al., 2002; MacLeod and Yaouancq, 2000; McNutt, 1984; Parsons and Sclater, 1977; Searle and Escartín, 2013; Shaw, 1992; Watts, 1978; Weissel and Karner, 1989).

During circulation, the fluids can achieve temperatures over 400°C while ocean floor seawater normally has a temperature range between 2 - 4°C (Kingston Tivey, 2013; Macdonald et al., 1980). Contact between hot hydrothermal fluids and cold seawater, which have extremely different chemical and physical characteristics, forms vents, called black or white smokers. These are geologically important because of their capacity to transport heat and high concentrations of chemical elements, some of which precipitate immediately after mixing with cold seawater, in many cases giving rise to large ore deposits (mainly sulfide) (Hannington et al., 2013; Hannington, 1988; Haymon, 1983; Koski, 1987). The fluid chemistry at vents provides an important record of the alteration, temperature and pressure conditions that the fluid experienced during passage within the crust. Geochemical analysis around plumes reveal that the steady state concentrations of dissolved species and their solubility are controlled by mineral phases occurring in the reaction zone. These occur in the deepest part of a submarine hydrothermal system where the circulation occurs just above the magmatic heating source, close to the brittle-ductile boundary. In this zone, the intensity of the alteration process achieves a maximum and the kinetics of chemical reactions are fast at high T and P condition. In the reaction zone, the fluid (mainly seawater) is modified during circulation mostly by: 1) temperature and pressure (which determine the state of the fluid both in supercritical and subcritical states); 2) water-rock interaction; 3) magmatic degassing (input of volatiles such as CO₂, CH₄, He, H₂S, SO₂, HCl, HF H₂); and (iv) redox reactions. Together, these factors determine the type of the hydrothermal alteration, the metals transported, the chemistry of the fluid and the final metals deposited on the seafloor (Bowers et al., 1988; Butterfield and Massoth, 1994; Campbell et al., 1988; German and Von Damm, 2004; Seyfried and Ding, 2013).

Figure 1.1. Schematic diagram of a typical hydrothermal system within an oceanic ridge axial zone showing the hydrothermal fluid circulation (blue arrows) at recharge, reaction and discharge zones (Coelho et al., 2015).

The terms *supercritical* and *subcritical* refer to conditions where a fluid has a temperature and pressure higher than its critical temperature (T_c) and critical pressure (P_c) or lower than T_c and P_c , respectively. This terminology needs to be used carefully and clarified when dealing with one- or multi-component systems (Liebscher and Heinrich, 2007). In a one-component system, such as pure water, conditions above the critical point ($T > 374^\circ\text{C}$, $P > 221$ bar for pure water) there is a single-phase present, i.e., liquid and vapour are physically indistinguishable. While at conditions below the critical point for a one component system, two phases can exist along the liquid-vapour curve (Fig. 2a-b).

In a two-component system such as H_2O - NaCl , the T_c and P_c differ from pure water and lie along the critical point curve that is dependent on NaCl concentration (Fig. 1.2). The T_c and P_c of seawater (3.2 wt.% NaCl equivalent) is $\sim 404^\circ\text{C}$ and 300 bars (Bischoff and Rosenbauer, 1984) which corresponds to a cold seawater depth of ~ 3000 m. At P - T conditions greater than the critical temperature (T_c) and critical pressure (P_c), seawater (e.g. $T = 407^\circ\text{C}$, 500 bar), a supercritical single phase is present. A decrease in pressure at temperature that intersects the liquid-vapour two-phase surface causes the fluid to undergo *phase separation*. When the fluid intersects the liquid-vapour two-phase surface on the liquid side of the critical curve, the system

starts to *boil*. In contrast, when the fluid intersects the liquid-vapour two-phase surface on the vapour side of the critical curve, the systems starts to *condense* (Liebscher and Heinrich, 2007). In both situations, two compositionally different fluid fractions form: a conjugate pair of low (vapour) and high (liquid) salinity and density aqueous solutions.

In this study, pressure (~500 bar) was consistently above the P_c for pure water, geothermal brine and seawater, thus, the term *supercritical* is defined here as conditions where temperature is above T_c for the fluid utilised. The term *subcritical* refers to conditions where temperature is below T_c for the fluid utilised.

Whether the hydrothermal circulation is under subcritical or supercritical conditions is one of the most important factors affecting hydrothermal alteration and reflecting the compositional variability observed at hydrothermal vents on the seafloor. Under subcritical conditions, the fluid is nearly incompressible, has low thermal expansion, a low molar heat capacity and an elevated dielectric constant. In contrast, the fluid under supercritical conditions has a low density, viscosity and dielectric constant (almost zero) but a high thermal expansion and heat capacity (Anisimov et al., 2004; Norton, 1984).

At elevated temperatures and pressures the properties of water change dramatically due to the modification of its density and molecular structure. Hydrogen bonds are stable at low and moderate temperature, while an assembly of isolated polar water molecules are present at high and supercritical temperatures. At this point water loses its solvent power for ionic species (electrolytes), which tend to form ion-pairs, and becomes a good solvent for non-polar components. Hydrothermal alteration occurring at supercritical and/or at subcritical conditions generates significant dissimilar effects on mineral solubility, complex formation and metal transport. At higher T-P, aqueous species become more associated as there cannot be charged species near the critical point. Also, metal mobility increases substantially (Brunner, 2014).

Metal transport is ultimately controlled by the availability of important ligands during hydrothermal circulation both in the vapour phase and in the liquid phase. This, in turn, can affect the resulting metal assemblage in seafloor mineral deposits. Both chloride and hydrosulfide (HS^-) have a major impact on the metal mobility during hydrothermal circulation. They form important aqueous metal complexes, affect the ionic strength of the fluid, and the charge balance. This influences mineral solubility and controls the total concentration of cationic species that can be present in the fluid. As a consequence, measurements of salinity at vents are

very important to constrain the evolution of the fluid during its residence in sub-seafloor reaction zones (Seyfried et al., 1991; Von Damm et al., 2002; Von Damm, 1988; Von Damm et al., 2003).

Figure 1.2. (a) Pressure-temperature solid-liquid-vapour phase relations of pure water showing the critical point and critical isochore line; (b) temperature – density relations in the pure water system; (c) two component system showing the critical behaviour of pure water dominated fluids. (d) phase diagram of H₂O–NaCl versus temperature–pressure–composition. (a-c) Liebscher and Heinrich, 2007; (d) Driesner and Heinrich, 2007).

1.2. Hydrothermal alteration during seawater circulation in submarine hydrothermal systems: field evidence

Over the past 40 years, since the initial discovery of the hot springs at the Galapagos spreading centre (Edmond et al., 1979), many studies have been undertaken to better understand the mechanisms that occur during hydrothermal alteration. Hydrothermal alteration can be described as a “metamorphic” process which involves hot fluid in contact with rocks causing the conversion of the primary mineralisation into a set of new minerals in equilibrium with the conditions of temperature, pressure and chemical composition of the fluid. Furthermore, considering that the fluid can move rapidly, slowly or be stagnant during its passage through the crust, flow rate and resident time can also have a significant impact on the alteration that forms. The original texture of the rock can be totally or partially altered and fluid chemistry substantially modified (Pirajno, 1992).

The “metamorphic” process where there is re-equilibration of the mineral assemblage due to the passage of the fluid, material transport and changes in fluid composition, is known as metasomatism (Putnis and Austrheim, 2010). Metasomatism occurs in an open system and differs from standard “metamorphism” in which rock deformation can take place, a fluid phase is not necessarily involved, and no appreciable bulk chemical alteration occurs. A metasomatic process can be associated with a metamorphic or igneous environment, can include ore mineralisation, or alteration of the mantle, the oceanic lithosphere, the subducted oceanic, or the continental crust (Harlov and Austrheim, 2013) .

At mid-ocean ridges, the intensity of hydrothermal alteration increases with the increase of temperature and pressure downwards into the oceanic crust (Fehn et al., 1983; Sleep, 1991). The grade of rock alteration and the changes in fluid composition are different for each zone in this environment. In the most recent studies of MORB alteration, three different metamorphic facies have been identified: (i) a zeolite facies in volcanic sediments and low greenschist facies in the upper sheeted dikes (recharge zone); (ii) a high greenschist facies in the lower dikes (shallowest part of the reaction zone) and (iii) an amphibolitic facies in the uppermost plutonic (gabbro) section (deepest part of the reaction zone) (Cann, 1971; Cann, 1969; Cann and Funnell, 1967; Melson et al., 1968; Melson and van Andel, 1966; Miyashiro et al., 1971; Quon, 1963; Shido et al., 1974).

The evidence that is available on the lithology and mineral composition of these zones is

from sub-aerial exposures of ophiolites (e.g. the Samail ophiolite, Oman) (Gillis, 2008; Gillis and Roberts, 1999; Nehlig et al., 1994; Nicolas and Boudier, 1991; Nicolas et al., 2008), and from the petrological and mineralogical studies of drill core from mid-ocean ridges carried out in the last 40 years. These latest include: the Deep Sea Drilling Program (DSDP) in 1968; the Ocean Drilling Program (ODP) in 1985 and the Integrated Ocean Drilling Program (IODP) in 2003 (Fig. 1.3) (Benoit et al., 2014).

Hole 504B of the ODP was drilled in the equatorial Pacific Ocean and was the deepest ever drilled within the ocean crust (2111mbfs). It showed the presence of hydrothermal alteration up to the lower sheeted dikes (Alt et al., 1996; Bach et al., 2003; Becker et al., 1989; Vanko and Laverne, 1998). Only in IODP, Hole 1256D, from the eastern Pacific Ocean (1507mbsf) it was possible to penetrate to the dike/gabbro (plutonic) boundary for the first time (Koepke et al., 2008; Patten et al., 2016; Wilson et al., 2006). Important data about the geological setting at MORB also come from the Iceland Deep Drilling Project (IDDP), in the Reykjanes Peninsula, from two wells in particular: well RN-17 from IDDP-1 (3100 m) (Marks et al., 2011) and well RN-15, from IDDP-2 (4659 m) the deepest geothermal well drilled to date (Friðleifsson et al., 2017). These projects offer a unique opportunity to study a high-temperature active hydrothermal system at supercritical conditions.

Figure 1.3. Map of ocean floor age, based on age grid by Muller et al. (2008) revised version 3 (www.earthbyte.org/). Symbols represent DSDP, ODP, and IODP holes drilled in ocean from 1974 to 2011.

Fluid-rock interaction at mid-ocean ridges starts at the recharge zone adjacent to the ridge. Seawater penetrates through fractures, crossing the first shallow layer of pillow lava and lava flows, overlain by pelagic sedimentary rocks (Alt, 2013). The first alteration process that takes place is a low temperature (up to 40°C) oxidation with the formation of Fe-oxyhydroxides which replace olivine and primary sulfide minerals, giving a typical red colour to the rock (Berndt and Seyfried Jr, 1986; Böhlke et al., 1981; Honnorez, 1983; Ridley et al., 1994).

Celadonite and nontronite (ferric mica and smectite, respectively) also precipitate, trapping elements such as Sb, As, Rb, Cs, B, K, and in some cases Mn. Chemical evidence shows the highest values of $\text{Fe}^{3+}/\text{Fe}^{\text{Total}}$ and K_2O in these altered rocks relative to unaltered rocks. The study of Vanko and Laverne (1998) on Hole 504B differentiates, at this stage, two different hydrothermal alterations at lower temperature (<100°C). One oxidative sea floor weathering zone in the upper half of the extrusive section and one non-oxidative alteration zone in the lower extrusive section (Figure 1.4).

Patten et al. (2016), from a recent analysis on the sulfide mineral evolution and metal mobility in Hole 1256D, recognized five main groups of sulfides: magmatic, metasomatised, high temperature, low temperature and patchy sulphides. In their study, it is reported that magmatic sulfides in the volcanic portion of the hole are replaced by secondary sulfides including as pyrite, marcasite and chalcopyrite during lower temperature hydrothermal alteration. Laverne et al. (2006) also report the breakdown of titanomagnetite to schorlomite in altered basalt from Hole 1256D, during low temperature hydrothermal alteration.

The temperature of hydrothermal fluids at this stage is less than 150°C. Zeolites and carbonates are also present but more off-axis from the ridge. A prevalent reaction that occurs in this recharge zone is the precipitation of Ca-Mg from seawater in the form of sulfate minerals. The most common sulfate mineral is anhydrite (CaSO_4) which precipitates at temperatures between 150-200°C. The formation of anhydrite involves depletion of Ca from seawater which prevents the formation of appreciable Ca-silicates. From Hole 504B and hole 1256D, anhydrite is present in veins in the lower volcanics. Contemporaneously, ferrous iron is trapped by the formation of Mg-smectite (saponite). This process contributes to the fixation of Mg from seawater with the highest Mg concentrations lost due to the formation of smectite at lower temperatures (<200°C) and chlorite at higher temperatures ($T > 200^\circ\text{C}$).

As the fluid migrates deeper, it encounters the transition between the basal volcanics and

the upper sheeted dikes, where temperature of the hydrothermal alteration increases up to 250-300°C (greenschist facies). Here albite replaces plagioclase (albitisation process) while chlorite and actinolite replace basaltic glass and olivine. Anhydrite is also present and suggests that sulfate is not completely lost in the low temperature reaction zone (Alt et al., 2010). Patten et al. (2016) report that in the upper sheeted dikes, magmatic sulfides such as pyrrhotite, chalcopyrite and marcasite are replaced by the formation of secondary sulfides such as pyrite (most abundant), chalcopyrite and sphalerite. During this stage, the first significant metal mobilisation occurs at moderate temperatures (~ 300°C).

Between the middle sheeted dike zone and the upper gabbro section, fluid temperatures reach 350-450°C (and higher) resulting in a significant change of metamorphic grade. This is where the most intense hydrothermal alteration occurs. The hydrothermal alteration at this reaction zone is not well-documented, however, early observations of this zone were reported from Hole 1256D by several authors (Figure 1.4). Wilson et al. (2006), Koepke et al. (2008) and Alt et al. (2010) report that within the lower sheeted dikes, the grade of alteration increases under reduced and more acidic fluid conditions. The mineral actinolite becomes more common than chlorite below 1300 mbsf. followed by the formation of Mg-hornblende with a greenish brown colour below 1350 mbfs. While the lowest ~ 60 m of the dikes (~1350 to 1407 mbsf), basalt is partially to completely recrystallized to distinctive granoblastic textures, because of contact metamorphism by the underlying gabbroic intrusions.

Koepe et al. (2008) concluded that the granoblastic dikes portion in Hole 1256D was formed by the intrusion of the magmatic chamber and its relative conductive boundary layer overlapping the previously altered sheeted dikes. Thin section analysis of the granoblastic section showed two stages of hydrothermal alteration by seawater circulation. The first stage formed prior to the granoblastic overprint forming a greenschist facies matrix including quartz, albite, actinolite, sulfides and magnetite. The second stage occurred as a result of an overprinting by circulating seawater-derived fluids. This formed pseudomorphs of Mg-hornblende from the actinolite aggregates of the earlier matrix. Plagioclase was converted to high Ab-rich compositions.

The top portion of the plutonic complex (gabbro and trondhjemite dikes between 1407_{mbsf} and 1500_{mbsf} approximately, Figure 1.5) in Hole 1256D was analysed by Wilson et al. (2006). Two major bodies of gabbros are separated by a layer of granoblastic dikes. The gabbros were

altered by hydrothermal fluids to hornblende, actinolite, epidote, chlorite, prehnite, laumontite and secondary plagioclase.

Analysis of sulphide mineral evolution and metal mobility in Hole 1256D by Patten et al. (2016) demonstrates that temperatures in the lower dikes, up to the gabbro contact, are higher than 350-400°C resulting in reducing and more acidic conditions of the fluid. This drives a progressive and pronounced leaching and dissolution processes of the sulfides. Accurate mass balance equation analysis of different rock samples shows that these processes are responsible for the release of significant amounts of Cu, Se and Au during hydrothermal alteration, while the mobilisation of elements such as Zn, Sb, As, and Pb is controlled by silicate reactions and not by sulfide leaching.

Vanko and Laverne (1998) describe the lower portion of the sheeted dike complex of ODP Hole 504B (Fig. 1.4) and compared it with the Cretaceous Semail ophiolite in Oman (Nicolas and Boudier, 1991). After the drilling of the IODP Hole 1256D, Nicolas and Boudier (1991) revisited their paper incorporating a new detailed map and new information on the Oman ophiolite and made a comparison with Hole 1256D (Nicolas et al., 2008).

Vanko and Laverne (1998) study of Hole 504B gives important information about the transition between the magmatic and hydrothermal and about the hydrothermal reaction zones at mid-ocean ridges. Hydrothermal alteration consists of amphibolitic metasomatism (giving pressures between 380-850 bar and temperatures higher than 425°C). The mineral assemblage found consists of abundant Mg-hornblende and minor secondary hydrothermal Na- and Ti-rich diopside that replaces primary clinopyroxene (augite) and secondary, hydrothermal calcic plagioclase replacing magmatic plagioclase (from An₅₅ to An₉₅). This is consistent with experimental results at 400°C and 400 bar of (Berndt and Seyfried, 1993). They showed that secondary plagioclase formation buffers the a_{Ca}/a_{Na}^2 of black smoker fluids.

Recent information on high-temperature alteration occurring at the reaction zones comes from the studies on cuttings recovered from the IDDP-1/RN-17 and IDDP-2/RN-15 wells (Friðleifsson et al., 2017; Marks et al., 2011; Marks et al., 2010). The Iceland geological setting is of great interest when studying hydrothermal alteration occurring at mid-ocean ridges, particular when there is direct evidence of supercritical conditions at depth (Elders and Friðleifsson, 2010). The Iceland rift is part of the Atlantic oceanic rift system. The geology and tectonic conditions are similar to those of seafloor mid-oceanic ridges. Shallow magmatic

activity facilitates the circulation of meteoric water and seawater through the crust. The geothermal systems are seawater-dominated and located inland on the extension of the Mid-Atlantic Ridge (Elders and Friðleifsson, 2010; Marks et al., 2011).

Many studies have been undertaken on the geological setting of Icelandic geothermal systems and many of these report information on the geochemistry of the fluid reservoirs at depth (Arnórsson, 1995; Arnórsson et al., 1978; Björnsson et al., 1970; Fowler et al., 2015; Franzson et al., 2008; Fridleifsson and Albertsson, 2000; Gudmundsson, 1986; Jakobsson et al., 1978; Kaasalainen and Stefánsson, 2012; Marks et al., 2011; Thordarson and Larsen, 2007; Weir et al., 2001; Ásmundsson et al., 2014). The recent completion of the Iceland Deep Drilling Project at Reykjanes region (IDDP-1 and IDDP-2, well RN-17 and well RN-15, respectively) has provided important insights into the geochemistry of supercritical geothermal systems. Well RN-15 achieved a total depth of 4659 m (~4.5 km vertical depth) and supercritical conditions have been found (427°C/340 bar). The goal is to produce fluid with a temperature higher than the critical temperature of seawater (407°C) and a pressure less than the critical pressure (298 bar), resulting in superheated steam. As this fluid rises quickly, the enthalpy decrease by conduction is insufficient to allow phase separation and the fluid reaches the surface with a greater power conversion efficiency. It is estimated that this well can yield to 50 MWe of electric power alone, tenfold better than a typical conventional subcritical two phase well (Fridleifsson and Elders, 2005; Fridleifsson et al., 2017).

Marks et al. (2010, 2011) studied the lower portion of the RN-17/ IDDP-1 (Fig. 1.4) where they observed hydrothermal alteration passing from the zeolite facies (~400 m) to the greenschist facies alteration at about 400 m depth. This alteration is composed of actinolite, albite, chlorite, quartz, epidote, titanite and magnetite (up to ~2300 m depth). Between 2300 m and 3100 m depth the mineral assemblage changes to amphibolite facies alteration in conjunction with granoblastic hornfels derived by contact metamorphism. The granoblastic texture shows evidence of being formed by recrystallisation of the greenschist facies minerals. Hydrothermal hornblende and clinopyroxene (from $\text{Wo}_{49}\text{En}_3\text{Fs}_{48}$ to $\text{Wo}_{53}\text{En}_{30}\text{Fo}_{17}$) are present in veins with calcic plagioclase, epidote and quartz.

Fridleifsson et al. (2017) reports on the active seawater-recharged hydrothermal system in well RN-15/IDDP-2 (Fig. 1.4). The lowest portion of this well is at supercritical conditions ($T = 427^\circ\text{C}$ and $P = 340$ bar). Between 1100 m and 1400 m depth, epidote-actinolite facies alteration

is present in basalt flows and pillow lavas. Between 1400 and 3600 m depth the extrusive and intrusive transition is found. Here, epidote, hornblende (replacing actinolite), chlorite and calcic plagioclase are present. Below 3600 m, typical amphibolite facies alteration occurs. Hornblende is the most abundant amphibole, with actinolite and chlorite being almost absent and igneous plagioclase remains relatively unaltered. From 4260 m to the lowermost portion of the core, igneous clinopyroxene is altered to hornblende. Hydrothermal biotite is found in fractures and is stained red by a coating of hematite (Figure 1.6). The presence of hematite is explained by the oxidation of iron when oxygenated water was pumped downhole for cooling. Cu-Fe sulfides and pyrrhotite were also found in the deepest core, although in minor amount.

Figure 1.4. A comparison of the lithologies between Hole 1256D and Hole 504B drilled during the IODP and ODP expeditions, respectively, and cores of RN-17 and RN-15 recovered during the development of the IDDP-1 and IDDP-2 in Reykjanes region (Iceland), respectively (Friðleifsson et al., 2017).

Figure 1.5. (A) Lithostratigraphic section of the plutonic complex, Hole 1256D. (B) dike sample with granoblastic texture; (C) dike-gabbro boundary (gabbro extremely altered by hydrothermal circulation); (D) diorite rich in quartz and oxide altered to actinolite, hornblende and secondary plagioclase, chlorite and epidote; (E) Gabbro with oxides and patchy texture; (F) Gabbro strongly altered by hydrothermal circulation with veins of chlorite and actinolite; (G) sample of intruded dike within gabbro (all from Wilson et al, 2006).

Figure 1.6. Photomicrographs of the core from the IDDP-2, well RN-15, at 4637.81 m depth (Friðleifsson et al., 2017) (a) euhedral crystals of hydrothermal biotite covered by hematite which gives them a red coloration, formed during coring operation (b) open-spaces filled by quartz overgrown on hydrothermal biotite covered by hematite.

The locations where fluids containing metals and sulfur rise to the seafloor in a submarine hydrothermal systems are referred to as zones of up-welling (Richardson et al., 1987). A large fluid/rock ratio results in a mineral assemblage controlled by the fluid chemistry rather than by the surrounding rock (Vanko and Laverne, 1998). It has been estimated that the residence time of this fluid, from the deep reaction zone to seafloor, is less than one year (Kadko et al., 1985; Kadko and Moore, 1988; Macdonald et al., 1980). The deepest zone of upwelling coincides with the deep reaction zone up to sea bottom. These portions of the crust are altered to granular epidote, quartz and titanite (epidosites). They can extend into quartz and epidote veins and can be linked to quartz, sulfide and epidote veins beneath sulfide deposits at sea floor (Bettison-Varga et al., 1992; Harper et al., 1988; Haymon et al., 1989; Nehlig et al., 1994). When compared to the fresh diabase, the epidiosites show high contents in Ca, Sr, $\text{Fe}^{3+}/\text{Fe}^{\text{T}}$ and are depleted in Mg, Na, K, Cu, Zn, and S indicating alteration processes occurring at temperatures between 300-400°C.

Ore deposit formation is strictly linked to vent activity at sea floor. This activity is essentially determined by parameters which control metal transport during hydrothermal circulation. The most important are pH, redox ($f\text{O}_2$), the fugacity of sulphur ($f\text{S}_2$), fluid mixing, and temperature decrease. These factors determine the carrying capacity which is directly proportional to the availability (*activity*) of ligands present in solution (such as Cl^- , HS^- and OH^-) which form complexes with metals.

The first observations of vents were made at Axial Seamount, Juan de Fuca Ridge (Hannington, 1988) and at 9°50 N, East Pacific Rise (Haymon et al., 1993). Recent studies suggest that the origin of their manifestations can be strictly attributed to magma intrusions close to sea floor, fracturing and sub-volcanic eruptions which permit the rise of the fluids.

In a submarine hydrothermal environment, at the seafloor, the two main deposit types formed are: 1) sulfate deposits, formed by white smokers, so-called because of the white colour of the plume due to the high concentration of Ba and Ca sulfate and silica particles (Hannington et al., 2013); and 2) sulfide deposits, formed by black smokers, so-called due to the black colour of the plume which contains high concentrations of metals (mostly Cu, Zn, Pb, Fe) and S. White smokers normally have lower temperatures (100-300°C) than black smokers and for this reason they are insufficient to transport metals and reduced sulfur. The typical mineral precipitation related to a white smoker consists of amorphous silica (SiO_2) and barite (BaSO_4) which are the

first, and last to precipitate, respectively. This is due to conductive cooling and mixing with the cold seawater rich in SO_4^{2-} . Anhydrite also forms, however, its solubility is retrograde. As a result, it dissolves back into cold seawater while the amorphous silica and barite remain.

In contrast, black smokers are typically hotter (350-400°C) with extensive deposits of ore metals and S. When hot fluids from vents mix with the cold surrounding seawater, the solubility of transition sulfides decreases dramatically, causing instantaneous precipitation and formation of massive sulfide layers on the seafloor. The typical mineral precipitates consist of an assemblage of chalcopyrite (CuFeS_2), pyrrhotite and wurtzite $[(\text{Zn,Fe})\text{S}]$ at high temperature and low $f\text{O}_2$ - $f\text{S}_2$ while an assemblage of pyrite, marcasite (orthorhombic FeS_2) and sphalerite (ZnS) forms at lower temperatures but higher $f\text{O}_2$ and $f\text{S}_2$ (Janecky and Seyfried, 1984). The main mineral precipitates at black smokers are sulfides but sulfate and silicate minerals are also observed. Anhydrite has also been identified but far from the vent plumes (Haymon, 1983; Tivey and Delaney, 1986). Other minerals found include Mg-silicates such as lizardite $[(\text{Mg}_3\text{Si}_2\text{O}_5(\text{OH})_4]$, stevensite $[(\text{Ca,Na})_x\text{Mg}_{3-x}\text{Si}_4\text{O}_{10}(\text{OH})_2]$ and some Mg-hydroxysulfates such as caminite $[\text{Mg}_7(\text{SO}_4)_5(\text{OH})_4\cdot\text{H}_2\text{O}]$ and starkeyite ($\text{MgSO}_4\cdot 4\text{H}_2\text{O}$) may also occur in minor amounts.

1.3. Experimental simulations of seawater-rock interaction: Previous work

Table 1.1 presents a summary of water-mafic/ultramafic rock interaction experiments conducted during the past ~40 years with relevance to mid-ocean ridge hydrothermal systems.

The earliest experiments were carried out in the mid-1970's. Hajash (1975) reacted basalt with seawater at low fluid/rock ratios under medium-high T and high P conditions (200-500°C/500-800 bar) using a cold-seal pressure vessel. The experiments revealed the role of rock composition in buffering pH and redox state. The main goal of the experiments was to determine the nature and the rate of chemical exchange and the nature of resulting mineral precipitates. At the time, there was lack of thermodynamic data to account for the relevant alteration minerals that formed in equilibrium with fluid.

Bischoff and Dickson (1975) improved on the above by using a Teflon-cell described in Dickson et al. (1963) and in Seyfried et al. (1987) that allowed sampling at higher fluid/rock ratios. They reacted seawater with tholeiitic basalt at 200°C/500 bar, conditions typical of geothermal systems of the Reykjanes area. In their experiments, a small amount of glass was dissolved, and the major secondary phases formed were anhydrite and montmorillonite (smectite group). Fluid analyses showed that SiO₂ was saturated with respect to amorphous silica while Mg and SO₄ decreased to below detection limit.

Seyfried and Bischoff (1977) used a similar approach to study the hydrothermal transport of trace metals, mineralogical changes and mineral reactions as a function of time, as well as the effect of water/rock ratio. The experiments were batch-type without fluid flow. They reacted seawater with basaltic glass at 260°C/500 bar with 50:1 water/rock ratio. The results showed efficient leaching from the rock of metals such as Cu, Zn and Ba, which achieved elevated concentrations in solution. These experiments were innovative for the time; however, it was not possible to reach the temperature and pressure regime present deep in the sub-seafloor using Teflon reaction vessel liners.

Bischoff and Seyfried (1978) investigated the kinetics of precipitation and compared results with theoretical solubilities of minerals including anhydrite, brucite, dolomite, magnesite and calcite in their experiments. They heated seawater to 350°C for approximately one month without the presence of rock material. This caused an increase in acidity of the fluid and the depletion of Mg, Ca and SO₄ from solution (Fig. 1.7). Mineral precipitates consisted of anhydrite

and magnesium hydroxysulfate (Fig. 1.8) but not brucite. The pH at experimental conditions was calculated to be 3.3.

Figure 1.7. (a) Mg, Ca, SO_4 and pH concentrations during the experiment of Bischoff and Seyfried (1978) from 25°C to 350°C/500bar; (b) Ion-Activity Products (IAP's) of brucite and anhydrite in thin lines calculated from the experiment from 25°C to 350°C compared to theoretical log K values for dissolution equilibrium (thick lines) at 500 bar (Helgeson and Kirkham, 1974; Helgeson and Kirkham, 1976).

Figure 1.8. (a-b) SEM pictures of the mineral precipitates from the experiment of Bischoff and Seyfried (1978) showing magnesium hydroxysulfate crystals (10µm scale increments) formed at 325°C/500 bar.

Using gold-lined pressure vessels, Seyfried and Bischoff (1979) and Mottl et al. (1978, 1979) were able to conduct experiments at higher temperature and pressure, closer to the conditions deep in sub-seafloor hydrothermal systems (Mottl et al., 1979). The results were significant in terms of understanding the chemical changes that occurred in the seawater at higher temperature and it was possible to study the behaviour of some important base metals under these conditions. The release and uptake of elements to and from the fluid phase such as Mg, Fe, Mn and Cu caused changes in H^+ concentration and a consequent variation in solution pH.

Mottl et al. (1978, 1979) performed forty experiments reacting seawater and artificial seawater with mid-ocean ridge basalts of varying crystallinity at different temperatures and pressures: 200°C/500 bar; 300°C/600 bar; 400°C/700 bar; and 500°C/1000 bar. The total experimental time was between 2 and 20 months. They used sealed 15 cm³ gold capsules filled with crushed rock (<149 µm size). Results for major elements showed two principal exchanges: Mg for Ca and Na for Ca. There was an almost complete loss of Mg from the seawater due to the formation of smectite and tremolite-actinolite. Ca-bearing phases including anhydrite, truscottite, tremolite and actinolite were the main alteration minerals. SiO₂ concentrations achieved quartz saturation at temperatures above 300°C. Sulfur, iron and manganese showed near-constant concentrations at high T (400-500°C), but not at lower temperatures (200-300°C). Oxide and sulfide minerals found in the experiments showed an assemblage of pyrite, pyrrhotite, chalcopyrite, and hematite.

Seyfried and Bischoff (1979) described three experiments where basaltic glass was reacted with seawater at 70°C/1 bar and 150°C/500 bar, and diabase was reacted with seawater at 150°C/500 bar. At low temperature (70°C) there was a loss of Mg, Na and K from solution and enrichment of SiO₂ and Ca in the fluid. At higher temperature (150°C) Mg and SO₄ were lost from the fluid in a greater amount, while Ca, SiO₂, Fe, Na, K, Mn and B were added to the seawater. Smectite was the major alteration product recovered from both basaltic glass and diabase experiments at 150°C.

Mottl (1983) discussed in detail how seawater-basalt interactions are influenced by the role of Mg. The formation of smectite, chlorite and other minerals such as brucite [Mg(OH)₂] and Mg hydroxysulfates rapidly removes Mg from the fluid, transferring high concentrations of

H⁺ into the solution. The low pH causes the alteration of the primary silicates, consuming H⁺ via hydrolysis reactions. This leads to extensive exchange of cations with the rock.

Further experimental work by Seyfried and Bischoff (1981), Seyfried and Mottl (1982), Seyfried and Janecky (1985), Seyfried et al. (1986), Gilles et al. (1987) and Berndt et al. (1989) investigated chemical reactions and mineralogical changes during fluid-rock interaction using an improved reaction cell design (Seyfried Jr, 1979; Seyfried et al., 1987). They demonstrated the importance of the pressure on fluid density (particularly under supercritical conditions) as well as the importance of chloro-complexes in determining metal mobility at subcritical and supercritical conditions. They used crystalline basalt, basalt glass and diabase and reacted these with seawater and NaCl solution at different water/rock ratios. Temperature (300-425°C) and pressure (250-500 bar) were changed from conditions below to above the T_c and P_c of seawater.

Seyfried and Bischoff (1981) found an increase in SiO₂, H₂S, Ca, Fe, Mn, K, Ba and Al in solution, while there was depletion of Mg and SO₄. Secondary minerals found included anhydrite, smectite, hematite in the basalt glass and layered chlorite/smectite, anhydrite and magnetite in diabase. Analysis for heavy metals showed low concentrations in the solution during the experiments. From these results, the authors concluded that chloride-complexing cannot be considered the dominant mechanism in regulating the heavy-metal solubility, at least at 300°C for seawater.

Seyfried and Mottl (1982) reacted basaltic glass and diabase at 150-300°C/500 bar at different fluid/rock ratios and found similar results to Seyfried and Bischoff (1981). The depletion of Mg and the consequent production of H⁺ was a very important as this mechanism regulates: (1) heavy metal mobility and (2) hydrolysis reactions. The reactive capacity of a hydrothermal solution (the capacity to hydrolytically decompose silicates) is determined largely by its acidity. The authors observed a significant increase in Fe, Mn and Zn in solution at low pH. In contrast, the concentrations drop markedly when Mg removal was near completion and the glass hydrolysed. At higher temperature (300°C) almost all Ca, Na, Zn, Cu and most of Ba, Sr, K and Mn were leached from the rock. Si, Al and H₂S were also mobilised while Cr, V and Ni, remained relatively immobile.

Seyfried and Janecky (1985) investigated heavy metal and sulfur transport during subcritical and supercritical hydrothermal alteration of rocks of basaltic composition. Diabase, basalt glass and crystalline basalt were reacted with a Na-Ca-K-Cl fluid of seawater composition

at 350-425°C/375-400 bar, with fluid/rock ratio of 1.0-0.5. The pH decreased with increasing temperature at constant pressure, changing from 4.8 to 2.7 at 350 and 425°C, respectively (Fig. 1.9). Fe and Mn concentrations increased with increasing temperature in all experiments except with basalt glass. Cu, Zn and H₂S showed maximum concentrations at 375-400°C/400 bar, however, they did not increase when temperature was increased to 425°C (Fig. 1.9). This suggests that sulfides are more insoluble under these conditions. From these studies, it was concluded that pressure plays a key role in metal transport and on H⁺ generation. Results from experiments at 425°C/400 bar showed that metal concentrations (especially Fe and Mn) were higher of those reported from experiments by Mottl and Holland (1978) and by Mottl et al. (1979) at 500°C/1000 bar. A pressure decrease at $T > T_c$ for seawater causes a decrease in solution density and a decrease of the dielectric constant causing an increase in the chloro-complex stability. The dominant alteration phase in these experiments was mixed layer chlorite/smectite (Fig. 1.10). Poorly crystalline tremolite and actinolite were found from the basalt glass experiment, while clinozoisite (epidote) was found only in the diabase experiment (Fig. 1.10). Secondary magnetite was identified only in the experiment at 425°C/400 bar. Pyrite formed at 400°C and 425°C/400 bar while pyrrhotite was found in experiments at $T \leq 375^\circ\text{C}$ (Fig. 1.10).

Figure 1.9. Fe, Mn, Cu and Zn concentrations (in μmol) versus temperature (350-375-400-425°C/400 bar) and pH by Seyfried and Janecky (1985).

Figure 1.10. SEM images from Seyfried and Janecky (1985) showing: (a) pyrrhotite crystals (hexagonal) (scale = 70 μ m); (b) pyrrhotite crystals with overgrowth pyrite (scale = 20 μ m); (c) pyrite overgrowth on pyrrhotite (scale = 5 μ m); (d) Tremolite/actinolite, fibrous crystals (scale = 20 μ m).

Berndt et al. (1989) showed the difference in the alteration process as a result of different dissolved SiO_2 concentrations and compositions of plagioclase. In diabase experiments (0.5 to 1 water/rock ratio), fluids were produced that were undersaturated with respect to quartz and caused the hydration of olivine and orthopyroxene. In contrast, basalt experiments produced fluids slightly oversaturated with respect to quartz, via the dissolution of the glass, and the formation of secondary smectite and amphibole. Fluid chemistry gave constraints on the equilibrium state which appeared to approach equilibrium with the albite and anorthite components of plagioclase. The pH values were consistent with equilibrium between plagioclase and epidote.

During the 1990's, the study of fluid-rock interaction became more advanced, using more sophisticated equipment, which provided better control on temperature and pressure. The combination of new exploration technologies, which permitted field investigations at deep sea vents, and better experimental methodologies, significantly increased the knowledge of the nature and geochemical evolution of fluids during hydrothermal alteration. This produced new and more reliable thermodynamic data allowing better numerical modelling, especially for the prediction of pH, redox constraints, mineral solubilities and the stability of metal complexes in solution. Experiments on talc-quartz equilibria and on the stability of magnesium chloride complexes below and near the critical point of seawater were undertaken by Saccocia and Seyfried (1990). The determination of the stability of Fe-Cl complexing was studied by Heinrich and Seward (1990). While the effect of redox on the relative solubilities of copper and iron in Cl-bearing aqueous fluids at elevated temperatures and pressures was studied by Ding and Seyfried (1992).

Further experiments (Seewald and Seyfried, 1990; Berndt, 1993) conducted at subcritical and near supercritical conditions of the fluid using crystalline basalt, provided evidence on the role of temperature during metal transport. Their work revealed that the dissolved concentrations of Zn, Cu, Fe and Mn measured at vents ($T < 375^{\circ}\text{C}$) were not consistent with those found during experimental simulations. The concentrations measured *in situ* could only be achieved or exceeded at temperatures $\geq 400^{\circ}\text{C}$. This result confirmed that hydrothermal vent fluids lost heat and possibly dissolved metals during ascent to the seafloor from a higher temperature reaction zone.

Since the beginning of the 21st century, only a few experimental fluid-rock simulations have been undertaken. Their goal was mainly focused on better assessment of hydrothermal alteration processes in the ultramafic systems at mid-ocean ridges. More information collected from field investigations and the experimental simulations allowed better understanding of the parameters that control chemical compositions at vents (Seyfried et al., 2013). These experiments reported significant information on redox and pH constraints.

Recent experiments used different mineral assemblages including olivine-orthopyroxene-clinopyroxene in reaction with NaCl and MgCl_2 at $400^{\circ}\text{C}/500$ bar (Allen and Seyfried, 2003); magnetite-bornite-anhydrite with a Na-K-Cl bearing aqueous fluid at $375\text{--}400^{\circ}\text{C}/500$ bar (Foustoukos and Seyfried, 2005); and peridotite in reaction with seawater at

200°C/500 bar (Seyfried and Foustoukos, 2007). These studies revealed the development of low pH values (4.9 – 5.2) with substantial changes in fluid composition and mineral solubilities; slower reaction of olivine with increasing T and P; and high concentrations of SiO₂ and Ca in the fluid. The increase in Ca concentration was attributed to the dissolution of pyroxene, with tremolite and talc becoming stable according to the observed pH values. High H_{2(aq)} concentrations, from the oxidation of ferrous silicates (especially pyroxene), confirmed high Fe solubilities which was consistent with measurements *in situ* at Rainbow and Logatchev, on the Mid-Atlantic-Ridge. Low H₂S concentrations and high dissolved Ni and Cu showed fluid equilibria with magnetite – bornite - chalcocite (Cu₂S) – heazlewoodite (Ni₃S₂). Experimental data revealed that Cu concentrations in solution were more sensitive to temperature changes than with respect to H₂S and Fe concentrations. In contrast, Fe concentrations were more sensitive to pH and chloride concentrations in the fluid.

More recently, Zhang et al. (2015) conducted a simulation reacting basalt with pure water and 5% NaCl using a flow-through reactor at temperatures from 20 to 400°C/230 bar. The aim was to better understand the nature of hydrothermal reactions in basaltic rocks and the genesis of the large magnetite ore deposits. Their study gave constraints on the changes in metal release rates under increasing temperature conditions. Unfortunately, their work did not address the possibility of the formation of secondary minerals phases, especially at higher temperatures, therefore, the interpretation of their work is somewhat problematic.

Table 1.1. Mafic/Ultramafic rock - fluid interaction experiments carried out from the 1970s to the present.

Authors	T-P conditions	Experimental set-up	Fluid	Rock	System conditions	Experimental time	Number of Samples
Hajash, 1975	200-500°C 500-800 bar	Cold-seal pressure vessel (Bridgman seal vessel)	seawater	basalt	static fluid		
Bischoff and Dickson, 1975	200°C 500 bar	Rocking Autoclaves For Hydrothermal Experiments (TEFLON cell); on-line sampling	seawater (300 g)	tholeiitic basalt (30 g)	static fluid	4752 hrs	19 samples of 6 ml
Seyfried and Bischoff, 1977	260°C 500 bar	Rocking Autoclaves For Hydrothermal Experiments (TEFLON cell and stainless steel pressure vessel); on-line sampling	artificial seawater (200 g)	basaltic glass (4 g)	static fluid	2400 hrs	6 samples of 10 ml
Bischoff and Seyfried, 1978	70-350°C 500 bar	Rocking Autoclaves For Hydrothermal Experiments (Gold cell); on-line sampling	seawater (100 ml)	no rock	static fluid	~1 month	
Mottl et al., 1978, 1979	200-500°C 500-1000 bar	Rocking Autoclaves For Hydrothermal Experiments (Gold cell); on-line sampling	seawater artificial seawater	basalt andesite (1:3 fluid/rock ratio)	static fluid	2 to 20 months	
Seyfried and Bischoff, 1979	70°C, 1 bar 150°C, 500 bar	Rocking Autoclaves For Hydrothermal Experiments (TEFLON cell); on-line sampling	seawater (200 g)	basalt (20 g) diabase (20 g)	static fluid	3600 hrs at 70°C with basalt 3564 hrs with basalt 11,058 hrs with diabase at 150°C	5 samples at 70°C 8 at 150°C with basalt glass 8 samples with diabase at 150°C
Seyfried and Bischoff, 1981	300°C 500 bar	NEW Rocking Autoclaves Design For Hydrothermal Experiments (Titanium-Gold cell and chrome-vanadium pressure vessel); on-line sampling	seawater NaCl solution	basalt glass diabase (fluid/rock ratio of 10)	static fluid	2028 hrs basalt glass-seawater exp. 1968 hrs diabase-seawater exp. 400 hrs basalt glass-NaCl solution exp.	9 samples for the basalt glass-seawater exp. 6 samples for the diabase-seawater exp. 4 samples for the basalt-glass-NaCl solution exp.
Seyfried and Mottl, 1982	150-300°C 500 bar	As above	seawater	basalt glass diabase (fluid/rock ratios of 50, 62 and 125)	static fluid	between 120 and 150 days	
Seyfried and Janecky, 1985	350-425°C 375-400 bar	As above	Na-Ca-K-Cl fluid	crystalline basalt diabase basalt glass	static fluid		4 samples at 350°C 4 samples at 375°C 4 samples at 400°C 4 samples at 425°C
Berndt et al., 1989	350-425°C 250-400 bar	As above	Na-Ca-K-Cl fluid	basalt glass diabase (fluid/rock ratio ranged between 0.5 to 5.0)	static fluid	~2500 hrs	2-3 samples at each T
Seewald and Seyfried (1990)	400°C, 400 bar 350°C, 400 bar 300°C, 400 bar	As above	Na-Ca-K-Cl fluid	crystalline basalt fluid/rock ratio of 1	static fluid	990.5 hrs at 400°C 1516 hrs at 350°C 2183 hrs at 300°C	4 samples at 400°C 3 samples at 350°C 3 samples at 300°C 1 samples at 400°C
Zhang et al. (2015)	between 25°C to 400°C 230 bar	Flow-Through reactor system	Pure water and NaCl (5 wt%) - pure water (flow-rate of 0.5 - 8.0 ml min ⁻¹)	basalt	Continuous flow		1 sample every 1 hr at constant T-P and flow-rate

1.4. Proposed research: framework and questions

In this study, experiments have been performed simulating the reaction of basalt with various fluids at near-supercritical/supercritical (400°C/500 bar) and subcritical (350°C/500 bar) conditions that would be typical of reaction zones in sub-seafloor hydrothermal systems.

Previous experimental studies, as summarised above, provided insight into the fluid-rock exchanges that give rise to the fluid's chemical signature; however, many fundamental questions involving the equilibrium and kinetic aspects of fluid-rock interaction, are still poorly constrained. To simulate fluid-rock interactions at supercritical and subcritical conditions, computer modelling is somewhat deficient due to a lack of reliable thermodynamic data. Therefore, the experimental approach offers the only alternative to directly duplicate fluid-mineral interactions that occur in the reaction zone in submarine hydrothermal systems. The experiments conducted in this study have used a novel experimental approach able to simulate high T-P conditions occurring where seawater reacts with basaltic rocks in the sub-seafloor. Using the results of the experiments, it has been possible to investigate the reaction-path chemistry of different fluids including pure water, geothermal brine, and seawater both at near-supercritical, supercritical, and subcritical conditions. For the first time, flow-through reaction of seawater with rocks with a high sampling frequency without altering P-T conditions of the system has been undertaken.

In previous experimental studies, important insight has been gained into the fluid-rock exchanges that give rise to a fluid's chemical signature. However, several fundamental questions that result from the hydrothermal alteration at supercritical, near-supercritical and subcritical conditions in flow-through (open-system), remain. The aims of this study are to investigate, in detail, the mineralogical changes, kinetic of reactions, chemical evolution of the fluid, and elementals fluxes of major and trace elements. This information is then compared with previous experimental data and to natural analogues.

The thesis is divided into seven chapters:

Chapter 1: Introduction

Chapter 2: Experimental Method

- description of the experimental apparatus used in for the experiments
- description of the unreacted experimental fluids and rock substrate used in the experiments
- the experimental protocols/methodology used for each set of experiments (distilled water, geothermal brine, seawater)
- the analytical techniques used to analyse the input solutions, effluent samples and unreacted and reacted rock substrate
- the methodology for the calculation of at temperature pH values, species concentrations and activities, and mineral saturation indices

Chapter 3: Basalt - water interactions under hydrothermal conditions

- an introduction to the experiments reacting basalt rock with distilled water at subcritical and supercritical conditions
- the presentation of the results of these experiments including fluid chemistry and mineralogical analysis
- discussion of the results of the experiments including major and trace elements fluxes, fluid-rock interaction path, implications to Na/K geothermometry, and geological implications

Chapter 4: Basalt – geothermal brine interactions under hydrothermal conditions

- an introduction to the experiments reacting basalt rock with geothermal brine at subcritical and supercritical conditions
- the presentation of the results of these experiments including fluid chemistry and mineralogical analysis
- discussion of the results of the experiments including major and trace elements fluxes, fluid-rock interaction path, implications to Na/K geothermometry, and geological implications
- a comparison between the distilled water and geothermal brine experiments.

Chapter 5: The experimental behaviour of seawater

- an introduction to the experiments preheating seawater to subcritical and near-supercritical conditions
- the presentation of the results of these experiments including fluid chemistry and mineralogical analysis
- discussion of the results of the experiments including major element fluxes and mineralogical implications

Chapter 6: Basalt – seawater interactions under hydrothermal conditions

- an introduction to the experiments reacting basalt rock with seawater at subcritical and near-supercritical conditions
- the presentation of the results of these experiments including fluid chemistry and mineralogical analysis
- discussion of the results of the experiments including major and trace elements fluxes, fluid-rock interaction path, implications to Na/K geothermometry, and geological implications

Chapter 7: Summary and conclusions

1.5. References

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Chapter 2: Experimental Method

2.1. Experimental Apparatus

A high pressure and temperature (P-T) titanium alloy autoclave system (Coretest Systems Ltd.) was used in this study (Fig. 2.1 – 2.2). The experimental set-up allows single-pass continuous flow of aqueous fluid through rock or mineral materials at a maximum temperature ($T_{\max}$) and pressure ($P_{\max}$) of 400°C and 500 bar, respectively. Continuous flow is achieved by a computer-controlled double-piston metering pump with a flow rate range from 0.001 to 15 ml min⁻¹ (Fig. 2.2). The pump (*a*, Fig. 2.1c) injects distilled water from the plastic reservoir (*h*, Fig. 2.1d) into the bottom of the 1 litre titanium accumulator vessel (*b*, Fig. 2.1c) containing a movable metal piston. The experimental fluid is located above the piston which separates the fluid from the distilled water. As distilled water is pumped into the bottom of the accumulator vessel, this forces the piston upwards pushing the experimental fluid out of the accumulator vessel and through the experimental apparatus (Fig. 2.1c). In this way, the stainless-steel metering pump does not come in contact with the potentially corrosive experimental solution.

The rock or mineral material is enclosed in a titanium pressure vessel (Reactor) (19.2 cm³) (*c*, Fig. 2.1c,d) which is externally-heated in one of the two high temperature furnace ($T_{\max}$ = 400 °C) (*g*, Fig. 2.1c,d). After passing through the pressure vessel, the fluid exits via the digital back pressure regulator (*d* - *e*, Fig. 2.1c,d) and collects in a standard disposable plastic syringe (*f*, Fig. 2.1d). All the components of the autoclave are connected using 1/8" titanium tubing (Fig. 2.1c,d).

The flow through autoclave is connected to a dedicated computer that records the experimental conditions using Quizix PumpWorks v. 7.03 for pressure logging and Coretest HFS-340 v. 1.20.2082 for temperature logging. The experimental temperature and pressure are recorded every 300 seconds.

Figure 2.1. (a,b) front and back view of the high temperature and pressure hydrothermal flow autoclave at the Experimental Geochemistry Laboratory of GNS Science, Wairakei Research Centre, Taupo, New Zealand; (c,d) individual components of the flow autoclave: *a*, double piston metering pump; *b*, accumulator vessel containing the piston which separates distilled water coming from the pump from the experimental fluid above the piston; *c*, pressure vessel (Reactor) containing the rock material enclosed by the furnace; *d*, back pressure regulator controller; *e*, back pressure regulator; *f*, collection syringe; *g*, partial cross section of the furnace assembly showing position of pressure vessel (Reactor); *h*, plastic reservoir containing distilled water used by the metering pump. Yellow lines represent 1/8" titanium tube connections between components. Blue arrows show the flow path.

Figure 2.2. Schematic diagram of the hydrothermal flow autoclave. Blue arrows show the path of distilled water coming from the metering pump. Red arrows show the path of the experimental fluid exiting the accumulator vessel, passing down the side of the furnace and into the bottom of the pressure vessel (Reactor). The fluid then passes through the Reactor vessel containing the rock material and exits out the top, after which it moves to the back pressure regulator and into the collection syringe.

2.2. Experimental Protocols

In this thesis, the results of eight experimental studies are presented (Table 2.1). Basalt of typical mid-ocean ridge lithology was the sole rock substrate. Three different aqueous fluids were utilised including: distilled water, geothermal brine and natural seawater. Each basalt – fluid reaction set was conducted at two temperatures: 350°C (sub-critical) and 400°C (supercritical/near-supercritical depending on the fluid) totalling six “rock” experiments. The pressure range during these experiments was 488-502 bar. Two further experiments were also undertaken to study possible heterogeneous equilibria which may occur when seawater (with no basalt) is heated to 342°C and 377°C/488 bar.

2.3. Experimental Substrate and Fluids

2.3.1. Unreacted basalt: mineralogy, texture and mineral chemistry

The lithology used in all rock-present experiments is a tholeiitic basalt sourced from the Eldvraphraun flow, Reykjanes, Iceland (Fig. 2.3). The unreacted basalt was studied in detail using: 1) electron microprobe analysis (EMPA) on a petrographic thin section for unreacted mineral and glass compositions; 2) scanning electron microscopy with electron dispersive spectroscopic analysis (SEM-EDS) for elemental mapping of unreacted rock textural information; and 3) quantitative X-ray diffraction analysis (XRD) to determine rock mineralogical composition.

Major and trace element data are reported in Table 2.2, in wt% and ppm, respectively (Peate et al., 2008). The basalt is completely devoid of secondary mineralisation or alteration.

Figure 2.3. Fragments of basalt from the Eldvarpahraun lava flow, Reykjanes Peninsula, Iceland.

Table 2.1. Experimental protocols for the eight experiments conducted in this study.

Experiment Designation	BW1	BW2	BGB1	BGB2	SW1	BSW1	SW2	BSW2
Rock Substrate	Basalt	Basalt	Basalt	Basalt		Basalt		Basalt
Type of fluid	Water (distilled)	Water (distilled)	Geothermal Brine	Geothermal Brine	Seawater (natural)	Seawater (natural)	Seawater (natural)	Seawater (natural)
Room T Period/°C	20	20	20	20	no Room T period	no Room T period	no Room T period	no Room T period
Time at Room T/hr	167.3	160.5	190.9	187.8				
T_{max}/°C	400	350	400	350	377 (Preheater)	377 (Preheater) 400 (Reactor)	342 (Preheater)	342 (Preheater) 350 (Reactor)
Time at T_{max}/hr	746.2	984.2	662.3	720	546.7	659	381.2	311
P_{max}/bar	502	490	483	486	488	488	488	488
Time at P_{max}/hr	913.5	1144.7	853.2	907.8	546.7	659	381.2	311
De-oxygenation	Deoxygenated solution	Deoxygenated solution	Deoxygenated solution	Deoxygenated solution	Solution not deoxygenated	Deoxygenated solution for 626.8 hr, Last 32.2 hr solution not deoxygenated	Solution not deoxygenated	Deoxygenated solution
Preheater vessel and/or Reactor vessel	Reactor Only	Reactor Only	Reactor Only	Reactor Only	Preheater Only	Preheater and Reactor	Preheater Only	Preheater and Reactor
ZrO₂ Beads Used/g	-	-	-	-	157.0	160.5	166.3	168.7
Basalt grains size/μm	355 - 500	355 - 500	355 - 500	355 - 500	-	355 - 500	-	355 - 500
Weight of basalt/g	26.2	26.6	27.0	26.4	-	22.5	-	23.3
Basalt Block Added	Yes	Yes	No	Yes	No	Yes	No	Yes
Total Fluid Flux/L	0.77	1.02	0.69	0.75	0.40	1.48	0.33	1.15
Time/hr: Flow-rate/ml hr⁻¹	819.1: 1 94.4: 0.5	1002.1: 1 142.6: 0.5	767.5: 1 85.7: 0.5	907.8: 1	546.7: 1	532.6: 1 50.2: 1.5 44: 10 24.5: 7.5 7.7: 5	381.2: 1	119.8: 1 47.5: 10 23.5: 5 73.5: 2.5 46.6: 1
Number of Samples	35	46	34	38	23	43	16	27
Total time/hr	913.5	1144.7	853.2	907.8	546.7	659	381.2	311

Table 2.2. Major and trace element composition of the basalt (Peate et al., 2008).

Major Elements	wt%	Trace Elements	ppm
SiO ₂	48.85	Sc	51
TiO ₂	2.13	V	467
Al ₂ O ₃	13.41	Cr	124
Fe ₂ O ₃ (T)	15.11	Co	56
MnO	0.24	Ni	65
MgO	6.5	Cu	167
CaO	10.94	Zn	124
Na ₂ O	2.35	Ga	20
K ₂ O	0.25	Rb	4.3
P ₂ O ₅	0.22	Sr	156
Volatiles	0.66	Y	35.3
Total	99.84	Zr	108
		Nb	13.5
		Ba	66.8
		La	9.19
		Ce	22.66
		Pr	3.25
		Nd	15.46
		Sm	4.36
		Eu	1.53
		Gd	5.38
		Dy	5.88
		Er	3.61
		Yb	3.33
		Lu	0.49

Electron Microprobe Analysis (EMPA)

EMPA analysis was undertaken on five areas of the petrographic thin section (Area A – E, Fig. 2.4). Areas A and B focused on mineral compositions while Areas C – E focused on the composition of the glass. Table 2.3 summarises the mineral compositions. Complete EMPA analyses and detailed SEM photographs of Area A – E are shown in Appendix A.

Table 2.3. Mineral phase, ID and average mineral compositions determined by EMPA.

Phase	Mineral Identified	Average Mineral Composition
Plagioclase	Bytownite	$\text{Ca}_{0.7}\text{Na}_{0.3}\text{Si}_{2.3}\text{Al}_{1.7}\text{O}_8$ (An ₇₆ -Ab ₂₄)
Pyroxene	Augite	$\text{Ca}_{0.7}\text{Mg}_{0.9}\text{Fe}_{0.3}\text{Al}_{0.1}\text{Si}_{1.9}\text{Al}_{0.1}\text{O}_6$
Olivine	Forsterite	$\text{Mg}_{1.4}\text{Fe}_{0.6}\text{SiO}_4$ (Fo ₇₀ -Fa ₃₀)
Oxide	Titanomagnetite	$\text{Fe}^{2+}(\text{Fe}^{3+}, \text{Ti})_2\text{O}_4$
Glass	-	wt%: SiO ₂ 67.88, Al ₂ O ₃ 16.22, FeO _(T) 4.08, TiO ₂ 0.65 Na ₂ O 6.13, K ₂ O 1.37, CaO 5.29, MgO 0.79 SO ₂ 0.04, Cl 0.09, P ₂ O ₅ 0.32, MnO 0.07

Figure 2.4. Thin section of the basalt showing the different areas analysed by EMPA (points A-B-C-D-E, in red rectangles). Yellow circles indicate the points where glass was analysed.

SEM-EDS analysis of unreacted basalt

SEM-EDS mapping was made on epoxy-mounted, polished basalt grains to examine their textural details and on different thin section areas to identify the volcanic glass. EDS measurements of selected mineral compositions were also undertaken to compare with the EMPA analyses and are listed in Appendix A. Figure 2.5 and Figure 2.6 show examples of one of these elemental maps for unreacted basalt grains texture and volcanic glass identification, respectively.

The basalt has an ophitic texture composed of interlocking plagioclase (bytownite) laths with interstitial pyroxene (augite). Olivine (forsterite) occurs as isolated anhedral crystals. These three minerals comprise >95% of the basalt. Titanomagnetite is the next most abundant phase followed by minor amounts of volcanic glass that contain inclusions of Fe-sulfide and apatite. The basalt is vesicular with plagioclase lathes projecting into the void spaces. SEM examination shows that the basalt has no hydrous phases and is completely unaltered.

Quantitative XRD analysis

The quantitative XRD analysis of the unaltered basalt is shown in Table 2.4 Results show the predominance of plagioclase and clinopyroxene (99%). According to the SEM analyses olivine and titanomagnetite are clearly present, however, they were not detected by the quantitative XRD analysis. This emphasises the poor sensitivity of this type of analysis. Nevertheless, these results are provided in order that the quantitative XRD analyses of the reacted basalt samples can be compared.

Table 2.4. Quantitative XRD analysis of unreacted basalt. Margin of error: Abundance estimate are determined through successive refinement of cell parameters; the position, width and orientation of each mineral. Values are given to the nearest whole number. The margin of error for phase concentration is as follow: 0 – 10% $\pm 10\%$; 10 – 50% $\pm 5\%$; 50 - 100% $\pm 2\%$.

	Abundance %
Plagioclase	60
Clinopyroxene	39
Other	1

Figure 2.5. SEM-EDS elemental map of an unreacted basalt grain: (a) grey scale image; (b) composite colour image combining maps for c) Mg, d) Ca and e) Na. In (b) the composite colour image shows plagioclase (violet), pyroxene (turquoise), olivine (light green) and titanomagnetite (white).

Figure 2.6. SEM-EDS images of the unaltered basalt: (a) Point C (Figure 2.4); (b) secondary electron image of the red rectangular area in (a); (c) composite colour image (b) combining maps for f) Al, g) Si, and h) P showing plagioclase (green), clinopyroxene (light red), volcanic glass (dark red), oxides (white) and apatite (blue-violet); (d) enlargement of yellow rectangle (n°1) in (c) showing volcanic glass (outlined in yellow) including apatite and sulfides; (e) enlargement of yellow rectangular area (n°2) in (c) showing other two areas of the volcanic glass (outlined in yellow).

SEM examination of unreacted basalt grains

Figure 2.6 shows SEM photographs of four unreacted basalt grains. Two distinctive fabric types are present: idiomorphic granular, composed of well-formed crystal faces of interlocking euhedral plagioclase lathes of tabular, prismatic shape; and allotriomorphic granular, composed of unbounded crystal faces of anhedral and interstitial clinopyroxene. Olivine and oxides are also interstitial to the plagioclase lathes. Appendix A provides the complete set of SEM photographs of unreacted grains.

Figure 2.7. SEM photographs of four different unreacted basalt grains: a) typical rough surface texture; b) - d) show euhedral lathes of plagioclase (plg) and anhedral interstitial clinopyroxene (cpx). The euhedral lathes are found as linings of the vesicles.

2.3.2. Experimental Fluids

Three experimental fluids were utilised in the experiments:

1. Doubly distilled water from an Arium® pro-Ultrapure water system;
2. Low-pressure flash geothermal brine, collected from the Nga Awa Purua geothermal power station, Rotokawa, New Zealand;
3. Natural seawater collected at the New Zealand National Aquarium, Napier, New Zealand.

Fluid compositions are reported in Table 2.5.

Table 2.5. Starting experimental fluid compositions including major cations, anions, H₂S and SO₄²⁻ (mmol kg⁻¹), trace elements (μmol kg⁻¹) and pH values at room temperature. Cells colours and number of the experiments refer to Table 2.1. n.a.: not analyzed.

Experiment	BW1	BW2	BGB1	BGB2	SW1	BSW1 (output SW1)	SW2	BSW2 (output SW2)
Fluid	Water (distilled)	Water (distilled)	Geothermal Brine	Geothermal Brine	Seawater (natural)	Seawater (natural)	Seawater (natural)	Seawater (natural)
pH (~21°C)	7.83	6.80	3.91	4.28	7.75	7.75	7.65	8.20
mmol kg ⁻¹								
As	< 0.0002	0.001	0.02	0.002	< 0.0002	< 0.0002	< 0.0002	0.02
B	< 0.03	0.2	4.5	5.1	0.2	0.6	0.5	0.5
Ca	0.01	0.02	0.08	0.2	9.4	2.1	8	1.4
Fe	< 0.001	< 0.001	0.001	< 0.001	0.002	1.3	0.002	1.7
K	< 0.02	0.08	3	3	9.4	8.4	8.6	8.4
Mg	0.001	0.004	0.01	0.04	45.8	24.4	36.7	22.8
Na	< 0.03	0.3	31.6	31.6	420	360	361	360
SiO ₂	< 0.01	0.04	12.6	14.7	0.1	0.9	0.1	0.25
Al	< 0.006	< 0.006	0.06	0.4	0.01	0.01	0.007	< 0.006
Li	< 0.001	< 0.001	0.8	1	0.02	0.02	0.02	0.02
H ₂ S	< 0.0003	< 0.0003	0.004	< 0.0003	< 0.0003	< 0.0003	< 0.0003	< 0.0003
Cl ⁻	0.004	< 0.003	26.5	27.1	432	447	439	450
SO ₄ ²⁻	0.001	< 0.001	4.2	4.2	22	1.2	23	2.7
μmol kg ⁻¹					Starting seawater SW1		Starting seawater SW2	
V	< 0.002	< 0.001	0.04	n.a.	0.04	0.04	0.04	0.04
Cr	< 0.004	< 0.004	0.06	n.a.	< 0.004	< 0.004	< 0.004	< 0.004
Co	< 0.002	< 0.002	< 0.002	0.001	< 0.002	< 0.002	< 0.002	< 0.002
Ni	< 0.003	< 0.003	0.1	0.2	< 0.003	< 0.003	< 0.003	< 0.003
Cu	< 0.0009	< 0.0009	0.3	0.8	< 0.0009	< 0.0009	< 0.0009	< 0.0009
Zn	< 0.008	< 0.008	1.9	2.9	< 0.008	< 0.008	< 0.008	< 0.008
Rb	< 0.001	< 0.001	8.5	n.a.	0.1	0.1	0.1	0.1
Mo	< 0.002	< 0.002	0.1	0.03	n.a.	n.a.	n.a.	n.a.
Ag	< 0.0005	< 0.0005	0.006	0.003	< 0.0005	< 0.0005	< 0.0005	< 0.0005
Cd	< 0.0009	< 0.0009	0.6	0.002	< 0.0009	< 0.0009	< 0.0009	< 0.0009
Ba	< 0.001	< 0.001	< 0.001	0.05	< 0.001	< 0.001	< 0.001	< 0.001
Au	< 0.001	< 0.001	1	0.04	0.01	0.01	0.01	0.01
Pb	< 0.001	< 0.001	0.01	0.02	< 0.001	< 0.001	< 0.001	< 0.001
Mn	< 0.13	< 0.13	< 0.13	2.5	< 0.13	< 0.13	< 0.13	< 0.13

2.4. Experimental Procedure

2.4.1. Preparation of the Reactor

The coarse basalt pieces were crushed and sieved to obtain different size fractions in the range of 155 μm to 2 mm (Fig. 2.8a-b). The different size fractions were ultrasonically cleaned using distilled water in order to remove powdered fines. This is necessary as fines are highly reactive and not representative of the true basalt surface. Basalt grains of the size fraction 355 - 500 μm were utilised in all the “rock present” experiments (Table 2.1, Fig. 2.7c).

The pressure vessel (15 cm length, 1.27 cm ID, 19.3 cm^3 internal volume), here after referred to as the Reactor, is composed of titanium alloy cylinder and two titanium alloy end caps (Fig. 2.9a). The top cap of the reactor has a hole into which a K-type thermocouple can be inserted to measure temperature during experiment. At each end of the column, 1.2 cm diameter titanium frits (0.45 μm pore size) are placed which acted as filters to prevent the passage of particles or reaction products from exiting the Reactor either from the bottom or top (Fig. 2.9b). The reactor vessel is sealed using two collars and thrust rings that compress the column into cone-typed seals in the caps (Fig. 2.9a).

After sealing one end of the Reactor, it is weighed, after which the basalt grains are added. It is re-weighed to determine the weight of rock present. The Reactor can contain a maximum of 19.2 cm^3 of fluid (without rock material). The weight of rock present in the Reactor (at maximum capacity and without fluid) is ~26-27 g, for all experiments. This is equal to a solid volume (V_s) of ~9 cm^3 considering a density of the basalt of 2.9 g cm^{-3} and it gives a pore volume (V_p) of ~10 cm^3 . At a flow rate of 1 ml hr^{-1} and assuming plug flow, the average residence time of fluid is about 10 hours, based on a porosity of ~53%, in the Reactor. Calculation of the porosity in the Reactor was made using the following equation:

$$\text{porosity } (Pt) (\%) = \frac{\text{pore volume } (V_p)}{\text{total volume } (V_t)} \cdot 100$$

Where V_t is the sum of the pore volume (V_p) and the solid volume (V_s).

In all “rock present” experiments (excluding basalt - geothermal brine experiment, BGB1) a small block of basalt (8 x 8 x 2 mm with one polished surface) (Fig. 2.8d) was positioned at the bottom of the Reactor. After sealing the top cap, the Reactor is ready for the experiment (Fig. 2.9c).

Figure 2.8. (a) sequential sieving equipment, Volcanic Petrology Laboratory, GNS Science, Taupo, (b) collected size fractions, (c) the typical appearance of the 355 – 500 μm basalt grains size fraction, (d) example of the basalt block, which was positioned at the bottom of the reactor in all “rock present” experiments (excluding the basalt geothermal brine experiment, BGB1). The front surface of the block has been highly polished.

Figure 2.9. (a) Titanium pressure vessel referred to as the Reactor in this study with end caps, collars and thrust rings. The thrust rings push against the collars to make a cone-type seal against the caps. (b) Reactor filled with basalt grains. Titanium filters are placed at each end of the reactor to prevent passage of rock materials or reaction products. (c) the Reactor assembled.

Once the Reactor is prepared, it is positioned in an aluminium and steel support (Fig. 2.10). The top of the Reactor is connected to a 1/4" titanium exit tube which is then connected to a titanium-lined high temperature and pressure (T-P) valve (Fig. 2.10a). The bottom of the Reactor is connected to 1/8" titanium tubing which provides the experimental fluid from the accumulator vessel. This assembly (Fig. 2.10b) is inserted into the furnace. The high T-P valve is connected with the back-pressure regulator (BPR) and can be closed when necessary to allow maintenance of the BPR.

Figure 2.10. (a) Reactor, 1/4" titanium exit tube, high T-P valve, and aluminium and steel support; (b) Reactor, exit tube, and high T-P valve assembled on the metal support.

2.4.2. Preparation of the Experimental Fluid

In order to remove atmospheric oxygen from the aqueous fluid, approximately 1.5 litre of solution was placed into a 2-litre glass flask (Fig. 2.11). A glass bubbler was inserted into the flask and this was connected to a high purity 100 ppm H₂ in N₂ composition compressed gas cylinder. The gas was bubbled typically for about 10 minutes.

After de-oxygenation, the flask was connected to the accumulator vessel with plastic

tubing and the connecting tubing was evacuated. The plastic tubing from the flask is attached to the accumulator vessel by way of a three-way titanium valve (Fig. 2.11). With both sides of the valve open and a vacuum applied, the entire assembly including the connecting tubing, the 1/8" titanium tubing and the Reactor are evacuated.

When filling the accumulator vessel with experimental fluid, the piston inside the accumulator vessel is positioned at the top (Fig. 2.12) and the volume below the piston is filled with distilled water. To fill the accumulator vessel, the glass flask is opened, filling the plastic tubing with fluid. The pump is then engaged in reverse mode. This causes the distilled water to be drawn out of the accumulator, causing the piston to lower and drawing in the experimental fluid from the flask. This is done at the maximum pump rate of 15 ml min^{-1} .

Figure 2.11. The de-oxygenation apparatus showing the experimental fluid contained in the glass flask. The flask is also connected to the three-way valve at the top of the accumulator vessel.

Figure 2.12. (a) main accumulator vessel; (b) internal view of the accumulator vessel with the movable piston that separates the experimental solution from distilled water below. The metering pump injects distilled water into the bottom of the accumulator vessel. This causes the experimental solution to be force from the top of the accumulator vessel and through the autoclave.

2.4.3. The Back-pressure Regulator and Temperature Control

Pressure in the autoclave is maintained by the back-pressure regulator (BPR) (Fig. 2.13). This is composed of the control unit (Fig. 2.13a,c) and the valve unit (Fig. 2.13b,d). The unit electronically controls the valve and relays pressure information to the computer software. The valve unit comprises back pressure regulation system in which a small reservoir (~1 ml) of vacuum oil is compressed against a PEEK or Teflon diaphragm by a piston. The pressure of the oil determines the pressure in the entire autoclave.

The BPR determines the internal pressure of the autoclave but the metering pump maintains the pressure. The experimental fluid is pushed out of the accumulator vessel and through the Reactor towards the BPR. As the reacted fluid pushes against the plastic diaphragm in the BPR its pressure builds until it equalises that of the vacuum oil, allowing the fluid to leak out into the syringe.

The temperature of the autoclave is controlled by a separate control unit to which are connected four thermocouples, two for each furnace and the analog signals from this unit are converted to digital and recorded by the computer software.

Figure 2.13. (a) the control unit of the back-pressure regulator (BPR); (b) the valve unit of the BPR; (c) schematic view of the BPR showing the vacuum oil syringe (vertical) and sample syringe (horizontal); (d) schematic view of the BPR valve box unit showing the diaphragm, vacuum oil syringe and sample syringe. Blue arrows indicate the direction of the experimental fluid coming from the Reactor.

2.4.4. Experimental Set-up: Water and Geothermal Brine

The experimental set-up for the basalt - water (BW1, BW2) and the basalt - geothermal brine (BGB1, BGB2) experiments is illustrated in Figure 2.14 and Figure 2.15, respectively. In these experiments a single pressure vessel (the Reactor) was used.

In the BW1 and BW2 experiments, the upper part of the accumulator vessel was filled with distilled water and the Reactor with basalt grains. In the BGB1 and BGB2 experiments, the upper chamber of the accumulator vessel was filled with geothermal brine and the Reactor with basalt grains.

Figure 2.14. (a) set-up for the BW1 experiment at 400°C/502 bar; (b) set-up for the BW2 experiment at 350°C/490 bar. In both experiments the upper chamber of the accumulator vessel was filled with water (distilled) which is pushed through the Reactor, up to the BPR, and collects in the collection syringe. Both experiments used basalt grains. The water is shown in blue. Red arrows show the direction of flow of the water.

Figure 2.15. (a) set-up for the BGB1 experiment at 400°C/483 bar; (b) set-up for the BGB2 experiment at 350°C/486 bar. In both experiments the upper chamber of the accumulator vessel was filled with geothermal brine which is pushed through the Reactor, up to the BPR, and collects in the collection syringe. Both experiments used basalt grains. The water is shown in blue. Red arrows show the direction of flow of the water.

2.4.5. Experimental Set-up: Seawater (A New Approach)

With distilled water and geothermal brine experiments, there is no expectation of mineral phases with retrograde solubility precipitating during heating. This, however, is not the case for seawater. The use of seawater as the experimental fluid in a flow-through situation is complicated by the retrograde solubility of minerals such as anhydrite, brucite and magnesium sulfate/hydroxysulfates (Bischoff and Seyfried, 1978b). At the slow flow rates used in the present experiments, mineral precipitation would occur in the 1/8" titanium inlet tubing before entry into the Reactor and would rapidly cause a blockage.

Figure 2.16 shows the saturation indices of four phases: anhydrite (CaSO_4), brucite ($\text{Mg}(\text{OH})_2$), magnesium hydroxysulfate ($\text{MHSH}(\text{Mg}_{1.5})$), and $\text{MgSO}_4(\text{c})$ as average seawater is heated from 25 to 300°C. These were calculated using Geochemist's Workbench[®] (GWB) v. 12 software package (Bethke et al., 2018; Bethke and Yeakel, 2009; Bethke and Yeakel, 2015). At 70°C, seawater saturates with respect to brucite; at 108°C it saturates with respect to anhydrite, and at 193°C, it saturates with respect to Mg hydroxysulfate. GWB's database is limited up to 300°C, however, it is also expected that anhydrous MgSO_4 will saturate just above 300°C. In a simulated GWB run including mineral precipitation, when heating 1 kg of average seawater to 300°C, 1.4 g of anhydrite and 1.3 g of Mg-hydroxysulfate will precipitate. In a flow-through situation, as used in this study, small bore tubing would become quickly blocked after a short period of time. One approach to avoid this is to use synthetic seawater without significant Ca or Mg (Berndt et al., 1989; Gilles et al., 1987; Seewald and Seyfried, 1990; Seyfried et al., 1986; Seyfried and Janecky, 1985). Alternatively, batch-type experiments can be used.

One of the objectives of this study was to develop a method by which natural seawater can be used in a flow-through water-rock interaction simulation. This would allow flow of seawater through the rock, continuously replenishing the rock with "fresh" pore fluid and greatly increasing the integrated fluid/rock ratio.

To our knowledge, there have been no published, geochemically-related, continuous-flow seawater/rock interaction studies. All previous published studies have used batch-type reactors (Berndt and Seyfried, 1993; Berndt et al., 1989; Bischoff and Dickson, 1975; Bischoff and Seyfried, 1978b; Gilles et al., 1987; Hajash, 1975; Mottl and Holland, 1978; Mottl et al., 1979; Seewald and Seyfried, 1990; Seyfried Jr, 1979; Seyfried Jr and Bischoff, 1979; Seyfried and Bischoff, 1977; Seyfried et al., 1986; Seyfried and Bischoff, 1981; Seyfried et al., 1987; Seyfried

and Janecky, 1985; Seyfried and Mottl, 1982; Seyfried et al., 1979).

Figure 2.16. The mineral saturation indices of selected Ca and Mg sulfate/hydroxysulfate phases in seawater with increasing temperature calculated using the Geochemist's Workbench[®] (GWB) v. 12 software package (Bethke et al., 2018).

In order to eliminate the problem of retrograde mineral precipitation when using flowing natural seawater, a new experimental method needed to be developed. It was conjectured that preheating of the water in a larger pressure vessel would allow retrograde phases to precipitate before entering the smaller bore tubing at the bottom of the Reactor containing the rock. It is, however, necessary that permeability along the flow path, while the seawater is being heated, be sufficiently high to prevent blockage. In order to accomplish this, a large pressure vessel was constructed (56 cm in length and 25 cm in diameter and has an internal volume of 71 cm³; Fig. 2.17a,b). The function of the pressure vessel, hereafter referred to as the Preheater, is to allow gradual heating of the seawater up to ~400°C at a sufficiently slow rate to allow precipitation of retrograde phases, thus preventing blockage of the small bore Ti tubing. The Preheater is connected in series with the Reactor containing the rock material (Fig. 2.17c). The seawater enters the top of the Preheater and moves “downwards” to the bottom after which it passes through the connecting tubing and into the bottom of the Reactor which contains the basalt rock.

It is expected that the actual path of the seawater in the Preheater is complex and consists of multiple convection cells, however, the overall result is $\sim 400^{\circ}\text{C}$ seawater leaving the bottom of the Preheater.

Figure 2.17. (a) the Preheater pressure vessel disassembled, (b) the Preheater assembled, (c) the Preheater connected in series with the Reactor vessel.

For the SW experiments using only seawater, the Preheater, without the Reactor, is mounted in the furnace using the metal support. The top 20 cm of the Preheater extends outside of the furnace while the remainder extends down towards the bottom of the furnace. An electric fan is used to cool the top of the Preheater. This creates a large temperature gradient between the top ($\sim 40^{\circ}\text{C}$) and bottom ($\sim 400^{\circ}\text{C}$) of the Preheater (Fig. 2.18).

As this approach had not previously been tested, it was necessary to conduct some preliminary experiments to determine its efficacy. These are included in this section as they are considered method development experiments (Fig. 2.17).

At the beginning of all experiments using seawater, the Preheater and connected tubing are filled with distilled water. This prevents mineral precipitation in the Ti tubing during heat-up. Once the required temperature and pressure are reached, seawater flow is initiated. Chemical analyses of the effluent solutions show that it takes 3 - 7 days for the distilled water to be completely displaced by seawater at 1 ml hr^{-1} depending on the temperature. This shows some degree of turbulent flow in the Preheater as with a plug flow regime it should take only about 71 hours.

The first method development experiment was conducted to test the efficiency of the Preheater at removing retrograde phases (set-up in Fig. 2.18). The temperature in the furnace was at 400°C while the temperature registered at the bottom of the Preheater was 377°C . The pressure was maintained at 490 bar. For expediency, it was performed using synthetic seawater made from Seachem reef salt powder (pH 8.4, $10.8\text{ mmol kg}^{-1}\text{ Ca}$, $53.5\text{ mmol kg}^{-1}\text{ Mg}$, $13.5\text{ mmol kg}^{-1}\text{ K}$ (<https://www.seachem.com/vibrant-sea.php>). Continuous flow at 1 ml hr^{-1} was maintained for 13 days indicating that about 300 g of seawater had passed through the Preheater. At 13 days, pump pressure increased to the safety pressure value (7500 psi/503 bar) and pump flow ceased indicating a blockage. Upon opening of the Preheater, a solid crystalline mineral layer was found at the bottom. This was responsible for the blockage.

Figure 2.18. Experimental set-up with synthetic seawater at 400°C/490 bar. The Preheater extended approximately 20 cm outside the top of the furnace while the remainder of the vessel extended down towards the bottom of the furnace. The Preheater was connected at the top to the main accumulator vessel containing the synthetic seawater (blue) and on the bottom to the back-pressure regulator (BPR). The BPR was fitted with a syringe that collected the synthetic seawater after passing through the Preheater. An electric fan cooled the top of the Preheater which created a temperature gradient from 40°C to 377°C at the bottom. There was no Reactor in this test experiment. The temperature of the Preheater was 377°C at the bottom. The yellow circle on bottom of the Preheater indicates the position of the retrograde phase precipitation which caused the blockage and exceeding of the safety pressure.

As anhydrite saturates at 106°C in seawater, it was expected that precipitates would be found on the walls of the Preheater at a higher level. However, this was not the case and evidently the titanium walls of the Preheater do not provide a suitable nucleation point for anhydrite crystal growth. We conjecture that the mechanism is nucleation in solution and once the crystallites reach a critical size, they settle to the bottom of the Preheater. This test experiment shows that the use of a Preheater vessel for removal of retrograde phases is successful, but the duration before blockage (~13 days) is too short to be useful for this study.

If the above precipitation mechanism is active, then the blockage of the exit point of the Preheater could be prevented by packing the pressure vessel with suitable material to: 1) increase the surface area for precipitation and; 2) prevent crystal nuclei from settling to the bottom. This material must not reduce permeability and be unreactive with the heated seawater. In this study, we used zirconia ceramic beads (2 mm dia) sourced from Zircoa, Inc. (Fig. 2.19). These beads are not large enough to impede fluid flow, provide greatly enhanced surface area in the Preheater and are relatively unreactive, even at high temperatures. The beads are composed of predominantly of ZrO_2 (~97%) and MgO (~3%), with minor concentrations at <0.30% each of SiO_2 , CaO , Fe_2O_3 , Al_2O_3 , TiO_2 . For all the experiments described in this thesis, the Preheater was filled 2/3 with zirconia beads (Fig. 2.19).

Figure 2.19. (a) zirconia beads sourced from Zircoa, Inc. (2 mm dia); (b) Preheater filled with zirconia beads 2/3rd full. Black circles indicate where thermocouples were positioned to measure the temperature at the top and bottom of the vessel during experiment.

To differentiate the effects of fluid-rock interaction from those caused by the fluid-zirconia interaction, two control experiments, SW1 and SW2, were conducted. The set-up for these experiments involves use of the Preheater vessel containing zirconia beads without use of the Reactor vessel (Fig. 2.20a and 2.21a). While, for the fluid-rock interaction experiments BSW1 and BSW2, the set-up involved the use of the Preheater filled with zirconia beads connected in series to the Reactor containing the basalt rock fragments (Fig. 2.20b and 2.21b).

The ideal temperature for the SW1 and BSW1 experiments was 400°C and 350°C for the SW2 and BSW2 experiments. The experimental configuration involved positioning the top 1/3 of the Preheater outside the furnace and the bottom 2/3 in the furnace. The top cooled by a fan resulting in a temperature ~40°C at the top of the Preheater, however, the maximum temperature at the bottom of the Preheater was 377°C in SW1 and BSW1 and 342°C for SW2 and BSW2. The temperature for the Reactor in BSW1 and BSW2 was 400°C and 350°C, respectively (Fig. 2.20b and 2.21b). The difference in temperature between the bottom of the Preheater and the Reactor is due to rapid heat conduction up the Preheater vessel and out of the furnace. A pressure of 488 bar was maintained constant for all experimental configurations.

Figure 2.20. (a) experimental set-up of the seawater-only experiment (SW1) at 400°C/488 bar. The Preheater extended approximately 20 cm outside the top of the furnace while the remainder of the vessel extended down towards the bottom of the furnace. The Preheater is 2/3 filled with zirconia beads. It was connected at the top to the main accumulator vessel containing the natural seawater (blue) and on the bottom to the back-pressure regulator (BPR). The BPR was fitted with a syringe that collected the seawater after passing through the zirconia beads. An electric fan cooled the top of the Preheater which created a temperature gradient from 40°C at the top to 377°C at the bottom. There was no Reactor in this experiment. (b) experimental set-up of the basalt-seawater experiment at 400°C/488 bar (BSW1). The Preheater was 2/3 filled with zirconia beads. It was connected at the top to the main accumulator vessel containing natural seawater (blue) and on the bottom to the Reactor containing the basalt fragments. The temperature gradient between the top and the bottom of the Preheater was 40°C to 377°C. The temperature of the Reactor was 400°C.

Figure 2.21. (a) experimental set-up of the seawater-only experiment (SW2) at 350°C/488 bar. The Preheater extended approximately 20 cm outside the top of the furnace while the remainder of the vessel extended down towards the bottom of the furnace. The Preheater is 2/3 filled with zirconia beads. It was connected at the top to the main accumulator vessel containing the natural seawater (blue) and on the bottom to the back-pressure regulator (BPR). The BPR was fitted with a syringe that collected the seawater after passing through the zirconia beads. An electric fan cooled the top of the Preheater which created a temperature gradient from 40°C at the top to 342°C at the bottom. There was no Reactor in this experiment. (b) experimental set-up of the basalt-seawater experiment at 350°C/488 bar (BSW2). The Preheater was 2/3 filled with zirconia beads. It was connected at the top to the main accumulator vessel containing natural seawater (blue) and on the bottom to the Reactor containing the basalt fragments. The temperature gradient between the top and the bottom of the Preheater is 40°C to 342°C. The temperature of the Reactor was 350°C.

2.5. Analytical Techniques

2.5.1. Rock material

The methods of analysis of the mineralogical and chemical composition both of unreacted and reacted rock material are listed in Table 2.6. These included:

1. scanning electron microscopy with energy dispersive spectroscopy (SEM-EDS) using instruments at the Research Centre for Surface and Materials Science, University of Auckland, New Zealand and at the Wairakei Research Centre, GNS Science, New Zealand;
2. X-ray diffraction (XRD) performed at the Callaghan Innovation Centre, Lower Hutt, New Zealand. The X-ray diffraction data was collected using a Philips X'Pert Pro (P1700 series) instrument utilising CoK α radiation and the following operating conditions:

Start Position [$^{\circ}2\theta$]	3.000
End Position [$^{\circ}2\theta$]	80.000
Step Size [$^{\circ}2\theta$]	0.050
Scan Step Time [s]	1.00
Generator Settings	40 kV, 35 mA

The mineralogy of the samples was determined using PANalytical interpretive software *X'Pert High Score*;

3. X-ray fluorescence (XRF) analysed by SpectraChem, CRL Energy Ltd, Lower Hutt, New Zealand. Multi-element analysis of the samples was performed using the following method: Pressed powder / X-ray spectrometry/ Spectraplus SQ46. The values are reported as wt% with Lower Level Detection (LLD) of 0.001; and
4. electron microprobe analysis (EMPA) performed at the College of Earth, Ocean, and Atmospheric Sciences, Electron Microprobe Laboratory, Oregon State University, Corvallis, United States. The EMPA analysis were conducted using a Cameca SX100 electron microprobe with a 30 nA beam current, 15 kV accelerating potential, and 5 μ m beam diameter.

2.5.2. Experimental Fluids (initial and reacted)

The methods used to analyse the experimental solutions (effluents), both initial and unreacted, are listed in Table 2.7. These included:

1. inductively-coupled plasma optical emission spectroscopy analysis (ICP-OES) for Li, Na,

K, Mg, Ca, Sr, Mn, Fe, As, Al, B and SiO₂ with detection limits of Li, 0.01; Na, 0.8; K, 0.9; Mg, 0.01; Ca, 0.05; Sr, 0.003; Mn, 0.007; Fe, 0.08; As, 0.015; Al, 0.15; B, 0.3; Si, 0.6 mg kg⁻¹. The major cation concentrations were measured by inductively-coupled plasma-optical emission spectroscopy (ICP-OES) with a Thermo Scientific iCap 7600 Duo ICP-OES with a ceramic plasma torch, quartz spray chamber and nebulizer with attached Cetac ASX-520 Autosampler, and Qtegra software. The aliquots for ICP-OES analysis were acidified with HNO₃;

2. ion chromatography analysis (IC) for chloride and sulfate with detection limits of Cl, 0.04 and SO₄, 0.1 mg kg⁻¹. Anions were analysed with a DIONEX ICS 5000 ion chromatograph with AS14 Column and attached AS 50 Autosampler, and Chromeleon software;
3. total reduced sulfur as H₂S by UV-Vis spectroscopy using the methylene blue method with a detection limit of 0.01 mg kg⁻¹. The concentrations of hydrogen sulfide were determined spectrophotometrically with a Dynamica DB-30 UV/VIS spectrophotometer;
4. quench (room temperature) pH, using a pH electrode and standard pH buffers. The pH of the experimental solutions was measured with a Metrohm pH meter (with a temperature probe). The pH meter was calibrated against standard buffer solutions daily.

All the above methods were performed at the Wairakei Research Centre, GNS Science, New Zealand. Samples for ICP-OES analysis were diluted and acidified using with HNO₃ to 0.5% acid by weight. Samples for IC and H₂S analysis were diluted with doubly-distilled water.

Selected effluents were also analysed for trace metal concentrations using inductively coupled plasma mass spectroscopy (ICP-MS) for Co, Ni, Cu, Zn, Mo, Ag, Cd, Ba, Au, Pb, Cr, V, Rb. Detection limits for elements were as follow: Co, < 0.05; Ni, < 0.20; Cu, < 0.06; Zn, < 0.50; Mo, < 0.20; Ag, < 0.05; Cd, < 0.10; Ba, < 0.20; Au, < 0.20; Pb, < 0.20; Cr, < 0.20; V, < 0.10; and Rb, < 0.10 µg L⁻¹. Solutions were diluted with doubly-distilled water and acidified to 0.5% using ultrapure HNO₃. Samples were analysed at Edith Cowan University, Science Analytical Facility Laboratories, Perth, Australia. Trace elements were analysed by ICP-MS system and autosampler iCAP Q ICP-MS (S/N IC76DC141606) ASX-520 AutoSampler by Thermo-Fisher Scientific; Teledyne Cetac (Omaha, USA).

Note that CO₂ concentrations were not measured on the effluent samples due to the large sample size required (50 ml). Four measurements of total inorganic carbon as HCO₃⁻ were measured during the BSW1 and BSW2 experiments when flow rate was 10 ml hr⁻¹. These ranged from 24 - 99 mg kg⁻¹. CO₂ in distilled water and the geothermal brine are both <20 mg kg⁻¹. The CO₂ quantification was made using a Metrohm 809 Titrino automatic titrator with a Metrohm 814 Sample Processor, Metrohm 834 Pump Station, and Tiamo software 2.5-2014.

Table 2.6. Mineralogical and chemical analytical methods for unreacted and reacted rock materials

	Unreacted Material	BW1	BW2	BGB1	BGB2	SW1	BSW1	SW2	BSW2
SEM-EDS	<ul style="list-style-type: none"> • Fresh basalt grains • Basalt blocks polished surface 	<ul style="list-style-type: none"> • Reacted basalt grains (bottom and top of Reactor) • Reacted basalt block surface 	<ul style="list-style-type: none"> • Reacted basalt grains • Reacted basalt block surface 	<ul style="list-style-type: none"> • Reacted basalt grains (bottom and top of Reactor) 	<ul style="list-style-type: none"> • Reacted basalt grains (bottom and top of Reactor) • Reacted basalt block surface 	<ul style="list-style-type: none"> • Zirconia beads (Preheater) 	<ul style="list-style-type: none"> • Reacted basalt grains (bottom, middle and top of Reactor) • Reacted basalt block 	<ul style="list-style-type: none"> • Zirconia beads (Preheater) 	<ul style="list-style-type: none"> • Reacted basalt grains (bottom, middle and top of the Reactor) • Reacted basalt block
XRD		<ul style="list-style-type: none"> • Reacted basalt grains (bottom and top of the Reactor) 	<ul style="list-style-type: none"> • Reacted basalt grains (bottom and top of the Reactor) 	<ul style="list-style-type: none"> • Reacted basalt grains (bottom and top of the Reactor) 	<ul style="list-style-type: none"> • Reacted basalt grains (bottom and top of the Reactor) 		<ul style="list-style-type: none"> • Reacted basalt grains (bottom, middle and top of Reactor) 		<ul style="list-style-type: none"> • Reacted basalt grains (bottom, middle and top of Reactor)
XRF	<ul style="list-style-type: none"> • Unreacted rock powder 						<ul style="list-style-type: none"> • Reacted basalt grains (bottom, middle and top of Reactor) 		<ul style="list-style-type: none"> • Reacted basalt grains (bottom, middle and top of Reactor)
EMPA	<ul style="list-style-type: none"> • Fresh basalt rock thin section 	<ul style="list-style-type: none"> • Reacted basalt grains (bottom of Reactor) 	<ul style="list-style-type: none"> • Reacted basalt grains (bottom of Reactor) 	<ul style="list-style-type: none"> • Reacted basalt grains (bottom of Reactor) 	<ul style="list-style-type: none"> • Reacted basalt grains (bottom of Reactor) 				

Table 2.7. Chemical analytical methods for experimental solutions

	Starting fluids	BW1	BW2	BGB1	BGB2	SW1	BSW1	SW2	BSW2
ICP-OES	Yes	Yes	Yes	Yes	Yes	Yes	Yes	Yes	Yes
IC	Yes	Yes	Yes	Yes	Yes	Yes	Yes	Yes	Yes
H₂S	No	Yes	Yes	Yes	Yes	No	Yes	No	Yes
ICP-MS	Yes	Yes	Yes	Yes	Yes	Yes	Yes	Yes	Yes

2.6. Determination of experimental pH and solute speciation at high temperature and pressure conditions (325-400°C and 500 bar)

The calculation of solute activities at high temperature and pressure is necessary to determine experimental pH and mineral saturation indices at experimental conditions. This requires consideration of all the relevant equilibria. Several computational software packages are available to calculate such equilibria but are restricted by the temperature limitation of their databases (e.g. Geochemist's Workbench[®], $\leq 300^\circ\text{C}$). However, all experiments in the current study were conducted at temperatures $\geq 342^\circ\text{C}$ and these software packages are not applicable.

To properly quantify the mechanisms that control the chemical exchanges between fluid and rock at hydrothermal conditions, several chemical and thermodynamic concepts must be considered. These include:

1. all relevant chemical equilibria (solution and mineral);
2. the concentrations of dissolved species (molal, m_i);
3. the activity coefficients all these species (γ_i);
4. the solution ionic strength (I).

The calculation of mineral solubility and solute concentration and speciation are based on equilibrium thermodynamics. To evaluate the state of equilibrium for a given reaction, the concentration of reactants and products and the equilibrium constant of the reaction, K , are required. For simple reaction,

The equilibrium constant is expressed as

$$K = \frac{a_{\text{C}}^z}{a_{\text{A}}^x \cdot a_{\text{B}}^y} \quad (2)$$

where $[a_i]$ are the species' activities.

A species activity [a_i] is related to its concentration (m_i) through the activity coefficient, γ_i , by

$$a_i = m_i \cdot \gamma_i \quad (3)$$

and Equation (2) can be written as

$$K = \frac{[m_C \cdot \gamma_C]^z}{[m_A \cdot \gamma_A]^x \cdot [m_B \cdot \gamma_B]^y} \quad (4)$$

Where $m_{(i)}$ and $\gamma_{(i)}$ is the concentration and the activity coefficient of species, i , respectively.

The activities coefficients are a function of ionic strength (I) as given by the extended Debye-Hückel expression (Helgeson, 1969)

$$-\log \gamma_i = \frac{A z_i^2 \sqrt{I}}{1 + B a_i \sqrt{I}} + \bar{B} \cdot I \quad (5)$$

and

$$I = \frac{1}{2} \sum m_i \cdot z_i^2 \quad (6)$$

where I is the ionic strength, z_i is the ion charge, A , B , and $\bar{B}$ are temperature dependent constants and a is the ion size parameter.

In this study, an iterative approach is taken to simplify the calculation. This method “tracks” all the species present, distributing the total concentration of each species in solution. An Excel spread-sheet has been developed that is linked to the software package EqSolvr (Stefan Mroczek and Ed Mroczek, 2017) (<https://github.com/shearwavesplitter/EqSolvr>), an equilibrium solver based on the Newton-Raphson method. This spreadsheet can perform iterative computations between all geochemical equations and parameters to calculate the speciation and, consequently, the pH at the experimental temperature and pressure.

The iterative approach uses a non-linear system of equations in including:

1. the mass action equations (e.g. Equation 1);
2. the mass balance equations;
3. the charge balance equation.

An example of a mass balance equation is, for example, that for Na

$$m_{\text{Na total}} = m_{\text{Na}^+} + m_{\text{NaOH}^\circ} + m_{\text{NaCl}^\circ} + m_{\text{NaSO}_4^{2-}} + m_{\text{NaCl}^-} \quad (7)$$

where m_i is the species' concentration in molality.

The charge balance equation (solutions are assumed to be electrically neutral) can be expressed as

$$\sum [\text{positive charge}] = \sum [\text{negative charge}] \quad (8)$$

All relevant aqueous species are considered and their thermodynamic data utilised including: $\log K$ (325, 350, 375, 400°C and 500 bar), A , B and $\tilde{B}$ parameters for Equation (6) (350, 375, 400°C and 500 bar), z_i and $\tilde{a}_i$, are listed in Table 2.8. Equilibrium constants ($\log K$) were calculated using Supcrt.92 slop98.dat (<https://reaktoro.org/thermodynamic-databases.html>). The Debye-Hückel parameters (A , B and $\tilde{B}$) data were sourced from (Helgeson and Kirkham, 1974).

Table 2.8. Aqueous species and parameters used in the equilibrium solver spread-sheet linked to EqSolvR (Stefan Mroczek and Ed Mroczek, 2017). Log K data taken from Supcrt.92 slop98.dat database (<http://geopig.asu.edu/?q=tools>). The Debye-Hückel parameters (*A*, *B* and *B-dot*) data were sourced from (Helgeson and Kirkham, 1974).

	Log K	Log K	Log K	Log K	<i>z</i>	$\bar{a}$ (10 ⁻⁸ cm)	<i>A</i>	<i>B</i>	<i>A</i>	<i>B</i>	<i>A</i>	<i>B</i>	<i>B-dot</i>	<i>B-dot</i>
	325°C/ 500 bar	350°C/ 500 bar	375°C/ 500 bar	400°C/ 500 bar			350°C/ 500 bar	350°C/ 500 bar	375°C/ 500 bar	375°C/ 500 bar	400°C/ 500 bar	400°C/ 500 bar	350, 375, 400°C	at 350, 375, 400°C
							1.3267	0.4004	1.5464	0.4104	1.8789	0.423	0	0
Aqueous species														
H ⁺					1	9								
OH ⁻					-1	4								
Cl ⁻					-1	3.5								
K ⁺					1	3								
Na ⁺					1	4								
SO ₄ ²⁻					-2	4								
Ca ²⁺					2	6								
Mg ²⁺					2	8								
Fe ²⁺					2	6								
H ₂ O	-10.976	-11.112	-11.159	-11.356										
NaCl°	-0.899	-1.184	-1.383	-1.737	0	0								
KCl°	-0.271	-0.590	-0.841	-1.236	0	0								
HCl°	-1.174	-1.601	-2.033	-2.689	0	0								
KOH°	-0.849	-1.080	-1.187	-1.446	0	0								
NaOH°	-0.615	-0.840	-0.922	-1.164	0	0								
NaSO ₄ ⁻	-2.725	-3.055	-3.219	-3.549	-1	4								
HSO ₄ ⁻	-6.190	-6.652	-6.975	-7.444	-1	4								
KSO ₄ ⁻	-3.003	-3.351	-3.541	-3.899	-1	4								
MgCl ⁺	-2.216	-2.594	-2.809	-3.180	1	8								
FeCl ⁺	-6.598	-6.476	-6.153	-5.745	1	6								
CaCl ⁺	-2.647	-3.061	-3.298	-3.692	1	6								
CaCl ₂ °	-2.932	-3.633	-4.048	-4.783	0	0								
MgOH ⁺	-5.197	-5.610	-5.800	-6.149	1	8								
CaOH ⁺	-4.724	-5.139	-5.308	-5.635	1	6								
CaSO ₄ °	-4.874	-5.424	-5.638	-6.173	0	0								
MgSO ₄ °	-4.898	-5.439	-5.565	-6.014	0	0								
FeSO ₄ °		-3.6129		-3.8140	0	0								

Mineral saturation index (SI)

A mineral saturation index (SI) is a measure of the degree to which a solution is in equilibrium with respect to a specific mineral. It is defined as the ratio of the ion activity product (IAP or Q) for that mineral's solubility reaction to equilibrium solubility product K_{sp} (Clark, 2015):

$$SI = \frac{IAP}{K_{sp}} \quad (9)$$

when

$SI > 1$ or $\log SI > 0$	the mineral is supersaturated
$SI = 1$ or $\log SI = 0$	the mineral is in equilibrium with solution
$SI < 1$ or $\log SI < 0$	the mineral is undersaturated

Activity-activity diagrams

Activity-activity diagrams show mineral stability fields in contact with the aqueous phase. They plot the activity of an un-associated free ion versus a second ion at the specified T and P. It is normal to plot the logarithm of the free ion's activity divided by the activity of the hydrogen ion (10^{-pH}) effectively allowing a third degree of freedom in the phase diagram (eg. Fig. 2.22). These diagrams provide a convenient graphical method of representing solution mineral saturations and for predicting the consequences of mineral reactions (Bowers et al., 1984).

In this study, experimental results have been plotted on these diagrams to evaluate the degree to which natural analogues match theoretical representations. Plotting multiple sample flow-through results allows monitoring of the path of fluid-rock interactions. These graphical representations can also give some information on the “speed” of the geochemical reactions.

Figure 2.22. An example of an activity-activity diagram used in this study. This diagram plots the ratio of the free activity of Na divided by the activity of the hydrogen ion versus the same for potassium at 400°C and 500 bar. The diagram shows the mineral stability fields in contact with an aqueous phase for the minerals: albite (alb), K-feldspar (K-spar), paragonite (parag), muscovite (musc) and andalusite (and).

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Chapter 3: Basalt - Water Interactions under Hydrothermal Conditions

3.1. A brief introduction

Water occurs ubiquitously throughout the Earth's crust where it can react with rocks at elevated temperatures and pressures. Of particular interest are basalt - water and basalt - seawater interactions which have important applications to sub-seafloor environments and the evolution of hydrothermal discharges into the oceans. Despite the fundamental importance of reactions, there are relatively few experimental studies designed to provide insight into the chemistry of heterogeneous basalt - water equilibria. A number of basalt - water reactions and dissolution rates have been studied at subcritical and supercritical conditions with pure water using packed-bed reactors systems (Ronghua et al., 2000; Ronghua et al., 2002; Zhang et al., 2011; Zhang et al., 1990; Zhang et al., 2007). More recently, Zhang et al. (2015) studied the dissolution and reaction kinetics of basalt - water interaction up to 400°C and 23 MPa using a packed-bed reactor.

In this chapter, we report the results of two experiments simulating basalt - water interaction carried out using a high T-P flow-through apparatus. These were named BW1 - 400°C/502 bar (supercritical water) and BW2 - 350°C/490 bar (subcritical water).

Our results indicate that water reacts aggressively with the basalt both at supercritical and subcritical conditions. Major changes in solution chemistry are evident, in both experiments, after the temperature shift. These changes consist of: 1) an increase in solution of all major ions and generation of H_2S , SO_4^{2-} and Cl^- ; 2) moderate mobility of the trace elements in solution; and 3) the rise of pH to alkaline values. Major ion concentrations were higher at 350°C than at 400°C whereas the concentrations of the trace elements were lower. Analysis of the reacted basalt was conducted on grains collected both from the bottom and top positions in the Reactor at the conclusion of the experiments. Results show that the bottom portion of the Reactor (first 1-2 mm), located at the entry point of the unreacted fluid, was the most altered portion of the basalt. While the top portion (upper 1-2 mm), located at the exit point of the reacted fluid into Reactor, represented the least altered portion of the basalt.

3.2. Results

In this chapter the results are presented for the:

- 1) major element analyses of experimental solutions;
- 2) trace element analyses of experimental solutions;
- 3) chemical, mineralogical and textural analyses of reacted basalt grains

Appendix B contains complete XRD, EMPA and SEM-EDS results as well as quantitative analyses for the reacted material for both experiments. Note that SEM-EDS and EMPA analysis cannot measure the hydrogen content. For this reason, all mineral chemistries were normalised to 100% anhydrous (ignoring water content), for both experiments.

3.2.1. BW1: Basalt – water at 400°C/502 bar

The first basalt - water experiment (BW1) ran for 913.5 hr. The first 144.2 hr were at room temperature and 502 bar and the remaining 769 hr were at 400°C and 502 bar. The flow rate was 1 ml hr⁻¹ up to 819.1 hr after which it was changed to 0.5 ml hr⁻¹ for the remaining 94.4 hr. The flow-rate was set-up to guarantee the collection of enough solution for all chemical analyses at each approximately 24 hours interval. During this experiment, analyses of major ions were conducted for the total number (36) of the fluid samples collected. Analyses of trace elements were made for the first 30 fluid samples collected.

3.2.1.1. Major element concentrations

Appendix B lists the complete experimental parameters (T, P, flow rate, chemistry). Figure 3.1 and Figure 3.2 show these results plotted against time in hours. The unreacted distilled water composition is shown at $t = 0$. Trace concentrations of Ca (0.01 mmol kg⁻¹) and K (0.01 mmol kg⁻¹) were detected in this analysis. All other major elements were below detection limit.

During the room temperature (~21°C) period, no significant changes in solution composition are evident. The pH values are on average lower than the starting blank but are quite irregular. Ca and K remain stable reflecting the composition of the input solution.

The change in temperature to 400°C was initiated at 144 hours and took about 3 hours, thus only about 3 ml of solution were in contact with the rock during heat-up. Major changes in solution chemistry are evident after the temperature shift.

Effluent quench pH (ambient temperature) slowly increases from just below 7 at 144 hours to about 9 by 450 hours. It remains near this alkaline value for the remainder of the experiment. The calculated *in situ* pH at 400°C declines from 7 after the temperature shift to 5.8 by the end of the experiment.

SiO₂ increases to 33.2 mmol kg⁻¹ (1994 ppm) which exceeds quartz saturation at 400°C/500 bar (1238 ppm, Supcrt92). Between 200 and 400 hours, silica concentration remains elevated but then after about 400 hours, the silica concentration rapidly decreases over about four days to 11 mmol kg⁻¹ then declines gradually to 7.8 mmol kg⁻¹ by the end of the experiment.

Both Na and K show a sharp increase after the temperature shift and then decline over the next five days before increasing again at 450 hours. After this, their behaviours diverge with Na slowly increasing to 1.8 mmol kg⁻¹ and remaining near this value for the remainder of the experiment. Potassium increases to a maximum of 0.35 mmol kg⁻¹ and then declines, rapidly at first, then slowly to about 0.075 mmol kg⁻¹ by 914 hours.

Al concentration remains at about 0.2 mmol kg⁻¹ up to 450 hours after which it increases sharply to 0.75 mmol kg⁻¹ within 24 hours, finally reaching a maximum of 0.9 mmol kg⁻¹ at 850 hours. Ca concentration is elevated in only the first four samples after the temperature increase, after which it decreases to about 0.02 mmol kg⁻¹ and remains near this value for the remainder of the experiment. Fe and Mg increase to 0.04 and 0.02 mmol kg⁻¹, respectively, immediately after temperature increase and then decline to values near or below detection limit over the remaining time.

SO₄ and Cl show similar behaviour to Fe with their maximum values of 0.2 and 0.5 mmol kg⁻¹, respectively, occurring immediately after temperature increase, then decline to near detection limit values over the remainder of the experiment. H₂S concentration increases to a maximum of 0.085 mmol kg⁻¹ two days after temperature increase. It then declines in a linear manner over the next ten days after which it remains at 0.01 mmol kg⁻¹ for the remaining time.

The change in flow rate to 0.5 ml hr⁻¹ (the final two effluent samples) did not cause any significant effects on elemental concentrations and pH values (i.e., fluid composition remains fairly stable during the last 94.4 hrs of experiment).

Figure 3.1. Major element concentrations in blank and effluent samples (mmol kg^{-1}) versus time (hr) for the basalt-water experiment at $400^\circ\text{C}/502$ bar (BW1). Yellow symbols are blank sample composition of the water. Blue symbols are for effluents at room T/502 bar and 1.0 ml hr^{-1} . Black symbols are effluents at $400^\circ\text{C}/502$ bar and 1.0 ml hr^{-1} flow rate. Red symbols are effluents at $400^\circ\text{C}/502$ bar and 0.5 ml hr^{-1} flow rate. *In situ* pH is the calculated pH at temperature. The limit of detection (LOD) is shown for each component.

Figure 3.2. Major element concentrations in blank and effluent samples (mmol kg^{-1}) versus time (hr) for the basalt-water experiment at $400^\circ\text{C}/502$ bar (BW1). Yellow symbols are blank sample composition of the water. Blue symbols are for effluents at room T/ 502 bar and 1.0 ml hr^{-1} . Black symbols are effluents at $400^\circ\text{C}/502$ bar and 1.0 ml hr^{-1} flow rate. Red symbols are effluents at $400^\circ\text{C}/502$ bar and 0.5 ml hr^{-1} flow rate. The limit of detection (LOD) is shown for each component.

3.2.1.2. Trace element concentrations

Appendix B lists the complete trace element results. Figure 3.3 and Figure 3.4 show these results plotted against time in hours. The unreacted distilled water composition is shown at $t = 0$. All trace element concentrations are below detection limit in the starting solution.

During the room temperature ($\sim 21^{\circ}\text{C}$) period, measurable overall increases in Co, Ni, Cr, Mo and, in particular, Zn are present. There are two elevated values for Au that are likely analytical noise. The high and erratic values of Zn, that are similar in magnitude to those found for the remainder of the experiment, suggest an artefact of the method rather than meaningful values due to water-rock interaction. The concentrations of Ag remain below detection limit throughout the experiment.

After the temperature shift to 400°C , several trace elements noticeably increase in concentration including Co, Au, Ni, Rb, Cd, Pb, Cr, Cu, Mo, Ba and Mn. For the remainder of the experiment several behaviours are observed. Co, Cr, and Cu decrease over 150 to 200 hours to relatively constant but elevated values. Mn declines below detection limit after 280 hours, while Mo decreases gradually over the whole experiment. Zn and Au display irregular values that show no particular trend over time. The Pb concentration increases slightly after temperature shift. V displays a gradual increase in concentration over time. Finally, Ba and Rb decline to minimums at 250 and 300 hours, respectively, after which they increase again to reach maximums at 330 and 400 hours, and then decrease over the remainder of the experiment.

Figure 3.3. Trace element concentrations in blank and effluent samples ($\mu\text{mol kg}^{-1}$) versus time (hr) for the basalt-water experiment at 400°C/502 bar (BW1). Yellow symbols are the blank sample composition of the water. Blue symbols are for effluents at room T/502 bar and 1.0 ml hr⁻¹ flow rate. Black symbols are effluents at 400°C/502 bar and 1.0 ml hr⁻¹ flow rate. *In situ* pH is the calculated pH at temperature. The limit of detection (LOD) is shown for each component.

Figure 3.4. Trace element concentrations in blank and effluent samples ($\mu\text{mol kg}^{-1}$) versus time (hr) for the basalt-water experiment at $400^\circ\text{C}/502$ bar (BW1). Yellow symbols are the blank sample composition of the water. Blue symbols are for effluents at room T/ 502 bar and 1.0 ml hr^{-1} flow rate. Black symbols are effluents at $400^\circ\text{C}/502$ bar and 1.0 ml hr^{-1} flow rate. The limit of detection (LOD) is shown for each component.

3.2.1.3. Mineralogy and Texture of Reacted Basalt: Bottom of the Reactor (Portion 1)

Upon the conclusion of the experiment, the reacted basalt grains were extracted from the Reactor onto absorbent paper. They were rinsed with distilled water to remove precipitated soluble salts such as NaCl and KCl and then air-dried. A portion of grains were collected from the bottom of the Reactor (Portion 1) and one portion was collected from the top of the Reactor (Portion 2) (Fig. 3.5). Note that no reacted grains in between Portion 1 and Portion 2 were collected for analysis. We estimate that there are more than 200,000 basalt grains in each experiment.

In this section we report the results of mineralogical and textural analysis of grains from the bottom of the Reactor (Portion 1). This portion is located at the entry point of the unreacted fluid into the Reactor.

Selected grains were mounted on aluminium stubs for textural analyses by SEM and several grains were epoxy-mounted and polished for SEM-EDS and EMPA analysis. Appendix B contains all SEM and EMPA results for Portion 1 (bottom of the Reactor).

Figure 3.5. Schematic diagram of the Reactor showing position (Portion 1 and Portion 2) of reacted basalt grains shown in SEM photographs and the position of the basalt block for the BW1 experiment. The picture is not to scale.

SEM-EDS and EMPA analysis

Grains from immediately adjacent to the fluid entry point of Portion 1 were examined. Extensive alteration of the basalt leading to strong residual Ca-metasomatism (in the sense that the resulting phases are predominantly Ca minerals, i.e., Ca was not added from the fluid) was observed. The minerals of secondary origin detected were: anorthite, wollastonite, grossular, chlorite and magnetite. The presence of remnant, unreacted primary bytownite, clinopyroxene, olivine, and titanomagnetite (Table 3.1) was noted.

Table 3.1. Mineral assemblage detected by EMPA and SEM-EDS analysis of reacted grains extracted from bottom (Portion 1) of the Reactor after the BW1 experiment. Appendix B contains all SEM and EMPA results for this portion of the rock.

Type of Analysis	Analysis Material	Mineral Identified	Average Mineral Composition
EMPA	polished grains	Anorthite	$\text{Ca}_{0.98}\text{Al}_2\text{Si}_2\text{O}_8$ (An ₉₈ -Ab ₂)
SEM-EDS	polished grains	Bytownite	$\text{Ca}_{0.68}\text{Na}_{0.28}\text{Si}_{2.40}\text{Al}_{1.65}\text{O}_8$ (An ₇₁ -Ab ₂₉)
EMPA	polished grains	Augite	$\text{Ca}_{0.70}\text{Mg}_{0.83}\text{Fe}_{0.36}\text{Si}_2\text{O}_6$
EMPA	polished grains	Forsterite	$\text{Mg}_{1.4}\text{Fe}_{0.6}\text{SiO}_4$ (Fo ₇₀ -Fa ₃₀)
SEM-EDS	polished grains	Titanomagnetite	$\text{Fe}^{2+}(\text{Fe}^{3+}, \text{Ti})_2\text{O}_4$
SEM-EDS	polished grains	Magnetite	$\text{Fe}^{3+}\text{Fe}^{2+}_2\text{O}_4$
EMPA	polished grains	Chlorite	$\text{Mg}_{3.6}\text{Fe}_{1.4}\text{Al}_{0.8}\text{Si}_{3.4}\text{Al}_{0.5}\text{O}_{10}(\text{OH})_8$ (calculated based on the anhydrous composition with 14 oxygens)
EMPA	polished grains	Wollastonite	$\text{Ca}_{0.98}\text{Si}_{0.96}\text{O}_3$
EMPA	polished grains	Grossular	$\text{Ca}_{6.32}\text{Mg}_{0.16}\text{Ti}_{0.27}\text{Fe}_{1.87}\text{Al}_{1.75}\text{Si}_{6.23}\text{O}_{24}$

Figure 3.6 shows SEM images of the most reacted grains from the position immediately next to the entry point of the fluid (Portion1, Fig. 3.5). Wollastonite appears in groupings of acicular crystals, surrounding and surrounded by euhedral grossular garnet crystals occurring in dense aggregates. Anorthite occurs as anhedral fenestral pseudomorphs of plagioclase. Chlorite appears as aggregates of dense flakes in botryoidal masses. The intense alteration indicates that this is the most reacted portion of the basalt coinciding with the entry point of the unreacted fluid. Petrographic observation shows that the wollastonite laths are white in colour while the garnets are brown, common with grossular (composition confirmed by EMPA analysis).

Figure 3.7 shows SEM backscatter images and EDS maps of a polished mount of one of the grains described above. The grain is highly corroded with primary clinopyroxene (violet), titanomagnetite (green), and minor amounts of remnant plagioclase remaining. Wollastonite laths (pink acicular) fill the void spaces left by primary plagioclase. The

hydrothermal (secondary) plagioclase is anorthitic, however, relicts of the primary bytownite were also found by SEM-EDS. Clinopyroxene appears relatively unaffected when compared with the plagioclase. SEM-EDS analysis confirm the presence of primary titanomagnetite as well as the formation of secondary magnetite.

Figure 3.6. (a-f) SEM images of reacted grains collected from the immediately adjacent to the fluid entry point (bottom, Portion 1) after the BW1 experiment (minerals were identified by SEM-EDS analysis): (a) grain entirely covered by wollastonite (Wo) occurring in groupings of acicular crystals and by garnet (Grt) which appears in well-formed dodecahedral crystals; (b) clusters of garnet crystals with sparse wollastonite; (c) enlargement of area in (b) (red rectangle) showing in more detail the wollastonite and garnet; (d) secondary plagioclase of anorthitic (An) composition, wollastonite (Wo) and visibly altered primary clinopyroxene (Cpx); (e) a reacted grain surface (enlargement) showing acicular wollastonite (Wo), euhedral garnet (Grt), and relict clinopyroxene (Cpx); (f) grain surface completely replaced by chlorite appearing as botryoidal masses composed of densely intergrown flakes.

Figure 3.7. SEM backscatter image and EDS compositional maps of an epoxy-mounted, polished grain from the bottom portion of the BW1 experiment: (a) backscatter image; (b) composite colour image combining the backscatter image and elemental maps for c) Fe in green, d) Mg in blue, and e) Ca in red. The composite image shows needles of wollastonite (pink acicular) and primary clinopyroxene (violet), plagioclase (anhedral pink remnants), and Fe oxide (green).

Figure 3.8 shows SEM backscatter images and EDS maps of a polished mount of one grain from about 2 mm further up the reactor (Portion 1) (Fig. 3.5). This grain shows the presence of garnet (pink in Fig. 3.8c) and plagioclase (green). No wollastonite is observed. Primary clinopyroxene is relatively unaltered while plagioclase is clearly altered but to a lesser extent than the grain in Figure 3.7a. The plagioclase displays a corroded fenestral texture and is anorthitic in composition. Titanomagnetite is unaltered.

Figure 3.9 shows a grain composed originally entirely of olivine (red) located from the same position in the Reactor as the previous grain. The grain is surrounded by a thick coating of chlorite (violet).

Figure 3.10a-e shows a further reacted grain from the same position in the Reactor as the above grains. In this grain the corroded nature of the plagioclase lathes is evident leaving a desiccated, fenestral texture. The plagioclase is anorthitic in composition with remnants of bytownite present, as observed in the large lath located inside the red square. Olivine (lime green) and titanomagnetite (white) appear internally unaffected. Close-up backscatter images of this grain are shown in Figure 3.10f, g. Clinopyroxene is relatively unaltered, however, the grain has coating of chlorite.

Figure 3.11 shows a further grain from a similar position to the above. This grain shows secondary chlorite with intergrowths of secondary magnetite.

Figure 3.8. SEM backscatter and EDS compositional maps of an epoxy-mounted, polished grain from the bottom portion of the BW1 experiment: (a) backscatter image of entire grain; (b) backscatter image of rectangular area in (a); (c) composite colour image combining the backscatter image and the elemental maps for c) Ca in red, d) Al in green, and e) Fe in blue. The image shows remnant anorthite (green) and two crystals of garnet (pink). The Fe elemental map shows that there is a detectable concentration of Fe in the garnet.

Figure 3.9. SEM backscatter and EDS compositional maps of an epoxy-mounted, polished grain of olivine from the bottom portion of the BW1 experiment: (a) backscatter image of entire grain; (b) composite colour image combining the backscatter image and the elemental maps for c) Mg in red, d) Al in blue, and e) Fe in green. The composite image shows remnant olivine (red) and a coating of chlorite (violet).

Figure 3.10. (a-e) SEM backscatter and EDS compositional maps of an epoxy-mounted, polished grain collected from about 2 mm further up the Reactor (bottom, Portion 1) after the BW1 experiment: (a) backscatter image of entire grain; (b) composite colour image combining the backscatter image and the elemental maps for c) Mg in green, d) Fe in red, and e) Ca in blue. The image shows highly-altered plagioclase (blue), relatively unaltered clinopyroxene (turquoise), Fe oxides (red), and olivine (yellow green). (f-g) SEM backscatter images of the two red rectangular areas in (a): (f) top of grain showing secondary plagioclase of anorthitic composition (An), primary clinopyroxene (Cpx), a remnant plagioclase of bytownite composition (Byt), grain edge coating of chlorite (Chl), and Fe-Ti oxide (Tnt); (g) bottom of grain showing extensive alteration of plagioclase to anorthite, a remnant lath of plagioclase of bytownite composition, chlorite, and Fe-Ti oxide.

Figure 3.11. SEM backscatter image of a reacted grain showing secondary plagioclase of anorthitic composition (An), primary clinopyroxene (Cpx), chlorite (Chl), primary Fe-Ti oxide (Tnt), and secondary magnetite (Mag).

3.2.1.4. Mineralogy and Texture of Reacted Basalt: Top of the Reactor (Portion 2)

Selected grains were taken of the rock basalt immediately next to the exit point of the fluid (Portion 2, Fig. 3.5). These were mounted on aluminium stubs for textural analyses by SEM. Selected grains were also mounted in epoxy and polished for SEM-EDS analysis. Appendix B lists complete results.

SEM-EDS analysis

Several grains adjacent to the fluid exit point were examined (Fig. 3.5). The results confirm a lower grade of alteration of the basalt grains when compared with the bottom portion of the Reactor (Portion 1). Minerals of secondary origin detected were: plagioclase of anorthitic composition, chlorite, a K-Na-Mg-Fe aluminosilicate and titanite. The data also confirm the presence of the primary, unreacted minerals clinopyroxene, olivine, and titanomagnetite (Table 3.2).

Figure 3.12 shows the surface texture of grains from the top portion of the vessel. EDS backscatter images at low magnification show the presence of relict clinopyroxene visibly altered, secondary plagioclase of anorthitic composition, the K-Na-Mg-Fe aluminosilicate and titanite. In detail, anorthite shows an allotriomorphic habit, with no crystal-faces boundaries, while titanite appears as euhedral crystals. The K-Na-Mg-Fe aluminosilicate forms dense foliated masses. No evidence of wollastonite and/or garnet was found during analysis.

Figure 3.13 and Figure 3.14 show SEM backscatter images and EDS maps for two examples of epoxy-mounted, polished grains collected from the top portion in the Reactor. The lower intensity of hydrothermal alteration is evident when compared with grains from near the bottom of the Reactor. Primary minerals appear moderately affected by the hydrothermal activity. Also present is the K-Na-Mg-Fe aluminosilicate composition that replaces olivine (Fig. 3.14c). Secondary Fe oxide was not observed in these grains.

Table 3.2. Mineral assemblage found during analysis of reacted grains extracted from top of the Reactor (Portion 2) after the BW1 experiment. Analysis is made by SEM-EDS. Appendix B contains all SEM and EMPA results for this portion of the rock.

Type of Analysis	Analysis Material	Mineral Identified	Average Mineral Composition
SEM-EDS	polished grains	Bytownite	-
SEM-EDS	polished grains	Augite	$\text{Ca}_{0.58}\text{Mg}_{0.87}\text{Fe}_{0.47}\text{Al}_{0.1}\text{Si}_2\text{O}_6$
SEM-EDS	polished grains	Forsterite	$\text{Mg}_{1.2}\text{Fe}_{0.8}\text{SiO}_4$ (Fo ₆₀ -Fa ₄₀)
SEM-EDS	polished grains	Titanomagnetite	$\text{Fe}^{2+}(\text{Fe}^{3+}, \text{Ti})_2\text{O}_4$
SEM-EDS	polished grains	Celadonite	$\text{K}_{0.27}\text{Na}_{0.14}\text{Mg}_{1.9}\text{Fe}_{0.9}\text{Al}_{0.26}\text{Si}_{3.19}\text{Al}_{0.81}\text{O}_{10}(\text{OH})_2$ (calculated based on the anhydrous composition with 11 oxygens)
SEM-EDS	grains surface	Celadonite	$\text{K}_{0.39}\text{Na}_{0.36}\text{Mg}_{1.5}\text{Fe}_{1.45}\text{Al}_{0.12}\text{Si}_{3.0}\text{Al}_{0.98}\text{O}_{10}(\text{OH})_2$ (calculated based on the anhydrous composition with 11 oxygens)
SEM-EDS	grain surface	Anorthite	$\text{Ca}_{0.84}\text{Al}_2\text{Si}_2\text{O}_8$ (An ₉₇ -Ab ₃)
SEM-EDS	grain surface	Sphene	$\text{Ca}_{0.99}\text{Ti}_{0.77}\text{Al}_{0.24}\text{SiO}_5$

SEM analyses of the K-Na-Mg-Fe aluminosilicate are shown in Table 3.3. It is possible that these growths (Fig. 3.14c) are a mixture of two or more phases. However, repeat SEM-EDS analyses, made both on epoxy-mounted polished grains and during morphology examination, show the mineral to be composed of fairly consistent concentrations of iron, aluminium, silica and magnesium with a significant concentration of sodium and potassium but no calcium. The presence of Na₂O and K₂O, the high percentage of FeO and MgO, the lack of calcium, and the micaceous habit suggest a phyllosilicate rather than an amphibole. The most likely phase to have these properties is celadonite. This mineral is a common constituent of altered mafic and andesitic volcanic rocks (Andrews, 1980; Baker et al., 2012; Chesworth et al., 2004; Li et al., 1997; Li et al., 2011; Parra et al., 1985). It's ideal formula is $\text{K}(\text{Mg}, \text{Fe}^{2+})(\text{Al}, \text{Fe}^{3+}) \text{Si}_4\text{O}_{10}(\text{OH})_2$ with possible substitutions of Na and/or Ca in the interlayer site (Hendricks and Ross, 1941; Wise and Eugster, 1964). This is consistent with chemical compositions reported in Table 3.3. Figure 3.15 shows the average composition of this mineral plotted on the dioctahedral mica ternary diagram (Tappert et al., 2013).

Figure 3.12. SEM images of grains from the top (Portion 2) of the reactor after the BW1 experiment (minerals were identified by SEM-EDS analysis): a) surface showing intense alteration of the primary plagioclase to secondary anorthite composition; b) reacted grain surface showing primary clinopyroxene (Cpx) and secondary titanite (Ttn); c) surface of a reacted grain showing rounded masses of the K-Na-Mg-Fe aluminosilicate phase of secondary origin, concluded to be celadonite (Cel).

Figure 3.13. SEM backscatter image and EDS compositional maps of an epoxy-mounted, polished grain from the top portion of the BW1 experiment: (a) backscatter image of entire grain; (b) composite colour image combining the backscatter image and the elemental maps for c) Ca in blue, d) Mg in green, and e) Fe in red. The composite image shows plagioclase (dark blue), unaltered clinopyroxene (turquoise), titanomagnetite (red), and olivine (yellow green).

Figure 3.14. SEM backscatter images and EDS compositional maps of an epoxy-mounted, polished grain from the top portion of the BW1 experiment: (a) backscatter image of entire grain; (b) composite colour image combining the backscatter image and the elemental maps for Ca, Mg, and Fe. The composite image shows plagioclase (dark blue), unaltered clinopyroxene (turquoise), titanomagnetite (red), and olivine (yellow green). (c) enlargement of the red rectangle in (b) showing an overgrowth celadonite (Cel) on the olivine (Ol).

Table 3.3. Average composition (by SEM-EDS analysis) of the micaceous phase (celadonite) found during study of the reacted grains collected from the top (Portion 2) of the Reactor after the BW1 experiment. Empirical formulas reported in Table 3.2.

oxide	Unpolished (N=10)		Polished (N=5)	
	average Wt %	$\pm 1\sigma$	average Wt %	$\pm 1\sigma$
Na₂O	2.55	0.9	1.08	0.2
MgO	14.07	3.2	18.81	1.6
Al₂O₃	12.89	1.1	13.41	0.5
SiO₂	42.22	3.4	47.28	0.9
K₂O	4.25	1.3	3.10	0.8
FeO	24.03	7.0	16.34	2.7
Total	100.01		100.02	

Figure 3.15. Dioctahedral mica ternary diagram (Al, Fe, Mg) (n° of atoms) with plotted results from the empirical formula of Table 3.2.

3.2.1.5. Mineralogy and Texture of Reacted Basalt: Basalt Block

The basalt block (8 x 8 x 4 mm) with one polished surface was positioned vertically near the bottom of the Reactor approximately 0.5 - 1.0 cm above the titanium frit (Fig. 3.5). The block was used to investigate the relationship between primary and secondary minerals along a simulated “fracture surface”. Upon the conclusion of the experiment, the reacted block was mounted on an aluminium stub for SEM-EDS analysis (Table 3.4). Composite mosaic images of the basalt block surface, before and after the experiment, are shown in Appendix B.

Table 3.4. Mineral composition of reacted basalt block surface after the BW1 experiment. Appendix B contains all SEM results.

Type of Analysis	Analysis Material	Mineral Identified	Average Mineral Composition
SEM-EDS	basalt block	Plagioclase	-
SEM-EDS	basalt block	Augite	$\text{Ca}_{0.65}\text{Mg}_{0.81}\text{Fe}_{0.44}\text{Al}_{0.1}\text{Si}_2\text{O}_6$
SEM-EDS	basalt block	Titanomagnetite	$\text{Fe}^{2+}(\text{Fe}^{3+}, \text{Ti})_2\text{O}_4$
SEM-EDS	basalt block	Fe-Ni-Cr Oxide	-
SEM-EDS	basalt block	Celadonite	$\text{K}_{0.46}\text{Na}_{0.33}\text{Mg}_{1.4}\text{Fe}_{1.6}\text{Al}_{0.07}\text{Si}_{2.9}\text{Al}_{1.1}\text{O}_{10}(\text{OH})_2$ (calculated based on the anhydrous composition with 11 oxygens)

Figure 3.16a shows an SEM backscatter image of the corner of the unreacted basalt block. It shows the ophitic texture, composed of interlocking plagioclase (bytownite) laths (darker grey) with interstitial clinopyroxene (lighter grey). Olivine occurs as isolated anhedral crystals (examples circled in yellow), while oxides (titanomagnetite) appear white. Figure 3.16b shows the same area above after reaction. At low magnification, the most significant observation is the growth of amoeboid masses of celadonite exclusively on primary olivine crystals. The growths of celadonite were large enough to be examined under the optical microscope and appeared green-blue in colour.

Figure 3.16c shows a higher magnification image of this phase. Table 3.5 shows the average of 24 SEM-EDS analyses of this phase. When compared to Table 3.3, the composition of the celadonite analysed on the basalt block surface is similar to that measured from reacted grains (Table 3.2). The mineral habit is similar to that shown in Figure 3.12c, thus they are interpreted to be the same phase. Figure 3.17 shows the average composition of this mineral plotted on the dioctahedral mica ternary diagram (Tappert et al., 2013).

At higher magnification, a further observation is the etching of the twin planes in plagioclase (Fig. 3.16d,e). EDS analysis shows the plagioclase has an increase in Na content relative to the original bytownite (Appendix B). It is uncertain to what depth this enrichment has occurred. Clinopyroxene and titanomagnetite appear unaffected.

Also observed is the growth of a Fe-Ni-Cr oxide. Figure 3.18a shows an area of the unreacted basalt block while Figure 3.18b shows the same area after reaction. Along the twin planes and edges of the plagioclase laths there appear bright lines of a secondary phase. These are evident in the higher magnification image (Fig. 3.18c). EDS analyses of this material shows it to be composed of Fe, Ni, and Cr. It is most likely an oxide phase.

Figure 3.16. (a-b) SEM backscatter images of the surface of the basalt block used in the BW1 experiment: a) unreacted block with interlocking lathes of plagioclase (dark gray), interstitial clinopyroxene (lighter gray), titanomagnetite (white), and isolated crystals of olivine (yellow ovals); b) reacted block showing celadonite replacing olivine. (c-d-e) SEM backscatter images of the basalt block surface after the BW1 experiment: c) enlargement of rectangular area in (b) showing celadonite (Cel) replacing olivine; d) SEM backscatter image showing celadonite (Cel), relatively unaltered clinopyroxene (Cpx) (lighter grey) and plagioclase with more Na content (Plg) coating primary plagioclase; e) SEM backscatter image of celadonite (Cel) replacing olivine (Ol) and altered plagioclase (Plg).

Table 3.5. Average composition (SEM-EDS analysis) of celadonite found during study of the reacted basalt surface collected from the bottom of the Reactor after the BW1. Empirical formula reported in Table 3.4.

Basalt Block (N=24)		
oxide	average Wt %	$\pm 1\sigma$
Na₂O	2.28	0.93
MgO	12.81	3.02
Al₂O₃	13.16	2.01
SiO₂	40.00	4.25
K₂O	4.91	1.90
FeO	26.85	8.59
Total	100.00	

Figure 3.17. Dioctahedral mica ternary diagram (Al, Fe, Mg) (n° of atoms) with plotted results from the empirical formula of Table 3.4.

Figure 3.18. SEM backscatter images of the basalt block surface after the BW1 experiment: a) area of the basalt block surface before the BW1 experiment; (b) same area after the BW1 experiment showing larger plagioclase microphenocrysts surrounded by ophitic textured plagioclase, clinopyroxene, olivine and titanomagnetite; c) enlargement of the red rectangular area in (b) showing secondary features in detail. Primary clinopyroxene (Cpx) is unaltered while the plagioclase (Plg), altered, has a major Na content when compared to the primary bytownite (Appendix B). Bright spots are Fe-Ni-Cr oxide.

3.2.2. BW2: Basalt – water at 350°C/490 bar

The second basalt-water experiment (BW2) ran for total time of 1145 hr. The first 136 hr were at room temperature and 490 bar and the remaining 1008 hr were at 350°C and 490 bar. The flow rate was 1 ml hr⁻¹ up to 1002 hr after which it was changed to 0.5 ml hr⁻¹ for the remaining 143 hr. Analyses of major ions were made for the total number (46) of fluid samples. Analyses of trace elements were made for the first 29 fluid samples.

3.2.2.1. Major element concentrations

Appendix B lists the complete experimental parameters (T, P, flow rate, chemistry). Figure 3.19 and Figure 3.20 show the major element results plotted against time in hours. The unreacted distilled water composition is shown at $t = 0$. Trace concentrations of Ca (0.02 mmol kg⁻¹), K (0.08 mmol kg⁻¹), Na (0.29 mmol kg⁻¹), and SiO₂ (0.04 mmol kg⁻¹), were detected. All other major elements were below detection limit.

During the room temperature (~21°C) period, no significant changes in solution composition are evident. The pH values are on average slightly higher (6.94) than the starting blank but are quite irregular. Ca, K and Na remain stable reflecting the composition of the input solution. SiO₂ slightly rises in concentration.

The change in temperature to 350°C was initiated at 136 hours. Major changes in solution chemistry are evident after the temperature shift. Effluent quench pH slowly increases from just above 7 at 184 hours to about 9 by 378 hours and remains near this alkaline value for the remainder of the experiment. The calculated *in situ* pH declines from 6.24 after the temperature shift to 5.3 - 5.4 by the end of the experiment.

SiO₂ increases to 32.25 mmol kg⁻¹ (1937 ppm) which is more than double quartz saturation at 350°C/500 bar (~981 ppm, Supcrt92). Between 184 and 403 hours, silica concentration remains elevated but decreases to about 20 mmol kg⁻¹. After about 400 hours, silica concentration rapidly decreases over about ten days to 10 mmol kg⁻¹ then declines gradually to 8.2 mmol kg⁻¹ by the end of the experiment.

Na and K both show a sharp increase after the temperature shift, then decline over the next five days and then increase again up to about 500 hours. After this, their concentrations diverge with Na stabilising at around 2.5 mmol kg⁻¹ up to 800 hours then decreasing to 2 mmol kg⁻¹ for the remainder of the experiment. Potassium increases to a maximum of 0.62 mmol kg⁻¹ and then concentrations decline to about 0.41 mmol kg⁻¹ by 800 hours after which they decrease sharply to 0.13 - 0.14 mmol kg⁻¹ for the remainder of the experiment.

Aluminium concentration increases to about 0.4 mmol kg^{-1} after the temperature shift and remains relatively constant up to 419 hours, after which it increases to about 1 mmol kg^{-1} and remains near this value until the change in flow rate at 1000 hours. At the lower flow rate, Al concentration decreases slightly. On average, Ca concentration increases after the temperature shift to a value around $0.04 \text{ mmol kg}^{-1}$ for the remaining experiment, however, it is highly irregular. Mg behaves similarly, displaying highly irregular, low values averaging around $0.09 \text{ mmol kg}^{-1}$. Fe increases sharply to $0.027 \text{ mmol kg}^{-1}$ immediately after temperature shift and then consistently declines to values near or below detection limit over the remaining experiment.

SO_4 concentration increases immediately after temperature shift to a value of $0.12 \text{ mmol kg}^{-1}$. It then declines to near detection limit values over the remainder of the experiment. Similarly, Cl concentration increases to $0.56 \text{ mmol kg}^{-1}$ after the temperature shift and then declines to between $0.01 - 0.02 \text{ mmol kg}^{-1}$ by the end of the experiment. H_2S concentration increases to a maximum of 0.3 mmol kg^{-1} three days after temperature increase. It then decreases in a linear manner over the next thirteen days after which it declines to values near or below detection limit for the remaining time.

The change in flow rate to 0.5 ml hr^{-1} (the final three effluent samples) did not cause any significant effects on elemental concentrations and pH values, i.e., fluid composition remains stable during the last 143 hrs of experiment.

Figure 3.19. Major element concentrations in blank and effluent samples (mmol kg^{-1}) versus time (hr) for the basalt-water experiment at $350^\circ\text{C}/490$ bar (BW2). Yellow symbols are the blank sample composition of the water. Blue symbols are for effluents at room T/ 490 bar and 1.0 ml hr^{-1} flow rate. Black symbols are effluents at $350^\circ\text{C}/490$ bar and 1.0 ml hr^{-1} flow rate. Red symbols are effluents at $350^\circ\text{C}/490$ bar and 0.5 ml hr^{-1} flow rate. *In situ* pH is the calculated pH at temperature. The limit of detection (LOD) is shown for each component.

Figure 3.20. Major element concentrations in blank and effluent samples (mmol kg^{-1}) versus time (hr) for the basalt-water experiment at $350^\circ\text{C}/490$ bar (BW2). Yellow symbols are the blank sample composition of the water. Blue symbols are for effluents at room T/ 490 bar and 1.0 ml hr^{-1} flow rate. Black symbols are effluents at $350^\circ\text{C}/490$ bar and 1.0 ml hr^{-1} flow rate. Red symbols are effluents at $350^\circ\text{C}/490$ bar and 0.5 ml hr^{-1} flow rate. *In situ* pH is the calculated pH at temperature. The limit of detection (LOD) is shown for each component.

3.2.2.2. Trace element concentrations

Appendix B lists the complete trace element results. Figure 3.21 and Figure 3.22 show these results plotted against experimental time in hours. The unreacted water composition is shown at $t = 0$. All trace element concentrations are below detection limit.

As with the basalt - water experiment at supercritical conditions (BW1), during the room temperature ($\sim 21^{\circ}\text{C}$) period, measurable consistent increases in trace elements Cr, Ni, Zn, Mo, and Au are observed. Zn concentrations are similar in magnitude to those found for the remainder of the experiment, suggesting an artefact of the method rather than meaningful values due to water-rock interaction.

After the temperature shift to 350°C , four trace elements sharply increase in concentration including Mn, Co, Rb, and Mo. V slowly increases over the remainder of the experiment while Mo decreases. Overall decreases are also observed for Cr, Mn, and perhaps Au. Rb peaks at 450 hours and then decreases. Other elements are low and erratic in concentration over the experiment (Co, Cu, Ag, Cd, Ba, Pb).

Figure 3.21. Trace element concentrations in blank and effluent samples ($\mu\text{mol kg}^{-1}$) versus time (hr) for the basalt-water experiment at 350°C/490 bar (BW2). Yellow symbols are the blank sample composition of the water. Blue symbols are for effluents at room T/490 bar and 1.0 ml hr⁻¹ flow rate. Black symbols are effluents at 350°C/490 bar and 1.0 ml hr⁻¹ flow rate. *In situ* pH is the calculated pH at temperature. The limit of detection (LOD) is shown for each component.

Figure 3.22. Trace element concentrations in blank and effluent samples ($\mu\text{mol kg}^{-1}$) versus time (hr) for the basalt-water experiment at $350^\circ\text{C}/490$ bar (BW2). Yellow symbols are the blank sample composition of the water. Blue symbols are for effluents at room T/ 490 bar and 1.0 ml hr^{-1} flow rate. Black symbols are effluents at $350^\circ\text{C}/490$ bar and 1.0 ml hr^{-1} flow rate. *In situ* pH is the calculated pH at temperature. The limit of detection (LOD) is shown for each component.

3.2.2.3. Mineralogy and Texture of Reacted Basalt: Bottom of the Reactor (Portion 1)

Upon conclusion of the experiment, the reacted basalt grains were extracted from the Reactor onto absorbent paper. They were rinsed with distilled water to remove precipitated soluble salts such as NaCl and KCl and were air-dried. Several grains were collected from the bottom of the Reactor (Portion 1) and from the top of the Reactor (Portion 2) (Fig. 3.23). Note that, no reacted grains in between Portion 1 and Portion 2 were collected for analysis.

Selected grains were mounted on aluminium stubs for textural analyses by SEM and several grains were epoxy-mounted and polished for SEM-EDS and EMPA analysis. Appendix B contains all SEM and EMPA results for this portion of the rock.

Figure 3.23. Schematic diagram of the Reactor showing position (Portion 1 and Portion 2) of reacted basalt grains shown in SEM photographs and the position of the basalt block for the BW2 experiment. The picture is not to scale.

SEM-EDS and EMPA analysis

Results confirm substantial alteration of the basalt caused by water-rock interaction. Minerals of secondary origin detected were: anorthite, chlorite, magnetite and titanite. Data also confirm the presence of the primary minerals clinopyroxene, olivine and titanomagnetite (Table 3.6).

