Insights into Late Holocene climate of the Ross Sea region, Antarctica,
from high resolution ice core chemistry

by

Rachael H. Rhodes

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Abstract

The Ross Sea is the most biologically productive sector of the Southern Ocean and a region of substantial bottom water formation. Modulation of these processes has the potential to influence both regional and global climate. Analysis of snow pit and ice core samples from Mt Erebus Saddle (MES) on Ross Island allows reconstruction of Late Holocene climate of this key region of Antarctica.

The biogenic sulphur species, methylsulphonate (MS^-), is shown to be a quantitative proxy for Ross Sea Polynya conditions. MS^- concentrations of the snow pit, dating from 1999-2005 AD, strongly correlate ($R^2 > 0.9$) with interannual changes in open water area and surface ocean primary productivity caused by the sea-ice-damming effect of large icebergs.

Trace element analysis of ice core samples allows delineation between: 1) terrestrial and marine sources, 2) anthropogenic Pb pollution, and 3) volcanic trace element deposition. To assess the contribution of mineral dust leaching to trace element concentrations, powdered rock standards were leached in 1 wt.% HNO_3 and periodically sampled for analysis. Results demonstrate that trace element leaching in acidified samples is time- and mineral-dependent. Incongruent leaching of trace elements from dust causes errors in crustal enrichment factors and produces trace element ratios, which do not reflect dust provenance.

Stable isotope (δD , $\delta^{18}\text{O}$, d-excess) and soluble chemistry records of the 120 m MES ice core document the climate of the Ross Sea region since 1446 AD. This includes the Little Ice Age (LIA) - the most recent global climate change event. Lithophile elements (e.g., Al), sourced from mineral dust, are proxies for katabatic wind speed whilst d-excess and marine elements (e.g., Na) are related to the incursion of cyclonic systems into the Ross Sea. δD values of 6.4‰ below the 1950-2006 mean characterise the LIA, suggesting a mean cooling of 1.6 °C. An abrupt 5‰ d-excess increase provides evidence for enhanced cyclonic activity between 1625 and 1875 AD. Mean lithophile element concentrations, which are > 50% higher in the LIA than post-1850 AD, demonstrate that katabatic wind speeds > 57 m s⁻¹ prevailed during the LIA.

Furthermore, MS^- concentrations indicate that the Ross Sea Polynya was larger and more productive prior to 1875 AD, relative to the ensuing time. As strong katabatic winds appear to have maintained a more extensive Ross Sea Polynya during the LIA, the associated increase in sea ice formation may have enhanced bottom water formation at this time.

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Chapter 1: Introduction

1.1 Foreword

Ice cores provide the most continuous and high resolution records of paleoclimate available for the past one million years of Earth's history [EPICA, 2004; Petit *et al.*, 1999]. High profile, internationally acclaimed ice coring projects, such as the European Project for Ice Coring in Antarctica (EPICA), have provided a wealth of information about past global temperature and atmospheric greenhouse gas concentrations, which is fundamental to our understanding of global climate change [EPICA, 2004; IPCC, 2007].

To further our advance understanding of Earth's climate system and to allow for more accurate predictions of future climate response to continued anthropogenic greenhouse gas emissions, the International Trans-Antarctic Scientific Expedition (ITASE) identified the retrieval and interpretation of short term (past 200 yr), high resolution ice core records as a primary aim [Mayewski *et al.*, 2005]. This goal was adopted by the International Partnership on Ice Coring Sciences (IPICS) and the targeted time period was extended to the past 2000 yr to include Late Holocene climate variability including the Medieval Warm Period and Little Ice Age events [IPICS, 2008]. The New Zealand Ice Core Program contributes to ITASE and IPICS by obtaining ice core and snow pit samples from coastal locations in the Ross Sea region, Antarctica. Coastal Antarctica experiences higher rates of snow accumulation, and ice cores from coastal locations therefore provide subannual resolution climate records, which permit decadal-scale climate variability to be resolved [e.g. van Ommen and Morgan, 1997].

Advances in analytical capability, allowing the determination of trace element concentrations [e.g. Barbante *et al.*, 1997], have introduced a new tool to ice core paleoclimatology. Trace element determination by inductively coupled plasma mass spectrometry (ICP-MS) is increasingly utilised alongside the conventional ice

core climate proxies, stable isotope ratios and major ion chemistry and has the potential to provide additional insights into paleoclimate.

1.2 Research aims

The aim of this thesis is to produce a record of the Late Holocene climate of the Ross Sea region, Antarctica, from glaciochemical proxies developed from a 2 m snow pit and 120 m ice core record. In order to achieve this, stable isotope ratios (oxygen and hydrogen), major ion, and major, minor and trace element concentrations, analysed at high temporal resolution, are correlated to instrumental and satellite data.

1.3 Rationale

The Ross Sea is a key region of Antarctica of which to understand past climate and to evaluate the potential future response to anthropogenically induced climate change. The Ross Sea is a principal site of sea ice production [Tamura *et al.*, 2008] in the Southern Hemisphere and this drives substantial amounts of bottom water formation [Jacobs and Giulivi, 1998], which contributes to the global thermohaline circulation of the oceans [Broecker, 1997]. Additionally, the Ross Sea Polynya provides an excellent habitat for phytoplankton, making the Ross Sea the most biologically productive region of the Southern Ocean [Arrigo *et al.*, 1998; Smith and Gordon, 1997] and a significant region of CO₂ drawdown from the atmosphere [Arrigo *et al.*, 1999]. Changes to any of these processes have the potential to create climate feedbacks which would affect not only regional climate, but also the global climate system.

Therefore, it is important to understand how the climate and environmental conditions of this region have varied in the past in order to provide a context in which to consider how the region may respond in the future. At present, there is a knowledge gap concerning the past climate variability of the Ross Sea region, the Antarctic continent, and the Southern Hemisphere as a whole, resulting from a lack of historical meteorological data from prior to the late-1950s and the restricted temporal coverage of satellite datasets (late-1970s onwards).

Ice core proxy records have the potential to extend our knowledge of past climate beyond the observational record. However, contrasting regional trends in temperature, sea ice cover, ocean temperatures and wind strength [Boning *et al.*, 2008;

Marshall et al., 2004; *Steig et al.*, 2009; *Zwally et al.*, 2002] have occurred in the Antarctic over the satellite era (Fig. 1.1), demonstrating that ice core climate proxy records from different locations in Antarctica will record regional signatures. The ITASE program takes this into account and aims to build up a network of climate proxy records from ice cores across the continent [*Mayewski et al.*, 2005].

Figure 1.1: Reconstructed Antarctic surface temperature trends and observed changes in sea ice fractional area for 1979 to 2003 (modified after *Steig et al.* [2009]).

The snow pit and ice core records considered in this thesis were retrieved from Mt Erebus Saddle on Ross Island, Antarctica, as components of a wider sampling array in the Ross Sea region (Fig. 1.2), which comprises the New Zealand contribution to ITASE. Mt Erebus Saddle is situated at a boundary between two meteorological systems - marine-based cyclones [*Carrasco and Bromwich*, 1993] and continental katabatic winds [*Bromwich et al.*, 1992], characterised by air masses of contrasting geochemical signatures [*Bertler et al.*, 2004a], facilitating climate reconstruction from the ice core record. In addition to this, Mt Erebus Saddle and other coastal Antarctic ice cores are also unique in that they have the potential to record local signatures of atmosphere-ocean interaction as a result of their proximity to seasonally open ocean and their low (< 2000 m) elevations.

Figure 1.2: Map of the Ross Sea region showing NZ-ITASE ice core sites. White-filled drops indicate locations of ice core sites drilled. A = Mt Erebus Saddle (this study), B = Evans Piedmont and Victoria Lower Glacier in the Dry Valleys, C = Whitehall Glacier. Grey-filled drops are locations of proposed future drill sites.

Several ice core records from the ITASE program have utilised oxygen and hydrogen stable isotope ratios and major ion concentrations as glaciochemical proxies for climatic and environmental parameters. Major ions are predominantly sourced from the ocean [Legrand and Delmas, 1984] and can provide little information about terrestrial contributions. However, ICP-MS analysis can accurately determine the concentrations of a wide array of elements including lithophile, rare earth and heavy volatile elements. To date, there are no published studies which directly relate trace element concentrations in ice cores to climate parameters on decadal to multi-decadal timescales.

1.4 Research objectives

Five research objectives were developed in order to fulfil the research aim of this thesis.

The **first objective** of this thesis was to date and interpret oxygen stable isotope and major ion concentration data from a snow pit sampled at Mt Erebus Saddle in order to examine the interannual variability of the climate record (Chapter 3). The oxygen isotope record proved suitable for annual layer counting and the record of methylsulphonate, a biogenic sulphur species, was developed as a proxy for both sea ice cover and primary productivity in the Ross Sea. This study is the first to directly link a snow or ice core record of methylsulphonate to variability in primary productivity and demonstrates the sensitivity of coastal ice core records to marine biogenic processes.

The Mt Erebus Saddle ice core was the first core to be processed and sampled at the New Zealand Ice Core Laboratory, GNS Science, Lower Hutt and the first to be analysed for trace elements at the Victoria University of Wellington Geochemistry Laboratory. A **second objective** was therefore to set up a continuous melter system (after *Osterberg et al.* [2006]) to ensure a clean and effective sampling procedure and to develop an accurate, precise and efficient method for ICP-MS analysis of element concentrations ranging from several hundred ppb (parts per billion) to sub-ppt (parts per trillion) levels (Chapter 4).

A **third objective** was to date the glaciochemical record accurately (Chapter 5). The high snow accumulation rate at Mt Erebus Saddle ($22 \text{ g cm}^{-3} \text{ yr}^{-1}$) facilitated annual layer counting of the stable isotope ratio (oxygen and hydrogen) records. Development of the annual layer count model was aided by back-diffusion of the stable isotopic records, results of a glacial flow model and the identification of age tie points related to chemical deposition from thermonuclear bomb tests and major volcanic eruptions.

A **fourth objective** of this thesis was to advance understanding of the controls on the trace element budget of ice cores (Chapter 6). In particular, a previous study by *Bull* [2009] had experienced reproducibility problems with ICP-MS measurements of snow samples, attributed to the presence of mineral dust particles within the samples which were acidified prior to analysis. A systematic experiment designed to assess the contribution of acid-leaching of mineral dust particles to trace element concentrations measured by ICP-MS was undertaken as a component of this study.

The **fifth and principal objective** of this thesis was to produce a paleoclimate record from glaciochemical proxies of the Mt Erebus ice core (Chapter 7). The stable isotopic and trace element record produced from the 120 m depth of ice core analysed encompasses the 1446 to 2006 AD time period and captures much of the Little Ice Age (LIA) climate event. Proxy relationships, identified through comparison between ice core chemistry (stable isotopes, marine chemical species and lithophile elements) and instrumental records, demonstrate that, compared to the present, cooler conditions with stronger katabatic winds and a larger, more productive Ross Sea Polynya prevailed during the LIA.

