Planktic foraminiferal proxy development and application to paleoceanographic change in the Southwest Pacific Ocean

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Abstract

This thesis investigates the use of foraminiferal calcite geochemical and physical properties as paleoceanographic proxies, to improve identification of past climatic change and provide a more quantitative basis for forecasts of future climate. I have developed and used these proxies on a high resolution, well-dated marine sediment core, MD97 2121 from north of the Subtropical Front (STF) off the eastern central North Island of New Zealand to determine paleoceanographic changes in the South Pacific Gyre since the last glacial period, 25 ka to present.

Various analytical methods to measure foraminiferal calcite trace element geochemistry were first investigated using core top samples. Two main analytical techniques were deployed; “pseudo” solution- or laser ablation-based ICPMS analysis. Ratios tested include Mg/Ca, Sr/Ca, Ba/Ca, Zn/Ca, Mn/Ca and Al/Ca. Trace element/calcium ratios Mg/Ca and Sr/Ca values were consistent between these methods, provided that currently recommended ‘Mg-cleaning’ protocols were followed for solution-based measurements. However, discrepancies of up to an order-of-magnitude for Zn/Ca, Mn/Ca and Ba/Ca occurred between solution and laser ablation-based measurements if both oxidative *and* reductive cleaning techniques were not employed prior to solution-based analysis.

Using down-core trace element values Mg/Ca, Zn/Ca, Mn/Ca and Ba/Ca from MD97 2121, coupled with modern core top and plankton-tow samples, multiple geochemical proxies for the SW Pacific Ocean were developed and/or tested. Results suggest that Zn/Ca may act as (i) a surface water mass tracer, in this case differentiating between subtropical and subantarctic surface waters and (ii) a proxy for nutrients. Mg/Ca and Zn/Ca values from different test chambers in *Globigerina bulloides* were also found to reliably re-construct surface ocean temperature and nutrient stratification. Using these new proxies, coupled with oxygen isotopes, standard Mg/Ca paleothermometry and foraminiferal assemblage data, I show that surface water nutrient and thermal stratification significantly reduced during the last glacial period. In addition, the relative strength of the South Pacific Gyre, which affects the inflow of subtropical water to New Zealand, was a major influence during the last glacial termination. In particular, the period from 17-14.5 ka, otherwise known as the ‘Mystery Interval’, appears to be genuinely anomalous with foraminifera indicating cooling trends while alkenones continue to warm. This may reflect changes to both gyre strength and Antarctic forcing prior to the Antarctic Cold Reversal (14.2-12.5ka) and an offset in the timing of species productivity.

The high resolution Mg/Ca paleotemperature record developed here, together with published alkenone paleotemperatures were compared to core MD97 2120, south of the STF to evaluate the relationship between Mg/Ca and alkenones temperatures and how these reflect environmental change. It appears that the season of maximum alkenone and *G. bulloides* flux

varied over the last 25kyr in response to insolation and water mass changes. During the glacial period north and south of the STF alkenone seasonal flux was summer dominated. However, during the Holocene while seasonal alkenone flux remained summer or annual dominated in the north, it shifted to a spring productivity cycle south of the STF. The foraminifera *G. bulloides* glacial period flux was likely have been spring dominated both north and south of the STF, maintaining a spring bloom cycle south of the STF, while shifting to a summer or annual cycle to the north during the Holocene. These seasonal offsets may have acted to dampen or exacerbate the glacial-Holocene temperature offsets by up to 4°C especially for the surface dwelling, alkenone producing coccolithophores. Seasonality changes of the coccolithophore and foraminifera make direct comparison of alkenone and Mg/Ca *G. bulloides* paleothermometers challenging. However, despite the complexity, offsets in the paleotemperatures may help to elucidate changes in the paleoceanography.

The use of *G. bulloides* size normalised weight (SNW) as a proxy for surface water carbonate ion concentration ($[\text{CO}_3^{2-}]$) was investigated by comparing modern SNW data sets from five different ocean regions to their specific environmental variables including $[\text{CO}_3^{2-}]$, chlorophyll-*a*, nutrient and temperature values. It was identified that the ‘ocean’ from which the foraminifera originated appeared to have the strongest control over shell SNW, potentially reflecting geographically distinct, genetic variations within the *G. bulloides* species. Within ‘ocean’ regions no consistent environmental variable(s) could be identified that appeared to control shell SNW in all regions. From the 25 ka to present, shell SNWs from the SW Pacific Ocean were compared to the North Atlantic and were found to be heavier during the glacial period regardless of ocean region. This may reflect multiple factors including increased surface ocean CO_3^{2-} , possibly combined with changes in primary productivity. Calcification of *G. bulloides* tests appears to be region specific; therefore, proxy calibrations based on shell SNW for one ocean are not applicable to other settings.

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List of commonly used acronyms and terms

Oceanographic

STW	Subtropical Surface Water
SAW	Subantarctic Surface Water
CSW	Circumpolar Surface Water
STF	Subtropical Front
SAW	Subantarctic Front
TF	Tropical Front
SPG	South Pacific Gyre
EAC	East Australian Current
EAUC	East Auckland Current
WE	Wairarapa Eddy
MIS	Marine Isotope Stage
SST	Sea Surface Temperature
AAIW	Antarctic Intermediate Water
SAMW	Subantarctic Mode Water

Foraminifera

<i>G. bulloides</i>	<i>Globigerina bulloides</i>
<i>G. ruber</i>	<i>Globigerinoides ruber</i>
Tests	Shells
Gametogenesis	reproduction

Analytical

SEM	Scanning electron microscope
LA-ICPMS	Laser ablation-inductively coupled plasma mass spectrometry
MilliQ	Ultrapure water (equivalent to $>18.2 \text{ M}\Omega \text{ H}_2\text{O}$)
$>18.2 \text{ M}\Omega \text{ H}_2\text{O}$	Ultrapure water (equivalent to MilliQ)
NIST	National Institute of Standards and Technology
TE	Trace element
LA-ICPMS	Laser ablation – inductively coupled plasma mass spectrometry

General

LGM	Last Glacial Maximum (<i>ca.</i> 25 ka)
ka	A specific time in the geological record
kyr	A length of time
CI	Confidence interval
SI	Supplementary information

Publications arising from this thesis

Journal articles

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Conference abstracts () indicates oral presentation*

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*Marr, J. P., J. A. Baker, L. Carter, A. S.R. Allan, K. Christensen, and H. C. Bostock, 2011. Horizontal and vertical water mass tracing of the SW Pacific Ocean during the last deglaciation, *Goldschmidt Conference, Prague, 14-19 August, 2011*, 1408pp.

Marr, J., Baker, J., Carter, L., Dunbar, G., 2009. LA-ICP-MS core-top Mg/Ca-temperature calibration for *G. bulloides* and a high resolution record of the last deglaciation in the

Southwest Pacific Ocean, *American Geophysical Union, San Francisco, Fall Meeting 2010*,
abstract #PP41B-1639

Chapter 1

Introduction

1.1 Thesis objectives and structure

This work focuses on the development and use of trace metals and physical properties measured in the planktic foraminifers, *Globigerina bulloides* and *Globigerinoides ruber* as paleoenvironmental proxies in the Southwest Pacific Ocean. These foraminifera are characterised by widespread biogeographical and paleoceanographical coverage, they live in the surface layers of the ocean (Bé, 1977; Bé and Hutson, 1977; Hemleben et al., 1989), and their shells (tests) are composed primarily of calcium carbonate, with minor inclusions of other trace elements (e.g. Boyle, 1981; Delaney et al., 1985). Previously, trace metal proxy development for foraminiferal calcite has primarily focused on the ratio of Mg to Ca as a paleothermometer (e.g. Anand et al., 2003; Bender et al., 1975; Rosenthal et al., 1997). However, fundamental challenges to the use and understanding of Mg/Ca as a paleotemperature proxy have been ongoing in the biogeochemical and paleoceanographical communities (e.g. Dekens et al., 2002; Eggins et al., 2003a; Erez, 2003). The emphasis on developing a more holistic understanding about changes in the ocean environment is also becoming more prominent as our understanding about the role of nutrients, surface ocean stratification, heat transportation and biology in global climate change develops (e.g. Ridgway and Hill, 2009; Rost and Riebesell, 2004). Further, it is vital that we identify natural temperature variability if we are to better isolate the current potential anthropogenic effect.

The central purpose of this thesis is to provide new perspectives on the use of foraminifera trace metal values and physical properties as paleoenvironmental proxies. I have used core top and plankton tow samples from the Southwest Pacific Ocean region, coupled with samples from a 25 ka cored sedimentary record from site MD97 2121 off Hawke Bay, New Zealand. My approach integrates geochemical data, electron microscope imaging, and trace element mapping of foraminifera tests to reconstruct the surface ocean paleoenvironment in the Southwest Pacific Ocean. Building on the existing geochemical data base from Marr (2011) and Bolton (2011), I establish new proxies for distinguishing between subantarctic (SAW) and subtropical water masses (STW), in addition to paleo surface ocean thermal and nutrient stratification based on the geochemical offsets between *G. bulloides* chambers and *G.*

ruber/ *G. bulloides* species. These proxies are then used to determine the interaction between these surface water masses overlying the core site from the last glacial maximum (LGM) to present. Further, I investigate (i) reasons behind the apparent differences between different paleothermometry proxy records, and (ii) the potential of the ratio of foraminifera weight to diameter to provide a reliable record of surface water carbonate ion concentration and therefore atmospheric CO₂ levels.

This work contributes to a well-established, yet still developing paleoceanographical research field. Techniques such as the bulk (solution) and in situ (e.g. laser ablation) geochemical analysis of foraminifera have been used by previous workers (e.g. Sadekov et al., 2008; Barker and Elderfield, 2002) to develop and apply paleoceanographic proxies to foraminifera recovered from sedimentary archives from all of the major ocean basins. However, some fundamental aspects concerning these approaches require further scrutiny. For example, little is known about the physical effects on the foraminiferal shell of the chemical pre-treatments applied prior to solution analysis.. Structural damage to the calcite shell may exacerbate the effect of the chemical e.g. untended dissolution of the primary calcite, thus potentially making the results incomparable. These aspects of foraminiferal cleaning procedures, and their implications for subsequent interpretations of geochemical data, are explored in this thesis. Further, because foraminifera live and calcify their shells within the ocean, they potentially provide a ‘snap-shot’ of ocean chemistry and/or conditions at the time of calcification. As such, in situ geochemical analysis of individual foraminifera has the potential to extend the utility of foraminifera in paleoceanographic reconstructions beyond the temperature reconstructions for which they are most widely currently used. Investigated in this thesis is whether foraminifera are able to be used as proxies for other part of the ocean system, e.g. changes to the water mass and stratification.

An inherent assumption surrounding the application of Mg/Ca values of foraminifera and alkenone ratios of coccolithophore as proxies is that these geochemical features primarily reflect temperature changes. However, comparison between where these particular temperature proxies have been applied (e.g. Barrows et al., 2007) clearly indicate that other factors, in addition to temperature, are influencing the geochemical signature. At present it is not clear what effect, if any, these ‘other influences’ may have on the validity of temperature estimates. For example, do the differences between foraminiferal versus coccolithophore temperature records in these studies (Barrows et al. 2007) reflect a breakdown of one or other

of the temperature proxies, or simply an indication that the two proxies are recording different aspects of the temperature (e.g. depth, season etc)? This thesis addresses what some of these other influences may be, explores to what extent they may affect the validity of such temperature estimates, and identifies ways in which contrasting records from foraminifera and coccolithophore may be interpreted to understanding wider hydrological and environmental changes. In addition to chemistry-based proxies, the weight of foraminiferal shells have previously been identified as having potential utility as a paleo-proxy (e.g. Barker and Elderfield, 2002). The current proposed applications include the use of foraminiferal weight as a proxy for surface ocean carbonate ion concentration, temperature and nutrient levels (e.g. Barker and Elderfield, 2002; Marr et al., 2011; Aldridge et al., 2012). A criticism of these studies is that the calibrations have tended to be developed for isolated and specific oceanic regions, and while it is theorised that their results may apply in a wider context, little actual comparison of size normalised weights, either in the modern or from the paleocean, has been attempted. In this thesis size-normalised foraminifera weights from modern day records from ocean basins including the Southwest Pacific, Southern Ocean, and North Atlantic are compared to assess whether there are consistent trends in data between ocean basins.

Hence, the primary objectives of this thesis are to:

- i) Determine the utility of the laser ablation technique for measurement of Mg/Ca and other trace element to calcium (TE/Ca) ratios in foraminifera.
- ii) Compare laser- and solution-based analytical techniques to understand the effect of the analytical method on TE/Ca results for use in established and novel geochemical paleo proxies.
- iii) Develop foraminiferal Mg/Ca and other 'trace elements' (TE/Ca) as proxies for thermal and nutrient concentration and potentially upper ocean stratification.
- iv) Apply thermal and nutrient paleo proxies to a paleoceanographic record from the Southwest Pacific to potential reveal major shifts the oceanography and climate over the last 25 kyr.
- v) Evaluate the reason(s) behind differences between various proxies used to determine sea surface temperatures.

vi) Investigate the potential use of *G. bulloides* test weights as a paleoceanographic proxy.

These specific aims are addressed within five interrelated chapters, structured around the central theme of developing, understanding and applying TE/Ca upper ocean paleoenvironmental proxies. The chapters are written in a science journal style suitable for publication, and are thus presented as self-contained studies, each building on findings from the previous chapter. As a result there is some necessary replication of information, in particular, that pertaining to the general setting of the study area and methods. Published or accepted papers have been modified only slightly (stylistically and in terms of formatting, but not in content) for incorporation into the thesis.

Chapter 1: Provides background information for the research including; the relative effects of ecology, biology, water geochemistry, physical oceanography and sedimentation processes on paleoceanographic records, and the theory behind the use of test weights as atmospheric CO₂ proxies, focusing on planktic foraminifera test calcite as archives of the paleocean environment.

Chapter 2: Compares analytical techniques for deriving trace element and ultra-trace element measurements from foraminiferal test calcite, including investigation of the efficacy of cleaning for laser ablation-ICPMS, and the compatibility between solution-based and laser ablation-based data.

Chapter 3: Presents modern and paleoceanographic geochemical data from *G. bulloides* and *G. ruber* to investigate the use of chamber specific Mg/Ca, Zn/Ca, Mn/Ca and Ba/Ca as paleoenvironmental proxies for the surface ocean conditions in the Southwest Pacific Ocean.

Chapter 4: Uses the MD97 2121 core record as a case study for assessing the use of two common paleothermometry techniques; alkenone undersaturation levels and foraminiferal Mg/Ca, to evaluate any differences and develop a coherent paleoceanographic record.

Chapter 5: Investigates the modern calibrations relating *G. bulloides* size-normalised test weights to temperature and carbonate ion levels in the surface ocean. Regional core top and LGM to present data, are evaluated from five different oceans, with the most detailed comparison made for the North Atlantic and Southwest Pacific Oceans.

Chapter 6: Integrates the primary findings of this doctoral work, and outlines new areas for targeted research in the future.

1.2 Background

1.2.1 Planktic foraminifera

Planktic foraminifera are unicellular, free-floating protozoa found throughout the major ocean basins. Although they represent a fairly minor proportion of the total living zooplankton, their calcium carbonate shells (tests) constitute a major component of the marine sedimentary record in areas of moderate to high productivity where the bottom waters are favourable for test preservation. The earliest taxonomic descriptions of foraminifera were given by d'Orbigny (1826; 1839) and later revised and updated by Brady (1876; 1884). Since that time studies on foraminiferal ecology and the chemical composition of their tests have provided the basis for a multitude of tools aimed at understanding paleoceanographic and environmental variability over timescales ranging from short-term seasonal and inter-decadal cycles to relatively long term changes over hundreds and millions of years (Hemleben et al., 1989).

The chemical composition of foraminiferal shells is primarily determined by the chemistry of the ambient seawater (Kucera, 2007). Foraminifera also have some control over trace metal incorporation into test calcite, either through passive mechanisms, such as a change in its habitat, or via actively controlling or 'pumping' the metal to remove it from its cytoplasm (e.g. de Nooijer et al., 2009; Lea, 2003). Foraminiferal vertical migration through the water column, and thus a change in calcification depth, is an example of passive control over test calcite trace metal incorporation. The fossil assemblage is also biased toward shells deposited during the time of maximum production. This means that, depending on the species and its ecological niche, the geochemical signal measured on any given sample of specimens may represent the yearly average, spring, summer, or autumn conditions. Therefore the use of these organisms as a basis for geochemical proxies is increasingly reliant upon a detailed knowledge of the ecology of the signal carrier (e.g. Allen et al., 2011; Rohling et al., 2004).

Planktonic foraminifera generally inhabit the surface mixed layer and upper thermocline of the oceans. Foraminifera species have a range of environmental preferences or tolerances. In addition, their growth and reproductive habits can vary between ocean basins and latitudes. These conditions can only be replicated with varying degrees of success in laboratory culture experiments (e.g. Bender et al., 1975; Lea et al., 1999; Lea and Spero, 1992; Lombard et al.,

2009). However, with improved understanding of these species specific complexities, opportunities for more paleo proxy tools may arise. Here, the properties of foraminiferal calcification, ecology and genetic diversity are described with reference to the species involved in this study.

1.2.2 Calcification of spinose foraminifera

Calcification of chambers in spinose species such as *G. bulloides* and *G. ruber* occur along the ‘ridges’ or undulations of the test surface between spines during the ontogenetic stages of growth (Fig. 1). During ontogenetic calcification, spines protrude from the intersection between the ridge sections, and small flat calcite plaques (*ca.* 0.2 μm in diameter) are secreted on top of each other forming the ridges that connect the spine bases (Fig. 1) (Bé et al., 1980). This calcite forms the basic structural units that make up the test wall and is hereafter referred to as ‘primary calcite’. Subsequent thickening of the test wall occurs with the secretion of calcite layers that accompany chamber-by-chamber growth (Fig. 1). Thin layers of organic material, similar in composition to the primary organic membrane on the inside of the test wall, are deposited between each subsequent layer of calcite associated with new chamber formation (Bé, 1980; Sen Gupta and Hansen, 2003). Prior to gametogenesis (reproduction) foraminifera migrate lower in the upper water column, possibly to the euphotic zone, and the final chamber is formed followed by the resorption of the spines into the rhizopodial (Bé et al., 1980; Erez et al., 1991). Gametes are then released before gametogenic calcification. This gametogenic calcite deposits euhedral crystallites over the ridges, and can infill pore basins and thereby smooth the appearance of the inter-pore ridges (Fig. 1) (Bé, 1980; Bé et al., 1980; Erez et al., 1991). When grown under laboratory conditions very few specimens carry out gametogenic calcification (Bé, 1980).

Figure 1. Calcification of the foraminifera test wall. (a) Electron backscattered image of *G. bulloides* chamber *f-1*, which has undergone oxidative and 1x acid leach cleaning. Spines of the foraminifera have been incompletely resorbed, leaving a remnant in the test wall, the top of which was subsequently covered with gametogenic calcite. (b) Schematic diagram illustrating wall and pore structure of an adult *G. bulloides* showing successive growth stages of ontogenetic calcification. Successive primary calcite/ontogenetic calcification layers are indicated by bricks with the thin, possibly organic layers between chamber formation indicated by blocks with crescents, inner test wall/primary organic membrane is indicated by dashed lines. Gametogenic calcification/surface layer is indicated by stippling. (Bé, 1980; Erez, 2003; Sadekov et al., 2005). (c) Cross-section through the test wall of foraminifera chamber *f-1*, which has undergone oxidative and reductive cleaning treatments. Complete resorption of spines has occurred, with remnants of the outer spine wall clearly visible after primary calcite layer separation. Also illustrated is the relationship between stronger calcite formed in the inner test wall and immediately around the spines, and primary calcite layers. No distinctive dark or light

banding was observed in these or other samples in this study to indicate the presence of organic layers (Erez, 2003). (d) SEM image of *G. bulloides* indicating key parts of the foraminifera including the chambers from oldest (*f*-2) to youngest (*f*) and the aperture.

1.2.3 Test calcite trace metal concentrations

Foraminifera tests are primarily composed of calcite, however within the calcite lattice are inclusions of small amounts of other elements such as Mg, Sr, Al, Mn, Zn, and Ba, which are known as ‘trace metals’. There are three potential primary influences on the concentration of trace metals in primary test calcite; 1) trace metal availability in the ambient water mass (Fig. 2) (Bruland and Lohan, 2003); 2) biological controls on metal incorporation including the minimum metal quota for phytoplankton growth; 3) the species depth in the water column at the time of calcification (Morel et al., 1991; Lea and Boyle et al., 1991; Anand et al., 2003). Post-deposition diagenetic effects can also affect trace metal concentrations in test calcite including dissolution, recrystallisation or adhesion of particles such as clay (e.g. Boyle, 1983; Pena et al., 2005; Sadekov et al., 2010).

Trace metal concentration through the water column varies depending on the elemental source(s), uptake and ocean residency times, and upper ocean stratification, which in turn affect its vertical distribution. Where the respective residency time is shorter than the mixing time required for water column homogenisation, and organic or inorganic demand exceeds supply, the element becomes depleted at the surface and increasingly replete with depth to give a nutrient-like profile, as in the case of Zn and Ba (Fig. 2). Alternatively, relatively high flux, low uptake and short residency times leads to scavenged-type profile where the element has maximum concentrations in surface waters e.g. Mn and Al (Fig. 2). Mg/Ca thermometry takes advantage of the conservative nature and long residency times of both Mg and Ca in seawater, providing a relatively uniform temporal and spatial distribution in the water column. As a result of the conservative nature of these elements, it is not the ambient concentration in the water mass that primarily causes variability of Mg/Ca in test calcite on time scales shorter than *ca.* 1 Ma, but rather biologically mediated, thermodynamically controlled incorporation of Mg into the calcite lattice (Fig. 2) (Bender et al., 1975; Broecker and Peng, 1982; Lea et al., 1999). Application of the Mg/Ca paleothermometer derives from the empirical observation that foraminiferal Mg/Ca values increase systematically with seawater temperature (e.g. Anand et al., 2003; Lohmann, 1995; Savin and Douglas, 1973). The usefulness of other trace metals in paleoceanographic research is derived from their close relationships with other

oceanographic properties such as nutrient distribution in the case of Zn and Cd (Boyle, 1981). In addition, the strong inter-basin fractionation of elements with such as Al or Ba short residency times may be a valuable source of information about circulation and mixing between water masses (Boyle and Keigwin, 1985; Bruland and Lohan, 2003; Lea and Spero, 1994).

Figure 2. Mean element distributions in seawater for the Pacific (pink symbols/line) and Atlantic Oceans (green symbols/line) of trace metals investigated in this study. (a) Mg, has a residency time of ca.13 Myr and thus a conservative distribution with higher values in the Atlantic due to higher salinity (Broecker and Peng, 1982); (b) Ca has a residency time of 1.1 Myr and is the fifth most abundant element in seawater with a nearly conservative distribution (Broecker and Peng, 1982); (c) Sr, has a residency time of 5.1 Myr and a near vertical profile with a slight surface depletion due to the strontium sulphate shell production of *Acantharia* plankton (Broecker and Peng, 1982; de Villiers, 1999); (d) Mn has a scavenged vertical profile, with a high surface concentration becoming increasingly replete with depth, and in certain regions, a subsurface maximum in places with low oxygen concentrations. Mn has a residency time of ca.60 yrs (Johnson et al., 1996; Klinkhammer and Bender, 1980; Martin and Knauer, 1980); (e) Al has an ocean residency time of ca.200 yrs and the vertical profile of a scavenged element (Orlans and Bruland, 1986). (f) Ba has a ocean residency time of 10 ka and a

nutrient-like vertical profile with depleted concentrations found at the surface and values increasing to a deep maximum (Chan et al., 1976). (g) Zn has a residency time of *ca.* 50 ka and a nutrient like vertical profile, highly correlated with Si (Shiller and Boyle, 1985). Graphs adapted from (Johnson et al., 1999).

The degree to which biology controls trace metal incorporation has been the subject of several studies (Delaney, 1989; Delaney et al., 1985; Hathorne et al., 2003; Hönisch et al., 2011; Lea et al., 1999; Nürnberg et al., 1996). For example, biology plays a significant role in controlling the incorporation of trace elements such as Mg. Surface seawater is supersaturated in Mg with respect to Ca, however foraminifera generally produce a test with a low Mg content indicating that the organism must actively remove Mg^{2+} from vacuolized seawater (seawater within the cytoplasm) prior to calcite precipitation (Bentov and Erez, 2006; Lea et al., 1999). This removal likely occurs in conjunction with pH elevation at the site of calcification to overcome Mg precipitation-inhibition (de Nooijer et al., 2009).

As a result of biologically mediated controls on foraminiferal test calcite Mg levels, the Mg/Ca ratios differ markedly from that predicted by thermodynamic calculations (Bender et al., 1975) in two fundamental ways. First, foraminifera contain 5-10 times less Mg than predicted by thermodynamics. Second, the response of shell Mg to temperature is *ca.* 3 times larger averaging 9-10 % per °C, than the thermodynamic prediction and inorganic observation of 3 % per °C (Cléroux et al., 2008; Lea et al., 1999; Marr et al., 2011; McConnell and Thunell, 2005). While it is possible that these biological controls also mediate the incorporation of bioactive trace metals such as Zn and Mn, or metals which appear to not have a biological function such as Ba and Sr, the mechanism(s) by which this may happen is currently unknown. Such biological effects are commonly referred to as ‘vital effects’ and are a source of natural ‘noise’ or variance within data (e.g. Bentov and Erez, 2006; Lear et al., 2002; Sadekov et al., 2005).

1.2.4 Foraminifera ecology

It is commonly recognised that upper ocean organisms inhabit specific depth(s), dependant on the prevailing surface water conditions and stage of lifecycle (Hemleben et al., 1989). Thus foraminiferal vertical migration pattern and depth of calcification determine what level in the water column the geochemical signal represents. Typically, the planktic foraminiferal lifecycle is no longer than a month. It takes less than 8 hours to fully calcify any one chamber, with final chamber calcification (chambers *f* to *f*-3 in *G. bulloides* or *f* to *f*-2 in *G. ruber* – Fig. 3) occurring in the final two weeks (Spero pers. comm, 2012). Therefore, the calcite of any

specific chamber preserves a ‘snapshot’ of surface water conditions at the time and depth of calcification (Bé et al., 1979; Hemleben et al., 1989).

Figure 3. Scanning electron microscope images of *G. ruber* (a) and *G. bulloides* (b) analysed using laser ablation inductively coupled plasma mass spectrometry (LA-ICPMS) in this study. The chambers are labelled such that *f* represents the final (youngest) chamber, *f-1* is the penultimate chamber, *f-2* is the antepenultimate chamber and *f-3* the oldest chamber analysed. Circular laser ablation pits are shown in each *G. bulloides* chamber.

When assessing how foraminiferal species trace metal geochemistry reflects paleocean conditions there are two types of depth that need to be taken into account: 1) the natural depth habitat of the species and known migrations within its lifecycle, 2) the depth that a particular proxy has been calibrated for. It is best practice to develop modern calibrations specific to the depth and species targeted for paleoceanographic analysis due to variations in surface water trace metal concentrations and wider environmental conditions such as light or nutrient levels. These factors, in addition to other species specific biology, such as the microhabitat created by algal symbionts associated with some species, may affect the kinetic or metabolic fractionations of an element and therefore its sensitivity to changing environmental conditions (Fig. 4) (Kucera et al., 2005; Lea et al., 1999; Rosenthal, 2007). For example, while *G. ruber* is restricted to the upper photic zone (0-50 m) due to its symbiotic activity, it also has a slightly lower Mg/Ca sensitivity to temperature change than *G. bulloides*, which

tends to dwell between 50-200 m depending on lifecycle stage (Bé, 1977; Condie and Dunn, 2006; Hemleben et al., 1989; Mortyn and Charles, 2003; Wilke et al., 2009b).

Figure 4. Species specific Mg/Ca-temperature calibrations for *G. bulloides* (blue) and *G. ruber* (red) from the Southwest Pacific Ocean (Bolton et al., 2011; Marr et al., 2011). Temperature curves extend beyond the species temperature tolerance levels to assist in the illustration of the calibration offset. The calibrations converge at lower temperatures and diverge at higher temperatures, illustrating the increased importance of species specific calibrations in warmer modern or paleoclimates. Note, calibrations have been extended beyond the typical species temperature ranges to better illustrate the calibration relationships.

1.2.5 Seasonality and depth habitat

Like physical proxies, geochemical proxies can only be applied as far back in time as the relationship between species ecology and the target chemical process are the same. Even if the metabolic or biochemical pathway responsible for incorporation of the chemical signal remains the same, any change in calcification depth or season(s) of peak productivity will alter the meaning of the reconstructed record (Kucera, 2007).

Species-specific stratification can be useful for the determination of stratified paleo surface water conditions. However, it can also lead to offsets between paleothermometry records with depth dependant variance in seasonal temperature range, as recorded in physical oceanographic data (e.g. Heath, 1985b; Locarnini et al., 2006). Organisms which have a specific surface water niche such as coccolithophores (ca. 0-20 m depth) experience a far greater seasonal range of temperatures at mid-latitudes of ca. 3-5 °C than for example, sub-

surface dwelling *G. bulloides*, which has a depth range of approximately 50-200 m (e.g. Condie and Dunn, 2006) and associated seasonal temperature range of <1 °C (Heath, 1985b; Locarnini et al., 2006). As a consequence, change in seasonal peak productivity for surface dwelling species will have an impact on any paleotemperature record. Seasonally specific productivity peaks vary between marine organisms depending on species-specific optimal conditions, e.g. nutrient and light availability, temperature for surface dwelling species, level of competition and physical mixing (e.g. Hemleben et al., 1989; Smyth et al., 2002). Modern ocean planktic foraminifera generally have a spring bloom productivity cycle when high nutrient levels are present following winter mixing, coupled with warmer temperatures, and higher light levels for those species with symboints (King and Howard, 2001; Kuroyanagi et al., 2002; Thunell and Reynolds, 1984). However, this foraminiferal spring productivity peak is offset from that of coccolithophores, which tend to peak in summer owing to increased light levels and surface water stratification accompanied by reduced competition (Sikes et al., 2005; Tyrrell and Merico, 2004). Furthermore, these productivity generalisations can change on a regional and inter-annual basis, and therefore as surface water conditions change through time, so too may the timing of species-specific productivity peaks (King and Howard, 2001; Murphy et al., 2001; Neil et al., 2004; Nodder and Northcote, 2001; Sikes et al., 2005).

1.2.6 Planktic foraminifera genotypes

Planktic foraminiferal species have a limited diversity compared to benthic forms, numbering at around fifty extant species, traditionally identified based on test shape (Hemleben et al., 1989). Diversity typically peaks in the sub-tropics and decreases steeply towards the poles (Rutherford et al., 1999). Recent genetic studies, however, show that individual species such as *G. bulloides* are actually comprised of several discrete genetic types (genotypes) (Darling and Wade, 2008; Kucera and Darling, 2002). Many of these genotypes have distinct ecologies and novel adaptations leading to distinctive biogeographies.

G. bulloides has seven distinct genotype groups ranging from tropical to polar latitudinal provinces (Fig. 5) (Darling et al., 2007; Darling et al., 2003; Darling and Wade, 2008; Darling et al., 1999; Darling et al., 2000). The *G. bulloides* genotypes are split principally into two groups (Type I and Type II), which have distinct ecologies. Two Type I genotypes are found in subtropical/tropical waters: Type Ia has been found in the Coral Sea and Arabian Sea (Darling and Wade, 2008; Darling et al., 1999) and Type Ib in the Mediterranean and off the Canary Islands (Darling and Wade, 2008; de Vargas et al., 1997).

Figure 5. The biogeographical distribution (shaded) and evolutionary relationships for genotypes of *G. bulloides*. Bipolar genotypes are underlined (from Darling et al., 2008).

The Type II genotypes are typically found in cooler waters in the subpolar and transitional zones. Five Type II genotypes have been identified (Types IIa–IIe). Type IIa and Type IIb are bipolar genotypes, also found in the subpolar Arctic and Antarctic (Darling et al., 2007; Darling et al., 2000). However, while Type IIa and IIb occur together they have distinct ecological preferences. Type IIa is found in greatest abundance in the coldest subpolar waters, where Type IIb is absent (Darling and Wade, 2008). Seasonality studies also indicate that Type IIa advances ahead of Type IIb with the spring plankton bloom (Darling and Wade, 2008). Type IIc has currently only been identified in the subpolar Antarctic (Darling et al., 2000).

The picture of genotype distribution of *G. bulloides* in the North Pacific, however, is entirely different from other ocean basins with distinctly different genotypes. Type IId is most commonly identified in subtropical regions while type IIe is only identified in subpolar waters (Darling et al., 2007).

The implications of this genetic diversity on trace metal incorporation or test development for *G. bulloides* has not been studied to date. However, the similarity of trace metal results from a number of ocean basins for *G. bulloides* (Marr et al., 2011) suggests that Mg/Ca paleothermometry at least is unlikely to be significantly affected by species genotype.

There are four distinct genotypes for the *G. ruber* species, increasing in diversity towards the tropical regions (Fig. 6) (Darling and Wade, 2008). There are two main genotype groups for this species, Type I and Type II with Type IIa likely to represent a species level distinction. A high degree of genetic distinction also exists between the two morphotypes of *G. ruber* pink and white which both fall within Type I. The difference in test morphotype between these genotypes is also clearly evident. The tests of the *G. ruber* (white) morphospecies exhibit extensive morphological variation aligned to the genotype groupings and may be indicative of unique species adaptations. *G. ruber* Mg/Ca ratios are also known to vary with the morphotype analysed, suggesting that genotype differences for this species may have a significant effect on its use as a paleothermometer (Steinke et al., 2005). In this study only *G. ruber* white was analysed and results assessed using regionally derived calibrations (Bolton et al., 2011), which have the advantage of naturally accounting for any Mg/Ca variation caused as a result of glacial-interglacial changes in regional genetic variability.

Figure 6. The biogeographical distribution (shaded) and evolutionary relationships for genotypes of the species *G. ruber* (from Darling et al., 2008).

1.2.7 Other controls on foraminifera calcification – The carbonate ion effect

Most of the surface ocean is supersaturated with respect to both the calcite and aragonite forms of calcium carbonate. Therefore, it is possible that small changes in surface-ocean carbonate chemistry would not have a significant effect on marine calcification (Fig. 7). For example, an increase in carbonate ion availability in the surface water may make it easier for foraminifera to produce the calcium carbonate required for chamber formation, potentially leads to an increase in the amount of calcite deposited (e.g. Spero et al., 1997). However, a range of studies have shown a strong dependence of carbonate production rates on the degree of supersaturation, concluding that the rate of carbonate production was positively correlated

with the carbonate saturation state of seawater (e.g. Kleypas et al., 1999; Langdon et al., 2000; Riebesell et al., 2000). Similar results have also been identified for planktic foraminiferal calcification and thus foraminiferal test weights (Barker, 2002b; Moy et al., 2009; Spero et al., 1997).

Figure 7. Bjerrum plot showing the relative contributions of CO_2 , bicarbonate (HCO_3^-) and carbonate (CO_3^{2-}) ions to total dissolved inorganic carbon as a function of pH. Typical surface seawater pH is indicated by the vertical red line i.e. $\text{pH} = \text{ca. } 8.2$, and is therefore dominated by HCO_3^- (modified from Barker et al., 2003b).

It is difficult to quantify how calcifying foraminifera have responded to changes in the surface ocean $[\text{CO}_3^{2-}]$ levels, or if in fact change in open ocean test weights are a direct result surface water $[\text{CO}_3^{2-}]$. However, recent modern observational and modelling studies have made significant inroads into establishing what variations might occur (Barker and Elderfield, 2002; Flynn et al., 2012; Moy et al., 2009). Spero et al. (1997) laboratory experiments suggested that higher rates of calcification in the symbiont-bearing species *Orbulina universa*, induced by increased carbonate ion concentrations ($[\text{CO}_3^{2-}] > 600 \mu\text{mol/kg}$), resulted in tests 37% heavier than those grown in ambient seawater. In addition, Moy et al. (2009) also found that post-industrial modern *G. bulloides* test weights were 30–35% lower than pre-industrial sediment samples in the Southern Ocean, linking this result to a decrease in modern ocean pH and carbonate saturation levels.

Other factors that may affect calcification include sea surface stratification, by reducing the available nutrients necessary for primary production in the euphotic zone (Barker et al., 2003b). Increasing vertical stratification also affects the CO₂ draw down by, in effect, reducing the oceanic volume available to CO₂ absorption from the atmosphere. Foraminiferal calcification also relies upon temperature, light (if symbiont-bearing) and potentially ‘food’ availability for grazing zooplankton species, which varies as a function of surface water nutrient levels (e.g. Gonzalez-Mora et al., 2008; Hemleben et al., 1989; Lombard et al., 2011; Lombard et al., 2009).

1.2.8 Regional Setting

The Southwest Pacific, east of New Zealand, is a challenging environment to undertake paleoceanographic studies because of the varying water masses and dynamic current and frontal systems. To the north of the subtropical front (STF) lies the South Pacific Gyre (SPG) (Fig. 8). The East Australian Current (EAC) flows south along eastern Australia, with a component detaching to form the eastward flowing Tasman Front (TF) (Ridgway and Dunn, 2007). This frontal flow attaches to northern New Zealand as the East Auckland Current (EAUC) and its southward continuation as the East Coast Current (ECC) continues to Chatham Rise before being steered eastward (Ridgway and Hill, 2009; Tilburg et al., 2001). Seaward of the ECC is the anticyclonic, warm-core Wairarapa Eddy (WE) associated with the East Cape Eddy system. Eddies shed near East Cape propagate southwest along the continental margin to Hawke Bay where they may stall or merge with a previous perturbation to form the Wairarapa Eddy (Chiswell, 2005; Roemmich and Sutton, 1998).

South of the STF, the inflow is dominated by the Antarctic Circumpolar Current (ACC) whose leading edge is the Subantarctic Front (SAF). The SAF is forced south around the bathymetric barrier of Campbell Plateau and then northeast separating Subantarctic Surface Water (SAW) from colder Circumpolar Surface Water (CSW) to the east and south (Fig. 8) (Heath, 1985a; Morris et al., 2001).

These subtropical and subantarctic inflows create a dynamically-driven modern upper ocean (Fig. 8). The boundary between the two inflows is the STF positioned along the east-west crest of Chatham Rise (Chiswell, 2002a). The front separates warm, saline, micronutrient-rich, macronutrient-poor subtropical surface water (STW) in the north from cold, less saline,

micronutrient-poor, macronutrient-rich SAW to the south (Boyd et al., 1999; Ellwood et al., 2008; Locarnini et al., 2006).

Figure 8. Generalised modern surface ocean currents and bathymetry surrounding New Zealand (modified from Carter et al., 1998). Black circles and triangles mark the core-top and plankton tow sites respectively where original modern data used in this thesis is derived from. Yellow star indicates core site MD97 2121 from which the 0-25ka paleoceanographic records contained in this thesis are derived. TF-Tasman Front; STF-Subtropical Front; SAF-Subantarctic Front; ECC-East Cape Current; STW-Subtropical Surface Water; SAW-Subantarctic Surface Water; MS-Mernoo Saddle; WE-Wairarapa Eddy; CVZ-Central volcanic zone; ^Southern Alps. Isobaths are in metres.

1.2.9 Glacial–Interglacial Oceanography

During the LGM changes in the dominance and influence of the specific currents occurs near the MD97 2121 site. At the sea surface, temperatures were 5°C colder than present (Pahnke and Sachs, 2006; Carter et al., 2008) and microfaunas contained *Neogloboquadrina pachyderma* with subtropical forms being either rare or absent (Weaver et al., 1998; Northcote et al., 2007) suggesting the region was dominated by SAW from the south. In part, this reflects an increase in strength of the ACC, forcing more water through Pukaki Saddle,

increasing the speed of the Bounty Gyre and forcing more SAW northwards through Mernoo Saddle (MS) onto the MD97 2121 site (Neil et al., 2004). In addition, the Southland Current (SC) had a more expansive role off southeastern North Island, carrying *ca.* 90% SAW, and an increased SC flow through the MS acted to force the subtropical waters of the East Cape Current and the Wairarapa Eddy further offshore along the northern side of the Chatham Rise (Sutton, 2003; Carter and Manighetti, 2006; Nelson et al., 2000).

The STF is today semi-locked into place by the bathymetric influence of the Chatham Rise. The currents that flow along the northern and southern flanks of the rise and dynamically position the STF to the rise crest (Heath, 1972 and Heath, 1981). Paleoceanographic studies suggest that, in the Chatham Rise region, the STF has remained in this position through recent glacial-interglacial cycles (Fenner et al., 1992; Nelson et al., 1993; Weaver et al., 1998; Sikes et al., 2002). However, during the glacial there was an increase in upwelling due to strengthening in zonal westerly winds (Nelson et al., 2000).

In Antarctica and the Southern Hemisphere an event referred to as the ‘Antarctic Cold Reversal’ (ACR) occurred at approximately 14.5 ka and lasted for two millennia. It is recognized in both terrestrial and marine settings and brought an average cooling of *ca.* 2-3 °C. (e.g. Carter et al., 2008; Putnam et al., 2010; Vandergoes et al., 2008). The Mystery Interval (MI) – a period of rapid and often contradictory change in the Northern Hemisphere (Denton et al., 2006). Millennial-scale MI events may be manifested in the Southern Hemisphere by the southward forcing of the Intertropical Convergence Zone (ITCZ) (Denton et al., 2010). In the Southern Hemisphere, the MI was accompanied by a poleward shift of zonal westerly winds, a general warming of the upper ocean (Barrows et al., 2007; Calvo et al., 2007), and increased Southern Ocean upwelling (Anderson et al., 2009).

Foraminiferal stable isotope, assemblage and trace metal values have been used extensively to understand hydrological and climatological changes (e.g. Carter et al., 2008; CLIMAP, 1976; Elderfield and Ganssen, 2000; Fenner et al., 1992; MARGO et al., 2009). Other techniques such as the use of alkenone undersaturation values as a paleothermometer compliment understandings derived from foraminifera (e.g. Pahnke and Sachs, 2006; Pahnke et al., 2003). The relative strengths and weaknesses of using foraminiferal trace metal values and alkenone values as paleoproxies and how they may assist us to understand changes which occurred during the last glacial maximum and subsequent transition will be explored in this thesis.

Chapter 2

DIFFERENTIAL EFFECTS OF CLEANING PROCEDURES ON THE TRACE ELEMENT CHEMISTRY OF PLANKTIC FORAMINIFERA

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Abstract

We have investigated the effects of different sample cleaning procedures on six trace element/Ca ratios in *Globigerina bulloides*, a planktic species widely used in paleoenvironmental reconstructions. Foraminifera from core-top and down-core sediments were cleaned using seven different methods. Individual foraminifera were analysed before and after cleaning using laser ablation inductively coupled plasma mass spectrometry (LA-ICPMS). We present a comparison between oxidative and reductive cleaning, and an analysis of the effect of using laser ablation versus solution-based ICPMS methods. Measurements of Mg/Ca and Sr/Ca values were identical whether samples were subjected to oxidative,

reductive treatments, two-four acid leach treatments or a combination thereof. However, ultra trace element ratios Al/Ca, Mn/Ca, Zn/Ca and Ba/Ca are much more sensitive to the cleaning method, with up to an order of magnitude difference between techniques. Al/Ca was progressively removed with more intensive cleaning, but six or more acid leach treatments were required for full removal of this contaminant phase. Mn/Ca and Ba/Ca required a combination of oxidative and reductive and/or acid leaching for contaminant phase removal. By contrast, Zn/Ca values increased after acid leaching cleaning procedures. This may be a reflection of preferential dissolution of low-Zn calcite. Accurate measurement of Zn/Ca in planktic foraminifera by solution methods requires oxidative and reductive treatment without acid leaching or alternatively, the use of an *in situ* method such as laser ablation ICPMS. Careful data processing following laser ablation ICPMS analysis appears to be the most effective method to ensure elimination of ultra trace metal TE/Ca contaminant phases.

1.0 Introduction

The use of the Mg/Ca compositions of planktic foraminifera test calcite as a paleothermometer is now well-established (e.g. Anand et al., 2003; Cléroux et al., 2008; Pahnke et al., 2003) and has stimulated further interest in the use of other trace metals as geochemical proxies to track paleo-productivity, nutrient, fluvial input and ocean front migration through time (Hall and Chan, 2004; Hönisch et al., 2011; Lea and Boyle, 1991; Marchitto et al., 2000; Marr et al., in press-b). However, while our understanding of how foraminiferal trace elements reflect the natural environment is rapidly developing and these elements are more commonly being measured, there has not yet been a clear study on the effects of pre-cleaning protocols, especially pertinent as different analytical methods commonly employ different cleaning techniques. This is especially critical for elements such

as Zn or Mn, for example, which have much lower concentrations in the test calcite than Mg or Sr, and are highly susceptible to contamination from organic matter, clays and ferromanganese oxide coatings.

Three main methods of analysing foraminiferal calcite have been established for determining trace element/Ca (TE/Ca) values. Two involve test calcite dissolution; either the complete dissolution prior to analysis (e.g. Barker et al., 2003a; Rosenthal et al., 2004) or progressive dissolution during analysis ('flow-through' method) (Haley and Klinkhammer, 2002; Klinkhammer et al., 2004). The third approach employs *in situ* analyses to target individual tests using electron microprobe, secondary ion mass spectrometry, or laser ablation inductively coupled plasma mass spectrometry (LA-ICPMS). Such techniques enable repeat analyses of individual tests at a high spatial resolution (2-35 μm) with minimal sample destruction (e.g. Eggins et al., 2003b; Sadekov et al., 2010). Due to the nature of the different techniques, a range of strategies are employed for mitigating the potential impact of contamination. Pre-cleaning procedures vary for dissolution-based analyses depending on the trace element ratio(s) being targeted and level of test calcite contamination (e.g. Barker et al., 2003a; Boyle, 1981). The suite of chemicals used may affect the trace element chemistry of the primary calcite, depending on how the solution and its constituents interact with test calcite. It is now well established that partial test dissolution can artificially lower Mg/Ca values of test calcite both in the natural and laboratory environments in response to preferential dissolution of Mg-rich portions of the calcite (Barker et al., 2003a; Benway et al., 2003; Dekens et al., 2002; Rosenthal and Lohmann, 2002). For example, Barker et al. (2003) showed that the combined effect of chemical-based cleaning techniques can reduce Mg/Ca values by as much 25%. The most affected elements however, are likely to be those that occur in ultra-low concentrations in foraminiferal calcite and are most susceptible to

contamination and the inefficient removal of contaminant phases. As an example, Lea and Boyle (1991) found that levels of Ba/Ca were reduced by up to 53% when different pre-cleaning methods were employed (Lea and Boyle, 1991). In addition, there has been recent speculation that the early loss of the fragile final chamber of planktic foraminifera during cleaning may produce offsets between the results of laser ablation and solution based methods (Marr et al., 2011). However, as traditional solution-based methods require complete dissolution of the tests prior to analysis, the mechanism(s) by which these cleaning techniques reduce sample TE/Ca cannot be readily resolved.

The more recently developed *in situ* LA-ICPMS technique takes a different approach, initially removing test surface contamination via ablation and later discriminating between contaminated or primary TE/Ca values during data processing (e.g. Eggins et al., 2003). As *in situ* methods have the ability to discriminate between foraminiferal samples after analysis it has been assumed that extensive pre-treatment is not required (Sadekov et al., 2009).

In this study we examine the differential effects of various cleaning methods on the measurement of trace element ratios in the planktic foraminifera, *G. bulloides*. The key benefit to using laser ablation for this study is that we are able to undergo one particular treatment on an individual foraminifera, analyse by LA-ICPMS, then chemically treat the same specimen before geochemical reanalysis and imaging. Using this technique we are able to build a progressive picture of how the different cleaning methods affect the test through different stages of the cleaning process.

2.0 Methods

2.1 Samples and sample preparation

Globigerina bulloides is a shallow dwelling (~ 60 m water depth) spinose, planktic foraminifera that calcifies multiple chambers, progressively adding calcite layers to older chambers with each new chamber addition (Fig. 9). The *G. bulloides* examined here were picked from sieved core-top sediment samples (size fraction 250-400 μm) from site D178, Southwest Pacific Ocean at 51.72°S, 169.83°E and water depth 629 m (Marr et al., 2011) with the antepenultimate or chamber *f*-2 targeted for analysis. Surface waters overlying D178 are characterised as cold, micronutrient-depleted, Subantarctic Water (Bowie et al., 2009; Boyd et al., 2001) and the radiocarbon age of the sediment is 4835 ± 33 yrs (Marr et al., 2011). *G. bulloides* samples previously investigated from this site (Marr et al., 2011) were determined to have experienced negligible post-depositional alteration as informed by examination under scanning electron microscopy (SEM).

A summary of the sample preparation procedures is given in figure 2, with further detail in Auxiliary information 1-3. All foraminifera were first treated with cleaning procedures typically used in LA-ICPMS analytical studies (e.g. Eggins et al., 2003; Sadekov et al., 2005). These are designed to remove clay contaminants and involve three ultrasonication washes in ultrapure water for 2-3 seconds, replacing the water after each ultrasonication. This was followed by two rinses in AR-grade methanol (AI. 1). Individual specimens were then mounted on a NIST610 silicate glass standard ready for LA-ICPMS analysis (analytical details described below). After this initial analysis of each test, individual foraminifera were then cleaned using various steps modified from common solution-based methods (Barker et al., 2003a; Boyle and Keigwin, 1985). Individual foraminifera were subjected to each

cleaning step separately so that each specific individual could be traced throughout the entire study ensuring all data presented are co-related.

Figure 9. Calcification of the foraminifera test wall. (a) Electron backscattered image of foraminifera-29 chamber *f-1*, which has undergone oxidative and 1x acid leach cleaning. Spines of the foraminifera have had incomplete resorption, leaving the remnant spine in the test wall the top of which was subsequently covered with gametogenic calcite. (b) Schematic diagram illustrating wall and pore structure of an adult *G. bulloides* showing successive growth stages of ontogenetic calcification. Successive primary calcite/ontogenetic calcification layers are indicated by ‘bricks’ with the thin layers between chamber formation indicated by blocks with ‘crescents’, inner test wall/primary organic membrane is indicated by dashed lines. Gametogenic calcification/surface layer is indicated by stippling. (Bé, 1980; Erez, 2003; Sadekov et al., 2005). (c) Cross-section through the test wall of foraminifera-18, chamber *f-1* which has undergone oxidative and reductive treatments. Complete resorption of spines has occurred, with remnants of the outer spine wall clearly visible after primary calcite layer separation. Also illustrated is the relationship between stronger calcite formed in the inner test wall and immediately around the spines, and primary calcite layers. No distinctive dark or light banding was observed in these or other samples to indicate the presence of organic layers (Erez, 2003).

Seven different chemical and physical cleaning techniques were used on seven subsets of tests prior to them being re-mounted for LA-ICPMS (Fig. 10). Foraminiferal tests were left whole during the cleaning process so that chamber specific variability could be assessed. This meant that any detritus located inside the test could only be removed via the test aperture.

While this would be an issue for dissolution analysis, it does not impact upon *in-situ* LA-ICPMS analyses. Inner test calcite has different crystallography to the primary test layers and typically acts as a barrier to dissolution (Sadekov et al., 2010). It is therefore likely to remain unaffected by the cleaning process.

The recommended sample cleaning method of Barker et al. (2003a) for solution-based Mg/Ca studies involves rinsing foraminifera fragments in ultraclean water and methanol, oxidative cleaning with hydrogen peroxide, followed by acid leaching in dilute nitric acid (AI 3). For measurement of other trace elements, including Cd, which is found in much lower concentrations than Mg, Boyle and Keigwin (1985) recommended the addition of a reductive cleaning step (AI. 5).

Figure 10. Flow diagram summary of the sample preparation and analytical procedures used during this study. Numbers in italics indicate the number of foraminifera involved in that particular experimental step e.g. *n*=35. See text for further details.

To evaluate the effects of these methods, 3-10 foraminifera with varying initial TE/Ca contents were treated individually using combinations of these cleaning steps with ultrasonication washes limited to 2-3 seconds, the steps are (Fig. 10):

- (1) oxidative clean only,
- (2) oxidative and reductive clean only,
- (3) oxidative clean and 1x acid leach,
- (4) 1x acid leach only,
- (5) 2x acid leach,
- (6) 4x acid leach,
- (7) > 6x acid leach treatments

After the final treatment, the foraminifera were rinsed in ultrapure water and placed in an oven at 40°C overnight to dry. When a foraminifera test fragmented during cleaning it was removed from the study. Whole specimens were then re-analysed using LA-ICPMS (Table 1, Fig. 10, 11).

Figure 11. Electron backscattered images of two adult *G. bulloides* which have undergone (a) no cleaning and (b) 10x acid leach cleaning treatments to assess changes to the surface texture prior to chamber separation. Larger circular holes in chamber test walls are ablation pits of 35 µm diameter. (c) and (d) are images of ablation pits from the foraminifera in (a) and (b) respectively, magnified 1500 x. Successive layers of calcite through the test wall are visible as lines in (c) and (d). Dark lines indicate where there has been increased dissolution at calcite layer boundaries. (a) and (c) have pore spaces that are smaller where visible, or loosely infilled with detritus such as nanofossils or clay. Detritus has been removed from pore spaces in (b) and (d), and pore spaces are generally larger. Fracturing between chambers and micro-fracturing on the surface of and through the test wall of (b) and (d) are also visible.