Table 3.6. Mineral assemblage detected by EMPA and SEM-EDS analysis of reacted grains extracted from bottom (Portion 1) of the Reactor after the BW2 experiment. Appendix B contains all SEM and EMPA results.

Type of Analysis	Analysis Material	Mineral Identified	Average Mineral Composition
EMPA	polished grains	Anorthite	$\text{Ca}_{0.88}\text{Na}_{0.09}\text{Al}_2\text{Si}_2\text{O}_8$ (An ₉₁ -Ab ₉)
EMPA	polished grains	Augite	$\text{Ca}_{0.44}\text{Mg}_{0.93}\text{Fe}_{0.60}\text{Ti}_{0.18}\text{Si}_2\text{O}_6$
EMPA	polished grains	Forsterite	$\text{Mg}_{1.43}\text{Fe}_{0.56}\text{SiO}_4$ (Fo ₇₂ -Fa ₂₈)
SEM-EDS	polished grains	Titanomagnetite	$\text{Fe}^{2+}(\text{Fe}^{3+}, \text{Ti})_2\text{O}_4$
SEM-EDS	polished grains	Magnetite	$\text{Fe}^{3+}\text{Fe}^{2+}_2\text{O}_4$
EMPA	polished grains	Chlorite	$\text{Mg}_{2.9}\text{Fe}_{1.8}\text{AlSi}_3\text{AlO}_{10}(\text{OH})_8$ (calculated based on the anhydrous composition with 14 oxygens)
SEM-EDS	grain surface	Sphene	$\text{CaTi}_{0.85}\text{Al}_{0.27}\text{SiO}_5$

Figure 3.24 show SEM images of the most reacted grains from the position immediately next to the entry point of the fluid (Fig. 3.23). In Figure 3.24a-b, the grain has chlorite as irregular masses of densely-packed flakes intergrown with euhedral titanite crystals. In Figure 3.24c-d, a second grain has anorthite occurring as subhedral fenestral pseudomorphs of plagioclase. Chlorite displays three habits: botryoidal masses of randomly oriented flakes; epitaxially-oriented pseudomorphs of clinopyroxene; and as intergrowths with anorthite.

Figure 3.25a-f shows SEM backscatter images and EDS maps of an epoxy-mounted, polished grain from the bottom of the Reactor. The grain is considerably altered, with highly-corroded plagioclase (blue), relatively unaffected clinopyroxene (turquoise), Fe-Ti and Fe oxides (red), and chlorite (green). Figure 3.25g is a higher magnification image of the rectangular area in Figure 3.25a showing chlorite (green) that has grown internally and outside the margin of the grain in a botryoidal habit, mostly replacing olivine. The chlorite is intergrown with secondary magnetite. Plagioclase is anorthitic in composition. Internally, primary clinopyroxene and titanomagnetite are relatively unaffected.

Figure 3.24. SEM images of grains collected from bottom (Portion 1) of the Reactor after the BW2 experiment (minerals were identified by SEM-EDS analysis): a) grain covered by secondary chlorite and secondary titanite; (b) enlargement of red rectangular area in (a) showing in more detail the chlorite (Chl) and titanite (Ttn) which appears as prismatic crystals. (c) surface of a reacted grain showing chlorite (Chl) as botryoidal masses composed of densely intergrown flakes; d) enlargement of the red rectangular area in (c) displaying intense alteration of the primary clinopyroxene (Cpx) to chlorite (Chl); (e) secondary chlorite formation (Chl) replacing the plagioclase (Plg). (f) grain entirely covered with chlorite of secondary origin appearing as botryoidal masses composed of densely intergrown flakes.

Figure 3.25. (a-f) SEM backscatter images and EDS compositional maps of an epoxy-mounted, polished grain collected from the bottom (Portion 1) of the Reactor after the BW2 experiment. (a) backscatter image of entire grain; (b) backscatter image of rectangular area in (a); (c) composite colour image combining the backscatter image and the elemental maps for d) Fe in red, e) Mg in green, and f) Ca in blue. The image shows remnant plagioclase (blue-purple), relatively unaltered clinopyroxene (turquoise), oxides (red) and a chlorite (green); (g) SEM backscatter image of the red rectangular area shown in (a) displaying secondary plagioclase of anorthitic composition (An), primary clinopyroxene (Cpx), secondary chlorite (Chl), primary Fe-Ti oxide (Tnt), and secondary magnetite (Mag).

3.2.2.4. Mineralogy and Texture of Reacted Basalt: Top of the Reactor (Portion 2)

Selected grains were taken on the top portion of the rock immediately next to the exit point of the fluid (Fig. 3.23). These were mounted on aluminium stubs for textural analyses by SEM. Selected grains were also mounted in epoxy and polished for SEM-EDS analysis. Appendix B lists complete results for these analyses.

SEM-EDS analysis

Results confirm less alteration of the basalt grains when compared with the bottom (Portion 1) of the Reactor. Minerals of secondary origin detected were celadonite and titanite. Primary plagioclase, clinopyroxene, olivine and titanomagnetite were also present (Table 3.7).

Table 3.7. Mineral assemblage found during analysis of reacted grains collected from the top (Portion 2) of the Reactor after the BW2 experiment. Appendix B contains all SEM results for this portion of the rock.

Type of Analysis	Analysis Material	Mineral Identified	Average Mineral Composition
SEM-EDS	polished grains	Bytownite	-
SEM-EDS	polished grains	Augite	-
SEM-EDS	polished grains	Forsterite	Mg _{1.14} Fe _{0.85} SiO ₄ , (Fo ₅₇ -Fa ₄₃)
SEM-EDS	polished grains	Celadonite	K _{0.17} Mg _{1.5} Fe _{1.3} Al _{0.3} Si _{3.2} Al _{0.8} O ₁₀ (OH) ₂ (calculated based on the anhydrous composition with 11 oxygens)
SEM-EDS	grain surface	Celadonite	K _{0.42} Na _{0.20} Mg _{1.23} Fe _{1.62} Al _{0.25} Si _{2.98} Al ₁ O ₁₀ (OH) ₂ (calculated based on the anhydrous composition with 11 oxygens)
SEM-EDS	grain surface	Sphene	Ca _{1.13} Fe _{0.13} Ti _{0.80} Al _{0.23} SiO ₅
SEM-EDS	polished grains	Titanomagnetite	-

Figure 3.26 shows surface textures of grains from the top portion of the Reactor. EDS backscatter images at low magnification show celadonite and titanite. Celadonite forms dense foliated masses while titanite appears as euhedral crystals. No evidence of chlorite or anorthite was found.

Figure 3.27a - e shows SEM backscatter images and EDS maps for epoxy-mounted, polished grains collected from the top portion in the Reactor. The lower intensity of hydrothermal alteration is evident when compared with grains from the bottom of the Reactor (Fig. 3.24). Primary minerals appear relatively unaffected. Also present (Fig. 3.27f) is

celadonite and relict olivine with substantial loss in Mg when compared to the unreacted olivine (Table 2.3). Secondary Fe oxide was not observed in these grains.

SEM results for celadonite are summarised in Table 3.8. Repeat SEM-EDS analyses of the epoxy-mounted polished grains show the mineral to contain high concentrations of iron and magnesium with a substantial amount of sodium and potassium but no calcium. Results are very similar to those obtained during analysis of the grains collected from Portion 2 (top of the Reactor) after the BW1 experiment and on the reacted basalt block from this experiment. Table 3.8 reports chemical compositions of the celadonite while Figure 3.28 shows results plotted on the dioctahedral mica ternary diagram (Tappert et al., 2013).

Figure 3.26. SEM images of grains collected from the top of the Reactor after the BW2 experiment (minerals were identified by SEM-EDS analysis: a) surface of a reacted grain; b) enlargement of the red rectangular area in (a) showing the K-Na-Mg-Fe aluminosilicate of secondary origin (Cel); c) surface of a reacted grain; d) enlargement of the red rectangular area in (c) showing the K-Na-Mg-Fe aluminosilicate (Cel) of secondary origin; e) portion of a reacted grain; f) enlargement of the red rectangular area in (e) displaying crystals of titanite (Ttn) of secondary origin.

Figure 3.27. SEM backscatter images and EDS compositional maps of an epoxy-mounted, polished grain collected from the top portion of the Reactor after the BW2 experiment: (a) backscatter image of entire grain; (b) composite colour image combining the backscatter image and the elemental maps for c) Mg in green, d) Ca in blue, and e) Fe in red. The composite image shows unaltered plagioclase (dark blue), unaltered clinopyroxene (turquoise), unaltered olivine (yellow), oxides (red), and celadonite (green); (f) SEM backscatter image of the red rectangular area in (a) displaying plagioclase (Plg), primary olivine (Ol) and celadonite (Cel).

Table 3.8. Average oxides composition (by SEM-EDS analysis) of celadonite found during the morphological examination and from the epoxy-mounted polished section study of grains collected from the top (Portion 2) of the Reactor after the BW2. Empirical formulas reported in Table 3.7. n.d.= not detected.

oxide	Unpolished (N=7)		Polished (N=3)	
	average Wt %	$\pm 1\sigma$	average Wt %	$\pm 1\sigma$
Na₂O	1.43	1.38	n.d.	-
MgO	11.37	3.18	14.40	1.22
Al₂O₃	14.76	2.22	13.88	1.28
SiO₂	41.15	3.65	46.74	1.82
K₂O	4.51	2.85	1.86	1.21
FeO	26.77	5.83	23.12	0.66
Total	100.01		100.00	

Figure 3.28. Dioctahedral mica ternary diagram (Al, Fe, Mg) (n° of atoms) with plotted results from the empirical formula of Table 3.7.

3.2.2.5. Mineralogy and Texture of Reacted Basalt: Basalt Block

The basalt block (8 x 8 x 4 mm) with one polished surface, was positioned vertically near the bottom of the Reactor approximately 0.5 - 1.0 cm above the titanium frit (Fig. 3.23). Upon the conclusion of the experiment, the reacted block was mounted on an aluminium stub for SEM-EDS analysis (Table 3.9). Composite mosaic images of the basalt block surface, before and after the experiment are provided in Appendix B.

Table 3.9. Mineral composition of the reacted basalt block after the BW2 experiment.

Type of Analysis	Analysis Material	Mineral Identified	Average Mineral Composition
SEM-EDS	basalt block	Anorthite	$\text{CaAl}_2\text{Si}_2\text{O}_8, (\text{An}_{94}\text{-Ab}_6)$
SEM-EDS	basalt block	Augite	$\text{Ca}_{0.40}\text{Mg}_{0.66}\text{Fe}_{0.90}\text{Al}_{0.19}\text{Si}_{1.52}\text{Al}_{0.48}\text{O}_6$
SEM-EDS	basalt block	Titanomagnetite	$\text{Fe}^{2+}(\text{Fe}^{3+}, \text{Ti})_2\text{O}_4$
SEM-EDS	basalt block	Fe-Ni-Cr Oxide	-
SEM-EDS	basalt block	Chlorite	$\text{Mg}_{1.9}\text{Fe}_{2.8}\text{Al}_{1.18}\text{Si}_{2.83}\text{Al}_{1.17}\text{O}_{10}(\text{OH})_8$ (calculated based on the anhydrous composition with 14 oxygens)

Figure 3.29a,e show SEM backscatter images of two areas of the unreacted basalt block. They show the ophitic texture, composed of interlocking plagioclase (bytownite) laths (darker grey) with interstitial clinopyroxene (lighter grey). Olivine occurs as isolated anhedral crystals (Fig. 3.29e, examples circled in yellow), while oxides (titanomagnetite) appear as bright white.

Figure 3.29b,f show the same areas above after reaction. Comparison with the unreacted surfaces show an increase in surface roughness. At low magnification, the most significant observation is the growth of chlorite which replaces clinopyroxene, olivine and, partially, plagioclase. Celadonite was not observed on the block.

Figure 3.29g,h show higher magnification images of the respective reacted areas (red rectangular areas) showing more in detail the replacement by chlorite. EDS analysis confirms the plagioclase has an anorthitic composition, at least on its surface and has inclusions of chlorite. Clinopyroxene is replaced by epitaxial growths of chlorite. Titanomagnetite appears unaffected. Also identified was the secondary Fe-Ni-Cr oxide phase shown in Figure 3.30 (also identified on basalt block from the BW1 experiment, Fig. 3.18c). In this case, it is found on a relict clinopyroxene grains.

Figure 3.29. SEM backscatter images: (a) portion (left border) of the basalt block surface before the BW2 experiment; (b) same portion (left border) of the basalt block after the BW2 experiment. In (a) primary plagioclase (Byt) appears in darker grey under backscatter electron detector, while clinopyroxene (Cpx) in lighter gray. In (b) both plagioclase and clinopyroxene are strongly altered; (c) enlargement of red rectangular area in (b); (d) enlargement of red rectangular area in (c) showing in detail the presence of secondary plagioclase of anorthitic composition (An) and secondary chlorite formation (Chl); (e) left border of the basalt block surface before the BW2 experiment with primary plagioclase (Byt) and clinopyroxene (Cpx) and isolated crystals of olivine (yellow ovals); (f) same same area in (e) after the BW2 experiment with strongly altered plagioclase, clinopyroxene and olivine; (g) enlargement of the red rectangular area 1 in (f) showing secondary plagioclase of anorthitic composition (An); (h) enlargement of the red rectangular area 2 in (f) showing secondary plagioclase of anorthitic composition (An) and secondary chlorite formation (Chl) where chlorite replaces all primary silicates (olivine, plagioclase and clinopyroxene).

Figure 3.30. SEM backscatter images of the basalt block after the BW2 experiment showing a relict clinopyroxene grain. The mineral has an unaltered inclusion of primary titanomagnetite and a secondary Fe-Ni-Cr oxide phase. Chlorite crystals surround the relict clinopyroxene.

3.3. Discussion

3.3.1. Major and trace element exchange during water – rock interaction

Major ions

The basalt-water experiments were conducted at room T for the first week and then conditions were shifted to 350°C (BW2) and 400°C (BW1). Pressure was maintained constant at 490 and 502 bar for BW2 and BW1, respectively. During room temperature conditions, several major ions (SiO₂, Al, Ca, Na, Fe, Mg and Cl) increase in the solution, but only in small amounts. In the same way, trace elements such as Cr, Co, Ni, Cu, Zn, Mo and Pb increase to a minor degree.

After temperature increase, silica concentrations remain oversaturated with respect to quartz in both experiments. After ~243 hr at subcritical condition and ~242 hr at supercritical conditions, they decrease below saturation with respect to quartz. The initial high SiO₂ values are attributed to the dissolution of volcanic glass after the shift in temperature, both at 350 and 400°C. The decrease in SiO₂ concentrations at ~240 hr indicates complete dissolution of basaltic glass in both experiments (Fig. 3.31).

In order to estimate the amount of volcanic glass present in the experiments, the integrated SiO₂ flux was calculated (Fig. 3.31a, e). This was done by summing the total volume of each sample multiplied by the silica concentration in that sample. For BW2 and BW1 this is equal to 896 and 769 mg, respectively. Note that after the loss of the volcanic glass, SiO₂ concentration decreases to a lower steady state value. If it is assumed that this SiO₂ flux is due to dissolution of primary basalt minerals (plagioclase, pyroxene, olivine), this can be subtracted from the total flux to estimate SiO₂ content released from glass. The SiO₂ flux from silicate minerals (Fig. 3.31b,f) was estimated using the average silica contents of the last two fluid samples and applying this over the whole experiment. This amounted to 489 and 347 mg for BW2 (including blank input mass composition supposing no fluid-rock exchange) and BW1, respectively. These values were subtracted from the total SiO₂ flux to estimate the amount of silica released from the glass. This resulted in a value of 405 and 422 mg of SiO₂ for BW2 and BW1, respectively. The total amount of glass can be then calculated from the EMPA analyses (Table 2.3). This gives ~597 mg of glass for the BW2 and ~622 of glass for the BW1. This means that the basalt contains about 2.5% glass by weight. This seems reasonable given the low abundance of glass found during petrographic examination.

It should be emphasised that this is an estimate as there is evidence that secondary minerals have formed in some of the voids where glass was present. Figure 3.32 shows the

typical “rosette structure” (Carstens, 1975; Jafri and Charan, 1992) left over during the glass devitrification process. The constituents of these minerals likely came from the original glass. This is supported by the low concentrations of Ca and Al in the fluid relative to that expected from congruent dissolution of the glass (Table 3.10). In addition, it is assumed that the dissolution of primary minerals is not suppressed by the high SiO₂ concentrations during glass dissolution, thus the calculation is a minimum estimate of the amount of glass. All details of the calculations are reported in Appendix B.

Table 3.10. Mass flux of major elements estimated by dissolution of volcanic glass and from the fluid sample compositions over the BW1 and BW2.

BW2 (350 °C / 490 bar)	K	Cl	SO₂	Ca	Na	Mg	Fe
Elements Estimated From Volcanic Glass / mg (over the entire experiment)	6.6	0.52	0.12	21.9	26.3	2.8	18
Total Elements Flux From Fluid Samples / mg (over the entire experiment)	9	2	S _{tot} = 1.5	0.6	38.1	0.11	0.37
BW1 (400 °C / 502 bar)	K	Cl	SO₂	Ca	Na	Mg	Fe
Elements Estimated From Volcanic Glass / mg (over the entire experiment)	7.1	0.56	0.12	23	28	3	20
Total Elements Flux From Fluid Samples / mg (over the entire experiment)	4.8	1.7	S _{tot} = 1.4	0.36	24.2	0.075	0.22

Figure 3.31. SiO_2 concentration (mmol kg^{-1}) vs time (hr) for the BW2 and the BW1 experiments: a) total SiO_2 flux for BW2 based on sample volume and solution composition (pink area); b) total SiO_2 flux from silicate minerals (green) based on the average SiO_2 concentration in the last two samples (0.5 ml hr^{-1} flow rate) less the input water composition (grey); c) the difference between a) and b) representing the net SiO_2 flux from glass for BW2 (orange area); d) total SiO_2 flux for BW2 (orange + green area); e) total SiO_2 flux for BW1 based on sample volume and solution composition (pink area); f) total SiO_2 flux from silicate minerals (green) based on the average SiO_2 concentration in the last two samples (0.5 ml hr^{-1} flow rate) (green area); g) difference between a) and b) representing the total SiO_2 flux from glass for BW1 (orange area).

Figure 3.32. Secondary mineral growths in voids left by the dissolution of volcanic glass with the typical “rosette structure”. This was found in the basalt block from the BW1 experiment (400°C/502 bar).

With an estimate of the amount of volcanic glass, the amount of its constituent elements can be estimated. This is done by multiplying the wt% of a component from the EMPA results by the weight of the volcanic glass estimated above. Total element flux from the experiment can also be calculated from the chemistry of the reacted fluid compositions. These results allow a comparison of the content of a component in the rock with its total flux from the experiment. For example, the concentration of Cl in the glass measured by EMPA analysis is 0.09 wt%. This is equal to ~0.6 mg of chlorine available in the glass during the experiments. The ΣCl flux measured from fluid chemistry is higher at ~2 mg in both experiments. The large difference could be explained by inhomogeneity in the glass Cl content and thus the amount of Cl may be underestimated based on EMPA analyses. For example, the glass contains distinct crystals of apatite which could contain a higher Cl content. The correlation of SiO_2 released during glass dissolution with Cl concentration over the same period (Fig. 3.33a,b) shows that Cl must have been derived from the glass.

Potassium is derived mainly from the volcanic glass (indeed glass was identified in the polished thin section by EDS maps of K). The plagioclase in the rock is also expected to contain a small amount of K. Microprobe analysis of the glass gave a concentration of K_2O of 1.37 wt%, or 1.14 wt% of K. This equates ~7 mg of K available in both experiments. The ΣK flux calculated from fluid chemistry is 9 mg (BW2) and 4.8 mg (BW1) from the rock. At 350°C, the higher amount of potassium calculated in the fluid flux indicates the complete release of K present in the glass plus an extra amount released by a stronger dissolution of the plagioclase. At 400°C, the lower amount of potassium calculated in the fluid flux indicates

precipitation of a greater amount of the secondary K-bearing mineral phase. The precipitation of a secondary K-bearing phase is supported by the SEM results and the negative correlation between K and SiO₂ during glass dissolution (Fig. 3.33c,d). Once the glass has been dissolved, concentrations of K are higher at the same time silica is low. At this point, the lower concentration of K is controlled by minerals in the basalt.

Figure 3.33. Plots of Cl and K (mmol kg⁻¹) versus SiO₂ (mmol kg⁻¹) for the BW1 and BW2. Symbols in red represent values during glass dissolution, while symbols in blue represent values after glass dissolution.

The presence of H₂S and SO₄²⁻ in the fluid are attributed to dissolution of SO₂ and immiscible sulfide blebs trapped in the volcanic glass. Hydrogen sulfide can be generated from dissolution of Fe sulfide (eq. 1):

It is also possible that some sulfide is generated by the reduction of SO₂ (eq. 2):

However, there is a strong correlation between SiO₂ and H₂S (Fig. 3.34a,b) showing that the sulfide is being released solely from the glass.

The release of SO₂ to the solution explains the presence of SO₄²⁻. This occurs when sulfurous acid (H₂SO₃) forms by the dissolution of SO₂ in the fluid (eq. 3), followed by its oxidation to sulfate possibly in either the experiment or in the sampling syringe (eq. 4):

The concentration of SO₂ in the glass (Table 2.3) is 0.04 wt% or 0.02 wt% of S. This is equal to 0.12 mg of S available in the unaltered glass in both experiments. The amount of total S (reduced and oxidized) calculated from the fluid chemistry (ΣH₂S and ΣSO₄²⁻ flux) after completion of the BW2 and BW1 is 1.5 mg. The higher flux of S calculated from the fluid samples is due to the dissolution of Fe sulfide blebs present in the volcanic glass which apparently were not encountered during EMPA measurements.

The release of S from the glass also explains the initial low quench pH values measured after the temperature change. Once the glass is depleted the quench pH values become basic at 9.6 and 9.2 at 350 and 400°C, respectively. However, the *in situ* pH at the experimental temperature is close to neutral, with an average value of 6.0 and 5.5 for BW1 and BW2, respectively.

At temperature the sulfite/sulfate anion created by the release of SO₂ from the glass is protonated forming bisulfite and/or bisulfate (eq. 5 and 6):

This buffers *in situ* pH to near neutral, however, these anions deprotonate upon cooling and thus room temperature pH is acid.

Once the volcanic glass is dissolved there is no longer a source for S. This results in pH increasing to basic values due to cation exchange with the rock minerals. In order to dissolve cations such as Ca, Na and K from the rock, it requires the consumption of H⁺ and which explains the pH increase. Figure 3.34a-f shows the correlations between H₂S and SO₄ versus SiO₂ and of Fe versus H₂S. There are clear correlations between H₂S and SO₄ versus SiO₂. There is also a strong correlation between Fe and H₂S. This confirms that the hydrogen sulfide formation is due to the dissolution of Fe-sulfide present in the volcanic glass.

Figure 3.34. Plots of H_2S and SO_4 (mmol kg^{-1}) versus SiO_2 (mmol kg^{-1}) and Fe (mmol kg^{-1}) versus H_2S (mmol kg^{-1}) for the BW1 and BW2. Symbols in red represent values during glass dissolution, while symbols in blue represent values after glass dissolution.

Trace elements

Trace element concentrations give important information about the capacity of basalt to release or retain these elements during water – rock interaction, both at subcritical and at supercritical experimental conditions (Fig. 3.3 - 3.4, Fig. 3.21 - 3.22). In the following discussion, only elements that show clear trends are considered. These include Cu, Co, Mo and V. Elements which do not show clear trends were excluded (Mn, Ni, Zn, Pb, Ba, Cr, Au and Ag).

Cu. At 400°C there is a good correlation between Cu and SiO₂ (Fig. 3.35a) indicating that Cu is being released during the dissolution of volcanic glass. The correlation between Cu and H₂S indicates that copper is hosted by the Fe sulfide blebs in the glass. At 350°C (Fig. 3.35b), there is ample evidence that the glass is dissolving (Fig. 3.34), however, there is essentially no detectable copper. This suggests the precipitation of a Cu-bearing phase.

Figure 3.35. Plots of Cu ($\mu\text{mol kg}^{-1}$) versus SiO₂ and H₂S ($\mu\text{mol kg}^{-1}$) for the BW1 and BW2. Symbols in red represent values during glass dissolution, while symbols in blue represent values after glass dissolution.

Co, Mo. At 350°C there appears to be no significant difference in Co concentrations during and after glass dissolution (Fig. 3.36b), however, at 400°C there is a positive relationship between Co and SiO₂ when glass is dissolving (Fig. 3.36a). This suggests that, as with copper, Co is derived from sulfides in the volcanic glass but that at 350°C its mobility is limited and it is precipitating in a secondary phase. For Mo, there is a positive correlation with SiO₂ at both temperatures (Fig. 3.36c,d). This suggests its derivation from the volcanic glass, or the sulfide blebs in the glass (Fig. 3.37).

V. At 350°C, there is a negative correlation between V and SiO₂ (Fig. 3.36f), while at 400°C, the highest V values are encountered after the glass has been removed (Fig. 3.36e). Vanadium occurs as a component of titanomagnetite (Hukkanen and Walden, 1985). It is possible that elevated Fe concentrations during glass dissolution could suppress titanomagnetite dissolution thus leading to lower V concentrations. This is a possible mechanism to explain the results at 350°C (Fig. 3.36h); however, at 400°C, this is not as clear. Figure 3.36g shows there is no clear correlation between Fe and SiO₂ at 400°C. As *in situ* pH does not vary significantly over the experiment, the difference in V mobility cannot be explained by pH change.

The results show that, from elements discussed above, there is higher mobility in solution at 400°C than at 350°C. As there is no significant difference in concentrations of Cl and H₂S released during glass dissolution, the most plausible explanation is that at 400°C there is higher mineral solubility and thus secondary trace element-containing phases do not precipitate. The release of significant concentrations of some of the trace elements in solution is mostly dependent on the dissolution from the volcanic glass and to a lesser degree from primary minerals (Fig. 3.35).

Figure 3.36. Plots of Co, Mo, V and Fe ($\mu\text{mol kg}^{-1}$) versus SiO_2 ($\mu\text{mol kg}^{-1}$) for BW1 and BW2. Symbols in red represent values during glass dissolution, while symbols in blue represent values after glass dissolution.

Figure 3.37. Plots of Co and Mo ($\mu\text{mol kg}^{-1}$) versus H_2S ($\mu\text{mol kg}^{-1}$) for BW1 and BW2. Symbols in red represent values during glass dissolution, while symbols in blue represent values after glass dissolution.

3.3.2. The path of fluid-rock interaction

Activity-activity diagrams

The path of fluid-rock interaction can be examined by plotting aqueous species' activities/activity ratios on activity phase diagrams. The software EqSolvR was used to determine the species activities and pH values (Chapter 2).

Activity diagrams were constructed for the experimental T (350 and 400°C) and a pressure of 500 bar, assuming unit activity of mineral phases. There was no period during the experiments where quartz was saturated, quartz was neither observed in the original basalt, nor in the reacted rock. This means that SiO₂ activity cannot be fixed by the presence of quartz, thus, for activity diagrams that do not plot SiO₂ activity as a variable, it is necessary to define SiO₂ activity. The average SiO₂ concentrations during and after the volcanic glass dissolution were used to determine SiO₂ activity. These were (in log units): -1.54 (during glass dissolution) and -2.0 (after glass dissolution) at 350°C/490 bar and -1.57 and -2.06 at 400°C/502 bar.

Activity diagrams show that the location of the fluid compositions in activity-activity space. When a fluid composition lies within a particular mineral stability field, this indicates that the composition is consistent with the stability of this mineral. Note, however, that these projections are two dimensional and are “projected” through other components. This means that, although, a particular mineral may be stable according to the phase diagram, another mineral may actually be more stable when other components are present. Selected diagrams are presented in the discussion below. All activity diagrams calculated are reported in Appendix B.

Fluid samples were collected approximately daily during the experiments. The cation activity ratios shown in the activity diagrams thus represent the average fluid composition over that period. At a flow rate of 1 ml hr⁻¹ and a porosity of ~53% (Chapter 2, §2.4.1) this constitutes approximately 2.2 pore volumes of fluid each day (ignoring expansion of the pressure vessel and rock). The average fluid composition plotted on the activity diagram thus indicates that 2.2 pore volumes reached this composition on average. Note that the *in situ* pH was relatively constant over the experiments, thus changes in cation activity ratios (e.g. $a_{Ca^{2+}}/a_{H^+}^2$) mainly reflect changes in cation concentration.

Figure 3.38a shows the activity diagram for the CaO-Al₂O₃-SiO₂-H₂O system at 400°C. This initial blank composition had detectable Ca and log a_{SiO_2} is assumed to be < -4,

thus the blank composition plots as shown (yellow circle). After 24 hours at 400°C, the average solution composition passes quartz saturation and $a_{Ca^{2+}}$ increases about two orders of magnitude. The average fluid composition lies in the grossular stability field. The rapid increase in SiO_2 activity highlights the fast rate of glass dissolution where the concentration of SiO_2 is controlled by the competition between the flow rate and the precipitation of secondary minerals (i.e., steady state). Over the next ~15 days, $\log(a_{SiO_2})$ remains elevated (-1.6) as glass dissolves, however, $\log(a_{Ca^{2+}})$ decreases gradually such that fluid passes through prehnite field, past the prehnite-anorthite-wairakite triple point and into the anorthite field. At this time, glass becomes depleted, $\log(a_{SiO_2})$ decreases to below quartz saturation, while $a_{Ca^{2+}}$ remains fairly constant. Once $\log(a_{SiO_2})$ reaches steady state at -2.1, $\log(a_{Ca^{2+}})$ begins to decrease again and the fluid composition passes into the margarite field.

The assemblage grossular-wollastonite was found immediately at the entry point of the fluid. This testifies to fast reaction rates that rapidly shift the blank composition to grossular stability. This is due to quantitative removal of Na and K and, to a much lesser degree Ca, from the rock leaving a Ca-silicate assemblage behind. If the experiment had continued for a longer period of time, it is expected that an alteration front, defined by the removal of Na and K from the rock, would be found to have moved up the column. This shows how water, with an absence of alkali cations, is effective at removing Na and K during hydrothermal alteration.

Figure 3.38b shows the same diagram (CaO-Al₂O₃-SiO₂-H₂O system) for the experiment at 350°C. Initial output fluid compositions do not reach the field of grossular at 350°C but lie in the prehnite field while glass was dissolving. This indicates that the lower temperature did not allow $\log(a_{Ca^{2+}}/a_{H^+}^2)$ to increase high enough to stabilise this mineral. No evidence of prehnite was found during SEM-EDS examination; however, the absence of grossular is in agreement with fluid chemistry. Once glass dissolution is complete, the equilibrium shifts to the prehnite-clinozoisite mineral phase boundary for almost 48 hours and then to the clinozoisite-anorthite mineral phase boundary for only 24 hours, finally passing through the anorthite field and into the margarite stability field. Of the above minerals only anorthite was found in the reacted basalt. This indicates that margarite was metastable perhaps due to the abundance of plagioclase to act as a substrate for anorthite precipitation or that margarite was not the stable phase due to the presence of Mg and Fe in the fluid stabilising celadonite. The presence of celadonite replacing olivine suggests that

while glass was dissolving, and K activity was higher, Mg/Fe released from olivine formed this mineral.

In the $K_2O-Al_2O_3-SiO_2-H_2O$ activity space (Fig. 3.39) the path of the fluid composition is similar at both temperatures. At 350°C, quartz immediately becomes supersaturated and fluid composition lies in the muscovite field (Fig. 3.39b) while at 400°C quartz is slightly undersaturated and also in the muscovite field (Fig. 3.39a). In both experiments, the concentration of K is elevated in the first sample after temperature shift, however, it declines over the following 5 days, in both experiments. The source of K in the basalt is primarily the glass. It would be expected that if K was being congruently released while glass was dissolving, its trend should follow that of SiO_2 . The decrease in K concentration thus indicates precipitation of a secondary K-bearing phase. Celadonite is the only K-bearing secondary phase observed in the run products of the experiments and its precipitation is concluded to be the cause of the decrease in K concentration. The incorporation of Na into celadonite also explains the decrease in Na over the same period.

Celadonite is a dioctahedral mica isostructural with muscovite, where $Fe^{VI}Si^{IV}$ and $Mg^{VI}Si^{IV}$ substitutes for $Al^{VI}Al^{IV}$, and Fe^{3+} for Al^{VI} , thus there will be fixed activity of muscovite in this mineral (Schmidt et al., 2001). This is consistent with the position of the fluid composition in the activity diagrams (Fig. 3.39). At both temperatures, the fluid path lies colinear with the muscovite-pyrophyllite join.

At 350°C, once quartz becomes undersaturated, $\log(a_{K^+}/a_{H^+})$ increases along the muscovite - andalusite join indicating that K was being released to the fluid. This suggests that celadonite (being the only K-bearing phase identified) is dissolving again, probably because of lower silica activities. At 400°C, the path is similar but the increase in $\log(a_{K^+}/a_{H^+})$ is less obvious.

For the last several days, both at 350 and 400°C, fluid composition moves to lower $\log(a_{K^+}/a_{H^+})$ into the andalusite and corundum fields, respectively. The chemistry results show that this is due to a substantial decrease in K concentration (Fig. 3.1 and 3.19) suggesting that the secondary mineral releasing K became exhausted. This, however, is inconsistent with the SEM results where the presence of celadonite was confirmed. The explanation for the significant decrease in K is therefore uncertain.

The overall path of fluid-rock interaction in the $K_2O-Al_2O_3-SiO_2-H_2O$ system at both temperatures is similar indicating that the mineral reactions involved are likely the same.

In Figure 3.39, the red crosses show positions of effluents collected at 0.5 ml hr⁻¹ flow rate for the last few days of the experiments. There is no noticeable difference from earlier samples collected at 1.0 ml hr⁻¹. This confirms that changes in flow rate did not affect cation activity ratios.

Figure 3.38. Activity diagrams for the CaO-Al₂O₃-SiO₂-H₂O system showing mineral stability fields for BW1(a) and BW2(b). Black and red crosses show position of effluent samples collected at 1.0 and 0.5 ml hr⁻¹ flow rate, respectively. Yellow circles show position of the unreacted fluid (water) at 400 and 350°C/500 bar. Black dotted line indicates quartz saturation while pink dotted lines represent the average of silica concentration (in log units) before and after dissolution of the basalt glass, calculated for the respective experiments. Blue arrows show the path of reacted fluids over the time of the experiments.

Figure 3.39. Activity diagrams for the $K_2O-Al_2O_3-SiO_2-H_2O$ system showing mineral stability fields for BW1(a) and BW2(b). Black and red crosses show position of effluent sample collected at 1.0 and 0.5 ml hr^{-1} flow rate, respectively. Yellow circles show position of the unreacted fluid (water) at 400 and 350°C/500 bar. Black dotted line indicates quartz saturation while pink dotted lines represent the average of silica concentration (in log units) during and after dissolution of the basalt glass, calculated for the respective experiments. Blue arrows show the path of reacted fluids over the time of the experiments.

Chlorite was also identified as a common secondary aluminosilicate in the experiments (Fig. 3.6 - 3.11, 3.24 - 3.25, 3.29 - 3.30). Figure 3.40 shows the activity ratio diagrams for the $MgO-Al_2O_3-SiO_2-H_2O$ systems at 350 and 400°C/500 bar. Both at 350 and 400°C, during and after the basalt glass dissolution, the decrease in cation activity ratios of $\log(a_{Mg^{2+}}/a_{H^+}^2)$ mainly reflect changes in cation concentration, as the *in situ* pH was relatively constant over the experiments.

This initial blank composition had detectable Mg and $\log a_{SiO_2}$ is assumed to be < -4 . After 24 hours in both experiments, the average solution compositions pass quartz saturation and $a_{Mg^{2+}}$ increases about two orders of magnitude. The average fluid compositions lie in the chlorite stability field (CL14A = clinocllore) both for the BW1 and BW2. Over the next ~11 days, $\log(a_{SiO_2})$ remains elevated (~ -1.6) as glass dissolves, however, $\log(a_{Mg^{2+}})$ decreases gradually to an activity of ~ -5.5 in both experiments. At this point, glass becomes

depleted, $\log (a_{\text{SiO}_2})$ decreases to below quartz saturation, while $a_{\text{Mg}^{2+}}$ remains fairly constant during BW1, while it visibly decreases during BW2. Once $\log (a_{\text{SiO}_2})$ reaches steady state at ~ -2.1 and -2.0 in BW1 and BW2, respectively, $a_{\text{Mg}^{2+}}$ begins to decrease again in both experiments and the fluid compositions remain the chlorite field by the end of the experiment.

In BW1 (400°C) chlorite was found intergrown with the other secondary mineral phases including grossular and wollastonite and replacing primary plagioclase, clinopyroxene and olivine. In BW2 (350°C), chlorite appears as the main secondary aluminosilicate. It was identified at the bottom of the Reactor after the conclusion of both experiments while no evidence of this mineral was found at the top of the Reactor after both simulations. The identification of the chlorite during rock analysis demonstrates that fluid compositions must have been saturated with respect to this mineral. This is consistent with the activity diagrams where the fluid compositions lie within the chlorite field in both experiments (Fig. 3.40).

Figure 3.40. Activity diagrams for the $\text{MgO-Al}_2\text{O}_3\text{-SiO}_2\text{-H}_2\text{O}$ systems showing mineral stability fields (CL14A = clinochlore) for BW1 and BW2. Black and red crosses show position of effluent sample collected at 1.0 and 0.5 ml hr^{-1} flow rate, respectively. Yellow circles show position of the unreacted fluid (water) at 400 and 350°C/500 bar. Black dotted line indicates quartz saturation while pink dotted lines represent the average of silica concentration (in log units) during and after dissolution of the basalt glass, calculated for the respective experiments. Blue arrows show the path of reacted fluids over the time of the experiments.

The fluid-mineral reactions that occurred during the experiments can provide information on the chemical path that the fluid took while passing through the rock and the resulting effects on the mineral assemblage.

At 400°C, exclusively Ca-aluminosilicate phases formed at bottom of the Reactor. The source of Ca, Al and SiO₂ was provided by the rock, as these components are not present in the input fluid. The extreme rearrangement of rock components during the alteration means that it is not possible to relate any particular secondary phase to a primary mineral. To form anorthite, grossular and wollastonite, both plagioclase and clinopyroxene can be the source for Ca, while plagioclase is the main source of Al. During the first approximately 15 days, the main source of SiO₂ was the volcanic glass.

SEM analysis shows that both clinopyroxene and plagioclase had almost completely dissolved in grains collected from immediately adjacent to the fluid entry point. The precipitation of anorthite, grossular and wollastonite (end-members in the reactions) at the expense of plagioclase and clinopyroxene in the experiments can be represented in Reactions 7-11:

All of these reactions consume H^+ explaining the high quench pH values during the experiment relative to the input water pH (after 400 hours, Fig. 3.1). The reactions also release the Na, Mg and Fe from the minerals to the fluid. After complete glass dissolution, Al concentrations also significantly increase.

Further up the Reactor, chlorite was observed with a lesser concentration of Ca-aluminosilicates. The source of Mg and Fe for chlorite is from olivine and clinopyroxene and cannot be from the input fluid, while Al could be provided directly from the dissolution of primary minerals as per Reactions 7–11. The formation of chlorite at the expense of clinopyroxene and olivine is represented in Reactions 12 and 13:

During these reactions, the formation of chlorite from clinopyroxene dissolution consumes H^+ while the formation of chlorite from olivine produces hydrogen ion.

Celadonite was observed at top of the Reactor. From SEM analysis of the basalt block, celadonite appeared in dense foliated masses that only replaced olivine. The celadonite contains both K and Na. Potassium was provided by the glass (as there are no K-bearing minerals in the basalt) while sodium is from plagioclase dissolution. As concentrations of both elements decrease from the beginning of glass dissolution (higher SiO_2 activity) (Fig. 3.1, §3.2.1.1) it indicates that celadonite began to form immediately after temperature shift. However, celadonite does not appear as a secondary mineral at bottom of the Reactor. This implies that when fresh fluid entered the Reactor, the extreme disequilibrium between the distilled water and the rock minerals caused rapid formation of grossular, wollastonite and chlorite. This only occurred in the very bottom millimetre of the Reactor and resulted in the extreme “leaching” of the cations Na, K, Fe and Mg from the rock. As these reactions occurred, the concentrations of these components would have increased leading to equilibration with celadonite.

The celadonite formation at the expense of olivine can be represented by Reaction 14:

The concentrations of Al, Na and K (Fig. 3.1, §3.2.1.1) show a sharp increase in solution at approximately 400 hrs. This coincides with values of silica at lower activity (after glass dissolution). The sudden rise of K, Al and Na in the solution suggests that celadonite started to dissolve at this point.

During these reactions it is evident that the consumption of H^+ by the formation of Ca-aluminosilicates and chlorite is greater than the production of H^+ by the formation of celadonite. Although it is not possible to determine a proportion between minerals dissolved and precipitated during experiment, the formation of Ca-aluminosilicates must have been greater than celadonite. This explains why the pH reached values highly basic in BW1.

In BW2, at 350°C, anorthite and chlorite were the main secondary minerals identified at the bottom of the Reactor. Neither grossular nor wollastonite was found. The formation of chlorite required a source for Mg, Fe and Al that could be provided only by the rock as these are not present in the distilled water. The formation of chlorite and anorthite at the expense of clinopyroxene, olivine and plagioclase can be represented in Reactions 15-17:

During these reactions, both clinopyroxene and olivine can be the source of Mg and Fe. The conversion of plagioclase to anorthite is a residual reaction whereby the albite

component is being removed by the fluid. This is supported by the textural evidence seen in SEM examination (Fig. 3.24 – 25 – 29).

Celadonite was only observed at top of the Reactor. The formation mechanism of the celadonite is similar to the experiment at 400°C, but in this case, it does not contain Na. The progressive increase of Na after T shift during glass dissolution (Fig. 3.19, §3.2.2.2) confirms that this element is not involved in the celadonite formation at 350°C. The sudden rise of K and Al in the solution at 350 - 400 hrs (lower silica activity) suggests that celadonite started to dissolve at this point, as in BW1 (Fig. 3.19, §3.2.2.2).

Celadonite formation at top of the Reactor at the expense of olivine can be represented in Reactions 18:

During these reactions it is evident that the consumption of H^+ by the formation of chlorite and anorthite is greater than the production of H^+ by the formation of celadonite. As with BW1, it is not possible to determine the proportion between minerals dissolved and precipitated. However, it is supposed that the formation of chlorite and anorthite must have been greater than celadonite. This explains why the pH reached basic values as with BW1.

3.3.3. Na/K geothermometers

Figure 3.41 shows the activity ratio diagrams for the $\text{Na}_2\text{O}-\text{K}_2\text{O}-\text{Al}_2\text{O}_3-\text{SiO}_2-\text{H}_2\text{O}$ systems at 350 and 400°C/500 bar. The diagrams show that at 350 and 400°C, during basalt glass dissolution, fluid compositions move towards equilibrium with muscovite. After glass dissolution, both at 350 and 400°C, fluid compositions move to lower $\log (a_{K^+}/a_{H^+})$ but constant $\log (a_{Na^+}/a_{H^+})$ into the andalusite field.

In these diagrams, many fluid compositions lie close to the metastable extension of the albite - K-feldspar join. If a fluid composition is on this line the Na/K ratio should reflect equilibrium at temperature and can be used as a geothermometer (Ellis, 1970; Ellis and Mahon, 1977; Fournier, 1981; Fournier and Truesdell, 1974; Fournier, 1979; Henley et al., 1984). Cation ratio geothermometers (eg. Na-K, Na-K-Ca) are used extensively to estimate aquifer temperatures in geothermal systems, however, it is of great interest to geochemists how quickly these geothermometers equilibrate.

Table 3.11 and Figure 3.42 report the average estimated temperature (°C) calculated both for the BW1 and BW2 fluid compositions utilising several cation geothermometers reported in literature (Arnórsson, 1983; Fournier and Truesdell, 1973; Fournier, 1979; Giggenbach, 1988b; Nieva and Nieva, 1987; Santoyo and Díaz-González, 2009; Tonani, 1980; Truesdell, 1976).

For the BW1 experiment, during glass dissolution (Sample 7-18), the estimated temperature by several Na-K geothermometers is close to 400°C within one standard deviation. The Na-K-Ca geothermometer gives an average estimate well below 400°C indicating that Ca concentration is far from the equilibrium concentration expected at this temperature. After glass dissolution ceases (Sample 19-35), temperature estimates for all geothermometers are well below the experimental temperature of 400°C. This is due to the decrease in K concentrations because of the loss of glass and the lower solubility of the secondary K-bearing minerals. Changing the flow rate to 0.5 ml hr⁻¹ (Sample 34 – 35) made no difference to the accuracy of temperature estimates.

In BW2, the situation is reversed. During glass dissolution (Sample 7–18), temperature estimates from the Na-K geothermometers are significantly higher than the experimental temperature, while the Na-K-Ca geothermometer gives a low temperature. After glass dissolution ceases, and while K concentrations are high due to celadonite dissolution, temperature estimates from several geothermometers are close to the experimental temperature of 350°C within one standard deviation. Again, the Na-K-Ca geothermometer

gives a low value. After K concentrations decrease (Sample 35 – 46), the estimates fall well below the actual experimental temperature.

Figure 3.42 shows estimated temperature (°C) plotted versus time. Also, in this figure are plotted the SiO₂, Na and K concentrations. The trends for silica are similar and the time taken for removal of glass is the same in both experiments, however, the estimated temperatures at 400°C are much closer than at 350°C. It is evident that during glass dissolution at 350°C, K concentrations are overall higher than at 400°C while Na concentrations are similar. This leads to overestimation of the temperature at 350°C. After glass dissolution, K concentrations remain higher at 350°C due to dissolution of celadonite, thus the assemblage of muscovite (in celadonite) and albite (in plagioclase) is maintaining fluid Na/K near the equilibrium value. It is evident that without a secondary K-bearing phase, Na/K ratios are not useful in estimating temperature.

Figure 3.41. Activity diagrams for the $\text{Na}_2\text{O}-\text{K}_2\text{O}-\text{Al}_2\text{O}_3-\text{SiO}_2-\text{H}_2\text{O}$ system showing mineral stability fields for BW1(a) and BW2(b) during and after glass dissolution. Black and red crosses show position of effluent samples collected at 1.0 and 0.5 ml hr^{-1} flow rate, respectively. Yellow circles show position of the unreacted fluid (water) at 400 and 350°C/500 bar. Blue arrows show the path of reacted fluids over the experiment.

Table 3.11. Average and 1σ of estimated temperature ($^{\circ}\text{C}$) during and after basalt glass dissolution using fluid compositions for the BW1 and BW2. Estimates were made using several geothermometers from literature (Arnórsson, 1983; Fournier and Truesdell, 1973; Fournier, 1979; Giggenbach, 1988b; Nieva and Nieva, 1987; Santoyo and Díaz-González, 2009; Tonani, 1980; Truesdell, 1976).

		Na/K (Fournier 1979)	Na/K (Truesdell 1976)	Na/K/Ca (Fournier and Truesdell 1973) ($\beta=1/3$)	Na/K (Santoyo and Díaz-González 2009)	Na/K (Arnórsson 1983) (250-350 $^{\circ}\text{C}$)	Na/K (Tonani 1980)	Na/K (Nieva and Nieva 1987)	Na/K (Giggenbach 1988)
BW1 400 $^{\circ}\text{C}$ /502 bar	During basalt glass dissolution (Sample 7-18)	383	424	254	408	364	451	366	382
	1σ	22	36	10	34	19	40	22	20
	After basalt glass dissolution (Sample 19-33)	250	233	205	224	246	244	236	263
	1σ	53	71	31	69	48	76	52	49
	After basalt glass dissolution (Sample 34-35) 0.5 ml hr $^{-1}$	190	154	166	147	191	160	177	207
	1σ								
BW2 350 $^{\circ}\text{C}$ /490 bar	During basalt glass dissolution (Sample 7-18)	390	437	222	420	370	466	374	388
	1σ	41	67	15	64	36	74	40	36
	After basalt glass dissolution (Sample 19-33)	348	368	216	354	333	390	332	351
	1σ	18	27	9	26	16	30	18	16
	After basalt glass dissolution (Sample 35-46)	234	209	159	200	231	218	220	248
	1σ	15	20	8	20	14	22	15	14

Figure 3.42. Estimated temperatures ($^{\circ}\text{C}$) calculated using several cation geothermometers (Arnórsson, 1983; Fournier, 1979; Giggenbach, 1988b; Nieva and Nieva, 1987; Santoyo and Díaz-González, 2009; Tonani, 1980; Truesdell, 1976) together with SiO_2 , Na and K concentrations for BW1 and BW2 plotted versus time. Dotted black lines separate value of SiO_2 above quartz saturation (during basalt glass dissolution) from those below quartz saturation (after basalt glass dissolution). Dotted red lines show experimental temperature of BW1 and BW2 over time. n: Sample number.

3.3.4. Geological implications

Although the interaction between basalt and (distilled) water is an unlikely scenario in the natural environment, the presence of celadonite as an alteration product is notable and significant. Celadonite was formed in both the 350°C and 400°C experiments. The experiments show that it can be formed by the interaction of deuteritic water and basalt without any other added components, provided that the basalt has sufficient glass as a source for SiO₂ and K and mafics as a source for Mg and Fe. Celadonite is known as a hydrothermal alteration product derived by the interaction between basalt and seawater where it is known to replace both olivine and pyroxene (Baker et al., 2012).

Examination of the basalt block shows that celadonite is replacing olivine (Fig. 3.16). As olivine is more soluble than the accompanying aluminosilicates (Brantley, 2008; Oelkers, 2001; Oelkers et al., 2018; Schott et al., 2009; Velbel, 2009), this resulted in it being the only mineral replaced by the celadonite (Hendricks and Ross, 1941). There was no evidence of augite and/or plagioclase replacement by celadonite. Our experiments demonstrate that celadonite can form by an “auto-metasomatic” process whereby only heated meteoric water in contact with fresh basalt is necessary. This conclusion implies that seawater is not necessary to supply K for celadonite formation if sufficient K is released from dissolving basaltic glass.

Celadonite occurred both at 350 and 400°C/500 bar with chlorite. This implies that the experiments reproduced a metamorphic grade up to lower greenschist facies (Brown, 1967; Velde, 2003; Wise and Eugster, 1964).

3.4. References

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Chapter 4: Basalt – Geothermal Brine Interactions Under Hydrothermal Conditions

4.1. A brief introduction

Basalt-geothermal brine interactions, both at supercritical and subcritical conditions, can reflect many real scenarios occurring in the geothermal environment. During circulation, a geothermal fluid achieves its temperature depending on the depth, path, and its proximity to the heat source. The higher the enthalpy content of the fluid, the more energy that can be extracted usefully.

The chemical composition of the hydrothermal fluid reflects the temperature, pressure and geological setting of the surrounding host rocks. It is therefore expected that the composition will be markedly different depending on whether the fluid is at subcritical or supercritical conditions. It is also expected that the fluid will be in equilibrium with its host rock minerals before extraction and will give an indication of its pressure and temperature conditions. For example, geothermometers using the cation concentrations in the fluid are used to estimate aquifer temperatures in geothermal systems (Fournier and Truesdell, 1973; Fournier, 1979; Giggenbach et al., 1983; Giggenbach, 1988b; Henley and Ellis, 1983; Marini, 2000).

One example of supercritical hydrothermal circulation is at the Reykjanes and Krafla geothermal fields in Iceland. Many studies have been carried out investigating these geothermal reservoirs especially during the Icelandic Deep Drilling Project, (Armannsson et al., 2014; Arnórsson, 1995; Arnórsson et al., 1978; Asmundsson et al., 2014; Elders and Friðleifsson, 2010; Fowler et al., 2015; Franzson et al., 2008; Fridleifsson and Elders, 2005; Fridleifsson et al., 2017; Friðleifsson et al., 2014; Marks et al., 2010; Mortensen et al., 2014; Pálsson et al., 2014; Thórhallsson et al., 2014; Weir et al., 2001). Icelandic geothermal systems are dominated by hydrothermal circulation involving seawater mixed with meteoric water, heated by a shallow magmatic source. As a result, supercritical fluids are located at relatively shallow depths when compared to geothermal fields elsewhere.

Few experimental simulations have been carried out to investigate geothermal brine – rock interactions at geothermal conditions. Examples include: greywacke (Taupo Volcanic Zone, New Zealand) and geothermal brine (Wairakei field, New Zealand) at 25 - 203°C/35 bar using a flow-through hydrothermal apparatus (Sonney and Mountain, 2013); between basaltic glass (Stapafell, Iceland) and natural geothermal brine (Krafla field, Iceland) at 260°C and 400 - 420°C/69 bar using a flow-through system (Heřmanská et al., 2019).

In the present study, tholeiitic basalt (Eldvarpahraun, Iceland) was reacted with natural geothermal brine (Rotokawa field, New Zealand) at 400°C/483 bar and at 350°C/486 bar, using a flow-through hydrothermal apparatus. The geothermal fluid used for these experiments contains significant concentrations of K, Na, Ca, SO₄, SiO₂ and Cl when compared to distilled water, but at the same time, it is more diluted when compared to natural seawater (Chapter 6). The brine has a low initial pH due to the addition of sulfuric acid (H₂SO₄) at the plant to inhibit silica polymerisation and subsequent silica scaling (Addison et al., 2015).

Our results indicate that the geothermal brine reacted aggressively with the basalt in both experiments. Major changes in solution chemistry occurred after temperature shift. These consisted of: (1) silica concentrations consistently over quartz saturation for two weeks at 400°C, while there was a progressive decrease from quartz supersaturation at 350°C; (2) pH values strongly correlated with silica concentrations mainly due to the dissolution of volcanic glass; (3) lower concentrations of K and SO₄²⁻ relative to the starting brine while there was a measurable depletion of Ca only at 350°C; (4) measurable concentrations of H₂S that were greater at 400°C than at 350°C; and (5) a moderate but higher mobility of the trace elements in solution at 400 rather than at 350°C.

Analysis of the reacted rock material was conducted on basalt grains collected both from the bottom and top portion of the Reactor. Results show that the bottom portion (first 1-2 mm), located at the entry point of the unreacted fluid, is the most altered portion of the basalt, while the top portion (last 1-2 mm), located at the exit point of the reacted fluid into Reactor, is the least altered portion of the basalt.

4.2. Results

In this chapter the results are presented for the:

- 1) major element analyses of experimental solutions;
- 2) trace element analyses of experimental solutions;
- 3) chemical, mineralogical and textural analyses of reacted basalt grains.

4.2.1. BGB1: Basalt – Geothermal brine at 400°C/483 bar

The first basalt - geothermal brine experiment (BGB1) ran for total time of 853 hrs (Fig. 4.1). The first 167 hr were at room temperature/483 bar and the remaining 687 hr were at 400°C/483 bar. The flow rate was 1 ml hr⁻¹ up to 768 hr after which it was changed to 0.5 ml hr⁻¹ for the remaining 86 hr. As for the BW experiments, the flow-rate was set-up to guarantee the collection of enough solution for all chemical analyses at the approximately 24 hours interval. For this experiment, analysis of major ions was undertaken for 34 fluid samples. Trace element analysis was undertaken for the first 30 fluid samples.

4.2.1.1. Major element concentrations

Appendix (C) lists the complete experimental parameters and results (T, P, flow rate, chemistry). Figure 4.1 and Figure 4.2 show selected elements plotted against experimental time in hours. The unreacted geothermal brine composition is shown at time = 0. Initial concentrations of major ions were measured as follow: As (0.02 mmol kg⁻¹), B (4.45 mmol kg⁻¹), Ca (0.08 mmol kg⁻¹), Fe (<0.08 mmol kg⁻¹), K (3.0 mmol kg⁻¹), Mg (0.01 mmol kg⁻¹), Na (31.6 mmol kg⁻¹), SiO₂ (12.6 mmol kg⁻¹), Al (0.06 mmol kg⁻¹), Sr (<0.003 mmol kg⁻¹), Li (0.82 mmol kg⁻¹), H₂S (<0.01 mmol kg⁻¹), Cl (26.54 mmol kg⁻¹) and SO₄ (4.22 mmol kg⁻¹).

During the room temperature (~21°C) period, the significant changes in solution composition are increases in Al, Ca, Fe and Mg. The pH values are on average higher (5.63) than the starting blank (3.91). Over the seven-day room temperature period Fe concentration increases while Ca and Al decrease.

The temperature shift to 400°C was initiated at 167 hours and took approximately 3 hours, thus only about 3 ml of the first sample were collected while heating was occurring. Major changes in solution chemistry are observed after the temperature shift. Effluent quench pH decreases to between 2.87 and 3.5 for approximately 250 hours and then increases to about 7 over the next 200 hours after which it remains between 7 and 8 for the remainder of

the experiment. The change in flow rate at 768 hours does not noticeably effect pH. Calculated *in situ* pH stays constant after the temperature shift at about 7.

SiO₂ increases to 34.6 mmol kg⁻¹ (~2080 ppm) which greatly exceeds quartz saturation at 400°C/500 bar (1238 ppm, Supcrt92). Between 215 and 550 hours, silica concentration remains elevated and relatively constant at an average value of 31.1 mmol kg⁻¹. It then decreases to about 16 mmol kg⁻¹ by 600 hours after which it remains relatively stable for the remainder of the experiment. The change in flow rate at 768 hours does not significantly affect SiO₂ concentration.

Na concentration decreases slightly after the temperature shift but only for three days after which it remains similar to the blank sample. K shows an increase after temperature shift, reaching ~5.0 mmol kg⁻¹ for two days. It decreases to 3.8 mmol kg⁻¹ after one day and then gradually decreases to 2.3 mmol kg⁻¹ 620 hours and then remains constant.

Al concentration decreases after the temperature shift to between 0.02 and 0.03 mmol kg⁻¹ up to 550 hours, after which it increases to 0.22 mmol kg⁻¹ by 768 hrs. After the flow rate change, it decreases to 0.16 mmol kg⁻¹ at 809 hrs and 0.17 mmol kg⁻¹ at 853 hrs.

Ca concentration decreases, after the temperature shift, to a minimum of 0.05 mmol kg⁻¹ at 215 hours and then increases up to 0.12 mmol kg⁻¹ by 550 hours. It remains stable around 0.10 - 0.11 mmol kg⁻¹ to 768 hours. After the change in flow rate, Ca concentration peaks at 0.14 mmol kg⁻¹ and decreases back to 0.1 mmol kg⁻¹ in the last sample.

Fe decreases to near or below detection limit after temperature shift and remains at this value for the remainder of the experiment. Mg concentration also decreases after temperature shift and remains near blank values for the next 450 hours after which it increases to between 0.01 and 0.02 mmol kg⁻¹ up until the flow rate change at 768 hours. Similar to Ca, Mg has a peak value of 0.03 mmol kg⁻¹ after the change in flow rate and then decreases to 0.05 mmol kg⁻¹ in the last sample.

SO₄ concentration decreases to a minimum of 2.50 mmol kg⁻¹ immediately after temperature shift. It then increases to a value of 3.8 mmol kg⁻¹ by 406 hours after which there is an overall small decrease to 3.2 mmol kg⁻¹ (1.0 mmol kg⁻¹ less the input solution) by 768 hours. The change in flow rate to 0.5 ml hr⁻¹ did not significantly affect its concentration. H₂S concentration increases to a maximum of ~0.05 mmol kg⁻¹ for three days after temperature increase. It then gradually decreases over the remainder of the experiment reaching a value of 0.01 mmol kg⁻¹ at 768 hours. The change in flow rate did not cause a significant change in concentration.

Cl concentration remains close to the input solution value throughout the experiment indicating that the apparatus was behaving correctly.

Figure 4.1. Major element concentrations in blank and effluent samples (mmol kg^{-1}) versus time (hr) for the basalt - geothermal brine experiment at $400^\circ\text{C}/483$ bar (BGB1). Yellow symbols are the blank sample composition of the geothermal brine. Blue symbols are for effluents at room T/ 483 bar and 1.0 ml hr^{-1} flow rate. Black symbols are effluents at $400^\circ\text{C}/483$ bar and 1.0 ml hr^{-1} flow rate. Red symbols are effluents at $400^\circ\text{C}/483$ bar and 0.5 ml hr^{-1} flow rate. *In situ* pH is the calculated pH at temperature.

Figure 4.2. Major element concentrations in blank and effluent samples (mmol kg^{-1}) versus time (hr) for the basalt – geothermal brine experiment at $400^\circ\text{C}/483$ bar (BGB1). Yellow symbols are the blank sample composition of the geothermal brine. Blue symbols are for effluents at room T/ 483 bar and 1.0 ml hr^{-1} flow rate. Black symbols are effluents at $400^\circ\text{C}/483$ bar and 1.0 ml hr^{-1} flow rate. Red symbols are effluents at $400^\circ\text{C}/483$ bar and 0.5 ml hr^{-1} flow rate. *In situ* pH is the calculated pH at temperature.

4.2.1.2. Trace element concentrations

Appendix (C) lists the complete trace element results. Figure 4.3 and Figure 4.4 show these results plotted against time in hours. The unreacted geothermal brine composition is shown at $t = 0$. All trace elements (except for Co and Ba) are detectable in the input solution. In particular, elevated values of Zn ($1.9 \mu\text{mol kg}^{-1}$), Rb ($8.5 \mu\text{mol kg}^{-1}$) and Au ($1.0 \mu\text{mol kg}^{-1}$) are notable.

During the room temperature ($\sim 21^\circ\text{C}$) period, measurable increases in trace element concentration, including Cr, Mn, Co, Ni, Ba, Pb and, in particular, Cu and Zn, are present in the effluent. V, Cd and Au decrease in solution, while Rb and Mo remain relatively unchanged. Ag has values near or below detection limit.

After the temperature shift to 400°C , several trace elements including Cr, Mn, Co, Ni, Cu, Ag, and Ba decrease sharply to values at or below the detection limit. V concentration remains below $0.1 \mu\text{mol kg}^{-1}$ until 600 hours after which it increases to between 0.2 and $0.3 \mu\text{mol kg}^{-1}$. Rb concentration decreases regularly to $1.9 \mu\text{mol kg}^{-1}$ by the end of the experiment. Mo concentration remains relatively unchanged for the entire experiment while Pb concentration is highly irregular.

Au displays interesting behaviour. The concentration in the blank geothermal brine is about $1 \mu\text{mol kg}^{-1}$. During the room temperature period it decreases regularly to $0.2 \mu\text{mol kg}^{-1}$ and, after the temperature shift, it continues to decline in a regular manner until near detection limit. The clear exponential decrease, which is independent of temperature, suggests precipitation in the separator before passage through the rock.

Zn is the only trace element that shows a consistent increase after the temperature shift reaching up to $42 \mu\text{mol kg}^{-1}$. The increase in Zn concentration correlates with elevated SiO_2 values suggesting that Zn is dissolving from the volcanic glass. Its concentration decreases after 550 hours and remains so over the remainder of the experiment.

Figure 4.3. Trace element concentrations in blank and effluent samples ($\mu\text{mol kg}^{-1}$) versus time (hr) for the basalt – geothermal brine experiment at 400°C/483 bar (BGB1). Yellow symbols are the blank sample composition of the geothermal brine. Blue symbols are for effluents at room T/483 bar and 1.0 ml hr⁻¹ flow rate. Black symbols are effluents at 400°C/483 bar and 1.0 ml hr⁻¹ flow rate.

Figure 4.4. Trace element concentrations in blank and effluent samples ($\mu\text{mol kg}^{-1}$) versus time (hr) for the basalt – geothermal brine experiment at 400°C/483 bar (BGB1). Yellow symbols are the blank sample composition of the geothermal brine. Blue symbols are for effluents at room T/483 bar and 1.0 ml hr⁻¹ flow rate. Black symbols are effluents at 400°C/483 bar and 1.0 ml hr⁻¹ flow rate.

4.2.1.3. Mineralogy and texture of reacted basalt: Bottom of Reactor (Portion 1)

Mineralogical and textural analysis were undertaken on reacted grains collected from the bottom (Portion 1) of the Reactor (Fig. 4.5). Upon completion of the experiment, the reacted basalt grains were extracted from the Reactor. The rinsing and drying procedure of the grains was the same as described for BW1 and BW2 (Chapter 3). The basalt block was not introduced at the bottom of Reactor for this experiment.

Selected grains were mounted on aluminium stubs for textural analyses by SEM and several grains were epoxy-mounted and polished for SEM-EDS and EMPA analysis. Appendix C contains all SEM and EMPA results for this portion of the rock.

Figure 4.5. Schematic diagram (not to scale) showing position (Portion 1 and Portion 2) of reacted basalt grains shown in SEM photographs.

SEM-EDS and EMPA analysis

Several grains (Fig. 4.6 - 4.8) from immediately adjacent to the fluid entry point (Portion 1, Fig. 4.5) were examined. Results confirm a high degree of alteration of the basalt caused by intense hydrothermal activity. Minerals of secondary origin identified were anhydrite, biotite, apatite (?), Cu-sulfide, and Fe oxides. Results also confirm the presence of the primary minerals bytownite, clinopyroxene, olivine, and titanomagnetite (Table 4.1).

Table 4.1. Mineral assemblage detected by EMPA and SEM-EDS analysis of reacted grains extracted from the bottom (Portion 1) of Reactor after the BGB1 experiment. Appendix (C) contains all SEM and EMPA results for this portion of the rock.

Type of Analysis	Analysis Material	Mineral Identified	Average Mineral Composition
SEM-EDS	polished grains	Bytownite	$\text{Ca}_{0.70}\text{Na}_{0.19}\text{Al}_{1.79}\text{Si}_{2.31}\text{O}_8$, (An ₇₈ -Ab ₂₂)
EMPA	polished grains	Augite	$\text{Ca}_{0.70}\text{Mg}_{0.90}\text{Fe}_{0.37}\text{Si}_2\text{O}_6$
EMPA	polished grains	Biotite	$\text{K}_{0.49}\text{Ca}_{0.1}\text{Na}_{0.07}\text{Mg}_{1.4}\text{Fe}_{1.4}\text{Ti}_{0.05}\text{Al}_{1.16}\text{Si}_{2.92}\text{Al}_{0.08}\text{O}_{10}(\text{OH})_2$ (calculated based on an anhydrous composition of 11 oxygens)
EMPA	polished grains	Anhydrite	(Ca,Fe)SO ₄
SEM-EDS	grain surface	Apatite	$\text{Ca}_5(\text{PO}_4)_3(\text{OH},\text{F},\text{Cl})$
SEM-EDS	grain surface	Cu-sulfide (covellite?)	$\text{Cu}_{0.79}\text{Fe}_{0.16}\text{S}_{1.16}$
SEM-EDS	polished grains	Fe-Ti Oxide Fe-Oxide	-

Figure 4.6 shows SEM images of the reacted grains from the position immediately next to the entry point of the fluid. Anhydrite appears as singular euhedral tabular crystals, surrounded by hexagonal aligned plates of biotite, occurring in dense aggregates. There was no evidence of primary plagioclase and clinopyroxene on the surface of these grains. Only a few grains with this intensity of alteration, shown by a noticeable change in colour, were observed. Petrographic observation shows that the anhydrite crystals are transparent.

Figure 4.7a,b shows SEM images of rare minerals in the reacted grains including a copper sulfide phase with a hexagonal habit. The EDS analysis shows a composition close to idaite (Cu_5FeS_6) or possibly covellite (CuS) with minor Fe substitution. Also found were radiating acicular crystals of apatite. The occurrence of the apatite in a void suggests that they may be remnant crystals that were originally trapped in volcanic glass.

Figure 4.8 shows SEM backscatter images and EDS maps of a polished mount of a grain from Portion 1. Both plagioclase and clinopyroxene (both blue) are highly corroded and are replaced by biotite (green). Biotite occurs along the margins and inside the grain. Isolated

anhydrite crystals (violet) surround the grain and small areas of anhydrite occur internally. A large olivine crystal (grey) appears unreacted as it was isolated from the brine by surrounding minerals (the crack likely occurred during sample prep). EDS analysis of the Fe and Ti oxides reveal secondary magnetite and TiO_2 , however, the primary titanomagnetite was also present.

Figure 4.6. SEM images of grains collected from the bottom (Portion 1) of the Reactor after the BGB1 experiment (minerals identified by SEM-EDS analysis): a) grain covered by anhydrite (Anh) occurring in isolated tabular euhedral crystals and biotite (Bt) in masses of foliated crystals; (b) reacted grain surface covered by a secondary mineral assemblage consisting of anhydrite and biotite; (c) enlargement of red rectangular area in (b) showing euhedral tabular crystals of anhydrite and stacked hexagonal plates of biotite; (e-f) are enlargements, respectively, of rectangular area in (d) showing biotite appearing in hexagonal stacked crystals.

Figure 4.7. SEM images from the bottom (Portion 1) of the Reactor after the BGB1 experiment (minerals identified by SEM-EDS analysis): (a) grain surface showing a Cu-sulfide crystal appearing in hexagonal shape; (b) apatite (Ap), occurring in a radiating group of acicular crystals.

Figure 4.8. SEM backscatter images and EDS compositional maps of an epoxy-mounted, polished grain collected from immediately adjacent to the fluid entry point at bottom (Portion 1) of the Reactor: (a) backscatter image; (b) composite colour image combining the backscatter image and elemental maps for c) K in green, d) Ca in blue, and e) S in red. The composite image shows the anhydrite crystals (violet), biotite (green), unreacted plagioclase and clinopyroxene (blue), olivine (grey), and Fe-Ti oxides (white).

4.2.1.4. Mineralogy and texture of reacted basalt: Top of Reactor (Portion 2)

Several grains (Fig. 4.9 – 4.10) from immediately adjacent to the fluid exit point (Portion 2, Fig. 4.5) were examined. These were mounted on aluminium stubs for textural analyses by SEM while several grains were mounted in epoxy and polished for SEM-EDS analysis. Appendix (C) lists complete results for this portion of the altered basalt.

SEM-EDS analysis

Results show less intense alteration of the basalt grains when compared with the bottom of the Reactor (Portion 1). Minerals of secondary origin detected were a K-Mg-Fe-bearing aluminosilicate, identified here as smectite. Data also confirm the presence of the primary minerals bytownite, clinopyroxene, olivine, and titanomagnetite (Table 4.2).

Table 4.2. Mineral assemblage found during analysis of reacted grains extracted from top (Portion 2) of the Reactor after the BGB1 experiment. Analysis were effectuated by SEM-EDS. Appendix (C) contains all SEM results for this Portion of the rock.

Type of Analysis	Analysis Material	Mineral Identified	Average Mineral Composition
SEM-EDS	grain surface	Bytownite	$\text{Ca}_{0.9}\text{Na}_{0.2}\text{Al}_{1.5}\text{Si}_{2.4}\text{O}_8$ (An ₈₁ -Ab ₁₉)
SEM-EDS	grain surface	Augite	$\text{Ca}_{0.3}\text{Mg}_{0.8}\text{Fe}_{0.6}\text{Al}_{0.2}\text{Si}_2\text{O}_6$
SEM-EDS	polished grains	Fayalite	$\text{Mg}_{0.7}\text{Fe}_{1.2}\text{SiO}_4$ (Fo ₃₇ -Fa ₆₃)
SEM-EDS	polished grains	Smectite	$\text{K}_{0.1}\text{Mg}_{1.5}\text{Fe}_{1.3}\text{Al}_{0.2}\text{Si}_{3.3}\text{Al}_{0.7}\text{O}_{10}(\text{OH})_2 \cdot n\text{H}_2\text{O}$ (calculated based on an anhydrous composition with 11 oxygens)
SEM-EDS	polished grains	Titanomagnetite	$\text{Fe}^{2+}(\text{Fe}^{3+}, \text{Ti})_2\text{O}_4$

Figure 4.9 shows surface textures of three different grains collected from the top (Portion 2) of the Reactor. EDS backscatter images at low magnification show the K-Mg-Fe-bearing secondary phase with a honeycomb texture similar to smectite, primary clinopyroxene and plagioclase. In detail, the smectite-like phase occurs as foliated masses. Clinopyroxene appears relatively unaffected. Anhydrite and biotite were not observed within or on these grains.

Figure 4.10a-e shows SEM backscatter images and EDS maps for an epoxy-mounted, polished grain from the top (Portion 2) of the Reactor. A lesser degree of alteration is evident when compared with the grains analysed from the bottom (Portion 1) of the Reactor (Fig. 4.8). Primary minerals (plagioclase, clinopyroxene, olivine and oxides) appear moderately affected internally by alteration.

Figure 4.10f is the enlargement of the rectangular area in Figure 4.10a. The average composition of the K-Mg-Fe aluminosilicate phase from EDS analyses of the epoxy mounted grain is shown in Table 4.3. It contains a high FeO and MgO content with lesser K₂O. The low percentage concentration of K₂O excludes celadonite. A smectite clay such as saponite or nontronite (Cheshire et al., 2018; Haldar, 2020) fits the composition, however, the high temperature would seem to exclude a swelling clay as they would not be expected to be stable at 400°C (Bird, 1984; Browne, 1978; Browne and Ellis, 1970; Essene and Peacor, 1995; Hedenquist et al., 2000; Henley and Ellis, 1983; Reyes, 1990; Steiner, 1977). However, Yardley et al (2014) found saponite as a run product when reacting hornfels with water up to 500°C. Another possibility is corrensite, a mixed-layer chlorite - trioctahedral smectite clay mineral (Beaufort et al., 1997). In the present study, the composition and smectite-like texture, lead us to conclude that this phase is smectite and it will be referred to as such. Without more detailed analysis using more sophisticated analytical techniques, it is difficult to refine this further.

Figure 4.9. SEM images of grains collected from the top of the Reactor (Portion 2) : (a) entire grain; (b) enlargement of rectangular area in (a) showing the smectite (Smc) and the primary plagioclase bytownite (Byt); (c) entire grain; (d) enlargement of rectangular area in (c) showing typical smectite texture (Smc); (e) image of reacted grain; (f) enlargement of rectangular area in (e) showing the smectite (Smc) and primary clinopyroxene (Cpx).

Figure 4.10. SEM backscatter images and EDS compositional maps of an epoxy-mounted, polished grain collected from the top (Portion 2) of the Reactor: (a) backscatter image of entire grain; (b) composite colour image combining the backscatter image and elemental maps for c) Mg in green, d) Ca in blue, and e) Fe in red that shows plagioclase (dark blue), clinopyroxene (turquoise), olivine (yellow green), Fe-Ti oxide (red) and the smectite (green); (f) SEM backscatter image of rectangular area in (a) showing olivine (Ol), titanomagnetite (Tnt) and the K-Mg-Fe aluminosilicate (Smc).

Table 4.3. Average EDS analysis (wt. %) of the smectite identified at top of the Reactor (epoxy mount). N: number of analyses.

Polished (N=5)		
oxide	average Wt %	$\pm 1\sigma$
K₂O	1.03	0.50
Al₂O₃	11.42	0.76
SiO₂	48.83	1.10
MgO	15.22	0.94
FeO	23.52	1.56
Total	100.00	

4.2.2. BGB2: Basalt – Geothermal brine at 350°C/486 bar

The second basalt - geothermal brine experiment (BGB2) ran for total time of 908 hrs (Fig. 4.12). The first 166 hrs were at room temperature, 486 bar and the remaining 742 hrs were at 350°C, 486 bar. The flow rate was 1 ml hr⁻¹ for the entire experiment. As for the BW experiments, the flow-rate was set-up to ensure the collection of sufficient solution for all chemical analyses at the approximately 24 hour interval. Analysis of major cations and anions were made for 38 fluid samples. Analysis of trace elements (except for V, Cr and Rb) were made for the first 29 fluid samples.

4.2.2.1. Major element concentrations

Appendix (C) lists the complete experimental parameters (T, P, flow rate, chemistry). Figure 4.11 and Figure 4.12 show these results plotted against time in hours. The unreacted geothermal brine composition is shown at t = 0. Initial concentrations of major ions in the unreacted fluid were detected as follow: As (0.00 mmol kg⁻¹), B (5.13 mmol kg⁻¹), Ca (0.18 mmol kg⁻¹), Fe (<0.08 mmol kg⁻¹), K (3 mmol kg⁻¹), Mg (0.04 mmol kg⁻¹), Na (31.6 mmol kg⁻¹), SiO₂ (14.70 mmol kg⁻¹), Al (0.35 mmol kg⁻¹), Sr (<0.003 mmol kg⁻¹), Li (0.97 mmol kg⁻¹), H₂S (<0.01 mmol kg⁻¹), Cl (27.14 mmol kg⁻¹) and SO₄ (4.23 mmol kg⁻¹).

During the room temperature (~21°C) period small decreases in B, Ca, K and in particular Na are present. The pH values are on average an order of magnitude higher (5.3) than the starting blank (4.28). As, Fe, SiO₂, Sr, Li, Cl and SO₄ remain unchanged reflecting the composition of the input solution.

The change in temperature to 350°C was initiated at 166 hours and took approximately 2.5 hours, thus only about 2.5 ml of solution were produced during heat-up. Major changes in solution chemistry are present after the temperature shift.

Effluent quench pH decreases to a minimum of 3.39 at 211 hours then slowly increases to ~4.5 at 260 hours to greater than 7 by 428 hours. It remains near this alkaline value for the remainder of the experiment, approaching 8.0 for the last eight days. The calculated *in situ* pH remains constant after the temperature shift to 6.80 by the end of the experiment.

SiO₂ increases to 30.97 mmol kg⁻¹ (~1860 ppm) at 211 hours, which exceeds quartz saturation at 350°C and 500 bar (~981 ppm, Supcrt92), after which it regularly decreases by the end of the experiment to a stable values of 13.7 mmol kg⁻¹, 1 mmol kg⁻¹ lower than the starting brine.

K shows a significant increase immediately after the temperature shift, reaching a peak value of $6.74 \text{ mmol kg}^{-1}$ at 211 hours. It then decreases to $2.97 \text{ mmol kg}^{-1}$ at 356 hours after which it remains near 3 mmol kg^{-1} for the remainder of the experiment. Na concentration decreases to a minimum of $24.97 \text{ mmol kg}^{-1}$ at 211 hours after which it increases to input value ($\sim 31 \text{ mmol kg}^{-1}$) for the remainder of the experiment.

After the temperature shift, Al concentration decreases to $0.01 \text{ mmol kg}^{-1}$ at 211 hours, after which it increases to $0.05 \text{ mmol kg}^{-1}$ within eight days (at 403 hrs). It decreases again up to $0.01 \text{ mmol kg}^{-1}$ by 571 hours and then rises again to stable values of $0.06 \text{ mmol kg}^{-1}$ by the end of the experiment. Concentrations are all below the starting brine value. Ca concentration decreases, after the temperature shift, to a minimum of $0.02 \text{ mmol kg}^{-1}$ at 236 hours and then stabilise between 0.05 and $0.06 \text{ mmol kg}^{-1}$ for the remainder of the experiment. Ca concentrations are all lower than in the starting brine.

Magnesium decreases to near detection limit two days after temperature increase after which it gradually rises to $0.01 \text{ mmol kg}^{-1}$ by 850 hours. The last three samples average $0.005 \text{ mmol kg}^{-1}$. All Mg concentrations are well below the input solution value.

Sulfate decreases to a minimum peak of $2.16 \text{ mmol kg}^{-1}$ two days after temperature increase and then increases to between 2.95 and $3.97 \text{ mmol kg}^{-1}$ for the remainder of the experiment. The H_2S concentrations reach a maximum of $0.06 \text{ mmol kg}^{-1}$ three days after temperature increase. It remains around $0.05 \text{ mmol kg}^{-1}$ for five days and then decreases over twenty-eight days to near or below detection limit. Chloride concentrations remain near the input brine values for the entire experiment showing that the apparatus behaved correctly without boiling or dilution.

Figure 4.11. Major element concentrations in blank and effluent samples (mmol kg^{-1}) versus time (hr) for the basalt-geothermal brine experiment at 350°C/486 bar (BGB2). Yellow symbols are the blank sample composition of the brine. Blue symbols are for effluents at room T/486 bar and 1.0 ml hr^{-1} flow rate. Black symbols are effluents at 350°C/486 bar and 1.0 ml hr^{-1} flow rate. *In situ* pH is the calculated pH at temperature.

Figure 4.12. Major element concentrations in blank and effluent samples (mmol kg^{-1}) versus time (hr) for the basalt-geothermal brine experiment at $350^\circ\text{C}/486$ bar (BGB2). Yellow symbols are the blank sample composition of the brine. Blue symbols are for effluents at room T/486 bar and 1.0 ml hr^{-1} flow rate. Black symbols are effluents at $350^\circ\text{C}/486$ bar and 1.0 ml hr^{-1} flow rate. *In situ* pH is the calculated pH at temperature.

4.2.2.2. Trace element concentration

Appendix (C) lists the complete trace element results. Figure 4.13 and Figure 4.14 show these results plotted against time in hours. The unreacted geothermal brine composition is shown at $t = 0$. All trace element concentrations (except for Ag and Mn) are present in the starting brine. In particular, are high values of Ni ($2.9 \mu\text{mol hr}^{-1}$), Cu ($5.9 \mu\text{mol hr}^{-1}$) and Zn ($27.2 \mu\text{mol hr}^{-1}$).

During the room temperature ($\sim 21^\circ\text{C}$) period, overall decreases in several trace elements including Co, Ni Zn, Mo, Au and Pb are present. While Cu, Cd, Ba and Mn increase in solution relative to the starting brine. Silver concentrations are near detection limit.

Except for Mo, which rises to $\sim 1.0 \mu\text{mol hr}^{-1}$, all the other trace elements decrease substantially after the temperature shift to 350°C . Co, Ni, Ag, Cd, Au and Mn are near or below detection limit, while only Cu ($0.07 \mu\text{mol hr}^{-1}$), Zn ($2.9 \mu\text{mol hr}^{-1}$), Mo ($0.37 \mu\text{mol hr}^{-1}$), Ba ($0.07 \mu\text{mol hr}^{-1}$) and Pb ($0.005 \mu\text{mol hr}^{-1}$) display measurable concentrations by the end of the experiment.

Figure 4.13. Trace element concentrations in blank and effluent samples ($\mu\text{mol kg}^{-1}$) versus time (hr) for the basalt-geothermal brine experiment at 350°C/486 bar (BGB2). Yellow symbols are the blank sample composition of the distilled water. Blue symbols are for effluents at room T/486 bar and 1.0 ml hr⁻¹ flow rate. Black symbols are effluents at 350°C/486 bar and 1.0 ml hr⁻¹ flow rate.

Figure 4.14. Trace element concentrations in blank and effluent samples ($\mu\text{mol kg}^{-1}$) versus time (hr) for the basalt-geothermal brine experiment at 350°C/486 bar (BGB2). Yellow symbols are the blank sample composition of the distilled water. Blue symbols are for effluents at room T/486 bar and 1.0 ml hr⁻¹ flow rate. Black symbols are effluents at 350°C/486 bar and 1.0 ml hr⁻¹ flow rate.

4.2.2.3. Mineralogy and Texture of Reacted Basalt: Bottom of Reactor (Portion 1)

Upon the conclusion of the experiment, the reacted basalt grains were extracted from the Reactor. The cleaning, drying and apportioning of the reacted material was as described for BW1 and BW2 (Chapter 3, §3.2.1.3). In this section we report the results of mineralogical and textural analysis of reacted grains from the bottom (Portion 1) of the Reactor (Fig. 4.15).

Selected grains were mounted on aluminium stubs for textural analyses by SEM while several grains were epoxy-mounted and polished for SEM-EDS analysis. Appendix C contains all SEM results for this Portion of the rock.

Figure 4.15. Schematic diagram showing position of Portion 1 and 2 of reacted basalt grains examined by SEM-EDS and the position of the basalt block (not to scale).

SEM-EDS analysis

Several grains from immediately adjacent to the fluid entry point (Portion 1, Fig. 4.15) are shown in Figure 4.16 – 4.19. The results confirm a substantial degree of alteration of the basalt due to fluid-rock interaction. Minerals of secondary origin detected were anhydrite, smectite and Cu-sulfide (Table 4.4). Results also confirm the presence of the original primary minerals plagioclase, clinopyroxene, olivine and titanomagnetite. Biotite was not observed in this portion of the rock.

Table 4.4. Mineral assemblage detected by SEM-EDS analysis of reacted grains extracted from the bottom (Portion 1) of the Reactor after the BGB2 experiment.

Type of Analysis	Analysis Material	Mineral Identified	Average Mineral Composition
SEM-EDS	polished grains	Bytownite	$\text{Ca}_{0.7}\text{Na}_{0.2}\text{Al}_{1.7}\text{Si}_{2.4}\text{O}_8$ (An ₇₇ -Ab ₂₃)
SEM-EDS	polished grains	Augite	$\text{Ca}_{0.7}\text{Mg}_{0.9}\text{Fe}_{0.4}\text{Si}_2\text{O}_6$
SEM-EDS	polished grains	Titanomagnetite	$\text{Fe}^{2+}(\text{Fe}^{3+}, \text{Ti})_2\text{O}_4$
SEM-EDS	grain surface	Smectite 1	$\text{K}_{0.1}\text{Na}_{0.3}\text{Ca}_{0.1}\text{Mg}_{1.5}\text{Fe}_{1.1}\text{Al}_{0.3}\text{Si}_{3.4}\text{Al}_{0.6}\text{O}_{10}(\text{OH})_2 \cdot n\text{H}_2\text{O}$ (calculated based on an anhydrous composition with 11 oxygens)
SEM-EDS	grain surface	Smectite 2	$\text{K}_{0.1}\text{Na}_{0.2}\text{Ca}_{0.3}\text{Mg}_{1.6}\text{Fe}_{1.2}\text{Al}_{0.1}\text{Si}_{3.4}\text{Al}_{0.6}\text{O}_{10}(\text{OH})_2 \cdot n\text{H}_2\text{O}$ (calculated based on an anhydrous composition with 11 oxygens)
SEM-EDS	grain surface	Anhydrite	CaSO_4
SEM-EDS	grain surface	Cu-sulfide (covellite?)	$\text{Cu}_{0.90}\text{Fe}_{0.15}\text{S}_{0.96}$

Figure 4.16 shows SEM images of two highly altered grains from the position immediately next to the fluid entry point. An assemblage of secondary minerals covers their surface consisting of isolated euhedral crystals of anhydrite (Fig. 4.16a) and smectite with two morphologies (Fig. 4.16b). Smectite 1 (Table 4.4) consists of densely packed, foliated layers resembling rose petals (Fig. 4.16c) and Smectite 2 (Table 4.4) has a honeycomb texture (Fig. 4.17d). SEM-EDS analysis of these two morphologies shows that they have similar compositions (Table 4.5). Only a few grains with this intensity of alteration were found at the bottom of the Reactor.

It is hypothesised here that in the BGB2 experiment, the ameboid densely-packed morphology is due to growth from olivine while the second texture is due to growth from either plagioclase or clinopyroxene (or possibly both).

Figure 4.17 shows two SEM images of copper sulfide crystals with a hexagonal habit similar to those found in BGB1. These could be idaite or possibly covellite.

Figure 4.18 shows SEM backscatter images and EDS maps of a polished mount of a grain from the bottom of the Reactor. It is moderately altered with the smectite occurring on the edge of the grain. Plagioclase and clinopyroxene are present, with olivine and Fe-Ti oxide. The average composition of the K-Na-Mg-Fe aluminosilicate phase from EDS analyses of the epoxy mounted grain is shown in Table 4.4. It contains almost identical composition of SiO₂, Al₂O₃, MgO, FeO and K₂O of the mineral identified in BGB1 (Table 4.3) with the addition of CaO and Na₂O. XRD results for Portion 1 (Appendix C) give small peaks for montmorillonite, confirming the presence of a swelling clay like smectite.

Figure 4.19a,b show two enlargements of rectangular areas in Figure 4.18a showing bytownite, the smectite, and Fe-Ti oxide of possible secondary origin, as well as primary minerals bytownite, clinopyroxene, olivine, and titanomagnetite.

Figure 4.16. SEM images of the surface of a grain collected from the bottom (Portion 1) of the Reactor after the BGB2 experiment: (a) grain with euhedral crystals of anhydrite (Anh), the smectite (Smc) appearing in masses of foliated crystals; (c) higher magnification view of smectite with interlocking rose petal-like morphology; (d) rectangular area shown in (b) the smectite (Na-K-Ca-Mg-Fe aluminosilicate) with rose petal-like morphology (bottom left) and with cornflake morphology (top right).

Figure 4.17. a) and b) SEM images of two Cu-sulfide crystals found on the surface of two reacted grains from the BGB2 experiment.

Figure 4.18. SEM backscatter image and EDS compositional maps of an epoxy-mounted polished grain from the bottom (Portion 1) of the Reactor after the BGB2 experiment: a) backscatter image of the entire grain; (b) composite colour image combining the backscatter image and the elemental maps for c) Mg in green, d) Ca in blue, and e) Fe in red. The image shows plagioclase (blue), clinopyroxene (turquoise), olivine (bright green), and the K-Na-Mg-Fe aluminosilicate (dark green) on the borders of the grain growing from olivine crystals.

Figure 4.19. (a) and (b) SEM backscatter images of enlargements of rectangular areas (n1 and n2) of Figure 4.18a, respectively, showing primary minerals bytownite (Byt), olivine (Ol), titanomagnetite (Tnt) and the K-Na-Mg-Fe aluminosilicate phase (Smc).

Table 4.5. Average EDS analysis (wt. %) of the smectite identified at bottom of the Reactor (grains morphology). N: number of analysis.

oxide	Smectite 2 Unpolished N=15		Smectite 1 Unpolished N=5	
	average Wt %	$\pm 1\sigma$	average Wt %	$\pm 1\sigma$
Na₂O	2.48	0.47	1.51	0.67
MgO	15.15	2.41	15.69	2.44
Al₂O₃	10.90	1.40	9.03	0.70
SiO₂	50.92	2.04	48.77	1.71
K₂O	0.60	0.44	1.53	0.36
FeO	18.58	2.88	19.89	3.18
CaO	1.33	0.58	3.58	0.28
Total	99.96		100.00	

4.2.2.4. Mineralogy and Texture of Reacted Basalt: Top of Reactor (Portion 2)

Several grains (Fig. 4.20 – 4.22) from the immediately adjacent to the fluid exit point at the top of the Reactor (Portion 2, Fig. 4.15) were examined. These were mounted on aluminium stubs for morphological analysis by SEM. Several grains were also mounted in epoxy and polished for SEM-EDS analysis. Appendix C lists the complete results for this Portion of the basalt.

SEM-EDS analysis

SEM examination confirms a lesser degree of alteration of the reacted grains when compared to the bottom (Portion 1) of the Reactor. Only one mineral of secondary origin was detected, a clay-like phase thought to be smectite. Data also confirm the presence of the primary minerals bytownite, clinopyroxene, olivine and titanomagnetite (Table 4.6). No evidence of biotite or anhydrite was found during analysis.

Table 4.6. Mineral assemblage found during analysis of reacted grains extracted from the top (Portion 2) of the Reactor after the BGB2. Analysis was effectuated by SEM-EDS. Appendix (C) contains all SEM results for this portion of the rock.

Type of Analysis	Analysis Material	Mineral Identified	Average Mineral Composition
SEM-EDS	polished grains	Bytownite	$\text{Ca}_{0.7}\text{Na}_{0.3}\text{Al}_{1.6}\text{Si}_{2.4}\text{O}_8$ (An ₇₃ -Ab ₂₇)
SEM-EDS	polished grains	Augite	$\text{Ca}_{0.5}\text{Mg}_{0.7}\text{Fe}_{0.7}\text{Al}_{0.8}\text{Si}_2\text{O}_6$
SEM-EDS	polished grains	Fayalite	$\text{Mg}_{0.7}\text{Fe}_{1.2}\text{SiO}_4$
SEM-EDS	polished grains	Titanomagnetite	$\text{Fe}^{2+}(\text{Fe}^{3+}, \text{Ti})_2\text{O}_4$
SEM-EDS	polished grains	Smectite	$\text{K}_{0.1}\text{Na}_{0.2}\text{Ca}_{0.1}\text{Mg}_{1.5}\text{Fe}_{1.3}\text{Al}_{0.2}\text{Si}_{3.5}\text{Al}_{0.5}\text{O}_{10}(\text{OH})_2 \cdot n\text{H}_2\text{O}$ (calculated based on an anhydrous composition with 11 oxygens)
SEM-EDS	grain surface	Smectite	$\text{K}_{0.1}\text{Na}_{0.3}\text{Ca}_{0.2}\text{Mg}_{1.6}\text{Fe}_{1.2}\text{Al}_{0.2}\text{Si}_{3.3}\text{Al}_{0.7}\text{O}_{10}(\text{OH})_2 \cdot n\text{H}_2\text{O}$ (calculated based on an anhydrous composition with 11 oxygens)

Figure 4.20 shows the surface textures of two different grains extracted from the top (Portion 2) of the Reactor. EDS backscatter images show that the surface is partially altered and covered by the aluminosilicate phase appearing in sparse globular masses. The mineral shows similar shape and chemical composition when compared with the phase identified at bottom (Portion 1) of the Reactor (Table 4.4). Figure 4.20c,d shows, in detail, the aluminosilicate appearing in globular masses of dense flakes.

Figure 4.21 shows SEM backscatter images and EDS maps for an epoxy-mounted, polished grain collected from the top (Portion 2) in the Reactor. The lower intensity of

hydrothermal alteration is evident when compared with grains collected at bottom of the Reactor (Portion 1, Fig. 4.18). Analysis of chemical composition by SEM-EDS show that primary plagioclase bytownite (dark blue) is essentially unaltered. Also present is a K-Na-Ca-Mg-Fe aluminosilicate phase (smectite). The primary clinopyroxene (turquoise) and titanomagnetite are relatively unaffected, while olivine (yellow) is richer in Fe rather than of Mg when compared with results of the unaltered material (Table 2.2).

Figure 4.22a,b are the two enlargements of red square areas in Figure 4.21a,b showing relict clinopyroxene, titanomagnetite and smectite. This mineral shows similar shape and chemical composition when compared with the phase identified from the bottom portion of the Reactor. It appears in isolated masses on the reacted grains surface suggesting that it replaces a single primary mineral, most likely olivine. Table 4.7 reports the average EDS analyses of this mineral both from the polished mount and from surface analysis.

Figure 4.20. SEM images of grains collected from the top (Portion 2) of Reactor after BGB2: (a-b) smectite (Smc) in globular dense masses covering partially the surface of both grains. (c-d) SEM microphotographs of the rectangular areas in (a) and (b) respectively, showing in more detail the smectite.

Figure 4.21. SEM backscatter and EDS compositional maps of an epoxy-mounted polished grain collected from the top (Portion 2) of Reactor after the BGB2 experiment. (a) backscatter image of the entire grain; (b) composite colour image combining the backscatter image and the elemental maps for c) Mg in green, d) Ca in blue, and e) Fe in red. The composite image shows plagioclase (dark blue), unaltered clinopyroxene (turquoise), olivine (yellow), Fe-Ti oxides (red), and smectite (green). All data set points in Appendix (C).

Figure 4.22. (a-b) SEM images of the rectangular areas of Figure 4.22a and Figure 4.22b, respectively, plagioclase (Plg), olivine (Ol), primary titanomagnetite and smectite (Smc). The smectite has replaced the primary olivine.

Table 4.7. Average EDS analysis (wt. %) of the K-Na-Ca-Mg-Fe aluminosilicate phase (smectite) identified at top of the Reactor (grains morphology and epoxy-mount). N: number of analysis. All data set points in Appendix (C).

	Unpolished N=2		Polished N=11	
oxide	average Wt %	$\pm 1\sigma$	average Wt %	$\pm 1\sigma$
Na₂O	2.02	0.37	0.99	0.86
MgO	15.04	1.62	15.06	2.14
Al₂O₃	11.22	0.64	8.68	0.54
SiO₂	47.74	0.83	50.70	1.32
K₂O	0.78	0.03	0.59	0.38
FeO	21.25	1.38	23.08	3.37
CaO	1.98	0.47	0.86	0.40
Total	100.00		99.95	

4.2.2.5 Mineralogy and Texture of Reacted Basalt: Basalt Block

The basalt block (8x8x4 mm) with one polished surface, was positioned vertically near the bottom of the Reactor approximately 0.5 - 1.0 cm above the titanium frit (Fig. 4.15). Upon the completion of the experiment, the block was mounted on an aluminium stub for SEM-EDS analysis (Table 4.8). Complete SEM results for the reacted basalt block surface are reported in Appendix (C).

Table 4.8. Mineral composition of the reacted basalt block surface after the BGB2.

Type of Analysis	Analysis Material	Mineral Identified	Average Mineral Composition
SEM-EDS	basalt block	Bytownite	$\text{Ca}_{0.7}\text{Na}_{0.3}\text{Al}_{1.6}\text{Si}_{2.4}\text{O}_8 (\text{An}_{75}\text{-Ab}_{25})$
SEM-EDS	basalt block	Anhydrite	CaSO_4
SEM-EDS	basalt block	Smectite	$\text{K}_{0.1}\text{Na}_{0.7}\text{Ca}_{0.3}\text{Mg}_{1.5}\text{Fe}_{1.6}\text{Si}_{3.1}\text{Al}_{0.7}\text{O}_{10}(\text{OH})_2 \cdot n\text{H}_2\text{O}$ (calculated based on an anhydrous composition with 11 oxygens)
SEM-EDS	basalt block	Unknown Na-Ca-Mg-Fe-Ti-Mn aluminosilicate	-

Figure 4.23 shows the complete surface of the reacted basalt block which appears visibly altered. The smectite and anhydrite are the main secondary minerals identified. Plagioclase is essentially unaffected. EDS analysis confirms that the dark spots with a subhedral shape are anhydrite. It is possible that the anhydrite crystals were partially dissolved during cleaning of the block with distilled water after extraction from the Reactor. Unfortunately, it was not possible to remove all the brine salt remnants from the surface thus

EDS analysis were found to contain measureable quantities of Na and Cl. This must be considered when interpreting the EDS results.

Figure 4.24 shows SEM backscatter images of rectangular areas of Figure 4.23. Primary bytownite, the smectite, anhydrite and the Ca-Na-Mg-Fe-Mn-Ti aluminosilicate. The primary minerals clinopyroxene and titanomagnetite were also identified. Anhydrite appears as tabular crystals, the smectite has flaky habit while the unknown Ca-Na-Mg-Fe-Mn-Ti aluminosilicate appears in platy crystals of hexagonal shape.

Figure 4.23. SEM backscatter image of the basalt block surface after the BGB2 experiment. Dark gray subhedral spots (white arrows) are voids left by anhydrite crystal that were lost after collection.

Figure 4.24. SEM backscatter images of the reacted basalt surface after the BGB2 experiment: (a) enlargement of the red area n°1 in Figure 4.23 showing two crystals of anhydrite surrounded by the smectite (Smc); (b) enlargement of the red area n°2 in Figure 4.23 showing spots of anhydrite partially dissolved after cleaning with distilled water; (c) enlargement of the red area n°3 in Figure 4.23 showing primary bytownite (Byt), the unknown Na-Ca-Mg-Fe-Ti-Mn aluminosilicate, anhydrite (Anh) and occurring on the plagioclase surface; (d) enlargement of the red area n°4 in Figure 4.23 showing primary plagioclase (Byt); (e-f) enlargements of the red areas in (c) and (d), respectively, showing in detail the hexagonal crystals of the unknown aluminosilicate.

4.3 Discussion

4.3.1. Major and trace element exchange during water – rock interaction

Major ions

The basalt - geothermal brine experiments were conducted at room temperature for the first week after which conditions were shifted to 350°C (BGB2) and 400°C (BGB1). After temperature increase to 400°C, SiO₂ concentrations remain oversaturated with respect to quartz for ~384 hours and at ~600 hr the concentrations decrease below saturation. In comparison, after temperature increase to 350°C, SiO₂ concentration also reaches oversaturation with respect to quartz (~30 mmol kg⁻¹) but, in contrast to the 400°C experiment, it immediately starts to decrease until it passes below quartz saturation at 740 hr. At the end of both experiments SiO₂ concentration is similar at ~15 mmol kg⁻¹. This suggests that there are similar mineral reactions controlling SiO₂ concentration. The initial high SiO₂ values in both experiments are attributed to the dissolution of volcanic glass after temperature shift. However, the plateau shaped trend and rapid decrease in SiO₂ concentrations at ~600 hr at 400°C indicate relatively constant release of silica until the glass is exhausted, while at 350°C, the constant decreasing trend indicates that released silica was incorporated into new minerals (Fig. 4.25).

In the brine experiments, the input solution initially contains dissolved silica (~12 mmol kg⁻¹). This concentration is well below quartz saturation at 350 and 400°C. The higher SiO₂ concentrations after temperature shift, in both brine experiments, confirm that volcanic glass was certainly dissolving; however, the silica concentrations reached are similar to those of the distilled water experiments. This is evidence of mineral precipitation controlling silica concentration, rather than a kinetic effect due to flow rate, i.e., fluid residence time. Using the same procedure described for the BW experiments (Chapter 3, §3.31) the amount of glass dissolved was estimated for BGB2 and BGB1 (Appendix C). This calculation gives ~330 mg of glass for BGB2 and ~530 mg for BGB1.

In the BW experiments, the correlation of some components, namely K, H₂S, SO₄ and Cl with SiO₂ concentration was evidence of release from volcanic glass (Chapter 3, §3.3.1). In the BGB experiments, geothermal brine was used which contains much higher concentrations of K, SO₄ and Cl, nevertheless, further increases in K were observed during glass dissolution in BGB1 at 400°C. This was not observed in BGB2 at 350°C, which is evidence of greater K incorporation into secondary minerals at this temperature. Any

correlation of SO_4 and Cl concentrations with glass dissolution are masked by the high initial concentrations in the brine.

Elevated concentrations of H_2S are observed during glass dissolution in both experiments but there is no clear correlation with SiO_2 concentrations suggesting sulfide mineral precipitation.

The presence of H_2S in the fluid is attributed to the dissolution of sulfide blebs and the generation of SO_3 by the release of SO_2 . H_2S and SO_2 are expected to be both trapped in the volcanic glass. The release of sulfur from the glass also explains the initial low quench pH values measured after the temperature change, especially at 400°C . Once the glass is depleted, the quench pH values change from 3.4 to 7.8 and from 2.9 to 7.7 at 350 and 400°C , respectively; however, the *in situ* pH is constant, with an average of 6.8 and 7.0 for BGB2 and BGB1. At temperature, the sulfite/sulfate anion created by the release of SO_2 from the glass is protonated forming bisulfite and/or bisulfate. This causes *in situ* pH to be near neutral, however, these anions deprotonate upon cooling and thus room temperature pH is acid. Once the volcanic glass is dissolved there is no longer a source of sulfur and the pH increases due to cation exchange with the rock minerals.

For the fluid to equilibrate with the rock it requires the consumption of H^+ and this explains the increase in pH. Unlike the distilled water experiments, much of the chemistry is controlled by the fluid and not by the rock. Ca, Na and K do not transfer to the fluid as these elements are already present in the geothermal brine. For this reason, the consumption of H^+ occurs to a lesser degree when compared to the experiments with distilled water. This explains why the quench pH increases to 7.7 - 7.8 during the BGB experiments while it reached values above 9 in the BW experiments.

Table 4.9 shows the input total mass (mg) and integrated elemental fluxes (mg) for selected components. The input total mass represents the amount of material that entered the Reactor based on the total fluid flux (0.75 L in BGB2 and 0.69 L in BGB1) and input brine composition. The integrated elemental flux is the net mass of component integrated over the entire experiment based on daily fluid flux and the effluent composition.

For the BGB2 (350°C), the integrated flux calculation shows a net flux of +226 mg SiO_2 to the fluid while BGB1 (400°C) has a net positive flux of +504 mg SiO_2 . This indicates that 55% less silica was released at 350°C than at 400°C . This can be explained by greater incorporation of released silica into secondary mineral phases.

Figure 4.25. SiO_2 concentration (mmol kg^{-1}) vs time (hr) for BGB1 and BGB2: a) total SiO_2 flux for BGB2 based on sample volume and solution compositions (pink area); b) total SiO_2 flux from the input brine; c) the difference between a) and b) representing the net SiO_2 flux from the rock for BGB2 (orange area); d) total SiO_2 flux for BGB1 based on sample volume and solution compositions (pink area); e) total SiO_2 flux from silicate minerals (green) based on the average SiO_2 concentration in the last two samples less the input brine composition (grey); f) the difference between d) and e) representing the total SiO_2 flux estimated from glass; g) total SiO_2 flux released from BGB1 (orange + green area).

Table 4.9. Total input mass (mg) and integrated elemental fluxes (mg) for selected components in BGB2 and BGB1.

BGB2 (350°C / 486 bar)		SiO₂	K	SO₄	H₂S	Ca	Na	Mg	Fe
Blank composition (mg kg ⁻¹)		884	116	406	< 0.01	7.2	725	0.9	<0.08
Total input mass (mg) (based on 0.75 L total brine)		662	86.9	305	-	5.4	543	0.7	-
Total integrated elemental flux (mg) (over the entire experiment)		+226	+15.4	-58	+0.3	-3.8	-4.7	-0.5	+0.07
BGB1 (400°C / 483 bar)		SiO₂	K	SO₄	H₂S	Ca	Na	Mg	Fe
Blank composition (mg kg ⁻¹)		759	116	404	0.2	3.4	725	0.2	0.08
Total input mass (mg) (based on 0.69 L total brine)		525	80	280	0.1	2.4	502	0.1	0.1
Total integrated elemental flux (mg) (over the entire experiment)		+504	+3.7	-45	+0.7	+0.2	-18	+0.1	+0.009

At 350°C, the total integrated flux for SO₄ is -58 mg (the negative sign indicates a loss from the fluid), -3.8 mg for Ca, +15.4 mg for K, -4.7 mg for Na, and -0.5 mg for Mg. H₂S and Fe show small positive values of +0.3 and +0.07 mg, respectively. The results agree with the mineralogy identified by SEM-EDS. The significant loss of SO₄ is explained by the precipitation of anhydrite. The small Ca flux relative to SO₄ indicates that the source of most of the Ca in anhydrite is from the rock. At 350°C, there is evidence for precipitation of K as smectite, however, the high concentration in the input brine masks any small changes in K due to glass dissolution and/or secondary mineral precipitation. The loss of Na is attributed to the formation of the secondary smectite, however, given the high concentration of Na in the brine this change may be within uncertainties. The total integrated flux for Fe (+0.07 mg) and Mg (-0.5 mg) are small. This shows that in terms of mass balance, Fe and Mg remain fixed in the rock in secondary minerals. Fe and Mg are both low in concentration in the input brine thus dissolution of primary minerals must be the source for secondary mica precipitation. The small positive total integrated flux for H₂S indicates that it is sourced from the rock.

At 400°C, the total integrated flux for SO₄ is -45 mg and for Na is -18 mg. Ca, Mg, H₂S, Fe and K all have small positive values of +0.2, +0.1, +0.7, +0.009 and +3.7 mg, respectively, meaning that they were conservative. As in BGB2, the significant loss of SO₄ is explained by the precipitation anhydrite with the primary source of Ca being clinopyroxene and/or plagioclase. At 400°C, there is evidence for precipitation of K as both biotite and smectite, however, the high concentration in the input brine masks any small changes in K due to glass dissolution and/or secondary mineral precipitation, as at 350°C. The loss of Na at 400°C is difficult to explain by mineral precipitation as the secondary minerals measured by

SEM-EDS did not contain significant Na. It is likely that, as with K, any small change may not be resolvable from due to the high input concentration.

Trace elements

Trace element concentrations give important information on the capacity of basalt to release or retain these elements during fluid – rock interaction, both at subcritical and supercritical experimental conditions (Fig. 4.3 - 4.4, Fig. 4.13 - 4.14). In the following discussion, only elements that show evident trends are considered. These include Zn Cu, Mo and V. Elements which do not show clear trends were excluded in the discussion (Ni, Pb, Mn, Ba, Co, Cr, Cd, Rb, Au and Ag). It should be noted that V, Cr and Rb were analysed only in BGB1 (400°C) and not in BGB2 (350°C). Also, for BGB2, trace elements analyses of the fluid samples collected after basalt glass dissolution are not available.

V, Cr, Co, Mn, Pb (only in BGB1), Cd (only in BGB2) and Ni, Cu, Zn, Mo, Ba in both experiments, are present in the geothermal brine at very low concentration, nevertheless they increase in solution at room temperature and pressure ~500 bar. This indicates that minor amounts of these elements were extracted from the rock at room temperature. Au and Ag are also present in the geothermal brine, but they show decreases over the experiment not related to temperature change. It is possible that the two trace elements actually precipitate in the fluid reservoir due to reaction in the experimental apparatus.

Zn, Cu. At 400°C there is a correlation between Zn and SiO₂ (Fig. 4.26a) supporting the conclusion that Zn is being released during the dissolution of volcanic glass. A correlation between Zn and H₂S (Fig. 4.26c) is not present indicating that Zn sulfide precipitation is not occurring. At 350°C, Zn values are very low when compared to 400°C (Fig. 4.26b). If Zn is being released by glass dissolution, then it must be re-precipitating at 350°C. This is supported by concurrent low sulfide concentrations (Fig. 4.26d).

Cu. The input concentration of Cu in the geothermal brine is very low (0.3 µmol kg⁻¹ in BGB1 and 0.8 µmol kg⁻¹ in BGB2). Cu is present in the volcanic glass in the Fe sulfide blebs as previously demonstrated in Chapter 3 (§3.3.1). In the effluent samples, both at 350 and 400°C, there is no clear correlation of Cu with either SiO₂ or H₂S (Fig. 4.26e-h). However, a Cu sulfide phase was identified in the run products in both experiments (Fig. 4.7 and 4.17). It may be that the concentrations of Cu are so low that statistically meaningful correlations with H₂S and SiO₂ are not possible.

Mo. At 400°C, there is no correlation between Mo and SiO₂ (Fig. 4.27a), while at 350°C there is a suggestion of a positive correlation (Fig. 4.27b). This is comparable to the

distilled water experiments. The effluent composition trends with time for Mo (Fig. 4.13) show a progressive increase over eight days while at the same time SiO_2 decreases, after which it parallels SiO_2 , decreasing over the remainder of the experiment. This suggests that Mo is derived from the volcanic glass but then precipitates as secondary mineral precipitation proceeds. Molybdenum has a siderophile rather than a chalcophile element behaviour (Lodders and Palme, 1991) and it is predominantly present in basaltic volcanic rocks in ilmenite, magnetite, but can also be present in the interstitial glass (Arnórsson and Óskarsson, 2007; Greaney et al., 2018; Greaney et al., 2017).

V. Geothermal brine contains a very low concentration of vanadium. At 400°C , there is a negative correlation between V and SiO_2 (Fig. 4.27e), while for the experiment at 350°C the analyses were not available. Higher V values are encountered after the glass has been removed. Vanadium, as discussed in the previous Chapter 3 (§3.3.1) occurs as a component of titanomagnetite (Hukkanen and Walden, 1985). It is possible that elevated Fe concentrations during glass dissolution could suppress titanomagnetite dissolution thus leading to lower V concentrations.

Figure 4.26. Zn and Cu ($\mu\text{mol kg}^{-1}$) versus SiO_2 and H_2S ($\mu\text{mol kg}^{-1}$) for BGB1 and BGB2. Symbols in red represent values during glass dissolution, while symbols in blue represent values after glass dissolution. In BGB2, there are no analyses available for trace elements of the reacted fluid compositions collected after glass dissolution.

Figure 4.27. Mo and V ($\mu\text{mol kg}^{-1}$) versus SiO_2 and Mo ($\mu\text{mol kg}^{-1}$) versus H_2S ($\mu\text{mol kg}^{-1}$) for BGB1 and BGB2. Symbols in red represent values during glass dissolution, while symbols in blue represent values after glass dissolution. In BGB2, there are no analyses available for trace elements of the reacted fluid compositions collected after basalt glass dissolution.

4.3.2. The path of fluid-rock interaction

The path of fluid-rock interaction was examined using activity diagrams based on aqueous species' activities and *in situ* pH calculated using the *EqSolvR* software package (Chapter 2).

Activity ratio diagrams were constructed for the experimental temperatures and 500 bar, assuming unit activity of mineral phases. There was no period during the experiments when quartz remained saturated thus SiO_2 activity for the diagrams must be adjusted based on solution chemistry (Chapter 3, §3.3.3). At 400°C, these limits were based on the average silica concentration when glass dissolution was occurring [$\log(a_{\text{SiO}_2}) = -1.52$] and after glass dissolution [$\log(a_{\text{SiO}_2}) = -1.8$]. At 350°C, there is no clear plateau for SiO_2 concentration during glass dissolution (Fig. 4.11) but instead a continuous decrease from a maximum after temperature change [$\log(a_{\text{SiO}_2}) = -1.51$] to a minimum near the end of the experiment [$\log(a_{\text{SiO}_2}) = -1.87$]. These limits are used for the diagrams at 350°C. All the phase diagrams for the BGB1 and the BGB2 are reported in Appendix C.

In the $\text{K}_2\text{O}-\text{Al}_2\text{O}_3-\text{SiO}_2-\text{H}_2\text{O}$ activity space (Fig. 4.28a,b), the fluid path is similar, but not identical, at both temperatures. The unreacted geothermal brine composition (yellow circles) lies on the muscovite-K-feldspar join, both at 350 and 400°C. At 400°C (Fig. 4.28a), after the shift in temperature, quartz immediately becomes supersaturated and compositions move into the K-feldspar stability field and reach maximum SiO_2 activity. Potassium feldspar was not observed during SEM examination of the top and bottom portions of the reacted rock. Potassium concentration reaches the highest values in the first samples after temperature shift and $\log(a_{\text{K}^+}/a_{\text{H}^+})$ remains higher than input value during removal of the glass. As the glass dissolves, $\log(a_{\text{K}^+}/a_{\text{H}^+})$ decreases. At 400°C, the ratio decreases at constant silica activity keeping the fluid in the K-feldspar field, while at 350°C, it decreases along with silica activity moving the fluid towards the muscovite field.

The decrease in K concentration in both experiments is due to the precipitation of secondary K-bearing phases. Biotite (found at the bottom of the Reactor) and smectite (found at the top) are observed at 400°C. The mineral precipitation appears to be occurring while $\log(a_{\text{SiO}_2})$ is relatively constant. At 350°C, $\log(a_{\text{K}^+}/a_{\text{H}^+})$ decreases simultaneously with the decrease in $\log(a_{\text{SiO}_2})$ indicating that K-bearing silicate mineral precipitation was occurring immediately after temperature change. Smectite was found both at the bottom and top of the Reactor while biotite was observed only at the bottom at 400°C. Evidently, the 50°C difference did not allow biotite to stabilise at the lower temperature.

The identification of the biotite at 400°C demonstrates that fluid compositions must have been saturated with respect to this mineral. This is consistent with the K_2O - MgO - Al_2O_3 - SiO_2 - H_2O activity diagram (Fig. 4.29a) where the fluid compositions lie within the phlogopite field. Biotite is a trioctahedral mica with the end members phlogopite and annite. At 400°C, the presence of biotite indicates that while glass was dissolving, K activity was sufficient to allow Mg and Fe released from clinopyroxene and olivine to form this mineral. Once the glass had been removed, K activities decreased, and any Mg and Fe released formed smectite.

At 350°C, in the K_2O - MgO - Al_2O_3 - SiO_2 - H_2O activity diagram (Fig. 4.29b), fluid compositions also lie in the phlogopite field, however, biotite was not observed. It would appear that immediate onset of mineral precipitation (smectite) at this temperature reduced K activities such that biotite did not stabilise.

In Figure 4.28a – 4.29a, the red crosses show positions of effluents collected at 0.5 ml hr^{-1} flow rate for the BGB1 experiment. There is no noticeable difference from earlier samples collected at 1.0 ml hr^{-1} . This confirms that changes in flow rate did not affect cation activity ratios and presumably mineral precipitation.

Figure 4.28. Activity diagrams for the $K_2O-Al_2O_3-SiO_2-H_2O$ system showing mineral stability fields for BGB1(a) and BGB2(b). Black and red crosses show position of effluent samples collected at 1.0 and 0.5 $ml\ hr^{-1}$ flow rate, respectively. Yellow circles show position of the unreacted brine at 400 and 350°C/500 bar. Black dotted line shows quartz saturation while pink dotted lines represent the average of silica concentration (in log units) during and after dissolution of the basalt glass, calculated for the respective experiments. Blue arrows show the path of reacted fluids over the time of the experiments.

Figure 4.29. Activity diagrams for the $\text{K}_2\text{O-MgO-Al}_2\text{O}_3\text{-SiO}_2\text{-H}_2\text{O}$ system showing mineral stability fields for BGB1(a) and BGB2(b). Black and red crosses show position of effluent sample collected at 1.0 and 0.5 ml hr^{-1} flow rate, respectively. Yellow circles show position of the unreacted fluid at 400 and 350°C/500 bar. Blue arrows show the path of reacted fluids over the time of the experiments.

The fluid-mineral reactions that occurred during the experiments can provide information on the chemical path that the fluid took while passing through the rock and the resulting effects on the mineral assemblage.

In both experiments, anhydrite was observed. The anhydrite could not have precipitated solely from the geothermal brine as this would have occurred while the brine was heating up in the tubing before the Reactor. The brine is the source of sulfate and dissolution of rock minerals the source of calcium. SEM analysis shows that both clinopyroxene and plagioclase dissolved. The precipitation of anhydrite at the expense of these minerals is represented by Reactions 1 and 2:

During both reactions, anhydrite precipitates, hydrogen ion is consumed, and Al is produced. In Reaction 2, the dissolution of clinopyroxene also supplies a source of Mg and Fe. At both temperatures, the release of Al initiates aluminosilicate precipitation at the high concentration of silica present.

At 400°C, in addition to anhydrite, biotite was also observed at bottom of the Reactor. Biotite formed when brine containing K entered the rock immediately adjacent to the fluid entry point. Although some K was supplied by glass dissolution, the bulk of the K is supplied by the brine. The local presence of Al and K initiated biotite precipitation at the expense of clinopyroxene and olivine. Mg and Fe were provided by the rock as concentrations of these components are very low in the brine. The formation of biotite at the expense of clinopyroxene and olivine at bottom of the Reactor is represented in Reactions 3 and 4:

In these reactions, biotite precipitates and the dissolution of clinopyroxene and olivine releases H^+ . The presence of Na in the mineral structure explains why sodium concentrations started to decrease after the T shift (Fig. 4.1, §4.2.1.1).

Smectite was observed at top of the Reactor in dense foliated masses that replaced olivine. Smectite does not appear at bottom of the Reactor with anhydrite and biotite. This implies that when fresh brine entered in contact with basalt, the formation of anhydrite and biotite occurred rapidly at the immediate bottom of the Reactor. K and SiO_2 concentrations reach their highest values after temperature shift (Fig. 4.1). It is suggested that these high concentrations caused biotite to be supersaturated. This initiated biotite precipitation and a decrease to lower K and SiO_2 values after 2 – 3 days. As more brine entered, biotite precipitation continued at the bottom of the column, keeping K and SiO_2 fixed, i.e., glass dissolution competes with biotite precipitation to maintain K, Al and SiO_2 at steady state (or equilibrium). At some point upwards in the Reactor, K/Al/ SiO_2 ratios must have changed sufficiently to stabilise smectite over biotite. As the fluid continued to move upwards, Mg and Fe was sourced mainly from olivine, Al from plagioclase, and K from the fluid to form smectite according to Reaction 5:

Although it is not possible to determine the relative extent of the above reactions, it is evident that the consumption of H^+ during anhydrite precipitation (Reaction 1 and 2) and the conversion of clinopyroxene and olivine to biotite (Reaction 3 - 4) must have been more than offset by the formation of smectite from olivine (Reaction 5) as the quench pH of the fluid becomes acid after temperature shift. This is a net shift of pH down about ~0.5 log units over the input brine pH (~4, Fig. 4.1). After the loss of volcanic glass, quench pH then increases above input brine pH indicating that Reactions 1 – 2 must have become more important than Reaction 5.

At 350°C, the formation of anhydrite is also represented by Reactions 1 and 2. Only smectite was found at bottom and top of the Reactor in this experiment. No biotite was identified. SEM analysis shows that at the bottom, smectite was observed to replace not only olivine but also other silicate minerals. Major element trends (Fig. 4.11 – 4.12) also show that mineral precipitation decreased K and SiO_2 concentrations substantially after temperature shift unlike at 400°C. The quench pH also shifted to more alkaline values above the input

brine pH much sooner than at 400°C. The conversion of olivine to smectite is represented by Reaction 5 while the conversion of plagioclase and clinopyroxene to smectite is represented by Reaction 6 and 7:

The more rapid shift of pH upwards suggests that Reactions 1 – 2 must have become more substantial than Reaction 6 – 7.

4.3.3. Na/K geothermometers

Figure 4.30a,b shows the activity ratio diagrams for the $\text{Na}_2\text{O}-\text{K}_2\text{O}-\text{Al}_2\text{O}_3-\text{SiO}_2-\text{H}_2\text{O}$ systems at 350 and 400°C/500 bar. The diagrams show that at 350 and 400°C, despite changes in silica activity, fluid compositions lie on or close to the albite – K-feldspar join, including the input brine composition. Only at 400°C, and after glass dissolution, is the fluid composition consistently above this phase boundary, albeit to a very small degree (Fig. 4.33).

The estimated temperatures for the BGB1 and BGB2 fluid compositions were calculated utilising several geothermometers for Na/K and Na-K-Ca reported in literature (Arnórsson, 1983; Fournier and Truesdell, 1973; Fournier, 1979; Giggenbach, 1988b; Nieva and Nieva, 1987; Santoyo and Díaz-González, 2009; Tonani, 1980; Truesdell, 1976). Table 4.10 reports the averages of these geothermometers calculated at silica concentrations during and after glass dissolution. The results show that all calculated values are well below the experimental temperatures.

Figure 4.31 shows the estimated temperatures using the geothermometers plotted versus time. Also shown are the SiO_2 , Na and K concentrations. The plots for silica concentration emphasise the difference in the two experiments. At 400°C there is a clear change when glass dissolution ceases while at 350°C this distinction is masked by mineral precipitation. At 400°C there appears to be an attempt by the rock to adjust the fluid composition towards equilibrium as the calculated temperatures move upwards. At 350°C no such attempt is evident.

Sodium concentrations are comparable in both experiments, while K is higher during glass dissolution at 400°C than at 350°C. The results show underestimation of all temperatures calculated from the reacted fluids. The predominant values coincide with the estimated temperature calculated from composition of the unreacted geothermal brine (blank in Fig. 4.31). This implies that the Na/K ratio did not change sufficiently during fluid-rock interaction.

It is evident that because of the absence of the K-bearing minerals in the basalt, and the high amount of Na and K continuously supplied by the unreacted brine, the Na/K ratio is controlled by the fluid and not by the rock. This is likely due to the short residence time of the fluid. The estimated residence time is only ~10 hrs at 1 ml hr^{-1} and ~20 hrs at 0.5 ml hr^{-1} . This is clearly too short to allow the Na/K ratio to shift sufficiently to the equilibrium value, both at 350 and 400°C.

Figure 4.30. Activity diagrams for the $\text{Na}_2\text{O}-\text{K}_2\text{O}-\text{Al}_2\text{O}_3-\text{SiO}_2-\text{H}_2\text{O}$ system showing mineral stability fields for BGB1(a) and BGB2(b) during and after glass dissolution. Black and red crosses show position of effluent samples collected at 1.0 and 0.5 ml hr^{-1} flow rate, respectively. Yellow circles show position of the unreacted fluid (geothermal brine) at 400 and 350°C/500 bar.

Tale 4.10. Average and 1σ of estimated temperature ($^{\circ}\text{C}$) during and after basalt glass dissolution using fluid compositions for the BGB1 and BGB2. Estimates were made using geothermometers from literature (Arnórsson, 1983; Fournier and Truesdell, 1973; Fournier, 1979; Giggenbach, 1988b; Nieva and Nieva, 1987; Santoyo and Díaz-González, 2009; Tonani, 1980; Truesdell, 1976).

		Na/K (Fournier 1979)	Na/K (Truesdell 1976)	Na/K/Ca (Fournier and Truesdell 1973) ($\beta=1/3$)	Na/K (Santoyo and Díaz-González 2009)	Na/K (Arnórsson 1983) (250-350 $^{\circ}\text{C}$)	Na/K (Tonani 1980)	Na/K (Nieva and Nieva 1987)	Na/K (Giggenbach 1988)
BGB1 400$^{\circ}\text{C}$ / 483 bar	Input brine	261	245	260	235	256	256	257	273
	During glass dissolution	287	280	278	269	279	294	272	296
	$\pm 1\sigma$	26	37	20	36	24	40	26	24
	After glass dissolution	242	220	244	211	239	229	228	256
	$\pm 1\sigma$	4	5	3	5	3	5	4	3
BGB1 350$^{\circ}\text{C}$ / 486 bar	Input brine	261	244	182	235	256	255	247	273
	During glass dissolution?	286	280	207	269	277	294	271	295
	$\pm 1\sigma$	41	61	21	59	36	66	40	37
	After glass dissolution?	261	245	193	235	256	256	247	273
	$\pm 1\sigma$	4	5	3	5	3	5	4	3

Figure 4.31. Estimated temperatures ($^{\circ}\text{C}$) calculated using several cation geothermometers (Arnórsson, 1983; Fournier, 1979; Giggenbach, 1988b; Nieva and Nieva, 1987; Santoyo and Díaz-González, 2009; Tonani, 1980; Truesdell, 1976) together with SiO_2 , Na and K concentrations for BGB1 and BGB2 plotted versus time. Dotted black lines separate value of SiO_2 above quartz saturation (during basalt glass dissolution) from those below quartz saturation (after basalt glass dissolution). Dotted red lines show experimental temperature of BGB1 and BGB2 over time. n: Sample number.

4.3.4. Comparison of Distilled Water and Brine Experiments

In the experiments described so far, the interaction was between a basalt (from Iceland) and either distilled water or geothermal brine (from New Zealand). The main purpose of these two sets of experiments was investigate fluid-rock interaction paths at subcritical and supercritical conditions for the different fluids as they react with basalt. To this effect, results from fluid chemistry and secondary mineralogy at same temperature are compared, i.e., BW1 with BGB1 (400°C) and BW2 with BGB2 (350°C). Table 4.11 summarises the identified secondary minerals that formed during the experiments. Figure 4.32 shows the comparison of chemistry results for all components at the same temperature but with the differing fluids.

In the following discussion, only pH and major aqueous species that show significant differences between experiments are considered. These include quench and *in situ* pH, SiO₂, K, Na, Al, Ca and SO₄. Aqueous species that do not show significant differences include Fe, Mg, and H₂S.

Table 4.11. Secondary mineral assemblage identified after completion of the experiments with water and geothermal brine at 400 and 350°C.

	Basalt-Water (BW1) 400°C	Basalt-Geothermal Brine (BGB1) 400°C	Basalt-Water (BW2) 350°C	Basalt-Geothermal Brine (BGB2) 350°C
Secondary Mineralogy	Anorthite Chlorite Wollastonite Grossular Celadonite Magnetite	Anhydrite Biotite Smectite Cu-sulfide Magnetite	Anorthite Chlorite Celadonite	Anhydrite Smectite Cu-sulfide

Distilled water and geothermal brine enter the Reactor with different initial chemical compositions and pH. Distilled water has a near zero ionic strength and neutral pH (~7 at 25°C) while geothermal brine contains a much higher ionic strength (0.04) and an acid pH (~4 at 25°C). These are the major difference in the input fluid compositions.

In terms of secondary mineralogy, at 400°C, a mineral assemblage composed by grossular, anorthite, wollastonite and chlorite was found at the bottom of the Reactor in the distilled water experiment. With geothermal brine at same temperature, anhydrite and biotite were the predominant secondary mineral phases. At the top of the Reactor, anorthite and celadonite were found as the major secondary phases at 400°C, while smectite was the only major secondary phase identified at 350°C.

At 350°C, in the water experiment, a mineral assemblage composed of chlorite and anorthite was found at the bottom of the Reactor. With geothermal brine, smectite was the only secondary mineral identified at the bottom of the Reactor. Celadonite and smectite were the dominant secondary phases in the upper part of the Reactor in the distilled water and brine experiment, respectively.

Quench pH. In all four experiments, after the T shift, the quench pH initially becomes more acidic than the input value. At 400°C quench pH rises to alkaline values in the distilled water experiment while it remains acidic while glass is dissolving with geothermal brine. At 350°C, both experiments behave similarly but the quench pH is ~2 log units higher than with the brine.

In situ pH. After temperature shift, the *in situ* pH is higher for the brine experiments than for the distilled water experiments. It is ~3 log units higher than the input brine pH at both temperatures indicating neutralisation of brine acidity by fluid-rock interactions. For the distilled water experiments, pH is initially ~1 log unit lower than the input pH and then decreases over time indicating production of acidity during fluid-rock interaction at both temperatures.

At high temperature, ionic species tend to associate and the H^+ and/or OH^- in solution forms complexes and ion pairs (Chapter 2, §2.6, Table 2.8). In contrast, when the solution cools down, these species dissociate and hydrogen and hydroxide ions are released to the solution. These reactions determine the shift of the pH to more acid or basic values at room temperature.

SiO₂. Distilled water contains only trace concentrations of silica while the geothermal brine has an input value of 14 - 15 mmol kg⁻¹. Despite the difference in the initial concentration, after the T shift, SiO₂ reached the same maximum value in both the distilled water and brine experiments at 400°C (Fig. 4.32). This indicates that SiO₂ concentrations were controlled by similar fluid-rock interactions rather than by the dissolution rate of the volcanic glass. SiO₂ concentrations remained elevated during glass dissolution for a longer period of time in the brine experiment due to the higher input SiO₂ concentrations. At 350°C, the time required for glass dissolution into distilled water is similar to that at 400°C and the final SiO₂ concentration is similar in both experiments.

The behaviour with geothermal brine at 350°C is markedly different with a gradual decrease of SiO₂ concentrations after temperature increase. This is due to the initiation of smectite precipitation immediately after T shift causing SiO₂ concentrations to decline even

though volcanic glass was dissolving. This is the only experiment where smectite was identified both at the bottom (with anhydrite) and at top of the Reactor. Unlike the brine experiment, with distilled water at same temperature, chlorite was the predominant phase identified at the bottom of the Reactor, rather than smectite.

K, Na. In the experiments with geothermal brine, Na and K are mainly supplied by the fluid. In contrast, in the experiments with distilled water, K was supplied entirely by the volcanic glass and Na by the dissolution of plagioclase. The high concentrations of these elements present in the brine when compared to the low concentrations in distilled water are evident in the results (Fig. 4.32).

At both temperatures with geothermal brine, there is an uptake of Na immediately after temperature increase, however, Na concentration remains relatively unchanged from input values for the remainder of the experiments. With distilled water, Na concentration increases but appears suppressed while glass dissolution is occurring after which it reaches similar values at both temperatures. This suggests uptake of Na into secondary minerals which cannot be detected at the high Na concentration in the brine.

The behaviour of K between brine and water experiments is markedly different. In all experiments, K concentration increases after temperature shift, however, the relative increase in the brine experiments is much larger. Given the much higher concentration of K in the geothermal brine this relative difference must be due to either the lower pH of the brine or to the high Cl concentration in the brine allowing formation of KCl ion pair (increasing K concentration in the brine). In either case, the effect does not continue as K concentration decreases again after a few days due to the formation of secondary K-bearing phases. It is also notable that, at 400°C, K remains elevated during glass dissolution and then decreases below the input value for the remainder of the experiments. This is not the case at 350°C indicating greater uptake of K by the rock at 400°C.

Al. At room temperature the brine experiments show much higher Al concentrations than the water experiments. This is attributed to the low pH of the brine which allowed some dissolution of aluminosilicates at room temperature. Upon temperature increase in both distilled water experiments, Al concentrations increase while in the brine experiments, they decrease to near detection limit values (except at 400°C after glass dissolution). This is attributed to immediate secondary mineral precipitation with the brine because of its high cation concentrations. Note the SiO₂ concentrations in both fluids are similar at this point. It is notable that Al concentrations are much higher in the distilled water experiments than in

the brine experiments. This is attributed to the higher SiO₂ concentrations in the brine after glass dissolution inducing greater secondary mineral formation during the brine experiments.

Ca and SO₄. At 400°C, brine Ca concentrations are consistently higher than with distilled water. They fall below the input value after temperature increase due to the precipitation of anhydrite. Sulfate also follows this trend (note the difference in ordinate scales for Ca and SO₄). In the water experiments, SO₄ increases slightly due to the dissolution of SO₂ from the glass with a possible contribution from H₂S oxidation in the sampling syringe. No anhydrite precipitated in the distilled water experiments.

A secondary Ca mineral assemblage consisting of grossular, wollastonite and anorthite was found with distilled water at 400°C, while in the brine experiment, anhydrite was the only secondary Ca-bearing mineral identified. The mineral saturations calculated for the brine experiment (Appendix C) reveal that fluid composition was also saturated with respect to grossular. It is suggested that the higher concentration of SO₄ in the input brine favoured the formation of anhydrite over grossular during the brine experiment. It is notable that while glass dissolution was occurring Ca concentration decreased markedly under the input value, however, once the glass was depleted it returns to the input value. Hence, the elevated SiO₂ concentrations triggered Ca fixation in the rock.

At 350°C, Ca reaches similar concentrations in both fluids, however, in the brine experiment, the final Ca concentrations are significantly lower than the input value. This shows significant fixation of Ca in the secondary phases. The Ca concentrations during the 400°C experiment are much higher indicating that there was less fixation of Ca at supercritical conditions (at least after SiO₂ concentration decreased).

Figure 4.32. pH and major ions concentrations in the water and geothermal brine experiments at each temperature.

4.4. References

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Chapter 5: The Experimental Behaviour of Seawater

5.1. Introduction

The seawater - basalt experiments described in Chapter 6 were performed using a new experimental design (Chapter 2, §2.4.5, Fig. 2.20b – 2.21b). The seawater-only experiments described in this chapter were carried out for the purpose of determining seawater behaviour in the absence of the basalt. These are essentially control experiments that use the Preheater only without the Reactor (Chapter 2, §2.4.5, Fig. 2.20a – 2.21a). As discussed in the Methods section, the retrograde solubility of sulfate minerals makes it difficult to conduct flow-through experiments with seawater. The other reason for conducting these experiments was to determine the influence of the ZrO₂ beads on the solution composition.

The experiments reproduced (on a small scale) the submarine hydrothermal process where seawater is depleted in Ca, Mg and SO₄ during its initial descent into the oceanic crust, crossing first the recharge zone before accessing the reaction zone (Babcock et al., 1998; Cann, 1971; Cann, 1969; Cann and Funnell, 1967; Chernysheva, 1971; Coelho et al., 2015; Detrick et al., 1987; Kent et al., 1990; Melson et al., 1968; Melson and van Andel, 1966; Miyashiro et al., 1971; Quon, 1963; Shido et al., 1974; Sinha and Evans, 2013; Sinton and Detrick, 1992). The set-up had a temperature gradient along the Preheater column which allowed entry of seawater at its top at a low enough temperature to avoid sulfate mineral precipitation. As the seawater descends through the Preheater, crystallisation of retrograde solubility minerals occurs.

The experiments did not reproduce, in total, the natural environmental conditions at MORBs. This is because the passage of seawater down the Preheater column occurred without influence from any sediments or basalt. However, the experiments allowed the measurement of the solubility of major elements in solution both at near-supercritical and at subcritical conditions, giving helpful insight into retrograde mineral precipitation phases and their reaction rates.

There are few laboratory experiments where seawater alone has been heated to supercritical and subcritical conditions to investigate retrograde mineral precipitation. The only experiment available in literature, describes these reactions when seawater is heated from 25 to 350°C/500 bar using a batch reactor without rock (Bischoff and Seyfried, 1978).

In our experiments, we used for the first time a novel method to test the thermal stability of seawater at near-supercritical (377°C/488 bar) and at subcritical (342°C/488 bar) conditions using a high T-P hydrothermal flow-through apparatus.

In Chapter 2 (§2.4.5, Fig. 2.17) we described an initial experiment with the Preheater to test its efficiency at removing retrograde phases. This used synthetic seawater (seawater powder) and the empty Preheater. The test ran for 12 days at 377°C/490 bar after which the pressure of the system suddenly exceeded the safety pressure (~517 bar). This was caused by a blockage at the exit point of the Preheater consisting of secondary mineral precipitates. The experimental set-up was modified to include 2 mm diameter ZrO₂ beads filled partway up the Preheater (Chapter 2, §2.4.5, Fig. 2.19). The use of the ZrO₂ beads had two aims: (1) to increase the surface area for retrograde mineral phase precipitation, and (2) to prevent crystal nuclei from settling to the bottom of the vessel and blocking the exit. This set-up was successful in preventing blockage of the exit point of the Preheater.

Two experiments were then conducted using this set-up and natural seawater: SW1 (377°C/488 bar) and SW2 (342°C/488 bar). The temperature of the furnace for the SW1 experiment was set to 400°C, however, a maximum temperature of 377°C was measured in the bottom cap of the Preheater (Chapter 2, §2.4.5, Fig. 2.20a). The temperature of the furnace for the SW2 experiment was set to 350°C, however, a maximum temperature of 342°C was measured in the bottom cap of the Preheater (Chapter 2, §2.4.5, Fig. 2.21a).

Our results show that significant changes in seawater chemistry occurred at both experimental conditions. These consisted of: 1) achievement of rapid steady state element concentrations in solution; 2) strong depletion of Ca, Mg and SO₄ from the seawater at both conditions; and 3) significant decreases of quench pH to acidic values.

5.2. Results

In this chapter the results for the development tests, SW1, and SW2 experiments are presented. These include:

- 1) major element analyses of experimental solutions for SW1 and SW2;
- 2) trace element analyses of experimental solutions for SW1 and SW2;
- 3) chemical, mineralogical and textural analyses of mineral precipitates from the Preheater for a) the initial method development test (Chapter 2, §2.4.5, Fig. 2.17) and b) from the SW1 and SW2 experiments.

Fluid chemistry results from the development test are not reported.

5.2.1. Method development test (377°C/490 bar): Mineralogy of precipitated phases

SEM analysis was performed on the precipitated mineral phases extracted from the bottom portion of the Preheater after the development test. This test used synthetic seawater in the absence of ZrO₂ beads (Chapter 2, §2.4.5, Fig. 2.17). During the experiment, a solid disc of secondary minerals formed at the bottom of the Preheater (Fig. 5.1a). During extraction, this disc broke into numerous clear crystal aggregates up to a millimetre in size (Fig. 5.1b). Samples of this material were mounted on aluminium stubs for SEM-EDS analyses. Appendix D contains all SEM results for this study.

Figure 5. 1. (a) Schematic diagram (not to scale) of the Preheater during the method development test with synthetic seawater (salt powder) without zirconia beads; (b) image of the solid mineral layer extracted from the bottom of the Preheater after completion of the test

SEM images of the mineral phases that precipitated at the bottom of the Preheater during the development are shown in Figure 5.2. The precipitated mineral layer is composed predominantly of aggregates of intergrown tabular anhydrite crystals. Closer examination reveals numerous hexagonal platelets of brucite. Associated exclusively with the brucite crystals are submicron aggregates of a Mg-silicate phase. It is uncertain which Mg-silicate phase this represents; however, talc is a likely candidate. It is interesting to note that no Mg sulfate phases were identified in the precipitate.

As discussed in Chapter 2, it is expected that anhydrite nucleated high in the column where it saturates at 108°C. These crystallites, however, did not adhere to the walls of the Preheater and descended by gravity to the bottom, continuing to grow in the process. It is also evident that brucite and its associated Mg-silicate (talc?) grew exclusively on the surface of anhydrite crystals.

Figure 5.2. SEM images of the mineral precipitates extracted from the bottom of the Preheater after the experiment with synthetic seawater. (a-b) mineral clusters composed primarily of euhedral tabular aggregates of anhydrite; (c) enlargement of rectangular area in (b) showing a hexagonal crystal of brucite; (d-e-f) brucite crystals (Brc) on anhydrite surfaces (Anh). Fine material associated with brucite is a Mg-silicate phase, possibly talc (Tlc).

5.2.2. SW1: Natural seawater (377°C/488 bar)

The first seawater experiment (SW1) ran for a total time of 547 hrs. Note that there was no room temperature period for these experiments. Initially, distilled water was pumped into the system and the experimental pressure of 488 bar was reached. The internal volume of the Preheater is 70 ml with approximately half of this volume taken up by the ZrO₂ beads. The heating procedure was started with the distilled water in the Preheater to prevent mineral precipitation in the apparatus during heat-up. The heating procedure took approximately 3 hrs. Once the experimental temperature was achieved at the bottom of the Preheater (377°C), flow was initiated allowing seawater to enter the Preheater. The flow rate was 1 ml hr⁻¹ for the entire experiment. Analysis of major and trace elements were made for the total number of fluid samples (23) collected.

5.2.2.1. Major element concentrations

Appendix D lists the complete experimental parameters (T, P, time, flow rate, *in situ* and room temperature pH, chemistry). Figure 5.3 and Figure 5.4 show these results plotted against time in hours. The unreacted natural seawater composition is shown at $t = 0$. The blank composition of distilled water is not shown. The concentrations of major ions for the first 163 hrs are essentially for distilled water as it required approximately 6 - 7 days for seawater to begin to exit the Preheater at 1 ml hr⁻¹.

The room temperature pH of the unreacted Napier seawater is 7.75. This seawater is more dilute (432 mmol kg⁻¹ Cl) with respect to average seawater (547 mmol kg⁻¹ Cl) due to freshwater inflow from the Clive River to the south of Napier. While distilled water was present, the quench and *in situ* pH values are irregular due to the low ionic strength of the solution. Once seawater begins to exit the Preheater, *in situ* pH stabilises at ~5.4 while quench pH decreases to ~3.2 for the remainder of the experiment.