1.5 Thesis outline

Chapters 3, 6 and 7 are each stand-alone papers, which are either, published or ready for submission to academic journals. A summary of the results obtained from this study is provided in Chapter 8. Additional information and all raw data obtained during the course of this study are contained in the Appendices. The content of each chapter is summarized briefly below. The chapters comprised of research papers include some contributions from co-authors other than thesis supervisors and these contributions are described.

Chapter 1: Introduction

Research aim, rationale and objectives

Chapter 2: Antarctic climate and ice core climate proxies

Background information concerning the climate of Antarctica and the Ross Sea region, glaciochemical proxies and ice core records of Late Holocene climate in Antarctica.

Chapter 3: Sea ice variability and primary productivity in the Ross Sea, Antarctica from methylsulphonate snow record

Snow pit study demonstrating the effectiveness of methylsulphonate (MS^-) concentration as a proxy for sea ice cover and primary productivity in the Ross Sea.

Paper published in Geophysical Research Letters (Section 1.6).

S. B. Sneed measured major ion concentrations and H. Oerter measured stable oxygen isotope ratios in the snow pit samples. K. R. Arrigo provided open water area and primary productivity time series data in addition to sharing his insight into the biochemistry of the Ross Sea.

Chapter 4: Methodology for ice core study

Details of ice core drilling, processing and sampling procedures. Analytical techniques for determination of stable isotope ratios ($\delta^{18}\text{O}$ and δD), major ion and trace element concentrations are provided and techniques used to date the ice core are summarised.

Chapter 5: Dating the ice core record

Dating of the ice core record by annual layer counting of stable isotope ratios, using thermonuclear bomb tritium fallout, and volcanic trace element deposition events as age tie points, is described.

Chapter 6: Factors affecting the reproducibility of trace element analyses of ice core samples

Series of laboratory experiments designed to quantify the effect of mineral dust leaching after sample acidification on the trace element budget of ice cores and its effect on measurement accuracy and reproducibility.

Paper accepted for publication in Chemical Geology (Section 1.6).

M-A. Millet provided input on experiment design and ideas for data interpretation.

Chapter 7: Increased katabatic wind speeds and greater Ross Sea Polynya extent in the Little Ice Age.

Climate proxy record of the ice core encompassing the time period 1446 to 2006 AD, including the Little Ice Age (LIA) and its termination. Comparisons between high resolution stable isotopic and geochemical records and the instrumental record develop a lithophile element proxy for katabatic wind strength. It is demonstrated that cooler, windier conditions and a larger, more productive Ross Sea Polynya prevailed during the LIA.

Paper prepared for submission to Climate of the Past (Section 1.6).

H. C. Steen-Larsen and S. J. Johnsen performed back-diffusion of the stable isotopic data and modelled the age-depth relationship down the ice core using a glacial flow model. S. B. Sneed measured some samples for major ion concentrations. U.

Morgenstern measured samples for tritium contents and provided tritium content data for precipitation at other Antarctic sites.

Chapter 8: Conclusions

Appendices

Appendix I: Mt Erebus Saddle 2004/05 2 m snow pit stable oxygen isotope ratios and major ion concentrations.

Appendix II: Procedural blanks for Mt Erebus Saddle ice core processing and sampling (ICP-MS and IC).

Appendix III: Accuracy, precision and detection limits of major ion concentration measurements on Mt Erebus Saddle 2006/07 ice core samples.

Appendix IV: Stable isotope data for Mt Erebus Saddle 2006/07 ice core.

Appendix V: Dansgaard-Johnsen glacial flow model.

Appendix VI: Back-diffusion of Mt Erebus Saddle 2006/07 ice core stable isotope ratios.

Appendix VII: Mt Erebus Saddle 2006/07 ice core tritium content measurements.

Appendix VIII: Mt Erebus Saddle 2006/07 ice core density measurements.

Appendix IX: Supplementary data tables for dust leaching investigation

Appendix X: Mt Erebus Saddle 2006/07 ice core major and minor element concentrations.

Appendix XI: Mt Erebus Saddle 2006/07 ice core age model.

1.6 Publications resulting from this thesis

Peer-reviewed journal articles

Rhodes, R. H., Baker, J. A., Millet, M-A., Bertler, N. A. N., 2011. Experimental investigation of the effects of mineral dust on the reproducibility and accuracy of ice core trace element analyses. *Chemical Geology*, doi: 10.1016/j.chemgeo.2011.05.006.

Purdie, H., Bertler, N. A. N., Mackintosh, A., Baker, J. A. and **Rhodes, R. H.**, 2010. Isotopic and elemental changes in winter snow accumulation on glaciers in the Southern Alps of New Zealand. *Journal of Climate* 23, doi: 10.1175/2010JCLI3701.1

Rhodes, R.H., Bertler, N. A. N., Baker, J. A., Sneed, S. B., Oerter, H., Arrigo, K. R., 2009. Sea ice variability and primary productivity in the Ross Sea, Antarctica, from methylsulphonate snow record. *Geophysical Research Letters* 36, L10704, doi:10.1029/2009GL037311.

Journal articles in preparation for submission

Rhodes, R. H., Bertler, N. A. N., Baker, J. A., Steen-Larsen, H. C., Sneed, S. B., Morgenstern, U., Johnsen, S. J., Increased katabatic wind speeds and greater Ross Sea Polynya extent in the Little Ice Age. *In preparation for Climate of the Past*.

Selected conference and workshop presentations

Rhodes, R. H., Baker, J. A., Millet, M-A., Bertler, N. A. N., Experimental investigation of the effects of mineral dust on the reproducibility and accuracy of ice core trace element analysis. *American Geophysical Union, Fall Meeting 2010*. San Francisco, USA. Abstract #C13B-0548. 13-17 December 2010. (Poster)

Rhodes, R. H., Bertler, N. A. N., Baker, J. A., Trace elements reveal 'Little Ice Age' in an Antarctic ice core. *European Research Course on Atmospheres*. Grenoble, France. 11 January to 12 February 2010.

Rhodes, R. H., Bertler, N. A. N., Baker, J. A., Trace elements reveal 'Little Ice Age' in an Antarctic ice core. *New Zealand Postgraduate Conference*. Victoria University of Wellington, Wellington, New Zealand, 20-21 November, 2009.

Rhodes, R. H., Bertler, N. A. N., Baker, J. A., Sneed, S. B., An ice core indicator of Ross Ice Shelf stability? *Geological Society of New Zealand, New Zealand Geophysical Society and New Zealand Geochemical & Mineralogical Society Joint Annual Conference*. Te Papa, Wellington, New Zealand, 23-26 November, 2008.

Rhodes, R. H., Bertler, N. A. N., Baker, J. A., Sneed, S. B., High resolution climate reconstruction utilizing trace element geochemistry and stable isotopes from Mt. Erebus Saddle. *SCAR/IASC IPY Open Science Conference, Polar Research – Arctic and Antarctic Perspectives in the International Polar Year*. St. Petersburg, Russia, 8-11th July 2008. (Poster)

Rhodes, R. H., Bertler, N. A. N., Baker, J. A., and Sneed, S. B., Effects of large icebergs on sea ice and primary productivity in the Ross Sea. *Annual Antarctic Conference - International Polar Year and the Next Generation*. Dunedin, New Zealand. July 2008 (Poster)

Chapter 2: Antarctic climate and ice core climate proxies

This chapter presents a review of literature that is relevant to the research aim, rationale and objectives of this study. Geographical locations of places and ice core sites referred to in this chapter are displayed in Figure 2.1.

Figure 2.1: Map of the Antarctic continent showing key locations and ice core sites referred to in the text. Ice core sites are as follows: DC= EPICA Dome C, DF = Dome Fuji, DM = EPICA Dronning Maud Land, LD = Law Dome, SD = Siple Dome, SP = South Pole, SS = Siple Station, TD = Talos Dome, TY = Taylor Dome, VK = Vostok. All locations are approximate.

2.1 Antarctica and the global climate system

Antarctica influences the global climate system primarily through its role as a sink for heat transported from the equator to high latitudes, mainly by extra-tropical cyclones [King and Turner, 1997] and ocean currents [Trenberth and Solomon, 2009]. The isolation of Antarctica within the Southern Ocean allows for the development of a persistent westerly circulation of cyclonic systems around the continent [King and Turner, 1997]. Another control on the Earth's energy budget is the high albedo of Antarctica and its associated sea ice, which cools the continent. It is the cooling of the air above the ice sheet surface which creates a temperature inversion causing persistent katabatic winds to flow off the continent [Parish, 1988] (Section 2.2). Katabatic winds are involved in the formation of polynyas [Bromwich *et al.*, 1992], areas of open water within the sea ice cover, where new sea ice is generated. The formation of sea ice ejects brine, which along with cooling of the ocean by cold katabatic winds, causes the dense ocean waters to sink. This is the process of bottom water formation, a crucial step in the thermohaline circulation of the world's ocean which transports heat and nutrients, and ventilates the deep ocean [Broecker, 1997]. Arguably the most important interaction between Antarctica and the global climate system is the delicate mass balance of the ice sheets which hold 61% of the fresh water on the planet. A negative shift in the mass balance and resultant melting of the marine-based portion of the West Antarctic ice sheet would result in a global eustatic sea level rise of 3.3 m [Bamber *et al.*, 2009].

2.2 Aspects of Antarctic meteorology

The meteorology of coastal Antarctica is dominated by the westerly-circulating belt of cyclones situated between 60-70 °S which is called the Antarctic circum-polar trough. This low pressure belt consists of synoptic-scale (> 1000 km diameter; >1 day lifetime) cyclones, which create strong westerly winds around the coast of Antarctica. These winds are important for cooling the ocean surface, promoting downwelling and bottom water formation [King and Turner, 1997]. The circum-polar trough is not perfectly circular in form because the path of the cyclones is obstructed by the Antarctic Peninsula, which obtrudes northwards from the continent into the Southern Ocean. As a result, three principal centres of low pressure form within the circum-polar trough (Fig. 2.2). The low pressure centre located off the coast of West Antarctica at 90-150 °W is the Amundsen Sea Low. The circum-polar trough is subject to a semi-annual oscillation in its latitudinal position and strength. The trough contracts in spring and autumn, creating lower pressures close to Antarctica. Whereas, in summer and winter, the trough expands and moves further north, creating a positive pressure anomaly [King and Turner, 1997]. The circum-polar trough and its cyclones rarely penetrate into the interior of the Antarctic continent because elevation increases steeply from sea level to 3000 m on the plateau. This causes the rapid decrease in accumulation between coastal regions and the interior [King and Turner, 1997] (Fig. 2.3).