	'LA processed' - before chemical cleaning (mmol/mol)					
Cleaning protocol	Mg/Ca	Al/Ca	Mn/Ca	Zn/Ca	Sr/Ca	Ba/Ca
Oxidative	1.81	0.06	0.003	0.003	1.34	0.002
Oxidative-Reductive	1.60	0.01	0.002	0.004	1.30	0.002
Oxidative-1x Leach	1.46	0.02	0.004	0.003	1.30	0.002
1x Leach	1.33	0.06	0.004	0.003	1.32	0.003
2x Leach	1.71	0.07	0.005	0.003	1.32	0.003
4x Leach	1.23	0.02	0.001	0.000	1.36	0.001
6x Leach	2.22	0.02	0.008	0.002	1.32	0.006
10x Leach	2.32	0.03	0.003	0.002	1.22	0.001
	'LA processed'- after chemical cleaning (mmol/mol)					
Oxidative	1.64	0.03	0.004	0.022	1.31	0.003
Oxidative-Reductive	1.45	0.01	0.001	0.006	1.31	0.001
Oxidative-1x Leach	1.26	0.01	0.002	0.006	1.29	0.002
1x Leach	1.38	0.03	0.004	0.006	1.32	0.003
2x Leach	1.41	0.02	0.003	0.005	1.33	0.003
4x Leach	1.17	0.00	0.000	0.001	1.37	0.001
6x Leach	2.61	0.01	0.007	0.002	1.33	0.004
10x Leach	1.33	0.00	0.000	0.000	1.28	0.001
	'Solution processed'- before chemical cleaning (mmol/mol)					
Oxidative	2.68	0.81	0.018	0.033	1.45	0.010
Oxidative-Reductive	2.27	0.39	0.009	0.013	1.39	0.008
Oxidative-1x Leach	2.13	0.98	0.010	0.012	1.37	0.009
1x Leach	2.17	0.49	0.014	0.015	1.38	0.009
2x Leach	2.25	0.42	0.013	0.010	1.38	0.004
4x Leach	1.93	0.39	0.007	0.008	1.40	0.021
6x Leach	2.57	0.39	0.342	0.013	1.37	0.008
10x Leach	2.24	0.24	0.007	0.007	1.30	0.010
	'Solution processed'- after chemical cleaning (mmol/mol)					
Oxidative	1.96	0.31	0.008	0.049	1.34	0.006
Oxidative-Reductive	1.72	0.07	0.001	0.002	1.32	0.002
Oxidative-1x Leach	1.55	0.12	0.004	0.021	1.32	0.004
1x Leach	1.84	0.42	0.016	0.027	1.37	0.022
2x Leach	1.74	0.24	0.011	0.032	1.35	0.009
4x Leach	1.38	0.05	0.003	0.044	1.61	0.003
6x Leach	2.48	0.02	0.010	0.011	1.34	0.004
10x Leach	1.40	0.02	0.004	0.006	1.34	0.001

Table 1. Mean TE/Ca values in primary test calcite calculated prior and subsequent to chemical cleaning using LA and solution data processing.

Following both LA-ICPMS analytical steps, pre- and post- cleaning, intact foraminifera tests were carbon coated and imaged using a Jeol JSM 6500F SEM at Victoria University of Wellington. After the second geochemical analysis, post-cleaning, tests were then broken

open (chamber separation), re-coated with carbon and re-imaged on the SEM to reveal internal structures.

2.2 Geochemical analysis

Trace element/Ca (TE/Ca) ratios of foraminiferal tests were carried out using a New Wave deep-UV (193 nm) solid-state laser ablation (LA) system coupled to an Agilent 7500CS ICPMS at Victoria University of Wellington. Laser ablation analyses were of 60 s duration. For each analysis, after subtraction of background signals, TE/Ca ratios were calculated by reference to TE/Ca ratios obtained from bracketing analyses of the NIST610 glass standard, and normalised to the preferred trace element values in this standard: Mg = 465, Al = 10798, Ca = 82191, Mn = 485, Zn = 456, Sr = 516, Ba = 435 ppm (Pearce et al., 1997). Analyses of NIST610 bracketed 5-20 analyses of foraminifera and showed no significant drift in TE/Ca ratios beyond the internal precision of the analyses. Eight analyses of chamber *f*-2 on a single *G. bulloides* from D178 were conducted to evaluate reproducibility during the course of an analytical run. The 95% confidence intervals for the single chamber analysis based on the mean TE/Ca chamber values are Mg/Ca 2.01 ± 0.27 (13%) mmol/mol, Al/Ca 0.11 ± 0.06 (50%) mmol/mol, Mn/Ca 0.002 ± 0.001 (51%) mmol/mol, Zn/Ca 0.002 ± 0.001 (41%) mmol/mol, Sr/Ca 1.34 ± 0.02 (2%) mmol/mol, Ba/Ca 0.002 ± 0.001 (28%) mmol/mol (all $n = 8$). We use the calculated 95% confidence intervals to assess intra-chamber variability due to the small sample size. While still assuming a Gaussian normal distribution similar to standard practice, this approach uses a t-statistic with the appropriate degrees of freedom to assess the probability that true values lie outside the 95% limits for the mean. Limits of detection for each of the measured elements are given in AI 1 and were calculated using Iolite data reduction software and assuming a stoichiometric value of 40.04 wt% Ca content of the test and monitoring ^{43}Ca as an internal standard (Paton et al., 2011). Typical concentrations of

Mg, Al, Sr and Ba are all well above detection limits. However, the background levels of Mn and Zn comprise a significant percentage of the total signal for a typical analysis of foraminiferal calcite (~29 and ~43%, respectively). Analytical profiles of these elements are therefore carefully scrutinised to ensure that TE/Ca values reflect test calcite (AI. 2).

2.3 Data processing

Trace element data obtained from the individual foraminifera after solution cleaning were processed in two ways. First, using a typical LA analysis procedure (“LA processing”), for which the integrated portion of the time-resolved compositional profile through the test is carefully screened to exclude any contamination adhering to the outer test wall (AI. 2) (Eggins et al., 2003a; Marr et al., 2011; Sadekov et al., 2008). When calculated in this manner, any offset in an individual foraminifer’s test chemistry as determined before and after solution cleaning protocols, reflect changes to the chemistry of the primary calcite test that have been induced by various the solution cleaning techniques. Secondly, the data were also processed by integrating the entire time-resolved signal including the outermost layer(s) to approximate the composition that would be obtained if the full test was dissolved for solution-based ICPMS analysis. Data processed this way are hereafter referred to as “solution-processed”. Trends in data processed this way for example, contamination reduction, appear to closely match those previously published for solution-ICPMS analysis in Barker et al. (2003a) and Hathorne et al. (2009). As opposed to crushing and dissolving the tests for true solution analysis this approach, importantly, leaves the foraminifera tests intact for SEM and backscattered electron (BS) imaging. Note trace element data was processed before and after chemical cleaning using both the solution and LA processing techniques, however, all samples processed ‘before chemical cleaning’ had still undergone the ‘*Laser Ablation Clean, Clay Removal*’ cleaning protocol (AI. 1.1).

3.0 Results

3.1 Prior to solution-based cleaning protocols

The range in test TE/Ca values analysed before application of solution-based cleaning techniques follows a normal Gaussian distribution (Fig. 12). The range in data for individual foraminifera is typical for a core-top sample (e.g. Bolton et al., 2011; Marr et al., 2011; Sadekov et al., 2008) and mean values fall within previous published ranges for Mn/Ca and Zn/Ca < 0.3 mmol/mol and Ba/Ca < 0.01 mmol/mol (Hathorne et al., 2003; Lea and Boyle, 1991; Pena et al., 2005; Rosenthal et al., 1999). However as core-top D178 is located in Subantarctic Water, low TE/Ca reflect low concentrations in the ambient water mass and a mean annual temperature of 7.4 °C at 60 m water depth (Bowie et al., 2009; M. Ellwood pers. comm., 2011; Neil et al., 2004).

3.2 After solution-based cleaning protocols

3.2.1 Test attrition rates

Of the initial 52 foraminifera, 36 remained whole after cleaning treatments. Comparison of test chemistry before cleaning shows that tests with elevated Mg/Ca values (4.6 mmol/mol) also had high Zn/Ca and Ba/Ca values of 0.012 and 0.011 mmol/mol respectively, and were lost due to fragmentation during the oxidative and leaching cleaning processes. Of the tests with <0.004 mmol/mol of Mn/Ca and/or Zn/Ca, more than 70% remained whole during the cleaning process, whereas the attrition rate for tests with >0.004 mmol/mol of Mn/Ca or Zn/Ca was 50%. The greatest loss in foraminifera tests was observed after oxidative and acid leach treatments, when 60% of the individuals fragmented. However, no unusual TE/Ca values were recorded prior to treatment with subsample means of Mg/Ca, 2.0 mmol/mol; Sr/Ca, 1.33 mmol/mol; Al/Ca, 0.044 mmol/mol; Mn/Ca, 0.005 mmol/mol; Zn/Ca, 0.006

mmol/mol; Ba/Ca, 0.005 mmol/mol in the tests selected for oxidative and acid leach treatment.

Figure 12. Histograms showing initial range in *G. bulloides* chamber f-2 TE/Ca values prior to chemical cleaning treatment. Blue bars indicate those foraminifera that remained whole after chemical treatment and were used for further TE/Ca analysis and imaging, and red bars are the initial TE/Ca values of those foraminifera that fragmented during cleaning.

3.2.2 'LA processing'

Here we present the TE/Ca data attained before and after chemical cleaning using only "LA processing" (Fig. 13-16, AI, 2). While a limited number of specimens remained after oxidative and 1x acid leach treatment (n=4), a Mg/Ca decrease of *ca.* 15% was observed, markedly higher than the *ca.* 3% decrease after 'a single' (1x) acid leach or *ca.* 10% decrease after oxidative treatment alone. A > 40% and 4% decrease in Mg/Ca and Sr/Ca, respectively, was observed after 10 acid leaching treatments. Mean Sr/Ca did not vary compared to the pre-cleaning measurements by more than 2% in all other treatments. The variability in Mg/Ca after up to 4 acid leach treatments was not significantly different to the pre-treatment values with a mean difference of $\pm 9.5\%$, which is less than natural heterogeneity ($\pm 13\%$) (Fig. 13). Distinctive Mg/Ca peaks in the laser profiles through individual tests of up to 1.5 mmol/mol higher than the surrounding portions of the profiles, were apparent in the analyses both before and after chemical cleaning (Fig. 16). These Mg/Ca peaks were not consistently associated with distinct layers identified in the test wall (e.g. Fig. 16). Published Mg/Ca and Sr/Ca values typically range between *ca.* 0.5-4 mmol/mol and ultra trace elements (ultra TE/Ca) Mn/Ca, Al/Ca, Ba/Ca and Zn/Ca have values typically between 0.00-0.04 mmol/mol (e.g. Marr et al., 2011; Sadekov et al., 2009).

Our results show no resolvable differences in primary test Mn/Ca and Ba/Ca values measured before and after the standard oxidative and acid leach techniques recommended by Barker et al. (2003) (Fig. 13). This is similar to findings on Late Pleistocene planktic foraminifera from Panama Basin, where Mn/Ca was identified as not being effectively removed by oxidative or oxidative + 1x acid leach treatments (Pena et al., 2005). For the D178 samples, a combination of oxidative and reductive cleanings, or multiple (> 2) acid leaches were required before primary calcite Mn/Ca levels were measurably reduced (Fig. 14, 15).

While Mn/Ca oscillations of up to 0.009 mmol/mol were present through some test walls, the magnitude of these oscillations was generally unchanged by the cleaning treatments (Fig. 16). These high/low Mn/Ca bands could not be identified as visually distinct calcite layers through the test wall (Fig. 16). Ba/Ca levels were not statistically different before and after solution-based cleaning treatments using LA processing (Fig. 10, 14, 15).

Mean test Zn/Ca values increased by > 60% of their measured pre-treatment values following chemical cleaning treatments, but not with tests subject to oxidative and reductive treatments or 10x acid leach treatment (Fig. 13-15). Patterns of high and low Zn/Ca banding through the test were also enhanced by chemical cleaning treatments. For example, prior to oxidative cleaning, bands in one foraminifera specimen had a maximum oscillation up to ± 0.003 mmol/mol with a mean value of 0.004 mmol/mol in the primary calcite (Fig. 16). However after cleaning, the oscillations increased to ± 0.009 mmol/mol around a central mean value of 0.017 mmol/mol (AI. 2). An increase in oscillations of this magnitude was not evident in the other elements measured. Al/Ca showed the strongest reduction following cleaning treatments, with values reduced from the pre-cleaning LA-ICPMS measurements by up to 90% (Table 1).

Figure 13. Comparison of TE/Ca for individual foraminifera prior and subsequent to oxidative only, and oxidative + 1x acid leach treatments. Coloured diamonds indicate individual foraminiferal values calculated using LA processing before and solution processing after cleaning (see text). Black triangles indicate samples processed using the LA processing before and after cleaning. Black line indicates a 1:1 relationship, shaded bar indicates the TE/Ca 95% confidence interval (CI) for natural heterogeneity within an individual foraminifera chamber. Overall sample means are indicated by horizontal lines on the graphs; blue –before chemical cleaning (LA processing), orange –after chemical cleaning (LA processing), red – sample mean derived using solution processing after chemical cleaning.

Figure 14. Comparison of TE/Ca for individual foraminifera prior and subsequent to oxidative and reductive cleaning treatments. Symbols as for Fig. 13. Black line indicates a 1:1 relationship, shaded bar indicates the TE/Ca 95% CI for natural heterogeneity within an individual foraminifera chamber.

Figure 15. Comparison of TE/Ca for individual foraminifera prior and subsequent to single and multiple acid leach treatments. Multiple leach treatments key: coloured diamonds = 2x acid leach), circles (6x acid leach), triangles (4x acid leach) and squares (10x acid leach) indicate sample mean values calculated using LA processing before and solution processing after cleaning for 1x acid leach. Black triangles indicate samples processed using the LA processing before and after cleaning. LA and solution processing before and after cleaning. Multiple leach treatments black symbol key: diamonds (2x acid leach), circles (6x acid leach), triangles (4x acid leach) and squares (10x acid leach) indicate samples processed using the LA technique before and after cleaning. Single acid leach treatment: all black diamonds indicate the use of LA processing technique before and after chemical pre-treatment. Black line indicates a 1:1 relationship, shaded bar indicates the TE/Ca 95% CI for natural heterogeneity within an individual foraminifera chamber. Overall sample means are indicated by horizontal lines for 1x acid leach, and 2x acid leach samples on the multi acid leach treatment graphs; blue –before chemical cleaning (LA processing), orange –after chemical cleaning (LA processing), red – derived using solution processing after chemical cleaning.

3.2.3 Solution- vs LA- Processing

Here we compare results obtained using ‘solution’ and ‘LA’ processing (Fig. 13-15, 17, AI. 2). The largest offset in Mg/Ca between solution and LA methods is following a single acid leach treatment where Mg/Ca solution values are 1.4 times higher than the LA. However, after 10 acid leach treatments, solution Mg/Ca values are 0.99 mmol/mol lower (or a 40 % decreased) than that recorded using LA prior to chemical cleaning (Fig. 17d). There is no significant difference between Mg/Ca values in test calcite that has been LA- and solution-processed after foraminifera were treated using oxidative $\pm$ reductive and oxidative $\pm$ 1x acid leach treatments, and foraminifera subject to 2-6x acid leach treatments (Fig. 17). Mean Sr/Ca values are the same within error, regardless of data processing method (Fig. 17d).

Figure 16. TE/Ca ablation profiles of foraminifera-20, as measured by laser ablation analysis through chamber *f*-2 before and after oxidative and reductive cleaning. Black and coloured lines indicate TE/Ca profiles before and after cleaning, respectively. Dashed lines indicate boundaries of progressive calcite layers through the test wall, as identified from the electron backscattered image images after cleaning. Note micro-fracturing and calcite dissolution through the test wall. The thin membrane of calcite deposited during gametogenic calcification is clearly visible on the inner-most test wall. Mg/Ca, Sr/Ca and Mn/Ca surface layer enrichment present prior to cleaning treatments is significantly reduced in Mg/Ca and Sr/Ca after cleaning, while Mn/Ca remains relatively unchanged. Zn/Ca levels increase in the surface layer after cleaning.

Figure 17. Comparison of sample means using the two different types of data acquisition. Graphs (a)-(c) give TE/Ca sample means from solution based data acquisition. Graphs (d) and (e) illustrate the factor of difference between TE/Ca (d) and ultra-TE/Ca (e) values derived using solution methods and values calculated by laser ablation data processing. The dashed line indicates a factor of 1 difference, or where there is no difference between solution or laser ablation results. The factor difference between solution and laser ablation methods for Zn/Ca after four acid leaches has been omitted as it was *ca.* 120 higher after chemical cleaning and therefore obscured other results.

Ultra TE/Ca values show the most sensitivity to the use of solution or LA processing methods (Fig. 16). Mean Mn/Ca and Ba/Ca values were 0.016 and 0.022 mmol/mol after using oxidative and reductive treatments followed by solution processing. However, if the same foraminiferal TE profiles used for solution processing are re-processed using LA processing methods those values were significantly reduced to 0.001 and 0.002 mmol/mol (Fig. 17). Comparison of samples processed using solution processing before and after chemical

cleaning indicated that there were some significant trends in TE/Ca values. After chemical cleaning, those foraminifera processed using solution processing indicated a significant increase in Zn/Ca values increase after using oxidative, oxidative and acid leach, and up to four acid leach only treatments (Table 1). Generally, all other TE/Ca values were reduced after using chemical treatments and solution processing (Table 1). Zn/Ca values were *ca.* 2-5x higher using solution processing compared to LA processing values before chemical cleaning treatment (Table 1; Fig. 16). Solution processed Al/Ca values were generally 2 times higher than LA processed values, only showing comparable values after 6x acid leaches (Fig. 17e).

3.3 Test imaging

All foraminifera tests for which chemical data are reported were imaged using SEM and BS imaging (Figs 1, 14, 16 and 17). The brightness of the SEM images reflect calcite density which in turn reflects an interplay of several factors including growth rate, nutrient levels and biological functions (e.g. Aldridge et al., 2012; Bé, 1980; Bentov and Erez, 2006; de Nooijer et al., 2009) (Fig. 11, 18). For example, the inner test wall, surface layer and spine appear brighter under BS imaging, indicating a higher density calcite (Fig. 11, 18). Detailed SEM images of the chamber wall indicate that calcite crystals on the inner and outer surface are different to those in the middle of the test wall (Fig. 19), similar to that previously identified in *Orbulina universa* (Allan et al., 1973).

The difference in inter-layer calcite density is most distinctive in samples that have undergone oxidative and reductive cleaning, or extensive acid leaching, where a 'patchy' appearance is suggestive of uneven test wall dissolution (Fig. 16, 18). Dissolution is most distinctive in surface layer calcite and adjacent to micro-fractures through the test wall. In these samples, etching into the outer calcite surface is evident and pore spaces are enlarged

(Fig. 11, 18). After 1-2x acid leach treatments the foraminifera test surface layer showed signs of dissolution, for example etching on the test surface, and after more than 2x acid treatments the final chamber calcite (*f*) appeared visibly more dissolved than the older chambers (Fig. 11).

Figure 18. SEM backscatter images through foraminifera test walls showing various signs of dissolution. (a) Patchy dissolution of *G. bulloides* middle test wall while the outer calcite shows minimal dissolution after oxidative and 1x acid leach cleaning. (b) *G. ruber* test *ca.* 14 ka from SW Pacific Ocean core site (MD97 2121, *ca.* 2000 m water depth) showing signs of natural preferential dissolution of the middle of the test wall. (c) *G. bulloides* spine not fully re-adsorbed prior to gametogenesis. Pitting/etching on surface layer calcite indicates where a single acid leach has begun to dissolve the outer test, while a lack of micro-fracturing leaves the inner test free from dissolution effects. Etching of the test surface can be clearly observed while dissolution of the inner test is limited.

Backscattered imaging of the ablation pit prior to chamber separation shows preferential dissolution of thin, distinctive layers in the middle test wall (Fig. 11). In addition, all samples imaged after chemical cleaning with ultrasonication have micro-fractures or cracking through the test wall (Fig. 11, 18). The extent of test wall micro-fractures increased with progressive chemical cleaning treatments (Fig. 11, 18). Fracturing along suture lines was evident after 2x or more acid leaches (e.g. Fig. 11). After the oxidative and reductive, and multiple acid leaches, chambers were readily divided into their component ‘layers’ once the chambers had been separated (Fig. 9, 10, 17).

Figure 19. SEM back scattered imaging images of calcite crystals through the test wall of foraminifera -18 chamber *f* which has undergone both oxidative and reductive treatments. (a) overview through the test wall (b) and (d) show the surface and inner layers magnified 22 000x and 35 000x, respectively. Both show a different arrangement of calcite platelets to (c), which is from a ridge section of test wall primary calcite, magnified 27 000x. (e) View through chamber *f*-2 wall to illustrate the layering of calcite as chambers are added. A thin calcite band *ca.* 0.1-0.2 μm width is evident between chamber *f*-2 and *f*-1, but absent between chamber *f*-1 and *f* where the chamber layers are separating. (f) Thin layer of calcite which appears to have been deposited between significant chamber calcification(s).

4.0 Discussion

4.1 Variability of Mg/Ca and Sr/Ca in test calcite

Neither Mg/Ca, nor Sr/Ca, values measured after chemical cleaning reveal a significant response to oxidative and 1x acid leach, or the combination of oxidative and reductive cleaning (Figs. 11, 13-14). The difference between oxidative and reductively cleaned samples after solution processing was < 0.15 mmol/mol or $< 10\%$ lower, on an equivalent scale to natural inter-test variability (Table 1, SI. 1) (Barker, 2002a; Bolton et al., 2011; Marr et al., 2011; Sadekov et al., 2008). When converted to temperature range this represents an offset of *ca.* 1.0-1.5 °C, similar to the difference between *G. bulloides* calibrations (e.g. Anand et al., 2003; Marr et al., 2011; McConnell and Thunell, 2005). This confirms that Mg/Ca data for planktic foraminifera such as *G. bulloides* attained via LA or solution protocols are comparable regardless of whether so-called solution ‘Mg-cleaning’ (oxidative only) or ‘Cd-cleaning’ (oxidative and reductive cleaning) -without acid leaching or LA methods with minimal pre-cleaning are used.

We found that Sr/Ca did not significantly respond to any of the cleaning protocols, similar to the findings of Barker et al. (2003a) (Fig. 13-15). Therefore, while unable to be used as a measure of test contamination beyond a first order assessment, Sr/Ca data are highly comparable between solution and LA ICPMS analytical techniques.

Before and after chemical cleaning, distinctive peaks in Mg/Ca of LA profiles through the test wall were identified in some specimens, suggesting possible Mg-rich and Mg-poor calcite banding (Fig. 17) similar to that previously observed for other species such as *Orbulina universa* and *Globorotalia inflata* in previous studies (e.g. Eggins et al., 2003b; Hathorne et al., 2003; Hathorne et al., 2009; Sadekov et al., 2005). However, when Mg/Ca

TE/Ca profiles were compared to structural layers through the test wall (as visible in SEM images), peaks were not generally associated with calcite layering (Fig. 16). This differs from previous studies using electron microprobe mapping that associated oscillations between thin high-Mg and thick low-Mg bands with different episodes of calcite deposition during the lifecycle of spinose planktic foraminifera with symboints (e.g. *Globigerinoides ruber*), and non-spinose deep-dwelling species (e.g. *G. inflata*) (Hathorne et al., 2009; Sadekov et al., 2005). High-low Mg/Ca banding in *G. bulloides* may simply be less pronounced than *G. inflata*, similar to *Globigerinoides sacculifer* (Sadekov et al., 2010) so that identification of structural layers is not evident. Regardless, whether the high-low Mg banding is muted or absent, this, combined with the results showing no bias introduced by dissolution methods, indicates that any preferential dissolution of high Mg/Ca layers associated with other species (e.g. Brown and Elderfield, 1996; Dekens et al., 2002; Rosenthal and Lohmann, 2002), would not have a significant effect on *G. bulloides* Mg/Ca values. *G. bulloides* is therefore likely to provide reliable paleothermometry even where dissolution may be present.

4.2 Sensitivity of ultra-trace element values to cleaning and analytical protocols

In contrast to Mg/Ca and Sr/Ca, ultra-trace element values investigated here, Mn/Ca, Ba/Ca, Zn/Ca and Al/Ca, are sensitive to the type of cleaning protocol/s employed and the method used for analysis. As these elements have particularly low concentrations in test calcite, any enrichment or depletion caused by adhering clays, re-crystallisation or laboratory cleaning protocols, are likely to generate offsets, beyond that expected from natural heterogeneity within a population.

Similar to previous studies (Barker et al., 2003a), we found that oxidative treatment alone was unable to significantly reduce Al/Ca, requiring a combination of oxidative and reductive and/or acid leach treatments (Fig. 17). However, even after oxidative and 1x acid leach ('Mg

cleaning'), Al/Ca values were still four times greater than that recorded in primary calcite, as determined using LA processing, and 5 times higher than those achieved using LA processing prior to cleaning (Fig. 17). Only after >4x acid leach are Al/Ca levels reduced to values comparable to those obtained by LA processing (Fig. 15). However, elevated Al/Ca values after chemical cleaning did not necessarily indicate or reflect contamination in other trace and ultra trace elements measured.

In contrast to other trace and ultra trace elements measured, Zn/Ca values generally increased with more intensive chemical cleaning procedures, regardless of whether LA or solution processing were used (Fig. 13-15). Similar to Yu (2007), we found that levels of Zn/Ca remained high after the application of oxidative treatments. For example, a combination of oxidative and acid leaching increased Zn/Ca levels by five times compared to primary calcite values measured prior to chemical cleaning (Fig. 13). Only the use of oxidative and reductive cleaning (without acid leaching) or >10x acid leaching were we able to replicate values identified prior to chemical treatment (Fig. 14, 15) and result in the same values regardless of analytical technique. As this enrichment was evident regardless of solution or LA processing, but was not present in the samples that had undergone the most handling during preparation (oxidative + reductive treatment), this suggests that it may be an indication of low-Zn calcite preferential removal rather than laboratory contamination (Table 1, Fig. 13-15) (Wasylenki et al., 2011). Another explanation may be preferential dissolution of low-Zn/Ca calcite bands observed in the LA profiles during the leaching process (Fig. 16), which would suggest that enrichment of Zn/Ca values in specimens that have undergone natural dissolution on the sea floor (e.g. Sadekov et al., 2010) may also be an issue.

We found that while oxidative cleaning and multiple acid leaches yield comparable results between LA- and solution-based methods for Mg/Ca, only the combination of oxidative *and*

reductive treatments (without acid leaching) yield comparable results between methods for all TE/Ca measured, except Al/Ca (Fig. 17).

4.3 Impact of cleaning protocols on test calcite

Ultrasonication used during the cleaning processes resulted in both physical damage to the test wall (micro-fracturing), and the destruction of *ca.* 30% of whole tests in our study (Fig. 9, 17). Based on SEM imaging undertaken after chemical treatment and before chamber separation, a correlation appears to exist between the level of damage to the test wall and the number of ultrasonications. While ‘large scale’ fracturing occurred at junctions between chambers, or within chambers, ‘micro-fracturing’ also became increasingly pervasive through the test wall as the number of repeat ultrasonications increased (Fig. 11). Test wall micro-fracturing increases the surface area for chemical interaction during cleaning. This enhances the effect of chemical cleaning procedures, not only on the outer test surface, but also allowing the chemicals to penetrate through to primary test calcite. Therefore, acid leaching after oxidative and/or reductive cleaning and ultrasonification has a greater impact on test calcite as it is effectively able to dissolve both at the surface, and through the foraminifera test wall. The consequence of test wall micro-fracturing prior to acid leaching is indicated by the greater effect of TE/Ca removal by oxidative + acid leaching treatments than can be achieved by either treatment in isolation (Fig. 17). In contrast to Barker (2003a) and Yu (2007), we found that it was not the specific use of reductive chemicals $\pm$ citric acid during cleaning that lowered trace metal content. Rather, we suggest that the dramatic reduction in trace element concentration was likely the result of acid leach treatments, which utilise nitric acid following the reductive step (AI. 3). After >17 ultrasonification treatments ranging from 3 s to 10 min long used during the full reductive cleaning protocol, the dilute

nitric acid used during final leaching process would have had larger surface area from which to dissolve both surface and primary test calcite, enhancing any preferential leaching effects.

SEM imaging after various cleaning protocols shows that etching was present on the surface wall of specimens that had undergone as little as 1x acid leaching (Fig. 18), while specimens, which had undergone >4x acid or oxidative + 1x acid treatments indicated preferential dissolution of layers within the test wall. The dissolution of thin primary calcite layers within the test wall resulted in a breakup of remaining layers, which otherwise had a marked prismatic structure (Fig. 19). This process was not observed during chamber separation for samples that had not been acid treated. It is likely that these foraminifera, that separated into distinct primary calcite layers, did not fragment during cleaning ± analysis due to the higher density inner calcite layer supporting the outer layers (Fig. 19). In addition, after extensive chemical treatment the test wall primary calcite appeared to be dissolving at a faster rate than the outer surface. This effect was especially notable where the primary calcite surface had been exposed by LA (Fig. 11). Tests were also more fragile after treatment with nitric acid. Up to 3 out of 10 tests fragmented after oxidative ± reductive treatment or a single acid leach. However, after oxidative + acid leach treatments the number of tests that fragmented doubled to 6 out of 10, indicative of the increased ability of even a single acid treatment following oxidative ± reductive treatments to corrode the test calcite after extensive micro-fracturing (AI. 2).

Preferential dissolution of calcite from the middle of the test wall is similar to the effects of natural dissolution previously reported for planktic species by Johnstone et al. (2010) using X-ray computed tomography on core-top samples. The effects of chemical pre-cleaning found in this study range between that defined by Johnstone et al. (2010) as *Dissolution Stage* XDX 1, with only the first signs of dissolution present e.g. surface etching, to *Dissolution*

stage XDX 2-3 after multiple acid leaches or oxidative + reductive treatment, characterised by the distinctive density differences between the middle and outer test wall of the largest chambers (Fig. 11, 18) (e.g. Johnstone et al., 2010; Petrizzo et al., 2008). The SEM and optical microscopy images of the test outer surfaces offered little visual indication as to the degree of primary calcite dissolution until after the tests were broken open.

4.4 Effects of cleaning techniques on laser ablation results

The efficacy of different ‘cleaning’ protocols for LA analysis was assessed via comparison of LA results before and after each chemical cleaning method. Potentially, remnants of contaminant material in a foraminifer’s pore space (Fig. 11) may remain after use of standard ultrapure water and methanol LA cleaning, introducing bias during progressive ablation through the test wall. While pre-ablation may remove contaminants from the outer test surface (Sadekov et al., 2008) it will not remove material that may be lodged within pore spaces (Fig. 12c). Modified chemical cleaning methods otherwise used for solution based analyses (partially) remove the outer test surface layer, penetrating the pore spaces, removing potential contaminants (AI. 1). Whether these cleaning methods therefore yield improved accuracy for foraminifera trace and ultra-trace element LA-ICPMS analysis is evaluated below.

This study indicates little change in either the mean or precision of Mg/Ca foraminiferal sample means following the use of oxidative ± reductive, ± acid leach treatments prior to LA analysis and using LA processing (Fig. 13-15, AI. 4). Thus, no change from the typical LA-Mg/Ca cleaning protocol is recommended for samples that have not undergone extensive post-depositional alteration, such as those reported from the Panama Basin (Pena et al., 2005).

Sr/Ca changed little regardless of the degree of treatment and is therefore not suitable as either a contamination or dissolution indicator. Pre-cleaning treatments however had a more

significant impact on ultra-trace element TE/Ca values (Fig. 13-15, 17). Zn/Ca test results indicate a strong response to intensive cleaning techniques, particularly those involving acid leaching, increasing the Zn/Ca after treatment (Fig. 17).

Al/Ca values are commonly used as an indicator of contamination, rather than as a paleoceanographic proxy. Intensive chemical pre-treatments were effective in their removal of contaminants such as Al. However, Al/Ca levels were using solution processing after chemical treatment still higher than those otherwise recorded using LA processing before chemical treatment (Table 1, Fig. 16). Despite persistent Al/Ca contamination, elevated Al/Ca levels were not linked to elevated levels of other TE/Ca measured and consequently Al/Ca was a poor indicator of overall TE/Ca contamination. Therefore, the application of more aggressive cleaning treatments such as acid leaching targeted at Al removal for LA analysis is not warranted, and may in fact act to inadvertently enrich other TE/Ca values.

Careful post-analysis processing of the *ca.* 400 data points collected across a test profile for individual foraminifera to isolate the most representative TE/Ca profile had the most significant impact on trace and ultra-trace element/Ca values. Careful data processing (AI. 4) can ensure that the integrated profile does not include TE-enriched calcite from the inner or outer test surfaces, reducing sample TE/Ca values by up to 400 % (e.g. Al/Ca). Use of any chemical cleaning treatments for LA-ICPMS analysis 1) did not effectively remove Al/Ca, 2) enriched Zn/Ca, and 3) did not alter sample values in a statistically significant way (Mg/Ca, Sr/Ca, Ba/Ca, Mn/Ca). The highest levels of contamination introduced into foraminifera test samples originate from the inner- and outer-most calcite layers and may be incorporated into the solution-based samples. However, these layers are excluded using LA-techniques where post-analytical processing allows the effective ‘cleaning’ of foraminifera via the selection of only primary calcite TE/Ca values for integrated means without the use of chemicals.

5.0 Conclusions

Various approaches have been used to study the effectiveness of foraminiferal cleaning techniques, including a comparison between foraminifera analysed using solution and LA-based techniques. Mg/Ca and Sr/Ca values for the commonly used species, *G. bulloides*, demonstrate the resilience of test calcite to alteration as a result of oxidative $\pm$ reductive cleaning methods, despite the extensive test micro-fracturing otherwise identified on acid leached samples. Minimal, if any discernible dissolution effects on sample Mg/Ca compositions were identified for up to 6x acid leach treatments, including little evidence of selective Mg-rich calcite dissolution. *G. bulloides* from down-core samples with suspected dissolution may also provide a superior paleothermometer as this species' Mg/Ca values remain relatively unchanged after induced dissolution by repeated acid leaching treatments. Foraminifera cleaned using 'Mg-cleaning' for solution analysis and ultrapure water and methanol for LA analysis yield reassuringly compatible results for Mg/Ca and Sr/Ca between techniques.

Ultra-trace element values (TE/Ca of <0.15 mmol/mol) are more susceptible to the effects of insufficient cleaning/differential cleaning methods. Zn/Ca values increase with progressive dissolution of test calcite using dilute nitric acid suggesting preferential low-Zn calcite dissolution. Elevated Al/Ca persists after extensive cleaning, however values of this TE/Ca does not generally reflect contamination of other elements including Mg/Ca, Zn/Ca, Sr/Ca, Ba/Ca or Mn/Ca and therefore is not an effective contamination indicator. Likewise, Sr/Ca values do not reflect other TE/Ca contamination or depletion and therefore should not be used as an indicator of post-depositional test alteration.

We conclude that analysis of ultra-trace elements (Mn/Ca, Zn/Ca, Ba/Ca) via solution techniques require oxidative and reductive cleaning steps, without acid leaching to avoid artificial Zn/Ca elevation. Laser ablation analysis of trace and ultra-trace elements do not require additional cleaning steps beyond those typically used, however careful data processing of individual specimens to exclude inner- and outer-most test calcite (highest TE contamination) is vital for reliable results.

Auxiliary Information

AI. 1.0. Stepwise cleaning procedure for the preparation of foraminiferal calcite for elemental analysis using laser ablation

Procedures in part modified after Boyle (1981), Boyle and Keigwin (2000) and Barker et al. (2003a).

AI. 1.1. Laser Ablation Clean, Clay Removal

Only steps 1.1 and 1.2 were necessary for laser ablation analysis.

During this stage, samples were treated individually in order to maximize cleaning effectiveness, although ultrasonication was conducted in batches. Separate pipettes were used for adding and removing reagents.

1. ¼ fill deep sided petri dish with $>18.3 \text{ M}\Omega \text{ H}_2\text{O}$ (ultrapure water) to, *ca.* 8 mL.
2. Placed lid on petri dish, suspended foraminifera in the water and ultrasonicated for 3–10 seconds, depending on test fragility and the volume of adhering material. Samples with a large amount of material on the outer surface required ultrasonication for up to 1 minute, provided the tests did not fragment. This encouraged separation of more tightly bound clays and nano-fossils from the test surfaces.
3. Sample were allowed to settle for 30 seconds or so. The side of dish was flicked to encourage foraminifer to settle.
4. The dish was placed on an angle and the overlying solution (supernatant) was removed using a separate pipette, taking care not to inadvertently remove foraminifera which floated on the liquid surface or stuck to the sides of the dish. A 2 mL disposable pipette was found to be suitable for removing most of the overlying liquid from the dish without risk of sample loss.
5. Steps (1) to (4) were repeated a further 3 times.
9. 10 mL of Aristar methanol was squirted into each dish.

10. Dishes were ultrasonicated for 3–10 seconds.

11. The sample was allowed to settle for a few seconds, before the methanol was removed. Foraminifera tend to be more buoyant in methanol and additional care was taken not to inadvertently remove foraminifera from the sample.

12. The sample was placed in the oven at 40 °C overnight or for at least 6 hrs to ensure it was dry for mounting or weighing.

13. Foraminifera were checked under a microscope to assess effectiveness of clay removal from the outer test. If clay and/or nannofossils were still visible in the outer test or within the test aperture, steps (1)-(13) were repeated and the length of time the sample was ultrasonicated was increased.

More repetitions were necessary if clay or nano-fossil material was found to be still visible on the outer test.

AI. 1.2. Mounting for Laser Ablation Analysis

The foraminifera were mounted directly onto a carefully polished and cleaned disk of NIST silicate glass standard.

In studies where foraminifera were to be weighed, this was done prior to mounting using the following procedure; Using a dry brush, foraminifera were either weighed individually or as a group Mettler Toledo (MX/UMX 2) ultramicro-balance (precision=0.1 µg). As the weights of foraminifera were very low (e.g. 8.7 µg), the machine was zeroed between samples, and regular calibrations were performed to account for changes in environmental conditions. Reproducibility was assessed via by repeated weighing of the same sample.

1. Adhesive material was placed over $\frac{3}{4}$ of the NIST glass. In this study we used the sticky side of a post-it note, adhered to the silicate glass with double sided tape. The back of a post-it note was used so that foraminifera were able to be easily removed without fragmentation.

2. Using methanol or a dry brush under an optical microscope, foraminifera were placed individually onto the sticky surface whorl side down with the chamber surface selected for ablation is as close to horizontal as possible for ablation. Care was taken to ensure minimal manipulation of the foraminifera on the post-it note Any foraminifera that fragmented during

cleaning, strongly discoloured or had persistent adhering material were removed from the sample at this stage.

AI. 1.3. Oxidative Clean- Oxidative treatment is design to remove organic matter.

Equipment preparation:

1. Using a moistened brush, the foraminifera were transferred to an acid cleaned 2000 µl micro-centrifuge tube. Foraminifera were treated individually so that the same foraminifera could be identified and TE/Ca values matched throughout the study. However, if foraminifera were to be analysed in batched, no more than 5 foraminifera were added to each tube to minimise the effects of fragmentation during ultrasonication.

Oxidative clean:

1. 250 µl of alkali buffered 1% H₂O₂ solution was added to each tube and the rack secured with a lid to prevent tubes popping open while under pressure.

2. The sample rack was placed into a boiling water bath for 10 minutes.

a) At 2.5 and 7.5 minutes the rack was removed momentarily and rapped on the bench top to release any gaseous build-up.

b) At 5 minutes the rack was placed in an ultrasonic bath for a few seconds and returned to the water bath after rapping on the bench.

3. The oxidizing reagent was removed using a pipette.

4. Steps (1) to (3) were repeated.

5. Any remaining oxidizing reagent was removed by filling the tube with ultrapure water and removing. The side of the tube was tapped to encourage foraminifera to settle to the bottom thereby ensuring that they were not inadvertently removed during this process. This step was repeated three times.

AI. 1.4. Reductive Clean – Reductive cleaning is designed to remove any Mn-rich oxide or Mn-rich carbonate coatings (Boyle, 1983)

1. 100 µL of reducing cleaning solution (see AI 3.0) was placed in each sample tube containing the foraminifera just prior to cleaning and the rack secured with a lid to prevent tubes popping open while under pressure.
2. The sample rack was placed in a boiling water bath for 30 minutes. After every 2 minutes the rack was placed in an ultrasonic tank for a few seconds and returned to the water bath after rapping on the bench.
3. Reducing agents were removed using a pipette.
4. Foraminifera were heated in two ultrapure water rinses (5 minutes each) and followed with a final rinse with room temperature ultrapure water.

AI. 1.5. Dilute Acid Leach – the acid leach is designed to remove adsorbed contaminants and further leaching may be used to dissolve a Mn-carbonate coating where necessary

1. 250 µl of 0.001M HNO₃ were added to individual sample tubes.
2. Each sample was ultrasonicated for 3 seconds.
3. Acid was then removed from samples.
4. Ultrapure water was added to each tube.

It was important to replace the leach acid with H₂O as soon as possible for all samples in order to prevent excess dissolution. This was best achieved by only undertaking this step with a few samples at a time.

5. Overlying H₂O was removed.
6. Steps (4) and (5) were repeated once.
7. Using a 2 mL disposable pipette, any remaining solution was carefully removed from each sample.
8. The sample was placed in the oven at 40 °C overnight (or for at least 6 hrs) with the tube only loosely covered to ensure the sample was dry for sample mounting or weighing.

9. Step *AI. 1.2. Mounting for Laser Ablation Analysis* was followed.

AI. 2.0. Stepwise procedure for laser ablation data processing

AI. 2.1 Individual foraminifera

1. The raw counts of Mg and Ca vs. time were plotted on a xy line graph. This showed when the machine had ablated through the test wall.
2. The raw counts were used to assess at what times test wall ablation had taken place. As the laser had not been set for progressive depth correction as it ablated through the test wall, a small natural decay in the raw count signal was evident; however there was a significant decline in the signal after the test wall was penetrated.
3. All elements ratioed to Ca were plotted after background and standard correction on a log graph. This enabled all TE/Ca to be viewed at the same time despite the wide range in values.
4. The corrected TE/Ca data within the test ablation time frame indicated by the raw counts was assessed. A stable signal through all TE/Ca was optimal for the 'integrated profile'. If there was any enrichment in the outer test from adsorbed contaminants for example, this part of the profile was not selected for inclusion in the integrated profile. Likewise, any inner test enrichment was also excluded.
5. 'Fliers' or spurious data generated during analysis were removed from the *ca.* 100-300 data points for each element included in the integrated profile. There were typically 1-3 measurements on a single TE/Ca which generated values that were orders of magnitude higher than sample TE/Ca mean values.
5. Once the part of the foraminifera TE/Ca profile was selected for integration, values within the integrated section were averaged to generate the mean values.
6. The percent standard error was calculated for the integrated profiles. Mg/Ca generally had a % SE of 1-3 %, any individuals with Mg/Ca >5 % SE were excluded. Low levels of natural TE/Ca variability through the test wall was expected due to the progressive ablation through calcite layers deposited at different water depths during the species lifecycle.

AI. 2.2. Sample processing

Once individual foraminifera integrated profiles were assessed, and mean TE/Ca values for individual foraminifera calculated; the individual *G. bulloides* values from the same sample (e.g. same cleaning method) were pooled to generate sample means.

1. Individual foraminiferal TE/Ca values were collated for a sample.

Note, for studies which used more than one core top sample for example, which may cover a range of environmental variables (e.g. Marr et al., 2011) the following procedures would also be added:

2. Threshold values appropriate for the regional environment e.g. water mass, temperature, fluvial input, were used to assess individual TE/Ca measurements and ensure that foraminifera which have undergone post-depositional alteration were not included in the sample mean. For example, foraminifera which had undergone post-depositional alteration of primary test calcite via clay contamination typically had elevated TE/Ca at least 200% higher than sample mean values. Alternatively, samples which have undergone calcite recrystallisation produced Mg/Ca values up to 50% lower than sample mean values.

3. After individual values were pooled to generate sample means, the number of foraminifera remaining within the sample was scrutinised. Natural heterogeneity within a population caused by biological factors or ‘vital effects’ (Marr et al., 2011; Sadekov et al., 2008) meant that samples needed to have a statistically significant number of foraminifera to ensure an environmentally representative value was attained. While the number of foraminifera required for sample values to reach statistical significance varies between species and location, it is typically >10 foraminifera.

AI. 3.0. Reagents used for chemical cleaning, sufficient for a 20 samples

Oxidising Reagent

Alkali buffered 1% H₂O₂ solution. 250 ml oxidising solution used per sample.

Prepare fresh mixture for each batch of samples.

Prepared from:-

Hydrogen peroxide 30% w/v (Aristar grade).

0.1 M sodium hydroxide (Aristar grade)

Reducing Reagent

0.25 M citric acid in 16 M ammonia. Prepared fresh mixture made up to 1 M in hydrazine (NH₂NH₂) immediately before cleaning step.

Prepared from:-

100 ml ammonia

5.254 g citric acid (if using powdered citric acid)

Hydrazine step preparation:

To 146 µl of ammonia/citric mix, add 1314 µl of hydrazine

Dilute Acid Leach

Optima™ ultra trace grade 0.001 M

Made up using conc. HNO₃ (15M) and ultra pure water

Auxiliary 4.0. Individual foraminifera TE/Ca data before and after chemical cleaning.

Stars indicate where a foraminifera has fragmented during cleaning and there been removed from the study.

	Before chemical cleaning - LA processing - TE/Ca (mmol/mol)						After chemical cleaning - LA processing - TE/Ca (mmol/mol)					
	Mg/Ca	Al/Ca	Mn/Ca	Zn/Ca	Sr/Ca	Ba/Ca	Mg/Ca	Al/Ca	Mn/Ca	Zn/Ca	Sr/Ca	Ba/Ca
Oxidative - 1	1.48	0.025	0.006	0.002	1.31	0.002	1.55	0.012	0.002	0.013	1.30	0.003
Oxidative - 2	1.65	0.113	0.007	0.006	1.28	0.002	1.49	0.099	0.003	0.010	1.37	0.007
Oxidative - 3	3.16	0.052	0.006	0.005	1.49	0.005	0.73	0.019	0.005	0.015	1.29	0.002
Oxidative - 4	1.94	0.269	0.013	0.011	1.32	0.007	*	*	*	*	*	*
Oxidative - 5	2.29	0.020	0.001	0.003	1.35	0.001	2.27	0.014	0.006	0.011	1.33	0.001
Oxidative - 6	0.84	0.034	0.000	0.002	1.28	0.001	1.20	0.011	0.005	0.083	1.28	0.004
Oxidative - 7	1.35	0.147	0.000	0.004	1.39	0.002	1.44	0.075	0.007	0.032	1.32	0.002
Oxidative - 8	1.36	0.055	0.000	0.000	1.29	0.001	1.41	0.053	0.001	0.012	1.32	0.001
Oxidative - 9	1.21	0.043	0.003	0.004	1.30	0.005	1.11	0.008	0.002	0.017	1.27	0.002
Oxidative - 10	2.98	0.039	0.003	0.004	1.37	0.002	3.58	0.015	0.002	0.008	1.31	0.001
Oxidative-Reductive - 11	3.21	0.037	0.012	0.005	1.32	0.002	*	*	*	*	*	*
Oxidative-Reductive - 12	2.40	0.052	0.008	0.008	1.28	0.006	*	*	*	*	*	*
Oxidative-Reductive - 13	0.91	0.005	0.001	0.0109	1.34	0.001	1.07	0.017	0.000	0.0004	1.39	0.001
Oxidative-Reductive - 14	1.64	0.041	0.006	0.0021	1.43	0.002	*	*	*	*	*	*
Oxidative-Reductive - 15	1.50	0.010	0.003	0.0049	1.32	0.002	1.26	0.002	0.003	0.0153	1.28	0.001
Oxidative-Reductive - 16	1.08	0.018	0.000	0.0000	1.32	0.001	1.02	0.017	0.000	0.0018	1.35	0.001
Oxidative-Reductive - 17	3.52	0.019	0.004	0.0038	1.31	0.004	3.24	0.003	0.001	0.0103	1.31	0.002
Oxidative-Reductive - 18	1.34	0.011	0.003	0.0009	1.29	0.002	1.03	0.002	0.000	0.0027	1.30	0.001
Oxidative-Reductive - 19	1.67	0.005	0.005	0.0031	1.31	0.001	1.39	0.001	0.002	0.0047	1.28	0.001
Oxidative-Reductive - 20	1.19	0.025	0.002	0.0013	1.24	0.002	1.09	0.014	0.002	0.0048	1.23	0.001
Oxidative-1x Leach - 21	0.67	0.002	0.000	0.002	1.28	0.001	0.73	0.012	0.001	0.001	1.25	0.001
Oxidative-1x Leach - 22	0.91	0.031	0.005	0.003	1.35	0.002	*	*	*	*	*	*
Oxidative-1x Leach - 23	1.70	0.035	0.002	0.002	1.30	0.002	1.40	0.008	0.000	0.011	1.32	0.001
Oxidative-1x Leach - 24	3.29	0.035	0.009	0.008	1.35	0.019	*	*	*	*	*	*
Oxidative-1x Leach - 25	1.73	0.183	0.006	0.017	1.38	0.006	*	*	*	*	*	*
Oxidative-1x Leach - 26	1.41	0.014	0.002	0.003	1.28	0.002	*	*	*	*	*	*
Oxidative-1x Leach - 27	4.54	0.043	0.010	0.012	1.33	0.011	*	*	*	*	*	*
Oxidative-1x Leach - 28	1.60	0.035	0.003	0.002	1.30	0.003	1.48	0.013	0.000	0.006	1.30	0.001
Oxidative-1x Leach - 29	1.86	0.021	0.010	0.006	1.31	0.004	1.42	0.009	0.007	0.005	1.28	0.006
Oxidative-1x Leach - 30	2.06	0.034	0.006	0.002	1.46	0.002	*	*	*	*	*	*
1x Leach - 31	2.23	0.016	0.001	0.002	1.37	0.001	*	*	*	*	*	*
1x Leach - 32	0.86	0.016	0.002	0.001	1.36	0.001	0.88	0.020	0.008	0.017	1.39	0.003
1x Leach - 33	2.04	0.110	0.010	0.008	1.23	0.005	2.39	0.020	0.010	0.017	1.24	0.002
1x Leach - 34	1.04	0.011	0.001	0.002	1.27	0.001	1.10	0.009	0.000	0.000	1.30	0.001
1x Leach - 35	0.98	0.060	0.009	0.005	1.28	0.003	0.83	0.068	0.006	0.003	1.30	0.006
1x Leach - 36	1.60	0.028	0.005	0.005	1.30	0.003	*	*	*	*	*	*
1x Leach - 37	1.91	0.030	0.015	0.007	1.31	0.004	*	*	*	*	*	*
1x Leach - r1	1.74	0.022	0.001	0.002	1.26	0.001	1.61	0.008	0.000	0.000	1.27	0.002
1x Leach - r2	1.41	0.041	0.004	0.002	1.37	0.007	1.41	0.041	0.004	0.002	1.37	0.007
1x Leach - r3	1.25	0.149	0.003	0.003	1.44	0.002	1.42	0.034	0.003	0.001	1.35	0.002
2x Leach - 38	1.43	0.085	0.001	0.001	1.35	0.001	1.40	0.034	0.000	0.003	1.36	0.002
2x Leach - 40	1.40	0.141	0.007	0.004	1.32	0.004	1.49	0.023	0.004	0.015	1.39	0.002
2x Leach - 43	2.06	0.092	0.009	0.007	1.29	0.006	1.42	0.025	0.004	0.009	1.31	0.003
2x Leach - 44	2.38	0.010	0.002	0.001	1.31	0.002	1.48	0.005	0.001	0.000	1.33	0.001
2x Leach - 48	1.27	0.023	0.005	0.004	1.30	0.003	1.26	0.035	0.005	0.000	1.25	0.007
2x Leach - 49	1.29	0.009	0.001	0.001	1.28	0.001	*	*	*	*	*	*
4x Leach - 41	1.23	0.023	0.001	0.000	1.36	0.001	1.17	0.003	0.000	0.001	1.37	0.001
4x Leach - 42	2.52	0.062	0.009	0.011	1.36	0.003	*	*	*	*	*	*
4x Leach - 50	1.43	0.030	0.004	0.004	1.37	0.001	*	*	*	*	*	*
6x Leach - 45	2.79	0.010	0.014	0.001	1.35	0.001	2.32	0.009	0.000	0.000	1.31	0.001
6x Leach - 46	1.64	0.034	0.002	0.002	1.29	0.011	2.90	0.014	0.013	0.004	1.34	0.006
10x Leach - 47	2.32	0.025	0.003	0.002	1.22	0.001	1.33	0.003	0.000	0.000	1.28	0.001

C2-AI - Table 1. Individual foraminifera TE/Ca data before and after chemical cleaning with laser ablation processing. Stars indicate where a foraminifera has fragmented during cleaning and there been removed from the study.