SiO₂ concentrations are low when distilled water is present. Once seawater begins to appear in the effluents (~150 hr), SiO₂ concentrations begin to increase and reach a value of ~1 mmol kg⁻¹ (Fig. 5.1). There is only ~0.1 mmol kg⁻¹ SiO₂ in seawater thus the elevated SiO₂ values must be derived from the ZrO₂ beads. As shown in Chapter 2, §2.4.5, Figure 2.19, the ZrO₂ beads are not pure and contain minor amounts of Si, Fe, Mg, Ca, and Al. However, SiO₂ concentrations are not elevated when distilled water was present at 377°C. The SiO₂ concentrations only increase when seawater passes through the column. This indicates that the lower *in situ* pH and much higher ionic strength is inducing SiO₂ release

from the beads. Note that a SiO_2 concentration of 1 mmol kg^{-1} is relatively insignificant when compared to concentrations encountered in experiments using basalt.

A similar explanation can be applied to the behavior of Fe and Al. Fe concentrations only increase when seawater passes through the Preheater. This is attributed to dissolution from the beads (Fig. 5.4). Aluminum concentrations are on average higher while seawater passes through the Preheater (Fig. 5.3) but they are consistently low, irregular, and relatively insignificant when compared to the basalt experiments.

For Na, K, and Cl, results show conservative behavior. Potassium concentrations return to seawater values after mixing with distilled water. Sodium concentrations attain lower values ($\sim 380 \text{ mmol kg}^{-1}$) than the input value (420 mmol kg^{-1}). The explanation for this decrease is uncertain and may be due to an analytical issue. There were no Na-bearing minerals identified in the precipitated phases. Chloride concentrations are conservative and show an expected mixing line with distilled water.

Significant changes are encountered with the other major components Ca, Mg, and SO_4 present in seawater. The seawater contains 9.4 mmol kg^{-1} Ca (Fig. 5.2). While distilled water is exiting the Preheater, Ca concentrations remain at detection limit. Once seawater begins to exit the Ca concentration rises to reach $\sim 2.1 \text{ mmol kg}^{-1}$ after two days and remains at this value for the remainder of the experiment. This represents a significant decrease in Ca concentration from the original seawater.

The Mg concentration in the seawater is $45.8 \text{ mmol kg}^{-1}$. While distilled water is exiting the Preheater, Mg concentrations remain low. Upon the exit of seawater, the Mg concentrations increase gradually and reach a final concentration of $24.4 \text{ mmol kg}^{-1}$. As with Ca, there is a significant loss of Mg during the experiment.

The above changes in Ca and Mg concentrations are mirrored in the changes in SO_4 . The input SO_4 concentration for the seawater is 22 mmol kg^{-1} (Fig. 5.2). While distilled water exits the Preheater SO_4 concentrations are low. Upon the exit of seawater, SO_4 increases and maintains a final concentration of 1.2 mmol kg^{-1} . The behaviour of Ca, Mg, and SO_4 indicates significant precipitation of secondary phases.

There were no detectable concentrations of H_2S during the experiment (Fig. 5.3). This indicates that no measurable amount of sulfate reduction was occurring at the experimental condition.

Figure 5.3. Major element concentrations in blank and effluent samples (mmol kg^{-1}) versus time (hr) for the SW1 experiment at $377^\circ\text{C}/488$ bar and 1.0 ml hr^{-1} flow rate. Yellow symbols are the blank sample composition of natural seawater. Blue symbols show where distilled water was exiting the Preheater. Black symbols are effluent compositions during mixing and replacement of distilled water by seawater.

Figure 5.4. Major element concentrations in blank and effluent samples (mmol kg^{-1}) versus time (hr) for the SW1 experiment at $377^\circ\text{C}/488$ bar and 1.0 ml hr^{-1} flow rate. Yellow symbols are the blank sample composition of natural seawater. Blue symbols show where distilled water was exiting the Preheater. Black symbols are effluent compositions during mixing and replacement of distilled water by seawater.

5.2.2.2. Trace element concentrations

Figure 5.5 and Figure 5.6 show the trace element results plotted against time in hours. The unreacted natural seawater concentrations are shown at $t = 0$. Most trace elements are below detection limit with only V, Rb, Au and Mn showing detectable concentrations. The distilled water concentrations are not shown but are generally lower than seawater. Complete trace element results are listed in Appendix D.

While distilled water exits the Preheater (0 - 163 hr) trace element concentrations are low and irregular with perhaps small increases in Cr, Zn, and Ba. This indicates that the ZrO_2 beads do not release significant amounts of trace elements at 377°C in the presence of distilled water.

Once seawater begins to exit the Preheater several elements including V, Co, Ni, and perhaps Pb, display increasing concentration with time over the experiment. The values are much higher than the input seawater values and therefore must be derived from the ZrO_2 beads. Unfortunately, we do not have trace element analyses for the beads. The *in situ* pH and ionic strength of the fluid are constant after about 300 hours, therefore, the reason for the upward trends over time is uncertain but is attributed to some kinetic surface area effect of the ZrO_2 beads.

Mn and Au show trends that are similar to Fe (Fig. 5.4) indicating regular extraction from the beads. The concentrations of Cr and Cu remain low and irregular while Zn concentrations shown no clear trend and are likely spurious and subject to contamination.

The results for Rb show a mixing line identical with Cl and this suggests derivation from the seawater. However, the blank value is not at the level expected for natural seawater. The average global concentration of Rb in seawater is $1.4 \mu\text{mol kg}^{-1}$ (Smith et al., 1965). Given that the seawater is slightly diluted, the final concentration of $1 \mu\text{mol kg}^{-1}$ seems reasonable.

Barium shows unique behaviour with its highest concentration of $7 \mu\text{mol kg}^{-1}$ found in the first sample after which it continuously decreases to a final value of $\sim 0.5 \mu\text{mol kg}^{-1}$. The average global concentration of Ba in seawater is only $0.04 \mu\text{mol kg}^{-1}$ (Field et al., 2007; Hsieh and Henderson, 2017), therefore, Ba must be efficiently extracted from the beads after which it declines to 10x seawater concentration. Also, Ba concentrations decrease with increasing SO_4 concentrations suggesting precipitation of barite. The minor amount of barite precipitated would be difficult to identify in SEM examination.

Figure 5.5. Trace element concentrations in blank and effluent samples ($\mu\text{mol kg}^{-1}$) versus time (hr) for the SW1 experiment at 377°C/488 bar and 1.0 ml hr⁻¹ flow rate. Yellow symbols are the blank sample composition of natural seawater. Blue symbols show where distilled water was exiting the Preheater. Black symbols are effluent compositions during mixing and replacement of distilled water by seawater.

Figure 5.6. Trace element concentrations in blank and effluent samples ($\mu\text{mol kg}^{-1}$) versus time (hr) for the SW1 experiment at $377^\circ\text{C}/488$ bar and 1.0 ml hr^{-1} flow rate. Yellow symbols are the blank sample composition of natural seawater. Blue symbols show where distilled water was exiting the Preheater. Black symbols are effluent compositions during mixing and replacement of distilled water by seawater.

5.2.2.3. Mineralogy of precipitated phases

Mineral precipitates and beads were selected from the bottom of the Preheater (Fig. 5.7, rectangular area). These were mounted on Al stubs for SEM-EDS analysis. Appendix D contains complete SEM results.

Figure 5.7. Schematic diagram (not to scale) of the Preheater for the SW1 experiment with natural seawater. Rectangular area in red indicates where reacted ZrO_2 beads were collected.

SEM-EDS analysis

SEM-EDS results confirm the white mineral precipitate to be composed of anhydrite, Mg sulfate or hydroxysulfate, and brucite (Table 5.1). No evidence of Mg-silicate/talc was found during analysis. The average SEM-EDS analysis of the Mg phase (Table 5.2) shows a Mg:S molar ratio of ~2.2:1.2. In nature, a mineral of this composition has not been identified. However, given the semi-quantitative nature of the EDS analyses (similar analyses of anhydrite gave a Ca:S ratio of ~2:2.2) it is likely that this is the mineral caminite ($\text{Mg}_7(\text{SO}_4)_5(\text{OH})_4 \cdot \text{H}_2\text{O}$ or $\text{MgSO}_4:0.4\text{Mg}(\text{OH})_2:0.2\text{H}_2\text{O}$) which has an ideal Mg:S ratio of 2:1.4. There is some variability in the $\text{Mg}(\text{OH})_2$ component in caminite which could accommodate slight differences in the Mg:S ratio (Haymon and Kastner, 1986).

Caminite has the crystal form of tetragonal bipyramidal which is consistent with crystals found in the experiments (Fig. 5.9, 5.15, 6.6). Caminite was identified as a naturally occurring mineral in precipitates from black smoker chimneys on the East Pacific Rise relatively recently (Haymon and Kastner, 1986). There are several different Mg-hydroxysulfate formulas in the literature such as $\text{MHSH}(0.67)$ or $\text{MgSO}_4:1/3\text{Mg}(\text{OH})_2:1/3\text{H}_2\text{O}$ (Hochella et al., 1983; Keefer et al., 1981), $\text{MHSH}(0.625)$ or $\text{MgSO}_4:1/4\text{Mg}(\text{OH})_2:1/2\text{H}_2\text{O}$, $\text{MHSH}(0.16)$ or $\text{MgSO}_4:1/6\text{Mg}(\text{OH})_2:2/3\text{H}_2\text{O}$, and $\text{MHSH}(0.75)$ or $\text{MgSO}_4:1/2\text{Mg}(\text{OH})_2$ (Bischoff and Rosenbauer, 1983; Fleet and Knipe, 1997; Janecky and Seyfried, 1983). The Mg-hydroxysulfate precipitate found in the experiments of Bischoff and Seyfried (1978) is also considered to be caminite.

Table 5.1. Mineral phases identified during analysis of the precipitates collected from the bottom of the Preheater (Fig. 5.8 – 5.9) after the SW1 experiment. Analysis were made by SEM-EDS. Appendix D contains all SEM for this study.

Type of Analysis	Mineral Identified	Mineral Composition
SEM-EDS	Anhydrite	CaSO_4
SEM-EDS	Caminite	$\text{Mg}_7(\text{SO}_4)_5(\text{OH})_4 \cdot \text{H}_2\text{O}$
SEM-EDS	Brucite	$\text{Mg}(\text{OH})_2$

Table 5.2. Average composition (SEM-EDS analysis) of caminite from the bottom of the Preheater (Fig. 5.8 – 5.9) after the SW1 experiment.

Caminite (N=5)		
oxide	average Wt %	$\pm 1\sigma$
MgO	46.10	3.33
SO₃	53.90	3.33
Total	100.00	

Figure 5.8 shows SEM backscatter images and EDS maps of the mineral phases collected from the bottom of the Preheater after the SW1 experiment (Fig. 5.7, rectangular area). The composite colour image shows crystals of anhydrite and caminite. Anhydrite appears as euhedral rectangular crystals while caminite occurs as polyhedral grains.

Figure 5.9 shows SEM images of reacted ZrO_2 beads collected from the bottom of the Preheater. The surface of the beads shows larger crystals of caminite with lesser anhydrite (Fig. 5.9a-c). Brucite was also identified as discrete polygonal crystals (Fig. 5.9d) and as diamond-shaped growths on the surface of the beads (Fig. 5.9a,e,f). These diamond-shaped growths are composed of contiguous crystals of brucite along the outside edge with isolated growths within (Fig 5.9e).

Figure 5.8. SEM backscatter images and EDS compositional maps of the precipitate collected from the bottom of the Preheater after the SW1 experiment: (a) digital camera image of the precipitate; (b) backscatter image of rectangular area in (a); (c) composite colour image combining the backscatter image and elemental maps for d) Ca in green, e) Mg in red, and f) S in blue.

Figure 5.9. SEM images of reacted ZrO_2 beads collected from the bottom of the Preheater after the SW1 experiment: a) SED image of a single bead with one caminite crystal and diamond-shaped growths of brucite; b) SED image of a single bead with several crystals of caminite; c) BED image of bead with of anhydrite (Anh) and caminite; (d) BED image showing a caminite crystal with intergrown brucite; (e) SEM backscatter image of rectangular area in (a) showing diamond-shaped growth of brucite; (f) composite colour image combining the backscatter image and elemental map for Mg in red.

5.2.3. SW2: Natural seawater (342°C/488 bar)

The second seawater-only experiment (SW2) ran for a total time of 381 hrs. There was no room temperature period. The heating procedure using distilled water, initially in the Preheater, was the same as utilised for SW1. The flow rate was 1 ml hr⁻¹ and analyses for major and trace elements were made for the total number of fluid samples collected (16).

5.2.3.1. Major element concentrations

Appendix D lists the complete experimental parameters (T, P, time, flow rate, *in situ* and room T pH, chemistry). Figure 5.10 and Figure 5.11 show these results plotted against time in hours. The unreacted natural seawater composition is shown at $t = 0$. The blank composition of distilled water is not shown. The concentrations of major ions for the first 50 hrs are essentially for distilled water as it required at least 2 days for seawater to begin to exit the Preheater at 1 ml hr⁻¹.

The room temperature pH for the unreacted seawater is 7.65. Once the seawater begins to exit the Preheater, *in situ* pH stabilises at ~5.5 while quench pH decreases to ~2.7 for the remainder of the experiment.

At ~80 hours, SiO₂ concentrations begin to increase and stabilised at a value of ~0.25 mmol kg⁻¹ (Fig. 5.10). As in SW1, SiO₂ is derived from the ZrO₂ beads. Note that this concentration is insignificant when compared to concentrations encountered in experiments using basalt.

A similar explanation can be applied the behavior of Fe. Aluminum concentrations do not show any consistent increase in concentration. Iron only increases when seawater passes through the Preheater. This is attributed to dissolution from the beads (Fig. 5.11). Iron reaches a maximum concentration of ~1.8 mmol kg⁻¹ while Al concentrations are at or below detection limit for the entire experiment. The Fe concentrations are insignificant when compared to the basalt experiments.

For Na, K, and Cl, results show conservative behavior, as in the experiment at 377°C. The K, Na and Cl concentrations reach seawater values after displacement of the distilled water at six days.

Significant changes are encountered with the other major components Ca, Mg, and SO₄ present in seawater. The seawater contains 8 mmol kg⁻¹ Ca (Fig. 5.11). While distilled water is exiting the Preheater, Ca concentrations remain at detection limit. Once seawater begins to exit the Ca concentration rises to reach ~1.7 mmol kg⁻¹ after six days and then

decreases to 1.4 mmol kg^{-1} for the remainder of the experiment. This represents a significant decrease in Ca concentration from the original seawater.

The Mg concentration in the seawater is $36.7 \text{ mmol kg}^{-1}$. While distilled water is exiting the Preheater, Mg concentrations remain low. Upon the exit of seawater, the Mg concentrations increase gradually and maintain a final concentration of $22.8 \text{ mmol kg}^{-1}$. As with Ca, there is a significant loss of Mg during the experiment.

The above changes in Ca and Mg concentrations reflect the changes in SO_4 . The input SO_4 concentration for the seawater is 23 mmol kg^{-1} (Fig. 5.11). While distilled water exits the Preheater, SO_4 concentrations are low. Upon exit of seawater, SO_4 increases and maintains a final concentration of 2.7 mmol kg^{-1} . The behavior of Ca, Mg, and SO_4 indicate significant precipitation of secondary phases. The total loss of Ca is 6.6 mmol kg^{-1} , for Mg $13.9 \text{ mmol kg}^{-1}$ and for SO_4 $20.3 \text{ mmol kg}^{-1}$. If it is assumed that all Ca came from the seawater, this implies that 6.6 mmol kg^{-1} of SO_4 precipitated as anhydrite. This means that there is $13.7 \text{ mmol kg}^{-1}$ left to form caminite which would require $19.2 \text{ mmol kg}^{-1}$ of Mg. This is greater than amount of Mg lost, thus implying another source of Mg other than the seawater. This must be from the ZrO_2 beads which contain 3% MgO.

There were no detectable concentrations of H_2S during the experiment (Fig. 5.11). This indicates that no measurable amount of sulfate reduction was occurring at 342°C .

Figure 5.10. Major element concentrations in blank and effluent samples (mmol kg^{-1}) versus time (hr) for the SW2 experiment at $342^\circ\text{C}/488$ bar and 1.0 ml hr^{-1} flow rate. Yellow symbols are the blank sample composition of natural seawater. Blue symbols show where distilled water was exiting the Preheater. Black symbols are effluent compositions during mixing and replacement of distilled water by seawater.

■ ▲ blank seawater
■ ▲ $342^\circ\text{C}/488 \text{ bar}/1 \text{ ml hr}^{-1}$ (distilled water)
■ ▲ $342^\circ\text{C}/488 \text{ bar}/1 \text{ ml hr}^{-1}$ (seawater)

Figure 5.11. Major element concentrations in blank and effluent samples (mmol kg^{-1}) versus time (hr) for the SW2 experiment at $342^\circ\text{C}/488$ bar and 1.0 ml hr^{-1} flow rate. Yellow symbols are the blank sample composition of natural seawater. Blue symbols show where distilled water was exiting the Preheater. Black symbols are effluent compositions during mixing and replacement of distilled water by seawater.

5.2.3.2. Trace element concentrations

Complete trace element results are listed in Appendix D. Figure 5.12 and Figure 5.13 show these results plotted against time in hours. The unreacted natural seawater concentrations are shown at $t = 0$. Most trace elements are below detection limit with only V, Rb, Au and Mn showing detectable concentrations.

While distilled water exits the Preheater (0 - 50 hr), trace element concentrations are low and irregular with perhaps small increases in Cr, Zn, Cd, Ba and Pb. This indicates that the ZrO_2 beads do not release significant amounts of trace elements also at 342°C in the presence of distilled water.

While seawater exits the Preheater, Ni displays increasing concentration with time over the experiment while Mn and Co reach a steady state in solution at ~ 35 and $15 \mu\text{mol kg}^{-1}$, respectively. The values are much higher than the input seawater values and therefore must be derived from the ZrO_2 beads.

V, Au and also Cd show linear trends indicating regular extraction from the beads. The Cr concentration remains low and irregular while Ag and Pb appear close to detection limit for the entire experiment.

The results for Rb show the same behaviour as at 377°C with a final concentration of $1 \mu\text{mol kg}^{-1}$. Given that the seawater used in the experiment was slightly dilute, this concentration seems reasonable.

The Zn and Cu concentrations initially show a significant increase in solution after full replacement of distilled water by seawater and then decrease to low values. The final concentrations for Zn and Cu are higher than the input seawater (~ 4.5 and $\sim 10 \mu\text{mol kg}^{-1}$, respectively). The absence of reduced S excludes precipitation of these elements in mineral phases. The Ba concentration drops to $\sim 0.1 \mu\text{mol kg}^{-1}$ as in SW1. This suggests the precipitation of barite at 342°C .

Figure 5.12. Trace element concentrations in blank and effluent samples ($\mu\text{mol kg}^{-1}$) versus time (hr) for the SW2 experiment at $342^\circ\text{C}/488$ bar and 1.0 ml hr^{-1} flow rate. Yellow symbols are the blank sample composition of natural seawater. Blue symbols show where distilled water was exiting the Preheater. Black symbols are effluent compositions during mixing and replacement of distilled water by seawater.

Figure 5.13. Trace element concentrations in blank and effluent samples ($\mu\text{mol kg}^{-1}$) versus time (hr) for the SW2 experiment at $342^\circ\text{C}/488$ bar and 1.0 ml hr^{-1} flow rate. Yellow symbols are the blank sample composition of natural seawater. Blue symbols show where distilled water was exiting the Preheater. Black symbols are effluent compositions during mixing and replacement of distilled water by seawater.

▲ blank seawater
 ▲ $342^\circ\text{C}/488 \text{ bar}/1 \text{ ml hr}^{-1}$ (distilled water)
 ▲ $342^\circ\text{C}/488 \text{ bar}/1 \text{ ml hr}^{-1}$ (seawater)

5.2.3.3. Mineralogy of precipitated phases

ZrO₂ beads and associated mineral precipitates were collected from the bottom of the Preheater (Fig. 5.14, rectangular area) and mounted on Al stubs for analysis by SEM-EDS. Appendix D contains complete SEM results.

Figure 5.14. Schematic diagram (not to scale) of the Preheater for the SW2 experiment with natural seawater. Rectangular area in red indicates where reacted ZrO₂ beads were collected.

SEM-EDS analysis

SEM-EDS results confirm that the white mineral precipitates are composed of anhydrite, Mg sulfate, and brucite (Table 5.4). SEM-EDS analysis of the Mg sulfate phase gives the Mg:S ratio of 2:1.2 which is consistent with caminite.

Table 5.3. Mineral phases identified during analysis of the precipitates from the bottom of the Preheater (Fig. 5.15) after the SW2 experiment. Analysis were made by SEM-EDS. Appendix D contains all SEM for this study.

Type of Analysis	Mineral Identified	Mineral Composition
SEM-EDS	Anhydrite	CaSO ₄
SEM-EDS	Caminite	Mg ₇ (SO ₄) ₅ (OH) ₄ ·H ₂ O
SEM-EDS	Brucite	Mg(OH) ₂

Table 5.4. Average composition (SEM-EDS analysis) of caminite from the bottom of the Preheater (Fig. 5.15) after the SW2 experiment.

Caminite (N=1)		
oxide	average Wt %	±1σ
MgO	45.58	-
SO₃	54.42	-
Total	100.00	

Figure 5.15 shows reacted ZrO₂ beads collected from the bottom of the Preheater. The bead surfaces are covered by a mixture of cube-like anhydrite, polyhedral caminite, and hexagonal brucite (Fig. 5.15).

Figure 5.15. SEM images of reacted ZrO_2 beads collected from the bottom of the Preheater: (a) image of three reacted beads with precipitated phases; (b) surface of a reacted bead with the caminite and anhydrite (Anh); (c) surface area of a reacted bead with crystals of brucite; (d) a single brucite crystal.

5.3. Discussion

Table 5.5 shows the input total mass (mg) and integrated elemental fluxes (mg) for selected components for the seawater-only experiments. The input total mass represents the amount of material that entered the Preheater based on the total fluid flux (0.33 L in SW2 and 0.40 L in SW1) and the input seawater composition. The integrated elemental flux is the total mass of component integrated over the entire experiment based on daily fluid flux and the effluent composition. The calculations excluded the first six samples in SW1 and the first two samples in SW2, due to the time necessary for seawater to displace distilled water in the system.

For the SW2 (342°C), the integrated flux calculation shows a positive net flux of +3.8 mg SiO₂ and +23 mg Fe to the fluid while SW1 (377°C) has a net positive flux of +17 mg SiO₂ and +25 mg Fe to the fluid. This can be explained by silica and iron released from the ZrO₂ beads during the interaction with seawater.

At 342°C, the total integrated flux is -669 mg for SO₄, -89 mg for Ca, and -130 mg for Mg. The results agree with the mineralogy identified by SEM-EDS. The significant decreases in Ca, Mg, and SO₄ concentration can be explained by the precipitation of anhydrite, caminite, and brucite.

At 377°C, the total integrated elemental flux is -814 mg for SO₄, -121 mg for Ca, and -235 mg for Mg. The SEM-EDS results also confirm that the significant decreases in Ca, Mg and SO₄ concentrations are explained by the precipitation anhydrite, caminite, and brucite. It is also noted that at 377°C there was significantly more SO₄, Ca, and Mg removed from solution when compared to the losses at 342°C. This is consistent with the retrograde solubility of the precipitated phases.

Table 5.5. Total input mass (mg) and integrated elemental fluxes (mg) for selected components for SW1 and SW2.

SW2 (342°C / 488 bar)		SiO₂	SO₄	Ca	Mg	Fe
Blank composition (mg kg ⁻¹)		5.8	2237	321	892	0.1
Total input mass (mg) (based on 0.33 L total natural seawater)		1.9	746	107	297	0.03
Total integrated elemental flux (mg) (over the entire experiment)		+3.8	-669	-89	-130	+23
SW1 (377°C / 488 bar)		SiO₂	SO₄	Ca	Mg	Fe
Blank composition (mg kg ⁻¹)		6.7	2117	377	1112	0.1
Total input mass (mg) (based on 0.40 L total natural seawater)		2.7	856	152	450	0.04
Total integrated elemental flux (mg) (over the entire experiment)		+17.3	-814	-121	-235	+25

The precipitation of brucite, anhydrite, and caminite, all produce H⁺ ion as can be seen in the following reactions:

At high temperature, SO₄ is mostly protonated, occurring as HSO₄⁻, which dissociates upon cooling to room temperature, liberating protons and lowering pH to highly acidic values.

Using the *in situ* pH and individual species' activities calculated as described previously, the ion activity product (log Q) were determined at 342 and 377°C (Fig. 5.16). The solubility product (log K_{sp}) for anhydrite and brucite were sourced from SUPCRT92 (Johnson et al., 1992). Log K_{sp} for MSH(0.625) and MSH(0.75) were sourced by Janecky and Seyfried (1983) up to 350°C. They observed MSH(0.625) as the stable phase above 300°C. The K_{sp} for this phase is plotted in Figure 5.16, extrapolated linearly to 400°C. The log Q for caminite was determined using the species' activities and *in situ* pH calculated from our experiment data. Appendix D reports all calculations for solution composition and mineral saturation indices.

The log Q for anhydrite and brucite show that, when only reacted seawater was exiting the Preheater, these minerals were at equilibrium with the fluid at both temperatures (Fig. 5.16). This is shown by log Q being comparable to the log K_{sp} at temperature for these minerals. The log Q for caminite, calculated using the precipitation reaction for

MSHS(0.625) from Janecky and Seyfried (1983) and our species's activities and pH (both at 342°C and 377°C), are within $\frac{1}{2}$ log unit of their extrapolated log K_{sp} . This supports the conclusion that the mineral identified in this study is caminite.

Figure 5.16. Log Q and log K_{sp} for anhydrite (a) and brucite (b). Log K_{sp} for anhydrite and brucite from SUPCRT92. Log K_{sp} for caminite (c) from Janecky and Seyfried (1983) (MHS(0.625)) and compared with log Q from the experiment data in this study.

Bischoff and Seyfried (1978) reported results from an experiment study in which seawater was heated to elevated temperature up to 350°C. Table 5.6 lists the fluid chemistry and fluxes from this work along with a summary of the results from our study. Bischoff and Seyfried used closed system, batch reactors to investigate the kinetics of precipitation of minerals from seawater. Their results show little change in solute concentrations or pH until above 150°C. This is contrary to the expectation of brucite saturation at 70°C and anhydrite saturation at 108°C for standard seawater (Fig. 2.16). Note, however, that brucite saturation is sensitive to pH while anhydrite saturation is not, at least at lower temperatures, possibly explaining the absence of brucite in their experiments. The explanation for the absence of anhydrite precipitation above 108°C is uncertain but is unlikely due to kinetics given that their experiments lasted one month.

At 200 and 250°C it appears that only anhydrite precipitated with no accompanying Mg-bearing phase. Mg hydroxysulfate was only identified at 300 and 350°C. Bischoff and Seyfried (1978) did not identify brucite in any of their experiments, however, the excess for Mg over sulfate (once anhydrite is removed) can be explain by the precipitation of caminite.

For caminite, the thermodynamic data from GWB show that MHSH(Mg_{1.5}) should saturate at ~193°C (Fig. 2.16). Evidently this was not the case in Bischoff and Seyfried (1978). Their results are more consistent with the precipitation of caminite at 300 and 350°C. In this study we do not have data for mineral precipitates at lower temperatures, however, the SEM-EDS data confirm that the Mg-bearing sulfate phase has a Mg:S ratio of ~2:1.2 is consistent with the precipitation of caminite at 350°C. The earlier study also measured a large decrease in quench pH above 250°C. This is consistent with our results.

It should be noted that there is a fundamental difference between this study and the earlier experiments. Bischoff and Seyfried (1978) used closed system, batch experiments while this study used open-system, continuous flow-through. In the former, mineral precipitates are controlled not only by thermodynamic properties but also on total mass of solute available. In our study, the latter was not restricted with fresh seawater being continuously supplied. This may explain some of the differences in mineral precipitates encountered.

As previously mentioned at the beginning of this chapter, the experiments using only seawater were performed to determine fluid behaviour in the absence of the basalt and to determine the influence of the ZrO₂ beads on the solution composition. At the conclusion of these simulations, the composition of the fluid exiting the Preheater from SW1 and SW2, can

be assumed as equal to that entering the Reactor in the basalt-seawater experiments, BSW1 and BSW2, respectively.

Table 5.6. Comparison between experimental results of Bischoff and Seyfried (1978) and this study.

Bischoff Seyfried (1978)			(mmol kg⁻¹)			Precipitated (mmol kg⁻¹)		
T (°C)	P (bar)	pH (room T)	SO₄	Mg	Ca	SO₄	Mg	Ca
25	-	7.63	27	51.1	9.8			
70	500	7.7	27	50.4	9.9			
150	500	6.43	27	50.4	9.9			
200	500	6.2	20	51	3	-6.9	-	-6.8
250	500	5.8	18	50.6	1.5	-8.4	-	-8.3
300	500	3.01	11	43.8	1	-15.3	-7.3	-8.7
350	500	2.52	9	40.2	1	-18	-10.9	-8.8
SW2						Precipitated		
25	1	7.75	input	23	36.7	8		
342	488	2.79	output	2.7	22.8	1.4	-20.3	-13.9
SW1								
25	1	7.75	input	22	45.8	9.4		
377	488	3.34	output	1.2	24.4	2.1	-20.8	-21.4

5.4. References

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Chapter 6: Basalt – Seawater Interactions under Hydrothermal Conditions

6.1. A brief introduction

The experimental approach adopted for the basalt - seawater interactions is the most innovative aspect of this study. Simulations were performed using a high T-P hydrothermal apparatus in an open system (flow-through) rather than in a closed system (batch reactor). This method used a Preheater, allowing pre-treatment of the seawater, and a Reactor, containing the basalt, connected in series. This permitted simulation of MORB conditions where seawater, first depleted in Ca, Mg and SO₄ descends through a temperature gradient into the reaction zone and comes into contact with the basalt (Chapter 2, §2.4.5, Fig. 2.19b - 2.20b). Note, however, this apparatus only reproduces the loss of retrograde phases upon descent and does not reproduce any seawater - rock interactions along the descent path.

The high T-P hydrothermal apparatus used in this study allowed collection of multiple samples allowing monitoring of fluid – rock interaction path and variation of flow rate to test equilibrium conditions.

There are several studies in the literature of laboratory experiments describing basalt - seawater interactions at supercritical, near-supercritical and at subcritical conditions, however, these were performed using only batch reactors. Nevertheless, these experimental simulations provided great insights and fundamental implications to understanding basalt-seawater interaction occurring in the reaction zones at MORBs (Berndt and Seyfried, 1993; Bischoff and Dickson, 1975; Bischoff and Seyfried, 1978; Cann, 1979; Hajash, 1975; Hochella et al., 1983; Janecky and E. Seyfried, 1983; Mottl and E. Seyfried, 2019; Mottl and Seyfried Jr, 1980; Mottl and Holland, 1978; Mottl et al., 1979; Ohmoto and Rye, 1974; Seewald and Seyfried, 1990; Seyfried and Mottl, 1977; Seyfried et al., 1988; Seyfried and Bischoff, 1981; Seyfried and Mottl, 1982).

In this section we describe two basalt - seawater interaction experiments carried out at near-supercritical and subcritical conditions using the continuous flow apparatus: BSW1 at 400°C/488 bar and BSW2 at 350°C/488 bar.

The results from both experiments indicate that seawater reacted aggressively with the basalt. Equilibrium (or steady state) was reached at different flow rates and rate of reactions occurred rapidly at both experimental conditions. Major changes in solution chemistry consisted of: (1) almost total depletion of Mg and SO₄ from solution; (2) significant changes in concentrations in Ca and Fe depending on flow rate; (3) SiO₂

solubilities well above quartz saturation during both experiments; (4) the absence of K in mineral precipitates from both experiments; (5) the generation of measurable concentrations of H₂S; (6) highly acidic quench pH values; and (7) low trace element mobility in both experiments.

Analysis of the reacted basalt was conducted on grains collected from the Reactor at the conclusion of the experiments. These results show a distinct mineralisation front occurring at the approximate middle of the rock column in both experiments. At 400°C, analysis revealed that the most highly reacted grains coincided with the Portion of rock situated at ~2-3 cm above the fluid entry point in the Reactor. However, at 350°C, the most highly reacted grains were found immediately adjacent of the fluid entry point in the Reactor. In both experiments, the least altered basalt was encountered immediately adjacent of the fluid exit point of the Reactor.

6.2. Results

In this chapter the results are presented for the:

- 1) major element analyses of experimental solutions collected;
- 2) trace element analyses of experimental solutions collected;
- 3) chemical, mineralogical and textural analyses of the reacted rock material.

Note also that retrograde mineral precipitates in the Preheater were not examined after the basalt – seawater experiments. These precipitates are assumed to be the same as in SW1 and SW2 (Chapter 5). It is also assumed that the input composition of the pre-treated seawater in the basalt - seawater experiments is equal to that of the effluent compositions in SW1 and SW2.

6.2.1. BSW1: Basalt-seawater at 400°C/488 bar

The laboratory set-up for the BSW1 experiment consisted of the Preheater containing zirconia beads and the Reactor filled with rock material mounted in series (Chapter 2, §2.4.5, Fig. 2.19b). The experimental configuration maintained a temperature gradient of 40°C at the top to 377°C at the bottom of Preheater, while the Reactor was kept at a temperature of 400°C. Pressure remained stable at 488 bar.

The experiment ran for a total time of 659 hrs. At the start of the experiment, distilled water was pumped through the system for the first 24 hrs until pressure was stable. After this, the heating procedure increased the oven temperature until a Reactor temperature of 400°C was reached (~3 hours), then fluid flow was switched to seawater. It required approximately three days for seawater to begin to exit the Reactor at 1 ml hr⁻¹ (See Cl concentrations in Fig. 6.2). Distilled water was completely displaced from the combined Preheater and Reactor after about four days.

After 400 hrs (approximately two weeks) the pressure of the system suddenly dropped due to a leak in the apparatus. This required the experiment to be shut down which provided an opportunity to collect basalt grains during an experiment. The Preheater and Reactor were removed, and the Reactor was opened and several grains were collected from immediately adjacent of the fluid entry and exit point. These grains were rinsed with distilled water, dried, and mounted on the aluminium stubs for SEM-EDS analysis.

The experiment was shut down for three hours, after which the start-up procedure was repeated. At 603 hr the separator was re-filled with seawater. In this case, the seawater was not de-oxygenated. The flow rate was varied during the experiment as follows:

- 1 ml hr⁻¹ for 533 hr (23 samples collected)
- 1.5 ml hr⁻¹ for 50 hr (2 samples collected)
- 10 ml hr⁻¹ for 44 hr (10 samples collected)
- 7.5 ml hr⁻¹ for 25 hr (5 samples collected)
- 5 ml hr⁻¹ for 8 hr (4 samples collected)

Analysis for major and trace elements was made for the total number of the fluid samples collected (46). Distilled water and seawater blanks were included.

6.2.1.1. Major Element Concentrations

Complete experimental parameters and results (T, P, time, flow rate, *in situ* and room T pH, chemistry) are listed in Appendix E. Figure 6.1 and Figure 6.2 show these results plotted versus time in hours. The unreacted seawater composition is shown at $t = 0$. The composition of unreacted distilled water is not shown. The concentrations of major ions for the first 70 hrs are essentially for distilled water as it required approximately 3 days for seawater to begin to exit the Reactor at 1 ml hr^{-1} .

The room temperature pH of the unreacted Napier seawater is 7.75 (Fig. 6.1). While distilled water was exiting the Reactor, quench pH decreases from 6.37 to 4.17 while the *in situ* pH decreases from 7.17 to 6.71. Once seawater displaces distilled water the quench pH stabilises at ~ 4.1 after about seven days which translates into a stable *in situ* pH of ~ 5.8 . After re-starting the experiment at 400 hours, the quench and *in situ* pH values return to the above values after two days. The quench pH increases marginally to ~ 4.5 when flow rate was changed to 10, 7.5 and 5 ml hr^{-1} , however, the *in situ* pH remains stable at ~ 5.80 for this period. The entry *in situ* pH of the pre-treated seawater into the Reactor is assumed to be ~ 5.4 based on the results of the SW1 experiment.

SiO_2 concentrations increases to $\sim 31 \text{ mmol kg}^{-1}$ ($\sim 1860 \text{ ppm}$) while distilled water is exiting the Reactor for the first three days (Fig. 6.1). Once seawater begins to appear in the effluents ($\sim 70 \text{ hr}$), SiO_2 concentration stabilises to $\sim 28 \text{ mmol kg}^{-1}$ and then remains at this value for the remainder of the experiment. The variation of the flow from $1 - 10 \text{ ml hr}^{-1}$ does not affect effluent SiO_2 concentrations. A SiO_2 concentration of 28 mmol kg^{-1} (1682 ppm) exceeds quartz saturation at $400^\circ\text{C}/500 \text{ bar}$ (1238 ppm). Note that it is assumed that the SiO_2 concentration entering the Reactor is 0.7 mmol kg^{-1} based on the SW1 experiment.

Sodium concentration remains low while distilled water is exiting the Reactor. Once seawater begins to appear in the effluents, Na concentrations begin to increase and reach a value of $\sim 400 \text{ mmol kg}^{-1}$ after seven days. Na concentration averages around this value for the next eleven days. Sodium was conservative in the SW1 experiment thus Na concentrations entering the Reactor are expected to be similar to input seawater. On average the Na concentrations appear to be slightly higher, however, this is believed to be an analytical artefact and not from release of Na from the rock. This is supported by the Na results after the experiment was restarted which show the Na concentration stable at the seawater value, irrespective of the flow rate.

The behaviour of K is also conservative. The K concentration exactly reflects the Na concentrations and Na/K ratio is essentially constant (Fig. 6.1). Potassium concentration is on average higher than the input value between 100 and 400 hours. This is also attributed to an analytical artefact. After the experiment was restarted at 400 hours, K concentration stabilises at the input value of 8 mmol kg^{-1} and remains independent of flow rate.

Aluminium concentrations are slightly elevated when distilled water is present in the Reactor. Once seawater begins to appear in the effluents, Al concentrations decrease to close to the detection limit and remain so for the remainder of the experiment irrespective of flow rate.

Calcium concentration is below detection limit while distilled water is exiting the Reactor (Fig. 6.2). Once seawater begins to appear in the effluents after three days, Ca concentration increases to a steady value of $\sim 20 \text{ mmol kg}^{-1}$. After restarting at 400 hours, Ca again reaches this concentration at $1 - 1.5 \text{ ml hr}^{-1}$ flow rate (Fig. 6.1). At 10 ml hr^{-1} , Ca concentration decreases to 15 mmol kg^{-1} . It then increases marginally upon decreasing the flow rate to 7.5 and 5 ml hr^{-1} . Note that the input Ca concentration from the Preheater is assumed to be 2 mmol kg^{-1} based on the results from the SW1 experiment (Fig. 5.4). This indicates that a significant amount of Ca is being added to the fluid by the rock.

Iron concentration is below detection limit while distilled water is exiting the Reactor (Fig. 6.2). Once seawater appears, Fe concentration increases over time from $\sim 0.8 \text{ mmol kg}^{-1}$ to $\sim 3 \text{ mmol kg}^{-1}$. After restarting at 400 hours, Fe remains near 1 mmol kg^{-1} at 1 and 1.5 ml hr^{-1} flow rate. Upon increase of flow rate to 10 ml hr^{-1} , Fe concentration increases significantly to 7.5 mmol kg^{-1} . It then decreases upon decreasing flow rate to 7.5 and 5 ml hr^{-1} . The input Fe concentration is assumed to be $\sim 1 \text{ mmol kg}^{-1}$ based on the results from the SW1 experiment (Fig. 5.4). The Fe results indicate that there may be a slight increase in Fe derived from the rock but, as with Ca, the Fe contributed is dependent on the flow rate.

The behaviour of Mg is significantly different between the BSW1 and SW1 experiments. In BSW1, Mg concentrations remain under detection limit ($< 0.0004 \text{ mmol kg}^{-1}$) both in presence with distilled water and also once the seawater begins to appear in the effluents, but only when flow rate is at 1 ml hr^{-1} (Fig. 6.2). At 1.5 ml hr^{-1} there is a detectable increase in Mg concentration while at 10 ml hr^{-1} a significant increase occurs with Mg concentration rising to 0.1 mmol kg^{-1} . Decreasing the flow rate to 7.5 ml hr^{-1} results in a decrease in Mg to $0.09 \text{ mmol kg}^{-1}$ while at 5 ml hr^{-1} Mg decreases to $0.07 \text{ mmol kg}^{-1}$. The input Mg concentration is assumed to be $\sim 24 \text{ mmol kg}^{-1}$ based on the results of the SW1

experiments (Fig. 5.4). This indicates that all Mg remaining from seawater after precipitation of retrograde phases is fixed in the basalt due to fluid – rock interaction. This fixation, however, is dependent on flow rate.

Sulfate concentration is irregular over the experiment (Fig. 6.2). While seawater is exiting the Reactor, several values of $\sim 0.05 \text{ mmol kg}^{-1}$ are reached. There is no significant increase when flow rate is increased to 1.5 ml hr^{-1} , however, when it is increased to 10 ml hr^{-1} , there are measurable increases in SO_4 up to 0.1 mmol kg^{-1} . This concentration is not maintained and SO_4 decreases back to $\sim 0.05 \text{ mmol kg}^{-1}$ over the following days regardless of flow rate. The input concentration of SO_4 is assumed to be $\sim 1 \text{ mmol kg}^{-1}$ based on results from SW1 (Fig. 5.4). This indicates that the remaining SO_4 in the pre-treated seawater is also precipitating during reaction with the basalt.

There are detectable H_2S concentrations in the effluents from the BSW1 experiment (Fig. 6.2). This differs from the SW1 experiment which show no detectable H_2S (Fig. 5.4). The highest H_2S concentrations occur just after seawater begins to exit the Reactor. This suggests release of H_2S from sulfide inclusions in volcanic glass. Also, H_2S increases again after restarting at 400 hours. There is also limited evidence that H_2S concentrations are also dependent on the flow rate. The overall gradual decrease in concentration over the experiment is attributed to gradual dissolution of basalt glass dissolution.

Chloride is conservative and reflects mixing between distilled water and seawater. The concentrations are independent of flow rate (Fig. 6.2).

Figure 6.1. Major element concentrations in blank and effluent samples (mmol kg^{-1}) versus time (hr) for the BSW1 experiment at $400^\circ\text{C}/488$ bar. Yellow squares at $t=0$ are the blank sample composition of seawater from SW1. Light blue symbols show where distilled water was exiting the Reactor at $400^\circ\text{C}/488$ bar and 1.0 ml hr^{-1} . Black symbols are effluent compositions (seawater) at $400^\circ\text{C}/488$ bar and 1.0 ml hr^{-1} flow rate. Other coloured symbols show effluent compositions at different flow rates. *In situ* pH is the calculated pH at temperature. LOD= limit of detection.

Figure 6.2. Major element concentrations in blank and effluent samples (mmol kg^{-1}) versus time (hr) for the BSW1 experiment at $400^\circ\text{C}/488$ bar. Yellow squares at $t=0$ are the input composition of seawater from SW1. Light blue symbols show where distilled water was exiting the Reactor at $400^\circ\text{C}/488$ bar and 1.0 ml hr^{-1} . Black symbols are effluent compositions at $400^\circ\text{C}/488$ bar and 1.0 ml hr^{-1} flow rate. Other coloured symbols are effluent compositions at differing flow rate. *In situ* pH is the calculated pH at temperature. LOD= limit of detection.

- blank seawater
- distilled water $400^\circ\text{C}/488 \text{ bar}/1 \text{ ml hr}^{-1}$
- seawater $400^\circ\text{C}/488 \text{ bar}/1 \text{ ml hr}^{-1}$
- seawater $400^\circ\text{C}/488 \text{ bar}/1.5 \text{ ml hr}^{-1}$
- seawater $400^\circ\text{C}/488 \text{ bar}/10 \text{ ml hr}^{-1}$
- seawater $400^\circ\text{C}/488 \text{ bar}/7.5 \text{ ml hr}^{-1}$
- seawater $400^\circ\text{C}/488 \text{ bar}/5 \text{ ml hr}^{-1}$

6.2.1.2. Trace Element Concentrations

In SW1, trace elements showed some mobility and semi-regular to irregular trends caused by the interaction between seawater and the ZrO₂ beads (Fig. 5.5 and 5.6). It is evident that the beads were releasing measurable concentrations of some trace elements including V, Mn, Co, Ni, Ba, and perhaps Au. Effluents also showed seawater concentrations of Rb.

Figure 6.3 and Figure 6.4 show trace element results plotted versus time in hours for the BSW1 experiment. The unreacted natural seawater composition is shown at $t = 0$. Most trace elements are below detection limit with only V, Rb, Au and Mn showing detectable concentrations. The distilled water concentrations are not shown but are generally lower than seawater. Complete trace element results are listed in Appendix E.

While seawater exits that Reactor, the only elements that show regular trends are Mn, Rb, Ba, Au and perhaps Pb. All other element concentrations are either below detection limit or are highly irregular. Mn shows a regular concentration of $\sim 0.5 \text{ mmol kg}^{-1}$ up to 400 hours. Mn concentration would at first appear to be dependent on flow rate, however, the concentration at 10 ml hr^{-1} is lower than at 1 ml hr^{-1} while at 7.5 and 5 ml hr^{-1} , the concentration is unchanged.

Except for the isolated high value at the start of the experiment, Rb concentrations reflect the input seawater (Fig. 6.4).

As with SW1, Ba concentration is highest at the beginning of the exit of seawater, it decreases over the remainder of the experiment. This is attributed to the precipitation of barite. Ba concentrations are independent of flow rate.

Au concentrations are interesting in that they are the highest once seawater begins egress from the Reactor after which they decline regularly to below detection limit by the end of the experiment. This behaviour differs from the seawater-only experiment where Au remained at a relatively steady value of $0.05 \text{ } \mu\text{mol kg}^{-1}$ (Fig. 5.6). This suggests possible release of Au from the ZrO₂ beads and then fixation in the rock.

The trace element results are rather unremarkable, nevertheless, it is evident that trace element mobility is less when the basalt is present. This suggests fixation of trace elements by the rock during fluid – rock interaction rather than release from it.

Figure 6.3. Trace element concentrations in blank and effluent samples ($\mu\text{mol kg}^{-1}$) versus time (hr) for the basalt-seawater experiment at $400^\circ\text{C}/488$ bar (BSW1). Yellow squares at $t=0$ are the blank composition of seawater from SW1. Light blue symbols show where distilled water was exiting the Reactor at $400^\circ\text{C}/488$ bar and 1.0 ml hr^{-1} . Black symbols are effluent compositions at $400^\circ\text{C}/488$ bar and 1.0 ml hr^{-1} flow rate. Other coloured symbols are effluent composition at differing flow rate. *In situ* pH is the calculated pH at temperature. LOD= limit of detection.

Figure 6.4. Trace element concentrations in blank and effluent samples ($\mu\text{mol kg}^{-1}$) versus time (hr) for the basalt-seawater experiment at $400^\circ\text{C}/488$ bar (BSW1). Yellow squares are the blank composition of seawater from SW1. Light blue symbols show where distilled water was exiting the Reactor at $400^\circ\text{C}/488$ bar and 1.0 ml hr^{-1} . Black symbols are effluent compositions at $400^\circ\text{C}/488$ bar and 1.0 ml hr^{-1} flow rate. Other coloured symbols are effluent compositions at differing flow rate. *In situ* pH is the calculated pH at temperature. LOD= limit of detection.

6.2.1.3. Mineralogy and Texture of Reacted Basalt

Upon the completion of the experiment (659 hrs), the reacted basalt was extracted from the Reactor onto absorbent paper. The run products were rinsed with distilled water to remove precipitated soluble salts and air-dried. The reacted material was initially divided into seven portions which were numbered from 1 (bottom of the Reactor) to 7 (top of the Reactor) (Fig. 6.5). The remnants of the basalt block from the bottom of the Reactor were extracted and rinsed with distilled water.

Figure 6.5 shows the reacted grains after extraction from the Reactor upon completion of the experiment. The change of colour of the grains from bottom to top shows that the rock is visibly altered. Also present is a large amount of fine material which indicates partial disintegration of the rock grains during alteration. Portion 1 is light green-gray, Portion 2 and 3 are also light green-gray but have an additional pinkish tone, Portion 4 is gray with no pink coloration, while Portions 5 to 7 show a gradual darkening of the rock to dark green.

In order to reduce the amount of analysis required, grains from Portion 2 and 3 were combined, and run products from Portions 1, 2-3, 4 and 7 were mounted on aluminium stubs for SEM analysis. Run products from these portions were also epoxy-mounted and polished for SEM analysis. Larger samples were also collected for XRD and XRF analysis.

Figure 6.5. Schematic diagram showing position of reacted rock extracted from the Reactor after the completion of the BSW1 (not to scale). On the left, the reacted grains are shown after extraction and rinsing. On the right, are the same grains divided in seven portions numbered from 1 (bottom of the Reactor) to 7 (top of the Reactor). Also shown is the position of the basalt block.

Qualitative XRD analysis

Qualitative XRD results for the reacted material are listed in Table 6.2. They show that plagioclase was detected in all portions while augite was identified only Portion 7, which is located at the top of the Reactor. These results indicate that at least some plagioclase remains after reaction while pyroxene has been almost completely removed, at least up to Portion 4. This coincides with the loss of the dark green coloration of the basalt. All other minerals identified are interpreted to be secondary in origin including chlorite, maghemite, hematite, calcite, smectite, and ankerite. Hematite is found only in Portion 2-3 which explains the pink coloration of the rock. Smectite and ankerite are found only in Portion 7. The identification of smectite is unusual as swelling clays should not form at the high temperature of the experiment. Complete XRD scans and qualitative results are reported in Appendix E.

Table 6.1. Qualitative XRD analysis of Portion 1, 2-3, 4 and 7 from BSW1.

	Portion 1	Portion 2-3	Portion 4	Portion 7
Chlorite	x	x	x	
Plagioclase	x	x	x	x
Maghemite	x			
Hematite		x		
Calcite	x			
Smectite				x
Ankerite				x
Augite				x

XRF analysis

The high degree of visible alteration indicated that whole rock analysis of the reacted basalt would show measurable differences in composition upwards through the Reactor. Table 6.2 lists the XRF results for the portions examined. Notable changes in rock chemistry are evident. In order to test for significant relationships between elements during fluid – rock exchange a correlation matrix was made (Table 6.3). At the 95% significance level and with $n = 5$, the level of significance of $r = \pm 0.88$ (± 0.95 for S). The correlation coefficients with values of $-0.88 \leq r \leq +0.88$ are highlighted in yellow. Based on these coefficients, selected elements are plotted in Figure 6.6. These show the oxide composition of the altered basalt plotted by position in the Reactor column. Also shown is the unreacted basalt composition for comparison.

There are several notable observations to be made from these graphs. It is evident that the chemical composition of the rock changes upward through the Reactor. This is also evidenced by the change in colour (Fig. 6.5). This supports the conclusion that the flow regime in the Reactor is by plug flow whereby little mixing occurs between horizontal fluid layers (Saldaña et al., 2016). If the Reactor were well-mixed through turbulent flow, zonation of chemistry with vertical distance up the column would not be expected.

It can be seen from the correlation matrix there is significant positive correlation between CaO, Na₂O and SiO₂ while with MgO these three elements show a significant negative correlation. There is also weaker positive correlation between CaO and Fe₂O₃ and weaker negative correlation between Fe₂O₃ and MgO.

The highest Al₂O₃ concentration is in Portions 2+3 plotted at position 2.5 in Figure 6.6. As there was no detectable Al in most effluent samples, it is assumed that Al was immobile during fluid – rock interaction. This means that the highest mass loss occurred a position 2-3 in the Reactor column. This is supported by lows in SiO₂, Na₂O, and CaO at this position. The only elements that appear to have gained appreciable mass are MgO and S. The S concentration is highest at position 4 (0.8%). Except for K₂O and TiO₂, all elements approach the unaltered composition at the top of the Reactor.

Table 6.2. XRF analysis of the reacted material collected from Portion 1, 2-3, 4 and 7 after the BSW1 experiment (wt%). Also shown is the composition of the unreacted basalt rock. n.d.: not detected, n.m.: not measured.

	Na ₂ O	CaO	MgO	SiO ₂	TiO ₂	Al ₂ O ₃	Fe ₂ O ₃	MnO	K ₂ O	P ₂ O ₅	S (ppm)
Portion 7	2.51	10.76	5.74	46.64	1.47	14.49	12.34	0.13	0.06	0.31	n.d.
Portion 4	1.31	3.76	23.38	39.58	1.87	15.21	6.72	0.01	0.06	0.28	8460
Portion 2-3	0.22	2.04	26.20	32.30	2.19	15.87	8.20	0.008	0.02	0.14	6410
Portion 1	0.63	3.83	23.05	38.29	1.97	13.87	7.66	0.02	0.03	0.25	610
Unreacted	2.35	10.94	6.50	48.85	2.13	13.41	15.11	0.24	0.25	0.22	n.m.

Table 6.3. Correlation matrix of major oxides and sulfur for analyses shown in Table 6.2. Correlation coefficients significant at the 95% level are highlighted in yellow.

	Na ₂ O	CaO	MgO	SiO ₂	TiO ₂	Al ₂ O ₃	Fe ₂ O ₃	MnO	K ₂ O	P ₂ O ₅	S
Na ₂ O	1										
CaO	0.96	1									
MgO	-0.95	-1.00	1								
SiO ₂	0.97	0.96	-0.94	1							
TiO ₂	-0.56	-0.45	0.47	-0.43	1						
Al ₂ O ₃	-0.56	-0.66	0.63	-0.75	0.07	1					
Fe ₂ O ₃	0.80	0.92	-0.92	0.84	-0.10	-0.63	1				
MnO	0.83	0.92	-0.91	0.89	-0.07	-0.70	0.98	1			
K ₂ O	0.65	0.70	-0.67	0.75	0.25	-0.67	0.82	0.90	1		
P ₂ O ₅	0.62	0.47	-0.45	0.59	-0.86	-0.36	0.09	0.15	0.00	1	
S	-0.41	-0.65	0.65	-0.56	0.53	0.81	-0.67	-0.68	-0.01	-0.40	1

Figure 6.6. Chemical composition (wt%) of rock Portions analysed by XRF plotted against position in Reactor column (red circles). The unreacted basalt compositions shown by blue line.

SEM-EDS analysis

SEM-EDS results are presented in this section for grains collected and divided into Portion 1, 2-3, 4 and 7 as shown in Figure 6.5. Also analysed were grains collected from the immediately adjacent to the fluid entry and exit point of the Reactor after 396 hours (§6.2.1). All SEM results are listed in Appendix E.

Reacted grains – Bottom of Reactor (396 h)

Table 6.4 lists the minerals identified from grains collected from the bottom of the Reactor sample at 396 hr. These grains represent reacted basalt from immediately adjacent to the fluid entry point. The grains display a high degree of alteration. Minerals of secondary origin identified were anhydrite, chlorite, and caminite (Fig. 6.7). No evidence of the primary plagioclase, clinopyroxene or olivine was found during SEM examination of the grains.

Figure 6.7 shows SEM images of reacted grains covered by the secondary mineral assemblage. Chlorite appears in masses as densely intergrown flakes. Anhydrite occurs as euhedral crystals while caminite appears with its tetragonal dipyrmaid shape.

Table 6.4. Mineral assemblage identified by SEM-EDS analysis of reacted grains extracted from the immediately adjacent to the fluid entry point into the Reactor after 396 hours of the BSW1 experiment.

Type of Analysis	Analysis Material	Mineral Identified	Average Mineral Composition
SEM-EDS	grain surface	Anhydrite	CaSO_4
SEM-EDS	grain surface	Caminite	$\text{Mg}_7(\text{SO}_4)_5(\text{OH})_4 \cdot \text{H}_2\text{O}$
SEM-EDS	grain surface	Chlorite	$\text{Mg}_{4.0}\text{Fe}_{0.4}\text{Al}_{1.4}\text{Si}_{3.1}\text{Al}_{0.9}\text{O}_{10}(\text{OH})_8$ (calculated based on an anhydrous composition with 14 oxygens)

Figure 6.7. SEM images of grains collected from the immediately adjacent fluid entry point (bottom) of the Reactor after 396 hrs of the BSW1 experiment: (a) example of a reacted grain; (b-c) enlargements of rectangular area in (a) showing densely-packed flakes of chlorite (Chl), euhedral crystals of anhydrite (Anh) and caminite with its tetragonal dipyramidal shape; (d) a different reacted grain; (e-f) enlargements of rectangular area in (d) showing an euhedral crystal of anhydrite (Anh) surrounded by chlorite (Chl).

Reacted grains – Top of Reactor (396 h)

Table 6.5 lists minerals identified by SEM-EDS examination of several grains collected from the top of the Reactor when the experiment was stopped at 396 hr. The results confirm a lower grade of alteration of the grains when compared to those from the bottom of the Reactor (Fig. 6.7). Minerals of secondary origin identified were a clay-like Na-Mg-Fe aluminosilicate and caminite (Fig. 6.8). Primary plagioclase and pyroxene were observed on the outer surface of the grains, however, the grains were almost completely covered with the secondary Na-Mg-Fe phase (Fig. 6.8).

SEM analyses of the Na-Mg-Fe aluminosilicate are shown in Table 6.6. Repeat SEM-EDS analyses show the mineral to be composed of fairly consistent concentrations of iron, aluminium, silica and magnesium with a measurable concentration of sodium and calcium but no potassium. It should be emphasised, however, that SEM-EDS analyses of such a delicate phase are at best approximate.

The presence of Na₂O and CaO, the high percentage of FeO and MgO, and the clay-like habit suggest a clay mineral. The XRD results of the final run products from the top of the Reactor gave a strong peak for montmorillonite suggesting the presence of a smectite phase such as Fe-saponite (Cheshire et al., 2018; Yardley et al., 2014) or nontronite (Halдар, 2020) or a related smectite phase. Seyfried and Bischoff (1979) found smectite as the major secondary phase in experiments reacting diabase and basaltic glass with seawater at 150°C. Another possibility is corrensite a mixed-layer chlorite - trioctahedral smectite clay mineral (Beaufort et al., 1997). The presence of a swelling clay is unusual given the high temperature of the experiments, however, Yardley et al (2014) found saponite as a run product when reacting hornfels with water up to 500°C. Thus, the composition, smectite-like texture, and XRD results lead us to conclude that this phase is smectite-related phase and it will be referred to as such. Without more detailed analysis using more sophisticated analytical techniques, it is difficult to refine this further.

Table 6.5. Mineral assemblage identified by SEM-EDS analysis of reacted grains extracted from the immediately adjacent to the fluid exit point of the Reactor after 396 hrs of the BSW1 experiment.

Type of Analysis	Analysis Material	Mineral Identified	Average Mineral Composition
SEM-EDS	grain surface	Bytownite	Ca _{0.8} Na _{0.1} Al _{1.9} Si _{2.2} O ₈ (An ₈₉ -Ab ₁₁)
SEM-EDS	grain surface	Augite	Ca _{0.1} Mg _{0.8} Fe _{0.9} Al _{0.2} Si _{1.9} Al _{0.1} O ₆
SEM-EDS	grain surface	Caminite	Mg ₇ (SO ₄) ₅ (OH) ₄ ·H ₂ O
SEM-EDS	grain surface	Smectite	Na _{0.4} Ca _{0.1} Mg _{1.6} Fe _{1.1} Al _{0.25} Si _{3.3} Al _{0.7} O ₁₀ (OH) ₂ · nH ₂ O (calculated based on an anhydrous composition with 11 oxygens)

Figure 6.8. SEM images of the reacted grains collected from near the fluid exit point of the Reactor after 396 hrs of the BSW1 experiment: (a) example of a reacted grain; (b) enlargement of rectangular area n°1 in (a) showing the Na-Fe-Mg phase identified as smectite (Smc); (c) enlargement of rectangular area n°2 in (a) showing caminite in pyramidal shape surrounded by smectite (Smc); (d-e-f) three different reacted grains collected from the same Portion at top of the Reactor.

Table 6.6. Average composition (by SEM-EDS analysis) of the clay-like phase found during study of the reacted grains collected from the immediately adjacent to the fluid exit point (top) of the Reactor after 393.6 hrs of the BSW1. This phase is tentatively identified as smectite.

Grain Surface (N=2)		
oxide	average Wt %	$\pm 1\sigma$
Na₂O	3.03	0.21
MgO	15.92	1.35
Al₂O₃	11.95	1.96
SiO₂	49.03	2.02
CaO	1.69	0.14
FeO	18.34	1.29
Total	99.95	

Portion 1 (659 hr)

Selected grains from Portion 1 (Fig. 6.5) were mounted on aluminium stubs for analyses by SEM and several grains were epoxy-mounted and polished. Results confirm a high grade of alteration due to fluid – rock interaction. Minerals of secondary origin identified were chlorite, caminite and Fe-Ni-Cr oxides. The results also confirm the presence of the primary minerals plagioclase, clinopyroxene, olivine and titanomagnetite (Table 6.7). Appendix E contains all SEM results for this Portion of the rock.

Table 6.7. Mineral assemblage identified by SEM-EDS analysis of reacted grains of Portion 1 after the BSW1 experiment.

Type of Analysis	Analysis Material	Mineral Identified	Average Mineral Composition
SEM-EDS	polished grains	Plagioclase	-
SEM-EDS	polished grains	Augite	$\text{Ca}_{0.60}\text{Mg}_{0.91}\text{Fe}_{0.42}\text{Si}_2\text{O}_6$
SEM-EDS	polished grains	Olivine	$\text{Mg}_{1.24}\text{Fe}_{0.75}\text{SiO}_4$
SEM-EDS	polished grains	Chlorite	$\text{Mg}_{4.2}\text{Fe}_{0.6}\text{Al}_{0.9}\text{Si}_{3.8}\text{Al}_{0.2}\text{O}_{10}(\text{OH})_8$ (calculated based on an anhydrous composition with 14 oxygens)
SEM-EDS	grain surface	Caminite	$\text{Mg}_7(\text{SO}_4)_5(\text{OH})_4 \cdot \text{H}_2\text{O}$
SEM-EDS	polished grains	Fe-Ti-Cr oxides	-

Figure 6.9 show secondary electron images of the reacted grains. There are surrounded by densely-packed plates of chlorite. Also present are isolated crystals of caminite. No evidence of the primary plagioclase and clinopyroxene were observed on the outside of the unpolished grains. No anhydrite was observed.

Figure 6.9. SEM images of reacted grains from Portion 1 after the BSW1 experiment: (a-b-c-d) grains covered by chlorite with caminite (e,f).

SEM examination of polished grains shows extensive chloritization with a significant amount of original plagioclase remaining but only remnants of the original clinopyroxene (Fig. 6.10). Chloritization is pervasive and has preferentially replaced clinopyroxene, however, plagioclase lathes also appear to have been partially replaced. Some olivine is also present and was likely isolated from the fluid and has been preserved. Titanomagnetite appears relatively unaffected.

Figure 6.10. SEM backscatter and EDS compositional maps of a polished grain from the Portion 1 of the BSW1 experiment: (a) backscatter image; (b) composite colour image combining the backscatter image and elemental maps for c) Mg in green, d) Fe in red, and e) Ca in blue showing plagioclase (blue), clinopyroxene (light blue), secondary chlorite (green), olivine (orange-yellow), and Fe-Ti oxides (red); (f-g) SEM backscatter images of the rectangular areas n°1 and n°2 in (a) showing secondary chlorite (Chl), plagioclase (Plg), clinopyroxene (Cpx), olivine (Ol) and titanomagnetite (Ox).

Portion 2 – 3 (659 hr)

Selected grains from Portion 2-3 (Fig. 6.5) were mounted on aluminium stubs for textural analyses and several grains were epoxy-mounted and polished for examination by SEM-EDS. Appendix E contains all SEM results for this Portion of the rock.

SEM examination of epoxy-mounted polished grains (Fig. 6.11) confirm this to be the most intensely altered portion of the basalt. The only minerals identified are chlorite with altered primary titanomagnetite (Table 6.8). No evidence of the primary plagioclase, clinopyroxene, or olivine was found. Hematite was identified in the XRD results and likely comprises some of the altered Fe-Ti oxides.

Table 6.8. Mineral assemblage detected by SEM-EDS analysis of reacted grains of Portion 2-3.

Analysis Material	Mineral Identified	Average Mineral Composition
polished grains	Chlorite	$\text{Mg}_{3.6}\text{Fe}_{0.7}\text{Al}_{1.3}\text{Si}_{3.1}\text{Al}_{0.9}\text{O}_{10}(\text{OH})_8$ (calculated based on an anhydrous composition with 14 oxygens)
polished grains	Altered oxides	-

Figure 6.11. SEM backscatter and EDS compositional maps of two polished grains collected from the Portion 2-3 after the BSW1 experiment. (a) backscatter image of a reacted grain; (b) composite colour image combining the backscatter image and elemental maps for c) Mg in green and d) Fe in red showing secondary chlorite (green) with Fe oxides (red); (e) backscatter image of a second reacted grain; (f) composite colour image combining the backscatter image and elemental maps for g) Mg in green and h) Fe in red showing only chlorite (green) with Fe oxides (red).

Figure 6.12. (a-b) SEM secondary electron images of the two red rectangular areas shown in Figure 6.11a; (c-d) SEM backscatter images of the same two areas in (a-b). They show that the grains are completely replaced by chlorite with some primary but altered titanomagnetite (white spots). No primary plagioclase, clinopyroxene or olivine are present. Black holes are spaces void left by plagioclase dissolution.

Portion 4 (659 hr)

SEM examination showed that these grains were less altered when compared to the results of Portion 2-3 (Fig. 6.13). The grain shown has a coating of a secondary Na-Mg-Fe aluminosilicate, tentatively identified as smectite. This phase is similar to that described previous portion and, at least for this grain, is the only secondary mineral present (Table 6.9). The original plagioclase is still present but highly corroded, while only minor amounts of remnant clinopyroxene and olivine are observed. These were preserved likely due to isolation from the fluids in the interior of the grain. Titanomagnetite appears altered. No clear evidence of chlorite was found in the grains analysed. This contradicts the XRD results which clearly chlorite present but no detectable clay mineral. The lack of XRD peaks for smectite may imply that there is <5% present, however, chlorite must be present but was not seen in the SEM examination.

Table 6.9. Mineral assemblage detected by SEM-EDS analysis of reacted grains of Portion 4 after the BSW1.

Type of Analysis	Analysis Material	Mineral ID	Average Mineral Composition
SEM-EDS	polished grains	Plagioclase	-
SEM-EDS	polished grains	Augite	$\text{Ca}_{0.6}\text{Mg}_{0.9}\text{Fe}_{0.3}\text{Al}_{0.1}\text{Si}_{1.8}\text{Al}_{0.2}\text{O}_6$
SEM-EDS	polished grains	Olivine	$\text{Mg}_{1.24}\text{Fe}_{0.75}\text{SiO}_4$
SEM-EDS	polished grains	Smectite	$\text{Na}_{0.2}\text{Mg}_{2.3}\text{Fe}_{0.5}\text{Al}_{0.3}\text{Si}_{3.2}\text{Al}_{0.8}\text{O}_{10}(\text{OH})_2 \cdot n\text{H}_2\text{O}$ (calculated based on an anhydrous composition with 11 oxygens)
SEM-EDS	polished grains	Altered Oxides	-

Numerous SEM-EDS analyses were made of the Na-Mg-Fe aluminosilicate phase that is tentatively identified as smectite (Table 6.10). These show fairly consistent concentrations of aluminium and silica comparable to the clay-like phase identified from the top of the Reactor after 396 hr. Note that this composition has a lower Al:Si ratio than previous identified chlorite (Table 6.7) and contains a measurable Na content.

Table 6.10. Average composition (SEM-EDS) of the clay mineral phase found in Portion 4 after the completion (659 hrs) of the BSW1 experiment. This phase is tentatively identified as smectite.

Polished (N=62)		
oxide	average Wt %	$\pm 1\sigma$
Na₂O	1.72	1.05
MgO	24.24	3.72
Al₂O₃	14.40	3.32
SiO₂	50.38	4.13
FeO	8.46	3.36
TiO₂	0.52	2.43
Total	99.7	

Figure 6.13. SEM backscatter and EDS compositional maps of a polished grain from the Portion 4 after the BSW1 experiment: (a) backscatter image; (b) composite colour image combining the backscatter image and elemental maps for c) Mg in green, d) Fe in red, and e) Ca in blue showing plagioclase (blue), clinopyroxene (light blue), olivine (yellow), oxides (red) and smectite (green); (g-h) SEM backscatter images of the two red rectangular areas shown in (a). The grain is covered around the margin and internally by smectite (Smc), with plagioclase (Plg), clinopyroxene (Cpx), olivine (Ol) and titanomagnetite (Ox).

Portion 7 (659 hr)

SEM analysis confirms a much lower intensity of alteration of the grains when compared to previous portions. The only secondary mineral identified was smectite with a composition similar to that described above (Table 6.11).

Table 6.11. Mineral assemblage detected by SEM-EDS analysis of reacted grains of Portion 7 after the BSW1.

Type of Analysis	Analysis Material	Mineral Identified	Average Mineral Composition
SEM-EDS	polished grains	Plagioclase	-
SEM-EDS	polished grains	Augite	$\text{Ca}_{0.7}\text{Mg}_{0.8}\text{Fe}_{0.4}\text{Si}_{1.9}\text{O}_6$
SEM-EDS	polished grains	Olivine	$\text{Mg}_{1.4}\text{Fe}_{0.6}\text{SiO}_4$
SEM-EDS	polished grains	Smectite	$\text{Na}_{0.3}\text{Mg}_{1.3}\text{Fe}_{1.4}\text{Al}_{0.3}\text{Si}_{3.5}\text{Al}_{0.5}\text{O}_{10}(\text{OH})_2 \cdot n\text{H}_2\text{O}$ (calculated based on an anhydrous composition with 11 oxygens)
SEM-EDS	polished grains	Titanomagnetite	-

Figure 6.14a-e shows SEM backscatter image and EDS maps of a polished mount of one grain collected from Portion 7. Plagioclase, clinopyroxene, olivine and oxides are mostly unaffected. The only secondary mineral detected is smectite occurring as a thin layer around the outside of the grain.

The average SEM-EDS analyses for smectite is shown in Table 6.12. Results show the mineral to be composed of similar concentrations of Al_2O_3 , SiO_2 and Na_2O the clay phase identified in Portion 4. The major difference is the higher Fe:Mg ratio.

Figure 6.15 shows a summary photo of the reacted basalt grains, the backscatter images, and the EDS compositional maps for comparison. The bleaching of the rock can be attributed to the replacement of primary clinopyroxene, olivine and plagioclase by chlorite up to Portion 3 and then by smectite from Portion 4 upwards. This implies a transition from chlorite to smectite as the dominant secondary phase about one third way up the Reactor. For Portions 5 to 7, the intensity of alteration decreases, and the colour of the grains darkens as more clinopyroxene remains unaltered and replacement by smectite is reduced.

Figure 6.14. SEM backscatter and EDS compositional maps of a polished grain collected from the Portion 7 after the BSW1 experiment: (a) backscatter image of the reacted grain; (b) composite colour image combining the backscatter image and elemental maps for c) Mg in green, d) Fe in red, and e) Ca in blue showing plagioclase (blue), clinopyroxene (turquoise), olivine (orange-yellow), Fe-Ti oxides (red), and smectite (green); (f-g) SEM backscatter images of the two rectangular areas shown in (a). Images show a thin covering of smectite (Smc) with primary plagioclase (Plg), clinopyroxene (Cpx), olivine (Ol) and titanomagnetite (Tnt).

Table 6.12. Average composition (SEM-EDS) of the Na-Fe-Mg aluminosilicate phase found during study of the reacted grains collected from Portion 7 after the completion (659 hrs) of the BSW1 experiment.

Polished (N=19)		
oxide	average Wt %	$\pm 1\sigma$
Na ₂ O	1.85	0.58
MgO	12.35	2.37
Al ₂ O ₃	10.46	1.13
SiO ₂	50.06	5.05
FeO	24.35	3.17
Total	99.06	

Figure 6.15. Composite image of reacted grains, backscatter images, and elemental maps of the epoxy-mounted, polished grains analysed from the BSW1 experiment. Flow direction is from the bottom of the figure to the top. The change in intensity of the alteration upwards is evident due to replacement by chlorite and smectite.

6.2.1.4. Mineralogy and Texture of Reacted Basalt: Basalt Block

The basalt block (8x8x4 mm), was positioned vertically near the bottom of the Reactor approximately 0.5 cm above the titanium frit (Fig. 6.5). Upon opening the Reactor, it was revealed that the block had disintegrated into several pieces (Fig. 6.16). SEM-EDS analysis was not performed on the block. It is evident, however, that there has been severe bleaching of the rock. This has completely penetrated the block. This attests to the intensity of the alteration at this position in the Reactor.

Figure 6.16. Digital photograph of the basalt block fragments extracted from the bottom of the Reactor after the BSW1 experiment. The block was originally 8 x 8 x 4 mm.

6.2.2. BSW2: Basalt-seawater experiment at 350°C/488 bar

The laboratory set-up for the BSW2 experiment consisted of the Preheater containing zirconia beads and the Reactor filled with rock material mounted in series (Chapter 2, §2.4.5, Fig. 2.20b). The experimental configuration maintained a temperature gradient of 40°C at the top to 342°C at the bottom of the Preheater, while the Reactor was kept at a temperature of 350°C. Pressure remained stable at 488 bar.

The experiment ran for a total time of 311 hours. At the start of the experiment, distilled water was pumped through the system until pressure was stable. After this, the heating procedure increased the oven temperature until a Reactor temperature of 350°C was reached (~3 hours), then fluid flow was switched to seawater. It required approximately 1 day for seawater to begin to exit the Reactor at 1 ml hr⁻¹ (See Cl concentrations in Fig. 6.18). Distilled water was completely displaced from the combined Preheater and Reactor after about four days. The flow rate was varied during the experiment changed as follow:

- 1 ml hr⁻¹ for the first 120 hrs (5 samples collected)
- 10 ml hr⁻¹ for 48 hrs (10 samples collected)
- 5 ml hr⁻¹ for 24 hrs (5 samples collected)
- 2.5 ml hr⁻¹ for 74 hrs (5 samples collected)
- 1 ml hr⁻¹ for the last 47 hrs (2 samples collected)

Analysis for major and trace elements was made for the total number of the fluid samples collected (29). Distilled water and seawater blanks were included.

6.2.2.1. Major Element Concentrations

Complete experimental parameters and results (T, P, time, flow rate, in situ and room T pH, chemistry) are listed in Appendix E. Figure 6.17 and Figure 6.18 show these results plotted versus time in hours. The unreacted seawater composition is shown at t = 0. The composition of unreacted distilled water is not shown. The concentrations of major ions for the first 24 hrs are essentially for distilled water as it required approximately 1 day for seawater to begin to exit the Reactor at 1 ml hr⁻¹.

The room temperature pH of the unreacted Napier seawater is 8.20 (Fig. 6.17). While distilled water is exiting the Reactor, quench pH is 5.15 while the *in situ* pH is 6.61. Once seawater displaces distilled water, the quench pH stabilises at ~4.7 after about 4 days which translates into a stable *in situ* pH of ~5.3. The quench pH increases marginally to ~4.3 when

flow rate was changed to 10, 5, 2.5 and again 1 ml hr⁻¹, however, the *in situ* pH remains stable at ~5.3 for this period. The entry *in situ* pH of the pre-treated seawater into the Reactor is assumed to be ~5.5 based on the results of the SW2 experiment.

SiO₂ concentration increases to ~32 mmol kg⁻¹ (~1930 ppm) while distilled water is exiting the Reactor for the first day (Fig. 6.17). Once seawater begins to appear in the effluents (~48 hr), SiO₂ concentration stabilises to ~35 mmol kg⁻¹ for four days. The change to 10 ml hr⁻¹ initially causes an increase in SiO₂ concentration to 42 mmol kg⁻¹. It then decreases over the next several hours back to 28 mmol kg⁻¹. There is an incremental decrease in SiO₂ concentration at 5 and 2.5 ml hr⁻¹ flow rates. Finally, at 1 ml hr⁻¹, the SiO₂ concentration is ~25 mmol kg⁻¹. This concentration (1500 ppm) exceeds quartz saturation at 350°C/500 bar (980 ppm). Note that it is assumed that the SiO₂ concentration entering the Reactor is 0.25 mmol kg⁻¹ based on the SW2 experiment.

Sodium concentration remains low while distilled water is exiting the Reactor. Once seawater begins to appear in the effluent, Na concentration increases and reaches a value of ~370 mmol kg⁻¹ after seven days. It remains at this value for the remainder of the experiment. This value is similar to the input seawater composition, thus Na behaviour is conservative and independent of flow rate.

In the first sample containing seawater in the effluent, K concentration is highly elevated (20 mmol kg⁻¹). This is much higher than the input seawater K concentration. However, after another 24 hours, the K concentration decreases to the input value and remains there for the remainder of the experiment. This value is similar to the input value and K concentrations are independent of flow rate.

The Al concentration is elevated in the single sample where distilled water was exiting the Reactor (~24 hr). Once seawater begins to appear in the effluents, Al concentrations are below detection limit and remain so for the remainder of the experiment irrespective of flow rate.

Calcium concentration is below detection limit while distilled water is exiting the Reactor (Fig. 6.18). Once seawater begins to appear in the effluent, Ca concentration increases to a value of 20 mmol kg⁻¹ at a flow rate of 1 ml hr⁻¹. A measurable decrease in Ca is evident when flow rate is changed to 10 ml hr⁻¹ where it stabilises at 19 mmol kg⁻¹. Further decreases in flow rate to 5, 2.5 and 1 ml hr⁻¹ result in a stable 22 mmol kg⁻¹ Ca for the remainder of the experiment. Note that the input Ca concentration from the Preheater is assumed to be 1.4 mmol kg⁻¹ based on the results from the SW2 experiment (Fig. 5.11). This indicates that a significant amount of Ca is being added to the fluid from the rock.

Iron concentration is 0.4 mmol kg^{-1} while distilled water is exiting the Reactor (Fig. 6.18). Once seawater appears, Fe remains under detection limit at 1 ml hr^{-1} flow rate. Upon increase of flow rate to 10 ml hr^{-1} , Fe concentration significantly increases to $\sim 6 \text{ mmol kg}^{-1}$ and then over the next several hours decreases to $\sim 3 \text{ mmol kg}^{-1}$. A further decrease in flow rate to 5 ml hr^{-1} appears to have little effect on Fe concentrations as they continue to decrease to below detection limit. At 2.5 and 1 ml hr^{-1} Fe concentrations remains near or below detection limit. The input Fe concentration is assumed to be $\sim 1.7 \text{ mmol kg}^{-1}$ based on the results from the SW2 experiment (Fig. 5.11).

The behaviour of Mg is significantly different between the BSW2 and SW2 experiments. In BSW2, Mg concentrations remain below detection limit ($< 0.0004 \text{ mmol kg}^{-1}$) both in presence of distilled water and as seawater begins to appear in the effluents at a flow rate of 1 ml hr^{-1} (Fig. 6.18). When flow rate is increased to 10 ml hr^{-1} , a significant increase in Mg concentration occurs, rising to 5 mmol kg^{-1} , after which it decreases to 1 mmol kg^{-1} . Decreasing the flow rate to 5 ml hr^{-1} results in a decrease in Mg to 0.4 mmol kg^{-1} while at 2.5 ml hr^{-1} it decreases further to 0.3 mmol kg^{-1} , and finally to $\sim 0.2 \text{ mmol kg}^{-1}$ at 1 ml hr^{-1} flow rate. The input Mg concentration is assumed to be $\sim 23 \text{ mmol kg}^{-1}$ based on the results of the SW2 experiments (Fig. 5.11). These results show that almost all Mg remaining in the seawater after passage through the Preheater is fixed in the rock.

Sulfate concentration is $\sim 0.25 \text{ mmol kg}^{-1}$ when in presence of distilled water (Fig. 6.18). When seawater is exiting the Reactor, it reaches a value of $0.05 - 0.1 \text{ mmol kg}^{-1}$ over the following four days. Upon increase of flow rate to 10 ml hr^{-1} , there are moderate increases in SO_4 up to $\sim 0.25 \text{ mmol kg}^{-1}$. This concentration is not maintained and SO_4 decreases back to $\sim 0.08 \text{ mmol kg}^{-1}$ over the following days independent of flow rate. The input concentration of SO_4 is assumed to be $\sim 1.7 \text{ mmol kg}^{-1}$ based on results from SW2 (Fig. 5.11). This indicates that the remaining SO_4 in the pre-treated seawater is precipitating during reaction with the basalt.

There are detectable H_2S concentrations in the effluents from the BSW2 experiment (Fig. 6.18). This differs from the SW2 experiment which show no detectable H_2S (Fig. 5.11). The highest H_2S concentrations occur just after seawater begins to exit the Reactor, as in BSW1. This suggests release of H_2S from sulfide inclusions trapped in volcanic glass. The overall decrease in concentration over the experiment is attributed to complete dissolution of volcanic glass.

Chloride is conservative and reflects mixing between distilled water and seawater. The concentrations are independent of flow rate (Fig. 6.18).

Figure 6.17. Major element concentrations in blank and effluent samples (mmol kg^{-1}) versus time (hr) for the BSW2 experiment at $350^\circ\text{C}/488$ bar. Yellow squares at $t=0$ are the blank sample composition of seawater from SW2. Light blue symbols show where distilled water was exiting the Reactor at $350^\circ\text{C}/488$ bar and 1.0 ml hr^{-1} . Black symbols are effluent compositions containing seawater at $350^\circ\text{C}/488$ bar and 1.0 ml hr^{-1} flow rate. Other coloured symbols show effluent compositions at different flow rates. *In situ* pH is the calculated pH at temperature. LOD= limit of detection.

- ▲ blank (seawater)
- ▲ distilled water $350^\circ\text{C}/488$ bar/ 1 ml hr^{-1}
- ▲ seawater $350^\circ\text{C}/488$ bar/ 1 ml hr^{-1}
- ▲ seawater $350^\circ\text{C}/488$ bar/ 10 ml hr^{-1}
- ▲ seawater $350^\circ\text{C}/488$ bar/ 5 ml hr^{-1}
- ▲ seawater $350^\circ\text{C}/488$ bar/ 2.5 ml hr^{-1}

Figure 6.18. Major element concentrations in blank and effluent samples (mmol kg^{-1}) versus time (hr) for the BSW2 experiment at $350^\circ\text{C}/488$ bar. Yellow squares at $t=0$ are the input composition of seawater from SW2. Light blue symbols show where distilled water was exiting the Reactor at $350^\circ\text{C}/488$ bar and 1.0 ml hr^{-1} . Black symbols are effluent compositions containing seawater at $350^\circ\text{C}/488$ bar and 1.0 ml hr^{-1} flow rate. Other coloured symbols show effluent compositions at different flow rates. *In situ* pH is the calculated pH at temperature. LOD= limit of detection.

6.2.2.2. Trace Element Concentrations

In the seawater-only experiment (SW2), trace elements showed some mobility and semi-regular to irregular trends caused by the interaction between seawater and the ZrO_2 beads (Fig. 5.12 and 5.13). It is evident that the beads were releasing measurable concentrations of some trace elements including V, Cr, Mn, Co, Ni, Cu, Zn, Cd, Ba, Pb and perhaps Au. Effluents also showed seawater concentrations of Rb.

Figure 6.19 and Figure 6.20 show trace element results plotted versus time in hours for the BSW2 experiment. The unreacted natural seawater composition is shown at $t = 0$. Most trace elements are below detection limit with Mn, Zn, Ag, Ba, Cd and Au showing low, but detectable concentrations. The distilled water concentrations are not shown but are generally lower than seawater. Complete trace element results for this experiment are listed in Appendix E.

While seawater exits that Reactor, elements that show regular trends are Mn, Rb, Ag, Ba and Au. The concentrations of Zn, Cu and Cd are elevated only at higher flow rates but overall their trends are highly irregular. The Mn concentrations reach values of $0.3 - 0.5 \text{ mmol kg}^{-1}$ and are not dependent on flow rate. All other element concentrations are near or below detection limit.

Except for the isolated high value at the start of the experiment, Rb concentrations reflect the input seawater, as in BSW1 (Fig. 6.20).

As with SW2, Ba concentration is highest at the beginning of the exit of seawater, it decreases over the remainder of the experiment. This is attributed to the precipitation of barite, Ba concentrations are independent of flow rate.

The Ag and Au concentrations are the highest once seawater begins to exit the Reactor after which Au decreases regularly to below detection limit, while Ag remains stable at $0.0015 \text{ } \mu\text{mol kg}^{-1}$ to the end of the experiment. Their behaviours differ from the seawater-only experiment in which Au remained at a relatively steady value of $0.03 \text{ } \mu\text{mol kg}^{-1}$ while Ag remained under detection limit after 200 hrs (Fig. 5.13). This suggest Au is released from the ZrO_2 beads but then is fixed in the rock. The concentrations of Ag are very close to the detection limit and are all of similar value. This suggests some caution using the Ag data.

The trace element results, as with BSW2, are unremarkable. However, the apparent lower mobility when the basalt is present suggests fixation of trace elements by the rock during fluid – rock interaction rather than release from it.

Figure 6.19. Trace element concentrations in blank and effluent samples ($\mu\text{mol kg}^{-1}$) versus time (hr) for the basalt-seawater experiment at $350^\circ\text{C}/488$ bar (BSW2). Yellow squares at $t=0$ are the blank composition of seawater from SW2. Light blue symbols show where distilled water was exiting the Reactor at $350^\circ\text{C}/488$ bar and 1.0 ml hr^{-1} . Black symbols are effluent compositions at $350^\circ\text{C}/488$ bar and 1.0 ml hr^{-1} flow rate. Other coloured symbols are effluent compositions at differing flow rate. *In situ* pH is the calculated pH at temperature. LOD= limit of detection.

Figure 6.20. Trace element concentrations in blank and effluent samples ($\mu\text{mol kg}^{-1}$) versus time (hr) for the basalt-seawater experiment at $350^\circ\text{C}/488$ bar (BSW2). Yellow squares at $t=0$ are the blank composition of seawater from SW2. Light blue symbols show where distilled water was exiting the Reactor at $350^\circ\text{C}/488$ bar and 1.0 ml hr^{-1} . Black symbols are effluent compositions at $350^\circ\text{C}/488$ bar and 1.0 ml hr^{-1} flow rate. Other coloured symbols are effluent compositions at differing flow rate. *In situ* pH is the calculated pH at temperature. LOD= limit of detection.

6.2.2.3. Mineralogy and Texture of Reacted Basalt

Upon the completion of the experiment (311 hrs), the reacted basalt was extracted from the Reactor onto absorbent paper. The run products were rinsed with distilled water to remove precipitated soluble salts and air-dried. The reacted material was initially divided into 5 portions numbered from 1 (bottom of the Reactor) to 5 (top of the Reactor) (Fig. 6.21). The basalt block from the bottom of the Reactor was extracted and rinsed with distilled water.

Figure 6.21 shows the reacted grains after extraction from the Reactor. The change of colour of the grains from bottom to top shows that the rock is visibly altered. Portion 1 is light gray, Portion 2 and 3 are light green-gray, while Portions 4 to 5 show the darker gray-green colour of the original basalt.

In order to reduce the amount of analyses required, grains from Portion 2 and 3 were combined as were grains from Portion 4 and 5. Run products from Portions 1, 2-3, 4-5 were mounted on aluminium stubs for SEM analysis. Run products from these portions were also epoxy-mounted and polished for SEM analysis. Larger samples were collected for XRD and XRF analysis.

Qualitative XRD analysis

The qualitative XRD results for all Portion 1, 2-3, and 4-5 are shown in Table 6.13. These confirm plagioclase is present in all Portions. This is assumed to be the original bytownite. Clinopyroxene was detected in only in Portion 2 - 5 showing that it has been essentially replaced by secondary phases. Secondary minerals identified are chlorite (which is found in all portions), magnetite, anhydrite and ankerite. Anhydrite was found only in Portion 1 at the bottom of the Reactor. Ankerite is found only at the top. All XRD results are reported in Appendix E.

Table 6.13. Qualitative XRD analysis of Portion 1, 2-3, 4-5 from BSW2.

	Portion 1	Portion 2-3	Portion 4-5
Chlorite	x	x	x
Plagioclase	x	x	x
Magnetite	x		
Anhydrite	x		
Ankerite			x
Augite		x	x

Figure 6.21. Schematic diagram showing position of reacted basalt portions extracted from the Reactor after completion of the BSW2 experiment (not to scale). On the right, are the reacted grains divided in 5 portions numbered from 1 (bottom of the Reactor) to 5 (top of the Reactor). Also shown is the position of the basalt block.

XRF analysis

Table 6.14 lists the XRF results for the portions examined. Significant changes in rock chemistry are evident. In order to determine the relationship between elements during fluid – rock exchange a correlation matrix, similar to that constructed for the 400°C experiment, was made (Table 6.15). At the 95% significance level and with $n = 4$, the level of significance of $r = \pm 0.95$ (± 0.997 for S). The correlation coefficients with values of $-0.95 \leq r \leq +0.95$ are highlighted in yellow in the table. Selected elements are plotted by position in Figure 6.22. Also shown is the unreacted basalt composition for comparison. It can be seen from the correlation matrix that there is a significant positive correlation between Na_2O and SiO_2 while MgO correlates negatively with Na_2O . There is also significant positive correlation between Fe_2O_3 and SiO_2 .

As there was no detectable Al in the effluent samples, it is assumed that Al was immobile during fluid – rock interaction. The highest Al value is in Portion 4 - 5 which should be the least altered portion near to the top of the Reactor. This suggests some variability in the unreacted rock Al_2O_3 content. It is evident that the greatest mass loss occurred in Portion 1 as indicated by substantial decreases in SiO_2 , Na_2O , CaO , and Fe_2O_3 without an accompanying increase in Al_2O_3 . K_2O is uniformly lost throughout the Reactor. As with the experiment at 400°C, MgO and S appear to be the only components to have increased in mass.

Table 6.14. XRF analysis of the reacted material collected from Portion 1, 2-3, 4-5 after the BSW2 experiment (wt%). Also shown is the composition of the unreacted basalt rock. n.m.: not measured.

	Na_2O	CaO	MgO	SiO_2	TiO_2	Al_2O_3	Fe_2O_3	MnO	K_2O	P_2O_5	S (ppm)
Portion 4-5	2.36	10.47	6.33	45.35	1.44	15.32	12.48	0.14	0.06	0.18	120
Portion 2-3	1.37	5.11	17.08	43.43	1.59	13.60	11.44	0.04	0.05	0.17	5330
Portion 1	0.42	6.00	22.55	34.87	1.80	13.66	9.08	0.03	0.03	0.13	19900
Unreacted rock	2.35	10.94	6.50	48.85	2.13	13.41	15.11	0.24	0.25	0.22	n.m.

Table 6.15. Correlation matrix of major oxides and sulfur for analyses shown in Table 6.14. Correlation coefficients significant at the 95% level are highlighted in yellow.

	Na ₂ O	CaO	MgO	SiO ₂	TiO ₂	Al ₂ O ₃	Fe ₂ O ₃	MnO	K ₂ O	P ₂ O ₅	S
Na ₂ O	1.00										
CaO	0.85	1.00									
MgO	-0.99	-0.92	1.00								
SiO ₂	0.95	0.71	-0.90	1.00							
TiO ₂	0.03	0.26	-0.07	0.19	1.00						
Al ₂ O ₃	0.42	0.42	-0.46	0.14	-0.74	1.00					
Fe ₂ O ₃	0.90	0.79	-0.89	0.96	0.43	0.00	1.00				
MnO	0.83	0.92	-0.87	0.82	0.55	0.05	0.93	1.00			
K ₂ O	0.63	0.68	-0.65	0.74	0.79	-0.36	0.89	0.91	1.00		
P ₂ O ₅	0.88	0.72	-0.86	0.97	0.41	-0.05	0.99	0.89	0.88	1.00	
S	-0.96	-0.58	0.90	-1.00	0.98	-0.68	-1.00	-0.74	-1.00	-0.99	1.00

The S concentration is highest at position 1 (2%). The host for the added S is anhydrite, thus, unlike the experiment at 400°C, the highest concentration of anhydrite is at the bottom of the Reactor. K₂O is almost completely removed at all positions in the column. This indicates that glass has been removed from the entire column, similar to the 400°C experiment. Except for K₂O and TiO₂ (not shown in Figure 6.22), all elements approach the unaltered composition at the top of the Reactor.

Figure 6.22. Chemical composition (wt%) of rock Portions analysed by XRF plotted against position in Reactor column (red circles). The unreacted basalt compositions shown by blue line.

Reacted grains - Portion 1

SEM examination shows a significant degree of alteration due to fluid – rock interaction. Minerals of secondary origin identified were chlorite and anhydrite. The results also confirm the presence of the primary minerals plagioclase, clinopyroxene, olivine and titanomagnetite (Table 6.16). No evidence of caminite was found. Appendix E contains all SEM results for this Portion of the rock.

Table 6.16. Mineral assemblage identified by SEM-EDS analysis of the surface of reacted grains of Portion 1 after completion of the BSW2 experiment.

Type of Analysis	Analysis Material	Mineral Identified	Average Mineral Composition
SEM-EDS	polished grains	Plagioclase	-
SEM-EDS	polished grains	Augite	$\text{Ca}_{0.7}\text{Mg}_{0.9}\text{Fe}_{0.2}\text{Al}_{0.1}\text{Si}_2\text{O}_6$
SEM-EDS	polished grains	Olivine	$\text{Mg}_{0.9}\text{FeSi}_{1.1}\text{O}_4 (\text{Fo}_{49}\text{-Fa}_{51})$
SEM-EDS	polished grains	Chlorite	$\text{Mg}_{3.8}\text{Fe}_{0.5}\text{Al}_{1.5}\text{Si}_{3.5}\text{Al}_{0.5}\text{O}_{10}(\text{OH})_8$ (calculated based on an anhydrous composition with 14 oxygens)
SEM-EDS	polished grains	Anhydrite	CaSO_4
SEM-EDS	polished grains	Titanomagnetite	-

Figure 6.23 shows SEM images of selected reacted grains from Portion 1. These are covered with a continuous layer of chlorite and isolated euhedral anhydrite crystals. No evidence of the primary plagioclase, clinopyroxene, and olivine is found on the surface of the grains.

Figure 6.24a-e shows SEM backscatter images and EDS maps of a polished mount of a grain collected from Portion 1. The images show the high degree of alteration where clinopyroxene is almost entirely replaced by chlorite. Remnant clinopyroxene is internal to the grain. Plagioclase is also highly corroded, but a significant amount remains. Fe-Ti oxides appear relatively unaltered although some titanite was identified. Remnant olivine persists and was likely isolated from the fluid.

Figure 6.24f,g are SEM backscatter detailed images of Figure 6.24a. EDS analyses reveal the Mg-Fe aluminosilicate to be chlorite with a higher concentration of magnesium than iron. The plagioclase remaining is the original bytownite. Fe-Ti oxides are relatively unaffected.

Figure 6.23. SEM images of reacted grains collected from Portion 1 of the Reactor after the BSW2 experiment: (a-f) grains covered by a surface coating of chlorite with isolated and intergrown anhydrite crystals.

Figure 6.24. SEM images and EDS compositional maps of an epoxy-mounted, polished grain collected from the Portion 1 after the BSW2 experiment: (a) backscatter image of the reacted grain; (b) composite colour image combining the backscatter image and elemental maps for (c) Mg in green, (d) Ca in blue, and (e) Fe in red showing plagioclase (blue) and clinopyroxene (light blue), olivine (yellow), Fe-Ti oxides (red), and chlorite (green); (f-g) SEM backscatter images of the red rectangular areas n°1 and n°2 in (a) showing secondary chlorite (Chl), the plagioclase (Plg) and clinopyroxene (Cpx), olivine (Ol) and oxides (Ox).

Portion 2-3

SEM results show a significant degree of alteration. Secondary minerals identified are chlorite, anhydrite and a smectite (Table 6.17). The primary minerals plagioclase, clinopyroxene, olivine and titanomagnetite were also identified.

Table 6.17. Mineral assemblage identified by SEM-EDS analysis of reacted grains from Portion 2-3 after the BSW2 experiment. Only the compositions of plagioclase, chlorite and smectite were measured.

Type of Analysis	Analysis Material	Mineral Identified	Average Mineral Composition
SEM-EDS	polished grains	Plagioclase	$\text{Ca}_{0.7}\text{Na}_{0.2}\text{Al}_{1.6}\text{Si}_{2.4}\text{O}_8 (\text{An}_{74}-\text{Ab}_{26})$
SEM-EDS	polished grains	Augite	-
SEM-EDS	polished grains	Olivine	-
SEM-EDS	polished grains	Chlorite	$\text{Mg}_{3.5}\text{Fe}_{0.7}\text{Al}_{1.3}\text{Si}_{3.5}\text{Al}_{0.5}\text{O}_{10}(\text{OH})_8$ (calculated based on an anhydrous composition with 14 oxygens)
SEM-EDS	grain surface	Anhydrite	CaSO_4
SEM-EDS	polished grains	Titanomagnetite	-
SEM-EDS	polished grains	Smectite	$\text{Na}_{0.1}\text{Mg}_{2.1}\text{Fe}_{0.6}\text{Al}_{0.3}\text{Si}_{3.4}\text{Al}_{0.5}\text{O}_{10}(\text{OH})_2 \cdot n\text{H}_2\text{O}$ (calculated based on an anhydrous composition with 11 oxygens)

Figure 6.25a-e shows SEM backscatter images and EDS maps of a polished mount of a grain collected from Portion 2-3. Clinopyroxene has been almost entirely replaced by chlorite while the remnant plagioclase is corroded but persists. Chlorite surrounds the rim of the grain and internally replaces clinopyroxene, plagioclase, and presumably olivine. Fe-Ti oxide appear relatively unaffected.

Figure 6.26a-e shows SEM backscatter images and EDS maps of a second polished grain collected from Portion 2-3. The grains show a high degree of alteration with clinopyroxene almost entirely replaced while plagioclase was more resistant. This grain differs from the previous shown in Figure 6.25 as the secondary phase surrounding and replacing the grain is not chlorite. The average SEM-EDS analysis of this mineral (Table 6.18) show measurable concentrations of Na, a lower Mg/Fe ratio and higher Si/Al ratio than that of the chlorite found in the previous grain and in Portion 1. This mineral replaces mainly clinopyroxene and surrounds the outside of the grain.

This phase is comparable in composition to the clay-like phase encountered in the BSW1 experiment at 400°C. Given that the XRD results from the latter experiment it is concluded that the most likely candidate for this mineral is smectite.

Figure 6.25. SEM images and EDS compositional maps of an epoxy-mounted, polished grain collected from the Portion 2-3 after the BSW2 experiment: (a) backscatter image; (b) composite colour image combining the backscatter image and elemental maps for c) Fe in red, d) Ca in blue and e) Mg in green showing plagioclase (blue), Fe-Ti oxides (red), and chlorite (green); (f-g) SEM backscatter images of the two rectangular areas shown in (a).

Figure 6.26. SEM images and EDS compositional maps of a polished grain collected from the Portion 2-3 after the BSW2 experiment: (a) backscatter image; (b) composite colour image combining the backscatter image and elemental maps for c) Mg in green, d) Ca in blue and e) Fe in red showing plagioclase (blue), Fe-Ti oxides (red), and smectite (green); f-g) SEM backscatter images of the two rectangular areas shown in (a). The grain has been largely replaced by smectite.

Table 6.18. Average composition (SEM-EDS) of smectite found in Portion 2-3 after the completion of the BSW2 experiment.

Polished (N=13)		
oxide	average Wt %	$\pm 1\sigma$
Na₂O	0.72	0.21
MgO	22.25	1.15
Al₂O₃	11.71	0.91
SiO₂	53.45	1.55
FeO	11.59	1.78
Total	99.82	

Portion 4-5

SEM analysis of grain from the top two portions of reacted grains show a lower intensity of alteration of the rock. The only secondary mineral identified is smectite. Note that no chlorite or anhydrite was identified in the top two portions of the Reactor. This is consistent with the XRD results.

Table 6.19. Mineral assemblage detected by SEM-EDS analysis of reacted grains of Portion 4-5 after the BSW2 experiment.

Type of Analysis	Analysis Material	Mineral Identified	Average Mineral Composition
SEM-EDS	polished grains	Plagioclase	-
SEM-EDS	polished grains	Augite	$\text{Ca}_{0.5}\text{Mg}_{0.9}\text{Fe}_{0.4}\text{Al}_{0.1}\text{Si}_2\text{O}_6$
SEM-EDS	polished grains	Titanomagnetite	-
SEM-EDS	polished grains	Smectite	$\text{Na}_{0.2}\text{Ca}_{0.1}\text{Mg}_{1.3}\text{Fe}_{1.2}\text{Al}_{0.4}\text{Si}_{3.4}\text{Al}_{0.6}\text{O}_{10}(\text{OH})_2 \cdot n\text{H}_2\text{O}$ (calculated based on an anhydrous composition with 11 oxygens)

Figure 6.27a-e show SEM backscatter images and EDS maps of a polished mount of a grain collected from Portion 4-5. Primary plagioclase and clinopyroxene are relatively unaffected with smectite growing only on the outside edge of the grain. Primary titanomagnetite is unaffected.

Figure 6.27f,g are SEM backscatter detailed images of the grain shown in Figure 6.27a. EDS analyses show the smectite is high in FeO and MgO and with measurable Na_2O . The plagioclase appears slightly altered when compared to the unaltered rock while clinopyroxene and olivine are unaffected.

The average SEM-EDS analysis for smectite is shown in Table 6.20. It has similar concentrations of Al_2O_3 and SiO_2 , but has higher Na_2O and CaO than the smectite found in Portion 2 – 3. Also, when compared to the smectite found at the top of the Reactor in the 350°C experiment (Table 6.12), it has a higher Fe:Mg ratio.

To summarise, Figure 6.28 shows a composite diagram of the reacted basalt grains, the backscatter images, and the EDS compositional maps for the BSW2 experiment at 350°C. The decrease in the intensity of alteration between Portions 1-3 and Portion 4-5 is evident. The bleaching of the rock can be attributed to the replacement of primary clinopyroxene, olivine, and plagioclase by chlorite up to Portion 2. Within Portion 2 and 3, replacement by chlorite and smectite are both present but do not occur together. This implies a transition from chlorite to smectite as the dominant secondary phase about one quarter the way up the

Reactor. For Portions 3 to 5, the intensity of alteration decreases, and the colour of the grains darkens as more clinopyroxene remains unaltered and replacement by smectite is reduced.

Figure 6.27. SEM images and EDS compositional maps of a polished grain from the Portion 4-5 after the BSW2 experiment: (a) backscatter image; (b) composite colour image combining the backscatter image and elemental maps for c) Mg in green, d) Ca in blue and e) Fe in red showing plagioclase (blue), and clinopyroxene (light blue), Fe-Ti oxides (red), and the secondary Na-Mg-Fe aluminosilicate (green) growing on the outside edge of the grain; (f-g) SEM backscatter images of the two rectangular areas shown in Figure 6.28(a).

Table 6.20. Average composition (by SEM-EDS analysis) of the clay mineral phase found during study of the reacted grains collected from Portion 4-5 after the BSW2.

Polished (N=26)		
oxide	average Wt %	$\pm 1\sigma$
Na₂O	1.57	0.76
MgO	13.02	2.43
Al₂O₃	12.11	1.14
SiO₂	50.28	1.73
CaO	0.87	0.39
FeO	22.12	4.38
Total	99.97	

Figure 6.28. Composite image showing the changing intensity of alteration of reacted grains analysed from the BSW2 experiment. Flow direction is from the bottom to the top of the image. The decreasing degree of alteration is evident from the bleaching of the rock due to replacement by chlorite and smectite.

6.2.2.4. Mineralogy and Texture of Reacted Basalt: Basalt Block

The basalt block (8x8x4 mm) (Fig. 6.29a) was positioned vertically near the bottom of the Reactor approximately 0.5 cm above the titanium frit (Fig. 6.21). Upon opening the Reactor, the basalt block was well-preserved, with abundant evidence of reaction on left side and left top corner of the block (Fig. 6.29b). Once extracted, the reacted basalt block was mounted on an aluminium stub for SEM analysis. Complete SEM results are reported in Appendix E.

Figure 6.30 shows SEM backscatter images of the reacted surface of the basalt block. The bright backscatter image shows that the block is covered by a higher atomic weight element than the expected Na, Mg, Ca, Al, and Si. EDS analysis shows this coating is composed of Ni oxide. For this reason, the underlying minerals could not be analysed. The only observation that can be made is that there is considerably more porosity in the rock due to the dissolution of primary minerals. The origin of this coating of Ni oxide is unknown. It was not observed in the grains from Portion 1 and suggests something acquired after extraction from the Reactor.

Figure 6.29. (a) SEM backscatter photomosaic of the basalt block surface before the BSW2 experiment. (b) SEM backscatter photomosaic of the basalt block surface after the BSW2 experiment.

Figure 6.30. SEM backscatter images of the reacted basalt block surface after the BSW2 experiment. This surface is covered by Ni- oxide.

6.3. Discussion

6.3.1. Major and trace element exchange during seawater - basalt interaction

Major elements

It is assumed that the composition of the fluid entering the Reactor in the seawater – basalt experiments has the same composition as the effluent from the seawater-only experiments (Chapter 5). For the purposes of discussion these values are summarised in Table 6.21 and Table 6.22 along with the “stable” effluent concentrations from the seawater–basalt experiments (listed according to flow rate).

Figure 6.31 shows major element concentrations in effluent samples from the seawater-only and seawater-basalt experiments plotted together versus time. This allows the comparison of SW1 with BSW1 (400°C) and SW2 with BSW2 (350°C).

Table 6.23 shows the input total mass (mg) and integrated elemental fluxes (mg) for selected components for BSW1 and BSW2. The input total mass represents the amount of material that entered the Reactor based on the total fluid flux (1.48 kg in BSW1 and 1.15 kg in BSW2) and output seawater composition from the Preheater. The integrated elemental flux is the total mass of component integrated over the entire experiment based on daily fluid flux and the effluent composition. Also shown is the elemental flux normalised to total fluid flux (mg per kg brine). Appendix E shows all data.

Quench pH. The quench pH of seawater exiting the Preheater during the SW1 and SW2 experiments stabilised at 3.3 and 2.8, respectively (Fig. 6.31). The difference in pH is likely due to greater reaction with the ZrO₂ beads at the higher temperature. In BSW1 and BSW2, after reaction with the basalt, quench pH values shift upwards to ~4.0 and ~3.7 at 1 ml hr⁻¹ flow rate. As previously noted, the acidic quench pH values in the seawater-only experiments are due to the release of hydrogen ion from HSO₄⁻ and H₂O during precipitation of retrograde phases (anhydrite, caminite, brucite). The increase of quench pH, in both seawater-basalt experiments shows the neutralisation of H⁺ by fluid-rock reaction.

Table 6.21. Input and output fluid compositions (mmol kg⁻¹) of seawater for selected components during the SW1 and BSW1 experiment.

	Experiment	T °C	Flow Rate (ml hr ⁻¹)	pH (25°C)	pH (<i>in situ</i>)	SiO ₂	Al	K	SO ₄	H ₂ S	Ca	Na	Mg	Fe
Input	SW1	377	-	7.75	-	0.1	0.01	8.4	22	-	9.4	360	45.8	0.002
Output	SW1	377	1	3.34	5.37	0.9	0.01	8.4	1.2	-	2.1	360	24.4	1.3
	↓	↓		↓	↓	↓	↓	↓	↓	↓	↓	↓	↓	↓
Input	BSW1	400	-	3.34	5.37	0.9	0.01	8.4	1.2	-	2.1	360	24.4	1.3
	BSW1	400	1	4.04	5.73	28.7	0.07	8	0.04	0.004	21.5	351	0.003	1.1
	BSW1	400	1.5	4.17	5.75	27.6	<0.006	8.2	0.05	0.004	20.7	362	0.02	1.5
Output	BSW1	400	10	4.53	5.82	28.6	<0.006	8.2	0.06	0.03	14.6	369	0.1	7.6
	BSW1	400	7.5	4.55	5.81	28.3	<0.006	8.2	0.05	0.02	14.8	362	0.08	7.2
	BSW1	400	5	4.55	5.80	28.7	<0.006	8.4	0.05	-	15.8	374	0.07	6.7

Table 6.22. Input and output fluid compositions (mmol kg⁻¹) of seawater for selected components during the SW2 and BSW2 experiment.

	Experiment	T °C	Flow Rate (ml hr ⁻¹)	pH (25°C)	pH (<i>in situ</i>)	SiO ₂	Al	K	SO ₄	H ₂ S	Ca	Na	Mg	Fe
Input	SW2	342	-	7.75	-	<0.01	0.007	8.4	23	-	8	360	36.7	0.002
Output	SW2	342	1	2.77	5.49	0.25	<0.006	8.4	2.7	-	1.4	360	22.8	1.7
	↓	↓		↓	↓	↓	↓	↓	↓	↓	↓	↓	↓	↓
Input	BSW2	350	-	2.77	5.49	0.25	<0.006	8.4	2.7	-	1.4	360	22.8	1.7
	BSW2	350	1	3.73	5.31	34.7	0.004	8	0.07	0.01	20.3	333	0.04	<0.001
	BSW2	350	10	4.11	5.28	28.3	0.001	8.9	0.09	<0.0003	18.6	366	1	2.8
Output	BSW2	350	5	4.26	5.27	27.5	0.002	8.8	0.05	<0.0003	21.7	368	0.4	0.4
	BSW2	350	2.5	4.31	5.29	25.6	0.007	8.6	0.07	0.002	22.1	372	0.3	0.2
	BSW2	350	1	4.36	5.29	24	0.005	8.4	0.06	0.001	23.2	374	0.2	<0.001

In situ pH. The calculated *in situ* pH for the SW1 and SW2 experiments was 5.3 and 5.5, respectively. Given the uncertainties in the high temperature thermodynamic data, these two values are comparable. After reaction with the rock, *in situ* pH for BSW1 and BSW2 is 5.8 and 5.3, respectively (Fig. 6.31). The 0.5 log unit of difference between these values suggests either a difference in the mineral reactions controlling the pH or alternatively, higher ion pairing at 400°C.

SiO₂. In BSW1 and BSW2, SiO₂ concentration remains oversaturated with respect to quartz for the duration of both experiments with a final value of ~25 mmol kg⁻¹ (Fig. 6.31). Output seawater from SW1 and SW2 contains low dissolved silica at 0.9 and 0.25 mmol kg⁻¹, respectively. This shows that SiO₂ released from the ZrO₂ beads makes only a small

contribution to the final SiO₂ in solution. Hence, SiO₂ is derived predominantly from fluid-rock interaction. At 350°C, SiO₂ concentration shows higher values for the first 150 hours which may be evidence of volcanic glass dissolution. At 400°C, SiO₂ concentration is constant over the experiment and there is no discernible evidence of glass dissolution. Since glass must have been dissolving, this implies that fluid-mineral reactions were buffering silica concentration.

The low concentration of SiO₂ in the input solution lead to aggressive attack by the fluid. This is aided by the high chloride concentrations promoting cation solubility. Note that the *in situ* pH of ~5.5 at both temperatures is near-neutral at 350 and 400°C/500 bar. The normalised SiO₂ flux is +1896 mg kg⁻¹ brine for BSW2(350°C) and +1640 mg kg⁻¹ brine for BSW1(400°C) (Table 6.23). This indicates that ~16% of more silica was released at 400°C than at 350°C. This can be explained by higher silicate mineral solubilities and faster kinetics at the higher temperature.

K, Na. The concentrations of K and Na in the SW2 and SW1 experiments are essentially conservative. The same is true after reaction with basalt in BSW1 and BSW2. This is demonstrated by their overall steady concentrations over most of the experiment and values similar to the input concentration (Fig. 6.31). Potassium does show initial high peaks at the beginning of the seawater experiments; however, the same high values are observed in BW1, BGB1, and BGB2 experiments. These high peaks are attributed to rapid K release from glass leading to supersaturation of secondary mineral phases when, once nucleated, quickly bring K concentration back down to input values.

The normalised flux for K (+15 mg kg⁻¹ brine at 350°C and -3.6 mg kg⁻¹ brine at 400°C) and Na (-99 mg kg⁻¹ brine at 350°C and -34 mg kg⁻¹ brine at 400°C) are relatively small compared to their total concentrations (Table 6.23) and are likely within the uncertainty of the calculation. Na was measured in the smectite but Na can also be sourced from plagioclase and overall there was no significant change in concentration.

Al. Aluminium concentrations in the effluent samples from the SW experiments are very low (<0.02 mmol kg⁻¹, Fig. 5.3 and 5.10). Aluminium in these experiments is derived from the ZrO₂ beads in which Al is an impurity. In BSW1 and BSW2, the same low concentrations are encountered (Fig. 6.1 and 6.17). This indicates that despite the high concentrations of Al in the unreacted basalt, Al was essentially immobile during fluid-rock interaction.

Figure 6.31. pH and major element concentrations in the seawater-only and seawater-basalt experiments at each temperature.

Ca. Calcium in the SW experiments is what remains in the seawater after anhydrite precipitation in the Preheater. These concentrations are assumed to be the input concentrations for the BSW experiments. At 350°C and 400°C, effluent Ca concentrations are similar at 1.4 – 2.1 mmol kg⁻¹ (Fig. 6.31). In contrast, steady state Ca concentrations in the BSW experiments are significantly higher at 21 – 23 mmol kg⁻¹. This Ca is derived from the dissolution of clinopyroxene and plagioclase. Anhydrite was identified both in BSW1 and BSW2. The normalised flux for Ca reveals a significant transfer of this element to the fluid (+592 mg kg⁻¹ brine in BSW1, and +630 mg kg⁻¹ brine in BSW2).

Table 6.23. Total input mass (mg) and integrated elemental fluxes (mg) for selected components for BSW2 and BSW1.

BSW1		SiO₂	K	SO₄	H₂S	Ca	Na	Mg	Fe
(400°C / 488 bar)									
Input composition (mg kg ⁻¹) based on SW1		54	328	115	-	84	8276	561	73
Total input mass (mg) (based on 1.48 kg total brine)		80	487	171	-	125	12278	832	108
Total integrated elemental flux (mg) (over the entire experiment)		+2427	-5.4	-143	+0.34	+876	-51	-657	+317
Normalised elemental flux (mg kg ⁻¹)		+1640	-3.6	-97	+0.23	+592	-34	-444	+214
BSW2		SiO₂	K	SO₄	H₂S	Ca	Na	Mg	Fe
(350°C / 488 bar)									
Input composition (mg kg ⁻¹) based on SW2		15	328	259	-	56	8276	524	95
Total input mass (mg) (based on 1.15 kg total brine)		17	377	298	-	64	9512	602	109
Total integrated elemental flux (mg) (over the entire experiment)		+2180	+17	-285	+0.13	+725	-114	-537	+159
Normalised elemental flux (mg kg ⁻¹)		+1896	+15	-248	+0.11	+630	-99	-467	+138

Fe. Final Fe concentrations in the effluent samples from the SW experiments are 1.3 – 1.7 mmol kg⁻¹ (Fig. 6.31). This Fe is derived from the ZrO₂ beads. After reaction with basalt, Fe concentrations are irregular but in general higher at 400°C. Iron concentration also shows a dependence on flow rate with significant increases at 10, 7.5 and 5 ml hr⁻¹. At 350°C, Fe concentration is near detection limit at 1 ml hr⁻¹ while at higher flow rate, Fe increases in concentration. The source of Fe is the dissolution of olivine and clinopyroxene with the latter likely dominating Fe transfer to the fluid as there is considerably more clinopyroxene in the rock. SEM-EDS analysis shows that some Fe is fixed chlorite and smectite, however, the normalised flux for Fe (Table 6.23) shows significant transfers of this element to solution (+214 mg kg⁻¹ brine in BSW1, and +138 mg kg⁻¹ brine in BSW2). The higher Fe flux at 400°C is due to higher silicate mineral solubility and faster dissolution kinetics. It is evident that although some Fe is fixed in secondary phases, the net flux of Fe is to the fluid.

Mg. Magnesium shows the most significant difference between the SW and BSW experiments. The large decrease in Mg concentration in the SW experiments is explained by the precipitation of caminite and brucite in the Preheater (Chapter 5). However, a high concentration is still available in the fluid exiting the Preheater (23 - 25 mmol kg⁻¹). After reaction with the basalt, Mg concentration decreases to very low values (0.003 mmol kg⁻¹ at 400°C and 0.2 mmol kg⁻¹). A small amount of Mg precipitated as caminite at 400°C, however, at 350°C, caminite was not identified. The majority of Mg was fixed in chlorite as evidenced by the high MgO concentrations in the XRD analyses of the lower portions from the Reactor. Some Mg was also fixed in smectite. The fixation of Mg through fluid-rock interaction is emphasised by the large negative normalised fluxes of Mg to the fluid (-444 mg kg⁻¹ brine at 400°C and -537 mg kg⁻¹ at 350°C).

SO₄. The significant decrease of SO₄ in the SW experiments is also attributed to the precipitation of anhydrite and caminite within the Preheater (Chapter 5). The output concentration differs between temperatures with 1.2 mmol kg⁻¹ at 400°C and 2.7 mmol kg⁻¹ at 350°C. The difference is explained by the lower solubility of anhydrite and caminite at the higher temperature (Fig. 5.16). The SO₄ concentration in the effluent samples from the BSW experiments are even lower at 0.05 – 0.06 mmol kg⁻¹. This is due to further sulfate mineral precipitation in the basalt. The normalised SO₄ flux shows negative transfers of -97 mg kg⁻¹ brine and -248 mg kg⁻¹ brine at 400°C and 350°C, respectively. The lower transfer of SO₄ to the rock at 400°C can be explained by the lower input SO₄ concentration at this temperature (Table 6.21 and 6.22).

H₂S. During the SW experiments, there are no measurable concentrations of H₂S in solution. In the BSW experiments, there is a small positive normalised flux in BSW2 (+0.11 mg kg⁻¹ brine) and BSW1 (+0.23 mg kg⁻¹ brine, Table 6.23). The highest values of H₂S are observed in first 3 - 4 samples after T shift (Fig. 6.31). This is attributed to rapid glass dissolution after temperature shift. The lower flux of H₂S at 350°C is perhaps due to greater sulfide mineral precipitation at this temperature.

Trace elements

The data sets available in the literature on trace elements mobility (i.e. Mn, Cu, Zn, Li) are found in laboratory investigations conducted at temperatures and pressures typical of the reaction zone using seawater batch-type reactors (Mottl et al., 1979; Seewald and Seyfried, 1990; Seyfried and Janecky, 1985). In this study, trace element mobility was monitored under dynamic conditions and at different flow rates but at similar temperature-pressure conditions of previous simulations. A comparison between trace elements concentrations measured from this study, and those reported from previous experimental investigations and *in situ* at vents, is shown in Figure 6.24.

The BW experiments show that at least Cu, Co, and Mo are released from the volcanic glass at 350°C due to the dissolution of sulfide inclusions. However, in the BGB and BSW experiments, because of the high concentrations of SiO₂ in the input and effluent samples, it is difficult to relate trace metal concentrations with glass dissolution.

The results do show that the mobility of trace elements, both at 350°C (BSW2) and 400°C (BSW1), is very low in the experiments. Only Mn shows significant concentrations at both temperatures while Zn appears clearly more mobile than Cu. The low concentrations of H₂S in solution do not permit any correlation between trace elements and sulfide mineral. Changes in flow rate did not have any significant influence on their mobility at both temperatures.

Comparing the results from previous studies (Table 6.24) and those of this study show some similarities and significant differences. In particular:

1. Room temperature pH values from previous studies and vents are predominantly between 3 and 4 while those from this study are typically between 4 and 4.5. They are comparable between the previous experimental studies, vents and this study.
2. H₂S concentrations are much higher in previous batch studies and in vent samples.
3. Fe concentrations are in many cases comparable between previous work and this

study although some vent samples show much higher concentrations.

4. Mn and other trace element concentrations are consistently lower in this study when compared to earlier work and vent samples.

It is proposed here that the lower H₂S, Fe, Mn and trace element concentrations in this study is due to the very short residence time of the fluid within the rock. At an estimated porosity of ~ 53% and a flow rate of 1 ml hr⁻¹, the average residence time of the fluid within the rock, i.e., within the Reactor, is approximately 10 hours. It is possible that some trace elements are being released, however, the concentrations are extremely low due to the short reaction period. This may demonstrate a drawback of flow-through studies when compared to batch experiments. Nevertheless, the results in this study show that vastly more information on major element chemistry, reaction rates, and secondary mineralogy is obtained using a flow-through approach.

Table 6.24. Comparison of Fe, Mn, Zn, Cu, Li ($\mu\text{mol kg}^{-1} = \mu\text{m}$) and H_2S ($\text{mmol kg}^{-1} = \text{mm}$) concentrations between previous experiments (Mottl et al., 1979, Seyfried and Janecky, 1985, Seewald and Seyfried, 1990), vent fluids (East Pacific Rise, Mid-Atlantic Ridge, Southern Juan de Fuca Ridge) and this study (BSW1 and BSW2) listed by sample number. Table also reports the value of temperature (T), pressure (P), flow-rate (ml hr^{-1}), number of samples (samp), pH at room T and *in situ* pH. ^aVon Damm et al., 1985 and Campbell et al., 1988; ^bdata by Bowers et al., 1988; ^cdata by Campbell et al., 1988; ^ddata by Von Damm and Bischoff, 1987; ^edata by Von Damm et al., 1988; ^fdata by Campbell et al., 1988. NA: not data available; n.a.: not analysed.

												BSW1 (400°C/488 bar)								BSW2 (350°C/488 bar)									
Rock Type		T (°C)	P bar	samp	pH (room T)	ΣH ₂ S (mm)	Fe (μm)	Mn (μm)	Zn (μm)	Cu (μm)	Li (μm)	samp	flow rate (ml hr ⁻¹)	pH 20.1 °C	ΣH ₂ S (mm)	Fe (μm)	Mn (μm)	Zn (μm)	Cu (μm)	Li (μm)	samp	flow rate (ml hr ⁻¹)	pH 20.1°C	ΣH ₂ S (mm)	Fe (μm)	Mn (μm)	Zn (μm)	Cu (μm)	Li (μm)
Mottl et al. (1979)	crystalline basalt	400	700	2A	4.1	5.9	0	0	NA	NA	NA	1	1	6.5	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.	1	1	5.2	< 0.0003	36	< 0.1	< 0.008	< 0.0009	32
	crystalline basalt	400	700	2F	3.9	6.2	0	0	NA	NA	NA	2	1	6.4	0.01	< 1	< 0.0001	117	0.2	17	2	1	4.0	0.07	< 1	< 0.1	< 0.008	< 0.0009	165
	basalt-glass > 90%	400	700	2B	3.9	6.5	0	0	NA	NA	NA	3	1	4.2	0.01	6	< 0.0001	38	0.01	114	3	1	3.8	0.01	< 1	95	8	< 0.0009	36
	crystalline + glassy: 40%	400	700	2C	3.6	7.3	0	0	NA	NA	NA	4	1	3.3	0.04	624	204	56	0.4	72	4	1	3.7	0.02	< 1	272	< 0.008	< 0.0009	36
	crystalline + glassy: 40%	400	700	2D	3.8	6.8	0	0	NA	NA	NA	5	1	4.3	0.04	3297	409	37	0.3	50	5	1	3.7	0.01	< 1	334	12	< 0.0009	38
	crystalline + glassy: 40%	400	700	2E	3.85	7	0	0	NA	NA	NA	6	10	3.6	0.04	892	524	22	n.a.	46	6	10	3.1	n.a.	4606	570	170	< 0.0009	25
Seyfried and Janecky (1985)	EPR-crystalline	350	400	1	4.8	6.8	192	125	16	0.6	NA	7	1	3.6	0.03	1271	564	24	< 0.0009	50	7	10	3.2	n.a.	5282	387	39	3	29
				2	4.4	6.2	247	167	19	0.9	NA	8	1	4	0.01	1168	475	20	0.02	39	8	10	3.4	n.a.	5829	423	47	< 0.0009	30
	EPR-crystalline	375	400	1	3.8	11.5	1754	451	37	2.5	NA	9	1	3.8	0.003	1706	540	22	< 0.0009	42	9	10	3.5	< 0.0003	4910	388	40	< 0.0009	33
				2	3.7	12.9	2328	688	92	2.2	NA	10	1	4.2	0.01	1991	472	< 0.008	n.a.	33	10	10	4.0	n.a.	2743	436	30	< 0.0009	30
	EPR-crystalline	400	400	1	3.3	17.7	8684	1202	121	22	NA	13	1	4	0.01	2329	495	3	0.2	39	13	10	4.0	n.a.	2725	439	10	< 0.0009	33
				2	3.6	9	8326	1256	43	7	NA	14	1	4.1	0.01	2764	533	9	0.1	43	14	10	4.1	< 0.0003	2643	431	10	< 0.0009	35
	EPR-crystalline	425	400	1	2.8	30	25067	3677	45	0.8	NA	15	1	4.1	0.004	2496	468	< 0.008	0.2	32	15	10	4.1	n.a.	2831	423	18	6	25
				2	2.7	30	26947	4400	32	0.6	NA	16	1	4.1	0.01	2783	456	21	0.1	35	16	5	4.2	n.a.	2152	415	15	< 0.0009	25
JDF-Basalt glass	400	375	1	3.7	10.9	2468	638	14	0.5	NA	17	1	4.1	0.01	2661	467	n.a.	n.a.	45	17	5	4.2	n.a.	1013	492	72	< 0.0009	30	
			2	3.5	11.8	2613	655	NA	1.6	NA	19	1	7.6	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.	18	5	4.2	n.a.	345	431	100	< 0.0009	32	
Seewald and Seyfried (1990)	crystalline basalt	400	400		3.2	17.5	3975	1005	214	31	274	20	1	4.9	0.02	700	100	2.7	< 0.0009	n.a.	19	5	4.3	< 0.0003	1	412	76	< 0.0009	29
	crystalline basalt	350	400		4.8	5	154	118	28	6	317	21	1	4.3	0.02	1500	200	3	< 0.0009	n.a.	20	5	4.3	n.a.	406	463	24	4	32
East Pacific Rise, 21° N ^a					pH (<i>in situ</i>)							22	1	4.1	0.005	1300	200	47	0.1	n.a.	21	2.5	4.3	0.003	< 1	312	76	< 0.0009	36
	NGS(1979)	350			NA	NA	1491	1030	NA	NA	997	22	2.5	4.2	n.a.	< 1	389	91	< 0.0009	31	23	2.5	4.2	n.a.	< 1	389	91	< 0.0009	31
	NGS(1981)	273			3.8	6.6	871	1002	40	< 2	1033	23	1	4	0.004	900	200	123	< 0.0009	n.a.	23	2.5	4.2	0.002	< 1	446	42	< 0.0009	30
	NGS(1985)	260			NA	6.8	646	864	NA	NA	1091	24	2.5	4.2	n.a.	< 1	497	78	< 0.0009	30	24	2.5	4.2	n.a.	< 1	497	78	< 0.0009	30
	OBS(1979)	350			NA	NA	NA	NA	NA	NA	896	25	2.5	4.3	< 0.0003	194	476	30	1	32	25	2.5	4.3	< 0.0003	194	476	30	1	32
	OBS(1981)	351			3.4	7.3	1664	960	106	35	891	26	1	4.3	0.001	< 1	323	37	< 0.0009	30	27	1	4.4	n.a.	< 1	317	63	< 0.0009	35
	OBS(1985)	340			3.4	7.6	1530	1024	NA	NA	926	26	10	4.3	n.a.	4654	421	9	n.a.	24	26	1	4.3	0.001	< 1	323	37	< 0.0009	30
	SW(1979)	350			NA	NA	NA	NA	NA	NA	956	27	10	4.3	n.a.	5612	378	11	n.a.	21	27	10	4.3	n.a.	< 1	317	63	< 0.0009	35
	SW(1981)	346/355 ^e			3.6	7.4	750	699	89	9.7	899	28	10	4.5	0.01	6829	269	n.a.	n.a.	21	28	10	4.5	0.01	6829	269	n.a.	n.a.	21
												32	10	4.5	n.a.	7265	256	< 0.008	< 0.0009	21	32	10	4.5	n.a.	7286	254	< 0.008	< 0.0009	22
	SW(1985)	335 ^f			4	8.1	660	763	NA	NA	969	33	10	4.5	n.a.	7430	256	< 0.008	< 0.0009	21	33	10	4.5	n.a.	7409	256	3	< 0.0009	21
	HQ(1981)	351			3.3	8.4	2429	878	104	44	1322	34	10	4.5	n.a.	7553	244	n.a.	n.a.	20	34	10	4.5	0.03	7553	244	n.a.	n.a.	20
HQ(1985)	332			3.6	7.9	1308	640	NA	NA	1448	35	10	4.5	n.a.	7409	256	3	< 0.0009	21	35	10	4.5	n.a.	7409	256	3	< 0.0009	21	
East Pacific Rise, 11°-13° N ^b												36	10	4.5	0.03	7553	244	n.a.	n.a.	20	36	10	4.5	0.03	7553	244	n.a.	n.a.	20
	Vent 4	347			3.1	8	5271	766	105	NA	884	37	7.5	4.6	n.a.	7663	250	5	0.2	20	37	7.5	4.6	n.a.	7663	250	5	0.2	20
Mid-Atlantic Ridge ^c												38	7.5	4.6	n.a.	7301	254	4	0.2	18	38	7.5	4.6	n.a.	7301	254	4	0.2	18
												39	7.5	4.6	n.a.	7119	250	3	0.5	28	39	7.5	4.6	n.a.	7119	250	3	0.5	28
Southern Juan de Fuca Ridge ^d												40	7.5	4.6	n.a.	7091	248	< 0.008	< 0.0009	32	40	7.5	4.6	n.a.	7091	248	< 0.008	< 0.0009	32
												41	7.5	4.6	0.02	7155	234	n.a.	n.a.	30	41	7.5	4.6	0.02	7155	234	n.a.	n.a.	30
MARK-1	350			3.9	5.9	2180	491	50	17	843	42	5	4.7	n.a.	7303	235	11	0.1	26	42	5	4.7	n.a.	7303	235	11	0.1	26	
	335			3.7	5.9	1832	493	47	10	849	43	5	4.6	n.a.	6912	248	9	< 0.0009	28	43	5	4.6	n.a.	6912	248	9	< 0.0009	28	
MARK-2												44	5	4.5	n.a.	6757	251	41	< 0.0009	30	44	5	4.5	n.a.	6757	251	41	< 0.0009	30
												45	5	4.6	n.a.	6653	247	13	< 0.0009	29	45	5	4.6	n.a.	6653	247	13	< 0.0009	29

6.3.2. Mass exchange and alteration fronts

Tables 6.3 and 6.15 show the correlation coefficients between major element concentrations at different levels in the Reactor. These correlations are indicative of related mass changes during alteration. It is also important to take into consideration the overall mass change of the rock to correctly interpret individual component changes. This calculation can be made using an element that is assumed (or demonstrated) to be immobile during the alteration process. Typically, elements such as Al, Ti, or Zr are chosen as the immobile component (Finlow-Bates and Stumpfl, 1981; Mathieu, 2018; Petersen, 1983). In this study, most major elements display mobility in that measurable concentrations were detected in the effluents. Ti analyses in the fluid are not available, however, at both 350 and 400°C, there is no detectable Al in most effluent samples. This justifies the assumption of overall immobility of Al during fluid-rock interaction. Note, however, that it must also be assumed that Al was not mobile within the Reactor, i.e., it did not move between the divided portions of run products.

Based on these assumptions, the individual mass changes for the major elements can be calculated using the equation:

$$\Delta M_i = \left[\frac{C_{Al_u}}{C_{Al_a}} C_{a_i} \right] - C_{u_i} \quad (1)$$

where ΔM_i is the mass change of component i in g 100g⁻¹ rock, C_{Al_u} is the Al₂O₃ concentration in the unreacted rock, C_{Al_a} is the Al₂O₃ concentration in the reacted rock, C_{a_i} and C_{u_i} are the measured concentrations of component i in the altered and unaltered rock, respectively. The Al₂O₃ concentration in the unreacted basalt is 13.41% (Table 2.2). Table 6.25 lists the mass changes calculated for both experiments using Al₂O₃ as the immobile element. Figure 6.32 plots these results versus position in the Reactor (bottom to top).

In both experiments there is a uniform loss of K₂O (~0.2 g 100g⁻¹ rock) in all portions examined, which is 80% of the original basalt concentration of 0.25% (Table 2.2). This loss is attributed to the complete removal of volcanic glass from the rock. It implies that an alteration front of glass dissolution passed completely through the Reactor at both temperatures. Note that the 350°C experiment lasted only two weeks, thus complete glass dissolution was accomplished in this time period. This is supported by the BW1, BW2, and BGB1 experiments where the passage of this front is shown by a sharp decrease in SiO₂ concentrations after about two weeks.

Table 6.25. Calculated mass changes (g 100g⁻¹ rock) for each portion of rock from the BSW1 and BSW2 experiments assuming Al₂O₃ immobility.

BSW1 (400°C / 488 bar)												
Portions		Na ₂ O	CaO	MgO	SiO ₂	TiO ₂	Al ₂ O ₃	Fe ₂ O ₃	MnO	K ₂ O	P ₂ O ₅	S _(T)
Top	7	-0.03	-0.98	-1.19	-5.69	-0.77	0.00	-3.69	-0.12	-0.19	0.07	0.00
	4	-1.20	-7.62	14.11	-13.95	-0.48	0.00	-9.19	-0.23	-0.20	0.03	0.75
	2-3	-2.16	-9.22	15.64	-21.56	-0.28	0.00	-8.18	-0.23	-0.23	-0.10	0.54
Bottom	1	-1.74	-7.24	15.79	-11.83	-0.23	0.00	-7.70	-0.22	-0.22	0.02	0.06
Unreacted		0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
BSW2 (350°C / 488 bar)												
Portions		Na ₂ O	CaO	MgO	SiO ₂	TiO ₂	Al ₂ O ₃	Fe ₂ O ₃	MnO	K ₂ O	P ₂ O ₅	S _(T)
Top	4.5	-0.29	-1.78	-0.96	-9.16	-0.87	0.00	-4.19	-0.12	-0.20	-0.06	0.01
	2-3	-0.99	-5.90	10.33	-6.04	-0.56	0.00	-3.84	-0.20	-0.20	-0.05	0.52
Bottom	1	-1.94	-5.05	15.64	-14.62	-0.36	0.00	-6.20	-0.21	-0.22	-0.09	1.95
Unreacted		0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00

At both temperatures, the rock has gained a significant amount of MgO of up to ~15 g 100g⁻¹ rock. At 400°C, this amount is gained in Portions 1 – 3 while the gain is only 1 g less in Portion 4. At Portion 7 (top of the Reactor) the mass gain is essentially zero. Portion 2 - 3 coincides with the most intense chloritization of the rock (the rock is essentially a chloritite at this point). This implies that 9 g 100g⁻¹ of basalt is the maximum uptake of Mg from the seawater after which Mg must pass further up the Reactor. This represents a second alteration front: chloritization of the basalt.

At 350°C, this maximum uptake of 15 g MgO is only found in Portion 1 and decreases to zero by Portion 4-5. Chlorite was identified by XRD in all portions of rock but was not observed as present during SEM analysis of Portion 4 - 5. Based on the results of the 400°C experiment, it is concluded that the chloritization front progressed completely only as far as the bottom portion of the rock at 350°C. However, it should be noted that this experiment was only two weeks in duration, half that of the 400°C experiment. It is also possible the slower reaction kinetics at 350°C reduced the rate of progression of chloritization through the Reactor. It can be concluded that ~9 g is the maximum uptake of Mg by the basalt at both temperatures.

The chloritization of the basalt is mirrored by significant losses of SiO₂ and CaO and, to a lesser extent, Na₂O and Fe₂O₃. This suggests that initially the major source of Fe and SiO₂ for the formation of chlorite is clinopyroxene (olivine constitutes only a minor component of the basalt). With intense chloritization, plagioclase is also consumed. This is supported by the SEM results in which plagioclase is shown to be more resistant than

clinopyroxene. In the case of Al_2O_3 , some is sourced from the dissolution of clinopyroxene but the major source for Al_2O_3 is plagioclase.

Figure 6.32. Mass changes ($\text{g } 100\text{g}^{-1}$ rock) of the Portions analysed by XRF plotted against position in Reactor column for the BSW1 (red) and for the BSW2 (yellow). The unreacted basalt composition is shown by black line.

Sulfur is only a trace component in the unreacted basalt. In the reacted basalt, S is hosted in the secondary minerals anhydrite and caminite as SO_4 . At 400°C , S mass change is near zero at the bottom of the Reactor (Portion 1). The S mass change increases in Portion 2 – 3 and reaches its maximum in Portion 4, halfway up the Reactor. At the top of the Reactor, S was not detected in the XRF analyses. The concentration of S in Portion 4 is only about 0.8% which explains why neither anhydrite nor caminite were detected in the XRD analyses (Table 6.1).

At 350°C , the largest mass increase in S ($2 \text{ g } 100\text{g}^{-1} \text{ rock}$) is found in the bottom portion of the rock. It then decreases to near essentially zero by Portion 4 – 5. This is reflected in the XRD results in which anhydrite was identified in Portion 1 (Table 6.13) due to the much larger S gain when compared to the 400°C experiment. The difference between the experiments in the amount of S added can be explained by the difference in the solution composition entering the Preheater. The input SO_4 concentration at 350°C is higher (2.7 mmol kg^{-1} , Table 6.21) than at 400°C (1.2 mmol kg^{-1} , Table 6.22). This means that if most of the SO_4 precipitated there should be $\sim 2.25\times$ more S at 350°C .

The results for S suggest that precipitation of anhydrite was facilitated by fluid-rock interaction where intense chloritization released Ca thereby inducing anhydrite precipitation. The implication is that this represents a third alteration front: anhydrite precipitation. Because of the shorter experimental time and lower temperature, this front only advanced into the bottom portion of the rock at 350°C .

It is proposed that once chloritization of the rock is complete, no further Ca can be released, and incoming seawater must have become undersaturated with respect to anhydrite causing it to dissolve again. This implies that, if the experiment were continued for sufficient time, the peak in anhydrite precipitation would progress through the rock, ahead of the chloritization front. The rock would be completely chloritized, and no anhydrite would be found in the run products.

The presence of hematite in in Portions 2 – 3 of BSW1 is explained by the oxidation of least some of the Fe released during intense chloritization. This may be an experimental artefact since, as noted previously, the second aliquot of seawater used to refill the separator was not deoxygenated.

6.3.3. The path of fluid-rock interaction

The path of fluid-rock interaction was examined using activity diagrams based on aqueous solution species' activities. The *EqSolvR* software package was used to calculate the species' activities and *in situ* pH values (Chapter 2).

Activity ratio diagrams were constructed for the respective experimental temperatures (350 and 400°C) and a pressure of 488 bar, assuming unit activity of pure mineral phases. There was no period during the experiments where quartz was saturated, thus SiO₂ activity for the diagrams must be based on solution chemistry (Chapter 3, §3.3.3). For the experiment at 350°C, the average log (a_{SiO_2}) is -1.52 while for the experiment at 400°C the average log (a_{SiO_2}) is -1.56. All the phase diagrams for the BSW1 and BSW2 experiments are provided in Appendix E.

Figure 3.33 shows the activity ratio diagrams for the MgO-Al₂O₃-SiO₂-H₂O system at 350 and 400°C/500 bar. At both temperatures, the changes in cation activity ratio mainly reflect changes in Mg²⁺ as the *in situ* pH values are relatively constant. The input composition of the preheated seawater is shown by the yellow circles (SW1 and SW2). Early effluent samples from both experiments were comprised of a mixture of distilled water and seawater. In these samples, SiO₂ concentration quickly reached elevated levels such that even the distilled water/seawater mixtures had high log (a_{SiO_2}) (black crosses in Fig. 6.33). At the same time, Mg must have been increasing in the fluid, however, it was also being fixed in the rock resulting in measurable but lower log ($a_{Mg^{2+}}/a_{H^+}^2$) values. At both temperatures, these early values lie below the clinocllore (CL-14A) field (distilled water effect in Fig. 6.33).

Once 100% preheated seawater was entering the Reactor, exit fluid compositions all lie in the clinocllore field. At 400°C, fluid flow rate was maintained at 1 ml hr⁻¹ for most of the experiment and these fluid compositions cluster at log ($a_{Mg^{2+}}/a_{H^+}^2$) = 5, however, there is a slight variation with flow rate. At 350°C, flow rate was increased to 10 ml hr⁻¹ once seawater was exiting the Reactor. This resulted in higher Mg concentrations in the fluid and, due to the relatively constant *in situ* pH, higher log ($a_{Mg^{2+}}/a_{H^+}^2$) values (Fig. 6.33, BSW2). Decreasing the flow rate at this temperature caused log ($a_{Mg^{2+}}/a_{H^+}^2$) to decrease but fluid compositions remain the clinocllore field.

Figure 6.33. Activity-activity diagrams showing mineral stability fields in the $\text{MgO} - \text{Al}_2\text{O}_3 - \text{SiO}_2 - \text{H}_2\text{O}$ system for a) the BSW1 (400°C/488 bar) and b) the BSW2 (350°C/488 bar) experiment. Yellow circles show position of the output fluid composition from SW1 and SW2 at 377 and 342°C/488 bar, respectively. Arrows indicate fluid-path. Symbol colour refers to different flow rates as shown in the legend below the figure.

The predominance of chlorite as a secondary phase demonstrates that fluid compositions were saturated with respect to this mineral. This is consistent with Figure 6.33. The overall path of fluid-rock interaction in the $\text{MgO-K}_2\text{O-Al}_2\text{O}_3\text{-SiO}_2\text{-H}_2\text{O}$ system at both temperatures is similar indicating that the mineral reactions involved are the same which agrees with the minerals observed. However, there is a noticeable effect of flow rate on cation activity ratios both at 350 and 400°C (more below).