Figure 2.2: Mean sea level pressure across Antarctica and the Southern Ocean for the time period Jan-1979 to Jan-2010. The low pressure belt (purple colours) around the Antarctic continent is the circum-polar trough. Values were calculated from monthly averages of surface level NCEP (National Centres for Environmental Prediction) reanalysis data for latitude range 90 °S to 50 °S and plotted using the interactive plotting tool at NOAA (National Oceanographic and Atmospheric Administration) Earth System Research Laboratory
<http://www.esrl.noaa.gov/psd/cgi-bin/data/getpage.pl>.

Figure 2.3: Map of Antarctica showing the rate of accumulation of precipitation (modified after *Mayewski et al. [2009]*).

The interior of the continent is dominated by a high pressure system and the wind regime is governed by katabatic winds. The high-elevation ice sheets cool radiatively and cool the layer of air just above the surface. This creates a temperature inversion, which causes the air to move down-slope under the pressure-gradient force [*Parish, 1988; van den Broeke and van Lipzig, 2003*]. Katabatic winds are therefore strongest during the winter months when the temperature inversion above the ice sheets is greatest. Their flow paths are strongly controlled by topography causing major outlet glaciers at the coast to funnel strong, cold winds down off the plateau (Fig. 2.4). Once katabatic winds have reached the relatively flat coastline or ice shelf the pressure-gradient force is weak but interaction with synoptic scale cyclones can cause strong katabatic wind flow across the ice shelves (Section 2.4).

Cold katabatic winds descending from the interior are one cause of baroclinic instability around the Antarctic coast which leads to the formation of mesoscale (< 1000 km diameter; < 24 hr lifetime) cyclones [*Carrasco and Bromwich, 1993*]. Baroclinic instability is caused by a thermal gradient which disrupts the stratification of the atmosphere. For this reason mesoscale cyclones also form at the northern edge of

the sea ice cover or at the boundary between land and open ocean in summer [King and Turner, 1997].

Figure 2.4: Major flowlines of katabatic winds off the Antarctic continent (modified after *Parish* [1988]). Thin black lines are ice sheet elevation contours.

2.3 Decadal drivers of Antarctic and Southern Hemisphere climate variability

The dominant driver of the climate variability of the Southern Hemisphere on seasonal to decadal timescales is an atmospheric phenomenon called the Southern Annular Mode (SAM) [Kidson, 1999], which is also referred to as the Antarctic Oscillation (AAO). The SAM index explains the variability in atmospheric flow that is additional to the variability associated with the semi-annual oscillation of the circum-polar trough (Section 2.2) [Gong and Wang, 1999]. A strong positive SAM index corresponds to contraction of the circum-polar trough and Antarctica is subject to generally colder temperatures, lower pressures and stronger flow around latitude 60°S [Thompson and Solomon, 2002]. Over the last few decades SAM has moved into a more positive state causing intensified westerly winds [Marshall, 2003], a change that has been linked to the presence of the Antarctic ozone hole [Thompson and Solomon, 2002] or anthropogenic greenhouse gas forcing [Cai *et al.*, 2003]. Model results suggest that stronger circum-polar circulation should result in higher temperatures over the Antarctic Peninsula, West Antarctica and the Weddell Sea, but cooler temperatures over East Antarctica, the Ross Ice Shelf and Marie Byrd Land [van den Broeke and van Lipzig, 2004]. These trends are appearing in Antarctic temperatures [van den Broeke, 2000]; 50% of the warming over the Antarctic Peninsula is attributed to the long-term trend in SAM [Thompson and Solomon, 2002]. Variations in SAM have also been linked to sea surface temperature (SST) across the Southern Ocean [Zhou and Yu, 2004], the distribution of sea ice around Antarctica [Hall and Visbeck, 2002] and change in ocean mixed layer depth [Sallee *et al.*, 2010].

The second most important driver of Southern Hemisphere variability is the El Niño Southern Oscillation (ENSO) [Kidson, 1999; Turner, 2004], a coupled ocean-atmosphere climatic cycle. The term El Niño, and its counterpart La Niña, refer to anomalies in the sea surface temperature observed in the tropical eastern Pacific Ocean [Trenberth, 1997]. The Southern Oscillation is the coupled atmospheric response to the change in sea surface temperature and causes changes in air pressure across the Pacific. The Southern Oscillation Index (SOI) is the normalised difference in surface pressure between Darwin (West Pacific) and Tahiti (East Pacific). Extreme negative SOI values indicate El Niño conditions whereas positive values indicate La Niña [Trenberth, 1997].

During an El Niño event, SST is increased in the tropical Pacific and a strong anti-cyclone develops in the atmosphere above [Renwick, 1998]. This atmospheric anomaly is transmitted to the high southern latitudes via a wave train called the Pacific South American Pattern (PSA) in a process that is not completely understood (see Turner [2004] or Yuan and Martinson [2000] for reviews). The teleconnection causes an anti-cyclonic anomaly over the Amundsen-Bellinghausen Sea and movement of the Amundsen Sea Low pressure centre 1400 km eastwards towards the Marie-Byrd Land coast [Cullather et al., 1996] (Section 2.4). The opposite sequence of events occurs during La Niña periods and the Amundsen Sea Low intensifies.

The ENSO signal has been shown to affect the moisture budget of West Antarctica and the Weddell Sea – Ronne Ice Shelf region [Bromwich et al., 2004; Bromwich et al., 2000; Cullather et al., 1996]. Links between ENSO and sea ice extent around the Antarctic continent have also been established [Carleton, 1989; Kwok and Comiso, 2002; Simmonds and Jacka, 1995].

Recent research suggests that ENSO needs to be positively correlated with SAM to exert a strong influence on Antarctic climate. If both the SAM index and the SOI are in a positive phase then negative pressure anomalies and positive geopotential height anomalies in the South Pacific are augmented. However, if SAM and ENSO are out of phase, the effect of SAM will effectively cancel out any ENSO forcing from the tropics [Fogt and Bromwich, 2006].

2.4 Climate of the Ross Sea region

The climate of the Ross Sea region is characterised by the interaction between cyclonic systems of the circum-polar trough and katabatic winds from the continent. Synoptic-scale cyclones provide moisture to the Victoria Land coast by either remaining quasi-stationary over the Ross Sea or by effectively detaching from the cyclone belt and tracking around the inland edge of the Ross Ice Shelf [Sinclair *et al.*, 2010].

Figure 2.5: Thermal infra-red satellite image of the Ross Ice Shelf in mid-winter. Darker shades indicate a warmer surface and red patches are open water. Warm katabatic winds can be seen originating from glaciers draining the Transantarctic Mountains and a well-developed katabatic surge is seen flowing across the ice shelf from the Siple Coast. Automatic weather station observation of wind (wind barbs = 5 ms^{-1}) and temperature ($^{\circ}\text{C}$) have been overlaid on the image (from study by Bromwich *et al.* [1992]).

Katabatic winds, originating from West Antarctica, via the Siple Coast, and East Antarctica via large outlet glaciers along the Transantarctic Mountains, such as the

Byrd Glacier, propagate in a northwest direction across the Ross Ice Shelf [Bromwich *et al.*, 1993]. The major katabatic flow path is diverted eastwards around Ross Island and is responsible for the formation of the Ross Sea Polynya at the edge of the Ross Ice Shelf (Fig. 2.5).

The cold air of the katabatic flows creates thermal gradients necessary for mesoscale cyclone formation. The region just to the north of Ross Island has a high rate of mesoscale cyclone formation [Carrasco and Bromwich, 1993] which contributes to the precipitation budget along the Victoria Land coast [Sinclair *et al.*, 2010].

Figure 2.6: Effect of El Niño and La Niña events on the position and strength of the Amundsen Sea Low (L_{AS}) pressure centre (modified after Bertler *et al.*[2004b]). Thickness of large arrows is indicative of the strength of the low pressure centre. Thin black lines depict the prevailing wind directions.

The southeast Pacific sector of Antarctica displays the strongest links to ENSO forcing from the tropics [Turner, 2004] through the modulation of the position of the Amundsen Sea Low (Fig. 2.6). The weakening and migration of the Amundsen Sea Low towards Marie Byrd Land during El Niño events causes the western Ross Sea to experience increase katabatic surges of cold, dry air from across the West Antarctic Ice Sheet [Bromwich *et al.*, 1993]. Incursion of marine air masses onto the Ross Ice Shelf is reduced [Bertler *et al.*, 2004b]. In contrast, during La Niña events the intensified

Amundsen Sea Low brings strong cyclonic circulation and relatively warm, moist air to the Ross Sea [Bertler *et al.*, 2004b]. In agreement with the later study of *Fogt and Bromwich* [2006], Bertler *et al.* [2004b] found that the ENSO influence on temperature in the Ross Sea region was more pronounced in the 1990s than the 1980s because SAM and ENSO were in-phase with one another. The advance and retreat of sea ice in the western Ross Sea is also associated with the interaction between SAM and ENSO [Stammerjohn *et al.*, 2008].

2.5 Ice core climate and environmental proxies

Ice cores extracted from the Antarctic ice sheets have the potential to extend the meteorological record back in time via the development of geochemical proxies for climate parameters. The stable isotopes of water, soluble major ion chemistry, and dust content of ice cores are conventional ice core climate proxies and the applications of ice core trace element measurements are being developed. The basic principles of each are summarised in the following sections.

2.5.1 Stable isotopes of water

The stable isotope ratios of oxygen ($\delta^{18}\text{O}$) and hydrogen (δD) are important proxies for ice core site temperature. The delta (δ) notation refers to the deviation of the ratio of the heavy isotope (^{18}O or ^2H) to the more abundant light isotope (^{16}O or ^1H) in the sample, from that of a standard, usually Vienna Standard Mean Ocean Water (V-SMOW). The equation for the calculation of $\delta^{18}\text{O}$ is:

$$\delta^{18}\text{O} (\text{‰}) = [({}^{18}\text{O}/{}^{16}\text{O}_{\text{sample}} - {}^{18}\text{O}/{}^{16}\text{O}_{\text{standard}}) / ({}^{18}\text{O}/{}^{16}\text{O}_{\text{standard}}) - 1] * 1000$$

(‰ = per mil)

Isotopic fractionation of the stable isotopes of water occurs during phase changes as water molecules containing heavy isotopes ($^1\text{H}^2\text{HO}$ and H_2^{18}O) will preferentially remain in the liquid during evaporation and move into the liquid or solid during condensation or freezing [Araguas-Araguas *et al.*, 2000]. When the two phase states of water are in equilibrium, the degree of fractionation between heavy and light isotopes (or the fractionation factor) will depend on the ratio of saturation vapour pressure of standard water (H_2O) to 'heavy' water ($^1\text{H}^2\text{HO}$ and H_2^{18}O) [Gat, 2005]. As the values of $\delta^{18}\text{O}$ and δD in the same air mass are controlled by the same processes, a bivariate plot of the two ratios produces a linear trend (Fig. 2.7). The slope of the line equates to a value of 8 because the equilibrium fractionation of hydrogen isotopes is 8 times greater than that of oxygen isotopes [Jouzel, 2003]. The linear relationship displayed by this graph is consistent for samples from across the world and it is therefore named the Global Meteoric Water Line (GMWL) [Craig, 1961].