	Before chemical cleaning - solution processing - TE/Ca (mmol/mol)						After chemical cleaning - solution processing - TE/Ca (mmol/mol)					
	Mg/Ca	Al/Ca	Mn/Ca	Zn/Ca	Sr/Ca	Ba/Ca	Mg/Ca	Al/Ca	Mn/Ca	Zn/Ca	Sr/Ca	Ba/Ca
Oxidative - 1	3.30	1.76	0.042	0.076	1.44	0.022	2.37	0.309	0.007	0.041	1.37	0.013
Oxidative - 2	2.41	0.72	0.024	0.030	1.40	0.009	2.11	0.545	0.011	0.039	1.48	0.020
Oxidative - 3	3.92	1.11	0.022	0.022	1.66	0.020	0.76	0.029	0.004	0.016	1.30	0.002
Oxidative - 4	*	*	*	*	*	*	*	*	*	*	*	*
Oxidative - 5	2.84	0.35	0.023	0.018	1.41	0.005	2.59	0.090	0.014	0.025	1.38	0.002
Oxidative - 6	2.00	0.81	0.015	0.042	1.35	0.019	1.45	0.086	0.009	0.152	1.25	0.008
Oxidative - 7	2.08	0.83	0.012	0.032	1.48	0.005	1.98	1.072	0.016	0.068	1.37	0.006
Oxidative - 8	2.12	0.54	0.005	0.028	1.41	0.013	1.58	0.247	0.004	0.031	1.31	0.002
Oxidative - 9	2.09	0.62	0.012	0.024	1.44	0.091	1.23	0.101	0.005	0.045	1.28	0.003
Oxidative - 10	3.39	0.52	0.011	0.026	1.44	0.006	3.61	0.304	0.005	0.021	1.36	0.003
Oxidative-Reductive - 11	*	*	*	*	*	*	*	*	*	*	*	*
Oxidative-Reductive - 12	*	*	*	*	*	*	*	*	*	*	*	*
Oxidative-Reductive - 13	2.47	0.32	0.005	0.010	1.46	0.006	1.82	0.046	0.000	0.0023	1.46	0.002
Oxidative-Reductive - 14	*	*	*	*	*	*	*	*	*	*	*	*
Oxidative-Reductive - 15	2.08	0.69	0.016	0.028	1.40	0.013	1.34	0.228	0.001	0.0053	1.32	0.003
Oxidative-Reductive - 16	2.13	0.89	0.010	0.024	1.48	0.017	1.20	0.083	0.000	0.0015	1.37	0.003
Oxidative-Reductive - 17	3.61	0.34	0.009	0.009	1.34	0.012	3.86	0.045	0.002	0.0029	1.32	0.003
Oxidative-Reductive - 18	1.85	0.06	0.004	0.003	1.33	0.003	1.30	0.011	0.002	0.0002	1.29	0.001
Oxidative-Reductive - 19	1.77	0.01	0.002	0.002	1.29	0.001	1.40	0.015	0.002	0.0023	1.29	0.001
Oxidative-Reductive - 20	1.94	0.41	0.012	0.013	1.45	0.006	1.15	0.048	0.002	0.0021	1.22	0.002
Oxidative-1x Leach - 21	0.88	0.11	0.004	0.006	1.27	0.002	0.77	0.023	0.003	0.008	1.28	0.001
Oxidative-1x Leach - 22	*	*	*	*	*	*	*	*	*	*	*	*
Oxidative-1x Leach - 23	2.19	1.69	0.010	0.011	1.41	0.008	1.46	0.063	0.003	0.019	1.33	0.001
Oxidative-1x Leach - 24	*	*	*	*	*	*	*	*	*	*	*	*
Oxidative-1x Leach - 25	*	*	*	*	*	*	*	*	*	*	*	*
Oxidative-1x Leach - 26	*	*	*	*	*	*	*	*	*	*	*	*
Oxidative-1x Leach - 27	*	*	*	*	*	*	*	*	*	*	*	*
Oxidative-1x Leach - 28	2.11	0.38	0.008	0.008	1.33	0.008	1.59	0.102	0.003	0.014	1.30	0.001
Oxidative-1x Leach - 29	3.34	1.74	0.019	0.024	1.46	0.022	2.37	0.309	0.007	0.041	1.37	0.013
Oxidative-1x Leach - 30	*	*	*	*	*	*	*	*	*	*	*	*
1x Leach - 31	*	*	*	*	*	*	*	*	*	*	*	*
1x Leach - 32	1.52	0.22	0.006	0.006	1.37	0.004	1.11	0.613	0.024	0.063	1.37	0.008
1x Leach - 33	2.15	0.38	0.014	0.012	1.26	0.007	2.62	0.046	0.013	0.031	1.27	0.003
1x Leach - 34	1.77	0.57	0.009	0.021	1.37	0.008	1.38	0.118	0.007	0.032	1.36	0.006
1x Leach - 35	2.72	0.57	0.025	0.014	1.35	0.011	1.53	0.870	0.034	0.020	1.43	0.032
1x Leach - 36	*	*	*	*	*	*	*	*	*	*	*	*
1x Leach - 37	*	*	*	*	*	*	*	*	*	*	*	*
1x Leach - r1	2.06	0.32	0.008	0.008	1.30	0.004	2.02	0.035	0.010	0.011	1.34	0.008
1x Leach - r2	2.76	0.45	0.009	0.018	1.39	0.026	2.19	0.766	0.014	0.013	1.46	0.091
1x Leach - r3	2.21	0.89	0.025	0.026	1.65	0.012	2.04	0.522	0.012	0.022	1.37	0.009
2x Leach - 38	2.04	0.49	0.008	0.009	1.38	0.004	1.68	0.213	0.007	0.019	1.38	0.006
2x Leach - 40	2.07	0.46	0.012	0.008	1.40	0.006	1.63	0.347	0.010	0.072	1.41	0.007
2x Leach - 43	2.59	0.68	0.012	0.013	1.41	0.013	2.04	0.313	0.016	0.051	1.32	0.010
2x Leach - 44	2.39	0.20	0.006	0.007	1.35	0.005	1.78	0.077	0.003	0.005	1.33	0.003
2x Leach - 48	2.16	0.27	0.026	0.013	1.33	0.009	1.57	0.264	0.018	0.014	1.29	0.017
2x Leach - 49	*	*	*	*	*	*	*	*	*	*	*	*
4x Leach - 41	1.93	0.39	0.007	0.008	1.40	0.009	1.38	0.049	0.003	0.044	1.61	0.003
4x Leach - 42	*	*	*	*	*	*	*	*	*	*	*	*
4x Leach - 50	*	*	*	*	*	*	*	*	*	*	*	*
6x Leach - 45	3.28	0.45	0.678	0.016	1.38	0.010	2.22	0.013	0.005	0.004	1.32	0.001
6x Leach - 46	1.87	0.33	0.007	0.010	1.35	0.011	2.74	0.028	0.014	0.018	1.36	0.007
10x Leach - 47	2.24	0.24	0.007	0.007	1.30	0.004	1.40	0.025	0.004	0.006	1.34	0.001

C2-AI - Table 2. Individual foraminifera TE/Ca data before and after chemical cleaning with solution processing. Stars indicate where a foraminifera has fragmented during cleaning and there been removed from the study.

Chapter 3

Southwest Pacific Ocean response to a warming world: using Mg/Ca, Zn/Ca and Mn/Ca in foraminifera to track surface ocean water masses during the last deglaciation

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Author Contributions:

Julene Marr; data collection, interpretation, manuscript writing

Lionel Carter, Helen Bostock; general supervision

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Annette Bolton; data contribution (modern *G. ruber*); general discussion.

Euan Smith; assistance with statistical analysis and interpretation.

Abstract

In situ measurements of Mg/Ca, Zn/Ca, Mn/Ca and Ba/Ca in *Globigerinoides bulloides* and *Globigerina ruber* from Southwest Pacific core top sites and plankton tow are reported and their potential as paleo-proxies explored. The modern samples cover 20° of latitude from 34-54°S, 7-19 °C water temperature, and variable influence of subantarctic (SAW) and subtropical (STW) surface waters. Trace element signatures recorded in core top and plankton tow planktic foraminifera are examined in the context of the chemistry and nutrient profiles of their modern water masses. Our observations suggest that Zn/Ca and Mn/Ca may have potential to trace SAW and STW. Intra- and inter-species offsets identified by *in situ* measurements of Mg/Ca and Zn/Ca indicate these ratios may also record changes in thermal and nutrient stratification in the upper ocean.

We apply these potential proxies to fossilised foraminifera from the high resolution core MD97-2121. At the Last Glacial Maximum, mean surface water temperatures from Mg/Ca were *ca.* 6-7°C lower than present, accompanied by low levels of Mn/Ca and Zn/Ca, with minimal thermal and nutrient stratification. This is consistent with regional dominance of SAW and reduced STW inflow associated with a reduced South Pacific Gyre (SPG). Upper ocean thermal and nutrient stratification collapsed during the Antarctic Cold Reversal, before poleward migration of the zonal winds and ocean fronts invigorated the SPG and increased STW inflow in the early Holocene. Together with reduced winds, this favoured a stratified upper ocean from *ca.* 10ka to present.

1.0. Introduction

The South Pacific Gyre (SPG) plays a dominant role in heat transportation, with surface currents transporting heat from the tropics to the subtropics. The SPG is also globally important as it links with other Southern Hemisphere mid-latitude gyres in the Indian and Atlantic oceans via the Tasman Leakage (Ridgway and Dunn, 2007; Roemmich, 2007). Recent climatic warming has been accompanied by increased wind stress curl over the South Pacific. This has resulted in a 'spin up' of the SPG, causing the poleward advance of the extended East Australian Current (Ridgway and Hill, 2009). However, the degree to which traditional paleoceanographic methods can investigate past SPG change, as reflected in the surface oceans, is limited restricting our understanding of the dynamic Southwest Pacific Ocean environment.

Previous work has indicated that the SPG contracted during the glacial, with a northward shift of the STF (Passlow et al., 1997; Sikes et al., 2009). The exception to this is along the Chatham Rise, east of New Zealand, where the STF is constrained by the topography and confined within 1-2° of latitude (Sikes et al., 2002). Evidence from eastern New Zealand suggests, however, that there may have been some flow through of cold subantarctic surface

waters (SAW) across the western end of Chatham Rise through the Mernoo Saddle (Fig. 1; Weaver et al., 1998; Nelson et al., 2000).

This paper firstly endeavours to develop new paleoceanographic proxies using trace element geochemistry of planktic foraminifers, which may aid in our understanding of surface water masses. *In situ* measurements of Mg/Ca, Ba/Ca, Zn/Ca and Mn/Ca in *Globigerina bulloides* (*G. bulloides*) and *Globigerinoides ruber* (*G. ruber*) were obtained using laser ablation inductively coupled plasma mass spectrometry (LA-ICPMS). Modern variations in foraminiferal core top and plankton tow trace metal concentrations are initially used to determine whether any distinctive chemical signatures could be used to distinguish between water masses (e.g. Lea and Boyle, 1991; Marchitto et al., 2000). These modern samples span a wide range of temperature and nutrient concentrations, and build on previous work that established regional calibration curves for foraminiferal Mg/Ca and ocean temperatures (Bolton et al., 2011; Marr et al., 2011).

In situ trace element measurements are then presented for foraminifera from the last 25 ka of core MD97 2121 in the Southwest Pacific Ocean (Fig. 1) located north of the modern STF, at the southern boundary of the SPG. We used this record to assess whether any changes in the water mass, including surface water thermal and nutrient stratification at the MD97 2121 site were recorded and preserved in the foraminiferal geochemistry. These novel geochemical water mass tracers are then used help enhance our understanding of how frontal surface waters of the SPG – in this case subtropical (STW) and subantarctic (SAW) surface waters near the STF – responded, expanding upon the findings of previous studies in the region.

Figure 20. Generalised modern surface ocean currents and bathymetry surrounding New Zealand (modified from Carter et al., 1998). Black and red circles mark the core-top sites, with red sites denoting those used for *G. ruber* only. Black triangle – plankton tow locations; yellow star – MD97 2121, green star – MD97 2120. TF-Tasman Front; STF-Subtropical Front; SAF-Subantarctic Front; ECC-East Cape Current; STW-Subtropical Surface Water; SAW-Subantarctic Surface Water; MS-Mernoo Saddle; WE-Wairarapa Eddy; CVZ-Central volcanic zone; WR-Waihou River; ^-Southern Alps. Isobaths are in metres.

In situ trace element measurements are then presented for foraminifera from the last 25 ka of core MD97 2121 in the Southwest Pacific Ocean (Fig. 20) located north of the modern STF, at the southern boundary of the SPG. We used this record to assess whether any changes in the water mass, including surface water thermal and nutrient stratification at the MD97 2121 site were recorded and preserved in the foraminiferal geochemistry. These novel geochemical

water mass tracers are then used help enhance our understanding of how frontal surface waters of the SPG – in this case subtropical (STW) and subantarctic (SAW) surface waters near the STF – responded, expanding upon the findings of previous studies in the region.

2.0. Background

2.1. Trace metal signatures in foraminiferal calcite

The incorporation of trace metals into foraminiferal calcite is likely to be influenced by the waters from which the organisms calcify (e.g. Hönisch et al., 2011). Here we focus on Mg/Ca, which is now well established as a temperature proxy (e.g. Anand et al., 2003; Cléroutx et al., 2008), and Zn/Ca, Mn/Ca and Ba/Ca as potential paleo water mass and environmental tracers.

Previously, Zn/Ca and Ba/Ca have been used as paleo tracers in benthic foraminifera (Lea and Boyle, 1990; Marchitto et al., 2000) and Ba/Ca in planktic foraminifera to track surface water changes in trace metal composition caused by changing fluvial input or upwelling (Hall and Chan, 2004; Lea and Boyle, 1991). However, values of Ba/Ca in planktic foraminifera are typically low (*ca.* 1-15 $\mu\text{mol/mol}$) making it challenging to measure statistically significant offsets in test calcite where a Ba-enriched fluvial source is absent (Hall and Chan, 2004; Lea and Spero, 1994; Weldeab et al., 2007). Also, the use of oxidative or reductive cleaning procedures prior to the measurements of Zn/Ca, Mn/Ca and Ba/Ca via solution-based analytical techniques can lead to marked differences in measurements (Marr et al., in press-a).

Zinc and Mn have roles similar to Fe, and are essential to biological processes associated with the primary productivity and enzymatic activity of phytoplankton (Bruland and Lohan, 2003; Croot and Hunter, 1998; Lea and Boyle, 1991; Morel and Price, 2003; Price and Morel, 1990). They are collectively referred to as ‘bioactive trace metals’ (Bruland and Lohan, 2003). The mechanisms by which planktic foraminifera incorporate and biologically mediate Mn, Zn or Ba into test calcite are, however, unclear.

There are various factors known to influence Mg incorporation, and which may also affect the other trace metals. Studies using *in situ* analytical techniques highlight the effect of day-night, high-low Mg/Ca banding through foraminifera test wall caused by light on symbiotic species (Eggins et al., 2004; Sadekov et al., 2005; Spero et al., 2008). While this can cause Mg/Ca offsets between calcite layers of up to 8 mmol/mol in species such as *Orbulina*

universa, which precipitates *ca.* 30% of its shell as high Mg/Ca calcite (Spero et al., 2008), high-Mg calcite precipitation is significantly less in other species such as *G. ruber* (Sadekov et al., 2008; Sadekov et al., 2005). *G. bulloides* is asymbiotic and there is no apparent high-low banding of Mg/Ca, Mn/Ca, Ba/Ca or Zn/Ca through test walls associated with ontogenic growth as revealed by LA-ICPMS profiles through test walls (Marr et al., 2011; Marr et al., in press-a). LA-ICPMS also enables the direct targeting of specific chambers for trace metal analysis, and thus allows assessment of changes in trace metal concentrations of different chambers during the foraminifera's lifecycle.

2.2 Surface ocean trace metal concentrations

Differences in concentrations of Zn and Mn in the surface waters have been observed across the modern STF in the South Pacific Ocean. Mean dissolved Zn levels of 0.22 nmol/kg in STW are higher than a mean of 0.04 nmol/kg in SAW (M. Ellwood pers. comm., 2011). STW Mn concentrations are *ca.* 1.2 nmol/kg, while those from SAW generally range from 0.3 to 0.7 nmol/kg (Klinkhammer and Bender, 1980). Thus, an increasing influence of nutrient-rich STW may potentially be indicated by elevated Zn/Ca or Mn/Ca in foraminifera.

Dissolved Ba concentrations, however, are relatively homogenous with as little as 10-20% difference between SAW and STW off southern Australia (Jacquet et al., 2004). While there is no major upwelling in this region to enhance Ba concentrations, there are many rivers that discharge along the lower eastern North Island, annually carrying *ca.* 83 Mt of suspended load to the continental shelf (Hicks and Shankar, 2003). The Waihou River, where the Mn and Zn concentrations have been measured, is the closest river to the core site MD97 2121, over 300 km to the northwest (Fig. 20). The Waihou, does however, drain a similar catchment to rivers discharging into Hawke Bay (Fig. 20). The Waihou River has dissolved Mn levels of 1.4-8.8 µg/kg and Zn of <0.1 µg/kg (Webster, 1995), lower than the global averages of 34 µg/l and 0.6 µg/l, respectively (Gaillardet et al., 2003). Unfortunately no dissolved Ba concentrations from rivers are available for the North Island (see Auxiliary Information).

2.3 Physical Oceanography

The East Australian Current (EAC) is the main western boundary current of the SPG (Ridgway and Hill, 2009). The EAC flows south along eastern Australia, with a component detaching to form the eastward flowing Tasman Front (TF) (Ridgway and Dunn, 2007). This

frontal flow attaches to northern New Zealand as the East Auckland Current (EAUC) and its southward continuation as the East Coast Current (ECC) continues to Chatham Rise before being steered eastward (Ridgway and Hill, 2009; Tilburg et al., 2001). Seaward of the ECC is the anticyclonic, warm-core Wairarapa Eddy (WE) associated with the East Cape Eddy system. Eddies shed near East Cape, and propagate southwest along the continental margin to Hawke Bay where they may stall or merge with a previous perturbation to form the WE (Chiswell, 2005; Roemmich and Sutton, 1998).

South of Chatham Rise, the inflow to southern New Zealand is dominated by the Antarctic Circumpolar Current (ACC) whose leading edge is the Subantarctic Front (SAF). The SAF separates Subantarctic Water (SAW) from colder Circumpolar Surface Water (CSW) and is forced south around the bathymetric barrier of Campbell Plateau (Fig. 20) (Heath, 1985a; Morris et al., 2001).

These subtropical and subantarctic inflows create a dynamically-driven modern surface ocean east of New Zealand (Fig. 20). The boundary between the two inflows is the STF positioned along the east-west crest of Chatham Rise (Chiswell, 2002a). The front separates warm, saline, micronutrient-rich, macronutrient-poor subtropical water (STW) in the north from cold, less saline, micronutrient-poor, macronutrient-rich SAW to the south (Boyd et al., 1999; Ellwood et al., 2008; Locarnini et al., 2006).

Off the eastern South island, the STF is represented by the northward flowing Southland Current. At Chatham Rise, a branch of the Southland Current extends east to the STF whereas another branch continues north through Mernoo Saddle (Fig. 20). On its passage north through the Mernoo Saddle, cool ($\sim 7^{\circ}\text{C}$), low salinity (~ 34.6 psu) Subantarctic Mode Water is forced from 580-800m water depth to at least 275m, and probably to the surface, via episodic wind-induced upwelling (Heath 1972a,b; Heath 1985; Morris et al., 2001).

3.0. Samples and Methods

3.1. Samples

Modern foraminifera were sampled from eleven core-top sites and three plankton tows spanning 20 degrees of latitude, three water masses, and water depths from 580-3003 m (Fig. 20). The deepest sites are close to the calcite saturation horizon, which locally lies at 2800-3100 m (Bostock et al., 2011). Accordingly, individual foraminifera from core-top sites >2500 m depth were examined visually and via scanning electron microscopy for signs

of test dissolution, which can indicate that preferential leaching of trace elements (e.g. Brown and Elderfield, 1996). Any individuals that were potentially compromised by dissolution were removed from the dataset.

Ancient foraminifera were sampled from the upper 9.15 m, corresponding to the last *ca.* 25 kyr of giant piston core, MD97 2121, situated north of the modern STF (40°22.935'S, 177°59.68'E) at a water depth of 2314 m (Carter et al., 2008). The oceanographic setting, high sedimentation rate (29-42 cm/kyr) and well constrained chronology (Carter et al., 2008) make this an optimal site to test these new geochemical proxies and learn more about the SPG over the last glacial/interglacial cycle.

Samples were taken in *ca.* 5-10 cm intervals yielding a *ca.* 300-600 year resolution (e.g. Carter et al., 2008). *G. ruber* and *G. bulloides* from core-tops and MD97 2121, were hand-picked from the 250-450 µm sieved fraction (Fig. 21). *G. bulloides* is present continuously throughout the glacial-interglacial record, however, *G. ruber*, which favours warmer waters, is rare during the cooler intervals and is only present in sufficient abundance for analysis from *ca.* 15.5 ka through the late Holocene.

Figure 21. Scanning electron microscopy image of *Globigerinoides ruber* (A) and *Globigerina bulloides* (B). The chambers are labelled such that *f* represents the final (youngest) chamber, *f-1* is the penultimate chamber, *f-2* is the antepenultimate chamber and *f-3* the oldest chamber analysed. Core-top study results for mean STW and SAW trace element/Ca values are based on the mean of *G. bulloides* chamber *f-3*, *f-2* and *f-1* values as this species present in both STW and SAW. For the down core MD97 2121 record, only chambers *f-2* and *f* were analysed for *G. bulloides* and chamber *f-2* for *G. ruber*. Laser ablation pits measuring 25 μm in diameter are visible. High magnification images of pore space and surrounding calcite in a glacial (C) and, Holocene ablation pit (D) *G. bulloides* shows no change in calcification through the test wall which indicates little to no dissolution and/or re-crystallisation has taken place. Image (E) is of an ablation pit through a *G. bulloides* from another Southwest Pacific location on which dissolution is clearly evident by the absence of thin calcite layers through the test wall.

3.2. Analytical Techniques

Foraminifera were cleaned and mounted on a NIST 610 silicate glass standard for trace element analysis by LA-ICPMS following the protocols outlined in Marr et al. (2011). Trace element/Ca ratios of foraminiferal tests were analysed using a New Wave deep-UV (193 nm) solid-state laser ablation system coupled to an Agilent 7500CS ICPMS at Victoria University of Wellington, New Zealand. Monitored isotopes were ^{24}Mg , ^{27}Al , ^{43}Ca , ^{55}Mn , ^{66}Zn , ^{88}Sr and ^{138}Ba . Laser ablation analyses were between 60 s and 120 s in duration depending on test wall thickness and/or density, to ensure consistent penetration of the *G. bulloides* and *G. ruber* test wall (e.g. Marr et al., 2011). After subtraction of background signals, trace element/Ca ratios were calculated by reference to bracketing LA-ICPMS analyses of the NIST610 glass standard, and normalisation to the preferred trace element values in this standard: Mg-465 ppm, Al-10798 ppm, Ca-82191 ppm, Mn-485 ppm, Zn-456 ppm, Sr-516 ppm, Ba-435 ppm (Pearce et al., 1997). Analyses of NIST610 bracketed every 5-20 analyses of foraminifera and showed no significant drift in trace element/Ca ratios beyond the internal precision of the analyses over the course of the analytical sessions. The internal precisions (% 2 standard error) of trace element/Ca ratios for a single foraminiferal analysis are typically: Mg/Ca ± 1.0 -2.5%, Al/Ca ± 5 -20%, Mn/Ca ± 3 -15%, Zn/Ca ± 6 -23%, Sr/Ca ± 1.0 -2.0%, Ba/Ca ± 3 -30%.

Previous LA-ICPMS studies of foraminifera demonstrated that trace element-depth profiles through a test wall are typically variable with a 'surface veneer' enriched in Mg and other trace elements (except Sr) and similar, highly localised, enrichment in Mg and other trace elements as the laser penetrates the inner test wall (e.g. Eggins et al., 2003b). This is especially true of Mn/Ca levels in foraminiferal calcite, which is known to be susceptible to post-deposition alteration (e.g. Boiteau et al., 2012; Boyle, 1983). Careful scrutiny of the time-resolved trace element depth profiles during processing, with exclusion of high Mn/Ca phases potentially representing post-depositional contamination or diagenesis (e.g. Boyle, 1983), ensures that only primary calcite is represented in sample means (Marr et al., 2011).

For the modern core-tops all four visible chambers of *G. bulloides* and chamber *f*-2 of *G. ruber* were analysed (Bolton et al., 2011). However, only data from *G. bulloides* older three visible chambers (*f*-3 to *f*-1) were used to determine the mean for the water mass, as final chamber (*f*) values show a large offset (Marr et al., 2011). Individual foraminifera values are grouped and presented as sample means for core-top and plankton tows ($n=10$ -37) to allow comparison with studies that use solution techniques (e.g. Anand et al., 2003; Pahnke and Sachs, 2006; Pahnke et al., 2003).

For the MD97 2121 down core samples only the anti-penultimate (*f*-2) and final (*f*) chambers of *G. bulloides* were analysed, because chamber *f*-2 yielded better within-chamber reproducibility than older *f*-3 or younger *f*-1 chambers and avoids issues associated with the kummerform chambers (Fig. 2) (Berger, 1971). Each sample mean (using chambers *f*-2 or *f*) were composed of measurements from 10-46 individual specimens with the 95% confidence interval describing the distribution of the data about the sample mean given in Auxiliary Information 1. The variance of values in each sample was also calculated. Paleo-temperature estimates were determined as follows:

$$G. \textit{bulloides} - \text{Mg/Ca (mmol/mol)} = 0.952 [\pm 0.041] \times e^{0.068 [\pm 0.002] \times T} (r^2 = 0.95)$$

Calibrated temperature range - *ca.* 7.0-31.0 °C (Marr et al., 2011)

$$G. \textit{ruber} - \text{Mg/Ca (mmol/mol)} = 0.798 [\pm 0.133] \times e^{0.070 [\pm 0.005] \times T} (r^2 = 0.89)$$

Calibrated temperature range - *ca.* 14.0-29.0 °C (Bolton et al., 2011)

4.0. Results

4.1. Mn/Ca, Zn/Ca and Ba/Ca ratios in the modern ocean

Mn/Ca and Zn/Ca typically occur in low (< 300 µmol/mol) and Ba/Ca in ultra low (<10 µmol/mol) levels in the modern and ancient foraminifera studied here (Fig. 23-25, Table 2) (e.g. Lea and Boyle, 1991; Rosenthal et al., 1999). Individual LA-ICPMS analyses of these elemental ratios can have large uncertainties, due to low concentrations of Mn, Zn and Ba and heterogeneity of the foraminiferal test wall. Multiple analyses (*n* = 3-5) of single chambers of an individual foraminifera show that the external reproducibility (2 sd) of trace element/Ca ratios for a single foraminifera analysis are better than: Mn/Ca ±15-60% (±9-33 µmol/mol), Zn/Ca ±14-52% (±4-19 µmol/mol), Ba/Ca ±27-157% (±2-14 µmol/mol). Some of this variability represents real heterogeneity within the foraminiferal test chambers and overestimates the analytical external reproducibility (Marr et al., 2011). Nevertheless, Mn/Ca and Zn/Ca mean values of *G. bulloides* from STW core-top sites are statistically different from SAW core-top sites, (Mn/Ca_{STW} = 23.7-120.2 vs Mn/Ca_{SAW} = 1.8-7.6 µmol/mol and Zn/Ca_{STW} = 19.7-65.6 vs Zn/Ca_{SAW} = 7.5-14.1 µmol/mol). The relative differences of these mean elemental ratios from *G. bulloides* between STW and SAW core-top sites, *ca.* 1700% for Mn and 400% Zn, are larger than analytically, or known biologically induced uncertainties (Fig. 22).

G. bulloides and *G. ruber* mean Zn/Ca and Ba/Ca values from individual core-top and plankton tow samples are in good agreement, suggesting that any post-depositional alteration of tests is not significant (Fig. 22, Table 2; AI 2). However, mean Mn/Ca of 0.6 $\mu\text{mol/mol}$ measured on the *G. bulloides* from U2309 plankton tow is 4-12 times lower than that of nearby core tops. Likewise, the mean Mn/Ca of 7.6 $\mu\text{mol/mol}$ measured on *G. ruber* from plankton tow U2315/U2322 from STW is 5 times less than adjacent core top ratios (Table 2; AI 2).

Mean Mn/Ca and Zn/Ca ratios for modern *G. bulloides* compared across all core-top and plankton tow samples show approximately an order of magnitude variation, with the largest difference evident across the STF (Fig. 20, 22, Table 2). *G. bulloides* Zn/Ca values from STW sites are four times greater than their SAW counterparts (Fig. 22). This broadly mirrors modern water chemistry, where mean STW Zn levels are >5 times higher than in SAW (Fig. 22g) (M. Ellwood pers. comm., 2011). *G. bulloides* STW and SAW foraminiferal Mn/Ca values also mimic the distinctive water mass trace metal concentrations, where particulate STW Mn is two to four times higher than that found in SAW south of Australia (Fig. 22d) (Bowie et al., 2009). *G. bulloides* Ba/Ca from SAW and STW does not vary significantly between samples, which are very low (0.5-5 $\mu\text{mol/mol}$) for distal sites P71, B32, D178, F111, dominated by carbonate-rich sediments (Fig. 22c). However, core-top and plankton tow Ba/Ca results from S938, R623, U2309 have values of up to 8.7 $\mu\text{mol/mol}$, and S793 up to 14 $\mu\text{mol/mol}$ or 400% higher (Fig. 22c). Corresponding enrichments or depletions in foraminiferal Zn/Ca, Mn/Ca or Mg/Ca are not apparent.

G. bulloides**(chamber f-3 - f-1)****(chamber f)**

Site	Water Depth (m)	n=	Latitude (°S)	Longitude (°E)	Water Mass ¹	Mn/Ca (μmol/mol)	Zn/Ca (μmol/mol)	Ba/Ca (μmol/mol)	Mn/Ca (μmol/mol)	Zn/Ca (μmol/mol)	Ba/Ca (μmol/mol)
P71	1919	18	33.86	174.69	STW	25.1	24.9	1.8	26.2	34.7	1.3
						5.2	6.6	0.3	5.8	6.7	0.3
S793	2411	18	36.32	176.80	STW	73.4	21.9	8.6	72.4	20.0	6.7
						33.6	3.7	3.0	42.6	5.2	3.5
P69	2195	14	40.40	178.00	STW	39.6	67.7	2.5	33.7	69.3	1.89
						10.9	15.3	0.6	6.8	20.3	0.4
S938	3003	12	40.03	180.00	STW	159.0	30.2	4.4	170.6	30.4	4.54
						79.9	13.3	1.3	65.7	12.1	1.6
R623	1128	16	43.20	186.00	STF: SAW/STW	42.7	77.5	4.7	36.9	80.7	3.8
						11.8	36.9	1.0	7.8	38.0	1.0
Q220	580	10	44.29	174.98	STF: SAW/STW	4.5	38.9	3.6	0.3	28.0	1.65
						0.3	10.0	0.5	0.1	6.0	0.2
ΔU2309	3585	37	46.40	178.30	STF: SAW/STW	0.6	33.3	2.7	5.2	22.8	2.3
						0.3	40.4	1.8	2.8	7.0	1.5
F111	704	22	48.95	174.98	SAW	2.8	9.8	1.9	3.4	15.8	1.63
						0.6	2.6	0.3	0.8	3.6	0.3
D178	629	19	51.72	169.83	SAW	2.6	4.6	1.8	3.4	4.7	1.48
						1.0	1.5	0.3	1.4	1.3	0.3
B32	799	23	53.63	169.87	SAW	7.6	12.6	2.4	9.7	13.4	2.05
						2.1	3.0	0.4	2.4	3.0	0.4

G. ruber (chamber f-1)

Site	Water Depth (m)	n=	Latitude (°S)	Longitude (°E)	Water Mass ¹	Mn/Ca (μmol/mol)	Zn/Ca (μmol/mol)	Ba/Ca (μmol/mol)
P71	1919	15	33.86	174.69	STW	38.9	27.2	2.2
						14.3	7.0	0.8
Z7003	430	18	36.69	176.24	STW	39.3	10.2	1.5
						9.2	4.9	0.4
ΔU2315		31	38.51	179.02	STW	7.6	103.7	1.11
ΔU2322			41.60	178.05		2.3	26.8	0.1
ODP1123	3290	13	41.94	188.50	STF: SAW/STW	53.5	49.9	5.8
						37.6	20.3	1.6

Table 2. Details of core-top and ^Δplankton tow locations, water depth and number of foraminifera analysed from 10 core-top and one plankton tow site in the Southwest Pacific Ocean, east of New Zealand used for calibrating the planktic foraminifera water mass proxies (Fig. 20). Also presented is a summary of trace element chemistry for *G. bulloides* three oldest chambers (*f1*, *f2*, *f3*), final chamber (*f*) and *G. ruber* outlined here as sample means with 95% confidence interval in italics. Note, where subtropical mean or subantarctic water means have been presented only those sites solely labelled STW or SAW have been used. For additional details about core-top sites see Marr et al. (2011).

¹ STW = Subtropical Water; SAW = Subantarctic Water; STF = Subtropical Front, Stanton (1973).

G. ruber samples are restricted to the warmer STW, however, their mean Mn/Ca, Zn/Ca and Ba/Ca values are similar to the mean for *G. bulloides* older chambers *f-3*, *f-2* and *f-1* from the same or nearby sites (ODP1123:R623, Z7003:S973, P71) (Fig. 22, Table 2).

Modern *G. bulloides* chamber *f* values tend to be more enriched in Zn/Ca than either *G. bulloides* chambers *f-1* to *f-3* by up to 40% or in *G. ruber* (chamber *f-2*) by up to 50% (Table 2). While the difference between *G. bulloides* chamber *f* and *G. ruber* chamber *f-2* is up to 50%, except the data from plankton tow sites U2322 and U2315, where *G. ruber* Zn/Ca values are more than 50% higher than core top sites suggesting these samples may contain some remnant Zn-enriched organic material (Fig. 22). The relationship between *G. bulloides* chamber *f* and *G. ruber* chamber *f-2* Zn/Ca may replicate the modern surface water concentration gradients, where Zn/Ca is *ca.* 50% higher at 100 m depth than at 30-40 m (Fig. 22H,I) (Martin et al., 1989).

All *G. bulloides* chambers and *G. ruber* Mn/Ca values from the same sample are indistinguishable (P71; Table 2). Ba/Ca is present in ultra low concentrations, and any inter-chamber variations are close to uncertainty; however the general trend is for *G. bulloides* older chambers *f-3*, *f-2* and *f-1* and *G. ruber* to be more enriched in Ba/Ca than *G. bulloides* chamber *f* (Table, 2).

Figure 22. Comparison of sample trace element/Ca ratios for modern *G. bulloides* chambers *f-1* to *f-3* (inclusive) and *G. ruber* chamber *f-2* with each sample mean comprised of measurements from multiple individual specimens. Core sites are presented according to their respective latitudes (Table 2) from north to south with those sites from the STW and SAW indicated either side of the STF sites (grey shaded box). “Box and whisker” plots in panels (A – C) illustrate values of all *G. bulloides* *f-2* analyses at a given site. Bar graphs in panels (D-F) represents *G. ruber* (orange) and *G. bulloides* (chambers *f-3-1* – dark blue; chamber *f* – light blue). Note *G. ruber* site Z7003 has been incorporated into S793 and ODP1123 into R623 due to their close proximity. The bar graph indicates mean site values for *G. bulloides* chambers *f-1-f-3* (dark blue) and *f* (light blue). The Zn/Ca and

Mn/Ca solid lines represent the mean values for the STW (red - P71, P81, S793, P69, S938) and SAW (blue - F111, D178, B32) sites. Site means are for *G. bulloides* chambers *f-1* to *f-3* only. Plankton tow values from U2309 (*G. bulloides*) and U2315 and U2322 (*G. ruber*) are indicated by hashed lines, note, *G. ruber* plankton tow values have been appended to site P69 due to location proximity. (G) STW and SAW water mass Zn concentrations sampled in October, 2000 (Elwood, unpub. data 2012) ca.41.2-46.5°S; 178.5-178.6°E, (H) Zn surface water concentrations from 0-500 m and (I) surface-deep water from 0-1500 m, 39.47°S; 179.35°E (Elwood, unpub. data 2012). (J) Modern surface ocean thermal stratification as measured by Mg/Ca thermometry of *G. bulloides* chamber *f-2* (dark blue diamonds) and *f*.

4.2. Glacial-interglacial Mg/Ca, Zn/Ca, Mn/Ca and Ba/Ca

MD97 2121 core data (Fig. 22, 23 and AI 1) show mean glacial Mg/Ca temperatures for *G. bulloides* (chamber *f-2*) and *G. ruber* (chamber *f-2*) are 10.4 and 12.4 °C, respectively from 25-21 ka. *G. bulloides* records an initial temperature increase of ca. 4 °C from ca. 22-18 ka followed by an equivalent decrease in temperature from 18 to 15 ka. From ca. 17 to 14 ka there is an apparent decoupling of *G. bulloides* and *G. ruber* temperature trends, while *G. ruber* indicates warming, *G. bulloides* displays continued, but highly variable, cooling (Fig. 23). Significant, but erratic, warming of ca. 6-7 °C is only indicated by *G. bulloides* after ca. 14 ka, during the Antarctic Cold Reversal (ACR- ca. 14.2-12.4 ka) (Fig. 23). Meanwhile *G. ruber* temperatures cool by ca. 4 °C during the ACR. Mean Holocene *G. ruber* and *G. bulloides* surface ocean temperatures (17.9 and 17.8 °C, respectively) are within error of each other and of modern regional surface ocean temperatures (Carter, unpublished report, 2000). However, ca. 9-6.5 ka and again in the late Holocene (<3 ka) *G. bulloides* (chamber *f-2*) records higher temperatures by up to 3 °C than *G. ruber*, the opposite of normal species stratification.

Previous laser ablation measurements of core-top and plankton tow *G. bulloides* show chamber *f* Mg/Ca values are ca. 20-30% lower than those of chamber *f-2* (Marr et al., 2011). Down core *G. bulloides* chamber *f-2* – *f* offset varies markedly during the glacial period, including times when chamber *f* temperatures are similar to, or occasionally higher than the older chambers (Fig. 23). During the ACR there is little significant difference in Mg/Ca values between chambers. Following the ACR, the offset between chambers is relatively consistent, equivalent to 3-4 °C throughout the Holocene (Fig. 23).

Figure 23. Geochemical and isotopic proxy data from MD97 2121 (A – D) and Antarctica (E) for the last 25 kyr. Laser ablation ICPMS data (this study, A – C) are shown for 2 chambers of *G. bulloides* as the dark blue line-*f*-2 (anti-penultimate chamber) and light blue line-*f* (final chamber) with each sample mean comprised of measurements from multiple individual specimens. Data for *G. ruber* (red line) are from laser ablation analyses of chamber *f*-2. (A) Mg/Ca - temperatures using the calibrations of Marr et al. (2011) and Bolton et al. (2011) (B) Zn/Ca – nutrient stratification, (C) Mn/Ca – productivity, (D) $\delta^{18}\text{O}$ profiles of three planktic foraminiferal species from the MD97 2121 record (Carter et al., 2008), (E) EPICA Dome C deuterium record (Jouzel et al., 2007). The Antarctic Cold Reversal (ACR) is indicated by the blue shaded bar. Grey shaded area highlights the difference in trace metal values between *G. bulloides* chambers *f* and *f*-2. Geochemical data are presented using a three point moving mean for trend comparison with typical 95% confidence interval (CI) about the moving mean shown as error bars to simplify the graph. Individual sample values are represented as points on the graph. Where the density of data is less than 2 samples/3ka no trend line has been drawn. Red dashed line from 13.5-12.5 kyr indicates a period of clear, appreciable variability evident in *G. bulloides* data for which a *G. ruber* record is absent, likely due to an influx of SAW water which is also evident in the faunal assemblage record (E).

Glacial to Holocene Zn/Ca, Mn/Ca and Ba/Ca trends of *G. bulloides* and *G. ruber* generally follow that of Mg/Ca (Fig. 22, 23) (Carter et al., 2008; Weaver et al., 1997). In the glacial the Zn/Ca values are similar to that from modern SAW core tops, while during the deglaciation, including the ACR, Zn/Ca values of *G. bulloides f*-2 increase dramatically from 9.3-24.4 $\mu\text{mol/mol}$ and Ba/Ca from 2.8-5.3 $\mu\text{mol/mol}$. *G. bulloides f*-2 Mn/Ca values are lowest during peak glacial conditions at ca. 40 $\mu\text{mol/mol}$ ca. 23-22 ka, gradually increasing until the ACR when they peak at ca. 300 $\mu\text{mol/mol}$, and maintain a range of ca. 100-300 $\mu\text{mol/mol}$ throughout the Holocene. Holocene mean *G. bulloides f*-2 Zn/Ca values of 24.4 $\mu\text{mol/mol}$ are similar to those of STW from core-tops.

Shallow dwelling *G. ruber* records the lowest Zn/Ca values, whereas deeper living *G. bulloides* has higher values, especially in chamber *f* (Fig. 23). Glacial *G. ruber* and *G. bulloides f*-2 Zn/Ca offsets and *G. bulloides* inter-chamber (*f*-2-*f*) Zn/Ca offsets are relatively consistent with *G. bulloides* chamber *f* more enriched in Zn/Ca by ca. 45% than chamber *f*-2 (Fig. 23). At the ACR, however, there is no offset in Zn/Ca values between chambers *f*-2 and *f* in *G. bulloides*, or *G. bulloides*-*G. ruber*. During the Holocene, the Zn/Ca offset between *G. bulloides*-*G. ruber* is variable, reaching a peak difference between ca. 10 and 6.5 ka when *G. bulloides* chamber *f* values are double those of *G. ruber*.

The variance of the trace element/Ca data within individual samples was also calculated. Mg/Ca variance of *G. bulloides* chamber *f*-2 averaged 0.92 mmol/mol from 25-18 ka, and 0.86 mmol/mol from 18-10 ka. From ca. 10 ka there is a ca. 50% increased Mg/Ca variance

increasing to 1.37 mmol/mol, with a similar result for chamber *f*. The scatter was further tested over the delineated periods to ascertain if the difference in population variance was significant by application of the 'F-test' (Dixon and Massey, 1969). A value of $F=1.09$ ($F_{inv}=1.74$, $df=48$) confirmed that the difference is significant. Similar variance trends were also found for Zn/Ca and Mn/Ca. T-test values of 17.6 between the periods 25-14 ka and 17.1 between 12.5 ka to present ($p<0.05$, $df=48$) clearly indicate a significant difference.

5.0. Discussion

5.1 Zn/Ca, Mn/Ca and Ba/Ca as tracers of ocean change

The evidence from the modern core tops and plankton tows suggests that these trace elements show distinct offsets between STW and SAW in the Southwest Pacific. If modern Zn/Ca concentrations in surface waters (Results 4.1 and Fig. 22) hold for the paleocean record, Zn/Ca concentrations in *G. bulloides* and *G. ruber* chambers potentially can track surface water masses. Zinc is also essential for phytoplankton photosynthesis, and has a spatial and vertical distribution similar to other micronutrients (Fig. 22H). The results from modern core tops in this study suggest that Zn/Ca in fossilised foraminiferal calcite may also be a paleo-nutrient proxy.

Manganese, after Fe, is the most important trace element for marine phytoplankton growth, and is *ca.* 10 times more abundant in seawater than Zn (Fig. 23, 24) (Ho et al., 2003; Morel et al., 2003). However, Mn/Ca ratios in foraminiferal test calcite are a conundrum. Core-top data reveal a clear distinction between sites underlying SAW (mean 4.3 $\mu\text{mol/mol}$) and STW (mean 74.3 $\mu\text{mol/mol}$), suggesting a link with those water masses. Such low SAW values are confirmed by a plankton tow from the STF (U2309) where there is a strong SAW influence via the subantarctic-dominant Southland Current (Fig. 20) (Sutton, 2003). The down-core variability suggests that change in measured Mn/Ca values is primarily a response to changing water masses. Minimum Mn/Ca values occur during the glacial, which is consistent with the dominance of SAW, as evinced by Mg/Ca, Zn/Ca, stable isotopes and foraminiferal assemblages (Fig. 23; Carter et al. 2008). We discount any possibility of Mn/Ca being influenced by terrigenous input, as terrigenous flux increased in the glaciation when Mn/Ca is low at MD97 2121 (Fig. 25) (Carter and Manighetti, 2006). During the Holocene, Mn/Ca is generally higher than glacial values, again consistent with STW dominance as identified by aforementioned proxies (e.g. Weaver et al., 1998). However, Holocene *G. bulloides* and *G. ruber* Mn/Ca is significantly elevated above the modern STW and while the cause of this

offset remains unknown, it raises the possibility of other influences (Fig. 25; Auxiliary Information-Chapter 3). Several peaks in Mn/Ca occur during the Holocene, including a distinct peak in *G. ruber* Mn/Ca centred on 11 ka. This coincides with a time of elevated carbonate and silicate MAR, and warmer SSTs from the subtropics suggesting some influence of increase STW inflow and potentially productivity.

In contrast to Zn/Ca and Mn/Ca, levels of Ba/Ca in the modern *G. ruber* and *G. bulloides* samples do not distinguish between STW and SAW. Core-top S793 has elevated Ba/Ca levels, which may reflect locally high fluvial input (Hicks and Shankar, 2003). However, foraminifera from other high fluvial inputs (P69, S938) do not have elevated Ba/Ca values (Fig. 22), suggesting that fluvial discharge is not a primary control on local Ba concentrations (Fig. 22). The higher Ba/Ca at S793 may also be due to the proximity to the volcanic-hydrothermally active White Island (Fig. 20), which produces rocks and hydrothermal fluids with high levels of Ba (rocks >1000 g/m³) (Hedenquist et al., 1993). The MD97 2121 record reveals a small offset between glacial and interglacial Ba/Ca values suggesting a change in Ba concentrations in the ambient water mass (Fig. 24). However, as fluctuations of Ba/Ca are unlikely to reflect terrestrial sources as seen in the core-top material, the reason for the offset is unresolved (Fig. 22).

Figure 24. Mg/Ca (A), Zn/Ca (B) and Ba/Ca (C) records of core MD97 2121 for the past 25 ka for *G. ruber* (red) and *G. bulloides* (blue) with each sample mean comprised of measurements from multiple individual specimens. Horizontal blue and red lines on the graph define SAW and STW water mass modern trace element /Ca means as determined from modern core-top analyses (from Fig. 22). Also presented is the $\delta^{13}\text{C}$ record for *G. bulloides* (blue) (D) (Carter et al., 2008) together with mean values of 0.51 and -0.95 for SAW and STW respectively are from repeat core-top *G. bulloides* analyses undertaken at NIWA and (E) the foraminiferal assemblages of species with known environmental preferences (Imbrie and Kipp, 1973), based on samples of >100 individuals (Northcote et al., 2007). The Antarctic Cold Reversal (ACR) is indicated by the blue shaded bar. See Fig. 23 for details on data presentation.

Figure 25. Geochemical, biogenic sediment based productivity indicators for the MD97 2121 paleo record and abundance of key faunal taxa. (A) Mn/Ca for *G. bulloides* (blue) and *G. ruber* (red). (B) Carbonate mass accumulation rate (MAR) and (C) terrigenous sediment and silica MARs for MD97 2121 (Carter et al., 2008). (D) Percentage of *G. ruber* (red) and *G. bulloides* (blue) from the total planktonic foraminifera species abundance, based on samples of >100 individuals (Northcote et al., 2007). The Antarctic Cold Reversal (ACR) is indicated by the blue shaded bar. See Fig. 23 for details on data presentation.

5.2. Thermal and nutrient stratification

Modern *G. bulloides* chamber *f* is lower in Mg/Ca compared to the previous chambers. This is likely to reflect a lower temperature at the time the chamber was calcified, an interpretation consistent with this species migrating to deeper depths near the end of its lifecycle (Fig. 22I) (Hemleben et al., 1989; Marr et al., 2011). Alternative reasons for offsets in Mg/Ca and other trace metal values between chambers may include diagenesis disproportionately affecting the thinner chamber *f*. However, diagenesis seems unlikely as Mg/Ca values (and therefore Mg/Ca paleotemperatures) decrease in chamber *f* relative to chamber *f*-2, while Zn/Ca values increase and Mn/Ca remains relatively unchanged (Fig. 23). *G. bulloides* Mg/Ca mean and chamber *f* values for core tops adjacent to the plankton tows are also consistent with the change in trace metal values originating from primary calcite (Fig. 22).

Core-top Mg/Ca-temperature data for *G. bulloides* reveal a systematic offset with final chamber (*f*) consistently yielding cooler temperatures (Fig. 22). The final chamber temperatures are *ca.* 5.5 °C (STW core tops) and 3 °C (SAW core tops) colder than corresponding chamber *f*-2 estimates for *G. bulloides* (Fig. 22I) (Marr et al., 2011). This temperature offset is comparable to the difference between the bottom of the mixed layer and base of the thermocline in modern surface waters off eastern New Zealand (Garner, 1961; Heath, 1975; Locarnini et al., 2006).

Zn/Ca offsets between chambers *f*-2 and *f* in core tops and plankton tows are also consistent with increasing Zn concentrations with water depth, following a nutrient-like distribution similar to Cd (Fig. 22) (Boyle, 1981). This indicates for the first time that inter-chamber differences in *G. bulloides* Zn/Ca could be used to elucidate nutrient stratification in the upper water column. The down core Zn/Ca offset between chambers *f*-2 and *f* shows a similar pattern to the Mg/Ca with reduced nutrient stratification in the glacial and no stratification/complete mixing of the upper water column during the ACR. Nutrient stratification appears to re-establish initially in the upper surface waters from *ca.* 11.5 ka, prior to the stabilisation of the mixed layer/thermocline after *ca.* 10.5 ka (Nelson et al., 2000).

5.3. Glacial/Interglacial Changes in the SPG

Changes in the wind fields across glacial-interglacial cycles probably affected the ancestral SPG, judging by the dependency of its modern counterpart on the wind stress curl (e.g. Ridgway and Dunn, 2007; Tilburg et al., 2001). Here we evaluate the glacial/interglacial changes in the SPG from the presence of STW sourced from the gyre via the TF – the trans-Tasman component of the SPG (Fig. 20). We combine the evidence from our new geochemical proxies, with previously published paleoceanographic data (Fig. 26, 27).

5.3.1 Glaciation

During the glacial period, SAW dominated the MD97 2121 site as reflected by Mg/Ca *G. bulloides* temperatures, typically $<11^{\circ}\text{C}$ (Fig. 23, 27), and supported by a planktonic foraminiferal assemblage, which includes the polar species *Neogloboquadrina pachyderma* (Fig. 24) (Nelson et al., 2000; Weaver et al., 1998). The concomitant low Zn/Ca and Mn/Ca also supports the presence of SAW north of the Chatham Rise (Fig. 22). This is the result of a strengthened branch of the ACC forced SAW northwards through Mernoo Saddle thus circumventing the STF that is constrained by Chatham Rise (Sikes et al., 2002; Sutton and Roemmich, 2001) (Fig. 20).

Between 25 and 15ka, Mg/Ca and Zn/Ca data from different chambers (chamber *f-2* minus *f*) of *G. bulloides* suggest reduced thermal (offset of $<3^{\circ}\text{C}$) and nutrient stratification of the upper ocean (Fig. 23, 27). This coincides with a reduction in the offset between *G. bulloides* and *G. inflata* $\delta^{18}\text{O}$ data as well (Carter et al., 2008; Fig. 23) and indicates that the upper water column was well mixed by the strong westerly winds during the glacial (Shulmeister et al., 2004). The variance in the Mg/Ca, Zn/Ca and Mn/Ca data from individual samples was also at its lowest during the glacial, suggesting that there may have been fewer or muted short term fluctuations such as that caused by ENSO activity (also modulated by the Southern Annular Mode) which affects storminess and ocean temperatures in the Hawke Bay region (Gomez et al., 2012). However, this lower glacial Mg/Ca variance may also reflect a more limited calcification depth range for *G. bulloides* owing to diminished upper ocean thermal stratification than during the interglacial period.

Figure 26. Compilation of regional water mass proxy data with global deglaciation trends. **Temperature** proxy data includes (A) regional high resolution alkenone data for site MD97 2121 (Pahnke and Sachs, 2006), for site MD03 2611, South Australia (Calvo et al., 2007), and site MD97 2120 –off the South Island, New Zealand (Pahnke et al., 2003); (B) Mg/Ca temperature data *G. ruber* (red), *G. bulloides* (blue) - this study, MD97 2121 and for site MD97 2120: *G. bulloides* (green) (Mg/Ca data from Pahnke et al., 2003 converted to temperature using calibration from Marr et al., 2011). **Water mass** proxies (C) Zn/Ca *G. bulloides* (blue), *G. ruber* (red) – this study, (D) $\delta^{13}\text{C}$ *G. bulloides* (blue), *G. ruber* (red) (Carter et al., 2008). All geochemical data are presented using a three point moving mean for trend comparison, except for MD97 2120 Mg/Ca and MD03 2611 alkenone data which are at a lower temporal resolution and therefore individual data points have been joined. The Antarctic Cold Reversal (ACR) is indicated by the blue shaded bar.

Warmer Mg/Ca SSTs at *ca.* 22-18 ka, accompanied by elevated Zn/Ca, lightened planktic $\delta^{18}\text{O}$ and warmer water foraminiferal assemblages point to an incursion of STW that is also present at ODP 1123, downstream of MD97 2121, (Fig. 23, 26) (Crundwell et al., 2008). No clear temperature change is recorded in Antarctica at this time period (Fig. 23) (Jouzel et al., 2007), but there is a coeval warming in the Greenland (NGRIP et al., 2004). We suggest that the perturbation may reflect Northern Hemispheric forcing of the equatorial region and mid-latitude winds that spin up the SPG under increased wind stress curl (cf. Denton et al., 2010; Roemmich, 2007).

5.3.2 17-14.5 ka or Mystery Interval, early deglacial

The Mystery Interval (MI) – a period of rapid and often contradictory change in the Northern Hemisphere (Denton et al., 2006) coincides with rapid change in MD97 2121 (Fig. 26, 27). Millennial-scale MI events may be manifested in the Southern Hemisphere by the southward forcing of the Intertropical Convergence Zone (ITCZ) (Denton et al., 2010). In the Southern Hemisphere, the MI was accompanied by a poleward shift of zonal westerly winds, a general warming of the upper ocean (Barrows et al., 2007; Calvo et al., 2007), and increased Southern Ocean upwelling (Anderson et al., 2009).

In contrast, *G. bulloides* Mg/Ca-temperatures at MD97 2121 cooled to the point that they converged on those of subantarctic site MD97 2120 (Pahnke et al., 2003). *G. bulloides* Zn/Ca and Mn/Ca levels increased slightly and subpolar and polar planktic species reached a maximum (Fig. 24, 25). *G. bulloides* Mg/Ca cooling coupled with high nutrient levels (Zn/Ca) and high $\delta^{13}\text{C}$, appear to confirm regional upwelling of cooler nutrient-rich water similar to, but on a much smaller scale than, that previously associated with diatom productivity blooms in the Southern Ocean (Anderson et al., 2009).

However, the alkenone temperatures from MD97 2121 maintained a consistent warming trend of *ca.* 0.4 °C/ka (Pahnke and Sachs, 2006), similar to SSTs from the eastern equatorial Pacific Ocean (e.g. Koutavas et al., 2002; Rosenthal et al., 2003) and consistent with an incursion of STW resulting from a spin up of the SPG. The decoupling of *G. bulloides* Mg/Ca from alkenone and later *G. ruber* temperatures may reflect changes in the species seasonality/ecological niches across this interval (Leduc et al., 2010; Marr et al., in-prep).

		Thermocline	Nutricline	Dominant Forcing	Comment
	Holocene 11 ka - present	Generally well mixed at the surface with a well stratified subsurface.	Generally well stratified, and strongly depleted at the surface. Well mixed period from ca. 5.5-7 ka.	STW dominant with possible SAW pulse from ca. 5.5-7 ka.	Poleward migration of ocean fronts, with strengthened South Pacific Gyre (SPG) brings an increased inflow of STW. Perturbation towards cooler temperatures and increased SAW inflow from ca. 5.5-7 ka a time of increased storminess ¹ .
	ACR 14-17.5 ka	Limited stratification. Temperature cools by up to 4 °C.	Limited stratification.	SAW dominant, but possibly under increased winds periodic increased inflow of STW.	Interplay between SAW and STW reduces stratification and induces large shift in temperature and nutrient surface water profiles.
	MI 14.5-17.5 ka	<i>G. bulloides</i> temp. decrease by ca. 1°C/ka, but alkenones increase by ca. 0.5 °C/ka.	Limited stratification. Generally low trace metal values.	SAW dominant with reduced inflow of STW.	Increased spring upwelling of cooler, nutrient depleted waters, coupled with higher summer insolation produced contrasting paleo-thermometer trends.
	SPG Spin-up 22-18 ka	Limited stratification. Temperature ca. 2-4 °C warmer than LGM.	Limited stratification. Increase in Zn/Ca.	SAW dominant with STW pulse.	SPG spin-up possibly due to northern hemisphere forcing ² . No corresponding warming identified south of STF ³ or in Antarctic ice records ⁴ .
	LGM 25-21 ka	Limited stratification. Temperature ca. 6-7 °C cooler than present.	Limited stratification. With generally low trace metal concentrations relative to modern.	SAW dominant with reduced inflow of STW.	Mean sub-surface water temperatures ca. 6-7 °C lower than present. Diminished SPG. Increased windiness or ocean turbulence likely reduced surface water stratification.

Figure 27. Summary of surface water changes in the thermocline, nutricline and dominant forcing from 25 ka - present. MI= Mystery Interval, or period from 17.5-14.5 ka ¹Gomez et al. (2012), ²Stuiver (1997), ³Lorrey et al. (2012), ⁴EPICA et al. (2004).