In the portions of reacted basalt above the zone of intense chloritization, smectite is present as the most common secondary phase. Unfortunately, there are no thermodynamic data available for common smectite minerals at 350 and 400°C so these cannot be incorporated in the activity diagrams. However, some insight can be gained by examining the

equilibrium between chlorite and smectite. Using clinochlore and Mg-saponite as proxies for chlorite and smectite, respectively, the following reaction (2) can be written:

This reaction shows that saponite stability is favoured by higher Mg^{2+} and SiO_2 activity, and higher pH. The relative positions of these minerals in the $\log (a_{\text{Mg}^{2+}}/a_{\text{H}^+}^2) - \log (a_{\text{SiO}_2})$ space can be seen by constructing a similar diagram to Figure 6.33 at 300°C using the same mineral phases, of which thermodynamic data are available (Fig. 6.34).

Figure 6.34. Activity-activity diagram showing mineral stability fields in the $\text{MgO} - \text{Al}_2\text{O}_3 - \text{SiO}_2 - \text{H}_2\text{O}$ system at 300°C using the phases in Figure 6.33 with the addition of Mg-saponite. Diagram constructed using GWB (Bethke, 1996).

At 350 and 400°C, the phase boundaries will move but the overall relative position of the minerals will not change. In the experiments, the dominant secondary phase switches from chlorite to smectite up the Reactor. This occurs closer to the bottom of the Reactor at 350°C and about halfway up the Reactor at 400°C. The position of the fluid compositions in Figure 6.33 are therefore conjectured to lie near the equilibrium phase boundary between chlorite and smectite in $\log (a_{\text{Mg}^{2+}}/a_{\text{H}^+}^2) - \log (a_{\text{SiO}_2})$ space. We cannot confirm this without thermodynamic data and end member mineral activities but the shift from chlorite to

smectite does occur in both experiments which indicates that a mineral phase boundary must have been traversed.

With the above information on the distribution of secondary minerals and some knowledge of the position of the fluid compositions in activity space, the reactions that occurred during fluid-rock interaction can be addressed. These reactions are complex as they involve multiple phases at the same time. To examine the fluid-rock interaction process, the reactions are broken down into individual mineral reactions.

In both BSW experiments, glass dissolution was the only pervasive “reaction” throughout the Reactor. As stated previously, a reaction front of glass dissolution passed through the rock in about two weeks but, unlike earlier experiments (BW1, BW2, BGB1), there are no elevated SiO₂ values directly relatable to glass dissolution. This indicates that secondary mineral precipitation was already controlling SiO₂ concentrations in the BSW experiments. The small amount of glass in the rock implies that glass dissolution did not have a major effect on the secondary minerals precipitated. The most significant result of glass dissolution was an 80% loss of K₂O from the rock.

The distilled water experiments (BW1 and BW2) show that after glass the next most reactive phase was olivine. The dissolution of olivine can provide a source for Fe, Mg, and SiO₂ but not Al. The conversion of olivine to chlorite requires a source for Al and this cannot be the seawater, thus the transformation of olivine to chlorite must occurred simultaneously with the dissolution of clinopyroxene and/or plagioclase. As with glass, the amount of olivine in the basalt is probably <5% as it was not detected in the XRD analysis of the unaltered rock.

The dominant secondary phase found at the bottom of the Reactor in both basalt seawater experiments is chlorite, with the chloritization front proceeding about twice as far up the column at 400°C than at 350°C. Pervasive chloritization shows that all minerals (except Fe-Ti oxides) were converted to chlorite. The reactions for the replacement of olivine, clinopyroxene and plagioclase by chlorite, assuming conservation of Al, can be written as:

Note that in this discussion we ignore ion pairing for convenience. If the cations were, for example, Cl complexed, the reaction would have the same form.

As stated above, the conversion of olivine to chlorite (Reaction 3) requires a source of Al thus dissolution of clinopyroxene or plagioclase must provide this, however, olivine is a minor phase and this reaction is not expected to be important during intense chloritization.

The SEM results show that the conversion of clinopyroxene to chlorite is the next reaction (Reaction 4) that goes to completion, followed finally by the conversion of the remaining plagioclase to chlorite (Reaction 5). Chloritization of clinopyroxene consumes H^+ and produces SiO_2 , Ca, Mg, and Fe. Chloritization of plagioclase consumes SiO_2 , Mg, and Fe, and produces H^+ , Na^+ and Ca, thus Ca is released by both chloritization reactions. Input preheated seawater Ca concentrations are 2.1 and 1.4 mmol kg^{-1} , at 400 and 350°C, respectively, while output Ca concentrations are 21.5 and 20.3 mmol kg^{-1} (at 1 ml hr^{-1}). This shows a 10 – 15-fold increase in Ca concentration in the effluent samples. This is due to the chloritization of the primary silicate minerals.

It is informative to combine Reaction 4 and 5 to see the combined effect of chloritization. This gives:

This reaction shows that complete chloritization of clinopyroxene and plagioclase requires addition of a significant amount of Mg, sourced from seawater, and releases significant Ca, from the primary minerals. Note that the clinopyroxene/plagioclase ratio in this reaction is 5.5:1 while in the rock it is about 0.5:1. This means that during chloritization, assuming conservation of Al, other components including Fe and SiO_2 must be moving within the column, i.e., chloritization is not just simply the addition of Mg and the removal of Ca.

Sulfate concentration entering the bottom of the Reactor ranges from 1.2 – 2.1 mmol kg⁻¹ while in the effluent it is much less at 0.04 – 0.07 mmol kg⁻¹. This indicates that most of the SO₄ precipitated in the Reactor. The peak in S concentration by XRF was found in Portion 4 approximately halfway up the column. The precipitation of anhydrite and caminite can be written as follows:

Both these reactions consume cation and HSO₄ from the fluid and produce H⁺.

It is assumed that the preheated seawater is in equilibrium with both minerals when entering the bottom of the Reactor, therefore any precipitation of these phases requires a change in solution chemistry. From Reactions 4 and 5, chloritization of both clinopyroxene and plagioclase releases Ca. This induces anhydrite precipitation according to Reaction 7. In addition, the chloritization of clinopyroxene consumes H⁺ increasing pH which can further induce sulfate mineral precipitation. Given the extensive amount of chloritization, this could be expected to surpass any H⁺ produced by anhydrite precipitation. Caminite was also present in the run products but was rare, possibly due to the precipitation of anhydrite which consumed SO₄?

As long as Ca is provided by clinopyroxene and plagioclase dissolution, and more SO₄ was entering the bottom of the column, anhydrite precipitation would continue. Once clinopyroxene begins to be depleted, chloritization of plagioclase would take over as the dominant reaction and pH would decrease according to Reaction 5, meaning that H⁺ would now be produced, pH would fall, and anhydrite would re-dissolve. This implies that the front of anhydrite precipitation will overlap the position where the dominant chloritization reaction switches from clinopyroxene to plagioclase.

At 350°C, the shorter experiment time and lower temperature meant that chloritization did not progress as far up the column and anhydrite precipitation is at a maximum near the entry point at the bottom of the Reactor.

During the BSW experiments, the flow rate was varied to test for the equilibrium state of the system. Figure 6.35 shows the Ca, Mg and Fe concentrations versus flow rate in both experiments. These results show that, at both temperatures, Mg and Fe concentrations

increase with increased flow rate while Ca concentration decreases. Both Al and SiO₂ (not shown) remain constant showing no relation to flow rate (Table 6.21 and 6.22).

Figure 6.35. The concentration of Ca, Mg and Fe (mmol kg⁻¹) versus flow rate (ml hr⁻¹) during the BSW experiments.

Both Mg and Fe can be sourced from olivine and clinopyroxene, but as stated above, it is assumed that olivine is not of sufficient abundance to significantly contribute to overall fluid-rock reactions. It is proposed that clinopyroxene is the primary source of Fe for chloritization. Note that the Mg concentrations in Figure 6.35 are very low when compared to the input values in the seawater (23 – 24 mmol kg⁻¹). This demonstrates the efficiency of Mg fixation by the rock, even at a flow rate of 10 ml hr⁻¹ where the average residence time of the fluid is only 1 hr.

The concentration of Ca decreases with increased flow rate, however, Ca remains much higher in concentration than in the preheated seawater (1.4 - 2.1 mmol kg⁻¹). Because Fe increases in concentration with flow rate, this indicates that the release of Ca from clinopyroxene should not be decreasing. The implication, therefore, is that the dissolution rate of plagioclase is slower and cannot compete with the increased flow rate. This would result in higher Fe but lower Ca.

Both Mg and Fe increase with increased flow rate. These elements should be consumed by the precipitation of chlorite. This shows that the rate of chloritization is also affected by flow rate resulting in retention of these elements in the fluid. This interpretation is also supported by the fact that, if a curve were fitted to the datapoints for Mg and Fe in Figure 6.35, the shape of this curve would be similar for Mg and Fe at each temperature.

A change to smectite as the dominant secondary phase within the Reactor was observed in both experiments. At 400°C this was observed in Portion 4 and at 350°C at Portion 2-3. These two secondary phases were not found together, however, this is not unexpected due to the limited number of grains analysed and the difficulty of preserving the exact position of the grains when extracted. Nevertheless, it is clear that chlorite precipitation ceased and smectite became the dominant secondary phase in both experiments. The basalt grain shown in Figure 6.26 shows complete replacement of olivine and clinopyroxene and partial replacement of plagioclase by smectite. This indicates that there is a zone of intense smectitization within the Reactor. Without further investigation it is uncertain how far this progresses. At the top of the Reactor, smectite occurs only as a thin layer around the outside of relatively unaltered basalt (Fig. 6.27).

The Mg/Fe ratio in the dominant secondary phases provides insight into the change from chlorite to smectite. The chlorites from the BSW experiments have Mg/Fe ratios of 5 – 10 (Table 6.4, 6.7, 6.8, 6.16, 6.17) and are a mixture of clinocllore ($\text{Mg}_5\text{Al}_2\text{Si}_3\text{O}_{10}(\text{OH})_8$) with a lesser chamosite ($\text{Fe}_5\text{Al}_2\text{Si}_3\text{O}_{10}(\text{OH})_8$) component. The smectite from the experiments are a mixture of montmorillonite ($(\text{Na,Ca})_{0.33}(\text{Al,Mg})_2(\text{Si}_4\text{O}_{10}(\text{OH})_2)$) and nontronite ($\text{Na}_{0.3}\text{Fe}_2(\text{Si, Al})_4\text{O}_{10}(\text{OH})_2$). However, it should be noted, there is the possibility that this phase is corrensite, which is an interlayered mixture of chlorite and smectite. In BSW1, smectite was found at Portion 4 where some grains display intense smectitization. The Mg/Fe ratio in this smectite is 4.6 (Table 6.9). In BSW2, smectite was found in Portion 2-3 and its Mg/Fe ratio is 3.5 (Table 6.17). Smectite was also identified in the top portions of both experiments with a Mg/Fe of 0.9 – 1.1 (Table 6.11 and 6.19).

It can be seen that the Mg/Fe ratio in smectite is much higher where the transition from chlorite occurs, while at the top of the Reactor its ratio is ~ 1 in both experiments. This supports the supposition that the dominant secondary mineral composition is controlled by the Mg activity in the fluid. The influx of seawater with a high Mg content drives chloritization, consuming the Mg and creating chlorite that is dominated by the clinocllore component. Upon the change from chloritization to smectitization, the Mg activity must still be high, forming smectites with high Mg/Fe ratio. At this point however, the Mg activity must decrease rapidly as the smectites at the top of the Reactor have much lower Mg/Fe ratio and there is essentially no Mg left in the fluid. In other words, at the top of the Reactor the composition of smectite is determined by the rock composition and not the fluid.

This is supported by the Mg/Fe ratios in: celadonite (0.7 – 2.1) from the BW experiments where distilled water was the fluid (Chapter 3); and biotite (1) and smectite (1.1 – 1.4) in the BGB experiments (Chapter 4) in which geothermal brine with low Mg was the fluid.

As stated above, there must be some position in the column where chlorite and smectite are both present, at which point the fluid composition must lie on the phase boundary, and as the fluid moves upwards its composition moves into the smectite stability field. Using the chlorite and smectite compositions in Potion 4 of BSW1, where both minerals are found (Table 6.8 and 6.9), the phase boundary can be represented by the following reaction:

Again, this reaction assumes conservation of Al. The reaction shows that an increase in Na, SiO₂, Mg or Fe activity, favours smectite stability while a decrease in pH activity favours chlorite. Na is released from plagioclase, but the Na activity is not expected to change significantly because of its high concentration in seawater. SiO₂ activity is also not expected to change significantly also due to its high concentration. This leaves Fe, Mg and pH to determine the chlorite/smectite equilibrium. T log K expression for Reaction 9 can be written as:

$$\log K_9 = -0.5 \log \left(\frac{a_{Mg^{2+}}}{a_{H^+}^2} \right) - 0.15 \log \left(\frac{a_{Fe^{2+}}}{a_{H^+}^2} \right) - 0.2 \log \left(\frac{a_{Na^+}}{a_{H^+}} \right) - 1.65 \log a_{SiO_2} + 1.5 \log H^+ \quad (10)$$

Assuming constant activity for Na and SiO₂, this shows the relative effects of Mg, Fe and pH on smectite stability. An increase in Mg or Fe favours smectite stability while a decrease in pH favours chlorite. Mg activity is expected to decrease in concentration at this point thus favouring chlorite. The explanation must be that increased Fe concentration and/or decreased pH is stabilising smectite over chlorite.

In comparison, using the smectite composition at the top of the Reactor (Portion 7) gives the following reaction between chlorite and smectite:

For this reaction the equilibrium expression is:

$$\log K_{11} = +1.75 \log \left(\frac{a_{Mg^{2+}}}{a_{H^+}^2} \right) - 0.96 \log \left(\frac{a_{Fe^{2+}}}{a_{H^+}^2} \right) - 0.3 \log \left(\frac{a_{Na^+}}{a_{H^+}} \right) - 0.73 \log a_{SiO_2} - 1.3 \log H^+ \quad (12)$$

In this case, both lower Mg activity and lower pH favour smectite stability. It is proposed that by the time the smectite composition is controlled by rock chemistry (mainly by Mg and Fe released from olivine and clinopyroxene), Mg concentration reaches the low values found in the effluent samples. The interpretation is that there is a sharp gradient in Mg concentration at the point where chlorite switches to smectite (Portion 4), the latter mineral consuming the remaining Mg in the fluid, and the composition of smectites forming further up the column being controlled solely by the rock.

At the top of the Reactor, smectite is present but occurs only as a thin coating around relatively unaltered rock (Fig. 6.14 and 6.27). As discussed previously it is concluded that all glass, accessible by the fluid, has been removed. This means that the Mg and Fe required to form smectite is sourced from the rock minerals. As the alteration is weak, olivine could have been contributing significant Mg and Fe, however, clinopyroxene is expected to have been the dominant source. The conversion of olivine, clinopyroxene and plagioclase, to smectite can be expressed as:

Reaction 13 shows that, if conservation of Al is assumed, Al must be sourced from either clinopyroxene or plagioclase to convert olivine to smectite. The conversion of clinopyroxene to smectite (Reaction 14) requires only a small amount of Fe, consumes H^+ , while producing Ca and Mg, thus this reaction can proceed without significant addition of outside components. The conversion of plagioclase to smectite requires a significant addition of Mg and Fe and is expected to be a relatively minor reaction by the time the fluid reaches the top of the Reactor.

Note the above interpretation is based mainly on the results from BSW1 at 400°C, however, it is concluded, based on the identical mineralogy, that the same processes were occurring at 350°C. In the case of BSW2 is it interpreted that the lower temperature and shorter experiment time lead to progression of the chloritization only within the immediate bottom of the Reactor.

6.3.4. Na/K geothermometers

Fluid chemistry results for both seawater experiments showed that Na and K were conservative during fluid-rock interaction. This implies that the rock was unable to affect their concentrations over the residence time of the fluid. As a result, the fluid Na/K ratio did not change from its original seawater value and any estimated temperatures based on this ratio will simply reflect the seawater composition. The same would be true for experiments of longer duration as pervasive chloritization does not alter the fluid's Na/K ratio. The precipitation of smectite did incorporate some Na but not enough to sufficiently adjust the high Na concentration in seawater. Table 6.26 confirms this, as all of the estimated temperatures are low and are similar to that estimated using the input seawater composition.

Table 6.26. Average and 1 σ of estimated temperature (°C) using fluid compositions for BSW1 and BSW2 and geothermometers provided in literature.

		Na/K (Fournier 1979)	Na/K (Truesdell 1976)	Na/K/Ca (Fournier and Truesdell 1973) ($\beta=1/3$)	Na/K (Santoyo and Díaz-González 2009)	Na/K (Arnorsson 1983) (250-350°C)	Na/K (Tonani 1980)	Na/K (Nieva and Nieva 1987)	Na/K (Giggenbach 1988)
BSW1 400°C/483 bar	Blank Seawater	148	105	175	99	152	108	136	167
	Samples	147	104	168	98	151	107	136	167
	$\pm 1\sigma$	1.6	1.8	3.5	1.7	1.5	1.9	1.5	1.5
BSW2 350°C/488 bar	Blank Seawater	150	108	109	102	154	111	139	169
	Samples	148	105	102	99	152	108	137	168
	$\pm 1\sigma$	1.4	1.7	1.6	1.6	1.4	1.7	1.4	1.4

6.3.5. Geological implications

The altered basalt from the BSW experiments contain several secondary minerals that have formed during seawater-basalt interaction. These include chlorite, smectite, anhydrite, caminite, calcite, ankerite and altered oxides (magnetite, maghemite, hematite). Of these minerals, chlorite is by far the most abundant, with smectite comprising the second most common secondary phase. Locally anhydrite is an important phase while caminite is rare. Calcite and ankerite were identified by XRD analyses but were not found during SEM examination. This secondary mineral assemblage is consistent with the observations made in the deeper section of the drill cuttings at Hole 1256D and Hole 504B (Alt et al., 2010; Koepke et al., 2008; Nicolas and Boudier, 1991; Nicolas et al., 2008; Vanko and Laverne, 1998; Wilson et al., 2006) and at the Reykjanes geothermal field (Fridleifsson et al., 2017; Marks et al., 2011; Marks et al., 2010).

The results from the BSW experiments show that the metamorphic grade is consistent with lower greenschist facies at both temperatures (Alt, 1995; Honnorez, 2003). One exception is the lack of actinolite and epidote. No evidence of these minerals was found and these are common in natural altered basalts at this grade (Honnorez, 2003; Nehlig et al., 1994). This could be the result of kinetic inhibition of these minerals. Another possibility is that to form these minerals, the fluid must be maintained at quartz saturation. Quartz is a common alteration mineral in altered MORB; however, it was not observed in our experiments. Experiments conducted in our lab with New Zealand basement greywacke at 400°C (unpublished data) have actinolite as the most abundant secondary phase. This rock contains up to 40% quartz and effluent samples maintained quartz saturation during the experiments. In all experiments conducted in the present study, SiO₂ concentrations were consistently above quartz saturation and chlorite was the dominant secondary mineral.

The experiments were designed to allow the interaction of seawater with basalt in a continuous flow regime. This required the use of the Preheater to remove retrograde phases including anhydrite, caminite and brucite which would have blocked the apparatus. This set-up mimics the process of seawater influx away from the mid-ocean ridge, heating as it descends into the Reaction zone, and alteration of the basaltic rocks. The main difference between the experiments and the natural situation, besides the geographic scale and time, is that lack of fluid-rock interaction in the influx zone. In the influx zone, fluid-rock interactions occur to modify solution chemistry other than just sulfate mineral precipitation so that the fluid entering the reaction zone will be much more complex than in the experiments.

Nevertheless, anhydrite is found in the Reaction zone in MORB (Lowell and Yao, 2002; Scheuermann et al., 2019) showing that the experiments do reproduce the process of Ca fixation in anhydrite rather than as secondary Ca-silicate minerals. This may also be evidence for the lack of actinolite and epidote in the experiments.

The lack of caminite as a common secondary mineral in naturally altered MORB is due to the presence of abundant aluminosilicate phases in the influx zone. The experiments demonstrate the effectiveness of the existing aluminosilicate phases in fixing essentially all Mg in the descending fluid. Caminite was identified as a naturally-occurring mineral only in black smoker pipes where the heating of seawater allowed its precipitation (Haymon, 1983; Haymon and Kastner, 1981; Haymon and Kastner, 1986).

The most notable result from the BSW experiments is the rate of reaction. The BSW1 experiment at 400°C contained 22.5 g of basalt and a total seawater flux of 1.48 kg. This represents a fluid/rock ratio of only 66:1. Even at this low fluid/rock ratio the seawater was able to alter ~40% of the rock to chloritite in four weeks. This shows the efficiency of Mg fixation during fluid-rock interactions. Indeed, even at a flow rate of 10 ml hr⁻¹, where the average fluid residence time would have been only 1 hour, all Mg was essentially removed from the fluid. This shows that, in the natural environment, the fixation of Mg by aluminosilicate phases is exceedingly fast.

Combining the observations from all experiments, it is possible to form a sequence of events that would occur during interaction of basalt with seawater. The first “phase” that would be removed is the volcanic glass. This would occur very rapidly at low fluid/rock ratio. This results in almost complete dissolution of K from the rock. The next most reactive mineral is olivine, which dissolves releasing Mg and Fe to the fluid. In the BW experiments this results in the formation of celadonite, using K from the glass and Mg and Fe from olivine. The formation of this mineral, however, requires Al. This Al is sourced from either the glass or minor dissolution of clinopyroxene and/or plagioclase.

From the BSW experiments, it is observed that clinopyroxene is the next most reactive phase with seawater. This releases Ca, Fe and Mg to the fluid, the latter two being immediately incorporated into chlorite, and with the high Mg in the seawater, this results in chlorites with a high Mg component. Beside the Fe-Ti oxides, which are the most refractory phase in the basalt, plagioclase is next phase to be replaced. It should be noted that albite was not encountered in the secondary mineral assemblage. This implies that even with the high

activity of Na in seawater, the conversion of plagioclase to chlorite was surpassed by Mg fixation.

The previous sequence of events emphasises the role of Al in the progression of fluid-rock interactions. The first “phase” removed was the glass. The glass contains significant Al (16%) however most of this Al remained in secondary minerals that formed in the glass voids (Fig. 3.32). Olivine contains little Al and was the next phase showing replacement. This is followed by clinopyroxene with a small Al component, and finally by plagioclase. This suggests that the relative resistance of the minerals to alteration is due to their Al content. This is supported by the lack of Al in the effluents from the experiments.

The trace element results from the distilled water-basalt experiments (BW1 and BW2) show that there is some release of elements from volcanic glass. In the seawater-only experiments (SW1 and SW2) the ZrO₂ beads appear to be releasing some of these elements. Trace element results from the seawater-basalt experiments, however, in general, show lower abundances. The suggestion is that, if higher trace element concentrations enter the Reactor, or are being released by the glass, these are being removed during fluid-rock interaction with the basalt. This implies that during initial interaction between seawater and unaltered basalt, trace elements are not produced but are consumed during interaction. It is only at deeper levels in mid-ocean ridges where higher grade alteration releases the elements necessary to form volcanogenic massive sulfide deposits.

6.4. References

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Chapter 7: Summary and conclusions

7.1. Summary

In this study six laboratory experiments simulating fluid-rock interactions between distilled water, geothermal brine, and seawater and a tholeiitic basalt from Reykjanes, Iceland, were performed at subcritical, near-supercritical and supercritical condition (350 - 400°C/500 bar). Two further experiments with seawater only were completed as controls. The important parameters and elemental fluxes are summarised in Table 7.1. Figure 7.1 shows a comparison of fluid chemistries over time for all simulations (seawater-only experiment results excluded).

7.1.1. Basalt - distilled water interaction (BW1, BW2)

Two experiments simulated the interaction between distilled water and basalt at supercritical and subcritical conditions (blue lines, Fig. 7.1).

Fluid chemistry results show that *in situ* pH values stabilise at 5.7 (400°C) and 5.3 (350°C) over the experiments. Upon cooling, the pH values increase to ~9.5 in both experiments. This is due to the dissociation of ion pairs containing OH⁻ during cooling, resulting in alkaline values. Such high pH values are indicative of H⁺ consumption from the fluid during cation exchange with the rock.

Elevated concentrations of SiO₂, well above quartz saturation, along with increases in K, H₂S, SO₄ and Cl are found for approximately 12 days after temperature increase in both experiments. This is attributed to the dissolution of volcanic glass and its included sulfide blebs. After complete removal of the volcanic glass, these elements decrease in concentration while Na and Al concentrations increase. The latter changes due to enhanced dissolution of plagioclase in the presence of lower SiO₂ concentrations.

Trace elements results at 400°C show correlations between Cu, Co, and Mo with H₂S, and SiO₂. This indicates that these elements are released by volcanic glass dissolution in the presence of distilled water. These correlations are not present at 350°C suggesting fixation by sulfide minerals at subcritical conditions.

SEM analysis of the basalt reacted at 400°C show intense alteration at the bottom of the Reactor with a Ca skarn-like assemblage of grossular, wollastonite, anorthite, and chlorite. At the top of the Reactor only celadonite was found as a secondary phase. At 350°C, the alteration assemblage at the bottom of the Reactor consisted of chlorite and anorthite. Celadonite was also found as the sole secondary phase at the top of the Reactor. The intensity

of alteration at the top of the reactor is weak in both experiments with only the conversion of olivine to celadonite as the dominant reaction. With the exception of particularly intense alteration adjacent to the entry point of the fluid, most primary rock minerals (plagioclase, clinopyroxene, Fe-Ti oxides) remain relatively unaffected.

The results show the effectiveness of distilled water, which lacks any alkali cations, at removing Na and K rapidly from the rock. Once levels of these cations increase in the fluid, the rate of alteration slows substantially. The presence of celadonite as a secondary phase replacing olivine is notable. This points to olivine as the next most reactive phase after the volcanic glass. Celadonite is found in nature as a replacement of olivine and clinopyroxene in basaltic rocks. The results from the distilled water experiments show that the release of K from volcanic glass, Mg and Fe from olivine, and sufficient Al from clinopyroxene and/or plagioclase can stabilise celadonite without addition of introduced cations in the fluid.

Na/K geothermometry results show temperatures close to the experimental value when quartz is supersaturated at 400°C while at 350°C, temperatures are close to the experiment value only when K is elevated after glass dissolution.

7.1.2 Basalt-geothermal brine interactions (BGB1, BGB2)

Two experiments simulated the interaction of geothermal brine from the Nga Awa Purua geothermal power station, New Zealand, with basalt at supercritical (BGB1, 400°C/483 bar) and subcritical (BGB2, 350°C/486 bar) conditions (red lines, Fig. 7.1). These experiments were undertaken to study the effect of re-injection of a geothermal brine, containing elevated cation concentrations, on fluid and rock chemistry. Unlike distilled water, the brine contains initial high concentrations of SiO₂, K, SO₄, Na, Cl and has an acidic pH (~4).

Fluid chemistry results show that *in situ* pH stabilises at ~7.0 (400°C) and 6.8 (350°C) over the experiments. At 400°C, the quench pH is low (~2.9) while glass dissolution was occurring. At 350°C, the quench pH is initially low (~3.4) and gradually rises to 7.9. The low quench pH values are attributed to the precipitation of anhydrite which releases H⁺ to the fluid. At high temperature H⁺ is held in protonated species such as HSO₄⁻ but is released on cooling leading to acidic quench pH values.

At 400°C, SiO₂ concentration remains oversaturated with respect to quartz for approximately two weeks after temperature increase. This is due to the dissolution of the volcanic glass which took longer than with distilled water due to the higher input SiO₂ concentration in the brine. At 350°C, SiO₂ concentration is initially elevated after the

temperature increase, however, it gradually decreases in concentration back to the input value over the experiment. This is attributed to onset of precipitation of secondary phases immediately after the increase in temperature.

At 400°C, other notable changes in fluid chemistry are: a sharp rise in K after temperature increase, followed by higher concentrations than the input value while glass is dissolving; and elevated Al concentrations after the glass is removed due to lower SiO₂ concentrations. At 350°C, the above changes are similar except for K which decreases back to the input values immediately after the initial rise. At both temperatures H₂S is detected during glass dissolution and Ca, Mg, and Fe concentrations are detectable but low.

Many trace element concentrations are higher in the unreacted geothermal brine and during fluid-rock interaction through the initial room temperature period. At higher temperature, many trace elements are undetected except Mo, Ba, and Au. The presence of Cu sulfide as a secondary phase suggests removal of trace elements from the fluid and fixation in the rock.

SEM examination of the basalt reacted at 400°C shows intense alteration to biotite and anhydrite immediately adjacent to the entry point of the brine. At the top of the Reactor, anhydrite and smectite are found as the secondary minerals. At 350°C, the alteration assemblage found at the bottom of the Reactor consists of smectite (with two distinct textures) and anhydrite. At the top of the Reactor only smectite is found as a secondary phase.

Mass balance results show significant uptake of SiO₂ and K by the fluid at 400°C but only SiO₂ at 350°C. This suggests greater secondary mineral precipitation at the lower temperature. SO₄ shows significant losses from the fluid due to anhydrite precipitation. All other elements are essentially conservative meaning that any Ca, Mg, or Fe released from the rock was precipitated as anhydrite and smectite.

7.1.3 Seawater-only experiments (SW1, SW2)

The seawater-only experiments were carried out to determine the behaviour of seawater in the absence of basalt and to provide the input solution compositions for the seawater-basalt experiments. These are essentially control experiments that used the Preheater only, without the Reactor.

Effluent chemistry results show *in situ* pH values of 5.3 – 5.4 (377°C) and 5.5 (342°C). Quench pH values are highly acidic at 3.2 – 3.9 (377°C) and 2.9 – 3.7 (342°C). These low quench pH values are due to retrograde solubility phases that release H⁺ during precipitation. The H⁺ is ion-paired at high temperature but upon cooling these complexes

deprotonate resulting in acidic solutions. Fluid chemistry and mass balance results from both experiments show significant decreases in Mg, Ca, and SO₄. Na, K and Cl are conservative. Elevated concentrations of SiO₂, Al, and Fe, which cannot be sourced from seawater, are derived from the ZrO₂ beads used in the Preheater. Trace element concentrations above blank seawater values are found including V, Cr, Mn, Co, Cu, Ni, Zn, Cd, Ba, and Au. These must also be derived from the ZrO₂ beads.

The mineral precipitates from both seawater-only experiments were the same. They consisted of anhydrite, caminite and brucite. These phases have retrograde solubility and hence precipitated during the heating of the seawater.

7.1.4 Basalt-seawater interactions (BSW1, BSW2)

The seawater-basalt experiments provide the first example of flow-through experiments using preheated seawater and rock. They were performed to simulate (at a much smaller scale) the descent of seawater into the recharge zone and its reaction with basaltic rocks in the reaction zone at mid-ocean ridges.

The results from both experiments (green lines, Fig. 7.1) indicate that seawater reacted aggressively with the basalt. Fluid chemistry results show calculated *in situ* pH values of ~5.8 (400°C) and 5.3 (350°C) while quench pH values are acidic at 3.6 – 4.7 (400°C) and 3.1 – 4.4 (350°C).

Major changes in fluid chemistry due to fluid-rock interaction are observed in both experiments. SiO₂ concentrations increase substantially, and are above quartz saturation, but are not specifically elevated during glass dissolution due to immediate precipitation of secondary minerals. Ca concentrations greatly increase while there are smaller increases in Fe. Most Mg concentrations decrease to near or below detection limit (at 1 ml hr⁻¹). Na, K and Cl are generally conservative. Increased flow rate results in decreases in Ca concentration and increases in Mg and Fe concentrations. This is attributed to the effect of shorter fluid residence time on plagioclase dissolution (resulting in less Ca) and chlorite precipitation (resulting in higher Mg and Fe). SiO₂ concentration is independent of flow rate showing that it is buffered by opposing mineral reactions.

Mass balance calculations show the highest uptake of Mg occurred in the bottom third to half of the Reactor at 400°C and only in the bottom portion of the rock at 350°C. This is attributed to a shorter experiment time and the lower temperature. Complete chloritization occurs and results in a maximum uptake ~9 g 100g⁻¹ rock of Mg at both temperatures.

Maximum uptake of S occurs approximately halfway up the Reactor at 400°C and at the bottom of the Reactor at 350°C. The uptake of S is due to the precipitation of anhydrite.

SEM examination of the reacted basalt from the 400°C experiment shows that the dominant secondary phase at the bottom of the Reactor is chlorite. Further up the Reactor, complete chloritization of the rock is found. At approximately halfway up the Reactor the dominant secondary mineral changes from chlorite to smectite. This change is accompanied by the highest anhydrite content. At the top of the Reactor, smectite occurs as the dominant secondary phase, albeit only as thin coatings on the surface of relatively unreacted grains. At 350°C, the observed distribution of minerals is similar, however, the alteration only proceeded within the very bottom of the Reactor near the entry point of the fluid. This is attributed to the lower temperature and shorter time of the experiment.

The results indicate that at least three alteration fronts occurred during seawater-basalt interaction in the experiments: the dissolution of volcanic glass; a chloritization front replacing all the primary minerals (excluding Fe-Ti oxides); and an accompanying peak in anhydrite precipitation which moves with the chloritization front.

Trace element results are perhaps informative. During the distilled water experiments, some trace elements are released during glass dissolution. In the seawater-only experiments, some trace elements are released from the ZrO₂ beads. However, the trace element concentrations measured from the BSW experiments show in general lower values. The suggestion is that if these elements are entering the rock or released during glass dissolution, they are fixed during alteration of the rock.

As Na and K are essentially conservative during fluid-rock interaction, the Na/K ratio in the fluid remains unchanged. As a result, estimated temperatures using common Na/K geothermometers are inaccurate and reflect solely the input seawater composition.

Table 7.1. Parameters and results from the experiments of this study.

Parameter	BW1 400°C / 502 bar	BW2 350°C / 490 bar	BGB1 400°C / 483 bar	BGB2 350°C / 486 bar	SW1 377°C / 488 bar	SW2 342°C / 488 bar	BSW1 400°C / 488 bar	BSW2 350°C / 488 bar
Fluid	Water (distilled)	Water (distilled)	Geothermal Brine	Geothermal Brine	Seawater (natural)	Seawater (natural)	Seawater (natural)	Seawater (natural)
Rock	Basalt	Basalt	Basalt	Basalt	No Rock	No Rock	Basalt	Basalt
Total time / hrs	913.5	1144.7	853.2	907.8	546.7	381.2	659	311
Pressure Vessels used	Reactor	Reactor	Reactor	Reactor	Preheater	Preheater	Preheater and Reactor	Preheater and Reactor
Weight of Rock / g	26.2	26.6	27	26.4	-	-	26.5	26.3
Total Fluid Flux / L	0.77	1.02	0.69	0.75	0.40	0.33	1.48	1.15
Flow-rate / ml hr ⁻¹	1 - 0.5	1 - 0.5	1 - 0.5	1	1	1	1 - 1.5 - 10 - 7.5 - 5	1 - 10 - 5 - 2.5 - 1
Glass dissolution Time / hr	314	288	407	550	-	-	Cannot be determined	Cannot be determined
Estimate of Glass / mg	620	600	530	330	-	-	Cannot be determined	Cannot be determined
ΣSiO ₂ Input flux / mg	0	0	525	661	2.7	1.9	80	17
ΣSiO ₂ Output flux / mg	+769	+894	+504	+226	+17	+3.8	+2427	+2180
ΣH ₂ S Input flux / mg	0	0	0.14	0	n.a.	n.a.	0	0
ΣH ₂ S Output flux / mg	+1	+1	+0.7	+0.3	n.a.	n.a.	+0.34	+0.13
ΣSO ₄ Input flux / mg	0	0	280	305	856	746	171	298
ΣSO ₄ Output flux / mg	+0.6	+2.1	-45	-58	-814	-669	-143	-285
ΣCa Input flux / mg	0	0	2	5	152	107	125	64
ΣCa Output flux / mg	+0.4	+0.6	+0.2	-4	-121	-89	+876	+725
ΣFe Input flux / mg	0	0	0.06	0	0.04	0.03	108	109
ΣFe Output flux / mg	+0.2	+0.4	+0.009	+0.07	+25	+23	+317	+159
ΣK Input flux / mg	0	0	80	87	-	-	487	377
ΣK Output flux / mg	+5	+9	+4	+15	-	-	-5.4	+17
ΣMg Input flux / mg	0	0	0.1	0.7	450	297	832	602
ΣMg Output flux / mg	+0.1	+0.1	+0.1	-0.5	-235	-130	-657	-537
ΣNa Input flux / mg	0	0	502	543	-	-	12278	9512
ΣNa Output flux / mg	+24	+38	-18	-5	-	-	-51	-114
Maximum pH at °T	6.76	6.37	7.12	6.84	5.39	5.53	5.82	5.31
Minimum pH at °T	5.66	5.30	7.00	6.66	5.25	5.51	5.73	5.22
Maximum quench pH	9.47	9.66	7.76	7.91	3.85	3.72	4.65	4.36
Minimum quench pH	5.04	5.50	2.87	3.39	3.19	2.92	3.58	3.11
Secondary Mineralogy	Anorthite Chlorite Wollastonite Grossular Celadonite Sphene Magnetite	Anorthite Chlorite Sphene Celadonite	Anhydrite Biotite Smectite Cu-sulfide Magnetite	Anhydrite Smectite Cu-sulfide	Anhydrite Caminite Brucite	Anhydrite Caminite Brucite	Anhydrite Caminite Chlorite Calcite Ankerite Smectite Hematite Maghemite	Anhydrite Chlorite Calcite Ankerite Smectite Magnetite

Figure 7.1. Summary of the pH and major species concentrations in the water, geothermal brine and seawater experiments.

7.2. Conclusions

Eight experiments have been conducted to investigate the interaction of three different fluids with basalt at subcritical, near-supercritical, and supercritical conditions. From the results of this study, the following conclusions can be made.

I. Experimental Method

1. A novel experimental method has been developed to allow continuous flow experiments between seawater and rock substrates without the hinderance of retrograde mineral precipitation.

II. Distilled Water – basalt

1. A skarn-like Ca-silicate assemblage can result from the extraction of alkali cations from basalt by pure water at high temperature.
2. The precipitation of celadonite can occur in basalt with K-bearing glass without the addition of outside components.
3. At 400°C reaction rates are extremely fast and result in the growth of phases such as garnet even on the time scale of a short experiment.
4. The alteration mineralogy is determined by the rock.
5. There is some evidence of Cu, Co, and Mo release during devitrification of volcanic glass.

III. Geothermal brine – basalt

1. The injection of SO₄-containing geothermal brine into basalt results in the precipitation of anhydrite at both temperatures.
2. The precipitation of biotite occurred immediately upon entry of the fluid at 400°C while smectite was found at 350°C. This is due to the faster precipitation rate of biotite at higher temperature.
3. The precipitation of K-bearing secondary phases is due to the higher K concentrations in the geothermal brine.
4. Hence, the alteration mineralogy is largely determined by the fluid composition.
5. The presence of metal sulfides as precipitates suggests fixation from the fluid rather than release from the rock.

IV. Seawater – only

1. The progressive heating of seawater results in the precipitation of anhydrite, caminite and brucite.
2. The preheated seawater is in equilibrium with anhydrite, caminite and brucite upon exit from the Preheater.
3. Preheated seawater has a near-neutral pH at 350 – 400°C, however, this becomes highly acidic upon cooling.
4. Many trace elements were released from the ZrO₂ beads used in the Preheater. They are not necessarily ideal for trace element experiments.

V. Seawater – basalt

1. The seawater-basalt experiments provide the first example of flow-through experiments using natural seawater and basalt.
2. *In situ* pH values were near-neutral in the effluent samples.
3. Mass balance calculations show a maximum uptake of ~9 g 100g⁻¹ rock of Mg after complete chloritization of the basalt, at both temperatures.
4. The alteration mineralogy shows at least three alteration fronts: dissolution of volcanic glass (which passed completely through the rock in all experiments); intense chloritization which switches to smectitization and results in consumption of all Mg in the fluid; and an anhydrite precipitation front that coincides with the switch between chlorite and smectite.
5. The alteration is driven by the high Mg concentration in the fluid thus alteration mineralogy is controlled by the fluid until Mg is consumed.
6. The rate of reaction is extremely fast at both temperatures with an estimate of a few hours to fix essentially all Mg from the seawater by the rock.
7. The relative resistance of phases to alteration, from lowest to highest, is glass – olivine – clinopyroxene – plagioclase - Fe-Ti oxides. For the silicate phases this is related to their relative Al contents (except glass which is an amorphous phase and highly soluble).
8. The trace element results show that they are fixed in the altered rock and not released. This suggests that chloritization of the basalt is not the source of metals for the generation of volcanogenic massive sulfide deposits.

7.3. Further Work

The experimental method developed for this study can be applied to many geochemical problems. It is specifically applicable to fluid-rock interactions experiments using seawater as the experimental fluid due to the problem of retrograde mineral solubility. The apparatus can be used to study the thermodynamic parameters for retrograde solubility phases.

In terms of basalt – seawater experiments, further experiments for a longer period of time would greatly contribute to the understanding of how fast the alteration fronts progress through the rock. The computer modelling of fluid-rock interactions in the Reactor using geochemical/hydrological modelling software such as CHEMTOUGH would greatly enhance the understanding of the chemical gradients during alteration and confirm the results found in our experiments.

APPENDICES

Appendix A - (Chapter 2)

Chapter 2: Experimental Method

2.3.1. Unreacted basalt: mineralogy, texture and mineral chemistry

Figure A.2.1. SEM photographs of the petrographic thin section points analysed by EMPA (Fig. 2.4, Area A-E in the thesis). (a) SEM picture of point A analysed by EMPA (red rectangle); (b) enlargement of picture in (a) showing plagioclase (darker grey), clinopyroxene (lighter grey) and olivine. Oxides appear in bright white

Figure A.2.2. SEM picture of point B. Photograph shows the presence of plagioclase, clinopyroxene and olivine. Oxides appear in a bright white

Figure A.2.3. Point D. SEM photographs. (a) glass area for chemical analysis marked in red rectangle; (b) enlargement of picture in (a) showing the areas (yellow lines) with presence of glass. In (c) composite colour image of picture in (b) shows plagioclase (in green), clinopyroxene (in light red), glass (in dark red), oxides (in white) and apatite (in blue-violet) trapped within the glass

Figure A.2.4. SEM-EDS elemental map off Point D for glass analysis. d) grey scale image. In e) composite colour image combining maps for a) Al, b) Si and c) P shows plagioclase (in green), clinopyroxene (in wine colour), glass (in reddish), oxides (in white) and apatite (in blue-violet) trapped within the glass

Figure A.2.5. Point E. SEM photographs. (a) glass area for chemical analysis marked in red rectangle; (b) enlargement of picture in (a) showing areas (yellow lines) with the presence of glass; In (c) composite colour image of picture in (b) shows plagioclase (in green), clinopyroxene (in light red), glass (in dark red), oxides (in white) and apatite (in blue-violet) trapped within the glass

Figure A.2.6. SEM-EDS elemental map of Point E for glass analysis. d) grey scale image. In e) composite colour image combining maps for a) Al, b) Si and c) P shows plagioclase (in green), clinopyroxene (in wine colour), glass (in reddish), oxides (in white) and apatite (in blue-violet) trapped within the glass

Table A.2.1. Electron Microprobe Analysis (EMPA) of the petrographic thin section (Fig. 2.4. - Area A-E)

Plg	Analysis Point	Na ₂ O	MgO	SiO ₂	Al ₂ O ₃	FeO	CaO	K ₂ O	TiO ₂	Total	Glass	Analysis Point	SiO ₂	Al ₂ O ₃	Na ₂ O	MgO	TiO ₂	Cl	SO ₂	K ₂ O	CaO	MnO	FeO _(T)	P ₂ O ₅	Total			
Point B	1	2.50	0.25	49.80	32.15	0.64	15.77	0.03	0.03	101.16	Point C	1	54.94	29.23	7.00	0.12	0.11	0.00	0.00	0.12	12.26	0.02	1.01	0.00	104.81			
	2	2.52	0.27	49.51	31.87	0.72	15.45	0.03	0.05	100.41		2	54.59	28.77	7.35	0.10	0.10	0.00	0.00	0.15	11.88	0.02	0.93	0.02	103.92			
	3	2.79	0.26	50.25	31.62	0.58	14.92	0.04	0.04	100.49		3	56.93	27.10	9.61	0.05	0.10	0.00	0.01	0.31	8.42	0.00	0.87	0.03	103.42			
	4	2.69	0.25	49.60	31.84	0.67	15.04	0.04	0.07	100.20		4	52.63	30.68	5.97	0.12	0.09	0.00	0.00	0.06	13.86	0.02	0.96	0.02	104.41			
	5	1.29	0.25	45.93	34.46	0.48	18.11	0.01	0.00	100.53		5	53.70	29.72	6.38	0.11	0.10	0.00	0.00	0.12	12.89	0.01	0.96	0.00	103.98			
	6	1.21	0.25	45.71	34.48	0.46	18.14	0.01	0.01	100.27		6	57.28	27.27	9.19	0.06	0.12	0.00	0.01	0.28	9.65	0.00	0.86	0.01	104.73			
	7	1.82	0.20	47.53	33.55	0.61	17.01	0.02	0.03	100.77		7	50.16	0.96	0.25	10.51	0.82	0.00	0.00	0.05	12.05	0.52	25.75	0.13	101.19			
	8	2.17	0.23	48.43	32.90	0.62	16.22	0.02	0.02	100.60		8	73.38	14.68	6.51	0.10	0.72	0.07	0.04	3.21	2.78	0.03	1.17	0.61	103.30			
	9	2.93	0.27	50.11	31.49	0.68	14.94	0.03	0.05	100.51		9	54.79	28.82	7.72	0.09	0.13	0.00	0.00	0.15	11.67	0.00	0.96	0.02	104.35			
	10	3.19	0.24	50.77	31.08	1.02	14.10	0.07	0.06	100.54		10	59.42	3.63	1.62	6.04	0.40	0.21	0.01	0.60	4.87	0.51	25.14	0.25	102.70			
Point C	11	2.83	0.19	50.04	31.49	0.91	14.73	0.07	0.05	100.30	11	59.77	25.61	10.63	0.04	0.10	0.01	0.00	0.32	7.76	0.00	0.90	0.04	105.18				
	12	3.01	0.29	50.58	31.00	0.90	14.52	0.03	0.07	100.41	12	76.23	11.71	6.68	0.03	0.57	0.15	0.01	2.14	2.64	0.02	1.13	1.19	102.50				
	13	1.98	0.22	47.60	33.44	0.65	16.54	0.02	0.03	100.48	13	60.25	24.49	10.34	0.09	0.16	0.07	0.01	0.32	8.01	0.00	1.04	0.66	105.42				
	14	2.48	0.24	48.36	32.46	0.66	15.58	0.05	0.04	99.87	Point E	14	75.53	12.19	2.21	0.02	0.90	0.21	0.01	5.83	0.58	0.05	1.67	0.10	99.31			
	15	2.07	0.23	48.11	32.95	0.59	16.15	0.03	0.03	100.15		15	76.81	10.93	2.05	0.05	0.85	0.29	0.03	5.55	0.54	0.02	2.42	0.13	99.66			
	16	2.73	0.26	50.27	31.88	0.62	15.14	0.04	0.05	100.98		16	67.42	10.20	2.61	0.22	3.86	0.12	0.05	4.23	1.26	0.16	11.95	0.13	102.21			
	17	2.58	0.26	49.44	32.14	0.64	15.45	0.03	0.04	100.58		17	60.39	25.40	10.99	0.04	0.10	0.00	0.00	0.41	7.26	0.03	0.84	0.02	105.47			
	18	2.59	0.27	49.09	31.76	0.62	15.20	0.04	0.06	99.63	18	68.93	11.32	6.18	0.02	0.29	0.17	0.01	2.88	4.33	0.01	1.10	1.85	97.09				
	19	3.28	0.21	50.68	30.42	0.88	13.64	0.08	0.11	99.31	19	87.32	5.68	3.13	0.00	0.15	0.08	0.01	0.15	0.93	0.00	0.47	0.01	97.93				
	20	4.41	0.14	53.48	28.85	0.93	11.59	0.14	0.11	99.66	20	63.31	24.11	12.38	0.00	0.07	0.01	0.00	0.75	5.29	0.01	0.52	0.00	106.46				
	21	3.49	0.20	50.80	30.28	0.98	13.60	0.07	0.09	99.52	21	93.83	3.29	1.51	0.01	0.18	0.01	0.00	0.11	0.43	0.00	0.59	0.00	99.96				
	22	2.88	0.25	49.01	31.79	1.20	14.89	0.05	0.06	100.12	Point D	22	96.71	1.48	1.09	0.00	0.23	0.01	0.01	0.01	0.11	0.03	0.62	0.00	100.30			
	23	3.58	0.24	51.43	30.18	1.03	13.64	0.08	0.09	100.28		23	80.65	11.11	6.37	0.04	0.66	0.03	0.01	0.56	2.07	0.00	0.99	0.11	102.58			
	24	3.12	0.27	50.11	31.02	0.88	14.37	0.05	0.06	99.88		24	57.28	26.37	9.59	0.05	0.36	0.01	0.00	0.27	8.92	0.00	1.43	0.02	104.30			
average	2.67	0.24	49.44	31.88	0.75	15.20	0.04	0.05	100.28	25		68.38	23.56	8.62	0.04	0.37	0.01	0.00	1.31	6.63	0.04	1.22	0.06	110.23				
Cpx	Analysis Point	SiO ₂	Al ₂ O ₃	K ₂ O	FeO	Na ₂ O	MgO	Cr ₂ O ₃	TiO ₂	CaO	NiO	MnO	Total	26	61.23	8.97	4.37	0.10	7.43	0.12	0.10	0.68	0.98	0.12	14.63	0.03	98.76	
														27	73.50	12.62	8.82	0.02	0.74	0.04	0.02	0.68	1.90	0.00	2.59	0.00	100.92	
														28	71.88	10.70	6.87	0.04	0.47	0.21	0.83	0.67	6.57	0.05	2.13	4.34	104.77	
														29	77.64	14.01	9.66	0.01	0.39	0.23	0.03	1.43	1.74	0.03	0.90	0.11	106.17	
														30	80.89	12.17	1.60	0.02	0.61	0.27	0.25	0.67	2.13	0.02	1.25	0.32	100.19	
														31	75.89	14.39	6.91	0.01	0.33	0.06	0.03	0.64	2.90	0.00	0.83	0.05	102.04	
														32	70.85	11.43	1.77	0.53	0.42	0.29	0.04	5.37	2.20	0.05	2.76	0.54	96.26	
														33	55.00	1.95	1.37	9.03	0.59	0.07	0.02	0.23	6.55	0.51	30.67	0.33	106.33	
														34	73.91	16.66	9.91	0.02	0.23	0.24	0.00	2.60	1.84	0.03	0.79	0.01	106.25	
														35	74.29	16.36	7.21	0.01	0.11	0.08	0.01	4.93	1.26	0.02	0.64	0.01	104.92	
Point B	5	51.97	3.60	0.01	7.40	0.22	17.64	0.47	0.50	18.13	0.00	0.14	100.07	average		67.88	16.22	6.13	0.79	0.65	0.09	0.04	1.37	5.29	0.07	4.08	0.32	102.91
	6	51.47	3.66	0.01	7.70	0.17	17.50	0.52	0.55	18.13	0.01	0.21	99.93															
	7	52.58	2.00	0.00	7.15	0.23	18.83	0.32	0.36	17.67	0.00	0.14	99.27															
	8	52.82	3.38	0.00	7.68	0.21	18.10	0.44	0.41	17.46	0.02	0.07	100.59															
	9	52.65	3.10	0.00	7.24	0.22	18.03	0.40	0.40	18.16	0.04	0.16	100.39															
	10	52.42	2.86	0.02	7.12	0.23	18.02	0.42	0.38	18.46	0.02	0.21	100.15															
	11	52.57	2.82	0.03	7.27	0.23	18.24	0.48	0.37	17.94	0.04	0.10	100.08															
	12	51.68	3.97	0.01	7.62	0.22	17.30	0.56	0.61	18.13	0.00	0.20	100.30															
	13	52.62	2.81	0.01	7.07	0.22	18.13	0.40	0.35	18.32	0.01	0.12	100.06															
	average	51.98	3.37	0.01	9.41	0.30	16.71	0.37	0.53	17.35	0.03	0.19	100.24															

Table A.2.2. Average mineral compositions determined by EMPA from Table A.2.1

Oxides	average wt %	average wt %	average wt %	average wt %
Na ₂ O	2.67	0.30	0.01	6.13
MgO	0.24	16.71	36.14	0.79
SiO ₂	49.44	51.98	37.27	67.88
Al ₂ O ₃	31.88	3.37	0.04	16.22
FeO _(T)	0.75	9.41	25.03	4.08
CaO	15.20	17.35	0.28	5.29
K ₂ O	0.04	0.01	0.01	
TiO ₂	0.05	0.53	0.01	0.65
Cr ₂ O ₃		0.37	0.01	
MnO		0.19	0.35	0.07
NiO			0.13	
Cl				0.09
SO ₂				0.04
P ₂ O ₅				0.32
Total	100.28	100.22	99.28	101.56
Mineral Composition	$K_{0.002}Ca_{0.74}Na_{0.24}Fe^{2+}_{0.025}Mg_{0.016}Fe^{3+}_{0.004}Ti_{0.002}Al_{1.72}Si_{2.26}O_8$ (An ₇₆ -Ab ₂₄)			
Phase and ID	Plagioclase (bytownite)	Clinopyroxene (augite)	Mg-Olivine (forsterite)	Glass
	$Na_{0.02}Ca_{0.68}Mg_{0.92}Fe_{0.29}Mn_{0.006}Cr_{0.011}Ti_{0.015}Al_{0.07}Si_{1.91}Al_{0.09}O_6$	$Ca_{0.008}Mn_{0.008}Fe^{2+}_{0.54}Mg_{1.43}Fe^{3+}_{0.015}Al_{0.001}Si_{0.99}O_4$ (Fo ₇₂ -Fa ₂₈)		

SEM-EDS analysis of unreacted polished basalt grains

Figure A.2.7. Unreacted basalt grain. a) grey scale image. In b) composite colour image combining maps for c) Mg, d) Ca and e) Na shows plagioclase (violet), pyroxene (in turquoise), olivine (light green) and titanomagnetite (white)

Figure A.2.8. (a-c) SEM photographs of unreacted basalt grains in Fig. (A.8) and in Fig. (A.9); b-d) enlargements of pictures in (a) and (c) (red rectangles), respectively, showing plagioclase, clinopyroxene, olivine and Fe-Ti oxides

Figure A.2.9. SEM photographs for EDS analysis of unreacted grains. Analysis points are marked in blue

Table A.2.3. SEM-EDS analysis of unreacted basalt grains in Fig. A.2.9(A.10,a) and Fig. A.2.9(A.10,c)

Plg Fig. A.10,a	Analysis Point	Na ₂ O	MgO	Al ₂ O ₃	SiO ₂	CaO	TiO ₂	FeO	Total
	4	3.85		29.78	53.15	13.22			100.00
	5	3.25		30.84	51.97	13.95			100.01
	6	5.29		26.86	57.78	10.07			100.00
	7	3.28		30.52	52.57	13.63			100.00
	8	3.06		30.55	52.27	14.12			100.00
	9	3.46		30.50	52.50	13.54			100.00
	10	3.67		30.58	52.83	12.93			100.01
	Analysis Point	Na ₂ O	MgO	Al ₂ O ₃	SiO ₂	CaO	TiO ₂	FeO	Total
	28	3.61		29.91	53.30	13.18			100.00
Plg Fig. A.10,c	29	4.63		28.02	56.39	10.97			100.01
	30	3.21		30.15	52.51	14.13			100.00
	31	3.09		30.70	52.29	13.92			100.00
	32	3.15		30.47	52.35	14.03			100.00
	43	3.09		30.82	52.43	13.67			100.01
	average	3.59		29.98	53.26	13.18			100.00
Cpx Fig. A.10,a	Analysis Point	Na ₂ O	MgO	Al ₂ O ₃	SiO ₂	CaO	TiO ₂	FeO	Total
	11		15.74	2.34	53.15	18.25		10.52	100.00
	12		13.52	3.58	49.98	17.55		15.37	100.00
	13		14.65	2.46	52.89	18.46		11.54	100.00
	14		15.93	2.96	52.55	18.33		10.23	100.00
	15		15.89	2.95	52.31	18.05		10.81	100.00
	16		15.75	2.21	53.36	18.56		10.12	100.00
	17		15.54	2.62	52.80	17.72		11.31	100.00
	18		9.88	1.38	50.87	12.97		24.89	100.00
	19		15.74	2.29	53.38	18.81		9.77	100.00
Cpx Fig. A.10,c	Analysis Point	Na ₂ O	MgO	Al ₂ O ₃	SiO ₂	CaO	TiO ₂	FeO	Total
	33		15.56	2.46	52.15	17.18		12.66	100.01
	34		14.79	2.47	52.82	16.83		13.09	100.00
	35		15.83	1.80	53.56	19.00		9.81	100.00
	36		15.18	2.40	53.18	19.02		10.22	100.00
	37		15.57	2.68	52.49	18.81		10.45	100.00
	average		14.97	2.47	52.54	17.82		12.20	100.00
Ol Fig. A.10,a	Analysis Point	Na ₂ O	MgO	Al ₂ O ₃	SiO ₂	CaO	TiO ₂	FeO	Total
	21		21.22		34.40			44.38	100.00
	22		20.77		32.13			47.10	100.00
	23		29.47		37.35			33.18	100.00
	24		27.77		35.80			36.43	100.00
	Analysis Point	Na ₂ O	MgO	Al ₂ O ₃	SiO ₂	CaO	TiO ₂	FeO	Total
Ol Fig. A.10,c	38		35.62		38.29			26.08	100.00
	39		30.68		37.13			32.19	100.00
	40		33.67		38.06			28.27	100.00
	41		36.01		38.55			25.44	100.00
	average		29.40		36.46			34.13	100.00
Ox Fig. A.10,a	Analysis Point	Na ₂ O	MgO	Al ₂ O ₃	SiO ₂	CaO	TiO ₂	FeO	Total
	1						26.49	73.51	100.00
	2						26.21	73.79	100.00
	3						27.36	72.64	100.00
	20						26.61	73.39	100.00
Ox Fig. A.10,c	Analysis Point	Na ₂ O	MgO	Al ₂ O ₃	SiO ₂	CaO	TiO ₂	FeO	Total
	25						26.64	73.36	100.00
	26						26.31	73.69	100.00
	27						27.21	72.79	100.00
	44						27.16	72.84	100.00
	45						26.58	73.42	100.00
	46						26.62	73.38	100.00
	47						26.66	73.34	100.00
	average						26.71	73.29	100.00

Table A.2.4. Average mineral compositions determined by EDS from Table A.2.3

Oxides	average wt%	average wt%	average wt%	average wt%
	Na ₂ O	3.59		
	MgO		14.97	29.40
	SiO ₂	53.26	52.54	36.46
	Al ₂ O ₃	29.98	2.47	
	FeO _(T)		12.20	34.13
	CaO	13.18	17.82	
	K ₂ O			
	TiO ₂			26.71
	Total	100.01	100.00	99.99
Mineral Composition	Ca _{0.7} Na _{0.3} Al _{1.6} Si _{2.4} O ₈ (An ₇₀ -Ab ₃₀)	Ca _{0.71} Mg _{0.83} Fe _{0.38} Al _{0.8} Si _{1.97} Al _{0.03} O ₆	Mg _{1.2} Fe _{0.8} SiO ₄ (Fo ₆₀ -Fa ₄₀)	Fe ²⁺ (Fe ³⁺ ,Ti) ₂ O ₄
	Phase and ID	Plagioclase (bytownite)	Clinopyroxene (augite)	Mg-olivine (forsterite)
Titanomagnetite				

SEM examination of unreacted basalt grains

Figure A.2.10. SEM photographs of different unreacted basalt grains for the morphology study

Appendix B - (Chapter 3)

Chapter 3: Basalt-Water Reaction under Hydrothermal Conditions

3.2. Results

BW1: Basalt – water at 400°C/502 bar

Table B.3.1. Major ions compositions and complete experimental parameters (number of samples collected, T, P, time, flow rate and pH) for the BW1 at 400°C / 502 bar. *In situ* pH is the calculated pH at temperature. Analysis of major ions are reported both in mg kg⁻¹ and in mmol kg⁻¹. n.c.: not calculated

n° sample	T (°C)	P (bar)	time (hrs)	flow-rate (ml hr ⁻¹)	pH (room T)	pH (400°C)	mg kg ⁻¹											mmol kg ⁻¹														
							As	B	Ca	Fe	K	Mg	Na	SiO ₂	Al	Li	H ₂ S	Cl	SO ₄	As	B	Ca	Fe	K	Mg	Na	SiO ₂	Al	Li	H ₂ S	Cl	SO ₄
blank water (distilled)	19.6	1.0	0.0	-	7.83	5.40	< 0.015	< 0.3	0.4	< 0.08	< 0.9	0.04	< 0.8	< 0.6	< 0.15	< 0.01	< 0.01	0.1	0.07	< 0.0002	< 0.03	0.01	< 0.001	< 0.02	0.001	< 0.03	< 0.01	< 0.006	< 0.001	< 0.0003	0.004	0.001
1	19.7	502.9	24.1	1	6.79	n.c.	< 0.015	< 0.3	0.6	< 0.08	< 0.9	0.09	< 0.8	2	< 0.15	0.3	< 0.01	0.2	0.4	< 0.0002	< 0.03	0.01	< 0.001	< 0.02	0.004	< 0.03	0.03	< 0.006	0.05	< 0.0003	0.01	0.004
2	19.4	502.2	48.4	1	6.90	n.c.	< 0.015	< 0.3	0.5	< 0.08	< 0.9	0.05	< 0.8	2.4	< 0.15	0.2	< 0.01	0.1	0.4	< 0.0002	< 0.03	0.01	< 0.001	< 0.02	0.002	< 0.03	0.04	< 0.006	0.03	< 0.0003	0.003	0.004
3	19.3	501.9	72.7	1	6.48	n.c.	< 0.015	< 0.3	0.5	< 0.08	< 0.9	0.05	< 0.8	2.2	< 0.15	0.2	< 0.01	0.2	0.5	< 0.0002	< 0.03	0.01	< 0.001	< 0.02	0.002	< 0.03	0.04	< 0.006	0.02	< 0.0003	0.01	0.01
4	19.4	502.3	96.3	1	7.17	n.c.	< 0.015	< 0.3	0.4	< 0.08	< 0.9	0.09	< 0.8	2.1	< 0.15	0.1	< 0.01	0.3	0.6	< 0.0002	< 0.03	0.01	< 0.001	< 0.02	0.004	< 0.03	0.04	< 0.006	0.02	< 0.0003	0.01	0.01
5	19.6	501.8	120.4	1	6.34	n.c.	< 0.015	< 0.3	0.7	< 0.08	< 0.9	0.1	< 0.8	1.9	< 0.15	0.1	< 0.01	0.2	0.5	< 0.0002	< 0.03	0.02	< 0.001	< 0.02	0.005	< 0.03	0.03	< 0.006	0.02	< 0.0003	0.01	0.01
6	19.5	502.2	144.2	1	6.18	n.c.	< 0.015	< 0.3	0.7	< 0.08	< 0.9	0.1	< 0.8	1.8	< 0.15	0.2	< 0.01	0.2	0.5	< 0.0002	< 0.03	0.02	< 0.001	< 0.02	0.004	< 0.03	0.03	< 0.006	0.02	< 0.0003	0.01	0.005
7	402.1	502.0	167.3	1	5.04	6.76	< 0.015	< 0.3	2.5	1.9	13.3	0.5	28	1003.7	5.1	1.5	1.6	18.2	18.5	< 0.0002	0.03	0.06	0.03	0.3	0.02	1.2	16.7	0.2	0.2	0.05	0.5	0.2
8	401.2	503.0	216.7	1	6.53	6.41	< 0.015	< 0.3	1.2	1.3	6.9	0.2	14.9	1898.2	5.3	0.1	2.9	6.7	4.9	< 0.0002	< 0.03	0.03	0.02	0.2	0.009	0.6	31.6	0.2	0.01	0.09	0.2	0.05
9	400.9	502.7	240.9	1	6.58	6.23	< 0.015	< 0.3	1.3	1.1	5.8	0.2	13.5	1974.6	5.3	0.1	2.9	6	3.8	< 0.0002	< 0.03	0.03	0.02	0.1	0.01	0.6	32.9	0.2	0.01	0.08	0.2	0.04
10	400.9	502.6	264.7	1	6.93	6.35	< 0.015	< 0.3	1	1.2	5.3	0.2	13.7	1993.6	6	0.1	2.3	8.8	4	< 0.0002	< 0.03	0.02	0.02	0.1	0.009	0.6	33.2	0.2	0.01	0.07	0.2	0.04
11	400.8	502.6	288.7	1	6.93	6.34	< 0.015	< 0.3	0.8	0.4	4.7	0.1	13	1761.9	7.1	0.1	2.2	5.3	3.3	< 0.0002	< 0.03	0.02	0.01	0.1	0.006	0.6	29.3	0.3	0.01	0.06	0.1	0.03
12	401.0	502.5	312.7	1	7.04	6.16	< 0.015	< 0.3	0.8	0.4	4.4	0.1	10.3	1706.9	6.3	0.1	1.4	3.3	2.3	< 0.0002	< 0.03	0.02	0.01	0.1	0.006	0.4	28.4	0.2	0.01	0.04	0.09	0.02
13	400.9	503.2	335.9	1	7.26	6.12	< 0.015	< 0.3	0.7	0.2	4.9	0.1	9.5	1694.3	5.8	0.1	1.1	2.9	2	< 0.0002	< 0.03	0.02	0.004	0.1	0.005	0.4	28.2	0.2	0.01	0.03	0.08	0.02
14	400.7	502.7	361.8	1	7.39	6.07	< 0.015	< 0.3	0.8	0.2	5.4	0.1	10.4	1674	5.5	0.1	0.8	2.6	1.8	< 0.0002	< 0.03	0.02	0.003	0.1	0.005	0.5	27.9	0.2	0.01	0.02	0.07	0.02
15	400.5	502.4	386.2	1	7.84	6.06	< 0.015	< 0.3	0.7	0.2	5.9	0.1	12.8	1666.3	5.2	0.1	1	2.1	1.7	< 0.0002	< 0.03	0.02	0.003	0.2	0.005	0.6	27.7	0.2	0.02	0.03	0.06	0.02
16	400.5	502.5	409.5	1	8.61	5.99	< 0.015	< 0.3	0.7	0.2	6.6	0.1	17.9	1654.2	4.7	0.1	0.8	1.8	1.3	< 0.0002	< 0.03	0.02	0.004	0.2	0.005	0.8	27.5	0.2	0.02	0.02	0.05	0.01
17	400.4	502.3	434.0	1	8.84	5.91	< 0.015	< 0.3	0.8	0.2	8.3	0.2	25.7	1466	8.2	0.4	0.5	1.4	1.2	< 0.0002	< 0.03	0.02	0.004	0.2	0.006	1.1	24.4	0.3	0.05	0.01	0.04	0.01
18	400.4	502.5	458.2	1	9.14	6.03	< 0.015	0.3	0.7	0.1	14.2	0.1	36.1	1271.9	21.3	1.6	0.3	1.1	1.4	< 0.0002	0.03	0.02	0.002	0.4	0.006	1.6	21.2	0.8	0.2	0.01	0.03	0.01
19	400.3	502.1	482.1	1	9.20	5.93	< 0.015	0.3	1	0.1	11.9	0.2	38	834.7	17.2	1.5	0.3	1.2	1.2	< 0.0002	0.03	0.02	0.001	0.3	0.007	1.7	13.9	0.6	0.2	0.01	0.03	0.01
20	400.4	502.4	506.1	1	9.25	6.01	< 0.015	< 0.3	0.8	< 0.08	10.4	0.1	38.4	683.9	17.5	0.5	0.3	1	1.3	< 0.0002	0.03	0.02	< 0.001	0.3	0.005	1.7	11.4	0.6	0.07	0.01	0.03	0.01
21	400.3	502.2	530.3	1	9.36	5.92	< 0.015	< 0.3	0.6	< 0.08	10	0.1	39.2	629.9	17.5	0.4	0.3	0.7	0.8	< 0.0002	< 0.03	0.02	< 0.001	0.3	0.004	1.7	10.5	0.6	0.05	0.01	0.02	0.01
22	400.3	502.2	554.3	1	9.40	5.94	< 0.015	< 0.3	0.7	< 0.08	9.6	0.1	40.6	594.6	19	0.3	0.3	0.8	0.9	< 0.0002	< 0.03	0.02	< 0.001	0.2	0.004	1.8	9.9	0.7	0.05	0.01	0.02	0.01
23	400.3	502.3	578.3	1	9.41	6.04	< 0.015	< 0.3	0.7	< 0.08	9.0	0.1	40.5	563.4	20.2	0.3	0.3	0.9	1.3	< 0.0002	< 0.03	0.02	< 0.001	0.2	0.004	1.8	9.4	0.7	0.04	0.01	0.03	0.01
24	400.4	502.2	602.3	1	9.45	5.88	< 0.015	< 0.3	0.7	< 0.08	7.7	0.1	40.9	531.5	21.7	0.3	0.3	0.7	0.7	< 0.0002	< 0.03	0.02	< 0.001	0.2	0.004	1.8	8.8	0.8	0.04	0.01	0.02	0.01
25	400.3	502.5	626.3	1	9.47	5.67	< 0.015	< 0.3	0.8	< 0.08	6.2	0.1	42	513.4	23	0.2	0.3	0.1	0.2	< 0.0002	< 0.03	0.02	< 0.001	0.2	0.004	1.8	8.5	0.9	0.03	0.01	0.003	0.002
26	400.3	502.4	650.3	1	9.41	5.66	< 0.015	< 0.3	0.8	< 0.08	5.1	0.1	42.4	494.3	23.6	0.2	0.3	0.1	0.2	< 0.0002	< 0.03	0.02	< 0.001	0.1	0.005	1.8	8.2	0.9	0.03	0.01	0.003	0.002
27	400.1	502.4	674.6	1	9.39	5.72	< 0.015	< 0.3	0.6	< 0.08	4.4	0.1	42.3	485.7	24.1	0.2	0.3	0.1	0.2	< 0.0002	< 0.03	0.01	< 0.001	0.1	0.003	1.8	8.1	0.9	0.03	0.01	0.003	0.002
28	400.1	502.0	699.3	1	9.39	5.70	< 0.015	< 0.3	0.7	< 0.08	3.9	0.1	42.3	472.9	24.5	0.2	0.3	0.2	0.2	< 0.0002	< 0.03	0.02	< 0.001	0.1	0.003	1.8	7.9	0.9	0.03	0.01	0.006	0.002
29	400.1	502.2	722.7	1	9.35	5.67	< 0.015	< 0.3	0.8	< 0.08	3.6	0.1	42.6	471.2	24.7	0.2	0.3	0.1	0.2	< 0.0002	< 0.03	0										

Table B.3.2. Trace elements compositions and complete experimental parameters (number of samples collected, T, P, time, flow rate and pH) for the BW1 at 400°C / 502 bar. *In situ* pH is the calculated pH at temperature. Analysis of trace elements are reported in µmol kg⁻¹. n.a.: not analysed / n.c.: not calculated

n° sample	T (°C)	P (bar)	time (hrs)	flow-rate (ml hr ⁻¹)	pH (room T)	pH (400°C)	μmol kg ⁻¹													
							V	Cr	Co	Ni	Cu	Zn	Rb	Mo	Ag	Cd	Ba	Au	Pb	Mn
blank water (distilled)	19.6	1	0.0	-	7.83	5.40	< 0.002	< 0.004	< 0.002	< 0.003	< 0.0009	< 0.008	< 0.001	< 0.002	< 0.0005	< 0.0009	< 0.001	< 0.001	< 0.001	< 0.13
1	19.7	502.9	24.1	1	6.79	n.c.	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.
2	19.4	502.2	48.4	1	6.90	n.c.	< 0.002	0.1	0.01	0.6	0.2	31.5	0.05	0.3	< 0.0005	0.02	0.06	< 0.001	< 0.001	< 0.13
3	19.3	501.9	72.7	1	6.48	n.c.	< 0.002	0.003	0.01	0.3	0.2	41.6	0.1	0.2	< 0.0005	0.001	0.003	0.01	0.02	< 0.13
4	19.4	502.3	96.3	1	7.17	n.c.	< 0.002	0.04	0.01	0.3	0.003	55.5	0.04	0.1	< 0.0005	< 0.0009	0.1	< 0.001	< 0.001	< 0.13
5	19.6	501.8	120.4	1	6.34	n.c.	< 0.002	0.1	0.01	0.5	0.3	43.1	0.02	0.1	< 0.0005	< 0.0009	0.2	< 0.001	< 0.001	< 0.13
6	19.5	502.2	144.2	1	6.18	n.c.	< 0.002	0.05	0.01	0.2	0.2	37.2	0.03	0.1	< 0.0005	< 0.0009	0.2	0.02	< 0.001	< 0.13
7	402.1	502.0	167.3	1	5.04	6.76	0.7	0.7	0.2	4.4	5.2	55.8	2.1	1	< 0.0005	0.02	13.4	0.03	0.06	0.4
8	401.2	503.0	216.7	1	6.53	6.41	1	0.6	0.1	2.4	15.3	37.9	1.5	0.7	< 0.0005	0.1	1.1	0.01	0.03	0.3
9	400.9	502.7	240.9	1	6.58	6.23	1.2	0.4	0.08	2.6	12.5	23.5	1.4	0.7	< 0.0005	0.2	0.9	0.03	0.03	0.2
10	400.9	502.6	264.7	1	6.93	6.35	3	0.3	0.1	0.9	7.9	22.5	1.3	1	< 0.0005	0.04	1	0.03	0.01	0.2
11	400.8	502.6	288.7	1	6.93	6.34	2.3	0.2	0.09	0.6	8.7	6.7	1.1	1.1	< 0.0005	0.03	2	0.02	0.01	< 0.13
12	401.0	502.5	312.7	1	7.04	6.16	1.7	0.1	0.07	1.1	9.1	53	1.1	0.9	< 0.0005	0.04	3.9	< 0.001	0.09	< 0.13
13	400.9	503.2	335.9	1	7.26	6.12	1.1	0.2	0.04	0.3	7.3	13.2	1.4	0.8	< 0.0005	0.001	4.2	0.01	0.08	< 0.13
14	400.7	502.7	361.8	1	7.39	6.07	0.8	0.2	0.04	0.7	6.3	19.1	1.9	0.7	< 0.0005	0.04	3.1	0.01	0.08	< 0.13
15	400.5	502.4	386.2	1	7.84	6.06	1.3	0.1	0.04	0.6	4.3	17.8	2.4	0.6	< 0.0005	< 0.0009	1.9	0.02	0.05	< 0.13
16	400.5	502.5	409.5	1	8.61	5.99	3.5	0.1	0.03	1	4	16.6	3	0.6	< 0.0005	< 0.0009	1.2	< 0.001	0.04	< 0.13
17	400.4	502.3	434.0	1	8.84	5.91	4.6	0.1	0.03	0.8	5.6	26	3.8	0.5	< 0.0005	0.03	0.8	< 0.001	0.02	< 0.13
18	400.4	502.5	458.2	1	9.14	6.03	0.5	0.1	< 0.002	0.4	0.1	2.9	1	0.1	< 0.0005	< 0.0009	0.05	< 0.001	< 0.001	< 0.13
19	400.3	502.1	482.1	1	9.20	5.93	0.4	0.1	< 0.002	0.3	0.004	2.3	0.4	0.1	< 0.0005	< 0.0009	0.001	< 0.001	< 0.001	< 0.13
20	400.4	502.4	506.1	1	9.25	6.01	2.8	0.2	0.02	0.9	0.5	47.4	1.8	0.6	< 0.0005	0.07	0.2	0.02	0.5	< 0.13
21	400.3	502.2	530.3	1	9.36	5.92	2.9	0.1	0.04	1	0.4	38.4	1.3	0.5	< 0.0005	0.04	0.1	0.001	0.1	< 0.13
22	400.3	502.2	554.3	1	9.40	5.94	6.3	0.2	0.02	0.6	0.2	37.6	1	0.3	< 0.0005	0.01	3.2	0.02	0.2	< 0.13
23	400.3	502.3	578.3	1	9.41	6.04	15.8	0.1	0.02	0.4	0.002	28.7	0.9	0.3	< 0.0005	0.03	0.2	< 0.001	0.04	< 0.13
24	400.4	502.2	602.3	1	9.45	5.88	17.5	0.1	0.01	0.3	< 0.0009	21.2	0.8	0.3	< 0.0005	< 0.0009	0.06	< 0.001	0.06	< 0.13
25	400.3	502.5	626.3	1	9.47	5.67	18.5	0.4	0.02	0.7	< 0.0009	21.6	0.7	0.3	< 0.0005	< 0.0009	0.05	0.01	0.1	< 0.13
26	400.3	502.4	650.3	1	9.41	5.66	15.8	0.1	0.02	0.5	< 0.0009	18.2	0.6	0.2	< 0.0005	< 0.0009	0.001	< 0.001	0.1	< 0.13
27	400.1	502.4	674.6	1	9.39	5.72	10.6	0.3	0.01	0.5	2.3	27.8	0.4	0.2	< 0.0005	< 0.0009	< 0.001	< 0.001	0.1	< 0.13
28	400.1	502.0	699.3	1	9.39	5.70	10.9	0.1	0.01	0.2	0.04	29.3	0.5	0.2	< 0.0005	0.01	0.9	< 0.001	0.2	< 0.13
29	400.1	502.2	722.7	1	9.35	5.67	12.9	0.1	0.01	3.9	< 0.0009	21.8	0.5	0.2	< 0.0005	0.02	0.03	< 0.001	0.06	< 0.13
30	400.2	502.0	746.6	1	9.37	5.68	11.7	0.1	0.01	0.3	< 0.0009	18.1	0.5	0.2	< 0.0005	0.01	0.02	< 0.001	0.06	< 0.13

Figure B.3.1. EDS analysis for the study of the morphology of reacted grains collected from the bottom (Portion 1) of the Reactor after the BW1 experiment

Figure B.3.2. SEM photographs of different reacted basalt grains collected from the bottom (Portion 1) of the Reactor for the study of the morphology after the BW1 experiment

Figure B.3.3. SEM photographs (epoxy-mounted) of reacted grains collected from the bottom (Portion 1) of Reactor after the BW1 experiment for EMPA examination. Analysis points are marked in red numbers

Table B.3.3. EMPA analysis of reacted grains 1-3-4-5-7-9-10 in Figure B.3.3.

Analysis Point	Grain 1	Na ₂ O	MgO	SiO ₂	K ₂ O	CaO	TiO ₂	FeO	MnO	Cl	Al ₂ O ₃	SO ₂	P ₂ O ₅	Total
2	Wo	0.03	0.04	29.02	0.00	25.92	0.01	0.85	0.04	0.29	0.56	0.09	0.04	56.91
5	Wo	0.00	0.04	18.54	0.00	16.17	0.01	0.52	0.00	0.36	0.25	0.06	0.01	35.97
7	Ox	0.00	0.62	0.16	0.00	0.35	19.94	71.01	0.43	0.01	1.45	0.02	0.00	94.00
8	Wo	0.02	0.38	29.48	0.01	26.61	0.17	2.01	0.06	0.28	1.01	0.08	0.04	60.14
9	Wo	0.01	0.05	32.29	0.00	31.80	0.03	1.05	0.03	0.24	0.49	0.05	0.01	66.05
10	Wo	0.03	0.04	28.51	0.00	26.57	0.00	0.92	0.02	0.27	0.53	0.13	0.30	57.32
11	Wo	0.00	0.03	31.73	0.02	30.45	0.01	1.11	0.01	0.25	0.48	0.07	0.01	64.16
Analysis Point	Grain 3	Na ₂ O	MgO	SiO ₂	K ₂ O	CaO	TiO ₂	FeO	MnO	Cl	Al ₂ O ₃	SO ₂	P ₂ O ₅	Total
1	Plg	0.03	0.20	34.33	0.01	14.39	0.05	0.73	0.01	0.02	28.94	0.25	0.03	78.99
3	Plg	0.00	0.01	9.34	0.01	5.10	0.02	0.67	0.02	0.00	8.10	0.01	0.01	23.30
Analysis Point	Grain 4	Na ₂ O	MgO	SiO ₂	K ₂ O	CaO	TiO ₂	FeO	MnO	Cl	Al ₂ O ₃	SO ₂	P ₂ O ₅	Total
1	Cpx	0.11	10.31	43.97	0.06	16.02	0.49	14.10	0.50	0.07	1.52	0.26	0.04	87.43
2	Grt	0.06	0.44	21.55	0.19	19.52	1.49	10.07	0.12	0.07	4.56	1.06	0.08	59.21
3	Cpx	0.20	19.15	53.48	0.01	17.02	0.33	9.11	0.29	0.01	1.71	0.01	0.02	101.33
4	Cpx	0.00	5.51	36.38	0.02	6.79	0.17	6.33	0.27	0.13	2.79	0.30	0.07	58.75
5	Grt	0.00	0.26	18.42	0.06	18.31	0.78	4.29	0.03	0.09	4.94	0.48	0.03	47.67
6	Grt	0.00	7.22	18.40	0.04	9.39	0.41	21.91	0.55	0.05	1.66	0.35	0.03	60.02
7	Cpx	0.10	12.87	40.45	0.01	17.72	0.55	10.76	0.20	0.03	1.64	0.09	0.03	84.45
Analysis Point	Grain 5	Na ₂ O	MgO	SiO ₂	K ₂ O	CaO	TiO ₂	FeO	MnO	Cl	Al ₂ O ₃	SO ₂	P ₂ O ₅	Total
1	OI	0.02	42.54	39.81	0.00	0.30	0.02	20.11	0.29	0.00	0.04	0.02	0.02	103.18
2	Chl	0.05	20.86	27.67	0.05	0.24	0.01	11.16	0.10	0.06	7.79	0.69	0.07	68.74
3	Chl	0.06	26.92	34.78	0.06	0.20	0.02	13.27	0.08	0.02	9.63	0.20	0.04	85.27
4	Chl	0.00	18.55	29.30	0.07	0.27	0.02	11.32	0.11	0.07	9.26	0.75	0.02	69.74
5	Chl	0.03	18.59	26.80	0.04	0.09	0.02	10.31	0.10	0.06	7.11	0.56	0.01	63.71
6	Chl	0.00	27.97	35.67	0.00	0.19	0.02	16.01	0.24	0.01	1.07	0.11	0.02	81.31
7	OI	0.01	43.46	43.62	0.00	0.31	0.01	19.38	0.33	0.01	0.08	0.00	0.02	107.22
8	OI	0.01	42.49	39.85	0.00	0.30	0.00	19.87	0.27	0.00	0.04	0.00	0.02	102.86
Analysis Point	Grain 7	Na ₂ O	MgO	SiO ₂	K ₂ O	CaO	TiO ₂	FeO	MnO	Cl	Al ₂ O ₃	SO ₂	P ₂ O ₅	Total
1	Wo	0.00	0.08	29.36	0.01	28.50	0.00	0.64	0.04	0.29	0.47	0.07	0.02	59.49
2	Wo	0.01	0.11	24.84	0.00	22.86	0.02	0.67	0.07	0.31	0.38	0.08	0.01	49.37
3	Wo	0.03	0.08	18.72	0.00	18.30	0.01	0.48	0.03	0.40	0.32	0.10	0.05	38.54
4	Wo	0.00	0.13	12.98	0.00	11.41	0.04	0.52	0.00	0.47	0.36	0.13	0.05	26.09
5	Cpx	0.16	16.88	52.61	0.00	18.80	0.48	10.00	0.24	0.01	2.04	0.00	0.03	101.26
Analysis Point	Grain 9	Na ₂ O	MgO	SiO ₂	K ₂ O	CaO	TiO ₂	FeO	MnO	Cl	Al ₂ O ₃	SO ₂	P ₂ O ₅	Total
1	Wo	0.00	0.04	30.58	0.00	29.50	0.03	0.91	0.06	0.24	0.53	0.09	0.02	62.01
2	Wo	0.00	0.05	39.24	0.01	37.83	0.03	1.17	0.04	0.15	0.70	0.05	0.02	79.29
3	Wo	0.03	0.06	27.94	0.00	26.91	0.04	1.11	0.01	0.27	1.31	0.12	1.00	58.82
4	Wo	0.00	0.04	29.08	0.02	29.42	0.02	0.99	0.04	0.24	0.64	0.09	0.02	60.60
5	Wo	0.00	0.03	17.10	0.01	17.29	4.49	1.55	0.00	0.31	5.08	0.19	0.03	46.09
6	Wo	0.04	0.04	26.87	0.01	25.85	0.02	0.84	0.05	0.22	0.53	0.26	0.03	54.74
7	Wo	0.01	0.05	40.14	0.02	38.79	0.03	1.06	0.05	0.12	0.68	0.05	0.04	81.02
8	Wo	0.02	0.05	32.27	0.00	31.45	0.02	0.89	0.05	0.21	0.56	0.08	0.04	65.65
9	Wo	0.04	0.04	28.01	0.00	28.91	0.02	0.91	0.02	0.24	0.44	0.08	0.04	58.74
10	Wo	0.00	0.05	34.10	0.00	33.97	0.01	1.04	0.05	0.19	0.51	0.06	0.00	69.97
11	Wo	0.01	0.14	14.68	0.00	14.62	0.03	0.71	0.00	0.35	0.35	0.16	0.01	31.06
12	Wo	0.02	0.12	19.37	0.00	21.07	0.01	0.77	0.01	0.28	0.49	0.15	0.02	42.31
13	Wo	0.01	0.23	15.85	0.00	15.43	0.03	0.85	0.00	0.35	0.58	0.17	0.01	33.51
14	Wo	0.00	0.06	32.47	0.00	29.85	0.02	1.00	0.03	0.20	0.60	0.12	0.03	64.37
15	Wo	0.01	0.05	24.64	0.03	15.91	0.05	0.83	0.00	0.23	0.64	0.62	0.27	43.28
Analysis Point	Grain 10	Na ₂ O	MgO	SiO ₂	K ₂ O	CaO	TiO ₂	FeO	MnO	Cl	Al ₂ O ₃	SO ₂	P ₂ O ₅	Total
1	Chl	0.05	16.56	26.31	0.02	0.38	0.07	20.30	0.40	0.12	15.12	0.37	0.06	79.78
2	Chl	0.02	11.96	20.00	0.04	0.28	0.04	15.00	0.27	0.27	12.07	0.14	0.04	60.11
3	Chl	0.00	0.17	0.35	0.02	0.10	0.02	0.28	0.00	0.66	0.33	0.11	0.00	2.03
4	Chl	0.00	3.90	6.48	0.03	0.59	0.02	5.08	0.07	0.52	4.62	0.24	0.02	21.57
5	Chl	0.01	0.01	0.05	0.00	0.03	0.00	0.14	0.00	0.79	0.02	0.16	0.00	1.22
6	Plg	0.25	0.02	42.82	0.00	19.65	0.02	0.41			36.16			99.33
7	Plg	0.39	0.00	43.27	0.00	19.30	0.02	0.41			36.24			99.63
8	Plg	0.20	0.00	42.07	0.01	19.67	0.00	0.39			36.57			98.91
9	Plg	0.06	0.00	42.86	0.00	20.21	0.38	0.01			36.99			100.52
	average	Na ₂ O	MgO	SiO ₂	K ₂ O	CaO	TiO ₂	FeO	MnO	Cl	Al ₂ O ₃	SO ₂	P ₂ O ₅	
	Plg	0.16	0.04	35.78	0.01	16.39	0.08	0.44			30.50			
	Cpx	0.12	12.94	45.38	0.02	15.27	0.40	10.06	0.30	0.05	1.94	0.13	0.04	
	Grt	0.03	0.35	19.99	0.12	18.91	1.14	7.18	0.08	0.08	4.75	0.77	0.05	
	Wo	0.01	0.08	26.71	0.01	25.41	0.21	0.94	0.03	0.27	0.74	0.13	0.09	
	Chl	0.02	14.55	20.74	0.03	0.24	0.02	10.29	0.14	0.26	6.70	0.33	0.03	
	Ox	0.00	0.62	0.16	0.00	0.35	19.94	71.01	0.43	0.01	1.45	0.02	0.00	
	OI	0.01	42.83	41.10	0.00	0.30	0.01	19.79	0.30	0.00	0.05	0.01	0.02	

Table B.3.4. Average mineral compositions determined by EMPA analysis from Table B.3.3

Oxides	average wt %	average wt %	average wt %	average wt %
Na ₂ O	0.16	0.12	0.01	
MgO		12.94	42.83	0.62
SiO ₂	35.78	45.38	41.10	0.16
K ₂ O	0.01	0.02		
CaO	16.39	15.27	0.30	0.35
TiO ₂	0.08	0.40	0.01	19.94
FeO _(T)	0.44	10.06	19.79	71.01
MnO		0.30	0.30	0.43
Cl		0.05		0.01
Al ₂ O ₃	30.50	1.94	0.05	1.45
SO ₂		0.13	0.01	0.02
P ₂ O ₅		0.04	0.02	
Total	83.36	86.64	104.39	94.00
Mineral Composition	Ca _{0.975} Na _{0.017} Fe ³⁺ _{0.02} Al _{1.996} Si _{1.987} O ₈ (An ₉₈ -Ab ₂)	Na _{0.01} Ca _{0.70} Mg _{0.83} Fe ²⁺ _{0.36} Mn _{0.01} Ti _{0.01} Al _{0.01} Si _{1.96} O ₆	Ca _{0.008} Mn _{0.008} Fe ²⁺ _{0.542} Mg _{1.56} Fe ³⁺ _{0.015} Si _{0.99} O ₄ (Fo ₇₂ -Fa ₂₈)	Fe ²⁺ (Fe ³⁺ ,Ti) ₂ O ₄
Phase and ID	Plagioclase (anorthite)	Clinopyroxene (augite)	Mg-olivine (forsterite)	Oxide (titanomagnetite)

Oxides	average wt %	average wt %	average wt %
Na ₂ O	0.02	0.01	0.03
MgO	14.55	0.08	0.35
SiO ₂	20.74	26.71	19.99
K ₂ O	0.03	0.01	0.12
CaO	0.24	25.41	18.91
TiO ₂	0.02	0.21	1.14
FeO _(T)	10.29	0.94	7.18
MnO	0.14	0.03	0.08
Cl	0.26	0.27	0.08
Al ₂ O ₃	6.70	0.74	4.75
SO ₂	0.33	0.13	0.77
P ₂ O ₅	0.03	0.09	0.05
Total	53.35	54.62	53.44
Mineral Composition	K _{0.01} Na _{0.01} Ca _{0.09} Mn _{0.04} Mg _{7.22} Fe _{2.87} Ti _{0.01} Al _{1.54} Si _{6.91} Al _{1.09} O ₂₀ (OH) ₁₆ (on the basis of 28 oxygen equivalents, ignoring H ₂ O)	K _{0.001} Na _{0.004} Ca _{5.89} Mn _{0.005} Mg _{0.026} Fe _{0.17} Ti _{0.034} Si _{5.77} Al _{0.19} O ₁₈ (on the basis of 18 oxygen equivalents)	Ca _{6.32} Mn _{0.02} Fe _{1.874} Mg _{0.163} Ti _{0.267} Si _{6.235} Al _{1.747} O ₂₄ (on the basis of 24 oxygen equivalent)
Phase and ID	Chlorite	Wollastonite	Garnet (grossular)

Figure B.3.4. SEM photographs (epoxy-mounted) for EDS examination of reacted grains collected from the bottom (Portion 1) of the Reactor. Analysis points are marked in blue

Table B.3.5. EDS analysis of reacted grains in Figure B.3.4

	Analysis Point	Na ₂ O	Al ₂ O ₃	SiO ₂	CaO	Total	
Plg	42	0.40	39.00	41.42	19.18	100.00	
	48	0.30	36.37	43.57	19.77	100.00	
	50	0.00	36.72	43.07	20.21	100.00	
	62	0.00	36.40	44.22	19.38	100.00	
	63	0.00	36.87	43.43	19.70	100.00	
	64	0.29	39.51	41.27	18.93	100.00	
	65	0.00	36.52	43.21	20.28	100.00	
	66	0.00	39.89	42.07	18.04	100.00	
	68	0.33	36.30	41.67	20.67	100.00	
	69	0.32	38.94	40.96	19.78	100.00	
	70	0.00	39.78	40.18	20.04	100.00	
	71	0.00	36.70	43.19	20.11	100.00	
	76	0.00	39.37	40.81	19.83	100.00	
	78	0.00	36.77	43.02	20.21	100.00	
	79	0.00	37.13	43.50	19.37	100.00	
	80	0.00	39.25	41.87	18.88	100.00	
	81	1.05	36.50	45.40	17.06	100.00	
average		0.16	37.77	42.52	19.50		
	Analysis Point	MgO	Al ₂ O ₃	SiO ₂	CaO	FeO	Total
Cpx	2	15.04	3.65	50.79	18.34	12.18	100.00
	3	15.59	2.40	52.78	19.32	9.91	100.00
	4	12.26	2.57	55.32	18.37	11.48	100.00
	6	13.13	1.94	51.30	11.37	22.27	100.00
	8	15.97	1.59	50.38	5.31	26.76	100.00
	11	16.40	0.80	51.76	4.44	26.59	100.00
	12	16.02	2.46	52.82	18.71	9.99	100.00
	23	13.91	6.50	49.75	19.50	10.33	100.00
	24	16.26	1.98	53.17	19.50	9.08	100.00
	25	16.07	2.10	52.89	17.92	11.03	100.00
	30	14.08	2.15	55.88	20.11	7.78	100.00
	32	15.39	1.59	51.46	8.28	23.27	100.00
	33	15.92	2.77	51.70	18.71	10.89	100.00
	43	14.12	2.11	56.03	20.40	7.35	100.00
	46	13.45	2.28	55.28	20.26	8.74	100.00
	52	16.18	2.27	52.55	19.86	9.14	100.00
	56	11.59	1.92	54.70	13.59	18.20	100.00
	67	12.20	2.29	55.67	20.21	9.63	100.00
	74	14.77	1.04	51.35	4.44	28.40	100.00
	75	13.46	2.33	55.27	20.01	8.94	100.00
	87	13.62	2.21	51.00	17.00	16.17	100.00
average		14.54	2.33	52.95	15.98	14.20	
	Analysis Point	MgO	SiO ₂	FeO	Al ₂ O ₃	Total	
Ol	14	30.48	36.81	32.70	0.00	100.00	
	9	30.38	36.19	32.84	0.59	100.00	
average		30.43	36.50	32.77	0.30		
	Analysis Point	Al ₂ O ₃	SiO ₂	CaO	Total		
Wo	5	0.91	53.86	45.23	100.00		
	1	1.74	52.03	46.23	100.00		
	34	1.26	52.76	45.98	100.00		
average	35	0.00	50.69	49.31	100.00		
		0.98	52.34	46.69			
	Analysis Point	Al ₂ O ₃	SiO ₂	CaO	TiO ₂	FeO	Total
Grt	77	15.79	35.19	38.69	0.00	10.33	100.00
	82	15.70	34.73	38.30	1.58	9.69	100.00
	83	18.48	37.13	36.28	0.00	8.11	100.00
	84	11.76	35.04	39.79	0.00	13.41	100.00
	85	17.89	35.44	38.86	0.00	7.81	100.00
	91	14.90	34.83	38.84	0.00	11.44	100.00
	average	15.75	35.39	38.46	0.26	10.13	
	Analysis Point	MgO	Al ₂ O ₃	SiO ₂	FeO	Total	
Chl	55	20.68	19.21	35.27	24.84	100.00	
	57	20.94	19.73	34.40	24.93	100.00	
	58	21.32	18.73	35.84	24.11	100.00	
	61	22.72	20.04	35.23	22.01	100.00	
	86	19.54	16.40	38.00	26.05	100.00	
	88	16.10	18.60	36.05	29.24	100.00	
	89	21.06	19.69	35.00	24.24	100.00	
average		20.34	18.91	35.68	25.06		
	Analysis Point	TiO ₂	FeO	Total			
Ox	22	30.39	69.61	100.00			
	26	28.62	71.38	100.00			
	31	28.62	71.38	100.00			
	44	25.73	74.27	100.00			
average		28.34	71.66				

Table B.3.6. Average mineral compositions determined by EDS from Table B.3.5

Oxides	average wt %	average wt %	average wt %	average wt %	average wt %	average wt %	average wt %
MgO		14.54	30.43		20.34		
Na ₂ O	0.16						
Al ₂ O ₃	37.77	2.33	0.30		18.91	0.98	15.75
SiO ₂	42.52	52.95	36.50		35.68	52.34	35.39
CaO	19.50	15.98				46.69	38.46
FeO _(T)		14.20	32.77	71.66	25.06		10.13
TiO ₂				28.34			0.26
Total	99.94	100.00	100.00	100.00	99.99	100.01	100.00
Mineral Composition	Ca _{0.97} Na _{0.01} Al _{2.06} Si _{1.97} O ₈ (An ₉₉ -Ab ₁)	Ca _{0.64} Mg _{0.81} Fe _{0.44} Al _{0.1} Si _{1.98} O ₆	Mg _{1.24} Fe _{0.75} SiO ₄ (Fo ₆₂ -Fa ₃₈)	Fe ²⁺ (Fe ³⁺ ,Ti) ₂ O ₄	Mg _{5.44} Fe _{3.76} Al _{2.4} Si _{6.4} Al _{1.6} O ₂₀ (OH) ₁₆ (on the basis of 28 oxygen equivalents, ignoring H ₂ O)	Ca _{5.76} Si _{6.02} Al _{0.13} O ₁₈ (on the basis of 18 oxygen equivalents)	Ca _{6.65} Fe _{1.37} Ti _{0.03} Al _{0.71} Si _{5.71} Al _{2.29} O ₂₄ (on the basis of 24 oxygen equivalent)
Phase nd ID	Plagioclase (anorthite)	Clinopyroxene (augite)	Mg-olivine (forsterite)	Oxide (titanomagnetite)	Chlorite	Wollastonite	Garnet (grossular)

Figure B.3.5. EDS analysis of grains collected from the bottom (Portion 1) of the Reactor

Figure B.3.6. EDS analysis of grains collected from the bottom (Portion 1) of the Reactor

Figure B.3.7. EDS analysis of grains collected from the bottom (Portion 1) of the Reactor

Figure B.3.8. XRD scan showing the mineralogy of reacted grains collected on the bottom portion of the Reactor

Figure B.3.9. Quantitative XRD analysis of reacted grains collected from the bottom portion of Reactor

Figure B.3.10. SEM-EDS morphology analysis of grains collected on top (Portion 2) of the Reactor

Figure B.3.11. SEM-EDS morphology analysis of grains collected from the top (Portion 2) of the Reactor

Table B.3.7a. EDS analysis and average mineral compositions of grains in Figure B.3.11 for the celadonite

Cel (Grains Morphology Study)	Analysis Point	Na ₂ O	MgO	Al ₂ O ₃	SiO ₂	K ₂ O	FeO	Total	Oxides	average wt%
	53	1.95	12.61	12.23	41.98	5.26	25.96	99.99	Na ₂ O	2.55
	54	1.99	13.28	13.9	41.91	5.22	23.7	100.00	MgO	14.07
	55	1.50	10.40	11.95	37.90	5.81	32.43	99.99	SiO ₂	42.22
	64	2.80	16.59	12.26	46.15	2.78	19.43	100.01	Al ₂ O ₃	12.89
	66	2.65	16.80	13.89	44.74	4.18	17.74	100.00	FeO _(T)	24.03
	68	4.23	19.27	13.91	45.79	2.21	14.60	100.01		
	70	1.85	10.51	10.89	36.32	4.88	35.54	99.99	K ₂ O	4.25
	71	1.67	10.02	12.46	39.36	5.43	31.06	100.00	Total	100.02
	74	3.75	15.58	13.80	44.09	3.40	19.47	100.09		
	75	3.13	15.66	13.56	43.96	3.36	20.33	100.00		
average		2.55	14.07	12.89	42.22	4.25	24.03	100.01	Mineral	K _{0.78} Na _{0.71} Mg _{3.0} Fe _{2.9} Al _{0.23} Si _{6.05} Al _{1.95} O ₂₀ (OH) ₄
±σ		0.93	3.18	1.07	3.38	1.25	7.00		Composition	(on the basis of 22 oxygen equivalents, ignoring H ₂ O)
									Phase and ID	Celadonite (grains morphology study)

Figure B.3.12. SEM photographs (epoxy-mounted) of reacted grains collected from the top portion of Reactor for EDS examination. Analysis points are marked in blue

Figure B.3.13. SEM-EDS of an epoxy-mount polished grain collected from the top (Portion 2) of the Reactor for the mineral celadonite (points 4-5-6 in Table B.3.7b)

Figure B.3.14. SEM-EDS of an epoxy-mount polished grain collected from the top (Portion 2) of the Reactor for the mineral celadonite (points 4-5-6 in Table B.3.7b)

Table B.3.7b. EDS analysis and average mineral compositions of grains in Figure B.3.12

Plg	Analysis Point	Na ₂ O	MgO	Al ₂ O ₃	SiO ₂	CaO	TiO ₂	Total	Oxides	average wt%	average wt%	average wt%	average wt%
	139	2.10		30.52	50.40	16.98		100.00	Na ₂ O	3.87			1.08
	140	5.91		27.42	57.52	9.15		100.00	MgO		15.59	27.15	18.81
	143	4.45		26.97	58.27	10.32		100.01	SiO ₂	54.82	52.80	36.23	47.28
	144	3.75		29.16	54.20	12.90		100.01	Al ₂ O ₃	28.94	2.24		13.41
	147	3.27		30.00	52.88	13.85		100.00	FeO _(T)		14.90	36.62	16.34
	148	3.53		29.78	53.61	13.08		100.00	CaO	12.37	14.47		
	149	4.40		28.07	56.65	10.88		100.00	K ₂ O				3.10
	153	3.90		28.37	55.97	11.76		100.00					
	155	3.18		30.41	52.64	13.77		100.00					
	157	3.79		29.06	54.58	12.57		100.00	Total	100.00	100.00	100.00	100.02
	159	4.25		28.33	55.87	11.54		99.99	Mineral Composition	Ca _{0.60} Na _{0.34} Al _{1.5} Si _{2.5} O ₈ (An ₆₄ -Ab ₃₆)	Ca _{0.58} Mg _{0.87} Fe _{0.47} Al _{0.1} Si ₂ O ₆	Mg _{1.2} Fe _{0.8} SiO ₄ (Fo ₆₀ -Fa ₄₀)	K _{0.53} Na _{0.28} Mg _{3.79} Fe _{1.84} Al _{0.51} Si _{6.38} Al _{1.62} O ₂₀ (OH) ₄ (on the basis of 22 oxygen equivalents, ignoring H ₂ O)
	160	4.38		27.25	57.86	10.51	100.00						
	162	3.35		29.97	53.32	13.36	100.00						
	163	3.18		29.72	52.88	14.22	100.00						
	165	3.54		29.62	53.98	12.86		100.00	Phase and ID	Plagioclase	Clinopyroxene (augite)	Mg-olivine (forsterite)	Celadonite
	166	3.55		29.62	54.46	12.38	100.01						
	168	5.20		27.78	56.84	10.18	100.00						
average		3.87		28.94	54.82	12.37	100.00						
Cpx	Analysis Point	Na ₂ O	MgO	Al ₂ O ₃	SiO ₂	CaO	FeO	Total					
	145		15.89	3.41	52.39	18.26	10.05	100.00					
	146		15.77	2.10	53.47	18.11	10.55	100.00					
	151		14.89	4.36	52.07	19.65	9.04	100.01					
	152		16.50	1.65	53.95	12.43	15.47	100.00					
	154		17.70	0.99	52.64	4.30	24.38	100.01					
	156		12.62	1.72	50.97	10.30	24.39	100.00					
	158		14.79	1.82	53.11	16.81	13.48	100.01					
	161		15.06	2.41	52.99	19.27	10.28	100.01					
	164		15.89	2.63	53.02	18.49	9.96	99.99					
	167		13.51	2.40	52.47	16.22	15.40	100.00					
	169		18.89	1.16	53.71	5.32	20.92	100.00					
average			15.59	2.24	52.80	14.47	14.90	100.00					
Ol	Analysis Point	Na ₂ O	MgO	Al ₂ O ₃	SiO ₂	CaO	FeO	Total					
	141		25.92		35.90		38.18	100.00					
	142		28.38		36.56		35.06	100.00					
	13		33.40		38.44		28.16	100.00					
	11		30.76		38.55		30.70	100.01					
average			29.62		37.36		33.03	100.00					
Cel (Epoxy-Mount Polished Grains Study)	Analysis Point	Na ₂ O	MgO	Al ₂ O ₃	SiO ₂	K ₂ O	FeO	Total					
	4	1.40	20.85	13.66	48.73	2.07	13.30	100.01					
	10	1.02	20.25	14.06	47.20	3.35	14.12	100.00					
	7	1.00	17.23	12.63	46.46	2.77	19.91	100.00					
	6	0.97	17.46	13.30	46.82	4.11	17.34	100.00					
	5	1.03	18.27	13.40	47.19	3.19	17.02	100.10					
average		1.08	18.81	13.41	47.28	3.10	16.34	100.02					
±σ		0.18	1.65	0.53	0.87	0.75	2.66	0.04					

Mineralogy and Texture of Reacted Basalt: Basalt Block. SEM-EDS analyses - BW1: bottom (Portion 1) of the Reactor

Figure B.3.15. SEM backscatter image of the UNREACTED basalt block surface by assembling singular photographs (mosaic composition)

Figure B.3.16. SEM backscatter image of the REACTED basalt block surface by assembling singular photographs (mosaic composition)

Figure B.3.17. SEM photographs of different areas of the reacted basalt block surface

Table B.3.8. EDS analysis and average mineral compositions of pictures in Figure B.3.17.

Plg	Analysis Point	Na ₂ O	Al ₂ O ₃	SiO ₂	CaO			Total
	18	3.93	26.47	55.04	14.56			100.00
	20	6.56	27.14	56.77	9.53			100.00
	21	3.3	26.55	55.12	15.00			100.00
	37	5.32	27.32	55.66	11.71			100.00
	41	2.15	33.06	48.03	16.76			100.00
	100	6.30	28.22	55.82	9.67			100.00
	120	5.30	28.10	55.76	10.83			100.00
average		4.69	28.12	54.60	12.58			100.00

Cpx	Analysis Point	MgO	Al ₂ O ₃	SiO ₂	CaO	FeO			Total
	19	13.64	3.44	53.83	18.21	10.88			100.00
	22	16.27	4.45	51.73	16.37	11.18			100.00
	29	12.39	4.25	49.98	14.74	18.64			100.00
	38	16.19	3.31	52.22	15.25	13.03			100.00
	39	12.94	3.77	50.55	11.73	21.01			100.00
	44	12.67	3.70	50.83	16.54	16.27			100.00
	80	15.72	2.50	52.80	17.79	11.19			100.00
	117	15.89	4.11	52.39	18.47	9.13			100.00
average		14.46	3.69	51.79	16.14	13.92			100.00

Cel (reacted basalt block)	Analysis Point	Na ₂ O	MgO	Al ₂ O ₃	SiO ₂	K ₂ O	FeO	Total
	15	3.46	17.38	10.51	39.10	1.55	27.99	100.00
	26	2.42	14.93	13.80	42.93	3.57	22.35	100.00
	27	2.65	13.58	13.22	42.29	4.07	24.18	100.00
	28	3.15	16.14	14.17	44.20	3.76	18.58	100.00
	72	1.67	13.45	15.34	40.36	7.32	21.86	100.00
	2	1.96	12.71	14.67	40.81	6.92	22.94	100.00
	75	3.02	14.58	13.92	43.42	4.00	21.05	100.00
	77	2.39	12.19	12.24	38.80	4.35	30.03	100.00
	82	3.68	15.91	15.47	43.34	3.13	18.47	100.00
	83	2.76	14.98	13.77	42.87	4.34	21.29	100.00
	84	2.75	15.51	14.60	43.40	4.61	19.13	100.00
	85	1.78	10.86	13.36	38.94	5.27	29.80	100.00
	89	1.47	13.58	15.06	41.73	7.25	20.91	100.00
	90	1.07	12.05	13.55	40.00	8.38	24.95	100.00
	91	0.49	5.29	7.69	29.40	6.50	50.63	100.00
	92	3.85	16.56	16.01	43.59	3.52	16.48	100.00
	93	2.20	12.48	13.83	41.18	4.78	25.53	100.00
	94	1.00	6.03	10.41	31.05	7.24	44.26	100.00
	95	3.14	10.66	13.59	33.62	5.35	33.65	100.00
	113	2.20	13.96	13.07	43.76	4.38	22.62	100.00
	114	3.26	12.36	13.85	40.40	2.98	27.15	100.00
	115	1.75	8.78	11.53	31.81	5.78	40.35	100.00
	116	1.67	11.46	9.24	40.67	1.26	35.71	100.00
	118	0.86	11.95	12.99	42.23	7.58	24.40	100.00
average		2.28	12.81	13.16	40.00	4.91	26.85	100.00
±σ		0.93	3.02	2.01	4.25	1.90	8.59	

Ox (reacted basalt block)	Analysis Point	TiO ₂	Cr ₂ O ₃	FeO	NiO			Total
	103	23.58		76.42				100.00
	104		20.48	70.57	8.95			100.00
	105		20.81	70.79	8.40			100.00
	106		21.16	70.04	8.80			100.00
	107	27.85		70.69				100.00
	108		20.02	71.21	8.77			100.00
	109	3.46	20.11	67.68	8.75			100.00
	110		20.25	69.76	9.99			100.00
	111		20.60	71.39	8.00			100.00
	112		20.20	70.57	9.23			100.00

Oxides	average wt %	average wt %	average wt %
MgO		14.46	12.81
Na ₂ O	4.69		2.28
Al ₂ O ₃	28.12	3.69	13.16
SiO ₂	54.60	51.79	40.00
CaO	12.58	16.14	
K ₂ O			4.91
FeO _(T)		13.92	26.85
Total	99.99	100.00	100.01
Mineral formula	Ca _{0.6} Na _{0.4} Al _{1.5} Si _{2.5} O ₈ (An ₅₉ -Ab ₄₁)	Ca _{0.65} Mg _{0.81} Fe _{0.44} Al _{0.1} Si _{1.94} Al _{0.06} O ₆	K _{0.92} Na _{0.65} Mg _{2.80} Fe _{3.29} Al _{0.13} Si _{5.86} Al _{2.14} O ₂₀ (OH) ₄ (on the basis of 22 oxygen equivalents, ignoring H ₂ O)
Mineral name	Plagioclase	Clinopyroxene (augite)	Celadonite

Figure B.3.18. EDS analysis for oxides. Reacted basalt-block surface

Figure B.3.20. Quantitative XRD analysis of reacted grains collected from the top portion of Reactor

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Sample Composition

Table 1. Mineral percentages for BW1 sample was determined and then normalized to exclude zinc oxide:

	Abundance %						
	BW1 Top – 400°C 2018002709						
Anorthite	77						
Augite	23						

Margin of Error: Abundance estimates are determined through successive refinement of cell parameters; the position, width and orientation of each mineral. Values are given to the nearest whole number. The margin of error for phase concentration is proposed as follows: 0 – 10% ±10%; 10 – 50% ±5%; 50 – 100% ±2%

3.2. Results

BW2: Basalt – water at 350°C/490 bar

Table B.3.9. Major ions compositions and complete experimental parameters (number of samples collected, T, P, time, flow rate and pH) for the BW2 at 350°C / 490 bar. *In situ* pH is the calculated pH at temperature. Analysis of major ions are reported both in mg kg⁻¹ and in mmol kg⁻¹. n.c.: not calculated

n° sample	T (°C)	P (bar)	time (hrs)	flow-rate (ml hr ⁻¹)	pH (room T)	pH (350°C)	mg kg ⁻¹												mmol kg ⁻¹													
							As	B	Ca	Fe	K	Mg	Na	SiO ₂	Al	Li	H ₂ S	Cl	SO ₄	As	B	Ca	Fe	K	Mg	Na	SiO ₂	Al	Li	H ₂ S	Cl	SO ₄
blank water (distilled)	19.6	1	0.00	-	6.80	5.29	0.04	2.5	1	<0.08	3.2	0.1	6.7	2.3	<0.15	<0.01	<0.01	<0.1	<0.1	0.001	0.2	0.02	<0.001	0.08	0.004	0.3	0.04	<0.006	<0.001	<0.0003	<0.003	<0.001
1	19.4	489.5	18.3	1	7.56	n.c.	0.02	2.1	1.2	0.08	4.3	0.3	12.5	7.8	<0.15	0.02	<0.01	5.9	1.9	0.0002	0.2	0.03	0.001	0.1	0.01	0.5	0.1	<0.006	0.003	<0.0003	0.2	0.02
2	19.7	488.9	43.3	1	6.65	n.c.	0.2	1.6	1.1	<0.08	2.5	0.2	7.3	27.4	<0.15	<0.01	<0.01	0.7	0.3	0.003	0.1	0.03	<0.001	0.06	0.01	0.3	0.5	<0.006	<0.001	<0.0003	0.02	0.003
3	19.5	488.9	67.6	1	7.58	n.c.	0.3	1.3	1	<0.08	1.8	0.1	6.2	23.1	<0.15	<0.01	<0.01	0.3	<0.1	0.004	0.1	0.02	<0.001	0.05	0.004	0.3	0.4	<0.006	<0.001	<0.0003	0.01	<0.001
4	19.6	488.8	88.5	1	6.50	n.c.	0.2	1.4	1	<0.08	1.9	0.1	5.8	19.8	<0.15	<0.01	<0.01	0.2	<0.1	0.002	0.1	0.02	<0.001	0.05	0.005	0.3	0.3	<0.006	<0.001	<0.0003	0.005	<0.001
5	19.3	488.8	112.4	1	6.53	n.c.	0.1	0.7	1	0.09	3.1	0.2	<0.8	18.8	<0.15	<0.01	<0.01	0.2	<0.1	0.002	0.06	0.02	0.002	0.08	0.01	<0.03	0.3	<0.006	<0.001	<0.0003	0.005	<0.001
6	19.5	488.8	136.4	1	6.80	n.c.	0.1	0.6	1	0.09	2.6	0.2	<0.8	17.5	<0.15	<0.01	<0.01	0.2	<0.1	0.002	0.05	0.02	0.002	0.07	0.01	<0.03	0.3	<0.006	<0.001	<0.0003	0.01	<0.001
7	351.8	488.8	160.5	1	5.50	6.24	0.2	0.7	2.0	1.5	14.3	0.7	25.6	1330.1	9.7	0.09	1.3	19.9	11.6	0.003	0.07	0.05	0.03	0.4	0.03	1.1	22.1	0.4	0.01	0.04	0.6	0.1
8	350.4	488.9	184.3	1	7.13	6.37	0.1	0.7	1.5	1.2	11.2	0.4	17.5	1937.5	9	0.08	3.4	10.6	10.9	0.002	0.06	0.04	0.02	0.3	0.02	0.8	32.2	0.3	0.01	0.1	0.3	0.1
9	350.6	488.9	211.6	1	7.59	6.09	0.06	1.2	2.5	1	12.8	0.4	7.6	1891.2	9.1	0.08	4.3	7.6	8.1	0.001	0.1	0.06	0.02	0.3	0.02	0.3	31.5	0.3	0.01	0.1	0.2	0.08
10	350.2	488.9	232.8	1	8.41	6.31	0.07	0.6	1.1	1.2	10.3	0.2	20.3	1902.4	9.9	0.09	4.5	6.2	7.7	0.001	0.06	0.03	0.02	0.3	0.01	0.9	31.7	0.4	0.01	0.1	0.2	0.08
11	350.6	489.0	256.5	1	8.50	6.08	0.05	0.7	1.9	1.1	10.7	0.3	19.6	1889.0	10.6	0.09	3.8	5.6	6.4	0.001	0.07	0.05	0.02	0.3	0.01	0.9	31.4	0.4	0.01	0.1	0.2	0.07
12	350.7	488.9	280.5	1	8.59	6.16	0.05	0.7	1.7	0.9	9.6	0.2	16.8	1802.9	9.6	0.09	3.9	5.4	6.4	0.001	0.07	0.04	0.02	0.2	0.01	0.7	30	0.4	0.01	0.1	0.2	0.07
13	350.6	489.0	304.0	1	8.78	6.18	0.05	0.7	1.7	0.9	8.1	0.3	20.4	1743.3	9.9	0.1	3.1	4.5	7.1	0.001	0.06	0.04	0.02	0.2	0.01	0.9	29	0.4	0.01	0.09	0.1	0.07
14	350.2	489.0	328.3	1	8.88	6.14	0.06	0.9	1.7	0.7	8.9	0.2	25.6	1721.3	11.4	0.1	3.2	4.2	6.2	0.001	0.08	0.04	0.01	0.2	0.01	1.1	28.7	0.4	0.02	0.09	0.1	0.06
15	350.4	488.9	353.0	1	8.96	6.08	0.05	1.2	2.1	0.5	10.1	0.2	24.1	1678.5	12.9	0.1	3	3.5	6.1	0.001	0.1	0.05	0.01	0.3	0.01	1	27.9	0.5	0.02	0.09	0.1	0.06
16	350.8	489.1	378.2	1	9.07	5.79	0.04	1.4	2.9	0.5	12.1	0.3	32.6	1522.5	11.4	0.09	2.2	2.5	3.9	0.0005	0.1	0.07	0.01	0.3	0.01	1.4	25.3	0.4	0.01	0.06	0.07	0.04
17	350.7	488.9	403.6	1	9.22	5.82	0.02	0.9	2.2	0.4	12	0.2	38.4	1553.3	10.8	0.05	1.7	1.9	3	0.0003	0.08	0.05	0.01	0.3	0.01	1.7	25.9	0.4	0.01	0.05	0.05	0.03
18	350.6	489.0	424.3	1	9.39	5.50	<0.015	0.9	2	0.4	13.7	0.3	45.6	1212.3	13.6	0.03	0.9	0.8	1	<0.0002	0.08	0.05	0.01	0.3	0.01	2	20.2	0.5	0.004	0.03	0.02	0.01
19	350.4	488.9	449.2	1	9.35	5.31	0.02	0.7	1.7	0.4	15.9	0.3	50.3	766.2	21.3	0.02	0.4	0.3	<0.1	0.0003	0.07	0.04	0.01	0.4	0.01	2.2	12.8	0.8	0.003	0.01	0.01	<0.001
20	350.6	489.1	472.5	1	9.48	5.30	0.06	1.8	2.2	0.3	19.9	0.3	51.7	715.1	23.7	0.02	0.3	0.2	<0.1	0.001	0.2	0.05	0.01	0.5	0.01	2.2	11.9	0.9	0.003	0.01	0.01	<0.001
21	350.8	488.9	496.3	1	9.47	5.52	<0.015	1.5	1.5	0.3	20.8	0.3	57.5	739.6	26.8	<0.01	0.3	0.6	0.7	<0.0002	0.1	0.04	0.005	0.5	0.01	2.5	12.3	1	<0.001	0.01	0.02	0.01
22	350.7	488.9	519.3	1	9.52	5.49	0.02	1.4	1.8	0.3	19.9	0.2	51.1	676.8	26.8	<0.01	0.2	0.5	0.6	0.0003	0.1	0.05	0.01	0.5	0.01	2.2	11.3	1	<0.001	0.01	0.01	0.01
23	350.5	489.6	546.3	1	9.64	5.65	0.02	1.2	0.5	0.2	24.3	0.03	64.7	628.9	43	0.01	0.4	0.3	0.4	0.0002	0.1	0.01	0.004	0.6	0.001	2.8	10.5	1.6	0.001	0.01	0.01	0.005
24	350.5	489.6	572.4	1	9.53	5.46	0.02	1.1	1.6	0.2	19	0.2	53.1	645.3	28	0.01	0.2	0.3	0.4	0.0003	0.1	0.04	0.004	0.5	0.01	2.3	10.7	1	0.001	0.005	0.01	0.004
25	350.7	489.5	592.6	1	9.59	5.48	0.04	1.1	1.6	0.2	19.7	0.2	50.3	638.6	28.8	0.01	0.2	0.3	0.5	0.0005	0.1	0.04	0.004	0.5	0.01	2.2	10.6	1.1	0.002	0.005	0.01	0.005
26	350.9	489.5	616.8	1	9.60	5.46	<0.015	1	1.6	0.1	18.8	0.2	51	626.7	29	0.02	0.1	0.3	0.4	<0.0002	0.09	0.04	0.002	0.5	0.01	2.2	10.4	1.1	0.003	0.004	0.01	0.004
27	350.7	488.1	644.5	1	9.62	5.64	0.02	0.8	0.8	0.1	20	0.1	62.7	615.2	30.4	0.01	0.2	0.3	0.6	0.0003	0.07	0.02	0.003	0.5	0.002	2.7	10.2	1.1	0.002	0.005	0.01	0.01
28	350.4	488.6	664.5	1	9.65	5.46	<0.015	0.8	1.7	0.3	19.2	0.3	61.7	596.6	29.4	0.01	0.1	0.3	0.5	<0.0002	0.07	0.04	0.01	0.5	0.01	2.7	9.9	1.1	0.002	0.004	0.01	0.01
29	350.6	489.5	688.3	1	9.61	5.48	0.01	0.6	1.5	0.2	18.2	0.2	58	573.7	28	0.02	0.1	0.2	0.5	0.0002												

Table B.3.10. Trace elements compositions and complete experimental parameters (number of samples collected, T, P, time, flow rate and pH) for the BW2 at 350°C / 490 bar. *In situ* pH is the calculated pH at temperature. Analysis of major ions are reported in µmol kg⁻¹. n.a.: not analysed / n.c.: not calculated

n° sample	T (°C)	P (bar)	time (hrs)	flow-rate (ml hr ⁻¹)	pH (room T)	pH (350°C)	µmol kg ⁻¹													
							V	Cr	Co	Ni	Cu	Zn	Rb	Mo	Ag	Cd	Ba	Au	Pb	Mn
blank water (distilled)	19.6	1	0.0	-	6.80	5.29	< 0.001	< 0.004	< 0.002	< 0.003	< 0.0009	< 0.008	< 0.001	< 0.002	< 0.0005	< 0.0009	< 0.001	< 0.001	< 0.001	< 0.13
1	19.4	489.5	18.3	1	7.56	n.c.	< 0.001	0.07	< 0.002	n.a.	0.2	1.7	0.05	0.3	< 0.0005	< 0.0009	< 0.001	n.a.	0.006	< 0.13
2	19.7	488.9	43.3	1	6.65	n.c.	< 0.001	0.1	< 0.002	0.2	< 0.0009	12.9	0.02	0.3	< 0.0005	< 0.0009	< 0.001	n.a.	0.008	< 0.13
3	19.5	488.9	67.6	1	7.58	n.c.	< 0.001	0.05	< 0.002	0.1	n.a.	16.3	0.01	0.2	< 0.0005	< 0.0009	< 0.001	n.a.	0.04	< 0.13
4	19.6	488.8	88.5	1	6.50	n.c.	< 0.001	1.2	< 0.002	0.2	< 0.0009	5.6	0.02	0.2	< 0.0005	< 0.0009	< 0.001	n.a.	< 0.001	< 0.13
5	19.3	488.8	112.4	1	6.53	n.c.	< 0.001	0.05	< 0.002	0.2	< 0.0009	16.8	0.01	0.1	< 0.0005	< 0.0009	< 0.001	n.a.	< 0.001	< 0.13
6	19.5	488.8	136.4	1	6.80	n.c.	0.01	0.06	< 0.002	0.04	< 0.0009	5.4	0.01	0.1	< 0.0005	< 0.0009	< 0.001	n.a.	< 0.001	< 0.13
7	351.8	488.8	160.5	1	5.50	6.24	< 0.001	0.08	0.006	0.4	< 0.0009	17.2	0.3	1	0.003	< 0.0009	< 0.001	0.02	0.006	0.3
8	350.4	488.9	184.3	1	7.13	6.37	0.1	0.06	0.01	0.1	< 0.0009	14.6	0.2	0.8	< 0.0005	< 0.0009	< 0.001	0.04	0.01	0.1
9	350.6	488.9	211.6	1	7.59	6.09	0.8	0.05	< 0.002	0.1	< 0.0009	7.8	0.2	0.5	< 0.0005	< 0.0009	< 0.001	0.04	< 0.001	< 0.13
10	350.2	488.9	232.8	1	8.41	6.31	0.8	0.04	0.007	0.2	< 0.0009	1.4	0.2	0.3	< 0.0005	< 0.0009	0.09	0.03	< 0.001	0.2
11	350.6	489.0	256.5	1	8.50	6.08	1.5	0.06	0.009	0.3	< 0.0009	1.7	0.3	0.4	< 0.0005	< 0.0009	0.1	0.02	< 0.001	< 0.13
12	350.7	488.9	280.5	1	8.59	6.16	1.1	0.04	0.005	0.1	< 0.0009	16.6	0.2	0.3	0.004	< 0.0009	0.03	0.01	< 0.001	< 0.13
13	350.6	489.0	304.0	1	8.78	6.18	1.5	0.02	< 0.002	n.a.	< 0.0009	3	0.2	0.2	< 0.0005	< 0.0009	< 0.001	0.05	< 0.001	< 0.13
14	350.2	489.0	328.3	1	8.88	6.14	1.7	< 0.004	< 0.002	0.1	< 0.0009	1	0.2	0.2	< 0.0005	< 0.0009	< 0.001	0.02	< 0.001	0.1
15	350.4	488.9	353.0	1	8.96	6.08	1.5	0.03	< 0.002	0.1	< 0.0009	1.1	0.2	0.2	< 0.0005	< 0.0009	< 0.001	0.04	0.008	< 0.13
16	350.8	489.1	378.2	1	9.07	5.79	1.6	0.04	< 0.002	0.003	< 0.0009	1.1	0.2	0.2	< 0.0005	< 0.0009	< 0.001	0.02	< 0.001	< 0.13
17	350.7	488.9	403.6	1	9.22	5.82	2	0.04	0.02	0.03	< 0.0009	0.4	0.4	0.1	< 0.0005	< 0.0009	0.05	0.01	< 0.001	0.2
18	350.6	489.0	424.3	1	9.39	5.50	2.3	< 0.004	< 0.002	< 0.003	< 0.0009	2.1	1	0.2	0.007	< 0.0009	0.02	0.01	< 0.001	< 0.13
19	350.4	488.9	449.2	1	9.35	5.31	2.8	< 0.004	< 0.002	0.04	< 0.0009	1.4	1.5	0.2	< 0.0005	0.006	0.03	0.01	< 0.001	0.1
20	350.6	489.1	472.5	1	9.48	5.30	3.3	< 0.004	< 0.002	0.002	< 0.0009	0.9	0.7	0.1	< 0.0005	< 0.0009	< 0.001	0.003	< 0.001	0.1
21	350.8	488.9	496.3	1	9.47	5.52	3.2	0.03	< 0.002	0.01	< 0.0009	10.4	0.4	0.1	0.003	< 0.0009	0.04	0.02	0.33	< 0.13
22	350.7	488.9	519.3	1	9.52	5.49	3.1	0.06	< 0.002	0.1	< 0.0009	20.5	0.4	0.1	0.004	< 0.0009	0.02	0.01	n.a.	< 0.13
23	350.5	489.6	546.3	1	9.64	5.65	0.6	0.02	0.005	0.1	< 0.0009	0.4	0.03	0.004	0.003	< 0.0009	< 0.001	0.005	< 0.001	< 0.13
24	350.5	489.6	572.4	1	9.53	5.46	3.7	< 0.004	0.005	0.04	< 0.0009	9.6	0.2	0.1	< 0.0005	< 0.0009	< 0.001	0.01	0.007	< 0.13
25	350.7	489.5	592.6	1	9.59	5.48	3.7	< 0.004	0.005	0.03	< 0.0009	12.2	0.2	0.1	0.004	0.005	< 0.001	0.02	0.03	< 0.13
26	350.9	489.5	616.8	1	9.60	5.46	3.6	< 0.004	0.01	0.1	< 0.0009	10.2	0.2	0.1	0.004	< 0.0009	0.03	0.01	0.02	< 0.13
27	350.7	488.1	644.5	1	9.62	5.64	4	< 0.004	< 0.002	0.1	1.7	9.6	0.2	0.1	< 0.0005	< 0.0009	0.005	0.01	0.03	0.1
28	350.4	488.6	664.5	1	9.65	5.46	3.8	< 0.004	0.007	< 0.003	< 0.0009	7.5	0.2	0.1	< 0.0005	0.009	0.02	0.01	0.007	< 0.13
29	350.6	489.5	688.3	1	9.61	5.48	3.9	< 0.004	0.01	< 0.003	< 0.0009	7.4	0.2	0.1	< 0.0005	< 0.0009	< 0.001	0.02	< 0.001	< 0.13

Figure B.3.21. EDS analysis for the study of morphology of reacted grains collected from the bottom (Portion 1) of the Reactor

Figure B.3.22. EDS analysis for the study of morphology of reacted grains collected from the bottom portion of Reactor

Figure B.3.23. SEM photographs (epoxy-mounted) of reacted grains collected from the bottom portion of Reactor, for EMPA examination. Analysis points are marked in red numbers

Table B.3.11. EMPA analysis of grains 1-3-4-5-7-9-10 in Figure B.3.23

Analysis Point	Grain 1	Na ₂ O	MgO	SiO ₂	Al ₂ O ₃	FeO	CaO	K ₂ O	TiO ₂	Total				
1	Plg	1.05	0.00	45.21	34.78	0.33	18.13	0.01	0.03	99.55				
2	Plg	0.77	0.02	43.24	34.09	0.46	18.44	0.00	0.02	97.05				
3	Plg	0.54	5.15	47.03	23.60	4.53	18.43	0.00	0.24	99.52				
7	Plg	1.55	0.00	46.66	34.07	0.24	17.15	0.01	0.00	99.67				
9	Plg	1.18	0.05	45.51	34.59	0.67	17.88	0.00	0.02	99.91				
11	Plg	2.95	0.14	49.48	30.84	1.01	14.29	0.06	0.08	98.86				
13	Plg	0.59	6.09	47.31	22.02	11.16	13.13	0.00	0.40	100.70				
Analysis Point	Grain 2	Na ₂ O	MgO	SiO ₂	Al ₂ O ₃	FeO	CaO	K ₂ O	TiO ₂	Total				
1	Plg	0.61	0.00	44.56	36.67	0.31	19.44	0.02	0.00	101.60				
2	Plg	1.04	0.00	44.44	34.84	0.34	17.76	0.00	0.00	98.42				
4	Plg	0.68	0.00	44.86	36.55	0.38	19.23	0.00	0.01	101.71				
5	Plg	0.29	0.35	41.04	34.28	1.22	18.44	0.01	0.01	95.63				
6	Plg	0.72	0.00	42.56	34.40	0.56	18.59	0.01	0.08	96.91				
8	Plg	0.69	0.00	44.85	36.24	0.29	19.03	0.01	0.01	101.14				
9	Cpx	52.89	2.48	0.00	12.95	0.17	16.82	0.06	0.73	102.06				
10	Cpx	52.25	1.08	0.00	24.70	0.02	19.96	0.01	0.47	103.19				
11	Cpx	52.63	0.65	0.00	26.22	0.04	19.24	0.01	0.49	104.05				
12	Cpx	53.28	0.82	0.00	25.63	0.05	19.52	0.02	0.49	104.76				
13	Cpx	53.53	1.18	0.01	22.89	0.06	21.03	0.01	0.51	104.33				
14	Cpx	51.97	1.41	0.00	25.06	0.15	15.50	0.08	0.86	104.23				
15	OI	34.89	0.03	0.00	38.57	0.03	25.08	0.01	0.02	99.44				
16	OI	34.74	0.02	0.01	41.64	0.00	22.26	0.01	0.05	99.55				
17	OI	34.59	0.04	0.00	43.92	0.00	20.66	0.00	0.09	100.25				
18	OI	36.01	0.02	0.02	32.29	0.00	30.46	0.02	0.03	99.58				
Analysis Point	Grain 3	SiO ₂	Al ₂ O ₃	K ₂ O	FeO	Na ₂ O	MgO	Cr ₂ O ₃	TiO ₂	CaO	NiO	MnO	Total	
1	Cpx	53.45	2.03	0.00	10.10	0.20	17.43	0.15	0.46	17.00	0.00	0.18	100.99	
2	Cpx	52.97	1.73	0.00	16.64	0.19	17.62	0.03	0.59	12.62	0.00	0.39	102.78	
3	Cpx	49.89	1.06	0.03	24.62	0.10	12.59	0.00	1.00	11.28	0.06	0.54	101.18	
6	Cpx	53.90	2.00	0.00	10.32	0.18	17.17	0.14	0.49	17.09	0.04	0.37	101.69	
7	Cpx	51.47	2.02	0.03	12.80	0.18	16.90	0.07	0.59	16.11	0.00	0.32	100.49	
8	Cpx	52.91	2.64	0.00	10.40	0.17	16.65	0.11	0.57	17.48	0.04	0.23	101.20	
9	Cpx	50.52	1.73	0.00	20.76	0.20	13.26	0.01	1.01	13.60	0.01	0.37	101.48	
10	Cpx	51.28	1.78	0.01	19.06	0.20	14.52	0.01	0.86	13.36	0.00	0.38	101.46	
11	Cpx	50.65	0.87	0.01	30.07	0.07	14.86	0.00	0.58	5.89	0.09	0.59	103.68	
4	OI	35.69	0.01	0.00	34.63	0.01	28.54	0.00	0.04	0.32	0.20	0.43	99.87	
5	OI	34.69	0.09	0.00	35.49	0.01	27.75	0.00	0.01	0.33	0.08	0.47	98.93	
Analysis Point	Grain 5	Na ₂ O	MgO	SiO ₂	K ₂ O	CaO	TiO ₂	FeO	MnO	Cl	Al ₂ O ₃	SO ₂	P ₂ O ₅	Total
1 Line 1	Chl	0.00	12.82	26.58	0.02	0.26	0.17	24.66	0.21	0.02	11.82	0.10	0.07	76.72
2 Line 1	Chl	0.00	14.67	26.43	0.02	0.62	0.06	22.29	0.24	0.02	12.68	0.11	0.32	77.46
3 Line 1	Chl	0.00	14.74	26.99	0.03	0.22	0.06	20.50	0.24	0.02	12.06	0.16	0.06	75.08
4 Line 1	Chl	0.00	12.40	24.62	0.02	0.28	0.03	18.46	0.20	0.03	11.10	0.19	0.22	67.55
5 Line 1	Chl	0.00	13.49	25.18	0.03	0.27	0.05	18.98	0.18	0.04	11.38	0.20	0.18	69.97
6 Line 1	Chl	0.00	10.11	22.91	0.05	0.19	0.05	18.84	0.27	0.04	10.61	0.20	0.06	63.33
7 Line 1	Chl	0.01	10.76	24.21	0.06	0.19	0.04	18.37	0.28	0.05	12.23	0.19	0.04	66.44
8 Line 1	Chl	0.01	12.53	24.84	0.05	0.28	0.05	18.23	0.21	0.04	12.06	0.17	0.19	68.66
9 Line 1	Chl	0.00	13.80	22.80	0.05	0.44	0.19	17.10	0.28	0.06	12.82	0.21	0.07	67.83
10Line 1	Chl	0.01	16.52	26.19	0.04	0.14	0.12	16.84	0.28	0.03	13.86	0.14	0.07	74.24
1 Line 2	Chl	0.01	13.62	26.58	0.04	0.25	0.15	24.79	0.25	0.01	11.78	0.12	0.06	77.64
2 Line 2	Chl	0.00	11.37	22.82	0.03	0.45	0.10	22.44	0.17	0.04	11.65	0.16	0.18	69.40
3 Line 2	Chl	0.00	13.63	25.48	0.04	0.22	0.05	23.32	0.26	0.02	12.24	0.16	0.07	75.49
4 Line 2	Chl	0.00	14.08	26.29	0.01	0.18	0.06	22.67	0.20	0.03	11.66	0.13	0.07	75.40
5 Line 2	Chl	0.03	15.03	27.49	0.01	0.21	0.03	22.86	0.22	0.02	11.33	0.10	0.10	77.43
6 Line 2	Chl	0.00	14.99	26.14	0.02	0.30	0.09	21.06	0.11	0.03	12.58	0.12	0.05	75.48
7 Line 2	Chl	0.00	14.90	27.27	0.04	0.20	0.20	20.08	0.18	0.02	14.68	0.09	0.02	77.69
8 Line 2	Chl	0.00	14.05	27.43	0.05	0.18	0.14	20.34	0.25	0.02	14.14	0.08	0.05	76.72
9 Line 2	Chl	0.01	13.09	26.48	0.05	0.16	0.13	19.36	0.28	0.03	14.18	0.12	0.06	73.94
10 Line 2	Chl	0.01	14.18	28.14	0.02	0.14	0.07	20.21	0.30	0.04	16.77	0.07	0.04	79.98
Analysis Point	Grain 7	Na ₂ O	MgO	SiO ₂	K ₂ O	CaO	TiO ₂	FeO	MnO	Cl	Al ₂ O ₃	SO ₂	P ₂ O ₅	Total
1	Chl	0.00	15.10	24.16	0.02	0.11	0.10	18.71	0.32	0.04	14.91	0.17	0.03	73.67
2	Chl	0.00	16.82	27.36	0.02	0.58	0.11	20.20	0.27	0.03	14.91	0.11	0.05	80.45
3	Chl	0.00	13.95	22.69	0.00	0.29	0.25	17.20	0.23	0.05	14.88	0.18	0.03	69.75
4	Chl	0.00	20.75	28.38	0.00	0.19	0.02	14.21	0.19	0.05	9.90	0.20	0.03	73.91
5	Chl	0.00	17.82	27.80	0.02	0.18	0.03	17.64	0.22	0.04	9.84	0.14	0.04	73.77
6	Chl	0.00	20.83	29.20	0.02	0.16	0.09	12.52	0.34	0.02	15.97	0.09	0.02	79.26
7	Chl	0.00	17.01	25.66	0.00	0.06	0.08	17.21	0.27	0.07	15.85	0.14	0.03	76.37
8	Chl	0.00	17.12	24.74	0.00	0.06	0.10	17.07	0.27	0.05	15.20	0.19	0.03	74.83
9	Chl	0.00	14.00	23.10	0.01	0.10	0.04	15.84	0.23	0.05	13.82	0.29	0.05	67.54
10	Chl	0.01	21.05	33.31	0.03	0.24	0.02	21.78	0.24	0.02	12.91	0.05	0.01	89.67
11	Chl	0.00	17.16	29.80	0.02	1.02	0.00	10.47	0.09	0.03	3.74	0.07	0.67	63.07
12	Chl	0.00	15.64	27.76	0.03	0.20	0.06	20.25	0.27	0.03	14.37	0.11	0.03	78.73
13	Chl	0.00	15.22	24.58	0.00	0.09	0.07	16.69	0.28	0.06	15.43	0.24	0.06	72.73
14	Chl	0.00	15.07	25.20	0.00	0.14	0.04	18.76	0.27	0.03	13.58	0.15	0.05	73.28
15	Chl	0.00	17.05	25.62	0.02	0.05	0.09	18.19	0.28	0.03	15.49	0.10	0.04	76.95
16	Chl	0.00	18.95	31.38	0.01	0.18	0.02	19.17	0.24	0.03	10.68	0.10	0.05	80.81
17	Chl	0.00	15.18	26.55	0.01	0.13	0.06	18.05	0.25	0.05	14.14	0.17	0.07	74.67
18	Chl	0.00	12.99	22.63	0.04	0.18	0.05	17.62	0.30	0.17	14.83	0.22	0.06	69.08
19	Chl	0.02	22.75	31.04	0.06	0.36	0.02	16.87	0.07	0.02	5.68	0.08	0.03	76.98
Analysis Point	Grain 9	Na ₂ O	MgO	SiO ₂	K ₂ O	CaO	TiO ₂	FeO	MnO	Cl	Al ₂ O ₃	SO ₂	P ₂ O ₅	Total
1 Line 1	Chl	0.00	17.97	27.21	0.01	0.24	0.05	16.18	0.29	0.02	13.85	0.11	0.00	75.93
2 Line 1	Chl	0.00	17.35	30.48	0.02	0.47	0.03	17.23	0.24	0.03	10.98	0.09	0.11	77.01
3 Line 1	Chl	0.00	18.35	30.45	0.02	0.49	0.05	19.01	0.19	0.03	11.24	0.08	0.11	80.01
4 Line 1	Chl	0.02	18.30	30.95	0.04	0.32	0.04	18.21	0.23	0.02	12.40	0.08	0.00	80.61
5 Line 1	Chl	0.00	19.03	30.19	0.04	0.23	0.05	18.19	0.26	0.01	13.97	0.19	0.03	82.19
6 Line 1	Chl	0.00	19.07	30.16	0.01	0.25	0.05	17.70	0.23	0.02	12.83	0.09	0.00	80.41
7 Line 1	Chl	0.00	16.83	27.87	0.04	0.34	0.18	16.09	0.21	0.01	12.27	0.13	0.03	74.00
8 Line 1	Chl	0.06	19.67	30.16	0.05	0.33	0.16	18.55	0.23	0.01	13.22	0.08	0.00	82.51
9 Line 1	Chl	0.02	19.25	29.38	0.04	0.24	0.08	16.66	0.28	0.02	15.02	0.09	0.05	81.11
10 Line 1	Chl	0.00	16.26	25.34	0.02	0.24	0.34	20.08	0.26	0.02	14.62	0.11	0.03	77.32
11 Line 1	Chl	0.00	16.13	25.34	0.03	0.10	0.14	15.73	0.27	0.03	14.89	0.13	0.01	72.80
12 Line 1	Chl	0.00	17.89	24.63	0.01	0.08	0.06	15.93	0.36	0.03	14.14	0.11	0.03	73.26
1 Line 2	Chl	0.18	9.68	36.03	0.02	13.57	3.16	11.00	0.23	0.03	9.78	0.14	0.23	84.03
2 Line 2	Chl	0.15	9.40	36.02	0.05	9.74	1.40	12.05	0.23	0.02	6.99	0.15	0.19	76.39
3 Line 2	Chl	0.24	13.24	32.64	0.12	0.60	0.03	13.03	0					