Figure 2.7: Global Meteoric Water Line (GMWL) of *Craig* [1961] with evaporation trend line of a moisture source located on the GMWL (after *Gat* [1996]). Samples with positive δ values that plot on the curved dashed line are from lakes and rivers in East Africa.

However, a state of equilibrium is usually not reached because vapour is often evaporated from open water into an atmosphere that is not fully saturated (relative humidity < 100%). In this case, the differences in the molecular diffusion of heavy and light water molecules through the water-air interface cause kinetic fractionation [*Merlivat and Jouzel, 1979*]. During evaporation of a moisture source which lies on the GMWL, the residual water of the moisture source moves to the right of the GMWL (Fig. 2.7) as the $\delta D/\delta^{18}O$ slope during kinetic fractionation is less than 8. The vapour produced must therefore lie to the left of the GMWL producing a different value of d-excess. The extent of kinetic fractionation which occurs during evaporation and condensation determines the value of the second-order stable isotopic parameter, deuterium excess (d-excess) [*Jouzel and Merlivat, 1984; Merlivat and Jouzel, 1979*], as defined by *Dansgaard* [1964].

$$\text{d-excess} = \delta D - 8 * \delta^{18}O$$

The intercept of a meteoric water line is the value of d-excess. The GMWL has a d-excess value of 10‰ (Fig. 2.7) but this value varies considerably with the extent of kinetic fractionation.

Kinetic fractionation is principally controlled by the relative humidity at the surface temperature of the water and d-excess of an air mass will therefore increase with decreased relative humidity [Merlivat and Jouzel, 1979] (Fig. 2.8). Secondary effects on d-excess values include sea surface temperature (SST) of the moisture source and wind speed [Petit *et al.*, 1991] (Fig. 2.8). Deuterium excess records from Antarctic ice cores can be used as proxies for a) vapour source temperature [Vimeux *et al.*, 2002] b) relative humidity [Jouzel *et al.*, 1982] and c) to identify abrupt changes in moisture source [Masson-Delmotte *et al.*, 2010].

Figure 2.8: Deuterium excess as a function of temperature in the initial cloud vapour for relative humidities of 50% (black), 70% (red) and 90% (blue) and wind speeds of 2 ms⁻¹ (dashed), 4 ms⁻¹ (dotted) and 6 ms⁻¹ (solid). Constructed from data of Merlivat and Jouzel [1979] (K. Sinclair, GNS Science, Personal communication).

Figure 2.9: Linear relationships between surface temperature and stable isotope ratios of snow and ice core samples from across Antarctica (from *Masson-Delmotte et al. [2008]*).

Stable isotope ratios of oxygen ($\delta^{18}\text{O}$) and hydrogen (δD) in Antarctic ice cores are well-established proxies for air temperature. Extensive spatial arrays that cover a wide range of temperatures have demonstrated strong correlations between mean temperature and $\delta^{18}\text{O}$ and δD (Fig. 2.9) [*Masson-Delmotte et al., 2008*]. Several other factors including, elevation, distance from the coast and snow accumulation will also influence $\delta^{18}\text{O}$ and δD so it is desirable to produce a δ -temperature calibration from samples taken along a local spatial slope [*Jouzel, 2003*]. For coastal locations the calibration developed for Taylor Dome, West Antarctica, is applicable: $0.5\text{‰ } \delta^{18}\text{O} / ^\circ\text{C}$ and $4\text{‰ } \delta\text{D} / ^\circ\text{C}$ [*Steig et al., 1998*].

Ice core stable isotopic records from both West and East Antarctic exhibit sensitivity to both SAM and ENSO forcing. *Gregory and Noone [2008]* and *Naik et al. [2010]* studied records from West Antarctica and Dronning Maud Land respectively, and found that, in agreement with the theory of *Fogt and Bromwich [2006]*, SAM is the dominant control on stable isotope ratios but ENSO influence is identifiable in periods when SAM and ENSO are in-phase. *Patterson et al. [2005]* also demonstrated that an ice core d-excess record from the Dry Valleys region reflected variations in moisture source and transport pathway caused by ENSO modulation of the position of the Amundsen Sea Low.

2.5.2 Soluble major ion chemistry

Concentrations of major ions dissolved within an ice core are determined by ion chromatography (IC), an analytical technique which separates ions according to their ionic radius and charge [Curran and Palmer, 2001; Morganti *et al.*, 2007]. The ions typically determined are Na^+ , Mg^{2+} , Ca^{2+} , K^+ , Cl^- , sulphate (SO_4^{2-}), nitrate (NO_3^-) and methylsulphonate (MS^-). Soluble Na^+ , Mg^{2+} , Ca^{2+} , Cl^- and SO_4^{2-} are principally sourced from the ocean whilst K^+ and NO_3^- have mixed sources [Legrand and Mayewski, 1997]. MS^- and SO_4^{2-} are produced by biogenic activity in the ocean [Legrand, 1997]. The following summary will only consider the source and transport of Na^+ , Ca^{2+} , SO_4^{2-} and MS^- because they have been developed as climate proxies relevant to this study.

Atmospheric aerosol species are transferred from the atmosphere to the ice sheet by either, wet or dry deposition. Wet deposition involves scavenging of chemical species by precipitation, which includes snow, rain, fog and diamond dust, whereas dry deposition can occur without precipitation. It involves either gravitational settling, diffusion or impaction of aerosol particles onto the ice sheet surface [Buseck and Schwartz, 2003]. The latter process is often referred to as wind pumping [Legrand and Mayewski, 1997]. At coastal locations, where cyclones are active and the air is relatively humid, wet deposition is the dominant process for marine aerosol [Benassai *et al.*, 2005].

There is considerable debate surrounding the mechanism by which Na^+ ions are transferred from the ocean into the polar atmosphere. Conventional understanding has favoured 'bubble bursting' which is the generation of marine aerosol droplets by breaking waves [Monahan *et al.*, 1986]. According to this mechanism, production of marine aerosol should be increased at locations or time periods of more intense cyclonic activity over the ocean [Petit *et al.*, 1981]. The alternative mechanism of transfer to the atmosphere is via the transport of frost flowers from the sea ice surface [Hall and Wolff, 1998]. Frost flowers are a well-documented feature on the surface of young sea ice and consist of salts precipitated from brine which migrates up through the sea ice [Rankin *et al.*, 2000; Rankin *et al.*, 2002]. Na^+ sourced from frost flowers can be differentiated from Na^+ from sourced bubble bursting by considering the

$\text{Na}^+/\text{SO}_4^{2-}$ in ice core samples because a major frost flower constituent is mirabalite ($\text{Na}_2\text{SO}_4 \cdot 10\text{H}_2\text{O}$), a salt which is depleted in SO_4^{2-} relative to Na^+ [Wagenbach *et al.*, 1998]. Na has been developed as a proxy for cyclonic activity [Kaspari *et al.*, 2005; Kreutz *et al.*, 2000] assuming an open water bubble bursting source by relating ice core concentrations to sea level pressure. However, Na^+ has also been employed as a proxy for sea ice extent assuming a frost flower source and correlating Na^+ levels with sea ice area [Wolff *et al.*, 2003].

Providing one assumes that all Na^+ present in ice cores is sourced from the ocean, the concentration of another ion (e.g. Ca^{2+}) which originates from a different source (non-sea salt = nss) can be calculated as follows,

$$[\text{nssCa}^{2+}] = [\text{Ca}^{2+}]_{\text{sample}} - [\text{Ca}^{2+}/\text{Na}^+]_{\text{sw}} * [\text{Na}^+]_{\text{sw}}$$

where $[\text{Ca}^{2+}]_{\text{sample}}$ refers to the concentration of Ca^{2+} in the sample and $[\text{Ca}^{2+}]_{\text{sw}}$ refers to the concentration of the ion in seawater [Legrand and Delmas, 1984].

Soluble Ca^{2+} ions can be sourced from the open ocean, terrestrial calcium carbonate (CaCO_3) dust [Banta *et al.*, 2008] and anhydrous CaCO_3 salts, such as ikaite, which are thought to form on the sea ice surface [Sala *et al.*, 2008]. nssCa^{2+} has been used as a tracer of terrestrial dust transport to both Greenland and Antarctic ice core sites [Fischer *et al.*, 2007; Mayewski *et al.*, 1994; Wolff *et al.*, 2006; Yan *et al.*, 2005] but the merit of this approach is questionable for Antarctica because soluble Ca concentrations are unlikely to be representative of dust inputs that are dominated by aluminosilicate minerals [Ayling and McGowan, 2006; Gaudichet *et al.*, 1988; Ruth *et al.*, 2008].

There are three recognised sources of nssSO_4^{2-} in Antarctic ice cores: volcanic activity (Section 4.3.3), anthropogenic industrial activity and biogenic processes. nssSO_4^{2-} and MS^- are oxidation products of dimethylsulphide (DMS), which is produced by marine phytoplankton associated with seasonal sea ice cover [Saltzman *et al.*, 1983]. Concentrations of both nssSO_4^{2-} [Dixon *et al.*, 2005] and MS^- [e.g. Abram *et al.*, 2010; Curran *et al.*, 2003; Welch *et al.*, 1993] in Antarctic ice cores have been used as proxies for sea ice extent of different sectors of Antarctica. The effectiveness of the proxy and

sign of correlation between MS^- and sea ice extent varies between ice core records from different locations due to site-specific factors [Abram *et al.*, 2007].

2.5.3 Mineral dust

In addition to marine salts, volcanic and biogenic aerosols, the atmosphere also contains wind-blown dust aerosol. Wind-blown dust is sourced from the entrainment of dust particles during dust storms over arid regions. In the Southern Hemisphere the dust aerosol load of the atmosphere is lower than that of the Northern Hemisphere because there are less arid areas and dust storms are less frequent [Prospero *et al.*, 2002]. Only around 1% of the total available dust is carried in vertical suspension after a dust storm and the particles have a maximum diameter of 20-50 μm [Gillette *et al.*, 1974]. In the Dry Valleys region of Antarctica there is a significant ice free area where a combination of mechanical weathering in the cold environment [Pye, 1987] and strong winds ($> 5.5 \text{ m s}^{-1}$) cause entrainment of dust particles [Ayling and McGowan, 2006].