5.3.3. ACR- late deglaciation

Large variability in foraminiferal Mg/Ca temperature and Zn/Ca from 14-11.5 ka is representative of a dynamically mixed upper ocean with competing SAW and STW during the ACR (Fig. 27). The ACR is bookended by peaks in *G. bulloides* and *G. ruber* abundance (Fig. 25) as water masses over MD97 2121 shifted dominance from SAW to STW. Large swings in foraminifera SSTs of *ca.* 7°C are similar to other Southern Hemisphere cores which switch from SAW to STW (Barrows et al., 2007; Calvo et al., 2007; Passlow et al., 1997; Sikes et al., 2009). These swings are accompanied here by marked changes in subsurface trace metal levels and an offset in planktic $\delta^{13}\text{C}$ (Fig. 23, 26). Thermal and nutrient surface water stratification during this time were also highly variable. There is a shift from moderate stratification during the early ACR, before stratification collapse during *ca.* 13.5-12.5 ka (Fig. 23) (Carter et al., 2008). This was followed by a decline in surface water productivity, before a gradual recovery and increase in thermal stratification by the late deglaciation (Fig. 23, 25). This condensed stratification during the ACR is likely the result of enhanced winds (Carter et al., 2008), either causing (i) increased physical mixing of the surface waters (Carter et al., 2008; Shulmeister et al., 2004) and/or (ii) regional upwelling along the nearby continental margin as seen in the modern ocean (e.g. Heath, 1972a; 1985).

This intense ACR variability is representative of the competing equatorial-southern forcing; the latter driving SAW northward through the Mernoo Saddle during the last glaciation and ACR, and the former forcing STW southward during the late deglaciation/early Holocene.

5.3.4 Holocene

At *ca.* 11.5 ka peak STW conditions were reached with a thermal maxima from *G. ruber* Mg/Ca SST. The TF shifted south, and likely found gaps in the Norfolk Ridge system that maximised the subtropical inflow to eastern New Zealand (Carter et al., 2008) (Fig. 27). Surface water thermal and nutrient stratification are strongest during the Holocene. Stratification is most prominent in the uppermost surface waters at 11.5 ka accompanied by a peak in biogenic siliceous and carbonate MAR/productivity (Fig. 25). For the remainder of the Holocene, upper ocean temperature stratification was consistent, as shown by the offset between *G. bulloides* chambers *f*-2 and *f* temperatures. However, isothermal conditions from

0 to *ca.* 75 m depth likely prevailed, as indicated by similarity between *G. bulloides* chamber *f*-2 and *G. ruber* temperatures (Fig. 23). Between 7 and 5.5 ka, *G. bulloides* Zn/Ca declines rapidly and merges with *G. ruber*. This convergence may represent a phase of reduced nutrient stratification in the mid-Holocene that is coeval with a period of high storm activity recorded in nearby onshore Lake Tutira (Gomez et al., 2012). A 50 % increase in the variance of the trace element/Ca data during the Holocene may suggest increased decadal or ENSO activity (Koutavas et al., 2006; Koutavas et al., 2002).

6.0 Conclusions

In situ measurements on modern foraminifera from a wide range of environmental settings indicate that Zn/Ca, Mn/Ca and Mg/Ca can act as proxies for the water masses and structure of the upper ocean. We show that Zn/Ca and Mn/Ca measurements in *G. bulloides* and *G. ruber* have the potential to trace SAW and STW surface water masses. Offsets between the Mg/Ca and Zn/Ca from chamber *f* and *f*-2 data may also function as a proxy for thermal and nutrient stratification of the upper ocean.

By applying these new proxies to down-core data from MD97 2121 we show that the ocean off eastern New Zealand underwent significant changes over the past 25 kyr. At the last glacial maximum, mean SSTs were *ca.* 6-7 °C colder than present, foraminiferal Mn/Ca and Zn/Ca were low, and ocean thermal and nutrient stratification were minimal. Such conditions reflect regional dominance of SAW under a strengthened ACC, and a reduced STW inflow associated with a weakened SPG. Warm SST perturbations from *ca.* 22-18 ka were likely due to early deglacial equatorial forcing that increased the STW inflow, raising Zn/Ca levels briefly. From 17.5-14.5ka an anomalous period occurred that coincides with the Northern Hemisphere 'Mystery Interval'. During this period *G. bulloides* SSTs cooled by *ca.* 1°C/ka, while alkenone temperatures indicate continued warming. Upper ocean thermal and nutrient stratification collapsed during the ACR when large swings in temperature and nutrient concentrations resulted from the interplay between polar forced SAW and equatorial derived STW. After the ACR, the continued poleward migration of strong zonal westerly winds strengthened the SPG and its STW inflow to eastern New Zealand. With this southward shift of strong winds, the upper ocean at core site MD97 2121 was dominated by generally well stratified STW from *ca.* 10ka to present.

Auxiliary information

AI 1.0. Table of Mg, Al, Mn, Zn, Sr and Ba/Ca ratios and sample means

C3-AI. Table 1. Table of Mg, Al, Mn, Zn, Sr and Ba/Ca ratios and sample mean, 95% confidence interval, of *G. bulloides* (chamber *f*-2 and *f*) and *G. ruber* (chamber *f*-2) from MD97 2121, with sample depth and age.

<i>G. bulloides</i> - chamber f-2	Age	Sediment sample depth	Mg/Ca	<i>Cl</i>	Al/Ca	<i>Cl</i>	Mn/Ca	<i>Cl</i>	Zn/Ca	<i>Cl</i>	Sr/Ca	<i>Cl</i>	Ba/Ca	<i>Cl</i>
(n)	(kyr)	(m)	(mmol/mol)		(μmol/mol)		(μmol/mol)		(μmol/mol)		(mmol/mol)		(μmol/mol)	
13	0.0	0.00-0.01	3.74	0.8	322.7	190.0	102.8	50.2	55.6	22.4	1.41	0.03	3.3	0.9
18	0.0	0.01-0.02	3.24	0.6	100.8	43.6	111.1	33.6	27.4	8.4	1.43	0.06	6.5	1.6
16	0.1	0.08-0.09	3.38	0.8	235.8	92.2	141.3	38.4	18.9	4.9	1.37	0.03	8.1	2.4
12	0.4	0.20-0.21	3.25	0.9	49.7	26.1	148.2	46.7	22.1	6.3	1.73	0.24	4.8	1.2
32	1.0	0.38-0.39	2.99	0.4	124.8	40.0	180.6	28.6	24.4	4.7	1.37	0.02	5.6	1.5
23	1.8	0.56-0.57	3.80	0.7	247.3	106.5	215.4	30.8	19.8	5.9	1.33	0.03		
16	2.6	0.80-0.81	3.52	0.7	125.0	50.1	242.6	43.3	19.7	8.0	1.36	0.02	5.1	1.6
12	2.9	0.90-0.91	3.28	0.8	72.2	40.4	276.5	56.2	66.3	35.5	1.39	0.05	4.1	2.0
13	4.3	1.40-1.41	3.62	1.2	132.6	63.5	286.4	80.1	20.6	11.3	1.39	0.05	6.0	1.6
21	4.8	1.60-1.61	4.01	0.9	146.0	50.4	328.0	49.3	27.8	10.8	1.42	0.04	6.6	1.1
17	5.3	1.80-1.81	3.25	0.7	168.2	132.0	241.2	102.3	22.3	10.5	1.41	0.09		
10	5.6	1.90-1.91	2.56	0.4	68.4	32.7	226.2	55.5	14.7	9.7	1.34	0.05	4.1	1.1
19	6.0	2.10-2.11	2.87	0.5	93.2	39.1	204.2	46.6			1.37	0.04	7.3	2.5
17	6.1	2.20-2.21	3.41	0.8	103.3	62.8	208.1	39.0	10.7	5.3	1.37	0.03	5.7	1.7
23	6.3	2.30-2.31	3.61	0.7	158.5	54.2	176.5	33.6	21.4	6.1	1.38	0.03	4.8	1.0
12	6.5	2.40-2.41	3.02	0.9	107.7	58.5	194.1	68.2	24.3	14.8	1.40	0.10	5.0	1.6
12	6.6	2.50-2.51	2.46	0.4	34.2	16.9	172.6	71.1	16.4	9.1	1.35	0.03	6.5	2.9
19	6.8	2.60-2.61	3.85	1.0	107.8	63.0	213.2	35.4	15.9	4.4	1.33	0.02	4.8	1.7
20	7.1	2.72-2.73	3.43	0.7	179.6	54.3	211.6	46.7	21.9	6.0	1.37	0.04	6.0	1.1
12	7.9	2.90-2.91	3.75	1.1	158.5	75.0	170.2	56.4	25.5	11.1	1.35	0.06	5.2	2.2
20	9.0	3.20-3.21	2.72	0.6	300.0	113.7	206.9	55.4	22.2	11.1	1.43	0.07	6.2	1.8
16	9.3	3.30-3.31	3.41	0.9	344.0	131.8	285.9	77.5			1.37	0.04	4.2	1.4
16	10.0	3.60-3.61	3.27	0.8	247.1	160.1	262.2	55.1	23.4	16.2	1.44	0.04	3.4	0.8
10	10.2	3.70-3.71	2.41	0.4	169.8	74.8	250.4	86.6	12.0	7.3	1.34	0.03	3.3	0.9
16	10.5	3.80-3.81	2.96	0.7	180.8	139.8	314.1	73.0	28.0	20.7	1.36	0.06	6.6	2.8
16	10.7	3.90-3.91	2.66	0.4	128.4	69.9	237.3	66.7			1.36	0.03	3.4	1.4
14	11.4	4.10-4.11	2.46	0.4	749.7	322.5	233.8	49.3	23.5	5.9	1.36	0.02	6.0	1.9
18	11.9	4.16-4.17	2.52	0.4	776.9	373.9	251.9	49.8	11.4	3.4	1.39	0.05		
12	12.2	4.20-4.21	3.15	0.8	229.2	92.9	303.1	121.1			1.37	0.02	3.4	1.0
19	12.4	4.30-4.31	2.39	0.3	448.3	155.1	262.7	45.8	20.2	5.2	1.41	0.04	4.3	1.5
10	12.5	4.36-4.37	2.63	0.6	194.9	85.4	298.0	91.5	20.6	15.0	1.31	0.04	4.2	0.7
11	12.6	4.40-4.41	2.18	0.6	159.1	96.0	222.6	74.3	9.8	5.8	1.34	0.04	3.6	1.9
15	12.6	4.44-4.45	3.15	0.9	209.2	85.1	301.0	70.2	24.7	13.4	1.39	0.03	4.1	1.6
12	12.8	4.50-4.51	1.98	0.3	154.7	93.0	224.5	80.0	29.7	21.2	1.32	0.05	3.1	0.7
15	12.8	4.54-4.55	1.75	0.3	390.5	223.0	192.4	58.5	8.3	8.7	1.31	0.05	4.5	1.1
15	12.9	4.56-4.57	2.16	0.4	97.0	31.6	197.7	56.4	6.4	2.3	1.39	0.02	2.7	0.7
18	12.9	4.60-4.61	2.54	0.5	106.7	49.7	253.0	97.9	20.4	11.7	1.38	0.04	3.1	0.6
15	13.1	4.70-4.71	2.57	0.5	215.0	102.9	253.6	55.8			1.38	0.03	4.9	2.0
15	13.3	4.80-4.81	2.62	0.9	198.1	93.9	211.9	88.2	23.6	12.4	1.41	0.05	4.9	1.5
14	13.4	4.90-4.91	2.12	0.4	359.7	176.8	196.7	63.0	10.7	4.9	1.32	0.04	4.4	1.9
10	13.6	5.04-5.05	2.10	0.5	157.1	94.6	148.0	62.6	7.2	6.3	1.36	0.04	2.6	0.7
13	13.8	5.08-5.09	1.33	0.2	83.9	57.0	44.6	23.3	1.1	2.9	1.33	0.05	1.5	0.3
10	13.8	5.12-5.13	1.56	0.5	97.3	31.0	119.3	61.9	9.8	12.5	1.37	0.07	2.3	0.6
18	14.1	5.20-5.21	2.50	0.5	320.2	149.6	213.5	90.7	10.7	6.6	1.36	0.02	3.9	1.4
21	14.3	5.26-5.27	1.39	0.2	101.6	40.1	83.1	38.8	3.6	1.3	1.34	0.02	1.6	0.7
15	14.5	5.30-5.31	2.44	0.5	264.4	97.1	171.2	60.8	13.3	7.5	1.36	0.03	3.6	1.1
19	14.6	5.35-5.36	1.68	0.4	201.9	109.8	110.8	50.3	5.6	6.6	1.41	0.03	3.3	0.8
16	14.8	5.40-5.41	2.30	0.4	306.3	114.4	182.2	57.6			1.36	0.03	3.5	1.5
21	15.1	5.50-5.51	1.58	0.3	129.4	87.9	103.7	54.3	5.9	3.0	1.37	0.03	2.2	0.7
15	15.5	5.60-5.61	1.76	0.6	129.3	68.6	141.5	55.3	8.4	4.2	1.33	0.04	2.9	1.1
12	15.8	5.68-5.69	1.91	0.3	312.1	174.4	138.7	46.9	9.5	4.2	1.41	0.10	4.1	1.4
17	16.0	5.76-5.77	2.19	0.8	198.8	93.8	113.7	59.7	8.1	5.0	1.35	0.03	3.0	1.0
18	16.5	5.90-5.91	1.96	0.4	264.6	143.8	145.1	50.2	10.0	4.7	1.41	0.03	4.1	1.4
16	17.2	6.10-6.11	1.94	0.5	185.9	90.2	102.7	43.9	9.1	4.1	1.36	0.04	1.7	0.5
12	18.1	6.40-6.41	2.03	0.6	73.5	46.3	100.5	63.3	6.7	4.8	1.33	0.04	2.7	0.8
16	18.8	6.70-6.71	2.67	0.6	127.7	51.7	151.0	56.8	13.4	8.7	1.36	0.04	3.6	0.8
14	19.0	6.78-6.79	1.75	0.4	173.3	99.6	69.1	36.5	9.9	7.0	1.42	0.04	4.3	1.3
21	19.3	6.90-6.91	2.57	0.8	140.2	75.7	89.4	38.2	12.1	6.6	1.38	0.03	2.6	1.0
21	19.5	7.00-7.01	2.64	0.5	88.9	33.1	123.0	47.5	11.4	5.6	1.39	0.03	2.4	0.9
15	20.0	7.20-7.21	2.31	0.6	151.0	54.0	89.3	43.5	11.5	6.1	1.39	0.04	4.0	1.0
21	20.2	7.30-7.30	1.90	0.3	179.9	94.8	48.6	27.2	9.9	5.7	1.37	0.03	2.2	0.8
14	20.7	7.50-7.50	2.23	0.7	63.8	24.7	82.9	51.2	11.9	12.7	1.28	0.04	3.0	1.1
15	21.2	7.70-7.71	1.61	0.4	126.0	58.2	32.2	18.5	7.6	4.1	1.36	0.03	2.0	0.7
13	21.6	7.88-7.89	1.86	0.6	134.9	68.8	33.4	24.0	6.4	4.2	1.39	0.03	1.7	0.5
12	21.7	7.90-7.91	1.50	0.2	187.4	102.4	19.1	18.9	3.7	3.4	1.42	0.04	2.0	0.7
16	21.7	8.01-8.02	2.31	0.8	265.7	138.2	40.8	15.4	7.9	4.0	1.39	0.04	2.9	1.3
15	22.1	8.10-8.11	1.80	0.2	93.5	45.5	38.1	19.6	6.5	4.4	1.35	0.03	1.8	0.6
24	22.4	8.22-8.23	1.37	0.2	93.0	47.7	26.6	8.3	4.9	2.6	1.35	0.02	1.8	0.5
19	23.1	8.50-8.51	2.73	1.0	105.9	52.6	80.2	32.0	17.6	10.6	1.36	0.03	3.2	0.8
19	23.6	8.70-8.71	2.38	0.5	150.8	70.7	68.9	20.2			1.39	0.03	3.6	1.2
18	23.8	8.80-8.81	1.78	0.3	115.9	61.8	49.8	13.5	14.9	6.8	1.36	0.02	2.3	0.6
21	24.3	9.00-9.01	1.73	0.2	120.1	49.6	48.9	15.0	11.5	5.8	1.34	0.03	2.6	0.6
17	24.5	9.10-9.11	1.91	0.3	88.3	33.6	67.7	18.9	9.2	4.4	1.36	0.03	3.1	1.0
10	25.0	9.30-9.31	2.10	0.6	63.6	32.1	48.0	36.2	9.7	6.9	1.42	0.05	1.8	0.5

<i>G. bulloides</i> - chamber <i>f</i>	Age	Sediment sample depth	Mg/Ca	<i>Cl</i>	Al/Ca	<i>Cl</i>	Mn/Ca	<i>Cl</i>	Zn/Ca	<i>Cl</i>	Sr/Ca	<i>Cl</i>	Ba/Ca	<i>Cl</i>
(n)	(kyr)	(m)	(mmol/mol)		(μmol/mol)		(μmol/mol)		(μmol/mol)		(mmol/mol)		(μmol/mol)	
13	0.0	0.00-0.01	3.74	0.8	322.7	233.0	102.8	31.9	55.6	23.4	1.41	0.03	3.3	0.9
24	0.0	0.01-0.02	2.58	0.4	46.0	20.5	125.7	18.6	38.4	8.4	1.41	0.05	6.3	1.2
24	0.1	0.08-0.09	2.73	0.5	129.5	59.9	140.6	21.4	26.7	5.7	1.37	0.04	7.4	1.3
16	0.4	0.20-0.21	2.81	0.9	32.0	18.2	152.2	21.2	19.1	4.3	1.61	0.14	5.0	1.0
46	1.0	0.38-0.39	2.39	0.3	86.1	27.7	167.3	15.4	26.8	3.9	1.36	0.02	5.6	1.2
25	1.8	0.56-0.57	3.02	0.7	251.7	138.8	196.2	25.6	29.5	15.1	1.34	0.02	10.0	2.2
21	2.6	0.80-0.81	2.59	0.4	73.1	42.3	205.6	29.3	18.1	5.6	1.35	0.02	4.7	1.2
15	2.9	0.90-0.91	2.76	0.6	55.9	39.3	232.5	39.9	87.4	35.7	1.39	0.02	3.4	1.3
9	3.6	1.10-1.11	2.17	0.3	196.9	117.5	177.8	36.5	28.6	13.6	1.39	0.06	6.3	2.6
16	4.3	1.40-1.41	2.89	0.7	109.7	53.6	239.3	54.7	23.7	11.6	1.39	0.04	5.6	1.9
23	4.8	1.60-1.61	3.20	0.6	117.7	61.5	259.0	44.6	26.9	10.5	1.41	0.02	5.3	1.0
27	5.3	1.80-1.81	2.46	0.4	88.3	44.8	194.3	36.9	24.0	12.3	1.39	0.06	7.6	3.4
13	5.6	1.90-1.91	2.20	0.4	27.1	18.4	216.0	34.8	21.2	8.6	1.36	0.04	5.6	1.5
22	6.0	2.10-2.11	2.40	0.3	84.7	35.6	164.2	17.3	55.6	16.3	1.37	0.03	4.6	0.7
19	6.1	2.20-2.21	2.69	0.6	19.8	12.3	193.5	30.7	12.8	4.4	1.36	0.03	4.5	1.3
27	6.3	2.30-2.31	2.54	0.4	98.3	38.5	177.2	30.2	28.5	6.7	1.36	0.03	4.6	0.7
16	6.5	2.40-2.41	2.82	0.7	67.2	56.9	170.0	29.1	19.4	9.4	1.38	0.03	4.1	1.0
14	6.6	2.50-2.51	2.47	0.4	33.5	23.0	187.7	77.3	13.2	6.6	1.38	0.05	5.7	1.8
21	6.8	2.60-2.61	2.57	0.8	80.8	55.2	179.7	34.9	14.5	5.5	1.36	0.03	3.0	1.1
14	7.0	2.69-2.70	2.18	0.4	159.0	42.8	218.3	43.9	47.4	17.8	1.78	0.17	3.8	0.9
21	7.1	2.72-2.73	2.48	0.4	132.8	48.1	198.4	34.4	24.9	6.5	1.34	0.03	5.7	1.5
15	7.9	2.90-2.91	3.05	0.9	124.5	67.9	168.3	24.4	38.6	18.5	1.34	0.06	4.7	1.9
25	8.4	3.20-3.21	2.31	0.4	147.8	88.7	196.0	30.7	35.0	20.2	1.47	0.05	4.9	1.2
21	9.0	3.30-3.31	2.35	0.4	61.5	25.4	244.3	48.3	30.2	15.1	1.39	0.04	3.8	1.5
20	9.3	3.60-3.61	2.76	0.6	131.0	71.1	220.2	37.6	31.9	17.3	1.44	0.04	2.9	0.7
14	10.0	3.70-3.71	1.89	0.5	77.7	58.5	204.3	49.4	14.7	7.6	1.36	0.03	2.2	0.5
22	10.2	3.80-3.81	2.40	0.5	81.6	42.7	274.7	40.2	31.2	16.4	1.38	0.03	4.5	1.1
19	10.5	3.90-3.91	1.87	0.5	80.1	46.4	201.5	62.7	26.9	23.7	1.39	0.02	2.0	0.5
22	10.7	4.00-4.01	2.62	0.5	149.4	71.0	301.4	52.6	22.6	5.8	1.38	0.04	4.5	1.3
23	11.4	4.10-4.11	2.35	0.4	343.8	148.9	230.6	31.7	19.7	4.2	1.38	0.03	5.2	1.2
16	11.9	4.16-4.17	1.97	0.2	785.0	480.1	223.0	54.9	9.2	2.4	1.41	0.04	6.6	1.4
16	12.2	4.20-4.21	2.40	0.4	69.0	34.9	260.1	50.2	25.1	8.5	1.40	0.03	3.7	1.6
17	12.4	4.30-4.31	1.78	0.3	472.2	273.2	247.6	33.4	20.7	4.3	1.39	0.04	3.7	1.0
12	12.5	4.36-4.37	1.96	0.6	112.1	66.4	206.2	58.8	25.7	12.9	1.36	0.04	4.1	0.7
14	12.6	4.40-4.41	1.89	0.4	177.7	76.5	243.4	52.9	16.8	6.0	1.33	0.04	4.9	1.6
14	12.6	4.44-4.45	2.55	0.9	115.5	104.0	271.3	33.1	17.7	8.8	1.42	0.03	4.1	1.3
17	12.8	4.50-4.51	1.74	0.2	97.4	57.5	239.7	40.7	19.1	7.9	1.33	0.04	3.7	1.0
21	12.8	4.54-4.55	1.44	0.2	364.7	179.4	250.9	41.0	11.6	5.6	1.31	0.04	4.1	1.3
12	12.9	4.56-4.57	1.74	0.6	77.9	43.5	207.6	61.1	7.9	3.0	1.39	0.03	2.2	0.5
21	12.9	4.60-4.61	2.01	0.3	35.8	21.8	207.8	47.3	24.8	13.6	1.39	0.04	2.6	0.8
18	13.1	4.70-4.71	2.38	0.4	237.5	124.3	212.1	47.4	45.6	21.7	1.40	0.04	4.7	1.4
18	13.3	4.80-4.81	2.45	0.6	173.6	71.9	233.5	46.1	40.2	18.2	1.41	0.03	5.4	1.2
20	13.4	4.90-4.91	1.83	0.3	156.6	60.3	224.8	47.2	20.2	8.8	1.37	0.03	4.9	1.4
19	13.6	5.04-5.05	1.58	0.2	82.8	50.7	174.9	33.8	17.3	10.8	1.36	0.03	3.1	0.9
17	13.8	5.08-5.09	1.40	0.1	98.2	39.7	121.0	36.7	3.7	1.6	1.32	0.05	1.9	0.4
12	13.8	5.12-5.13	1.36	0.2	86.5	41.6	149.6	52.4	16.3	9.7	1.39	0.04	2.8	0.6
19	14.1	5.20-5.21	1.96	0.4	166.7	77.7	193.8	52.6	13.3	6.4	1.39	0.03	3.3	1.0
20	14.3	5.26-5.27	1.42	0.2	89.2	38.4	139.1	51.8	4.9	2.1	1.39	0.03	2.5	0.8
23	14.5	5.30-5.31	1.77	0.3	95.8	55.5	169.1	35.7	16.8	7.0	1.38	0.03	3.3	1.4
19	14.6	5.35-5.36	1.50	0.2	209.6	89.6	133.4	33.5	7.8	3.5	1.42	0.03	4.9	1.2
21	14.8	5.40-5.41	1.98	0.3	270.0	84.6	180.5	45.8	40.5	18.2	1.38	0.03	3.2	0.9
25	15.1	5.50-5.51	1.74	0.3	147.8	59.1	163.3	41.9	14.0	6.1	1.39	0.04	3.5	0.8
18	15.5	5.60-5.61	1.63	0.3	130.7	66.4	138.0	35.6	10.2	3.7	1.34	0.03	2.5	0.5
19	15.8	5.68-5.69	1.71	0.2	302.7	128.2	153.6	27.5	17.8	6.6	1.39	0.05	4.1	0.9
26	16.0	5.76-5.77	1.99	0.4	179.5	66.4	138.3	30.3	10.5	3.4	1.37	0.03	3.9	0.8
24	16.5	5.90-5.91	1.81	0.3	168.0	75.4	143.7	29.3	8.3	3.0	1.41	0.02	3.2	0.6
22	17.2	6.10-6.11	1.87	0.3	53.0	28.0	122.0	28.6	12.7	5.8	1.38	0.04	1.7	0.4
17	18.1	6.40-6.41	1.86	0.4	65.6	39.8	92.6	39.6	8.2	4.1	1.33	0.04	2.8	0.6
10	18.3	6.50-6.51	2.47	0.6	22.5	13.2	108.6	41.4	17.8	8.0	1.39	0.04	2.0	0.7
22	18.6	6.60-6.61	2.80	0.6	61.6	42.2	137.5	33.2	13.1	3.7	1.37	0.04	2.5	1.0
22	18.8	6.70-6.71	2.19	0.3	101.1	53.2	117.6	31.0	16.0	7.9	1.39	0.04	3.4	0.7
11	19.0	6.78-6.79	1.88	0.5	132.5	86.3	79.0	28.5	14.4	8.6	1.38	0.04	3.7	0.9
19	19.3	6.90-6.91	2.24	0.7	110.3	80.5	80.3	30.4	27.6	18.1	1.41	0.04	3.3	1.4
27	19.5	7.00-7.01	2.37	0.4	71.1	25.3	106.1	24.1	14.3	3.9	1.41	0.03	2.4	1.2
14	20.0	7.20-7.21	1.95	0.5	109.4	41.6	78.8	26.7	20.6	9.0	1.40	0.05	2.9	0.6
26	20.2	7.30-7.30	2.18	0.5	176.0	63.7	56.5	18.2	12.4	5.2	1.38	0.04	2.7	0.4
13	20.7	7.50-7.50	2.09	0.5	99.2	59.9	93.8	45.7	11.3	6.3	1.37	0.05	2.9	0.8
17	21.0	7.60-7.61	2.31	0.5	76.1	36.9	67.5	22.5	28.1	14.1	1.39	0.03	2.7	0.8
20	21.2	7.70-7.71	1.81	0.2	141.3	62.1	60.1	15.0	32.5	10.3	1.42	0.03	3.3	1.1
14	21.6	7.88-7.89	1.67	0.5	120.4	64.9	51.2	29.1	12.2	6.6	1.40	0.05	2.4	0.5
15	21.7	7.90-7.91	1.55	0.2	255.0	112.2	36.5	15.3	5.5	2.6	1.43	0.04	3.1	0.9
19	21.7	8.01-8.02	1.93	0.4	129.8	84.9	45.5	14.7	8.5	3.2	1.43	0.04	3.7	0.9
18	22.1	8.10-8.11	1.65	0.2	56.6	36.1	43.3	10.8	10.3	4.6	1.36	0.04	1.8	0.5
27	22.4	8.22-8.23	1.53	0.2	97.5	44.0	41.5	11.0	6.9	2.5	1.37	0.03	2.4	0.6
22	23.1	8.50-8.51	2.12	0.5	107.9	45.0	78.4	20.3	19.5	11.0	1.36	0.03	3.2	0.7
21	23.6	8.70-8.71	2.53	0.4	107.5	37.5	90.9	16.9	30.1	11.6	1.39	0.03	4.3	1.2
16	23.8	8.80-8.81	2.01	0.3	75.2	42.0	76.8	10.8	23.5	6.9	1.37	0.03	3.7	0.6
21	24.3	9.00-9.01	1.88	0.2	72.1	28.7	69.2	18.4	12.9	6.2	1.35	0.03	3.1	0.7
23	24.5	9.10-9.11	2.16	0.2	65.1	29.5	89.2	14.5	11.9	3.3	1.37	0.03	4.0	0.7
12	25.0	9.30-9.31	2.16	0.6	33.8	22.3	50.6	15.2	12.8	7.7	1.40	0.04	2.1	0.3

<i>G. ruber</i> - chamber f-1	Age	Sediment sample depth	Mg/Ca	<i>Cl</i>	Al/Ca	<i>Cl</i>	Mn/Ca	<i>Cl</i>	Zn/Ca	<i>Cl</i>	Sr/Ca	<i>Cl</i>	Ba/Ca	<i>Cl</i>
(n)	(kyr)	(m)	(mmol/mol)		(μmol/mol)		(μmol/mol)		(μmol/mol)		(mmol/mol)		(μmol/mol)	
7	1.0	0.38-0.39	2.42	0.4	227.8	171.2	254.9	113.7	21.6	14.2	1.43	0.08	8.9	1.8
15	1.8	0.56-0.57	2.63	0.3	213.2	91.0	194.8	43.6	18.3	8.3	1.39	0.04	5.6	1.4
9	2.6	0.80-0.81	3.33	0.7	200.0	106.2	205.2	52.5	17.3	9.5	1.35	0.02	3.8	1.6
6	4.3	1.40-1.41	3.04	1.0	44.1	92.8	269.7	102.8	7.1	3.3	1.44	0.06	5.6	1.8
14	5.3	1.80-1.81	3.01	0.5	147.0	165.3	214.5	92.6	12.7	8.3	1.42	0.06	6.6	2.4
6	5.6	1.90-1.91	3.07	0.5	90.6	129.3	298.5	118.5	29.1	30.7	1.42	0.08	8.3	2.4
15	6.1	2.10-2.11	2.65	0.3	156.6	117.2	263.8	49.0	23.0	13.4	1.41	0.03	4.7	1.2
11	6.4	2.20-2.21	3.29	0.4	134.0	101.3	256.1	59.5	9.8	6.1	1.43	0.06	5.3	1.7
8	6.9	2.40-2.41	2.36	0.7	139.6	129.7	170.9	87.1	13.9	11.9	1.41	0.06	5.5	3.8
14	7.1	2.50-2.51	2.74	0.6	144.2	64.7	184.1	64.0	10.2	7.5	1.39	0.04	4.5	1.3
11	7.4	2.60-2.61	2.69	0.3	114.5	100.2	229.4	89.9	17.2	17.0	1.39	0.04	4.9	1.7
8	7.6	2.69-2.70	2.47	0.2	120.4	134.0	260.9	75.2	12.1	7.1	1.34	0.06	2.9	1.5
9	7.9	2.90-2.91	2.58	0.3	109.6	81.0	151.1	65.9	14.6	13.4	1.47	0.06	2.9	0.9
10	8.4	3.00-3.01	2.52	0.6	235.2	156.1	181.1	75.5	14.7	17.5	1.39	0.04	3.8	1.6
7	9.0	3.30-3.31	2.96	0.8	275.7	492.7	275.5	83.2	35.8	74.1	1.38	0.10	5.4	0.8
15	9.3	3.60-3.61	2.51	0.5	375.5	234.1	243.7	34.7	7.9	8.7	1.43	0.05	2.4	0.5
7	10.0	3.70-3.71	3.01	0.5	29.5	21.0	350.9	105.8	10.9	8.3	1.37	0.03	3.2	0.8
13	10.2	3.80-3.81	2.76	0.6	128.2	91.1	295.5	126.1	19.7	20.0	1.42	0.04	3.6	1.3
5	10.5	3.90-3.91	3.05	0.5	91.0	53.2	409.1	184.9	4.7	2.7	1.35	0.03	4.2	1.0
7	10.7	4.00-4.01	2.89	0.5	129.8	146.5	358.7	145.4	16.4	23.2	1.40	0.09	3.5	1.0
5	11.5	4.20-4.21	2.50	1.2	347.9	319.1	159.9	183.3	35.8	42.4	1.45	0.08	5.8	5.3
11	11.8	4.44-4.45			73.0	47.7	62.1	29.1	4.5	2.1	1.43	0.05	1.3	0.2
8	12.8	4.50-4.51	3.25	0.3	255.3	171.3	390.3	201.0	84.2	133.5	1.37	0.04	5.7	2.3
6	13.1	4.70-4.71	1.80	0.3	323.8	417.8	105.7	66.2	15.9	18.8	1.40	0.05	2.9	1.6
5	13.6	5.04-5.05	2.20	1.1	83.2	125.7	195.9	108.0	5.7	8.0	1.38	0.02	3.8	0.8
10	14.1	5.20-5.21	2.57	0.7	295.5	295.4	209.9	171.8	13.8	17.4	1.24	0.04	3.5	2.5
7	14.5	5.30-5.31	2.19	0.5	95.3	76.0	77.3	33.9	5.8	3.6	1.37	0.07	2.1	0.9
15	14.8	5.40-5.41	2.29	0.5	174.4	162.8	143.9	70.5	25.4	23.3	1.43	0.05	2.2	0.9
11	15.5	5.60-5.61	1.87	0.3	154.9	68.3	105.0	45.4	8.4	5.1	1.42	0.03	2.6	1.2
4	15.8	5.68-5.69	1.75	0.4	93.7	67.3	72.3	38.3	3.7	2.3	1.45	0.09	1.5	0.8
4	16.0	5.76-5.77	1.98	0.8	134.2	260.1	115.1	123.8	9.1	12.7	1.37	0.14	3.4	2.2
4	19.0	6.78-6.79	2.65	1.5	157.6	291.5	123.3	181.4	6.6	3.8	1.36	0.15	4.4	5.6
5	19.5	7.00-7.01	2.62	1.1	127.7	230.9	172.9	147.1	12.2	14.6	1.39	0.04	5.3	5.5
5	22.1	8.10-8.11	1.73	0.2	51.6	38.2	27.5	27.7	9.6	7.8	1.44	0.09	1.1	0.5
4	22.4	8.22-8.23	2.08	1.4	165.6	206.7	58.1	97.5	7.1	9.9	1.4	0.11	2.6	3.3

AI 2.0. Trace metal concentrations in the surface ocean and foraminiferal test calcite

AI 2.1. Surface ocean trace metal concentrations

Differences in the modern water mass concentrations of Zn and Mn have been observed across the modern STF. Mean dissolved Zn levels of 0.22 nmol/kg in STW are higher than a mean of 0.04 nmol/kg in SAW (M. Ellwood pers. comm., 2011). Subtropical surface water Mn concentrations from the Southwest Pacific Ocean are *ca.* 1.2 nmol/kg while those from the subantarctic waters generally range from 0.3 to 0.7 nmol/kg (Klinkhammer and Bender, 1980). Dissolved Ba concentrations, however, are relatively homogenous with as little as 10-20% difference between SAW and STW off southern Australia (Jacquet et al., 2004). The closest river record of Mn, Zn or Ba levels to the core sites of this study is from the Waihou River, located 300 km west of Hawke Bay (Fig. 20). The river drains a greywacke/volcanic catchment similar to that of rivers discharging off Hawke Bay near MD97 2121. The Waihou River has dissolved Mn levels of 1.4-8.8 µg/kg and Zn of <0.1 µg/kg (Webster, 1995), lower than the global averages of 34 µg/l and 0.6 µg/l, respectively (Gaillardet et al., 2003). No dissolved Ba concentrations are available for the North Island. Rivers draining the lower eastern North Island annually carry *ca.* 83 Mt of suspended load to the continental shelf (Hicks and Shankar, 2003). Modern core-top and plankton-tow sites in STW or SAW, which are adjacent to high-input rivers (P69, S938, U2309, Q220) are then compared to sites that are more distal from major fluvial point sources (P71, S793, F111, D178, B32, R623 or ODP1123).

AI 2.2 Trace metal values in foraminifera

Zinc follows a nutrient-like profile in the water column similar to that of cadmium and phosphate. Zinc is depleted in surface waters, becoming increasingly replete with depth (Ellwood, 2004; Frew and Hunter, 1995; Hunter and Boyd, 1999; Morel et al., 1991). Variable concentrations of Zn/Ca in foraminifera may therefore offer insights into nutrient depletion/repletion in surface waters. Diatom blooms may potentially affect Zn/Ca concentrations, as Zn is an essential element for many diatom enzymatic processes. However, even after diatom blooms in Southern Ocean, surface water Zn levels reduced by only *ca.* 50% (Frew et al., 2001), which is likely to only affect surface dwelling *G. ruber*.

Although vital for phytoplankton growth, the relatively low uptake of Mn by marine phytoplankton results in high ambient Mn surface water concentrations (Learman et al., 2011;

Morel et al., 2003; Sunda and Huntsman, 1988). Manganese concentrations are in excess of those that would otherwise limit growth and/or productivity and are therefore generally higher in surface than deep waters (Morel et al., 2003). Fluctuations in the Mn excess may be regulated by terrestrial or volcanic inputs relative to a background concentration in the ambient water mass (Bruland and Lohan, 2003).

Barium is incorporated into foraminifera via passive substitution for Ca either in a biologically mediated process and/or by adhering to the test (Bruland and Lohan, 2003; Lea and Boyle, 1991). Accordingly, depletion of Ba in surface waters (as low as 20% of the highest deep water values) is smaller than observed for bio-active trace metals that can limit productivity (Bacon and Edmond, 1972; Chan et al., 1977; Lea and Boyle, 1989). Laboratory foraminifera culturing experiments have established that Ba is incorporated into test calcite in equilibrium with ambient water concentrations (Hönisch et al., 2011; Lea and Spero, 1992) with Ba/Ca levels homogeneous across the test wall regardless of diurnal cycles (Spero et al., 2008). Previously, links between foraminiferal Ba/Ca and fluvial discharge and upwelling have been made (Hall and Chan, 2004; Lea and Boyle, 1990; Weldeab et al., 2007). In addition, a relationship between marine sediment Ba/Al values and diatom productivity in the Southwest Pacific Ocean has been proposed (Weedon and Hall, 2004). A core-top validation of Ba/Ca in planktic foraminifera as a water mass tracer proxy has not previously been established. Plankton tow and core-top material utilised in this study span zones of high-low productivity (e.g. King and Howard, 2001; Murphy et al., 2001) and variable fluvial input (see Hicks and Shankar, 2003) thereby providing the opportunity to evaluate any modern relationship between trace metal levels in foraminiferal test calcite and the environment.

AI 3.0. Complexity in interpretation of test trace metal values as paleo-ocean proxies

AI 3.1. Core-top diagenesis

Southern core-tops are mainly from the carbonate-mantled Campbell Plateau (e.g. Neil et al., 2004) whereas the northern core-tops come from the high terrigenous input, Hikurangi Margin and Plateau (Hicks and Shankar, 2003; Orpin et al., 2008). This raises the possibility that the high terrigenous fluvial flux may contribute to the elevated northern Mn/Ca values in contrast to the terrigenous-starved Campbell Plateau and its minimal Mn/Ca ratios (Fig. 24). However, northern plankton tows, in particular U2322 from near MD97 2121, captured *G. ruber* with Mn/Ca of *ca.* 8 $\mu\text{mol/mol}$, similar to SAW values (Fig. 24). Bearing in mind that

this tow data are a single “snapshot” of the austral autumn water conditions of 2001, it raises the following possibilities; namely, the Mn/Ca ratio is low because of (i) the presence of SAW-bearing water, which can extend to MD97 2121, but is unlikely because under the modern conditions, SAW modified water is confined mainly to the continental shelf and MD97 2121, which is located off the continental slope, is overlain by STW (Chiswell, 2000), (ii) low fluvial input as reflected by the low precipitation at the time of the plankton tows (NIWA, 2012), and/or (iii) it is the normal dissolved Mn level for the surface waters. If the last point is valid, it implies that the elevated Mn/Ca of the core tops and down-core section of MD97 2121 may be affected by post-depositional processes.

C3-AI. Fig. 1. (a) X-ray map of Mn/Ca relative intensity of a single *G. bulloides* test as measured by WDS electron microprobe with two adult and juvenile chambers indicated. (b) Time-resolved laser ablation profile for *G. bulloides* chamber *f* from MD97 2121, 2.4 m depth (6.5 ka). The colour spectrum on (a) has been linearly scaled to enable distinction between the inner and outer test compositions. Values of Mn/Ca above *ca.* 1 mmol/mol are coloured pink or higher on this intensity scale. The spatial resolution of the WDS map is *ca.* 1 μm^2 . Contaminant phases are indicated in red/pink on the outer test surface in the elemental map with very high relative amounts of Mn/Ca (*ca.* > 1 mmol/mol) compared to the inner test coloured in blue/green (*ca.* 0.3 mmol/mol). The contaminant phase on the outer test can also be clearly identified on the laser ablation profile (indicated by the red bar). This section is completely removed during the first 10–15 seconds of ablation and the test trace metal profile indicated by the red bar is excluded when calculating individual foraminifera and sample mean elemental ratios.

Any post-depositional contamination of foraminiferal tests has the potential to affect trace element concentrations, for example, Boyle (1981; 1983) highlighted enrichment in Mn due to the formation of manganese carbonate outgrowths and ferromanganese coatings on test surfaces. In addition, as noted in the Methods, any surface enrichment seen in the trace element maps are detectable in the laser ablation profiles (C3-AI. Fig. 1). Hence trace element measurements are restricted to the test's primary calcite layer. Element maps of the test wall also confirm a lack of obvious Mn/Ca contamination within test pore spaces (C3-AI. Fig. 1) and the primary test calcite (C3-AI. Fig. 1). Our LA-ICPMS analyses and EPMA element mapping can only resolve Mn contamination within the acknowledged spatial and analytical capabilities of those instruments, and we cannot discount the potential presence of pervasive sub-micron films of Mn precipitation within the pores, a feature which would likely only be resolvable using NanoSIMS methods (e.g. Kunioka et al., 2006). Given low

concentrations of Mn in the test calcite of plankton tow samples, any film may act leverage the analysis. Nonetheless, clearly resolvable differences exist between core top foraminifera underlying SAW and STW.

AI 3.2 Measurement of trace element data

Trace metal data was measured here using laser ablation ICP-MS. This technique involves the removal of a very small volume of material from the foraminiferal shell, associated with a circular laser beam of 35 μm diameter. Any foraminiferal shell spot likely only represents data from up to ~one month which the foraminifera takes to undergo its full life cycle (Hemleben et al., 1989) and thus only offers a ‘snap shot’ of environmental conditions at the time and depth at which the shell was calcified. As such, a spot analysis of a single foraminifera is unlikely to be representative of annual conditions prevailing at (for example) 60 m water depth. However, spot analyses of multiple foraminifera reduces the uncertainty (see discussion of uncertainty in the *methods* section 3.2) of a single spot and generates results which, in their totality, offer an insight into conditions over a time span for which the age of the foraminifera range. For example, in a high sedimentation region a core top sample of 30 foraminifera may provide the average conditions over a 200 year time span for spring conditions under a regional spring dominated productivity cycle.

Uncertainty of individual data points (% 2 standard error) of trace element/Ca ratios for a single foraminiferal analysis are typically: Mg/Ca ± 1.0 -2.5%, Al/Ca ± 5 -20%, Mn/Ca ± 3 -15%, Zn/Ca ± 6 -23%, Sr/Ca ± 1.0 -2.0%, Ba/Ca ± 3 -30%. This level of uncertainty on an individual-by-individual basis affects the uncertainty of a sample mean at a given horizon within a down-core record. The use of multiple foraminifera in a sample is therefore vital to ensure that uncertainty associated an individual measurement is reduced. Uncertainty is reduced by the increase in the number of foraminifera in a sample, this can be clearly illustrated using t-statistics. For example, by going from 30 to 10 foraminifera in a sample would increase the ‘degrees of freedom’ from 2.04 to 2.6 or an inflation of the uncertainty of approximately 10%. This variability will introduce uncertainty into the sample. However, inter-sample variability varies from 10-30 %, therefore this is far more significant than for an individual data point.

C3-AI. Fig. 2. (a) Mg/Ca and (b) Zn/Ca sample values with individual sample 95% confidence intervals.

Inter sample variability like those above represent natural heterogeneity within the sample (Fig. C3-AI. Fig. 2). This natural heterogeneity is a result of the different depths at which the foraminifera dwell (e.g. Mortyn and Charles, 2003), the different season(s) of productivity and related surface water trace metal concentrations (e.g. Neil and Northcote, 2004; Gault-Ringold et al. 2012) and natural differences in the biological incorporation of trace metals between individuals (pers. comm. Spero, 2012). Using laser ablation we are able to further investigate this variability. In the text of chapter 3 we use the intra-sample variability to investigate if this may act as a potential proxy for changes in ENSO following the work of Koutavas et al. (2006). However this intra-sample variability, which is only resolvable using in situ geochemical techniques, also emphasises the need to use the smoothing technique to highlight trends through time, rather than be reliant on a single sample. In addition, it also emphasises the need to look for similar trends in other independent proxy records e.g. foraminifera assemblages or key indicator species indicating a cooling trend at a similar time

thus supporting the interpretation and clearly distinguish between natural background ‘noise’ and changes reflecting wider environmental conditions.

AI 3.3 Benthic Conditions

Trace element ratios over a glacial-interglacial cycle may be affected by changing benthic conditions. In the case of ODP 1123, *ca.* 900 km east of MD97 2121, glacial to interglacial changes from (i) terrigenous-dominant to carbonate-dominant sedimentation, (ii) a reduced the organic carbon flux (Lean and McCave, 1998) and (iii) relatively fast flowing Antarctic-sourced Circumpolar Deep Water to relatively slower North Atlantic Deep Water (Hall et al., 2001), all have the potential to change the trace element supply and benthic geochemical conditions. In contrast, sedimentation at MD97 2121 is continually rapid (30-40 cm/kyr compared to 4 cm/kyr at ODP 1123), and the terrigenous input remained high and carbonate low (<20%) over the last glacial/interglacial cycle without major changes in the benthic water mass compared to the marked changes in the surface ocean (Carter and Manighetti, 2006). Thus the trace element/Ca ratios, in particular Zn/Ca, potentially reflect the concentrations of trace elements at the time of calcification at MD97 2121.

AI 3.4 Water column concentrations

Interpretations of Zn/Ca trace metal values in foraminifera require consideration of the Zn water-column profile at the time of calcification. *G. bulloides* mainly calcifies in the New Zealand spring (King and Howard, 2001) when strong seasonal winds affect deep mixing and local upwelling at the continental margin (Chang et al., 2003; Sutton and Roemmich, 2001). Such conditions, in particular upwelling, are liable to bring Zn-enriched deeper waters to the surface and so disrupt the Zn nutrient profile causing calcifying tests to have an elevated Zn/Ca ratio compared to the profile data available to us (Fig. 23). This situation would be reversed for Mn, which is enriched in surface waters and declines with depth.

Chapter 4

IMPACT OF SEASONALITY AND CHANGING OCEANOGRAPHY ON PALEOTHERMOMETRY RECORDS

Marr, J. P., H. C. Bostock, L. Carter, in review. Impact of seasonality on paleothermometry records: implications for paleothermometry records derived from frontal regions, *Paleoceanography Paleoclimatology Paleoecology*

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Abstract

Modern sediment trap studies have illustrated a distinct seasonal offset in foraminiferal and alkenone flux to the sea floor between the subantarctic and subtropical water masses. However, the potential effect of a change in species seasonality on paleothermometry records where there has been a change in dominant water mass is yet to be illustrated. Here we present a comparison between temperature records of two independent paleothermometers, alkenone and Mg/Ca analysed on planktonic foraminifera, from a high-resolution core situated close to a subtropical frontal region. The long term temperature trends in alkenone and *Globigerina bulloides* (*G. bulloides*) Mg/Ca-based estimates generally agree. The offset between *G. bulloides* and alkenone temperatures varies between *ca.* 3-7 °C during the glacial period and the subsequent transition to the Holocene. During the last glacial to early deglaciation (25-16 ka) the study site was bathed by SAW and alkenone production was most likely limited to summer, as favourable conditions for coccolithophore productivity including stratified surface waters and optimal light levels is unlikely to be achieved at other time during the year. This has the effect of producing warmer glacial alkenone temperatures, dampening glacial-interglacial variability. However, during the glacial period *G. bulloides* is likely to have followed a spring bloom cycle, similar to modern subantarctic sites with temperature further dampened by wind induced upwelling or mixing of the upper ocean. This resulted in cooler Mg/Ca-*G. bulloides* glacial temperature estimates and a greater offset with

between alkenone and Mg/Ca temperature records as compared to the Holocene. Holocene based alkenone-*G. bulloides* temperatures are generally the same within error, signalling a return to modern surface water conditions and a common season(s) (spring and summer) of productivity. This study highlights the susceptibility of foraminiferal Mg/Ca and alkenone-based temperature estimates to the effects of seasonality and changing regional hydrology.

1.0 Introduction

Global temperature has been warming since 1880s, and the more recent acceleration of this increase since the late 1970s has alarmed scientists (e.g. Cole and McCarthy, 2012; Root et al., 2003; IPCC 4th Assessment). However, it is also known that global temperature naturally fluctuates, thus it is important to establish a base line for natural temperature variability in order to identify any anthropogenic impact on global climate (e.g. Mayewski et al., 2004). Paleotemperature reconstructions largely rely on geochemical measurements or floral/faunal assemblages (e.g. Otto-Bliesner et al., 2009). However, when data from different proxies are compared discrepancies commonly arise as identified previously in the CLIMAP (Climate Long-Range Investigation, Mapping and Prediction) (e.g. CLIMAP, 1976; CLIMAP, 1981; Rind and Peteet, 1985), or more recently the MARGO projects (Multiproxy Approach for the Reconstruction of the Glacial Ocean surface) (Kucera et al., 2005; MARGO et al., 2009). From these global research projects it has become clear that a greater understanding is required of what temperatures these proxies are actually recording. In this study we tackle this issue by comparing multiple paleothermometer analyses which use different planktic organisms/species preserved in well-dated, well-preserved marine sediment cores.

Geochemical proxies can only be applied as far back in time as the relationship between species ecology and biology, and the target chemical process remain stable (Kucera, 2007; MARGO et al., 2009; Sikes et al., 2009). Even if the metabolic or biochemical pathway responsible for incorporation of the chemical signal remains the same, any change in the season of production, or the environmental niche, can alter the reconstructed record (Bemis et al., 2002; Kucera, 2007). Depending on the environmental preference/s of a particular species and its adaptive capacity, this may result in an attenuated record as an organism attempts to maintain optimal habitat conditions by ceasing productivity in specific region(s) (Kucera et al., 2005; Tyrrell and Merico, 2004). Previously, it was suggested that a change in species seasonality may be affecting paleoceanographic records, however details regarding the

degree to which seasonality impacts upon the paleotemperature record are currently unknown (Barrows et al., 2007; Leduc et al., 2010; Sikes et al., 2009).

Here we present a comparison between paleotemperature records of two independent paleothermometers; alkenones and Mg/Ca measured on planktonic foraminifera, *Globigerina bulloides*, from a high-resolution core MD97 2121 from north of the Chatham Rise, east of New Zealand (Carter et al., 2002). The core sits just north of the Subtropical Front (STF; Fig. 28) and while the surface waters currently bathing the core site are subtropical water (STW), the region was overlain by subantarctic water (SAW) during the glacial period (Carter et al., 2008; Marr et al., in press-b; Weaver et al., 1998). Therefore this site provides the ideal opportunity to investigate how changes in the dominant water mass(es), both of which have distinctive temperature and nutrient profiles, have affected the ecological response of coccolithophores and foraminifers and thus the paleotemperature records derived from these organisms.

2.0 Background

2.1 Paleothermometry tools

There are two sources of paleotemperature records used in this study; alkenone records and Mg/Ca ratios measured on planktic foraminifera *Globigerina bulloides* (*G. bulloides*). Alkenone-based surface water temperatures are determined from the organic remnants of the phytoplankton coccolithophores in sediment, using the alkenone undersaturation index. This index uses the degree of unsaturation of the C₃₇ alkenones, which increases with decreasing temperature of the water in which the microalgae grow (Brassell et al., 1986; Prahl and Wakeham, 1987). For temperature estimation, this unsaturation is generally expressed as the U_{37}^K ratio, which is the ratio of the amount of di-unsaturated to the total di- plus tri-unsaturated C₃₇ alkenones in the sample ($[37:2]/[37:2+37:3]$). *Emiliania huxleyi* (*E. huxleyi*) and *Gephyrocapsa oceanica* (*G. oceanica*) are the two species of coccolithophore, which are the principal alkenone synthesizers in the modern ocean (Conte et al., 1994; Volkman et al., 1995) and both are commonly found in the New Zealand region (Rhodes et al., 1995; Hoe Chang, pers. comm.).

Mg/Ca-based thermometry uses the geochemical trace element composition of foraminiferal shells (tests), which reflect i) the chemistry of the ambient seawater, and ii) in the case of the Mg incorporation into test calcite, the thermodynamic relationship between Mg and Ca,

which leads to an exponential increase in the level of Mg relative to Ca with increasing temperature (e.g. Bender et al., 1975; Lea et al., 1999). While multiple species of planktic foraminifera have been calibrated for Mg/Ca paleothermometry, here we use the temperate species, *G. bulloides* due to its wide geographic distribution at southern mid-latitudes (Hemleben et al., 1989) and continuous presence in Quaternary cores from the eastern New Zealand region (Hayward et al., 2008; Marr et al., in press-b; Pahnke et al., 2003).

Figure 28. Generalised modern surface ocean currents and bathymetry surrounding New Zealand (modified from Carter et al., 1998). Yellow star marks the core site MD97 2121 used in this study. Circles mark location of *G. bulloides* and alkenone sediment trap studies, NCR=North of Chatham Rise, SCR=South of Chatham Rise: King and Howard (2001), Sikes et al. (Sikes et al., 2005); PR=Pukaki Rise, CF=Campbell Flank: Northcote and Neil (2005); TF = Tasman Front; STF = Subtropical Front; SAF = Subantarctic Front; STW = Subtropical

Surface Water; SAW = Subantarctic Surface Water; MS = Mernoo Saddle; DWBC=Deep western boundary current; ECC=East Coast Current; WE=Wairarapa Eddy. Isobaths are in metres.