Table B.3.12. Average mineral compositions determined by EMPA from Table B.3.11

Oxides	average wt%	average wt%	average wt%	average wt%
Na ₂ O	0.97	0.13	0.01	0.03
MgO	0.91	16.87	25.79	16.16
SiO ₂	45.13	52.24	35.10	28.44
K ₂ O	0.01	0.01	0.01	0.04
CaO	17.69	11.07	0.30	0.99
TiO ₂	0.07	0.65	0.04	0.15
FeO _(T)	1.65	19.48	37.76	17.57
MnO		0.41	0.47	0.23
Cl				0.03
Al ₂ O ₃	32.84	1.56	0.04	11.81
NiO		0.03	0.08	
Cr ₂ O ₃		0.05	0.01	
SO ₂				0.13
P ₂ O ₅				0.07
Total	99.28	102.50	99.61	75.65
Mineral Composition	Ca _{0.88} Na _{0.09} Mg _{0.06} Fe ³⁺ _{0.06} Ti _{0.002} Al _{1.8} Si _{2.1} O ₈ (An ₉₁ -Ab ₉)	Na _{0.09} Ca _{0.44} Mg _{0.93} Fe _{0.60} Mn _{0.01} Cr _{0.001} Ti _{0.18} Si _{1.93} Al _{0.07} O ₆	Ca _{0.008} Mn _{0.008} Fe ²⁺ _{0.542} Mg _{1.434} Fe ³⁺ _{0.015} Si _{0.99} Al _{0.001} O ₄ (Fo ₇₂ -Fa ₂₈)	Ca _{0.25} K _{0.01} Na _{0.01} Mn _{0.05} Mg _{5.71} Fe _{3.49} Ti _{0.03} Al _{2.05} Si _{6.75} Al _{1.25} O ₂₀ (OH) ₁₆ (on the basis of 28 oxygen equivalents, ignoring H ₂ O)
Phase and ID	Plagioclase (anorthite)	Clinopyroxene (augite)	Mg-olivine (forsterite)	Chlorite

Figure B.2.24. SEM photographs (epoxy-mounted) of reacted grains collected from the bottom portion of Reactor, for EDS examination. Analysis points are marked in blue

Table B.3.13. EDS analysis and average mineral compositions of grains in Figure B.3.24

	Analysis Point	Na ₂ O	Al ₂ O ₃	SiO ₂	CaO	Total	Oxides	average wt%	average wt%	average wt%
Plg	2	0.94	37.31	44.18	17.58	100.00	Na ₂ O	0.63		
							MgO		13.56	18.48
	11	0.83	37.86	43.15	18.16	100.00	SiO ₂	42.41	55.52	36.76
	13	0.48	39.18	42.05	18.29	100.00	Al ₂ O ₃	38.51	2.65	17.13
	14	0.67	38.74	42.95	17.63	100.00	FeO _(T)		10.09	27.63
	15	0.70	38.62	42.88	17.81	100.00	CaO	18.45	18.19	
	16	0.30	38.37	40.52	20.81	100.00	K ₂ O			
	17	0.51	38.79	42.48	18.22	100.00	TiO ₂			
	18	0.35	39.25	39.96	20.44	100.00				
	20	1.46	37.31	45.54	15.69	100.00	Total	100	100	100
	21	0.66	39.80	43.40	16.14	100.00				
	22	0.61	37.95	42.25	19.19	100.00	Mineral Composition	Ca _{0.91} Na _{0.06} Al _{2.09} Si _{1.95} O ₈	Ca _{0.71} Mg _{0.74} Fe _{0.31} Al _{0.11} Si _{2.03} O ₆	Mg _{4.99} Fe _{4.19} Al _{2.32} Si _{6.66} Al _{1.34} O ₂₀ (OH) ₁₆
	32	0.55	38.84	41.80	18.81	100.00		(An ₉₄ -Ab ₆)		(on the basis of 28 oxygen equivalents, ignoring H ₂ O)
	34	0.35	37.91	39.84	21.90	100.00				
	42	0.30	39.02	41.68	19.00	100.00	Phase and ID	Plagioclase (anorthite)	Clinopyroxene (augite)	Chlorite
	43	0.68	38.71	43.47	17.13	100.00				
average		0.63	38.51	42.41	18.45					
Cpx	Analysis Point	MgO	Al ₂ O ₃	SiO ₂	CaO	FeO	Total	<div> point n°26 [Oxides wt% and elements mass % and atomic %] FeO (wt%) 95.10 Fe: (wt%) 73.93 - (at%) 47.34 O: (wt%) 23.55 - (at%) 52.66 Fe³⁺₂Fe²⁺O₄ Oxide (magnetite?) </div>		
	3	14.02	2.14	55.62	20.07	8.14	100.00			
	4	13.51	1.78	56.30	11.96	16.45	100.00			
	19	13.40	4.26	54.64	20.80	6.90	100.00			
	29	13.30	2.40	55.50	19.93	8.87	100.00			
average		13.56	2.65	55.52	18.19	10.09				
Ox	Analysis Point	TiO ₂	FeO				Total			
	26		100.00				100.00			
Chl	Analysis Point	MgO	Al ₃ O ₃	SiO ₂	FeO		Total			
	1	11.14	19.64	32.89	36.33		100.00			
	5	13.45	15.73	33.65	37.18		100.00			
	24	25.39	20.77	37.27	16.56		100.00			
	25	18.30	19.21	34.96	27.53		100.00			
	35	27.09	12.71	43.02	17.17		100.00			
	36	17.41	19.05	36.30	27.24		100.00			
	37	16.32	13.94	37.20	32.54		100.00			
	38	17.71	14.87	38.14	29.28		100.00			
	39	18.29	15.14	39.04	27.53		100.00			
	40	18.71	19.03	34.94	27.32		100.00			
	41	19.50	18.35	36.93	25.22		100.00			
average		18.48	17.13	36.76	27.63		100.00			

Figure B.3.25. EDS analysis of grains collected from the bottom portion of Reactor

Figure B.3.26. SEM-EDS elemental maps of a reacted grain (epoxy-mounted) collected from the bottom portion of Reactor: a) grey scale image. In b), composite colour image combining maps for c) Mg, d) Ca and e) Fe shows plagioclase (blue-purple), pyroxene (turquoise), olivine, Fe-Mg- aluminosilicate (chlorite) (light green) and oxides (red)

Figure B.3.28. Quantitative XRD analysis of reacted grains collected from the bottom portion of Reactor

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Sample Composition

Table 1. Mineral percentages for BW2 sample was determined and then normalized to exclude zinc oxide:

	Abundance %						
		BW2 Bottom – 350°C 2018002710					
Anorthite		67					
Augite		29					
Kaolinite		4					

Margin of Error:

Abundance estimates are determined through successive refinement of cell parameters; the position, width and orientation of each mineral. Values are given to the nearest whole number. The margin of error for phase concentration is proposed as follows:0 – 10% ±10%; 10 – 50% ±5%; 50 – 100% ±2%

Figure B.3.29. SEM photographs for EDS analysis of the morphology of reacted grains collected on the top portion of Reactor

Table B.3.14. EDS analysis and average mineral compositions of grains in Figure B.3.29

Plg	Analysis Point	Na ₂ O	Al ₂ O ₃	SiO ₂	CaO	Total		
	69	5.27	24.92	59.96	9.85	100.00		
	70	2.41	31.26	51	15.33	100.00		
	71	5.72	28.31	56.17	9.8	100.00		
average		4.47	28.16	55.71	11.66	100.00		

Cel (Grains Morphology Study)	Analysis Point	Na ₂ O	MgO	Al ₂ O ₃	SiO ₂	K ₂ O	FeO	Total
	51	4.21	14.98	15.64	43.98	0.00	21.18	99.99
	52	1.47	11.16	16.38	41.31	2.82	26.86	100.00
	53	1.64	14.01	14.55	43.76	4.47	21.57	100.00
	55	2.24	14.33	13.25	45.86	1.46	22.86	100.00
	61	0.00	7.19	12.44	35.63	8.38	36.37	100.01
	65	0.00	10.18	18.49	39.46	6.19	25.68	100.00
	66	0.48	7.76	12.60	38.05	8.26	32.84	99.99
average		1.43	11.37	14.76	41.15	4.51	26.77	100.00
±σ		1.38	3.18	2.22	3.65	2.85	5.83	

Ttn	Analysis Point	MgO	Al ₂ O ₃	SiO ₂	CaO	TiO ₂	FeO	Total
	73	0.62	4.85	23.74	33.83	30.94	6.03	100.01
	74	0.7	6.65	29.1	28.49	32.18	2.89	100.01
average		0.66	5.75	26.42	31.16	31.56	4.46	100.01

Oxides	average wt%	average wt%	average wt%
Na ₂ O	4.47	1.43	
MgO		11.37	0.66
SiO ₂	55.71	41.15	26.42
Al ₂ O ₃	28.16	14.76	5.75
FeO _(T)		26.77	4.46
CaO	11.66		31.16
K ₂ O		4.51	
TiO ₂			31.56
Total	100.00	99.99	100.01
Mineral Composition	Ca _{0.57} Na _{0.39} Al _{1.51} Si _{2.53} O ₈ (An ₅₉ -Ab ₄₁)	K _{0.83} Na _{0.40} Mg _{2.45} Fe _{3.24} Al _{0.49} Si _{5.96} Al _{2.03} O ₂₀ (OH) ₄ (on the basis of 22 oxygen equivalents, ignoring H ₂ O)	Ca _{1.13} Fe _{0.13} Ti _{0.80} Al _{0.23} Si _{0.9} O ₅
Phase and ID	Plagioclase	Celadonite	Titanite (sphene)

Figure B.3.30. SEM photographs (epoxy-mounted) of reacted grains collected from the top portion of Reactor, for EDS analysis

Table B.3.15. EDS analysis and average mineral compositions of grain in Figure B.3.30

Plg	Analysis Point	Na ₂ O	Al ₂ O ₃	SiO ₂	CaO	Total	
	4	4.07	29.05	55.11	11.77	100.00	
Ol	Analysis Point	MgO	SiO ₂	FeO	Total		
	5	27.51	36.18	36.3	99.99		
Cel (Epoxy-Mount Study)	Analysis Point	MgO	Al ₂ O ₃	SiO ₂	K ₂ O	FeO	Total
	1	13.08	15.35	44.76	3.13	23.68	100.00
	6	15.48	13.28	47.12	1.72	22.40	100.00
	8	14.64	13.01	48.33	0.73	23.29	100.00
	average	14.40	13.88	46.74	1.86	23.12	100.00
±σ	1.22	1.28	1.82	1.21	0.66		

Oxides	average wt%	average wt%	average wt%
Na ₂ O	4.07		
MgO		27.51	14.40
SiO ₂	55.11	36.18	46.74
Al ₂ O ₃	29.05		13.88
FeO _(T)		36.30	23.12
CaO	11.77		
K ₂ O			1.86
Total	100.00	99.99	100.00
Mineral Composition	Ca _{0.60} Na _{0.34} Al _{1.5} Si _{2.5} O ₈ (An ₆₄ -Ab ₄₆)	Mg _{1.14} Fe _{0.85} SiO ₄ (Fo ₅₇ -Fa ₄₃)	K _{0.33} Mg _{2.95} Fe _{2.65} Al _{0.68} Si _{6.43} Al _{1.57} O ₂₀ (OH) ₄ (on the basis of 22 oxygen equivalents, ignoring H ₂ O)
Phase and ID	Plagioclase	Mg-olivine (forsterite)	Celadonite

Figure B.3.32. Quantitative XRD analysis of reacted grains collected from the top portion of Reactor

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Sample Composition

Table 1. Mineral percentages for BW2 sample was determined and then normalized to exclude zinc oxide:

	Abundance %					
			BW2 Top – 350°C 2018002711			
Anorthite			67			
Albite			11			
Augite			22			

Margin of Error:

Abundance estimates are determined through successive refinement of cell parameters; the position, width and orientation of each mineral. Values are given to the nearest whole number. The margin of error for phase concentration is proposed as follows:0 – 10% ±10%; 10 – 50% ±5%; 50 – 100% ±2%

Figure B.3.33. SEM backscatter image of the UNREACTIONED basalt block surface by assembling singular photographs (mosaic composition)

Figure B.3.34. SEM backscatter image of the REACTED basalt block surface by assembling singular photographs (mosaic composition)

Figure B.3.35. SEM photographs of different areas of the reacted basalt block surface

Table B.3.16. EDS analysis of points in Figure B.3.35

Plg	Analysis Point		Al ₂ O ₃	SiO ₂	CaO			Total	
	5		38.47	41.07	20.46			100.00	
	13		36.06	44.59	19.35			100.00	
	15		35.64	44.70	19.65			99.99	
	16		36.64	43.82	19.54			100.00	
	17		36.65	43.98	19.36			99.99	
	35		37.07	43.37	19.57			100.01	
Cpx	Analysis Point		MgO	Al ₂ O ₃	SiO ₂	CaO	FeO	Total	
	36		9.60	8.88	46.90	16.33	18.28	99.99	
	37		9.80	20.82	30.23	3.15	36.00	100.00	
	38		10.68	4.21	53.61	20.12	11.37	99.99	
	39		12.86	5.83	53.46	16.08	11.78	100.01	
	41		11.57	21.92	28.11	0.00	38.40	100.00	
	42		15.45	19.16	31.92	0.00	33.46	99.99	
Chl	Analysis Point		MgO	Al ₃ O ₃	SiO ₂	CaO	FeO	TiO ₂	Total
	3		16.82	24.21	32.10		26.88		100.01
	7		11.97	16.25	22.74		43.81	5.24	94.77
	8		11.14	22.84	29.80		36.21		99.99
	9		14.39	23.34	32.13		30.14		100.00
	11		15.92	22.70	28.96		32.43		100.01
	12		14.58	21.32	28.42		35.68		100.00
	32		15.43	23.60	29.86	0.83	30.28		100.00
	34		11.87	21.79	29.25		37.09		100.00

Figure B.3.36. SEM photographs of different areas of the reacted basalt block surface

Table B.3.17. EDS analysis of grain in Figure B.3.36

Plg	Analysis Point	NaO	Al ₂ O ₃	SiO ₂	CaO		Total
	28	0.58	35.12	42.24	22.06		100.00
	29	0.74	34.79	42.63	21.84		100.00
Cpx	Analysis Point	MgO	Al ₂ O ₃	SiO ₂	CaO	FeO	Total
	1	10.24	11.56	37.66	13.89	26.66	100.01
	2	7.62	23.40	32.32	6.38	30.28	100.00
	3	12.62	20.87	29.18	1.09	36.24	100.00
	4	13.28	3.83	51.79	17.79	13.31	100.00
	14	9.42	13.96	31.79	9.20	35.63	100.00
	15	13.12	21.41	31.96	3.05	30.45	99.99
	25	9.47	14.25	34.15	10.15	31.98	100.00
	26	10.90	10.17	40.96	13.75	24.22	100.00
Ox	Analysis Point	Cr ₂ O ₃	FeO	NiO	TiO ₂	FeO	Total
	13	19.73	71.91	8.35			99.99
	17	20.01	71.89	8.10			100.00
	18	19.54	71.30	9.15			99.99
	19	20.48	71.21	8.31			100.00
	20				23.72	76.28	100.00
	23				23.02	76.98	100.00
	24				21.98	78.02	100.00
Chl	Analysis Point	MgO	Al ₃ O ₃	SiO ₂	CaO	FeO	Total
	21	12.38	19.94	30.30	3.15	34.23	100.00
	27	12.84	19.68	30.00		37.48	100.00

Table B.3.18. Average of EDS analysis from Table B.3.16 and Table B.3.17

average	NaO	MgO	Al₃O₃	SiO₂	CaO	FeO
Plg	0.66		36.31	43.30	20.23	
Cpx		11.19	14.31	38.15	9.36	27.00
Chl		13.94	22.27	30.09		33.70

Table B.3.19. Average mineral compositions from Table B.3.18

Oxides	average wt%	average wt%	average wt%
Na ₂ O	0.66		
MgO		11.19	13.94
SiO ₂	43.30	38.15	30.09
Al ₂ O ₃	36.31	14.31	22.27
FeO _(T)		27.00	33.70
CaO	20.23	9.36	
Total	100.50	100.01	100.00
Mineral Composition	Ca _{0.99} Na _{0.06} Al _{1.96} Si _{1.99} O ₈ (An ₉₄ -Ab ₆)	Ca _{0.399} Mg _{0.663} Fe _{0.898} Al _{0.188} Si _{1.517} Al _{0.483} O ₆	Mg _{3.79} Fe _{5.58} Al _{2.36} Si _{5.66} Al _{2.34} O ₂₀ (OH) ₁₆ (on the basis of 28 oxygen equivalents, ignoring H ₂ O)
Phase and ID	Plagioclase (anorthite)	Clinopyroxene (augite)	Chlorite

3.3. Discussion

Elements Flux Calculation

Table B.3.20. BW1 experiment (400°C / 502 bar). Elements flux calculation and amount of glass dissolved

	Time	Total Time	Time	Reactor Temp	Pressure	SiO ₂	Cl	K	SO ₄	H ₂ S	Ca	Na	Mg	Fe	Volume*	SiO ₂ Flux	diff. Cl	Cl Flux	K Flux	diff. SO ₄	SO ₄ Flux	H ₂ S Flux	diff. Ca	Ca Flux	Na Flux	diff. Mg	Mg Flux	Fe Flux		
		day	day	°C	bar	mg kg ⁻¹	mg kg ⁻¹	mg kg ⁻¹	mg kg ⁻¹	mg kg ⁻¹	mg kg ⁻¹	mg kg ⁻¹	mg kg ⁻¹	mg kg ⁻¹	L	mg	mg kg ⁻¹	mg	mg	mg kg ⁻¹	mg	mg	mg kg ⁻¹	mg	mg	mg kg ⁻¹	mg	mg	mg	
Blank		0	0	room T	1	< 0.6	0.14	< 0.9	0.07	< 0.01	0.39	< 0.8	0.04	< 0.08																SiO ₂ Flux Area for subtraction
1	10:17:00	1.0		room T	1																									
2	10:40:00	2.02	1.02	room T	1																									
3	11:00:00	3.03	1.01	room T	1																									
4	10:40:00	4.02	0.99	room T	1																									
5	10:45:00	5.02	1.00	room T	1																									
6	10:30:00	6.01	0.99	room T	1																									
7	9:40:00	6.97	0.97	400	502	1003.70	18.21	13.27	1.64	18.53	2.49	28.03	0.49	1.87	0.023	23.3	18.07	0.419	0.31	1.57	0.036	0.429	2.099	0.049	0.649	0.452	0.010	0.043	11.2	
8	11:10:00	9.04	2.06	400	502	1898.24	6.74	6.88	2.90	4.91	1.16	14.88	0.22	1.26	0.050	94.0	6.60	0.327	0.34	2.83	0.140	0.243	0.768	0.038	0.737	0.180	0.009	0.062	11.2	
9	11:15:00	10.07	1.03	400	502	1974.56	5.97	5.78	2.86	3.82	1.29	13.48	0.25	1.14	0.025	49.0	5.83	0.145	0.14	2.79	0.069	0.095	0.898	0.022	0.335	0.207	0.005	0.028	11.2	
10	11:00:00	11.07	0.99	400	502	1993.63	8.78	5.32	2.25	4.01	0.95	13.74	0.23	1.24	0.024	47.5	8.64	0.206	0.13	2.18	0.052	0.096	0.560	0.013	0.328	0.189	0.005	0.029	11.2	
11	11:00:00	12.07	1.00	400	502	1761.91	5.26	4.72	2.15	3.29	0.79	13.02	0.15	0.45	0.024	42.3	5.12	0.123	0.11	2.08	0.050	0.079	0.405	0.010	0.312	0.108	0.003	0.011	11.2	
12	11:00:00	13.07	1.00	400	502	1706.92	3.35	4.36	1.38	2.27	0.75	10.28	0.15	0.36	0.024	41.0	3.21	0.077	0.10	1.31	0.031	0.054	0.364	0.009	0.247	0.106	0.003	0.009	11.2	
13	10:15:00	14.03	0.97	400	502	1694.33	2.91	4.94	1.14	2.00	0.73	9.53	0.12	0.24	0.023	39.4	2.77	0.064	0.11	1.07	0.025	0.046	0.335	0.008	0.222	0.080	0.002	0.006	11.2	
14	12:10:00	15.11	1.08	400	502	1673.99	2.59	5.39	0.77	1.79	0.75	10.43	0.12	0.16	0.026	43.4	2.45	0.063	0.14	0.70	0.018	0.047	0.363	0.009	0.270	0.080	0.002	0.004	11.2	
15	12:30:00	16.17	1.06	400	502	1666.32	2.09	5.90	0.98	1.69	0.72	12.75	0.12	0.19	0.025	42.2	1.95	0.049	0.15	0.91	0.023	0.043	0.333	0.008	0.323	0.077	0.002	0.005	11.2	
16	11:40:00	17.13	0.97	400	502	1654.21	1.84	6.64	0.77	1.35	0.71	17.86	0.12	0.20	0.023	38.3	1.70	0.039	0.15	0.70	0.016	0.031	0.322	0.007	0.414	0.077	0.002	0.005	11.2	
17	12:10:00	18.20	1.06	400	502	1466.00	1.39	8.29	0.50	1.18	0.85	25.69	0.15	0.23	0.026	37.4	1.25	0.032	0.21	0.43	0.011	0.030	0.456	0.012	0.655	0.111	0.003	0.006	11.2	
18	12:25:00	19.25	1.05	400	502	1271.92	1.09	14.21	0.33	1.42	0.71	36.07	0.14	0.09	0.025	32.1	0.95	0.024	0.36	0.26	0.007	0.036	0.323	0.008	0.911	0.098	0.002	0.002	11.2	
19	12:15:00	20.21	0.96	400	502	834.74	1.17	11.92	0.28	1.25	0.96	37.96	0.17	0.06	0.023	19.3	1.03	0.024	0.28	0.21	0.005	0.029	0.574	0.013	0.877	0.132	0.003	0.001	11.2	
20	12:15:00	21.21	1.00	400	502	683.88	1.02	10.40	0.31	1.33	0.80	38.40	0.13	< 0.08	0.024	16.4	0.88	0.021	0.25	0.24	0.006	0.032	0.410	0.010	0.922	0.087	0.002		11.2	
21	12:30:00	22.21	1.00	400	502	629.92	0.70	9.97	0.32	0.80	0.61	39.17	0.09	< 0.08	0.024	15.1	0.56	0.013	0.24	0.25	0.006	0.019	0.225	0.005	0.940	0.053	0.001		11.2	
22	12:30:00	23.21	1.00	400	502	594.62	0.78	9.63	0.32	0.92	0.73	40.58	0.10	< 0.08	0.024	14.3	0.64	0.015	0.23	0.25	0.006	0.022	0.335	0.008	0.974	0.059	0.001		11.2	
23	12:30:00	24.21	1.00	400	502	563.40	0.89	8.97	0.34	1.32	0.75	40.51	0.10	< 0.08	0.024	13.5	0.75	0.018	0.22	0.27	0.007	0.032	0.356	0.009	0.972	0.059	0.001		11.2	
24	12:30:00	25.21	1.00	400	502	531.51	0.70	7.72	0.33	0.70	0.70	40.87	0.09	< 0.08	0.024	12.8	0.56	0.013	0.19	0.26	0.006	0.017	0.311	0.007	0.981	0.049	0.001		11.2	
25	12:30:00	26.21	1.00	400	502	513.41	0.10	6.20	0.34	0.18	0.78	42.02	0.09	< 0.08	0.024	12.3	< 0.1		0.15	0.27	0.006	0.004	0.391	0.009	1.008	0.054	0.001		11.2	
26	12:30:00	27.21	1.00	400	502	494.32	0.10	5.06	0.30	0.18	0.78	42.35	0.11	< 0.08	0.024	11.9	< 0.1		0.12	0.23	0.006	0.004	0.390	0.009	1.016	0.072	0.002		11.2	
27	12:43:00	28.22	1.01	400	502	485.73	0.11	4.40	0.29	0.19	0.59	42.32	0.07	< 0.08	0.024	11.8	< 0.1		0.11	0.22	0.005	0.005	0.201	0.005	1.025	0.026	0.001		11.2	
28	13:31:00	29.23	1.01	400	502	472.86	0.22	3.93	0.29	0.20	0.68	42.32	0.08	< 0.08	0.024	11.5	< 0.1		0.10	0.22	0.005	0.005	0.289	0.007	1.025	0.037	0.001		11.2	
29	12:50:00	30.20	0.97	400	502	471.20	0.11	3.61	0.31	0.20	0.77	42.60	0.10	< 0.08	0.023	11.0	< 0.1		0.08	0.24	0.006	0.005	0.378	0.009	0.993	0.059	0.001		11.2	
30	12:45:00	31.20	1.00	400	502	466.64	0.11	3.39	0.36	0.21	0.72	42.73	0.09	< 0.08	0.024	11.2	< 0.1		0.08	0.29	0.007	0.005	0.332	0.008	1.022	0.055	0.001		11.2	
31	11:10:00	32.13	0.93	400	502	461.72	0.11	3.17	0.38	0.21	0.81	42.09	0.11	< 0.08	0.022	10.4	< 0.1		0.07	0.31	0.007	0.005	0.416	0.009	0.944	0.070	0.002		11.2	
32	13:05:00	33.21	1.08	400	502	457.55	0.12	3.39	0.32	0.22	0.72	42.85	0.08	< 0.08	0.026	11.9	< 0.1		0.09	0.25	0.006	0.006	0.325	0.008	1.111	0.035	0.001		11.2	
33	13:15:00	34.26	1.05	400	502	447.39	0.12	3.16	0.37	0.22	0.82	42.24	0.12	0.25	0.025	11.3	< 0.1		0.08	0.30	0.008	0.005	0.432	0.011	1.063	0.080	0.002	0.006	11.2	
34 (48 hrs)	12:12:00	36.22	1.96	400	502	463.39	0.12	2.95	0.40	0.23	0.83	41.33	0.11	< 0.08	0.047	21.8	< 0.1		0.14	0.33	0.016	0.011	0.439	0.021	1.941	0.065	0.003		21.8	
34 (24 hrs)																10.9														
34 (24 hrs)																10.9	</													

Table B.3.21. BW2 experiment (350°C / 490 bar). Elements flux calculation and amount of glass dissolved

Sample No.	Time	Total Time	Time	Reactor Temp	Pressure	SiO ₂ mg kg ⁻¹	Cl mg kg ⁻¹	K mg kg ⁻¹	SO ₄ mg kg ⁻¹	H ₂ S mg kg ⁻¹	Ca mg kg ⁻¹	Na mg kg ⁻¹	Mg mg kg ⁻¹	Fe mg kg ⁻¹	Volume* L		diff. SiO ₂ mg kg ⁻¹	SiO ₂ Flux mg	Cl Flux mg	diff. K mg kg ⁻¹	K Flux mg	SO ₄ Flux mg	H ₂ S Flux mg	diff. Ca mg kg ⁻¹	Ca Flux mg	diff. Na mg kg ⁻¹	Na Flux mg	diff. Mg mg kg ⁻¹	Mg Flux mg	Fe Flux mg	SiO ₂ Flux Area for subtraction	
		day	day	°C	bar																											
Blank		0	0	room T	1	2.34	< 0.1	3.17	< 0.1	< 0.01	0.96	6.67	0.10	< 0.08																		
1	10:15:00	1.0		room T	1																											
2	12:20:00	2.1	1.1	room T	1																											
3	12:35:00	3.1	1.1	room T	1																											
4	9:30:00	4.0	0.9	room T	1																											
5	9:25:00	5.0	1.0	room T	1																											
6	9:25:00	6.0	1.0	room T	1																											
7	9:30:00	7.0	1.0	350	490	1330.1	19.88	14.32	11.64	1.30	2.03	25.63	0.68	1.50	0.024	32.03	1327.81	31.98	0.479	11.15	0.27	0.280	0.031	1.07	0.026	18.961	0.457	0.577	0.014	0.036	11.7	
8	9:20:00	8.0	1.0	350	490	1937.5	10.55	11.24	10.94	3.43	1.46	17.54	0.39	1.15	0.024	46.18	1935.15	46.12	0.251	8.07	0.19	0.261	0.082	0.50	0.012	10.866	0.259	0.287	0.007	0.027	11.7	
9	12:35:00	9.1	1.1	350	490	1891.2	7.61	12.79	8.09	4.30	2.53	7.56	0.41	0.95	0.027	51.54	1888.87	51.47	0.207	9.62	0.26	0.220	0.117	1.57	0.043	0.893	0.024	0.310	0.008	0.026	11.7	
10	9:45:00	10.0	0.9	350	490	1902.4	6.22	10.26	7.74	4.52	1.11	20.34	0.20	1.18	0.021	40.27	1900.08	40.22	0.132	7.09	0.15	0.164	0.096	0.15	0.003	13.670	0.289	0.098	0.002	0.025	11.7	
11	9:30:00	11.0	1.0	350	490	1889.0	5.59	10.69	6.37	3.81	1.95	19.56	0.31	1.06	0.024	44.86	1886.71	44.81	0.133	7.52	0.18	0.151	0.090	0.99	0.023	12.887	0.306	0.209	0.005	0.025	11.7	
12	9:30:00	12.0	1.0	350	490	1802.9	5.44	9.59	6.44	3.87	1.70	16.78	0.22	0.87	0.024	43.27	1800.59	43.21	0.131	6.42	0.15	0.155	0.093	0.74	0.018	10.106	0.243	0.117	0.003	0.021	11.7	
13	9:00:00	13.0	1.0	350	490	1743.3	4.52	8.15	7.06	3.13	1.68	20.41	0.27	0.92	0.024	40.97	1740.92	40.91	0.106	4.98	0.12	0.166	0.074	0.72	0.017	13.736	0.323	0.175	0.004	0.022	11.7	
14	9:15:00	14.0	1.0	350	490	1721.3	4.23	8.95	6.18	3.23	1.66	25.64	0.20	0.70	0.024	41.74	1718.99	41.69	0.103	5.78	0.14	0.150	0.078	0.70	0.017	18.969	0.460	0.102	0.002	0.017	11.7	
15	10:00:00	15.0	1.0	350	490	1678.5	3.47	10.11	6.10	3.02	2.11	24.10	0.21	0.51	0.025	41.54	1676.14	41.48	0.086	6.94	0.17	0.151	0.075	1.15	0.028	17.426	0.431	0.105	0.003	0.013	11.7	
16	11:10:00	16.1	1.0	350	490	1522.5	2.53	12.13	3.85	2.19	2.87	32.59	0.32	0.53	0.025	38.32	1520.13	38.26	0.064	8.96	0.23	0.097	0.055	1.91	0.048	25.916	0.652	0.221	0.006	0.013	11.7	
17	12:35:00	17.1	1.1	350	490	1553.3	1.92	12.03	2.98	1.70	2.16	38.43	0.20	0.37	0.025	39.48	1550.99	39.42	0.049	8.86	0.23	0.076	0.043	1.20	0.030	31.759	0.807	0.097	0.002	0.009	11.7	
0.0	9:15:00	18.0	0.9	350	490	1212.3	0.78	13.67	0.95	0.87	2.04	45.61	0.29	0.39	0.021	25.05	1209.94	25.01	0.016	10.50	0.22	0.020	0.018	1.08	0.022	38.937	0.805	0.186	0.004	0.008	11.7	
19	10:10:00	19.1	1.1	350	490	766.2	0.31	15.95	0.02	0.39	1.69	50.28	0.25	0.38	0.026	19.86	763.82	19.80	0.008	12.78	0.33	0.001	0.010	0.73	0.019	43.605	1.130	0.150	0.004	0.010	11.7	
20	9:30:00	20.1	1.0	350	490	715.1	0.22	19.87	0.05	0.33	2.16	51.71	0.28	0.33	0.023	16.69	712.75	16.63	0.005	16.70	0.39	0.001	0.008	1.20	0.028	45.040	1.051	0.179	0.004	0.008	11.7	
21	9:15:00	21.0	1.0	350	490	739.6	0.55	20.79	0.73	0.27	1.47	57.48	0.26	0.26	0.024	17.57	737.29	17.51	0.013	17.62	0.42	0.017	0.006	0.51	0.012	50.812	1.207	0.159	0.004	0.006	11.7	
22	9:15:00	22.0	1.0	350	490	676.8	0.45	19.87	0.61	0.24	1.82	51.11	0.19	0.29	0.024	16.24	674.48	16.19	0.011	16.70	0.40	0.015	0.006	0.86	0.021	44.439	1.067	0.094	0.002	0.007	11.7	
23	11:15:00	23.1	1.1	350	490	628.9	0.29	24.32	0.44	0.39	0.53	64.72	0.03	0.25	0.026	16.35	626.52	16.29	0.008	21.15	0.55	0.011	0.010			58.054	1.509			0.006	11.7	
24	13:25:00	24.2	1.1	350	490	645.3	0.28	19.03	0.43	0.16	1.65	53.14	0.20	0.22	0.026	16.99	642.948	16.93	0.007	15.86	0.42	0.011	0.004	0.69	0.018	46.473	1.224	0.095	0.003	0.006	11.7	
25	9:35:00	25.3	1.1	350	490	638.6	0.31	19.71	0.45	0.15	1.63	50.34	0.15	0.24	0.027	17.13	636.30	17.07	0.008	16.54	0.44	0.012	0.004	0.67	0.018	43.666	1.172	0.054	0.001	0.007	11.7	
26	9:45:00	26.3	1.0	350	490	626.7	0.25	18.80	0.40	0.15	1.60	50.97	0.16	0.13	0.024	14.94	624.36	14.88	0.006	15.63	0.37	0.010	0.003	0.64	0.015	44.302	1.056	0.061	0.001	0.003	11.7	
27	13:31:00	27.5	1.2	350	490	615.2	0.26	19.97	0.57	0.16	0.84	62.70	0.06	0.15	0.028	17.08	612.90	17.02	0.007	16.80	0.47	0.016	0.004			56.030	1.556			0.004	11.7	
28	9:30:00	28.3	0.8	350	490	596.6	0.26	19.20	0.50	0.14	1.75	61.69	0.26	0.29	0.020	11.92	594.26	11.88	0.005	16.03	0.32	0.010	0.003	0.79	0.016	55.024	1.100	0.161	0.003	0.006	11.7	
29	9:15:00	29.3	1.0	350	490	573.7	0.17	18.17	0.45	0.15	1.51	57.99	0.18	0.21	0.024	13.62	571.32	13.57	0.004	15.00	0.36	0.011	0.004	0.55	0.013	51.317	1.219	0.079	0.002	0.005	11.7	
30	11:35:00	30.4	1.1	350	490	566.2	0.24	17.50	0.44	0.13	0.94	58.18	0.12	0.14	0.026	14.91	563.85	14.85	0.006	14.33	0.38	0.012	0.003			51.509	1.356	0.020	0.001	0.004	11.7	
31	12:02:00	31.4	1.0	350	490	539.1	0.01	16.55	0.45	0.10	1.43	59.38	0.12	0.10	0.024	12.69	536.79	12.63	0.000	13.38	0.31	0.011	0.002	0.47	0.011	52.710	1.240	0.020	0.0005	0.002	11.7	
32	10:05:00	32.3	0.9	350	490	533.3	0.23	16.20	0.42	0.13	1.43	57.59	0.10	0.04	0.022	11.75	530.99	11.70	0.005	13.03	0.29	0.009	0.003	0.47	0.010	50.920	1.122	0.004	0.0001	0.001	11.7	
33	9:10:00	33.2	0.9	350	490	530.3	0.20	16.15	0.43	0.10	1.91	60.88	0.19	0.19	0.022	11.71	527.96	11.66	0.004	12.98	0.29	0.009	0.002	0.95	0.021	54.208	1.197	0.089	0.002	0.004	11.7	
34	9:50:00	34.3	1.0	350	490	561.4	0.10	11.86	0.41	0.03	1.86	64.72	0.21	0.26	0.025	13.85	559.05	13.79	0.002	8.69	0.21	0.010	0.001	0.90	0.022	58.050	1.432	0.106	0.003	0.006	11.7	
35	9:00:00	35.2	1.0	350	490	515.4	0.48	6.80	0.52	< 0.01	1.54	47.25	0.19	0.01	0.023	11.94	513.02	11.88	0.011	3.63	0.08	0.012	0.001	0.58	0.013	40.575	0.940	0.094	0.002	0.0	11.7	
36	13:15:00	36.4	1.2	350	490	514.9	0.37	5.32	0.11	0.08	0.82	43.43	0.10	0.15	0.028	14.55	512.57	14.48	0.010	2.15	0.06	0.003	0.002			36.761	1.039			0.004	11.7	
37	11:40:00	37.3	0.9	350	490	505.1	0.57	5.28	0.02	0.11	1.52	41.46	0.17	0.19	0.022	11.32	502.80	11.27	0.013	2.11	0.05	0.0004	0.003	0.56	0.013	34.793	0.780	0.069	0.002	0.004	11.7	
38	8:10:00	38.2	0.9	350	490	497.3	0.42	5.11	0.07	0.10	1.05	46.30	0.11	0.11	0.021	10.20	494.99	10.15	0.009	1.94	0.04	0.001	0.002	0.09	0.002	39.630	0.812	0.007	0.0001	0.002	11.7	
39	8:15:00	39.2	1.0	350	490	493.2	0.44	5.25	0.10	0.10	1.28	48.48	0.14	0.09	0.024	11.88	490.84	11.82	0.011	2.08	0.05	0.002	0.002	0.32	0.008	41.815	1.007	0.035	0.001	0.002	11.7	
40	8:20:00	40.2	1.0	350	490	485.3	0.36	5.28	0.07	0.08	1.52	48.70	0.22	0.15	0.024	11.69	482.99	11.63	0.009	2.11	0.05	0.002	0.002	0.56	0.013	42.030	1.012	0.122				

Table B.3.22. Major elements estimated in the unaltered volcanic glass, and Σ major elements flux calculation from fluid samples compositions, both for the BW1 and BW2

BW1 400° C / 502 bar (26.2 g of rock)		BW2 350° C / 490 bar (26.6 g of rock)	
Elements Estimated From Volcanic Glass	Total Elements Flux From Fluid Samples	Elements Estimated From Volcanic Glass	Total Elements Flux From Fluid Samples
(EMPA) wt% K ₂ O = 1.37 wt% K = 1.14 glass calculated (g) = 0.621 K in glass (g) = 0.0071 K in glass (mg) = 7.1	Σ K flux (g) = 0.0048 Σ K flux (mg) = 4.8	wt% (by EMPA) K ₂ O = 1.37 wt% K = 1.14 glass calculated (g) = 0.579 K in glass (g) = 0.0066 K in glass (mg) = 6.6	Σ K flux (g) = 0.0090 Σ K flux (mg) = 9.0
wt% (by EMPA) Cl = 0.09 glass (g) = 0.621 Cl in glass (g) = 0.00056 Cl in glass (mg) = 0.56	Σ Cl flux (g) = 0.0017 Σ Cl flux (mg) = 1.7	wt% (by EMPA) Cl = 0.09 glass (g) = 0.579 Cl in glass (g) = 0.00052 Cl in glass (mg) = 0.52	Σ Cl flux (g) = 0.002 Σ Cl flux (mg) = 2.0
wt% (by EMPA) SO ₂ = 0.04 wt% S = 0.02 glass (g) = 0.621 S in glass (g) = 0.00012 S in glass (mg) = 0.12	Σ H ₂ S flux (mg) = 1.40 Σ S (reduced) flux (mg) = 1.28 Σ SO ₄ flux (mg) = 0.60 Σ S (oxidized) flux (mg) = 0.20 <div> S_(Ox) + S_(Red) in (mg) = 1.5 S_(Ox) + S_(Red) in (g) = 0.0015 </div>	wt% (by EMPA) SO ₂ = 0.04 wt% S = 0.02 glass (g) = 0.579 S in glass (g) = 0.00012 S in glass (mg) = 0.12	Σ H ₂ S flux (mg) = 0.90 Σ S (reduced) flux (mg) = 0.82 Σ SO ₄ flux (mg) = 2.1 Σ S (oxidized) flux (mg) = 0.70 <div> S_(Ox) + S_(Red) in (mg) = 1.5 S_(Ox) + S_(Red) in (g) = 0.0015 </div>
(EMPA) wt% CaO = 5.29 wt% Ca = 3.78 glass calculated (g) = 0.621 Ca in glass (g) = 0.023 Ca in glass (mg) = 23.5	Σ Ca flux (g) = 0.00036 Σ Ca flux (mg) = 0.36	(EMPA) wt% CaO = 5.29 wt% Ca = 3.78 glass calculated (g) = 0.579 Ca in glass (g) = 0.0219 Ca in glass (mg) = 21.9	Σ Ca flux (g) = 0.0006 Σ Ca flux (mg) = 0.60
(EMPA) wt% Na ₂ O = 6.13 wt% Na = 4.55 glass calculated (g) = 0.621 Na in glass (g) = 0.028 Na in glass (mg) = 28.2	Σ Na flux (g) = 0.0242 Σ Na flux (mg) = 24.2	(EMPA) wt% Na ₂ O = 6.13 wt% Na = 4.55 glass calculated (g) = 0.579 Na in glass (g) = 0.0263 Na in glass (mg) = 26.3	Σ Na flux (g) = 0.0381 Σ Na flux (mg) = 38.1
(EMPA) wt% MgO = 0.79 wt% Mg = 0.48 glass calculated (g) = 0.621 Mg in glass (g) = 0.0030 Mg in glass (mg) = 3.0	Σ Mg flux (g) = 0.000075 Σ Mg flux (mg) = 0.075	(EMPA) wt% MgO = 0.79 wt% Mg = 0.48 glass calculated (g) = 0.579 Mg in glass (g) = 0.0028 Mg in glass (mg) = 2.8	Σ Mg flux (g) = 0.0001 Σ Mg flux (mg) = 0.11
(EMPA) wt% FeO = 4.08 wt% Fe = 3.17 glass calculated (g) = 0.621 Fe in glass (g) = 0.020 Fe in glass (mg) = 19.7	Σ Mg flux (g) = 0.00022 Σ Mg flux (mg) = 0.22	(EMPA) wt% FeO = 4.08 wt% Fe = 3.17 glass calculated (g) = 0.579 Fe in glass (g) = 0.018 Fe in glass (mg) = 18.4	Σ Mg flux (g) = 0.00037 Σ Mg flux (mg) = 0.37

Activity calculation

Table B.3.23. Ions activity and logarithm of activity calculated by the R package (linked to EqSolvR by Mroczek S. and Mroczek E., 2017) for the BW1 experiment (400°C / 502 bar). Table also reports values of quench pH, *in situ* pH, experimental time, flow-rate, T and P. Red column indicates effluents collected at 0.5 ml hr⁻¹ flow rate. LOD: limit of detection

samples	water (distilled) blank	7	8	9	10	11	12	13	14	15	16	17	18	19	20	21	22	23	24	25	26	27	28	29	30	31	32	33	34	35	
$a = m \cdot a_{\gamma}$																															
H ⁺	3.95E-06	1.74E-07	3.89E-07	5.86E-07	4.49E-07	4.59E-07	6.98E-07	7.54E-07	8.57E-07	8.63E-07	1.01E-06	1.22E-06	9.29E-07	1.17E-06	9.77E-07	1.20E-06	1.15E-06	9.12E-07	1.31E-06	2.13E-06	2.21E-06	1.92E-06	2.00E-06	2.12E-06	2.08E-06	2.18E-06	1.97E-06	2.21E-06	2.15E-06	2.14E-06	
OH ⁻	1.11E-06	2.53E-05	1.13E-05	7.52E-06	9.81E-06	9.59E-06	6.32E-06	5.84E-06	5.14E-06	5.10E-06	4.34E-06	3.62E-06	4.74E-06	3.77E-06	4.51E-06	3.67E-06	3.83E-06	4.83E-06	3.35E-06	2.07E-06	2.00E-06	2.30E-06	2.20E-06	2.08E-06	2.12E-06	2.02E-06	2.24E-06	1.99E-06	2.05E-06	2.06E-06	
Na ⁺	< LOD	9.50E-04	5.49E-04	5.03E-04	5.13E-04	4.90E-04	3.94E-04	3.66E-04	3.98E-04	4.81E-04	6.58E-04	9.15E-04	1.23E-03	1.29E-03	1.31E-03	1.34E-03	1.38E-03	1.38E-03	1.39E-03	1.43E-03	1.44E-03	1.44E-03	1.45E-03	1.45E-03	1.46E-03	1.44E-03	1.46E-03	1.44E-03	1.42E-03	1.39E-03	
K ⁺	9.06E-06	2.60E-04	1.51E-04	1.29E-04	1.18E-04	1.06E-04	9.92E-05	1.13E-04	1.23E-04	1.33E-04	1.47E-04	1.79E-04	2.97E-04	2.49E-04	2.17E-04	2.09E-04	2.01E-04	1.87E-04	1.62E-04	1.30E-04	1.06E-04	9.21E-05	8.24E-05	7.57E-05	7.10E-05	6.65E-05	7.11E-05	6.63E-05	6.20E-05	6.03E-05	
Cl ⁻	2.92E-05	1.11E-03	7.06E-04	6.56E-04	6.43E-04	5.90E-04	5.00E-04	4.84E-04	5.28E-04	6.21E-04	8.16E-04	1.11E-03	1.53E-03	1.56E-03	1.54E-03	1.55E-03	1.59E-03	1.57E-03	1.56E-03	1.58E-03	1.57E-03	1.55E-03	1.54E-03	1.55E-03	1.55E-03	1.53E-03	1.55E-03	1.54E-03	1.50E-03	1.47E-03	
SO ₄ ²⁻	5.71E-09	1.15E-05	2.46E-06	1.41E-06	1.90E-06	1.59E-06	8.09E-07	6.74E-07	5.38E-07	5.01E-07	3.41E-07	2.45E-07	3.42E-07	2.51E-07	3.12E-07	1.62E-07	1.91E-07	3.26E-07	1.32E-07	2.32E-08	2.26E-08	2.72E-08	2.62E-08	2.58E-08	2.67E-08	2.63E-08	2.98E-08	2.64E-08	2.85E-08	2.98E-08	
Ca ²⁺	5.58E-06	1.63E-06	1.96E-06	2.93E-06	1.87E-06	1.68E-06	2.23E-06	2.29E-06	2.46E-06	2.21E-06	2.01E-06	2.04E-06	1.28E-06	1.78E-06	1.45E-06	1.16E-06	1.33E-06	1.31E-06	1.33E-06	1.57E-06	1.58E-06	1.20E-06	1.38E-06	1.57E-06	1.47E-06	1.67E-06	1.45E-06	1.70E-06	1.74E-06	1.75E-06	
Mg ²⁺	5.33E-07	3.54E-07	3.88E-07	6.35E-07	4.70E-07	3.17E-07	4.62E-07	4.12E-07	4.51E-07	4.33E-07	4.68E-07	6.35E-07	4.40E-07	6.29E-07	4.19E-07	3.49E-07	3.60E-07	3.10E-07	3.50E-07	5.73E-07	3.20E-07	3.78E-07	5.01E-07	4.75E-07	5.65E-07	3.68E-07	6.18E-07	5.43E-07	5.33E-07		
Fe ²⁺	1.67E-07	6.74E-06	6.48E-06	6.16E-06	6.78E-06	2.60E-06	2.34E-06	1.57E-06	1.01E-06	1.05E-06	9.31E-07	8.70E-07	2.56E-07	1.71E-07	< LOD	< LOD	< LOD	< LOD	< LOD	< LOD	< LOD	< LOD	< LOD	< LOD	< LOD	< LOD	< LOD	< LOD	< LOD	< LOD	
a ³⁺ H ⁺	1.56E-11	3.03E-14	1.52E-13	3.44E-13	2.02E-13	2.11E-13	4.87E-13	5.68E-13	7.35E-13	7.45E-13	1.03E-12	1.48E-12	8.63E-13	1.37E-12	9.54E-13	1.44E-12	1.33E-12	8.31E-13	1.73E-12	4.55E-12	4.87E-12	3.67E-12	4.02E-12	4.50E-12	4.31E-12	4.74E-12	3.87E-12	4.89E-12	4.64E-12	4.57E-12	
log (a SiO ₂)	-5.8	-1.5	-1.5	-1.5	-1.5	-1.5	-1.5	-1.6	-1.6	-1.6	-1.6	-1.7	-1.9	-1.9	-2.0	-2.0	-2.0	-2.1	-2.1	-2.1	-2.1	-2.1	-2.1	-2.1	-2.1	-2.1	-2.1	-2.1	-2.1	-2.1	
log (a K ⁺ /a H ⁺)	0.4	3.2	2.6	2.3	2.4	2.4	2.2	2.2	2.2	2.2	2.2	2.2	2.5	2.3	2.3	2.2	2.2	2.3	2.1	1.8	1.7	1.7	1.6	1.6	1.5	1.5	1.6	1.5	1.5	1.5	
log (a Na ⁺ /a H ⁺)	< LOD	3.7	3.1	2.9	3.1	3.0	2.8	2.7	2.7	2.7	2.8	2.9	3.1	3.0	3.1	3.0	3.1	3.2	3.0	2.8	2.8	2.9	2.9	2.8	2.8	2.8	2.9	2.8	2.8	2.8	
log (a Ca ₂₊ /a ² H ⁺)	5.6	7.7	7.1	6.9	7.0	6.9	6.7	6.6	6.5	6.5	6.3	6.1	6.2	6.1	6.2	5.9	6.0	6.2	5.9	5.5	5.5	5.5	5.5	5.5	5.5	5.5	5.6	5.5	5.6	5.6	
log (a Fe ₂₊ /a ² H ⁺)	4.0	8.3	7.6	7.3	7.5	7.1	6.7	6.4	6.1	6.1	6.0	5.8	5.5	5.1	< LOD	< LOD	< LOD	< LOD	< LOD	< LOD	< LOD	< LOD	< LOD	< LOD	< LOD	< LOD	< LOD	< LOD	< LOD	< LOD	
log (a Mg ₂₊ /a ² H ⁺)	4.5	7.1	6.4	6.3	6.4	6.2	6.0	5.9	5.8	5.8	5.7	5.6	5.7	5.7	5.6	5.4	5.4	5.6	5.3	5.0	5.1	4.9	5.0	5.0	5.0	5.1	5.0	5.1	5.1	5.1	
log a Na ⁺	< LOD	-3.0	-3.3	-3.3	-3.3	-3.3	-3.4	-3.4	-3.4	-3.3	-3.2	-3.0	-2.9	-2.9	-2.9	-2.9	-2.9	-2.9	-2.9	-2.8	-2.8	-2.8	-2.8	-2.8	-2.8	-2.8	-2.8	-2.8	-2.8	-2.8	
log a K ⁺	-5.0	-3.6	-3.8	-3.9	-3.9	-4.0	-3.9	-3.9	-3.9	-3.9	-3.8	-3.7	-3.5	-3.6	-3.7	-3.7	-3.7	-3.7	-3.8	-3.9	-4.0	-4.0	-4.1	-4.1	-4.1	-4.2	-4.1	-4.2	-4.2	-4.2	
log a Cl ⁻	-4.5	-3.0	-3.2	-3.2	-3.2	-3.2	-3.3	-3.3	-3.3	-3.2	-3.1	-3.0	-2.8	-2.8	-2.8	-2.8	-2.8	-2.8	-2.8	-2.8	-2.8	-2.8	-2.8	-2.8	-2.8	-2.8	-2.8	-2.8	-2.8	-2.8	
log a SO ₄ ²⁻	-8.2	-4.9	-5.6	-5.8	-5.7	-5.8	-6.1	-6.2	-6.3	-6.3	-6.5	-6.6	-6.5	-6.6	-6.5	-6.8	-6.7	-6.5	-6.9	-7.6	-7.6	-7.6	-7.6	-7.6	-7.6	-7.6	-7.5	-7.6	-7.5	-7.5	
log a Ca ²⁺	-5.3	-5.8	-5.7	-5.5	-5.7	-5.8	-5.7	-5.6	-5.6	-5.7	-5.7	-5.7	-5.9	-5.7	-5.8	-5.9	-5.9	-5.9	-5.9	-5.8	-5.8	-5.9	-5.9	-5.8	-5.8	-5.8	-5.8	-5.8	-5.8	-5.8	
log a Mg ²⁺	-6.3	-6.5	-6.4	-6.2	-6.3	-6.5	-6.3	-6.4	-6.3	-6.4	-6.3	-6.2	-6.4	-6.2	-6.4	-6.5	-6.4	-6.5	-6.5	-6.3	-6.2	-6.5	-6.4	-6.3	-6.3	-6.2	-6.4	-6.2	-6.3	-6.3	
log a Fe ²⁺	-6.8	-5.2	-5.2	-5.2	-5.2	-5.6	-5.6	-5.8	-6.0	-6.0	-6.0	-6.1	-6.6	-6.8	< LOD	< LOD	< LOD	< LOD	< LOD	< LOD	< LOD	< LOD	< LOD	< LOD	< LOD	< LOD	< LOD	< LOD	< LOD	< LOD	
T	400	402	401	401	401	401	401	401	401	401	401	400	400	400	400	400	400	400	400	400	400	400	400	400	400	400	400	400	401	401	
P	500	502	503	503	503	503	502	503	503	502	502	502	503	502	502	502	502	502	502	502	502	502	502	502	502	502	502	502	502	502	502
in situ pH (400°C)	5.4	6.76	6.41	6.24	6.35	6.33	6.16	6.13	6.07	6.06	5.99	6.03	6.03	5.93	6.01	5.92	5.94	6.04	5.88	5.67	5.66	5.72	5.70	5.67	5.68	5.66	5.71	5.66	5.67	5.67	
room T pH	7.83	5.04	6.53	6.58	6.93	6.93	7.04	7.26	7.39	7.84	8.61	8.84	9.14	9.2	9.25	9.36	9.4	9.41	9.45	9.47	9.41	9.39	9.39	9.35	9.37	9.29	9.38	9.39	9.38	9.21	
flow rate (ml hr ⁻¹)	1	1	1	1	1	1	1	1	1	1	1	1	1	1	1	1	1	1	1	1	1	1	1	1	1	1	1	1	0.5	0.5	
time (hrs)	0.00	167.3	216.7	240.9	264.7	288.7	312.7	335.9	361.8	386.2	409.5	434.0	458.2	482.1	506.1	530.3	554.3	578.3	602.3	626.3	650.3	674.6	699.3	722.7	746.6	769.0	794.9	819.1	866.0	913.5	

Table B.3.24. Values of the activity coefficients (a_i) calculate by the R package for the BW1

sample		H ⁺	OH ⁻	Na ⁺	K ⁺	Cl ⁻	SO ₄ ²⁻	Ca ²⁺	Mg ²⁺	Fe ²⁺	NaSO ₄ ⁻	HSO ₄ ⁻	KSO ₄ ⁻	NaCl [°]	KCl [°]	HCl [°]	KOH [°]	NaOH [°]	CaSO ₄ [°]	MgSO ₄ [°]	MgCl ⁺	CaCl ⁺	CaCl ₂ [°]	MgOH ⁺	CaOH ⁺	FeCl [°]	FeSO ₄ [°]
water (distilled) blank	m	4.06E-06	1.14E-06		9.30E-06	3.00E-05	6.35E-09	6.20E-06	5.93E-07	1.85E-07		6.45E-07	4.21E-10		4.56E-09	5.64E-08	2.82E-10		3.15E-09	2.42E-08	8.23E-07	2.89E-10	8.60E-07	8.60E-07	2.76E-06	1.16E-08	6.20E-12
	a _i	9.74E-01	9.74E-01		9.74E-01	9.74E-01	8.99E-01	8.99E-01	9.00E-01	8.99E-01		9.74E-01	9.74E-01		1.00E+00	1.00E+00	1.00E+00		1.00E+00	1.00E+00	9.74E-01	9.74E-01	1.00E+00	9.74E-01	9.74E-01	9.74E-01	1.00E+00
	activity	3.95E-06	1.11E-06		9.06E-06	2.92E-05	5.71E-09	5.58E-06	5.33E-07	1.67E-07		6.28E-07	4.10E-10		4.56E-09	5.64E-08	2.82E-10		3.15E-09	2.42E-08	8.02E-07	2.81E-10	8.60E-07	8.38E-07	2.68E-06	1.13E-08	6.20E-12
7	m	2.01E-07	2.98E-05	1.12E-03	3.06E-04	1.31E-03	2.19E-05	3.01E-06	6.38E-07	1.24E-05	4.55E-05	6.53E-05	2.79E-05	5.77E-05	4.98E-06	9.44E-08	1.84E-07	3.52E-07	2.78E-05	4.16E-06	6.84E-07	1.04E-05	1.04E-05	1.45E-05	2.07E-05	2.01E-05	5.00E-07
	a _i	8.62E-01	8.52E-01	8.52E-01	8.50E-01	8.51E-01	5.27E-01	5.37E-01	5.47E-01	5.37E-01	8.52E-01	8.52E-01	8.52E-01	1.00E+00	1.00E+00	1.00E+00	1.00E+00	1.00E+00	1.00E+00	1.00E+00	8.60E-01	8.56E-01	1.00E+00	8.60E-01	8.56E-01	8.56E-01	1.00E+00
	activity	1.74E-07	2.54E-05	9.50E-04	2.60E-04	1.11E-03	1.15E-05	1.62E-06	3.49E-07	6.65E-06	3.88E-05	5.56E-05	2.38E-05	5.77E-05	4.98E-06	9.44E-08	1.84E-07	3.52E-07	2.78E-05	4.16E-06	5.88E-07	8.87E-06	1.04E-05	1.25E-05	1.77E-05	1.72E-05	5.00E-07
8	m	4.39E-07	1.27E-05	6.20E-04	1.71E-04	7.99E-04	3.99E-06	3.18E-06	6.19E-07	1.06E-05	5.37E-06	3.00E-05	3.31E-06	2.12E-05	1.84E-06	1.35E-07	4.75E-08	9.03E-08	7.20E-06	9.82E-07	4.67E-07	7.74E-06	7.74E-06	6.93E-06	1.08E-05	1.23E-05	1.05E-07
	a _i	8.91E-01	8.85E-01	8.85E-01	8.84E-01	8.84E-01	6.14E-01	6.21E-01	6.28E-01	6.21E-01	8.85E-01	8.85E-01	8.85E-01	1.00E+00	1.00E+00	1.00E+00	1.00E+00	1.00E+00	1.00E+00	1.00E+00	8.90E-01	8.88E-01	1.00E+00	8.90E-01	8.88E-01	8.88E-01	1.00E+00
	activity	3.91E-07	1.13E-05	5.49E-04	1.51E-04	7.07E-04	2.45E-06	1.98E-06	3.89E-07	6.61E-06	4.76E-06	2.66E-05	2.93E-06	2.12E-05	1.84E-06	1.35E-07	4.75E-08	9.03E-08	7.20E-06	9.82E-07	4.16E-07	6.87E-06	7.74E-06	6.17E-06	9.60E-06	1.09E-05	1.05E-07
9	m	6.44E-07	8.59E-06	5.65E-04	1.45E-04	7.37E-04	2.30E-06	4.56E-06	9.64E-07	9.57E-06	2.89E-06	2.60E-05	1.65E-06	1.80E-05	1.45E-06	1.85E-07	2.75E-08	5.61E-08	6.21E-06	9.19E-07	6.84E-07	1.05E-05	1.05E-05	7.43E-06	1.07E-05	1.04E-05	5.70E-08
	a _i	8.96E-01	8.90E-01	8.90E-01	8.89E-01	8.89E-01	6.27E-01	6.34E-01	6.40E-01	6.34E-01	8.90E-01	8.90E-01	8.90E-01	1.00E+00	1.00E+00	1.00E+00	1.00E+00	1.00E+00	1.00E+00	1.00E+00	8.94E-01	8.92E-01	1.00E+00	8.94E-01	8.92E-01	8.92E-01	1.00E+00
	activity	5.76E-07	7.64E-06	5.03E-04	1.29E-04	6.55E-04	1.44E-06	2.89E-06	6.17E-07	6.07E-06	2.57E-06	2.31E-05	1.47E-06	1.80E-05	1.45E-06	1.85E-07	2.75E-08	5.61E-08	6.21E-06	9.19E-07	6.12E-07	9.33E-06	1.05E-05	6.65E-06	9.54E-06	9.25E-06	5.70E-08
10	m	4.93E-07	1.12E-05	5.76E-04	1.33E-04	7.22E-04	3.07E-06	2.94E-06	6.90E-07	1.06E-05	3.94E-06	2.66E-05	2.03E-06	1.80E-05	1.30E-06	1.39E-07	3.28E-08	7.46E-08	5.38E-06	8.82E-07	4.81E-07	6.62E-06	6.62E-06	6.95E-06	9.01E-06	1.13E-05	8.48E-08
	a _i	8.96E-01	8.90E-01	8.90E-01	8.89E-01	8.90E-01	6.29E-01	6.35E-01	6.41E-01	6.35E-01	8.90E-01	8.90E-01	8.90E-01	1.00E+00	1.00E+00	1.00E+00	1.00E+00	1.00E+00	1.00E+00	1.00E+00	8.95E-01	8.93E-01	1.00E+00	8.95E-01	8.93E-01	8.93E-01	1.00E+00
	activity	4.42E-07	9.97E-06	5.13E-04	1.18E-04	6.43E-04	1.93E-06	1.87E-06	4.43E-07	6.74E-06	3.50E-06	2.37E-05	1.80E-06	1.80E-05	1.30E-06	1.39E-07	3.28E-08	7.46E-08	5.38E-06	8.82E-07	4.30E-07	5.91E-06	6.62E-06	6.22E-06	8.04E-06	1.01E-05	8.48E-08
11	m	5.15E-07	1.06E-05	5.47E-04	1.18E-04	6.60E-04	2.43E-06	2.64E-06	4.82E-07	4.00E-06	3.03E-06	2.25E-05	1.47E-06	1.58E-05	1.08E-06	1.34E-07	2.81E-08	6.78E-08	3.99E-06	5.10E-07	3.14E-07	5.54E-06	5.54E-06	4.69E-06	7.80E-06	3.98E-06	2.65E-08
	a _i	9.00E-01	8.95E-01	8.95E-01	8.94E-01	8.95E-01	6.43E-01	6.49E-01	6.55E-01	6.49E-01	8.95E-01	8.95E-01	8.95E-01	1.00E+00	1.00E+00	1.00E+00	1.00E+00	1.00E+00	1.00E+00	1.00E+00	9.00E-01	8.98E-01	1.00E+00	9.00E-01	8.98E-01	8.98E-01	1.00E+00
	activity	4.64E-07	9.49E-06	4.90E-04	1.06E-04	5.91E-04	1.56E-06	1.71E-06	3.16E-07	2.59E-06	2.71E-06	2.02E-05	1.31E-06	1.58E-05	1.08E-06	1.34E-07	2.81E-08	6.78E-08	3.99E-06	5.10E-07	2.82E-07	4.97E-06	5.54E-06	4.22E-06	7.00E-06	3.57E-06	2.65E-08
12	m	7.57E-07	7.08E-06	4.35E-04	1.09E-04	5.53E-04	1.24E-06	3.32E-06	6.75E-07	3.75E-06	1.28E-06	1.76E-05	7.20E-07	1.07E-05	8.49E-07	1.68E-07	1.77E-08	3.67E-08	2.77E-06	3.93E-07	3.81E-07	6.06E-06	6.06E-06	4.55E-06	6.82E-06	3.24E-06	1.37E-08
	a _i	9.08E-01	9.04E-01	9.04E-01	9.03E-01	9.03E-01	6.68E-01	6.73E-01	6.78E-01	6.73E-01	9.04E-01	9.04E-01	9.04E-01	1.00E+00	1.00E+00	1.00E+00	1.00E+00	1.00E+00	1.00E+00	1.00E+00	9.07E-01	9.06E-01	1.00E+00	9.07E-01	9.06E-01	9.06E-01	1.00E+00
	activity	6.88E-07	6.40E-06	3.93E-04	9.88E-05	4.99E-04	8.31E-07	2.23E-06	4.58E-07	2.52E-06	1.16E-06	1.59E-05	6.51E-07	1.07E-05	8.49E-07	1.68E-07	1.77E-08	3.67E-08	2.77E-06	3.93E-07	3.46E-07	5.49E-06	6.06E-06	4.13E-06	6.18E-06	2.93E-06	1.37E-08
13	m	8.20E-07	6.52E-06	4.03E-04	1.24E-04	5.33E-04	1.02E-06	3.35E-06	6.04E-07	2.17E-06	9.79E-07	1.57E-05	6.75E-07	9.62E-06	9.35E-07	1.76E-07	1.85E-08	3.15E-08	2.32E-06	2.92E-07	3.31E-07	5.94E-06	5.94E-06	3.77E-06	6.37E-06	1.82E-06	6.58E-09
	a _i	9.10E-01	9.06E-01	9.06E-01	9.05E-01	9.05E-01	6.73E-01	6.78E-01	6.83E-01	6.78E-01	9.06E-01	9.06E-01	9.06E-01	1.00E+00	1.00E+00	1.00E+00	1.00E+00	1.00E+00	1.00E+00	1.00E+00	9.09E-01	9.07E-01	1.00E+00	9.09E-01	9.07E-01	9.07E-01	1.00E+00
	activity	7.46E-07	5.90E-06	3.65E-04	1.13E-04	4.83E-04	6.86E-07	2.27E-06	4.12E-07	1.47E-06	8.87E-07	1.42E-05	6.12E-07	9.62E-06	9.35E-07	1.76E-07	1.85E-08	3.15E-08	2.32E-06	2.92E-07	3.01E-07	5.39E-06	5.94E-06	3.43E-06			

Table B.3.25. Ions activity and logarithm of activity calculate by the R package (linked to EqSolvR by Mroczek S. and Mroczek E., 2017) for the BW2 experiment (350°C / 490 bar). Table also reports values of quench pH, *in situ* pH, experimental time, flow-rate, T and P

samples	water (distilled) blank	7	8	9	10	11	12	13	14	15	16	17	18	19	20	21	22	23	24	25	26
$a = m \cdot a_{\gamma}$																					
H ⁺	5.14E-06	5.74E-07	4.29E-07	8.11E-07	4.88E-07	8.23E-07	6.94E-07	6.58E-07	7.17E-07	8.29E-07	1.61E-06	1.51E-06	3.14E-06	4.88E-06	5.04E-06	2.99E-06	3.23E-06	2.24E-06	3.49E-06	3.32E-06	3.44E-06
OH ⁻	1.50E-06	1.35E-05	1.80E-05	9.53E-06	1.58E-05	9.39E-06	1.11E-05	1.17E-05	1.08E-05	9.32E-06	4.79E-06	5.13E-06	2.46E-06	1.58E-06	1.53E-06	2.58E-06	2.39E-06	3.45E-06	2.22E-06	2.32E-06	2.25E-06
Na ⁺	2.71E-04	9.58E-04	6.70E-04	2.98E-04	7.79E-04	7.53E-04	6.50E-04	7.85E-04	9.81E-04	9.22E-04	1.23E-03	1.43E-03	1.68E-03	1.84E-03	1.88E-03	2.07E-03	1.86E-03	2.31E-03	1.93E-03	1.83E-03	1.86E-03
K ⁺	7.61E-05	3.15E-04	2.49E-04	2.95E-04	2.29E-04	2.42E-04	2.18E-04	1.84E-04	2.01E-04	2.28E-04	2.71E-04	2.67E-04	3.02E-04	3.49E-04	4.33E-04	4.50E-04	4.33E-04	5.22E-04	4.15E-04	4.30E-04	4.11E-04
Cl ⁻	3.95E-04	1.25E-03	8.60E-04	6.13E-04	9.73E-04	1.01E-03	8.67E-04	9.62E-04	1.18E-03	1.16E-03	1.57E-03	1.74E-03	2.05E-03	2.26E-03	2.40E-03	2.57E-03	2.35E-03	2.85E-03	2.40E-03	2.32E-03	2.32E-03
SO ₄ ²⁻	< LOD	1.40E-05	1.80E-05	8.51E-06	1.23E-05	6.80E-06	8.08E-06	9.00E-06	7.29E-06	6.34E-06	2.42E-06	2.06E-06	4.04E-07	6.22E-09	1.48E-08	3.19E-07	2.54E-07	2.43E-07	1.71E-07	1.86E-07	1.62E-07
Ca ²⁺	1.21E-05	5.64E-06	3.62E-06	1.08E-05	3.32E-06	8.09E-06	6.64E-06	6.10E-06	6.27E-06	8.62E-06	1.42E-05	1.02E-05	1.03E-05	8.41E-06	1.03E-05	6.34E-06	8.45E-06	2.10E-06	7.63E-06	7.69E-06	7.56E-06
Mg ²⁺	1.95E-06	2.31E-06	1.07E-06	2.07E-06	6.61E-07	1.59E-06	9.91E-07	1.18E-06	9.34E-07	1.06E-06	2.57E-06	1.52E-06	3.07E-06	2.97E-06	3.25E-06	2.52E-06	2.01E-06	2.66E-07	2.05E-06	1.62E-06	1.71E-06
Fe ²⁺	5.47E-07	1.09E-05	9.77E-06	9.37E-06	9.67E-06	8.63E-06	7.59E-06	7.67E-06	5.33E-06	3.90E-06	3.55E-06	2.33E-06	2.22E-06	2.04E-06	1.71E-06	1.30E-06	1.51E-06	1.15E-06	1.13E-06	1.29E-06	6.89E-07
a ² H ⁺	2.64E-11	3.29E-13	1.84E-13	6.57E-13	2.38E-13	6.77E-13	4.81E-13	4.33E-13	5.14E-13	6.87E-13	2.60E-12	2.27E-12	9.88E-12	2.38E-11	2.54E-11	8.95E-12	1.04E-11	5.03E-12	1.21E-11	1.11E-11	1.18E-11
log (a SiO ₂)	-4.4	-1.7	-1.5	-1.5	-1.5	-1.5	-1.5	-1.5	-1.5	-1.6	-1.6	-1.6	-1.7	-1.9	-1.9	-1.9	-1.9	-2.0	-2.0	-2.0	-2.0
log (a K ⁺ /a H ⁺)	1.2	2.7	2.8	2.6	2.7	2.5	2.5	2.4	2.4	2.4	2.2	2.2	2.0	1.9	1.9	2.2	2.1	2.4	2.1	2.1	2.1
log (a Na ⁺ /a H ⁺)	2.4	3.2	3.2	2.6	3.2	3.0	3.0	3.1	3.1	3.0	2.9	3.0	2.7	2.6	2.6	2.8	2.8	3.0	2.7	2.7	2.7
log (a Ca ²⁺ /a ² H ⁺)	5.7	7.2	7.3	7.2	7.1	7.1	7.1	7.1	7.1	7.1	6.7	6.7	6.0	5.5	5.6	5.9	5.9	5.6	5.8	5.8	5.8
log (a Fe ²⁺ /a ² H ⁺)	4.3	7.5	7.7	7.2	7.6	7.1	7.2	7.2	7.0	6.8	6.1	6.0	5.4	4.9	4.8	5.2	5.2	5.4	5.0	5.1	4.8
log (a Mg ²⁺ /a ² H ⁺)	4.9	6.8	6.8	6.5	6.4	6.4	6.3	6.4	6.3	6.2	6.0	5.8	5.5	5.1	5.1	5.5	5.3	4.7	5.2	5.2	5.2
log a Na ⁺	-3.6	-3.0	-3.2	-3.5	-3.1	-3.1	-3.2	-3.1	-3.0	-3.0	-2.9	-2.8	-2.8	-2.7	-2.7	-2.7	-2.7	-2.6	-2.7	-2.7	-2.7
log a K ⁺	-4.1	-3.5	-3.6	-3.5	-3.6	-3.6	-3.7	-3.7	-3.7	-3.6	-3.6	-3.6	-3.5	-3.5	-3.4	-3.3	-3.4	-3.3	-3.4	-3.4	-3.4
log a Cl ⁻	-3.4	-2.9	-3.1	-3.2	-3.0	-3.0	-3.1	-3.0	-2.9	-2.9	-2.8	-2.8	-2.7	-2.6	-2.6	-2.6	-2.6	-2.5	-2.6	-2.6	-2.6
log a SO ₄ ²⁻	< LOD	-4.9	-4.7	-5.1	-4.9	-5.2	-5.1	-5.0	-5.1	-5.2	-5.6	-5.7	-6.4	-8.2	-7.8	-6.5	-6.6	-6.6	-6.8	-6.7	-6.8
log a Ca ²⁺	-4.9	-5.2	-5.4	-5.0	-5.5	-5.1	-5.2	-5.2	-5.2	-5.1	-4.8	-5.0	-5.0	-5.1	-5.0	-5.2	-5.1	-5.7	-5.1	-5.1	-5.1
log a Mg ²⁺	-5.7	-5.6	-6.0	-5.7	-6.2	-5.8	-6.0	-5.9	-6.0	-6.0	-5.6	-5.8	-5.5	-5.5	-5.5	-5.6	-5.7	-6.6	-5.7	-5.8	-5.8
log a Fe ²⁺	-6.3	-5.0	-5.0	-5.0	-5.0	-5.1	-5.1	-5.1	-5.3	-5.4	-5.4	-5.6	-5.7	-5.7	-5.8	-5.9	-5.8	-5.9	-5.9	-5.9	-6.2
T	350	352	350	351	350	351	351	351	350	350	351	351	351	350	351	351	351	351	351	351	351
P	500	489	489	489	489	489	489	489	489	489	489	489	489	489	489	489	489	490	490	490	490
<i>in situ</i> pH (350°C)	5.29	6.24	6.37	6.09	6.31	6.08	6.16	6.18	6.14	6.08	5.79	5.82	5.50	5.31	5.30	5.52	5.49	5.65	5.46	5.48	5.46
room T pH	6.8	5.50	7.13	7.59	8.41	8.50	8.59	8.78	8.88	8.96	9.07	9.22	9.39	9.35	9.48	9.47	9.52	9.64	9.53	9.59	9.60
flow rate (ml hr ⁻¹)	-	1	1	1	1	1	1	1	1	1	1	1	1	1	1	1	1	1	1	1	1
time (hrs)	0.0	160.5	184.3	211.6	232.8	256.5	280.5	304.0	328.3	353.0	378.2	403.6	424.3	449.2	472.5	496.3	519.3	546.3	572.4	592.6	616.8

Table B.3.26. Ions activity and logarithm of activity calculate by the R package (linked to EqSolvR by Mroczek S. and Mroczek E., 2017) for the BW2 experiment (350°C / 490 bar). Table also reports values of quench pH, *in situ* pH, experimental time, flow-rate, T and P

samples																				
	27	28	29	30	31	32	33	34	35	36	37	38	39	40	41	42	43	44	45	46
$a = m \cdot a_{\gamma}$																				
H ⁺	2.31E-06	3.50E-06	3.28E-06	2.80E-06	3.04E-06	3.06E-06	3.53E-06	refilling	3.58E-06	3.38E-06	3.60E-06	4.75E-06	3.92E-06	4.06E-06	4.66E-06	4.62E-06	4.81E-06	3.57E-06	3.76E-06	4.45E-06
OH	3.35E-06	2.21E-06	2.36E-06	2.76E-06	2.54E-06	2.52E-06	2.19E-06	refilling	2.16E-06	2.29E-06	2.15E-06	1.63E-06	1.97E-06	1.90E-06	1.66E-06	1.67E-06	1.61E-06	2.17E-06	2.06E-06	1.73E-06
Na ⁺	2.25E-03	2.21E-03	2.09E-03	2.10E-03	2.14E-03	2.08E-03	2.19E-03	refilling	2.33E-03	1.75E-03	1.62E-03	1.55E-03	1.72E-03	1.80E-03	1.80E-03	1.82E-03	1.69E-03	1.78E-03	1.70E-03	1.70E-03
K ⁺	4.31E-04	4.14E-04	3.94E-04	3.80E-04	3.58E-04	3.52E-04	3.49E-04	refilling	2.56E-04	1.51E-04	1.19E-04	1.18E-04	1.14E-04	1.16E-04	1.17E-04	1.14E-04	1.22E-04	1.21E-04	1.11E-04	1.12E-04
Cl ⁻	2.70E-03	2.69E-03	2.54E-03	2.51E-03	2.54E-03	2.47E-03	2.60E-03	refilling	2.65E-03	1.95E-03	1.77E-03	1.73E-03	1.87E-03	1.96E-03	1.98E-03	1.99E-03	1.87E-03	1.93E-03	1.85E-03	1.87E-03
SO ₄ ²⁻	3.09E-07	1.93E-07	1.87E-07	2.12E-07	1.99E-07	1.86E-07	1.66E-07	refilling	1.57E-07	2.21E-07	4.79E-08	6.67E-09	2.78E-08	3.78E-08	2.33E-08	3.38E-09	9.91E-09	3.03E-08	4.53E-08	0.00E+00
Ca ²⁺	3.46E-06	7.43E-06	6.67E-06	4.11E-06	6.30E-06	6.42E-06	8.32E-06	refilling	8.00E-06	8.22E-06	4.73E-06	9.13E-06	5.87E-06	6.96E-06	8.30E-06	7.83E-06	6.47E-06	4.61E-06	6.36E-06	7.32E-06
Mg ²⁺	5.17E-07	2.61E-06	1.81E-06	1.16E-06	1.18E-06	1.04E-06	1.93E-06	refilling	2.10E-06	2.19E-06	1.15E-06	2.22E-06	1.30E-06	1.63E-06	2.75E-06	2.18E-06	3.46E-06	7.95E-07	1.02E-06	1.71E-06
Fe ²⁺	7.03E-07	1.41E-06	1.04E-06	6.83E-07	4.82E-07	2.01E-07	9.26E-07	refilling	1.26E-06	< LOD	9.19E-07	1.18E-06	6.64E-07	5.23E-07	8.55E-07	8.36E-07	8.01E-07	6.84E-07	4.80E-07	1.12E-06
a ² H ⁺	5.33E-12	1.23E-11	1.07E-11	7.82E-12	9.26E-12	9.39E-12	1.24E-11	refilling	1.28E-11	1.14E-11	1.30E-11	2.26E-11	1.53E-11	1.65E-11	2.17E-11	2.13E-11	2.32E-11	1.27E-11	1.41E-11	1.98E-11
log (a SiO ₂)	-2.0	-2.0	-2.0	-2.0	-2.0	-2.1	-2.1	refilling	-2.0	-2.1	-2.1	-2.1	-2.1	-2.1	-2.1	-2.1	-2.1	-2.1	-2.1	-2.1
log (a K ⁺ /a H ⁺)	2.3	2.1	2.1	2.1	2.1	2.1	2.0	refilling	1.9	1.6	1.5	1.4	1.5	1.5	1.4	1.4	1.4	1.5	1.5	1.4
log (a Na ⁺ /a H ⁺)	3.0	2.8	2.8	2.9	2.8	2.8	2.8	refilling	2.8	2.7	2.7	2.5	2.6	2.6	2.6	2.6	2.5	2.7	2.7	2.6
log (a Ca ²⁺ /a ² H ⁺)	5.8	5.8	5.8	5.7	5.8	5.8	5.8	refilling	5.8	5.9	5.6	5.6	5.6	5.6	5.6	5.6	5.4	5.6	5.7	5.6
log (a Fe ²⁺ /a ² H ⁺)	5.1	5.1	5.0	4.9	4.7	4.3	4.9	refilling	5.0		4.9	4.7	4.6	4.5	4.6	4.6	4.5	4.7	4.5	4.8
log (a Mg ²⁺ /a ² H ⁺)	5.0	5.3	5.2	5.2	5.1	5.0	5.2	refilling	5.2	5.3	4.9	5.0	4.9	5.0	5.1	5.0	5.2	4.8	4.9	4.9
log a Na ⁺	-2.6	-2.7	-2.7	-2.7	-2.7	-2.7	-2.7	refilling	-2.6	-2.8	-2.8	-2.8	-2.8	-2.7	-2.7	-2.7	-2.8	-2.7	-2.8	-2.8
log a K ⁺	-3.4	-3.4	-3.4	-3.4	-3.4	-3.5	-3.5	refilling	-3.6	-3.8	-3.9	-3.9	-3.9	-3.9	-3.9	-3.9	-3.9	-3.9	-4.0	-4.0
log a Cl ⁻	-2.6	-2.6	-2.6	-2.6	-2.6	-2.6	-2.6	refilling	-2.6	-2.7	-2.8	-2.8	-2.7	-2.7	-2.7	-2.7	-2.7	-2.7	-2.7	-2.7
log a SO ₄ ²⁻	-6.5	-6.7	-6.7	-6.7	-6.7	-6.7	-6.8	refilling	-6.8	-6.7	-7.3	-8.2	-7.6	-7.4	-7.6	-8.5	-8.0	-7.5	-7.3	
log a Ca ²⁺	-5.5	-5.1	-5.2	-5.4	-5.2	-5.2	-5.1	refilling	-5.1	-5.1	-5.3	-5.0	-5.2	-5.2	-5.1	-5.1	-5.2	-5.3	-5.2	-5.1
log a Mg ²⁺	-6.3	-5.6	-5.7	-5.9	-5.9	-6.0	-5.7	refilling	-5.7	-5.7	-5.9	-5.7	-5.9	-5.8	-5.6	-5.7	-5.5	-6.1	-6.0	-5.8
log a Fe ²⁺	-6.2	-5.9	-6.0	-6.2	-6.3	-6.7	-6.0	refilling	-5.9		-6.0	-5.9	-6.2	-6.3	-6.1	-6.1	-6.1	-6.2	-6.3	-6.0
T	351	350	351	351	351	350	351	refilling	350	351	351	350	351	351	350	350	351	351	350	350
P	488	489	490	490	490	489	488	refilling	490	490	490	490	490	489	489	490	490	490	489	489
in situ pH (350°C)	5.64	5.46	5.48	5.55	5.52	5.51	5.45	refilling	5.45	5.47	5.44	5.32	5.41	5.39	5.33	5.34	5.32	5.45	5.43	5.35
room T pH	9.62	9.65	9.61	9.61	9.60	9.57	9.63	refilling	8.91	9.56	9.57	9.57	9.58	9.62	9.61	9.64	9.66	9.65	9.62	9.62
flow rate (ml hr ⁻¹)	1	1	1	1	1	1	1	refilling	1	1	1	1	1	1	1	1	1	0.5	0.5	0.5
time (hrs)	644.5	664.5	688.3	714.6	739.1	761.1	785.2	refilling	809.8	833.0	862.3	883.7	904.2	928.3	952.3	976.7	1002.1	1049.8	1096.5	1144.7

Table B.3.27. Molal (m), activity coefficients (a_γ) and activity of the ions species in solution calculated by the R package for the BW2

sample		H ⁺	OH ⁻	Na ⁺	K ⁺	Cl ⁻	SO ₄ ²⁻	Ca ²⁺	Mg ²⁺	Fe ²⁺	NaSO ₄ ⁺	HSO ₄ ⁻	KSO ₄ ⁻	NaCl ⁰	KCl ⁰	HCl ⁰	KOH ⁰	NaOH ⁰	CaSO ₄ ⁰	MgSO ₄ ⁰	MgCl ⁺	CaCl ⁺	CaCl ₂ ⁰	MgOH ⁺	CaOH ⁺	FeCl ⁰	FeSO ₄ ⁰		
water (distilled)	m	5.45E-06	1.60E-06	2.88E-04	8.10E-05	4.21E-04		1.54E-05	2.48E-06	6.98E-07				1.64E-06	1.17E-07	8.10E-08	1.38E-09	2.82E-09			3.21E-07	5.83E-06	8.09E-09	1.27E-06	2.66E-06	1.39E-07			
blank	a _γ	9.42E-01	9.40E-01	9.40E-01	9.39E-01	9.40E-01		7.83E-01	7.86E-01	7.83E-01				1.00E+00	1.00E+00	1.00E+00	1.00E+00	1.00E+00			9.42E-01	9.41E-01	1.00E+00	9.42E-01	9.41E-01	9.41E-01			
	activity	5.14E-06	1.50E-06	2.71E-04	7.61E-05	3.95E-04		1.21E-05	1.95E-06	5.47E-07				1.64E-06	1.17E-07	8.10E-08	1.38E-09	2.82E-09			3.03E-07	5.49E-06	8.09E-09	1.20E-06	2.50E-06	1.31E-07			
7	m	6.38E-07	1.51E-05	1.07E-03	3.53E-04	1.40E-03	2.21E-05	8.78E-06	3.55E-06	1.70E-05	1.71E-05	4.04E-05	1.11E-05	1.83E-05	1.53E-06	2.87E-08	5.09E-08	8.93E-08	2.09E-05	8.87E-06	1.26E-06	9.07E-06	3.79E-08	1.41E-05	1.17E-05	9.21E-06	6.24E-07		
	a _γ	8.99E-01	8.92E-01	8.92E-01	8.90E-01	8.91E-01	6.33E-01	6.42E-01	6.50E-01	6.42E-01	8.92E-01	8.92E-01	8.92E-01	1.00E+00	1.00E+00	1.00E+00	1.00E+00	1.00E+00	1.00E+00	1.00E+00	8.98E-01	8.95E-01	1.00E+00	8.98E-01	8.95E-01	8.95E-01	1.00E+00		
	activity	5.74E-07	1.35E-05	9.58E-04	3.15E-04	1.25E-03	1.40E-05	5.64E-06	2.31E-06	1.09E-05	1.52E-05	3.60E-05	9.87E-06	1.83E-05	1.53E-06	2.87E-08	5.09E-08	8.93E-08	2.09E-05	8.87E-06	1.13E-06	8.12E-06	3.79E-08	1.27E-05	1.05E-05	8.25E-06	6.24E-07		
8	m	4.70E-07	1.99E-05	7.39E-04	2.75E-04	9.48E-04	2.65E-05	5.30E-06	1.56E-06	1.43E-05	1.51E-05	3.81E-05	1.11E-05	8.80E-06	8.33E-07	1.47E-08	5.40E-08	8.36E-08	1.73E-05	5.30E-06	3.97E-07	3.94E-06	1.15E-08	8.65E-06	9.89E-06	5.59E-06	7.19E-07		
	a _γ	9.12E-01	9.07E-01	9.07E-01	9.06E-01	9.06E-01	6.77E-01	6.83E-01	6.90E-01	6.83E-01	9.07E-01	9.07E-01	9.07E-01	1.00E+00	1.00E+00	1.00E+00	1.00E+00	1.00E+00	1.00E+00	1.00E+00	9.11E-01	9.09E-01	1.00E+00	9.11E-01	9.09E-01	9.09E-01	1.00E+00		
	activity	4.29E-07	1.80E-05	6.70E-04	2.49E-04	8.60E-04	1.80E-05	3.62E-06	1.07E-06	9.77E-06	1.37E-05	3.45E-05	1.00E-05	8.80E-06	8.33E-07	1.47E-08	5.40E-08	8.36E-08	1.73E-05	5.30E-06	3.62E-07	3.58E-06	1.15E-08	7.88E-06	8.99E-06	5.08E-06	7.19E-07		
9	m	8.76E-07	1.03E-05	3.23E-04	3.20E-04	6.65E-04	1.18E-05	1.49E-05	2.83E-06	1.29E-05	3.12E-06	3.36E-05	6.11E-06	2.79E-06	7.03E-07	1.98E-08	3.38E-08	1.96E-08	2.44E-05	4.84E-06	5.38E-07	8.26E-06	1.74E-08	8.69E-06	1.54E-05	3.76E-06	3.27E-07		
	a _γ	9.25E-01	9.21E-01	9.21E-01	9.21E-01	9.21E-01	7.21E-01	7.26E-01	7.30E-01	7.26E-01	9.21E-01	9.21E-01	9.21E-01	1.00E+00	1.00E+00	1.00E+00	1.00E+00	1.00E+00	1.00E+00	1.00E+00	9.24E-01	9.23E-01	1.00E+00	9.24E-01	9.23E-01	9.23E-01	1.00E+00		
	activity	8.11E-07	9.53E-06	2.98E-04	2.95E-04	6.13E-04	8.51E-06	1.08E-05	2.07E-06	9.37E-06	2.87E-06	3.09E-05	5.63E-06	2.79E-06	7.03E-07	1.98E-08	3.38E-08	1.96E-08	2.44E-05	4.84E-06	4.98E-07	7.63E-06	1.74E-08	8.04E-06	1.42E-05	3.47E-06	3.27E-07		
10	m	5.37E-07	1.75E-05	8.61E-04	2.54E-04	1.08E-03	1.84E-05	4.92E-06	9.69E-07	1.43E-05	1.20E-05	2.97E-05	6.98E-06	1.16E-05	8.68E-07	1.90E-08	4.36E-08	8.52E-08	1.08E-05	2.23E-06	2.78E-07	4.10E-06	1.35E-08	4.69E-06	7.97E-06	6.28E-06	4.86E-07		
	a _γ	9.10E-01	9.04E-01	9.04E-01	9.03E-01	9.03E-01	6.68E-01	6.75E-01	6.81E-01	6.75E-01	9.04E-01	9.04E-01	9.04E-01	1.00E+00	1.00E+00	1.00E+00	1.00E+00	1.00E+00	1.00E+00	1.00E+00	9.09E-01	9.06E-01	1.00E+00	9.09E-01	9.06E-01	9.06E-01	1.00E+00		
	activity	4.88E-07	1.58E-05	7.79E-04	2.29E-04	9.73E-04	1.23E-05	3.32E-06	6.61E-07	9.67E-06	1.08E-05	2.69E-05	6.31E-06	1.16E-05	8.68E-07	1.90E-08	4.36E-08	8.52E-08	1.08E-05	2.23E-06	2.52E-07	3.71E-06	1.35E-08	4.26E-06	7.23E-06	5.69E-06	4.86E-07		
11	m	9.05E-07	1.04E-05	8.33E-04	2.68E-04	1.12E-03	1.02E-05	1.20E-05	2.34E-06	1.28E-05	6.43E-06	2.78E-05	4.08E-06	1.16E-05	9.53E-07	3.33E-08	2.73E-08	4.89E-08	1.46E-05	2.97E-06	6.96E-07	1.04E-05	3.57E-08	6.70E-06	1.15E-05	5.84E-06	2.41E-07		
	a _γ	9.09E-01	9.04E-01	9.04E-01	9.02E-01	9.03E-01	6.67E-01	6.74E-01	6.80E-01	6.74E-01	9.04E-01	9.04E-01	9.04E-01	1.00E+00	1.00E+00	1.00E+00	1.00E+00	1.00E+00	1.00E+00	1.00E+00	9.08E-01	9.06E-01	1.00E+00	9.08E-01	9.06E-01	9.06E-01	1.00E+00		
	activity	8.23E-07	9.39E-06	7.53E-04	2.42E-04	1.01E-03	6.80E-06	8.09E-06	1.59E-06	8.63E-06	5.81E-06	2.51E-05	3.69E-06	1.16E-05	9.53E-07	3.33E-08	2.73E-08	4.89E-08	1.46E-05	2.97E-06	6.32E-07	9.43E-06	3.57E-08	6.08E-06	1.05E-05	5.30E-06	2.41E-07		
12	m	7.58E-07	1.22E-05	7.15E-04	2.40E-04	9.53E-04	1.18E-05	9.61E-06	1.42E-06	1.10E-05	6.55E-06	2.76E-05	4.34E-06	8.61E-06	7.35E-07	2.40E-08	2.92E-08	5.01E-08	1.42E-05	2.20E-06	3.69E-07	7.26E-06	2.14E-08	4.92E-06	1.12E-05	4.37E-06	2.51E-07		
	a _γ	9.15E-01	9.10E-01	9.10E-01	9.09E-01	9.09E-01	6.85E-01	6.91E-01	6.97E-01	6.91E-01	9.10E-01	9.10E-01	9.10E-01	1.00E+00	1.00E+00	1.00E+00	1.00E+00	1.00E+00	1.00E+00	1.00E+00	9.14E-01	9.12E-01	1.00E+00	9.14E-01	9.12E-01	9.12E-01	1.00E+00		
	activity	6.94E-07	1.11E-05	6.50E-04	2.18E-04	8.67E-04	8.08E-06	6.64E-06	9.91E-07	7.59E-06	5.96E-06	2.51E-05	3.95E-06	8.61E-06	7.35E-07	2.40E-08	2.92E-08	5.01E-08	1.42E-05	2.20E-06	3.37E-07	6.62E-06	2.14E-08	4.50E-06	1.02E-05	3.98E-06	2.51E-07		
13	m	7.23E-07	1.30E-05	8.68E-04	2.03E-04	1.06E-03	1.34E-05	8.99E-06	1.72E-06	1.13E-05	8.86E-06	2.94E-05	4.10E-06	1.15E-05	6.87E-07	2.53E-08	2.59E-08	6.38E-08	1.46E-05	2.91E-06	4.88E-07	7.44E-06	2.42E-08	6.18E-06	1.09E-05	4.92E-06	2.83E-07		
	a _γ	9.11E-01	9.05E-01	9.05E-01	9.04E-01	9.05E-01	6.72E-01	6.79E-01	6.85E-01	6.79E-01	9.05E-01	9.05E-01	9.05E-01	1.00E+00	1.00E+00	1.00E+00	1.00E+00	1.00E+00	1.00E+00	1.00E+00	9.10E-01	9.08E-01	1.00E+00	9.10E-01	9.08E-01	9.08E-01	1.00E+00		
	activity	6.58E-07	1.17E-05	7.85E-04	1.84E-04	9.62E-04	9.00E-06	6.10E-06	1.18E-06	7.67E-06	8.02E-06	2.66E-05	3.71E-06	1.15E-05	6.87E-07	2.53E-08	2.59E-08	6.38E-08	1.46E-05	2.91E-06	4.44E-07	6.75E-06	2.42E-08	5.63E-06	9.86E-06	4.46E-06	2.83E-07		
14	m	7.94E-07	1.20E-05	1.09E-03	2.24E-04	1.31E-03	1.13E-05	9.56E-06	1.41E-06	8.12E-06	9.05E-06	2.62E-05	3.67E-06	1.76E-05	9.20E-07	3.37E-08	2.60E-08	7.31E-08	1.21E-05	1.87E-06	4.78E-07	9.43E-06	3.73E-08	4.54E-06	1.03E-05	4.22E-06	1.59E-07		
	a _γ	9.04E-01	8.97E-01	8																									

Activity-activity diagrams

Figure B.3.37. Activity diagrams for the BW1 showing mineral stability fields in the $\text{CaO} - \text{MgO} - \text{Al}_2\text{O}_3 - \text{H}_2\text{O}$. Diagrams were constructed on the base of two different silica averages, during and after glass dissolution. Black and red crosses show position of effluent samples collected at 1.0 and 0.5 ml hr^{-1} flow rate, respectively. Yellow circles show position of the unreacted fluid (water) at $400^\circ\text{C} / 500 \text{ bar}$. Blue arrows show the path of reacted fluids over the time of the experiments.

Figure B.3.38. Activity diagrams for the BW2 showing mineral stability fields in the $\text{CaO} - \text{MgO} - \text{Al}_2\text{O}_3 - \text{H}_2\text{O}$. Diagrams were constructed on the base of two different silica averages, during and after glass dissolution process. Black and red crosses show position of effluent samples collected at 1.0 and 0.5 ml hr^{-1} flow rate, respectively. Yellow circles show position of the unreacted fluid (water) at $350^\circ\text{C} / 490 \text{ bar}$. Blue arrows show the path of reacted fluids over the time of the experiments.

Figure B.3.39. Activity diagrams for the BW1 and BW2 showing mineral stability fields in the CaO – FeO – Al₂O₃ – H₂O. Diagrams for each experiment were constructed on the base of two different silica averages, during and after glass dissolution. Black and red crosses show position of effluent samples collected at 1.0 and 0.5 ml hr⁻¹ flow rate, respectively. Yellow circles show position of the unreacted fluid (water) at 400 - 350°C / 500 bar. Blue arrows show the path of reacted fluids over the time of the experiments

Figure B.3.40. Activity diagrams for the BW1 and BW2 showing mineral stability fields in the $\text{CaO} - \text{K}_2\text{O} - \text{Al}_2\text{O}_3 - \text{H}_2\text{O}$. Diagrams for each experiment were constructed on the base of two different silica averages, during and after glass dissolution. Black and red crosses show position of effluent samples collected at 1.0 and 0.5 ml hr^{-1} flow rate, respectively. Yellow circles show position of the unreacted fluid (water) at 400 - 350°C / 500 bar. Blue arrows show the path of reacted fluids over the time of the experiments

Figure B.3.41. Activity diagrams for the BW1 and BW2 showing mineral stability fields in the $\text{CaO} - \text{Na}_2\text{O} - \text{Al}_2\text{O}_3 - \text{H}_2\text{O}$. Diagrams for each experiment were constructed on the base of two different silica averages, during and after glass dissolution. Black and red crosses show position of effluent samples collected at 1.0 and 0.5 ml hr^{-1} flow rate, respectively. Yellow circles show position of the unreacted fluid (water) at 400 - 350°C / 500 bar. Blue arrows show the path of reacted fluids over the time of the experiments

Figure B.3.42. Activity diagrams for the BW1 and BW2 showing mineral stability fields in the FeO – MgO – Al₂O₃ – H₂O. Diagrams for each experiment were constructed on the base of two different silica averages, during and after glass dissolution. Black and red crosses show position of effluent samples collected at 1.0 and 0.5 ml hr⁻¹ flow rate, respectively. Yellow circles show position of the unreacted fluid (water) at 400 - 350°C / 500 bar. Blue arrows show the path of reacted fluids over the time of the experiments

Figure B.3.43. Activity diagrams for the BW1 and BW2 showing mineral stability fields in the $K_2O - MgO - Al_2O_3 - H_2O$. Diagrams for each experiment were constructed on the base of two different silica averages, during and after glass dissolution. Black and red crosses show position of effluent samples collected at 1.0 and 0.5 ml hr^{-1} flow rate, respectively. Yellow circles show position of the unreacted fluid (water) at 400 - 350°C / 500 bar. Blue arrows show the path of reacted fluids over the time of the experiments

Figure B.3.44. Activity diagrams for the BW1 and BW2 showing mineral stability fields in the $\text{SiO}_2 - \text{MgO} - \text{Al}_2\text{O}_3 - \text{H}_2\text{O}$. Diagrams for each experiment were constructed on the base of two different silica averages, during and after glass dissolution. Black and red crosses show position of effluent samples collected at 1.0 and 0.5 ml hr^{-1} flow rate, respectively. Yellow circles show position of the unreacted fluid (water) at 400 - 350°C / 500 bar. Blue arrows show the path of reacted fluids over the time of the experiments.

Na/K geothermometers

Table B.3.28. Values of the estimate temperatures for the BW1 calculated with the geothermometers equations by Fournier (1979), Truesdell (1976), Fournier and Truesdell (1973), Santoyo and Díaz-González (2009), Arnorsson (1983), Tonani (1980), Nieva and Nieva (1987) and Giggenbach (1988)

BW1 - 400°C																																							
±15°C																																							
				mg kg ⁻¹																																			
n° samples	time	T (°C)	P (bar)	Ca	K	Na		T(°C)	T(°C)	T(°C)	T(°C)	T(°C)	T(°C)	T(°C)	T(°C)	T(°C)																							
								Na/K (Fournier 1979)	Na/K (Truesdell 1976)	Na/K/Ca (Fournier and Truesdell 1973) β=1/3	Na/K (Santoyo and Díaz-González 2009)	Na/K (Arnorrsson 1983)	Na/K (Tonani 1980)	Na/K (Nieva and Nieva 1987)	Na/K (Giggenbach 1988)																								
blank	0.00	19.6	1	0.4	< 0.9	< 0.8																																	
1		room T	502																																				
2		room T	502																																				
3		room T	502																																				
4		room T	502																																				
5		room T	502																																				
6		room T	502																																				
T-shift	7	167.3	402	502	2.5	13.3	28.0		400	451	264	434	379	481	383	397																							
	8	216.7	401	503	1.2	6.9	14.9		396	445	256	428	375	474	380	394																							
	9	240.9	401	503	1.3	5.8	13.5		384	425	247	409	365	453	368	383																							
	10	264.7	401	503	1.0	5.3	13.7		369	401	244	386	352	425	353	370																							
	11	288.7	401	503	0.8	4.7	13.0		359	386	240	372	343	409	343	361																							
	12	312.7	401	502	0.8	4.4	10.3		383	422	246	407	363	449	366	382																							
	13	335.9	401	503	0.7	4.9	9.5		415	476	259	458	392	509	398	410																							
	14	361.8	401	503	0.8	5.4	10.4		414	474	261	457	391	507	397	409																							
	15	386.2	401	502	0.7	5.9	12.8		396	444	258	428	375	474	379	393																							
	16	409.5	401	502	0.7	6.6	17.9		363	392	251	377	346	415	347	364																							
	17	434.0	400	502	0.8	8.3	25.7		343	361	247	348	329	382	328	347																							
	18	458.2	400	503	0.7	14.2	36.1		372	405	273	390	354	430	355	372																							
							T(°C) AVERAGE (SiO ₂ above quartz saturation)																																
							383									424			254			408			364			451			366			382					
							STDEV									22			36			10			34			19			40			22			20		
19	482.1	400	502	1.0	11.9	38.0		339	355	253	342	326	376	324	344																								
20	506.1	400	502	0.8	10.4	38.4		320	327	245	315	309	345	305	327																								
21	530.3	400	502	0.6	10.0	39.2		313	317	244	305	302	334	298	320																								
22	554.3	400	502	0.7	9.6	40.6		304	304	238	292	294	319	289	312																								
23	578.3	400	502	0.7	9.0	40.5		297	293	233	282	288	308	282	305																								
24	602.3	400	502	0.7	7.7	40.9		278	268	223	257	271	280	264	288																								
25	626.3	400	503	0.8	6.2	42.0		253	234	207	224	248	244	239	265																								
26	650.3	400	502	0.8	5.1	42.4		233	208	195	200	231	217	220	248																								
27	674.6	400	502	0.6	4.4	42.3		220	192	190	184	219	199	207	235																								
28	699.3	400	502	0.7	3.9	42.3		210	179	182	171	209	186	197	226																								
29	722.7	400	502	0.8	3.6	42.6		203	170	176	163	203	176	190	219																								
30	746.6	400	502	0.7	3.4	42.7		198	164	173	157	198	170	185	215																								
31	769.0	400	502	0.8	3.2	42.1		195	160	170	153	195	165	182	211																								
32	794.9	400	502	0.7	3.4	42.9		198	164	173	157	198	170	185	214																								
33	819.1	400	502	0.8	3.2	42.2		194	159	169	152	195	165	182	211																								
							T(°C) AVERAGE (SiO ₂ below quartz saturation)																																
							250									233			205			224			246			244			236			263					
							STDEV									53			71			31			69			48			76			52			49		
34	866.0	401	502	0.8	2.9	41.3		188	152	165	145	189	158	176	206																								
35	913.5	401	502	0.8	2.9	40.5		190	154	166	147	191	160	177	207																								
							T(°C) AVERAGE (SiO ₂ below quartz saturation)																																
							190									154			166			147			191			160			177			207					
							STDEV									1			1			1			1			1			1			1					

Table B.3.29. Values of the estimate temperatures for the BW2 calculated with the geothermometers equations by Fournier (1979), Truesdell (1976), Fournier and Truesdell (1973), Santoyo and Díaz-González (2009), Arnorsson (1983), Tonani (1980), Nieva and Nieva (1987) and Giggenbach (1988)

BW2 - 350°C ±15°C				mg kg ⁻¹														
n° samples	time	T (°C)	P (bar)	Ca	K	Na				T(°C)	T(°C)	T(°C)	T(°C)	T(°C)	T(°C)	T(°C)	T(°C)	
							Na/K (Fournier 1979)	Na/K (Truesdell 1976)	Na/K/Ca (Fournier and Truesdell 1973)	Na/K (Santoyo and Díaz-González 2009)	Na/K (Arnorrsson 1983)	Na/K (Tonani 1980)	Na/K (Nieva and Nieva 1987)	Na/K (Giggenbach 1988)				
blank	0.00	19.6	1	1.0	3.2	6.7												
1		room T	490															
2		room T	490															
3		room T	490															
4		room T	490															
5		room T	490															
6		room T	490															
T-shift	7	160.5	352	489	2.0	14.3	25.6	428	498	237	479	403	533	411	421			
	8	184.3	350	489	1.5	11.2	17.5	453	541	246	521	424	583	435	442			
	9	211.6	351	489	2.5	12.8	7.6											
	10	232.8	350	489	1.1	10.3	20.3	410	468	235	450	388	500	393	406			
	11	256.5	351	489	1.9	10.7	19.6	424	491	233	473	399	526	407	418			
	12	280.5	351	489	1.7	9.6	16.8	432	505	236	486	406	541	415	424			
	13	304.0	351	489	1.7	8.1	20.4	374	408	215	393	356	434	357	374			
	14	328.3	350	489	1.7	8.9	25.6	354	378	209	364	339	400	338	357			
	15	353.0	350	489	2.1	10.1	24.1	381	420	217	404	362	447	365	380			
	16	378.2	351	489	2.9	12.1	32.6	363	392	210	377	347	416	347	365			
	17	403.6	351	489	2.2	12.0	38.4	339	355	204	342	325	375	323	343			
	18	424.3	351	489	2.0	13.7	45.6	333	347	204	334	320	366	318	338			
								T(°C) AVERAGE (SiO ₂ above quartz saturation)										
								390 437 222 420 370 466 374 388										
								STDEV										
								41 67 15 64 36 74 40 36										
	19	449.2	350	489	1.7	15.9	50.3	341	358	210	345	327	378	325	345			
	20	472.5	351	489	2.2	19.9	51.7	368	399	220	384	351	424	352	369			
21	496.3	351	489	1.5	20.8	57.5	359	385	221	371	343	409	343	361				
22	519.3	351	489	1.8	19.9	51.1	370	402	222	387	352	427	353	370				
23	546.3	351	490	0.5	24.3	64.7	365	394	236	379	348	418	348	366				
24	572.4	351	490	1.6	19.0	53.1	358	383	218	369	342	406	342	360				
25	592.6	351	490	1.6	19.7	50.3	371	403	224	389	353	428	354	371				
26	616.8	351	490	1.6	18.8	51.0	362	390	220	375	345	414	346	364				
27	644.5	351	488	0.8	20.0	62.7	342	359	220	345	327	379	326	345				
28	664.5	350	489	1.7	19.2	61.7	338	354	210	341	325	374	323	343				
29	688.3	351	490	1.5	18.2	58.0	339	355	212	342	326	376	324	344				
30	714.6	351	490	0.9	17.5	58.2	334	347	214	334	321	367	318	339				
31	739.1	351	490	1.4	16.5	59.4	324	333	205	320	312	351	309	330				
32	761.1	350	489	1.4	16.2	57.6	325	334	206	322	313	353	310	331				
33	785.2	351	488	1.9	16.2	60.9	318	324	200	312	307	341	303	324				
blank - refilling	34	20	1	1.4	2.2	6.1	-	-	-	-	-	-	-	-	-			
							T(°C) AVERAGE (SiO ₂ below quartz saturation)											
							348 368 216 354 333 390 332 351											
							STDEV											
35	809.8	350	490	1.9	11.9	64.7	275	263	180	253	268	276	261	286				
36	833.0	351	490	1.5	6.8	47.2	250	230	166	221	246	240	236	263				
37	862.3	351	490	0.8	5.3	43.4	235	211	162	202	232	219	221	249				
38	883.7	350	490	1.5	5.3	41.5	239	215	159	206	235	224	225	252				
39	904.2	351	490	1.0	5.1	46.3	226	198	156	190	223	206	212	240				
40	928.3	351	489	1.3	5.3	48.5	224	196	154	188	222	204	211	239				
41	952.3	350	489	1.5	5.3	48.7	224	196	152	188	222	204	211	239				
42	976.7	350	490	1.4	5.2	49.3	221	192	151	184	219	200	208	236				
43	1002.1	351	490	1.1	5.5	45.5	233	208	159	200	230	217	220	247				
44	1049.8	351	490	0.8	5.5	48.1	228	202	159	194	226	210	215	243				
45	1096.5	350	489	1.1	5.0	45.8	224	197	154	189	222	205	211	239				
46	1144.7	350	489	1.3	5.0	45.8	225	198	154	189	223	206	212	240				
							T(°C) AVERAGE (SiO ₂ below quartz saturation)											
							234 209 159 200 231 218 220 248											
							STDEV											
							15 20 8 20 14 22 15 14											

Table B.3.30. Geothermometers equations utilized for the calculation of the estimate temperature values reported in Table 3.28 and Table 3.29

Na/K : Fournier (1979)	$T(^{\circ}C) = \frac{1217}{1.438 + \log\left(\frac{Na}{K}\right)} - 273,15 (^{\circ}K)$
Na/K : Truesdell (1976)	$T(^{\circ}C) = \frac{855,6}{0.8573 + \log\left(\frac{Na}{K}\right)} - 273,15 (^{\circ}K)$
Na/K : Santoyo and Gonzalez (2009)	$T(^{\circ}C) = \frac{876.3(\pm 26.26)}{0.8775(\pm 0.0508) + \log\left(\frac{Na}{K}\right)} - 273,15 (^{\circ}K)$
Na/K : Arnorsson (1983)	$T(^{\circ}C) = \frac{1319}{1.699 + \log\left(\frac{Na}{K}\right)} - 273,15 (^{\circ}K)$
Na/K : Tonani (1980)	$T(^{\circ}C) = \frac{883}{0.78 + \log\left(\frac{Na}{K}\right)} - 273,15 (^{\circ}K)$
Na/K : Nieva and Nieva (1987)	$T(^{\circ}C) = \frac{1178}{1.483 + \log\left(\frac{Na}{K}\right)} - 273,15 (^{\circ}K)$
Na/K : Giggenbach (1988)	$T(^{\circ}C) = \frac{1390}{1.75 + \log\left(\frac{Na}{K}\right)} - 273,15 (^{\circ}K)$
Na/K/Ca : Fournier and Truesdall (1973)	$T(^{\circ}C) = \frac{1647}{\log\left(\frac{Na}{K}\right) + \beta [\log(\sqrt{Ca}/Na) + 2.06] + 2.47} - 273,15 (^{\circ}K)$

Appendix C - (Chapter 4)

Chapter 4: Basalt – Geothermal Brine Interactions Under Hydrothermal Conditions

4.2. Results

4.2.1. BGB1: Basalt – geothermal brine at 400°C/483 bar

Table C.4.1. Major ions compositions and complete experimental parameters (n° of samples collected, T, P, experimental time, flow rate and pH) for the BGB1 (400°C / 483 bar). *In situ* pH is the calculated pH at temperature. Analysis of major ions are reported both in mg kg⁻¹ and in mmol kg⁻¹. n.c.: not calculated

n° sample	T (°C)	P (bar)	time (hrs)	flow-rate (ml hr ⁻¹)	pH (room T)	pH (400°C)	mg kg ⁻¹												mmol kg ⁻¹													
							As	B	Ca	Fe	K	Mg	Na	SiO ₂	Al	Li	H ₂ S	Cl	SO ₄	As	B	Ca	Fe	K	Mg	Na	SiO ₂	Al	Li	H ₂ S	Cl	SO ₄
blank geothermal brine	20.1	1	0.0	-	3.91	7.14	1.8	48.2	3.4	0.08	116.2	0.2	725.3	758.7	1.5	5.7	0.2	941	404.9	0.02	4.5	0.08	0.001	3	0.01	31.6	12.6	0.06	0.8	0.004	26.5	4.2
1	20.4	485.8	20.6	1	5.90	n.c.	0.4	48.2	7.1	0.2	106.7	1.2	710.5	710.6	8.8	5.6	0.1	935.6	401.3	0.01	4.5	0.2	0.004	2.7	0.05	30.9	11.8	0.3	0.8	0.004	26.5	4.2
2	20.2	483.4	45.6	1	6.00	n.c.	0.2	48.2	5.9	0.4	122.3	0.8	710.9	733.9	10.5	5.6	0.2	842.7	350.4	0.003	4.5	0.1	0.01	3.1	0.03	30.9	12.2	0.4	0.8	0.01	26.4	3.6
3	20.7	484.0	72.8	1	5.64	n.c.	0.2	48.2	6.1	0.9	117.2	0.6	720	803.8	8	5.7	0.3	963.6	397.6	0.003	4.5	0.2	0.02	3	0.02	31.3	13.4	0.3	0.8	0.01	27.2	4.1
4	20.6	483.5	94.8	1	5.50	n.c.	0.2	48.2	5.6	1.3	116	0.6	724.5	815.1	7.2	5.7	0.2	824.1	345.1	0.003	4.5	0.1	0.02	3	0.03	31.5	13.6	0.3	0.8	0.01	23.2	3.6
5	20.5	484.2	118.9	1	5.49	n.c.	0.3	48.2	5.1	1.5	115	0.7	716.9	804.9	7.1	5.7	0.2	891.8	373.9	0.004	4.5	0.1	0.03	2.9	0.03	31.2	13.4	0.3	0.8	0.01	25.2	3.9
6	20.7	485.4	143.1	1	5.55	n.c.	0.4	48.2	5.2	1.6	113.8	0.8	712	802.1	6.7	5.6	0.3	951.7	394.7	0.005	4.5	0.1	0.03	2.9	0.03	31	13.3	0.2	0.8	0.01	26.8	4.1
7	20.4	484.5	166.7	1	5.35	n.c.	0.4	48.2	4.9	1.3	114.6	0.8	716.9	807.9	5.8	5.7	0.3	970.5	400	0.01	4.5	0.1	0.02	2.9	0.03	31.2	13.4	0.2	0.8	0.01	27.4	4.2
8	397.6	478.9	190.9	1	3.23	7.00	2.1	48.2	3.2	0.5	192.5	0.4	597.7	1531.1	2.6	4.4	0.1	900.9	239.8	0.03	4.5	0.08	0.01	4.9	0.02	26	25.5	0.1	0.6	0.003	25.4	2.5
9	400.1	483.1	214.7	1	2.87	7.06	1	48.2	2	0.1	196.5	0.2	623.5	2081.2	0.8	5	1.6	934.4	272.7	0.01	4.5	0.05	0.001	5	0.01	27.1	34.6	0.03	0.7	0.05	26.4	2.8
10	400.4	483.5	239.3	1	3.25	7.10	0.8	48.2	2.2	0.1	149.5	0.2	666.1	2000.7	0.6	5.4	5.3	964.6	326.8	0.01	4.5	0.06	0.002	3.8	0.01	29	33.3	0.02	0.8	0.2	27.2	3.4
11	400.7	483.8	262.6	1	3.32	7.11	0.7	48.2	2.8	<0.08	144.8	0.3	684.6	1798.4	0.6	5.3	8.6	969.2	350.2	0.01	4.5	0.07	<0.001	3.7	0.01	29.8	29.9	0.02	0.8	0.3	27.3	3.6
12	400.8	484.1	287.9	1	3.25	7.11	1	48.2	2.6	<0.08	150.9	0.2	692.5	1813.4	0.6	5.1	5.2	906.1	347.9	0.01	4.5	0.06	<0.001	3.9	0.01	30.1	30.2	0.02	0.7	0.2	25.6	3.6
13	400.4	484.4	313.4	1	3.31	7.11	1.2	48.2	2.3	<0.08	151.5	0.1	697.6	1814.9	0.5	5.1	1.6	903.4	351.1	0.02	4.5	0.06	<0.001	3.9	0.01	30.3	30.2	0.02	0.7	0.05	25.5	3.7
14	400.4	484.3	334.4	1	3.53	7.12	1.4	48.2	2.5	<0.08	148.7	0.2	689.8	1810.1	0.6	5	1.8	938.8	366	0.02	4.5	0.06	<0.001	3.8	0.01	30	30.1	0.02	0.7	0.05	26.5	3.8
15	400.8	484.4	359.0	1	3.55	7.12	1.5	48.2	2.7	<0.08	147.9	0.2	696.9	1829.5	0.5	5.1	1.2	921	367.4	0.02	4.5	0.07	<0.001	3.8	0.01	30.3	30.5	0.02	0.7	0.04	26	3.8
16	400.6	484.2	382.7	1	3.50	7.12	1.6	48.2	2.7	<0.08	145.3	0.2	681.6	1844.5	0.8	5.1	1	914.3	364.1	0.02	4.5	0.07	<0.001	3.7	0.01	29.6	30.7	0.03	0.7	0.03	25.8	3.8
17	400.7	483.5	406.0	1	3.40	7.12	1.7	48.2	3	0.1	141.6	0.2	684.8	1852.9	0.8	5.1	0.9	923.4	368.8	0.02	4.5	0.07	0.001	3.6	0.01	29.8	30.8	0.03	0.7	0.03	26	3.8
18	400.9	483.6	430.6	1	3.45	7.11	1.7	48.2	3.8	<0.08	136.2	0.2	688.8	1859.6	0.8	5.1	0.6	928.6	369.1	0.02	4.5	0.09	<0.001	3.5	0.01	30	31	0.03	0.7	0.02	26.2	3.8
19	400.7	483.8	457.3	1	3.57	7.10	1.7	48.2	3.7	<0.08	132.1	0.4	694.3	1887.6	0.7	5.1	0.7	894.6	361.5	0.02	4.5	0.09	<0.001	3.4	0.02	30.2	31.4	0.03	0.7	0.02	25.2	3.8
20	400.6	483.8	480.7	1	3.71	7.09	1.7	48.2	4.3	<0.08	122.6	0.4	693.2	1886.4	0.6	5.1	0.2	883.8	348.4	0.02	4.5	0.1	<0.001	3.1	0.02	30.2	31.4	0.02	0.7	0.01	24.9	3.6
21	400.6	484.7	503.3	1	3.76	7.08	1.7	48.2	4	0.1	114.4	0.4	710.1	1898.7	0.7	5.2	0.6	822.2	333.8	0.02	4.5	0.1	0.001	2.9	0.02	30.9	31.6	0.02	0.7	0.02	23.2	3.5
22	400.9	484.2	527.7	1	3.78	7.10	1.6	48.2	4.3	<0.08	106.3	0.5	706	1897.8	0.7	5.1	0.4	907.7	360.2	0.02	4.5	0.1	<0.001	2.7	0.02	30.7	31.6	0.02	0.7	0.01	25.6	3.8
23	400.5	483.5	550.4	1	4.05	7.09	1.6	48.2	4.9	0.1	103.1	0.5	713.4	1841	0.7	5.1	0.5	918.7	366.9	0.02	4.5	0.1	0.002	2.6	0.02	31	30.6	0.03	0.7	0.02	25.9	3.8
24	400.7	483.5	574.8	1	4.60	7.10	1.7	48.2	3.9	<0.08	100.4	0.4	714.8	1463.6	1.2	5	0.5	920.1	352.7	0.02	4.5	0.1	<0.001	2.6	0.02	31.1	24.4	0.05	0.7	0.01	26	3.7
25	400.6	483.9	597.6	1	6.23	7.08	1.7	48.2	4.2	<0.08	98.8	0.5	701.6	1101.8	2.8	4.8	0.5	893.8	337.1	0.02	4.5	0.1	<0.001	2.5	0.02	30.5	18.3	0.1	0.7	0.01	25.2	3.5
26	400.5	484.0	625.7	1	6.51	7.11	1.7	48.2	3.3	<0.08	96.3	0.3	699.7	1009.7	2.9	4.8	<0.01	925.3	338.3	0.02	4.5	0.1	<0.001	2.5	0.01	30.4	16.8	0.1	0.7	<0.0003	26.1	3.5
27	400.7	483.9	647.5	1	6.77	7.11	1.7	48.2	3.8	<0.08	95.1	0.4	694.6	1004.2	3	4.8	0.2	933.1	354.8	0.02	4.5	0.1	<0.001	2.4	0.02	30.2	16.7	0.1	0.7	0.01	26.3	3.7
28	400.4	483.6	670.8	1	7.07	7.09	1.7	48.2	4.4	<0.08	95.3	0.5	727.2	988.3	3.7	4.9	0.2	942.6	351.8	0.02	4.5	0.1	<0.001	2.4	0.02	31.6	16.4	0.1	0.7	0.01	26.6	3.7
29	400.5	483.6	694.4	1	7.44	7.05	1.6	48.2	4.4	<0.08	95.4	0.5	718.4	976.9	4.4	4.9	0.3	828.4	303.2	0.02	4.5	0.1	<0.001	2.4	0.02	31.2	16.3	0.2	0.7	0.01	23.4	3.2
30	400.2	483.4	718.8	1	7.52	7.10	1.7	48.2	3.8	<0.08	95.1	0.4	724.5	987.2	4	5	0.2	916.1	346.4	0.02	4.5	0.1	<0.001	2.4	0.02	31.5	16.4	0.1	0.7	0.01	25.8	3.6
31	400.4	483.6	743.4	1	7.41	7.08	1.7	48.2	4	<0.08	94.8	0.4	722.1	980.5	4.3	5	0.2	874.2	332	0.02	4.5	0.1	<0.001	2.4	0.02	31.4	16.3	0.2	0.7	0.01	24.7	3.5
32	400.6	483.1	767.5	1	7.66	7.08	1.5	48.2	4	<0.08	92.3	0.3	711.8	930.3	5.9	5	0.3	891.4	309.2	0.02	4.5	0.1	<0.001	2.4	0.01	31	15.5	0.2	0.7	0.01	25.1	3.2
33	400.7	477.0	809.2	0.5	7.30	7.05	2	48.2	5.7	<0.08	93.3	0.7	741.6	954.2	4.5	5.2	0.1	918.3	330.2	0.03	4.5	0.1	<0.001	2.4	0.03	32.3	15.9	0.2	0.8	0.00	25.9	3.4
34	400.5	482.3	853.2	0.5	7.76	7.09	1.9	48.2	3.9	<0.08	92.1	0.4	735.9	1023.2	4.6	5.1	0.2	915.2	333.3	0.03	4.5	0.1	<0.001	2.4	0.01	32	17	0.2	0.7	0.01	25.8	3.5

Table C.4.2. Trace element compositions and complete experimental parameters (n° of samples collected, T, P, experimental time, flow rate and pH) for the BGB1 (400°C / 483 bar). *In situ* pH is the calculated pH at temperature. Analysis of trace elements are reported in µmol kg⁻¹. n.c.: not calculated

n° sample	T (°C)	P (bar)	time (hrs)	flow-rate (ml hr ⁻¹)	pH (room T)	pH (400°C)	µmol kg ⁻¹													
							V	Cr	Co	Ni	Cu	Zn	Rb	Mo	Ag	Cd	Ba	Au	Pb	Mn
blank geothermal brine	20.1	1	0.0	-	3.91	7.14	0.04	0.06	< 0.002	0.1	0.3	1.9	8.5	0.1	0.006	0.6	< 0.001	1	0.01	< 0.13
1	20.4	485.8	20.6	1	5.90	n.c.	0.02	0.3	0.2	4.7	0.1	23.3	6.2	0.1	0.004	0.03	0.1	0.8	0.3	3.1
2	20.2	483.4	45.6	1	6.00	n.c.	0.02	0.6	0.2	4.4	12.7	23.1	8.5	0.07	0.002	0.04	0.3	0.5	0.2	3.5
3	20.7	484.0	72.8	1	5.64	n.c.	0.01	2.3	0.4	5.8	36.3	13.4	8.3	0.09	< 0.0005	0.02	0.4	0.4	0.8	3.7
4	20.6	483.5	94.8	1	5.50	n.c.	0.02	3.7	0.3	5.5	29.4	20.3	7.5	0.1	0.003	0.05	0.5	0.3	1.1	3.0
5	20.5	484.2	118.9	1	5.49	n.c.	0.03	5	0.3	6.1	31	14.5	7.2	0.2	< 0.0005	0.03	0.4	0.3	1.1	2.5
6	20.7	485.4	143.1	1	5.55	n.c.	0.05	5	0.3	5.6	23.1	26.9	7	0.1	0.003	0.03	0.3	0.2	1.4	2.2
7	20.4	484.5	166.7	1	5.35	n.c.	0.07	6.2	0.4	6.8	27.6	35.4	9.7	0.3	0.003	0.03	0.4	0.3	1.1	1.6
8	397.6	478.9	190.9	1	3.23	7.00	0.1	0.6	0.04	1.0	7.9	30.2	6.7	0.06	< 0.0005	0.04	0.09	0.1	0.3	0.2
9	400.1	483.1	214.7	1	2.87	7.06	0.003	0.1	0.01	0.6	0.3	37.1	5.8	0.2	< 0.0005	0.01	0.01	0.1	0.8	< 0.13
10	400.4	483.5	239.3	1	3.25	7.10	0.01	0.1	0.005	0.5	0.2	42.6	6	0.2	< 0.0005	0.04	< 0.001	0.1	1.3	< 0.13
11	400.7	483.8	262.6	1	3.32	7.11	0.04	< 0.004	< 0.002	0.7	1.7	42	10.9	0.3	< 0.0005	0.01	< 0.001	0.1	0.2	< 0.13
12	400.8	484.1	287.9	1	3.25	7.11	0.03	0.1	< 0.002	0.4	0.1	33	11.4	0.1	< 0.0005	0.01	< 0.001	0.1	1	< 0.13
13	400.4	484.4	313.4	1	3.31	7.11	0.05	0.02	< 0.002	0.6	0.1	39.4	7.5	0.1	< 0.0005	0.03	< 0.001	0.1	0.3	< 0.13
14	400.4	484.3	334.4	1	3.53	7.12	0.08	0.02	< 0.002	0.6	0.1	33.1	6.1	0.1	< 0.0005	0.03	< 0.001	0.1	0.1	< 0.13
15	400.8	484.4	359.0	1	3.55	7.12	0.08	0.03	< 0.002	0.6	0.1	30.1	5.5	0.1	< 0.0005	0.003	< 0.001	0.1	0.1	< 0.13
16	400.6	484.2	382.7	1	3.50	7.12	0.07	0.03	0.005	0.6	0.2	38.1	5.1	0.1	< 0.0005	0.02	< 0.001	0.1	0.1	< 0.13
17	400.7	483.5	406.0	1	3.40	7.12	0.07	0.03	< 0.002	0.7	0.2	34.1	4.5	0.1	< 0.0005	0.02	< 0.001	0.1	0.1	< 0.13
18	400.9	483.6	430.6	1	3.45	7.11	0.05	0.03	< 0.002	0.3	0.1	30.8	4.1	0.1	< 0.0005	0.03	< 0.001	0.1	0.3	< 0.13
19	400.7	483.8	457.3	1	3.57	7.10	0.03	0.04	< 0.002	0.2	0.1	21.1	3.8	0.09	< 0.0005	0.03	0.02	0.03	0.4	< 0.13
20	400.6	483.8	480.7	1	3.71	7.09	0.03	0.04	< 0.002	0.6	0.2	34.7	3.1	0.1	< 0.0005	0.03	< 0.001	0.1	0.5	0.2
21	400.6	484.7	503.3	1	3.76	7.08	0.06	0.03	0.008	0.9	0.1	38.5	3.5	0.1	< 0.0005	0.03	< 0.001	0.04	0.2	< 0.13
22	400.9	484.2	527.7	1	3.78	7.10	0.03	0.03	0.006	0.6	0.1	35.7	2.7	0.08	< 0.0005	0.04	< 0.001	0.04	0.2	< 0.13
23	400.5	483.5	550.4	1	4.05	7.09	0.03	0.04	0.005	0.5	0.3	26.4	2.4	0.07	< 0.0005	0.03	< 0.001	0.03	0.5	< 0.13
24	400.7	483.5	574.8	1	4.60	7.10	0.08	< 0.004	< 0.002	0.2	0.1	17.1	2.3	0.09	< 0.0005	0.04	< 0.001	0.03	0.1	< 0.13
25	400.6	483.9	597.6	1	6.23	7.08	0.3	0.1	< 0.002	0.2	0.1	11.7	2	0.3	< 0.0005	0.03	< 0.001	0.03	0.03	< 0.13
26	400.5	484.0	625.7	1	6.51	7.11	0.3	0.04	< 0.002	0.3	0.2	8.4	2	0.1	< 0.0005	0.02	< 0.001	0.03	0.03	0.2
27	400.7	483.9	647.5	1	6.77	7.11	0.2	0.1	< 0.002	0.2	0.3	16.2	1.8	0.1	< 0.0005	0.03	< 0.001	0.02	0.2	< 0.13
28	400.4	483.6	670.8	1	7.07	7.09	0.3	0.1	< 0.002	0.4	0.3	15.5	1.8	0.1	0.003	0.03	< 0.001	0.03	0.3	0.14
29	400.5	483.6	694.4	1	7.44	7.05	0.3	0.03	0.004	0.2	0.2	11.4	1.6	0.1	< 0.0005	0.02	< 0.001	0.02	0.2	< 0.13
30	400.2	483.4	718.8	1	7.52	7.10	0.2	0.02	< 0.002	0.2	0.1	14.4	1.5	0.1	< 0.0005	0.01	< 0.001	0.02	0.3	< 0.13

Figure C.4.1. EDS analysis for the study of the morphology of reacted grains collected from the bottom (Portion 1) of the Reactor after the BGB1 experiment

Figure C.4.2. EDS analysis for the study of the morphology of reacted grains collected from the bottom (Portion 1) of the Reactor after the BGB1 experiment

Figure C.4.3. SEM photographs (epoxy-mount) of reacted grains collected from the bottom (Portion 1) of Reactor for EMPA examination. Analysis points are marked in red numbers

Table C.4.3. EMPA analysis of grains 1-2-3-4 in Fig. C.4.3

Analysis Point	Grain 1	Na ₂ O	MgO	SiO ₂	K ₂ O	CaO	TiO ₂	FeO	MnO	Cl	Al ₂ O ₃	SO ₂	P ₂ O ₅	Total	Analysis Point	Grain 4	Na ₂ O	MgO	SiO ₂	K ₂ O	CaO	TiO ₂	FeO	MnO	Cl	Al ₂ O ₃	SO ₂	P ₂ O ₅	Total																
1	Mca	0.13	6.16	19.74	3.07	0.23	0.12	10.81	0.18	0.34	7.23	0.11		48.12	1	Mca	0.38	10.86	35.91	6.38	0.49	0.51	20.98	0.31	0.03	14.53	0.07	0.03	90.48																
2	Mca	0.45	8.17	25.12	2.03	0.82	0.38	20.88	0.18	0.13	8.50	0.19	0.06	66.92	2	Mca	0.37	10.73	35.44	6.16	0.63	0.44	20.57	0.31	0.05	13.96	0.07	0.03	88.75																
3	Mca	0.49	11.00	29.51	0.26	0.63	0.09	12.88	0.10	0.19	5.61	0.25	0.07	61.07	4	Mca	0.46	10.35	35.69	5.92	0.52	0.65	22.93	0.31	0.02	12.33	0.07	0.04	89.29																
4	Mca	0.22	5.57	21.21	3.28	0.95	0.17	11.50	0.14	0.17	8.03	0.40	0.02	51.64	5	Mca	0.33	11.80	38.07	6.84	0.39	0.36	22.80	0.29	0.04	13.99	0.01	0.02	94.95																
5	Mca	0.42	10.90	35.51	5.19	0.98	0.32	20.05	0.35	0.06	12.69	0.09	0.29	86.84	12	Mca	0.17	7.13	21.24	2.54	0.68	0.20	12.65	0.25	0.27	9.55	0.06	0.01	54.74																
6	Mca	0.38	10.02	31.50	4.86	0.61	0.21	18.67	0.32	0.10	10.52	0.14	0.04	77.37	13	Mca	0.39	9.78	31.08	4.63	0.79	0.68	18.90	0.29	0.16	12.05	0.09	0.03	78.86																
7	Mca	0.23	9.17	32.45	6.25	0.40	0.26	19.24	0.27	0.09	11.63	0.06	0.02	80.06	3	Cpx	0.26	16.71	49.37	0.60	15.00	0.53	12.33	0.28	0.02	3.89	0.03	0.02	99.04																
8	Plg	3.87	0.19	52.35	0.09	13.79	0.06	1.02	0.01		30.86		0.02	102.25	8	Cpx	0.23	15.93	51.12	0.01	17.97	0.93	11.08	0.26		3.53	0.01	0.04	101.10																
															14	Cpx	0.22	16.41	52.57	0.03	18.44	0.58	11.19	0.27		2.05	0.01	0.03	101.80																
9	Cpx	0.21	16.09	51.69		18.50	0.64	11.45	0.30		2.17	0.01	0.02	101.08	6	Plg	3.73	0.20	51.54	0.07	13.83	0.07	1.03	0.05		30.96		0.01	101.50																
															15	Plg	3.56	0.15	52.31	0.05	14.13	0.05	0.75		0.01	31.35		0.02	102.38																
Analysis Point	Grain 2	Na ₂ O	MgO	SiO ₂	K ₂ O	CaO	TiO ₂	FeO	MnO	Cl	Al ₂ O ₃	SO ₂	P ₂ O ₅	Total	10	Anh			0.04		40.17	0.02	0.20		0.01	0.02	34.82	0.05	75.32																
															16	Ox		1.06	0.02	0.01	0.17	42.96	47.20	0.60	0.01	0.09		0.01	92.12																
															average	Na ₂ O	MgO	SiO ₂	K ₂ O	CaO	TiO ₂	FeO	MnO	Cl	Al ₂ O ₃	SO ₂	P ₂ O ₅																		
																Mca	0.35	9.99	31.10	4.11	1.04	0.76	17.86	0.25	0.12	11.18	0.16	0.28																	
																Plg	3.92	0.18	52.25	0.08	13.72	0.07	0.94	0.03	0.01	30.92	0.01	0.02																	
																Cpx	0.22	15.88	50.01	0.16	17.04	0.62	11.46	0.26	0.02	2.58	0.03	0.03																	
																Ox		1.06	0.02	0.01	0.17	42.96	47.20	0.60	0.01	0.09		0.01																	
																Anh			0.03	0.01	39.24	0.02	0.14		0.02	0.02	34.84	0.04																	
																7	Plg	4.51	0.17	52.79	0.11	13.11	0.09	0.96	0.01		30.51	0.01		102.28															
																13	Anh			0.03	0.01	38.31		0.07		0.03	0.03	34.87	0.03	73.38															
																Analysis Point	Grain 3	Na ₂ O	MgO	SiO ₂	K ₂ O	CaO	TiO ₂	FeO	MnO	Cl	Al ₂ O ₃	SO ₂	P ₂ O ₅	Total	1	Mca	0.38	9.81	30.40	2.92	0.90	0.17	16.27	0.19	0.10	11.96	0.17	0.07	73.33
																															2	Mca	0.46	9.57	34.15	5.53	1.60	1.09	22.97	0.34	0.04	12.16	0.10	0.76	88.74
																															3	Mca	0.30	9.08	31.82	5.41	1.88	0.87	23.21	0.31	0.05	12.18	0.11	0.97	86.22
																															4	Mca	0.25	8.55	29.98	5.38	0.53	0.40	19.44	0.21	0.12	11.38	0.13		76.36
																															5	Mca	0.57	13.27	37.01	3.76	0.59	0.92	23.84	0.19	0.04	12.07	0.03	0.03	92.33
																															6	Mca	0.21	6.33	17.67	1.20	0.56	0.10	8.89	0.10	0.43	6.87	0.07	0.02	42.44
7	Mca	0.57	13.27	37.47	3.91	0.67	0.81	18.25	0.29	0.06	12.95	0.06	0.02	88.34																															
8	Mca	0.43	12.72	37.38	4.37	0.66	1.13	19.19	0.29	0.06	12.84	0.06	0.03	89.17																															
9	Mca	1.12	11.35	32.22	2.87	0.77	0.78	20.54	0.18	0.07	10.93	0.12	0.07	81.02																															
10	Mca	0.70	14.17	39.02	4.03	0.88	0.32	17.87	0.23	0.04	12.98	0.04	0.05	90.34																															
13	Mca	0.40	9.51	32.06	5.61	0.68	0.20	18.87	0.20	0.13	12.34	0.08	0.03	80.10																															
14	Mca	0.33	7.19	23.44	3.77	7.99	0.16	13.23	0.16	0.23	8.55	0.09	6.41	71.56																															
15	Mca	0.58	9.75	32.15	2.80	1.37	0.69	16.85	0.20	0.08	11.17	0.16	0.03	75.82																															
16	Mca	0.46	11.03	34.40	5.94	0.80	0.61	20.47	0.26	0.06	12.44	0.15	0.10	86.73																															
18	Mca	0.36	12.51	36.96	4.62	0.78	0.91	19.30	0.22	0.05	12.30	0.10	0.05	88.15																															
19	Mca	0.36	14.01	39.66	4.47	0.87	0.25	18.04	0.24	0.04	13.82	0.05	0.04	91.84																															
11	Cpx		13.62	42.88	0.02	13.00	0.49	12.17	0.23	0.02	1.76	0.10		84.28																															
12	Cpx	0.17	16.51	52.40		19.32	0.53	10.52	0.23		2.10			101.78																															

Table C.4.4. Average mineral compositions from Table C.4.3

Oxides	average wt%			average wt%			average wt%	average wt%
Na ₂ O	0.18			0.35				
MgO	15.88			9.99			1.06	
SiO ₂	50.01			31.10			0.02	0.03
K ₂ O	0.11			4.11			0.01	0.01
CaO	17.04			1.04			0.17	39.24
TiO ₂	0.62			0.76			42.96	0.01
FeO _(T)	11.46			17.86			47.20	0.14
MnO	0.26			0.25			0.60	
Cl	0.01			0.12			0.01	0.02
Al ₂ O ₃	2.58			11.18			0.09	0.02
SO ₂	0.03			0.16				34.84
P ₂ O ₅	0.02			0.27			0.01	0.04
Total	98.18			77.19			92.12	74.35
Mineral Composition	Na _{0.013} Ca _{0.70} Mg _{0.90} Fe _{0.37} Mn _{0.01} Ti _{0.02} Al _{0.03} Si _{1.91} Al _{0.09} O ₆			K _{0.98} Ca _{0.21} Na _{0.13} Mg _{2.80} Fe _{2.80} Mn _{0.04} Ti _{0.11} Al _{0.31} Si _{5.84} Al _{2.16} O ₂₀ (OH) ₄ (on the basis of 22 oxygen equivalents, ignoring H ₂ O)				CaSO ₄
Phase and ID	Clinopyroxene (augite)			Mica (biotite)			Oxide (titanomagnetite)	Sulphate (anhydrite)

Figure C.4.4. SEM photographs (epoxy-mount) of reacted grains collected from the bottom (Portion 1) of the Reactor for SEM-EDS examination. Analysis points are marked in blue

Figure C.4.5. SEM backscatter and EDS compositional maps of further epoxy-mounted, polished grain collected from the bottom (Portion 1) of Reactor after the BGB1 experiment: (a) backscatter image; (b) composite colour image combining the backscatter image and elemental maps for c) K in green, d) Ca in blue, and e) S in red. The composite image shows the anhydrite crystals (pink), biotite (green), the primary plagioclase (darker blue) and clinopyroxene (lighter blue), primary olivine and Fe-Ti oxides (grey)

Table C.4.5. EDS analysis of grains in Fig. C.4.4

Plg	Analysis Point	Na ₂ O	Al ₂ O ₃	SiO ₂	CaO	FeO	Total
	2	2.21	32.77	50.32	13.78	0.93	100.00
	8	2.54	32.01	52.11	13.34	0.00	100.00
	23	2.09	33.09	49.97	14.85	0.00	100.00
	25	2.13	33.35	50.11	14.41	0.00	100.00
	27	2.25	34.06	49.61	14.07	0.00	100.00
	36	2.17	33.61	49.60	13.52	1.10	100.00
	38	2.37	32.58	51.98	13.07	0.00	100.00
	44	1.83	34.01	48.89	15.27	0.00	100.00
	72	2.10	32.59	50.61	14.71	0.00	100.00
	75	2.09	33.10	50.16	14.65	0.00	100.00
average		2.18	33.12	50.34	14.17	0.20	100.00

Cpx	Analysis Point	MgO	Al ₂ O ₃	SiO ₂	CaO	FeO	Total
	3	12.01	2.20	55.18	19.04	11.57	100.00
	7	3.80	6.09	33.06	26.02	31.03	100.00
	9	14.08	2.06	55.77	20.50	7.60	100.00
	11	9.32	2.69	54.66	13.22	20.11	100.00
	12	5.98	1.64	42.98	17.94	31.47	100.00
	22	10.61	2.06	54.88	17.77	14.68	100.00
	26	9.35	1.89	55.28	17.95	15.53	100.00
	29	13.87	2.24	55.83	19.90	8.16	100.00
	33	13.66	2.74	55.66	19.64	8.30	100.00
	37	12.90	4.13	53.77	20.65	8.55	100.00
	45	13.61	3.62	54.86	20.14	7.78	100.00
	60	14.09	2.18	56.28	19.27	8.18	100.00
	68	9.58	2.16	54.45	17.42	16.40	100.00
	69	9.53	2.45	53.70	17.81	16.52	100.00
	76	13.09	2.48	55.22	19.99	9.22	100.00
	77	13.22	4.56	53.54	19.95	8.73	100.00
	78	13.15	2.38	55.23	20.54	8.70	100.00
	79	12.82	4.72	53.01	19.38	10.07	100.00
	80	13.62	3.31	54.67	18.43	9.97	100.00
average		11.49	2.93	53.05	19.24	13.29	100.00

Mca	Analysis Point	MgO	Al ₂ O ₃	SiO ₂	K ₂ O	FeO	Total
	1	12.06	15.34	46.06	7.02	19.53	100.00
	4	11.00	14.12	45.45	7.43	22.00	100.00
	5	10.90	15.84	45.22	7.81	20.23	100.00
	6	10.58	14.54	44.83	8.12	21.93	100.00
	21	12.01	14.51	46.58	6.54	20.36	100.00
	24	10.19	13.73	46.16	7.86	22.06	100.00
	28	10.20	14.34	43.94	7.55	23.97	100.00
	30	11.34	12.78	46.70	3.87	25.32	100.00
	31	12.90	11.69	41.97	1.63	31.81	100.00
	32	9.85	13.47	44.65	5.69	26.33	100.00
	35	8.45	14.40	46.04	8.32	22.79	100.00
	41	12.70	17.27	47.51	1.92	20.61	100.00
	42	12.45	15.53	46.67	6.97	18.38	100.00
	43	11.09	15.74	44.90	7.18	21.09	100.00
	59	10.66	15.64	44.66	7.52	21.52	100.00
	61	12.09	15.13	45.78	7.47	19.53	100.00
	64	12.15	14.78	46.34	6.14	20.59	100.00
average		11.21	14.64	45.50	6.41	22.24	100.00

Anh	Analysis Point	CaO	SO ₃	Total
	40	42.16	57.84	100.00
	62	37.07	62.77	100.00
	63	39.10	60.90	100.00
average		39.44	60.50	99.95

Ox	Analysis Point	FeO	TiO ₂	Total
	55	52.10	47.90	100.00
	56	98.77	1.23	100.00

Tnt	Analysis Point	FeO	TiO ₂	Total
	34	70.26	29.74	100.00
	59	69.96	30.04	100.00
	61	74.44	25.56	100.00
	62	66.47	33.53	100.00
	63	75.83	24.17	100.00
	64	73.15	26.85	100.00
average		71.69	28.32	100.00

Table C.4.6. Average mineral compositions from Table C.4.5

Oxides	average wt%	average wt%	average wt%	average wt%	average wt%	point n°56 wt%
Na ₂ O	2.18					
Al ₂ O ₃	33.12	2.93	14.64			
SiO ₂	50.34	53.05	45.50			
CaO	14.17	19.24		39.44		
FeO	0.20	13.29	22.24		71.69	98.77
MgO		11.49	11.21			
K ₂ O			6.41			
TiO ₂					28.32	1.23
SO ₃				60.50		
Total	100.00	100.00	100.00	99.94	100.01	100.00
Mineral Composition	Ca _{0.70} Na _{0.19} Al _{1.79} Si _{2.31} O ₈ (An ₇₈ -Ab ₂₂)	Ca _{0.77} Mg _{0.64} Fe _{0.42} Al _{0.12} Si _{1.99} Al _{0.01} O ₆	K _{1.15} Mg _{2.35} Fe _{2.62} Al _{0.84} Si _{6.41} Al _{1.59} O ₂₀ (OH) ₄ (on the basis of 22 oxygen equivalents, ignoring H ₂ O)	CaSO ₄	Fe ²⁺ (Fe ³⁺ ,Ti) ₂ O ₄	
Phase and ID	Plagioclase (bytownite)	Clinopyroxene (augite)	Mica (biotite)	Sulphate (anhydrite)	Oxide (titanomagnetite)	Oxide

Figure C.4.6. XRD scan showing the mineralogy of reacted grains collected from the bottom (Portion 1) of the Reactor after the BGB1 experiment

Figure C.4.7. Quantitative XRD analysis of reacted grains collected from the bottom (Portion 1) of the Reactor after the BGB1 experiment

Report Number: PSR2018/16_2018041205
Report Date: 30/04/2018

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Sample Composition

Table 1. Mineral percentages for BGB1 sample was determined and then normalized to exclude zinc oxide:

	Abundance %						
				BGB1 Bottom – 400°C 2018002712			
Anorthite				32			
Albite				42			
Augite				19			
Illite				7			

Margin of Error: Abundance estimates are determined through successive refinement of cell parameters; the position, width and orientation of each mineral. Values are given to the nearest whole number. The margin of error for phase concentration is proposed as follows: 0 – 10% ±10%; 10 – 50% ±5%; 50 – 100% ±2%

4.2.1.4. Mineralogy and Texture of Reacted Basalt: Top of Reactor (Portion 2)

Figure C.4.8. SEM photographs for EDS analysis of epoxy-mounted polished grains collected from the top portion of Reactor. Analysis points are marked in blue

Table C.4.7. EDS analysis of grains in Fig. C.4.8

OI	Analysis Point	MgO	Al ₂ O ₃	SiO ₂	CaO	FeO	Total
	16	15.75	1.18	33.14	0.54	49.4	100.00

Ox	Analysis Point	TiO ₂	FeO	Total
	19	25.6	74.4	100.00

Smc	Analysis Point	MgO	Al ₂ O ₃	SiO ₂	K ₂ O	FeO	Total
	7	13.73	11.12	48.05	1.07	26.03	100.00
	8	15.83	10.97	50.43	0.38	22.39	100.00
	9	16.07	12.64	47.57	1.50	22.22	100.00
	10	14.88	10.73	48.95	1.50	23.94	100.00
	15	15.57	11.62	49.13	0.68	23.00	100.00
average		15.22	11.42	48.83	1.03	23.52	100.00
±σ		0.94	0.76	1.10	0.50	1.56	

Table C.4.8. Average mineral compositions from Table (A.4.7)

Oxides	average wt%	average wt%	average wt%
Na ₂ O			
Al ₂ O ₃	1.18	11.42	
SiO ₂	33.14	48.83	
CaO	0.54		
FeO	49.39	23.52	74.41
MgO	15.75	15.22	
TiO ₂			25.59
K ₂ O		1.03	
Total	100.00	100.02	100.00
Mineral Composition	Mg _{0.7} Fe _{1.2} SiO ₄ (Fo ₃₇ -Fa ₆₃)	K _{0.1} Mg _{1.5} Fe _{1.3} Al _{0.2} Si _{3.3} Al _{0.7} O ₁₀ (OH) ₂ (on the basis of 11 oxygen equivalents, ignoring H ₂ O)	Fe ²⁺ (Fe ³⁺ ,Ti) ₂ O ₄
Phase and ID	Fe-olivine (fayalite)	Smectite (epoxy-mount)	Oxide (titanomagnetite)

Figure C.4.10. Quantitative XRD analysis of reacted grains collected from the top (Portion 2) of the Reactor after the BGB1 experiment

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Report Date: 30/04/2018

Confidential 2018

Sample Composition

Table 1. Mineral percentages for BGB1 sample was determined and then normalized to exclude zinc oxide:

	Abundance %						
					BGB1 Top – 400°C 2018002713		
Anorthite					58		
Albite					22		
Augite					20		

4.2.