Dust particles can be carried in suspension for days or weeks, depending on size and composition. Larger particles have a much shorter lifetime in suspension because they are rapidly removed by gravitational settling leading to a mean particle size of 2-3 μm involved in long-range transport [Schulz *et al.*, 1998]. Dust aerosols are transferred to the ice sheet by the same mechanisms as described in Section 2.5.2. On a global scale, wet deposition is the dominant removal process for smaller particles ($< 2 \mu\text{m}$) and dry deposition for larger particles [Buseck and Schwartz, 2003].

Where there are dust sources proximal to the ice core site, as is the case for sites close to the Dry Valleys, it is common practice to distinguish between 'global' dust, transported from elsewhere in the Southern Hemisphere, and 'local' dust, by grain size. 'Global' dusts have diameters of 2-6 μm [Delmonte *et al.*, 2004], whereas 'local' dust particles are $> 10 \mu\text{m}$ in diameter [Atkins and Dunbar, 2009]. More diagnostic provenance is achieved either by study of the mineralogy of the mineral dust

[*Gaudichet et al.*, 1988] or by determining Sr and Nd isotope ratios, which fingerprint the samples to potential source regions [*Bory et al.*, 2010; *Delmonte et al.*, 2010].

2.5.4 Trace elements

Inductively coupled plasma mass spectrometry (ICP-MS) provides excellent analytical capability for determination of trace element concentrations in Antarctic ice core samples. Additionally, analysis is rapid, has the capability to determine many elements simultaneously and only a small amount of sample is consumed.

Analysis of melted ice samples involves introducing samples into an argon-generated plasma, which ionizes the elements present. The ion beam is focused by lenses which direct it towards the mass analyser where the ions are separated before colliding with the detector [*Thomas*, 2001]. Most ICP-MS systems have a quadrupole mass analyser which separate ions according to their mass to charge ratio [*Thomas*, 2001]. The disadvantage with this system is that the difference between two chemical species with the same mass to charge ratio, i.e., $^{56}\text{Fe}^+$ and $^{40}\text{Ar}^{16}\text{O}^+$, cannot be resolved. In response to this, several other mass analysers including collision cell technology and double focusing magnetic sector or sector field (SF) analysers were developed. Many Antarctic snow and ice trace element studies [e.g. *Barbante et al.*, 1997; *Gabrielli et al.*, 2006; *Planchon et al.*, 2001] used SF-ICP-MS systems, but *Grotti et al.* [2008] and *Bull* [2009] have demonstrated that quadrupole ICP-MS is suitable for trace element determinations in coastal ice core samples.

Initial measurements of trace elements in Antarctic snow and ice were conducted before the advent of ICP-MS instruments and yet were able to define 20th century baseline concentrations of several trace elements and classify these elements into three source groups: marine, terrestrial and another, speculated to be volcanism [*Boutron and Lorius*, 1979; *Liu et al.*, 1988]. The development of analytical techniques for ICP-MS analysis of snow and ice samples [*Barbante et al.*, 1997; *Gabrielli et al.*, 2006; *Krachler et al.*, 2004; *Planchon et al.*, 2001; *Townsend and Edwards*, 1998] prompted a proliferation of trace element studies.

Analyses of snow pit and ice core samples dating from the last few centuries have focused on assessing the level of anthropogenic pollution to reach the Antarctic ice sheets and on understanding the broad sources, i.e., marine, terrestrial, volcanic, anthropogenic, of the trace elements measured. Both of these objectives involve calculating crustal enrichment factors according to the following equation:

$$\text{Crustal Enrichment Factor (EF}_c\text{) for element E} \quad E = \left(\frac{[E]_{\text{sample}}}{[X]_{\text{sample}}} \right) / \left(\frac{[E]_{\text{crust}}}{[X]_{\text{crust}}} \right)$$

[E] is the concentration of the element concerned and [X] is the concentration of another element that is considered to be sourced solely from terrestrial dust. The ratio of these elements in the sample is normalised to the same ratio of elements in the upper continental crust, values for which are obtained from the literature. Any relative contribution from element E above that of the terrestrial tracer, element X, is classed as being enriched i.e., from a source other than the crust, and any lower relative contribution from element E means that it is depleted relative to the crust. Anthropogenic pollution produces crustal enrichment factors greater than unity.

Wolff et al. [1999] identified only Cu as showing inputs from anthropogenic pollution in Coats Land, East Antarctica but *Planchon et al.* [2002b] added Cr, Zn, Ag, Pb, Bi and U to the list and attributed most these anthropogenic inputs to mining activities in the Southern Hemisphere. Anthropogenic input of Cu, Pb and As has also been recorded on the opposite side of East Antarctica in the Lambert Glacier basin [*Hur et al.*, 2007]. Both an increase in Pb pollution resulting from the use of leaded petrol and a decrease in Pb pollution since the 1980s due to heavily reduced leaded petrol use is recorded in Antarctic ice [*Planchon et al.*, 2003].

Defining the sources of trace elements in Antarctic snow and ice has proven to be difficult and complex. Each element tends to exhibit large variations in concentration [*Bull*, 2009; *Hur et al.*, 2007; *Planchon et al.*, 2002b], and variability in behaviour between elements is high [*Bull*, 2009; *Planchon et al.*, 2002b]. Where temporal resolution of the sampled time period is high enough, seasonal cycles have been noted in some trace elements (Ba and Mn, *Hur et al.* [2007]). Crustal enrichment factor values greater than unity can be interpreted as input from either anthropogenic or

volcanic sources; this has led to Cu, Zn and Pb being classified as both volcanic [Vallelonga *et al.*, 2004] and anthropogenic [Planchon *et al.*, 2002a] in origin.

Trace element concentrations have also been determined for sections of the deep ice cores from EPICA Dome C and Vostok which record glacial-interglacial climate cycles. Results from both cores show higher trace element concentrations in glacial periods than interglacial periods [Gabrielli *et al.*, 2005a; Gabrielli *et al.*, 2005b; Marteel *et al.*, 2008; Marteel *et al.*, 2009]. Peaks in mineral dust levels recorded in the Dome C core closely correspond to maxima in trace element concentrations indicating that elements such as Li, Mg, Cr, Mn, Co, Cu, As, Rb, Ba and Bi are sourced from terrestrial dust in glacial periods [Gabrielli *et al.*, 2005a]. Gabrielli *et al.* [2005a; 2005b] argued that in interglacial periods, when both dust concentrations and trace element concentrations are reduced, input of Cd, Bi and As from volcanic sources becomes important. Plots of trace element concentration against the stable isotope ratio $\delta^{18}\text{O}$ suggest a threshold low temperature has to be reached before the transport to, and/or deposition of, trace elements on the ice sheet can increase [Gabrielli *et al.*, 2005a; Gabrielli *et al.*, 2005b]. Marteel *et al.* [2009] identified a trend of decreasing trace element concentrations in successive glacial periods which they tentatively relate to a “change in the size distribution of dust particles transported from the mid-latitudes.”

A further study on the EPICA Dome C ice core considered only Fe concentrations measured after leaching the samples, which contain mineral dust particles, in acid for 24 hr (pH1, HNO_3). The relatively high concentration of Fe in the last glacial period is seen to decrease at the glacial termination as atmospheric CO_2 concentration rises [Gaspari *et al.*, 2006]. This adds some support to the ‘biological pump hypothesis’, which links iron availability to phytoplankton growth, CO_2 uptake, and temperature decrease during glacial periods [Sigman and Boyle, 2000]. Gabrielli *et al.* [2010] also studied the transition from the Last Glacial Maximum to the Holocene and measured concentrations of rare earth elements by ICP-MS. Discrepancies in the rare earth element signatures of the samples between the two periods are interpreted as representing a change in the composition of aeolian dust transported to Antarctica, and therefore a possible source region shift.

2.6 Ice core records of decadal-scale climate variability in the Antarctic

The study of *Schneider et al.* [2006] examined stable isotopic records from five ice cores across Antarctica to assess temperature changes since 1800 AD. The records showed that 17% of the variance in temperature, across time and space, could be explained by SAM. Additionally a cooler ($-0.2\text{ }^{\circ}\text{C}$) period was identified between the mid-19th and early-20th centuries. High resolution sea salt concentration records from Law Dome, East Antarctica, revealed that this cool period was also characterised by increased sea salt deposition and stronger atmospheric circulation during the winter months [*Souney et al.*, 2002]. *Goodwin et al.* [2004] expanded on this study by correlating the Na^+ record from Law Dome with winter sea level pressure to develop a proxy for the strength of SAM. The reconstructed SAM record shows that temporal variations in SAM became slower after 1500 AD and the SAM index started to trend towards a weakly positive state. The Law Dome ice core record suggests that the positive shift in the SAM since 1970 is part of natural climate variability rather than the result of anthropogenic greenhouse gases or the ozone hole, as others have proposed [*Thompson and Solomon*, 2002].

Kreutz et al. [2000] correlated the marine aerosol record from Siple Dome, West Antarctica, with sea level pressure of the Amundsen Sea region to produce a proxy for the strength of the Amundsen Sea Low. ENSO periodicities of 2.2 and 7.1 yr were identified in the marine aerosol spectrum between 1890 and 1994 AD, indicating that the ENSO teleconnection to Antarctica was effective during this period. Furthermore, evolutionary spectrum analysis of the sea salt record showed that a strong 45 yr periodicity ended ca. 1600 AD, suggesting that a change in forcing of sea level pressure occurred.

Another ice core proxy for ENSO influence on Antarctica is the biogenic sulphur species methylsulphonate (MS^-), which is linked to sea ice extent. *Meyerson et al.* [2002] found that the MS^- record of an ice core from the South Pole correlated with the SOI and developed a proxy for the SOI. This record shows that between 1600 and 1800 AD the ENSO teleconnection to the Antarctic was weak and Pacific sector sea ice extent was

reduced. At 1800 AD a shift occurs in the proxy record towards higher frequency El Niño events and the stable isotopic record also shows a cooling at this time.

Figure 2.10: Na concentration records from Siple Dome (red) and Law Dome (blue) (25 year running means) used as proxies for the Amundsen Sea Low (ASL) and East Antarctic High (EAH) respectively (modified after *Mayewski et al. [2009]*) Grey shading highlights the anomalous period in which the records are in-phase.

Mayewski et al. [2004] combined the proxy records of *Souney et al. [2002]* (for the East Antarctic High, see Fig. 2.2)), *Kreutz et al. [2000]* (for the Amundsen Sea Low) and *Meyerson et al. [2002]* (for El Niño events) and argue that atmospheric circulation underwent a ‘mode switch’ during the period 1700 to 1850 AD in which the East Antarctic High and Amundsen Sea Low, which are normally out-of-phase, came into phase (Fig. 2.10). The authors also observe that this time period is coincident with a minimum in solar variability. The same time period sees the increased in El Niño activity identified by *Meyerson et al. [2002]*. *Mayewski et al. [2009]* propose a potential link between the termination of this anomalous period and the beginning of atmospheric CO₂ concentration rise.