2.2 Ecological niches

Coccolithophore are distributed in the upper mixed layer, while planktonic foraminifera are present throughout the whole water column. Particular species are restricted in their vertical and spatial distribution by species-specific ecological requirements (e.g. Hemleben et al., 1989; Kuroyanagi and Kawahata, 2004; Tyrrell and Merico, 2004). Phytoplankton *E. huxleyi* and *G. oceanica* are recognised as being relatively cosmopolitan living north and south of the STF. However, *G. oceanica* tends to be more dominant in STW, while *E. huxleyi* is more prominent in SAW (Duncan, 2012; Rhodes et al., 1995). There are a number of potential constraints on coccolithophore depth habitat, including the key physiological requirement of light for the photosynthesis (Tyrrell and Merico, 2004). Light requirements generally restrict coccolithophore to the upper 30 m of the water column (Nanninga and Tyrrell, 1996; Tyrrell and Merico, 2004).

Foraminifera are zooplankton. The foraminifera *G. bulloides* is asymbiotic and thus its depth habitats are not constrained by light levels. North and south of the STF the distribution of *G. bulloides* through the water column, as identified by stratified plankton tows, does not significantly change (NIWA, Cruise Report TAN 9814, unpublished report, 1998) despite the significant differences in water mass properties including temperature and seasonal surface water mixing (Heath, 1985b; Morris et al., 2001; Sutton, 2001). The highest concentrations of *G. bulloides* are typically found between 50-100 m depth (Mortyn and Charles, 2003; Wilke et al., 2009a), however they have also been recovered alive from depths of 400 m in the New Zealand region (NIWA, Voyage Report TAN 9814, unpublished report, 1998).

2.3 Oceanography

Modern surface waters east of New Zealand feature a suite of dynamically-driven water masses (e.g. Chiswell, 2002a; Heath, 1985b; Morris et al., 2001). Off eastern Australia, the East Australian Current (EAC) flows south, with a component detaching to form the eastward flowing Tasman Front (TF) (Fig. 28) (Ridgway and Dunn, 2007). The Tasman Front flows across the Tasman Basin and re-attaches to northern New Zealand as the East Auckland Current (EAUC) and its southward continuation, the East Coast Current (ECC) (Ridgway and

Hill, 2009; Tilburg et al., 2001). Seaward of the ECC is the anticyclonic, warm-core Wairarapa Eddy (WE) associated with the East Cape Eddy system. Eddies shed near East Cape and propagate southwest along the continental margin to Hawke Bay where they may stall or merge with a previous perturbation to form the Wairarapa Eddy, which is proximal to our core site MD97 2121 (Chiswell, 2005; Roemmich and Sutton, 1998).

East of New Zealand the STF is situated approximately along the east-west crest of Chatham Rise (Fig. 28). This front separates the warm, micronutrient-rich, saline STW which have flowed in to the region via the TF from Australia, from micronutrient poor, cool, fresher SAW (e.g. Bowie et al., 2009; Chiswell, 2002a; Hamilton, 2006) (Fig. 28). Modern sea surface temperatures (SSTs) north of the Chatham Rise vary by *ca.* 3.5-4°C at the ocean surface between spring and summer (Locarnini et al., 2006).

South of Chatham Rise, the inflow to southern New Zealand is dominated by the Antarctic Circumpolar Current (ACC) whose leading edge is the Subantarctic Front (SAF). The SAF separates the SAW from colder Circumpolar Surface Water (CSW) is forced south around the bathymetric barrier of Campbell Plateau (Fig. 28) (Heath, 1985a; Morris et al., 2001).

2.4 Modern seasonality of coccolithophores and *G. bulloides* production

Timing of coccolithophore, and thus alkenone, production varies north and south of the STF (Sikes et al., 2005). Evidence from sediment traps show that to the north of the STF in STW, alkenone flux peaks in late December, during the Austral summer, with smaller peaks approximately half the size in spring and autumn (Fig. 29). Alkenone STW temperatures from sediment traps generally agreed with the satellite derived SST throughout the year, but gave cooler than predicted temperatures by up to 4 °C during late summer to early autumn—possibly due to reduced nutrients (Sikes et al., 2005). South of the STF in SAW, a more sustained, but single peak in alkenone flux occurs from September-November, Austral spring (Fig. 29), with warmer alkenone derived temperatures than expected found during late summer to early winter – possibly due to light limitation (Sikes et al., 2005).

In STW, north of the STF, *G. bulloides* mainly blooms in spring to early summer, with smaller peaks in productivity (approximately half the flux) in spring and autumn, similar to alkenones (Fig. 29) (King and Howard, 2001). South of the STF, in SAW, *G. bulloides* peak flux occurs during spring, also at the same time as the alkenones (Fig. 29) (King and Howard, 2001; Northcote and Neil, 2005).

3.0 Methods

Paleotemperatures used in this study have been derived from the marine sediment core MD97 2121. The top 9.15 m of the giant piston core covers the period from 25 ka-present giving a mean sedimentation rate of *ca.* 40 cm/ka. The core site is located just north of the Chatham Rise (40°22'S; 177°60'E, water depth 2314 m). A robust chronology is based on 20 Accelerator Mass Spectrometry (AMS) ¹⁴C and nine tephra dates (Carter et al., 2008).

3.1 Alkenone temperature estimates

Alkenone-based SSTs for core MD97 2121 were published by Pahnke and Sachs (2006). We have calibrated the temperatures using the Sikes and Volkman (1993) calibration due to the regional dominance of SAW at this site during the glacial period (Marr et al., in press-b; Nelson et al., 2000; Weaver et al., 1998). The Sikes and Volkman (1993) calibration was developed for the Southern Ocean, but in modern subtropical waters can lead to temperature estimates 1-2 °C warmer than expected from satellite temperature measurements (Sikes et al., 2005; Sikes and Volkman, 1993). Errors of ± 1.5 °C are associated with alkenone temperatures derived from the Southern Ocean (Sikes et al., 2009), comparable to the errors associated with Mg/Ca SST estimates. The Sikes and Volkman (1993) alkenone calibrations are based on alkenone concentrations of both *E. huxleyi* and *G. oceanica* whereas the Prahl et al. (1988), calibration is based only on *E. huxleyi*. Neither calibration is likely to be suitable for samples containing only *G. oceanica* (Volkman et al., 1995), and the performance of both alkenone calibrations is poor below 6 °C (Sikes et al., 1997).

Previously, the use of either the global (Prahl et al., (1988) or SW Pacific regional (Sikes and Volkman, (1993) alkenone calibrations for marine sediment cores MD97 2121 and MD97 2120 (south of the Chatham Rise) have been discussed in Pahnke and Sachs (2006). Typically, the Sikes and Volkman (1993) temperature calibration generates warmer temperatures by 1-4 °C, equivalent to summer SST estimates. While the global Prahl et al. (1988) calibration reflects annual mean SST. The difference between Prahl et al. (1988) and Sikes and Volkman (1993) temperature estimates are more pronounced at the MD97 2120 site. At MD97 2121 the difference between the calibrations is typically 1-2 °C, only exceeding the calibration error of ± 1.5 °C during the glacial period (AI. 1). During the glacial period the difference between the Sikes and Prahl calibrations at MD97 2121 increases to between 1.5-2 °C, with the Prahl calibration producing cooler temperatures. The increased

glacial offset is likely the effect of increased SAW influence at the MD97 2121 site during the glacial period (Marr et al., in press-b; Nelson et al., 2000; Weaver et al., 1998). As the Sikes and Volkman (1993) calibration was developed for SAW we use this for comparison, noting that during times of peak alkenone production this calibration may produce warmer SSTs by 1-2 °C in subtropical water and will provide summer rather than annual SSTs (Prah et al., 1988; Sikes et al., 2005; Sikes and Volkman, 1993).

Figure 29. Alkenone and foraminiferal seasonal productivity fluxes north (a) and south (b) of the Subtropical Front. NCR-North Chatham Rise, SCR-South Chatham (*G. bulloides*-King and Howard, 2001; Alkenone-Sikes et al., 2005), CF-Campbell Flank, PR-Pukaki Rise (Northcote and Neil, 2005). Note, the Sikes et al. (2005) data is presented as the non-normalised total daily fluxes as this is more likely to represent alkenone accumulation in the marine sediment core record.

3.2 Mg/Ca temperature estimates

Mg/Ca-temperatures from MD97 2121 *G. bulloides* anti-penultimate chamber (*f*-2) has previously been published (Marr et al., in press-b) using a regional SW Pacific species-

specific calibration (Marr et al., 2011). While there are small errors associated with the specific calibrations (Anand et al., 2003; Marr et al., 2011), the errors on the Mg/Ca paleotemperatures used in this study are *ca.* ± 1.5 °C (Marr et al., in press-b).

3.3 SEM identification of coccolithophore species

Seven 1 cm sections interspersed throughout marine isotope stages (MIS) 1 and 2 were selected for SEM imaging. This was carried out on the <40 μ m grain size fraction to determine the dominant species of alkenone producing coccolithophore (Fig. 30). SEM images were taken using Jeol JSM 6500F at Victoria University of Wellington. Carbon tape was attached to an SEM stub, with a silicon wafer placed on top. A drop of sediment, diluted in MilliQ water, was placed on to a stub. Stubs were then dried under a heat lamp before being carbon coated.

Figure 30. Example of an SEM image of coccolithophore and terrigenous material from sample 6.10-6.11 m. Favourable sample preservation has allowed for species level identification of *G. oceanica* and *E. huxleyi* (red

circles). However, all *G. oceanica* were included in the category *Gephyrocapsa* spp. as identification to species level was not always possible.

For each sample, images were taken from random fields of view (FOV) at 1500-3000x magnification and used to identify coccolithophore specimens. The total number of specimens identified for each sample varied from 11 to 85 (Al. 2). These data were turned into percentages to look at major changes in the assemblage over the last 25 ka (Fig. 31). This is a semi-quantitative approach, since the total numbers of coccolithophore per gram of sediment were not determined, but the method highlights significant changes that could be evaluated with a more quantitative approach in the future. The use of the SEM rather than a light microscope had benefits and limitations. Very small specimens of *E. huxleyi* and *Gephyrocapsa* spp. are easier to identify with a SEM. However, the traditional data collection method of counting a specific number of coccolithophore per sample (e.g., 300 to 500) takes significantly longer. In addition, coccolithophore in SEM images are occasionally obscured from view by terrigenous sediment. Poor preservation of some samples also made species identification difficult. For this reason, geophyrocapsids were grouped into *Gephyrocapsa* spp.. However, in samples where preservation permitted specimens to be identified to species level, most geophyrocapsids were identified as being *G. oceanica*.

3.4 Determination of the difference between alkenone and Mg/Ca temperature proxies

The difference in temperature between the proxies has been determined by measuring the difference between the proxies temperature estimates after a three point moving mean was applied to the data. Smoothing of the data is an attempt to find better representation over time, reducing the scatter point by point by assuming that the general background conditions are fairly constant over a period of time –in the case of Mg/Ca this is *ca.* 700 yr. The statistical basis for this is the reduction in the uncertainty of the mean of N numbers by $1/\sqrt{N}$. We note that after a 3 point moving mean is used every 3rd point will be independent.

Figure 31. Relative abundances of alkenone producing coccolithophore identified under SEM from the <40 μ m sediment size fraction, and relative temperature offset between alkenone and *G. bulloides* paleotemperatures for the selected time slices (Marr et al., in press-b; Pahnke and Sachs, 2006).

4.0 Results

4.1 Difference between alkenone and Mg/Ca temperature proxies

There are two distinct periods of temperature difference between alkenone and *G. bulloides* Mg/Ca paleotemperatures at the MD97 2121 site (Fig. 32). From 25 ka to the initiation of the Antarctic Cold Reversal (ACR) at 14.2 ka, alkenone SSTs were 3 to 7 °C warmer than their Mg/Ca counterparts (Marr et al., in press-b; Pahnke and Sachs, 2006). The largest offset(s) occurred during the early ACR, from *ca.* 14.2-13.7 ka reaching up to 10 °C (Fig. 32). However, during the late deglaciation from *ca.* 13.5 ka, the difference between the two paleotemperature estimates declines. From *ca.* 10 ka the alkenone-Mg/Ca temperature estimates are indistinguishable based on the associated proxy errors of ± 1.5 °C (Marr et al., in press-b; Pahnke and Sachs, 2006; Sikes et al., 2009).

Figure 32. 25 ka-present faunal and paleotemperature records from MD97 2121 and MD97 2120. (a) paleotemperature data in blue derived from MD97 2121 alkenones-solid line (Pahnke and Sachs, 2006) and *G. bulloides* chamber *f*-2 –dashed line Mg/Ca (Marr et al., in press-b), and in grey MD97 2120 derived from alkenones-solid line and *G. bulloides*–dashed line (Pahnke et al., 2003) (b) foraminiferal assemblages of species with known environmental preferences (Imbrie and Kipp, 1973), based on samples of >100 individuals (Northcote et al., 2007). Geochemical data are presented using a three point moving mean for trend comparison. For consistency, the Sikes and Volkman (1993) calibration is used for alkenone data, and Marr et al. (2011) calibration for *G. bulloides* Mg/Ca. The Antarctic Cold Reversal (ACR) is indicated by the blue shaded bar. Vertical orange lines indicate the timing of the seven 1 cm core sections selected for further analysis via SEM and x-ray imaging.

4.2 Identification of alkenone producing coccolithophore species

Both *Gephyrocapsa* spp. and *E. huxleyi* were able to be identified in SEM images (Fig. 30). During the glacial-interglacial period the total number of *Gephyrocapsa* spp. and *E. huxleyi* identified fluctuated depending on the amount of clay in the sample (which obscured lith view) and sample preservation (AI. 2). *Gephyrocapsa* spp. was typically identified in greater numbers than *E. huxleyi*, which likely reflects the wider range of species morphology included in this category (AI. 2). However during the transition period, including the ACR, *E.*

huxleyi was absent from both 15.5 and 13.7 ka samples despite a strong presence of *Gephyrocapsa* spp. (Fig. 31).

5.0 Discussion

Paleothermometry records derived from foraminiferal and coccolithophore based material can be affected by a number of issues; 1) transport or post-depositional alteration to the record after the organism has completed its lifecycle and the material is deposited in the sediment (e.g. Boyle, 1995; Mollenhauer et al., 2003; Pena et al., 2005), 2) the organisms' environmental preferences or niches (depth in the water column), and 3) the season of their peak productivity and thus highest flux to the sea floor (Northcote and Neil, 2005; Sikes et al., 2005).

5.1 Alteration to samples following completion of its life cycle

Previous work has shown that the carbonate proxy records from MD97 2121 have not been affected by post-depositional alteration/diagenesis (Carter et al., 2008; Marr et al., in press-b; Pahnke and Sachs, 2006; Weaver et al., 1998), as it sits above the modern calcite saturation horizon (Bostock et al., 2011), which would have only deepened during the glacial period (Marchitto et al., 2005). In addition, there was little change in the sediment flux to the seabed (Holocene=30 g/cm²/kyr; Glacial=37 g/cm²/kyr; Carter and Manighetti, 2006) and minimal bottom water currents in the region (Carter and Manighetti, 2006; Carter et al., 2002). Thus re-working and re-distribution of sediment is unlikely. Significant changes between glacial and interglacial sedimentary structures were also not identified in core x-ray images (AI. 3).

During the interglacial period the dominant inflow at the MD97 2121 site was from the north, while during the glacial period it was from the south (Marr et al., in press-b; Nelson et al., 2000). Transportation of the fine sediment size fraction had been previously highlighted as a source of error for alkenone thermometry (Mollenhauer et al., 2003; Ohkouchi et al., 2002). The alkenone-based glacial SSTs at MD97 2121 are *ca.* 15 °C, which is only 4 °C colder than those for the Holocene (Marr et al., in press-b; Pahnke and Sachs, 2006), however this is greater than proxy uncertainty ± 1.5 °C. Such temperatures would preclude alkenones being swept to the site from the south where alkenone based SSTs are *ca.* 8 °C during the glacial period (Pahnke et al., 2003). Such a preclusion is counter to the documented northward transport of SAW to MD97 2121 as supported by the presence of subpolar/polar foraminifera

assemblages (Carter et al., 2008; Weaver et al., 1998) and to a lesser extent by the modern physical oceanography (e.g. Chiswell, 2000; Orpin et al., 2008). Therefore we believe that the most likely reasons for the differences between the two paleotemperature estimates in this core are due to changes in the foraminifera or coccolithophore ecological niche, or season of productivity.

5.2 Change in the organisms' environmental preferences or niches

Coccolithophore dependence on light for photosynthesis means that it is unlikely to significantly change its depth of maximum production between the glacial-Holocene periods (Nanninga and Tyrrell, 1996; Tyrrell and Merico, 2004). However, asymbiont *G. bulloides* is not constrained by light limitation and therefore depth of greatest production may change. There is no direct evidence to indicate that *G. bulloides* productivity depth changed during the glacial period, or, that it remained stable. Inter-species Mg/Ca and oxygen isotope records from MD97 2121 indicate that inter-species stratification was present during the glacial period with *G. bulloides* dwelling at lower depths than *Globigerinoides ruber* and higher than *Globorotalia inflata*, similar to the modern period (Carter et al., 2008; Marr et al., in press-a). However, it should be noted that during the ACR this inter-species stratification relationship changed as previously noted in Marr et al., (submitted a) and Carter et al., (2008), with little to no stratification present at times. As the temperature and environmental information derived from this species is consistent with our current understanding of the MD97 2121 region (e.g. Nelson et al., 2000; Weaver et al., 1998), there is little evidence to suggest any significant change in the *G. bulloides* habitat depth.

5.3 Changes in the seasonality of productivity

If alkenone and *G. bulloides* season's of maximum flux responded in a similar way to the glacial presence of SAW at MD97 2121, then based on modern conditions, it may be expected both species would bloom during spring. This would result in a consistent temperature offset between the paleothermometry records throughout the glacial-Holocene record. The change in alkenone and *G. bulloides* Mg/Ca temperature offset between the glacial and Holocene periods indicates that, 1) the species response to the changing environmental conditions were different, and 2) there were factors beyond a change in water mass properties which influenced species' ecology. As coccolithophore are photosynthesisers a change in glacial-Holocene light levels is likely to have been a significant additional factor,

in addition to nutrient levels, and stratification, affecting the timing of species productivity and water column depth (e.g. Nanninga and Tyrrell, 1996).

In the modern ocean wind intensity at southern mid-latitudes affects regional upwelling and depth of the mixed layer, following a seasonal cycle; peaking during winter, subsiding during spring, before reaching a summer minima (Sallée et al., 2010b; Young, 1999). This seasonal wind cycle has a significant effect on the surface water stratification and upwelling and mixing (e.g. Pollard et al., 1972; Sallée et al., 2010a). In the Southern Ocean under modern conditions, maximum surface water stratification typically occurs during summer (Morris et al., 2001; Sallée et al., 2010b). Optimal bloom conditions for coccolithophore requires relatively stable surface water stratification, especially for species such as *E. huxleyi* (Tyrrell and Merico, 2004).

5.3.1 Glacial-early deglacial (25-16 ka)

During the glacial period, wind intensity increased (Shulmeister et al., 2004) and thus it is likely that this delayed the establishment of stable surface water stratification and thus coccolithophore blooms. At MD97 2121 well mixed winter surface water conditions prevailed at least until spring (Marr et al., in press-b) creating more turbid surface water conditions and filtering light levels. Thus, during the glacial period it is likely that coccolithophore peak productivity was restricted to summer when there was maximum surface ocean stratification and increased levels of light transmitted to the surface waters (Fig. 33). Asymbiotic *G. bulloides*, however, was likely able to maintain a spring bloom cycle, consistent with modern SAW (Fig. 32) (King and Howard, 2001; Northcote and Neil, 2005). This offset in seasonal bloom times likely contributed to *ca.* 3-4 °C of the total temperature offset between alkenone-*G. bulloides* paleotemperature estimates.

The increased wind intensity during the glacial period (Shulmeister et al., 2004) is also likely to have encouraged the upwelling of cooler, deeper Antarctic Intermediate and/or Subantarctic Mode Waters (AAIW/SAMW) over the Mernoo Saddle, in an intensification of the modern processes (Carter et al., 2000; Chiswell, 2000; Heath, 1975). Mixing with overlying SAW, the cooler upwelled waters may have contributed to the appearance of several polar planktic foraminiferal species in the MD97 2121 region, including *Neogloboquadrina pachyderma*, which formed up to 20 % of the faunal abundance during the glacial period (Nelson et al., 2000; Northcote et al., 2007; Weaver et al., 1998). Thus, if *G.*

bulloides maintained a spring bloom cycle it is likely that temperature estimates would be further cooled due to this upwelling phenomenon by at least another 2 °C (Sutton, 2003).

South of the STF at MD97 2120, glacial period *G. bulloides*-Mg/Ca and alkenone temperature offsets were also larger during the glacial period, similar to MD97 2121 (Pahnke et al., 2003). However, between 25-18 ka, temperature offsets at MD97 2120 averaged 7-8 °C, greater than that of MD97 2121, narrowing to a 3-4 °C offset during the Holocene. The difference in alkenone-*G. bulloides*- Mg/Ca temperature relationship between the sites indicates that there are likely to be different factors affecting the MD97 2120 region (Fig. 32).

Compounding factors during the glacial period at MD97 2120 for alkenone-*G. bulloides*-Mg/Ca temperature offsets include, 1) the poor performance of the alkenone paleothermometer at temperatures at or below 6 °C (Sikes et al., 1997), which depending on which temperature calibration is used, surface ocean temperatures at the MD97 2120 may have been close to this threshold (Pahnke and Sachs, 2006); 2) The influx of very cold CSW into the Bounty Trough with more intense winds, changes in the SAF and intensification of the ACC around Campbell Plateau (Hayward et al., 2008; Neil et al., 2004), significantly lowering *G. bulloides* temperatures, also taking them outside the calibrated range of the *G. bulloides* Mg/Ca paleothermometer(s) (Fig. 32) (Anand et al., 2003; Hayward et al., 2008; Marr et al., 2011). We suggest the seasons of maximum flux during the glacial period at MD97 2120 are similar to MD97 2121, with alkenones during the summer and *G. bulloides* in the spring, due to similar insolation and seasonality in surface water mixing conditions (Berger and Loutre, 1992; Sallée et al., 2010b; Shulmeister et al., 2004).

5.4 Deglacial (16-11 ka)

During the transition from glacial to Holocene conditions there was significant variability in surface water temperature recorded by both *G. bulloides* and *G. ruber* Mg/Ca which are absent from the alkenone record (Fig. 32). (Marr et al., in press-b; Pahnke and Sachs, 2006). The difference between *G. bulloides* and alkenone paleotemperature records during this period is up to 10 °C (Fig. 32), which is greater than the proxy associated uncertainty of ± 1.5 °C. Such a difference cannot be accounted for solely by species seasonality or regional upwelling, thus they are likely to be other contributing factors. It is known that SSTs during this period reflected the dynamic interplay between SAW and STW as the region shifted from glacial-SAW dominated to interglacial-STW dominated conditions (Carter et al., 2008; Marr et al., in press-b; Nelson et al., 2000; Northcote et al., 2007).

Period	Stratification ¹	Dominant surface water ^{1,2,3,4}	Nutrient levels ¹	Season of maximum flux	Main coccolithophore species
Holocene	Increased surface water stratification.	STW	High micronutrient with typically low macronutrient levels with occasional incursion(s) of SAW (and thus elevated macronutrient concentrations) from the south ⁵ .	Coccolithophore and <i>G. bullioides</i> have a main period of peak productivity in summer, with additional smaller peaks in spring and autumn ^{5,7} .	<i>G. oceanica</i> and <i>E. huxleyi</i>
Deglaciation	Reduced surface water stratification.	STW/SAW with AAIW/SAMW upwelling	Typically high macronutrient levels from SAW with entrainment of upwelled micronutrient enriched water. After the ACR macronutrient levels are reduced as volumes of SAW transported to the site decline.	Offset seasons of species peak productivity: <i>G. bullioides</i> : spring; coccolithophore: summer.	<i>G. oceanica</i>
Glacial	Reduced surface water stratification. Wind conditions ⁸ prolong the mixed surface water conditions into spring.	SAW	High macronutrient with typically low micronutrient levels.	Offset seasons of species peak productivity: <i>G. bullioides</i> : spring; coccolithophore: summer.	<i>G. oceanica</i> and <i>E. huxleyi</i>

Figure 33. Summary of surface water stratification, nutrient, seasonality, and species changes from 25 ka - present. ¹Marr et al., (in press-b); ²Nelson et al., (2000); ³Weaver et al., (1998); ⁴Carter et al., (2008); ⁵Boyd et al., (1999); ⁶King and Howard, (2001); ⁷Sikes et al. (2005); ⁸Shulmeister et al., (2004); ⁹Northcote and Neil (2005).

During the glacial-Holocene transitional SAW flow through Mernoo saddle is likely to have increased initially as sea level rose, reducing the bathymetric constraints. However, at *ca.* 14 ka the glacial land bridge between the New Zealand North and South islands opened, swamping the region with STW (Carter et al., 2000). While clearly evident in the *G. bulloides* Mg/Ca record, neither of these events are captured in the alkenone record. This suggests that there may have been other factors which affected the MD97 2121 alkenone record during this time, which in effect acted to smooth out the dynamic glacial-Holocene changes in this region (Fig. 32) (Pahnke and Sachs, 2006). SEM imaging of the <40 µm size fraction of the sediment revealed that a change in the alkenone-producing coccolithophore species also occurred during the transition period. Whereas *Gephyrocapsa* spp. and *E. huxleyi* were typically present throughout the glacial-interglacial period, the two samples taken immediately preceding and during the Antarctic Cold Reversal, revealed that *E. huxleyi* may have been absent (Fig. 31).

Reasons for the absence of the ‘cosmopolitan’ *E. huxleyi* are unknown, as they are typically identified throughout the modern surface waters north and south of the STF (Rhodes et al., 1995). Previously, *G. oceanica* blooms were observed in Jervis Bay, Australia, after eddy induced continental slope water upwelling increased nutrient supply (Blackburn and Cresswell, 1993). Northern sourced AAIW currently bathes the continental slope adjacent to core site MD97 2121, similar to that in the Jervis Bay region (Bostock et al., 2013; Chiswell, 2000; Stanton, 2002). Thus, it is possible that a shift in the wind (and/or eddy regime) to favour the regional upwelling of AAIW (Chiswell, 2002b) during the ACR may have favoured a similar dominance of large-scale, monospecific *G. oceanica* blooms, whilst the cool water upwelling resulted in depressed *G. bulloides* temperatures (Fig. 33, Fig. 32) (Weaver et al., 1998). Furthermore, the lack of surface water stratification (Marr et al., in press-b) during this transition period is likely to have further inhibited the growth of *E. huxleyi* (Nanninga and Tyrrell, 1996; Tyrrell and Merico, 2004). Thus neither the Sikes and Volkman (1993) nor Prahl et al. (1988) alkenone calibrations may be appropriate for this

interval and application of these calibrations may have contributed to the apparently muted alkenone temperature record.

During the deglacial period (16-13.5 ka) the *G. bulloides* Mg/Ca temperatures from MD97 2121 and MD97 2120 converge following a period of sustained warming as indicated by *G. bulloides* at MD97 2120 from *ca.* 19-16 ka (Fig. 32). The increase in *G. bulloides* temperature at MD97 2120 is likely a reflection of reduced CSW inflow to the region (Hayward et al., 2008). This is consistent with nearby DSDP 594 faunal assemblage records which also indicate the diminished presence of polar planktic species (*Neogloboquadrina pachyderma* (s), and *Globigerina quinqueloba*) (Nelson et al., 1993). After the reduction of CSW inflow it is likely that a very similar mix of SAW and AAIW/SAMW bathed both the MD97 2121 and MD97 2120 sites, causing the *G. bulloides* temperatures to converge (Fig. 32).

5.5 Holocene (ca. 11 ka-present)

Throughout the Holocene and in the modern ocean, STW has dominated surface waters above MD97 2121 (Marr et al., in press-b; Nelson et al., 2000). Under Holocene conditions, deeper surface water stratification at MD97 2121 relative to the glacial period allowed increased light penetration (Marr et al., in press-b). Coupled with higher summer insolation and influx of micro-nutrient rich STW, coccolithophore are able to bloom multiple times throughout the year similar to modern *G. bulloides* flux(s) (Sikes et al., 2005). As a result, the temperature relationship between alkenone and *G. bulloides* paleothermometry records is largely consistent from *ca.* 11 ka to present bearing in mind ± 1.5 °C errors for the two proxies.

In the early Holocene alkenone temperatures from both MD97 2121 and MD97 2120 converge *ca.* 12.5-11 ka, suggesting an increased influence of STW at both sites (Fig. 32). The increased volume of STW is consistent with a peak in the faunal abundance of *G. ruber* at MD97 2121 (Northcote et al., 2007). The increased volume of STW and thus micronutrient concentrations at MD97 2120 may have also influenced the seasonality of peak alkenone productivity in the region, bringing the alkenone temperatures closer to MD97 2121. Thus, in the early Holocene due to the STW influence alkenone temperatures at MD97 2120 were recording an annual average temperature which was warmer than in the mid-late Holocene.

The mid-late Holocene (*ca.* 9-3 ka) 3-4 °C offset between alkenone and *G. bulloides* temperature estimates at MD97 2120 suggests a sustained seasonal offset in peak flux, however this is contradictory to modern observations of similar seasons of alkenone-*G. bulloides* peak flux in SAW (Fig. 29) (King and Howard, 2001; Sikes et al., 2005). Modern stratified plankton tow records also do not indicate that *G. bulloides* dwell significantly deeper in MD97 2120 region (NIWA, Cruise Report TAN 0103, unpublished report, 2001). Therefore, why there appears to be a clear discrepancy between modern observed and seasonality inferred from the MD97 2120 Holocene temperature records is unknown. However, the apparently clear changes in alkenone seasonal flux between the glacial and Holocene periods does suggest that it may be appropriate to alternate the use of the Sikes and Volkman (1993) and Prahl et al. (1988) calibrations within paleocean records depending on the dominant timing of regional seasonal alkenone production, or new calibrations are required.

6.0 Conclusions

Understanding how environmental changes affect species ecology is vital for an improved interpretation of the paleotemperature record. At site MD97 2121 the relationship between alkenone and Mg/Ca *G. bulloides* derived paleotemperatures changed over the last 25 ka. Glacial temperature estimate offsets of *ca.* 3-7 °C are all but eliminated during the Holocene, suggesting that the planktic species' ecology and the local hydrology changed. We suggest the organisms' season of maximum productivity, and thus the annual timing of the temperature records, changed between glacial-interglacial periods. This was in response to variations in surface water conditions with SAW dominating the region during the glacial period and STW during the Holocene. Glacial-Holocene environmental changes such as wind and light conditions also altered surface water stratification and insolation levels. As a consequence of the change in the environmental conditions and changes in the surface waters, alkenone production at MD97 2121 shifted from glacial-summer to Holocene-annual and *G. bulloides* from glacial-spring to Holocene-annual productivity peak. For surface dwelling coccolithophore, changes to the season of maximum production had a significant impact on the associated paleotemperature record, offsetting glacial temperature estimates toward warmer values and dampening the apparent glacial-interglacial temperature change. However, *G. bulloides* is a sub-surface species and thus the (limited) effect of seasonality productivity

changes on the paleotemperature records was unable to be resolved within the errors associated with Mg/Ca paleothermometry, and therefore more likely affected by regional upwelling. The findings of the study suggest that paleotemperature records from regions where a change in surface water mass are likely to have occurred between glacial-interglacial periods should be carefully assessed.

Auxiliary Information

AI 1.0. Difference in alkenone based temperature estimates from 25ka-present at MD97 2121-blue and MD97 2120-grey using two different temperature calibrations.

C4-AI. Fig. 1. Difference in alkenone based temperature estimates from 25ka-present at MD97 2121-blue (Pahnke and Sachs, 2006) and MD97 2120-grey (Sachs et al., 2003) using two different temperature calibrations. The global derived Prahll et al. (1988) is indicated by the dashed line and regionally derived Sikes and Volkman (1993) by the solid line. Note, the calibration error of ± 1.5 °C is only exceeded at MD97 2121 during the glacial period, with a mean offset 1.7 °C towards cooler temperatures using the Prahll et al. (1988) calibration.

AI 2.0. Total number of *Gephyrocapsa* spp. and *E. huxleyi* identified in SEM images.

	Glacial			Termination (ACR)		Interglacial	
	Depth (m)						
	9.01-9.02	7.21-7.22	6.10-6.11	5.60-5.61	5.04-5.05	3.79-3.80	2.10-2.11
	Age (ka)						
	Species	24.3	20.0	17.2	15.5	13.7	10.5
<i>Coccolithus palagicus</i>	9	4	7	17	15	7	1
<i>Calcidiscus leptoporus</i>	25	13	12	7		1	8
<i>Gephyrocapsa</i> spp.	22	27	43	37	5	19	1
<i>Emiliana huxleyi</i>	24	9	19			9	1
<i>Umbilicosphaera</i>	1	2	4	1			
<i>Helicosphaera carteri</i>		1		1	1	1	
<i>Oolithotus antillarum</i>				1			
Total identified	81	56	85	64	21	37	11

C4-AI. Fig. 2. Total number of *Gephyrocapsa* spp. and *E. huxleyi* identified in SEM images of MD97 2121 samples.

AI 2.0. Core X-Ray imaging

X-radiographs of longitudinally split sediment cores, approximately 5.75 cm max thickness, were made using a Varian PaxScan 4030E flat panel digital imaging system and an Ecotron EPX-F2800 portable veterinary X-ray generator at NIWA, Wellington (C4-AI. Fig. 3). Exposures were compensated on the core edges by placing the half-core into a milled PVC cradle, ensuring consistent cross-sectional thickness. Exposure, grey-level mapping and window/level were controlled via proprietary Varian software (ViVA 2.0, Revision L.04), and typical energy settings for this study were [60] kV and [20] mA. The X-radiographs are displayed herein as negatives; low densities in dark shades and the highest density as white, and the area outside the core of zero density as black.

X-ray images help identify features from density differences, which cannot be seen by visual examination. In addition, these images help identify bioturbation structures especially where different lithologies are involved, e.g. if a burrow fill is different from the ambient sediment. Where the core appears featureless, this may indicate that only one lithology is dominant, or there has been significant bioturbation which has homogenised the sediment (e.g. Pouderoux et al., 2012).

(A) **C4-AI. Fig. 3.** MD97 2121 core x-ray images from (A) 7.3-7.1 m, covering the 7.2-7.21 m or 20.0 ka interval, (B) 9.0-9.2 m, covering the 9.01-9.02 m or 24.3 ka interval. X-ray images of the MD97 2121 sediment core were largely featureless possibly reflecting limited bioturbation and the high volume of terrigenous material deposited at this site (Carter et al., 2002). However, two sections from 20.0 and 24.3 ka had visible burrows.

(B)

Chapter 5

WEIGHING IN: ARE SIZE-NORMALISED FORAMINIFERA WEIGHTS A PROXY FOR SURFACE WATER CARBONATE ION CONCENTRATIONS?

Marr, J. P., H. C. Bostock, L. Carter and E. Smith, in review. Weighing in: are size-normalised foraminifera weights a proxy for surface water carbonate ion concentrations? *Marine Micropaleontology*.

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Abstract

Studies in the North Atlantic have suggested that higher calcium carbonate ion concentrations ($[\text{CO}_3^{=}]$) are the primary cause of increased calcification of the planktic foraminifer, *Globigerina bulloides*. However, *G. bulloides* in the Southern Ocean calcify heavier shells, in a region which has low surface water $[\text{CO}_3^{=}]$ relative to the North Atlantic. Such ocean differences have been largely overlooked. Here we assess differences in calcification, as expressed by shell size normalised weight (SNW), of modern *G. bulloides* shells from five ocean regions. Comparison of trends between different modern water masses showed no consistent relationship between any single environmental factor and shell calcification. Instead linear models suggest that SNW responds to an “ocean effect,” that is a combination of various environmental variables such as temperature, nutrients, or $[\text{CO}_3^{=}]$. The differences between the oceans/regions appear to be consistent with previously identified spatial patterns of genetic variability. Comparison of environmental proxy and SNW data from the last glacial maximum to the Holocene from the North Atlantic and SW Pacific Oceans confirms that at mid-latitudes, regardless of ocean region, *G. bulloides* shell SNW increased during the glacial period. We suggest that this may reflect multiple factors including increased surface

ocean [$\text{CO}_3^{=}$], possibly combined with changes in primary productivity. There is no apparent relationship in the SW Pacific between *G. bulloides* SNW and down core productivity or *G. bulloides* abundance. We conclude that calcification of *G. bulloides* appears to be region specific; therefore, proxy calibrations based on shell SNW for one ocean will not be applicable to other settings.

1.0 Introduction

Carbonate-bearing marine organisms play a critical role in the global carbon cycle, transferring carbon dioxide from the atmosphere and depositing it as calcium carbonate (CaCO_3) on the sea floor (Archer and Maier-Reimer, 1994; Broecker and Clark, 2002; Milliman, 1993). A significant reduction in this carbon removal mechanism through ocean acidification and reduced shell calcification would likely have a large impact on the global carbon cycle. However, to strengthen the link between atmospheric carbon dioxide levels and shell calcification requires a greater understanding of the controls of modern calcification in order to interpret changes in the past (Caldeira and Wickett, 2003). The notion that surface water carbonate ion concentration ($[\text{CO}_3^{=}]$) controls planktic foraminiferal shell weight, derives from the idea that additional ions in the surface water are likely to reduce the energy required for, and thus increase the rate of calcification (Barker and Elderfield, 2002; Lohmann, 1995).

Previous studies have generally focused either on a single oceanic region, weighing and measuring *G. bulloides* shells on samples derived from core-top, down core, sediment trap, plankton tow, or on laboratory cultured material. They have then linked the shell weight or size normalised weight (SNW) to changes in a variety of environmental variables including, species optimal environment (e.g. de Villiers, 2004; Hecht, 1976), temperature (e.g. Lombard et al., 2009), $[\text{CO}_3^{=}]$ (e.g. Barker and Elderfield, 2002; Spero et al., 1997) and nutrient concentration (Aldridge et al., 2012).

In this study we combine previously published data from 5 different ocean regions to see if any one environmental variable can explain the changes in SNW. We then compare down core data from the North Atlantic (Barker et al., 2002) and SW Pacific to see if past changes can provide more information about what causes the changes in SNW.

2.0 Background

2.1 *G. bulloides*

Globigerina bulloides is generally described as most productive at warmer temperatures (10–18°C) with higher salinity, and lower nutrient levels (Bé, 1977; Bé and Hutson, 1977; Hemleben et al., 1989). It is also associated with weak and shallow thermocline environments with highest faunal abundances in subtropical waters (Bé, 1977; Bé and Hutson, 1977; Hemleben et al., 1989). This species has no symbiotic algae, being a heterotroph that feeds off phyto- and other zooplankton (Hemleben et al., 1989).

2.2 Shell calcification

In foraminifera, the shell's function is to protect the organism, and in the case of spinose species, such as *G. bulloides*, the shell also serves as base for the spines (Erez, 2003). The spines then allow for the construction of a wide pseudopodial “spider web” to help catch algal prey, move, build their shell, respire and extract waste (Hemleben et al., 1989). Thus, maintenance of these networks is especially critical for planktic species such as *G. bulloides* which dwells in turbulent, shallow water (ter Kuile and Erez, 1984).

There is a large discrepancy between $[\text{Ca}^{2+}]$ and $[\text{CO}_3^{=}]$, in seawater. In the modern ocean $[\text{Ca}^{2+}]$ is between 10 and 11 mM while $[\text{CO}_3^{=}]$ is only 100–300 μM , *ca.* 50 times lower than $[\text{Ca}^{2+}]$ (Tyrrell and Zeebe, 2004). Thus, it is $[\text{CO}_3^{=}]$ and not $[\text{Ca}^{2+}]$ which is the limiting factor for CaCO_3 precipitation (Erez, 2003). Foraminifera also raise their internal pH to *ca.* 8.5 to 9 to increase the internal $[\text{CO}_3^{=}]$ levels (de Nooijer et al., 2009; Erez, 2003). This provides enough $[\text{CO}_3^{=}]$ to match the amount of $[\text{Ca}^{2+}]$ in the seawater vacuoles.

2.3 Regional SW Pacific setting

The giant piston core, MD97 2121, was recovered off the east coast of New Zealand, in the SW Pacific Ocean (40°22.935'S, 177°59.68'E) from a water depth of 2314 m (Carter et al., 2002; Carter et al., 2008) (Fig. 34). The modern site is overlain by warm, saline, micronutrient-rich, macronutrient-poor subtropical surface waters (STW) (Boyd et al., 1999; Ellwood et al., 2008; Frew et al., 2001; Locarnini et al., 2006). During the LGM, cold, less saline, micronutrient-poor, macronutrient-rich subantarctic water (SAW) from the south (Boyd et al., 1999; Ellwood et al., 2008; Frew et al., 2001; Locarnini et al., 2006) flowed north over the core site (Marr et al., in press-b; Nelson et al., 2000).

Figure 34. Global (a) location map of core-top, plankton tow, sediment trap and down core locations referred to in this study. Regional maps are provided for sites used in linear regression models: (b) **North Atlantic:** Barker and Elderfield (2002b); Aldridge et al. (2012); (c) **Arabian Sea:** Beer et al. (2010b); (d) **SW Pacific:** this study and Marr et al. (2011); (e) **Southern Ocean:** Moy et al. (2009). Note, individual core site longitudes were not provided for South Atlantic sites, thus for illustrative purposes only core sites have been evenly spaced within the stated 14° range at their given latitudes (figures generated using Schlitzer, 2011). Stars indicate the location of down core sites referred to in text.

At 2314 m depth, the core site is situated above the modern day calcite saturation horizon which in the SW Pacific Ocean lies at 2800 m depth (Bostock et al., 2011). The site is bathed by low- $\delta^{13}\text{C}$, oxygen, macronutrient-rich North Pacific Deep Water (NPDW) (Broecker and Maier-Reimer, 1992; McCave et al., 2008). During the glacial period, MD97 2121 was bathed in upper Circumpolar Deep Water (UCDW) of similar origin and nutrient content to NPDW (Gordon, 1975; McCave et al., 2008). While the change in bottom water mass may potentially enhance post-depositional alteration at MD97 2121, there is little evidence by way of fragmentation indices to suggest that foraminifera preservation was adversely affected by the change in bottom water during the glacial (Northcote et al., 2007; Weaver et al., 1998).

3.0 Data and Methods

We combine the results from previous studies using core-top and plankton-tow data from the North Atlantic (Aldridge et al., 2012; Barker and Elderfield, 2002) and South Atlantic (de Villiers, 2004), Southern Ocean (Moy et al., 2009), SW Pacific Ocean (Marr et al., 2011) and Arabian Sea (Beer et al., 2010b), as well as culturing studies (Lombard et al., 2010; Lombard et al., 2009). The core-top, sediment trap and plankton tow data collated here cover a range of environmental gradients including mean annual sea-surface temperature (SST) ranges from *ca.* 5 to 28 °C (Locarnini et al., 2010), surface water $[\text{CO}_3^{2-}]$ from *ca.* 120 to 250 $\mu\text{mol/kg}$, nutrient phosphate and nitrate concentrations from *ca.* 0.1-2.3 $\mu\text{mol/L}$ and 0.01-18 $\mu\text{mol/L}$ respectively (Garcia et al., 2010), and six of the seven genotypes (genetic variations within the same species) recognised for *G. bulloides* by Darling and Wade (2008).

New down core *G. bulloides* SNW data were generated from core MD97 2121 for the last 25 ka. Systematic samplings at *ca.* 12 cm intervals of the upper 9.15 m of the core were made. Measured shell weights, and lengths (diameter) for the planktonic foraminiferal species *G. bulloides* were determined for all samples. The species *G. bulloides* was selected as it was

continuously present throughout the Late Pleistocene and thus able to be compared to previous core-top, plankton tow and down core studies in other regions (e.g. Aldridge et al., 2012; Barker and Elderfield, 2002; de Villiers, 2004). Shell-weight values presented for MD97 2121 represent the mean specimen weight based on a sample size of 10-32 specimens from a size range of 250-400 μm , avoiding ones with kummerform chambers. All foraminiferal shells were cleaned to removing loosely adhering clay and other detrital material via 2–3 ultrasonication rinses for 2–3 s in $>18.2\text{ M}\Omega$ ultra-clean water, followed by two AR-grade methanol rinses. Samples were subsequently examined under a binocular microscope and any individuals with visible adhering material were treated to a further one or two ultrasonic cycles in $\text{M}\Omega$ ultra-clean water. Foraminifera were then dried in an oven at 40°C for 24 hr. Any shells broken during the cleaning process were discarded. Shells were then batch weighed using a Mettler Toledo (MX/UMX 2) ultramicro-balance (precision= $0.1\text{ }\mu\text{g}$). Analytical uncertainty on these weight measurements is $< \pm 5\%$ (2 sd relative) based upon 15 replicate measurements of a single *G. bulloides* shell weighing $8.7\text{ }\mu\text{g}$. Foraminifera lengths were then individually measured prior to laser ablation using the laser ablation systems optical microscopy.

The same foraminifera samples used for weighing were analysed for their Mg/Ca values using a New Wave deep-UV (193 nm) solid-state laser ablation system coupled to an Agilent 7500CS ICP-MS at Victoria University of Wellington. The anti-penultimate (*f*-2) chamber of *G. bulloides* was analysed as chamber *f*-2 generally shows better within-chamber reproducibility than older *f*-3 or younger *f*-1 chambers (Marr et al., 2011; Marr et al., in press-a).

3.1 Size normalisation

Shell weights used in this study were normalised to shell size (maximum diameter) so that the results may be compared between ocean regions. Previously it has been shown that the use of shell area or length does not make a significant difference to normalisation data with an r^2 correlation of >0.95 (Aldridge et al., 2012; Barker, 2002b; Beer et al., 2010a; Beer et al., 2010b). However, the method of shell weight ‘size normalisation’ has varied between studies, typically concluding with multiplication of the final value by an arbitrary amount, normally the average shell size of a number of foraminifera from the region (e.g. Aldridge et al., 2012; Barker, 2002b). In addition, some studies which measured shell weights elected not to

measure shell size, instead choosing to confine sample selection to a narrow sieved size range instead (e.g. Moy et al., 2009). Issues associated with sieving foraminifera are fully discussed in Beer et al. (2010a), with the primary problem being that sieving alone does not always guarantee a narrow size range due to the irregular shape of the foraminifera.

In cases where measured shell lengths are not available, the sieved size range midpoint has been used for size normalisation so the data may be compared to other sites. As the samples used in this study were from a number of regions, and data for foraminiferal surface area not available for all samples, the simplest approach to size normalisation has been applied. Shell weight measured in micrograms was divided by the shell length or midpoint of the sieved size range measured in microns and the final result given in g/m. SW Pacific individual core top weight and length measurements of *G. bulloides* from STW (n=13) and SAW (n=18) samples indicate that the 95% confidence intervals for a sample weight/length measurements based on the mean values are: 0.020 g/m $\pm$ 0.003 g/m (STW), or 0.045 g/m $\pm$ 0.007 g/m (SAW).

3.2 Modern oceanographic data

Core-top temperature and nutrient data were obtained from the World Ocean Atlas, 2009 (Garcia et al., 2010; Locarnini et al., 2010). Annual mean data from 60 m depth was used as *G. bulloides* is a subsurface species, and seasonality effects at this depth are limited (e.g. Kuroyanagi and Kawahata, 2004; Wilke et al., 2009a). Sixty meters water depth is also within the range of plankton tow depths for samples presented here and thus depth of measured environmental values (Aldridge et al., 2012; Beer et al., 2010b). However, it should be noted plankton tow environmental variable values will only provide a ‘snapshot’ of conditions at the time of the tow. These values depend on the season and ocean hydrology in the days immediately preceding data collection. As the *G. bulloides* lifecycle is at least one month long (Hemleben et al., 1989) these measurements provide a limited impression of sample growth conditions. Thus, an offset between ‘instantaneous’ measured plankton tow values from the annual averages calculated for core-top values are expected.

Core-top carbonate ion values are derived from Global Ocean Data Analysis Project (GLODAP) and CLIVAR databases. Barker and Elderfield (2002) had previously converted this data to preindustrial values. However, we have avoided this approach due to the number

of assumptions required, including the need to estimate anthropogenic CO₂ contribution according to the region and water depth. The difference between post- and pre-industrial values is on the order of *ca.* 20 to 50 µmol/kg decrease in [CO₃²⁻] depending on a number of oceanographic factors including regional surface water temperature, hydrology and productivity. Therefore, direct comparison between [CO₃²⁻] in the pre-industrial oceans is not possible where the difference in concentration is less than 50 µmol/kg. Chlorophyll-*a* data is derived from the Giovanni NASA online database (Acker and Leptoukh, 2007). As depth stratified chlorophyll-*a* data are sparse, surface ocean measurements have been used. Longitudes for South Atlantic core sites were not able to be sourced, however core-tops were identified as spanning a 14° longitudinal range (de Villiers, 2004). Therefore only the information previously presented in de Villiers (2004) is presented here including: temperature, [CO₃²⁻] and latitude oceanographic data, limiting its use for inter-ocean comparison. All hydrographic information for the sites discussed is listed in the auxiliary material (AI. 1).

3.3 Regression of SNW against environmental variables and temperature

Simple linear regression between SNW and one environmental variable were initially undertaken to assess any common trends within ocean regions (Fig. 35). Subsequently, multiple linear regression models were constructed using more than one environmental variable. The latter included the observed data for five environmental variables, and also an “ocean effect”, described below. SW Pacific data are presented two ways; firstly as a combined regional dataset for simple regressions, and secondly by dividing sites by the dominant water mass, and thus presenting the information in a similar way to other regions a single dominant surface water mass.

This has the effect of creating two SW Pacific ‘oceans’ denoted as SW Pacific – Subantarctic waters (SAW) and SW Pacific – Subtropical waters (STW). Plankton tow data have also been treated separately to core-top data. Thus, North Atlantic core-top and plankton tow data have been divided to form two North Atlantic ‘oceans’ denoted North Atlantic – plankton tow (P) and North Atlantic – core-top (C). Arabian Sea data which were also included as an ‘ocean’ was derived from plankton tow material. This gives a total of six modelled ‘oceans’, excluding the South Atlantic and Gulf of Mexico for which limited datasets were available.

Figure 35. *G. bulloides* SNW-environmental variable comparison between water mass: North Atlantic core-top-dark blue (Barker and Elderfield, 2002) and plankton tow-light blue (Aldridge et al., 2012); South Atlantic-dark blue (de Villiers, 2004); SW Pacific-red (Marr et al., 2011), note: SW Pacific (STW) sites are in filled with a lighter red colour, while results from site R623 are unfilled as it has not been included in the water mass specific relationships due to its location within the subtropical front, SAW dark red in-filled triangle with a black outline; Southern Ocean-green (Moy et al., 2009); Arabian Sea-purple (Beer et al., 2010b) locations.

Within panel (a): Vertical grey lines indicate species ecological niches as calculated from *G. bulloides* relative sedimentary abundances by latitude, dark grey (> 20%), medium grey (10-20%), light grey (5-10%), white (< 5%) (from Bé, 1977). Ecological preferences as indicated by dashed vertical black lines with species genotypes written in grey after Darling and Wade (2008). Latitudes of down core sites from NEAP 8K-Barker and Elderfield (2002), MD97 2121-this study, and GC17-Moy et al. (2009) are indicated by red crosses..

Panels (b-e): *G. bulloides* shell SNWs plotted against (b) temperature; (c) $[\text{CO}_3^{2-}]$; (d) phosphate; (e) chlorophyll-*a* data, see in text for details regarding data acquisition and AI. 1 for data sources. Black lines within panels (b)-(e) indicate data linear regressions with r^2 values given in Table 4.

Here we use the term “ocean effect” to describe where data has been grouped by water mass or “ocean” and pre- or post-industrial age. Grouped by ‘ocean’, the data reflect a combination of factors which contribute to a specific ocean environment which may, or may not, be measured here, including seasonality, terrestrial input, regional hydrology and any anthropogenic changes. The term ‘environmental variable’ is used to describe different ocean parameters used for the multiple linear regression model for example; temperature, $[\text{CO}_3^{2-}]$, concentration of nutrients phosphate and nitrate, and chlorophyll-*a* concentration.

The linear models are in the form:

$$y = X \beta$$

where y is the pooled vector of SNW for the six oceans, X is the model matrix of dimensions (number of data) $\times$ (number of parameters) and β is the vector of parameters to be solved.

For a simple regression of SNW against one environmental variable, X would have the structure that the first column would be all 1, and the second would be the observed values of the variable. The two components of β are then the intercept ($\beta(1)$) and slope ($\beta(2)$) of the regression.

The following is the set of models considered.

- 1) Multiple regression of SNW on all five measurement variables (β comprises five slope parameters plus a constant);
- 2) An “ocean effect” only model, being a separate constant for each ocean without additional variables (β comprises six parameters);

- 3) An “ocean effect” plus measurement variables model, being a separate constant for each ocean plus a slope parameter for each measurement variable (β comprises six ocean parameters plus five slope parameters);
- 4) Five models consisting of a separate parameter for each ocean plus one slope parameter for each measurement variable in turn (β comprises six ocean parameters plus one slope parameter);

Each model was solved by least squares, in which all SNW data had the same weight and no allowance was made for the covariance between the measurement variables. The *relative regression parameters* have been obtained by subtracting the column means (X and y=SNW), from that column and then dividing by the column standard deviation. This has the effect of shifting the origin for the variable (subtracted mean) in the model and rescaling the variables to make them of comparable size (in the approximate range -2 to 2), but not changing the relationship between variables. This re-scaling enables the relative contributions of the different environmental variables to be compared visually. After rescaling, the null model is zero, so the significance of each individual parameter can be assessed according to whether its 95% confidence interval includes zero. For example, if the environmental parameter crosses the null model or zero line then this indicates that it has no significant contribution to shell SNW changes. The results, discussed below, show that the “ocean effect” is dominant. We conclude that alternative approaches to least squares, such as canonical correlation analysis (Hair et al., 2005) will not be successful unless an “ocean effect” is included, and so has not been attempted.

4.0 Results

4.1 Modern ocean

4.1.1 Inter-ocean parameter comparison

Firstly, environmental and temperature data were correlated, as shown in Table 3a. From this it is clear that the different environmental variables are moderate-highly correlated (Table 3a). This indicates that these variables are not independent, and thus highlights the difficulty in isolating the effect of any single variable on shell SNW.

In addition, this relationship becomes distinctly stronger if the ‘ocean’ environmental variable mean value is subtracted (Table 3b). This is evidence for what we have termed the “ocean effect”.