Margin of Error: Abundance estimates are determined through successive refinement of cell parameters; the position, width and orientation of each mineral. Values are given to the nearest whole number. The margin of error for phase concentration is proposed as follows: 0 – 10% ±10%; 10 – 50% ±5%; 50 – 100% ±2%

4.2. Results

4.2.2. BGB2: Basalt – geothermal brine at 350°C/486 bar

Table C.4.9. Major ions compositions and complete experimental parameters (n° of samples collected, T, P, time, flow rate and pH) for the BGB2 at 350°C and 486 bar. *In situ* pH is the calculated pH at temperature. Analysis of major ions are reported both in mg kg⁻¹ and in mmol kg⁻¹. n.c.: not calculated

n° sample	T (°C)	P (bar)	time (hrs)	flow-rate (ml hr ⁻¹)	pH (room T)	pH (350°C)	mg kg ⁻¹												mmol kg ⁻¹													
							As	B	Ca	Fe	K	Mg	Na	SiO ₂	Al	Li	H ₂ S	Cl	SO ₄	As	B	Ca	Fe	K	Mg	Na	SiO ₂	Al	Li	H ₂ S	Cl	SO ₄
blank geothermal brine	20.1	1	0.0	-	4.28	6.75	0.1	55.4	7.2	< 0.08	116	0.9	725.1	883.3	9.6	6.7	< 0.01	962.1	406.3	0.002	5.1	0.2	< 0.001	3	0.04	31.6	14.7	0.4	1	< 0.0003	27.1	4.2
1	20.4	488.3	21.2	1	5.77	n.c.	1.5	41.2	2.9	0.1	97.4	0.2	647	760.3	1.4	4.8	< 0.01	899.2	348.2	0.02	3.8	0.07	0.001	2.5	0.01	28.1	12.7	0.1	0.7	< 0.0003	27.1	3.6
2	20.3	488.0	47.3	1	5.43	n.c.	0.1	46.8	5.4	0.1	115.1	0.8	723.6	766.7	9.1	5.6	< 0.01	901.4	377.4	0.0009	4.3	0.1	0.001	2.9	0.03	31.5	12.8	0.3	0.8	< 0.0003	25.4	3.9
3	20.6	488.0	71.4	1	5.10	n.c.	0.5	48.4	4.3	0.3	115.9	0.5	733.3	840	5.8	5.7	< 0.01	951.1	398.3	0.01	4.5	0.1	0.01	3	0.02	31.9	14	0.2	0.8	< 0.0003	26.8	4.1
4	20.5	487.8	93.7	1	5.20	n.c.	0.4	46.4	4.1	0.3	115.2	0.6	723.2	821.4	7.3	5.6	< 0.01	892.2	363	0.01	4.3	0.1	0.01	2.9	0.02	31.5	13.7	0.3	0.8	< 0.0003	25.2	3.8
5	20.5	487.9	118.2	1	5.19	n.c.	0.4	46.3	4.2	0.6	115	0.7	724.8	821.9	7	5.6	< 0.01	498.1	195.6	0.01	4.3	0.1	0.01	2.9	0.03	31.5	13.7	0.3	0.8	< 0.0003	14.1	2
6	20.1	487.9	141.8	1	5.23	n.c.	0.5	46.4	3.7	0.9	114.8	0.6	722	819.8	6.5	5.6	< 0.01	990.6	421.2	0.01	4.3	0.1	0.02	2.9	0.03	31.4	13.6	0.2	0.8	< 0.0003	27.9	4.4
7	20.4	487.8	165.7	1	5.06	n.c.	0.7	46.2	4.1	1.1	114.9	0.9	721.7	823.8	6.2	5.6	< 0.01	965.3	388.2	0.01	4.3	0.1	0.02	2.9	0.04	31.4	13.7	0.2	0.8	< 0.0003	27.2	4
8	352.3	486.3	187.8	1	4.43	6.66	0.9	46.3	4.2	0.3	218.3	0.6	620.2	1395	3.7	4	< 0.01	990.3	225.4	0.01	4.3	0.1	0.005	5.6	0.02	27	23.2	0.1	0.6	< 0.0003	27.9	2.3
9	350.4	486.2	211.4	1	3.39	6.68	2	47.8	2.2	0.1	263.5	0.2	574.2	1860.4	0.4	4.3	0.9	957.2	207.5	0.03	4.4	0.06	0.002	6.7	0.01	25	31	0.01	0.6	0.03	27	2.2
10	350.5	486.3	236.2	1	3.56	6.76	0.6	45.9	1.7	0.1	246.3	0.1	634.7	1690	0.8	4.8	2	885.1	283.4	0.01	4.2	0.04	0.003	6.3	0.002	27.6	28.1	0.03	0.7	0.06	25	2.9
11	350.7	486.2	260.3	1	4.58	6.82	1.1	47.6	1	0.1	172.9	0.01	713.7	1516.8	1.1	5.4	1.6	980	341.5	0.01	4.4	0.02	0.001	4.4	0.000	31	25.2	0.04	0.8	0.05	27.6	3.6
12	350.6	486.2	286.3	1	4.65	6.80	1	46.8	1.2	0.1	131.4	0.04	710.3	1491.7	1.1	5.3	1.5	909.3	304.1	0.01	4.3	0.03	0.001	3.4	0.002	30.9	24.8	0.04	0.8	0.04	25.7	3.2
13	350.8	486.2	310.3	1	5.40	6.80	0.8	47.7	2.1	0.1	121.1	0.1	726.9	1554.1	0.7	5.4	1.6	961	331.5	0.01	4.4	0.05	0.002	3.1	0.01	31.6	25.9	0.03	0.8	0.05	27.1	3.5
14	350.7	486.2	334.0	1	6.05	6.80	1.6	46.2	1.6	0.1	118.1	0.1	730.9	1463.1	0.7	5.4	1.8	914.3	315.6	0.02	4.3	0.04	0.001	3	0.003	31.8	24.4	0.03	0.8	0.05	25.8	3.3
15	350.4	486.3	355.5	1	6.31	6.82	1.6	47.1	1.9	0.1	116.2	0.1	715.8	1443.3	0.8	5.3	1.6	972.3	345	0.02	4.4	0.05	0.001	3	0.005	31.1	24	0.03	0.8	0.05	27.4	3.6
16	350.6	486.2	381.8	1	6.72	6.78	1.7	46.8	1.9	0.1	117	0.2	725.3	1325	0.9	5.6	0.8	878.3	299.2	0.02	4.3	0.05	0.001	3	0.01	31.5	22.1	0.03	0.8	0.02	24.8	3.1
17	350.8	486.4	403.3	1	6.72	6.79	1.7	47.5	2	0.1	122	0.2	734.1	1377.3	1.3	5.6	0.4	908	320.5	0.02	4.4	0.05	0.001	3.1	0.01	31.9	22.9	0.05	0.8	0.01	25.6	3.3
18	350.6	486.2	428.1	1	7.01	6.81	1.7	46	2.1	0.1	124.6	0.2	718.8	1308.3	1.4	5.5	0.2	925.3	349	0.02	4.3	0.05	0.001	3.2	0.01	31.3	21.8	0.05	0.8	0.005	26.1	3.6
19	350.7	486.2	451.8	1	7.25	6.82	1.7	47.2	1.9	0.1	127.3	0.1	743.1	1250.1	1.1	5.6	0.1	930.1	363.2	0.02	4.4	0.05	0.001	3.3	0.01	32.3	20.8	0.04	0.8	0.002	26.2	3.8
20	350.8	486.1	475.8	1	7.21	6.79	1.7	48.4	2.1	0.1	131.9	0.1	746.9	1211.6	0.9	5.6	0.1	896.4	327.1	0.02	4.5	0.05	0.002	3.4	0.01	32.5	20.2	0.03	0.8	0.003	25.3	3.4
21	350.3	486.2	498.9	1	7.17	6.83	1.7	45.9	1.6	< 0.08	131.1	0.04	725.9	1200.9	1	5.5	0.1	952.1	363.2	0.02	4.2	0.04	< 0.001	3.4	0.002	31.6	20	0.04	0.8	0.002	26.9	3.8
22	350.5	486.3	523.6	1	7.21	6.82	1.7	48.1	2.1	< 0.08	131.6	0.2	743.7	1125.9	0.6	5.3	0.1	947.4	364.3	0.02	4.5	0.05	< 0.001	3.4	0.01	32.3	18.7	0.02	0.8	0.003	26.7	3.8
23	350.5	486.3	547.8	1	7.21	6.82	1.7	48.2	2.4	< 0.08	130.8	0.2	739.4	1179.8	0.4	5.3	0.1	996.3	381.4	0.02	4.5	0.06	< 0.001	3.3	0.01	32.2	19.6	0.02	0.8	0.002	28.1	4
24	350.4	486.2	571.4	1	7.30	6.82	1.7	48.3	2.3	< 0.08	129.3	0.2	747.4	1149.7	0.4	5.3	0.1	956.4	379.3	0.02	4.5	0.06	< 0.001	3.3	0.01	32.5	19.1	0.01	0.8	0.001	27	3.9
25	350.6	486.2	595.7	1	7.31	6.78	1.7	47.9	2.2	< 0.08	128.4	0.2	747	1126.4	0.3	5.3	0.1	881.2	318.5	0.02	4.4	0.05	< 0.001	3.3	0.01	32.5	18.7	0.01	0.8	0.002	24.9	3.3
26	350.8	486.2	619.5	1	7.46	6.79	1.7	48.2	2.3	< 0.08	127.6	0.2	751.1	1142	0.3	5.2	0.1	870.4	332.5	0.02	4.5	0.06	< 0.001	3.3	0.01	32.7	19	0.01	0.8	0.002	24.6	3.5
27	350.7	486.2	645.3	1	7.51	6.83	1.7	46.1	2	0.2	127.3	0.2	716.7	1061.5	0.3	5.3	0.04	943.2	373.1	0.02	4.3	0.05	0.003	3.3	0.01	31.2	17.7	0.01	0.8	0.001	26.6	3.9
28	350.7	486.2	668.7	1	7.73	6.81	1.7	45.8	2.2	0.1	125.8	0.3	704.2	1011.4	0.3	5.3	0.05	950.1	338.2	0.02	4.2	0.06	0.001	3.2	0.01	30.6	16.8	0.01	0.8	0.001	26.8	3.5
29	350.4	486.2	692.9	1	7.69	6.77	1.7	46	2.2	< 0.08	124.4	0.2	709.1	1009.1	0.2	5.3	0.04	872.2	291	0.02	4.3	0.05	< 0.001	3.2	0.01	30.8	16.8	0.01	0.8	0.001	24.6	3
30	350.6	486.3	715.6	1	7.70	6.78	1.7	48.3	2.7	0.1	125	0.3	746	1031.6	0.3	5.4	< 0.01	901.5	321.1	0.02	4.5	0.07	0.002									

Table C.4.10. Trace element compositions and complete experimental parameters (n° of samples collected, T, P, time, flow rate and pH) for the BGB2 (350°C / 486 bar). *In situ* pH is the calculated pH at temperature. Analysis of trace elements are reported in µmol kg⁻¹. n.c.: not calculated. Effluents were not analysed for V, Cr and Rb

n° sample	T (°C)	P (bar)	time (hrs)	flow-rate (ml hr ⁻¹)	pH (room T)	pH (350°C)	µmol kg ⁻¹										
							Co	Ni	Cu	Zn	Mo	Ag	Cd	Ba	Au	Pb	Mn
blank geothermal brine	20.1	1	0.0	-	4.28	6.75	0.001	0.2	0.8	2.9	0.03	0.003	0.002	0.05	0.04	0.02	2.5
1	20.4	488.3	21.2	1	5.77	n.c.	0.07	3.1	73.3	11.9	0.04	< 0.0005	0.01	0.6	0.005	0.001	1.8
2	20.3	488.0	47.3	1	5.43	n.c.	0.02	0.6	38.7	3.5	0.02	< 0.0005	0.006	0.4	0.003	0.001	0.5
3	20.6	488.0	71.4	1	5.10	n.c.	0.05	0.9	37.9	2.2	0.01	< 0.0005	0.005	0.3	0.002	< 0.001	1
4	20.5	487.8	93.7	1	5.20	n.c.	0.04	0.6	36.8	1.6	0.02	< 0.0005	0.005	0.3	0.002	< 0.001	0.9
5	20.5	487.9	118.2	1	5.19	n.c.	0.04	0.6	37.5	1.3	0.01	< 0.0005	0.004	0.2	0.002	< 0.001	0.8
6	20.1	487.9	141.8	1	5.23	n.c.	0.04	0.5	28.7	0.9	0.01	< 0.0005	0.007	0.2	0.002	< 0.001	0.8
7	20.4	487.8	165.7	1	5.06	n.c.	0.03	2	23.2	2.8	1.1	< 0.0005	0.001	0.1	0.001	0.007	0.7
8	352.3	486.3	187.8	1	4.43	6.66	0.002	0.1	2.3	0.7	0.07	< 0.0005	< 0.0009	0.1	0.001	< 0.001	< 0.13
9	350.4	486.2	211.4	1	3.39	6.68	< 0.002	0.2	0.1	0.3	0.2	< 0.0005	< 0.0009	0.03	0.001	< 0.001	< 0.13
10	350.5	486.3	236.2	1	3.56	6.76	0.01	0.02	0.2	0.1	0.5	< 0.0005	< 0.0009	0.03	0.001	< 0.001	< 0.13
11	350.7	486.2	260.3	1	4.58	6.82	0.01	0.008	0.04	0.1	0.6	< 0.0005	< 0.0009	0.03	0.001	< 0.001	< 0.13
12	350.6	486.2	286.3	1	4.65	6.80	0.01	0.01	0.1	0.1	0.9	< 0.0005	< 0.0009	0.04	0.001	< 0.001	< 0.13
13	350.8	486.2	310.3	1	5.40	6.80	0.01	< 0.003	0.04	0.1	0.9	< 0.0005	< 0.0009	0.05	0.001	< 0.001	< 0.13
14	350.7	486.2	334.0	1	6.05	6.80	0.01	0.008	0.1	0.1	1	< 0.0005	< 0.0009	0.1	0.001	< 0.001	< 0.13
15	350.4	486.3	355.5	1	6.31	6.82	0.002	< 0.003	0.1	0.2	1.1	< 0.0005	0.001	0.1	0.001	< 0.001	< 0.13
16	350.6	486.2	381.8	1	6.72	6.78	< 0.002	0.04	0.1	0.3	0.8	< 0.0005	0.002	0.1	0.001	< 0.001	< 0.13
17	350.8	486.4	403.3	1	6.72	6.79	< 0.002	< 0.003	0.1	0.4	1	< 0.0005	< 0.0009	0.1	0.001	< 0.001	< 0.13
18	350.6	486.2	428.1	1	7.01	6.81	< 0.002	0.02	0.1	5.7	0.9	< 0.0005	< 0.0009	0.1	0.001	0.001	< 0.13
19	350.7	486.2	451.8	1	7.25	6.82	< 0.002	0.02	0.1	2	0.7	< 0.0005	< 0.0009	0.1	0.001	0.004	< 0.13
20	350.8	486.1	475.8	1	7.21	6.79	< 0.002	0.03	1.2	1.9	0.7	< 0.0005	< 0.0009	0.1	0.001	0.003	< 0.13
21	350.3	486.2	498.9	1	7.17	6.83	< 0.002	< 0.003	0.1	1.6	0.6	< 0.0005	< 0.0009	0.1	0.001	0.001	< 0.13
22	350.5	486.3	523.6	1	7.21	6.82	< 0.002	< 0.003	0.1	2.7	0.6	< 0.0005	< 0.0009	0.1	0.001	0.005	< 0.13
23	350.5	486.3	547.8	1	7.21	6.82	< 0.002	0.004	0.2	2.9	0.5	< 0.0005	< 0.0009	0.1	< 0.001	0.001	< 0.13
24	350.4	486.2	571.4	1	7.30	6.82	< 0.002	< 0.003	0.04	1.1	0.4	< 0.0005	< 0.0009	0.05	0.001	0.002	< 0.13
25	350.6	486.2	595.7	1	7.31	6.78	< 0.002	< 0.003	0.03	2.4	0.5	< 0.0005	< 0.0009	0.1	0.001	< 0.001	< 0.13
26	350.8	486.2	619.5	1	7.46	6.79	< 0.002	0.03	0.1	1.4	0.5	< 0.0005	< 0.0009	0.1	0.001	0.02	< 0.13
27	350.7	486.2	645.3	1	7.51	6.83	< 0.002	0.02	0.04	1.5	0.5	< 0.0005	< 0.0009	0.1	< 0.001	0.02	< 0.13
28	350.7	486.2	668.7	1	7.73	6.81	< 0.002	< 0.003	0.05	3.6	0.4	< 0.0005	< 0.0009	0.1	< 0.001	0.004	< 0.13
29	350.4	486.2	692.9	1	7.69	6.77	< 0.002	< 0.003	0.1	2.9	0.4	< 0.0005	< 0.0009	0.1	< 0.001	0.005	< 0.13

Figure C.4.11. EDS analysis of the smectite (Smc 2) from the study of the morphology

Figure C.4.12. EDS analysis of the smectite (Smc 1) from the study of the morphology

Figure C.4.13. EDS analysis of the Cu-sulfide from the study of the morphology (Portion 1, BGB2)

Table C.4.11. EDS analysis from Fig. C.4.11-13

Anh	Analysis Point 3	SO ₃ 43.75					CaO 56.25		Total 100.00
Cu-sulfide	Analysis Point 31 34	SO ₃ 29.47 33.03	CuO 68.22 65.68					FeO 2.31 1.39	Total 100.00 100.10
average		31.25	66.95					1.85	100.05
Smc 2 (morphology)	Analysis Point	Na ₂ O	MgO	Al ₂ O ₃	SiO ₂	K ₂ O	CaO	FeO	Total
	2	2.35	14.28	10.80	50.74	0.00	0.62	21.20	99.99
	4	2.47	14.12	10.60	51.85	0.00	0.00	20.27	99.31
	7	3.31	14.08	12.06	50.80	0.00	1.39	18.35	99.99
	8	2.77	13.58	11.75	52.25	0.00	1.17	18.47	99.99
	10	2.51	14.58	8.87	48.40	1.20	1.21	23.20	99.97
	15	2.74	17.83	9.44	44.67	0.98	2.53	21.82	100.01
	16	2.82	21.80	9.44	50.89	0.55	1.78	12.73	100.01
	18	2.29	13.71	10.26	51.13	0.91	0.00	21.71	100.01
	20	2.38	15.28	10.71	51.93	0.73	2.02	16.94	99.99
	22	2.56	14.14	12.54	50.50	1.44	1.85	16.99	100.02
	23	1.26	14.95	9.80	51.88	0.00	2.26	19.84	99.99
	29	2.03	17.41	10.39	52.99	0.54	1.43	15.22	100.01
	44	2.12	11.47	14.36	51.40	1.87	2.45	16.33	100.00
	49	2.70	13.92	11.54	52.28	0.00	0.00	19.56	100.00
	51	2.86	16.04	10.92	52.10	0.77	1.28	16.03	100.00
average		2.48	15.15	10.90	50.92	0.60	1.33	18.58	99.95
±σ		0.47	2.41	1.40	2.04	0.44	0.58	2.88	
Smc 1 (morphology)	Analysis Point	Na ₂ O	MgO	Al ₂ O ₃	SiO ₂	K ₂ O	CaO	FeO	Total
	21	2.15	15.72	8.93	47.31	1.01	3.61	21.28	100.01
	26	0.58	12.42	8.07	49.31	1.98	3.61	24.02	99.99
	33	1.06	15.05	9.76	51.51	1.65	3.97	17.00	100.00
	45	2.06	19.24	9.66	48.11	1.37	3.17	16.38	99.99
	46	1.68	16.00	8.74	47.62	1.64	3.55	20.76	99.99
average		1.51	15.69	9.03	48.77	1.53	3.58	19.89	100.00
±σ		0.67	2.44	0.70	1.71	0.36	0.28	3.18	

Table C.4.12. Average mineral compositions from Table C.4.11

Oxides	Point n°3	average wt%	average wt%	average wt%
Na ₂ O			2.48	1.51
Al ₂ O ₃			10.90	9.03
SiO ₂			50.92	48.77
CaO	56.25		1.33	3.58
FeO		1.85	18.58	19.89
MgO			15.15	15.69
K ₂ O			0.60	1.53
SO ₃	43.75	31.25		
CuO		66.95		
Total	100.00	100.05	99.96	100.00
Mineral Composition	CaSO ₄	CuS	K _{0.1} Na _{0.3} Ca _{0.1} Mg _{1.5} Fe _{1.1} Al _{0.29} Si _{3.43} Al _{0.57} O ₁₀ (OH) ₂ (11 oxygen equivalents, ignoring H ₂ O)	K _{0.1} Na _{0.2} Ca _{0.3} Mg _{1.6} Fe _{1.2} Al _{0.1} Si _{3.4} Al _{0.6} O ₁₀ (OH) ₂ (11 oxygen equivalents, ignoring H ₂ O)
Phase and ID	Sulfate	Cu-sulfide	Smectite 1	Smectite 2

Figure C.4.15. Quantitative XRD analysis of reacted grains collected from the top (Portion 1) of the Reactor after the BGB2 experiment

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Sample Composition

Table 1. Mineral percentages for BGB2 sample was determined and then normalized to exclude zinc oxide:

	Abundance %						
						BGB 2 Bottom – 350°C 2017002714	
Anorthite						49	
Albite						21	
Augite						29	
Montmorillonite						1	

Margin of Error: Abundance estimates are determined through successive refinement of cell parameters; the position, width and orientation of each mineral. Values are given to the nearest whole number. The margin of error for phase concentration is proposed as follows: 0 – 10% ±10%; 10 – 50% ±5%; 50 – 100% ±2%

Figure C.4.16. EDS analysis of reacted grains collected from the top (Portion 2) of the Reactor

Table C.4.13. EDS analysis of grains in Fig. C.4.16

Smc (morphology)	Analysis Point	Na ₂ O	MgO	Al ₂ O ₃	SiO ₂	K ₂ O	CaO	FeO	Total
	1	2.28	16.18	11.67	47.15	0.80	1.64	20.27	99.99
	2	1.75	13.89	10.76	48.32	0.76	2.31	22.22	100.01
average		2.02	15.04	11.22	47.74	0.78	1.98	21.25	100.00
$\pm\sigma$		0.37	1.62	0.64	0.83	0.03	0.47	1.38	

Table C.4.14. Average mineral compositions from Table C.4.13

Oxides	average wt%
Na ₂ O	2.02
Al ₂ O ₃	11.22
SiO ₂	47.74
CaO	1.98
FeO	21.25
MgO	15.04
K ₂ O	0.78
Total	100.01
Mineral Composition	K _{0.05} Na _{0.25} Ca _{0.15} Mg _{1.6} Fe _{1.2} Al _{0.2} Si _{3.3} Al _{0.7} O ₁₀ (OH) ₂ (11 oxygen equivalents, ignoring H ₂ O)
Phase and ID	Smectite (morphology study)

Figure C.4.17. SEM photographs for EDS analysis of epoxy-mount polished grains collected from the top (Portion 2) of the Reactor. Analysis points are marked in blue

Table C.4.14. EDS analysis of grains in Fig. C.4.17

Plg	Analysis Point	Na ₂ O		Al ₂ O ₃	SiO ₂		CaO		Total
	20	2.96		30.31	52.30		14.43		100.00
Cpx	Analysis Point		MgO	Al ₂ O ₃	SiO ₂		CaO	FeO	Total
	3		12.50	2.23	51.82		11.99	21.46	100.00
	21		13.49	1.21	51.49		4.71	29.11	100.00
	29		7.57	1.69	49.56		10.71	30.47	100.00
	30		5.22	2.93	50.05		11.64	30.15	100.00
	32		15.10	2.08	53.37		18.55	10.89	100.00
	34		14.84	3.08	53.32		18.13	10.63	100.00
average			11.45	2.20	51.60		12.62	22.12	100.00
Ol	Analysis Point		MgO		SiO ₂			FeO	Total
	23		16.57		32.66			50.77	100.00
Ox	Analysis Point	TiO ₂						FeO	Total
	1	27.59						72.41	100.00
	2	28.18						71.82	100.00
	11	26.94						73.06	100.00
	31	26.01						73.99	100.00
average		27.18						72.82	100.00

Smc (epoxy-mount)	Analysis Point	Na ₂ O	MgO	Al ₂ O ₃	SiO ₂	K ₂ O	CaO	FeO	Total
	9	0.00	14.46	9.78	50.17	0.62	1.07	23.90	100.00
	10	0.00	12.59	8.75	48.43	0.38	1.35	28.51	100.00
	13	1.52	15.68	8.35	51.14	0.79	0.50	22.01	100.00
	14	2.02	16.70	8.84	51.06	0.74	0.38	19.69	100.00
	15	0.96	15.78	8.46	51.28	0.68	0.81	22.03	100.00
	16	0.89	15.29	8.40	52.88	0.00	0.65	21.89	100.00
	17	0.57	13.78	7.90	51.20	0.20	1.60	24.76	100.00
	18	3.16	17.04	7.99	50.21	0.37	1.22	20.02	100.00
	19	0.80	18.93	9.03	52.28	0.30	0.37	18.29	100.00
	24	0.00	11.32	8.79	48.86	1.50	0.78	28.74	100.00
	26	0.95	14.04	9.14	50.19	0.89	0.76	24.04	100.00
average		0.99	15.06	8.68	50.70	0.59	0.86	23.08	99.95
±σ		0.86	2.14	0.54	1.32	0.38	0.40	3.37	

Table C.4.15. Average mineral compositions from Table C.4.14

Oxides	Point n°20	Point n°23	average wt%	average wt%	average wt%
Na ₂ O	2.96				0.99
Al ₂ O ₃	30.31		2.20		8.68
SiO ₂	52.30	32.66	51.60		50.70
CaO	14.43		12.62		0.86
FeO		50.77	22.12	72.82	23.08
MgO		16.57	11.45		15.06
K ₂ O					0.59
Cl					0.05
TiO ₂				27.18	
Total	100.00	100.00	99.99	100.00	100.01
Mineral Composition	Ca _{0.71} Na _{0.26} Al _{1.64} Si _{2.39} O ₈ (An ₇₃ -Ab ₂₇)	Mg _{0.74} Fe _{1.24} Si _{0.98} O ₄ (Fo ₃₇ -Fa ₆₃)	Ca _{0.52} Mg _{0.66} Fe _{0.71} Al _{0.8} Si _{1.98} Al _{0.02} O ₆	Fe ²⁺ (Fe ³⁺ ,Ti) ₂ O ₄	K _{0.05} Na _{0.15} Ca _{0.05} Mg _{1.5} Fe _{1.3} Al _{0.2} Si _{3.5} Al _{0.5} O ₁₀ (OH) ₂ (11 oxygen equivalents, ignoring H ₂ O)
Phase and ID	Plagioclase (bytownite)	Fe-olivine (fayalite)	Clinopyroxene (augite)	Oxide (titanomagnetite)	Smectite (epoxy study)

Figure C.4.19. Quantitative XRD analysis of reacted grains collected from the top (Portion 2) of the Reactor after the BGB2 experiment

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Sample Composition

Table 1. Mineral percentages for BGB2 sample was determined and then normalized to exclude zinc oxide:

	Abundance %						BGB2 Top – 350°C 2018002715
Anorthite							56
Albite							16
Augite							26
Montmorillonite							2

Margin of Error: Abundance estimates are determined through successive refinement of cell parameters; the position, width and orientation of each mineral. Values are given to the nearest whole number. The margin of error for phase concentration is proposed as follows: 0 – 10% ±10%; 10 – 50% ±5%; 50 – 100% ±2%

Reacted Basalt Block

Figure C.4.20. EDS analysis of the reacted basalt block surface from the bottom (Portion 1) of the reactor after the BGB2 experiment

Figure C.4.21. EDS analysis of the reacted basalt block surface from the bottom (Portion 1) of the reactor after the BGB2 experiment

Table C.4.16. EDS analysis of points from Fig. C.4.20-21.

Plg	Analysis Point	Na ₂ O	Al ₂ O ₃	SiO ₂	CaO								Total
average	25	3.19	29.67	52.45	14.69								100.00
	56	2.45	30.92	51.23	15.51								100.11
		2.82	30.30	51.84	15.10								100.06
Anh	Analysis Point	SO ₃	CaO									Total	
average	8	60.61	39.39									100.00	
	9	59.00	41.00									100.00	
	50	58.97	41.03									100.00	
	47	58.18	41.82									100.00	
	46	58.54	41.46									100.00	
		59.06	40.94									100.00	
Smc	Analysis Point	Na ₂ O	MgO	Al ₂ O ₃	SiO ₂	SO3	Cl	K ₂ O	CaO	TiO ₂	FeO	Total	
average	26	4.77	16.29	9.00	47.54	2.04	1.12	0.89	3.18	0.00	15.17	100.00	
	31	6.85	11.25	7.29	37.32		1.00	1.10	3.01	0.00	23.54	91.36	
	33	3.68	11.14	7.33	33.73		0.00	1.35	3.14	0.00	39.63	100.00	
	7	2.51	8.27	6.96	39.76		1.74	1.25	0.60	0.00	38.91	100.00	
	15	5.93	16.81	10.69	46.96		1.12	0.65	0.77	0.00	17.08	100.01	
	32	4.16	10.94	6.12	37.29	0.16	0.89	0.65	4.50	2.87	32.41	99.99	
	61	3.05	16.81	6.94	50.17		0.54	0.71	11.77	0.00	10.01	100.00	
		4.42	13.07	7.76	41.82		0.92	0.94	3.86	0.41	25.25	98.77	

Na-Ca-Mg-Fe-Mn-Ti aluminosilicate	Analysis Point	Na ₂ O	MgO	Al ₂ O ₃	SiO ₂	CaO	TiO ₂	MnO	FeO				Total
average ±σ	76	4.30	1.51	6.74	11.48	2.55	36.25	1.86	35.31				100.00
	75	3.23	1.12	10.76	18.57	3.80	30.92	0.00	31.61				100.01
	74	3.76	0.92	13.94	21.67	4.63	26.51	0.00	28.56				99.99
	73	1.97	1.16	7.84	11.50	2.18	36.95	0.00	38.41				100.01
	79	2.77	0.00	17.71	22.68	7.63	24.07	0.00	25.14				100.00
	78	0.80	0.00	5.75	6.75	3.85	38.61	2.47	41.77				100.00
		2.81	0.79	10.46	15.44	4.11	32.22	0.72	33.47				100.00
		1.27	0.64	4.64	6.45	1.95	6.00	1.13	6.22				

Table C.4.17. Average mineral compositions from Table C.4.16

Oxides	average wt%	average wt%	average wt%
Na ₂ O	2.82		4.42
Al ₂ O ₃	30.30		7.76
SiO ₂	51.84		41.82
CaO	15.10	40.94	3.86
TiO ₂			0.41
SO ₃		59.06	
FeO			25.25
MgO			13.07
K ₂ O			0.94
Cl			0.92
Total	100.06	100.00	98.45
Mineral Composition	Ca _{0.74} Na _{0.25} Al _{1.64} Si _{2.37} O ₈ (An ₇₅ -Ab ₂₅)	CaSO ₄	K _{0.1} Na _{0.65} Ca _{0.3} Mg _{1.45} Fe _{1.55} Si _{3.1} Al _{0.7} O ₁₀ (OH) ₂ (11 oxygen equivalents, ignoring H ₂ O)
Phase and ID	Plagioclase (bytownite)	Sulphate (anhydrite)	Smectite

4.3. Discussion

Elements Flux Calculation

Table C.4.18. Elements flux calculation and amount of glass dissolved during the BGB1 experiment (400°C / 483 bar)

Sample No.	Time	Total Time	Time	Reactor Temp	Pressure	SiO ₂ mg kg ⁻¹	K mg kg ⁻¹	SO ₄ mg kg ⁻¹	H ₂ S mg kg ⁻¹	Ca mg kg ⁻¹	Na mg kg ⁻¹	Mg mg kg ⁻¹	Fe mg kg ⁻¹	Volume L	diff. SiO ₂ mg kg ⁻¹	SiO ₂ Flux mg	∫ SiO ₂ Flux mg	diff. K mg kg ⁻¹	∫ K Flux mg	diff. SO ₄ mg kg ⁻¹	∫ SO ₄ Flux mg	diff. H ₂ S mg kg ⁻¹	∫ H ₂ S Flux mg	diff. Ca mg kg ⁻¹	∫ Ca Flux mg	diff. Na mg kg ⁻¹	∫ Na Flux mg	diff. Mg mg kg ⁻¹	∫ Mg Flux mg	diff. Fe mg kg ⁻¹	∫ Fe Flux mg	SiO ₂ Flux Area (mg) for subtraction and glass calculation		
Blank		day 0	day 0	room T	bar 1	Total Input Mass (mg) in 0.69 L supposing no fluid-rock exchange																												
						525.3	80.4	279.7	0.14	2.4	502.1	0.14	0.06																					
1	9:25:00	1.0		room T	1																													
2	9:40:00	2.01	1.01	room T	1																													
3	12:56:00	3.15	1.14	room T	1																													
4	10:53:00	4.02	0.87	room T	1																													
5	11:00:00	4.98	0.96	room T	1																													
6	10:10:00	5.98	0.99	room T	1																													
7	9:45:00	6.95	0.98	room T	1																													
8	10:00:00	7.96	1.01	400	483	1531.08	192.50	239.79	0.12	3.19	597.71	0.43	0.45	0.024	772.4	37.1	18.7	76.3	1.85	-164.2	-3.98	-0.08	-0.002	-0.21	-0.005	-127.6	-3.09	0.23	0.006	0.371	0.00900	23.16		
9	9:45:00	8.95	0.99	400	483	2081.20	196.51	272.69	1.59	1.96	623.52	0.15	0.07	0.024	1322.5	49.4	31.4	80.3	1.91	-131.3	-3.12	1.39	0.033	-1.44	-0.034	-101.8	-2.42	-0.05	-0.001	-0.007	-0.00016	23.16		
10	10:20:00	9.98	1.02	400	483	2000.67	149.50	326.81	5.27	2.22	666.09	0.17	0.09	0.025	1242.0	49.2	30.5	33.3	0.82	-77.2	-1.90	5.07	0.125	-1.18	-0.029	-59.2	-1.46	-0.03	-0.001	0.012	0.00030	23.16		
11	9:40:00	10.95	0.97	400	483	1798.41	144.77	350.16	8.58	2.78	684.57	0.25	0.08	0.023	1039.7	42.0	24.3	28.6	0.67	-53.8	-1.26	8.38	0.195	-0.62	-0.015	-40.7	-0.95	0.05	0.001	0.000	0.00000	23.16		
12	11:00:00	12.00	1.06	400	483	1813.37	150.87	347.90	5.21	2.58	692.50	0.22	0.08	0.025	1054.7	45.9	26.7	34.7	0.88	-56.1	-1.42	5.01	0.127	-0.82	-0.021	-32.8	-0.83	0.02	0.001	0.000	0.00000	23.16		
13	12:30:00	13.07	1.06	400	483	1814.86	151.54	351.12	1.57	2.31	697.57	0.15	0.08	0.026	1056.2	46.3	26.9	35.3	0.90	-52.9	-1.35	1.37	0.035	-1.09	-0.028	-27.7	-0.71	-0.05	-0.001	0.000	0.00000	23.16		
14	9:30:00	13.94	0.88	400	483	1810.07	148.75	365.98	1.82	2.51	689.80	0.00	0.08	0.021	1051.4	38.0	22.1	32.5	0.68	-38.0	-0.80	1.62	0.034	-0.89	-0.019	-35.5	-0.75	-0.20	-0.004	0.000	0.00000	23.16		
15	10:10:00	14.97	1.03	400	483	1829.52	147.88	367.39	1.23	2.74	696.93	0.20	0.08	0.025	1070.8	45.1	26.4	31.7	0.78	-36.6	-0.90	1.03	0.025	-0.66	-0.016	-28.4	-0.70	0.00	0.000	0.000	0.00000	23.16		
16	9:45:00	15.95	0.98	400	483	1844.48	145.26	364.11	0.96	2.70	681.56	0.21	0.08	0.024	1085.8	43.5	25.6	29.1	0.69	-39.9	-0.94	0.76	0.018	-0.70	-0.016	-43.7	-1.03	0.01	0.000	0.000	0.00000	23.16		
17	9:05:00	16.92	0.97	400	483	1852.93	141.55	368.78	0.89	2.96	684.75	0.22	0.08	0.023	1094.2	43.2	25.5	25.4	0.59	-35.2	-0.82	0.69	0.016	-0.44	-0.010	-40.5	-0.95	0.02	0.000	-0.005	-0.00011	23.16		
18	9:40:00	17.95	1.02	400	483	1859.60	136.19	369.06	0.57	3.80	688.77	0.24	0.08	0.025	1100.9	45.7	27.1	20.0	0.49	-34.9	-0.86	0.37	0.009	0.40	0.010	-36.5	-0.90	0.04	0.001	0.000	0.00000	23.16		
19	12:10:00	19.05	1.10	400	483	1887.56	132.13	361.47	0.66	3.72	694.34	0.40	0.08	0.026	1128.9	50.0	29.9	15.9	0.42	-42.5	-1.13	0.46	0.012	0.32	0.009	-31.0	-0.82	0.20	0.005	0.000	0.00000	23.16		
20	11:45:00	20.03	0.98	400	483	1886.37	122.62	348.38	0.21	4.33	693.20	0.42	0.08	0.024	1127.7	44.5	26.6	6.4	0.15	-55.6	-1.31	0.01	0.000	0.93	0.022	-32.1	-0.76	0.22	0.005	0.000	0.00000	23.16		
21	10:25:00	20.98	0.94	400	483	1898.72	114.40	333.82	0.56	3.98	710.05	0.43	0.08	0.023	1140.0	42.9	25.7	-1.8	-0.04	-70.2	-1.58	0.36	0.008	0.58	0.013	-15.2	-0.34	0.23	0.005	-0.002	-0.00004	23.16		
22	10:45:00	21.99	1.01	400	483	1897.81	106.31	360.24	0.37	4.27	705.96	0.47	0.08	0.024	1139.1	46.2	27.7	-9.9	-0.24	-43.8	-1.06	0.17	0.004	0.87	0.021	-19.3	-0.47	0.27	0.007	0.000	0.00000	23.16		
23	9:30:00	22.94	0.95	400	483	1840.99	103.09	366.90	0.53	4.86	713.37	0.54	0.10	0.023	1082.3	41.9	24.6	-13.1	-0.30	-37.1	-0.84	0.33	0.007	1.46	0.033	-11.9	-0.27	0.34	0.008	0.022	0.00050	23.16		
24	9:50:00	23.95	1.01	400	483	1463.64	100.37	352.66	0.49	3.93	714.76	0.39	0.08	0.024	704.9	35.6	17.2	-15.8	-0.39	-51.3	-1.25	0.29	0.007	0.53	0.013	-10.5	-0.26	0.19	0.005	0.000	0.00000	23.16		
25	8:40:00	24.90	0.95	400	483	1101.77	98.77	337.10	0.48	4.23	701.63	0.53	0.08	0.023	343.1	25.2	7.8	-17.4	-0.40	-66.9	-1.53	0.28	0.006	0.83	0.019	-23.7	-0.54	0.33	0.008	0.000	0.00000	23.16		
26	12:45:00	26.03	1.13	400	483	1009.71	96.33	338.31	0.10	3.31	699.67	0.31	0.08	0.027	251.0	27.3	6.8	-19.9	-0.54	-65.7	-1.78	-0.10	-0.003	-0.09	-0.002	-25.6	-0.69	0.11	0.003	0.000	0.00000	23.16		
27	10:35:00	26.94	0.91	400	483	1004.23	95.14	354.79	0.24	3.85	694.58	0.45	0.08	0.022	245.5	21.9	5.4	-21.1	-0.46	-49.2	-1.07	0.04	0.001	0.45	0.010	-30.7	-0.67	0.25	0.005	0.000	0.00000	23.16		
28	9:55:00	27.91	0.97	400	483	988.25	95.28	351.76	0.20	4.37	727.24	0.50	0.08	0.023	229.6	23.1	5.4	-20.9	-0.49	-52.2	-1.22	0.00	0.000	0.97	0.023	1.9	0.05	0.30	0.007	0.000	0.00000	23.16		
29	9:30:00	28.90	0.98	400	483	976.90	95.39	303.18	0.27	4.44	718.40	0.52	0.08	0.024	218.2	23.0	5.1	-20.8	-0.49	-100.8	-2.38	0.07	0.002	1.04	0.025	-6.9	-0.16	0.32	0.008	0.000	0.00000	23.16		
30	9:55:00	29.91	1.02	400	483	987.17	95.07	346.37	0.22	3.77	724.46	0.38	0.08	0.024	228.5	24.1	5.6	-21.1	-0.52	-57.6	-1.41	0.02	0.001	0.37	0.009	-0.8	-0.02	0.18	0.005	0.000	0.00000	23.16		
31	10:30:00	30.89	0.98	400	483	980.52	94.81	331.99	0.19	4.01	722.13	0.44	0.08	0.023	221.8	23.0	5.2	-21.4	-0.50	-72.0	-1.69	-0.01	0.000	0.61	0.014	-3.2	-0.07	0.24	0.006	0.000	0.00000	23.16		
32	10:35:00	31.89	1.00	400	483	930.27	92.33	309.17	0.34	4.01	711.77	0.31	0.08	0.024	171.6	22.2	4.1	-23.9	-0.57	-94.8	-2.27	0.14	0.003	0.61	0.015	-13.5	-0.32	0.11	0.003	0.000	0.00000	23.16		
33 (48 hrs)	13:30:00	33.97	2.08	400	483	954.17	93.25	330.23	0.14	5.67	741.55	0.69	0.08	0.050	195.5	47.6	9.8	-22.9	-1.15	-73.8	-3.68	-0.06	-0.003	2.27	0.113	16.3	0.81	0.49	0.024	0.000	0.00000	47.60		
33 (24 hrs)						477.09	46.63	165.11	0.07	2.84	370.78	0.34				23.8																		
33 (24 hrs)						477.09	46.63	165.11	0.07	2.84	370.78	0.34				23.8																		
34 (48 hrs)	9:30:00	35.80	1.83	400	483	1023.20	92.11	330.26	0.19	3.89	735.78	0.36	0.08	0.044	264.5	45.0	11.6	-24.1	-1.06	-73.7	-3.24	-0.01	0.00	0.49	0.02	10.480	0.46	0.160	0.007	0.000	0.00000	45.00		
34 (24 hrs)						511.60	46.06	165.13	0.10	1.95	367.89	0.18				22.5																		
34 (24 hrs)						511.60	46.06	165.13	0.10	1.95	367.89	0.18				22.5																		
Total brine (L)															0.69																			
Σ SiO ₂ flux (blank included) (mg)																												1029						
Σ ∫ SiO ₂ flux released (blank excluded) (mg)																												504						
Σ SiO ₂ flux subtracted from the Σ SiO ₂ flux (blank include d) (mg)																														672				
SiO ₂ from the glass (mg)																												357						
Σ ∫ K flux (mg)																												3.7						
Σ ∫ SO ₄ flux (mg)																												-44.8						
Σ ∫ H ₂ S flux (mg)																												0.66						
Σ ∫ Ca flux (mg)																												0.17						
Σ ∫ Na flux (mg)																												-17.9						
Σ ∫ Mg flux (mg)																												0.11						
Σ ∫ Fe flux (mg)																												0.009						
EMPA Wt% SiO ₂ in glass= 67.88																												average for subtraction						
Effective Amount of Glass (mg)		357 / 0.6788 = 526																										23.16						

Table C.4.19. Elements flux calculation and amount of glass dissolved during the BGB2 experiment (350°C / 486 bar)

Sample No.	Time	Total Time	Time	Reactor Temp	Pressure	SiO ₂ mg kg ⁻¹	K mg kg ⁻¹	SO ₄ mg kg ⁻¹	H ₂ S mg kg ⁻¹	Ca mg kg ⁻¹	Na mg kg ⁻¹	Mg mg kg ⁻¹	Fe mg kg ⁻¹	Volume L	diff. SiO ₂ mg kg ⁻¹	SiO ₂ Flux mg	f SiO ₂ Flux mg	diff. K mg kg ⁻¹	K Flux mg	diff. SO ₄ mg kg ⁻¹	SO ₄ Flux mg	H ₂ S Flux mg	diff. Ca mg kg ⁻¹	Ca Flux mg	diff. Na mg kg ⁻¹	Na Flux mg	diff. Mg mg kg ⁻¹	Mg Flux mg	Fe Flux mg		
		day	day	°C	bar																										
Blank		0	0	room T	1	883.3	116	406.3	< 0.01	7.2	725	0.9	<0.08																		
						Total Input Max (mg) in 0.75 L supposing no fluid-rock exchange																									
1	9:27	1.0		room T	1																										
2	10:58	2.0	1.02	room T	1																										
3	11:00	3.0	1.00	room T	1																										
4	9:45	4.1	1.05	room T	1																										
5	9:45	5.1	1.00	room T	1																										
6	9:25	6.1	0.99	room T	1																										
7	9:15	7.1	0.99	room T	1																										
8	9:30	8.1	1.01	350	486	1395.0	218.3	225.4	0.01	4.23	620.2	0.59	0.27	0.024	511.74	33.83	12.41	102.3	2.5	-181.0	-4.388	0.000	-3.0	-0.072	-104.8	-2.541	-0.3	-0.008	0.006		
9	9:07	9.0	0.98	350	486	1860.4	263.5	207.5	0.94	2.24	574.2	0.17	0.12	0.024	977.11	43.76	22.98	147.5	3.5	-198.8	-4.675	0.022	-5.0	-0.117	-150.8	-3.548	-0.7	-0.017	0.003		
10	9:55	10.1	1.03	350	486	1690.0	246.3	283.4	2.03	1.68	634.7	0.05	0.14	0.025	806.71	41.91	20.01	130.3	3.2	-122.9	-3.049	0.050	-5.5	-0.137	-90.3	-2.240	-0.8	-0.021	0.003		
11	10:05	11.1	1.01	350	486	1516.8	172.9	341.5	1.59	1.00	713.7	0.01	0.07	0.024	633.45	36.65	15.31	56.9	1.4	-64.8	-1.566	0.038	-6.2	-0.150	-11.3	-0.272	-0.9	-0.022	0.002		
12	12:00	12.2	1.08	350	486	1491.7	131.4	304.1	1.48	1.19	710.3	0.04	0.06	0.026	608.45	38.66	15.77	15.4	0.4	-102.2	-2.649	0.038	-6.0	-0.156	-14.7	-0.382	-0.9	-0.022	0.001		
13	12:05	13.2	1.00	350	486	1554.1	121.1	331.5	1.58	2.05	726.9	0.13	0.11	0.024	670.76	37.30	16.10	5.1	0.1	-74.8	-1.795	0.038	-5.1	-0.124	1.9	0.045	-0.8	-0.019	0.003		
14	11:44	14.1	0.99	350	486	1463.1	118.1	315.6	1.83	1.64	730.9	0.06	0.07	0.024	579.75	34.60	13.71	2.1	0.0	-90.8	-2.146	0.043	-5.6	-0.131	5.9	0.140	-0.8	-0.020	0.002		
15	9:15	15.3	1.10	350	486	1443.3	116.2	345.0	1.59	1.90	715.8	0.12	0.07	0.026	559.98	38.24	14.84	0.2	0.0	-61.3	-1.624	0.042	-5.3	-0.140	-9.2	-0.243	-0.8	-0.021	0.002		
16	11:30	16.3	1.09	350	486	1325.0	117.0	299.2	0.83	1.89	725.3	0.18	0.08	0.026	441.73	34.66	11.56	1.0	0.0	-107.1	-2.802	0.022	-5.3	-0.139	0.3	0.008	-0.7	-0.019	0.002		
17	9:05	17.2	0.90	350	486	1377.3	122.0	320.5	0.41	1.96	734.1	0.18	0.08	0.022	494.00	29.73	10.66	6.0	0.1	-85.8	-1.852	0.009	-5.2	-0.113	9.1	0.195	-0.7	-0.016	0.002		
18	9:50	18.3	1.03	350	486	1308.3	124.6	349.0	0.16	2.13	718.8	0.19	0.07	0.025	425.02	32.37	10.52	8.6	0.2	-57.3	-1.417	0.004	-5.1	-0.125	-6.2	-0.153	-0.7	-0.018	0.002		
19	9:30	19.3	0.99	350	486	1250.1	127.3	363.2	0.07	1.93	743.1	0.14	0.06	0.024	366.80	29.59	8.68	11.3	0.3	-43.1	-1.020	0.002	-5.3	-0.125	18.1	0.428	-0.8	-0.018	0.001		
20	9:30	20.3	1.00	350	486	1211.6	131.9	327.1	0.11	2.06	746.9	0.14	0.11	0.024	328.27	29.08	7.88	15.9	0.4	-79.2	-1.900	0.003	-5.1	-0.123	21.9	0.525	-0.8	-0.018	0.003		
21	8:40	21.2	0.97	350	486	1200.9	131.1	363.2	0.08	1.61	725.9	0.04	0.08	0.023	317.64	27.82	7.36	15.1	0.3	-43.1	-0.999	0.002	-5.6	-0.130	0.9	0.021	-0.9	-0.020	0.002		
22	9:20	22.3	1.03	350	486	1125.9	131.6	364.3	0.11	2.10	743.7	0.22	0.08	0.025	242.56	27.75	5.98	15.6	0.4	-42.0	-1.035	0.003	-5.1	-0.126	18.7	0.460	-0.7	-0.017	0.002		
23	9:30	23.3	1.00	350	486	1179.8	130.8	381.4	0.07	2.38	739.4	0.22	0.08	0.024	296.52	28.32	7.12	14.8	0.4	-24.9	-0.598	0.002	-4.8	-0.116	14.4	0.347	-0.7	-0.016	0.002		
24	9:10	24.3	1.01	350	486	1149.7	129.3	379.3	0.05	2.27	747.4	0.23	0.08	0.024	266.41	27.98	6.48	13.3	0.3	-27.0	-0.657	0.001	-4.9	-0.120	22.4	0.545	-0.7	-0.016	0.002		
25	9:25	25.3	1.01	350	486	1126.4	128.4	318.5	0.06	2.16	747.0	0.17	0.08	0.024	243.14	27.30	5.89	12.4	0.3	-87.8	-0.122	0.002	-5.0	-0.122	22.0	0.534	-0.7	-0.018	0.002		
26	9:15	26.2	0.97	350	486	1142.0	127.6	332.5	0.07	2.30	751.1	0.23	0.08	0.023	258.69	26.65	6.04	11.6	0.3	-73.8	-1.722	0.002	-4.9	-0.114	26.1	0.609	-0.7	-0.016	0.002		
27	11:00	27.3	1.07	350	486	1061.5	127.3	373.1	0.04	2.01	716.7	0.20	0.15	0.026	178.15	27.33	4.59	11.3	0.3	-33.2	-0.856	0.001	-5.2	-0.134	-8.3	-0.214	-0.7	-0.018	0.004		
28	10:25	28.3	0.98	350	486	1011.4	125.8	338.2	0.05	2.21	704.2	0.26	0.07	0.023	128.10	23.68	3.00	9.8	0.2	-68.1	-1.594	0.001	-5.0	-0.117	-20.8	-0.487	-0.6	-0.015	0.002		
29	10:40	29.3	1.01	350	486	1009.1	124.4	291.0	0.04	2.16	709.1	0.24	0.08	0.024	125.81	24.46	3.05	8.4	0.2	-115.3	-2.795	0.001	-5.0	-0.122	-15.9	-0.385	-0.7	-0.016	0.002		
30	9:20	30.3	0.94	350	486	1031.6	125.0	321.1	0.01	2.68	746.0	0.27	0.09	0.023	148.34	23.38	3.36	9.0	0.2	-85.2	-1.930	0.000	-4.5	-0.102	21.0	0.475	-0.6	-0.014	0.002		
31	9:30	31.3	1.00	350	486	899.1	122.4	381.4	0.01	1.76	712.2	0.17	0.08	0.024	15.79	21.58	0.38	6.4	0.2	-24.9	-0.598	0.000	-5.4	-0.131	-12.8	-0.307	-0.7	-0.018	0.002		
32	10:30	32.3	1.04	350	486	889.3	125.3	379.3	0.01	2.59	749.2	0.26	0.08	0.025	5.98	22.20	0.15	9.3	0.2	-27.0	-0.673	0.000	-4.6	-0.115	24.2	0.605	-0.6	-0.016	0.002		
33	10:05	33.3	0.98	350	486	847.7	118.7	318.5	0.01	2.31	751.3	0.27	0.12	0.024	-35.56	19.99	-0.84	2.7	0.1	-87.8	-2.071	0.000	-4.9	-0.115	26.3	0.619	-0.6	-0.015	0.003		
34	12:15	34.4	1.09	350	486	848.2	116.3	332.5	0.01	2.53	747.2	0.30	0.12	0.026	-35.05	22.19	-0.92	0.3	0.0	-73.8	-1.930	0.000	-4.7	-0.122	22.2	0.580	-0.6	-0.016	0.003		
35	11:20	35.3	0.96	350	486	790.6	114.3	373.1	0.01	2.49	705.7	0.30	0.08	0.023	-92.66	18.25	-2.14	-1.7	0.0	-33.2	-0.767	0.000	-4.7	-0.109	-19.3	-0.446	-0.6	-0.014	0.002		
36	9:55	36.3	0.95	350	486	827.4	117.8	338.2	0.01	1.88	756.3	0.11	0.12	0.023	-55.91	18.82	-1.21	1.8	0.0	-68.1	-1.549	0.000	-5.3	-0.121	31.3	0.711	-0.8	-0.018	0.003		
37	9:35	37.3	0.99	350	486	813.4	113.2	291.0	0.01	1.95	724.1	0.15	0.08	0.024	-69.91	19.25	-1.45	-2.8	-0.1	-115.3	-2.728	0.000	-5.3	-0.124	-0.9	-0.022	-0.7	-0.018	0.002		
38	9:30	38.3	1.00	350	486	827.6	113.3	321.1	0.01	2.08	712.3	0.14	0.07	0.024	-55.69	19.86	-1.34	-2.7	-0.1	-85.2	-2.044	0.000	-5.1	-0.123	-12.7	-0.306	-0.8	-0.018	0.002		
Total fluid in contact with the basalt (L)														0.75																	
Σ SiO2 flux (blank included) (mg)															887																
Σ SiO2 flux released (blank excluded) = SiO2 from the glass (mg)															226																
Σ f K flux (mg)																	15.4														
Σ f SO4 flux (mg)																			-57.6												
Σ f H2S flux (mg)																			0.3												
Σ f Ca flux (mg)																					-3.8										
Σ f Na flux (mg)																							-4.7								
Σ f Mg flux (mg)																									-0.5						
Σ f Fe flux (mg)																												0.07			

Table C.4.20. Amount of major elements estimated in the unaltered volcanic glass and Σ major elements flux calculated from the fluid samples compositions, for the BGB1 and BGB2

BGB1 400°C / 483 bar (27.0 g of rock)			BGB2 350°C / 486 bar (26.4 g of rock)		
Amount of major elements estimated in the unaltered volcanic glass		Σ major elements flux calculated from the fluid samples compositions:	Amount of major elements estimated in the unaltered volcanic glass		Σ major elements flux calculated from the fluid samples compositions:
EMPA wt% SO ₂ = 0.04 wt% S = 0.02 glass (g) = 0.527 S in glass (g) = 0.00011 S in glass (mg) = 0.11		Σ H ₂ S flux (mg) = 0.66 Σ S (reduced) flux (mg) = 0.60 Σ SO ₄ flux (mg) = - Σ S (oxidized) flux (mg) = -	EMPA wt% SO ₂ = 0.04 wt% S = 0.02 glass (g) = 0.408 S in glass (g) = 0.00008 S in glass (mg) = 0.08		Σ H ₂ S flux (mg) = 0.30 Σ S (reduced) flux (mg) = 0.27 Σ SO ₄ flux (mg) = - Σ S (oxidized) flux (mg) = -
		S _(Ox) + S _(Red) in (mg) = 0.60 S _(Ox) + S _(Red) in (g) = 0.00060			S _(Ox) + S _(Red) in (mg) = 0.27 S _(Ox) + S _(Red) in (g) = 0.00027

Activity calculation

Table C.4.21. Ions activity and logarithm of activity calculate by the R package (linked to EqSolvR by Mroczek S. and Mroczek E., 2017) for the BGB1 (400°C / 483 bar). Table also reports values of quench pH, *in situ* pH, experimental time, flow-rate, T and P. Red column indicates effluents collected at 0.5 ml hr⁻¹ flow rate. LOD: limit of detection

samples	blank geothermal brine	8	9	10	11	12	13	14	15	16	17	18	19	20	21	22	23	24	25	26	27	28	29	30	31	32	33	34
<i>a</i> = <i>m</i> • <i>a</i> _γ																												
H ⁺	7.21E-08	9.92E-08	8.79E-08	7.89E-08	7.79E-08	7.84E-08	7.71E-08	7.55E-08	7.61E-08	7.57E-08	7.55E-08	7.69E-08	7.90E-08	8.12E-08	8.28E-08	7.93E-08	8.01E-08	7.91E-08	8.23E-08	7.84E-08	7.80E-08	8.11E-08	8.82E-08	7.96E-08	8.23E-08	8.40E-08	8.85E-08	8.17E-08
OH ⁻	6.11E-05	4.44E-05	5.01E-05	5.58E-05	5.66E-05	5.62E-05	5.72E-05	5.83E-05	5.79E-05	5.82E-05	5.83E-05	5.73E-05	5.58E-05	5.42E-05	5.32E-05	5.55E-05	5.50E-05	5.57E-05	5.35E-05	5.62E-05	5.65E-05	5.43E-05	4.99E-05	5.53E-05	5.35E-05	5.24E-05	4.98E-05	5.39E-05
Na ⁺	1.24E-02	1.07E-02	1.10E-02	1.17E-02	1.19E-02	1.20E-02	1.21E-02	1.20E-02	1.21E-02	1.19E-02	1.19E-02	1.20E-02	1.21E-02	1.21E-02	1.23E-02	1.23E-02	1.24E-02	1.24E-02	1.22E-02	1.22E-02	1.22E-02	1.26E-02	1.25E-02	1.25E-02	1.25E-02	1.24E-02	1.28E-02	1.27E-02
K ⁺	1.20E-03	2.21E-03	2.21E-03	1.62E-03	1.54E-03	1.61E-03	1.61E-03	1.57E-03	1.56E-03	1.54E-03	1.50E-03	1.44E-03	1.40E-03	1.31E-03	1.23E-03	1.12E-03	1.09E-03	1.06E-03	1.06E-03	1.03E-03	1.01E-03	1.01E-03	1.04E-03	1.01E-03	1.01E-03	1.00E-03	9.99E-04	9.85E-04
Cl ⁻	1.08E-02	1.13E-02	1.13E-02	1.10E-02	1.10E-02	1.12E-02	1.12E-02	1.10E-02	1.11E-02	1.09E-02	1.08E-02	1.09E-02	1.10E-02	1.10E-02	1.12E-02	1.09E-02	1.09E-02	1.10E-02	1.10E-02	1.09E-02	1.07E-02	1.11E-02	1.14E-02	1.11E-02	1.12E-02	1.13E-02	1.15E-02	1.14E-02
SO ₄ ²⁻	4.10E-05	2.36E-05	2.64E-05	3.29E-05	3.50E-05	3.42E-05	3.43E-05	3.63E-05	3.62E-05	3.66E-05	3.71E-05	3.72E-05	3.63E-05	3.54E-05	3.37E-05	3.71E-05	3.77E-05	3.63E-05	3.51E-05	3.56E-05	3.77E-05	3.60E-05	3.10E-05	3.56E-05	3.41E-05	3.20E-05	3.30E-05	3.39E-05
Ca ²⁺	4.17E-07	4.74E-07	2.75E-07	2.95E-07	3.60E-07	3.33E-07	2.97E-07	3.20E-07	3.49E-07	3.47E-07	3.78E-07	4.86E-07	4.80E-07	5.65E-07	5.21E-07	5.47E-07	6.22E-07	5.06E-07	5.59E-07	4.31E-07	4.98E-07	5.62E-07	5.97E-07	4.85E-07	5.23E-07	5.34E-07	7.46E-07	5.04E-07
Mg ²⁺	3.80E-08	1.16E-07	3.76E-08	3.76E-08	5.40E-08	4.87E-08	3.13E-08	3.99E-08	4.18E-08	4.51E-08	4.58E-08	4.98E-08	8.73E-08	9.41E-08	9.74E-08	1.01E-07	1.17E-07	8.36E-08	1.19E-07	6.64E-08	9.65E-08	1.10E-07	1.24E-07	8.36E-08	9.80E-08	7.04E-08	1.61E-07	7.95E-08
Fe ²⁺	< LOD	1.67E-07	2.68E-08	3.44E-08	< LOD	< LOD	< LOD	< LOD	< LOD	< LOD	< LOD	2.84E-08	< LOD	< LOD	< LOD	2.85E-08	< LOD	3.81E-08	< LOD	< LOD	< LOD	< LOD	< LOD	< LOD	< LOD	< LOD	< LOD	< LOD
a ³ H ⁺	5.19E-15	9.84E-15	7.73E-15	6.23E-15	6.07E-15	6.14E-15	5.94E-15	5.70E-15	5.79E-15	5.73E-15	5.71E-15	5.91E-15	6.24E-15	6.60E-15	6.86E-15	6.29E-15	6.41E-15	6.26E-15	6.77E-15	6.14E-15	6.09E-15	6.57E-15	7.78E-15	6.34E-15	6.78E-15	7.06E-15	7.83E-15	6.68E-15
log (<i>a</i> SiO ₂)	-1.9	-1.6	-1.5	-1.5	-1.5	-1.5	-1.5	-1.5	-1.5	-1.5	-1.5	-1.5	-1.5	-1.5	-1.5	-1.5	-1.5	-1.6	-1.7	-1.8	-1.8	-1.8	-1.8	-1.8	-1.8	-1.8	-1.8	-1.8
log (<i>a</i> K ⁺ / <i>a</i> H ⁺)	4.2	4.3	4.4	4.3	4.3	4.3	4.3	4.3	4.3	4.3	4.3	4.3	4.2	4.2	4.2	4.2	4.1	4.1	4.1	4.1	4.1	4.1	4.1	4.1	4.1	4.1	4.1	4.1
log (<i>a</i> Na ⁺ / <i>a</i> H ⁺)	5.2	5.0	5.1	5.2	5.2	5.2	5.2	5.2	5.2	5.2	5.2	5.2	5.2	5.2	5.2	5.2	5.2	5.2	5.2	5.2	5.2	5.2	5.2	5.2	5.2	5.2	5.2	5.2
log (<i>a</i> Ca ²⁺ / <i>a</i> ² H ⁺)	7.9	7.7	7.6	7.7	7.8	7.7	7.7	7.7	7.8	7.8	7.8	7.9	7.9	7.9	7.9	7.9	8.0	7.9	7.9	7.8	7.9	7.9	7.9	7.9	7.9	7.9	8.0	7.9
log (<i>a</i> Fe ²⁺ / <i>a</i> ² H ⁺)	< LOD	7.2	6.5	6.7	< LOD	< LOD	< LOD	< LOD	< LOD	< LOD	6.7	< LOD	< LOD	< LOD	6.6	< LOD	6.8	< LOD	< LOD	< LOD	< LOD	< LOD	< LOD	< LOD	< LOD	< LOD	< LOD	< LOD
log (<i>a</i> Mg ²⁺ / <i>a</i> ² H ⁺)	6.9	7.1	6.7	6.8	6.9	6.9	6.7	6.8	6.9	6.9	6.9	6.9	7.1	7.2	7.2	7.2	7.3	7.1	7.2	7.0	7.2	7.2	7.2	7.1	7.2	7.0	7.3	7.1
log <i>a</i> Na ⁺	-1.9	-2.0	-2.0	-1.9	-1.9	-1.9	-1.9	-1.9	-1.9	-1.9	-1.9	-1.9	-1.9	-1.9	-1.9	-1.9	-1.9	-1.9	-1.9	-1.9	-1.9	-1.9	-1.9	-1.9	-1.9	-1.9	-1.9	-1.9
log <i>a</i> K ⁺	-2.9	-2.7	-2.7	-2.8	-2.8	-2.8	-2.8	-2.8	-2.8	-2.8	-2.8	-2.8	-2.9	-2.9	-2.9	-2.9	-3.0	-3.0	-3.0	-3.0	-3.0	-3.0	-3.0	-3.0	-3.0	-3.0	-3.0	-3.0
log <i>a</i> Cl ⁻	-2.0	-1.9	-1.9	-2.0	-2.0	-2.0	-1.9	-2.0	-2.0	-2.0	-2.0	-2.0	-2.0	-2.0	-1.9	-2.0	-2.0	-2.0	-2.0	-2.0	-2.0	-2.0	-1.9	-2.0	-2.0	-1.9	-1.9	-1.9
log <i>a</i> SO ₄ ²⁻	-4.4	-4.6	-4.6	-4.5	-4.5	-4.5	-4.5	-4.4	-4.4	-4.4	-4.4	-4.4	-4.4	-4.5	-4.5	-4.4	-4.4	-4.4	-4.5	-4.4	-4.4	-4.4	-4.5	-4.4	-4.5	-4.5	-4.5	-4.5
log <i>a</i> Ca ²⁺	-6.4	-6.3	-6.6	-6.5	-6.4	-6.5	-6.5	-6.5	-6.5	-6.5	-6.4	-6.3	-6.3	-6.2	-6.3	-6.3	-6.2	-6.3	-6.3	-6.4	-6.3	-6.2	-6.2	-6.3	-6.3	-6.3	-6.1	-6.3
log <i>a</i> Mg ²⁺	-7.4	-6.9	-7.4	-7.4	-7.3	-7.3	-7.5	-7.4	-7.4	-7.3	-7.3	-7.3	-7.1	-7.0	-7.0	-7.0	-6.9	-7.1	-6.9	-7.2	-7.0	-7.0	-6.9	-7.1	-7.0	-7.2	-6.8	-7.1
log <i>a</i> Fe ²⁺	< LOD	-6.78	-7.57	-7.46	< LOD	< LOD	< LOD	< LOD	< LOD	< LOD	-7.55	< LOD	< LOD	< LOD	-7.54	< LOD	-7.42	< LOD	< LOD	< LOD	< LOD	< LOD	< LOD	< LOD	< LOD	< LOD	< LOD	< LOD
T(°C)	400	397.6	400.1	400.4	400.7	400.8	400.4	400.4	400.8	400.6	400.7	400.9	400.7	400.6	400.6	400.9	400.5	400.7	400.6	400.5	400.7	400.4	400.5	400.2	400.4	400.6	400.7	400.5
P (bar)	500	478.9	483.1	483.5	483.8	484.1	484.4	484.3	484.4	484.2	483.5	483.6	483.8	483.8	484.7	484.2	483.5	483.5	483.9	484.0	483.9	483.6	483.6	483.4	483.6	483.1	477.0	482.3
<i>in situ</i> pH (400°C)	7.14	7.00	7.06	7.10	7.11	7.11	7.11	7.12	7.12	7.12	7.12	7.11	7.10	7.09	7.08	7.10	7.10	7.10	7.08	7.11	7.11	7.09	7.05	7.10	7.08	7.08	7.05	7.09
room T pH	3.91	3.23	2.87	3.25	3.32	3.25	3.31	3.53	3.55	3.5	3.4	3.45	3.57	3.71	3.76	3.78	4.05	4.6	6.23	6.51	6.77	7.07	7.44	7.52	7.41	7.66	7.3	7.76
flow rate (ml hr ⁻¹)	-	1	1	1	1	1	1	1	1	1	1	1	1	1	1	1	1	1	1	1	1	1	1	1	1	1	0.5	0.5
time (hrs)	0.0	190.9	214.7	239.3	262.6	287.9	313.4	334.4	359.0	382.7	406.0	430.6	457.3	480.7	503.3	527.7	550.4	574.8	597.6	625.7	647.5	670.8	694.4	718.8	743.4	767.5	809.2	853.2
Anhydrite																												
Log <i>Ksp</i> (Supert92)		4.27	4.27	4.27	4.27	4.27	4.27	4.27	4.27	4.27	4.27	4.27	4.27	4.27	4.27	4.27	4.27	4.27	4.27	4.27	4.27	4.27	4.27	4.27	4.27	4.27	4.27	4.27
Log <i>Q</i> (IAP)		3.51	3.69	3.57	3.45	3.50	3.55	3.49	3.45	3.45	3.41	3.30	3.32	3.26	3.31	3.25	3.18	3.29	3.27	3.37	3.28	3.25	3.29	3.32	3.31	3.32	3.17	3.32
Log <i>SI</i>		-0.76	-0.58	-0.70	-0.82	-0.77	-0.72	-0.78	-0.82	-0.82	-0.86	-0.97	-0.95	-1.01	-0.96	-1.02	-1.09	-0.98	-1.00	-0.90	-0.99	-1.02	-0.98	-0.95	-0.96	-0.95	-1.10	-0.95

Table C.4.22. Values of the activity coefficients (a_v) calculate by the R package for the BGB1

		H ⁺	OH ⁻	Na ⁺	K ⁺	Cl ⁻	SO ₄ ²⁻	Ca ²⁺	Mg ²⁺	Fe ²⁺	NaSO ₄ ⁻	HSO ₄ ⁻	KSO ₄ ⁻	NaCl ⁻	KCl ⁻	HCl ⁻	KOH ⁻	NaOH ⁻	CaSO ₄	MgSO ₄	MgCl ⁺	CaCl ⁺	CaCl ₂	MgOH ⁺	CaOH ⁺	FeCl ⁻	FeSO ₄ ⁻	
blank																												
	geothermal brine	m	1.10E-07	1.04E-04	2.11E-02	2.09E-03	1.86E-02	3.38E-04	2.82E-06	2.19E-07																		
8	a ₁	m	6.58E-01	5.90E-01	5.90E-01	5.74E-01	5.82E-01	1.21E-01	1.48E-01	1.74E-01																		
	activity	m	7.21E-08	6.11E-05	1.24E-02	1.20E-03	1.08E-02	4.10E-05	4.17E-07	3.80E-08																		
	m	1.49E-07	7.42E-05	1.79E-02	3.80E-03	1.91E-02	1.84E-04	3.06E-06	6.39E-07	1.08E-06																		
9	a ₁	m	6.64E-01	5.99E-01	5.99E-01	5.83E-01	5.91E-01	1.29E-01	1.55E-01	1.81E-01	1.55E-01	5.99E-01	5.99E-01	5.99E-01	1.00E+00	1.00E+00	1.00E+00	1.00E+00	1.00E+00	1.00E+00	1.00E+00	1.00E+00	6.52E-01	6.27E-01	1.00E+00	6.52E-01	6.27E-01	1.00E+00
	activity	m	9.92E-08	4.44E-05	1.07E-02	2.21E-03	1.13E-02	2.36E-05	4.74E-07	1.16E-07	1.67E-07	8.96E-04	6.51E-05	4.14E-04	6.59E-03	4.29E-04	5.46E-07	2.74E-06	6.95E-06	2.82E-06	3.03E-06	2.73E-05	2.29E-06	1.11E-05	9.44E-06	4.38E-06	1.61E-08	0.00E+00
	m	1.33E-07	8.42E-05	1.85E-02	3.82E-03	1.93E-02	2.10E-04	1.81E-06	2.11E-07	1.76E-07	1.73E-03	1.08E-04	7.77E-04	6.82E-03	4.31E-04	4.86E-07	3.09E-06	8.07E-06	1.02E-06	9.91E-07	1.60E-05	1.34E-06	2.46E-05	2.14E-06	4.08E-06	9.54E-06	1.13E-06	4.60E-09
10	a ₁	m	6.61E-01	5.95E-01	5.95E-01	5.79E-01	5.87E-01	1.26E-01	1.52E-01	1.78E-01	1.52E-01	5.95E-01	5.95E-01	5.95E-01	1.00E+00	1.00E+00	1.00E+00	1.00E+00	1.00E+00	1.00E+00	1.00E+00	1.00E+00	6.50E-01	6.24E-01	1.00E+00	6.50E-01	6.24E-01	1.00E+00
	activity	m	8.79E-08	5.01E-05	1.10E-02	2.21E-03	1.13E-02	2.64E-05	2.75E-07	3.76E-08	2.68E-08	1.03E-03	6.45E-05	4.63E-04	6.82E-03	4.31E-04	4.86E-07	3.09E-06	8.07E-06	1.02E-06	9.91E-07	1.60E-05	1.34E-06	4.08E-06	6.20E-06	7.05E-07	2.87E-09	0.00E+00
	m	1.19E-07	9.39E-05	1.97E-02	2.80E-03	1.88E-02	2.63E-04	1.95E-06	2.12E-07	2.28E-07	2.29E-03	1.21E-04	7.10E-04	7.03E-03	4.37E-04	4.25E-07	2.52E-06	9.52E-06	1.28E-06	9.67E-07	1.56E-05	1.17E-06	4.56E-06	1.14E-05	1.42E-06	7.37E-09	0.00E+00	
11	a ₁	m	6.61E-01	5.94E-01	5.94E-01	5.78E-01	5.86E-01	1.25E-01	1.51E-01	1.77E-01	1.51E-01	5.94E-01	5.94E-01	5.94E-01	1.00E+00	1.00E+00	1.00E+00	1.00E+00	1.00E+00	1.00E+00	1.00E+00	1.00E+00	6.49E-01	6.24E-01	1.00E+00	6.49E-01	6.24E-01	1.00E+00
	activity	m	7.89E-08	5.58E-05	1.17E-02	1.62E-03	1.10E-02	3.29E-05	2.95E-07	3.76E-08	3.44E-08	1.36E-03	7.21E-05	4.22E-04	7.03E-03	3.07E-04	4.25E-07	2.52E-06	9.52E-06	1.28E-06	9.67E-07	1.66E-05	1.35E-06	4.56E-06	7.38E-06	8.82E-07	4.60E-09	0.00E+00
	m	1.18E-07	9.55E-05	2.01E-02	2.68E-03	1.89E-02	2.84E-04	2.40E-06	3.07E-07																			
12	a ₁	m	6.59E-01	5.92E-01	5.92E-01	5.76E-01	5.84E-01	1.23E-01	1.50E-01	1.76E-01																		
	activity	m	7.79E-08	5.66E-05	1.19E-02	1.51E-03	1.10E-02	3.50E-05	3.60E-07	5.40E-08																		
	m	1.19E-07	9.51E-05	2.03E-02	2.84E-03	1.92E-02	2.80E-04	2.25E-06	2.79E-07																			
13	a ₁	m	6.58E-01	5.91E-01	5.91E-01	5.74E-01	5.83E-01	1.22E-01	1.48E-01	1.75E-01																		
	activity	m	7.84E-08	5.62E-05	1.20E-02	1.61E-03	1.12E-02	3.42E-05	3.33E-07	4.87E-08																		
	m	1.17E-07	9.70E-05	2.04E-02	2.82E-03	1.93E-02	2.84E-04	2.01E-06	1.80E-07																			
14	a ₁	m	6.58E-01	5.90E-01	5.90E-01	5.74E-01	5.82E-01	1.21E-01	1.48E-01	1.74E-01																		
	activity	m	7.70E-08	5.72E-05	1.21E-02	1.62E-03	1.12E-02	3.44E-05	2.97E-07	3.13E-08																		
	m	1.15E-07	9.86E-05	2.02E-02	2.73E-03	1.88E-02	2.97E-04	2.15E-06	2.28E-07																			
15	a ₁	m	6.59E-01	5.92E-01	5.92E-01	5.75E-01	5.84E-01	1.23E-01	1.49E-01	1.75E-01																		
	activity	m	7.55E-08	5.83E-05	1.20E-02	1.57E-03	1.10E-02	3.63E-05	3.20E-07	3.99E-08																		
	m	1.16E-07	9.80E-05	2.04E-02	2.72E-03	1.90E-02	2.97E-04	2.35E-06	2.40E-07																			
16	a ₁	m	6.58E-01	5.91E-01	5.91E-01	5.74E-01	5.83E-01	1.22E-01	1.48E-01	1.74E-01																		
	activity	m	7.61E-08	5.79E-05	1.21E-02	1.56E-03	1.11E-02	3.62E-05	3.49E-07	4.18E-08																		
	m	1.15E-07	9.81E-05	2.00E-02	2.67E-03	1.85E-02	2.96E-04	2.31E-06	2.56E-07																			
17	a ₁	m	6.60E-01	5.93E-01	5.93E-01	5.77E-01	5.85E-01	1.24E-01	1.50E-01	1.76E-01																		
	activity	m	7.57E-08	5.82E-05	1.19E-02	1.54E-03	1.09E-02	3.66E-05	3.47E-07	4.51E-08																		
	m	1.15E-07	9.84E-05	2.01E-02	2.60E-03	1.85E-02	3.00E-04	2.52E-06	2.60E-07																			
18	a ₁	m	6.59E-01	5.93E-01	5.93E-01	5.76E-01	5.85E-01	1.24E-01	1.50E-01	1.76E-01																		
	activity	m	7.55E-08	5.83E-05	1.19E-02	1.50E-03	1.08E-02	3.71E-05	3.78E-07	4.58E-08																		
	m	1.17E-07	9.67E-05	2.02E-02	2.49E-03	1.86E-02	3.01E-04	3.24E-06	2.83E-07																			
19	a ₁	m	6.59E-01	5.93E-01	5.93E-01	5.76E-01	5.85E-01	1.23E-01	1.50E-01	1.76E-01																		
	activity	m	7.69E-08	5.73E-05	1.20E-02	1.44E-03	1.09E-02	3.72E-05	4.86E-07	4.98E-08																		
	m	1.20E-07	9.41E-05	2.04E-02	2.43E-03	1.88E-02	2.95E-04	3.21E-06	4.97E-07																			
20	a ₁	m	6.59E-01	5.92E-01	5.92E-01	5.76E-01	5.84E-01	1.23E-01	1.50E-01	1.76E-01																		
	activity	m	7.90E-08	5.58E-05	1.21E-02	1.40E-03	1.10E-02	3.63E-05	4.80E-07	8.73E-08																		
	m	1.23E-07	9.15E-05	2.04E-02	2.27E-03	1.88E-02	2.86E-04	3.76E-06	5.34E-07																			
21	a ₁	m	6.60E-01	5.93E-01	5.93E-01	5.77E-01	5.85E-01	1.24E-01	1.50E-01	1.76E-01																		
	activity	m	8.12E-08	5.42E-05	1.21E-02	1.31E-03	1.10E-02	3.54E-05	5.65E-07	9.41E-08																		
	m	1.26E-07	8.99E-05	2.08E-02	2.14E-03	1.93E-02	2.76E-04	3.50E-06	5.57E-07	1.92E-07																		
22	a ₁	m	6.58E-01	5.91E-01	5.91E-01	5.75E-01	5.83E-01	1.22E-01	1.49E-01	1.75E-01	1.49E-01	5.91E-01	5.91E-01	5.91E-01	1.00E+00	1.00E+00	1.00E+00	1.00E+00	1.00E+00	1.00E+00	1.00E+00	1.00E+00	6.47E-01	6.21E-01	1.00E+00	6.47E-01	6.21E-01	1.00E+00
	activity	m	8.28E-08	5.32E-05	1.23E-02	1.23E-03	1.12E-02	3.37E-05	5.21E-07	9.74E-08	2.85E-08	1.47E-03	7.76E-05	3.28E-04	7.56E-03	2.37E-04	4.55E-07	1.82E-06	9.57E-06	2.61E-05	3.39E-06	1.66E-06	2.88E-05	3.98E-06	7.30E-06	1.20E-05	7.46E-07	6.27E-09
	m	1.20E-07	9.36E-05	2.07E-02	1.95E-03	1.86E-02	3.00E-04	3.64E-06	5.75E-07																			
23	a ₁	m	6.60E-01	5.93E-01	5.93E-01	5.77E-01	5.85E-01	1.24E-01	1.50E-01	1.76E-01																		
	activity	m	7.93E-08	5.55E-05	1.23E-02	1.12E-03	1.09E-02	3.71E-05	5.47E-07	1.01E-07																		
	m	1.21E-07	9.29E-05	2.09E-02	1.89E-03	1.87E-02	3.06E-04	4.16E-06	6.65E-07	2.55E-07	2.78E-03	1.42E-04	5.48E-04	7.35E-03	2.04E-04	4.27E-07	1.67E-06	9.92E-06	4.55E-06	2.98E-06	5.37E-05	4.49E-06	1.40E-05	2.37E-05	1.56E-06	9.37E-09	0.00E+00	
24	a ₁	m	6.59E-01	5.92E-01	5.92E-01	5.76E-01	5.84E-01	1.23E-01	1.50E-01	1.76E-01	1.50E-01	5.92E-01	5.92E-01	5.92E-01	1.00E+00	1.00E+00	1.00E+00	1.00E+00	1.00E+00	1.00E+00	1.00E+00	1.00E+00	6.48E-01	6.22E-01	1.00E+00	6.48E-01	6.22E-01	1.00E+00
	activity	m	8.01E-08	5.50E-05	1.24E-02	1.09E-03	1.09E-02	3.77E-05	6.22E-07	1.17E-07	3.81E-08	1.65E-03	8.39E-05	3.25E-04														

Table C.4.23. Ions activity and logarithm of activity calculate by the R package (linked to EqSolvR by Mroczek S. and Mroczek E., 2017) for the BGB2 experiment (350°C / 486 bar). Table also reports values of quench pH, *in situ* pH, experimental time, flow-rate, T and P. LOD: limit of detection

samples	blank geothermal brine	8	9	10	11	12	13	14	15	16	17	18	19	20	21	22	23	24	25	26	27	28	29	30	31	32	33	34	35	36	37	38	
$a = m \cdot a_{\gamma}$																																	
H ⁺	1.79E-07	2.19E-07	2.09E-07	1.74E-07	1.53E-07	1.59E-07	1.57E-07	1.59E-07	1.51E-07	1.66E-07	1.61E-07	1.54E-07	1.51E-07	1.61E-07	1.47E-07	1.53E-07	1.50E-07	1.50E-07	1.64E-07	1.62E-07	1.48E-07	1.56E-07	1.70E-07	1.67E-07	1.44E-07	1.51E-07	1.66E-07	1.63E-07	1.48E-07	1.57E-07	1.68E-07	1.58E-07	
OH ⁻	4.32E-05	3.53E-05	3.69E-05	4.44E-05	5.06E-05	4.85E-05	4.92E-05	4.86E-05	5.10E-05	4.65E-05	4.80E-05	5.03E-05	5.12E-05	4.79E-05	5.25E-05	5.06E-05	5.17E-05	5.15E-05	4.71E-05	4.76E-05	5.23E-05	4.94E-05	4.54E-05	4.63E-05	5.38E-05	5.10E-05	4.65E-05	4.75E-05	5.21E-05	4.94E-05	4.60E-05	4.89E-05	
Na ⁺	1.92E-02	1.48E-02	1.38E-02	1.49E-02	1.64E-02	1.65E-02	1.68E-02	1.69E-02	1.66E-02	1.68E-02	1.69E-02	1.66E-02	1.70E-02	1.72E-02	1.67E-02	1.70E-02	1.69E-02	1.71E-02	1.72E-02	1.72E-02	1.65E-02	1.63E-02	1.65E-02	1.72E-02	1.64E-02	1.71E-02	1.73E-02	1.72E-02	1.63E-02	1.73E-02	1.68E-02	1.65E-02	
K ⁺	1.82E-03	3.15E-03	3.86E-03	3.46E-03	2.34E-03	1.81E-03	1.65E-03	1.62E-03	1.57E-03	1.61E-03	1.67E-03	1.68E-03	1.71E-03	1.79E-03	1.76E-03	1.76E-03	1.74E-03	1.72E-03	1.75E-03	1.73E-03	1.70E-03	1.71E-03	1.73E-03	1.63E-03	1.67E-03	1.62E-03	1.58E-03	1.53E-03	1.59E-03	1.57E-03	1.55E-03		
Cl ⁻	1.79E-02	1.61E-02	1.59E-02	1.60E-02	1.59E-02	1.58E-02	1.57E-02	1.59E-02	1.53E-02	1.60E-02	1.60E-02	1.54E-02	1.57E-02	1.63E-02	1.54E-02	1.58E-02	1.55E-02	1.57E-02	1.63E-02	1.62E-02	1.51E-02	1.53E-02	1.59E-02	1.62E-02	1.49E-02	1.57E-02	1.63E-02	1.60E-02	1.48E-02	1.61E-02	1.60E-02	1.54E-02	
SO ₄ ²⁻	8.92E-05	5.52E-05	5.06E-05	6.83E-05	8.46E-05	7.85E-05	8.54E-05	8.11E-05	9.09E-05	7.70E-05	8.18E-05	9.06E-05	9.20E-05	8.14E-05	9.34E-05	9.18E-05	9.67E-05	9.57E-05	7.95E-05	8.28E-05	9.74E-05	8.88E-05	7.52E-05	8.03E-05	1.01E-04	9.58E-05	7.98E-05	8.41E-05	1.00E-04	8.50E-05	7.52E-05	8.47E-05	
Ca ²⁺	2.63E-06	1.98E-06	1.07E-06	7.10E-07	3.88E-07	4.78E-07	8.03E-07	6.50E-07	7.33E-07	7.65E-07	7.74E-07	8.19E-07	7.29E-07	8.05E-07	6.06E-07	7.91E-07	8.86E-07	8.43E-07	8.53E-07	8.95E-07	7.55E-07	8.63E-07	8.91E-07	1.06E-06	6.52E-07	9.63E-07	9.15E-07	9.88E-07	9.38E-07	7.25E-07	7.98E-07	8.25E-07	
Mg ²⁺	5.71E-07	5.05E-07	1.49E-07	3.79E-08	3.82E-09	2.47E-08	8.12E-08	4.21E-08	7.35E-08	1.23E-07	1.16E-07	1.21E-07	8.51E-08	9.13E-08	2.36E-08	1.37E-07	1.34E-07	1.37E-07	1.12E-07	1.51E-07	1.22E-07	1.67E-07	1.66E-07	1.83E-07	9.68E-08	1.60E-07	1.81E-07	1.95E-07	1.78E-07	6.92E-08	1.05E-07	8.79E-08	
Fe ²⁺	< LOD	2.59E-07	1.15E-07	1.36E-07	7.14E-08	5.56E-08	1.03E-07	6.96E-08	6.79E-08	7.85E-08	7.90E-08	6.68E-08	5.68E-08	1.05E-07	< LOD	< LOD	< LOD	< LOD	< LOD	< LOD	1.50E-07	7.41E-08	< LOD	8.80E-08	8.14E-08	< LOD	1.17E-07	1.17E-07	8.00E-08	1.18E-07	7.72E-08	6.75E-08	
a ⁺ H ⁺	3.20E-14	4.80E-14	4.37E-14	3.03E-14	2.33E-14	2.54E-14	2.47E-14	2.52E-14	2.29E-14	2.76E-14	2.60E-14	2.36E-14	2.28E-14	2.60E-14	2.17E-14	2.34E-14	2.24E-14	2.25E-14	2.70E-14	2.63E-14	2.18E-14	2.45E-14	2.90E-14	2.78E-14	2.06E-14	2.29E-14	2.76E-14	2.64E-14	2.20E-14	2.45E-14	2.82E-14	2.50E-14	
log (<i>a</i> SiO ₂)	-1.83	-1.63	-1.51	-1.55	-1.60	-1.61	-1.59	-1.61	-1.62	-1.66	-1.64	-1.66	-1.68	-1.70	-1.70	-1.73	-1.71	-1.72	-1.73	-1.72	-1.75	-1.77	-1.77	-1.77	-1.82	-1.83	-1.85	-1.85	-1.88	-1.86	-1.87	-1.86	
log (<i>a</i> K ⁺ / <i>a</i> H ⁺)	4.01	4.16	4.27	4.30	4.19	4.06	4.02	4.01	4.02	3.99	4.01	4.04	4.05	4.05	4.08	4.06	4.07	4.06	4.03	4.03	4.06	4.04	4.01	4.01	4.05	4.04	3.99	3.99	4.01	4.01	3.97	3.99	
log (<i>a</i> Na ⁺ / <i>a</i> H ⁺)	5.03	4.83	4.82	4.93	5.03	5.02	5.03	5.03	5.04	5.01	5.02	5.03	5.05	5.03	5.05	5.05	5.05	5.06	5.02	5.03	5.05	5.02	4.99	5.01	5.06	5.05	5.02	5.02	5.04	5.04	5.00	5.02	
log (<i>a</i> Ca ₂₊ / <i>a</i> ² H ⁺)	7.92	7.62	7.39	7.37	7.22	7.27	7.51	7.41	7.50	7.44	7.47	7.54	7.51	7.49	7.45	7.53	7.60	7.57	7.50	7.53	7.54	7.55	7.49	7.58	7.50	7.62	7.52	7.57	7.63	7.47	7.45	7.52	
log (<i>a</i> Fe ₂₊ / <i>a</i> ² H ⁺)	< LOD	6.73	6.42	6.65	6.49	6.34	6.62	6.44	6.47	6.45	6.48	6.45	6.40	6.61	< LOD	< LOD	< LOD	< LOD	< LOD	< LOD	< LOD	6.84	6.48	< LOD	6.50	6.60	< LOD	6.63	6.64	6.56	6.68	6.44	6.43
log (<i>a</i> Mg ₂₊ / <i>a</i> ² H ⁺)	7.25	7.02	6.53	6.10	5.22	5.99	6.52	6.22	6.51	6.65	6.65	6.71	6.57	6.55	6.04	6.77	6.78	6.78	6.62	6.76	6.75	6.83	6.76	6.82	6.67	6.84	6.82	6.87	6.91	6.45	6.57	6.55	
log <i>a</i> Na ⁺	-1.72	-1.83	-1.86	-1.83	-1.79	-1.78	-1.77	-1.77	-1.78	-1.77	-1.77	-1.78	-1.77	-1.77	-1.78	-1.77	-1.77	-1.77	-1.76	-1.76	-1.78	-1.79	-1.78	-1.77	-1.79	-1.77	-1.76	-1.76	-1.79	-1.76	-1.77	-1.78	
log <i>a</i> K ⁺	-2.74	-2.50	-2.41	-2.46	-2.63	-2.74	-2.78	-2.79	-2.80	-2.79	-2.78	-2.77	-2.77	-2.75	-2.75	-2.75	-2.76	-2.76	-2.76	-2.76	-2.76	-2.77	-2.77	-2.76	-2.77	-2.79	-2.78	-2.79	-2.80	-2.82	-2.80	-2.81	
log <i>a</i> Cl ⁻	-1.75	-1.79	-1.80	-1.80	-1.80	-1.80	-1.80	-1.80	-1.82	-1.80	-1.80	-1.81	-1.80	-1.79	-1.81	-1.80	-1.81	-1.80	-1.79	-1.82	-1.79	-1.82	-1.82	-1.80	-1.79	-1.83	-1.79	-1.83	-1.79	-1.80	-1.81		
log <i>a</i> SO ₄ ²⁻	-4.05	-4.26	-4.30	-4.17	-4.07	-4.11	-4.07	-4.09	-4.04	-4.11	-4.09	-4.04	-4.04	-4.09	-4.03	-4.04	-4.01	-4.02	-4.10	-4.08	-4.01	-4.05	-4.12	-4.10	-4.00	-4.02	-4.10	-4.08	-4.00	-4.07	-4.12	-4.07	
log <i>a</i> Ca ²⁺	-5.58	-5.70	-5.97	-6.15	-6.41	-6.32	-6.10	-6.19	-6.13	-6.12	-6.11	-6.09	-6.14	-6.09	-6.22	-6.10	-6.05	-6.07	-6.07	-6.05	-6.12	-6.06	-6.05	-5.97	-6.19	-6.02	-6.04	-6.01	-6.03	-6.14	-6.10	-6.08	
log <i>a</i> Mg ²⁺	-6.24	-6.30	-6.83	-7.42	-8.42	-7.61	-7.09	-7.38	-7.13	-6.91	-6.94	-6.92	-7.07	-7.04	-7.63	-6.86	-6.87	-6.86	-6.95	-6.82	-6.91	-6.78	-6.78	-6.74	-7.01	-6.80	-6.74	-6.71	-6.75	-7.16	-6.98	-7.06	
log <i>a</i> Fe ²⁺	< LOD	-6.59	-6.94	-6.87	-7.15	-7.26	-6.99	-7.16	-7.17	-7.11	-7.10	-7.18	-7.25	-6.98	< LOD	< LOD	< LOD	< LOD	< LOD	< LOD	-6.82	-7.13	< LOD	-7.06	-7.09	< LOD	-6.93	-6.93	-7.10	-6.93	-7.11	-7.17	
T(°C)	350	352.3	350.4	350.5	350.7	350.6	350.8	350.7	350.4	350.6	350.8	350.6	350.7	350.8	350.3	350.5	350.5	350.4	350.6	350.8	350.7	350.7	350.4	350.6	350.6	350.5	350.7	350.8	350.5	350.3	350.6	350.4	
P(bar)	500	486.3	486.2	486.3	486.2	486.2	486.2	486.2	486.3	486.2	486.4	486.2	486.2	486.1	486.2	486.3	486.3	486.2	486.2	486.2	486.2	486.2	486.2	486.3	486.2	486.2	486.2	486.3	486.2	486.3	486.2	486.3	
in situ pH (350°C)	6.75	6.66	6.68	6.76	6.82	6.80	6.80	6.80	6.82	6.78	6.79	6.81	6.82	6.79	6.83	6.82	6.83	6.82	6.78	6.79	6.83	6.81	6.77	6.78	6.84	6.82	6.78	6.79	6.83	6.81	6.77	6.80	
room T pH	4.28	4.43	3.39	3.56	4.58	4.65	5.40	6.05	6.31	6.72	6.72	7.01	7.25	7.21	7.17	7.21	7.21	7.30	7.31	7.46	7.51	7.73	7.69	7.70	7.87	7.87	7.91	7.86	7.85	7.85	7.91	7.84	
flow rate (ml hr ⁻¹)	-	1	1	1	1	1	1	1	1	1	1	1	1	1	1	1	1	1	1	1	1	1	1	1	1	1	1	1	1	1	1	1	
time (hrs)	0.0	187.8																															

Table C.4.24. Values of the activity coefficients (a_i) calculate by the R package for the BGB2

	H ⁺	OH ⁻	Na ⁺	K ⁺	Cl ⁻	SO ₄ ²⁻	Ca ²⁺	Mg ²⁺	Fe ²⁺	NaSO ₄ ⁻	HSO ₄ ⁻	KSO ₄ ⁻	NaCl ⁰	KCl ⁰	HCl ⁰	KOH ⁰	NaOH ⁰	CaSO ₄ ⁰	MgSO ₄ ⁰	MgCl ⁺	CaCl ⁺	CaCl ₂ ⁰	MgOH ⁺	CaOH ⁺	FeCl ⁰	FeSO ₄ ⁰
m	2.50E-07	6.64E-05	2.95E-02	2.87E-03	2.78E-02	4.98E-04	1.24E-05	2.32E-06		2.99E-03	1.10E-04	5.60E-04	5.23E-03	1.26E-04	1.27E-07	9.46E-07	5.73E-06	6.24E-05	1.40E-05	5.69E-06	7.96E-05	3.60E-06	1.43E-05	2.31E-05		
a _i	7.15E-01	6.51E-01	6.51E-01	6.34E-01	6.42E-01	1.79E-01	2.13E-01	2.46E-01		6.51E-01	6.51E-01	6.51E-01	1.00E+00	1.00E+00	1.00E+00	1.00E+00	1.00E+00	1.00E+00	1.00E+00	7.04E-01	6.79E-01	1.00E+00	7.04E-01	6.79E-01		
activity	1.79E-07	4.32E-05	1.92E-02	1.82E-03	1.79E-02	8.92E-05	2.63E-06	5.71E-07		1.94E-03	7.16E-05	3.65E-04	5.23E-03	1.26E-04	1.27E-07	9.46E-07	5.73E-06	6.24E-05	1.40E-05	4.00E-06	5.41E-05	3.60E-06	1.01E-05	1.57E-05		
m	3.01E-07	5.25E-05	2.20E-02	4.80E-03	2.43E-02	2.72E-04	8.38E-06	1.89E-06	1.10E-06	1.38E-03	8.09E-05	5.82E-04	3.63E-03	1.98E-04	1.41E-07	1.34E-06	3.60E-06	2.90E-05	7.67E-06	4.44E-06	5.26E-05	2.21E-06	1.01E-05	1.38E-05	3.62E-06	5.87E-08
a _i	7.29E-01	6.71E-01	6.71E-01	6.57E-01	6.64E-01	2.03E-01	2.36E-01	2.68E-01	2.36E-01	6.71E-01	6.71E-01	6.71E-01	1.00E+00	1.00E+00	1.00E+00	1.00E+00	1.00E+00	1.00E+00	1.00E+00	7.19E-01	6.97E-01	1.00E+00	7.19E-01	6.97E-01	6.97E-01	1.00E+00
activity	2.19E-07	3.53E-05	1.48E-02	3.15E-03	1.61E-02	5.52E-05	1.98E-06	5.05E-07	2.59E-07	9.26E-04	5.43E-05	3.91E-04	3.63E-03	2.39E-04	1.33E-07	1.71E-06	3.52E-06	2.08E-05	7.67E-06	3.20E-06	3.67E-05	2.21E-06	7.26E-06	9.61E-06	2.53E-06	5.87E-08
m	2.86E-07	5.48E-05	2.05E-02	5.85E-03	2.39E-02	2.46E-04	4.49E-06	5.53E-07	4.83E-07	1.18E-03	7.06E-05	6.51E-04	3.36E-03	2.39E-04	1.33E-07	1.71E-06	3.52E-06	2.08E-06	1.30E-06	2.81E-05	1.17E-06	3.12E-06	7.80E-06	1.59E-06	2.40E-08	0.00E+00
a _i	7.31E-01	6.74E-01	6.74E-01	6.59E-01	6.67E-01	2.06E-01	2.39E-01	2.70E-01	2.39E-01	6.74E-01	6.74E-01	6.74E-01	1.00E+00	1.00E+00	1.00E+00	1.00E+00	1.00E+00	1.00E+00	1.00E+00	7.21E-01	6.99E-01	1.00E+00	7.21E-01	6.99E-01	6.99E-01	1.00E+00
activity	2.09E-07	3.69E-05	1.38E-02	3.86E-03	1.59E-02	5.06E-05	1.07E-06	1.49E-07	1.15E-07	7.92E-04	4.75E-05	4.38E-04	3.36E-03	2.39E-04	1.33E-07	1.71E-06	3.52E-06	2.08E-06	1.30E-06	2.03E-05	8.18E-07	3.12E-06	5.62E-06	1.11E-06	1.68E-08	0.00E+00
m	2.39E-07	6.64E-05	2.22E-02	5.29E-03	2.42E-02	3.42E-04	3.05E-06	1.43E-07	5.84E-07	1.72E-03	7.97E-05	7.92E-04	3.64E-03	2.15E-04	1.11E-07	1.85E-06	4.57E-06	7.10E-07	3.32E-07	1.88E-05	7.83E-07	9.55E-07	6.25E-06	1.90E-06	3.81E-08	0.00E+00
a _i	7.27E-01	6.69E-01	6.69E-01	6.54E-01	6.61E-01	2.00E-01	2.33E-01	2.65E-01	2.33E-01	6.69E-01	6.69E-01	6.69E-01	1.00E+00	1.00E+00	1.00E+00	1.00E+00	1.00E+00	1.00E+00	1.00E+00	7.17E-01	6.95E-01	1.00E+00	7.17E-01	6.95E-01	6.95E-01	1.00E+00
activity	1.74E-07	4.44E-05	1.49E-02	3.46E-03	1.60E-02	6.83E-05	7.10E-07	3.79E-08	1.36E-07	1.15E-03	5.33E-05	5.30E-04	3.64E-03	2.15E-04	1.11E-07	1.85E-06	4.57E-06	7.10E-07	3.32E-07	1.35E-05	5.44E-07	9.55E-07	4.49E-06	1.32E-06	2.65E-08	0.00E+00
m	2.10E-07	7.61E-05	2.46E-02	3.60E-03	2.42E-02	4.31E-04	1.69E-06	1.46E-08	3.11E-07	2.36E-03	8.70E-05	6.69E-04	3.99E-03	1.45E-04	9.70E-08	1.43E-06	5.75E-06	8.88E-08	3.34E-08	1.03E-05	4.23E-07	1.10E-07	3.91E-06	9.94E-07	2.48E-08	0.00E+00
a _i	7.25E-01	6.66E-01	6.66E-01	6.51E-01	6.58E-01	1.96E-01	2.30E-01	2.61E-01	2.30E-01	6.66E-01	6.66E-01	6.66E-01	1.00E+00	1.00E+00	1.00E+00	1.00E+00	1.00E+00	1.00E+00	1.00E+00	7.15E-01	6.92E-01	1.00E+00	7.15E-01	6.92E-01	6.92E-01	1.00E+00
activity	1.53E-07	5.06E-05	1.64E-02	2.34E-03	1.59E-02	8.46E-05	3.88E-07	3.82E-09	7.14E-08	1.57E-03	5.79E-05	4.45E-04	3.99E-03	1.45E-04	9.70E-08	1.43E-06	5.75E-06	8.88E-08	3.34E-08	7.35E-06	2.93E-07	1.10E-07	2.79E-06	6.88E-07	1.71E-08	0.00E+00
m	2.19E-07	7.25E-05	2.47E-02	2.77E-03	2.39E-02	3.93E-04	2.05E-06	9.33E-08	2.38E-07	2.20E-03	8.41E-05	4.78E-04	3.98E-03	1.11E-04	1.00E-07	1.06E-06	5.54E-06	5.33E-07	2.13E-07	1.25E-05	5.11E-07	6.80E-07	4.59E-06	7.64E-07	1.79E-08	0.00E+00
a _i	7.27E-01	6.69E-01	6.69E-01	6.54E-01	6.61E-01	2.00E-01	2.33E-01	2.65E-01	2.33E-01	6.69E-01	6.69E-01	6.69E-01	1.00E+00	1.00E+00	1.00E+00	1.00E+00	1.00E+00	1.00E+00	1.00E+00	7.17E-01	6.95E-01	1.00E+00	7.17E-01	6.95E-01	6.95E-01	1.00E+00
activity	1.59E-07	4.85E-05	1.65E-02	1.81E-03	1.58E-02	7.86E-05	4.77E-07	2.47E-08	5.55E-08	1.47E-03	5.62E-05	3.19E-04	3.98E-03	1.11E-04	1.00E-07	1.06E-06	5.54E-06	5.33E-07	2.13E-07	8.96E-06	3.55E-07	6.80E-07	3.29E-06	5.31E-07	1.24E-08	0.00E+00
m	2.16E-07	7.37E-05	2.51E-02	2.53E-03	2.38E-02	4.30E-04	3.46E-06	3.08E-07	4.46E-07	2.44E-03	9.02E-05	4.73E-04	4.02E-03	1.01E-04	9.84E-08	9.75E-07	5.71E-06	1.90E-06	6.98E-07	2.09E-05	8.51E-07	2.27E-06	7.85E-06	1.42E-06	3.63E-08	0.00E+00
a _i	7.27E-01	6.68E-01	6.68E-01	6.53E-01	6.60E-01	1.99E-01	2.32E-01	2.64E-01	2.32E-01	6.68E-01	6.68E-01	6.68E-01	1.00E+00	1.00E+00	1.00E+00	1.00E+00	1.00E+00	1.00E+00	1.00E+00	7.17E-01	6.94E-01	1.00E+00	7.17E-01	6.94E-01	6.94E-01	1.00E+00
activity	1.57E-07	4.92E-05	1.68E-02	1.65E-03	1.57E-02	8.54E-05	8.04E-07	8.11E-08	1.04E-07	1.63E-03	6.02E-05	3.16E-04	4.02E-03	1.01E-04	9.84E-08	9.75E-07	5.71E-06	1.90E-06	6.98E-07	1.50E-05	5.90E-07	2.27E-06	5.62E-06	9.84E-07	2.52E-08	0.00E+00
m	2.19E-07	7.28E-05	2.54E-02	2.48E-03	2.41E-02	4.09E-04	2.81E-06	1.60E-07	3.01E-07	2.33E-03	8.66E-05	4.40E-04	4.11E-03	1.00E-04	1.01E-07	9.45E-07	5.69E-06	1.40E-05	9.37E-07	3.68E-07	1.72E-05	7.07E-07	1.16E-06	6.27E-06	9.66E-07	2.31E-08
a _i	7.26E-01	6.67E-01	6.67E-01	6.52E-01	6.60E-01	1.98E-01	2.31E-01	2.63E-01	2.31E-01	6.67E-01	6.67E-01	6.67E-01	1.00E+00	1.00E+00	1.00E+00	1.00E+00	1.00E+00	1.00E+00	1.00E+00	7.16E-01	6.94E-01	1.00E+00	7.16E-01	6.94E-01	6.94E-01	1.00E+00
activity	1.59E-07	4.86E-05	1.69E-02	1.62E-03	1.59E-02	8.10E-05	6.50E-07	4.21E-08	6.96E-08	1.55E-03	5.78E-05	2.94E-04	4.11E-03	1.00E-04	1.01E-07	9.45E-07	5.69E-06	1.40E-05	9.37E-07	2.63E-07	1.19E-05	7.07E-07	8.34E-07	4.35E-06	6.70E-07	2.31E-08
m	2.08E-07	7.62E-05	2.47E-02	2.40E-03	2.30E-02	4.52E-04	3.13E-06	2.76E-07	2.91E-07	2.55E-03	9.22E-05	4.78E-04	3.85E-03	9.32E-05	9.22E-08	9.64E-07	5.84E-06	1.77E-05	1.83E-06	6.13E-07	1.85E-05	7.34E-07	2.13E-06	7.41E-06	9.04E-07	2.54E-08
a _i	7.28E-01	6.70E-01	6.70E-01	6.55E-01	6.63E-01	2.01E-01	2.34E-01	2.66E-01	2.34E-01	6.70E-01	6.70E-01	6.70E-01	1.00E+00	1.00E+00	1.00E+00	1.00E+00	1.00E+00	1.00E+00	1.00E+00	7.18E-01	6.96E-01	1.00E+00	7.18E-01	6.96E-01	6.96E-01	1.00E+00
activity	1.51E-07	5.10E-05	1.65E-02	1.57E-03	1.53E-02	9.09E-05	7.34E-07	7.34E-08	6.81E-08	1.71E-03	6.18E-05	3.20E-04	3.85E-03	9.32E-05	9.22E-08	9.64E-07	5.84E-06	1.77E-05	1.83E-06	4.40E-07	1.29E-05	7.34E-07	1.53E-06	5.16E-06	6.29E-07	2.54E-08
m	2.29E-07	6.96E-05	2.52E-02	2.47E-03	2.42E-02	3.87E-04	3.30E-06	4.65E-07	3.39E-07	2.20E-03	8.59E-05	4.17E-04	4.10E-03	1.00E-04	1.06E-07	9.02E-07	5.41E-06	1.56E-05	2.60E-06	1.07E-06	2.03E-05	8.37E-07	3.25E-06	7.06E-06	1.10E-06	2.49E-08
a _i	7.27E-01	6.68E-01	6.68E-01	6.53E-01	6.61E-01	1.99E-01	2.32E-01	2.64E-01	2.32E-01	6.68E-01	6.68E-01	6.68E-01	1.00E+00	1.00E+00	1.00E+00	1.00E+00	1.00E+00	1.00E+00	1.00E+00	7.17E-01	6.94E-01	1.00E+00	7.17E-01	6.94E-01	6.94E-01	1.00E+00
activity	1.66E-07	4.65E-05	1.68E-02	1.61E-03	1.60E-02	7.70E-05	7.66E-07	1.23E-07	7.88E-08	1.47E-03	5.74E-05	2.79E-04	4.10E-03	1.00E-04	1.06E-07	9.02E-07	5.41E-06	1.56E-05	2.60E-06	7.69E-07	1.41E-05	8.37E-07	2.33E-06	4.90E-06	7.61E-07	2.49E-08
m	2.22E-07	7.19E-05	2.54E-02	2.56E-03	2.42E-02	4.14E-04	3.35E-06	4.40E-07	3.42E-07	2.36E-03	8.87E-05	4.59E-04	4.13E-03	1.03E-04	1.03E-07	9.61E-07	5.62E-06	2.60E-06	1.01E-06	2.05E-05	8.47E-07	3.15E-06	7.38E-06	1.10E-06	2.65E-08	0.00E+00
a _i	7.26E-01	6.67E-01	6.67E-01	6.52E-01	6.59E-01	1.97E-01	2.31E-01	2.62E-01	2.31E-01	6.67E-01	6.67E-01	6.67E-01	1.00E+00	1.00E+00	1.00E+00	1.00E+00	1.00E+00	1.00E+00	1.00E+00	7.16E-01	6.93E-01	1.00E+00	7.16E-01	6.93E-01	6.93E-01	1.00E+00
activity	1.61E-07	4.80E-05	1.69E-02	1.67E-03	1.60E-02	8.18E-05	7.74E-07	1.16E-07	7.90E-08	1.57E-03	5.91E-05	3.06E-04	4.13E-03	1.03E-04	1.03E-07	9.61E-07	5.62E-06	2.60E-06	1.01E-06	1.47E-05	5.87E-07	3.15E-06	5.28E-06	7.63E-07	1.84E-08	0.00E+00
m	2.11E-07	7.52E-05	2.48E-02	2.58E-03	2.33E-02	4.53E-04	3.52E-06	4.56E-07	2.87E-07	2.55E-03	9.33E-05	5.11E-04	3.91E-03	1.01E-04	9.46E-08	1.02E-06	5.78E-06	1.97E-05	3.00E-06	1.02E-06	2.09E-05	8.36E-07	3.45E-06	8.16E-06	8.98E-07	2.48E-08
a _i	7.27E-01	6.69E-01	6.69E-01	6.54E-01	6																					

Activity-activity diagrams

Figure C.4.22. Activity diagrams for the BGB1 showing mineral stability fields in the CaO – MgO – Al₂O₃ –H₂O. Diagrams were constructed on the base of two different silica averages, during and after glass dissolution. Black and red crosses show position of effluent samples collected at 1.0 and 0.5 ml hr⁻¹ flow rate, respectively. Yellow circles show position of the unreacted fluid (water) at 400°C / 483 bar

Figure C.4.23. Activity diagrams for the BGB1 showing mineral stability fields in the CaO – MgO – Al₂O₃ –H₂O. Diagrams were constructed on the base of two different silica averages, during and after glass dissolution. Black and red crosses show position of effluent samples collected at 1.0. Yellow circles show position of the unreacted fluid (water) at 350°C / 500 bar

Figure C.4.24. Activity diagrams for the BGB1 showing mineral stability fields in the CaO – FeO – Al₂O₃ –H₂O. Diagrams for each experiment were constructed on the base of two different silica averages, during and after glass dissolution. Black and red crosses show position of effluent samples collected at 1.0 and 0.5 ml hr⁻¹ flow rate, respectively. Yellow circles show position of the unreacted fluid (water) at 400°C / 500 bar. Blue arrows show the path of reacted fluids over the time of the experiments

Figure C.4.25. Activity diagrams for the BGB2 showing mineral stability fields in the CaO – FeO – Al₂O₃ –H₂O. Diagrams for each experiment were constructed on the base of two different silica averages, during and after glass dissolution. Black and red crosses show position of effluent samples collected at 1.0. Yellow circles show position of the unreacted fluid (water) at 350°C / 500 bar. Blue arrows show the path of reacted fluids over the time of the experiments

Figure C.4.26. Activity diagrams for the BGB1 showing mineral stability fields in the $\text{CaO} - \text{K}_2\text{O} - \text{Al}_2\text{O}_3 - \text{H}_2\text{O}$. Diagrams for each experiment were constructed on the base of two different silica averages, during and after glass dissolution. Black and red crosses show position of effluent samples collected at 1.0 and 0.5 ml hr^{-1} flow rate, respectively. Yellow circles show position of the unreacted fluid (water) at $400^\circ\text{C} / 500 \text{ bar}$. Blue arrows show the path of reacted fluids over the time of the experiments

Figure C.4.27. Activity diagrams for the BGB2 showing mineral stability fields in the $\text{CaO} - \text{K}_2\text{O} - \text{Al}_2\text{O}_3 - \text{H}_2\text{O}$. Diagrams for each experiment were constructed on the base of two different silica averages, during and after glass dissolution. Black and red crosses show position of effluent samples collected at 1.0. Yellow circles show position of the unreacted fluid (water) at $350^\circ\text{C} / 500 \text{ bar}$. Blue arrows show the path of reacted fluids over the time of the experiments

Figure C.4.28. Activity diagrams for the BGB1 showing mineral stability fields in the $\text{CaO} - \text{Na}_2\text{O} - \text{Al}_2\text{O}_3 - \text{H}_2\text{O}$. Diagrams for each experiment were constructed on the base of two different silica averages, during and after glass dissolution. Black and red crosses show position of effluent samples collected at 1.0 and 0.5 ml hr^{-1} flow rate, respectively. Yellow circles show position of the unreacted fluid (water) at $400^\circ\text{C} / 500 \text{ bar}$. Blue arrows show the path of reacted fluids over the time of the experiments

Figure C.4.29. Activity diagrams for the BGB2 showing mineral stability fields in the $\text{CaO} - \text{Na}_2\text{O} - \text{Al}_2\text{O}_3 - \text{H}_2\text{O}$. Diagrams for each experiment were constructed on the base of two different silica averages, during and after glass dissolution. Black and red crosses show position of effluent samples collected at 1.0. Yellow circles show position of the unreacted fluid (water) at $350^\circ\text{C} / 500 \text{ bar}$. Blue arrows show the path of reacted fluids over the time of the experiments

Figure C.4.30. Activity diagrams for the BGB1 showing mineral stability fields in the FeO – MgO – Al₂O₃ – H₂O. Diagrams for each experiment were constructed on the base of two different silica averages, during and after glass dissolution. Black and red crosses show position of effluent samples collected at 1.0. Yellow circles show position of the unreacted fluid (water) at 400°C / 500 bar. Blue arrows show the path of reacted fluids over the time of the experiments

Figure C.4.31. Activity diagrams for the BGB2 showing mineral stability fields in the FeO – MgO – Al₂O₃ – H₂O. Diagrams for each experiment were constructed on the base of two different silica averages, during and after glass dissolution. Black and red crosses show position of effluent samples collected at 1.0. Yellow circles show position of the unreacted fluid (water) at 350°C / 500 bar. Blue arrows show the path of reacted fluids over the time of the experiments

Figure C.4.32. Activity diagrams for the BGB1 and BGB2 showing mineral stability fields in the $\text{MgO} - \text{SiO}_2 - \text{Al}_2\text{O}_3 - \text{H}_2\text{O}$. Diagrams for each experiment were constructed on the base of two different silica averages, during and after glass dissolution. Black and red crosses show position of effluent samples collected at 1.0 and 0.5 ml hr^{-1} flow rate, respectively. Yellow circles show position of the unreacted fluid (water) at 400-350°C / 500 bar. Blue arrows show the path of reacted fluids over the time of the experiments

Figure C.4.33. Activity diagrams for the BGB1 and BGB2 showing mineral stability fields in the $\text{Na}_2\text{O} - \text{SiO}_2 - \text{Al}_2\text{O}_3 - \text{H}_2\text{O}$. Diagrams for each experiment were constructed on the base of two different silica averages, during and after glass dissolution. Black and red crosses show position of effluent samples collected at 1.0 and 0.5 ml hr^{-1} flow rate, respectively. Yellow circles show position of the unreacted fluid (water) at 400-350°C / 500 bar. Blue arrows show the path of reacted fluids over the time of the experiments

Figure C.4.34. Activity diagrams for the BGB1 and BGB2 showing mineral stability fields in the CaO – SiO₂ – Al₂O₃ – H₂O. Diagrams for each experiment were constructed on the base of two different silica averages, during and after glass dissolution. Black and red crosses show position of effluent samples collected at 1.0 and 0.5 ml hr⁻¹ flow rate, respectively. Yellow circles show position of the unreacted fluid (water) at 400-350°C / 500 bar. Blue arrows show the path of reacted fluids over the time of the experiments

Na/K geothermometers

Table C.4.25. Values of the estimate temperatures for the BGB1 calculated with the geothermometers equations by Fournier (1979), Truesdell (1976), Fournier and Truesdell (1973), Santoyo and Díaz-González (2009), Arnorsson (1983), Tonani (1980), Nieva and Nieva (1987) and Giggenbach (1988)

BGB1 - 400°C / 483 bar																
n° samples	time	T (°C)	P (bar)	mg kg ⁻¹				T(°C)	T(°C)	T(°C)	T(°C)	T(°C)	T(°C)	T(°C)	T(°C)	
				Ca	K	Na		Na/K (Fournier 1979)	Na/K (Truesdell 1976)	Na/K/Ca (Fournier and Truesdell 1973) β=1/3	Na/K (Santoyo and Díaz-González 2009)	Na/K (Arnorsson 1983)	Na/K (Tonani 1980)	Na/K (Nieva and Nieva 1987)	Na/K (Giggenbach 1988)	
blank	0.0	room T	1	3.4	116.2	725.3		261	245	260	235	256	256	247	273	
	1	20.6	room T	1	7.1	106.73	710.52									
	2	45.6	room T	1	5.9	122.32	710.95									
	3	72.8	room T	1	6.1	117.18	720.04									
	4	94.8	room T	1	5.6	115.97	724.53									
	5	118.9	room T	1	5.1	114.99	716.89									
	6	143.1	room T	1	5.2	113.79	711.96									
	7	166.7	room T	1	4.9	114.6	716.9									
T-shift	8	190.9	400	483	3.2	192.5	597.7		343	361	314	348	329	382	347	
	9	214.7	400	483	2.0	196.5	623.5		340	357	320	343	326	377	344	
	10	239.3	400	483	2.2	149.5	666.1		298	295	290	284	289	310	306	
	11	262.6	400	483	2.8	144.8	684.6		291	285	283	274	283	299	300	
	12	287.9	400	483	2.6	150.9	692.5		294	290	287	279	286	305	303	
	13	313.4	400	483	2.3	151.5	697.6		294	290	288	279	285	304	303	
	14	334.4	400	483	2.5	148.7	689.8		293	288	286	277	285	303	302	
	15	359.0	400	483	2.7	147.9	696.9		291	286	284	275	283	300	300	
	16	382.7	400	483	2.7	145.3	681.6		292	287	284	276	283	301	301	
	17	406.0	400	483	3.0	141.6	684.8		288	282	281	271	280	296	298	
	18	430.6	400	483	3.8	136.2	688.8		283	275	274	264	276	288	293	
	19	457.3	400	483	3.7	132.1	694.3		279	269	271	259	272	282	289	
	20	480.7	400	483	4.3	122.6	693.2		271	258	264	248	265	270	282	
	21	503.3	400	483	4.0	114.4	710.1		262	245	258	236	256	256	273	
	22	527.7	400	483	4.3	106.3	706.0		255	236	252	227	250	247	267	
	23	550.4	400	483	4.9	103.1	713.4		251	231	248	222	246	241	264	
	24	574.8	400	483	3.9	100.4	714.8		248	227	249	218	244	237	261	
								T(°C) AVERAGE (SiO ₂ above quartz saturation)								
								287	280	278	269	279	294	272	296	
								1σ	26	37	20	36	24	40	26	24
	25	597.6	400	483	4.2	98.8	701.6		248	228	247	218	244	237	234	261
	26	625.7	400	483	3.3	96.3	699.7		246	225	249	216	242	234	232	259
	27	647.5	400	483	3.8	95.1	694.6		246	224	246	215	242	234	232	259
	28	670.8	400	483	4.4	95.3	727.2		241	219	243	210	238	228	228	255
	29	694.4	400	483	4.4	95.4	718.4		243	220	243	211	239	230	229	256
	30	718.8	400	483	3.8	95.1	724.5		241	219	245	210	238	228	228	255
	31	743.4	400	483	4.0	94.8	722.1		241	219	244	210	238	228	228	255
	32	767.5	400	483	4.0	92.3	711.8		240	217	243	209	237	227	227	254
	33	809.2	400	483	5.7	93.3	741.6		237	214	237	205	234	223	224	251
	34	853.2	400	483	3.9	92.1	735.9		237	213	241	204	234	222	223	251
							T(°C) AVERAGE (SiO ₂ below quartz saturation)									
							242	220	244	211	239	229	228	256		
							1σ	4	5	3	5	3	5	4	3	

Table C.4.26. Values of the estimate temperatures for the BGB2 calculated with the geothermometers equations by Fournier (1979), Truesdell (1976), Fournier and Truesdell (1973), Santoyo and Díaz-González (2009), Amorrsson (1983), Tonani (1980), Nieva and Nieva (1987) and Giggenbach (1988)

BGB2 - 350°C / 486 bar

n° samples	time	T (°C)	P (bar)	mg kg ⁻¹				T(°C)	T(°C)	T(°C)	T(°C)	T(°C)	T(°C)	T(°C)	T(°C)
				Ca	K	Na		Na/K (Fournier 1979)	Na/K (Truesdell 1976)	Na/K/Ca (Fournier and Truesdell 1973) β=1/3	Na/K (Santoyo and Díaz-González 2009)	Na/K (Amorrsson 1983)	Na/K (Tonani 1980)	Na/K (Nieva and Nieva 1987)	Na/K (Giggenbach 1988)
blank	0.0	room T	1	7.2	116.0	725.0		261	244	182	235	256	255	247	273
1	21.2	room T	1												
2	47.3	room T	1												
3	71.4	room T	1												
4	93.7	room T	1												
5	118.2	room T	1												
6	141.8	room T	1												
7	165.7	room T	1												
8	187.8	350	486	4.2	218.3	620.2		395	442	259	426	374	472	378	392
9	211.4	350	486	2.2	263.5	574.2		395	442	259	426	374	472	378	392
10	236.2	350	486	1.7	246.3	634.7		369	401	252	387	352	426	353	370
11	260.3	350	486	1.0	172.9	713.7		307	308	226	296	297	324	292	314
12	286.3	350	486	1.2	131.4	710.3		276	265	207	255	269	277	262	287
13	310.3	350	486	2.1	121.1	726.9		265	250	196	240	259	261	251	277
14	334.0	350	486	1.6	118.1	730.9		262	246	197	236	256	257	248	274
15	355.5	350	486	1.9	116.2	715.8		262	246	195	237	257	258	248	274
16	381.8	350	486	1.9	117.0	725.3		262	245	195	236	256	257	248	274
17	403.3	350	486	2.0	122.0	734.1		265	250	196	240	259	261	251	276
18	428.1	350	486	2.1	124.6	718.8		269	256	198	246	263	267	255	280
19	451.8	350	486	1.9	127.3	743.1		268	254	198	244	262	266	254	279
20	475.8	350	486	2.1	131.9	746.9		271	258	200	248	265	270	257	282
21	498.9	350	486	1.6	131.1	725.9		273	261	203	251	267	274	259	284
22	523.6	350	486	2.1	131.6	743.7		271	258	200	248	265	270	257	282
23	547.8	350	486	2.4	130.8	739.4		271	258	198	248	265	271	257	282
24	571.4	350	486	2.3	129.3	747.4		269	255	198	245	263	267	255	280
25	595.7	350	486	2.2	128.4	747.0		268	254	198	244	262	266	254	280
26	619.5	350	486	2.3	127.6	751.1		267	253	196	243	261	264	253	278
27	645.3	350	486	2.0	127.3	716.7		272	259	200	249	265	271	257	283
28	668.7	350	486	2.2	125.8	704.2		272	260	199	250	266	272	258	283
29	692.9	350	486	2.2	124.4	709.1		270	257	198	247	264	269	256	282
30	715.6	350	486	2.7	125.0	746.0		266	251	194	241	260	262	251	277
								T(°C) AVERAGE (SiO ₂ above quartz saturation)							
								286	280	207	269	277	294	271	295
								1σ	41	61	21	59	36	66	37
31	739.8	350	486	1.8	122.4	712.2		268	254	199	244	262	266	254	280
32	764.8	350	486	2.6	125.3	749.2		265	250	194	241	260	262	251	277
33	788.5	350	486	2.3	118.7	751.3		260	243	192	233	254	254	245	272
34	814.5	350	486	2.5	116.3	747.2		258	241	190	231	253	251	244	270
35	837.6	350	486	2.5	114.3	705.7		262	246	192	236	257	257	248	274
36	860.2	350	486	1.9	117.8	756.3		258	241	193	231	253	252	244	270
37	883.8	350	486	2.0	113.2	724.1		259	241	193	232	253	252	244	271
38	907.8	350	486	2.1	113.3	712.3		260	244	193	234	255	255	246	272
								T(°C) AVERAGE (SiO ₂ below quartz saturation)							
								261	245	193	235	256	256	247	273
								1σ	4	5	3	5	3	5	3

Table C.4.27. Geothermometers equations utilized for the calculation of the estimate temperature values reported in Table C.4.25-26

Na/K : Fournier (1979)	$T(^{\circ}C) = \frac{1217}{1.438 + \log\left(\frac{Na}{K}\right)} - 273,15 (^{\circ}K)$
Na/K : Truesdell (1976)	$T(^{\circ}C) = \frac{855,6}{0.8573 + \log\left(\frac{Na}{K}\right)} - 273,15 (^{\circ}K)$
Na/K : Santoyo and Gonzalez (2009)	$T(^{\circ}C) = \frac{876.3(\pm 26.26)}{0.8775(\pm 0.0508) + \log\left(\frac{Na}{K}\right)} - 273,15 (^{\circ}K)$
Na/K : Arnorsson (1983)	$T(^{\circ}C) = \frac{1319}{1.699 + \log\left(\frac{Na}{K}\right)} - 273,15 (^{\circ}K)$
Na/K : Tonani (1980)	$T(^{\circ}C) = \frac{883}{0.78 + \log\left(\frac{Na}{K}\right)} - 273,15 (^{\circ}K)$
Na/K : Nieva and Nieva (1987)	$T(^{\circ}C) = \frac{1178}{1.483 + \log\left(\frac{Na}{K}\right)} - 273,15 (^{\circ}K)$
Na/K : Giggenbach (1988)	$T(^{\circ}C) = \frac{1390}{1.75 + \log\left(\frac{Na}{K}\right)} - 273,15 (^{\circ}K)$
Na/K/Ca : Fournier and Truesdall (1973)	$T(^{\circ}C) = \frac{1647}{\log\left(\frac{Na}{K}\right) + \beta [\log(\sqrt{Ca}/Na) + 2.06] + 2.47} - 273,15 (^{\circ}K)$

Appendix D - (Chapter 5)

Chapter 5: The Experimental Behaviour of Seawater

5.2. Results

5.2.1. Method development test (377°C/490 bar)

Figure D.5.1. EDS analysis of texture of the solid layer extracted from the bottom portion of the Preheater after the efficiency test with synthetic seawater and zirconia beads excluded

5.2.1. SW1: Natural seawater at 377°C/488 bar

Table D.5.1. Major ions compositions and complete experimental parameters (n° of samples collected, T, P, time, flow rate and pH) for the SW1 at 377°C / 488 bar. *In situ* pH is the calculated pH at temperature. Analysis of major ions are reported both in mg kg⁻¹ and in mmol kg⁻¹. n.c.: not calculated. n.a: not analysed

n° sample	T (°C)	P (bar)	time (hrs)	flow-rate (ml hr ⁻¹)	pH (room T)	pH (375°C)	mg kg ⁻¹												mmol kg ⁻¹													
							As	B	Ca	Fe	K	Mg	Na	SiO ₂	Al	Li	H ₂ S	Cl	SO ₄	As	B	Ca	Fe	K	Mg	Na	SiO ₂	Al	Li	H ₂ S	Cl	SO ₄
blank water (distilled)	19.6	1	-	-	6.78	n.c.	0.03	< 0.3	< 0.05	0.1	4.7	< 0.01	9.2	5.1	0.2	0.02	n.a.	1.1	< 0.1	0.0004	< 0.03	< 0.001	0.002	0.12	< 0.0004	0.4	0.1	0.01	0.002	n.a.	0.03	< 0.001
blank seawater (natural)	19.6	1	0.0	-	7.75	n.c.	< 0.015	2.2	376.7	0.1	365.4	1112.1	9653.6	6.7	0.1	0.2	< 0.01	15318.4	2117.3	< 0.002	0.2	9.4	0.002	9.4	45.8	420	0.1	0.01	0.02	< 0.0003	432	22
1	377	487.1	24.2	1	6.70	5.32	0.03	< 0.3	< 0.05	< 0.08	7.0	5.0	43.9	5.4	0.5	0.01	< 0.01	26.6	6.5	0.0004	< 0.03	< 0.001	< 0.001	0.18	0.20	1.9	0.1	0.02	0.002	< 0.0003	0.7	0.07
2	377	487.7	44.5	1	5.96	5.95	< 0.015	< 0.3	0.4	0.08	4.3	0.7	22.8	9.7	0.1	0.02	< 0.01	14.5	3.6	< 0.0002	< 0.03	0.01	0.001	0.11	0.03	1	0.2	0.005	0.003	< 0.0003	0.4	0.04
3	377	486.8	68.9	1	5.56	6.49	< 0.015	< 0.3	< 0.05	< 0.08	2.2	< 0.01	13.3	6.1	0.3	0.01	< 0.01	5.8	3.1	< 0.0002	< 0.03	< 0.001	< 0.001	0.06	< 0.0004	0.6	0.1	0.01	0.002	< 0.0003	0.2	0.03
4	377	486.5	93.0	1	5.21	6.38	0.04	< 0.3	< 0.05	0.1	0.8	< 0.01	4.6	5	0.2	< 0.01	< 0.01	6.2	1.9	0.0005	< 0.03	< 0.001	0.003	0.02	< 0.0004	0.2	0.1	0.01	< 0.001	< 0.0003	0.2	0.02
5	377	486.8	115.8	1	5.53	6.21	0.05	< 0.3	< 0.05	< 0.08	0.4	< 0.01	9.1	3.8	0.3	0.02	< 0.01	2.6	1.3	0.0007	< 0.03	< 0.001	< 0.001	0.01	< 0.0004	0.4	0.1	0.01	0.003	< 0.0003	0.1	0.01
6	377	488.2	138.8	1	4.69	5.21	< 0.015	< 0.3	< 0.05	0.4	5.2	7.7	174.7	3.3	0.3	0.01	< 0.01	198.8	2.6	< 0.0002	< 0.03	< 0.001	0.008	0.13	0.32	7.6	0.1	0.01	0.001	< 0.0003	5.6	0.03
7	377	487.6	163.4	1	3.85	5.25	0.03	< 0.3	36.3	7.0	90.7	170.3	2553.8	3.8	0.5	0.1	< 0.01	4793.1	22.3	0.0004	< 0.03	0.9	0.1	2.3	7	111.1	0.1	0.02	0.008	< 0.0003	135.2	0.2
8	377	487.6	186.6	1	3.42	5.33	0.02	< 0.3	76.5	40.7	194.6	356.3	5322.4	5.9	0.8	0.1	< 0.01	9832.7	61.3	0.0003	< 0.03	1.9	0.7	5	14.7	231.5	0.1	0.03	0.01	< 0.0003	277.4	0.6
9	377	487.2	211.0	1	3.45	5.37	0.03	< 0.3	80.7	59.4	242.7	434.1	6620.9	8	0.5	0.1	< 0.01	12226.4	84.2	0.0004	< 0.03	2	1.1	6.2	17.9	288	0.1	0.02	0.02	< 0.0003	344.9	0.9
10	377	487.7	238.6	1	3.47	5.37	0.02	< 0.3	79.1	51.3	278.9	496.9	7505.4	20.4	0.3	0.2	< 0.01	13535.9	99.5	0.0003	< 0.03	2	0.9	7.1	20.4	326.5	0.3	0.01	0.02	< 0.0003	381.8	1
11	377	487.4	261.8	1	3.40	5.37	< 0.015	< 0.3	79.9	54.1	305.0	535.7	8093.6	36.2	0.4	0.2	< 0.01	14553.6	104.5	< 0.0002	< 0.03	2	1	7.8	22	352	0.6	0.01	0.02	< 0.0003	410.5	1.1
12	377	487.6	283.2	1	3.37	5.38	< 0.015	< 0.3	79.5	56.7	301.8	542.7	8199.2	46.0	0.5	0.2	< 0.01	15074.7	109.8	< 0.0002	< 0.03	2	1	7.7	22.3	356.6	0.8	0.02	0.02	< 0.0003	425.2	1.1
13	377	487.7	309.0	1	3.36	5.38	< 0.015	< 0.3	83.5	60.2	324.0	561.5	8508.6	51.9	0.4	0.2	< 0.01	14681.9	113.0	< 0.0002	< 0.03	2.1	1.1	8.3	23.1	370.1	0.9	0.02	0.02	< 0.0003	414.2	1.2
14	377	487.7	331.0	1	3.31	5.38	< 0.015	< 0.3	80.6	62.5	321.0	559.8	8466.7	55.1	0.1	0.2	< 0.01	14687.4	115.2	< 0.0002	< 0.03	2	1.1	8.2	23	368.3	0.9	0.005	0.03	< 0.0003	414.3	1.2
15	377	487.7	354.3	1	3.30	5.39	< 0.015	< 0.3	78.2	63.9	315.6	556.2	8383.3	56.4	0.3	0.1	< 0.01	15430.3	116.1	< 0.0002	< 0.03	2	1.1	8.1	22.9	364.7	0.9	0.01	0.02	< 0.0003	435.3	1.2
16	377	487.4	378.1	1	3.29	5.37	< 0.015	5.2	77.0	66.3	343.8	585.6	8470.3	63.5	0.5	0.2	< 0.01	15609.1	113.5	< 0.0002	0.49	1.9	1.2	8.8	24.1	368.4	1.1	0.02	0.02	< 0.0003	440.3	1.2
17	377	487.8	405.2	1	3.27	5.37	< 0.015	4.3	81.5	72.0	369.1	620.3	8885.7	58.7	< 0.006	0.2	< 0.01	15088.7	115.7	< 0.0002	0.40	2	1.3	9.4	25.5	386.5	1	< 0.005	0.02	< 0.0003	425.6	1.2
18	377	487.9	428.4	1	3.25	5.37	< 0.015	3.8	83.7	74.7	372.2	627.6	9019.9	57.2	0.2	0.1	< 0.01	15233.9	119.5	< 0.0002	0.36	2.1	1.3	9.5	25.8	392.3	1	0.01	0.02	< 0.0003	429.7	1.2
19	377	487.7	450.4	1	3.24	5.38	< 0.015	3.5	79.2	73.1	356.4	605.9	8715.0	56.2	0.3	0.1	< 0.01	15166.1	123.2	< 0.0002	0.32	2	1.3	9.1	24.9	379.1	0.9	0.01	0.02	< 0.0003	427.8	1.3
20	377	487.6	474.5	1	3.22	5.36	< 0.015	3.4	77.7	72.6	347.5	588.6	8500.4	55.6	0.2	0.1	< 0.01	15154.8	106.0	< 0.0002	0.31	1.9	1.3	8.9	24.2	369.7	0.9	0.01	0.02	< 0.0003	427.5	1.1
21	377	487.9	498.5	1	3.21	5.38	< 0.015	3.2	76.1	73.6	346.3	591.2	8503.8	53.6	< 0.006	0.1	< 0.01	15391.5	119.6	< 0.0002	0.30	1.9	1.3	8.9	24.3	369.9	0.9	< 0.005	0.02	< 0.0003	434.2	1.2
22	377	487.3	522.6	1	3.19	5.35	< 0.015	3.0	81.9	79.5	361.6	628.4	9014.3	53.5	0.5	0.2	< 0.01	15334.3	105.1	< 0.0002	0.28	2	1.4	9.2	25.9	392.1	0.9	0.02	0.02	< 0.0003	432.6	1.1
23	377	487.5	546.7	1	3.22	5.38	< 0.015	2.9	83.7	74.6	345.9	593.3	8530.3	52.1	0.2	0.1	< 0.01	15586.5	119.7	< 0.0002	0.26	2.1	1.3	8.8	24.4	371	0.9	0.01	0.01	< 0.0003	439.7	1.2