Chapter 3: Sea ice variability and primary productivity in the Ross Sea, Antarctica, from methylsulphonate snow record

This chapter constitutes a paper published in Geophysical Research Letters (Section 1.6).

Abstract

The Ross Sea contains the most biologically productive continental shelf in Antarctica and is a region where the annual formation of sea ice drives substantial amounts of bottom water formation. We present snow pit chemistry data from Mt Erebus Saddle that provide a quantitative proxy to reconstruct summer sea ice conditions and rates of marine primary production. The methylsulphonate (MS^-) record is strongly correlated with changes in the area of open water ($R^2 = 0.903$, $p < 0.05$) caused by differences in atmospheric circulation and the sea-ice-damming effect of large icebergs, B-15 and C-19, which calved from the Ross Ice Shelf in 2000 and 2002 respectively. Furthermore, MS^- and phytoplankton net primary production correlate significantly ($R^2 = 0.927$, $p < 0.01$). Our results demonstrate the potential of the Mt Erebus Saddle ice core to reconstruct sea ice and primary productivity variability in the Ross Sea beyond the observational record.

3.1 Introduction

Sea ice drives one of the strongest polar feedback mechanisms in the natural climate system, with reduced sea ice extent (SIE) causing amplification of greenhouse-gas-induced warming of the Earth. In addition, sea ice plays a key role in ocean circulation [Goose and Fichefet, 1999], ocean-atmosphere heat exchange and climate modulation [Yuan and Martinson, 2000], as well as providing a habitat for thriving marine ecosystems [Eicken, 1992]. Global temperature rise is predicted to continue at a rate of 0.2 °C per decade and climate models predict that sea ice will respond sensitively to increased sea surface temperature [IPCC, 2007]. Whilst Arctic sea ice is declining at a rapid and accelerating speed [Comiso *et al.*, 2008], Antarctic sea ice trends are less discernable.

Large interannual variability caused by the oscillating nature of regional climate drivers [Turner, 2004] provides a complicated view showing either no trend or opposing trends in sea ice behaviour around Antarctica between adjacent ocean sectors [Liu *et al.*, 2004; Zwally *et al.*, 2002]. In addition, reliable satellite data are only available from 1979 onwards, complicating the delineation of a long-term trend. The current observational data set therefore limits the evaluation of a temporal Antarctic SIE trend, including the possible response to observed ocean and atmospheric changes, such as the warming of the Southern Ocean [Boning *et al.*, 2008] and strong positive changes in the Southern Annular Mode [Stammerjohn *et al.*, 2008]. An accurate sea ice proxy extending the observational data set is crucial in order to establish the response of Antarctic sea ice to oceanic and atmospheric forcings and to quantify its potential as a positive feedback mechanism.

Ice cores provide particularly high resolution and continuous records of environmental conditions at high latitudes. Several ice core studies have identified a statistical relationship between the biogenic sulphur species, methylsulphonate (MS⁻), and SIE [Abram *et al.*, 2007; Curran *et al.*, 2003; Meyerson *et al.*, 2002; O'Dwyer *et al.*, 2000; Pasteur *et al.*, 1995; Sun *et al.*, 2002; Welch *et al.*, 1993] but the nature of this correlation is variable.

MS⁻ has a single source through the oxidation of dimethylsulphide (DMS) [Saltzman *et al.*, 1983] that, in the Southern Ocean, is a by-product of the dimethylsulphonioacetate (DMSP) produced by phytoplankton, such as *Phaeocystis antarctica* [DiTullio *et al.*, 2003; Liss *et al.*, 1994] and diatoms that are found in close association with sea ice [Bunt, 1963; Bunt and Wood, 1963; DiTullio *et al.*, 2003]. Here we report a snow pit MS⁻ record that demonstrates the causal link between MS⁻ emission, sea ice cover, and marine primary production in the Ross Sea, Antarctica.

3.2 Sea ice behaviour in the Ross Sea region

The Ross Sea is a globally important site of sea ice production [Tamura *et al.*, 2008] and bottom water formation [Jacobs and Giulivi, 1998]. However, current knowledge of sea ice behaviour in the Ross Sea is limited. Satellite data indicates that SIE has increased over the last 30 years [Stammerjohn *et al.*, 2008; Zwally *et al.*, 2002] despite a rise in the heat content of the Pacific sector of Southern Ocean [Levitus *et al.*, 2005]. In contrast, analyses of whaling records suggest that sea ice cover was more extensive either in the summer [Cotté and Guinet, 2007], or in the winter and spring months [de la Mare, 2009], during the pre-satellite era. In addition, there is increasing evidence that the Ross Sea freshened between 1960 and 2000, with a decrease in salinity of about 0.1 psu observed along the western Ross Ice Shelf, causing the Ross Sea shelf water to now be less dense than that of the Weddell Sea [Jacobs *et al.*, 2002].

The Ross Sea Polynya is maintained by katabatic winds that drive newly-formed ice offshore, allowing further sea ice formation [Bromwich *et al.*, 1992]. During this process, dense brine is ejected into the ocean and sinks to form a precursor to Antarctic Bottom Water [Jacobs and Giulivi, 1998], a major contributor to the global thermohaline circulation.

As the Ross Sea Polynya is located on the Antarctic continental shelf, nutrient concentrations are relatively high [Sedwick and DiTullio, 1997]. Consequently, during the austral spring and summer, phytoplankton biomass reaches very high levels [Arrigo and McClain, 1994; Arrigo *et al.*, 1999; Arrigo *et al.*, 2000; Smith and Gordon, 1997] making the Ross Sea the most productive sector of the Southern Ocean [Arrigo *et al.*, 1998; Smith and Gordon, 1997]. The Ross Sea Polynya itself is thought to be responsible for half the annual biological production on the entire Antarctic continental shelf (48 Tg C yr^{-1}) [Arrigo and van Dijken, 2003b].

3.3 Field site and methodology

Mt Erebus Saddle is situated on Ross Island at the edge of the Ross Ice Shelf (77°30.90'S, 167°40.59'E) (Fig. 3.1). As a result of its proximity (~15 km) to the seasonally open water of the Ross Sea Polynya, the snow accumulation rate at Mt Erebus Saddle is high (40 cm of snow per year). This allows sub-seasonal resolution of the snow and ice core record and limits post-depositional loss of MS^- [Weller *et al.*, 2004].

The predominant summer wind direction is north-easterly, entraining air masses that originate over the sea ice zone (Fig. 3.1). As a result, the marine aerosol signal in the Mt Erebus Saddle record is highly sensitive to the environmental conditions of the Ross Sea.

A 2 m deep snow pit was sampled in 2004/05, and a 180 m ice core was recovered from Mt Erebus Saddle in 2006/07. The snow pit was sampled at 1 cm resolution using methods reported previously [Bertler *et al.*, 2004a]. Samples were analysed for $\delta^{18}O$ at Alfred Wegener Institute for Polar and Marine Research to an accuracy of better than $\pm 0.1\text{‰}$ (MS Finnigan DeltaE) and for MS^- and major ions (Na^+ , K^+ , Mg^{2+} , Ca^{2+} , Cl^- , SO_4^{2-} , NO_3^-) by ion chromatography [Bertler *et al.*, 2004a] at the Climate Change Institute, University of Maine.

Figure 3.1: Location of Mt Erebus Saddle on (a) Radarsat Image of Antarctica (white box) and (b) on LIMA false colour satellite image, USGS. Rose diagram (C) displays wind direction and speed for summer months (Nov. to Feb.) at nearby Scott Base (available online at <http://www.cliflo.niwa.co.nz>).

Open water areas were determined using the algorithm of *Markus and Burns* [1995] from daily Special Sensor Microwave Imager (SSM/I) data obtained from the National Snow and Ice Data Center, University of Colorado, Boulder, CO. Sea-viewing Wide Field-of-view Sensor (SeaWiFS) chlorophyll *a* concentration data were acquired from the Goddard Earth Sciences (GES) Data and Information Services Center (DISC). Primary productivity was calculated using the algorithm of *Arrigo et al.* [2008]. Iceberg positions were projected from Moderate Resolution Imaging Spectroradiometer (MODIS) imagery.

3.4 Sea ice extent, primary productivity and methylsulphonate

The Mt Erebus Saddle snow pit record (Fig. 3.2A) was dated utilising the $\delta^{18}\text{O}$ record. $\delta^{18}\text{O}$ maxima represent peak annual temperatures and were assigned the timing of January 1st. Corresponding discrete annual summer peaks in MS^- concentration are clearly identifiable and vary between successive years of the record by almost an order of magnitude (11-68 ppb).

Figure 3.2: (A) Mt Erebus Saddle snow pit MS^- record (3-point running mean) plotted with $\delta^{18}\text{O}$ (3-point mean), (B) daily open water area of Ross Sea during summer (5-point running mean), and (C) daily primary productivity of the Ross Sea Polynya (3-point running mean). Grey shaded bars indicate summer (Nov. to Feb.).

To test the sensitivity of our MS^- record to sea ice conditions, for each year of the record, we compared MS^- concentrations to the area of open water (rather than the more commonly used ice edge latitude) present in the Ross Sea during austral summer (Fig. 3.2B). We chose to use open water area because ice cover in the south-western Ross Sea is controlled by the dynamics of the Ross Sea Polynya, a feature whose size is not readily characterized by latitude. Additionally, open water area is effectively the inverse of SIE but is better able to account for the influence of the polynya. The interannual variability of open water area over the time period of the snow pit record is high (Fig. 3.2B), ranging between a mean annual value of 63,000 km² in 2002/03 and 141,000 km² in 2001/02.

Austral summers that experienced increased open water area (decreased sea ice cover) in the Ross Sea (e.g., 2001/02) are associated with higher concentrations of MS^- in the snow pit record (Fig. 3.2B). However, the MS^- and open water area time series are both highly auto-correlated, which undermines the validity of direct cross-correlation. Therefore, we regressed annual mean MS^- concentration against annual mean open water area (Appendix I). This analysis yielded a strong, positive correlation ($R^2 = 0.903$, $p < 0.05$), indicating that an increase in open water area leads to a proportional increase in MS^- concentration in the snow pit record and vice versa.

In addition, we were able to identify for the first time why increased MS^- concentrations in a snow or ice core record are associated with higher open water area. This was achieved by comparing the MS^- record to the rate of marine primary production calculated for the Ross Sea over the same time period (Fig. 3.2C). In 2002/03, when the MS^- concentration was low, the maximum rate of primary production reached was only 895 mg C m⁻² d⁻¹ (Fig. 3.2C), less than a quarter of the rate reached in 2001/02, when the MS^- concentration peaks. Annual primary production and mean annual MS^- concentration correlate strongly ($R^2 = 0.927$, $p < 0.01$) (Appendix I). This identifies MS^- as a proxy for the mean annual rate of primary production. It also demonstrates that the MS^- concentration in the Mt Erebus Saddle record is controlled by sea ice conditions via the modulation of open water area available for primary production, whereby reduced summer sea ice leads directly to

greater marine primary productivity, higher DMS production, and elevated levels of MS^- in the snow pit.