(a)	Temperature	Phosphate	Nitrate	Carbonate ion	Chlorophyll- <i>a</i>
Temperature	1	-0.44	-0.77	0.36	0.17
Phosphate	-0.44	1	0.79	-0.52	-0.10
Nitrate	-0.77	0.79	1	-0.64	-0.02
Carbonate ion	0.36	-0.52	-0.64	1	0.05
Chlorophyll- <i>a</i>	0.17	-0.10	-0.02	0.05	1
(b)	Temperature	Phosphate	Nitrate	Carbonate ion	Chlorophyll- <i>a</i>
Temperature	1	-0.75	-0.91	0.90	-0.32
Phosphate	-0.75	1	0.83	-0.68	0.20
Nitrate	-0.91	0.83	1	-0.89	0.33
Carbonate ion	0.90	-0.68	-0.89	1	-0.39
Chlorophyll- <i>a</i>	-0.32	0.20	0.33	-0.39	1

Table 3. Environmental variable correlation coefficients from linear regressions shown to illustrate the close relationship between environmental data. Negative values indicate a negative correlation between variables. A: original data; B: with ‘ocean’ environmental variable mean value subtracted. Note, the relationship becomes distinctly stronger after the ‘ocean’ mean value is subtracted.

4.1.2 Shell SNW and environmental variables

To further illustrate the difficulty in isolating the influence of a single environmental control on shell SNW, a series of SNW-environmental variable relationships have been calculated (Fig. 35, Table 4). From this it is clear that no single parameter appears to consistently co-vary with shell SNW between ocean regions. For example, the Southern and SW Pacific (SAW) have the inverse relationship between temperature and nutrient concentrations and SNW relative to the other oceans (Table 4). The strengths of global SNW-surface ocean linear relationships were not improved by exclusion of the two plankton tow data sets from the North Atlantic and Arabian Sea which may have been affected by anthropogenic changes and thus offset from core top sample values (Fig. 35).

	North Atlantic (C)	North Atlantic (P)	South Atlantic	Southwest Pacific	Southwest Pacific (STW)	Southwest Pacific (SAW)	Southern Ocean	Arabian Sea
Temperature	0.69	0.44	0.79	0.81	0.55	-0.71	-0.08	0.18
Phosphate	-0.65	-0.61	n/a	0.62	0.00	0.88	0.11	0.00
Nitrate	-0.68	-0.42	n/a	0.71	-0.80	0.93	0.07	-0.20
Carbonate ion	0.73	0.33	0.59	-0.74	-0.31	0.53	-0.08	0.16
Chlorophyll- <i>a</i>	-0.60	0.11	n/a	0.00	-0.34	-0.93	-0.12	-0.18

Table 4. Correlation coefficient table of single environmental variables with *G. bulloides* shell SNW. SW Pacific STW includes core-tops: P71, P81, S793, P69, S938 and SAW includes core-tops: Q220, F111, D178 and B32. Negative values indicate a negative correlation between variables.

Model results for the relative regression parameters and their 95% confidence intervals are shown in Figure 3a and Table 4. Multi-parameter models have been used in two different ways, firstly to look at the five environmental variables in isolation which are then compared to the “ocean effect” (Fig. 36a). Secondly, the “ocean effect” has been combined with a single environmental variable (Fig. 36b). The r^2 values for each of these models are given in Table 4. Based on the models, the following are evident: 1) the contribution of the “ocean effect” is much larger than the environmental variables, in all models which include them (Fig. 36a) and r^2 is distinctly better for models that include the “ocean effect” ($r^2 > 0.9$ compared to a maximum of 0.75 for environmental variables only).

Figure 36. An illustration of the relative environmental and ‘ocean’ significance in controlling shell SNW, as determined by multiple linear regression modelling. The relative distance from the 0-fit line indicates the relative influence of the variable on shell SNW. Model results have been separated into ocean and environmental variable categories. The apparent ocean influence or “ocean effect” is significantly larger than that of the environmental variables, highlighting its importance in determining *G. bulloides* shell SNW. In addition, the model fit is little improved with addition of the environmental variables and model error is increased. Model r^2 values are given in Table 5. Error bars indicate 95% confidence intervals for the regression values.

Model	r^2 value
Five environmental variables only	0.75
Six 'oceans' only	0.91
Six 'oceans' & five environmental variables	0.92
Six 'oceans' & temperature	0.918
Six 'oceans' & phosphate	0.914
Six 'oceans' & nitrate	0.916
Six 'oceans' & carbonate ion	0.911
Six 'oceans' & chlorophyll- <i>a</i>	0.923

Table 5. The r^2 values for models illustrated in Figure 36 with addition values for model + a single environmental variable to indicate how well change in environmental conditions are able to explain the *G. bulloides* shell SNWs.

Generally, there is very little difference between the modelled significance of different environmental variable estimates (Fig. 36). This suggests that these estimates are stable and not model dependent. Inclusion of some, or all parameters, produces an insignificant improvement in r^2 compared to the “ocean effect” only model ($r^2 = 0.911$ to 0.923 compared to 0.909 for ocean effects only). Large error-bars for the six ‘oceans’ plus five environmental variables arise from the close variable correlation (Fig. 36b). This has the effect of inflating the covariance matrix even though the root-mean-square residual is reduced. Thus, inclusion of all environmental variables is statistically no better than a model which includes only the best single variable (chlorophyll-*a*), a conclusion confirmed by the r^2 values (Table 4).

Therefore, it appears that the SNW values of *G. bulloides* are dominated by an effect which is ‘ocean’ specific.

4.2 Paleoceanography

Shell SNW of *G. bulloides* from 25 ka to present in MD97 2121 (Fig. 37; AI. 2) range from 4 to 20 μg and length between 263 to 434 μm . Shell SNW is highest during the last glacial and early termination period, peaking twice at *ca.* 22.0 and 14.5 ka respectively before a decrease in size of *ca.* 50% by the early Holocene at *ca.* 11.0 ka. Heavier weights during the glacial period relative to the interglacial are also seen at other sites including the Southern Ocean (29.3 (glacial) vs. 24.7 (interglacial) μg) (Moy et al., 2009), Indian Ocean (13 vs. 6 μg) (Naik et al., 2010) and North Atlantic (20 vs. 11 μg) (Barker and Elderfield, 2002). Previous studies using modern core-tops from the SW Pacific region suggested that foraminifera weights may be strongly linked to SSTs (Marr et al., 2011), with cooler temperatures predicted to produce heavier shell weights during the glacial period. MD97 2121 *G. bulloides* SNWs have a good relationship ($r^2 = 0.58$) with temperature, significantly greater than the $r^2 = 0.10$ in the North Atlantic. However, *G. bulloides* SNW from the SW Pacific Ocean are consistently lower than those from the North Atlantic for the same temperature range (Fig. 38). Shell SNW in the SW Pacific decreases by *ca.* 0.002 $\text{m/g/}^\circ\text{C}$, significantly less than the 0.015 $\text{m/g/}^\circ\text{C}$ which occurs between the LGM and Holocene in the North Atlantic (Barker and Elderfield, 2002).

There is little relationship between shell SNW and Zn/Ca (representative of nutrients; Marr et al., submitted) or *G. bulloides* abundance (Fig. 37f). A weak relationship between *G. bulloides* SNW and foraminiferal fragmentation index at the SW Pacific core site is present (Fig. 37d), indicating that while dissolution may have occurred it was not the major factor controlling shell weight (Northcote et al., 2007). Moreover, scanning electron micrograph (SEM) imaging of foraminifera down core did not identify any changes consistent with dissolution. SEM images also did not show any calcite overgrowths and thus we do not believe that that post-depositional alteration has added or reduced mass to foraminiferal shells in the MD97 2121 record (Marr et al., in press-b). There is also no apparent relationship between *G. bulloides* SNW and biosiliceous or carbonate mass accumulation rates at MD97 2121 (Fig. 37e; AI. 3) (Carter and Manighetti, 2006).

Figure 37. Summary of *G. bulloides* data from SW Pacific core site, MD97 2121 from 25 ka-present. SNW data is indicate in red, and compared to; (a) temperature, (b) Zn/Ca derived using *G. bulloides* chamber *f*-2 trace metal values (see Marr et al., in press-b), (c) $\delta^{18}\text{O}$ (Carter et al., 2008), (d) faunal fragmentation (Northcote et al., 2007), (e) carbonate mass accumulation rate (Carter and Manighetti, 2006), and (f) *G. bulloides* abundance (Northcote et al., 2007). Note, individual geochemical and SNW measurements are shown as dots, while the solid line indicates the three point moving mean shown for trend comparison. Antarctic cold reversal (ACR) is indicated by the blue bar.

5.0 Discussion

Surface water conditions, which may lead to optimal *G. bulloides* growth, have been discussed extensively (e.g. Barker and Elderfield, 2002; Gonzalez-Mora et al., 2008; Kucera, 2007; Moy et al., 2009). Yet, there is still no agreement on what controls the shell weight of modern tests in different ocean regions (Fig. 35). The foraminifers' location, e.g. the water mass from which it hails, is likely to dictate its shell weight. However, what environmental variable(s) cause changes within water masses remains unclear (Fig. 36). In addition, *G. bulloides* shell SNW generally increases from the last glacial period to Holocene independent of ocean location, despite the records at MD97 2121 being punctuated by a brief mid-Holocene period of shell SNW lightening (Fig. 38). This suggests that there is an environmental variable which changes over a glacial-interglacial cycle which universally affects calcification (Fig. 38) (e.g. Barker and Elderfield, 2002; Gonzalez-Mora et al., 2008).

Development of a *G. bulloides* SNW proxy for an oceanic variable(s) is desirable as shell weight and size measurements are arguably easier to obtain than geochemical proxy data. However, significant changes in regional shell development may preclude the use of this proxy in certain water masses, or demand basin-specific calibrations. In the first part of the discussion we evaluate each of the leading theories on *G. bulloides* shell calcification against the modern environmental variables. Secondly, these findings are compared with data from high resolution cores from the North Atlantic and SW Pacific Ocean for the last 25 ka to ascertain if a single parameter can be identified as a control of *G. bulloides* SNW over glacial/interglacial timescales (Fig. 38) (Barker, 2002b; Kucera, 2007; Moy et al., 2009).

Figure 38. Comparison between *G. bulloides* North Atlantic NEAP 8K (Barker and Elderfield, 2002) (*blue*) and SW Pacific MD97 2121 (Marr et al., 2011) (*red*); temperature, oxygen isotopes and SNW (*purple*) values.

Temperature values (a,c) were derived from *G. bulloides* Mg/Ca values and converted to temperature using the calibration from Marr et al., (2011). Oxygen isotope values (b,d) are from Barker and Elderfield (2002) -North Atlantic and Carter et al. (2008) -SW Pacific. Note, individual geochemical and SNW measurements are shown as dots, while the solid line indicates the sample 3 point moving mean shown for trend for comparison.

5.1 Modern Observations

5.1.1 Optimal growth conditions

The theory of optimal growth conditions was proposed initially from down-core relationship between larger shell size during glacial periods, and has been used to explain modern and ancient changes in *G. bulloides* shell calcification (e.g. Hecht, 1976; Malmgren and Kennett, 1978). De Villiers (2004) noted that the heaviest planktic foraminifera weights occurred at the latitude of ‘optimal growth conditions’ as defined by the highest abundances of the particular species. In addition, higher *G. bulloides* abundances have been suggested as a productivity and upwelling indicator (e.g. Clemens et al., 1991; Clemens and Prell, 2003; Weaver et al., 1998). Modelling has also linked increased foraminiferal abundance to elevated shell growth (Lombard et al., 2011). However, while the modelled growth-abundance relationship was strong for symbiotic species like *Globigerinoides ruber* ($r^2=0.4$), the relationship for the asymbiotic *G. bulloides*, at $r^2=0.19$, is tenuous at best (Lombard et al., 2011). No single environmental variable has yet been isolated which reflects *G. bulloides* ‘optimal conditions’.

While modern North Atlantic SNWs plotted against *G. bulloides* abundance in core tops (Bé, 1977) indicate a possible relationship (Fig. 35a), this is not consistent for the Southern Hemisphere where heavier SNWs occur outside the latitudes of high abundance as defined by Bé (1977). Plankton tow samples from the North Atlantic also indicated a weak link between species abundance and shell SNW (Aldridge et al., 2012; Beer et al., 2010b). Therefore species abundance and/or ‘optimal conditions’ are unlikely to control *G. bulloides* SNW (Fig. 35a). However, elements of whatever comprises this species ‘optimal growth conditions’ are potentially incorporated into the “ocean effect” recognised here.

5.1.2 Temperature

Previously it was recognised that temperature may control shell size in planktonic foraminifera (Hecht, 1976; Malmgren and Kennett, 1976). Temperature is likely to be an important environmental factor in shell growth as foraminifera do not regulate their own temperature (Kooijman, 2000). Thus a change in temperature may affect foraminiferal feeding processes such as the speed of prey capture and digestion (Kooijman, 2000), which may in turn affect shell calcification. Recent computer modelling using temperature coupled with foraminiferal enzyme activity indicated that the simple combination of these factors could effectively model species growth patterns. Modelled and observed peak shell growth in the laboratory for *G. bulloides* occurred between *ca.* 23-27 °C (Lombard et al., 2009).

These temperatures of peak growth rate for *G. bulloides* fall within the temperature range of Arabian Sea plankton tow samples (Beer et al., 2010b). However, even though mean shell length (290-330 µm) was comparable with other samples presented here, Arabian Sea samples had significantly lower shell SNWs. In addition, these samples indicated little relationship between SNW and temperature (Table 4). Thus, while temperature may limit a species biogeographical range, within its biogeographical range temperature does not appear to be a primary control on *G. bulloides* shell SNW. Linear relationships between SNW-temperature indicate a normally positive relationship between the parameters including SW Pacific (STW). However, SW Pacific (SAW) and Southern Ocean samples indicate a weak negative relationship (Table 4, Fig. 35b). Coupled with the “ocean effect”, temperature alone produced an insignificant improvement to the modelled relationship (Table 5). This suggests that temperature may only co-vary with other controlling environmental factor(s).

5.1.3 Surface water carbonate ion concentration

Changing surface water [CO₃²⁻] between different water masses is illustrated in the North Atlantic-SW Pacific/Southern Ocean comparison (Fig. 39). Foraminifera use [CO₃²⁻] to construct their shell, therefore changes in surface water concentrations may have a direct impact on their calcification (e.g. Barker et al., 2003b; Spero et al., 1997). However, surface ocean [CO₃²⁻] varies as a function of temperature and atmospheric CO₂ levels, thus making it difficult to distinguish between the relative effects of those three variables (Lynch-Stieglitz et al., 1995).

North Atlantic core-top samples have a strong positive relationship between surface ocean $[\text{CO}_3^{=}]$ and shell SNW (Table 4, Fig. 35c) (Barker and Elderfield, 2002). In the SW Pacific, however, if (SAW) and (STW) samples are combined, shell SNW progressively decreases with increased surface ocean $[\text{CO}_3^{=}]$ concentrations (Table 4, Fig. 35c) (Marr et al., 2011). However, if SW Pacific (SAW) samples are isolated, these exhibit a weak negative relationship with $[\text{CO}_3^{=}]$ (Table 4). Inter-ocean comparison indicates that the heaviest *G. bulloides* SNWs occur in surface waters with the lowest $[\text{CO}_3^{=}]$ and lowest temperatures in the South Atlantic and Southern Ocean (Fig. 35c) (de Villiers, 2004; Moy et al., 2009). Coupled with the “ocean effect”, $[\text{CO}_3^{=}]$ did not significantly improve upon the “ocean effect” only fit (Table 5, Fig. 36). $[\text{CO}_3^{=}]$ therefore does not appear to be the primary control over modern shell size and/or weight globally, a finding consistent with *Orbulina universa* and *Globigerinoides sacculifer* laboratory results (Lombard et al., 2010).

All post-industrial *G. bulloides* SNWs derived from sediment trap and plankton tow samples, except that from the Southern Ocean (Moy et al., 2009), have SNWs at or below 0.02 g/m (Fig. 35). This is lower than 95 % of core-top sample SNWs measured. The Southern Ocean sediment trap sample is *ca.* 40 % lighter than mean Holocene weights from core tops in the same water mass (Fig. 35) (Moy et al., 2009). Low plankton tow SNWs may suggest that those specimens had not undergone the full foraminiferal lifecycle and therefore lacked calcification that may otherwise be associated with the core-top samples. However, Arabian Sea *G. bulloides* plankton net samples obtained from 2200 m water column depth did not suggest any significant change in SNW compared to samples from shallower depths (Beer, 2010). The cause of the reduced post-industrial calcification of *G. bulloides* is uncertain and does not appear to have a direct relationship with temperature or carbonate ion concentration. It may, instead, be associated with the modern response of the phytoplankton algal prey to environmental change (see below).

Figure 39. Surface water $[\text{CO}_3^{=}]$ in (a) the North Atlantic core-tops-*solid line* (Barker and Elderfield, 2002) and plankton tow samples-*dashed lines* (Aldridge et al., 2012), (b) SW Pacific core-top samples (Marr et al., 2011) and (c) Southern Ocean core-top-*solid lines* and sediment trap-*dashed line* samples (Moy et al., 2009). Colour scale indicates modern $[\text{CO}_3^{=}]$ in $\mu\text{mol/kg}$ (CLIVAR data set). Site line length corresponds to the deepest site at or above the calcite saturation horizon (CSH). Stars above core sites indicate locations where core falls below the CSH, the line length for these sites correspond to actual site depth. Sites which fell below the CSH were assessed in the original studies, however no signs of dissolution were indicated (Marr et al., 2011; Moy et al., 2009). Horizontal dashed line indicates regional calcite saturation horizons (Bostock et al., 2011). Figures constructed using Ocean Data View (Schlitzer, 2011).

5.1.4 Nutrients and chlorophyll-*a*

A change in nutrient concentration is unlikely to have a direct effect on *G. bulloides* as it is a predatory species of zooplankton (Hemleben et al., 1989). However, *G. bulloides* graze on phyto- and other zooplankton algae, which directly respond to changes in nutrient levels (e.g. Carpenter et al., 1985; Frew et al., 2001). As some sites are situated in the Southern Ocean, which is the largest high-nutrient low-chlorophyll (HNLC) region of the global ocean (Trull et al., 2001). As high nutrient levels do not necessarily reflect high productivity both nutrient and chlorophyll-*a* data are presented here.

North Atlantic sites have a negative relationship between phosphate, with *G. bulloides* shell SNW decreasing with increasing phosphate levels (Fig. 35d) (Aldridge et al., 2012; Barker and Elderfield, 2002). However, this is inconsistent with the other water masses: either there is no change in the case of Arabian Sea and SW Pacific (STW) (Beer et al., 2010b; Marr et al., 2011), or a positive relationship in the case of SW Pacific (SAW) and Southern Ocean (Fig. 35d) (Marr et al., 2011; Moy et al., 2009). The positive *G. bulloides* shell SNW-nutrient concentration relationship is consistent with faunal association data, which links higher *G. bulloides* abundance with nutrient-rich upwelling environments (e.g. deMenocal et al., 2000; Kipp, 1976; Weaver et al., 1997). However, at phosphate levels of 2.3 μmol , which is at least double those from the North Atlantic or SW Pacific, shells from the Gulf of California were still of comparable size/weight to the other locations, indicating that shell development in this water mass was not enhanced by the increased nutrient levels (Fig. 35d) (McConnell and Thunell, 2005). Addition of either nitrate or phosphate to the “ocean effects” model did not significantly improve the model fit (Table 5, Fig. 3). Therefore nutrient concentration does not appear to be a primary control over global *G. bulloides* shell SNW.

Planktonic foraminiferal shell calcification is dependent on feeding (Bé et al., 1982; Hemleben et al., 1989). An indicator of algal abundance, and thus *G. bulloides* food source is the concentration of surface water chlorophyll-*a*. Chlorophyll-*a* is the only environmental variable presented here which appears to have a relatively consistent, albeit very weak trend, with *G. bulloides* SNW across all the global water masses (Table 4, Fig. 35e). The weak relationship indicates that as chlorophyll-*a* decreases *G. bulloides* SNW shows a subtle increase (Fig. 35e). However, Southern Ocean samples are still offset to heavier SNW values.

Surface ocean chlorophyll-*a* concentration also had the best relationship in the “ocean effect” plus variable model (Fig. 36). The negative relationship between chlorophyll-*a* and *G. bulloides* shell SNWs is somewhat contradictory to the observation that the highest species abundance usually co-varies positively with elevated chlorophyll-*a* concentrations (Kuroyanagi and Kawahata, 2004; Schiebel et al., 2001). This re-affirms that shell SNW does not appear to reflect species abundance. It is possible however, that in response to less favourable conditions for growth, including low chlorophyll-*a* concentrations *G. bulloides* may slow shell growth. In effect this would increase the time available for calcite formation in the internal Calcite-pool (Anderson and Faber, 1984; Bentov and Erez, 2005), thereby increasing the amount of calcite available for chamber calcification.

5.1.5 Genotypes

There are at least seven *G. bulloides* genotypes (Darling and Wade, 2008; Kucera and Darling, 2002), suggesting that discrepancies between observed and modelled data for growth rates may originate from the species genetic diversity (Fig. 35a). Previous plankton tow, core-top, sediment trap and culturing studies have been generally based on specimens from a narrow range of locations (e.g. Aldridge et al., 2012; Lombard et al., 2009), or did not cover a wide range of inter-basin surface ocean conditions (e.g. Marr et al., 2011). Here we explore a new idea that a change in genotype, may have a significant effect on shell calcite and its geochemical composition. For example, *G. bulloides* calcifying in highly saline Mediterranean waters are known to incorporate trace metals differently to other locations (Ferguson et al., 2008) and have a distinctive *G. bulloides* genotype (Darling and Wade, 2008). While the geographical conditions, which lead to the formation of the Mediterranean surface water environment are limited, the possibility remains that other *G. bulloides* genotypes with distinct ecological preferences, e.g. Type-IIc, may change their latitudinal, biogeographic range as the prevailing environmental conditions vary.

Darling and Wade (2008) noted that while genotypes may occur together, there was a distinct difference in their ecologies. Of the seven *G. bulloides* genotypes types Type-IIa and -IIb are characterised as bipolar, subpolar species (Darling and Wade, 2008). However, Type-IIa had the highest abundance in cooler subpolar waters, blooming first in spring (Darling and Wade, 2008). Type-Ia was a unique subtropical water genotype present in both the Coral and Arabian Seas (Darling and Wade, 2008). Type IIc is unique to Antarctic waters (Darling and

Wade, 2008). Grouping *G. bulloides* samples by their genotypes may aid in explanation of the differences in SNW under relatively similar environmental conditions (Fig. 35a). Samples from the Southern Ocean (including SW Pacific (SAW)), which have much heavier SNW than the other water masses, fall within the regionally distinct Type-IIc boundaries, although the relative regional abundance of IIc compared to IIa or IIb is as yet unknown (Darling and Wade, 2008).

SW Pacific (STW) sites have some of the lightest shell modern core-top SNWs and appear distinctly offset from the geographically close SAW samples (Table 4, Fig. 35a). Darling and Wade (2008) genotype results suggest that this SW Pacific STW-SAW divide may be due to the presence of Type-Ia at STW sites, which is absent from SAW water. In addition, the SW Pacific STW SNWs are most similar to those from the Arabian Sea where this Type-Ia genotype has been previously identified (Fig. 35a). In the Southern Ocean, the *ca.* 3 sites north of the subtropical frontal zone tend towards lighter shell weights (Fig. 35). This may suggest the increased influence of other *G. bulloides* genotypes such as the subpolar/transitional Type IIa and IIb relative to Type IIc present in the circumpolar surface water masses, south of the subtropical frontal zone (Fig. 35a). The relative dominance of specific genotypes at any given site may aid in explanation of the large offsets between *G. bulloides* SNWs and the apparently strong “ocean effect” evident in the statistical modelling. However, it does not account for shell SNW variation within a specific genotype region (Fig. 35a) (Aldridge et al., 2012).

5.1.6 Ocean Effect

This work has identified an ocean effect on shell SNW not currently captured in these other environmental variables (Fig. 36). This “ocean effect” is most likely related to the different combination of environmental variables that exists within any one water mass (Table 3). Water mass specific SNW variation therefore may be a reflection of species’ environmental adaptations, which optimise shell development and other life cycle properties to ensure the species’ success in each region. This suggests that the “ocean effect” may actually reflect the evolutionary process evident in regional genetic variations (Fig. 35) (Darling and Wade, 2008). Based on the parameters measured here there does not appear to be any dominant environmental factor which causes the regional variation in weight (Fig. 36). The dominance of the “ocean effect” on *G. bulloides* shell calcification implies that any proxy calibrated to

modern surface ocean condition which utilises shell SNW is unlikely to be applicable outside the localised water mass.

5.2 LGM-Present

The primary cause(s) of modern geospatial shell SNW variation remains unresolved, potentially due to the wide distribution of sample sites and therefore the increased number of potential environmental influences. Thus, down-core samples taken from a single location where changes in surface water conditions are geographically constrained, may reduce the number of variables, and narrow the possibilities for that site or local region.

5.2.1 *Environmental forcing of species ecological optimum*

The down-core variance of *G. bulloides* shell size with SST has long been recognized, with use of the size-temperature relationship as a SST proxy first pioneered by Malmgren and Kennett (1978) following the work of Kennett (1976) and Hecht (1976). In this work the systematic shift in mean shell size of *G. bulloides* was linked to isotopically and faunally defined glacial stages (marine isotope stages (MIS) 2-8) that displayed a negative relationship between size and temperature. However, as the Indian Ocean core on which these findings were based was located north of the present-day *G. bulloides* ‘ecological optimum’ or *ca.* 50° latitude (Hecht, 1976), the possibility was raised that the change in shell size was merely an artefact of the species optimal growth conditions. During the glacial stages environmental forcing shifted the latitudinal range for optimal growth conditions northwards (Kucera, 2007; Schmidt et al., 2003), and closer to the Indian Ocean core site. Therefore by extension, if a core was analysed from a site located in waters within, or slightly cooler than, the ecological optimum, shell size should exhibit the opposite trend, decreasing in size during the glacial period.

Cores NEAP 8K and MD97 2121 provide an opportunity to test theories relating to the primary control over shell calcification with high resolution shell SNW weight, isotope and trace metal data available for *G. bulloides* from the LGM-present, in addition to regional core-top data to compare to (Fig. 34, 38) (Barker, 2002b; Carter et al., 2008; Marr et al., 2011; Marr et al., in press-b). North Atlantic core NEAP 8K at *ca.* 60°N is located within waters which are cooler, or outside, the *G. bulloides* preferred modern ‘ecological optimum’. At 40 °S, MD97 2121 is located in SW Pacific STW, which are within the modern ‘ecological

optimum' (Fig. 35a) (Bé, 1977). Therefore these two core sites should show the inverse shell SNW trends from the LGM to present with latitudinal migration of the species optimum conditions. However, in MD97 2121 and NEAP 8K *G. bulloides* shell SNWs are heavier during the glacial period relative to the Holocene (Fig. 38) (Barker and Elderfield, 2002). Further, *G. bulloides* from the Southern Ocean site GC17 at 47.5° S, which are significantly heavier under modern ocean conditions relative to other global locations, also increased shell weight during the last glacial period (Fig. 34,b38) (Moy et al., 2009). The *G. bulloides* abundance at MD97 2121 indicates that optimal conditions occurred immediately preceding the Antarctic Cold Reversal (Northcote et al., 2007); but there is no corresponding peak in shell SNW during this period (Fig. 37f, AI 3) (Northcote et al., 2007). The lack of correlation between *G. bulloides* abundance, carbonate or biosiliceous mass accumulation rates and test SNW indicates that the *G. bulloides* abundance, or SNW, of this species is not a reliable paleo-productivity indicator in this region (Fig. 37 e,f, AI. 3) (Carter and Manighetti, 2006; Northcote et al., 2007). These data agree with core-top and plankton tow studies, which show little relationship between optimal growth conditions and shell SNW in the SW Pacific (Marr et al., 2011), and therefore support previous findings which suggest that changes in 'ecological optimum conditions' are unlikely to be the cause of glacial shell SNW increase (Fig. 35) (Beer et al., 2010b).

5.2.2 SST and carbonate ion concentration

Temperature alone, as described by the Marr et al. (2011) SNW-temperature calibration, is unable to fully explain the glacial SNWs, with *ca.* 30% offset between those weights predicted from the down core Mg/Ca *G. bulloides* estimated temperatures (Marr et al., submitted). When other MD97 2121 proxy data are matched to shell SNW records, it also becomes immediately apparent that shell weights do not appear to be responding to surface water micronutrient/nutrient content as suggested by Zn/Ca (Marr et al., in press-b). Therefore, if it is not temperature or nutrient content which is the primary cause of increased shell calcification, other factors which are known to increase during the glacial period such as surface water $[\text{CO}_3^{=}]$ and primary productivity need to be investigated.

During glacial periods surface water $[\text{CO}_3^{=}]$ and pH were higher than the pre-industrial Holocene (e.g. Foster, 2008; Lynch-Stieglitz et al., 1995; Tyrrell and Zeebe, 2004). Glacial conditions may have assisted foraminifera in CaCO_3 formation by reducing the amount of

energy required to produce sufficient internal $[\text{CO}_3^{=}]$ concentrations to match the $[\text{Ca}^{2+}]$. Greater water turbulence is also been shown to increase test calcification, possibly to ensure the integrity of the spine network which is integral for this species survival (ter Kuile and Erez, 1984). As surface water turbulence is likely to have increased during the glacial period (e.g. Carter et al., 2008; Mulitza et al., 1997), this possibly also contributed to higher shell SNWs (Fig. 38). Elevated glacial primary productivity increased the *G. bulloides* food source (Hayward et al., 2012; Kumar et al., 1995; Sarnthein et al., 1988), reducing the energy needed for prey capture and increasing the energy able to be allocated to calcification.

In summary, during the glacial period colder, more turbulent surface waters may have increased the foraminifera's shell calcification requirements so that the spine network was maintained. The increased demand for calcification was made easier as there was higher surface water $[\text{CO}_3^{=}]$. Despite the negative relationship between increased food abundance and calcification in the modern ocean, during the glacial period the increased ease of prey capture may have actually provided the foraminifera with the additional energy required. This may then have enabled the foraminifera to create larger internal CaCO_3 -pools for shell calcification thus creating larger, heavier shells to be calcified regardless of the species genotype (Fig. 38).

6.0 Conclusions

These results suggest that there is an “ocean effect” not captured by the environmental variables, which may explain variations in SNW. We suggest that this “ocean effect” likely reflects *G. bulloides* genetic variations. However, this cannot account for the variations within the same water mass. Shell SNW appears to vary as a function of several environmental factors, including; temperature, surface water $[\text{CO}_3^{=}]$, nutrient concentrations, chlorophyll-*a* levels and genotype. As shell calcification tends towards heavier weights during the last glacial period, this study supports the theory that changes in foraminiferal shell weight are potentially related to changes in ambient $[\text{CO}_3^{=}]$, however changes in other environmental factors over glacial/interglacial cycles, such as food availability could also be significant. However, due to regional variation in shell calcification any modern proxy calibrations based on shell SNW are unlikely to be widely applicable. Modern (post-industrial) shell calcification is significantly lighter than Holocene samples from core-top

locations, even within the same genotype groupings. However, as there appears to be no consistent relationship between $[\text{CO}_3^-]$ and shell SNW, these post-industrial changes may reflect changes in foraminifera's food source and/or quantity. The quality and/or abundance of food may then in turn be affecting modern, post-industrial shell calcification.

Auxiliary Information

AI 1.0. Modern environmental, core-top and plankton tow data used in this study.

C5-AI. Table 1. Modern environmental, core-top and plankton tow data used in this study. Core top and sediment trap data: world ocean atlas (WOA)- temperature (Locarnini et al., 2010), nutrients (Garcia et al., 2010). Core-top and sediment trap carbonate ion values for SW Pacific and Southern Ocean core sites are derived from Global Ocean Data Analysis Project (GLODAP) and CLIVAR databases. Chlorophyll-*a* data is from the Giovanni NASA online database (Acker and Leptoukh, 2007) for all sites except R and T from Aldridge et al. (2012), due to their proximity to the coast. Unless otherwise stated, plankton tow data is that from the original Beer et al., (2010b) and Aldridge et al. (2012) papers, and North Atlantic pre-industrial core top carbonate ion values from Barker et al. (2003). South Atlantic temperature and carbonate ion values from de Villiers (2004).

Core ID	Depth	Location			Length (μm)	Weight (μg)	SNW (g/m)	Temperature ($^{\circ}\text{C}$)	WOA		Carbonate ion		
		Latitude ($^{\circ}$) ($^{\circ}\text{N}$)	Longitude ($^{\circ}$) ($^{\circ}\text{W}$)	Phosphate micromoles/l					Nitrate micromoles/l	Pre-industrial (μMkg^{-1})	Modern (μMkg^{-1})		
Barker et al., 2002 - core top													
T88 15B	2585	38.6	25.0	436		0.039	15.6	0.2	2.6	249			
T88 15aB	2738	38.9	25.0	445		0.043	15.6	0.2	2.6	249			
T88 14B	2858	40.4	25.8	449			15.0	0.6	6.3	245			
T90 12B	5085	40.6	20.1	422			14.7	0.2	3.3	246			
T86 9B	2026	40.8	27.5	420		0.043	15.4	0.3	2.9	244			
T86 8B	3232	42.3	25.7	435		0.040	14.6	0.3	3.7	241			
T88 13B	3133	42.9	25.3	462		0.044	14.6	0.3	3.7	240			
T86 7B	2664	43.9	25.0	398		0.033	14.2	0.3	4.0	238			
T90 13B	4016	44.0	20.0	437			13.8	0.3	4.7	237			
T88 12B	3052	44.1	24.9	448		0.038	14.2	0.3	4.4	238			
T90 11B	3208	45.0	24.7	449		0.036	14.2	0.3	4.4	236			
T88 11B	2741	45.4	25.4	447		0.032	13.7	0.4	4.6	235			
T90 5B	3069	46.0	23.8	439		0.030	13.5	0.4	5.0	234			
T90 8B	3393	46.2	23.7	450		0.032	13.2	0.4	5.4	234			
T86 5B	3121	46.9	25.4	417			13.5	0.4	5.1	232			
T88 9B	3074	48.4	25.1	451		0.032	12.7	0.5	6.3	229			
T86 3B	3113	50.2	27.0	421		0.031	11.3	0.6	7.8	225			
T88 7B	3013	50.5	26.5	448		0.030	11.4	0.6	7.8	225			
T88 6B	3381	51.4	25.8	451		0.027	10.7	0.6	8.8	222			
T90 2B	2731	53.1	20.8	451		0.029	10.6	0.6	9.9	222			
T86 1B	2580	53.4	27.5	443		0.029	9.1	0.8	10.4	215			
T88 5B	2812	53.6	27.1	406		0.029	9.1	0.8	10.4	216			
T88 4B	2821	55.0	28.3	452		0.029	8.5	0.8	11.1	211			
T88 3B	2819	56.4	27.8	443		0.026	8.9	0.9	11.6	209			
T88 2B	2767	57.9	26.0	427		0.027	9.0	0.8	11.6	209			
T90 1B	2911	58.5	20.5	468		0.027	9.3	0.7	11.3	212			
T88 1B	2010	59.7	27.4	435		0.030	8.1	0.9	12.3	206			
Marr et al., 2011 - core top													
P71	1919	33.9	174.7	352	8.9	0.025	17.8	0.4	3.8				
P81	2036	34.0	173.5	302	6.9	0.023	16.5	0.4	4.7				
S793	2411	36.3	176.8	272	4.5	0.016	16.5	0.5	5.5				
P69	2195	40.4	178.0	236	4.7	0.020	16.9	0.4	5.6				
S938	3003	40.0	180.0	279	5.2	0.019	16.5	0.3	6.0				
R623	1128	43.2	186.0	318	8.4	0.026	10.2	1.0	13.7				
Q220	580	44.3	175.0	312	12.1	0.039	9.7	0.7	11.8				
F111	704	49.0	175.0	391	19.7	0.050	8.0	1.0	14.9				
D178	629	51.7	169.8	397	17.0	0.043	8.1	0.9	12.6				
B32	799	53.6	169.9	407	19.3	0.047	7.8	1.0	14.8				
Moy et al., 2009 - core top + x1 sed trap													
SO136-140BX	1636	49°10'84"	150°10'13"		24.6	0.076	8.8	1.1	13.3		128		
SO136-153BX	1874	47°46'85"	149°23'73"		24.5	0.075	10.2	0.9	10.7		140		
MD972108BX	2140	48°29'28"	149°06'33"		28.5	0.088	9.5	1.0	12.0		135		
SO136-147BX	2177	48°29'99"	149°06'75"		31.6	0.097	9.5	1.0	12.0		135		
GC11	2406	45°44'02"	144°53'06"		24.4	0.075	11.0	0.8	9.4		157		
KR8807	2890	47°08'87"	145°47'80"		26.5	0.082	9.8	1.0	11.5		143		
MD972107	2950	47°42'70"	145°46'59"		30.5	0.094	9.8	1.0	11.5		141		
GC17	3001	47°45'04"	145°49'00"		24.4	0.075	9.8	1.0	11.5		141		
GC14	3360	46°26'98"	145°14'47"		26.2	0.081	10.5	0.8	10.2		147		
SO136-161BX	3685	46°33'18"	149°04'96"		22.8	0.070	10.9	0.8	9.4		147		
GC21	4132	49°00'16"	145°59'37"		23.7	0.073	8.4	1.2	14.5		130		
GC18	4368	48°05'37"	145°03'97"		20.2	0.062	9.2	1.1	12.9		138		
GC13	4452	46°10'01"	144°15'99"		18.6	0.057	10.4	0.9	10.7		150		
sed trap	1000	46°46' S,	142°04' E		16.9	0.052	10.2	0.9	10.9		145		

Core ID	Depth	Location			Length (µm)	Weight (µg)	SNW (g/m)	Temperature (°C)	WOA		Carbonate Ion		
		Latitude (°)	Longitude (°)	(°W)					Phosphate micromoles/l	Nitrate micromoles/l	Pre-industrial (µMkg ⁻¹)	Modern (µMkg ⁻¹)	
Aldridge et al., 2012 - plankton tow													
IB195		(°N)	(°W)		215.3	1.8	0.009	10.4	0.3		12.4	152	
IB16		62°40'	19°40'		243.8	2.6	0.010	10.7	0.3		12.4	148	
IB14		60°50'	20°00'		235.6	1.8	0.008	10.9	0.4		13.6	149	
IB13		61°00'	20°00'		250.9	2.5	0.010	11.0	0.3		11.1	166	
IB10		60°30'	20°00'		248.7	2.4	0.009	11.4	0.2		4.4	163	
IB6		59°40'	18°42'		243.8	2.3	0.009	11.3	0.2		5.3	175	
IB4		58°57'	17°11'		243.8	2.3	0.010	11.8	0.2		5.2	167	
K		58°30'	16°00'		235.8	2.4	0.010	11.8	0.2		4.0	175	
R		57°40'	10°87'		229.6	2.1	0.009	12.2	0.2		2.2	180	
T		57°00'	09°00'		231.6	2.4	0.011	12.7	0.1		0.0	181	
		56°50'	08°20'		245.8	2.9	0.011	12.7	0.0				
McConnell and Thunnell, 2005 - sed trap													
sed trap		(°N)	(°W)		283.5	6.0	0.021		2.3		18.0		129
de Villiers, 2004 - core top													
S1		(°S)	(°E)										
S2		48.9	1-14		327.5	25.0	0.076						142
S3		48.7				24.5	0.075						142
S4		48.3				22.0	0.067						142
S5		48.2				21.5	0.066						142
S6		47.0				20.1	0.061						135
S7		46.8				15.6	0.048						135
		46.4				15.0	0.046						135
Beer, 2010 - Arabian Sea - plankton tow													
SO120-17		(°N)	(°W)										
SO120-38		56.9	23.7		315.1	3.3	0.011	0.5	4.4		3.3	194	
SO120-41		57.6	23.6		332.0	4.7	0.014	0.5	4.4		4.7	171	
SO120-43		57.7	24.1		319.8	4.0	0.013	0.5	4.4		4.0	174	
M32-5-423		57.9	23.9		322.4	3.6	0.011	0.5	4.4		3.6	170	
M32-5-443		62.0	25.8		306.3	4.3	0.014	0.5	2.3		4.3	231	
M32-5-446		58.1	23.7		296.5	4.3	0.015	0.6	4.3		4.3	204	
M32-5-462		58.9	26.0		289.1	3.8	0.013	0.5	2.7		3.8	238	
M32-5-414		62.0	25.7		313.7	4.9	0.016	0.5	2.6		4.9	216	
		65.0	27.3		328.1	4.6	0.014	0.3	0.4		4.6	277	
Beer, North Atlantic - plankton tow													
M21-1		(°N)	(°W)										
M21-2		47.0	19.3		323.2	4.9	0.015	14.0	0.3		3.7		
M36-5		47.1	18.6		281.6	3.4	0.012	13.8	0.4		0.1		
M21-1		47.1	17.4		290.7	3.6	0.012	13.8	0.1		0.1		
M12-3		47.1	19.3		335.5	4.9	0.015	14.0	0.3		3.3		
M36-6		47.2	19.3		303.7	4.1	0.014	14.0	0.3		3.7		
M12-3		47.2	19.6		312.0	4.1	0.013	14.0	0.3		0.8		
M21-1		47.3	18.5		301.0	4.3	0.014	13.8	0.4		0.8		
M21-2		47.3	19.5		324.1	5.6	0.017	14.0	0.3		3.7		
M21-1		47.3	19.1		273.3	3.7	0.013	14.0	0.3		3.7		
M21-1		47.3	19.7		318.7	5.5	0.017	14.0	0.3		3.7		
M21-1		47.3	19.5		298.8	4.8	0.016	14.0	0.3		3.7		
M21-2		47.3	18.6		271.0	3.3	0.012	13.8	0.4		0.8		
M21-2		47.4	18.9		261.4	4.1	0.016	13.8	0.4		0.8		
M21-2		47.4	18.9		299.4	5.0	0.017	13.8	0.4		0.8		
M26-1		47.5	19.5		315.2	5.2	0.016	14.0	0.3		3.7		
M21-1		47.5	19.1		295.2	3.9	0.013	14.0	0.3		3.7		
M36-5		47.6	22.4		305.8	5.0	0.016	14.1	0.2		2.0		
M21-3		47.6	19.5		301.3	4.6	0.015	14.0	0.3		3.7		
M21-2		47.7	19.8		248.3	2.9	0.012	14.0	0.3		3.7		
M21-3		47.7	19.7		310.0	4.2	0.013	14.0	0.3		3.7		
M21-3		52.5	20.0		347.0	5.4	0.015	11.7	0.5		5.4		
M21-3		54.7	22.5		306.6	4.7	0.015	11.5					
M21-3		54.8	20.7		361.0	6.5	0.018	11.5	0.5		7.6		

AI 2.0. 25ka-present data used in this study.

C5-AI. Table 2. 25ka-present data used in this study.

Number of foraminifera in sample	Age (kyrs)	Depth	<i>G. bulloides</i>		
			T °C	Weight (µg)	Length (µm)
13	0.0	0.00-0.01 m	20.1	4.05	263.3
18	0.0	0.01-0.02 m	18.0	5.50	310.7
16	0.1	0.08-0.09m	18.6	5.24	301.6
12	0.4	0.20-0.21m	18.0	4.56	274.1
32	1.0	0.38-0.39m	16.8	4.99	301.6
23	1.8	0.56-0.57 m	20.3	5.67	309.2
16	2.6	0.80-0.81m	19.2	5.14	303.5
12	2.9	0.90-0.91m	18.1	5.20	295.8
13	3.6	1.40-1.41 m	19.6	5.51	307.8
21	4.3	1.60-1.61 m	21.1	5.33	307.4
17	4.8	1.80-1.81 m	18.0	5.76	294.5
10	5.3	1.90-1.91 m	14.5	7.73	343.7
19	5.6	2.10-2.11 m	16.2	7.41	292.0
17	6.0	2.20-2.21 m	18.7	7.41	318.5
23	6.1	2.30-2.31 m	19.6	6.67	313.0
12	6.3	2.40-2.41 m	16.9	5.25	282.1
12	6.5	2.50-2.51 m	13.9	5.70	304.4
19	6.6	2.60-2.61 m	20.5	6.30	304.9
11	6.8	2.69-2.70 m	11.0	9.53	362.3
20	7.0	2.72-2.73 m	18.8	6.17	302.6
12	7.1	2.90-2.91 m	20.1	4.98	288.3
20	7.9	3.20-3.21 m	15.4	5.53	288.0
16	8.4	3.30-3.31 m	18.7	7.68	347.4
16	9.0	3.60-3.61 m	18.1	6.04	319.2
10	9.3	3.70-3.71 m	13.6	8.46	366.5
16	10.0	3.80-3.81 m	16.6	5.62	315.9
16	10.2	3.90-3.91 m	15.0	7.60	360.0
14	10.5	4.10-4.11 m	13.9	6.27	303.3
18	10.7	4.16-4.17 m	14.3	7.04	334.9
12	11.0	4.20-4.21 m	17.5	5.89	298.1
19	11.4	4.30-4.31 m	13.5	5.98	310.4
10	11.9	4.36-4.37 m	14.9	7.16	317.0
11	12.2	4.40-4.41 m	12.1	7.09	328.0
15	12.4	4.44-4.45 m	17.6	6.00	314.0
12	12.5	4.50-4.51 m	10.7	8.62	347.6
15	12.6	4.54-4.55 m	8.9	9.65	366.4
15	12.6	4.56-4.57m	12.0	12.70	358.5
18	12.8	4.60-4.61 m	14.4	7.50	331.7
15	12.8	4.70-4.71 m	14.6	6.92	324.1
15	12.9	4.80-4.81 m	14.8	13.64	375.7
14	12.9	4.90-4.91 m	11.7	10.06	381.6
10	13.1	5.04-5.05 m	11.6	13.64	375.7
13	13.3	5.08-5.09 m	4.9	15.10	417.4
10	13.4	5.12-5.13 m	7.2	11.02	375.7
18	13.6	5.20-5.21 m	14.2	11.10	369.1
21	13.8	5.26-5.27 m	5.6	19.80	434.0
15	13.8	5.30-5.31 m	13.8	11.69	385.8
19	14.1	5.35-5.36 m	8.3	12.23	372.8
16	14.3	5.40-5.41 m	12.9	12.45	366.7
21	14.5	5.50-5.51 m	7.4	17.47	374.0
15	14.6	5.60-5.61 m	9.0	11.40	374.0
12	14.8	5.68-5.69 m	10.2	11.05	380.7
17	15.1	5.76-5.77 m	12.2	12.57	383.1
18	15.5	5.90-5.91 m	10.5	12.66	382.5
16	15.8	6.10-6.11 m	10.5	12.22	393.9
12	16.0	6.40-6.41 m	11.1	5.70	310.5
16	16.5	6.60-6.61 m	19.4	6.88	340.5
16	17.2	6.70-6.71 m	15.1	8.83	341.1
14	18.1	6.78-6.79 m	8.9	7.93	310.8
21	18.3	6.90-6.91 m	14.5	8.96	323.4
21	18.5	7.00-7.01 m	15.0	9.25	348.6
15	18.8	7.20-7.21 m	13.0	8.94	384.9
21	19.0	7.30-7.30 m	10.1	10.02	354.2
14	19.3	7.50-7.50 m	12.5	10.07	349.9
15	19.5	7.60-7.61 m	19.8	12.69	345.5
15	20.0	7.70-7.71 m	7.6	12.72	366.7
13	20.2	7.88-7.89 m	9.8	13.19	367.4
12	20.7	7.90-7.91 m	6.6	13.63	356.2
16	21.0	8.01-8.02 m	13.0	0.94	301.9
15	21.2	8.10-8.11 m	9.3	12.67	352.4
24	21.6	8.22-8.23 m	5.3	13.62	376.5
19	21.7	8.50-8.51 m	15.5	10.89	367.3
19	21.9	8.70-8.71 m	13.4	9.45	351.2
18	22.1	8.80-8.81 m	9.2	9.41	351.1
21	22.4	9.00-9.01 m	8.7	11.27	356.4
17	23.1	9.10-9.11 m	10.2	11.27	366.1
10	23.6	9.30-9.31 m	11.6	12.88	352.2

AI 3.0. MD97 2121 *G. bulloides* SNW compared to biogenic carbonate and silica mass accumulation rates.

C5-AI. Fig. 1. MD97 2121 *G. bulloides* SNW (red) compared to biogenic carbonate (a-brown-repeated from Fig. 37) and silica (b-blue) mass accumulation rates (MAR) (Carter and Manighetti, 2006). There is no apparent relationship between the variables. Note, the relationship between surface ocean production and particulate export to the sea floor can be decoupled (Buesseler, 1998). In addition, productivity as measured by carbonate MARs are limited to organisms which produce a calcium carbonate shell, and are bias towards larger zooplankton organisms such as foraminifera (200-700 μm). Therefore phytoplankton productivity from organisms such as coccolithophore (*ca.* 4-7 μm) which are vital to the ‘biological pump’ are not well represented in carbonate MARs (Frenz et al., 2005; Legendre and Le Fevre, 1995). Carbonate and silicate MAR records at MD 97 2121 confirm that; 1) silica MARs are low compared to carbonate. There is a small increase in silica MARs of 0.38 $\text{g/cm}^2/\text{kyr}$ and therefore an increase in production and/or preservation in the Holocene; 2) Mean carbonate MAR values between the last glacial and Holocene periods change little (3.74 vs. 3.96 $\text{g/cm}^2/\text{kyr}$), however, carbonate MAR are more consistent during the glacial periods as compared to the Holocene.

Chapter 6

Conclusions and Future Work

Conclusions

This thesis has generated a high resolution data set from off the eastern North Island of New Zealand that identifies changes in the regional climate and ocean over the last 25 kyr. Highlighted is the dynamic interaction between STW and SAW, which has led to a new understanding of how foraminiferal geochemical and physical paleoceanographic proxies reflect their environment. Each of the six central objectives of this thesis, set out in Chapter 1, are summarized here.

- ❖ Determine the reliability of the laser ablation technique for Mg/Ca and other trace elements ratioed to calcium (TE/Ca) in foraminifera, and
- ❖ Compare geochemical techniques for measuring TE/Ca.

The second chapter in this thesis presents an investigation into the effects of different sample cleaning procedures on six trace element/Ca ratios in *G. bulloides*, a planktic species widely used in paleoenvironmental reconstructions. Foraminifera from core-top and down-core sediments were cleaned using seven different methods. Individual foraminifera were analysed before and after cleaning using laser ablation inductively coupled plasma mass spectrometry (LA-ICPMS). Oxidative and reductive cleaning and subsequent analyses using laser ablation and “pseudo” solution-based ICPMS methods were compared. Measurements of Mg/Ca and Sr/Ca values were identical whether samples were subjected to oxidative and reductive treatments, or 2-4 acid leach treatments. However, ultra trace elements Al/Ca, Mn/Ca, Zn/Ca and Ba/Ca are much more sensitive to the cleaning method, with up to an order-of-magnitude difference between techniques depending on the cleaning employed. Al/Ca was progressively removed with more intense cleaning, but six or more acid leach treatments were required for full removal of this contaminant. Mn/Ca and Ba/Ca required a combination of oxidative and reductive and/or acid leaching for contaminant phase removal. By contrast, Zn/Ca values increased after acid leaching cleaning procedures, potentially indicating the preferential dissolution of low-Zn calcite. Accurate measurement of Zn/Ca in planktic foraminifera by solution methods

was found to require oxidative and reductive treatment without acid leaching or alternatively, the use of an *in situ* method such as laser LA- ICPMS. Careful data processing following LA- ICPMS analysis was found to be as the most effective method to ensure ultra trace metal contaminant phases were eliminated.

- ❖ Develop foraminiferal Mg/Ca and other ‘trace elements’ (TE/Ca) as proxies for thermal and nutrient concentration and thus determine upper ocean stratification and,
- ❖ Test these proxies against modern core top and plankton tow samples before applying them to a paleoceanographic record that reveals major shifts the oceanography and climate over the last 25 kyr.

The third chapter presents data from SW Pacific core tops and down-core data from the high resolution sediment core, MD97 2121. Core-top data showed that Zn/Ca and Mn/Ca measurements in *G. ruber* and *G. bulloides* have the potential to trace SAW and STW surface waters, the latter tending to be elevated in these trace elements. In addition, intra-chamber offsets between chambers *f* and *f*-2 of *G. bulloides* and inter-species offsets of the 0-50m dwelling *G. ruber* and deeper dwelling *G. bulloides* showed potential to reveal upper ocean nutrient and thermal stratification via Zn/Ca and Mg/Ca ratios, respectively. Furthermore, Zn/Ca and Mn/Ca data analysed from MD97 2121, paired with Mg/Ca paleothermometry, alkenones, foraminiferal assemblages, carbonate and silicate contents, and stable isotopes, revealed major changes in the ocean over the past 25 kyr as follows. At the Last Glacial Maximum, mean surface water temperatures were *ca.* 6-7 °C lower than present, accompanied by low levels of Mn/Ca and Zn/Ca, and minimal thermal and nutrient stratification. These findings are consistent with a regional dominance of SAW and reduced STW inflow associated with a reduced South Pacific Gyre. From 17.5-14.5 ka an anomalous period occurred, coinciding with the previously recognised ‘Mystery Interval’ when *G. bulloides* paleotemperatures cooled by *ca.* 1 °C/ka, accompanied by an increase in polar species faunal abundance, whereas alkenone temperatures continued to warm. It is likely that this offset was caused by seasonal upwelling, which due to the sub-surface position of *G. bulloides* in the water column and its tendency to bloom in spring in the subantarctic waters, was significantly affected relative to the summer blooming, surface dwelling coccolithophores. Upper ocean

thermal and nutrient stratification appeared to collapse during the Antarctic Cold Reversal. After this, the poleward migration of zonal winds and ocean fronts increased the STW inflow, and together with reduced winds, favoured a predominantly stratified upper ocean from *ca.* 10 ka to present.

- ❖ Evaluate the reason(s) behind differences between various proxies used to determine sea surface temperatures.

In Chapter Five a comparison between two independent paleothermometry records from the LGM to modern is presented. The broad, long term trends in alkenone and *G. bulloides* Mg/Ca based temperature estimates generally agree. There was, however, an inconsistent offset between *G. bulloides* and alkenone temperature records up to 6 °C during the glacial period. The relative influence of the STW and SAW waters that overlay MD97 2121 had a significant influence on paleo-temperature estimates. During the glacial period (25-16 ka), when the study site was bathed by SAW, the alkenones production was probably limited to summer. However, during this same period, *G. bulloides* most likely followed a spring bloom cycle. During the Holocene, alkenones and *G. bulloides* peak fluxes are likely closely aligned with the modern accumulation periods during summer north of and spring south of the Subtropical Front. Therefore, the lack of offset between the paleothermometer temperature estimates is consistent with a return to modern ocean conditions. The findings of this study highlighted the susceptibility of foraminiferal and alkenone-based paleothermometry records to the influence of changing regional hydrology and highlights the complimentary nature of combining different proxies (from a single site).

- ❖ Investigate the potential use of *G. bulloides* test weights as a paleoceanographic proxy.