Table D.5.2. Trace element compositions and complete experimental parameters (n° of samples collected, T, P, time, flow rate and pH) for the SW1 at 377°C, 488 bar. *In situ* pH is the calculated pH at temperature. Analysis of trace elements are reported in µmol kg⁻¹. n.c.: not calculated / n.a: not analysed

n° sample	T (°C)	P (bar)	time (hrs)	flow-rate (ml hr ⁻¹)	pH (room T)	pH (375°C)	µmol kg ⁻¹												mmol kg ⁻¹	
							V	Cr	Co	Ni	Cu	Zn	Rb	Ag	Cd	Ba	Au	Pb	Mn	
blank water (distilled)	20.1	1	-	-	6.78	n.c.	< 0.002	< 0.004	< 0.002	< 0.003	< 0.0009	< 0.008	< 0.001	< 0.0005	< 0.0009	< 0.001	< 0.001	< 0.001	< 0.13	
blank seawater (natural)	20.1	1	0.0	-	7.75	n.c.	0.04	< 0.004	< 0.002	< 0.003	< 0.0009	< 0.008	0.1	< 0.0005	< 0.0009	< 0.001	0.01	< 0.001	< 0.13	
1	377	487.1	24.2	1	6.70	5.32	0.2	0.2	0.02	0.4	1.6	10	0.03	< 0.0005	< 0.0009	0.4	< 0.001	0.01	<0.0001	
2	377	487.7	44.5	1	5.96	5.95	0.2	0.09	0.02	0.3	1.6	10.7	0.03	< 0.0005	0.01	0.5	< 0.001	0.002	0.0001	
3	377	486.8	68.9	1	5.56	6.49	0.02	0.2	0.03	0.9	0.2	1.8	0.02	< 0.0005	< 0.0009	0.4	< 0.001	0.002	0.0007	
4	377	486.5	93.0	1	5.21	6.38	0.01	0.1	0.02	0.6	1	2.1	0.01	< 0.0005	0.01	0.3	< 0.001	< 0.001	0.0005	
5	377	486.8	115.8	1	5.53	6.21	0.004	0.1	0.02	0.4	0.2	1.9	0.01	< 0.0005	< 0.0009	0.3	< 0.001	0.002	0.0003	
6	377	488.2	138.8	1	4.69	5.21	0.01	0.1	0.05	0.9	0.2	7.2	0.02	< 0.0005	< 0.0009	0.5	< 0.001	0.01	0.003	
7	377	487.6	163.4	1	3.85	5.25	0.06	0.2	0.4	1.5	0.2	15.3	0.3	< 0.0005	0.01	7	0.06	0.02	0.02	
8	377	487.6	186.6	1	3.42	5.33	0.4	0.2	3.3	14.4	0.1	6.3	0.6	< 0.0005	0.05	4.8	0.06	< 0.001	0.03	
9	377	487.2	211.0	1	3.45	5.37	0.5	0.2	2.2	7.4	1	5.3	0.8	< 0.0005	0.08	3	0.06	< 0.001	0.02	
10	377	487.7	238.6	1	3.47	5.37	0.5	0.2	1.6	4.7	0.2	4.5	0.9	< 0.0005	< 0.0009	1.8	0.06	< 0.001	0.02	
11	377	487.4	261.8	1	3.40	5.37	0.8	0.2	2.3	8.1	0.1	3.8	0.9	< 0.0005	0.03	1.1	0.06	< 0.001	0.02	
12	377	487.6	283.2	1	3.37	5.38	0.9	0.1	2.5	9.3	0.3	16.3	0.9	< 0.0005	0.02	0.8	0.06	< 0.001	0.02	
13	377	487.7	309.0	1	3.36	5.38	1	0.1	2.8	11.1	0.1	11.3	1	< 0.0005	0.05	0.6	0.06	< 0.001	0.02	
14	377	487.7	331.0	1	3.31	5.38	1	0.1	3.1	13.1	0.1	2.5	0.9	< 0.0005	0.02	0.4	0.05	< 0.001	0.02	
15	377	487.7	354.3	1	3.30	5.39	1.1	1	3.5	14.9	33.1	41.3	0.9	< 0.0005	0.06	0.5	0.06	0.02	0.02	
16	377	487.4	378.1	1	3.29	5.37	1.2	0.2	3.8	16.8	0.1	5.7	1	< 0.0005	< 0.0009	0.4	0.05	< 0.001	0.02	
17	377	487.8	405.2	1	3.27	5.37	1.3	0.1	4.4	19.8	0.1	14.6	1	< 0.0005	0.03	0.4	0.05	0.03	0.02	
18	377	487.9	428.4	1	3.25	5.37	1.3	0.1	4.7	23.6	0.2	52.9	0.9	< 0.0005	0.03	0.5	0.05	0.05	0.02	
19	377	487.7	450.4	1	3.24	5.38	1.3	0.1	5	25.2	0.2	14.4	1	< 0.0005	0.01	0.4	0.05	0.04	0.02	
20	377	487.6	474.5	1	3.22	5.36	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.	0.02	
21	377	487.9	498.5	1	3.21	5.38	1.5	0.1	5.4	29.1	0.2	19.6	1	< 0.0005	0.06	0.5	0.06	0.05	0.02	
22	377	487.3	522.6	1	3.19	5.35	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.	0.02	
23	377	487.5	546.7	1	3.22	5.38	1.2	0.09	5.9	31.5	0.3	20.5	1	< 0.0005	0.06	0.4	0.04	0.05	0.02	

Figure D.5.2. EDS analysis of texture of the mineral phases and zirconia beads extracted from the bottom portion of the Preheater after the SW1 experiment (377°C / 488 bar)

Figure D.5.3. EDS analysis of texture of zirconia beads extracted from the bottom portion of the Preheater after the SW1 experiment (377°C / 488 bar)

Figure D.5.4. SEM backscatter and EDS compositional maps of the polygonal shape found on a zirconia bead surface collected from the bottom (Portion 3) of Preheater after the SW1 experiment (377°C / 488 bar): (a) backscatter image; (b) composite colour image combining the backscatter image and elemental map for c) Mg in red

5.2.2. SW2: Natural seawater at 342°C/488 bar

Table D.5.3. Major ions compositions and complete experimental parameters (n° of samples collected, T, P, time, flow rate and pH) for the SW2 at 342°C / 488 bar. *In situ* pH is the calculated pH at temperature. Analysis of major ions are reported both in mg kg⁻¹ and in mmol kg⁻¹. n.c.: not calculated. n.a: not analysed

n° sample	T (°C)	P (bar)	time (hrs)	flow-rate (ml hr ⁻¹)	pH (room T)	pH (340°C)	mg kg ⁻¹												mmol kg ⁻¹													
							As	B	Ca	Fe	K	Mg	Na	SiO ₂	Al	Li	H ₂ S	Cl	SO ₄	As	B	Ca	Fe	K	Mg	Na	SiO ₂	Al	Li	H ₂ S	Cl	SO ₄
blank water (distilled)	20.1	1	-	-	7.65	n.c.	0.02	< 0.3	< 0.05	< 0.08	3.8	0.1	6.8	< 0.6	0.2	< 0.01	n.a.	< 0.1	0.2	0.0003	< 0.03	< 0.001	< 0.001	0.1	0.005	0.3	< 0.01	0.007	< 0.001	n.a.	< 0.003	0.002
blank seawater (natural)	20.1	1	0.0	-	7.65	n.c.	< 0.015	5.3	321.3	0.1	335.5	891.5	8308.5	5.8	0.2	0.2	< 0.01	15556.1	2236.7	< 0.0002	0.5	8	0.002	8.6	36.7	361	0.1	0.007	0.02	< 0.0003	439	23
1	342	486.4	21.3	1	5.83	4.81	< 0.015	0.2	0.5	1.6	5.5	5.6	9.9	2.4	0.2	0.03	< 0.01	2.3	3	< 0.0002	0.02	0.01	0.03	0.1	0.2	0.4	0.04	0.007	0.004	< 0.0003	0.07	0.03
2	342	486.8	45.3	1	5.24	5.50	< 0.015	< 0.3	< 0.05	0.2	2.2	0.1	5.8	< 0.6	< 0.15	0.02	< 0.01	1.9	0.1	< 0.0002	< 0.03	< 0.001	0.004	0.06	0.003	0.3	< 0.01	< 0.006	0.003	< 0.0003	0.05	0.001
3	342	486.9	67.0	1	5.05	5.31	0.02	< 0.3	11	1.6	47	87.6	1198.1	< 0.6	0.6	0.04	< 0.01	1933.6	27.1	0.0003	< 0.03	0.3	0.03	1.2	3.6	52.1	< 0.01	0.02	0.006	< 0.0003	54.5	0.3
4	342	487.1	92.1	1	4.31	5.40	0.03	0.4	39.2	10.2	166.3	317.4	4224.1	0.7	0.5	0.1	< 0.01	8925.8	102.3	0.0004	0.04	1	0.2	4.3	13.1	183.7	0.01	0.02	0.02	< 0.0003	251.8	1.1
5	342	487.3	116.1	1	3.41	5.46	< 0.015	0.9	58.9	39	251.5	455.5	6414.3	1.8	0.2	0.1	< 0.01	11845	168.8	< 0.0002	0.09	1.5	0.7	6.4	18.7	279	0.03	0.008	0.01	< 0.0003	334.1	1.8
6	342	487.4	140.1	1	3.12	5.49	< 0.015	1	64.2	54.3	291.1	520	7362.2	4.2	0.2	0.1	< 0.01	14511.4	214.2	< 0.0002	0.09	1.6	1	7.4	21.4	320.2	0.07	0.008	0.02	< 0.0003	409.3	2.2
7	342	487.2	166.6	1	2.96	5.51	< 0.015	1.2	61.8	64	312.2	552.1	7850.7	9.6	0.2	0.1	< 0.01	14436.9	250.1	< 0.0002	0.1	1.5	1.1	8	22.7	341.5	0.2	0.008	0.02	< 0.0003	407.2	2.6
8	342	487.2	189.8	1	2.88	5.53	< 0.015	1.4	63.9	73	322	559.2	8062.7	14.4	< 0.15	0.1	< 0.01	14974.5	282.4	< 0.0002	0.1	1.6	1.3	8.2	23	350.7	0.2	< 0.006	0.02	< 0.0003	422.4	2.9
9	342	487.4	213.3	1	2.81	5.53	< 0.015	1.3	63.7	81.2	333.1	572.2	8340.8	16.4	0.1	0.2	< 0.01	15096.2	286.7	< 0.0002	0.1	1.6	1.5	8.5	23.5	362.8	0.3	< 0.006	0.02	< 0.0003	425.8	3
10	342	487.3	236.8	1	2.85	5.53	< 0.015	1	67.8	89.8	333.7	572.3	8447.7	17.4	< 0.15	0.2	< 0.01	15461.8	286.1	< 0.0002	0.09	1.7	1.6	8.5	23.5	367.5	0.3	< 0.006	0.02	< 0.0003	436.2	3
11	342	487.3	261.6	1	2.75	5.53	< 0.015	0.9	59	93.5	335.3	564.9	8415.8	16.7	< 0.15	0.1	< 0.01	15472.3	275.3	< 0.0002	0.08	1.5	1.7	8.6	23.2	366.1	0.3	< 0.006	0.02	< 0.0003	436.5	2.9
12	342	487.2	284.7	1	2.73	5.53	< 0.015	0.6	57.9	95.1	336.9	565.8	8462.2	16.1	< 0.15	0.2	< 0.01	15383.1	274.9	< 0.0002	0.06	1.4	1.7	8.6	23.3	368.1	0.3	< 0.006	0.02	< 0.0003	433.9	2.9
13	342	487.3	311.7	1	2.75	5.53	< 0.015	0.7	55.4	90	325.9	542.3	8141.4	15.6	< 0.15	0.2	< 0.01	15465.7	270.2	< 0.0002	0.07	1.4	1.6	8.3	22.3	354.1	0.3	< 0.006	0.02	< 0.0003	436.3	2.8
14	342	487.3	335.3	1	2.73	5.52	< 0.015	0.1	57.9	98.6	340.2	572.5	8610.8	15.2	0.2	0.2	< 0.01	15383.6	262.7	< 0.0002	0.01	1.4	1.8	8.7	23.6	374.5	0.3	0.009	0.02	< 0.0003	434	2.7
15	342	487.3	357.3	1	2.72	5.53	< 0.015	0.1	56.4	96	332.6	557.6	8367.9	14.5	< 0.15	0.1	< 0.01	15391.2	271.7	< 0.0002	0.01	1.4	1.7	8.5	22.9	364	0.2	< 0.006	0.02	< 0.0003	434.2	2.8
16	342	487.2	381.2	1	2.72	5.52	< 0.015	0.1	56	94.5	333.9	554.4	8353	14.6	< 0.15	0.1	< 0.01	15238.3	260.2	< 0.0002	0.01	1.4	1.7	8.5	22.8	363.3	0.2	< 0.006	0.02	< 0.0003	429.9	2.7

Table D.5.4. Trace element compositions and complete experimental parameters (n° of samples collected, T, P, time, flow rate and pH) for the SW2 at 342°C / 488 bar. *In situ* pH is the calculated pH at temperature. Analysis of trace elements are reported in µmol kg⁻¹. n.c.: not calculated / n.a: not analysed

n° sample	T (°C)	P (bar)	time (hrs)	flow-rate (ml hr ⁻¹)	pH (room T)	pH (340°C)	µmol kg ⁻¹												mmol kg ⁻¹	
							V	Cr	Co	Ni	Cu	Zn	Rb	Ag	Cd	Ba	Au	Pb	Mn	
blank water (distilled)	20.1	1	-	-	7.65	n.c.	< 0.002	< 0.004	< 0.002	< 0.003	< 0.0009	< 0.008	< 0.001	< 0.0005	< 0.0009	< 0.001	< 0.001	< 0.001	0.00	
blank seawater (natural)	20.1	1	0.0	-	7.65	n.c.	0.04	< 0.004	< 0.002	< 0.003	< 0.0009	< 0.008	0.1	< 0.0005	< 0.0009	< 0.001	0.01	< 0.001	<0.0001	
1	342.0	486.4	21.3	1	5.83	4.81	0.02	0.1	0.05	1.3	1.4	9.8	0.05	0.01	< 0.0009	0.6	< 0.001	0.05	0.0002	
2	342.0	486.8	45.3	1	5.24	5.50	0.01	0.1	0.01	0.4	1.4	24.5	0.01	< 0.0005	0.02	0.2	< 0.001	0.02	<0.0001	
3	342.0	486.9	67.0	1	5.05	5.31	0.02	0.3	0.07	6.1	13.4	18	0.1	< 0.0005	0.02	4.6	0.02	0.3	0.0009	
4	342.0	487.1	92.1	1	4.31	5.40	0.05	0.4	2.7	5.2	110.5	28.9	0.5	< 0.0005	0.02	7.7	0.03	0.1	0.009	
5	342.0	487.3	116.1	1	3.41	5.46	0.6	0.9	6	37.7	112.1	35	0.7	0.01	0.02	5.1	0.04	0.08	0.01	
6	342.0	487.4	140.1	1	3.12	5.49	0.4	0.7	8.2	57	68.4	53	0.9	0.01	0.03	2.6	0.04	0.2	0.02	
7	342.0	487.2	166.6	1	2.96	5.51	0.3	0.5	9.6	77.6	40.4	38.4	0.9	0.01	0.01	1.3	0.03	0.07	0.02	
8	342.0	487.2	189.8	1	2.88	5.53	0.3	0.5	10.7	104.6	24.4	47.2	1	< 0.0005	0.06	0.7	0.04	0.1	0.02	
9	342.0	487.4	213.3	1	2.81	5.53	0.3	0.7	11.7	128.8	17	7.8	0.9	< 0.0005	0.02	0.7	0.03	0.02	0.03	
10	342.0	487.3	236.8	1	2.85	5.53	0.3	0.3	13	148.2	13.4	44.4	1	< 0.0005	0.02	0.6	0.03	0.4	0.03	
11	342.0	487.3	261.6	1	2.75	5.53	0.4	1.1	13.6	159.5	11.5	8.1	1	< 0.0005	0.03	0.8	0.03	0.02	0.03	
12	342.0	487.2	284.7	1	2.73	5.53	0.4	0.6	13.9	164.9	11	5.8	1	< 0.0005	0.02	1	0.03	0.01	0.03	
13	342.0	487.3	311.7	1	2.75	5.53	0.4	0.6	13.8	n.a.	10.5	6.6	1	< 0.0005	0.02	1.7	0.03	0.01	0.03	
14	342.0	487.3	335.3	1	2.73	5.52	0.3	0.5	14.6	186.8	9.9	4.6	1	< 0.0005	< 0.0009	0.5	0.03	0.02	0.03	
15	342.0	487.3	357.3	1	2.72	5.53	0.3	n.a.	15	192.5	9.4	5.3	0.9	< 0.0005	0.05	0.2	0.03	0.03	0.03	
16	342.0	487.2	381.2	1	2.72	5.52	0.3	0.4	14.8	197.6	9.7	4.4	1	< 0.0005	0.06	0.1	0.03	0.02	0.03	

Figure D.5.5. EDS analysis of the precipitate collected from the bottom portion of the Preheater after the SW2 experiment (342°C / 488 bar)

5.3. Discussion

Elements Flux Calculation

Table D.5.5. Elements flux calculation for the SW1 experiment (377°C / 488 bar)

Sample No.	Time	Total Time	Time	Reactor Temp	Pressure	SiO ₂ mg kg ⁻¹	K mg kg ⁻¹	SO ₄ mg kg ⁻¹	Ca mg kg ⁻¹	Na mg kg ⁻¹	Mg mg kg ⁻¹	Fe mg kg ⁻¹	Volume L	diff. SiO ₂ mg kg ⁻¹	SiO ₂ Flux mg	diff. K mg kg ⁻¹	K Flux mg	diff. SO ₄ mg kg ⁻¹	SO ₄ Flux mg	diff. Ca mg kg ⁻¹	Ca Flux mg	diff. Na mg kg ⁻¹	Na Flux mg	diff. Mg mg kg ⁻¹	Mg Flux mg	diff. Fe mg kg ⁻¹	Fe Flux mg					
	day	day	°C	bar		6.7	365.4	2117.3	376.7	9653.6	1112.1	0.1																				
Blank	0	0	room T	1	Total Input Mass (mg) in 0.40 L supposing no fluid-rock exchange	2.7	147.7	855.7	152.2	3901.6	449.5	0.040																				
1	15:24:00	1.0	377	488		5.4	7.0	6.5	0.0	43.9	4.98	0.0	0.024	-1.3	0.1	-358.4	-8.60	-2110.8	-50.66	-376.70	-9.041	-9609.7	-230.63	-1107.12	-26.571	-0.100	-0.00240					
2	11:45:00	1.851	0.85	377	488	9.66	4.32	3.6	0.4	22.8	0.7	0.1	0.020	3.0	0.2	-361.1	-7.37	-2113.7	-43.17	-376.28	-7.685	-9630.8	-196.70	-1111.36	-22.698	-0.018	-0.00036					
3	12:05:00	2.86	1.01	377	488	6.06	2.20	3.1	0.0	13.3	0.0	0.0	0.024	-0.6	0.1	-363.2	-8.84	-2114.2	-51.44	-376.70	-9.165	-9640.3	-234.55	-1112.10	-27.057	-0.100	-0.00243					
4	12:15:00	3.86	1.00	377	488	5.04	0.79	1.9	0.0	4.6	0.0	0.1	0.024	-1.7	0.1	-364.6	-8.75	-2115.4	-50.77	-376.70	-9.041	-9649.0	-231.58	-1112.10	-26.690	0.040	0.00095					
5	11:00:00	4.81	0.95	377	488	3.82	0.35	1.3	0.0	9.1	0.0	0.0	0.023	-2.9	0.1	-365.0	-8.32	-2116.0	-48.25	-376.70	-8.589	-9644.5	-219.89	-1112.10	-25.356	-0.100	-0.00228					
6	10:00:00	5.77	0.96	377	488	3.34	5.18	2.6	0.0	174.7	7.7	0.4	0.023	-3.4	0.1	-360.2	-8.30	-2114.7	-48.72	-376.70	-8.679	-9478.9	-218.39	-1104.43	-25.446	0.333	0.00768					
7	10:35:00	6.79	1.02	377	488	3.83	90.72	22.27	36.35	2553.79	170.35	7.01	0.024	-2.9	0.1	-274.7	-6.72	-2095.0	-51.29	-340.35	-8.332	-7099.8	-173.80	-941.75	-23.054	6.913	0.16923					
8	9:50:00	7.76	0.97	377	488	5.85	194.64	61.29	76.53	5322.44	356.29	40.74	0.023	-0.8	0.1	-170.8	-3.98	-2056.0	-47.86	-300.17	-6.988	-4331.2	-100.83	-755.81	-17.595	40.638	0.94605					
9	10:05:00	8.77	1.01	377	488	8.00	242.73	84.15	80.65	6620.87	434.09	59.36	0.024	1.3	0.2	-122.7	-2.97	-2033.2	-49.28	-296.05	-7.176	-3032.7	-73.51	-678.01	-16.435	59.264	1.43656					
10	13:47:00	9.90	1.13	377	488	20.43	278.88	99.51	79.14	7505.39	496.91	51.29	0.027	13.7	0.6	-86.5	-2.35	-2017.8	-54.72	-297.56	-8.070	-2148.2	-58.26	-615.19	-16.684	51.187	1.38820					
11	13:00:00	10.87	0.97	377	488	36.23	304.99	104.51	79.85	8093.56	535.71	54.07	0.023	29.5	0.8	-60.4	-1.41	-2012.8	-46.86	-296.85	-6.911	-1560.0	-36.32	-576.39	-13.418	53.970	1.25642					
12	10:25:00	11.72	0.85	377	488	46.01	301.80	109.84	79.50	8199.23	542.65	56.66	0.020	39.3	0.9	-63.6	-1.30	-2007.5	-40.95	-297.20	-6.063	-1454.4	-29.67	-569.45	-11.617	56.559	1.15380					
13	12:10:00	12.79	1.07	377	488	51.89	324.02	112.97	83.53	8508.62	561.48	60.24	0.026	45.2	1.3	-41.4	-1.06	-2004.3	-51.47	-293.17	-7.529	-1145.0	-29.40	-550.62	-14.140	60.135	1.54427					
14	10:15:00	13.71	0.92	377	488	55.07	320.96	115.22	80.57	8466.66	559.82	62.46	0.022	48.4	1.2	-44.4	-0.98	-2002.1	-44.21	-296.13	-6.538	-1186.9	-26.21	-552.28	-12.194	62.360	1.37691					
15	9:30:00	14.68	0.97	377	488	56.37	315.61	116.06	78.25	8383.32	556.22	63.92	0.023	49.7	1.3	-49.8	-1.16	-2001.2	-46.59	-298.45	-6.948	-1270.3	-29.57	-555.88	-12.941	63.819	1.48570					
16	9:20:00	15.67	0.99	377	488	63.47	343.80	113.46	77.00	8470.26	585.56	66.31	0.024	56.8	1.5	-21.6	-0.51	-2003.8	-47.61	-299.70	-7.121	-1183.3	-28.12	-526.54	-12.511	66.206	1.57306					
17	12:25:00	16.74	1.07	377	488	58.66	369.14	115.71	81.50	8885.74	620.26	72.02	0.026	52.0	1.5	3.7	0.10	-2001.6	-51.40	-295.20	-7.581	-767.9	-19.72	-491.84	-12.630	71.922	1.84695					
18	11:35:00	17.69	0.95	377	488	57.22	372.23	119.46	83.65	9019.89	627.61	74.67	0.023	50.5	1.3	6.8	0.16	-1997.8	-45.55	-293.05	-6.682	-633.7	-14.45	-484.49	-11.046	74.571	1.70023					
19	9:35:00	18.61	0.92	377	488	56.15	356.43	123.16	79.18	8714.98	605.89	73.10	0.022	49.5	1.2	-9.0	-0.20	-1994.1	-44.03	-297.52	-6.569	-938.6	-20.72	-506.21	-11.177	73.002	1.61189					
20	9:45:00	19.61	1.00	377	488	55.58	347.51	105.98	77.69	8500.43	588.59	72.65	0.024	48.9	1.3	-17.9	-0.43	-2011.3	-48.27	-299.01	-7.176	-1153.2	-27.68	-523.51	-12.564	72.548	1.74115					
21	9:45:00	20.61	1.00	377	488	53.61	346.33	119.63	76.09	8503.79	591.23	73.58	0.024	46.9	1.3	-19.1	-0.46	-1997.7	-47.94	-300.61	-7.215	-1149.8	-27.60	-520.87	-12.501	73.484	1.76362					
22	9:50:00	21.61	1.00	377	488	53.50	361.61	105.13	81.88	9014.33	628.41	79.46	0.024	46.8	1.3	-3.8	-0.09	-2012.2	-48.29	-294.82	-7.076	-639.3	-15.34	-483.69	-11.608	79.359	1.90462					
23	9:55:00	22.61	1.00	377	488	52.14	345.92	119.70	83.70	8530.31	593.34	74.64	0.024	45.4	1.3	-19.5	-0.47	-1997.6	-47.94	-293.00	-7.032	-1123.3	-26.96	-518.76	-12.450	74.536	1.78885					
Total brine (L)													0.40																			
ΣSiO2 flux (mg)													17																			
ΣK flux (mg)													-24																			
ΣSO4 flux (mg)													-814																			
ΣH2S flux (mg)																																
ΣCa flux (mg)													-121																			
ΣNa flux (mg)													-738																			
ΣMg flux (mg)													-235																			
ΣFe flux (mg)													25																			

Table D.5.6. Elements flux calculation for the SW2 experiment (342°C / 488 bar)

Reactor Temp	Pressure	SiO ₂ mg kg ⁻¹	K mg kg ⁻¹	SO ₄ mg kg ⁻¹	Ca mg kg ⁻¹	Na mg kg ⁻¹	Mg mg kg ⁻¹	Fe mg kg ⁻¹	Volume L	diff. SiO ₂ mg kg ⁻¹	SiO ₂ Flux mg	diff. K mg kg ⁻¹	K Flux mg	diff. SO ₄ mg kg ⁻¹	SO ₄ Flux mg	diff. Ca mg kg ⁻¹	Ca Flux mg	diff. Na mg kg ⁻¹	Na Flux mg	diff. Mg mg kg ⁻¹	Mg Flux mg	diff. Fe mg kg ⁻¹	Fe Flux mg
°C	bar																						
room T	1	5.8	336	2237	321	8309	892	0.1															
		Total Input Mass (mg) in 0.33 L supposing no fluid-rock exchange																					
342	488	2.4	5.5	3.0	0.5	9.9	5.6	1.6	0.024	-3.4	0.1	-330.0	-7.92	-2233.8	-53.61	-320.83	-7.700	-8298.6	-199.17	-885.89	-21.261	1.527	0.03665
342	488	0.0	2.2	0.1	0.0	5.8	0.1	0.2	0.024	-5.8	0.0	-333.3	-8.00	-2236.6	-53.68	-321.30	-7.711	-8302.7	-199.26	-891.42	-21.394	0.125	0.00300
342	488	0.0	47.0	27.1	11.0	1198.1	87.6	1.6	0.022	-5.8	0.0	-288.5	-6.30	-2209.6	-48.26	-310.34	-6.778	-7110.4	-155.29	-803.90	-17.557	1.526	0.03333
342	488	0.7	166.3	102.3	39.2	4224.1	317.4	10.2	0.025	-5.1	0.0	-169.2	-4.22	-2134.4	-53.27	-282.09	-7.041	-4084.4	-101.95	-574.11	-14.330	10.068	0.25130
342	488	1.8	251.5	168.8	58.9	6414.3	455.5	39.0	0.023	-4.0	0.0	-84.0	-1.94	-2067.9	-47.64	-262.41	-6.046	-1894.2	-43.64	-436.04	-10.046	38.877	0.89573
342	488	4.2	291.1	214.2	64.2	7362.2	520.0	54.3	0.024	-1.6	0.1	-44.4	-1.07	-2022.5	-48.54	-257.14	-6.171	-946.3	-22.71	-371.49	-8.916	54.222	1.30133
342	488	9.6	312.2	250.1	61.8	7850.7	552.1	64.0	0.026	3.8	0.3	-23.3	-0.61	-1986.7	-52.45	-259.52	-6.851	-457.8	-12.09	-339.45	-8.961	63.933	1.68784
342	488	14.4	322.0	282.4	63.9	8062.7	559.2	73.0	0.023	8.6	0.3	-13.5	-0.31	-1954.3	-45.03	-257.36	-5.930	-245.8	-5.66	-332.33	-7.657	72.915	1.67997
342	488	16.4	333.1	286.7	63.7	8340.8	572.2	81.2	0.024	10.6	0.4	-2.4	-0.06	-1950.0	-45.86	-257.62	-6.059	32.3	0.76	-319.31	-7.510	81.070	1.90678
342	488	17.4	333.7	286.1	67.8	8447.7	572.3	89.8	0.024	11.6	0.4	-1.8	-0.04	-1950.6	-45.88	-253.48	-5.962	139.2	3.27	-319.16	-7.507	89.694	2.10959
342	488	16.7	335.3	275.3	59.0	8415.8	564.9	93.5	0.025	10.9	0.4	-0.2	0.00	-1961.4	-48.49	-262.33	-6.485	107.3	2.65	-326.63	-8.074	93.396	2.30876
342	488	16.1	336.9	274.9	57.9	8462.2	565.8	95.1	0.023	10.3	0.4	1.4	0.03	-1961.8	-45.20	-263.38	-6.068	153.7	3.54	-325.71	-7.504	94.997	2.18873
342	488	15.6	325.9	270.2	55.4	8141.4	542.3	90.0	0.026	9.8	0.4	-9.6	-0.25	-1966.5	-50.97	-265.89	-6.892	-167.1	-4.33	-349.15	-9.050	89.867	2.32935
342	488	15.2	340.2	262.7	57.9	8610.8	572.5	98.6	0.024	9.4	0.4	4.7	0.11	-1974.0	-46.43	-263.38	-6.195	302.3	7.11	-318.98	-7.502	98.457	2.31570
342	488	14.5	332.6	271.7	56.4	8367.9	557.6	96.0	0.022	8.7	0.3	-2.9	-0.06	-1965.0	-43.39	-264.93	-5.850	59.4	1.31	-333.86	-7.372	95.944	2.11845
342	488	14.6	333.9	260.2	56.0	8353.0	554.4	94.5	0.024	8.8	0.3	-1.6	-0.04	-1976.5	-47.44	-265.34	-6.368	44.5	1.07	-337.10	-8.090	94.364	2.26474
									0.33														
										3.8													
												-15											
														-669									
																-89							
																		-326					
																				-130			
																						23	

Activity calculation

Table D.5.7. Ions activity and logarithm of activity calculate by the R package (linked to EqSolvR by Mroczek S. and Mroczek E., 2017) for the SW1 experiment (377°C / 488 bar). Table also reports values of quench pH, *in situ* pH, experimental time, flow-rate, T, P and values of *Log (Kps)*, *Log (Q)* and *SI* for minerals anhydrite and brucite

samples	1	2	3	4	5	6	7	8	9	10	11	12	13	14	15	16	17	18	19	20	21	22	23
$a = m \cdot a_{\gamma}$																							
H ⁺	4.31E-06	1.16E-06	3.78E-07	4.73E-07	6.83E-07	6.80E-06	7.13E-06	5.82E-06	5.40E-06	5.28E-06	5.31E-06	5.22E-06	5.22E-06	5.17E-06	5.14E-06	5.33E-06	5.41E-06	5.36E-06	5.21E-06	5.51E-06	5.23E-06	5.67E-06	5.24E-06
OH ⁻	1.61E-06	6.00E-06	1.83E-05	1.47E-05	1.02E-05	1.02E-06	9.73E-07	1.19E-06	1.28E-06	1.31E-06	1.30E-06	1.33E-06	1.33E-06	1.34E-06	1.35E-06	1.30E-06	1.28E-06	1.29E-06	1.33E-06	1.26E-06	1.33E-06	1.22E-06	1.32E-06
Na ⁺	1.56E-03	8.65E-04	5.21E-04	1.89E-04	3.65E-04	5.25E-03	3.68E-02	5.85E-02	6.70E-02	7.24E-02	7.59E-02	7.65E-02	7.82E-02	7.80E-02	7.75E-02	7.78E-02	8.00E-02	8.07E-02	7.91E-02	7.79E-02	7.79E-02	8.07E-02	7.80E-02
K ⁺	1.51E-04	9.72E-05	5.05E-05	1.90E-05	8.33E-06	9.72E-05	9.48E-04	1.61E-03	1.87E-03	2.06E-03	2.20E-03	2.17E-03	2.30E-03	2.28E-03	2.25E-03	2.44E-03	2.57E-03	2.58E-03	2.50E-03	2.46E-03	2.45E-03	2.51E-03	2.44E-03
Cl ⁻	1.90E-03	9.67E-04	5.19E-04	1.76E-04	3.52E-04	5.63E-03	4.09E-02	6.50E-02	7.41E-02	7.98E-02	8.35E-02	8.42E-02	8.61E-02	8.58E-02	8.53E-02	8.62E-02	8.88E-02	8.96E-02	8.77E-02	8.65E-02	8.64E-02	8.96E-02	8.66E-02
SO ₄ ²⁻	9.78E-07	2.08E-06	5.05E-06	3.18E-06	1.47E-06	2.42E-07	6.96E-07	1.36E-06	1.67E-06	1.83E-06	1.83E-06	1.91E-06	1.92E-06	1.97E-06	2.00E-06	1.91E-06	1.88E-06	1.93E-06	2.05E-06	1.77E-06	2.02E-06	1.68E-06	2.01E-06
Ca ²⁺	< LOD	1.75E-06	< LOD	< LOD	< LOD	< LOD	5.04E-06	5.75E-06	5.07E-06	4.50E-06	4.27E-06	4.20E-06	4.28E-06	4.15E-06	4.06E-06	3.94E-06	4.00E-06	4.06E-06	3.95E-06	3.96E-06	3.88E-06	3.98E-06	4.25E-06
Mg ²⁺	4.29E-05	4.20E-06	< LOD	< LOD	< LOD	3.88E-05	1.28E-04	1.60E-04	1.68E-04	1.77E-04	1.82E-04	1.82E-04	1.84E-04	1.84E-04	1.84E-04	1.92E-04	1.96E-04	1.97E-04	1.94E-04	1.92E-04	1.93E-04	1.97E-04	1.93E-04
Fe ²⁺	2.71E-07	5.68E-07	4.02E-07	1.75E-06	6.49E-07	7.81E-07	1.46E-06	4.83E-06	5.99E-06	4.72E-06	4.71E-06	4.89E-06	5.06E-06	5.26E-06	5.43E-06	5.56E-06	5.82E-06	5.97E-06	6.00E-06	6.07E-06	6.14E-06	6.35E-06	6.22E-06
a ² _{H+}	1.85E-11	1.33E-12	1.43E-13	2.24E-13	4.67E-13	4.63E-11	5.08E-11	3.39E-11	2.92E-11	2.79E-11	2.82E-11	2.73E-11	2.73E-11	2.67E-11	2.65E-11	2.84E-11	2.93E-11	2.87E-11	2.72E-11	3.03E-11	2.74E-11	3.21E-11	2.74E-11
log (a SiO ₂)	-4.0	-3.8	-4.0	-4.1	-4.2	-4.3	-4.2	-4.0	-3.9	-3.5	-3.2	-3.1	-3.1	-3.0	-3.0	-3.0	-3.0	-3.0	-3.0	-3.0	-3.0	-3.1	-3.1
log (a _{K+} /a _{H+})	1.5	1.9	2.1	1.6	1.1	1.2	2.1	2.4	2.5	2.6	2.6	2.6	2.6	2.6	2.6	2.7	2.7	2.7	2.7	2.6	2.7	2.6	2.7
log (a _{Na+} /a _{H+})	2.6	2.9	3.1	2.6	2.7	2.9	3.7	4.0	4.1	4.1	4.2	4.2	4.2	4.2	4.2	4.2	4.2	4.2	4.2	4.2	4.2	4.2	4.2
log (a _{Ca2+} /a ² _{H+})	< LOD	6.1	< LOD	< LOD	< LOD	< LOD	5.0	5.2	5.2	5.2	5.2	5.2	5.2	5.2	5.2	5.1	5.1	5.2	5.2	5.1	5.2	5.1	5.2
log (a _{Fe2+} /a ² _{H+})	4.2	5.6	6.4	6.9	6.1	4.2	4.5	5.2	5.3	5.2	5.2	5.3	5.3	5.3	5.3	5.3	5.3	5.3	5.3	5.3	5.4	5.3	5.4
log (a _{Mg2+} /a ² _{H+})	6.4	6.5	< LOD	< LOD	< LOD	5.9	6.4	6.7	6.8	6.8	6.8	6.8	6.8	6.8	6.8	6.8	6.8	6.8	6.9	6.8	6.8	6.8	6.8
log a _{Na+}	-2.8	-3.1	-3.3	-3.7	-3.4	-2.3	-1.4	-1.2	-1.2	-1.1	-1.1	-1.1	-1.1	-1.1	-1.1	-1.1	-1.1	-1.1	-1.1	-1.1	-1.1	-1.1	-1.1
log a _{K+}	-3.8	-4.0	-4.3	-4.7	-5.1	-4.0	-3.0	-2.8	-2.7	-2.7	-2.7	-2.7	-2.6	-2.6	-2.6	-2.6	-2.6	-2.6	-2.6	-2.6	-2.6	-2.6	-2.6
log a _{Cl-}	-2.7	-3.0	-3.3	-3.8	-3.5	-2.2	-1.4	-1.2	-1.1	-1.1	-1.1	-1.1	-1.1	-1.1	-1.1	-1.1	-1.1	-1.0	-1.1	-1.1	-1.1	-1.0	-1.1
log a _{SO42-}	-6.0	-5.7	-5.3	-5.5	-5.8	-6.6	-6.2	-5.9	-5.8	-5.7	-5.7	-5.7	-5.7	-5.7	-5.7	-5.7	-5.7	-5.7	-5.7	-5.8	-5.7	-5.8	-5.7
log a _{Ca2+}	< LOD	-5.8	< LOD	< LOD	< LOD	< LOD	-5.3	-5.2	-5.3	-5.3	-5.4	-5.4	-5.4	-5.4	-5.4	-5.4	-5.4	-5.4	-5.4	-5.4	-5.4	-5.4	-5.4
log a _{Mg2+}	-4.4	-5.4	< LOD	< LOD	< LOD	-4.4	-3.9	-3.8	-3.8	-3.8	-3.7	-3.7	-3.7	-3.7	-3.7	-3.7	-3.7	-3.7	-3.7	-3.7	-3.7	-3.7	-3.7
log a _{Fe2+}	-6.6	-6.2	-6.4	-5.8	-6.2	-6.1	-5.8	-5.3	-5.2	-5.3	-5.3	-5.3	-5.3	-5.3	-5.3	-5.3	-5.2	-5.2	-5.2	-5.2	-5.2	-5.2	-5.2
T (°C)	377.0	377.0	377.0	377.0	377.0	377.0	377.0	377.0	377.0	377.0	377.0	377.0	377.0	377.0	377.0	377.0	377.0	377.0	377.0	377.0	377.0	377.0	377.0
P (bar)	487.1	487.7	486.8	486.5	486.8	488.2	487.6	487.6	487.2	487.7	487.4	487.6	487.7	487.7	487.7	487.4	487.8	487.9	487.7	487.6	487.9	487.3	487.5
<i>in situ</i> pH _(375°C)	5.32	5.94	6.42	6.33	6.17	5.17	5.15	5.23	5.27	5.28	5.27	5.28	5.28	5.29	5.29	5.27	5.27	5.27	5.28	5.26	5.28	5.25	5.28
room T pH	5.37	5.96	5.56	5.21	5.53	4.69	3.85	3.42	3.45	3.47	3.40	3.37	3.36	3.31	3.30	3.29	3.27	3.25	3.24	3.22	3.21	3.19	3.22
flow rate (ml hr ⁻¹)	1	1	1	1	1	1	1	1	1	1	1	1	1	1	1	1	1	1	1	1	1	1	1
time (hr)	24.2	44.5	68.9	93.0	115.8	138.8	163.4	186.6	211.0	238.6	261.8	283.2	309.0	331.0	354.3	378.1	405.2	428.4	450.4	474.5	498.5	522.6	546.7
Anhydrite																							
Log Ksp (Supcrt92) @375°C		3.98					3.98	3.98	3.98	3.98	3.98	3.98	3.98	3.98	3.98	3.98	3.98	3.98	3.98	3.98	3.98	3.98	3.98
Log Q		4.46					4.48	4.14	4.09	4.11	4.14	4.12	4.11	4.11	4.11	4.15	4.15	4.13	4.12	4.18	4.13	4.20	4.09
Log (Q/K)		0.48					0.50	0.16	0.11	0.13	0.16	0.14	0.13	0.13	0.13	0.17	0.17	0.15	0.14	0.20	0.15	0.22	0.11
Brucite																							
Log Ksp (Supcrt92) @375°C		-6.51				-6.51	-6.51	-6.51	-6.51	-6.51	-6.51	-6.51	-6.51	-6.51	-6.51	-6.51	-6.51	-6.51	-6.51	-6.51	-6.51	-6.51	-6.51
Log Q		-6.50				-5.92	-6.40	-6.67	-6.76	-6.80	-6.81	-6.83	-6.83	-6.84	-6.84	-6.83	-6.83	-6.84	-6.85	-6.80	-6.85	-6.79	-6.85
Log (Q/K)		0.01				0.59	0.11	-0.16	-0.25	-0.29	-0.30	-0.32	-0.32	-0.33	-0.33	-0.32	-0.32	-0.33	-0.34	-0.29	-0.34	-0.28	-0.34
Caminite (MHSH 0.625)																							
Log Ksp = Log Q	8.81	9.43				9.55	8.45	8.00	7.86	7.79	7.78	7.75	7.75	7.73	7.72	7.73	7.72	7.71	7.69	7.77	7.70	7.78	7.70

Table D.5.8. Values of the activity coefficients (a_i) calculated by the R package for the SW1 experiment (377°C / 488 bar)

	sample		H ⁺	OH ⁻	Na ⁺	K ⁺	Cl ⁻	SO ₄ ²⁻	Ca ²⁺	Mg ²⁺	Fe ²⁺	NaSO ₄	HSO ₄ ⁻	KSO ₄	NaCl	KCl	HCl	KOH	NaOH	CaSO ₄	MgSO ₄	MgCl	CaCl ⁺	CaCl ₂	MgOH ⁺	CaOH ⁺	FeCl	FeSO ₄	
1	m		4.99E-06	1.89E-06	1.83E-03	1.78E-04	2.23E-03	1.86E-06		7.80E-05	5.03E-07	2.97E-06	4.67E-05	6.02E-07	7.16E-05	1.99E-06	8.82E-07	3.74E-09	2.10E-08		-	-			-		1.38E-09	0.00E+00	
	a _i		8.63E-01	8.52E-01	8.52E-01	8.49E-01	8.51E-01	5.26E-01		5.50E-01	5.39E-01	8.52E-01	8.52E-01	8.52E-01	1.00E+00	1.00E+00	1.00E+00	1.00E+00	1.00E+00		-	-			-		8.57E-01	1.00E+00	
	activity		4.31E-06	1.61E-06	1.56E-03	1.51E-04	1.90E-03	9.78E-07		4.29E-05	2.71E-07	2.53E-06	3.97E-05	5.13E-07	7.16E-05	1.99E-06	8.82E-07	3.74E-09	2.10E-08		-	-			-		1.18E-09	0.00E+00	
2	m		1.29E-06	6.73E-06	9.69E-04	1.09E-04	1.08E-03	3.29E-06	2.74E-06	6.47E-06	8.85E-07	3.34E-06	2.55E-05	7.89E-07	2.02E-05	6.52E-07	1.20E-07	8.98E-09	4.34E-08	1.59E-06	3.21E-06	2.91E-06	3.76E-06	1.83E-08	1.77E-05	2.39E-06	6.09E-07	6.14E-09	
	a _i		8.99E-01	8.92E-01	8.92E-01	8.91E-01	8.92E-01	6.34E-01	6.41E-01	6.49E-01	6.41E-01	8.92E-01	8.92E-01	8.92E-01	1.00E+00	1.00E+00	1.00E+00	1.00E+00	1.00E+00	1.00E+00	1.00E+00	8.97E-01	8.95E-01	1.00E+00	8.97E-01	8.95E-01	8.95E-01	1.00E+00	
	activity		1.16E-06	6.00E-06	8.65E-04	9.72E-05	9.67E-04	2.08E-06	1.75E-06	4.20E-06	5.68E-07	2.98E-06	2.27E-05	7.04E-07	2.02E-05	6.52E-07	1.20E-07	8.98E-09	4.34E-08	1.59E-06	3.21E-06	2.61E-06	3.37E-06	1.83E-08	1.59E-05	2.14E-06	5.45E-07	6.14E-09	
3	m		4.10E-07	2.00E-05	5.68E-04	5.50E-05	5.65E-04	7.12E-06			5.64E-07	4.75E-06	1.96E-05	9.65E-07	6.53E-06	1.81E-07	2.12E-08	1.42E-08	7.99E-08								0.00E+00	0.00E+00	
	a _i		9.21E-01	9.18E-01	9.18E-01	9.17E-01	9.17E-01	7.09E-01			7.14E-01	9.18E-01	9.18E-01	9.18E-01	1.00E+00	1.00E+00	1.00E+00	1.00E+00	1.00E+00								9.19E-01	1.00E+00	
	activity		3.78E-07	1.83E-05	5.21E-04	5.05E-05	5.19E-04	5.05E-06			4.02E-07	4.36E-06	1.80E-05	8.86E-07	6.53E-06	1.81E-07	2.12E-08	1.42E-08	7.99E-08								0.00E+00	0.00E+00	
4	m		4.98E-07	1.55E-05	1.99E-04	2.01E-05	1.85E-04	3.93E-06			2.15E-06	1.05E-06	1.50E-05	2.22E-07	8.02E-07	2.31E-08	8.96E-09	4.29E-09	2.32E-08								0.00E+00	0.00E+00	
	a _i		9.50E-01	9.49E-01	9.49E-01	9.48E-01	9.48E-01	8.10E-01			8.12E-01	9.49E-01	9.49E-01	9.49E-01	1.00E+00	1.00E+00	1.00E+00	1.00E+00	1.00E+00								9.49E-01	1.00E+00	
	activity		4.73E-07	1.47E-05	1.89E-04	1.90E-05	1.76E-04	3.18E-06			1.75E-06	9.96E-07	1.42E-05	2.10E-07	8.02E-07	2.31E-08	8.96E-09	4.29E-09	2.32E-08								0.00E+00	0.00E+00	
5	m		7.30E-07	1.09E-05	3.91E-04	8.93E-06	3.77E-04	1.94E-06			8.52E-07	9.52E-07	1.02E-05	4.56E-08	3.10E-06	2.03E-08	2.59E-08	1.30E-09	3.10E-08								0.00E+00	0.00E+00	
	a _i		9.35E-01	9.33E-01	9.33E-01	9.32E-01	9.33E-01	7.57E-01			7.61E-01	9.33E-01	9.33E-01	9.33E-01	1.00E+00	1.00E+00	1.00E+00	1.00E+00	1.00E+00								9.34E-01	1.00E+00	
	activity		6.83E-07	1.02E-05	3.65E-04	8.33E-06	3.52E-04	1.47E-06			6.49E-07	8.88E-07	9.48E-06	4.25E-08	3.10E-06	2.03E-08	2.59E-08	1.30E-09	3.10E-08								0.00E+00	0.00E+00	
6	m		8.60E-06	1.34E-06	6.88E-03	1.29E-04	7.42E-03	7.15E-07		1.02E-04	2.16E-06	2.76E-06	2.04E-05	1.07E-07	7.14E-04	3.80E-06	4.13E-06	1.52E-09	4.47E-08	1.54E-30	3.45E-06	1.79E-04			3.17E-05		5.64E-06	9.81E-10	
	a _i		7.91E-01	7.63E-01	7.63E-01	7.56E-01	7.60E-01	3.39E-01		3.82E-01	3.61E-01	7.63E-01	7.63E-01	7.63E-01	1.00E+00	1.00E+00	1.00E+00	1.00E+00	1.00E+00	1.00E+00	1.00E+00	1.00E+00	7.86E-01			7.86E-01		7.75E-01	1.00E+00
	activity		6.80E-06	1.02E-06	5.25E-03	9.72E-05	5.63E-03	2.42E-07		3.88E-05	7.81E-07	2.10E-06	1.55E-05	8.18E-08	7.14E-04	3.80E-06	4.13E-06	1.52E-09	4.47E-08	1.54E-30	3.45E-06	1.41E-04			2.49E-05		4.37E-06	9.81E-10	
7	m		1.18E-05	1.97E-06	7.46E-02	2.05E-03	8.56E-02	1.18E-05	5.74E-05	1.08E-03	1.66E-05	8.60E-05	9.50E-05	4.65E-06	3.64E-02	2.69E-04	3.15E-05	1.42E-08	2.99E-07	3.28E-05	5.76E-03	7.52E-04	9.42E-05	1.34E-04	1.83E-06	1.09E-04	5.28E-09	0.00E+00	
	a _i		6.05E-01	4.93E-01	4.93E-01	4.63E-01	4.78E-01	5.90E-02	1.18E-01	8.78E-02	4.93E-01	4.93E-01	4.93E-01	4.93E-01	1.00E+00	1.00E+00	1.00E+00	1.00E+00	1.00E+00	1.00E+00	1.00E+00	1.00E+00	5.87E-01	5.44E-01	1.00E+00	5.87E-01	5.44E-01	5.44E-01	1.00E+00
	activity		7.13E-06	9.73E-07	3.68E-02	9.48E-04	4.09E-02	6.96E-07	5.04E-06	1.28E-04	1.46E-06	4.24E-05	4.68E-05	2.29E-06	3.64E-02	2.69E-04	3.15E-05	1.42E-08	2.99E-07	3.28E-05	5.76E-03	4.41E-04	5.13E-05	1.34E-04	1.07E-06	5.93E-05	2.87E-09	0.00E+00	
8	m		1.04E-05	2.83E-06	1.39E-01	4.23E-03	1.62E-01	4.37E-05	1.04E-04	1.91E-03	8.70E-05	3.14E-04	1.78E-04	1.82E-05	9.19E-02	7.28E-04	4.09E-05	2.96E-08	5.82E-07	8.00E-05	1.24E-02	1.53E-03	2.71E-04	2.23E-04	2.86E-06	6.42E-04	3.42E-08	0.00E+00	
	a _i		5.61E-01	4.20E-01	4.20E-01	3.82E-01	4.01E-01	3.11E-02	5.55E-02	8.39E-02	5.55E-02	4.20E-01	4.20E-01	4.20E-01	1.00E+00	1.00E+00	1.00E+00	1.00E+00	1.00E+00	1.00E+00	1.00E+00	1.00E+00	5.38E-01	4.85E-01	1.00E+00	5.38E-01	4.85E-01	4.85E-01	1.00E+00
	activity		5.82E-06	1.19E-06	5.85E-02	1.61E-03	6.50E-02	1.36E-06	5.75E-06	1.60E-04	4.83E-06	1.32E-04	7.49E-05	7.64E-06	9.19E-02	7.28E-04	4.09E-05	2.96E-08	5.82E-07	8.00E-05	1.24E-02	8.23E-04	1.32E-04	2.23E-04	1.54E-06	3.12E-04	1.66E-08	0.00E+00	
9	m		9.84E-06	3.21E-06	1.68E-01	5.22E-03	1.95E-01	6.52E-05	1.04E-04	2.21E-03	1.23E-04	4.64E-04	2.13E-04	2.72E-05	1.20E-01	9.63E-04	4.32E-05	3.70E-08	7.19E-07	1.03E-04	1.53E-02	1.59E-03	3.11E-04	2.59E-04	2.82E-06	9.40E-04	5.20E-08	0.00E+00	
	a _i		5.49E-01	4.00E-01	4.00E-01	3.59E-01	3.80E-01	2.56E-02	4.86E-02	7.61E-02	4.86E-02	4.00E-01	4.00E-01	4.00E-01	1.00E+00	1.00E+00	1.00E+00	1.00E+00	1.00E+00	1.00E+00	1.00E+00	1.00E+00	5.25E-01	4.69E-01	1.00E+00	5.25E-01	4.69E-01	4.69E-01	1.00E+00
	activity		5.40E-06	1.28E-06	6.70E-02	1.87E-03	7.41E-02	1.67E-06	5.07E-06	1.68E-04	5.99E-06	1.86E-04	8.53E-05	1.09E-05	1.20E-01	9.63E-04	4.32E-05	3.70E-08	7.19E-07	1.03E-04	1.53E-02	8.35E-04	1.46E-04	2.59E-04	1.48E-06	4.41E-04	2.44E-08	0.00E+00	
10	m		9.73E-06	3.38E-06	1.86E-01	5.96E-03	2.17E-01	8.00E-05	1.00E-04	2.46E-03	1.05E-04	5.65E-04	2.35E-04	3.38E-05	1.40E-01	1.14E-03	4.55E-05	4.17E-08	7.95E-07	1.19E-04	1.76E-02	1.55E-03	3.20E-04	2.83E-04	2.61E-06	8.13E-04	4.49E-08	0.00E+00	
	a _i		5.43E-01	3.89E-01	3.89E-01	3.47E-01	3.68E-01	2.29E-02	4.50E-02	7.20E-02	4.50E-02	3.89E-01	3.89E-01	3.89E-01	1.00E+00	1.00E+00	1.00E+00	1.00E+00	1.00E+00	1.00E+00	1.00E+00	1.00E+00	5.18E-01	4.61E-01	1.00E+00	5.18E-01	4.61E-01	4.61E-01	1.00E+00
	activity		5.28E-06	1.31E-06	7.24E-02	2.06E-03	7.98E-02	1.83E-06	4.50E-06	1.77E-04	4.72E-06	2.20E-04	9.13E-05	1.31E-05	1.40E-01	1.14E-03	4.55E-05	4.17E-08	7.95E-07	1.19E-04	1.76E-02	8.02E-04	1.47E-04	2.83E-04	1.35E-06	3.75E-04	2.07E-08	0.00E+00	
11	m		9.87E-06	3.41E-06	1.98E-01	6.49E-03	2.31E-01	8.55E-05	9.93E-05	2.61																			

Table D.5.9. Ions activity and logarithm of activity calculate by the R package (linked to EqSolvR by Mroczek S. and Mroczek E., 2017) for the SW2 experiment (342°C / 488 bar). Table also reports values of quench pH, *in situ* pH, experimental time, flow-rate, T, P and values of *Log (Kps)*, *Log (Q)* and *SI* for minerals anhydrite and brucite

samples	1	2	3	4	5	6	7	8	9	10	11	12	13	14	15	16
$a = m \cdot a_{\gamma}$																
H ⁺	1.132E-05	3.014E-06	6.925E-06	5.838E-06	5.239E-06	4.923E-06	4.675E-06	4.415E-06	4.421E-06	4.419E-06	4.471E-06	4.476E-06	4.427E-06	4.599E-06	4.470E-06	4.554E-06
OH	6.823E-07	2.563E-06	1.116E-06	1.324E-06	1.475E-06	1.569E-06	1.653E-06	1.750E-06	1.748E-06	1.749E-06	1.728E-06	1.726E-06	1.745E-06	1.680E-06	1.729E-06	1.697E-06
Na ⁺	3.857E-04	2.400E-04	2.515E-02	5.964E-02	7.825E-02	8.543E-02	8.899E-02	9.053E-02	9.252E-02	9.329E-02	9.311E-02	9.345E-02	9.121E-02	9.450E-02	9.280E-02	9.271E-02
K ⁺	1.269E-04	5.401E-05	6.635E-04	1.704E-03	2.285E-03	2.536E-03	2.666E-03	2.726E-03	2.791E-03	2.787E-03	2.806E-03	2.815E-03	2.754E-03	2.829E-03	2.788E-03	2.803E-03
Cl ⁻	9.000E-04	3.048E-04	2.806E-02	6.636E-02	8.646E-02	9.422E-02	9.796E-02	9.945E-02	1.015E-01	1.023E-01	1.020E-01	1.024E-01	9.989E-02	1.035E-01	1.016E-01	1.016E-01
SO ₄ ²⁻	3.498E-07	6.139E-08	1.846E-06	3.712E-06	4.876E-06	5.716E-06	6.447E-06	7.222E-06	7.180E-06	7.120E-06	6.871E-06	6.839E-06	6.913E-06	6.446E-06	6.817E-06	6.524E-06
Ca ²⁺	4.187E-06	< LOD	4.565E-06	5.697E-06	6.093E-06	5.933E-06	5.425E-06	5.501E-06	5.333E-06	5.624E-06	4.909E-06	4.801E-06	4.742E-06	4.735E-06	4.717E-06	4.689E-06
Mg ²⁺	1.024E-04	1.251E-06	1.615E-04	2.416E-04	2.613E-04	2.715E-04	2.757E-04	2.740E-04	2.744E-04	2.723E-04	2.698E-04	2.694E-04	2.648E-04	2.699E-04	2.675E-04	2.665E-04
Fe ²⁺	1.400E-05	2.793E-06	9.068E-07	2.141E-06	6.026E-06	7.592E-06	8.547E-06	9.573E-06	1.039E-05	1.139E-05	1.190E-05	1.205E-05	1.174E-05	1.233E-05	1.228E-05	1.209E-05
a ² _{H+}	1.282E-10	9.086E-12	4.796E-11	3.408E-11	2.744E-11	2.424E-11	2.185E-11	1.949E-11	1.954E-11	1.953E-11	1.999E-11	2.003E-11	1.960E-11	2.115E-11	1.998E-11	2.074E-11
log (a SiO ₂)	-4.4	< LOD	< LOD	-4.9	-4.5	-4.2	-3.8	-3.6	-3.6	-3.5	-3.6	-3.6	-3.6	-3.6	-3.6	-3.6
log (a _{K+} /a _{H+})	1.0	1.3	2.0	2.5	2.6	2.7	2.8	2.8	2.8	2.8	2.8	2.8	2.8	2.8	2.8	2.8
log (a _{Na+} /a _{H+})	1.5	1.9	3.6	4.0	4.2	4.2	4.3	4.3	4.3	4.3	4.3	4.3	4.3	4.3	4.3	4.3
log (a _{Ca2+} /a ² _{H+})	4.5	< LOD	5.0	5.2	5.3	5.4	5.4	5.5	5.4	5.5	5.4	5.4	5.4	5.3	5.4	5.4
log (a _{Fe2+} /a ² _{H+})	5.0	5.5	4.3	4.8	5.3	5.5	5.6	5.7	5.7	5.8	5.8	5.8	5.8	5.8	5.8	5.8
log (a _{Mg2+} /a ² _{H+})	5.9	5.1	6.5	6.9	7.0	7.0	7.1	7.1	7.1	7.1	7.1	7.1	7.1	7.1	7.1	7.1
log a _{Na+}	-3.4	-3.6	-1.6	-1.2	-1.1	-1.1	-1.1	-1.0	-1.0	-1.0	-1.0	-1.0	-1.0	-1.0	-1.0	-1.0
log a _{K+}	-3.9	-4.3	-3.2	-2.8	-2.6	-2.6	-2.6	-2.6	-2.6	-2.6	-2.6	-2.6	-2.6	-2.5	-2.6	-2.6
log a _{Cl-}	-3.0	-3.5	-1.6	-1.2	-1.1	-1.0	-1.0	-1.0	-1.0	-1.0	-1.0	-1.0	-1.0	-1.0	-1.0	-1.0
log a _{SO42-}	-6.5	-7.2	-5.7	-5.4	-5.3	-5.2	-5.2	-5.1	-5.1	-5.1	-5.2	-5.2	-5.2	-5.2	-5.2	-5.2
log a _{Ca2+}	-5.4	< LOD	-5.3	-5.2	-5.2	-5.2	-5.3	-5.3	-5.3	-5.2	-5.3	-5.3	-5.3	-5.3	-5.3	-5.3
log a _{Mg2+}	-4.0	-5.9	-3.8	-3.6	-3.6	-3.6	-3.6	-3.6	-3.6	-3.6	-3.6	-3.6	-3.6	-3.6	-3.6	-3.6
log a _{Fe2+}	-4.9	-5.6	-6.0	-5.7	-5.2	-5.1	-5.1	-5.0	-5.0	-4.9	-4.9	-4.9	-4.9	-4.9	-4.9	-4.9
T (°C)	340	340	340	340	340	340	340	340	340	340	340	340	340	340	340	340
P (bar)	486.4	486.8	486.9	487.1	487.3	487.4	487.2	487.2	487.4	487.3	487.3	487.2	487.3	487.3	487.3	487.2
<i>in situ</i> pH _(340°C)	4.94	5.52	5.16	5.23	5.28	5.31	5.33	5.36	5.35	5.35	5.35	5.35	5.35	5.34	5.35	5.34
room T pH	5.83	5.24	5.05	4.31	3.41	3.12	2.96	2.88	2.81	2.85	2.75	2.73	2.75	2.73	2.72	2.72
flow rate (ml hr ⁻¹)	1	1	1	1	1	1	1	1	1	1	1	1	1	1	1	1
time (hr)	21.3	45.3	67.0	92.1	116.1	140.1	166.6	189.8	213.3	236.8	261.6	284.7	311.7	335.3	357.3	381.2
Anhydrite																
Log Ksp (Supcrt92) @350°C	3.86		3.86	3.86	3.86	3.86	3.86	3.86	3.86	3.86	3.86	3.86	3.86	3.86	3.86	3.86
Log Q	5.19		4.42	4.03	3.88	3.82	3.80	3.74	3.77	3.75	3.82	3.83	3.84	3.86	3.84	3.86
Log (Q/K)	1.33		0.56	0.17	0.02	-0.04	-0.06	-0.12	-0.09	-0.11	-0.04	-0.03	-0.02	0.00	-0.02	0.00
Brucite																
Log Ksp (Supcrt92) @350°C	-6.60	-6.60	-6.60	-6.60	-6.60	-6.60	-6.60	-6.60	-6.60	-6.60	-6.60	-6.60	-6.60	-6.60	-6.60	-6.60
Log Q	3.99	5.90	3.79	3.62	3.58	3.57	3.56	3.56	3.56	3.56	3.57	3.57	3.58	3.57	3.57	3.57
Log (Q/K)	10.59	12.50	10.39	10.22	10.18	10.17	10.16	10.16	10.16	10.16	10.17	10.17	10.18	10.17	10.17	10.17
Caminite (MHSB 0.625)																
Log Ksp = Log Q	8.97					7.05	6.97	6.91	6.92	6.93	6.95	6.95	6.96	6.98	6.96	6.98

Table D.5.10. Values of the activity coefficients (a_γ) calculated by the R package for the basalt-geothermal brine experiment (342°C / 488 bar)

sample		H ⁺	OH ⁻	Na ⁺	K ⁺	Cl ⁻	SO ₄ ²⁻	Ca ²⁺	Mg ²⁺	Fe ²⁺	NaSO ₄ ⁻	HSO ₄ ⁻	KSO ₄ ⁻	NaCl [°]	KCl [°]	HCl [°]	KOH [°]	NaOH [°]	CaSO ₄ [°]	MgSO ₄ [°]	MgCl ⁺	CaCl ⁺	CaCl ₂ [°]	MgOH ⁺	CaOH ⁺	FeCl [°]	FeSO ₄ [°]
1	m	1.24E-05	7.54E-07	4.26E-04	1.40E-04	9.95E-04	5.22E-07	6.18E-06	1.50E-04	2.07E-05	1.69E-07	1.96E-05	1.10E-07	5.30E-06	4.44E-07	4.07E-07	1.04E-09	1.82E-09	3.89E-07	9.84E-06	3.98E-05	4.78E-06	1.46E-08	3.13E-05	4.34E-07	8.41E-06	2.01E-08
	a _γ	9.10E-01	9.05E-01	9.05E-01	9.04E-01	9.04E-01	6.70E-01	6.77E-01	6.84E-01	6.77E-01	9.05E-01	9.05E-01	9.05E-01	1.00E+00	1.00E+00	1.00E+00	1.00E+00	1.00E+00	1.00E+00	1.00E+00	9.09E-01	9.07E-01	1.00E+00	9.09E-01	9.07E-01	9.07E-01	1.00E+00
	activity	1.13E-05	6.82E-07	3.86E-04	1.27E-04	9.00E-04	3.50E-07	4.19E-06	1.02E-04	1.40E-05	1.53E-07	1.78E-05	9.96E-08	5.30E-06	4.44E-07	4.07E-07	1.04E-09	1.82E-09	3.89E-07	9.84E-06	3.62E-05	4.34E-06	1.46E-08	2.85E-05	3.93E-07	7.63E-06	2.01E-08
2	m	3.18E-06	2.71E-06	2.53E-04	5.70E-05	3.22E-04	7.62E-08		1.54E-06	3.46E-06	1.76E-08	8.76E-07	7.85E-09	1.12E-06	6.40E-08	3.67E-08	1.66E-09	4.26E-09		2.11E-08	1.58E-07			1.38E-06		5.44E-07	7.03E-10
	a _γ	9.49E-01	9.47E-01	9.47E-01	9.47E-01	9.47E-01	8.06E-01		8.11E-01	8.08E-01	9.47E-01	9.47E-01	9.47E-01	1.00E+00	1.00E+00	1.00E+00	1.00E+00	1.00E+00		1.00E+00	9.49E-01			9.49E-01		9.48E-01	1.00E+00
	activity	3.01E-06	2.56E-06	2.40E-04	5.40E-05	3.05E-04	6.14E-08		1.25E-06	2.79E-06	1.67E-08	8.30E-07	7.44E-09	1.12E-06	6.40E-08	3.67E-08	1.66E-09	4.26E-09		2.11E-08	1.50E-07			1.31E-06		5.15E-07	7.03E-10
3	m	1.01E-05	1.83E-06	4.12E-02	1.13E-03	4.68E-02	1.34E-05	2.63E-05	7.78E-04	5.23E-06	8.64E-05	9.41E-05	4.51E-06	1.08E-02	7.24E-05	7.75E-06	8.90E-09	1.94E-07	8.19E-05	2.64E-03	2.28E-04	1.54E-05	1.09E-04	1.09E-06	2.39E-05	6.86E-09	0.00E+00
	a _γ	6.88E-01	6.10E-01	6.10E-01	5.89E-01	6.00E-01	1.38E-01	1.73E-01	2.08E-01	1.73E-01	6.10E-01	6.10E-01	6.10E-01	1.00E+00	1.00E+00	1.00E+00	1.00E+00	1.00E+00	1.00E+00	1.00E+00	6.75E-01	6.45E-01	1.00E+00	6.75E-01	6.45E-01	6.45E-01	1.00E+00
	activity	6.93E-06	1.12E-06	2.51E-02	6.63E-04	2.81E-02	1.85E-06	4.57E-06	1.62E-04	9.07E-07	5.27E-05	5.74E-05	2.75E-06	1.08E-02	7.24E-05	7.75E-06	8.90E-09	1.94E-07	8.19E-05	2.64E-03	1.54E-04	9.96E-06	1.09E-04	7.34E-07	1.54E-05	4.43E-09	0.00E+00
4	m	9.53E-06	2.72E-06	1.23E-01	3.78E-03	1.42E-01	6.66E-05	6.46E-05	1.96E-03	2.43E-05	5.17E-04	2.00E-04	2.92E-05	6.05E-02	4.40E-04	1.55E-05	2.71E-08	5.46E-07	2.46E-04	1.06E-02	7.98E-04	1.08E-04	2.20E-04	1.91E-06	1.58E-04	3.26E-08	0.00E+00
	a _γ	6.13E-01	4.86E-01	4.86E-01	4.51E-01	4.69E-01	5.57E-02	8.82E-02	1.23E-01	8.82E-02	4.86E-01	4.86E-01	4.86E-01	1.00E+00	1.00E+00	1.00E+00	1.00E+00	1.00E+00	1.00E+00	1.00E+00	5.92E-01	5.45E-01	1.00E+00	5.92E-01	5.45E-01	0.00E+00	1.00E+00
	activity	5.84E-06	1.32E-06	5.96E-02	1.70E-03	6.64E-02	3.71E-06	5.70E-06	2.42E-04	2.14E-06	2.51E-04	9.72E-05	1.42E-05	6.05E-02	4.40E-04	1.55E-05	2.71E-08	5.46E-07	2.46E-04	1.06E-02	4.73E-04	5.87E-05	2.20E-04	1.13E-06	8.60E-05	0.00E+00	0.00E+00
5	m	8.87E-06	3.29E-06	1.75E-01	5.61E-03	2.02E-01	1.21E-04	8.66E-05	2.50E-03	8.56E-05	9.67E-04	2.56E-04	5.58E-05	1.03E-01	7.69E-04	1.81E-05	4.05E-08	7.99E-07	3.50E-04	1.56E-02	1.18E-03	1.96E-04	2.76E-04	2.40E-06	6.12E-04	1.20E-07	0.00E+00
	a _γ	5.91E-01	4.48E-01	4.48E-01	4.08E-01	4.28E-01	4.03E-02	7.04E-02	1.04E-01	7.04E-02	4.48E-01	4.48E-01	4.48E-01	1.00E+00	1.00E+00	1.00E+00	1.00E+00	1.00E+00	1.00E+00	1.00E+00	5.68E-01	5.15E-01	1.00E+00	5.68E-01	5.15E-01	0.00E+00	0.00E+00
	activity	5.24E-06	1.47E-06	7.83E-02	2.29E-03	8.65E-02	4.88E-06	6.09E-06	2.61E-04	6.03E-06	4.33E-04	1.15E-04	2.50E-05	1.03E-01	7.69E-04	1.81E-05	4.05E-08	7.99E-07	3.50E-04	1.56E-02	6.69E-04	1.01E-04	2.76E-04	1.37E-06	3.15E-04	0.00E+00	0.00E+00
6	m	8.43E-06	3.60E-06	1.96E-01	6.44E-03	2.27E-01	1.58E-04	9.08E-05	2.75E-03	1.16E-04	1.27E-03	2.90E-04	7.46E-05	1.23E-01	9.30E-04	1.85E-05	4.79E-08	9.28E-07	4.26E-04	1.79E-02	1.27E-03	2.26E-04	3.10E-04	2.54E-06	8.56E-04	1.78E-07	0.00E+00
	a _γ	5.84E-01	4.36E-01	4.36E-01	3.94E-01	4.16E-01	3.61E-02	6.54E-02	9.88E-02	6.54E-02	4.36E-01	4.36E-01	4.36E-01	1.00E+00	1.00E+00	1.00E+00	1.00E+00	1.00E+00	1.00E+00	1.00E+00	5.61E-01	5.06E-01	1.00E+00	5.61E-01	5.06E-01	5.06E-01	1.00E+00
	activity	4.92E-06	1.57E-06	8.54E-02	2.54E-03	9.42E-02	5.72E-06	5.93E-06	2.71E-04	7.59E-06	5.54E-04	1.26E-04	3.25E-05	1.23E-01	9.30E-04	1.85E-05	4.79E-08	9.28E-07	4.26E-04	1.79E-02	7.13E-04	1.14E-04	3.10E-04	1.42E-06	4.33E-04	9.00E-08	0.00E+00
7	m	8.05E-06	3.84E-06	2.07E-01	6.88E-03	2.39E-01	1.88E-04	8.59E-05	2.86E-03	1.35E-04	1.51E-03	3.14E-04	8.96E-05	1.33E-01	1.02E-03	1.83E-05	5.30E-08	1.02E-06	4.89E-04	1.90E-02	1.22E-03	2.24E-04	3.33E-04	2.46E-06	1.01E-03	2.26E-07	0.00E+00
	a _γ	5.81E-01	4.30E-01	4.30E-01	3.88E-01	4.10E-01	3.43E-02	6.32E-02	9.64E-02	6.32E-02	4.30E-01	4.30E-01	4.30E-01	1.00E+00	1.00E+00	1.00E+00	1.00E+00	1.00E+00	1.00E+00	1.00E+00	5.57E-01	5.01E-01	1.00E+00	5.57E-01	5.01E-01	5.01E-01	1.00E+00
	activity	4.67E-06	1.65E-06	8.90E-02	2.67E-03	9.80E-02	6.45E-06	5.43E-06	2.76E-04	8.55E-06	6.51E-04	1.35E-04	3.86E-05	1.33E-01	1.02E-03	1.83E-05	5.30E-08	1.02E-06	4.89E-04	1.90E-02	6.80E-04	1.12E-04	3.33E-04	1.37E-06	5.07E-04	1.13E-07	0.00E+00
8	m	7.61E-06	4.09E-06	2.11E-01	7.08E-03	2.44E-01	2.15E-04	8.83E-05	2.87E-03	1.54E-04	1.73E-03	3.34E-04	1.03E-04	1.38E-01	1.05E-03	1.75E-05	5.74E-08	1.10E-06	5.44E-04	1.92E-02	1.26E-03	2.34E-04	3.51E-04	2.65E-06	1.15E-03	2.84E-07	0.00E+00
	a _γ	5.80E-01	4.28E-01	4.28E-01	3.85E-01	4.07E-01	3.36E-02	6.23E-02	9.55E-02	6.23E-02	4.28E-01	4.28E-01	4.28E-01	1.00E+00	1.00E+00	1.00E+00	1.00E+00	1.00E+00	1.00E+00	1.00E+00	5.56E-01	5.00E-01	1.00E+00	5.56E-01	5.00E-01	5.00E-01	1.00E+00
	activity	4.41E-06	1.75E-06	9.05E-02	2.73E-03	9.94E-02	7.22E-06	5.50E-06	2.74E-04	9.57E-06	7.42E-04	1.43E-04	4.42E-05	1.38E-01	1.05E-03	1.75E-05	5.74E-08	1.10E-06	5.44E-04	1.92E-02	7.01E-04	1.17E-04	3.51E-04	1.48E-06	5.76E-04	1.42E-07	0.00E+00
9	m	7.65E-06	4.11E-06	2.18E-01	7.31E-03	2.51E-01	2.19E-04	8.71E-05	2.91E-03	1.70E-04	1.77E-03	3.35E-04	1.06E-04	1.44E-01	1.10E-03	1.79E-05	5.87E-08	1.12E-06	5.41E-04	1.97E-02	1.25E-03	2.36E-04	3.53E-04	2.58E-06	1.28E-03		

Appendix E - (Chapter 6)

Chapter 6: Basalt – Seawater Interactions under Hydrothermal Conditions

6.2. Results

6.2.1. BSW1: Basalt-seawater experiment at 400°C/488 bar

Table E.6.1. Major ions compositions and complete experimental parameters (n° of samples collected, T, P, experimental time, flow rate and pH) for the BSW1 at 400°C / 488 bar. *In situ* pH is the calculated pH at temperature. Analysis of major ions are reported both in mg kg⁻¹ and in mmol kg⁻¹. In light-blue colour are distilled water mixed to seawater effluents. In green colour are effluents at 1.5 ml hr⁻¹ flow rate. In orange are effluents at 10 ml hr⁻¹ flow rate. In pink are effluents at 7.5 ml hr⁻¹ flow rate and in dark-blue are effluents at 5.0 ml hr⁻¹ flow rate. n.c.: not calculated. n.a: not analysed

n° sample	T (°C)	P (bar)	time (hrs)	flow-rate (ml hr ⁻¹)	pH (room T)	pH (400°C)	mg Kg ⁻¹											mmol Kg ⁻¹															
							As	B	Ca	Fe	K	Mg	Na	SiO ₂	Al	Li	H ₂ S	Cl ⁻	SO ₄ ²⁻	HCO ₃ ⁻	As	B	Ca	Fe	K	Mg	Na	SiO ₂	Al	Li	H ₂ S	Cl ⁻	SO ₄ ²⁻
Water (distilled) as starting fluid in the system	20.1	1.00	-	-	7.57	n.c.	<0.015	3.9	<0.05	<0.08	3.4	<0.01	<0.8	3.6	0.4	<0.01	<0.01	1.5	<0.1	n.a.	<0.0002	0.4	<0.001	<0.001	0.09	<0.0004	<0.03	0.06	0.02	<0.001	<0.0003	0.04	<0.001
Output seawater from SW1	20.1	1.00	0.00	-	7.75	5.96	-	-	-	-	-	-	-	-	-	-	-	-	-	-	<0.0002	0.26	2.1	1.3	8.8	24.4	371	0.9	0.01	0.01	<0.0003	439.7	1.2
Water (distilled) mixed seawater circulating in the system - 1	20.1	1.00	23.9	-			n.a.	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.	
2	401.3	485.4	45.3	1	6.37	7.17	0.04	1.5	<0.05	<0.08	27.2	<0.01	46.6	1451.5	13.1	0.1	0.3	5.3	49.5	n.a.	0.0005	0.1	<0.001	<0.001	0.7	<0.0004	2	24.2	0.5	0.02	0.01	0.1	0.5
3	400.7	486.1	68.1	1	4.17	6.71	0.05	1.4	<0.05	0.3	130.2	<0.01	206.8	1796	1.9	0.8	0.4	297.9	25.8	n.a.	0.0007	0.1	<0.001	0.01	3.3	<0.0004	9	29.9	0.07	0.1	0.01	8.4	0.3
4	400.6	486.1	92.3	1	3.29	5.95	<0.015	2.7	117.8	34.8	580.3	<0.01	4092.8	1687.6	<0.15	0.5	1.5	7164.2	4	n.a.	<0.0002	0.2	2.9	0.6	14.8	<0.0004	178	28.1	<0.006	0.07	0.04	202.1	0.04
5	400.4	486.1	116.7	1	4.34	5.77	<0.015	3.4	675.3	184.1	303.2	0.2	7245.3	1765.9	<0.15	0.4	1.4	13060.2	5.3	n.a.	<0.0002	0.3	16.8	3.3	7.8	0.01	315.2	29.4	<0.006	0.05	0.04	368.4	0.06
6	400.7	486.2	141.3	1	3.63	5.75	<0.015	3.4	827.7	49.8	334.3	<0.01	8089.6	1830	<0.15	0.3	1.4	14395.5	5.1	n.a.	<0.0002	0.3	20.7	0.9	8.6	<0.0004	351.9	30.5	<0.006	0.05	0.04	406.1	0.05
7	400.4	486.1	164.3	1	3.58	5.75	<0.015	3.4	929.6	71	376	<0.01	9123.4	1751.4	<0.15	0.4	1	14770.7	4.9	n.a.	<0.0002	0.3	23.2	1.3	9.6	<0.0004	396.8	29.2	<0.006	0.05	0.03	416.7	0.05
8	400.5	485.7	189.5	1	3.80	5.77	<0.015	3	799.4	65.2	316.2	<0.01	7991.4	1591.9	<0.15	0.3	0.2	15143.3	7.4	n.a.	<0.0002	0.3	19.9	1.2	8.1	<0.0004	347.6	26.5	<0.006	0.04	0.01	427.2	0.08
9	400.3	358.9	212.7	1	3.79	5.73	<0.015	3.4	921.2	95.3	378.4	<0.01	9317.2	1631.7	0.4	0.3	0.1	15061.1	0.2	n.a.	<0.0002	0.3	23	1.7	9.7	<0.0004	405.3	27.2	0.02	0.04	0.003	424.9	0.002
10	400.7	485.9	235.7	1	3.98	5.78	<0.015	3.2	817.3	128.3	366.3	<0.01	9103.1	1569.3	<0.15	0.2	0.4	15142.4	5.2	n.a.	<0.0002	0.3	20.4	2.3	9.4	<0.0004	396	26.1	<0.006	0.03	0.01	427.1	0.05
11	400.4	486.2	260.3	1	4.03	5.76	<0.015	3	829.2	101.4	330.4	<0.01	8553.8	1587.8	<0.15	0.3	0.4	15330.7	4.8	n.a.	<0.0002	0.3	20.7	1.8	8.5	<0.0004	372.1	26.4	<0.006	0.04	0.01	432.5	0.05
12	400.8	486.0	284.2	1	4.23	5.76	<0.015	3	840.3	111.2	343.7	<0.01	8742.6	1603	<0.15	0.2	0.4	15216.6	5	n.a.	<0.0002	0.3	21	2	8.8	<0.0004	380.3	26.7	<0.006	0.03	0.01	429.2	0.05
13	400.4	485.9	308.5	1	4.04	5.77	<0.015	1.2	879.5	130.1	366.1	<0.01	9193	1644.6	<0.15	0.3	0.3	15340.8	6.4	n.a.	<0.0002	0.1	21.9	2.3	9.4	<0.0004	399.9	27.4	<0.006	0.04	0.01	432.7	0.07
14	400.5	485.8	332.2	1	4.05	5.74	<0.015	1.3	948.2	154.4	396.5	0.2	9899.1	1742.2	0.2	0.3	0.3	15282.5	0.4	n.a.	<0.0002	0.1	23.7	2.8	10.1	0.007	430.6	29	0.008	0.04	0.01	431.1	0.004
15	400.2	367.6	352.7	1	4.09	5.74	<0.015	1	832.7	139.4	347.8	0.02	8825.7	1612.4	<0.15	0.2	0.1	15297.1	0.2	n.a.	<0.0002	0.1	20.8	2.5	8.9	0.0008	383.9	26.8	<0.006	0.03	0.004	431.5	0.002
16	400.7	485.1	374.8	1	4.10	5.78	<0.015	1	831.2	155.4	353.7	0.1	8941.7	1626.2	<0.15	0.2	0.3	15380.1	6.4	n.a.	<0.0002	0.1	20.7	2.8	9	0.005	388.9	27.1	<0.006	0.03	0.01	433.9	0.07
17	400.4	485.5	396.3	1	4.10	5.76	<0.015	3.4	804.1	148.6	329.8	<0.01	8522.8	1522.7	0.4	0.3	0.3	15515.2	3.4	n.a.	<0.0002	0.3	20.1	2.7	8.4	<0.0004	370.7	25.3	0.01	0.04	0.01	437.7	0.03
Re-starting heating procedure and re-filling with fresh seawater de-oxygenated	20.1	1.0	-	-	7.75	n.c.	<0.015	6.4	323	0.2	329.4	935.2	8405.6	8.4	<0.15	0.1	<0.01	15831.2	1910.9	n.a.	<0.0002	0.6	8.1	0.003	8.4	38.5	366	0.1	0.004	0.02	<0.0003	447	20
Water (distilled) mixed seawater circulating in the system - 19	400.8	486.6	411.9	1			n.a.	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.	
20	400.5	486.4	437.2	1	4.89	5.13	<0.015	<0.3	584.7	39.3	103.6	<0.01	2528.8	1606.8	<0.15	0.5	0.7	5094.3	0.5	n.a.	<0.0002	<0.03	14.6	0.7	2.6	<0.0004	110	26.7	<0.006	0.07	0.02	143.7	0.01
21	400.6	486.5	460.7	1	4.27	5.52	<0.015	1	849.4	84.9	199	<0.01	5405.9	1677.1	<0.15	0.2	0.8	10534.9	2	n.a.	<0.0002	0.09	21.2	1.5	5.1	<0.0004	235.1	27.9	<0.006	0.03	0.02	297.2	0.02
22	400.7	486.4	484.3	1	4.08	5.68	<0.015	1.2	832.7	72.5	261.4	<0.01	6896.6	1706.9	<0.15	0.3	0.2	12985.4	4.3	n.a.	<0.0002	0.1	20.8	1.3	6.7	<0.0004	300	28.4	<0.006	0.04	0.005	366.3	0.04
23	400.8	486.4	509.6	1	3.99	5.71	<0.015	1.4	843.3	52.2	295.2	0.2	7618.9	1707.2	0.2	0.3	0.1	14330.7	3.1	n.a.	<0.0002	0.1	21	0.9	7.5	0.008	331.4	28.4	0.007	0.04	0.004	404.2	0.03
24	400.6	486.5	532.6	1	4.04	5.73	<0.015	1.1	861	64.1	312.3	0.1	8069	1723.3	0.2	0.3	0.1	14902.1	4.2	n.a.	<0.0002	0.1	21.5	1.1	8	0.003	351	28.7	0.007	0.04	0.004	420.4	0.04
25	400.4	486.5	556.9	1.5	4.12	5.74	<0.015	5.6	842.5	69	315.8	0.4	8122.8	1648.8	<0.15	0.2	0.1	15269	4.5	n.a.	<0.0002	0.5	21	1.2	8.1	0.02	353.3	27.4	<0.006	0.03	0.004	430.7	0.05
26	400.6	486.4	582.8	1.5	4.17	5.75	<0.015	4.5	828.4	83	321.9	0.5	8314.6	1660.4	<0.15	0.2	0.1	15642.2	4.9	n.a.	<0.0002	0.4	20.7	1.5	8.2	0.02	361.7	27.6	<0.006	0.02	0.004	441.2	0.05
27	400.7	486.5	583.8	10	4.53	5.77	<0.015	4	779.9	112.6	315.1	0.4	8163.1	1622.9	<0.15	0.2	n.a.	15681.3	5.4	n.a.	<0.0002	0.4	19.5	2	8.1	0.02	355.1	27	<0.006	0.03	n.a.	442.4	0.06
28	400.3	486.8	584.8	10	4.27	5.79	<0.015	3.9	772.2	259.9	320	1.4																					

Table E.6.2. Trace element compositions and complete experimental parameters (n° of samples collected, T, P, experimental time, flow rate and pH) for the BSW1 at 400°C / 488 bar. *In situ* pH is the calculated pH at temperature. Analysis of trace elements are reported in µg kg⁻¹ and in µmol kg⁻¹. In light-blue colour are distilled water mixed to seawater effluents. In green colour are effluents at 1.5 ml hr⁻¹ flow rate. In orange are effluents at 10 ml hr⁻¹ flow rate. In pink are effluents at 7.5 ml hr⁻¹ flow rate and in dark-blue are effluents at 5.0 ml hr⁻¹ flow rate. Data of Mn are reported mg kg⁻¹ and in mmol kg⁻¹. n.c.: not calculated. n.a: not analysed

n° sample	T (°C)	P (bar)	time (hrs)	flow-rate (ml hr ⁻¹)	pH (room T)	pH (400°C)	µg kg ⁻¹										mg kg ⁻¹	µmol kg ⁻¹										mmol kg ⁻¹
							V	Cr	Cu	Zn	Rb	Ag	Cd	Ba	Au	Pb		Mn	V	Cr	Cu	Zn	Rb	Ag	Cd	Ba	Au	
Water (distilled) as starting fluid in the system	20.1	1.0	-	-	7.57	n.c.	<0.1	<0.2	<0.06	<0.5	<0.1	<0.05	<0.1	<0.2	<0.2	<0.2	<0.007	<0.002	<0.004	<0.0009	<0.008	<0.001	<0.0005	<0.0009	<0.001	<0.001	<0.001	<0.0001
Output seawater from SW1	20.1	1.0	0.0	-	7.75	5.96	-	-	-	-	-	-	-	-	-	-	-	1.2	0.09	0.3	20.5	1	<0.0005	0.06	0.4	0.04	0.05	0.02
Water (distilled) mixed seawater circulating in the system - 1	20.1	1.0	23.9	-	n.a.	n.c.	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.
2	401.3	485.4	45.3	1	6.37	7.17	14.8	<0.2	10.1	7632.5	56.7	0.9	7.8	66.9	3	3.1	<0.007	0.3	<0.004	0.2	116.7	0.7	0.009	0.07	0.5	0.02	0.03	<0.0001
3	400.7	486.1	68.1	1	4.17	6.71	<0.1	<0.2	0.6	2517	274.3	<0.05	6.6	46.9	4.7	4.9	<0.007	<0.002	<0.004	0.01	38.5	3.2	<0.0005	0.06	0.3	0.02	0.2	<0.0001
4	400.6	486.1	92.3	1	3.29	5.95	<0.1	<0.2	23.3	3665.1	1563	<0.05	7.5	203.8	15.1	15.9	11.2	<0.002	<0.004	0.4	56	18.6	<0.0005	0.07	1.5	0.08	0.4	0.2
5	400.4	486.1	116.7	1	4.34	5.77	<0.1	<0.2	17	2416.5	82.1	<0.05	2.8	4785.6	21.4	22.5	22.5	<0.002	<0.004	0.3	37	1.5	<0.0005	0.03	34.8	0.11	0.04	0.4
6	400.7	486.2	141.3	1	3.63	5.75	<0.1	<0.2	n.a.	1441.7	32.2	<0.05	<0.1	4964.2	16.7	17.6	28.8	<0.002	<0.004		22	1.1	<0.0005	<0.0009	36.1	0.08	0.04	0.5
7	400.4	486.1	164.3	1	3.58	5.75	<0.1	<0.2	<0.06	1591.5	20	<0.05	7.8	2486.1	14.9	15.6	31	<0.002	<0.004	<0.0009	24.3	1.1	<0.0005	0.07	18.1	0.08	0.04	0.6
8	400.5	485.7	189.5	1	3.80	5.77	<0.1	<0.2	1.3	1317.6	12.5	<0.05	4.9	1473.5	12.6	13.2	26.1	<0.002	<0.004	0.02	20.1	1.1	<0.0005	0.04	10.7	0.06	0.04	0.5
9	400.3	358.9	212.7	1	3.79	5.73	<0.1	<0.2	<0.06	1463.3	4.3	<0.05	6.7	1173.1	10.8	11.3	29.6	<0.002	<0.004	<0.0009	22.4	1	<0.0005	0.06	8.5	0.05	0.07	0.5
10	400.7	485.9	235.7	1	3.98	5.78	<0.1	<0.2	7.3	1141.8	10.3	<0.05	6.5	925.6	10.4	11	26.5	<0.002	<0.004	0.1	17.5	1.1	<0.0005	0.06	6.7	0.05	0.04	0.5
11	400.4	486.2	260.3	1	4.03	5.76	<0.1	<0.2	5	1725	7.8	<0.05	1.8	959.3	7.5	7.9	24.1	<0.002	<0.004	0.1	26.4	1	<0.0005	0.02	7	0.04	0.03	0.4
12	400.8	486.0	284.2	1	4.23	5.76	<0.1	<0.2	n.a.	<0.5	3.4	<0.05	5.7	818.8	7.6	8	25.9	<0.002	<0.004		<0.008	1	<0.0005	0.05	6	0.04	0.03	0.5
13	400.4	485.9	308.5	1	4.04	5.77	<0.1	<0.2	10.6	185.2	4.9	<0.05	6	725.8	9	9.5	27.2	<0.002	<0.004	0.2	2.8	1	<0.0005	0.05	5.3	0.05	0.03	0.5
14	400.5	485.8	332.2	1	4.05	5.74	<0.1	<0.2	5.8	619.2	6.1	<0.05	1.9	901.9	4.5	4.7	29.3	<0.002	<0.004	0.1	9.5	1	<0.0005	0.02	6.6	0.02	0.01	0.5
15	400.2	367.6	352.7	1	4.09	5.74	<0.1	<0.2	12.9	<0.5	6.1	<0.05	7.9	687.4	4.5	4.7	25.7	<0.002	<0.004	0.2	<0.008	1	<0.0005	0.07	5	0.02	0.01	0.5
16	400.7	485.1	374.8	1	4.10	5.78	<0.1	<0.2	7.5	1386.1	7.2	<0.05	4.9	698.2	6.2	6.6	25.1	<0.002	<0.004	0.1	21.2	1	<0.0005	0.04	5.1	0.03	0.03	0.5
17	400.4	485.5	396.3	1	4.10	5.76	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.	25.6	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.	0.5
Re-starting heating procedure and re-filling with fresh seawater de-oxygenated	20.1	1.0	-	-	7.75	n.c.	2	<0.2	<0.06	<0.5	8.5	<0.05	<0.1	<0.2	2	<0.2	<0.007	0.04	<0.004	<0.0009	<0.008	0.1	<0.0005	<0.0009	<0.001	0.01	<0.001	<0.0001
Water (distilled) mixed seawater circulating in the system - 19	400.8	486.6	411.9	1	7.57	n.c.	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.
20	400.5	486.4	437.2	1	4.89	5.13	<0.1	31.2	<0.06	175.3	38	<0.05	7.3	1418.5	8.7	9.2	7	<0.002	0.6	<0.0009	2.7	0.02	<0.0005	0.07	10.3	0.04	0.04	0.1
21	400.6	486.5	460.7	1	4.27	5.52	<0.1	133.2	<0.06	197.5	23.7	<0.05	7.4	625.4	1.1	1.1	13.1	<0.002	2.6	<0.0009	3	0.5	<0.0005	0.07	4.6	0.01	0.02	0.2
22	400.7	486.4	484.3	1	4.08	5.68	<0.1	58.8	3.5	3093.7	18.5	<0.05	2.9	1673.4	2.4	2.6	12.1	<0.002	1.1	0.1	47.3	0.6	<0.0005	0.03	12.2	0.01	0.03	0.2
23	400.8	486.4	509.6	1	3.99	5.71	<0.1	<0.2	<0.06	8017.5	8.1	<0.05	<0.1	539.4	<0.2	<0.2	12.5	<0.002	<0.004	<0.0009	122.6	0.8	<0.0005	<0.0009	3.9	<0.001	0.02	0.2
24	400.6	486.5	532.6	1	4.04	5.73	<0.1	<0.2	<0.06	4425.6	<0.1	<0.05	4.5	415	2.9	3	20.9	<0.002	<0.004	<0.0009	67.7	0.9	<0.0005	0.04	3	0.01	0.01	0.4
25	400.4	486.5	556.9	1.5	4.12	5.74	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.	30	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.	0.5
26	400.6	486.4	582.8	1.5	4.17	5.75	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.	27.9	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.	0.5
27	400.7	486.5	583.8	10	4.53	5.77	<0.1	<0.2	<0.06	3866.5	5.8	<0.05	<0.1	179.1	2.8	2.9	22.4	<0.002	<0.004	<0.0009	59.1	1	<0.0005	<0.0009	1.3	0.01	0.009	0.4
28	400.3	486.8	584.8	10	4.27	5.79	<0.1	<0.2	<0.06	590.5	7.7	2.1	0.4	207.3	2.3	2.5	23.1	<0.002	<0.004	<0.0009	9	1	0.02	0.004	1.5	0.01	0.007	0.4
29	400.7	486.5	585.8	10	4.28	5.80	<0.1	<0.2	<0.06	733.7	<0.1	<0.05	<0.1	227.1	3.4	3.5	19.9	<0.002	<0.004	<0.0009	11.2	1	<0.0005	<0.0009	1.7	0.02	0.02	0.4
30	400.5	486.8	586.8	10	4.50	5.81	<0.1	<0.2	<0.06	769.6	2.6	<0.05	<0.1	280.7	1.1	1.2	17.8	<0.002	<0.004	<0.0009	11.8	1.1	<0.0005	<0.0009	2	0.01	0.006	0.3
Re-filling with fresh seawater NOT de-oxygenated	20.1	1.0	-	-	7.75	n.c.	2	<0.2	<0.06	<0.5	8.5	<0.05	<0.1	<0.2	2	<0.2	<0.007	0.04	<0.004	<0.0009	<0.008	0.1	<0.0005	<0.0009	<0.001	0.01	<0.001	<0.0001
31	400.8	487																										

Figure E.6.2. XRD scan showing the mineralogy of Portion 2-3

Figure 1. XRD scan showing the mineralogy of BSW1 **Portion 2-3** sample as indicated by the labelled scan peaks

Figure E.6.4. XRD scan showing the mineralogy of Portion 7

Figure 3. XRD scan showing the mineralogy of BSW1 – **Portion 7** sample as indicated by the labelled scan peaks

Figure E.6.5. Qualitative XRD analysis of Portion 1, 2-3, 4 and 7

Report Number: PSR2017/64a_2017101106
Report Date: 31/10/2017

Confidential 2017

Sample Composition

Table 1. Mineralogical Composition of BSW1 Samples

	Mineralogical Composition			
	Portion 1	Portion 2-3	Portion 4	Portion 7
	2017007017	2017007535	2017007019	2017007021
Chlorite	x	x	x	
Plagioclase	x	x	x	x
Maghemite	x			
Hematite		x		
Calcite	x			
Smectite				x
Ankerite				x
Augite				x

Figure E.6.6. XRF analysis of Portion 1. BSW1 experiment

Figure E.6.7. XRF analysis of Portion 2-3. BSW1 experiment

Report Number: PSR2017/88b_2017103103
Report Date: 10/11/2017

Confidential 2017

Sample Identification: BSW1 – Portion 2-3

Laboratory Reference No:2017007536

X-ray fluorescence
SPECTRA^{plus}
Multi-element Analysis

CLIENT : GNS SCIENCE - WAIRAKEI
PROJECT : SA19938
DATE : 10/11/2017
SAMPLE : SAMPLE #1, LAB#2017007536, BSW1-Portion 2-3
COMMENTS : 100% - Total = sum of unmeasured elements (i.e H, B, C, N, O)
:
:

Carbon	C	–	Zinc	Zn	0.005	Iodine	I	nd
Fluorine	F	nd	Gallium	Ga	nd	Caesium	Cs	nd
Sodium	Na	0.160	Germanium	Ge	nd	Barium	Ba	nd
Magnesium	Mg	15.8	Arsenic	As	nd	Lanthanum	La	nd
Aluminium	Al	8.40	Selenium	Se	nd	Cerium	Ce	–
Silicon	Si	15.1	Bromine	Br	nd	Hafnium	Hf	–
Phosphorus	P	0.059	Rubidium	Rb	nd	Tantalum	Ta	nd
Sulphur	S	0.641	Strontium	Sr	0.007	Tungsten	W	nd
Chlorine	Cl	0.171	Yttrium	Y	0.003	Rhenium	Re	–
Potassium	K	0.013	Zirconium	Zr	0.010	Osmium	Os	–
Calcium	Ca	1.46	Niobium	Nb	nd	Iridium	Ir	–
Scandium	Sc	nd	Molybdenum	Mo	0.002	Platinum	Pt	–
Titanium	Ti	1.31	Rhodium	Rh	–	Gold	Au	–
Vanadium	V	0.038	Palladium	Pd	–	Mercury	Hg	nd
Chromium	Cr	0.017	Silver	Ag	–	Thallium	Tl	nd
Manganese	Mn	0.006	Cadmium	Cd	nd	Lead	Pb	nd
Iron	Fe	5.75	Indium	In	–	Bismuth	Bi	nd
Cobalt	Co	0.010	Tin	Sn	nd	Thorium	Th	nd
Nickel	Ni	0.029	Antimony	Sb	nd	Uranium	U	nd
Copper	Cu	nd	Tellurium	Te	–	Total		49.0

Values are weight %

nd = not detected

– = not measured

Figure E.6.8. XRF analysis of Portion 4, BSW1 experiment

Report Number: PSR2017/84b_2017101108
Report Date: 1/11/2017

Confidential 2017

Sample Identification: BSW1 – Portion 4 Laboratory Reference No:2017007020

X-ray fluorescence
SPECTRA^{plus}
Multi-element Analysis

CLIENT : GNS SCIENCE - WAIRAKEI
PROJECT : SA19893
DATE : 31/10/2017
SAMPLE : SAMPLE #2, LAB#2017007020, BSW1-Portion 4
COMMENTS : 100% - Total = sum of unmeasured elements (i.e H, B, C, N, O)
:
:

Carbon	C	—	Zinc	Zn	nd	Iodine	I	nd
Fluorine	F	nd	Gallium	Ga	nd	Caesium	Cs	nd
Sodium	Na	0.971	Germanium	Ge	nd	Barium	Ba	nd
Magnesium	Mg	14.1	Arsenic	As	nd	Lanthanum	La	nd
Aluminium	Al	8.05	Selenium	Se	nd	Cerium	Ce	—
Silicon	Si	18.5	Bromine	Br	nd	Hafnium	Hf	—
Phosphorus	P	0.120	Rubidium	Rb	nd	Tantalum	Ta	nd
Sulphur	S	0.846	Strontium	Sr	0.008	Tungsten	W	nd
Chlorine	Cl	0.299	Yttrium	Y	nd	Rhenium	Re	—
Potassium	K	0.046	Zirconium	Zr	0.007	Osmium	Os	—
Calcium	Ca	2.69	Niobium	Nb	nd	Iridium	Ir	—
Scandium	Sc	nd	Molybdenum	Mo	nd	Platinum	Pt	—
Titanium	Ti	1.12	Rhodium	Rh	—	Gold	Au	—
Vanadium	V	0.049	Palladium	Pd	—	Mercury	Hg	nd
Chromium	Cr	0.012	Silver	Ag	—	Thallium	Tl	nd
Manganese	Mn	0.010	Cadmium	Cd	nd	Lead	Pb	nd
Iron	Fe	4.70	Indium	In	—	Bismuth	Bi	nd
Cobalt	Co	0.009	Tin	Sn	nd	Thorium	Th	nd
Nickel	Ni	0.011	Antimony	Sb	nd	Uranium	U	nd
Copper	Cu	nd	Tellurium	Te	—	Total		51.5

Values are weight %

nd = not detected

— = not measured

Figure E.6.9. XRF analysis of Portion 7. BSW1 experiment

SEM results of the grains collected from the immediately adjacent fluid entry point after 396.3 hours of the experiment

Figure E.6.10. EDS analysis of texture of reacted grains collected from the bottom of the Reactor

Figure E.6.11. EDS analysis of texture of reacted grains collected from the bottom of the Reactor

Table E.6.3. EDS analysis of reacted grains in Figures A.6.10-11

Anh	Analysis Point	CaO	SO ₃					Total
	5	57.74	42.26					100.00
Sulfate	Analysis Point	MgO	SO ₃	Total	O	Mg	S	Total
	1	40.08	59.92	100.00	51.83	24.17	24.00	100.00
	7	43.34	56.66	100.00	51.17	26.14	22.69	100.00
average		41.71	58.29					100.00
Chl	Analysis Point	MgO	Al ₂ O ₃	SiO ₂	FeO	TiO ₂	Total	
	6	33.72	21.19	38.79	6.30	0.00	100.00	
	33	27.11	20.60	34.55	12.24	5.49	99.99	
	34	32.26	22.19	38.38	7.18	0.00	100.01	
	52	31.34	22.54	38.21	7.91	0.00	100.00	
	53	33.98	23.29	38.52	4.22	0.00	100.01	
	54	35.10	24.22	37.13	3.55	0.00	100.00	
	56	34.28	22.73	37.60	5.39	0.00	100.00	
	57	33.97	24.83	36.94	4.27	0.00	100.01	
	58	34.71	23.05	37.73	4.52	0.00	100.01	
	60	33.52	26.28	36.78	3.42	0.00	100.00	
	61	32.34	22.96	39.30	5.40	0.00	100.00	
average		32.94	23.08	37.63	5.85	0.50	100.00	

Table E.6.4. Average mineral compositions determined by EDS from Table E.6.3

Oxides	average wt%	average wt%	average wt%
MgO		41.71	32.94
Al ₂ O ₃			23.08
SiO ₂			37.63
CaO	57.74		
FeO			5.85
SO ₃	42.26	58.29	
TiO ₂			0.50
Total	100.00	100.00	100.00
Mineral Composition	CaSO ₄	Mg ₇ (SO ₄) ₅ (OH) ₄ ·H ₂ O	Mg _{8.0} Fe _{0.8} Al _{2.7} Ti _{0.1} Si _{6.2} Al _{1.8} O ₂₀ (OH) ₁₆ (on the basis of 28 oxygen equivalents, ignoring H ₂ O)
Phase and ID	Anhydrite	Caminite	Chlorite

Figure E.6.12. SEM photographs of reacted grains collected from the bottom of the Reactor

SEM results of the grains collected from the immediately adjacent fluid exit point after 396.3 hours of the experiment

Figure E.6.13. EDS analysis of texture of reacted grains collected from the top of the Reactor

Table E.6.5. EDS analysis of reacted grains in Figure E.6.13

Plg	Analysis Point	Na ₂ O	CaO	Al ₂ O ₃	SiO ₂				Total
	7	0.97	16.83	34.38	47.81				99.99
	8	1.18	15.80	34.55	48.48				100.01
average		1.08	16.32	34.47	48.15				100.00
Cpx	Analysis Point	MgO	Al ₂ O ₃	SiO ₂			CaO	FeO	Total
	60	13.39	7.02	48.27			2.94	28.38	100.00
Sulfate	Analysis Point	MgO	SO ₃	Total	O	Mg	S	Total	
	4	47.73	52.27	100.00	50.28	28.78	20.94	100.00	
	6	40.25	59.75	100.00	51.80	24.27	23.93	100.00	
average		43.99	56.01	100.00					
Smc	Analysis Point	Na ₂ O	MgO	Al ₂ O ₃	SiO ₂	CaO	FeO	Total	
	2	3.18	16.87	13.33	47.60	1.59	17.43	100.00	
	3	2.88	14.96	10.56	50.46	1.79	19.25	100.00	
average		3.03	15.92	11.95	49.03	1.69	18.34	99.95	
±σ		0.21	1.35	1.96	2.02	0.14	1.29		

Table E.6.6. Average mineral compositions determined by EDS from Table E.6.5

Oxides	average wt%	average wt%	average wt%	average wt%
Na ₂ O	1.08			3.03
MgO		13.39	43.99	15.92
Al ₂ O ₃	34.47	7.02		11.95
SiO ₂	48.15	48.27		49.03
CaO	16.32	2.94		1.69
FeO		28.38		18.34
SO ₃			56.01	
TiO ₂				
Total	100.02	100.00	100.00	99.96
Mineral Composition	Ca _{0.8} Na _{0.1} Al _{1.9} Si _{2.2} O ₈ (An ₈₉ -Ab ₁₁)	Ca _{0.1} Mg _{0.8} Fe _{0.9} Al _{0.2} Si _{1.9} Al _{0.1} O ₆	Mg ₇ (SO ₄) ₅ (OH) ₄ ·H ₂ O	Na _{0.8} Ca _{0.2} Mg _{3.2} Fe _{2.1} Al _{0.5} Si _{6.6} Al _{1.4} O ₂₀ (OH) ₄ (on the basis of 22 oxygen equivalents, ignoring H ₂ O)
Phase and ID	Bytownite	Augite	Caminite	Smectite

Figure E.6.14. SEM photographs of reacted grains collected from the top of the Reactor

BSW1: Portion 1

Figure E.6.15. EDS analysis of texture of reacted grains from Portion 1

Figure E.6.16. SEM pictures for EDS analysis of epoxy-mounted polished grains collected from **Portion 1**. Analysis points are marked in blue

Table E.6.7. SEM-EDS analysis results of grains in Figure E.6.16

	Analysis Point	Na ₂ O	Al ₂ O ₃	SiO ₂	CaO	MgO	Total			Analysis Point	MgO	Al ₂ O ₃	SiO ₂	TiO ₂	FeO	Total
Plg	4	3.86	30.29	52.50	13.35	0.00	100.00		Chl	35	32.38	12.80	43.28	1.12	10.43	100.00
	5	3.61	30.13	52.14	14.12	0.00	100.00			37	33.43	14.86	40.76	0.00	10.95	100.00
	6	3.63	30.17	52.51	13.69	0.00	100.00			41	32.56	13.91	42.61	0.00	10.91	100.00
	8	3.20	30.66	51.87	14.27	0.00	100.00			42	29.13	16.56	38.00	0.00	16.31	100.00
	34	3.88	31.72	51.61	12.57	0.22	100.00			43	32.42	12.48	42.74	0.00	12.37	100.00
	77	5.58	27.60	57.23	9.59	0.00	100.00			48	31.93	16.67	39.25	0.00	12.15	100.00
	79	4.27	29.06	54.42	12.25	0.00	100.00			49	27.51	16.99	37.63	0.00	17.87	100.00
	103	4.10	30.30	52.86	12.74	0.00	100.00			50	34.18	13.75	42.04	0.00	10.03	100.00
	104	3.34	30.66	51.57	14.43	0.00	100.00			51	37.01	13.10	43.65	0.00	6.25	100.00
average		3.94	30.07	52.97	13.00	0.02	100.00		52	32.47	15.11	40.25	0.00	12.18	100.00	
									53	31.00	13.49	42.17	0.00	13.34	100.00	
									54	31.21	16.72	40.00	0.00	12.07	100.00	
									55	31.98	18.18	41.58	0.00	8.26	100.00	
	Analysis Point	MgO	Al ₂ O ₃	SiO ₂	CaO	FeO	TiO ₂	Total		56	29.91	15.74	39.51	0.00	14.84	100.00
Cpx	28	16.97	2.32	52.97	15.85	11.88	0.00	100.00	58	40.37	11.18	46.05	0.00	2.40	100.00	
	29	14.88	2.22	52.24	17.91	12.75	0.00	100.00	59	23.40	18.11	36.30	0.00	22.18	100.00	
	73	18.54	0.73	53.13	4.40	23.20	0.00	100.00	60	24.49	16.98	36.50	0.00	22.03	100.00	
	81	15.18	2.85	52.20	19.09	9.73	0.94	100.00	61	19.58	13.94	31.56	0.00	34.92	100.00	
	102	16.49	1.77	53.41	18.33	10.01	0.00	100.00	62	34.02	22.11	41.83	0.00	2.04	100.00	
	average		16.41	1.98	52.79	15.12	13.51	0.19	99.81	63	31.45	16.81	38.96	0.00	12.78	100.00
									68	24.98	11.76	38.21	0.00	25.05	100.00	
									69	25.00	17.00	37.36	0.00	20.64	100.00	
									70	23.91	17.35	37.81	0.00	20.93	100.00	
									71	35.93	13.00	41.66	0.00	9.42	100.00	
									84	36.94	4.43	57.47	0.00	1.16	100.00	
									85	34.27	2.01	62.53	0.00	1.19	100.00	
Ol	2	25.34	35.60	39.06				100.00	86	34.10	3.68	60.65	0.00	1.56	100.00	
	32	17.22	33.86	48.92				100.00	87	35.65	4.24	59.69	0.42	0.00	100.00	
	74	22.25	35.43	42.32				100.00	88	33.29	4.05	58.76	1.85	2.05	100.00	
	99	30.73	37.37	31.90				100.00	89	35.65	4.24	59.69	0.42	0.00	100.00	
	average		23.89	35.57	40.55				100.00	90	33.29	4.05	58.76	1.85	2.05	100.00
									91	25.03	17.39	36.74	0.00	20.85	100.00	
									92	30.01	15.88	38.46	0.00	15.65	100.00	
									93	25.03	17.39	36.74	0.00	20.85	100.00	
									94	31.76	15.13	41.18	0.00	11.93	100.00	
Ox	Analysis Point	TiO ₂	FeO					Total	105	39.35	6.79	52.38	0.00	1.47	100.00	
	1	33.94	66.06					100.00	106	38.18	9.59	45.52	1.43	5.28	100.00	
	3	41.15	58.85					100.00	107	33.38	2.23	62.92	0.00	1.46	100.00	
	10	37.92	62.08					100.00	109	35.29	12.11	41.01	2.00	9.59	100.00	
	30	44.9	55.1					100.00	112	33.48	14.37	41.38	0.00	10.77	100.00	
	75	27.87	72.13					100.00	113	36.06	15.60	42.31	0.00	6.03	100.00	
	119	1.99	98.01					100.00	115	39.95	12.27	44.19	0.00	3.59	100.00	
									116	34.30	5.79	55.12	0.92	3.86	100.00	
									117	33.63	3.62	59.16	0.68	2.91	100.00	
								118	34.09	2.48	60.07	1.65	1.70	100.00		
								average		32.07	12.13	45.21	0.27	10.32	100.00	

Figure E.6.17. SEM pictures for EDS analysis of epoxy-mounted polished grains collected from **Portion 1**. Analysis points are marked in blue

Table E.6.8. SEM-EDS analysis results of grains in Figure E.6.17

	Analysis Point	MgO	Al ₂ O ₃	SiO ₂	TiO ₂	FeO	Total
Chl	104	30.23	18.60	40.29	0.00	10.88	100.00
	105	29.72	18.38	39.54	0.00	12.37	100.00
	106	31.31	16.43	40.30	0.00	11.96	100.00
	107	36.44	10.48	45.56	0.00	7.51	100.00
	108	36.40	13.14	42.92	0.00	7.55	100.00
	109	25.74	19.82	36.96	0.00	17.48	100.00
	110	36.99	11.76	43.60	0.00	7.64	100.00
	111	35.48	4.37	58.46	0.00	1.68	100.00
	115	35.23	10.65	44.39	2.63	7.09	100.00
	116	40.06	9.86	46.70	0.00	3.38	100.00
	117	32.68	4.69	59.29	0.00	3.33	100.00
	118	31.03	13.68	40.90	0.00	14.39	100.00
	119	37.30	12.55	42.86	0.00	7.29	100.00
	120	38.76	11.07	45.28	0.00	4.89	100.00
	121	38.31	11.81	43.63	0.00	6.25	100.00
	122	40.21	11.37	43.34	0.00	5.07	100.00
	123	37.38	10.83	44.38	0.00	7.41	100.00
	124	35.41	14.09	42.29	0.00	8.22	100.00
	125	32.13	1.82	63.87	0.00	2.19	100.00
	126	33.01	3.06	62.26	0.00	1.67	100.00
	127	30.92	15.35	39.65	0.00	14.08	100.00
	128	33.53	5.49	57.25	0.00	3.74	100.00
	129	32.97	3.28	61.90	0.00	1.84	100.00
	130	32.32	13.23	41.07	0.00	13.39	100.00
	120	35.47	12.43	42.85	0.00	9.25	100.00
	121	38.13	11.63	44.22	0.00	6.02	100.00
	136	37.70	12.84	42.57	0.00	6.89	100.00
	137	37.22	12.39	42.53	0.00	7.86	100.00
	138	34.76	4.63	58.85	0.00	1.76	100.00
	140	33.14	15.59	41.84	0.00	9.43	100.00
	141	32.58	13.87	41.17	0.00	12.38	100.00
	142	30.43	21.75	38.56	0.00	9.26	100.00
	143	31.52	17.33	38.92	0.00	12.23	100.00
	144	38.57	10.54	47.76	0.00	3.13	100.00
	145	30.36	15.49	39.38	0.00	14.77	100.00
	146	33.18	2.30	58.41	0.00	6.10	100.00
	147	35.96	4.77	56.88	0.00	2.39	100.00
	148	37.48	6.12	54.27	0.00	2.13	100.00
	149	40.56	8.77	47.50	0.00	3.18	100.00
	150	34.09	16.19	40.64	0.00	9.07	100.00
	151	32.34	3.68	61.42	0.00	2.56	100.00
	152	41.64	9.93	45.03	0.00	3.40	100.00
	153	39.63	11.55	43.51	0.00	5.30	100.00
	154	42.23	9.99	44.98	0.00	2.80	100.00
	155	41.96	9.47	45.70	0.00	2.86	100.00
	156	41.48	10.03	45.15	0.00	3.35	100.00
	157	42.50	9.83	44.81	0.00	2.86	100.00
	158	40.19	9.94	45.55	0.00	4.32	100.00
	160	40.52	10.45	44.33	0.00	4.69	100.00
	161	34.87	12.40	41.99	0.00	10.74	100.00
	162	32.03	2.30	63.20	0.00	2.46	100.00
	163	36.57	13.79	43.00	0.00	6.63	100.00
average		35.59	10.88	46.76	0.05	6.71	

Table E.6.9. Average mineral compositions from Table E.6.7 and Table E.6.8

	average wt%	average wt%	average wt%	point n°75	point n°119 [Oxides wt% and elements mass % and atomic %]	average wt%
Oxides						
MgO	0.02	16.41	23.89			33.83
Na ₂ O	3.94					
Al ₂ O ₃	30.07	1.98				11.51
SiO ₂	52.97	52.79	35.57			45.99
CaO	13.00	15.12				
FeO		13.51	40.55	72.13	FeO (wt%) 98.01	8.52
TiO ₂				27.87	TiO₂ (wt%) 1.99	0.16
					Fe: (wt%) 76.18 - (at%) 48.66	
					Ti: (wt%) 1.19.18 - (at%) 0.89	
					O: (wt%) 22.62 - (at%) 50.46	
Total	100.00	99.81	100.01	100.00		100.01
Mineral Composition	Ca _{0.63} Na _{0.35} Al _{1.6} Si _{2.4} O ₈ (An ₆₅ -Ab ₃₅)	Ca _{0.60} Mg _{0.91} Fe _{0.42} Al _{0.06} Si ₂ O ₆	Mg _{1.24} Fe _{0.75} SiO ₄ (Fo ₅₁ -Fa ₄₉)	Fe ²⁺ (Fe ³⁺ ,Ti) ₂ O ₄		Mg _{8.30} Fe _{1.17} Al _{1.80} Si _{7.57} Al _{0.43} O ₂₀ (OH) ₁₆ (on the basis of 28 oxygen equivalents, ignoring H ₂ O)
Phase and ID	Plagioclase (labradorite)	Clinopyroxene (augite)	Mg-olivine (forsterite)	Oxide (titanomagnetite)	Oxide (magnetite?)	Chlorite

Portion 2-3

Figure E.6.18. SEM pictures for EDS analysis of epoxy-mounted polished grains collected from **Portion 2-3**. Analysis points are marked in blue

Table E.6.10. SEM-EDS analysis results of grains in Figure E.6.18

Chl	Analysis Point	MgO	Al ₂ O ₃	SiO ₂	TiO ₂	FeO	Total	Ox						
								Analysis Point	TiO ₂	FeO	Total	SiO ₂	TiO ₂	FeO
	1	28.21	25.01	37.56	0.00	9.23	100.01	140	28.79	36.62	33.41	0.00	1.18	100.00
	7	26.34	22.62	36.86	0.00	14.18	100.00	141	29.58	24.94	36.36	0.00	9.11	99.99
	8	24.78	19.08	36.65	0.00	19.48	99.99	142	27.49	24.57	35.69	0.00	12.25	100.00
	12	27.07	21.79	37.70	0.00	13.44	100.00	143	29.45	33.11	34.27	0.00	3.17	100.00
	14	27.29	21.55	37.09	0.00	14.06	99.99	144	30.36	28.50	35.94	0.00	5.20	100.00
	15	24.97	25.10	38.25	0.00	11.68	100.00	145	30.56	32.27	34.24	0.00	2.92	99.99
	28	26.36	32.22	35.81	0.00	5.61	100.00	146	30.42	20.10	40.07	0.00	9.40	99.99
	29	26.06	21.52	36.51	0.00	15.90	99.99	147	30.61	20.69	39.64	0.00	9.06	100.00
	30	27.73	22.03	38.04	0.00	12.20	100.00	148	28.69	20.35	38.61	0.00	12.35	100.00
	31	27.87	21.38	38.51	0.00	12.24	100.00	149	31.38	21.22	38.61	0.00	8.79	100.00
	32	24.58	20.11	35.55	0.00	19.77	100.01	150	32.84	21.50	38.99	0.00	6.68	100.01
	33	27.75	21.17	35.57	0.00	15.51	100.00	151	24.11	19.01	37.98	0.00	18.89	99.99
	34	28.07	21.32	37.63	0.00	12.98	100.00	152	27.09	19.51	37.62	0.00	15.78	100.00
	35	29.17	21.50	37.97	0.00	11.37	100.01	153	25.00	19.22	37.30	0.00	18.49	100.01
	36	28.19	20.78	37.33	0.00	13.70	100.00	154	31.66	20.34	39.01	2.29	6.71	100.01
	37	26.39	21.46	35.56	0.00	16.60	100.01	157	28.40	19.24	38.62	1.76	11.97	99.99
	38	27.05	21.23	36.09	0.00	15.63	100.00	158	27.63	38.90	32.23	0.00	1.25	100.01
	39	24.25	21.76	36.30	0.00	17.70	100.01	159	31.25	36.71	30.69	0.00	1.35	100.00
	41	27.95	23.92	36.63	1.79	9.71	100.00	160	26.37	34.23	35.41	0.00	3.99	100.00
	42	26.50	22.04	38.92	0.00	12.53	99.99	162	31.66	21.16	38.93	0.00	8.26	100.01
	44	27.87	22.80	37.42	0.00	11.92	100.01	163	31.88	20.13	40.18	0.00	7.81	100.00
	45	27.38	35.83	34.04	0.00	2.75	100.00	164	31.95	21.62	40.16	0.00	6.26	99.99
	46	27.03	21.36	37.91	2.31	11.40	100.01	165	30.69	21.97	40.81	0.00	6.53	100.00
	47	24.15	19.62	35.78	0.00	20.45	100.00	166	33.82	20.78	40.11	0.00	5.29	100.00
	48	25.82	22.33	36.58	0.00	15.27	100.00	167	29.78	20.51	39.09	0.00	10.62	100.00
	49	20.89	17.94	31.11	10.16	19.91	100.01	168	30.12	20.43	40.54	0.00	8.90	99.99
	50	26.99	22.50	37.07	0.00	13.45	100.01	169	32.29	21.58	39.07	0.00	7.06	100.00
	51	26.94	23.73	35.78	0.00	13.56	100.01	170	30.04	19.97	38.68	2.08	9.22	99.99
	52	26.08	21.22	37.02	0.00	15.68	100.00	171	26.59	18.74	33.15	0.00	21.52	100.00
	53	26.06	20.11	36.91	0.00	16.92	100.00	average	28.15	23.83	36.99	0.33	10.69	
	54	29.21	21.84	38.24	0.00	10.71	100.00							
	56	27.47	22.23	37.11	0.00	13.19	100.00							
	58	28.47	21.02	38.36	0.00	12.15	100.00							
	59	27.85	21.74	36.39	0.00	14.02	100.00							
	94	30.51	20.58	39.92	0.00	8.99	100.00							
	96	31.62	20.63	38.90	0.00	8.85	100.00							
	97	32.03	21.51	40.20	0.00	6.27	100.01							
	103	30.88	19.67	40.34	0.00	9.10	100.00							
	104	25.60	35.45	35.84	0.00	3.11	100.00							
	106	25.03	37.45	35.87	0.00	1.65	100.00							
	107	26.49	36.44	35.21	0.00	1.86	100.00							
	108	24.61	18.19	35.15	4.33	17.72	100.00							
	109	27.05	19.75	37.35	0.00	15.85	100.00							
	138	30.45	36.96	31.44	0.00	1.14	99.99							
	139	29.86	37.00	31.45	0.00	1.69	100.00							

Figure E.6.19. SEM pictures for EDS analysis of epoxy-mounted polished grains collected from **Portion 2-3**. Analysis points are marked in blue

Table E.6.11. SEM-EDS analysis results of grains in Figure E.6.19

Chl	Analysis Point	MgO	Al ₂ O ₃	SiO ₂	FeO	Total		MgO	Al ₂ O ₃	SiO ₂	FeO	Total
	117	30.14	22.45	37.60	9.80	99.99	175	29.29	22.31	37.75	10.65	100.00
	118	29.85	22.90	39.78	7.46	99.99	176	29.82	22.07	37.04	11.07	100.00
	119	21.19	20.02	40.13	18.67	100.01	178	31.30	22.01	36.98	9.71	100.00
	120	27.44	21.42	36.78	14.36	100.00	179	32.36	22.65	37.00	7.99	100.00
	121	29.69	21.96	37.66	10.69	100.00	180	30.79	21.98	37.89	9.33	99.99
	122	31.88	23.84	37.99	6.29	100.00	181	30.43	21.98	37.29	10.30	100.00
	123	29.66	22.26	37.26	10.83	100.01	182	25.20	19.25	35.85	19.71	100.01
	124	30.42	22.17	36.76	10.65	100.00	183	28.45	23.40	36.67	11.48	100.00
	125	31.74	22.36	38.02	7.89	100.01	187	32.91	20.99	38.97	7.14	100.01
	126	30.20	22.35	37.64	9.81	100.00	189	32.10	20.63	38.90	8.38	100.01
	127	31.55	22.46	37.70	8.29	100.00	190	30.39	20.63	38.02	10.96	100.00
	128	28.36	20.92	37.96	12.75	99.99	191	28.21	19.46	38.58	13.76	100.01
	129	27.29	21.74	37.06	13.91	100.00	192	31.49	20.39	38.53	9.59	100.00
	130	31.88	22.57	38.02	7.53	100.00	193	30.05	19.87	37.65	12.43	100.00
	131	29.22	21.91	37.35	11.52	100.00	194	32.51	20.91	38.73	7.86	100.01
	133	30.31	21.08	37.34	11.27	100.00	195	31.58	20.48	38.48	9.47	100.01
	134	28.73	20.02	37.44	13.81	100.00	196	33.25	21.25	39.88	5.62	100.00
	135	22.06	19.15	36.38	22.42	100.01	197	34.89	21.30	39.32	4.49	100.00
	136	29.49	21.54	37.76	11.21	100.00	198	33.04	23.30	38.87	4.79	100.00
	137	29.17	22.84	37.54	10.45	100.00	199	36.35	21.78	39.47	2.40	100.00
	138	31.16	21.81	37.11	9.93	100.01	200	31.35	33.34	33.58	1.73	100.00
	139	28.00	20.48	35.39	16.13	100.00	201	30.03	21.47	37.27	11.22	99.99
	140	32.23	22.23	35.51	10.04	100.01	202	26.26	20.38	37.32	16.03	99.99
	141	30.59	22.62	38.29	8.50	100.00	203	30.00	21.85	37.22	10.93	100.00
	142	28.57	21.13	36.33	13.97	100.00	204	30.37	20.94	38.25	10.43	99.99
	143	31.25	22.86	37.30	8.60	100.01	205	29.97	21.67	37.36	11.00	100.00
	144	29.31	21.74	36.95	12.00	100.00	206	31.31	22.02	37.70	8.98	100.01
	145	29.94	24.31	38.07	7.68	100.00	207	31.91	21.31	37.44	9.35	100.01
	146	28.30	20.17	38.95	12.57	99.99	209	26.06	19.58	38.81	15.55	100.00
	147	30.48	22.55	37.09	9.89	100.01	210	31.68	20.26	40.88	7.17	99.99
	148	30.32	21.68	39.12	8.88	100.00	211	27.36	19.59	36.82	16.22	99.99
	149	29.13	23.42	38.65	8.80	100.00	213	29.89	22.28	36.61	11.23	100.01
	150	29.27	21.75	37.80	11.18	100.00	214	33.10	23.08	37.84	5.98	100.00
	151	29.73	21.26	37.11	11.90	100.00	215	31.56	22.14	37.11	9.18	99.99
	172	30.64	22.20	37.78	9.38	100.00	216	30.71	22.32	35.89	11.08	100.00
	173	31.42	22.15	37.78	8.65	100.00	217	29.08	21.78	38.01	11.13	100.00
	174	28.62	21.86	37.44	12.08	100.00		30.06	21.79	37.68	10.47	
						average						

Table E.6.12. Average mineral compositions from Table E.6.10 and Table E.6.11

Oxides	average wt%	average wt%
MgO		29.11
Al ₂ O ₃		22.81
SiO ₂		37.34
FeO _(T)		10.58
TiO ₂		0.17
Total		100.00
Mineral Composition	Altered Compositions in FeO -TiO ₂	Mg _{7.25} Fe _{1.48} Al _{2.73} Si _{6.24} Al _{1.76} O ₂₀ (OH) ₁₆ (on the basis of 28 oxygen equivalents, ignoring H ₂ O)
Phase and ID	Oxide (titanomagnetite present)	Chlorite

Portion 4

Figure E.6.20. SEM pictures for EDS analysis of epoxy-mounted polished grains collected from **Portion 4**. Analysis points are marked in blue

Table E.6.13. SEM-EDS analysis results of grains in Figure E.6.20

	Analysis Point	Na ₂ O	Al ₂ O ₃	SiO ₂	CaO	Total		Smc	Analysis Point	Na ₂ O	MgO	Al ₂ O ₃	SiO ₂	CaO	TiO ₂	FeO	Total	
Plg	4	2.96	30.27	51.89	14.89	100.01			5	2.60	23.29	14.54	49.35	0.54	0.00	9.69	100.00	
	20	3.36	27.44	56.56	12.63	99.99			6	1.49	21.89	14.20	48.70	0.39	0.91	12.43	100.00	
	25	4.84	29.18	55.18	10.79	99.99			7	2.00	20.86	14.11	51.28	0.50	0.00	11.24	100.00	
	35	2.59	30.54	52.64	14.24	100.01			8	1.56	25.32	15.15	51.48	0.00	0.00	6.51	100.00	
	38	4.07	31.51	52.71	11.72	100.01			9	1.82	25.78	16.95	47.32	0.00	0.00	8.14	100.00	
	39	2.68	30.46	52.28	14.58	100.00			10	1.75	27.16	14.55	50.75	0.00	0.00	5.78	100.00	
average		3.42	29.90	53.54	13.14	100.01			11	1.44	24.21	11.65	53.25	0.00	0.86	8.59	100.00	
									12	1.00	28.03	17.13	46.56	0.00	0.00	7.27	100.00	
									13	1.34	24.99	7.97	54.78	0.98	6.17	3.78	100.00	
									14	4.14	15.49	17.81	55.46	3.19	0.00	3.62	100.00	
									15	1.76	24.18	11.46	54.55	1.58	0.00	6.47	100.00	
									26	2.59	22.07	11.49	51.68	0.48	0.00	11.68	100.00	
Cpx	3	12.44	8.96	47.41	18.41	12.79	100.01		27	1.77	21.31	13.75	50.72	0.00	0.00	12.46	100.00	
	24	20.17	4.75	52.97	13.68	8.42	99.99		29	1.41	22.88	13.61	55.04	0.00	0.00	7.06	100.00	
average		16.31	6.86	50.19	16.05	10.61	99.99		32	0.99	23.88	14.56	49.98	0.00	0.00	10.60	100.00	
									33	0.99	20.42	11.53	48.81	2.74	3.37	12.15	100.00	
									43	0.46	29.86	30.35	37.90	0.00	0.00	1.42	100.00	
									46	0.76	32.17	19.59	43.51	0.00	0.00	3.97	100.00	
									47	1.38	31.78	20.02	41.76	0.00	0.00	5.06	100.00	
									48	0.47	26.06	13.53	41.24	0.38	8.47	9.85	100.00	
									50	0.54	27.02	12.17	55.77	0.63	0.00	3.87	100.00	
Ol	1	24.27	35.39	40.35			100.01		51	0.53	31.79	15.42	47.79	0.48	0.00	4.00	100.00	
									52	0.78	28.94	16.20	51.00	0.45	0.00	2.63	100.00	
Ox									53	0.47	30.60	20.34	43.51	0.00	0.00	5.07	100.00	
	2	29.47	70.53				100.00		55	4.34	25.11	18.70	46.36	0.00	0.00	5.49	100.00	
	16	38.60	61.40				100.00		56	1.18	28.96	18.69	45.51	0.41	0.00	5.25	100.00	
	17	30.93	69.07				100.00		57	0.58	26.47	14.89	49.26	0.54	1.46	6.80	100.00	
	18	28.87	71.13				100.00		58	0.94	27.47	16.08	51.11	0.00	0.00	4.40	100.00	
	21	27.96	72.04				100.00		59	0.71	30.55	17.66	41.52	0.00	3.12	6.43	100.00	
	22	19.71	80.29				100.00		60	1.07	29.46	17.03	44.88	0.77	0.79	6.00	100.00	
	23	13.88	86.12				100.00		61	0.46	30.63	18.52	43.98	0.00	0.00	6.41	100.00	
	28	27.34	72.66				100.00		68	1.19	25.32	10.99	56.29	0.00	0.00	6.22	100.00	
	36	31.55	68.45				100.00		69	2.12	21.58	13.27	47.61	0.00	2.65	12.77	100.00	
	37	48.81	51.19				100.00		70	2.25	22.85	10.63	53.96	0.00	1.66	8.65	100.00	
	65	40.31	59.69				100.00		71	1.87	23.49	11.41	54.66	0.00	0.00	8.57	100.00	
	average		30.68	69.32				100.00		72	1.41	24.39	14.83	49.62	0.00	0.00	9.75	100.00
										73	2.20	22.06	10.54	54.89	0.00	0.00	10.32	100.00
									74	2.47	19.11	12.88	51.22	0.00	0.87	13.46	100.00	
									75	1.40	19.78	12.15	50.96	0.00	2.08	13.63	100.00	
									76	0.98	15.29	11.99	52.46	0.00	0.00	19.28	100.00	
									77	0.49	23.28	13.70	55.88	0.00	0.00	6.65	100.00	
									79	1.87	22.08	13.52	51.78	0.00	0.00	10.74	100.00	
									80	0.60	24.42	14.30	52.17	0.00	0.00	8.51	100.00	
									156	2.60	19.21	12.08	52.52	0.84	0.00	12.74	100.00	
									157	3.23	24.36	14.54	49.41	0.35	0.00	8.11	100.00	
									158	2.20	22.26	13.04	50.91	0.00	0.00	11.59	100.00	
									159	2.75	22.73	12.97	51.68	1.13	0.00	8.73	100.00	
									160	1.74	22.13	12.63	54.34	0.00	0.00	9.14	100.00	
									161	4.51	23.86	12.62	50.67	0.00	0.00	8.34	100.00	
									162	5.30	22.96	10.02	53.87	0.00	0.00	7.85	100.00	
									163	3.75	21.22	12.38	52.45	0.00	0.00	10.20	100.00	
									164	1.82	20.63	11.56	55.11	0.00	0.00	10.87	100.00	
									165	2.68	25.32	10.85	53.65	0.60	0.00	6.89	100.00	
									166	2.00	22.53	14.66	51.92	0.00	0.00	8.89	100.00	
									181	2.31	21.29	13.71	50.41	0.00	0.00	12.28	100.00	
									182	1.13	18.60	13.52	50.06	0.00	0.00	16.70	100.00	
									183	1.50	23.15	14.82	52.35	0.00	0.00	8.18	100.00	
									184	1.33	23.75	12.15	54.11	0.00	0.00	8.66	100.00	
									185	1.62	24.10	15.16	50.61	0.00	0.00	8.52	100.00	
									186	1.50	25.60	16.53	47.66	0.00	0.00	8.71	100.00	
									187	1.07	25.90	15.73	49.05	0.00	0.00	8.24	100.00	
									188	1.12	21.28	13.79	56.64	0.00	0.00	7.17	100.00	
								average	1.72	24.24	14.40	50.38	0.27	0.52	8.46	100.00		
								±σ	1.05	3.72	3.32	4.13	0.79	2.43	3.36			

Table E.6.13. Average mineral compositions from Table E.6.12.