This is in contrast to several other ice core proxy studies [*Curran et al.*, 2003; *Meyerson et al.*, 2002; *Welch et al.*, 1993], which identify a positive relationship between MS^- and winter SIE. This difference is accounted for by considering the characteristics each site [cf. *Abram et al.*, 2007]. At Law Dome, for example, *Curran et al.* [2003] recognised that the sea ice adjacent to Law Dome breaks out uniformly each summer and therefore the Law Dome MS^- record is sensitive to differences in winter SIE. In contrast, Ross Sea summer sea ice conditions vary greatly. The range between maximum and minimum extent is almost twice that of the sector adjacent to Law Dome ($4.4 \times 10^6 \text{ km}^2$ compared to $2.4 \times 10^6 \text{ km}^2$) [*Zwally et al.*, 2002]. The influence of highly variable summer sea ice conditions on primary productivity and DMS production in the Ross Sea overrides any variability caused by changes in winter SIE.

3.5 Interannual variability

The five-year period of the Mt Erebus Saddle snow pit is characterised by high variability in sea ice conditions and primary productivity (Fig. 3.3) in the Ross Sea. The anomalously high sea ice cover and consequent low primary productivity of austral summers 2000/01 and 2002/03 have been linked to the presence of icebergs B-15 and C-19. These were large icebergs (10,000 km² and 6,400 km² in areal extent respectively) and their slow drift across the Ross Sea restricted the summer breakout of sea ice [Arrigo and van Dijken, 2003a].

Figure 3.3: MS⁻ time series with images showing distribution of photosynthetic pigment, chlorophyll *a*, concentrations in the south-western Ross Sea (160-190°E, 71-86°S) in mid-December of each austral summer. High concentrations of chlorophyll *a* in the surface ocean indicate primary production is high. Iceberg locations are indicated and the effect on sea ice is described.

The impact of these icebergs on SIE is visible in satellite imagery and is also represented in our proxy record (Fig. 3.3). In 2000/01, (Fig. 3.3) a barrier formed by descendants of B-15 limited sea ice drift and restricted the open water area available for primary production [Arrigo *et al.*, 2002] causing lower MS⁻ concentrations than in the neighbouring years. The iceberg-effect is even greater in 2002/03 when C-19 was positioned perpendicular to the path of sea ice drift [Arrigo and van Dijken, 2003a]. The area of open water and primary productivity were severely limited (Fig. 3.3) and

the concentration of MS^- was reduced. *Harangozo and Connolley* [2006] show that weak atmospheric circulation during this summer also contributed to the heavy sea ice cover observed.

In 1999/00, neither of the large icebergs had yet calved, and in 2001/02, iceberg B-15A was grounded off the north of Ross Island (Fig. 3.3), to the west of the main polynya, and had little influence on sea ice behaviour. In both summers, complete sea ice breakout occurred across the entire Ross Sea area, phytoplankton biomass reached 10 mg chlorophyll *a* m^{-3} over large areas (Fig. 3.3), resulting in high rates of primary production and peak MS^- concentrations above 50 ppb (Fig. 3.2a).

3.6 Conclusions

This snow pit study has identified the MS^- record from Mt Erebus Saddle as a robust proxy for Ross Sea summer sea ice conditions via a strong, significant correlation with open water area. Furthermore, the annual mean MS^- concentration at Mt Erebus Saddle is demonstrated to be a direct measure of the rate of marine primary productivity.

Strong, significant correlations between MS^- , primary productivity, and open water area are established at Mt Erebus Saddle primarily as a result of the proximity of the Ross Sea Polynya and the predominant north-easterly wind direction, which directs MS^- transport from the sea ice zone (Fig. 3.1). This ensures that atmospheric MS^- concentration is not depleted by a long transport distance [Preunkert *et al.*, 2008]. It is also important that coastal Antarctic regions are strongly affected by regional cyclonic activity [Carrasco and Bromwich, 1993] and receive little stratospheric air, which carries a low latitude MS^- signature [Minikin *et al.*, 1998].

Future work will concentrate on the application of this proxy to the longer-term record of the 180 m deep Mt Erebus Saddle ice core. Through the use of a multi-proxy approach, involving stable isotopes, major ions, and trace elements, it is anticipated that a better understanding of the response of sea ice to drivers such as temperature and atmospheric circulation patterns will be established. Analysis of the ice core also has unique potential to produce a high-resolution record of Ross Sea primary production and its response to climatic change. Together, these longer-term records would improve our understanding of the past, and possible future, influence of ice dynamics on bottom water formation and of primary production on CO_2 uptake in a key region of the Southern Ocean.

Chapter 4: Methodology for ice core study

4.1 Ice core sampling and processing

4.1.1 Site description

Mt Erebus Saddle is located between the peaks of Mt Erebus and Mt Terra Nova at an altitude of 1600 m on Ross Island, western Ross Sea region, Antarctica (Fig. 3.1) (77°30.90'S, 167°40.59'E). The average annual temperature determined by 15 m depth firn temperature at the site is -25.6 °C. A ground penetrating radar survey, conducted in late-2003, indicated a depth to bedrock of 220 m and suggested that ice flow off the saddle in NNW and SSE directions. The ice core was drilled at the centre of the ridge where ice flow is at a minimum. The radar survey imaged parallel isochrones or annual layers of snow deposition in the top 30-60 m and relatively flat bedrock topography, suggesting favourable glaciological conditions for the preservation of a continuous, annually-resolved ice core record (Fig. 4.1).

Figure 4.1: Ground penetrating radar (35 MHz frequency) profile from Mt Erebus Saddle showing bedrock topography, ice thickness and parallel isochrones (modified after Bertler [2004]).

This particular site was selected for ice core retrieval for two reasons. Firstly, the site was identified as having an anomalously high snow accumulation rate for coastal Antarctica (Fig. 4.2) [Bromwich, 1988; Monaghan *et al.*, 2005], indicating that an ice

core would capture a record of past climate at a high temporal resolution. Secondly, the firn-ice transition occurs between 60-67 m depth (Section 4.3.4), which is relatively shallow for an Antarctic ice core [Bender *et al.*, 1997]. A shallow firn-ice transition causes the closure of gas bubbles in the firn to occur more rapidly, resulting in a reduced age difference between the ice and the gas trapped inside it and a higher resolution gas record [Bender *et al.*, 2006]. Analysis of atmospheric gases trapped in the Mt Erebus Saddle ice core is being conducted by researchers at National Institute of Water and Atmospheric Research (NIWA), Wellington, New Zealand.

Figure 4.2: Map of annual precipitation in the McMurdo Sound region produced by the Antarctic Mesoscale Prediction System (AMPS) (modified after *Monaghan et al.* [2005]). The location of Mt Erebus Saddle is marked by a black circle. The 3.3 km domain model resolves the topography of Ross Island.

4.1.2 Ice core retrieval

The Mt Erebus Saddle ice core was drilled between 10th and 27th December 2006 using the Alfred Wegener Institute shallow drill and a drill depth of 168 m was reached. Once retrieved, the 10 cm diameter core was cut into sections of 1 m length using a band saw and each 1 m section was weighed in the field for calculation of density

(Section 5.4). To minimise contamination of the core during the drilling operation, all core processing personnel in the drill trench wore Tyvek® clean suits with hoods, powder-free polyethylene gloves and face masks. After processing, the core sections were transported at temperatures below -18 °C to the New Zealand Ice Core Laboratory, GNS Science, Lower Hutt, New Zealand and stored at -35 °C.

4.1.3 Ice core processing

4.1.3.1 Ice core preparation

The portion of ice core assigned to this study was prepared in the cold laboratory (-18 °C) of the New Zealand Ice Core Laboratory. Each 1 m length section of ice core was cut twice lengthways using a band saw to create a quasi-quarter sized portion (Fig. 4.3). Each exposed end surface was scraped with a ceramic knife to remove ice that may have been contaminated and this portion of core was then bagged into plastic lay flats for storage prior to melter processing. The remaining sections of core were also bagged into plastic lay flats and returned to storage.

Figure 4.3: Plan view of the Mt Erebus Saddle ice core showing the portion of core used in this study, outlined by a thick black line. Concentric grey circles indicate the positions of the inner circles of each melt disk used in processing (see text). Grey dashed lines are band saw cut lines.

The uppermost 120 m of the Mt Erebus Saddle ice core processed for this study were generally of good physical quality with few core breaks. The depths of all core breaks were recorded to check for chemical contamination or loss of material.

4.1.3.2 *Continuous-melter-discrete sampling system*

The ice core was processed in the clean laboratory of the New Zealand Ice Core Laboratory using a continuous-melter-discrete sampling system, described in detail by *Osterberg et al.* [2006], in order to obtain ultra-clean samples necessary for chemical analysis. To process the core each metre-length section was removed from the plastic lay flat and placed on a heated nickel disk situated inside a stand-alone freezer unit cooled to -10 °C. As the ice core melts on the nickel disk, sample is pumped away through radial slits on the surface of the disk. The melted sample is pumped to three Gilson fraction collectors which direct it into separate vials for three different types of analyses: determination of stable isotope ratios, ion chromatography (IC) and inductively coupled plasma mass spectrometry (ICP-MS). The fraction collector for the IC samples controls the sampling sequence by monitoring the number of drops of sample it receives. Once a drop number equivalent to the required sample volume is reached, the IC fraction collector signals all the fraction collectors to move to the next sample vial simultaneously.

Material from the interior of the core which has had no contact with the atmosphere or processing equipment is sampled for IC and ICP-MS analysis. The surface of the nickel disk has a raised inner circle which acts to isolate material melted from the interior of the core (Figs. 4.3 and 4.4). Material from the outer region of the core is sampled for stable isotope analysis and for archival storage. The diameter of the inner circle on the nickel disk dictates the ratio of inner to outer material collected from a 1 m length of core and therefore the sampling resolution that is achieved. A nickel disk with a 2 cm diameter inner circle was used to process the ice core down to a depth of 65 m with a mean sampling resolution of 2.3 cm depth. Each 2.3 cm depth of core melted equated to the following approximate sample volumes: 4 mL ICP-MS, 4 mL IC, 4.5 mL stable isotopes and up to 28 mL archive material. Between 66 m and 120 m

depth, a nickel disk with an inner circle diameter of 3.0 cm was used to process the ice core. A larger inner circle diameter increased the ratio of inner material to outer material and allowed a higher mean sampling resolution of 1.6 cm to be achieved whilst still obtaining the sample volumes required for chemical analysis.