Chapter Six investigates published hypotheses that higher surface water carbonate ion concentrations are the primary cause of an increased *G. bulloides* shell calcification during glacial periods. This hypothesis is largely based on studies from a North Atlantic setting. However, this chapter takes a novel approach by comparing data from the SW Pacific with previously published data from around the world to assess any inter-basin ocean differences in species calcification. Modern ocean general linear

models indicated that an ‘ocean effect,’ which reflects a combination of factors that contribute to a specific ocean environment, was the most significant factor in determining shell size normalised weight (SNW) ($r^2 > 0.90$). This effect is likely reflected in the various combinations of environmental parameters by the geographic distribution of species genotypes. However, comparison of linear regional trends between oceans showed no consistent relationship between temperature, nutrient or carbonate ion concentrations and shell calcification. A weak negative inter-basin correlation between shell SNW and chlorophyll-*a* concentration was identified, highlighting the importance of food in the dynamics of foraminiferal calcification. Comparison of geochemical and SNW data back to the LGM from the North Atlantic and SW Pacific Oceans confirmed that at mid-latitudes *G. bulloides* shell SNW increased during the glacial period, regardless of ocean region. This may reflect multiple factors including increased surface ocean carbonate ion concentration and pH and elevated levels of primary productivity. However, as calcification of *G. bulloides* appears to be region specific, shell SNW proxy is limited to the local environment it was developed for.

Overall, the work presented in this thesis demonstrates that trace metals in foraminiferal test calcite as measured using LA-ICPMS are potentially reliable paleoenvironmental recorders. Furthermore, the offset in Mg/Ca and Zn/Ca between the chambers of *G. bulloides* can respectively reconstruct the thermal and nutrient surface water stratification of the paleocean. This information, combined with regional paleoceanographic data, enabled the reconstruction of dynamics of the SW Pacific surface ocean under polar and subtropical forcing from the LGM to present. Moreover, the impact of the interaction between these competing water masses on the seasonality of plankton species, and thus their paleotemperature estimates, highlighted the need for caution when interpreting multi-proxy records. Finally, Darwinian Theory of species evolution was born out when looking at *G. bulloides* SNW after it was found that shell calcification appears to reflect species specific adaptations to regional environments. However, the universal trend towards heavier SNW during glacial periods suggests that an increase in surface water carbonate ion concentrations, higher pH and a change to more turbulent surface water likely encouraged

calcification in all genotypes. As these parameters are likely to be region specific, a universal SNW based paleo-proxy is unlikely.

Future Work

Foraminifera shells act as time capsules, in essence capturing and preserving information about their environment and thus the wider ocean climate in which they grew. If both the geochemical and physical information contained within the calcite shells is able to be understood, this can provide key insights about how climate may change in the future. Work in this thesis raises several exciting possibilities that can be further advanced along the following lines;

- ❖ Analyse multiple core tops from the SW Pacific Ocean, first using laser ablation-ICPMS, and then using solution-ICPMS on the same foraminifera samples to enable a direct comparison between the two techniques for trace and ultra-trace element measurements.
- ❖ Conduct trials on the use of Zn/Ca as a water mass/micronutrient tracer in different ocean regions using laser ablation techniques on plankton tow samples concomitant with water mass chemistry and physical oceanography for selected sites around NZ including use of long term sediment trap data to assess any inter-annual variability.
- ❖ Investigate multiple high resolution paleothermometry multi-proxy records to assess the offset between thermometers to see if there is a consistent trend, e.g. change in frontal movements, and therefore water mass influence, seasonal variability in algal and foraminiferal blooms. This investigation could be extended to compare to other types of paleotemperature proxies such as TEX-86.
- ❖ Conduct systematic sampling of *G. bulloides* from different ocean regions with distinctive genotypes. Those samples would be the basis for further research including, size normalised weight, trace metal and isotope analysis to assess any systematic offset which may be a function of genotype-specific trait.

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Single element/Ca smoothed profile comparisons - oxidative clean - foraminifera 1 - f-2

	Before cleaning - LA processing - TE/Ca (mmol/mol)						n=	After cleaning - LA processing - TE/Ca (mmol/mol)						n=	After cleaning - bulk processing - TE/Ca (mmol/mol)						n=
	Mg/Ca	Al/Ca	Mn/Ca	Zn/Ca	Sr/Ca	Ba/Ca	200	Mg/Ca	Al/Ca	Mn/Ca	Zn/Ca	Sr/Ca	Ba/Ca	190	Mg/Ca	Al/Ca	Mn/Ca	Zn/Ca	Sr/Ca	Ba/Ca	390
mean	1.482	0.025	0.006	0.002	1.305	0.002		1.551	0.012	0.002	0.013	1.305	0.003		2.366	0.309	0.007	0.041	1.371	0.013	
% 2se	2.4	7.3	14.5	64.6	3.2	7.2		2.3	12.3	46.1	18.0	1.9	7.0		5.1	5.3	0.0	0.2	1.4	0.1	

Single element/Ca smoothed profile comparisons -
oxidative clean - foraminifera 2-f-2

J. Marr
G. bulloides - D178

Oxidative - 2 - TE/Ca test wall profiles

	Before cleaning - LA processing - TE/Ca (mmol/mol)							n=	After cleaning - LA processing - TE/Ca (mmol/mol)							n=	After cleaning - bulk processing - TE/Ca (mmol/mol)							n=
	Mg/Ca	Al/Ca	Mn/Ca	Zn/Ca	Sr/Ca	Ba/Ca	300	Mg/Ca	Al/Ca	Mn/Ca	Zn/Ca	Sr/Ca	Ba/Ca	90	Mg/Ca	Al/Ca	Mn/Ca	Zn/Ca	Sr/Ca	Ba/Ca	390			
mean	1.648	0.113	0.007	0.006	1.282	0.002		1.486	0.099	0.003	0.010	1.372	0.007		2.106	0.545	0.011	0.039	1.478	0.020				
% 2se	2.1	5.8	11.7	17.5	2.2	5.7		2.4	7.6	49.2	35.0	2.6	19.5		10.4	28.6	21.4	35.2	6.6	27.5				

Single element/Ca smoothed profile comparisons - oxidative clean - foraminifera 3-f-2

J. Marr
G. bulloides - D178

Oxidative - 3 - TE/Ca test wall profiles

	Before cleaning - LA processing - TE/Ca (mmol/mol)							n=	After cleaning - LA processing - TE/Ca (mmol/mol)							n=	After cleaning - bulk processing - TE/Ca (mmol/mol)							n=
	Mg/Ca	Al/Ca	Mn/Ca	Zn/Ca	Sr/Ca	Ba/Ca		200	Mg/Ca	Al/Ca	Mn/Ca	Zn/Ca	Sr/Ca	Ba/Ca		110	Mg/Ca	Al/Ca	Mn/Ca	Zn/Ca	Sr/Ca	Ba/Ca		390
mean	3.163	0.052	0.006	0.005	1.486	0.005			0.729	0.019	0.005	0.015	1.294	0.002			0.761	0.029	0.004	0.016	1.300	0.002		
% 2se	2.5	6.7	12.0	25.3	3.1	76.8			2.7	10.7	21.1	17.1	2.6	11.6			2.2	15.4	18.1	13.4	1.9	8.5		

Single element/Ca smoothed profile comparisons - oxidative clean - foraminifera 5-f-2

	Before cleaning - LA processing - TE/Ca (mmol/mol)						n=	After cleaning - LA processing - TE/Ca (mmol/mol)						n=	After cleaning - bulk processing - TE/Ca (mmol/mol)					
mean	Mg/Ca	Al/Ca	Mn/Ca	Zn/Ca	Sr/Ca	Ba/Ca	270	Mg/Ca	Al/Ca	Mn/Ca	Zn/Ca	Sr/Ca	Ba/Ca	210	Mg/Ca	Al/Ca	Mn/Ca	Zn/Ca	Sr/Ca	Ba/Ca
% 2se	2.290	0.020	0.001	0.003	1.347	0.001		2.274	0.014	0.006	0.011	1.332	0.001		2.591	0.090	0.014	0.025	1.381	0.002
	2.0	13.6	50.3	29.8	2.4	6.5		1.8	9.7	15.4	16.5	1.7	8.5		3.3	45.7	20.4	19.8	2.2	18.6

Single element/Ca smoothed profile comparisons -
oxidative clean - foraminifera 6-f-2

	Before cleaning - LA processing - TE/Ca (mmol/mol)						n=	After cleaning - LA processing - TE/Ca (mmol/mol)						n=	After cleaning - bulk processing - TE/Ca (mmol/mol)						n=
	Mg/Ca	Al/Ca	Mn/Ca	Zn/Ca	Sr/Ca	Ba/Ca	250	Mg/Ca	Al/Ca	Mn/Ca	Zn/Ca	Sr/Ca	Ba/Ca	100	Mg/Ca	Al/Ca	Mn/Ca	Zn/Ca	Sr/Ca	Ba/Ca	390
mean	0.836	0.034	0.000	0.002	1.280	0.001		1.203	0.011	0.005	0.083	1.279	0.004		1.449	0.086	0.009	0.152	1.246	0.008	
% 2se	2.7	7.1	-39.0	44.6	1.7	6.0		2.1	45.1	24.3	5.9	2.7	7.3		5.3	60.6	17.3	18.0	1.9	18.2	

J. Marr
G. bulloides - D178

Oxidative - 6 - TE/Ca test wall profiles

Single element/Ca smoothed profile comparisons - oxidative clean - foraminifera 7-f-2

	Before cleaning - LA processing - TE/Ca (mmol/mol)						n=	After cleaning - LA processing - TE/Ca (mmol/mol)						n=	After cleaning - bulk processing - TE/Ca (mmol/mol)						n=
	Mg/Ca	Al/Ca	Mn/Ca	Zn/Ca	Sr/Ca	Ba/Ca	180	Mg/Ca	Al/Ca	Mn/Ca	Zn/Ca	Sr/Ca	Ba/Ca	130	Mg/Ca	Al/Ca	Mn/Ca	Zn/Ca	Sr/Ca	Ba/Ca	390
mean	1.345	0.147	0.000	0.004	1.392	0.002		1.436	0.075	0.007	0.032	1.322	0.002		1.978	1.072	0.016	0.068	1.370	0.006	
% 2se	2.3	15.6	39.3	32.8	1.6	20.2		2.6	6.3	16.2	10.8	2.0	9.0		8.4	83.9	29.6	21.3	2.7	20.4	

J. Marr
G. bulloides - D178

Oxidative - 7 - TE/Ca test wall profiles

Single element/Ca smoothed profile comparisons -
oxidative clean - foraminifera 8-f-2

	Before cleaning - LA processing - TE/Ca (mmol/mol)						n=	After cleaning - LA processing - TE/Ca (mmol/mol)						n=	After cleaning - bulk processing - TE/Ca (mmol/mol)						n=
	Mg/Ca	Al/Ca	Mn/Ca	Zn/Ca	Sr/Ca	Ba/Ca	230	Mg/Ca	Al/Ca	Mn/Ca	Zn/Ca	Sr/Ca	Ba/Ca	110	Mg/Ca	Al/Ca	Mn/Ca	Zn/Ca	Sr/Ca	Ba/Ca	390
mean	1.362	0.055	0.000	0.000	1.291	0.001		1.406	0.053	0.001	0.012	1.323	0.001		1.580	0.247	0.004	0.031	1.311	0.002	
% 2se	1.8	4.3	12.3	-903.5	2.4	7.0		2.4	10.8	82.5	20.8	2.4	12.3		5.9	27.6	16.4	21.2	1.7	14.2	

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G. bulloides - D178

Oxidative - 8 - TE/Ca test wall profiles

Single element/Ca smoothed profile comparisons - oxidative clean - foraminifera 9-f-2

	Before cleaning - LA processing - TE/Ca (mmol/mol)							n=	After cleaning - LA processing - TE/Ca (mmol/mol)							n=	After cleaning - bulk processing - TE/Ca (mmol/mol)							n=
	Mg/Ca	Al/Ca	Mn/Ca	Zn/Ca	Sr/Ca	Ba/Ca	210	Mg/Ca	Al/Ca	Mn/Ca	Zn/Ca	Sr/Ca	Ba/Ca	195	Mg/Ca	Al/Ca	Mn/Ca	Zn/Ca	Sr/Ca	Ba/Ca	390			
mean	1.206	0.043	0.003	0.004	1.304	0.005		1.108	0.008	0.002	0.017	1.268	0.002		1.228	0.101	0.005	0.045	1.284	0.003				
% 2se	2.1	6.3	20.5	20.8	1.5	9.6		1.7	13.9	36.1	17.3	1.4	6.5		4.9	59.6	18.9	24.5	2.4	16.1				

Single element/Ca smoothed profile comparisons - oxidative clean - foraminifera 10 - f-2

	Before cleaning - LA processing - TE/Ca (mmol/mol)							n=	After cleaning - LA processing - TE/Ca (mmol/mol)							n=	After cleaning - bulk processing - TE/Ca (mmol/mol)							n=
	Mg/Ca	Al/Ca	Mn/Ca	Zn/Ca	Sr/Ca	Ba/Ca	250	Mg/Ca	Al/Ca	Mn/Ca	Zn/Ca	Sr/Ca	Ba/Ca	100	Mg/Ca	Al/Ca	Mn/Ca	Zn/Ca	Sr/Ca	Ba/Ca	390			
mean	2.975	0.039	0.003	0.004	1.368	0.002		3.584	0.015	0.002	0.008	1.313	0.001		3.609	0.304	0.005	0.021	1.356	0.003				
% 2se	1.5	9.2	28.5	30.0	1.7	5.2		2.2	13.1	69.9	29.9	2.1	12.6		3.1	35.5	19.2	19.7	2.7	17.3				

Single element/Ca smoothed profile comparisons - oxidative - reductive clean - foraminifera 13 - f-2

	Before cleaning - LA processing - TE/Ca (mmol/mol)							n=	After cleaning - LA processing - TE/Ca (mmol/mol)							n=	After cleaning - bulk processing - TE/Ca (mmol/mol)							n=
	Mg/Ca	Al/Ca	Mn/Ca	Zn/Ca	Sr/Ca	Ba/Ca	200	Mg/Ca	Al/Ca	Mn/Ca	Zn/Ca	Sr/Ca	Ba/Ca	150	Mg/Ca	Al/Ca	Mn/Ca	Zn/Ca	Sr/Ca	Ba/Ca	390			
mean	0.913	0.005	0.001	0.011	1.343	0.001		1.074	0.017	0.000	0.000	1.387	0.001		1.816	0.046	0.000	0.002	1.456	0.002				
% 2se	2.7	13.5	74.3	233	2.2	10.3		2.8	25.4	134	20.6	1.9	16.0		6.4	17.9	183	44.8	2.5	66.3				

Single element/Ca smoothed profile comparisons - oxidative - reductive clean - foraminifera 15 - f-2

	Before cleaning - LA processing - TE/Ca (mmol/mol)							n=	After cleaning - LA processing - TE/Ca (mmol/mol)							n=	After cleaning - bulk processing - TE/Ca (mmol/mol)							n=
	Mg/Ca	Al/Ca	Mn/Ca	Zn/Ca	Sr/Ca	Ba/Ca		240	Mg/Ca	Al/Ca	Mn/Ca	Zn/Ca	Sr/Ca	Ba/Ca		210	Mg/Ca	Al/Ca	Mn/Ca	Zn/Ca	Sr/Ca	Ba/Ca		390
mean	1.497	0.010	0.003	0.005	1.318	0.002			1.261	0.002	0.003	0.015	1.279	0.001			1.343	0.228	0.001	0.005	1.321	0.003		
% 2se	1.5	11.7	48.0	17.7	1.3	8.6			2.2	42.4	32.9	12.9	1.8	11.0			2.0	148.9	56.0	17.6	1.4	15.4		

Single element/Ca smoothed profile comparisons - oxidative - reductive clean - foraminifera 16 - f-2

	Before cleaning - LA processing - TE/Ca (mmol/mol)						n=	After cleaning - LA processing - TE/Ca (mmol/mol)						n=	After cleaning - bulk processing - TE/Ca (mmol/mol)						n=
	Mg/Ca	Al/Ca	Mn/Ca	Zn/Ca	Sr/Ca	Ba/Ca	230	Mg/Ca	Al/Ca	Mn/Ca	Zn/Ca	Sr/Ca	Ba/Ca	150	Mg/Ca	Al/Ca	Mn/Ca	Zn/Ca	Sr/Ca	Ba/Ca	390
mean	1.08	0.018	0.000	0.000	1.32	0.001		1.02	0.017	0.000	0.002	1.35	0.001		1.20	0.083	0.000	0.002	1.37	0.003	
% 2se	1.5	15.1	19.0	68.8	1.5	6.5		2.1	12.7	387	106	2.4	13.5		3.3	27.5	-45	68	2.0	14.6	

Single element/Ca smoothed profile comparisons - oxidative - reductive clean - foraminifera 17 - f-2

	Before cleaning - LA processing - TE/Ca (mmol/mol)						n=	After cleaning - LA processing - TE/Ca (mmol/mol)						n=	After cleaning - bulk processing - TE/Ca (mmol/mol)						n=
	Mg/Ca	Al/Ca	Mn/Ca	Zn/Ca	Sr/Ca	Ba/Ca	260	Mg/Ca	Al/Ca	Mn/Ca	Zn/Ca	Sr/Ca	Ba/Ca	180	Mg/Ca	Al/Ca	Mn/Ca	Zn/Ca	Sr/Ca	Ba/Ca	390
mean	3.52	0.019	0.004	0.004	1.31	0.004		3.24	0.003	0.001	0.010	1.31	0.002		3.86	0.045	0.002	0.003	1.32	0.003	
% 2se	2.9	34.0	121	17.4	1.7	9.3		2.0	49.1	15.5	15.8	1.1	5.3		1.7	35.8	29.6	25.8	1.4	6.8	

Single element/Ca smoothed profile comparisons - oxidative - reductive clean - foraminifera 18 - f-2

	Before cleaning - LA processing - TE/Ca (mmol/mol)						n=	After cleaning - LA processing - TE/Ca (mmol/mol)						n=	After cleaning - bulk processing - TE/Ca (mmol/mol)						n=
	Mg/Ca	Al/Ca	Mn/Ca	Zn/Ca	Sr/Ca	Ba/Ca	300	Mg/Ca	Al/Ca	Mn/Ca	Zn/Ca	Sr/Ca	Ba/Ca	200	Mg/Ca	Al/Ca	Mn/Ca	Zn/Ca	Sr/Ca	Ba/Ca	390
mean	1.34	0.011	0.003	0.001	1.29	0.002		1.03	0.002	0.000	0.003	1.30	0.001		1.30	0.011	0.002	0.000	1.29	0.001	
% 2se	1.8	9.7	14.5	56.2	1.1	6.7		2.2	57.1	-175	52.8	1.3	15.0		2.6	14.6	28	269.6	1.5	9.8	

Single element/Ca smoothed profile comparisons -
oxidative and reductive cleaning - foraminifera 20 - f-2

	Before cleaning - LA processing - TE/Ca (mmol/mol)						n=	After cleaning - LA processing - TE/Ca (mmol/mol)						n=	After cleaning - bulk processing - TE/Ca (mmol/mol)						n=
	Mg/Ca	Al/Ca	Mn/Ca	Zn/Ca	Sr/Ca	Ba/Ca	260	Mg/Ca	Al/Ca	Mn/Ca	Zn/Ca	Sr/Ca	Ba/Ca	190	Mg/Ca	Al/Ca	Mn/Ca	Zn/Ca	Sr/Ca	Ba/Ca	390
mean	1.19	0.025	0.002	0.001	1.24	0.002		1.09	0.014	0.002	0.005	1.23	0.001		1.40	0.015	0.002	0.002	1.29	0.001	
% 2se	1.9	6.3	47.5	41.4	1.3	44.6		2.5	17.7	80.7	39.6	1.5	11.8		2.5	85.2	22.2	27.8	1.5	6.5	

Single element/Ca smoothed profile comparisons - oxidative - 1x leach clean - foraminifera 21 - f-2

	Before cleaning - LA processing - TE/Ca (mmol/mol)						n=	After cleaning - LA processing - TE/Ca (mmol/mol)						n=	After cleaning - bulk processing - TE/Ca (mmol/mol)						n=
	Mg/Ca	Al/Ca	Mn/Ca	Zn/Ca	Sr/Ca	Ba/Ca	300	Mg/Ca	Al/Ca	Mn/Ca	Zn/Ca	Sr/Ca	Ba/Ca	200	Mg/Ca	Al/Ca	Mn/Ca	Zn/Ca	Sr/Ca	Ba/Ca	390
mean	0.67	0.002	0.000	0.002	1.28	0.001		0.73	0.012	0.001	0.001	1.25	0.001		0.77	0.023	0.003	0.008	1.28	0.001	
% 2se	1.4	13.0	30.9	49.4	1.2	7.7		2.6	48.8	153.8	81.7	2.1	13.7		7.9	47.7	53.2	19.7	2.0	27.3	

J. Marr
G. bulloides - D178

Oxidative-1x leach - 21 - TE/Ca test wall profiles

Single element/Ca smoothed profile comparisons -

oxidative - 1x leach clean - foraminifera 23 - f-2

	Before cleaning - LA processing - TE/Ca (mmol/mol)						n=	After cleaning - LA processing - TE/Ca (mmol/mol)						n=	After cleaning - bulk processing - TE/Ca (mmol/mol)						n=
	Mg/Ca	Al/Ca	Mn/Ca	Zn/Ca	Sr/Ca	Ba/Ca	270	Mg/Ca	Al/Ca	Mn/Ca	Zn/Ca	Sr/Ca	Ba/Ca	160	Mg/Ca	Al/Ca	Mn/Ca	Zn/Ca	Sr/Ca	Ba/Ca	390
mean	1.70	0.035	0.002	0.002	1.30	0.002		1.40	0.008	0.000	0.011	1.32	0.001		1.46	0.063	0.003	0.019	1.33	0.001	
% 2se	1.8	6.2	24.1	26.3	1.4	5.3		2.5	19.6	336	22.1	2.7	10.8		4.0	50.5	17	13.2	3.4	9.7	

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G. bulloides - D178

Oxidative-1x leach - 23 - TE/Ca test wall profiles

Single element/Ca smoothed profile comparisons - oxidative - 1x leach clean - foraminifera 28 - f-2

	Before cleaning - LA processing - TE/Ca (mmol/mol)						n=	After cleaning - LA processing - TE/Ca (mmol/mol)						n=	After cleaning - bulk processing - TE/Ca (mmol/mol)						n=
	Mg/Ca	Al/Ca	Mn/Ca	Zn/Ca	Sr/Ca	Ba/Ca	250	Mg/Ca	Al/Ca	Mn/Ca	Zn/Ca	Sr/Ca	Ba/Ca	210	Mg/Ca	Al/Ca	Mn/Ca	Zn/Ca	Sr/Ca	Ba/Ca	390
mean	1.60	0.035	0.003	0.002	1.30	0.003		1.48	0.013	0.000	0.006	1.30	0.001		1.59	0.102	0.003	0.014	1.30	0.001	
% 2se	1.6	11.4	16.0	25.8	1.3	7.6		2.3	11.6	388	31.7	2.0	9.8		3.3	37.5	17	19.2	1.8	8.3	

Single element/Ca smoothed profile comparisons - oxidative - 1x leach clean - foraminifera 29 - f-2

J. Marr
G. bulloides - D178

Oxidative-1x leach - 29 - TE/Ca test wall profiles

	Before cleaning - LA processing - TE/Ca (mmol/mol)						n=	After cleaning - LA processing - TE/Ca (mmol/mol)						n=	After cleaning - bulk processing - TE/Ca (mmol/mol)						n=
	Mg/Ca	Al/Ca	Mn/Ca	Zn/Ca	Sr/Ca	Ba/Ca	300	Mg/Ca	Al/Ca	Mn/Ca	Zn/Ca	Sr/Ca	Ba/Ca	160	Mg/Ca	Al/Ca	Mn/Ca	Zn/Ca	Sr/Ca	Ba/Ca	390
mean	1.86	0.021	0.010	0.006	1.31	0.004		1.42	0.009	0.007	0.005	1.28	0.006		2.37	0.309	0.007	0.041	1.37	0.013	
% 2se	2.7	8.6	6.8	13.7	1.1	4.9		2.6	23.5	18.6	48.0	2.7	6.2		10.9	86.9	34.4	27.9	5.4	41.3	

Single element/Ca smoothed profile comparisons -
1x acid leach clean - foraminifera 32 - f-2

	Before cleaning - LA processing - TE/Ca (mmol/mol)						n=	After cleaning - LA processing - TE/Ca (mmol/mol)						n=	After cleaning - bulk processing - TE/Ca (mmol/mol)						n=
	Mg/Ca	Al/Ca	Mn/Ca	Zn/Ca	Sr/Ca	Ba/Ca	200	Mg/Ca	Al/Ca	Mn/Ca	Zn/Ca	Sr/Ca	Ba/Ca	90	Mg/Ca	Al/Ca	Mn/Ca	Zn/Ca	Sr/Ca	Ba/Ca	390
mean	0.86	0.016	0.002	0.001	1.36	0.001		0.88	0.020	0.008	0.017	1.39	0.003		1.11	0.613	0.024	0.063	1.37	0.008	
% 2se	2.46	12.1	29.0	62.8	1.65	9.29		2.7	12.7	16.6	15.9	2.3	10.9		12.4	81.2	58.5	104.0	2.9	53.9	

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G. bulloides - D178

1x leach - 32 - TE/Ca test wall profiles

Single element/Ca smoothed profile comparisons - 1x acid leach clean - foraminifera 33 - f-2

	Before cleaning - LA processing - TE/Ca (mmol/mol)						n=	After cleaning - LA processing - TE/Ca (mmol/mol)						n=	After cleaning - bulk processing - TE/Ca (mmol/mol)						n=
	Mg/Ca	Al/Ca	Mn/Ca	Zn/Ca	Sr/Ca	Ba/Ca	200	Mg/Ca	Al/Ca	Mn/Ca	Zn/Ca	Sr/Ca	Ba/Ca	260	Mg/Ca	Al/Ca	Mn/Ca	Zn/Ca	Sr/Ca	Ba/Ca	390
mean	2.04	0.110	0.010	0.008	1.23	0.005		2.39	0.020	0.010	0.017	1.24	0.002		2.62	0.046	0.013	0.031	1.27	0.003	
% 2se	1.6	4.2	5.9	9.2	1.3	8.3		1.6	9.3	8.3	9.7	1.4	5.3		5.8	22.8	11.4	24.7	2.4	18.9	

Single element/Ca smoothed profile comparisons -
1x acid leach clean - foraminifera 34 - f-2

J. Marr
G. bulloides - D178

1x leach - 34 - TE/Ca test wall profiles

	Before cleaning - LA processing - TE/Ca (mmol/mol)							n=	After cleaning - LA processing - TE/Ca (mmol/mol)							n=	After cleaning - bulk processing - TE/Ca (mmol/mol)							n=
	Mg/Ca	Al/Ca	Mn/Ca	Zn/Ca	Sr/Ca	Ba/Ca		250	Mg/Ca	Al/Ca	Mn/Ca	Zn/Ca	Sr/Ca	Ba/Ca		240	Mg/Ca	Al/Ca	Mn/Ca	Zn/Ca	Sr/Ca	Ba/Ca		390
mean	1.04	0.011	0.001	0.002	1.27	0.001			1.10	0.009	0.000	0.000	1.30	0.001			1.38	0.118	0.007	0.032	1.36	0.006		
% 2se	1.4	11.9	75.7	29.6	1.4	5.4			1.6	12.1	-183.0	420.0	1.2	7.7			6.3	65.3	94.4	67.5	2.2	27.7		

Single element/Ca smoothed profile comparisons - 1x acid leach clean - foraminifera 35 - f-2

	Before cleaning - LA processing - TE/Ca (mmol/mol)						n=	After cleaning - LA processing - TE/Ca (mmol/mol)						n=	After cleaning - bulk processing - TE/Ca (mmol/mol)						n=
	Mg/Ca	Al/Ca	Mn/Ca	Zn/Ca	Sr/Ca	Ba/Ca	250	Mg/Ca	Al/Ca	Mn/Ca	Zn/Ca	Sr/Ca	Ba/Ca	190	Mg/Ca	Al/Ca	Mn/Ca	Zn/Ca	Sr/Ca	Ba/Ca	390
mean	0.98	0.060	0.009	0.005	1.28	0.003		0.83	0.068	0.006	0.003	1.30	0.006		1.53	0.870	0.034	0.020	1.43	0.032	
% 2se	2.4	6.3	9.9	16.2	1.1	26.9		1.5	5.1	16.5	69.9	1.3	8.1		15.1	33.7	29.3	26.8	5.5	33.1	

J. Marr
G. bulloides - D178

1x leach - 35 - TE/Ca test wall profiles

Single element/Ca smoothed profile comparisons -
1x acid leach clean - foraminifera r1 - f-2

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G. bulloides - D178

1x leach - r1 - TE/Ca test wall profiles

	Before cleaning - LA processing - TE/Ca (mmol/mol)						n=	After cleaning - LA processing - TE/Ca (mmol/mol)						n=	After cleaning - bulk processing - TE/Ca (mmol/mol)						n=
	Mg/Ca	Al/Ca	Mn/Ca	Zn/Ca	Sr/Ca	Ba/Ca	280	Mg/Ca	Al/Ca	Mn/Ca	Zn/Ca	Sr/Ca	Ba/Ca	160	Mg/Ca	Al/Ca	Mn/Ca	Zn/Ca	Sr/Ca	Ba/Ca	390
mean	1.74	0.022	0.001	0.002	1.26	0.001		1.61	0.008	0.000	0.000	1.27	0.002		2.02	0.035	0.010	0.011	1.34	0.008	
% 2se	4.1	7.2	43.0	31.6	1.0	5.1		2.3	23.3	3675	-168	1.5	6.9		5.2	77.4	112	87	4.1	35.5	

Single element/Ca smoothed profile comparisons -
1x acid leach clean - foraminifera r2 - f-2

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G. bulloides - D178

1x leach - r2 - TE/Ca test wall profiles

	Before cleaning - LA processing - TE/Ca (mmol/mol)						n=	After cleaning - LA processing - TE/Ca (mmol/mol)						n=	After cleaning - bulk processing - TE/Ca (mmol/mol)						n=
	Mg/Ca	Al/Ca	Mn/Ca	Zn/Ca	Sr/Ca	Ba/Ca	250	Mg/Ca	Al/Ca	Mn/Ca	Zn/Ca	Sr/Ca	Ba/Ca	160	Mg/Ca	Al/Ca	Mn/Ca	Zn/Ca	Sr/Ca	Ba/Ca	390
mean	1.25	0.149	0.003	0.003	1.44	0.002		1.41	0.041	0.004	0.002	1.37	0.007		2.19	0.766	0.014	0.013	1.46	0.091	
% 2se	2.5	56.7	30.2	41.4	2.2	27.5		1.6	8.0	96.6	91.2	1.6	10.5		10.5	44.0	28.0	42.9	3.1	63.3	

Single element/Ca smoothed profile comparisons -
1x acid leach clean - foraminifera r3 - f-2

J. Marr
G. bulloides - D178

1x leach - r3 - TE/Ca test wall profiles

	Before cleaning - LA processing - TE/Ca (mmol/mol)						n=	After cleaning - LA processing - TE/Ca (mmol/mol)						n=	After cleaning - bulk processing - TE/Ca (mmol/mol)						n=
	Mg/Ca	Al/Ca	Mn/Ca	Zn/Ca	Sr/Ca	Ba/Ca	50	Mg/Ca	Al/Ca	Mn/Ca	Zn/Ca	Sr/Ca	Ba/Ca	180	Mg/Ca	Al/Ca	Mn/Ca	Zn/Ca	Sr/Ca	Ba/Ca	390
mean	1.25	0.149	0.003	0.003	1.44	0.002		1.42	0.034	0.003	0.001	1.35	0.002		2.04	0.522	0.012	0.022	1.37	0.009	
% 2se	2.5	56.7	30.2	41.4	2.2	27.5		1.3	14.3	38.0	154	1.4	7.0		9.4	51.0	20.4	33	1.6	24.3	

Single element/Ca smoothed profile comparisons -
2x acid leach clean - foraminifera 38 - f-2

J. Marr
G. bulloides - D178

2x leach - 38 - TE/Ca test wall profiles

	Before cleaning - LA processing - TE/Ca (mmol/mol)						n=	After cleaning - LA processing - TE/Ca (mmol/mol)						n=	After cleaning - bulk processing - TE/Ca (mmol/mol)						n=
	Mg/Ca	Al/Ca	Mn/Ca	Zn/Ca	Sr/Ca	Ba/Ca	150	Mg/Ca	Al/Ca	Mn/Ca	Zn/Ca	Sr/Ca	Ba/Ca	200	Mg/Ca	Al/Ca	Mn/Ca	Zn/Ca	Sr/Ca	Ba/Ca	390
mean	1.43	0.085	0.001	0.001	1.35	0.001		1.40	0.034	0.000	0.003	1.36	0.002		1.68	0.213	0.007	0.019	1.38	0.006	
% 2se	0.32	0.7	0.007	0.007	0.24	0.001		0.32	0.023	0.013	0.025	0.33	0.002		4.14	31.5	20.5	23.1	1.96	24.0	

Single element/Ca smoothed profile comparisons -

2x acid leach clean - foraminifera 40 - f-2

	Before cleaning - LA processing - TE/Ca (mmol/mol)							n=	After cleaning - LA processing - TE/Ca (mmol/mol)							n=	After cleaning - bulk processing - TE/Ca (mmol/mol)							n=
	Mg/Ca	Al/Ca	Mn/Ca	Zn/Ca	Sr/Ca	Ba/Ca	40	Mg/Ca	Al/Ca	Mn/Ca	Zn/Ca	Sr/Ca	Ba/Ca	230	Mg/Ca	Al/Ca	Mn/Ca	Zn/Ca	Sr/Ca	Ba/Ca	390			
mean	1.40	0.141	0.007	0.004	1.32	0.004		1.49	0.023	0.004	0.015	1.39	0.002		1.63	0.347	0.010	0.072	1.41	0.007				
% 2se	4.7	41.8	18.9	32.5	3.6	18.9		1.7	11.6	21.8	11.1	1.2	6.2		7.5	56.9	25.6	35.4	1.4	30.5				

Single element/Ca smoothed profile comparisons -

2x acid leach clean - foraminifera 43 - f-2

J. Marr
G. bulloides - D178

2x leach - 43 - TE/Ca test wall profiles

	Before cleaning - LA processing - TE/Ca (mmol/mol)						n=	After cleaning - LA processing - TE/Ca (mmol/mol)						n=	After cleaning - bulk processing - TE/Ca (mmol/mol)						n=
	Mg/Ca	Al/Ca	Mn/Ca	Zn/Ca	Sr/Ca	Ba/Ca	260	Mg/Ca	Al/Ca	Mn/Ca	Zn/Ca	Sr/Ca	Ba/Ca	110	Mg/Ca	Al/Ca	Mn/Ca	Zn/Ca	Sr/Ca	Ba/Ca	390
mean	2.06	0.092	0.009	0.007	1.29	0.006		1.42	0.025	0.004	0.009	1.31	0.003		2.04	0.313	0.016	0.051	1.32	0.010	
% 2se	2.3	3.9	7.3	8.2	1.2	5.2		4.0	9.3	37.7	31.1	2.2	8.1		10.5	49.9	28.5	39.6	1.8	26.7	

Single element/Ca smoothed profile comparisons -

2x acid leach clean - foraminifera 44 - f-2

	Before cleaning - LA processing - TE/Ca (mmol/mol)						n=	After cleaning - LA processing - TE/Ca (mmol/mol)						n=	After cleaning - bulk processing - TE/Ca (mmol/mol)						n=
	Mg/Ca	Al/Ca	Mn/Ca	Zn/Ca	Sr/Ca	Ba/Ca	250	Mg/Ca	Al/Ca	Mn/Ca	Zn/Ca	Sr/Ca	Ba/Ca	140	Mg/Ca	Al/Ca	Mn/Ca	Zn/Ca	Sr/Ca	Ba/Ca	390
mean	2.38	0.010	0.002	0.001	1.31	0.002		1.48	0.005	0.001	0.000	1.33	0.001		1.78	0.077	0.003	0.005	1.33	0.003	
% 2se	3.0	18.4	18.3	31.8	1.1	4.9		3.4	25.6	84.6	71.3	1.5	9.4		4.4	93.9	18.2	24.0	1.4	20.6	

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G. bulloides - D178

2x leach - 44 - TE/Ca test wall profiles

Single element/Ca smoothed profile comparisons -

2x acid leach clean - foraminifera 48 - f-2

	Before cleaning - LA processing - TE/Ca (mmol/mol)							n=	After cleaning - LA processing - TE/Ca (mmol/mol)							n=	After cleaning - bulk processing - TE/Ca (mmol/mol)							n=
	Mg/Ca	Al/Ca	Mn/Ca	Zn/Ca	Sr/Ca	Ba/Ca	260	Mg/Ca	Al/Ca	Mn/Ca	Zn/Ca	Sr/Ca	Ba/Ca	110	Mg/Ca	Al/Ca	Mn/Ca	Zn/Ca	Sr/Ca	Ba/Ca	390			
mean	1.27	0.023	0.005	0.004	1.30	0.003		1.26	0.035	0.005	0.000	1.25	0.007		1.57	0.264	0.018	0.014	1.29	0.017				
% 2se	1.9	12.9	10.1	25.7	1.6	6.3		2.6	9.2	16.2	351	1.3	5.5		6.1	53.5	18.2	30	1.7	22.3				

Single element/Ca smoothed profile comparisons -

4x acid leach clean - foraminifera 41 - f-2

	Before cleaning - LA processing - TE/Ca (mmol/mol)						n=	After cleaning - LA processing - TE/Ca (mmol/mol)						n=	After cleaning - bulk processing - TE/Ca (mmol/mol)						n=
	Mg/Ca	Al/Ca	Mn/Ca	Zn/Ca	Sr/Ca	Ba/Ca	200	Mg/Ca	Al/Ca	Mn/Ca	Zn/Ca	Sr/Ca	Ba/Ca	150	Mg/Ca	Al/Ca	Mn/Ca	Zn/Ca	Sr/Ca	Ba/Ca	390
mean	1.23	0.023	0.001	0.000	1.36	0.001		1.17	0.003	0.000	0.001	1.37	0.001		1.38	0.049	0.003	0.044	1.61	0.003	
% 2se	1.6	18.0	58.6	153	1.6	6.5		1.8	44.5	-69.0	123	1.9	13.0		7.6	45.8	27.5	54	23.0	39.9	

Single element/Ca smoothed profile comparisons -

6x acid leach clean - foraminifera 45 - f-2

	Before cleaning - LA processing - TE/Ca (mmol/mol)						n=	After cleaning - LA processing - TE/Ca (mmol/mol)						n=	After cleaning - bulk processing - TE/Ca (mmol/mol)						n=
	Mg/Ca	Al/Ca	Mn/Ca	Zn/Ca	Sr/Ca	Ba/Ca	280	Mg/Ca	Al/Ca	Mn/Ca	Zn/Ca	Sr/Ca	Ba/Ca	230	Mg/Ca	Al/Ca	Mn/Ca	Zn/Ca	Sr/Ca	Ba/Ca	390
mean	2.79	0.010	0.014	0.001	1.35	0.001		2.32	0.009	0.000	0.000	1.31	0.001		2.22	0.013	0.005	0.004	1.32	0.001	
% 2se	1.8	47.3	9.8	54.1	1.6	4.6		2.9	13.3	246	-69.1	1.2	7.8		2.6	21.3	19	17.9	1.2	6.2	

J. Marr
G. bulloides - D178

6x leach - 45 - TE/Ca test wall profiles

Single element/Ca smoothed profile comparisons -

6x acid leach clean - foraminifera 46 - f-2

	Before cleaning - LA processing - TE/Ca (mmol/mol)						n=	After cleaning - LA processing - TE/Ca (mmol/mol)						n=	After cleaning - bulk processing - TE/Ca (mmol/mol)						n=
	Mg/Ca	Al/Ca	Mn/Ca	Zn/Ca	Sr/Ca	Ba/Ca	280	Mg/Ca	Al/Ca	Mn/Ca	Zn/Ca	Sr/Ca	Ba/Ca	130	Mg/Ca	Al/Ca	Mn/Ca	Zn/Ca	Sr/Ca	Ba/Ca	390
mean	1.64	0.034	0.002	0.002	1.29	0.011		2.90	0.014	0.013	0.004	1.34	0.006		2.74	0.028	0.014	0.018	1.36	0.007	
% 2se	5.6	7.1	25.2	26.4	1.4	8.9		2.2	9.4	8.1	34.3	1.4	4.8		2.3	50.8	8.0	96.9	1.7	9.1	

J. Marr
G. bulloides - D178

6x leach - 46 - TE/Ca test wall profiles

Single element/Ca smoothed profile comparisons - 10x acid leach clean - foraminifera 47 - f-2

	Before cleaning - LA processing - TE/Ca (mmol/mol)							n=	After cleaning - LA processing - TE/Ca (mmol/mol)							n=	After cleaning - bulk processing - TE/Ca (mmol/mol)							n=
	Mg/Ca	Al/Ca	Mn/Ca	Zn/Ca	Sr/Ca	Ba/Ca	240	Mg/Ca	Al/Ca	Mn/Ca	Zn/Ca	Sr/Ca	Ba/Ca	190	Mg/Ca	Al/Ca	Mn/Ca	Zn/Ca	Sr/Ca	Ba/Ca	390			
mean	2.32	0.025	0.003	0.002	1.22	0.001		1.33	0.003	0.000	0.000	1.28	0.001		1.40	0.025	0.004	0.006	1.34	0.001				
% 2se	1.6	5.6	16.6	26.6	1.3	7.0		2.3	31.6	515.1	-61.7	1.8	11.4		2.6	73.3	18.7	26.5	2.7	14.7

Sample:	Oxidative - 1							
		Mg/Ca	Al/Ca					
		(mmol/mol)	(mmol/mol)					
Before cleaning								
	intergrated profile mean	1.48	0.025		0.006	0.002	1.31	0.002
	2 sd	0.50	0.026		0.012	0.015	0.59	0.002
After cleaning								
	intergrated profile mean	1.55	0.012		0.002	0.013	1.30	0.003
	2 sd	0.50	0.020		0.015	0.031	0.35	0.003
Difference								
	mean	-0.07	0.013		0.004	-0.011	0.00	-0.001

Sample:	Oxidative - 10							
		Mg/Ca (mmol/mol)	Al/Ca (mmol/mol)		Mn/Ca (mmol/mol)	Zn/Ca (mmol/mol)	Sr/Ca (mmol/mol)	Ba/Ca (mmol/mol)
Before cleaning								
	intergrated profile mean	2.975	0.039		0.003	0.004	1.368	0.002
	% 2se	1.5	9.2		28.5	30.0	1.7	5.2
After cleaning								
	intergrated profile mean	3.584	0.015		0.002	0.008	1.313	0.001
	% 2se	2.2	13.1		69.9	29.9	2.1	12.6
Difference								
	mean	-0.609	0.025		0.001	-0.004	0.055	0.001

Sample:	Oxidative - 2							
		Mg/Ca (mmol/mol)	Al/Ca (mmol/mol)		Mn/Ca (mmol/mol)	Zn/Ca (mmol/mol)	Sr/Ca (mmol/mol)	Ba/Ca (mmol/mol)
Before cleaning								
	intergrated profile mean	1.65	0.113		0.007	0.006	1.28	0.002
	2 sd	0.55	0.105		0.014	0.016	0.45	0.002
After cleaning								
	intergrated profile mean	1.49	0.099		0.003	0.010	1.37	0.007
	2 sd	0.33	0.072		0.016	0.032	0.34	0.012
Difference								
	mean	0.16	0.013		0.004	-0.004	-0.09	-0.004

Sample:	Oxidative - 3							
		Mg/Ca	Al/Ca		Mn/Ca	Zn/Ca	Sr/Ca	Ba/Ca
		(mmol/mol)	(mmol/mol)		(mmol/mol)	(mmol/mol)	(mmol/mol)	(mmol/mol)
Before cleaning								
	intergrated profile mean	3.16	0.052		0.006	0.005	1.49	0.005
	2 sd	1.12	0.049		0.011	0.019	0.66	0.055
After cleaning								
	intergrated profile mean	0.73	0.019		0.005	0.015	1.29	0.002
	2 sd	0.21	0.021		0.011	0.028	0.35	0.002
Difference								
	mean	2.43	0.033		0.001	-0.010	0.19	0.004

Sample:	Oxidative - 5							
		Mg/Ca	Al/Ca		Mn/Ca	Zn/Ca	Sr/Ca	Ba/Ca
	Before cleaning	(mmol/mol)	(mmol/mol)		(mmol/mol)	(mmol/mol)	(mmol/mol)	(mmol/mol)
	intergrated profile mean	2.29	0.020		0.001	0.003	1.35	0.001
	2 sd	0.74	0.046		0.010	0.016	0.53	0.001
	After cleaning							
	intergrated profile mean	2.27	0.014		0.006	0.011	1.33	0.001
	2 sd	0.60	0.019		0.014	0.026	0.34	0.001
Difference								
	mean	0.02	0.007		-0.005	-0.008	0.02	0.000

Sample:	Oxidative - 6							
		Mg/Ca	Al/Ca		Mn/Ca	Zn/Ca	Sr/Ca	Ba/Ca
Before cleaning		(mmol/mol)	(mmol/mol)		(mmol/mol)	(mmol/mol)	(mmol/mol)	(mmol/mol)
	intergrated profile mean	0.84	0.034		0.000	0.002	1.28	0.001
	2 sd	0.36	0.039		0.010	0.015	0.35	0.001
After cleaning								
	intergrated profile mean	1.20	0.011		0.005	0.083	1.28	0.004
	2 sd	0.26	0.051		0.012	0.049	0.35	0.003
Difference								
	mean	-0.37	0.023		-0.005	-0.081	0.00	-0.003

Sample:	Oxidative - 7							
		Mg/Ca	Al/Ca		Mn/Ca	Zn/Ca	Sr/Ca	Ba/Ca
Before cleaning		(mmol/mol)	(mmol/mol)		(mmol/mol)	(mmol/mol)	(mmol/mol)	(mmol/mol)
	intergrated profile mean	1.35	0.147		0.000	0.004	1.39	0.002
	2 sd	0.42	0.309		0.011	0.018	0.31	0.004
After cleaning								
	intergrated profile mean	1.44	0.075		0.007	0.032	1.32	0.002
	2 sd	0.43	0.054		0.013	0.040	0.30	0.002
Difference								
	mean	-0.09	0.072		-0.007	-0.028	0.07	-0.001

Sample:	Oxidative - 8							
		Mg/Ca (mmol/mol)	Al/Ca (mmol/mol)		Mn/Ca (mmol/mol)	Zn/Ca (mmol/mol)	Sr/Ca (mmol/mol)	Ba/Ca (mmol/mol)
Before cleaning								
	intergrated profile mean	1.36	0.055		0.000	0.000	1.29	0.001
	2 sd	0.38	0.036		0.011	0.022	0.47	0.001
After cleaning								
	intergrated profile mean	1.41	0.053		0.001	0.012	1.32	0.001
	2 sd	0.36	0.060		0.012	0.027	0.33	0.001
Difference								
	mean	-0.04	0.003		-0.001	-0.013	-0.03	0.0001

Sample:	Oxidative - 9							
		Mg/Ca	Al/Ca		Mn/Ca	Zn/Ca	Sr/Ca	Ba/Ca
Before cleaning		(mmol/mol)	(mmol/mol)		(mmol/mol)	(mmol/mol)	(mmol/mol)	(mmol/mol)
	intergrated profile mean	1.21	0.043		0.003	0.004	1.30	0.005
	2 sd	0.36	0.039		0.010	0.013	0.29	0.007
After cleaning								
	intergrated profile mean	1.11	0.008		0.002	0.017	1.27	0.002
	2 sd	0.27	0.015		0.011	0.040	0.25	0.002
Difference								
	mean	0.10	0.035		0.001	-0.012	0.04	0.003

Outer test

► Inner test

Ablation time (s)

oxidative-reductive - 13-chamber *f-1*

BS

***surface
veneer***

f

f-1

inside layer

NONE

COMPO

15.0kV

X1,500

10 μ m

WD 9.3mm

Sample:	Oxidative-Reductive - 15							
		Mg/Ca (mmol/mol)	Al/Ca (mmol/mol)		Mn/Ca (mmol/mol)	Zn/Ca (mmol/mol)	Sr/Ca (mmol/mol)	Ba/Ca (mmol/mol)
Before cleaning								
	intergrated profile mean	1.50	0.010		0.003	0.005	1.32	0.002
	2 sd	0.34	0.019		0.020	0.013	0.26	0.003
After cleaning								
	intergrated profile mean	1.26	0.002		0.003	0.015	1.28	0.001
	2 sd	0.40	0.015		0.013	0.029	0.33	0.001
Difference								
	mean	0.24	0.008		0.000	-0.010	0.04	0.001

oxidative-reductive - 15-
chamber *f*

oxidative-reductive - 15-
chamber f-2, f-3

Sample:	Oxidative-Reductive - 16							
		Mg/Ca	Al/Ca		Mn/Ca	Zn/Ca	Sr/Ca	Ba/Ca
Before cleaning		(mmol/mol)	(mmol/mol)		(mmol/mol)	(mmol/mol)	(mmol/mol)	(mmol/mol)
	intergrated profile mean	1.08	0.018		0.000	0.000	1.32	0.001
	% 2se	1.5	15.1		-19.0	-68.8	1.5	6.5
After cleaning								
	intergrated profile mean	1.02	0.017		0.000	0.002	1.35	0.001
	% 2se	2.1	12.7		-387	106	2.4	13.5
Difference								
	mean	0.06	0.000		0.000	-0.002	-0.03	0.001

oxidative-reductive - 16-
chamber *f-1, f-2*

Sample:	Oxidative-Reductive - 17							
		Mg/Ca (mmol/mol)	Al/Ca (mmol/mol)		Mn/Ca (mmol/mol)	Zn/Ca (mmol/mol)	Sr/Ca (mmol/mol)	Ba/Ca (mmol/mol)
Before cleaning								
	intergrated profile mean	3.52	0.019		0.004	0.004	1.31	0.004
	2 sd	1.16	0.148		0.009	0.010	0.23	0.004
After cleaning								
	intergrated profile mean	3.24	0.003		0.001	0.010	1.31	0.002
	2 sd	1.25	0.013		0.011	0.024	0.30	0.002
Difference								
	mean	0.28	0.016		0.003	-0.006	0.00	0.002

**oxidative-reductive - 17 -
chamber f-2, f-3**

Sample:	Oxidative-Reductive - 18							
		Mg/Ca (mmol/mol)	Al/Ca (mmol/mol)		Mn/Ca (mmol/mol)	Zn/Ca (mmol/mol)	Sr/Ca (mmol/mol)	Ba/Ca (mmol/mol)
Before cleaning								
	intergrated profile mean	1.34	0.011		0.003	0.001	1.29	0.002
	2 sd	0.41	0.019		0.009	0.009	0.24	0.002
After cleaning								
	intergrated profile mean	1.03	0.002		0.000	0.003	1.30	0.001
	2 sd	0.32	0.013		0.012	0.020	0.25	0.002
Difference								
	mean	0.31	0.010		0.004	-0.002	-0.01	0.001

oxidative-reductive - 18 -
chamber *f*

oxidative-reductive - 18 -
chamber *f-1*

oxidative-reductive - 18 -
chamber f-2

oxidative-reductive - 18 -
chamber *f-3*

oxidative-reductive - 18 -
chamber *f* - crystallography

oxidative-reductive - 18 - chamber *f* - crystallography - surface veneer

**oxidative-reductive - 18 - chamber *f* - crystallography -
primary calcite (used for trace element values)**

**oxidative-reductive - 18 - chamber *f* - crystallography -
primary calcite (used for trace element values)**

oxidative-reductive - 18 - chamber *f* - crystallography -
inside layer

Sample:	Oxidative-Reductive - 19							
		Mg/Ca	Al/Ca		Mn/Ca	Zn/Ca	Sr/Ca	Ba/Ca
	Before cleaning	(mmol/mol)	(mmol/mol)		(mmol/mol)	(mmol/mol)	(mmol/mol)	(mmol/mol)
	intergrated profile mean	1.67	0.005		0.005	0.003	1.31	0.001
	2 sd	0.70	0.014		0.009	0.009	0.26	0.001
	After cleaning							
	intergrated profile mean	1.39	0.001		0.002	0.005	1.28	0.001
	2 sd	0.43	0.013		0.014	0.024	0.23	0.001
Difference								
	mean	0.28	0.004		0.002	-0.002	0.02	0.001

oxidative-reductive - 19 - chamber f-2

oxidative-reductive - 19 - chamber f-3

Sample:	Oxidative-Reductive - 20							
		Mg/Ca	Al/Ca		Mn/Ca	Zn/Ca	Sr/Ca	Ba/Ca
		(mmol/mol)	(mmol/mol)		(mmol/mol)	(mmol/mol)	(mmol/mol)	(mmol/mol)
Before cleaning								
	intergrated profile mean	1.19	0.025		0.002	0.001	1.24	0.002
	2 sd	0.36	0.025		0.018	0.009	0.26	0.015
After cleaning								
	intergrated profile mean	1.09	0.014		0.002	0.005	1.23	0.001
	2 sd	0.38	0.034		0.025	0.026	0.25	0.001
Difference								
	mean	0.10	0.011		0.000	-0.003	0.01	0.001

**oxidative-reductive - 20 -
chamber *f***

oxidative-reductive - 20 - chamber *f* and *f-1* suture line

oxidative-reductive - 20 -
chamber *f-1*

oxidative-reductive - 20 -
chamber f-2

oxidative-reductive - 20 -
chamber *f-3*

Sample:	Oxidative-1x Leach - 21							
		Mg/Ca	Al/Ca		Mn/Ca	Zn/Ca	Sr/Ca	Ba/Ca
		(mmol/mol)	(mmol/mol)		(mmol/mol)	(mmol/mol)	(mmol/mol)	(mmol/mol)
Before cleaning								
	intergrated profile mean	0.67	0.002		0.000	0.002	1.28	0.001
	2 sd	0.25	0.013		0.012	0.024	0.38	0.001
After cleaning								
	intergrated profile mean	0.73	0.012		0.001	0.001	1.25	0.001
	2 sd	0.18	0.026		0.007	0.008	0.26	0.001
Difference								
	mean	-0.06	-0.010		-0.001	0.001	0.03	0.000

oxidative, 1x leach - 21 - chamber *f*

Sample:	Oxidative-1x Leach - 23							
		Mg/Ca	Al/Ca		Mn/Ca	Zn/Ca	Sr/Ca	Ba/Ca
		(mmol/mol)	(mmol/mol)		(mmol/mol)	(mmol/mol)	(mmol/mol)	(mmol/mol)
Before cleaning								
	intergrated profile mean	1.70	0.035		0.002	0.002	1.30	0.002
	2 sd	0.50	0.036		0.009	0.010	0.30	0.002
After cleaning								
	intergrated profile mean	1.40	0.008		0.000	0.011	1.32	0.001
	2 sd	0.44	0.019		0.014	0.030	0.45	0.001
Difference								
	mean	0.30	0.028		0.002	-0.008	-0.02	0.001