Oxides	average wt%	average wt%	average wt%	average wt%	average wt%
MgO		16.31	24.27		24.24
Na ₂ O	3.42				1.72
Al ₂ O ₃	29.90	6.86			14.40
SiO ₂	53.54	50.19	35.39		50.38
CaO	13.14	16.05			0.27
K ₂ O					
FeO		10.61	40.35	69.32	8.46
TiO ₂				30.68	0.52
Total	100.00	100.02	100.01	100.00	99.99
Mineral Composition	Ca _{0.65} Na _{0.30} Al _{1.6} Si _{2.4} O ₈ (An ₆₈ -Ab ₃₂)	Ca _{0.63} Mg _{0.89} Fe _{0.33} Al _{0.14} Si _{1.84} Al _{0.16} O ₆	Mg _{1.03} Fe _{0.96} SiO ₄ (Fo ₅₂ -Fa ₄₈)	Fe ²⁺ (Fe ³⁺ ,Ti) ₂ O ₄	Na _{0.42} Mg _{4.61} Fe _{0.89} Al _{0.62} Si _{6.40} Al _{1.60} O ₂₀ (OH) ₄ (22 oxygen equivalents, ignoring H ₂ O)
Phase and ID	Plagioclase	Clinopyroxene (augite)	Mg-olivine (forsterite)	Oxide (titanomagnetite)	Smectite

Portion 7

Figure E.6.21. SEM pictures for EDS analysis of epoxy-mounted polished grains collected from **Portion 7**. Analysis points are marked in blue

Table E.6.14. SEM-EDS analysis results of grains in Figure E.6.21

Plg	Analysis Point	Na ₂ O	Al ₂ O ₃	SiO ₂	CaO					Total
	6	2.81	29.93	53.22	14.03					100.00
	7	4.11	25.53	59.36	11.00					100.00
	13	2.92	29.95	52.79	14.34					100.00
	16	4.47	28.92	53.91	12.70					100.00
	19	2.60	30.01	52.51	14.88					100.00
	21	3.26	29.95	52.26	14.53					100.00
average		3.36	29.05	54.01	13.58					100.00

Cpx	Analysis Point	MgO	Al ₂ O ₃	SiO ₂	CaO	FeO					Total
	4	14.68	2.53	52.84	18.11	11.85					100.00
	20	13.24	3.05	52.79	19.96	10.95					100.00
	22	13.41	3.00	51.64	17.92	14.02					100.00
	23	15.42	2.79	53.54	16.56	11.70					100.00
average		14.19	2.84	52.70	18.14	12.13					100.00

Ol	Analysis Point	MgO	SiO ₂	FeO						Total
	5	35.81	38.09	26.10						100.00

Ox	Analysis Point	TiO ₂	FeO							Total
	8	26.06	73.94							100.00
	9	26.04	73.96							100.00
average		26.05	73.95							100.00
	17	50.29	49.71							100.00

Smc	Analysis Point	Na ₂ O	MgO	Al ₂ O ₃	SiO ₂	K ₂ O	CaO	FeO	Total
	2	1.59	13.66	11.46	50.13	0.00	0.46	22.70	100.00
	11	1.86	12.06	10.77	48.43	0.00	0.00	26.88	100.00
	12	2.06	12.82	11.04	47.82	0.31	0.00	25.95	100.00
	14	1.80	5.10	6.12	70.58	0.00	0.00	16.39	99.99
	15	1.94	9.08	10.00	47.12	0.00	0.75	31.11	100.00
	24	2.28	12.11	10.15	48.67	0.83	0.00	25.05	99.09
	25	2.06	10.71	10.69	47.50	0.69	0.00	27.43	99.08
	26	2.22	11.45	10.72	48.08	0.51	0.00	27.02	100.00
	27	2.11	10.07	10.10	47.83	1.19	0.00	27.81	99.11
	28	1.80	11.87	10.69	48.74	0.99	0.00	25.92	100.01
	29	2.93	14.09	11.31	50.15	0.00	0.49	21.04	100.01
	30	1.76	13.12	11.09	49.41	0.62	0.00	23.99	99.99
	96	1.19	13.82	10.48	49.58	0.78	0.54	23.63	100.02
	97	0.70	13.33	10.65	49.85	0.45	1.03	23.99	100.00
	98	2.72	13.50	9.95	48.68	0.33	0.68	24.14	100.00
	99	2.17	15.09	10.95	49.45	0.32	0.63	21.39	100.00
	100	1.95	13.99	10.59	49.62	0.56	0.38	22.92	100.01
	101	1.07	14.44	11.17	49.91	0.25	0.86	22.30	100.00
	103	0.85	14.40	10.74	49.64	0.44	0.86	23.07	100.00
average		1.85	12.35	10.46	50.06	0.44	0.35	24.35	99.86
±σ		0.58	2.37	1.13	5.05	0.28	0.21	3.17	

Table E.6.15. Average mineral compositions from Table E.6.14

	average wt%	average wt%	average wt%	average wt%	point n°17 [Oxides wt% and elements mass % and atomic %]	average wt%
Oxides						
MgO		14.19	35.81		FeO (wt%) 49.71	12.35
Na ₂ O	3.36				TiO ₂ (wt%) 50.29	1.85
Al ₂ O ₃	29.05	2.84			Fe: (wt%) 38.64 - (at%) 21.13	10.46
SiO ₂	54.01	52.70	38.09		Ti: (wt%) 30.14 - (at%) 19.23	50.06
CaO	13.58	18.14			O: (wt%) 31.22 - (at%) 59.63	0.35
K ₂ O						0.44
FeO		12.13	26.10	73.95		24.35
TiO ₂				26.05		
Total	100.00	100.00	100.00	100.00		99.86
Miceral Composition	Ca _{0.67} Na _{0.30} Al _{1.57} Si _{2.47} O ₈ (An ₆₉ -Ab ₃₁)	Ca _{0.72} Mg _{0.79} Fe _{0.38} Al _{0.09} Si _{1.96} Al _{0.04} O ₆	Mg _{1.41} Fe _{0.58} SiO ₄ (Fo ₇₁ -Fa ₂₉)	Fe ²⁺ (Fe ³⁺ ,Ti) ₂ O ₄	Fe ²⁺ TiO ₃	Na _{0.49} Mg _{2.53} Fe _{2.80} Al _{0.59} Si _{6.89} Al _{1.11} O ₂₀ (OH) ₄ (on the basis of 22 oxygen equivalents, ignoring H ₂ O)
Phase and ID	Plagioclase	Clinopyroxene (augite)	Mg-olivine (forsterite)	Oxide (titanomagnetite)	Oxide (ilmenite?)	Smectite

6.2. Results

6.2.2. BSW2: Basalt-seawater experiment at 350°C/488 bar

Table E.6.16. Major ions compositions and complete experimental parameters (n° of samples collected, T, P, experimental time, flow rate and pH) for the BSW2 at 350°C / 488 bar. *In situ* pH is the calculated pH at temperature. Analysis of major ions are reported both in mg kg⁻¹ and in mmol kg⁻¹. In orange are effluents at 10 ml hr⁻¹ flow rate. In pink symbols are effluents at 5 ml hr⁻¹ flow rate and in blue are effluents at 2.5 ml hr⁻¹ flow rate. Data of H₂S are also reported in μmol kg⁻¹

							mg kg ⁻¹													mmol kg ⁻¹													
n° sample	T (°C)	P (bar)	time (hrs)	flow-rate (ml·hr ⁻¹)	pH (room T)	pH (350°C)	As	B	Ca	Fe	K	Mg	Na	SiO ₂	Al	Li	H ₂ S	Cl ⁻	SO ₄ ²⁻	HCO ₃ ⁻	As	B	Ca	Fe	K	Mg	Na	SiO ₂	Al	Li	H ₂ S	Cl ⁻	SO ₄ ²⁻
blank water (distilled)	20.1	1	-	-	7.10	n.c.	< 0.015	0.7	< 0.05	< 0.08	2.4	< 0.01	4.2	0.5	< 0.15	0.006	n.a.	5.5	0.2	n.a.	< 0.0002	0.06	< 0.001	< 0.001	0.06	< 0.0004	0.2	0.01	< 0.006	0.01	n.a.	0.2	0.004
Output seawater from SW2	20.1	1	0.0	-	8.20	5.70	-	-	-	-	-	-	-	-	-	-	-	-	-	n.a.	< 0.0002	0.01	1.4	1.7	8.5	22.8	363.3	0.2	< 0.006	0.02	< 0.0003	429.9	2.7
1	352.4	487.5	18.5	1	5.15	6.61	0.004	0.7	< 0.05	< 0.08	33.8	< 0.01	69.5	1928.4	13.5	0.2	1.3	31.3	23.3	n.a.	< 0.0002	0.07	< 0.001	0.04	0.9	< 0.0004	3	32.1	0.5	0.03	< 0.0003	0.9	0.2
2	350.7	487.4	48.2	1	3.97	5.78	< 0.015	1.2	3.2	< 0.08	780	< 0.01	2253.1	2041.8	< 0.15	1.1	2.4	4217.2	6.1	n.a.	< 0.0002	0.1	0.08	< 0.001	20	< 0.0004	98	34	< 0.006	0.2	0.07	119	0.06
3	350.5	487.5	74.6	1	3.81	5.38	< 0.015	2.3	400.9	< 0.08	364.9	< 0.01	5390.3	2010.6	< 0.15	0.3	0.2	9614.5	5.4	n.a.	< 0.0002	0.2	10	< 0.001	9.3	< 0.0004	234.5	33.5	< 0.006	0.04	0.01	271.2	0.06
4	350.2	487.4	97.8	1	3.71	5.35	< 0.015	2.6	712.7	< 0.08	291.7	0.7	6927.6	2092.9	< 0.15	0.2	0.7	12248.1	9.4	n.a.	< 0.0002	0.2	17.8	< 0.001	7.5	0.03	301.3	34.8	< 0.006	0.04	0.02	345.5	0.1
5	350.7	487.0	119.8	1	3.73	5.31	< 0.015	2.9	814.5	< 0.08	313.6	1	7664.8	2082.3	< 0.15	0.3	0.5	13274	6.6	n.a.	< 0.0002	0.3	20.3	< 0.001	8	0.04	333.4	34.7	< 0.006	0.04	0.01	374.4	0.07
6	350.6	487.0	121.3	10	3.11	5.26	< 0.015	2.9	534.7	257.2	329.7	70	8297.2	2282.9	< 0.15	0.2	n.a.	14240	17	n.a.	< 0.0002	0.3	13.3	4.6	8.4	2.9	360.9	38	< 0.006	0.03	n.a.	401.7	0.2
7	350.8	487.1	123.3	10	3.23	5.22	< 0.015	3.1	467.2	295	335.4	115.1	8511.6	2361.3	< 0.15	0.2	n.a.	14592.3	22	n.a.	< 0.0003	0.3	11.7	5.3	8.6	4.7	360.9	39.3	< 0.006	0.03	n.a.	411.6	0.2
8	350.5	487.1	125.3	10	3.36	5.23	< 0.015	3.4	531.9	325.5	365.3	111.8	9168.5	2501.6	< 0.15	0.2	n.a.	14745.7	21.6	n.a.	< 0.0004	0.3	13.3	5.8	9.3	4.6	370.2	41.6	< 0.006	0.03	n.a.	416	0.2
9	350.3	486.9	127.3	10	3.47	5.28	< 0.015	6.1	512.8	274.2	328.4	85.1	8248.9	2261.1	< 0.15	0.2	< 0.01	14722.2	22.6	n.a.	< 0.0005	0.6	12.8	4.9	8.4	3.5	398.8	37.6	< 0.006	0.03	< 0.0003	415.3	0.2
10	350.5	487.0	143.3	10	4.05	5.28	< 0.015	4.8	629.5	202	321	42.4	8162.6	2036.8	< 0.15	0.2	n.a.	n.a.	12.1	n.a.	< 0.0006	0.4	15.7	3.6	8.2	1.7	358.8	33.9	< 0.006	0.03	n.a.	n.a.	0.1
11	350.6	487.0	145.3	10	3.98	5.29	< 0.015	4.2	719.4	150.1	326.7	25.3	8372.4	1840.7	< 0.15	0.3	n.a.	14556.7	10.6	n.a.	< 0.0007	0.4	18	2.7	8.4	1	355	30.6	< 0.006	0.04	n.a.	410.6	0.1
12	350.4	486.9	147.3	10	4.01	5.31	< 0.015	4	724.9	153.2	327	24.9	8413.9	1806.8	< 0.15	0.2	n.a.	n.a.	12.3	n.a.	< 0.0008	0.4	18.1	2.7	8.4	1	364.2	30.1	< 0.006	0.03	n.a.	n.a.	0.1
13	350.3	486.9	149.3	10	4.01	5.30	< 0.015	3.5	737	152.2	323.9	24.4	8491.1	1783.9	< 0.15	0.2	n.a.	14614.3	10.4	n.a.	< 0.0009	0.3	18.4	2.7	8.3	1	366	29.7	< 0.006	0.03	n.a.	412.3	0.1
14	350.7	486.9	151.1	10	4.05	5.30	< 0.015	3.4	736.6	147.6	322.4	23.4	8415.4	1740.4	< 0.15	0.2	< 0.01	14569.1	9.6	n.a.	< 0.0010	0.3	18.4	2.6	8.2	1	369.3	29	< 0.006	0.03	< 0.0003	411	0.1
15	350.7	486.9	167.3	10	4.11	5.28	< 0.015	6.2	745.6	158.1	348.2	24.8	8517.3	1701.2	< 0.15	0.2	n.a.	14621.3	9.1	83	< 0.0011	0.6	18.6	2.8	8.9	1	366	28.3	< 0.006	0.02	n.a.	412.4	0.09
16	350.8	486.9	169.3	5	4.17	5.30	< 0.015	5.3	755.8	120.2	339.9	20.1	8373.7	1613.2	0.2	0.2	n.a.	n.a.	9.1	n.a.	< 0.0002	0.5	18.9	2.2	8.7	0.8	370.5	26.9	0.006	0.03	n.a.	n.a.	0.1
17	350.4	486.9	171.3	5	4.17	5.29	< 0.015	5	836.4	56.6	341.8	14	8415.9	1659	< 0.15	0.2	n.a.	14802	8.1	n.a.	< 0.0002	0.5	20.9	1	8.7	0.6	364.2	27.6	< 0.006	0.03	n.a.	417.5	0.08
18	350.7	487.0	173.3	5	4.24	5.29	< 0.015	4.6	872.9	19.3	338.8	10.3	8374.1	1628.7	0.2	0.2	n.a.	14588.8	7.3	n.a.	< 0.0002	0.4	21.8	0.3	8.7	0.4	366.1	27.1	< 0.006	0.03	n.a.	411.5	0.08
19	350.4	486.9	175.3	5	4.26	5.30	< 0.015	4.4	889.4	0.06	345.1	8.2	8457.4	1628.1	< 0.15	0.2	< 0.01	14543.4	8.3	n.a.	< 0.0002	0.4	22.2	0.001	8.8	0.3	364.2	27.1	< 0.006	0.03	< 0.0003	410.3	0.09
20	350.7	487.4	190.8	5	4.26	5.27	< 0.015	4.3	870.5	22.7	344.2	9.9	8526.1	1654.6	< 0.15	0.2	n.a.	15849.6	4.5	24	< 0.0002	0.4	21.7	0.4	8.8	0.4	367.9	27.5	0.002	0.03	n.a.	447.1	0.05
21	350.2	486.8	199.0	2.5	4.26	5.29	0.022	6.6	905.1	< 0.08	340.2	5.9	8531.5	1555.5	0.3	0.2	0.09	15077.1	6.5	n.a.	< 0.0002	0.6	22.6	< 0.001	8.7	0.2	370.9	25.9	0.011	0.04	0.003	425.3	0.07
22	350.6	487.0	215.3	2.5	4.22	5.30	< 0.015	5.7	929.8	< 0.08	331.1	5	8457.6	1530.3	0.2	0.2	n.a.	15047.9	7.5	n.a.	< 0.0002	0.5	23.2	< 0.001	8.5	0.2	371.1	25.5	0.006	0.03	n.a.	424.5	0.08
23	350.9	487.1	222.3	2.5	4.24	5.30	0.013	5.5	912.1	< 0.08	333.9	5.2	8552.4	1550	< 0.15	0.2	0.08	15053.1	7.5	n.a.	< 0.0002	0.5	22.8	< 0.001	8.5	0.2	367.9	25.8	< 0.006	0.03	0.002	424.6	0.08
24	350.7	487.1	240.8	2.5	4.21	5.29	< 0.015	5.3	898.6	< 0.08	331.7	6.3	8559.2	1604.1	0.5	0.2	n.a.	15224.4	6.7	27	< 0.0002	0.5	22.4	< 0.001	8.5	0.3	372	26.7	0.02	0.03	n.a.	429.5	0.07
25	350.5	487.2	264.3	2.5	4.31	5.29	0.016	5.1	886.1	10.8	337	8.1	8701.7	1538.8	0.2	0.2	< 0.01	15189.7	6.6	n.a.	< 0.0002	0.5	22.1	0.2	8.6	0.3	372.3	25.6	0.007	0.03	< 0.0003	428.5	0.07
26	350.6	487.1	288.4	1	4.27	5.30	< 0.015	4.7	883.3	< 0.08	330.4	5.6	8603.2	1494.5	< 0.15	0.2	0.05	15333.6	6.6	n.a.	< 0.0002	0.4	22	< 0.001	8.4	0.2	378.5	24.9	< 0.006	0.03	0.001	432.5	0.07
27	350.8	486.9	311.0	1	4.36	5.29	< 0.015	4.7	929.1	< 0.08	329.4	4.2	8598.3	1440.6	< 0.15	0.2	n.a.	15262.4	6.2	n.a.	< 0.0002	0.4	23.2	< 0.001	8.4	0.2	374.2	24	< 0.006	0.03	n.a.	430.5	0.06

Table E.6.17. Trace elements compositions and complete experimental parameters (n° of samples collected, T, P, experimental time, flow rate and pH) for the BSW2 at 350°C / 488 bar. *In situ* pH is the calculated pH at temperature. Analysis of major ions are reported in µmol kg⁻¹. In orange are effluents at 10 ml hr⁻¹ flow rate. In pink symbols are effluents at 5 ml hr⁻¹ flow rate and in blue are effluents at 2.5 ml hr⁻¹ flow rate. Data of Mn are reported mg kg⁻¹ and in mmol kg⁻¹

							µg kg ⁻¹											mg kg ⁻¹	µmol kg ⁻¹											mmol kg ⁻¹
n° sample	T (°C)	P (bar)	time (hrs)	flow-rate (ml·hr ⁻¹)	pH (room T)	pH (350°C)	V	Cr	Co	Cu	Zn	Rb	Ag	Cd	Ba	Au	Pb	Mn	V	Cr	Co	Cu	Zn	Rb	Ag	Cd	Ba	Au	Pb	Mn
blank water (distilled)	20.1	1	-	-	7.10	n.c.	<0.1	<0.2	<0.05	<0.06	<0.5	<0.1	<0.05	<0.1	<0.2	<0.2	<0.2	<0.007	<0.002	<0.004	<0.002	<0.0009	<0.008	<0.001	<0.0005	<0.0009	<0.001	<0.001	<0.001	<0.0001
Output seawater from SW2	20.1	1	0.0	-	8.20	5.70	-	-	-	-	-	-	-	-	-	-	-	-	0.3	0.4	14.8	9.7	4.4	1	<0.0005	0.06	0.1	0.03	0.02	0.03
1	352.4	487.5	18.5	1	5.15	6.61	9.5	<0.2	<0.05	<0.06	<0.5	45.3	0.7	1	<0.2	92.6	<0.2	0.02	0.2	<0.004	<0.002	<0.0009	<0.008	0.5	0.006	0.009	<0.001	0.5	<0.001	<0.0001
2	350.7	487.4	48.2	1	3.97	5.78	1.8	<0.2	<0.05	<0.06	<0.5	1791.8	0.4	<0.1	<0.2	374.8	<0.2	<0.007	0.04	<0.004	<0.002	<0.0009	<0.008	21.4	0.004	0.000	<0.001	1.9	<0.001	<0.0001
3	350.5	487.5	74.6	1	3.81	5.38	<0.1	<0.2	<0.05	<0.06	534.7	785.1	<0.05	<0.1	2518.1	356.4	<0.2	5.2	<0.002	<0.004	<0.002	<0.0009	8.18	9.8	0.003	<0.0009	18.3	1.8	<0.001	0.1
4	350.2	487.4	97.8	1	3.71	5.35	<0.1	<0.2	<0.05	<0.06	<0.5	115.3	<0.05	1.9	4320.3	211	<0.2	15	<0.002	<0.004	<0.002	<0.0009	<0.008	2.1	0.003	0.02	31.5	1.1	<0.001	0.3
5	350.7	487.0	119.8	1	3.73	5.31	<0.1	<0.2	<0.05	<0.06	755.6	51.4	<0.05	2.6	3532.4	147.4	2.7	18.4	<0.002	<0.004	<0.002	<0.0009	11.6	1.4	<0.0005	0.02	25.7	0.7	0.01	0.3
6	350.6	487.0	121.3	10	3.11	5.26	<0.1	<0.2	<0.05	<0.06	11130.7	18.4	<0.05	0.7	1602.3	107.7	28.4	31.3	<0.002	<0.004	<0.002	<0.0009	170.2	1	0.001	0.006	11.7	0.5	0.14	0.6
7	350.8	487.1	123.3	10	3.23	5.22	<0.1	<0.2	<0.05	178.5	2524.4	15.5	0.06	<0.1	1453.6	75.2	<0.2	21.3	<0.002	<0.004	<0.002	2.8	38.6	1	0.001	<0.0009	10.6	0.4	<0.001	0.4
8	350.5	487.1	125.3	10	3.36	5.23	<0.1	<0.2	<0.05	<0.06	3101.5	16.4	0.3	<0.1	1525.7	54.6	<0.2	23.3	<0.002	<0.004	<0.002	<0.0009	47.4	1	0.003	0.001	11.1	0.3	<0.001	0.4
9	350.3	486.9	127.3	10	3.47	5.28	<0.1	<0.2	<0.05	<0.06	2647.4	20	<0.05	0.4	1399.6	30.8	<0.2	21.3	<0.002	<0.004	<0.002	<0.0009	40.5	1.1	<0.0005	0.003	10.2	0.2	<0.001	0.4
10	350.5	487.0	143.3	10	4.05	5.28	<0.1	<0.2	<0.05	2199.6	2004.3	19.5	0.4	0.9	1348.9	45.8	216.5	23.2	<0.002	<0.004	<0.002	34.6	30.7	1.1	0.003	0.008	9.8	0.2	1	0.4
11	350.6	487.0	145.3	10	3.98	5.29	<0.1	<0.2	<0.05	<0.06	1869.1	16.5	<0.05	<0.1	1028.4	25.7	<0.2	24.2	<0.002	<0.004	<0.002	<0.0009	28.6	1	0.001	0.003	7.5	0.1	<0.001	0.4
12	350.4	486.9	147.3	10	4.01	5.31	<0.1	<0.2	<0.05	<0.06	1970.8	16.9	<0.05	1	865.7	33.6	1.7	24	<0.002	<0.004	<0.002	<0.0009	30.1	1	0.001	0.009	6.3	0.2	0.008	0.4
13	350.3	486.9	149.3	10	4.01	5.30	<0.1	<0.2	<0.05	<0.06	630.6	17.2	<0.05	<0.1	729.6	23.1	<0.2	24.1	<0.002	<0.004	<0.002	<0.0009	9.6	1	0.001	<0.0009	5.3	0.1	<0.001	0.4
14	350.7	486.9	151.1	10	4.05	5.30	<0.1	<0.2	<0.05	<0.06	642.1	17.5	<0.05	<0.1	699.6	22.9	<0.2	23.7	<0.002	<0.004	<0.002	<0.0009	9.8	1	0.001	<0.0009	5.1	0.1	<0.001	0.4
15	350.7	486.9	167.3	10	4.11	5.28	<0.1	<0.2	<0.05	406.5	1206	14.3	<0.05	2.7	491.7	17.4	32.8	23.2	<0.002	<0.004	<0.002	6.4	18.4	1	0.001	0.02	3.6	0.09	0.2	0.4
16	350.8	486.9	169.3	5	4.17	5.30	<0.1	<0.2	<0.05	<0.06	962.7	15.1	<0.05	<0.1	435	24.3	<0.2	22.8	<0.002	<0.004	<0.002	<0.0009	14.7	1	0.001	<0.0009	3.2	0.1	<0.001	0.4
17	350.4	486.9	171.3	5	4.17	5.29	<0.1	<0.2	<0.05	<0.06	4686.6	16	<0.05	<0.1	471.3	21.2	<0.2	27	<0.002	<0.004	<0.002	<0.0009	71.7	1	0.001	<0.0009	3.4	0.1	<0.001	0.5
18	350.7	487.0	173.3	5	4.24	5.29	<0.1	<0.2	<0.05	<0.06	6542.9	15.8	<0.05	<0.1	479	16.5	<0.2	23.7	<0.002	<0.004	<0.002	<0.0009	100.1	1	0.001	<0.0009	3.5	0.08	<0.001	0.4
19	350.4	486.9	175.3	5	4.26	5.30	<0.1	<0.2	<0.05	<0.06	4941.6	17.1	<0.05	2.9	428.5	17.2	<0.2	22.6	<0.002	<0.004	<0.002	<0.0009	75.6	1	0.001	0.03	3.1	0.09	<0.001	0.4
20	350.7	487.4	190.8	5	4.26	5.27	<0.1	<0.2	<0.05	228.4	1579.1	8.2	<0.05	0.02	362.6	13.6	69.1	25.4	<0.002	<0.004	<0.002	3.6	24.1	0.9	0.001	<0.0009	2.6	0.07	0.3	0.5
21	350.2	486.8	199.0	2.5	4.26	5.29	<0.1	<0.2	<0.05	<0.06	4938.3	14.3	<0.05	<0.1	375.7	12.5	33.7	17.1	<0.002	<0.004	<0.002	<0.0009	75.5	1	0.001	0.002	2.7	0.06	0.2	0.3
22	350.6	487.0	215.3	2.5	4.22	5.30	<0.1	<0.2	<0.05	<0.06	5947	13.5	<0.05	<0.1	334.4	10.8	0.45	21.4	<0.002	<0.004	<0.002	<0.0009	90.9	1	0.001	0.003	2.4	0.06	0.002	0.4
23	350.9	487.1	222.3	2.5	4.24	5.30	<0.1	<0.2	<0.05	<0.06	2730.6	14.4	<0.05	<0.1	303.1	10.6	<0.2	24.5	<0.002	<0.004	<0.002	<0.0009	41.8	1	0.001	<0.0009	2.2	0.05	<0.001	0.4
24	350.7	487.1	240.8	2.5	4.21	5.29	<0.1	<0.2	<0.05	<0.06	5111.2	13.2	<0.05	<0.1	266.6	12	1.6	27.3	<0.002	<0.004	<0.002	<0.0009	78.2	1	0.001	<0.0009	1.9	0.06	0.008	0.5
25	350.5	487.2	264.3	2.5	4.31	5.29	<0.1	<0.2	<0.05	50.2	1985.9	14.2	<0.05	1.3	230.4	10.4	53.8	26.2	<0.002	<0.004	<0.002	0.8	30.4	1	0.001	0.01	1.7	0.05	0.3	0.5
26	350.6	487.1	288.4	1	4.27	5.30	<0.1	<0.2	<0.05	<0.06	2433.9	13.3	<0.05	2	222.5	10.1	<0.2	17.7	<0.002	<0.004	<0.002	<0.0009	37.2	1	0.001	0.02	1.6	0.05	<0.001	0.3
27	350.8	486.9	311.0	1	4.36	5.29	<0.1	<0.2	<0.05	<0.06	4089.2	11.7	<0.05	<0.1	240.1	8	28.7	17.4	<0.002	<0.004	<0.002	<0.0009	62.5	1	0.001	<0.0009	1.7	0.04	0.1	0.3

Figure E.6.24. XRD scan showing the mineralogy of Portion 4-5

Report Number: PSR2017/68a_2017103103
Report Date: 7/11/2017

Confidential 2017

Sample Identification: BSW2 - Portion 4-5 Laboratory Reference No: 2017007541

Figure E.6.25. Qualitative XRD analysis of Portion 1, 2-3 and 4-5

Report Number: PSR2017/68a_2017103103
Report Date: 7/11/2017

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Sample Composition

Table 1. Mineralogical Composition of BSW2 Samples

	Mineralogical Composition		
	Portion 1	Portion 2-3	Portion 4-5
	2017007537	2017007539	2017007541
Chlorite	X	X	X
Plagioclase	X	X	X
Magnetite	X		
Anhydrite	X		
Ankerite			X
Augite/ CPX		X	X

Figure E.6.26. XRF analysis of Portion 1

Report Number: PSR2017/88b_2017103103
Report Date: 10/11/2017

Confidential 2017

Sample Identification: BSW2 - Portion 1 Laboratory Reference No:2017007538

X-ray fluorescence
SPECTRA^{plus}
Multi-element Analysis

CLIENT : GNS SCIENCE - WAIRAKEI
PROJECT : SA19938
DATE : 10/11/2017
SAMPLE : SAMPLE #2, LAB#2017007538, Portion 1
COMMENTS : 100% - Total = sum of unmeasured elements (i.e H, B, C, N, O)
:
:

Carbon	C	–	Zinc	Zn	0.005	Iodine	I	nd
Fluorine	F	nd	Gallium	Ga	nd	Caesium	Cs	nd
Sodium	Na	0.310	Germanium	Ge	nd	Barium	Ba	nd
Magnesium	Mg	13.6	Arsenic	As	nd	Lanthanum	La	nd
Aluminium	Al	7.23	Selenium	Se	nd	Cerium	Ce	–
Silicon	Si	16.3	Bromine	Br	nd	Hafnium	Hf	–
Phosphorus	P	0.056	Rubidium	Rb	nd	Tantalum	Ta	nd
Sulphur	S	1.99	Strontium	Sr	0.016	Tungsten	W	nd
Chlorine	Cl	0.046	Yttrium	Y	nd	Rhenium	Re	–
Potassium	K	0.022	Zirconium	Zr	0.007	Osmium	Os	–
Calcium	Ca	4.29	Niobium	Nb	nd	Iridium	Ir	–
Scandium	Sc	nd	Molybdenum	Mo	nd	Platinum	Pt	–
Titanium	Ti	1.08	Rhodium	Rh	–	Gold	Au	–
Vanadium	V	0.035	Palladium	Pd	–	Mercury	Hg	nd
Chromium	Cr	0.012	Silver	Ag	–	Thallium	Tl	nd
Manganese	Mn	0.026	Cadmium	Cd	nd	Lead	Pb	nd
Iron	Fe	6.35	Indium	In	–	Bismuth	Bi	nd
Cobalt	Co	0.011	Tin	Sn	nd	Thorium	Th	nd
Nickel	Ni	0.287	Antimony	Sb	nd	Uranium	U	nd
Copper	Cu	0.006	Tellurium	Te	–	Total		51.7

Values are weight %

nd = not detected

– = not measured

Figure E.6.27. XRF analysis of Portion 2-3

Report Number: PSR2017/88b_2017103103
Report Date: 10/11/2017

Confidential 2017

Sample Identification: BSW2 – Portion 2-3 Laboratory Reference No:2017007540

X-ray fluorescence
SPECTRA^{plus}
Multi-element Analysis

CLIENT : GNS SCIENCE - WAIRAKEI
PROJECT : SA19938
DATE : 10/11/2017
SAMPLE : SAMPLE #3, LAB#2017007540, Portion 2-3
COMMENTS : 100% - Total = sum of unmeasured elements (i.e H, B, C, N, O)
:
:

Carbon	C	–	Zinc	Zn	nd	Iodine	I	nd
Fluorine	F	nd	Gallium	Ga	nd	Caesium	Cs	nd
Sodium	Na	1.02	Germanium	Ge	nd	Barium	Ba	nd
Magnesium	Mg	10.3	Arsenic	As	nd	Lanthanum	La	nd
Aluminium	Al	7.20	Selenium	Se	nd	Cerium	Ce	–
Silicon	Si	20.3	Bromine	Br	nd	Hafnium	Hf	–
Phosphorus	P	0.075	Rubidium	Rb	nd	Tantalum	Ta	nd
Sulphur	S	0.533	Strontium	Sr	0.010	Tungsten	W	nd
Chlorine	Cl	0.077	Yttrium	Y	nd	Rhenium	Re	–
Potassium	K	0.044	Zirconium	Zr	0.008	Osmium	Os	–
Calcium	Ca	3.65	Niobium	Nb	nd	Iridium	Ir	–
Scandium	Sc	nd	Molybdenum	Mo	nd	Platinum	Pt	–
Titanium	Ti	0.953	Rhodium	Rh	–	Gold	Au	–
Vanadium	V	0.039	Palladium	Pd	–	Mercury	Hg	nd
Chromium	Cr	0.015	Silver	Ag	–	Thallium	Tl	nd
Manganese	Mn	0.031	Cadmium	Cd	nd	Lead	Pb	nd
Iron	Fe	8.00	Indium	In	–	Bismuth	Bi	nd
Cobalt	Co	0.013	Tin	Sn	nd	Thorium	Th	nd
Nickel	Ni	0.013	Antimony	Sb	nd	Uranium	U	nd
Copper	Cu	0.007	Tellurium	Te	–	Total		52.3

Values are weight %

nd = not detected

– = not measured

Figure E.6.28. XRF analysis of Portion 4-5

Report Number: PSR2017/88b_2017103103
Report Date: 10/11/2017

Confidential 2017

Sample Identification: BSW2 – Portion 4-5

Laboratory Reference No:2017007542

X-ray fluorescence
SPECTRA^{plus}
Multi-element Analysis

CLIENT : GNS SCIENCE - WAIRAKEI		
PROJECT : SA19938		
DATE : 10/11/2017		
SAMPLE : SAMPLE #4, LAB#2017007542, Portion 4-5		
COMMENTS : 100% - Total = sum of unmeasured elements (i.e H, B, C, N, O)		
:		
:		
Carbon	C	–
Fluorine	F	nd
Sodium	Na	1.75
Magnesium	Mg	3.82
Aluminium	Al	8.11
Silicon	Si	21.2
Phosphorus	P	0.078
Sulphur	S	0.012
Chlorine	Cl	0.025
Potassium	K	0.050
Calcium	Ca	7.48
Scandium	Sc	nd
Titanium	Ti	0.861
Vanadium	V	0.031
Chromium	Cr	0.007
Manganese	Mn	0.107
Iron	Fe	8.73
Cobalt	Co	0.013
Nickel	Ni	0.008
Copper	Cu	nd
Zinc	Zn	0.008
Gallium	Ga	nd
Germanium	Ge	nd
Arsenic	As	nd
Selenium	Se	nd
Bromine	Br	nd
Rubidium	Rb	nd
Strontium	Sr	0.011
Yttrium	Y	0.003
Zirconium	Zr	0.007
Niobium	Nb	nd
Molybdenum	Mo	nd
Rhodium	Rh	–
Palladium	Pd	–
Silver	Ag	–
Cadmium	Cd	nd
Indium	In	–
Tin	Sn	nd
Antimony	Sb	nd
Tellurium	Te	–
Iodine	I	nd
Caesium	Cs	nd
Barium	Ba	nd
Lanthanum	La	nd
Cerium	Ce	–
Hafnium	Hf	–
Tantalum	Ta	nd
Tungsten	W	nd
Rhenium	Re	–
Osmium	Os	–
Iridium	Ir	–
Platinum	Pt	–
Gold	Au	–
Mercury	Hg	nd
Thallium	Tl	nd
Lead	Pb	nd
Bismuth	Bi	nd
Thorium	Th	nd
Uranium	U	nd
Total		52.3

Values are weight %

nd = not detected

– = not measured

Portion 1

Figure E.6.29. SEM pictures for EDS analysis of epoxy-mounted polished grains collected from **Portion 1**. Analysis points are marked in blue

Table E.6.18. SEM-EDS analysis results of grains in Figure E.6.29

Plg	Analysis Point	Na ₂ O	Al ₂ O ₃	SiO ₂	CaO	Total		Chl	Analysis Point	MgO	Al ₂ O ₃	SiO ₂	FeO	Total
	1	2.98	30.91	52.99	13.12	100.00			4	32.15	12.06	47.88	7.91	100.00
	14	3.57	30.64	54.27	11.52	100.00			5	34.35	16.14	43.77	5.73	100.00
	16	2.62	32.08	52.20	13.09	100.00			6	35.12	11.95	46.77	6.17	100.00
	28	3.52	30.48	54.69	11.31	100.00			7	31.92	15.82	43.38	8.88	100.00
	42	3.20	30.77	53.76	12.27	100.00			9	32.93	17.72	43.92	5.43	100.00
average		3.18	30.98	53.58	12.26	100.00			10	32.85	13.90	45.50	7.75	100.00
									11	34.36	11.69	47.80	6.16	100.00
Cpx	Analysis Point	MgO	Al ₂ O ₃	SiO ₂	CaO	FeO	Total		12	34.53	14.90	45.02	5.54	100.00
	15	16.36	2.82	55.55	17.15	8.12	100.00		13	32.25	16.13	43.93	7.68	100.00
									17	30.98	14.89	45.01	9.12	100.00
									18	34.34	12.34	48.56	4.75	100.00
									19	33.78	15.53	45.15	5.54	100.00
Ol	Analysis Point	MgO	SiO ₂	FeO	Total				20	33.00	15.43	44.60	6.97	100.00
	2	21.62	38.34	40.03	100.00				21	26.29	32.56	34.43	6.71	100.00
									22	34.29	14.28	44.70	6.73	100.00
									23	33.61	14.30	45.71	6.38	100.00
									24	32.64	14.62	45.10	7.64	100.00
Ox	Analysis Point	TiO ₂	FeO	Total					30	27.67	20.27	42.37	9.70	100.00
	3	29.93	70.07	100.00					31	26.02	18.20	37.98	17.79	100.00
	8	31.46	68.54	100.00					32	34.87	13.44	47.10	4.59	100.00
	26	29.02	70.98	100.00					33	29.97	16.83	42.67	10.54	100.00
	29	29.53	70.47	100.00					34	35.31	14.04	45.20	5.44	100.00
	43	15.45	84.55	100.00					35	28.30	34.30	34.32	3.07	100.00
average		27.08	72.92	100.00					36	27.96	19.07	41.76	11.22	100.00
									37	32.49	19.59	41.97	5.95	100.00
									38	27.82	17.43	41.94	12.81	100.00
Anh	Analysis Point	SO ₃	CaO	Total					39	30.69	16.67	43.05	9.58	100.00
	25	57.04	42.96	100.00					40	40.22	10.40	45.72	3.67	100.00
	27	56.63	43.37	100.00					41	29.07	17.80	41.81	11.32	100.00
	44	55.96	44.04	100.00					45	30.45	16.40	42.70	10.45	100.00
average		56.54	43.46	100.00					46	31.26	15.74	43.69	9.31	100.00
									47	31.86	15.50	43.71	8.92	100.00
									48	30.32	17.68	42.14	9.87	100.00
									49	30.47	16.43	42.50	10.60	100.00
									50	28.80	17.88	41.57	11.76	100.00
									51	30.80	15.55	44.02	9.62	100.00
									52	30.59	19.26	42.89	7.27	100.00
									53	30.17	17.38	41.48	10.97	100.00
									54	27.61	31.43	36.32	4.64	100.00
									55	32.72	15.34	43.49	8.45	100.00
									56	27.23	21.85	42.83	8.08	100.00
									57	33.91	6.10	56.48	3.51	100.00
								average		31.57	16.88	43.59	7.96	100.00

Table E.6.19. Average mineral compositions from Table E.6.18

	average wt%	average wt%	average wt%	average wt%	average wt%	average wt%
Oxides						
MgO		16.36	21.62		31.57	
Na ₂ O	3.18					
Al ₂ O ₃	30.98	2.82			16.88	
SiO ₂	53.58	55.55	38.34		43.59	43.46
CaO	12.26	17.15				
FeO		8.12	40.03	72.92	7.96	
TiO ₂				27.08		
SO ₃						56.64
Total	100.00	100.00	99.99	100.00	100.00	100.10
Mineral Composition	Ca _{0.60} Na _{0.28} Al _{1.67} Si _{2.45} O ₈ (An ₆₈ -Ab ₃₂)	Ca _{0.67} Mg _{0.88} Fe _{0.25} Al _{0.12} Si _{2.01} O ₆	Mg _{0.93} Fe _{0.97} Si _{1.1} O ₄ (Fo ₄₉ -Fa ₅₁)	Fe ²⁺ (Fe ³⁺ ,Ti) ₂ O ₄	Mg _{7.72} Fe _{1.09} Al _{3.17} Si _{7.15} Al _{0.85} O ₂₀ (OH) ₁₆ (on the basis of 28 oxygen equivalents, ignoring H ₂ O)	Ca(SO ₄)
Phase and ID	Plagioclase	Clinopyroxene (augite)	Fe-olivine (fayalite)	Oxide (titanomagnetite)	Chlorite	Sulfate (anhydrite)

Portion 2-3

Figure E.6.30. SEM pictures for EDS analysis of epoxy-mounted polished grains collected from **Portion 2-3**. Analysis points are marked in blue

Table E.6.20. SEM-EDS analysis results of grains in Figure E.6.30

Plg	Analysis Point	Na ₂ O	Al ₂ O ₃	SiO ₂	CaO	Total
	14	2.72	30.59	52.23	14.46	100.00
	15	2.73	30.14	51.67	15.45	99.99
	16	3.20	30.49	52.71	13.60	100.00
	17	2.36	31.14	51.93	14.57	100.00
average		2.75	30.59	52.14	14.52	100.00

Chl	Analysis Point	MgO	Al ₂ O ₃	SiO ₂	FeO	TiO ₂	Total
	39	28.22	17.31	43.58	10.89	0.00	100.00
	40	25.91	17.78	42.29	14.02	0.00	100.00
	41	27.12	18.00	43.32	11.56	0.00	100.00
	42	31.51	19.25	41.72	7.51	0.00	100.00
	43	29.65	17.82	43.73	8.80	0.00	100.00
	44	29.16	17.43	43.95	9.46	0.00	100.00
	45	31.01	18.31	43.89	6.78	0.00	100.00
	47	25.75	24.08	38.27	11.90	0.00	100.00
	48	31.09	19.48	41.49	7.93	0.00	100.00
	49	30.06	19.47	41.78	8.69	0.00	100.00
	50	29.35	21.37	41.16	8.12	0.00	100.00
	51	29.60	18.46	42.63	9.30	0.00	100.00
	52	26.53	17.12	41.76	14.58	0.00	100.00
	53	28.13	19.25	41.59	11.03	0.00	100.00
	54	26.74	17.30	38.27	14.98	2.72	100.00
	55	27.98	19.95	40.71	11.36	0.00	100.00
	56	26.72	11.78	49.14	8.01	4.35	100.00
average		28.50	18.48	42.31	10.29	0.42	100.00

Smc	Analysis Point	Na ₂ O	MgO	Al ₂ O ₃	SiO ₂	K ₂ O	CaO	TiO ₂	FeO	Total
	2	0.82	22.52	12.46	52.68	0.00	0.00	0.00	11.52	100.00
	3	1.00	21.64	12.82	49.87	0.51	0.00	0.00	14.16	100.00
	4	1.19	21.76	12.22	53.67	0.73	0.00	0.00	10.43	100.00
	5	0.42	21.68	11.92	53.39	0.00	0.00	0.00	12.59	100.00
	23	0.78	20.21	11.49	52.64	0.00	0.00	0.00	14.87	100.00
	24	0.67	21.45	13.07	52.87	0.00	0.00	0.00	11.94	100.00
	25	0.44	22.92	11.76	52.77	0.00	0.00	0.00	12.10	100.00
	26	0.64	20.86	11.84	53.62	0.00	0.00	0.00	13.04	100.00
	27	0.66	22.81	12.34	53.21	0.00	0.00	0.00	10.98	100.00
	28	0.57	22.19	10.41	56.03	0.00	0.00	0.00	10.80	100.00
	29	0.67	24.11	10.59	55.27	0.00	0.40	0.00	8.95	100.00
	30	0.71	22.94	11.08	53.48	0.26	0.39	1.32	9.81	100.00
	31	0.85	24.11	10.18	55.40	0.00	0.00	0.00	9.46	100.00
average		0.72	22.25	11.71	53.45	0.12	0.06	0.10	11.59	100.00
±σ		0.21	1.15	0.92	1.55	0.24	0.01		1.78	

Ox	Analysis Point	TiO ₂	FeO	Total
	11	27.26	72.74	100.00
	12	26.32	73.68	100.00
	13	27.15	72.85	100.00
	32	30.05	69.95	100.00
	33	28.51	71.49	100.00
average		27.86	72.14	100.00

Table E.6.21 Average mineral compositions from Table E.6.20

	average wt%	average wt%	average wt%	average wt%
Oxides				
MgO			28.50	22.25
Na ₂ O	2.75			0.72
Al ₂ O ₃	30.59		18.48	11.71
SiO ₂	52.14		42.31	53.45
CaO	14.52			0.06
FeO		72.14	10.29	11.59
TiO ₂		27.86	0.42	0.10
K ₂ O				0.12
Total	100.00	100.00	100.00	100.00
Mineral Composition	Ca _{0.71} Na _{0.24} Al _{1.65} Si _{2.39} O ₈ (An ₇₄ -Ab ₂₆)	Fe ²⁺ (Fe ³⁺ ,Ti) ₂ O ₄	Mg _{7.04} Fe _{1.43} Ti _{0.05} Al _{2.65} Si _{7.04} Al _{0.96} O ₂₀ (OH) ₁₆ (on the basis of 28 oxygen equivalents, ignoring H ₂ O)	Na _{0.18} Mg _{4.26} Fe _{1.24} Al _{0.63} Si _{6.86} Al _{1.14} O ₂₀ (OH) ₄ (on the basis of 22 oxygen equivalents, ignoring H ₂ O)
Phase and ID	Plagioclase (bytownite)	Oxide (titanomagnetite)	Chlorite	Smectite

Portion 4-5

Figure E.6.31. SEM pictures for EDS analysis of epoxy-mounted polished grains collected from **Portion 4-5**. Analysis points are marked in blue

Table E.6.22. SEM-EDS analysis results of grains in Figure E.6.31

Plg	Analysis Point	Na ₂ O	Al ₂ O ₃	SiO ₂	CaO			Total
	9	4.89	27.78	58.31	9.03			100.00
	11	3.08	31.10	53.07	12.75			100.00
average		3.99	29.44	55.69	10.89			100.01
Cpx	Analysis Point	MgO	Al ₂ O ₃	SiO ₂	CaO	TiO ₂	FeO	Total
	20	16.95	3.23	55.44	15.47	0.00	8.90	99.99
	7	17.54	1.85	54.79	3.67	0.00	22.15	100.00
	8	14.41	3.16	52.98	13.47	0.00	15.97	99.99
	10	14.28	6.13	52.04	16.00	1.29	10.26	100.00
average		15.80	3.59	53.81	12.15	0.32	14.32	100.00
Ox	Analysis Point	TiO ₂	FeO					Total
	19	27.22	72.78					100.00
	21	30.69	69.31					100.00
average		28.96	71.05					100.00
Smc	Analysis Point	Na ₂ O	MgO	Al ₂ O ₃	SiO ₂	CaO	FeO	Total
	12	0.78	12.55	11.60	50.44	0.75	23.87	100.00
	13	0.51	11.74	11.79	48.80	0.38	26.78	100.00
	14	1.47	6.94	10.77	44.34	1.43	35.06	100.00
	16	0.85	11.87	11.09	50.34	1.01	24.84	100.00
	17	0.00	12.38	11.22	50.93	0.99	24.48	100.00
	18	1.86	15.37	14.25	50.74	1.15	16.63	100.00
	1	0.91	17.11	10.67	53.23	0.34	17.74	100.00
	2	0.92	15.18	10.21	52.41	0.87	20.42	100.00
	3	1.12	15.28	11.67	52.24	0.87	18.82	100.00
	4	0.83	10.06	10.65	48.46	0.88	29.12	100.00
	5	0.75	13.96	12.07	51.95	0.50	20.41	100.00
	6	1.59	15.10	12.30	50.49	1.42	19.11	100.00
	22	2.42	16.12	12.43	51.71	0.60	16.73	100.00
	23	2.93	12.13	12.07	49.65	0.73	22.48	100.00
	24	2.49	14.09	13.01	51.21	0.49	18.71	100.00
	26	2.59	14.53	14.04	50.87	0.91	17.07	100.00
	27	2.06	12.21	12.06	49.66	1.37	22.64	100.00
	28	1.87	11.54	15.06	48.00	1.67	21.88	100.00
	29	2.02	12.31	12.43	48.88	0.67	23.69	100.00
	30	1.96	13.36	11.80	50.03	0.73	21.72	100.00
	31	2.33	14.86	12.37	50.95	1.08	18.40	100.00
	32	2.32	15.13	12.58	50.39	0.66	18.92	100.00
	33	2.09	12.59	11.78	49.61	0.72	23.22	100.00
	34	0.81	7.11	11.29	49.85	1.48	29.47	100.00
	35	1.70	12.43	13.11	51.39	0.84	20.53	100.00
	37	1.52	12.69	12.50	50.80	0.00	22.49	100.00
average		1.57	13.02	12.11	50.28	0.87	22.12	99.97
±σ		0.70	2.43	1.14	1.73	0.36	4.38	

Table E.6.23. Average mineral compositions from Table E.6.22

	average wt%	average wt%	average wt%	average wt%
Oxides				
MgO		15.80		13.02
Na ₂ O	3.99			1.57
Al ₂ O ₃	29.44	3.59		12.11
SiO ₂	55.69	53.81		50.28
CaO	10.89	12.15		0.87
FeO _(T)		14.32	71.05	22.12
TiO ₂		0.32	28.96	
Total	100.01	99.99	100.01	99.97
Mineral Composition	Ca _{0.53} Na _{0.35} Al _{1.58} Si _{2.54} O ₈ (An ₆₀ -Ab ₄₀)	Ca _{0.48} Mg _{0.87} Fe _{0.44} Al _{0.14} Si _{1.98} Al _{0.02} O ₆	Fe ²⁺ (Fe ³⁺ ,Ti) ₂ O ₄	Na _{0.41} Ca _{0.13} Mg _{2.63} Fe _{2.51} Al _{0.74} Si _{6.81} Al _{1.19} O ₂₀ (OH) ₄ (on the basis of 22 oxygen equivalents, ignoring H ₂ O)
Phase and ID	Plagioclase	Clinopyroxene (augite)	Oxide (titanomagnetite)	Smectite

Figure E.6.32. SEM photographs of different areas of the basal block surface after the BSW2 experiment

6.3. Discussion

Elements Flux Calculation

Table E.6.24. Elements flux calculation and amount of glass dissolved during the BSW1 experiment (400°C / 488 bar). Light blue colour indicates samples excluded from calculation

Sample No.	Time	Total Time	Time	Reactor T	Pressure	SiO ₂ mg kg ⁻¹	K mg kg ⁻¹	SO ₄ mg kg ⁻¹	H ₂ S mg kg ⁻¹	Ca mg kg ⁻¹	Na mg kg ⁻¹	Mg mg kg ⁻¹	Fe mg kg ⁻¹	Volume L	diff. SiO ₂ mg kg ⁻¹	SiO ₂ Flux mg	diff. K mg kg ⁻¹	K Flux mg	diff. SO ₄ mg kg ⁻¹	SO ₄ Flux mg	H ₂ S Flux mg	diff. Ca mg kg ⁻¹	Ca Flux mg	diff. Na mg kg ⁻¹	Na Flux mg	diff. Mg mg kg ⁻¹	Mg Flux mg	diff. Fe mg kg ⁻¹	Fe Flux mg	
	day	day		°C	bar																									
Output SW1	0	0	0	room T	1	54	328	115	0	84	8276	561	73																	
						Total Input Mass (mg) in 1.48 L supposing no fluid-rock exchange	80	487	171	0	125	12278	832	108																
Water (distilled) mixed seawater circulating in the system - 1	11:30:00	1.0		400	488	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.	0.024																
2	8:55:00	1.89	0.89	400	488	1451.50	27.24	49.46	0.34	< 0.05	46.55	< 0.01	< 0.08	0.021	1397.5	29.9	-301.2	-6.43	-65.8	-1.41				-8229.5	-175.78			-37.773	-0.90655	
3	8:55:00	2.89	1.00	400	488	1795.95	130.21	25.75	0.35	< 0.05	206.80	< 0.01	0.32	0.024	1742.0	41.8	-198.2	-4.76	-89.6	-2.15	0.008			-8069.2	-193.66			-72.283	-1.73480	
4	9:10:00	3.89	1.00	400	488	1687.58	580.31	3.95	1.46	117.81	4092.78	< 0.01	34.83	0.024	1633.6	39.2	251.9	6.05	-111.4	-2.67	0.008	33.61	0.807	-4183.2	-100.40			-37.773	-0.90655	
5	9:30:00	4.90	1.01	400	488	1765.86	303.24	5.33	1.43	675.28	7245.34	0.18	184.14	0.024	1711.9	41.5	-25.2	-0.61	-110.0	-2.67	0.035	591.08	14.328	-1030.7	-24.98	-560.82	-13.594	111.542	2.70378	
6	10:10:00	5.93	1.03	400	488	1830.01	334.31	5.13	1.41	827.70	8089.60	< 0.01	49.83	0.025	1776.0	43.8	5.9	0.15	-110.2	-2.72	0.035	743.50	18.326	-186.4	-4.59			-22.765	-0.56112	
7	9:10:00	6.89	0.96	400	488	1751.44	375.98	4.86	1.00	929.63	9123.35	< 0.01	71.00	0.023	1697.4	39.1	47.6	1.10	-110.4	-2.54	0.032	845.43	19.479	847.4	19.52			-1.595	-0.03676	
8	10:24:00	7.90	1.01	400	488	1591.93	316.23	7.36	0.19	799.35	7991.40	< 0.01	65.22	0.024	1537.9	37.3	-12.2	-0.30	-107.9	-2.62	0.024	715.15	17.335	-284.6	-6.90			-7.375	-0.17878	
9	9:30:00	8.86	0.96	400	488	1631.72	378.38	0.24	0.09	921.22	9317.18	< 0.01	95.25	0.023	1577.7	36.4	50.0	1.15	-115.1	-2.65	0.004	837.02	19.285	1041.2	23.99			22.655	0.52196	
10	8:30:00	9.82	0.96	400	488	1569.31	366.30	5.17	0.43	817.26	9103.08	< 0.01	128.34	0.023	1515.3	34.9	37.9	0.87	-110.1	-2.54	0.002	733.06	16.890	827.1	19.06			55.745	1.28436	
11	9:10:00	10.85	1.03	400	488	1587.80	330.39	4.79	0.42	829.19	8553.83	< 0.01	101.35	0.025	1533.8	37.9	2.0	0.05	-110.5	-2.73	0.011	744.99	18.416	277.8	6.87			28.755	0.71082	
12	9:00:00	11.85	1.00	400	488	1602.96	343.67	4.98	0.35	840.32	8742.55	< 0.01	111.17	0.024	1549.0	37.2	15.3	0.37	-110.3	-2.65	0.010	756.12	18.147	466.5	11.20			38.575	0.92579	
13	9:20:00	12.86	1.01	400	488	1644.61	366.06	6.43	0.33	879.47	9192.97	< 0.01	130.06	0.024	1590.6	38.6	37.7	0.91	-108.9	-2.64	0.008	795.27	19.277	917.0	22.23			57.465	1.39294	
14	9:00:00	13.85	0.99	400	488	1742.23	396.50	0.38	0.31	948.23	9899.06	0.18	154.37	0.024	1688.2	40.1	68.1	1.62	-114.9	-2.73	0.008	864.03	20.529	1623.1	38.56	-560.82	-13.325	81.775	1.94297	
15	13:11:00	15.02	1.17	400	488	1612.36	347.79	0.17	0.14	832.72	8825.73	0.02	139.38	0.028	1558.4	43.8	19.4	0.54	-115.1	-3.23	0.009	748.52	21.018	549.7	15.44	-560.98	-15.752	66.785	1.87531	
16	11:20:00	15.94	0.92	400	488	1626.21	353.69	6.41	0.29	831.19	8941.72	0.11	155.39	0.022	1572.2	34.7	25.3	0.56	-108.9	-2.40	0.003	746.99	16.494	665.7	14.70	-560.89	-12.384	82.795	1.82811	
17	8:45:00	16.83	0.89	400	488	1522.66	329.79	3.35	0.25	804.14	8522.84	< 0.01	148.61	0.021	1468.7	31.4	1.4	0.03	-112.0	-2.39	0.006	719.94	15.378	246.8	5.27			76.014	1.62365	
Re-starting heating procedure and re-filling with fresh seawater de-oxygenated																														
Water (distilled) mixed seawater circulating in the system - 19	8:55:00	17.83	1.00	400	488	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.	0.024																
20	10:10:00	18.88	1.05	400	488	1606.78	103.56	0.49	0.74	584.67	2528.76	< 0.01	39.35	0.025	1552.8	39.1	-224.8	-5.67	-114.8	-2.89		500.47	12.612	-5747.2	-144.83			-33.250	-0.83791	
21	9:40:00	19.86	0.98	400	488	1677.08	199.00	1.98	0.77	849.36	5405.86	< 0.01	84.86	0.024	1623.1	38.2	-129.4	-3.04	-113.3	-2.67	0.017	765.16	17.997	-2870.1	-67.51			12.264	0.28844	
22	9:05:00	20.83	0.97	400	488	1706.88	261.43	4.30	0.17	832.73	6896.60	< 0.01	72.51	0.023	1652.9	38.5	-67.0	-1.56	-111.0	-2.58	0.018	748.53	17.426	-1379.4	-32.11			-0.090	-0.00209	
23	10:20:00	21.88	1.05	400	488	1707.20	295.15	3.14	0.05	843.32	7618.94	0.18	52.21	0.025	1653.2	41.7	-33.2	-0.84	-112.2	-2.83	0.004	759.12	19.130	-657.1	-16.56	-560.82	-14.133	-20.393	-0.51390	
24	9:20:00	22.84	0.96	400	488	1723.30	312.30	4.23	0.07	860.98	8069.00	0.07	64.09	0.023	1669.3	38.5	-16.1	-0.37	-111.1	-2.56	0.001	776.78	17.897	-207.0	-4.77	-560.93	-12.924	-8.506	-0.19598	
25	9:40:00	23.85	1.01	400	488	1648.83	315.79	4.51	0.11	842.55	8122.78	0.39	69.04	0.036	1594.8	58.0	-12.6	-0.46	-110.8	-4.03	0.003	758.35	27.574	-153.2	-5.57	-560.61	-20.384	-3.561	-0.12947	
26	11:30:00	24.93	1.08	400	488	1660.41	321.95	4.89	0.08	828.39	8314.58	0.48	83.04	0.039	1606.4	62.5	-6.5	-0.25	-110.4	-4.29	0.004	744.19	28.934	38.6	1.50	-560.52	-21.793	10.441	0.40595	
27	13:15:00	25.00	0.073	400	488	1622.92	315.12	5.40	n.a.	779.90	8163.09	0.44	112.62	0.018	1568.9	27.5	-13.3	-0.23	-109.9	-1.93	0.001	695.70	12.189	-112.9	-1.98	-560.56	-9.821	40.024	0.70122	
28	14:15:00	25.08	0.08	400	488	1686.36	320.02	9.56	n.a.	772.18	8300.55	1.35	259.91	0.020	1632.4	32.5	-8.4	-0.17	-105.7	-2.11		687.98	13.705	24.6	0.49	-559.65	-11.148	187.310	3.73121	
29	15:15:00	25.17	0.08	400	488	1692.59	320.07	7.71	n.a.	705.28	8316.79	1.63	313.42	0.020	1638.6	32.6	-8.3	-0.17	-107.6	-2.14		621.08	12.372	40.8	0.81	-559.37	-11.143	240.815	4.79704	
30	16:15:00	25.25	0.08	400	488	1716.97	321.85	8.22	n.a.	648.91	8466.09	1.83	349.73	0.020	1663.0	33.1	-6.5	-0.13	-107.1	-2.13		564.71	11.249	190.1	3.79	-559.17	-11.139	277.135	5.52052	
Re-filling with fresh seawater NOT de-oxygenated		</																												

Table E.6.25. Elements flux calculation and amount of glass dissolved during the BSW2 experiment (350°C / 488 bar). Light blue colour indicates samples excluded from calculation

Sample No.	Time	Total Time	Time	Reactor T	Pressure	SiO ₂ mg kg ⁻¹	K mg kg ⁻¹	SO ₄ mg kg ⁻¹	H ₂ S mg kg ⁻¹	Ca mg kg ⁻¹	Na mg kg ⁻¹	Mg mg kg ⁻¹	Fe mg kg ⁻¹	Volume L	diff. SiO ₂ mg kg ⁻¹	SiO ₂ Flux mg	diff. K mg kg ⁻¹	K Flux mg	diff. SO ₄ mg kg ⁻¹	SO ₄ Flux mg	H ₂ S Flux mg	diff. Ca mg kg ⁻¹	Ca Flux mg	diff. Na mg kg ⁻¹	Na Flux mg	diff. Mg mg kg ⁻¹	Mg Flux mg	Fe Flux mg																															
Output SW2	0	0	0	room T	1	15	328	259	0	56	8276	524	95																																														
	Total Input Mass (mg) in 1.15 L supposing no fluid-rock exchange																																																										
1	8:50:00	1.0		350	488	1928.4	33.8	23.3	1.3	< 0.05	69.5	< 0.01	< 0.08	0.024	1913.43	45.92	-294.2	-7.1	-235.7	-5.657	0.030			-8206.5	-196.957																																		
2	9:50:00	2.0	1.04	350	488	2041.8	780.0	6.1	2.4	3.2	2253.1	< 0.01	< 0.08	0.025	2026.78	50.59	452.0	11.3	-252.9	-6.313	0.059	-52.9	-1.321	-6022.9	-150.331																																		
3	12:12:00	3.1	1.02	350	488	2010.6	364.9	5.4	0.2	400.9	5390.3	< 0.01	< 0.08	0.024	1995.56	48.85	36.9	0.9	-253.6	-6.207	0.006	344.8	8.440	-2885.7	-70.643																																		
4	11:30:00	4.0	0.97	350	488	2092.9	291.7	9.4	0.7	712.7	6927.6	0.7	< 0.08	0.023	2077.93	48.37	-36.3	-0.8	-249.6	-5.811	0.017	656.6	15.286	-1348.4	-31.391	-523.3	-12.183																																
5	9:30:00	5.0	0.92	350	488	2082.3	313.6	6.6	0.5	814.5	7664.8	1.0	< 0.08	0.022	2067.26	45.65	-14.4	-0.3	-252.5	-5.574	0.010	758.4	16.746	-611.2	-13.496	-523.0	-11.549																																
6	11:00:00	6.0	1.06	350	488	2282.9	329.7	17.0	n.a.	534.7	8297.2	70.0	257.2	0.254	2267.86	576.94	1.7	0.4	-242.0	-61.567		478.6	121.752	21.2	5.405	-454.0	-115.487	65.434																															
7	13:00:00	6.1	0.08	350	488	2361.3	335.4	22.0	n.a.	467.2	8511.6	115.1	295.0	0.020	2346.30	46.74	7.4	0.1	-237.0	-4.721		411.1	8.189	235.6	4.694	-408.9	-8.145	5.876																															
8	15:00:00	6.2	0.08	350	488	2501.6	365.3	21.6	n.a.	531.9	9168.5	111.8	325.5	0.020	2486.56	49.53	37.3	0.7	-237.4	-4.729		475.8	9.479	892.5	17.779	-412.2	-8.210	6.484																															
9	17:00:00	6.3	0.08	350	488	2261.1	328.4	22.6	< 0.01	512.8	8248.9	85.1	274.2	0.020	2246.06	44.74	0.4	0.0	-236.4	-4.708		456.7	9.097	-27.1	-0.539	-438.9	-8.742	5.462																															
10	9:00:00	6.9	0.67	350	488	2036.8	321.0	12.1	n.a.	629.5	8162.6	42.4	202.0	0.161	2021.83	325.11	-7.0	-1.1	-246.9	-39.703	0.0	573.4	92.198	-113.4	-18.241	-481.6	-77.443	32.480																															
11	11:00:00	7.0	0.08	350	488	1840.7	326.7	10.6	n.a.	719.4	8372.4	25.3	150.1	0.020	1825.65	36.37	-1.3	0.0	-248.4	-4.949		663.3	13.213	96.4	1.921	-498.7	-9.935	2.989																															
12	13:00:00	7.1	0.08	350	488	1806.8	327.0	12.3	n.a.	724.9	8413.9	24.9	153.2	0.020	1791.80	35.69	-1.0	0.0	-246.7	-4.915		668.8	13.323	137.9	2.746	-499.2	-9.943	3.051																															
13	15:00:00	7.2	0.08	350	488	1783.9	323.9	10.4	n.a.	737.0	8491.1	24.4	152.2	0.020	1768.87	35.24	-4.1	-0.1	-248.6	-4.952		680.9	13.563	215.0	4.284	-499.6	-9.952	3.032																															
14	16:45:00	7.3	0.11	350	488	1740.4	322.4	9.6	< 0.01	736.6	8415.4	23.4	147.6	0.026	1725.43	45.55	-5.6	-0.1	-249.4	-6.585	0.0	680.5	17.964	139.4	3.679	-500.6	-13.217	3.897																															
15	9:00:00	8.0	0.68	350	488	1701.2	348.2	9.1	n.a.	745.6	8517.3	24.8	158.1	0.163	1686.17	275.18	20.2	3.3	-249.9	-40.782		689.5	112.534	241.3	39.375	-499.2	-81.472	25.798																															
16	11:00:00	8.1	0.08	350	488	1613.2	339.9	9.1	n.a.	755.8	8373.7	20.1	120.2	0.010	1598.18	15.92	11.9	0.1	-249.9	-2.489		699.7	6.969	97.7	0.973	-503.9	-5.019	1.197																															
17	13:00:00	8.1	0.08	350	488	1659.0	341.8	8.1	n.a.	836.4	8415.9	14.0	56.6	0.010	1644.04	16.37	13.8	0.1	-250.9	-2.499		780.3	7.772	139.9	1.393	-510.0	-5.080	0.564																															
18	15:00:00	8.2	0.08	350	488	1628.7	338.8	7.3	n.a.	872.9	8374.1	10.3	19.3	0.010	1613.67	16.07	10.8	0.1	-251.7	-2.507		816.8	8.135	98.1	0.977	-513.7	-5.117	0.192																															
19	17:00:00	8.3	0.08	350	488	1628.1	345.1	8.3	< 0.01	889.4	8457.4	8.2	0.1	0.010	1613.07	16.07	17.1	0.2	-250.7	-2.497	0.0	833.3	8.300	181.4	1.807	-515.8	-5.137	0.001																															
20	8:30:00	9.0	0.65	350	488	1654.6	344.2	4.5	n.a.	870.5	8526.1	9.9	22.7	0.078	1639.62	127.89	16.2	1.3	-254.5	-19.851		814.4	63.520	250.1	19.507	-514.1	-40.100	1.767																															
fresh seawater (natural)																																																											
21	16:40:00	9.0	0.08	350	488	1555.5	340.2	6.5	0.1	905.1	8531.5	5.9	< 0.08	0.005	1540.52	7.67	12.2	0.1	-252.5	-1.258	0.0004	849.0	4.228	255.5	1.272	-518.1	-2.580																																
22	9:00:00	9.7	0.64	350	488	1530.3	331.1	7.5	n.a.	929.8	8457.6	5.0	< 0.08	0.038	1515.27	58.19	3.1	0.1	-251.5	-9.658		873.7	33.549	181.6	6.973	-519.0	-19.928																																
23	16:00:00	10.0	0.29	350	488	1550.0	333.9	7.5	0.1	912.1	8552.4	5.2	< 0.08	0.017	1534.97	26.71	5.9	0.1	-251.5	-4.376	0.001	856.0	14.894	276.4	4.810	-518.8	-9.027																																
24	10:25:00	10.7	0.77	350	488	1604.1	331.7	6.7	n.a.	898.6	8559.2	6.3	< 0.08	0.046	1589.10	73.42	3.7	0.2	-252.3	-11.656		842.5	38.923	283.2	13.084	-517.7	-23.920																																
25	10:00:00	11.7	0.98	350	488	1538.8	337.0	6.6	< 0.01	886.1	8701.7	8.1	10.8	0.059	1523.80	89.60	9.0	0.5	-252.4	-14.842		830.0	48.802	425.7	25.030	-515.9	-30.337	0.638																															
26	10:05:00	12.7	1.00	350	488	1494.5	330.4	6.6	0.1	883.3	8603.2	5.6	< 0.08	0.024	1479.49	35.51	2.4	0.1	-252.4	-6.057	0.001	827.2	19.853	327.2	7.854	-518.4	-12.442																																
27	8:40:00	13.7	0.94	350	488	1440.6	329.4	6.2	n.a.	929.1	8598.3	4.2	< 0.08	0.023	1425.57	32.16	1.4	0.0	-252.8	-5.702		873.0	19.694	322.3	7.272	-519.8	-11.727																																
Total brine (L)														1.15																																													
ΣSiO ₂ flux (mg)																								2180																																			
ΣK flux (mg)																																		17																									
ΣSO ₄ flux (mg)																																		-285																									
ΣH ₂ S flux (mg)																																		0.13																									
ΣCa flux (mg)																																												725															
ΣNa flux (mg)																																												-114															
ΣMg flux (mg)																																												-537															
ΣFe flux (mg)																																																	159										

Activity calculation

Table E.6.26. Ions activity and logarithm of activity calculate by the R package (linked to EqSolvR by Mroczek S. and Mroczek E., 2017) for the BSW1 (400°C / 488 bar). Table also reports values of quench pH, *in situ* pH, experimental time, flow-rate, T, P and values of *Log (Kps)*, *Log (Q)* and *SI* for mineral anhydrite. LOD= limit of detection

samples	Blank seawater (natural) de-oxygenated	Water (distilled) mixed seawater circulating in the system - 1 (not considered)	2	3	4	5	6	7	8	9	10	11	12	13	14	15	16	17	Re-starting heating procedure and re-filling with fresh seawater de-oxygenated (not considered)	Water (distilled) mixed seawater circulating in the system - 19 (not considered)	20	21	22
$a = m \cdot a_{\gamma}$																							
H ⁺	1.09E-06		6.82E-08	1.95E-07	1.13E-06	1.69E-06	1.77E-06	1.76E-06	1.70E-06	1.85E-06	1.67E-06	1.73E-06	1.72E-06	1.69E-06	1.81E-06	1.82E-06	1.67E-06	1.74E-06		3.79E-07	7.36E-06	3.03E-06	2.11E-06
OH ⁻	4.05E-06		6.46E-05	2.26E-05	3.90E-06	2.61E-06	2.49E-06	2.50E-06	2.59E-06	2.39E-06	2.64E-06	2.54E-06	2.56E-06	2.61E-06	2.43E-06	2.42E-06	2.64E-06	2.53E-06		1.16E-05	5.99E-07	1.45E-06	2.09E-06
Na ⁺	5.47E-02		1.41E-03	4.89E-03	3.74E-02	5.24E-02	5.61E-02	6.02E-02	5.58E-02	6.09E-02	6.02E-02	5.80E-02	5.87E-02	6.04E-02	6.30E-02	5.90E-02	5.95E-02	5.78E-02		2.38E-03	1.44E-03	2.59E-02	4.34E-02
K ⁺	1.63E-03		4.42E-04	2.03E-03	4.29E-03	1.82E-03	1.93E-03	2.07E-03	1.84E-03	2.07E-03	2.03E-03	1.87E-03	1.93E-03	2.01E-03	2.12E-03	1.94E-03	1.97E-03	1.87E-03		1.09E-04	1.40E-03	1.63E-03	1.73E-03
Cl ⁻	6.09E-02		1.30E-03	6.69E-03	4.15E-02	5.71E-02	6.05E-02	6.47E-02	6.00E-02	6.54E-02	6.44E-02	6.23E-02	6.31E-02	6.49E-02	6.77E-02	6.35E-02	6.39E-02	6.23E-02		2.47E-03	1.18E-02	3.50E-02	4.96E-02
SO ₄ ²⁻	1.98E-05		3.49E-05	4.41E-06	7.61E-08	6.84E-08	6.00E-08	5.19E-08	8.76E-08	2.51E-09	5.63E-08	5.42E-08	5.56E-08	6.91E-08	3.86E-09	2.11E-09	7.08E-08	3.81E-08		1.07E-06	8.70E-09	3.89E-08	6.36E-08
Ca ²⁺	7.58E-06		< LOD	< LOD	5.12E-06	1.84E-05	2.09E-05	2.12E-05	2.03E-05	2.07E-05	1.88E-05	2.00E-05	1.99E-05	1.99E-05	2.02E-05	1.95E-05	1.93E-05	1.94E-05		< LOD	1.36E-04	4.70E-05	2.80E-05
Mg ²⁺	1.48E-04		< LOD	< LOD	< LOD	3.51E-08	< LOD	< LOD	< LOD	< LOD	< LOD	< LOD	< LOD	< LOD	2.72E-08	4.20E-09	2.08E-08	< LOD		< LOD	< LOD	< LOD	< LOD
Fe ²⁺	7.44E-09		< LOD	2.17E-07	2.69E-06	9.33E-06	2.34E-06	3.04E-06	3.10E-06	4.04E-06	5.54E-06	4.56E-06	4.93E-06	5.56E-06	6.24E-06	6.13E-06	6.77E-06	6.71E-06		2.86E-06	1.42E-05	8.13E-06	4.41E-06
a ² H ⁺	1.18E-12		4.66E-15	3.81E-14	1.28E-12	2.86E-12	3.13E-12	3.11E-12	2.89E-12	3.41E-12	2.79E-12	3.01E-12	2.96E-12	2.84E-12	3.27E-12	3.31E-12	2.78E-12	3.04E-12		1.43E-13	5.41E-11	9.19E-12	4.43E-12
log (a SiO ₂)	-3.95		-1.62	-1.52	-1.55	-1.53	-1.52	-1.54	-1.58	-1.57	-1.58	-1.58	-1.57	-1.56	-1.54	-1.57	-1.57	-1.60		-1.60	-1.57	-1.55	-1.55
log (a _{K+/a H+})	3.18		3.81	4.02	3.58	3.03	3.04	3.07	3.03	3.05	3.08	3.03	3.05	3.08	3.07	3.03	3.07	3.03		2.46	2.28	2.73	2.91
log (a _{Na+/a H+})	4.70		4.31	4.40	4.52	4.49	4.50	4.53	4.52	4.52	4.56	4.52	4.53	4.55	4.54	4.51	4.55	4.52		3.80	2.29	3.93	4.31
log (a _{Ca2+/a 2 H+})	6.81		< LOD	< LOD	6.60	6.81	6.82	6.83	6.85	6.78	6.83	6.82	6.83	6.85	6.79	6.77	6.84	6.80		< LOD	6.40	6.71	6.80
log (a _{Fe2+/a 2 H+})	3.80		< LOD	6.76	6.32	6.51	5.87	5.99	6.03	6.07	6.30	6.18	6.22	6.29	6.28	6.27	6.39	6.34		7.30	5.42	5.95	6.00
log (a _{Mn2+/a 2 H+})	8.10		< LOD	< LOD	< LOD	4.09	< LOD	< LOD	< LOD	< LOD	< LOD	< LOD	< LOD	< LOD	3.92	3.10	3.87	< LOD		< LOD	< LOD	< LOD	< LOD
log a Na ⁺	-1.26		-2.85	-2.31	-1.43	-1.28	-1.25	-1.22	-1.25	-1.22	-1.22	-1.24	-1.23	-1.22	-1.20	-1.23	-1.23	-1.24		-2.62	-2.84	-1.59	-1.36
log a K ⁺	-2.79		-3.35	-2.69	-2.37	-2.74	-2.71	-2.68	-2.74	-2.68	-2.69	-2.73	-2.71	-2.70	-2.67	-2.71	-2.71	-2.73		-3.96	-2.86	-2.79	-2.76
log a Cl ⁻	-1.22		-2.89	-2.17	-1.38	-1.24	-1.22	-1.19	-1.22	-1.18	-1.19	-1.21	-1.20	-1.19	-1.17	-1.20	-1.19	-1.21		-2.61	-1.93	-1.46	-1.30
log a SO ₄ ²⁻	-4.70		-4.46	-5.36	-7.12	-7.16	-7.22	-7.28	-7.06	-8.60	-7.25	-7.27	-7.26	-7.16	-8.41	-8.68	-7.15	-7.42		-5.97	-8.06	-7.41	-7.20
log a Ca ²⁺	-5.12		< LOD	< LOD	-5.29	-4.73	-4.68	-4.67	-4.69	-4.68	-4.73	-4.70	-4.70	-4.70	-4.69	-4.71	-4.71	-4.71		< LOD	-3.87	-4.33	-4.55
log a Mg ²⁺	-3.83		< LOD	< LOD	< LOD	-7.45	< LOD	< LOD	< LOD	< LOD	< LOD	< LOD	< LOD	< LOD	-7.56	-8.38	-7.68	< LOD		< LOD	< LOD	< LOD	< LOD
log a Fe ²⁺	-8.13		< LOD	-6.66	-5.57	-5.03	-5.63	-5.52	-5.51	-5.39	-5.26	-5.34	-5.31	-5.26	-5.21	-5.17	-5.17	-5.17		-5.54	-4.85	-5.09	-5.36
T(°C)	400		401.3	400.7	400.6	400.4	400.7	400.4	400.5	400.3	400.7	400.4	400.8	400.4	400.5	400.2	400.7	400.4		400.8	400.5	400.6	400.7
P(bar)	500		485.4	486.1	486.1	486.1	486.2	486.1	485.7	358.9	485.9	486.2	486.0	485.9	485.8	367.6	485.1	485.5		486.6	486.4	486.5	486.4
<i>in situ</i> pH _(400°C)	5.96		7.17	6.71	5.95	5.77	5.75	5.75	5.77	5.73	5.78	5.76	5.76	5.77	5.74	5.74	5.78	5.76		6.42	5.13	5.52	5.68
room T pH	7.75		6.37	4.17	3.29	4.34	3.63	3.58	3.8	3.79	3.98	4.03	4.23	4.04	4.05	4.09	4.10	4.10		6.27	4.89	4.27	4.08
flow rate (ml hr ⁻¹)		1	1	1	1	1	1	1	1	1	1	1	1	1	1	1	1	1		1	1	1	1
time (hrs)	0.0		45.3	68.1	92.3	116.7	141.3	164.3	189.5	212.7	235.7	260.3	284.2	308.5	332.2	352.7	374.8	396.3		411.9	437.2	460.7	484.3
Anhydrite																							
<i>Log Ksp</i> (Supert92) @400°C			4.27	4.27	4.27	4.27	4.27	4.27	4.27	4.27	4.27	4.27	4.27	4.27	4.27	4.27	4.27	4.27		4.27	4.27	4.27	4.27
<i>Log Q</i> (or log IAP)			< LOD	< LOD	4.96	4.46	4.46	4.52	4.31	5.84	4.53	4.52	4.52	4.42	5.67	6.00	4.42	4.69		< LOD	3.69	4.55	4.37
<i>Log SI</i>			< LOD	< LOD	0.69	0.19	0.19	0.25	0.04	1.57	0.26	0.25	0.25	0.15	1.40	1.73	0.15	0.42		< LOD	-0.58	0.28	0.10

Table E.6.27. Ions activity and logarithm of activity calculate by the R package (linked to EqSolvR by Mroczek S. and Mroczek E., 2017) for the BSW1 (400°C / 488 bar). Table also reports values of quench pH, *in situ* pH, experimental time, flow-rate, T, P and values of *Log (Kps)*, *Log (Q)* and *SI* for mineral anhydrite. LOD= limit of detection

samples	23	24	25	26	27	28	29	30	Re-filling with fresh seawater NOT de-oxygenated (not considered)	31	32	33	34	35	36	37	38	39	40	41	42	43	44	45
$a = m \cdot a_{\gamma}$																								
H ⁺	1.96E-06	1.86E-06	1.80E-06	1.78E-06	1.71E-06	1.63E-06	1.60E-06	1.54E-06		1.55E-06	1.67E-06	1.54E-06	1.55E-06	1.51E-06	1.53E-06	1.53E-06	1.56E-06	1.55E-06	1.57E-06	1.55E-06	1.54E-06	1.58E-06	1.58E-06	1.57E-06
OH ⁻	2.25E-06	2.37E-06	2.44E-06	2.48E-06	2.58E-06	2.71E-06	2.75E-06	2.85E-06		2.85E-06	2.63E-06	2.86E-06	2.84E-06	2.92E-06	2.88E-06	2.88E-06	2.83E-06	2.84E-06	2.80E-06	2.84E-06	2.86E-06	2.79E-06	2.79E-06	2.81E-06
Na ⁺	5.07E-02	5.40E-02	5.60E-02	5.62E-02	5.71E-02	5.61E-02	5.67E-02	5.68E-02		5.75E-02	5.73E-02	5.77E-02	5.76E-02	5.80E-02	5.82E-02	5.75E-02	5.79E-02	5.80E-02	5.77E-02	5.77E-02	5.69E-02	5.76E-02	5.77E-02	5.81E-02
K ⁺	1.80E-03	1.84E-03	1.83E-03	1.86E-03	1.81E-03	1.86E-03	1.83E-03	1.82E-03		1.81E-03	1.84E-03	1.83E-03	1.83E-03	1.84E-03	1.81E-03	1.84E-03	1.86E-03	1.86E-03	1.85E-03	1.81E-03	1.87E-03	1.86E-03	1.84E-03	1.85E-03
Cl ⁻	5.59E-02	5.88E-02	6.05E-02	6.07E-02	6.13E-02	6.12E-02	6.16E-02	6.16E-02		6.21E-02	6.21E-02	6.24E-02	6.24E-02	6.27E-02	6.28E-02	6.23E-02	6.26E-02	6.28E-02	6.24E-02	6.23E-02	6.17E-02	6.23E-02	6.24E-02	6.27E-02
SO ₄ ²⁻	4.06E-08	5.11E-08	5.28E-08	5.72E-08	6.24E-08	1.14E-07	9.03E-08	9.76E-08		6.74E-08	2.00E-28	6.61E-08	6.38E-08	8.46E-08	6.11E-08	6.63E-08	5.67E-08	6.53E-08	5.57E-08	5.49E-08	7.04E-08	4.79E-08	5.45E-08	5.75E-08
Ca ²⁺	2.38E-05	2.26E-05	2.12E-05	2.08E-05	1.93E-05	1.91E-05	1.73E-05	1.59E-05		1.45E-05	1.45E-05	1.44E-05	1.45E-05	1.43E-05	1.39E-05	1.42E-05	1.45E-05	1.48E-05	1.48E-05	1.42E-05	1.46E-05	1.47E-05	1.52E-05	1.51E-05
Mg ²⁺	3.91E-08	1.38E-08	7.11E-08	8.85E-08	7.86E-08	2.44E-07	2.90E-07	3.24E-07		4.07E-07	3.82E-07	3.79E-07	3.92E-07	4.10E-07	4.14E-07	3.75E-07	3.78E-07	3.59E-07	3.53E-07	3.58E-07	3.49E-07	3.41E-07	3.11E-07	3.09E-07
Fe ²⁺	2.72E-06	3.12E-06	3.24E-06	3.88E-06	5.20E-06	1.20E-05	1.43E-05	1.60E-05		1.73E-05	1.84E-05	1.83E-05	1.87E-05	1.85E-05	1.88E-05	1.93E-05	1.83E-05	1.77E-05	1.78E-05	1.80E-05	1.86E-05	1.74E-05	1.70E-05	1.66E-05
a ² H ⁺	3.84E-12	3.47E-12	3.25E-12	3.16E-12	2.92E-12	2.65E-12	2.57E-12	2.38E-12		2.40E-12	2.80E-12	2.37E-12	2.40E-12	2.27E-12	2.34E-12	2.35E-12	2.43E-12	2.41E-12	2.47E-12	2.40E-12	2.37E-12	2.50E-12	2.50E-12	2.47E-12
log (a SiO ₂)	-1.55	-1.54	-1.56	-1.56	-1.57	-1.55	-1.55	-1.54		-1.59	-1.54	-1.55	-1.54	-1.54	-1.61	-1.55	-1.55	-1.55	-1.55	-1.62	-1.55	-1.55	-1.54	-1.54
log (a _{K+} /a _{H+})	2.96	2.99	3.01	3.02	3.02	3.05	3.06	3.08		3.07	3.04	3.08	3.07	3.09	3.07	3.08	3.08	3.08	3.07	3.07	3.08	3.07	3.07	3.07
log (a _{Na+} /a _{H+})	4.41	4.46	4.49	4.50	4.52	4.54	4.55	4.57		4.57	4.53	4.57	4.57	4.59	4.58	4.57	4.57	4.57	4.56	4.57	4.57	4.56	4.56	4.57
log (a _{Ca2+} /a ² _{H+})	6.79	6.81	6.81	6.82	6.82	6.86	6.83	6.82		6.78	6.72	6.78	6.78	6.80	6.77	6.78	6.78	6.79	6.78	6.77	6.79	6.77	6.78	6.79
log (a _{Fe2+} /a ² _{H+})	5.85	5.95	6.00	6.09	6.25	6.66	6.75	6.83		6.86	6.82	6.89	6.89	6.91	6.91	6.92	6.88	6.87	6.86	6.87	6.90	6.84	6.83	6.83
log (a _{Mg2+} /a ² _{H+})	4.01	3.60	4.34	4.45	4.43	4.96	5.05	5.13		5.23	5.14	5.20	5.21	5.26	5.25	5.20	5.19	5.17	5.16	5.17	5.17	5.14	5.09	5.10
log a Na ⁺	-1.29	-1.27	-1.25	-1.25	-1.24	-1.25	-1.25	-1.25		-1.24	-1.24	-1.24	-1.24	-1.24	-1.24	-1.24	-1.24	-1.24	-1.24	-1.24	-1.25	-1.24	-1.24	-1.24
log a K ⁺	-2.74	-2.74	-2.74	-2.73	-2.74	-2.74	-2.74	-2.74		-2.74	-2.74	-2.74	-2.74	-2.73	-2.74	-2.73	-2.73	-2.73	-2.73	-2.74	-2.73	-2.73	-2.73	-2.73
log a Cl ⁻	-1.25	-1.23	-1.22	-1.22	-1.21	-1.21	-1.21	-1.21		-1.21	-1.21	-1.21	-1.21	-1.20	-1.20	-1.21	-1.20	-1.20	-1.20	-1.21	-1.21	-1.21	-1.20	-1.20
log a SO ₄ ²⁻	-7.39	-7.29	-7.28	-7.24	-7.20	-6.94	-7.04	-7.01		-7.17	-27.70	-7.18	-7.20	-7.07	-7.21	-7.18	-7.25	-7.19	-7.25	-7.26	-7.15	-7.32	-7.26	-7.24
log a Ca ²⁺	-4.62	-4.65	-4.67	-4.68	-4.72	-4.72	-4.76	-4.80		-4.84	-4.84	-4.84	-4.84	-4.84	-4.86	-4.85	-4.84	-4.83	-4.83	-4.85	-4.84	-4.83	-4.82	-4.82
log a Mg ²⁺	-7.41	-7.86	-7.15	-7.05	-7.10	-6.61	-6.54	-6.49		-6.39	-6.42	-6.42	-6.41	-6.39	-6.38	-6.43	-6.42	-6.44	-6.45	-6.45	-6.46	-6.47	-6.51	-6.51
log a Fe ²⁺	-5.57	-5.51	-5.49	-5.41	-5.28	-4.92	-4.84	-4.80		-4.76	-4.74	-4.74	-4.73	-4.73	-4.73	-4.71	-4.74	-4.75	-4.75	-4.74	-4.73	-4.76	-4.77	-4.78
T(°C)	400.8	400.6	400.4	400.6	400.7	400.3	400.7	400.5		400.8	400.4	400.3	400.6	400.50	400.60	400.40	400.60	400.80	400.30	400.50	400.70	400.30	400.70	400.40
P(bar)	486.4	486.5	486.5	486.4	486.5	486.8	486.5	486.8		487.3	487.2	487.2	487.3	487.18	487.20	487.20	487.15	487.16	487.20	487.24	487.24	487.26	487.28	487.27
in situ pH _(400°C)	5.71	5.73	5.74	5.75	5.77	5.79	5.80	5.81		5.81	5.78	5.81	5.81	5.82	5.82	5.81	5.81	5.81	5.80	5.81	5.81	5.80	5.80	5.80
room T pH	3.99	4.04	4.12	4.17	4.53	4.27	4.28	4.5		4.48	4.54	4.5	4.53	4.54	4.53	4.59	4.62	4.63	4.6	4.55	4.65	4.55	4.53	4.55
flow rate (ml hr ⁻¹)	1	1	1.5	1.5	10	10	10	10		10	10	10	10	10	10	7.5	7.5	7.5	7.5	7.5	5	5	5	5
time (hrs)	509.6	532.6	556.9	582.8	583.8	584.8	585.8	586.8		603.3	605.3	607.3	609.3	611.3	626.8	628.8	630.8	632.8	634.8	651.3	653.3	655.3	657.3	659.0
Anhydrite																								
Log Ksp (Supert92) @400°C	4.27	4.27	4.27	4.27	4.27	4.27	4.27	4.27		4.27	4.27	4.27	4.27	4.27	4.27	4.27	4.27	4.27	4.27	4.27	4.27	4.27	4.27	4.27
Log Q (or log IAP)	4.34	4.58	4.51	4.51	4.49	4.46	4.25	4.38		4.41	4.60	< LOD	4.58	4.59	4.49	4.62	4.61	4.63	4.58	4.65	4.65	4.55	4.70	4.64
Log SI	0.07	0.31	0.24	0.24	0.22	0.19	-0.02	0.11		0.14	0.33	< LOD	0.31	0.32	0.22	0.35	0.34	0.36	0.31	0.38	0.38	0.28	0.43	0.37

Table E.6.28. Values of the activity coefficients (a_i) calculated by the R package for the BSW1 (400°C / 488 bar)

sample		H ⁺	OH ⁻	Na ⁺	K ⁺	Cl ⁻	SO ₄ ²⁻	Ca ²⁺	Mg ²⁺	Fe ²⁺	NaSO ₄ ⁻	HSO ₄ ⁻	KSO ₄ ⁻	NaCl ⁺	KCl ⁺	HCl ⁺	KOH ⁺	NaOH ⁺	CaSO ₄ ⁰	MgSO ₄ ⁰	MgCl ⁺	CaCl ⁺	CaCl ₂ ⁰	MgOH ⁺	CaOH ⁺	FeCl ⁺	FeSO ₄ ⁰
blank seawater (natural)	m	2.27E-06	1.27E-05	1.72E-01	5.91E-03	2.04E-01	1.92E-03	3.19E-04	3.50E-03	3.13E-07	1.20E-02	1.88E-03	8.03E-04	1.82E-01	1.71E-03	3.24E-05	1.84E-07	3.23E-06	2.23E-04	3.03E-03	3.01E-02	5.78E-03	1.70E-03	1.86E-03	3.37E-05	2.69E-06	9.60E-10
	a _i	4.80E-01	3.19E-01	3.19E-01	2.76E-01	2.98E-01	1.03E-02	2.38E-02	4.24E-02	2.38E-02	3.19E-01	3.19E-01	3.19E-01	1.00E+00	1.00E+00	1.00E+00	1.00E+00	1.00E+00	1.00E+00	1.00E+00	4.54E-01	3.93E-01	1.00E+00	4.54E-01	3.93E-01	3.93E-01	1.00E+00
	activity	1.09E-06	4.05E-06	5.47E-02	1.63E-03	6.09E-02	1.98E-05	7.58E-06	1.48E-04	7.44E-09	3.84E-03	5.99E-04	2.56E-04	1.82E-01	1.71E-03	3.24E-05	1.84E-07	3.23E-06	2.23E-04	3.03E-03	1.37E-02	2.27E-03	1.70E-03	8.46E-04	1.32E-05	1.05E-06	9.60E-10
2	m	8.14E-08	7.83E-05	1.71E-03	5.38E-04	1.58E-03	7.54E-05				2.11E-04	8.03E-05	1.48E-04	9.98E-05	9.88E-06	4.33E-08	7.97E-07	1.33E-06									
	a _i	8.39E-01	8.25E-01	8.25E-01	8.22E-01	8.23E-01	4.63E-01				8.25E-01	8.25E-01	8.25E-01	1.00E+00	1.00E+00	1.00E+00	1.00E+00	1.00E+00									
	activity	6.82E-08	6.46E-05	1.41E-03	4.42E-04	1.30E-03	3.49E-05				1.74E-04	6.62E-05	1.22E-04	9.98E-05	9.88E-06	4.33E-08	7.97E-07	1.33E-06									
3	m	2.68E-07	3.27E-05	7.10E-03	2.99E-03	9.78E-03	1.95E-05			8.70E-07	1.11E-04	3.47E-05	1.03E-04	1.79E-03	2.34E-04	6.39E-07	1.28E-06	1.61E-06								0.00E+00	0.00E+00
	a _i	7.30E-01	6.89E-01	6.89E-01	6.80E-01	6.85E-01	2.26E-01			2.50E-01	6.89E-01	6.89E-01	6.89E-01	1.00E+00	1.00E+00	1.00E+00	1.00E+00	1.00E+00								7.07E-01	1.00E+00
	activity	1.95E-07	2.26E-05	4.89E-03	2.03E-03	6.69E-03	4.41E-06			2.17E-07	7.64E-05	2.39E-05	7.10E-05	1.79E-03	2.34E-04	6.39E-07	1.28E-06	1.61E-06								0.00E+00	0.00E+00
4	m	2.13E-06	9.73E-06	9.33E-02	1.17E-02	1.08E-01	2.95E-06	1.14E-04			5.99E-05	2.51E-05	5.97E-06	6.46E-06	8.47E-02	3.07E-03	2.29E-05	4.67E-07	2.13E-06	0.00E+00		0.00E+00	1.87E-05	5.64E-04	1.33E-09	0.00E+00	0.00E+00
	a _i	5.31E-01	4.01E-01	4.01E-01	3.66E-01	3.84E-01	2.58E-02	4.49E-02			4.49E-02	4.01E-01	4.01E-01	4.01E-01	1.00E+00	1.00E+00	1.00E+00	1.00E+00	1.00E+00		0.00E+00	4.60E-01	1.00E+00	5.10E-01	4.60E-01	4.60E-01	1.00E+00
	activity	1.13E-06	3.90E-06	3.74E-02	4.29E-03	4.15E-02	7.61E-08	5.12E-06			2.69E-06	1.01E-05	2.39E-06	2.59E-06	8.47E-02	3.07E-03	2.29E-05	4.67E-07	2.13E-06	0.00E+00		0.00E+00	1.87E-05	2.88E-04	6.13E-10	0.00E+00	0.00E+00
5	m	3.40E-06	7.53E-06	1.52E-01	5.96E-03	1.75E-01	4.77E-06	6.20E-04	7.06E-07	3.14E-04	3.67E-05	9.29E-06	2.86E-06	1.63E-01	1.79E-03	4.72E-05	1.33E-07	1.99E-06	2.48E-09	6.43E-06	1.25E-02	3.65E-03	2.73E-07	4.99E-05	2.99E-03	4.16E-09	0.00E+00
	a _i	4.97E-01	3.46E-01	3.46E-01	3.06E-01	3.26E-01	1.43E-02	2.97E-02	4.98E-02	2.97E-02	3.46E-01	3.46E-01	3.46E-01	1.00E+00	1.00E+00	1.00E+00	1.00E+00	1.00E+00	1.00E+00	1.00E+00	4.72E-01	4.15E-01	1.00E+00	4.72E-01	4.15E-01	4.15E-01	1.00E+00
	activity	1.69E-06	2.61E-06	5.24E-02	1.82E-03	5.71E-02	8.84E-08	1.84E-05	3.51E-08	9.33E-06	1.27E-05	3.21E-06	9.89E-07	1.63E-01	1.79E-03	4.72E-05	1.33E-07	1.99E-06	2.48E-09	6.43E-06	5.90E-03	1.51E-03	2.73E-07	2.36E-05	1.24E-03	1.73E-09	0.00E+00
6	m	3.60E-06	7.40E-06	1.67E-01	6.53E-03	1.91E-01	4.66E-06	7.56E-04		8.46E-05	3.54E-05	8.76E-06	2.73E-06	1.85E-01	2.01E-03	5.23E-05	1.34E-07	2.04E-06	0.00E+00			0.00E+00	5.51E-05		9.13E-10	0.00E+00	0.00E+00
	a _i	4.91E-01	3.37E-01	3.37E-01	2.96E-01	3.17E-01	1.29E-02	2.76E-02		2.76E-02	3.37E-01	3.37E-01	3.37E-01	1.00E+00	1.00E+00	1.00E+00	1.00E+00	1.00E+00	1.00E+00		4.08E-01	1.00E+00			4.08E-01	4.08E-01	1.00E+00
	activity	1.77E-06	2.49E-06	5.61E-02	1.93E-03	6.05E-02	6.00E-08	2.09E-05		2.34E-06	1.19E-05	2.95E-06	9.19E-07	1.85E-01	2.01E-03	5.23E-05	1.34E-07	2.04E-06	0.00E+00			0.00E+00	5.51E-05		3.72E-10	0.00E+00	0.00E+00
7	m	3.64E-06	7.66E-06	1.85E-01	7.31E-03	2.12E-01	4.60E-06	8.38E-04		1.20E-04	3.39E-05	7.81E-06	2.62E-06	2.12E-01	2.31E-03	5.58E-05	1.45E-07	2.19E-06	0.00E+00			0.00E+00	5.73E-05		1.03E-09	0.00E+00	0.00E+00
	a _i	4.85E-01	3.26E-01	3.26E-01	2.84E-01	3.05E-01	1.13E-02	2.53E-02		2.53E-02	3.26E-01	3.26E-01	3.26E-01	1.00E+00	1.00E+00	1.00E+00	1.00E+00	1.00E+00	1.00E+00		3.99E-01	1.00E+00			3.99E-01	3.99E-01	1.00E+00
	activity	1.76E-06	2.50E-06	6.02E-02	2.07E-03	6.47E-02	5.19E-08	2.12E-05		3.04E-06	1.11E-05	2.55E-06	8.54E-07	2.12E-01	2.31E-03	5.58E-05	1.45E-07	2.19E-06	0.00E+00			0.00E+00	5.73E-05		4.11E-10	0.00E+00	0.00E+00
8	m	3.45E-06	7.67E-06	1.65E-01	6.19E-03	1.89E-01	6.71E-06	7.28E-04		1.11E-04	5.12E-05	1.22E-05	3.78E-06	1.83E-01	1.90E-03	4.98E-05	1.33E-07	2.11E-06	0.00E+00			0.00E+00	5.56E-05		1.77E-09	0.00E+00	0.00E+00
	a _i	4.92E-01	3.38E-01	3.38E-01	2.97E-01	3.18E-01	1.31E-02	2.79E-02		2.79E-02	3.38E-01	3.38E-01	3.38E-01	1.00E+00	1.00E+00	1.00E+00	1.00E+00	1.00E+00	1.00E+00		4.09E-01	1.00E+00			4.09E-01	4.09E-01	1.00E+00
	activity	1.70E-06	2.59E-06	5.58E-02	1.84E-03	6.00E-02	8.76E-08	2.03E-05		3.10E-06	1.73E-05	4.14E-06	1.28E-06	1.83E-01	1.90E-03	4.98E-05	1.33E-07	2.11E-06	0.00E+00			0.00E+00	5.56E-05		7.23E-10	0.00E+00	0.00E+00
9	m	3.82E-06	7.36E-06	1.88E-01	7.35E-03	2.15E-01	2.27E-07	8.29E-04		1.62E-04	1.67E-06	3.98E-07	1.27E-07	2.17E-01	2.33E-03	5.90E-05	1.38E-07	2.12E-06	0.00E+00			0.00E+00	5.36E-05		6.62E-11	0.00E+00	0.00E+00
	a _i	4.84E-01	3.24E-01	3.24E-01	2.82E-01	3.04E-01	1.11E-02	2.49E-02		2.49E-02	3.24E-01	3.24E-01	3.24E-01	1.00E+00	1.00E+00	1.00E+00	1.00E+00	1.00E+00	1.00E+00		3.97E-01	1.00E+00			3.97E-01	3.97E-01	1.00E+00
	activity	1.85E-06	2.39E-06	6.09E-02	2.07E-03	6.54E-02	2.51E-09	2.07E-05		4.04E-06	5.42E-07	1.29E-07	4.13E-08	2.17E-01	2.33E-03	5.90E-05	1.38E-07	2.12E-06	0.00E+00			0.00E+00	5.36E-05		2.63E-11	0.00E+00	0.00E+00
10	m	3.44E-06	8.07E-06	1.84E-01	7.12E-03	2.10E-01	4.92E-06	7.38E-04		2.18E-04	3.66E-05	7.97E-06	2.76E-06	2.12E-01	2.25E-03	5.26E-05	1.49E-07	2.32E-06	0.00E+00			0.00E+00	5.35E-05		2.03E-09	0.00E+00	0.00E+00
	a _i	4.85E-01	3.27E-01	3.27E-01	2.85E-01	3.06E-01	1.14E-02	2.54E-02		2.54E-02	3.27E-01	3.27E-01	3.27E-01	1.00E+00	1.00E+00	1.00E+00	1.00E+00	1.00E+00	1.00E+00		3.99E-01	1.00E+00			3.99E-01	3.99E-01	1.00E+00
	activity	1.67E-06	2.64E-06	6.02E-02	2.03E-03	6.44E-02	5.61E-08	1.88E-05		5.55E-06	1.20E-05	2.60E-06	9.01E-07	2.12E-01	2.25E-03	5.26E-05	1.49E-07	2.32E-06	0.00E+00			0.00E+00	5.35E-05		8.09E-10	0.00E+00	0.00E+00
11	m	3.55E-06	7.65E-06	1.75E-01	6.44E-03	2.00E-01	4.46E-06	7.53E-04		1.72E-04	3.35E-05	7.87E-06	2.42E-06	1.97E-01	2.01E-03	5.28E-05	1.33E-07	2.15E-06	0.00E+00			0.00E+00	5.43E-05		1.61E-09	0.00E+00	0.00E+00
	a _i	4.88E-01	3.32E-01	3.32E-01	2.91E-01	3.12E-01	1.21E-02	2.66E-02		2.66E-02	3.32E-01	3.32E-01	3.32E-01	1.00E+00	1.00E+00	1.00E+00	1.00E+00	1.00E+00	1.00E+00		4.04E-01	1.00E+00			4.04E-01	4.04E-01	1.00E+00
	activity	1.73E-06	2.54E-06	5.80E-02	1.87E-03	6.23E-02	5.42E-08	2.00E-05		4.56E-06	1.11E-05	2.61E-06	8.04E-07	1.97E-01	2.01E-03	5.28E-05	1.33E-07	2.15E-06	0.00E+00			0.00E+00	5.43E-05		6.50E-10	0.00E+00	0.00E+00
12	m	3.54E-06	7.74E-06	1.78E-01	6.69E-03	2.04E-01	4.67E-06	7.62E-04		1.89E-04	3.49E-05	8.04E-06	2.57E-06	2.02E-01	2.10E-03	5.31E-05	1.38E-07	2.19E-06	0.00E+00			0.00E+00	5.46E-05		1.78E-09	0.00E+00	0.00E+00
	a _i	4.87E-01	3.30E-01	3.30E-01	2.88E-01	3.10E-01	1.19E-02	2.61E-02		2.61E-02	3.30E-01	3.30E-01	3.30E-01	1.00E+00	1.00E+00	1.00E+00	1.00E+00	1.00E+00	1.00E+00		4.02E-01	1.00E+00			4.02E-01	4.02E-01	1.00E+00
	activity	1.72E-06	2.56E-06	5.87E-02	1.93E-03	6.31E-02	5.54E-08	1.99E-05		4.93E-06	1.15E-05	2.65E-06	8.47E-07	2.02E-01	2.10E-03	5.31E-05	1.38E-07	2.19E-06	0.00E+00			0.00E+00	5.46E-05		7.16E-10	0.00E+00	0.00E+00
13	m	3.48E-06	8.04E-06	1.86E-01	7.11E-03	2.13E-01	6.16E-06	7.91E-04		2.21E-04	4.54E-05	9.93E-06	3.38E-06	2.14E-01	2.25E-03	5.35E-05	1.47E-07	2.31E-06	0.00E+00			0.00E+00	5.64E-05		2.50E-09	0.00E+00	0.00E+00
	a _i	4.84E-01	3.25E-01	3.25E-01	2.83E-01	3.05E-01	1.12E-02	2.52E-02		2.52E-02	3.25E-01	3.25E-01	3.25E-01	1.00E+00	1.00E+0												

Table E.6.29. Ions activity and logarithm of activity calculate by the R package (linked to EqSolvR by Mroczek S. and Mroczek E., 2017) for the BSW2 (350°C / 488 bar). Table also reports values of quench pH, *in situ* pH, experimental time, flow-rate, T, P and values of *Log (Kps)*, *Log (Q)* and *SI* for mineral anhydrite. LOD= limit of detection

samples	Blank seawater (natural) de-oxygenated																											
$a = m \cdot a_{\gamma}$	1	2	3	4	5	6	7	8	9	10	11	12	13	14	15	16	17	18	19	20	21	22	23	24	25	26	27	
H ⁺	2.02E-06	2.45E-07	1.64E-06	4.20E-06	4.53E-06	4.92E-06	5.45E-06	6.00E-06	5.99E-06	5.22E-06	5.24E-06	5.07E-06	4.87E-06	5.03E-06	5.07E-06	5.19E-06	5.05E-06	5.13E-06	5.16E-06	5.03E-06	5.39E-06	5.10E-06	5.04E-06	5.01E-06	5.10E-06	5.13E-06	5.01E-06	5.17E-06
OH ⁻	3.83E-06	3.16E-05	4.70E-06	1.84E-06	1.71E-06	1.57E-06	1.42E-06	1.29E-06	1.29E-06	1.48E-06	1.47E-06	1.52E-06	1.59E-06	1.54E-06	1.52E-06	1.49E-06	1.53E-06	1.51E-06	1.50E-06	1.54E-06	1.43E-06	1.51E-06	1.53E-06	1.54E-06	1.51E-06	1.51E-06	1.54E-06	1.49E-06
Na ⁺	8.94E-02	2.38E-03	3.82E-02	7.10E-02	8.34E-02	8.89E-02	9.35E-02	9.33E-02	9.45E-02	9.99E-02	9.32E-02	9.25E-02	9.40E-02	9.43E-02	9.49E-02	9.42E-02	9.50E-02	9.39E-02	9.43E-02	9.40E-02	9.46E-02	9.51E-02	9.51E-02	9.46E-02	9.54E-02	9.54E-02	9.66E-02	9.57E-02
K ⁺	2.59E-03	6.75E-04	9.32E-03	3.56E-03	2.65E-03	2.76E-03	2.83E-03	2.87E-03	3.10E-03	2.74E-03	2.76E-03	2.82E-03	2.80E-03	2.77E-03	2.75E-03	2.98E-03	2.90E-03	2.93E-03	2.90E-03	2.96E-03	2.94E-03	2.90E-03	2.82E-03	2.85E-03	2.82E-03	2.87E-03	2.80E-03	2.80E-03
Cl ⁻	9.77E-02	2.81E-03	4.68E-02	7.61E-02	8.94E-02	9.53E-02	1.00E-01	1.01E-01	1.03E-01	1.06E-01	9.98E-02	9.93E-02	1.01E-01	1.01E-01	1.02E-01	1.01E-01	1.02E-01	1.01E-01	1.01E-01	1.01E-01	1.01E-01	1.02E-01	1.02E-01	1.01E-01	1.02E-01	1.02E-01	1.03E-01	1.03E-01
SO ₄ ²⁻	5.13E-05	2.91E-05	4.15E-07	2.15E-07	3.10E-07	1.99E-07	4.78E-07	6.04E-07	5.79E-07	6.11E-07	3.56E-07	3.05E-07	3.57E-07	3.00E-07	2.70E-07	2.56E-07	2.57E-07	2.30E-07	2.05E-07	2.36E-07	1.34E-07	1.88E-07	2.15E-07	2.16E-07	1.88E-07	1.87E-07	1.86E-07	1.60E-07
Ca ²⁺	2.62E-05	< LOD	7.24E-07	4.93E-05	7.13E-05	7.48E-05	4.59E-05	4.00E-05	4.45E-05	4.10E-05	5.45E-05	6.26E-05	6.19E-05	6.27E-05	6.24E-05	6.32E-05	6.39E-05	7.15E-05	7.43E-05	7.60E-05	7.37E-05	7.62E-05	7.82E-05	7.73E-05	7.56E-05	7.44E-05	7.35E-05	7.77E-05
Mg ²⁺	3.80E-04	< LOD	< LOD	< LOD	3.92E-07	5.09E-07	3.50E-05	5.74E-05	5.46E-05	4.00E-05	2.12E-05	1.28E-05	1.23E-05	1.20E-05	1.15E-05	1.23E-05	9.89E-06	6.93E-06	5.11E-06	4.09E-06	4.92E-06	2.87E-06	2.50E-06	2.52E-06	3.10E-06	3.93E-06	2.72E-06	2.02E-06
Fe ²⁺	< LOD	< LOD	< LOD	< LOD	< LOD	< LOD	3.36E-05	3.83E-05	4.13E-05	3.35E-05	2.65E-05	1.98E-05	1.99E-05	1.97E-05	1.90E-05	2.04E-05	1.54E-05	7.31E-06	2.49E-06	7.75E-09	2.95E-06	< LOD	< LOD	< LOD	< LOD	1.36E-06	< LOD	< LOD
a ² H ⁺	4.06E-12	5.99E-14	2.70E-12	1.77E-11	2.05E-11	2.42E-11	2.97E-11	3.59E-11	3.59E-11	2.73E-11	2.75E-11	2.57E-11	2.37E-11	2.53E-11	2.57E-11	2.69E-11	2.55E-11	2.63E-11	2.66E-11	2.53E-11	2.90E-11	2.60E-11	2.54E-11	2.51E-11	2.60E-11	2.63E-11	2.51E-11	2.68E-11
log (a SiO ₂)	-3.8	-1.5	-1.5	-1.5	-1.5	-1.5	-1.4	-1.4	-1.4	-1.4	-1.5	-1.5	-1.5	-1.5	-1.5	-1.5	-1.6	-1.6	-1.6	-1.6	-1.6	-1.6	-1.6	-1.6	-1.6	-1.6	-1.6	-1.6
log (a K ₊ /a H ₊)	3.1	3.4	3.8	2.9	2.8	2.7	2.7	2.7	2.7	2.7	2.7	2.7	2.8	2.7	2.7	2.8	2.8	2.7	2.8	2.7	2.8	2.7	2.8	2.7	2.7	2.7	2.7	2.7
log (a Na ₊ /a H ₊)	4.6	4.0	4.4	4.2	4.3	4.3	4.2	4.2	4.2	4.3	4.2	4.3	4.3	4.3	4.3	4.3	4.3	4.3	4.3	4.3	4.2	4.3	4.3	4.3	4.3	4.3	4.3	4.3
log (a Ca ₂₊ /a ² H ₊)	6.8	< LOD	5.4	6.4	6.5	6.5	6.2	6.0	6.1	6.2	6.3	6.4	6.4	6.4	6.4	6.4	6.4	6.4	6.4	6.5	6.4	6.5	6.5	6.5	6.5	6.5	6.5	6.5
log (a Fe ₂₊ /a ² H ₊)	< LOD	< LOD	< LOD	< LOD	< LOD	< LOD	6.1	6.0	6.1	6.1	6.0	5.9	5.9	5.9	5.9	5.9	5.8	5.4	5.0	< LOD	5.0	< LOD	< LOD	< LOD	< LOD	< LOD	< LOD	< LOD
log (a Mg ₂₊ /a ² H ₊)	8.0	< LOD	< LOD	< LOD	4.3	4.3	6.1	6.2	6.2	6.2	5.9	5.7	5.7	5.7	5.7	5.7	5.6	5.4	5.3	5.2	5.2	5.0	5.0	5.0	5.1	5.2	5.0	4.9
log a Na ⁺	-1.0	-2.6	-1.4	-1.1	-1.1	-1.1	-1.0	-1.0	-1.0	-1.0	-1.0	-1.0	-1.0	-1.0	-1.0	-1.0	-1.0	-1.0	-1.0	-1.0	-1.0	-1.0	-1.0	-1.0	-1.0	-1.0	-1.0	-1.0
log a K ⁺	-2.6	-3.2	-2.0	-2.4	-2.6	-2.6	-2.5	-2.5	-2.5	-2.6	-2.6	-2.5	-2.6	-2.6	-2.6	-2.5	-2.5	-2.5	-2.5	-2.5	-2.5	-2.5	-2.5	-2.5	-2.5	-2.5	-2.6	-2.6
log a Cl ⁻	-1.0	-2.6	-1.3	-1.1	-1.0	-1.0	-1.0	-1.0	-1.0	-1.0	-1.0	-1.0	-1.0	-1.0	-1.0	-1.0	-1.0	-1.0	-1.0	-1.0	-1.0	-1.0	-1.0	-1.0	-1.0	-1.0	-1.0	-1.0
log a SO ₄ ²⁻	-4.3	-4.5	-6.4	-6.7	-6.5	-6.7	-6.3	-6.2	-6.2	-6.2	-6.4	-6.5	-6.4	-6.5	-6.6	-6.6	-6.6	-6.6	-6.7	-6.6	-6.9	-6.7	-6.7	-6.7	-6.7	-6.7	-6.7	-6.8
log a Ca ²⁺	-4.6	< LOD	-6.1	-4.3	-4.1	-4.1	-4.3	-4.4	-4.4	-4.4	-4.3	-4.2	-4.2	-4.2	-4.2	-4.2	-4.2	-4.1	-4.1	-4.1	-4.1	-4.1	-4.1	-4.1	-4.1	-4.1	-4.1	-4.1
log a Mg ²⁺	-3.4	< LOD	< LOD	< LOD	-6.4	-6.3	-4.5	-4.2	-4.3	-4.4	-4.7	-4.9	-4.9	-4.9	-4.9	-4.9	-5.0	-5.2	-5.3	-5.4	-5.3	-5.5	-5.6	-5.6	-5.5	-5.4	-5.6	-5.7
log a Fe ²⁺	< LOD	< LOD	< LOD	< LOD	< LOD	< LOD	-4.5	-4.4	-4.4	-4.5	-4.6	-4.7	-4.7	-4.7	-4.7	-4.7	-4.8	-5.1	-5.6	-8.1	-5.5	< LOD	< LOD	< LOD	< LOD	< LOD	< LOD	< LOD
T (°C)	350	352.4	350.7	350.5	350.2	350.7	350.6	350.8	350.5	350.3	350.5	350.6	350.4	350.3	350.7	350.7	350.8	350.4	350.7	350.4	350.7	350.2	350.6	350.9	350.7	350.5	350.6	350.8
P (bar)	500	487.5	487.4	487.5	487.4	487.0	487.0	487.1	487.1	486.9	487.0	487.0	486.9	486.9	486.9	486.9	486.9	486.9	487.0	486.9	487.4	487.0	487.1	487.1	487.2	487.1	487.1	486.9
<i>in situ</i> pH (350°C)	5.70	6.61	5.78	5.38	5.34	5.31	5.26	5.22	5.22	5.28	5.28	5.29	5.31	5.30	5.29	5.29	5.30	5.29	5.29	5.30	5.27	5.29	5.30	5.30	5.29	5.29	5.30	5.29
room T pH	8.20	5.15	3.97	3.81	3.71	3.73	3.11	3.23	3.36	3.47	4.05	3.98	4.01	4.01	4.05	4.11	4.17	4.17	4.24	4.26	4.26	4.26	4.22	4.24	4.21	4.31	4.27	4.36
flow rate (ml hr ⁻¹)	-	1	1	1	1	1	10	10	10	10	10	10	10	10	10	10	5	5	5	5	5	2.5	2.5	2.5	2.5	2.5	1	1
time (hrs)	0.0	18.5	48.2	74.6	97.8	119.8	121.3	123.3	125.3	127.3	143.3	145.3	147.3	149.3	151.1	167.3	169.3	171.3	173.3	175.3	190.8	199.0	215.3	222.3	240.8	264.3	288.4	311.0
Anhydrite																												
Log Ksp (Supcrt92) @350°C			3.86	3.86	3.86	3.86	3.86	3.86	3.86	3.86	3.86	3.86	3.86	3.86	3.86	3.86	3.86	3.86	3.86	3.86	3.86	3.86	3.86	3.86	3.86	3.86	3.86	3.86
Log Q (or log IAP)			5.86	4.32	4.01	4.17	4.01	3.97	3.94	3.96	4.07	4.07	4.01	4.08	-0.72	4.13	4.13	4.13	4.16	4.09	4.38	4.21	4.13	4.13	4.20	4.21	4.22	4.22
Log SI			2.00	0.46	0.15	0.31	0.15	0.11	0.08	0.10	0.21	0.21	0.15	0.22	-4.58	0.27	0.27	0.27	0.30	0.23	0.52	0.35	0.27	0.27	0.34	0.35	0.36	0.36

Table E.6.30. Values of the activity coefficients (a_i) calculated by the R package for the BSW2 (350°C / 488 bar)

sample		H ⁺	OH ⁻	Na ⁺	K ⁺	Cl ⁻	SO ₄ ²⁻	Ca ²⁺	Mg ²⁺	Fe ²⁺	NaSO ₄ ⁻	HSO ₄ ⁻	KSO ₄ ⁻	NaCl ⁻	KCl ⁻	HCl ⁻	KOH ⁻	NaOH ⁻	CaSO ₄ ⁻	MgSO ₄ ⁻	MgCl ⁻	CaCl ⁺	CaCl ₂ ⁻	MgOH ⁺	CaOH ⁺	FeCl ⁻	FeSO ₄ ⁻
blank seawater (natural)	m	3.50E-06	9.10E-06	2.12E-01	6.88E-03	2.44E-01	1.63E-03	4.39E-04	4.10E-03		1.24E-02	1.10E-03	7.09E-04	1.33E-01	9.85E-04	7.86E-06	1.20E-07	2.37E-06	3.57E-04	5.36E-03	2.64E-02	5.95E-03	1.07E-03	1.07E-03	2.80E-05		
	a _i	5.76E-01	4.21E-01	4.21E-01	3.77E-01	4.00E-01	3.15E-02	5.97E-02	9.26E-02		4.21E-01	4.21E-01	4.21E-01	1.00E+00	1.00E+00	1.00E+00	1.00E+00	1.00E+00	1.00E+00	1.00E+00	5.52E-01	4.94E-01	1.00E+00	5.52E-01	4.94E-01		
	activity	2.02E-06	3.83E-06	8.94E-02	2.59E-03	9.77E-02	5.13E-05	2.62E-05	3.80E-04		5.21E-03	4.65E-04	2.99E-04	1.33E-01	9.85E-04	7.86E-06	1.20E-07	2.37E-06	3.57E-04	5.36E-03	1.46E-02	2.94E-03	1.07E-03	5.93E-04	1.38E-05		
1	m	2.85E-07	3.74E-05	2.82E-03	8.03E-04	3.34E-03	5.75E-05	0.00E+00			9.33E-05	3.79E-05	5.22E-05	1.02E-04	7.39E-06	2.75E-08	2.56E-07	5.20E-07	0.00E+00			0.00E+00	0.00E+00		1.07E-06		
	a _i	8.58E-01	8.43E-01	8.43E-01	8.40E-01	8.42E-01	5.06E-01	5.21E-01			8.43E-01	8.43E-01	8.43E-01	1.00E+00	1.00E+00	1.00E+00	1.00E+00	1.00E+00	1.00E+00			8.49E-01	1.00E+00		8.49E-01		
	activity	2.45E-07	3.16E-05	2.38E-03	6.75E-04	2.81E-03	2.91E-05	0.00E+00			7.86E-05	3.20E-05	4.40E-05	1.02E-04	7.39E-06	2.75E-08	2.56E-07	5.20E-07	0.00E+00			0.00E+00	0.00E+00		9.10E-07		
2	m	2.51E-06	8.84E-06	7.07E-02	1.83E-02	8.90E-02	5.16E-06				3.51E-05	5.90E-06	1.70E-05	2.73E-02	1.70E-03	3.02E-06	5.36E-07	1.26E-06							0.00E+00		
	a _i	6.45E-01	5.40E-01	5.40E-01	5.11E-01	5.26E-01	8.48E-02				5.40E-01	5.40E-01	5.40E-01	1.00E+00	1.00E+00	1.00E+00	1.00E+00	1.00E+00							5.88E-01		
	activity	1.62E-06	4.77E-06	3.82E-02	9.34E-03	4.68E-02	4.38E-07				1.90E-05	3.18E-06	9.18E-06	2.73E-02	1.70E-03	3.02E-06	5.36E-07	1.26E-06							0.00E+00		
3	m	6.98E-06	3.92E-06	1.51E-01	8.27E-03	1.69E-01	4.46E-06	6.19E-04			3.69E-05	8.65E-06	3.67E-06	8.25E-02	1.06E-03	1.28E-05	7.88E-08	9.02E-07	8.13E-03			2.35E-05	0.00E+00		0.00E+00		
	a _i	6.03E-01	4.68E-01	4.68E-01	4.31E-01	4.50E-01	4.82E-02	7.97E-02			4.68E-01	4.68E-01	4.68E-01	1.00E+00	1.00E+00	1.00E+00	1.00E+00	1.00E+00				5.31E-01	1.00E+00		5.31E-01		
	activity	4.20E-06	1.84E-06	7.10E-02	3.56E-03	7.61E-02	2.15E-07	4.93E-05			1.73E-05	4.05E-06	1.72E-06	8.25E-02	1.06E-03	1.28E-05	7.88E-08	9.02E-07	8.13E-03			1.25E-05	0.00E+00		0.00E+00		
4	m	7.68E-06	3.83E-06	1.87E-01	6.54E-03	2.10E-01	7.86E-06	1.03E-03	3.80E-06		6.58E-05	1.41E-05	4.13E-06	1.14E-01	9.20E-04	1.62E-05	5.43E-08	9.84E-07	3.34E-08	2.43E-05	1.43E-02	2.45E-03	4.81E-07	3.26E-05	0.00E+00		
	a _i	5.89E-01	4.45E-01	4.45E-01	4.05E-01	4.26E-01	3.94E-02	6.93E-02	1.03E-01		4.45E-01	4.45E-01	4.45E-01	1.00E+00	1.00E+00	1.00E+00	1.00E+00	1.00E+00	1.00E+00	1.00E+00	5.67E-01	5.13E-01	1.00E+00	5.67E-01	5.13E-01		
	activity	4.53E-06	1.71E-06	8.34E-02	2.65E-03	8.94E-02	3.10E-07	7.13E-05	3.92E-07		2.93E-05	6.30E-06	1.84E-06	1.14E-01	9.20E-04	1.62E-05	5.43E-08	9.84E-07	3.34E-08	2.43E-05	8.10E-03	1.26E-03	4.81E-07	1.85E-05	0.00E+00		
5	m	8.41E-06	3.60E-06	2.04E-01	6.99E-03	2.29E-01	5.47E-06	1.14E-03	5.13E-06		4.59E-05	1.00E-05	2.82E-06	1.29E-01	1.02E-03	1.87E-05	5.21E-08	9.66E-07	3.40E-05	1.62E-02	2.92E-03	5.81E-07	3.20E-05	0.00E+00	0.00E+00		
	a _i	5.84E-01	4.37E-01	4.37E-01	3.95E-01	4.16E-01	3.63E-02	6.56E-02	9.91E-02		4.37E-01	4.37E-01	4.37E-01	1.00E+00	1.00E+00	1.00E+00	1.00E+00	1.00E+00	1.00E+00	1.00E+00	5.61E-01	5.06E-01	1.00E+00	5.61E-01	5.06E-01		
	activity	4.92E-06	1.57E-06	8.89E-02	2.76E-03	9.53E-02	1.99E-07	7.48E-05	5.09E-07		2.00E-05	4.38E-06	1.23E-06	1.29E-01	1.02E-03	1.87E-05	5.21E-08	9.66E-07	3.40E-05	1.62E-02	1.64E-03	2.94E-07	3.20E-05	0.00E+00	0.00E+00		
6	m	9.39E-06	3.30E-06	2.18E-01	7.32E-03	2.45E-01	1.41E-05	7.31E-04	3.65E-04	5.36E-04	1.18E-04	2.72E-05	7.07E-06	1.43E-01	1.10E-03	2.18E-05	4.82E-08	9.17E-07	4.60E-06	2.47E-03	1.06E-02	1.98E-03	3.63E-05	1.79E-05	4.07E-03	6.59E-08	0.00E+00
	a _i	5.80E-01	4.29E-01	4.29E-01	3.86E-01	4.09E-01	3.40E-02	6.28E-02	6.28E-02	4.29E-01	4.29E-01	4.29E-01	1.00E+00	1.00E+00	1.00E+00	1.00E+00	1.00E+00	1.00E+00	1.00E+00	1.00E+00	5.57E-01	5.01E-01	1.00E+00	5.57E-01	5.01E-01	5.01E-01	1.00E+00
	activity	5.45E-06	1.42E-06	9.35E-02	2.83E-03	1.00E-01	4.78E-07	4.59E-05	3.50E-05	3.36E-05	5.07E-05	1.17E-05	3.03E-06	1.43E-01	1.10E-03	2.18E-05	4.82E-08	9.17E-07	4.60E-06	2.47E-03	1.06E-02	1.98E-03	3.63E-05	1.79E-05	4.07E-03	6.59E-08	0.00E+00
7	m	1.04E-05	3.00E-06	2.18E-01	7.45E-03	2.47E-01	1.78E-05	6.42E-04	6.00E-04	6.13E-04	1.48E-04	3.78E-05	9.04E-06	1.43E-01	1.12E-03	2.41E-05	4.44E-08	8.30E-07	9.48E-06	4.08E-03	9.29E-03	1.74E-03	5.41E-05	1.42E-05	4.67E-03	9.45E-08	0.00E+00
	a _i	5.80E-01	4.29E-01	4.29E-01	3.86E-01	4.08E-01	3.38E-02	6.25E-02	9.57E-02	6.25E-02	4.29E-01	4.29E-01	4.29E-01	1.00E+00	1.00E+00	1.00E+00	1.00E+00	1.00E+00	1.00E+00	1.00E+00	5.56E-01	5.00E-01	1.00E+00	5.56E-01	5.00E-01	5.00E-01	1.00E+00
	activity	6.00E-06	1.29E-06	9.33E-02	2.87E-03	1.01E-01	6.01E-07	4.01E-05	5.74E-05	3.83E-05	6.36E-05	1.62E-05	3.87E-06	1.43E-01	1.12E-03	2.41E-05	4.44E-08	8.30E-07	9.48E-06	4.08E-03	5.17E-03	8.72E-04	5.41E-05	7.92E-06	2.33E-03	4.72E-08	0.00E+00
8	m	1.04E-05	3.03E-06	2.22E-01	8.09E-03	2.53E-01	1.76E-05	7.24E-04	5.77E-04	6.73E-04	1.46E-04	3.66E-05	9.45E-06	1.48E-01	1.24E-03	2.45E-05	4.80E-08	8.43E-07	8.68E-06	3.96E-03	1.05E-02	2.01E-03	5.17E-05	1.59E-05	5.16E-03	9.82E-08	0.00E+00
	a _i	5.79E-01	4.26E-01	4.26E-01	3.83E-01	4.05E-01	3.29E-02	6.15E-02	9.46E-02	6.15E-02	4.26E-01	4.26E-01	4.26E-01	1.00E+00	1.00E+00	1.00E+00	1.00E+00	1.00E+00	1.00E+00	1.00E+00	5.55E-01	4.98E-01	1.00E+00	5.55E-01	4.98E-01	4.98E-01	1.00E+00
	activity	5.99E-06	1.29E-06	9.45E-02	3.10E-03	1.03E-01	5.79E-07	4.45E-05	5.46E-05	4.13E-05	6.21E-05	1.56E-05	4.02E-06	1.48E-01	1.24E-03	2.45E-05	4.80E-08	8.43E-07	8.68E-06	3.96E-03	5.85E-03	1.00E-03	5.17E-05	8.79E-06	2.57E-03	4.89E-08	0.00E+00
9	m	9.11E-06	3.49E-06	2.37E-01	7.26E-03	2.65E-01	1.90E-05	6.85E-04	4.31E-04	5.60E-04	1.61E-04	3.35E-05	8.76E-06	1.62E-01	1.13E-03	2.22E-05	4.85E-08	1.02E-06	6.60E-06	3.02E-03	1.01E-02	1.98E-03	4.35E-05	1.68E-05	4.35E-03	8.25E-08	0.00E+00
	a _i	5.76E-01	4.22E-01	4.22E-01	3.78E-01	4.00E-01	3.16E-02	5.98E-02	9.28E-02	5.98E-02	4.22E-01	4.22E-01	4.22E-01	1.00E+00	1.00E+00	1.00E+00	1.00E+00	1.00E+00	1.00E+00	1.00E+00	5.52E-01	4.95E-01	1.00E+00	5.52E-01	4.95E-01	4.95E-01	1.00E+00
	activity	5.25E-06	1.47E-06	9.99E-02	2.74E-03	1.06E-01	6.00E-07	4.10E-05	4.00E-05	3.35E-05	6.81E-05	1.41E-05	3.69E-06	1.62E-01	1.13E-03	2.22E-05	4.85E-08	1.02E-06	6.60E-06	3.02E-03	1.01E-02	1.98E-03	4.35E-05	1.68E-05	4.35E-03	8.25E-08	0.00E+00
10	m	9.08E-06	3.41E-06	2.17E-01	7.13E-03	2.44E-01	1.01E-05	8.64E-04	2.21E-04	4.21E-04	8.49E-05	1.90E-05	4.97E-06	1.42E-01	1.07E-03	2.10E-05	4.86E-08	9.45E-07	2.01E-06	1.49E-03	1.25E-02	2.33E-03	2.28E-05	2.19E-05	3.20E-03	3.75E-08	0.00E+00
	a _i	5.81E-01	4.30E-01	4.30E-01	3.87E-01	4.09E-01	3.42E-02	6.30E-02	9.63E-02	6.30E-02	4.30E-01	4.30E-01	4.30E-01	1.00E+00	1.00E+00	1.00E+00	1.00E+00	1.00E+00	1.00E+00	1.00E+00	5.57E-01	5.01E-01	1.00E+00	5.57E-01	5.01E-01	5.01E-01	1.00E+00
	activity	5.27E-06	1.47E-06	9.35E-02	2.76E-03	9.99E-02	3.45E-07	5.44E-05	2.12E-05	2.65E-05	3.65E-05	8.17E-06	2.14E-06	1.42E-01	1.07E-03	2.10E-05	4.86E-08	9.45E-07	2.01E-06	1.49E-03	6.95E-03	1.17E-03	2.28E-05	1.22E-05	1.60E-03	1.88E-08	0.00E+00
11	m	8.73E-06	3.53E-06	1.17E-03	7.27E-03	2.42E-01	8.87E-06	9.92E-04	1.32E-04	3.13E-04	1.48E-04	3.78E-05	9.04E-06	1.43E-01	1.09E-03	2.01E-05	5.16E-08	9.73E-07	1.07E-06	8.93E-04	1.43E-02	2.66E-03	1.42E-05	2.62E-05	2.38E-03	2.48E-08	0.00E+00
	a _i	5.81E-01	4.31E-01	4.31E-01	3.88E-01	4.10E-01	3.44E-02	6.33E-02	9.66E-02	6.33E-02	4.31E-01	4.31E-01	4.31E-01	1.00E+00	1.00E+00	1.00E+00	1.00E+00	1.00E+00	1.00E+00	1.00E+00	5.57E-01	5.02E-01	1.00E+00	5.57E-01	5.02E-01	5.02E-01	1.00E+00
	activity	5.08E-06	1.52E-06	9.24E-02	2.82E-03	9.93E-02	3.05E-07	6.28E-05	1.28E-05	1.98E-05	3.20E-05	6.95E-06	1.93E-06	1.40E-01	1.09E-03	2.01E-05	5.16E-08	9.73E-07	1.07E-06	8.93E-04	7.98E-03	1.34E-03	1.42E-05	1.46E-05	1.19E-03	1.24E-08	0.00E+00
12	m	8.42E-06	3.																								

Activity-activity diagrams

Figure E.6.33. Activity-activity diagrams for the basalt-seawater experiment showing mineral stability fields for the BSW1 experiment (400°C/488 bar) and the BSW2 experiment (350°C/488 bar) showing mineral stability fields in the $\text{SiO}_2 - \text{Al}_2\text{O}_3 - \text{CaO} - \text{H}_2\text{O}$ and in the $\text{CaO} - \text{Na}_2\text{O} - \text{Al}_2\text{O}_3 - \text{H}_2\text{O}$. Yellow circles show position of the output fluid composition from SW1 and SW2 at 377 and 342°C/488 bar, respectively. Blue arrows indicate fluid-path chemistry, in relation to different flow rate. In BSW1, black crosses show position of effluent samples collected at 1.0 ml hr⁻¹ flow rate. Green crosses show position of effluent samples collected at 1.5 ml hr⁻¹ (not visible on graphs). Orange crosses show position of effluent samples collected at 10 ml hr⁻¹. Violet crosses show position of effluent samples collected at 7.5 ml hr⁻¹, while blue crosses show position of effluent samples collected at 5 ml hr⁻¹. In BSW2, black crosses show position of effluent samples collected at 1.0 ml hr⁻¹ flow rate. Orange crosses show position of effluent samples collected at 10 ml hr⁻¹. Violet crosses show position of effluent samples collected at 5.0 ml hr⁻¹ while blue crosses show position of effluent samples collected at 2.5 ml hr⁻¹.

Figure E.6.34. Activity-activity diagrams showing mineral stability fields for the BSW1 (400°C / 488bar) and BSW2 (350°C / 488 bar) in the MgO – FeO – Al₂O₃ – H₂O and in the CaO – FeO – Al₂O₃ – H₂O system. Yellow circles show position of the output fluid composition from SW1 and SW2 at 377 and 342°C/488 bar, respectively. Arrows indicate fluid-path chemistry, in relation to different flow rate. For the BSW1 experiment, black crosses show position of effluent samples collected at 1.0 ml hr⁻¹ flow rate. Green crosses show position of effluent samples collected at 1.5 ml hr⁻¹. Orange crosses show position of effluent samples collected at 10 ml hr⁻¹. Violet crosses show position of effluent samples collected at 7.5 ml hr⁻¹ while blue crosses show position of effluent samples collected at 5 ml hr⁻¹. For the BSW2 experiment, black crosses show position of effluent samples collected at 1.0 ml hr⁻¹ flow rate. Orange crosses show position of effluent samples collected at 10 ml hr⁻¹. Violet crosses show position of effluent samples collected at 5 ml hr⁻¹ while blue crosses show position of effluent samples collected at 2.5 ml hr⁻¹

Figure E.6.35. Activity-activity diagrams showing mineral stability fields for the BSW1 (400°C / 488bar) and BSW2 (350°C / 488 bar) in the $K_2O - SiO_2 - Al_2O_3 - H_2O$ system. Yellow circles show position of the output fluid composition from SW1 and SW2 at 377 and 342°C/488 bar, respectively. Arrows indicate fluid-path chemistry, in relation to different flow rate. For the BSW1 experiment, black crosses show position of effluent samples collected at 1.0 $ml\ hr^{-1}$ flow rate. Green crosses show position of effluent samples collected at 1.5 $ml\ hr^{-1}$. Orange crosses show position of effluent samples collected at 10 $ml\ hr^{-1}$. Violet crosses show position of effluent samples collected at 7.5 $ml\ hr^{-1}$ while blue crosses show position of effluent samples collected at 5 $ml\ hr^{-1}$. For the BSW2 experiment, black crosses show position of effluent samples collected at 1.0 $ml\ hr^{-1}$ flow rate. Orange crosses show position of effluent samples collected at 10 $ml\ hr^{-1}$. Violet crosses show position of effluent samples collected at 5 $ml\ hr^{-1}$ while blue crosses show position of effluent samples collected at 2.5 $ml\ hr^{-1}$.

Figure E.6.36. Activity-activity diagrams showing mineral stability fields for the BSW1 (400°C / 488bar) and BSW2 (350°C / 488 bar) in the MgO – CaO – SiO₂ – Al₂O₃ – H₂O system. Yellow circles show position of the output fluid composition from SW1 and SW2 at 377 and 342°C/488 bar, respectively. Arrows indicate fluid-path chemistry, in relation to different flow rate. For the BSW1 experiment, black crosses show position of effluent samples collected at 1.0 ml hr⁻¹ flow rate. Green crosses show position of effluent samples collected at 1.5 ml hr⁻¹. Orange crosses show position of effluent samples collected at 10 ml hr⁻¹. Violet crosses show position of effluent samples collected at 7.5 ml hr⁻¹ while blue crosses show position of effluent samples collected at 5 ml hr⁻¹. For the BSW2 experiment, black crosses show position of effluent samples collected at 1.0 ml hr⁻¹ flow rate. Orange crosses show position of effluent samples collected at 10 ml hr⁻¹. Violet crosses show position of effluent samples collected at 5 ml hr⁻¹ while blue crosses show position of effluent samples collected at 2.5 ml hr⁻¹

Na/K geothermometers

Table E.6.31. Values of the estimate temperatures for the BSW1 calculated with the geothermometers equations by Fournier (1979), Truesdell (1976), Fournier and Truesdell (1973), Santoyo and Díaz-González (2009), Arnorsson (1983), Tonani (1980), Nieva and Nieva (1987) and Giggenbach (1988)

n° samples	time	T (°C)	P (bar)	flow-rate ml hr ⁻¹	mg kg ⁻¹					T(°C)	T(°C)	T(°C)	T(°C)	T(°C)	T(°C)	T(°C)	T(°C)
					Ca	K	Mg	Na		Na/K (Fournier 1979)	Na/K (Truesdell 1976)	Na/K/Ca (Fournier and Truesdell 1973) β=1/3	Na/K (Santoyo and Díaz-González 2009)	Na/K (Arnorsson 1983)	Na/K (Tonani 1980)	Na/K (Nieva and Nieva 1987)	Na/K (Giggenbach 1988)
Blank seawater (natural) de-oxygenated	0.0	room T	1	-	323.0	329.4	935.24	8405.6		148	105	175	99	152	108	136	167
Water (distilled) mixed seawater circulating in the system - 1	23.9	400	488	1	n.a.	n.a.	n.a.	n.a.		-	-	-	-	-	-	-	-
2	45.3	400	488	1	< 0.05	27.24	< 0.01	46.55		436	512	-	493	410	549	419	428
3	68.1	400	488	1	< 0.05	130.21	< 0.01	206.8		450	535	-	515	421	576	432	439
4	92.3	400	488	1	117.8	580.31	< 0.01	4092.78		249	228	250	219	245	238	235	262
5	116.7	400	488	1	675.3	303.24	0.18	7245.34		152	110	170	104	155	113	140	171
6	141.3	400	488	1	827.7	334.31	< 0.01	8089.6		151	109	169	103	155	112	140	170
7	164.3	400	488	1	929.6	376.0	< 0.01	9123.4		151	108	170	103	155	112	139	170
8	189.5	400	488	1	799.4	316.2	< 0.01	7991.4		149	105	167	100	152	109	137	168
9	212.7	400	488	1	921.2	378.4	< 0.01	9317.2		150	107	170	102	154	110	139	169
10	235.7	400	488	1	817.3	366.3	< 0.01	9103.1		150	107	170	101	153	110	138	169
11	260.3	400	488	1	829.2	330.4	< 0.01	8553.8		147	104	167	98	151	107	135	166
12	284.2	400	488	1	840.3	343.7	< 0.01	8742.6		148	105	168	99	152	108	137	167
13	308.5	400	488	1	879.5	366.1	< 0.01	9193.0		149	106	169	100	152	109	137	168
14	332.2	400	488	1	948.2	396.5	0.18	9899.1		149	106	170	101	153	109	138	168
15	352.7	400	488	1	832.7	347.8	0.02	8825.7		148	105	168	99	152	108	137	167
16	374.8	400	488	1	831.2	353.7	0.11	8941.7		149	105	169	100	152	108	137	168
17	396.3	400	488	1	804.1	329.8	< 0.01	8522.8		147	104	167	98	151	107	136	166
Re-starting heating procedure and re-filling with fresh seawater de-oxygenated		room T	1	-						-	-	-	-	-	-	-	-
Water (distilled) mixed seawater circulating in the system - 19	411.9	400	488	1	n.a.	n.a.	n.a.	n.a.		-	-	-	-	-	-	-	-
20	437.2	400	488	1	584.7	103.6	< 0.01	2528.8		151	108	152	102	154	111	139	170
21	460.7	400	488	1	849.4	199.0	< 0.01	5405.9		144	100	156	95	148	103	132	163
22	484.3	400	488	1	832.7	261.4	< 0.01	6896.6		146	102	162	97	150	105	134	165
23	509.6	400	488	1	843.3	295.2	0.18	7618.9		147	104	165	98	151	107	136	166
24	532.6	400	488	1	861.0	312.3	0.07	8069.0		147	104	165	98	151	107	136	166
25	556.9	400	488	1.5	842.5	315.8	0.39	8122.8		147	104	166	98	151	107	136	167
26	582.8	400	488	1.5	828.4	321.9	0.48	8314.6		147	104	166	98	151	107	136	166
27	583.8	400	488	10	779.9	315.1	0.44	8163.1		147	104	166	98	151	107	135	166
28	584.8	400	488	10	772.2	320.0	1.35	8300.6		147	104	167	98	151	107	135	166
29	585.8	400	488	10	705.3	320.1	1.63	8316.8		147	103	167	98	150	106	135	166
30	586.8	400	488	10	648.9	321.9	1.83	8466.1		146	103	168	97	150	105	134	165
Re-filling with fresh seawater NOT de-oxygenated	-	room T	1	-						-	-	-	-	-	-	-	-
31	603.3	400	488	10	601.4	319.7	2.3	8434.3		146	102	168	97	150	105	134	165
32	605.3	400	488	10	600.3	323.9	2.2	8512.9		146	103	168	97	150	106	135	165
33	607.3	400	488	10	598.2	323.7	2.2	8499.9		146	103	169	97	150	106	135	165
34	609.3	400	488	10	603.3	322.7	2.2	8603.6		145	102	168	96	149	104	134	165
35	611.25	400	488	10	601.3	327.5	2.4	8624.1		146	102	169	97	150	105	134	165
36	626.75	400	488	10	583.0	321.5	2.4	8474.8		146	102	169	97	150	105	134	165
37	628.75	400	488	7.5	590.4	325.6	2.1	8564.3		146	103	169	97	150	105	134	165
38	630.75	400	488	7.5	606.1	329.1	2.2	8611.7		146	103	169	97	150	106	135	166
39	632.75	400	488	7.5	623.3	330.8	2.1	8518.5		147	104	169	98	151	107	136	167
40	634.75	400	488	7.5	618.6	328.1	2.0	8512.4		147	104	169	98	151	107	135	166
41	651.25	400	488	7.5	591.3	320.1	2.0	8328.7		147	103	169	98	150	106	135	166
42	653.25	400	488	5	596.4	328.1	2.0	8506.0		147	104	169	98	151	107	135	166
43	655.25	400	488	5	612.6	329.1	2.0	8516.6		147	104	169	98	151	107	135	166
44	657.25	400	488	5	630.9	325.7	1.8	8608.0		146	102	168	97	149	105	134	165
45	659	400	488	5	631.6	328.0	1.8	8599.2		146	103	168	97	150	106	135	166
									T(°C) AVERAGE (SiO ₂ above quartz saturation)	147	104	168	98	151	107	136	167
									1σ	1.6	1.8	3.5	1.7	1.5	1.9	1.5	1.5

Table E.6.32. Values of the estimate temperatures for the BSW2 calculated with the geothermometers equations by Fournier (1979), Truesdell (1976), Fournier and Truesdell (1973), Santoyo and Díaz-González (2009), Arnorsson (1983), Tonani (1980), Nieva and Nieva (1987) and Giggenbach (1988)

n° samples	time	T (°C)	P (bar)	flow-rate ml hr ⁻¹	mg kg ⁻¹					T(°C)	T(°C)	T(°C)	T(°C)	T(°C)	T(°C)	T(°C)	T(°C)
					Ca	K	Mg	Na		Na/K (Fournier 1979)	Na/K (Truesdell 1976)	Na/K/Ca (Fournier and Truesdell 1973) β=1/3	Na/K (Santoyo and Díaz-González 2009)	Na/K (Arnorsson 1983)	Na/K (Tonani 1980)	Na/K (Nieva and Nieva 1987)	Na/K (Giggenbach 1988)
blank seawater (natural)	0.0	room T	1	-	314.6	335.0	897.0	8228.2		150	108	109	102	154	111	139	169
1	18.5	350	488	1	< 0.05	33.8	< 0.01	69.5		404	458	-	441	382	489	387	400
2	48.2	350	488	1	3.2	780.0	< 0.01	2253.1		353	376	251	362	338	398	337	356
3	74.6	350	488	1	400.9	364.9	< 0.01	5390.3		186	149	125	142	187	154	173	203
4	97.8	350	488	1	712.7	291.7	0.7	6927.6		153	110	104	104	156	113	141	172
5	119.8	350	488	1	814.5	313.6	1.0	7664.762		151	108	103	102	154	111	139	170
6	121.3	350	488	10	534.7	329.7	70.0	8297.246		149	106	105	100	152	109	137	168
7	123.3	350	488	10	467.2	335.4	115.1	8511.64		148	105	105	99	152	108	137	168
8	125.3	350	488	10	531.9	365.3	111.8	9168.5		149	106	105	100	153	109	137	168
9	127.3	350	488	10	512.8	328.4	85.1	8248.9		149	106	105	100	152	109	137	168
10	143.3	350	488	10	629.5	321.0	42.4	8162.6		148	105	103	99	152	108	137	167
11	145.3	350	488	10	719.4	326.7	25.3	8372.4		148	104	102	99	151	107	136	167
12	147.3	350	488	10	724.9	327.0	24.9	8413.9		147	104	102	98	151	107	136	167
13	149.3	350	488	10	737.0	323.9	24.4	8491.1		146	103	101	97	150	106	135	166
14	151.1	350	488	10	736.6	322.4	23.4	8415.4		147	103	101	97	150	106	135	166
15	167.3	350	488	10	745.6	348.2	24.8	8517.3		151	108	104	102	154	111	139	170
16	169.3	350	488	5	755.8	339.9	20.1	8373.7		150	107	103	101	154	110	139	169
17	171.3	350	488	5	836.4	341.8	14.0	8415.9		150	107	103	102	154	110	139	169
18	173.3	350	488	5	872.9	338.8	10.3	8374.1		150	107	102	101	153	110	138	169
19	175.3	350	488	5	889.4	345.1	8.2	8457.4		151	108	103	102	154	111	139	170
20	190.8	350	488	5	870.5	344.2	9.9	8526.1		150	107	102	101	153	110	138	169
21	199.0	350	488	2.5	905.1	340.2	5.9	8531.5		149	106	102	100	153	109	137	168
22	215.3	350	488	2.5	929.8	331.1	5.0	8457.6		148	105	101	99	151	108	136	167
23	222.3	350	488	2.5	912.1	333.9	5.2	8552.4		148	104	101	99	151	107	136	167
24	240.8	350	488	2.5	898.6	331.7	6.3	8559.2		147	104	101	98	151	107	136	166
25	264.3	350	488	2.5	886.1	337.0	8.1	8701.7		147	104	101	98	151	107	136	166
26	288.4	350	488	1	883.3	330.4	5.6	8603.2		147	103	101	98	150	106	135	166
27	311.0	350	488	1	929.1	329.4	4.2	8598.3		147	103	100	97	150	106	135	166
									T(°C) AVERAGE (SiO ₂ above quartz saturation)	148	105	102	99	152	108	137	168
									1σ	1.4	1.7	1.6	1.6	1.4	1.7	1.4	1.4

Table E.6.33. Geothermometers equations utilized for the calculation of the estimate temperature values reported in Table E.6.31-32

Na/K : Fournier (1979)	$T(^{\circ}C) = \frac{1217}{1.438 + \log\left(\frac{Na}{K}\right)} - 273,15 (^{\circ}K)$
Na/K : Truesdell (1976)	$T(^{\circ}C) = \frac{855,6}{0.8573 + \log\left(\frac{Na}{K}\right)} - 273,15 (^{\circ}K)$
Na/K : Santoyo and Gonzalez (2009)	$T(^{\circ}C) = \frac{876.3(\pm 26.26)}{0.8775(\pm 0.0508) + \log\left(\frac{Na}{K}\right)} - 273,15 (^{\circ}K)$
Na/K : Arnorsson (1983)	$T(^{\circ}C) = \frac{1319}{1.699 + \log\left(\frac{Na}{K}\right)} - 273,15 (^{\circ}K)$
Na/K : Tonani (1980)	$T(^{\circ}C) = \frac{883}{0.78 + \log\left(\frac{Na}{K}\right)} - 273,15 (^{\circ}K)$
Na/K : Nieva and Nieva (1987)	$T(^{\circ}C) = \frac{1178}{1.483 + \log\left(\frac{Na}{K}\right)} - 273,15 (^{\circ}K)$
Na/K : Giggenbach (1988)	$T(^{\circ}C) = \frac{1390}{1.75 + \log\left(\frac{Na}{K}\right)} - 273,15 (^{\circ}K)$
Na/K/Ca : Fournier and Truesdall (1973)	$T(^{\circ}C) = \frac{1647}{\log\left(\frac{Na}{K}\right) + \beta [\log(\sqrt{Ca}/Na) + 2.06] + 2.47} - 273,15 (^{\circ}K)$