**oxidative-1 x leach - 23 -
chamber *f-2* - ablation pit
- after cleaning**

**oxidative-1 x
leach - 23 -
chamber *f* -
*pore space***

Sample:	Oxidative-1x Leach - 28							
		Mg/Ca	Al/Ca		Mn/Ca	Zn/Ca	Sr/Ca	Ba/Ca
		(mmol/mol)	(mmol/mol)		(mmol/mol)	(mmol/mol)	(mmol/mol)	(mmol/mol)
Before cleaning								
	intergrated profile mean	1.60	0.035		0.003	0.002	1.30	0.003
	2 sd	0.40	0.063		0.008	0.010	0.28	0.003
After cleaning								
	intergrated profile mean	1.48	0.013		0.000	0.006	1.30	0.001
	2 sd	0.49	0.022		0.014	0.027	0.38	0.002
Difference								
	mean	0.12	0.022		0.003	-0.004	0.00	0.002

**oxidative-1 x leach - 23 -
chamber f-2**

Sample:	Oxidative-1x Leach - 29							
		Mg/Ca	Al/Ca		Mn/Ca	Zn/Ca	Sr/Ca	Ba/Ca
		(mmol/mol)	(mmol/mol)		(mmol/mol)	(mmol/mol)	(mmol/mol)	(mmol/mol)
Before cleaning								
	intergrated profile mean	1.86	0.021		0.010	0.006	1.31	0.004
	2 sd	0.88	0.032		0.012	0.015	0.25	0.003
After cleaning								
	intergrated profile mean	1.42	0.009		0.007	0.005	1.28	0.006
	2 sd	0.46	0.028		0.016	0.032	0.45	0.005
Difference								
	mean	0.44	0.012		0.003	0.001	0.03	-0.002

oxidative- 1x leach - 29-
chamber *f-1*

oxidative-1x leach - 29- chamber f-1 - spine

Sample:	1x Leach - 32							
		Mg/Ca (mmol/mol)	Al/Ca (mmol/mol)		Mn/Ca (mmol/mol)	Zn/Ca (mmol/mol)	Sr/Ca (mmol/mol)	Ba/Ca (mmol/mol)
Before cleaning								
	intergrated profile mean	0.86	0.016		0.002	0.001	1.36	0.001
	2 sd	0.30	0.027		0.007	0.008	0.32	0.002
After cleaning								
	intergrated profile mean	0.88	0.020		0.008	0.017	1.39	0.003
	2 sd	0.22	0.025		0.012	0.026	0.31	0.003
Difference								
	mean	-0.02	-0.004		-0.006	-0.016	-0.03	-0.002

NONE COMPO 15.0kV X2,000 10µm WD 9.5mm

NONE

COMPO 15.0kV

X270

100µm

WD 9.6mm

Image
Ablation pits

After
cleaning

Before
cleaning

Sample: 1x Leach - 33								
		Mg/Ca	Al/Ca		Mn/Ca	Zn/Ca	Sr/Ca	Ba/Ca
Before cleaning		(mmol/mol)	(mmol/mol)		(mmol/mol)	(mmol/mol)	(mmol/mol)	(mmol/mol)
	intergrated profile mean	2.04	0.110		0.010	0.008	1.23	0.005
	2 sd	0.48	0.066		0.008	0.010	0.24	0.006
After cleaning								
	intergrated profile mean	2.39	0.020		0.010	0.017	1.24	0.002
	2 sd	0.63	0.030		0.013	0.026	0.29	0.002
Difference								
	mean	-0.35	0.090		0.000	-0.009	-0.01	0.003

Sample:	1x Leach - 34							
		Mg/Ca	Al/Ca		Mn/Ca	Zn/Ca	Sr/Ca	Ba/Ca
		(mmol/mol)	(mmol/mol)		(mmol/mol)	(mmol/mol)	(mmol/mol)	(mmol/mol)
Before cleaning								
	intergrated profile mean	1.04	0.011		0.001	0.002	1.27	0.001
	2 sd	0.23	0.020		0.007	0.008	0.27	0.001
After cleaning								
	intergrated profile mean	1.10	0.009		0.000	0.000	1.30	0.001
	2 sd	0.27	0.017		0.012	0.024	0.25	0.002
Difference								
	mean	-0.05	0.002		0.001	0.001	-0.03	0.000

Sample:	1x Leach - 35							
		Mg/Ca	Al/Ca					
		(mmol/mol)	(mmol/mol)					
Before cleaning								
	intergrated profile mean	0.98	0.060					
	2 sd	0.37	0.059					
After cleaning								
	intergrated profile mean	0.83	0.068					
	2 sd	0.17	0.048					
Difference								
	mean	0.15	-0.008

Sample:	1x Leach - r1							
		Mg/Ca	Al/Ca		Mn/Ca	Zn/Ca	Sr/Ca	Ba/Ca
Before cleaning		(mmol/mol)	(mmol/mol)		(mmol/mol)	(mmol/mol)	(mmol/mol)	(mmol/mol)
	intergrated profile mean	1.74	0.022		0.001	0.002	1.26	0.001
	2 sd	1.20	0.026		0.007	0.008	0.20	0.001
After cleaning								
	intergrated profile mean	1.61	0.008		0.000	0.000	1.27	0.002
	2 sd	0.49	0.024		0.012	0.021	0.26	0.002
Difference								
	mean	0.13	0.014		0.001	0.002	0.00	-0.001

Sample:	1x Leach - r2							
		Mg/Ca (mmol/mol)	Al/Ca (mmol/mol)		Mn/Ca (mmol/mol)	Zn/Ca (mmol/mol)	Sr/Ca (mmol/mol)	Ba/Ca (mmol/mol)
Before cleaning								
	intergrated profile mean	1.25	0.149		0.003	0.003	1.44	0.002
	2 sd	0.22	0.603		0.006	0.010	0.22	0.004
After cleaning								
	intergrated profile mean	1.41	0.041		0.004	0.002	1.37	0.007
	2 sd	0.29	0.042		0.052	0.029	0.27	0.009
Difference								
	mean	-0.17	0.108		-0.001	0.001	0.06	-0.005

Sample:	1x Leach - r3							
		Mg/Ca (mmol/mol)	Al/Ca (mmol/mol)		Mn/Ca (mmol/mol)	Zn/Ca (mmol/mol)	Sr/Ca (mmol/mol)	Ba/Ca (mmol/mol)
Before cleaning								
	intergrated profile mean	1.25	0.149		0.003	0.003	1.44	0.002
	2 sd	0.22	0.603		0.006	0.010	0.22	0.004
After cleaning								
	intergrated profile mean	1.42	0.034		0.003	0.001	1.35	0.002
	2 sd	0.25	0.066		0.013	0.026	0.26	0.002
Difference								
	mean	-0.17	0.114		0.000	0.002	0.08	-0.001

(1x leach - r-3)

Sample:	2x Leach - 38							
		Mg/Ca (mmol/mol)	Al/Ca (mmol/mol)		Mn/Ca (mmol/mol)	Zn/Ca (mmol/mol)	Sr/Ca (mmol/mol)	Ba/Ca (mmol/mol)
Before cleaning								
	intergrated profile mean	1.43	0.085		0.001	0.001	1.35	0.001
	2 sd	0.32	0.695		0.007	0.007	0.24	0.001
After cleaning								
	intergrated profile mean	1.40	0.034		0.000	0.003	1.36	0.002
	2 sd	0.32	0.023		0.013	0.025	0.33	0.002
Difference								
	mean	0.04	0.051		0.001	-0.001	-0.02	-0.001

(2x leach - 38)

Sample:	2x Leach - 40							
		Mg/Ca	Al/Ca		Mn/Ca	Zn/Ca	Sr/Ca	Ba/Ca
		(mmol/mol)	(mmol/mol)		(mmol/mol)	(mmol/mol)	(mmol/mol)	(mmol/mol)
Before cleaning								
	intergrated profile mean	1.40	0.141		0.007	0.004	1.32	0.004
	2 sd	0.42	0.378		0.008	0.008	0.31	0.004
After cleaning								
	intergrated profile mean	1.49	0.023		0.004	0.015	1.39	0.002
	2 sd	0.39	0.041		0.015	0.025	0.25	0.002
Difference								
	mean	-0.10	0.118		0.003	-0.011	-0.07	0.002

Sample: 2x Leach - 43							
		Mg/Ca	Al/Ca				
		(mmol/mol)	(mmol/mol)				
Before cleaning							
	intergrated profile mean	2.06	0.092				
	2 sd	0.75	0.059				
After cleaning							
	intergrated profile mean	1.42	0.025				
	2 sd	0.59	0.025				
Difference							
	mean	0.64	0.067

Sample:	2x Leach - 44							
		Mg/Ca (mmol/mol)	Al/Ca (mmol/mol)		Mn/Ca (mmol/mol)	Zn/Ca (mmol/mol)	Sr/Ca (mmol/mol)	Ba/Ca (mmol/mol)
Before cleaning								
	intergrated profile mean	2.38	0.010		0.002	0.001	1.31	0.002
	2 sd	1.12	0.029		0.007	0.007	0.23	0.001
After cleaning								
	intergrated profile mean	1.48	0.005		0.001	0.000	1.33	0.001
	2 sd	0.59	0.014		0.011	0.022	0.23	0.001
Difference								
	mean	0.91	0.005		0.001	0.001	-0.01	0.001

Sample:	2x Leach - 48							
		Mg/Ca	Al/Ca		Mn/Ca	Zn/Ca	Sr/Ca	Ba/Ca
Before cleaning		(mmol/mol)	(mmol/mol)		(mmol/mol)	(mmol/mol)	(mmol/mol)	(mmol/mol)
	intergrated profile mean	1.27	0.023		0.005	0.004	1.30	0.003
	2 sd	0.40	0.048		0.008	0.015	0.34	0.003
After cleaning								
	intergrated profile mean	1.26	0.035		0.005	0.000	1.25	0.007
	2 sd	0.48	0.046		0.013	0.025	0.23	0.006
Difference								
	mean	0.02	-0.012		0.000	0.003	0.06	-0.004

Sample:	4x Leach - 41							
		Mg/Ca	Al/Ca		Mn/Ca	Zn/Ca	Sr/Ca	Ba/Ca
Before cleaning		(mmol/mol)	(mmol/mol)		(mmol/mol)	(mmol/mol)	(mmol/mol)	(mmol/mol)
	intergrated profile mean	1.23	0.023		0.001	0.000	1.36	0.001
	2 sd	0.28	0.058		0.006	0.008	0.31	0.001
After cleaning								
	intergrated profile mean	1.17	0.003		0.000	0.001	1.37	0.001
	2 sd	0.26	0.015		0.013	0.023	0.32	0.001
Difference								
	mean	0.07	0.020		0.001	-0.001	-0.01	0.000

(6x leach - 46)

Sample:	6x Leach - 46							
		Mg/Ca (mmol/mol)	Al/Ca (mmol/mol)		Mn/Ca (mmol/mol)	Zn/Ca (mmol/mol)	Sr/Ca (mmol/mol)	Ba/Ca (mmol/mol)
Before cleaning								
	intergrated profile mean	1.64	0.034		0.002	0.002	1.29	0.011
	2 sd	1.54	0.041		0.007	0.009	0.31	0.016
After cleaning								
	intergrated profile mean	2.90	0.014		0.013	0.004	1.34	0.006
	2 sd	0.73	0.015		0.012	0.017	0.22	0.003
Difference								
	mean	-1.26	0.020		-0.011	-0.002	-0.05	0.005

Sample:	10x Leach - 47							
		Mg/Ca	Al/Ca		Mn/Ca	Zn/Ca	Sr/Ca	Ba/Ca
Before cleaning		(mmol/mol)	(mmol/mol)		(mmol/mol)	(mmol/mol)	(mmol/mol)	(mmol/mol)
	intergrated profile mean	2.32	0.025		0.003	0.002	1.22	0.001
	2 sd	0.57	0.022		0.007	0.008	0.25	0.002
After cleaning								
	intergrated profile mean	1.33	0.003		0.000	0.000	1.28	0.001
	2 sd	0.42	0.013		0.013	0.021	0.32	0.001
Difference								
	mean	0.99	0.022		0.003	0.002	-0.05	0.001

Chap. 2 - Table 1

'LA processed' - before chemical cleaning (mmol/mol)							
Cleaning protocol	Mg/Ca	Al/Ca	Mn/Ca	Zn/Ca	Sr/Ca	Ba/Ca	n=
Oxidative	1.81	0.06	0.003	0.003	1.34	0.002	8
Oxidative-Reductive	1.60	0.01	0.002	0.004	1.30	0.002	7
Oxidative-1x Leach	1.46	0.02	0.004	0.003	1.30	0.002	4
1x Leach	1.33	0.06	0.004	0.003	1.32	0.003	7
2x Leach	1.71	0.07	0.005	0.003	1.32	0.003	5
4x Leach	1.23	0.02	0.001	0.000	1.36	0.001	1
6x Leach	2.22	0.02	0.008	0.002	1.32	0.006	2
10x Leach	2.32	0.03	0.003	0.002	1.22	0.001	1
'LA processed' - after chemical cleaning (mmol/mol)							
							n=
Oxidative	1.64	0.03	0.004	0.022	1.31	0.003	8
Oxidative-Reductive	1.45	0.01	0.001	0.006	1.31	0.001	7
Oxidative-1x Leach	1.26	0.01	0.002	0.006	1.29	0.002	4
1x Leach	1.38	0.03	0.004	0.006	1.32	0.003	7
2x Leach	1.41	0.02	0.003	0.005	1.33	0.003	5
4x Leach	1.17	0.00	0.000	0.001	1.37	0.001	1
6x Leach	2.61	0.01	0.007	0.002	1.33	0.004	2
10x Leach	1.33	0.00	0.000	0.000	1.28	0.001	1
'Solution processed' - before chemical cleaning (mmol/mol)							
							n=
Oxidative	2.68	0.81	0.018	0.033	1.45	0.010	8
Oxidative-Reductive	2.27	0.39	0.009	0.013	1.39	0.008	7
Oxidative-1x Leach	2.13	0.98	0.010	0.012	1.37	0.009	4
1x Leach	2.17	0.49	0.014	0.015	1.38	0.009	7
2x Leach	2.25	0.42	0.013	0.010	1.38	0.004	5
4x Leach	1.93	0.39	0.007	0.008	1.40	0.021	1
6x Leach	2.57	0.39	0.342	0.013	1.37	0.008	2
10x Leach	2.24	0.24	0.007	0.007	1.30	0.010	1
'Solution processed' - after chemical cleaning (mmol/mol)							
							n=
Oxidative	1.96	0.31	0.008	0.049	1.34	0.006	8
Oxidative-Reductive	1.72	0.07	0.001	0.002	1.32	0.002	7
Oxidative-1x Leach	1.55	0.12	0.004	0.021	1.32	0.004	4
1x Leach	1.84	0.42	0.016	0.027	1.37	0.022	7
2x Leach	1.74	0.24	0.011	0.032	1.35	0.009	5
4x Leach	1.38	0.05	0.003	0.044	1.61	0.003	1
6x Leach	2.48	0.02	0.010	0.011	1.34	0.004	2
10x Leach	1.40	0.02	0.004	0.006	1.34	0.001	1

Chap. 2 - SI 3.0

Element	Isotope measured	Mean concentration (ppm)	Mean LOD (ppm)
Mg	24	441	0.22
Al	27	16.2	0.48
Mn	55	2.87	0.84
Zn	64	2.75	1.17
Sr	88	1218	0.05
Ba	138	3.54	0.05

Chap. 2 - SI 4.0

	Before chemical cleaning - LA processing- TE/Ca (mmol/mol)						After chemical cleaning - LA processing- TE/Ca (mmol/mol)						Before chemical cleaning - solution processing- TE/Ca (mmol/r						After chemical cleaning - solution processing- TE/Ca (mmol/mo					
	Mg/Ca	Al/Ca	Mn/Ca	Zn/Ca	Sr/Ca	Ba/Ca	Mg/Ca	Al/Ca	Mn/Ca	Zn/Ca	Sr/Ca	Ba/Ca	Mg/Ca	Al/Ca	Mn/Ca	Zn/Ca	Sr/Ca	Ba/Ca	Mg/Ca	Al/Ca	Mn/Ca	Zn/Ca	Sr/Ca	Ba/Ca
Oxidative - 1	1.48	0.025	0.006	0.002	1.31	0.002	1.55	0.012	0.002	0.013	1.30	0.003	3.30	1.76	0.042	0.076	1.44	0.022	2.37	0.309	0.007	0.041	1.37	0.013
Oxidative - 2	1.65	0.113	0.007	0.006	1.28	0.002	1.49	0.099	0.003	0.010	1.37	0.007	2.41	0.72	0.024	0.030	1.40	0.009	2.11	0.545	0.011	0.039	1.48	0.020
Oxidative - 3	3.16	0.052	0.006	0.005	1.49	0.005	0.73	0.019	0.005	0.015	1.29	0.002	3.92	1.11	0.022	0.022	1.66	0.020	0.76	0.029	0.004	0.016	1.30	0.002
Oxidative - 4	1.94	0.269	0.013	0.011	1.32	0.007	*	*	*	*	*	*	*	*	*	*	*	*	*	*	*	*	*	*
Oxidative - 5	2.29	0.020	0.001	0.003	1.35	0.001	2.27	0.014	0.006	0.011	1.33	0.001	2.84	0.35	0.023	0.018	1.41	0.005	2.59	0.090	0.014	0.025	1.38	0.002
Oxidative - 6	0.84	0.034	0.000	0.002	1.28	0.001	1.20	0.011	0.005	0.083	1.28	0.004	2.00	0.81	0.015	0.042	1.35	0.019	1.45	0.086	0.009	0.152	1.25	0.008
Oxidative - 7	1.35	0.147	0.000	0.004	1.39	0.002	1.44	0.075	0.007	0.032	1.32	0.002	2.08	0.83	0.012	0.032	1.48	0.005	1.98	1.072	0.016	0.068	1.37	0.006
Oxidative - 8	1.36	0.055	0.000	0.000	1.29	0.001	1.41	0.053	0.001	0.012	1.32	0.001	2.12	0.54	0.005	0.028	1.41	0.013	1.58	0.247	0.004	0.031	1.31	0.002
Oxidative - 9	1.21	0.043	0.003	0.004	1.30	0.005	1.11	0.008	0.002	0.017	1.27	0.002	2.09	0.62	0.012	0.024	1.44	0.091	1.23	0.101	0.005	0.045	1.28	0.003
Oxidative - 10	2.98	0.039	0.003	0.004	1.37	0.002	3.58	0.015	0.002	0.008	1.31	0.001	3.39	0.52	0.011	0.026	1.44	0.006	3.61	0.304	0.005	0.021	1.36	0.003
Oxidative-Reductive - 11	3.21	0.037	0.012	0.005	1.32	0.002	*	*	*	*	*	*	*	*	*	*	*	*	*	*	*	*	*	*
Oxidative-Reductive - 12	2.40	0.052	0.008	0.008	1.28	0.006	*	*	*	*	*	*	*	*	*	*	*	*	*	*	*	*	*	*
Oxidative-Reductive - 13	0.91	0.005	0.001	0.0109	1.34	0.001	1.07	0.017	0.000	0.0004	1.39	0.001	2.47	0.32	0.005	0.010	1.46	0.006	1.82	0.046	0.000	0.0023	1.46	0.002
Oxidative-Reductive - 14	1.64	0.041	0.006	0.0021	1.43	0.002	*	*	*	*	*	*	*	*	*	*	*	*	*	*	*	*	*	*
Oxidative-Reductive - 15	1.50	0.010	0.003	0.0049	1.32	0.002	1.26	0.002	0.003	0.0153	1.28	0.001	2.08	0.69	0.016	0.028	1.40	0.013	1.34	0.228	0.001	0.0053	1.32	0.003
Oxidative-Reductive - 16	1.08	0.018	0.000	0.0000	1.32	0.001	1.02	0.017	0.000	0.0018	1.35	0.001	2.13	0.89	0.010	0.024	1.48	0.017	1.20	0.083	0.000	0.0015	1.37	0.003
Oxidative-Reductive - 17	3.52	0.019	0.004	0.0038	1.31	0.004	3.24	0.003	0.001	0.0103	1.31	0.002	3.61	0.34	0.009	0.009	1.34	0.012	3.86	0.045	0.002	0.0029	1.32	0.003
Oxidative-Reductive - 18	1.34	0.011	0.003	0.0009	1.29	0.002	1.03	0.002	0.000	0.0027	1.30	0.001	1.85	0.06	0.004	0.003	1.33	0.003	1.30	0.011	0.002	0.0002	1.29	0.001
Oxidative-Reductive - 19	1.67	0.005	0.005	0.0031	1.31	0.001	1.39	0.001	0.002	0.0047	1.28	0.001	1.77	0.01	0.002	0.002	1.29	0.001	1.40	0.015	0.002	0.0023	1.29	0.001
Oxidative-Reductive - 20	1.19	0.025	0.002	0.0013	1.24	0.002	1.09	0.014	0.002	0.0048	1.23	0.001	1.94	0.41	0.012	0.013	1.45	0.006	1.15	0.048	0.002	0.0021	1.22	0.002
Oxidative-1x Leach - 21	0.67	0.002	0.000	0.002	1.28	0.001	0.73	0.012	0.001	0.001	1.25	0.001	0.88	0.11	0.004	0.006	1.27	0.002	0.77	0.023	0.003	0.008	1.28	0.001
Oxidative-1x Leach - 22	0.91	0.031	0.005	0.003	1.35	0.002	*	*	*	*	*	*	*	*	*	*	*	*	*	*	*	*	*	*
Oxidative-1x Leach - 23	1.70	0.035	0.002	0.002	1.30	0.002	1.40	0.008	0.000	0.011	1.32	0.001	2.19	1.69	0.010	0.011	1.41	0.008	1.46	0.063	0.003	0.019	1.33	0.001
Oxidative-1x Leach - 24	3.29	0.035	0.009	0.008	1.35	0.019	*	*	*	*	*	*	*	*	*	*	*	*	*	*	*	*	*	*
Oxidative-1x Leach - 25	1.73	0.183	0.006	0.017	1.38	0.006	*	*	*	*	*	*	*	*	*	*	*	*	*	*	*	*	*	*
Oxidative-1x Leach - 26	1.41	0.014	0.002	0.003	1.28	0.002	*	*	*	*	*	*	*	*	*	*	*	*	*	*	*	*	*	*
Oxidative-1x Leach - 27	4.54	0.043	0.010	0.012	1.33	0.011	*	*	*	*	*	*	*	*	*	*	*	*	*	*	*	*	*	*
Oxidative-1x Leach - 28	1.60	0.035	0.003	0.002	1.30	0.003	1.48	0.013	0.000	0.006	1.30	0.001	2.11	0.38	0.008	0.008	1.33	0.008	1.59	0.102	0.003	0.014	1.30	0.001
Oxidative-1x Leach - 29	1.86	0.021	0.010	0.006	1.31	0.004	1.42	0.009	0.007	0.005	1.28	0.006	3.34	1.74	0.019	0.024	1.46	0.022	2.37	0.309	0.007	0.041	1.37	0.013
Oxidative-1x Leach - 30	2.06	0.034	0.006	0.002	1.46	0.002	*	*	*	*	*	*	*	*	*	*	*	*	*	*	*	*	*	*
1x Leach - 31	2.23	0.016	0.001	0.002	1.37	0.001	*	*	*	*	*	*	*	*	*	*	*	*	*	*	*	*	*	*
1x Leach - 32	0.86	0.016	0.002	0.001	1.36	0.001	0.88	0.020	0.008	0.017	1.39	0.003	1.52	0.22	0.006	0.006	1.37	0.004	1.11	0.613	0.024	0.063	1.37	0.008
1x Leach - 33	2.04	0.110	0.010	0.008	1.23	0.005	2.39	0.020	0.010	0.017	1.24	0.002	2.15	0.38	0.014	0.012	1.26	0.007	2.62	0.046	0.013	0.031	1.27	0.003
1x Leach - 34	1.04	0.011	0.001	0.002	1.27	0.001	1.10	0.009	0.000	0.000	1.30	0.001	1.77	0.57	0.009	0.021	1.37	0.008	1.38	0.118	0.007	0.032	1.36	0.006
1x Leach - 35	0.98	0.060	0.009	0.005	1.28	0.003	0.83	0.068	0.006	0.003	1.30	0.006	2.72	0.57	0.025	0.014	1.35	0.011	1.53	0.870	0.034	0.020	1.43	0.032
1x Leach - 36	1.60	0.028	0.005	0.005	1.30	0.003	*	*	*	*	*	*	*	*	*	*	*	*	*	*	*	*	*	*
1x Leach - 37	1.91	0.030	0.015	0.007	1.31	0.004	*	*	*	*	*	*	*	*	*	*	*	*	*	*	*	*	*	*
1x Leach - r1	1.74	0.022	0.001	0.002	1.26	0.001	1.61	0.008	0.000	0.000	1.27	0.002	2.06	0.32	0.008	0.008	1.30	0.004	2.02	0.035	0.010	0.011	1.34	0.008
1x Leach - r2	1.41	0.041	0.004	0.002	1.37	0.007	1.41	0.041	0.004	0.002	1.37	0.007	2.76	0.45	0.009	0.018	1.39	0.026	2.19	0.766	0.014	0.013	1.46	0.091
1x Leach - r3	1.25	0.149	0.003	0.003	1.44	0.002	1.42	0.034	0.003	0.001	1.35	0.002	2.21	0.89	0.025	0.026	1.65	0.012	2.04	0.522	0.012	0.022	1.37	0.009
2x Leach - 38	1.43	0.085	0.001	0.001	1.35	0.001	1.40	0.034	0.000	0.003	1.36	0.002	2.04	0.49	0.008	0.009	1.38	0.004	1.68	0.213	0.007	0.019	1.38	0.006
2x Leach - 40	1.40	0.141	0.007	0.004	1.32	0.004	1.49	0.023	0.004	0.015	1.39	0.002	2.07	0.46	0.012	0.008	1.40	0.006	1.63	0.347	0.010	0.072	1.41	0.007
2x Leach - 43	2.06	0.092	0.009	0.007	1.29	0.006	1.42	0.025	0.004	0.009	1.31	0.003	2.59	0.68	0.012	0.013	1.41	0.013	2.04	0.313	0.016	0.051	1.32	0.010
2x Leach - 44	2.38	0.010	0.002	0.001	1.31	0.002	1.48	0.005	0.001	0.000	1.33	0.001	2.39	0.20	0.006	0.007	1.35	0.005	1.78	0.077	0.003	0.005	1.33	0.003
2x Leach - 48	1.27	0.023	0.005	0.004	1.30	0.003	1.26	0.035	0.005	0.000	1.25	0.007	2.16	0.27	0.026	0.013	1.33	0.009	1.57	0.264	0.018	0.014	1.29	0.017
2x Leach - 49	1.29	0.009	0.001	0.001	1.28	0.001	*	*	*	*	*	*	*	*	*	*	*	*	*	*	*	*	*	*
4x Leach - 41	1.23	0.023	0.001	0.000	1.36	0.001	1.17	0.003	0.000	0.001	1.37	0.001	1.93	0.39	0.007	0.008	1.40	0.009	1.38	0.049	0.003	0.044	1.61	0.003
4x Leach - 42	2.52	0.062	0.009	0.011	1.36	0.003	*	*	*	*	*	*	*	*	*	*	*	*	*	*	*	*	*	*
4x Leach - 50	1.43	0.030	0.004	0.004	1.37	0.001	*	*	*	*	*	*	*	*	*	*	*	*	*	*	*	*	*	*
6x Leach - 45	2.79	0.010	0.014	0.001	1.35	0.001	2.32	0.009	0.000	0.000	1.31	0.001	3.28	0.45	0.678	0.016	1.38	0.010	2.22	0.013	0.005	0.004	1.32	0.001
6x Leach - 46	1.64	0.034	0.002	0.002	1.29	0.011	2.90	0.014	0.013	0.004	1.34	0.006	1.87	0.33	0.007	0.010	1.35	0.011	2.74	0.028	0.014	0.018	1.36	0.007
10x Leach - 47	2.32	0.025	0.003	0.002	1.22	0.001	1.33	0.003	0.000	0.000	1.28	0.001	2.24	0.24	0.007	0.007	1.30	0.004	1.40	0.025	0.004	0.006	1.34	0.001

G. bullides - chamber f-2																G. bullides - chamber f																G. ruber - chamber f-1															
Age	Sediment sample depth	Mg/Ca	Al/Ca	Mn/Ca	Zn/Ca	Sr/Ca	Ba/Ca	Age	Sediment sample depth	Mg/Ca	Al/Ca	Mn/Ca	Zn/Ca	Sr/Ca	Ba/Ca	Age	Sediment sample depth	Mg/Ca	Al/Ca	Mn/Ca	Zn/Ca	Sr/Ca	Ba/Ca	Age	Sediment sample depth	Mg/Ca	Al/Ca	Mn/Ca	Zn/Ca	Sr/Ca	Ba/Ca																
(yr)	(cm)	(mmol/mol)	(mmol/mol)	(mmol/mol)	(mmol/mol)	(mmol/mol)	(mmol/mol)	(yr)	(cm)	(mmol/mol)	(mmol/mol)	(mmol/mol)	(mmol/mol)	(mmol/mol)	(mmol/mol)	(yr)	(cm)	(mmol/mol)	(mmol/mol)	(mmol/mol)	(mmol/mol)	(mmol/mol)	(mmol/mol)	(yr)	(cm)	(mmol/mol)	(mmol/mol)	(mmol/mol)	(mmol/mol)	(mmol/mol)	(mmol/mol)																
13	0.0	0.00-0.01	3.74	0.8	322.7	190.0	102.8	50.2	55.6	22.4	1.41	0.03	8.3	0.9	7	1.0	0.38-0.39	2.42	0.4	227.8	171.2	254.9	113.7	21.6	14.2	1.43	0.08	8.9	1.8	18	0.0	0.00-0.01	3.74	0.8	322.7	190.0	102.8	50.2	55.6	22.4	1.41	0.03	8.3	0.9			
18	0.0	0.01-0.02	3.24	0.6	100.8	43.6	111.1	33.6	27.4	8.4	1.43	0.06	6.5	1.6	24	0.0	0.01-0.02	2.58	0.4	46.0	20.5	125.7	18.6	38.4	8.4	1.41	0.05	6.3	1.2	15	1.8	0.56-0.57	2.63	0.3	213.2	91.0	194.8	43.6	18.3	8.3	1.39	0.04	5.6	1.4			
16	0.1	0.08-0.09	3.38	0.8	235.8	92.2	141.3	38.4	18.9	4.9	1.37	0.03	8.1	2.4	24	0.1	0.08-0.09	2.73	0.5	129.5	59.9	140.6	21.4	26.7	5.7	1.37	0.04	7.4	1.3	9	2.6	0.80-0.81	3.33	0.7	200.0	106.2	205.2	52.5	17.3	9.5	1.35	0.02	3.8	1.6			
12	0.4	0.20-0.21	3.25	0.9	48.7	26.1	148.2	46.7	22.1	6.3	1.73	0.24	4.8	1.2	16	0.4	0.20-0.21	2.81	0.9	32.0	18.2	152.2	21.2	19.1	4.3	1.61	0.14	5.0	1.0	6	4.3	1.40-1.41	3.04	1.0	44.1	92.8	269.7	102.8	7.1	3.3	1.44	0.06	5.6	1.8			
32	1.0	0.38-0.39	2.99	0.4	124.8	40.0	180.6	28.6	24.4	4.7	1.37	0.02	5.6	1.5	46	1.0	0.38-0.39	2.39	0.3	86.1	27.7	167.3	15.4	26.8	3.9	1.36	0.02	5.6	1.2	14	5.3	1.80-1.81	3.01	0.9	147.0	165.1	214.5	92.6	12.7	8.3	1.42	0.06	6.6	2.4			
21	1.8	0.56-0.57	3.80	0.7	247.3	108.5	218.1	30.8	19.8	5.9	1.33	0.03	6.3	1.7	25	1.8	0.56-0.57	3.02	0.7	251.7	108.8	196.2	25.6	29.5	15.1	1.34	0.03	10.0	2.2	6	5.6	1.90-1.91	3.07	0.8	90.6	129.3	298.5	118.5	29.1	30.7	1.42	0.08	8.3	2.4			
16	2.6	0.80-0.81	3.52	0.7	125.0	50.1	126.6	43.3	19.7	8.0	1.36	0.02	5.1	1.6	21	2.6	0.80-0.81	2.59	0.4	73.1	42.3	205.6	29.3	18.1	5.6	1.35	0.02	4.7	1.2	15	6.1	2.10-2.11	2.65	0.3	156.6	117.2	263.8	49.0	23.0	13.4	1.41	0.03	4.7	1.2			
12	2.9	0.90-0.91	3.28	0.8	72.2	40.4	276.5	56.2	66.3	35.5	1.39	0.05	4.1	2.0	15	2.9	0.90-0.91	2.76	0.6	55.9	39.3	232.5	39.9	87.4	35.7	1.39	0.02	3.4	1.3	11	6.4	2.20-2.21	3.29	0.4	134.0	101.3	256.1	59.5	9.8	6.1	1.43	0.06	5.3	1.7			
13	4.3	1.40-1.41	3.62	1.2	132.6	63.5	286.4	80.1	20.6	11.3	1.39	0.05	6.0	1.6	9	4.3	1.10-1.11	2.17	0.3	196.9	117.5	177.8	36.5	28.6	13.6	1.39	0.06	6.3	2.6	8	6.9	2.40-2.41	2.36	0.7	139.6	129.7	170.9	87.1	13.9	11.9	1.41	0.06	5.5	1.8			
21	4.8	1.60-1.61	4.01	0.9	146.0	50.4	328.0	49.3	27.8	10.8	1.42	0.04	6.6	1.1	16	4.3	1.40-1.41	2.89	0.7	109.7	53.6	239.3	54.7	23.7	11.6	1.39	0.04	5.6	1.9	14	7.1	2.50-2.51	2.74	0.6	144.2	64.7	184.1	64.0	10.2	7.5	1.39	0.04	4.5	1.3			
17	5.3	1.80-1.81	3.25	0.7	168.2	132.0	241.2	102.3	22.3	10.5	1.41	0.09			23	4.8	1.60-1.61	3.20	0.6	117.7	61.5	259.0	44.6	26.9	10.5	1.41	0.02	5.3	1.0	11	7.4	2.60-2.61	2.69	0.3	114.5	100.2	229.4	89.9	17.2	17.0	1.39	0.04	4.9	1.7			
10	5.6	1.90-1.91	2.56	0.4	68.4	32.7	226.2	55.5	14.7	9.7	1.34	0.05	4.1	2.1	27	5.3	1.80-1.81	2.46	0.4	88.3	44.8	194.3	36.9	24.0	12.3	1.39	0.06	7.6	3.4	8	7.6	2.69-2.70	2.47	0.2	120.4	134.0	260.9	75.2	12.1	7.1	1.34	0.06	2.9	1.5			
19	6.0	2.10-2.11	2.87	0.5	93.2	39.1	204.2	46.6			1.37	0.04	7.3	2.5	13	5.6	1.90-1.91	2.20	0.4	27.1	18.4	216.0	34.8	21.2	8.6	1.36	0.04	5.6	1.5	9	7.9	2.90-2.91	2.58	0.3	109.6	81.0	151.1	65.9	14.6	13.4	1.47	0.06	2.9	0.9			
23	6.1	2.20-2.21	3.41	0.8	103.3	62.8	208.1	50.5	10.7	5.3	1.37	0.03	5.7	1.7	22	6.0	2.10-2.11	2.40	0.3	84.7	35.6	164.2	31.7	24.0	13.2	1.37	0.03	4.6	0.7	10	8.4	3.00-3.01	2.52	0.6	125.2	156.1	181.1	75.5	14.7	17.5	1.39	0.04	3.8	1.6			
23	6.3	2.30-2.31	3.61	0.7	158.5	54.2	176.5	33.6	21.4	6.1	1.38	0.03	4.8	1.0	19	6.1	2.20-2.21	2.69	0.6	19.8	12.3	193.5	30.7	12.8	4.4	1.36	0.03	4.5	1.3	7	9.0	3.30-3.31	2.96	0.8	275.7	492.7	275.5	83.2	35.8	74.1	1.38	0.10	5.4	0.8			
12	6.5	2.40-2.41	3.02	0.9	107.7	58.5	194.1	68.2	24.3	14.8	1.40	0.10	5.0	1.6	27	6.3	2.30-2.31	2.54	0.4	98.3	38.5	177.2	30.2	28.5	6.7	1.36	0.03	4.6	0.7	15	9.3	3.60-3.61	2.51	0.5	375.5	234.1	243.7	34.7	7.9	8.7	1.43	0.05	2.4	0.5			
12	6.6	2.50-2.51	2.46	0.4	182	16.9	172.6	71.1	16.4	9.1	1.35	0.03	6.5	2.9	16	6.5	2.40-2.41	2.82	0.7	67.2	36.9	170.0	29.1	19.4	9.4	1.38	0.03	4.1	1.0	7	10.0	3.70-3.71	3.01	0.9	29.5	21.0	350.9	105.8	10.9	8.3	1.37	0.03	3.2	0.8			
19	6.8	2.60-2.61	3.85	1.0	107.8	63.0	213.2	35.4	15.9	4.4	1.33	0.02	4.8	1.7	14	6.6	2.50-2.51	2.47	0.4	33.5	23.0	187.7	77.3	13.2	6.6	1.38	0.05	5.7	1.8	13	10.2	3.80-3.81	2.76	0.8	128.2	91.1	295.5	126.1	19.7	20.0	1.42	0.04	3.6	1.3			
20	7.1	2.72-2.73	3.43	0.7	179.6	54.3	211.6	46.7	21.9	6.0	1.37	0.04	6.0	1.1	21	6.8	2.60-2.61	2.57	0.8	80.8	55.2	179.7	34.9	14.5	5.5	1.36	0.03	3.0	1.1	5	10.5	3.90-3.91	3.05	0.5	91.0	53.2	409.1	184.9	4.7	2.7	1.35	0.03	4.2	1.0			
12	7.9	2.90-2.91	3.75	1.1	158.5	75.0	170.2	56.4	25.5	11.1	1.35	0.06	5.2	2.2	14	7.0	2.90-2.91	2.18	0.4	159.0	42.8	218.3	43.9	47.4	17.8	1.37	0.17	3.8	0.9	7	10.7	4.00-4.01	2.89	0.5	129.8	146.5	358.7	145.4	16.4	23.2	1.40	0.09	3.5	1.0			
20	9.0	3.20-3.21	2.72	0.6	300.0	113.7	206.9	55.4	22.2	11.1	1.43	0.07	6.2	1.8	21	7.1	2.72-2.73	2.48	0.4	132.8	48.1	198.4	34.4	24.9	6.5	1.34	0.03	5.7	1.5	5	11.5	4.20-4.21	2.50	1.2	347.9	319.1	399.9	188.3	35.8	42.4	1.45	0.08	5.8	5.3			
9	9.3	3.30-3.31	3.41	0.9	344.0	131.8	285.9	77.5			1.37	0.04	4.2	1.4	15	7.9	2.90-2.91	3.05	0.9	124.5	67.9	168.1	24.4	38.6	18.5	1.34	0.06	4.7	1.9	11	11.8	4.44-4.45			73.0	42.7	62.1	29.1	4.5	2.1	1.43	0.05	1.3	0.2			
16	10.0	3.60-3.61	3.27	0.8	247.1	160.1	262.2	55.1	23.4	16.2	1.44	0.04	3.4	0.8	25	8.4	3.20-3.31	2.31	0.4	147.8	88.7	196.0	30.7	35.0	20.2	1.47	0.05	4.9	1.2	8	12.8	4.50-4.51	3.25	0.3	255.3	171.3	390.3	201.0	84.2	133.5	1.37	0.04	5.7	2.3			
10	10.2	3.70-3.71	2.41	0.4	169.8	74.8	250.4	86.6	12.0	7.3	1.34	0.03	3.3	0.9	20	9.0	3.30-3.31	2.35	0.4	61.5	25.4	244.3	48.3	30.2	15.1	1.39	0.04	3.8	1.5	6	13.1	4.70-4.71	1.80	0.1	332.8	417.8	105.7										

Chap. 4 - SI 2

	Glacial			Termination (ACR)		Interglacial	
	Depth (m)						
	9.01-9.02	7.21-7.22	6.10-6.11	5.60-5.61	5.04-5.05	3.79-3.80	2.10-2.11
	Age (ka)						
Species	24.3	20.0	17.2	15.5	13.7	10.5	6.0
<i>Coccolithus palagicus</i>	9	4	7	17	15	7	1
<i>Calcidiscus leptoporus</i>	25	13	12	7		1	8
<i>Gephyrocapsa</i> spp.	22	27	43	37	5	19	1
<i>Emiliana huxleyi</i>	24	9	19			9	1
<i>Umbilicosphaera</i>	1	2	4	1			
<i>Helicosphaera carteri</i>		1		1	1	1	
<i>Oolithotus antillarum</i>				1			
Total identified	81	56	85	64	21	37	11

Chap. 5 - SI 1

Core ID	Depth (m)	Location		G. bullioides			WOA			Carbonate ion [CO ₃ ²⁻]		Chlorophyll a conc. Sep, 1997-Dec, 2010 mg/m**3
		Latitude	Longitude	Length (µm)	Weight (µg)	SNW (g/m)	Temperature (°C)	Phosphate micromoles/l	Nitrate micromoles/l	Pre-industrial (µMkg ⁻¹)	Modern (µMkg ⁻¹)	
		(°N)	(°E)									
Barker et al., 2002 - core top												
T88 15B	2585	38.6	-25.0	436		0.039	15.6	0.2	2.6	249		0.2
T88 15aB	2738	38.9	-25.0	445		0.043	15.6	0.2	2.6	249		0.3
T88 14B	2858	40.4	-25.8	449			15.0	0.6	6.3	245		0.3
T90 12B	5085	40.6	-20.1	422			14.7	0.2	3.3	246		0.3
T86 9B	2026	40.8	-27.5	420		0.043	15.4	0.3	2.9	244		0.3
T86 8B	3232	42.3	-25.7	435		0.040	14.6	0.3	3.7	241		0.3
T88 13B	3133	42.9	-25.3	462		0.044	14.6	0.3	3.7	240		0.3
T86 7B	2664	43.9	-25.0	398		0.033	14.2	0.3	4.0	238		0.3
T90 13B	4016	44.0	-20.0	437			13.8	0.3	4.7	237		0.4
T88 12B	3052	44.1	-24.9	448		0.038	14.2	0.3	4.4	238		0.4
T90 11B	3208	45.0	-24.7	449		0.036	14.2	0.3	4.4	236		0.4
T88 11B	2741	45.4	-25.4	447		0.032	13.7	0.4	4.6	235		0.4
T90 5B	3069	46.0	-23.8	439		0.030	13.5	0.4	5.0	234		0.4
T90 8B	3393	46.2	-23.7	450		0.032	13.2	0.4	5.4	234		0.4
T86 5B	3121	46.9	-25.4	417			13.5	0.4	5.1	232		0.5
T88 9B	3074	48.4	-25.1	451		0.032	12.7	0.5	6.3	229		0.6
T86 3B	3113	50.2	-27.0	421		0.031	11.3	0.6	7.8	225		0.6
T88 7B	3013	50.5	-26.5	448		0.030	11.4	0.6	7.8	225		0.7
T88 6B	3381	51.4	-25.8	451		0.027	10.7	0.6	8.8	222		0.7
T90 2B	2731	53.1	-20.8	451		0.029	10.6	0.6	9.9	222		0.6
T86 1B	2580	53.4	-27.5	443		0.029	9.1	0.8	10.4	215		0.8
T88 5B	2812	53.6	-27.1	406		0.029	9.1	0.8	10.4	216		0.8
T88 4B	2821	55.0	-28.3	452		0.029	8.5	0.8	11.1	211		0.9
T88 3B	2819	56.4	-27.8	443		0.026	8.9	0.9	11.6	209		0.8
T88 2B	2767	57.9	-26.0	427		0.027	9.0	0.8	11.6	209		0.8
T90 1B	2911	58.5	-20.5	468		0.027	9.3	0.7	11.3	212		1.0
T88 1B	2010	59.7	-27.4	435		0.030	8.1	0.9	12.3	206		1.0
Marr et al., 2011 - core top												
P71	1919	-33.9	174.7	352	8.9	0.025	17.8	0.4	3.8		166	0.2
P81	2036	-34.0	173.5	302	6.9	0.023	16.5	0.4	4.7		165	0.3
S793	2411	-36.3	176.8	272	4.5	0.016	16.5	0.5	5.5		160	0.3
P69	2195	-40.4	178.0	236	4.7	0.020	16.9	0.4	5.6		155	0.5
S938	3003	-40.0	180.0	279	5.2	0.019	16.5	0.3	6.0		155	0.4
R623	1128	-43.2	186.0	318	8.4	0.026	10.2	1.0	13.7		150	0.4
Q220	580	-44.3	175.0	312	12.1	0.039	9.7	0.7	11.8		145	0.7
F111	704	-49.0	175.0	391	19.7	0.050	8.0	1.0	14.9		140	0.2
D178	629	-51.7	169.8	397	17.0	0.043	8.1	0.9	12.6		137	0.4
B32	799	-53.6	169.9	407	19.3	0.047	7.8	1.0	14.8		135	0.3
Moy et al., 2009 - core top + x1 sed. trap												
SO136-1408X	1636	-49.2	150.2		24.6	0.076	8.8	1.1	13.3		128	0.3
SO136-1538X	1874	-47.8	149.4		24.5	0.075	10.2	0.9	10.7		140	0.3
MD9721088X	2140	-48.5	149.1		28.5	0.088	9.5	1.0	12.0		135	0.3
SO136-1478X	2177	-48.5	149.1		31.6	0.097	9.5	1.0	12.0		135	0.3
GC11	2406	-45.7	144.9		24.4	0.075	11.0	0.8	9.4		157	0.4
KR8807	2890	-47.2	145.8		26.5	0.082	9.8	1.0	11.5		143	0.3
MD972107	2950	-47.7	145.8		30.5	0.094	9.8	1.0	11.5		141	0.3
GC17	3001	-47.8	145.8		24.4	0.075	9.8	1.0	11.5		141	0.3
GC14	3360	-46.5	145.2		26.2	0.081	10.5	0.8	10.2		147	0.4
sed. trap	1000	-46.8	142.1		16.9	0.052	10.2	0.9	10.9		145	0.3
Aldridge et al., 2012 - plankton tow												
IB195		62.7	-19.7	215.3	1.8	0.009	10.4	0.3	12.4	152		2.5
IB16		60.8	-20.0	243.8	2.6	0.010	10.7	0.3	12.4	148		0.7
IB14		61.0	-20.0	235.6	1.8	0.008	10.9	0.4	13.6	149		0.7
IB13		60.5	-20.0	250.9	2.5	0.010	11.0	0.3	11.1	166		0.7
IB10		59.7	-18.7	248.7	2.4	0.009	11.4	0.2	4.4	163		1.0
IB6		59.0	-17.2	243.8	2.3	0.009	11.3	0.2	5.3	175		0.7
IB4		58.5	-16.0	235.8	2.4	0.010	11.8	0.2	5.2	167		1.0
K		57.7	-11.5	229.6	2.1	0.009	12.2	0.2	4.0	175		1.0
R		57.0	-9.0	231.6	2.4	0.011	12.7	0.1	2.2	180		1.2
T		56.8	-8.3	245.8	2.9	0.011	12.7	0.0	0.0	181		1.2
McConnell and Thunnell, 2005 - sed. trap												
sed trap		27.9	-111.7	283.5	6.0	0.021		2.3	18.0		129	1.0
de Villiers, 2004 - core top												
S1		48.9	1-14	327.5	25.0	0.076	7.3				142	
S2		48.7			24.5	0.075	6.8				142	
S3		48.3			22.0	0.067	6.6				142	
S4		48.2			21.5	0.066	5.3				142	
S5		47.0			20.1	0.061	5.2				135	
S6		46.8			15.6	0.048	4.9				135	
S7		46.4			15.0	0.046	4.7				135	
Beer, 2010 - Arabian Sea - plankton tow												
SO120-17		56.9	-23.7	315.1	3.3	0.011	0.5	4.4	3.3	194		1.0
SO120-38		57.6	-23.6	332.0	4.7	0.014	0.5	4.4	4.7	171		1.0
SO120-41		57.7	-24.1	319.8	4.0	0.013	0.5	4.4	4.0	174		1.0
SO120-43		57.9	-23.9	322.4	3.6	0.011	0.5	4.4	3.6	170		0.8
M32-5-423		62.0	-25.8	306.3	4.3	0.014	0.5	2.3	4.3	231		0.8
M32-5-443		58.1	-23.7	296.5	4.3	0.015	0.6	4.3	4.3	204		1.0
M32-5-446		58.8	-26.0	289.1	3.8	0.013	0.5	2.7	3.8	238		0.7
M32-5-462		62.0	-25.7	313.7	4.9	0.016	0.5	2.6	4.9	216		0.5
M32-5-414		65.0	-27.3	328.1	4.6	0.014	0.3	0.4	4.6	277		0.5

Chap. 5 - SI 2

MD97 2121			
Age (ka)	Weight (µg)	Length (µm)	SNW (g/m)
0.0	4.0	263	0.015
0.0	5.5	311	0.018
0.1	5.2	302	0.017
0.4	4.6	274	0.017
1.0	5.0	302	0.017
1.8	5.7	309	0.018
2.6	5.1	303	0.017
2.9	5.2	296	0.018
4.3	5.5	308	0.018
4.8	5.3	307	0.017
5.3	5.8	295	0.019
5.6	7.7	344	0.022
6.0	7.4	292	0.025
6.1	7.4	318	0.023
6.3	6.7	313	0.021
6.5	5.3	282	0.019
6.6	5.7	304	0.019
6.8	6.3	305	0.021
7.1	6.2	303	0.020
7.9	5.0	288	0.017
9.0	5.5	288	0.019
9.3	7.7	347	0.022
10.0	6.0	319	0.019
10.2	8.5	367	0.023
10.5	5.6	316	0.018
10.7	7.6	360	0.021
11.4	6.3	303	0.021
11.9	7.0	335	0.021
12.2	5.9	298	0.020
12.4	6.0	310	0.019
12.5	7.2	317	0.023
12.6	7.1	328	0.022
12.6	6.0	314	0.019
12.8	8.6	348	0.025
12.8	9.6	366	0.026
12.9	12.7	358	0.035
12.9	7.5	332	0.023
13.1	6.9	324	0.021
13.3	13.6	376	0.036
13.4	10.1	382	0.026
13.6	13.6	376	0.036
13.8	15.1	417	0.036
13.8	11.0	376	0.029
14.1	11.1	369	0.030
14.3	19.8	434	0.046
14.5	11.7	386	0.030
14.6	12.2	373	0.033
14.8	12.4	367	0.033
15.1	17.5	374	0.047
15.5	11.4	374	0.030
15.8	11.1	381	0.029
16.0	12.6	383	0.033
16.5	12.7	383	0.033
17.2	12.2	394	0.031
18.1	5.7	310	0.018
18.8	8.8	341	0.026
19.0	7.93	311	0.026
19.3	8.96	323	0.028
19.5	9.2	349	0.027
20.0	8.9	385	0.023
20.2	10.0	354	0.028
20.7	10.1	350	0.029
21.2	12.7	367	0.031
21.6	13.2	367	0.036
21.7	13.6	356	0.038
21.9	8.1	302	0.027
22.1	12.7	364	0.035
22.4	13.6	377	0.036
23.1	10.9	367	0.030
23.6	9.5	351	0.027
23.8	9.4	351	0.027
24.3	11.3	356	0.032
24.5	11.3	366	0.031
25.0	12.9	352	0.036

This thesis investigates the use of foraminiferal calcite geochemical and physical properties as paleoceanographic proxies, to improve identification of past climatic change and provide a more quantitative basis for forecasts of future climate.

Various analytical methods to measure foraminiferal calcite trace element geochemistry were first investigated using core top samples. Two main analytical techniques were deployed; “pseudo” solution- or laser ablation-based ICPMS analysis. Ratios tested include Mg/Ca, Sr/Ca, Ba/Ca, Zn/Ca, Mn/Ca and Al/Ca. Trace element/calcium ratios Mg/Ca and Sr/Ca values were consistent between these methods, provided that currently recommended ‘Mg-cleaning’ protocols were followed for solution-based measurements. However, discrepancies of up to an order-of-magnitude for Zn/Ca, Mn/Ca and Ba/Ca occurred between solution and laser ablation-based measurements if both oxidative *and* reductive cleaning techniques were not employed prior to solution-based analysis.

Using down-core trace element values Mg/Ca, Zn/Ca, Mn/Ca and Ba/Ca from MD97 2121, coupled with modern core top and plankton-tow samples, multiple geochemical proxies for the SW Pacific Ocean were developed and/or tested. Results suggest that Zn/Ca may act as (i) a surface water mass tracer, in this case differentiating between subtropical and subantarctic surface waters and (ii) a proxy for nutrients. Mg/Ca and Zn/Ca values from different test chambers in *Globigerina bulloides* were also found to reliably re-construct surface ocean temperature and nutrient stratification. Using these new proxies, coupled with oxygen isotopes, standard Mg/Ca paleothermometry and foraminiferal assemblage data, surface water nutrient and thermal stratification significantly reduced during the last glacial period.

The high resolution Mg/Ca paleotemperature record developed here, together with published alkenone paleotemperatures were compared to core MD97 2120, south of the STF to evaluate the relationship between Mg/Ca and alkenones temperatures and how these reflect environmental change. It appears that the season of maximum alkenone and *G. bulloides* flux varied over the last 25kyr in response to insolation and water mass changes. These seasonal offsets may have acted to dampen or exacerbate the glacial-Holocene temperature offsets by up to 4°C especially for the surface dwelling, alkenone producing coccolithophores. Seasonality changes of the coccolithophore and foraminifera make direct comparison of alkenone and Mg/Ca *G. bulloides* paleothermometers challenging.

The use of *G. bulloides* size normalised weight (SNW) as a proxy for surface water carbonate ion concentration ($[\text{CO}_3^{2-}]$) was investigated by comparing modern SNW data sets from five different ocean regions to their specific environmental variables including $[\text{CO}_3^{2-}]$, chlorophyll-*a*, nutrient and temperature values. It was identified that the ‘ocean’ from which the foraminifera originated appeared to have the strongest control over shell SNW, potentially reflecting geographically distinct, genetic variations within the *G. bulloides* species. Within ‘ocean’ regions no consistent environmental variable(s) could be identified that appeared to control shell SNW in all regions. From the 25 ka to present, shell SNWs from the SW Pacific Ocean were compared to the North Atlantic and were found to be heavier during the glacial period regardless of ocean region. Calcification of *G. bulloides* tests appears to be region specific; therefore, proxy calibrations based on shell SNW for one ocean are not applicable to other settings.