Figure 4.4: Photograph of nickel melt disk used on the continuous melter system. Raised inner circle (2 cm diameter) and radial slits can be seen.

4.1.3.3 Improvements to the melter system

The original design of the continuous-melter-discrete sampling system was improved in May 2010 by the development of software which monitors both the drop-counting sequence of the Gilson fraction collectors and the depth of core being sampled over time. This allows samples to be traced back to their original depth in the 1 m length of ice core melted. Another improvement was the addition of an optional setting which reduces the depth resolution of ICP-MS sampling by half; for every two stable isotope or IC samples produced, one ICP-MS sample is produced. This proved advantageous for this study because it was not practical or necessary to analyse every ICP-MS sample obtained and ICP-MS sample vials require a lengthy and laborious cleaning process. ICP-MS samples between 77 and 120 m were sampled at 3.2 cm resolution, whilst maintaining 1.64 cm resolution sampling for IC and stable isotope analysis. A total of

6669 samples for IC and stable isotope analysis and 5225 samples for ICP-MS were obtained.

4.1.3.4 *Vial cleaning procedures*

All vials used to sample material intended for IC or ICP-MS analysis were rigorously cleaned prior to use to prevent chemical contamination. The polypropylene vials used for IC samples were triple-rinsed with ultra-pure water ($> 18.2 \text{ M}\Omega$), soaked for a minimum of three days and triple-rinsed again. The polypropylene vials used for ICP-MS samples were first triple-rinsed with ultra-pure water then soaked in 5 wt.% analytical reagent grade HNO_3 for a minimum of 10 days, triple-rinsed, soaked in ultra-pure water for a minimum of 5 days and triple-rinsed with ultra-pure water. Vial cleaning was conducted under HEPA Class 100 clean room conditions whilst wearing a Tyvek® clean suit with hood and powder-free polyethene gloves.

4.1.3.5 *Procedural blanks*

Procedural blanks monitor the potential contribution of the processing and sampling procedure to the concentrations of chemical species measured. Fabricated ice cores of frozen ultra-pure water ($> 18.2 \text{ M}\Omega$) were processed, melted and sampled daily by the same methods as described above to provide procedural blanks. Chemical concentrations recorded in the procedural blanks are summarized in Tables 4.1 and 4.2. The procedural blank concentrations equate to: $< 10\%$ of the mean ice core concentrations of Na, Mg, As, Rb, Sr, Tl, Bi Th, K^+ and SO_4^{2-} ; $< 15\%$ of the mean ice core concentrations of Al, V, Mn, Cs, Ce, La and Pr; $< 20\%$ of the mean ice core concentrations of Y, Zr, U, NO_3^- and Cl^- ; $< 25\%$ of the mean ice core concentrations of Ti and Ba, and $< 30\%$ of the mean ice core concentration of Pb. Contamination of Ca was a problem as the ICP-MS procedural blank accounts for 70% of the mean concentration. The Ca and Zr in the ICP-MS procedural blanks originate from the ceramic knives used to prepare the ice core for melting. The Ca^{2+} concentration of the procedural blanks measured by IC is significantly higher than the Ca concentration measured by ICP-MS.

This is likely to be the result of interference from Ni, sourced from the melt disk, which is known to elute close to Ca^{2+} on the CS-12A column [Osterberg *et al.*, 2006]. During the processing of the ice core using the continuous melter system it was noted that dust particles can become lodged in connectors or tubing causing contamination of procedural blanks. It is recommended that connectors and tubing are checked for dust accumulation daily. Procedural blanks should also be sampled after several successive metres of ice core are melted to test whether the background concentrations increase.

Tables 4.1 and 4.2: Mean procedural blanks for Mt Erebus Saddle ice core processing and sampling. Raw data are provided in Appendix II.

Table 4.1: ICP-MS (ppt, except where indicated)

Element	Concentration
Na ^a	1.12
Mg ^a	0.29
Al ^a	0.56
Ca ^a	6.89
Ti	78.5
V	0.70
Mn	10.9
As	0.29
Rb	0.47
Sr	4.50
Y	0.50
Zr	3.05
Cs	0.05
Ba	5.28
La	0.66
Ce	1.42
Pr	0.17
Tl	0.00
Pb	4.67
Bi	0.09
Th	0.07
U	0.04

^a Concentrations in ppb

Table 4.2: IC (ppb)

Ion	Concentration
Na ⁺	0.34
Mg ²⁺	0.66
K ⁺	0.10
Ca ²⁺	20.3
MS ⁻	0.00
Cl ⁻	26.6
SO ₄ ²⁻	4.50
NO ₃ ⁻	6.27

4.2 Analytical techniques

4.2.1 Stable isotope analysis

The stable isotope ratios of oxygen ($\delta^{18}\text{O}$) and hydrogen (δD) were measured at the Stable Isotope Laboratory, GNS Science, Lower Hutt. Two different systems were used to analyse samples from different sections of the 120 m depth of ice core processed for this study and both are described below.

Samples from the top 91 m depth of ice core were analysed by a conventional isotope ratio mass spectrometer instrument. $\delta^{18}\text{O}$ measurement was conducted using a GVI AquaPrep system linked to a dual inlet GVI mass spectrometer. 400 μL of sample was equilibrated with 300 μL of CO_2 for 24 hr at 25.5 °C. The CO_2 was then extracted and transferred to the mass spectrometer for analysis. δD analyses were performed by directly reducing 100 μL of sample to H_2 gas in a PyrOH reaction column and measuring the gas on the same dual inlet GVI mass spectrometer. $\delta^{18}\text{O}$ and δD are reported with respect to V-SMOW and normalized to internal standards: INS9 with reported values of -17.4‰ for $\delta^{18}\text{O}$ and, -131.0‰ for δD , and INS11 with reported values of -0.4‰ for $\delta^{18}\text{O}$ and, -4.6‰ for δD . The analytical precision is $\pm 0.1\text{‰}$ for $\delta^{18}\text{O}$ and $\pm 1.0\text{‰}$ for δD .

Samples from 92 m to 120 m depth were analysed using a LGR Liquid-Water Isotope Analyser which measures $\delta^{18}\text{O}$ and δD simultaneously by laser absorption spectroscopy. Laser absorption is measured within a cavity containing high-reflectivity mirrors to generate laser path lengths of several km resulting in clear separation of laser absorption lines of different water molecules. $\delta^{18}\text{O}$ and δD are reported with respect to V-SMOW and normalized to the internal standards mentioned above. The analytical precision for this instrument is $\pm 0.2\text{‰}$ for $\delta^{18}\text{O}$ and $\pm 0.6\text{‰}$ for δD . Tests were carried out to assess the degree of comparability between the measurements of the two analytical instruments. $\delta^{18}\text{O}$ and δD values determined using the LGR Liquid-Water Isotope Analyser were corrected to make them directly comparable to the mass spectrometer measurements (Appendix IV).

Deuterium excess (d-excess) is a second order parameter derived from $\delta^{18}\text{O}$ and δD values:

$$d - \text{excess} = \delta\text{D} - 8 * \delta^{18}\text{O} \text{ [Dansgaard, 1954]}$$

Uncertainty (u) resulting from analytical precision can be estimated as:

$$u(d - \text{excess}) = \sqrt{(u\delta\text{D})^2 + (8 * u\delta^{18}\text{O})^2}$$

Measurements conducted on the mass spectrometer result in an uncertainty of 1.3‰ on d-excess, compared to 1.7‰ on the laser system. The combined uncertainty on d-excess values for the entire record is 2.14‰ (Appendix IV).

4.2.2 Ion chromatography

Ion chromatography (IC) analysis for major ions (Na^+ , K^+ , Mg^{2+} , Ca^{2+} , MS^- , Cl^- , NO_3^{2-} , SO_4^{2-}) was conducted at the Climate Change Institute, University of Maine using Dionex ion chromatographs with chemical suppression and conductivity detectors. Two ion chromatographs paired to a Gilson 215 Liquid Handler autosampler allowed for simultaneous anion and cation analysis. Anions were measured using an AS-18 column, 400 μL sample loop, and a Dionex Reagent Free Controller producing a KOH eluent concentration of 35 mM. Cations were measured using a CS-12A column and a 500 μL loop with 25 mM methanesulphonic acid eluent.

Table 4.3: Concentrations of major ions (ppb) in IC calibration standards

Calibration std.	Na^+	K^+	Mg^{2+}	Ca^{2+}	MS^-	Cl^-	NO_3^{2-}	SO_4^{2-}
1	1200	50	150	250	100	2000	150	1200
2	400	17	50	83	33	667	50	400
3	133	6	17	28	11	222	17	133
4	44	2	6	9	4	74	6	44
5	15	1	2	3	1	25	2	15

The chromatograph was calibrated at the beginning of each week by analyzing five calibration standards which bracketed the expected concentration range (Table 4.3). Correlation coefficients of $r^2 > 0.99$ were routinely achieved for all major ions. Calibration standard 2 was run daily to check the calibration. Calibration results were verified using the external standard ION-92 (National Water Research Institute, Canada), which was run at dilutions of 100 and 1000 times to reflect the range of concentrations measured in the ice core samples. The accuracy, precision and detection limits of major ion measurements are provided in Appendix III.

4.2.3 *Inductively coupled plasma mass spectrometry*

4.2.3.1 *Hardware and operating conditions*

ICP-MS analyses were conducted at the Geochemistry Laboratory of the School of Geography, Environment and Earth Sciences, Victoria University of Wellington using an Agilent 7500cs Series instrument. Ice core samples were analysed for concentrations of 22 major, minor and trace elements (Na, Mg, Al, Ca, Ti, V, Mn, As, Rb, Sr, Y, Zr, Cs, Ba, La, Ce, Pr, Tl, Pb, Bi, Th, U). The operating conditions employed for ICP-MS analysis are displayed in Table 4.4. The octopole collision cell was not used for this study because it inhibits the detection of very low (sub-ppt) concentrations of trace elements. An ASX-520 micro-volume autosampler linked to the ICP-MS introduced sample to the PFA Teflon nebuliser (0.2 mL min⁻¹ flow rate) via a peristaltic pump. The temperature of the quartz spray chamber was maintained at 2 °C to reduce the water content of aerosol entering the plasma and limit molecular interferences [Hutton and Eaton, 1987]. The formation of oxides in the plasma was monitored by aspirating a 1 ppb solution of Ce. Tuning parameters were adjusted to maintain the proportion of the ¹⁴⁰Ce converted to ¹⁴⁰Ce¹⁶O at below 2%.

Nickel sampling and skimmer cones were cleaned and the sample introduction system was circulated with 5 wt.% HNO₃ (Seastar) for 1 hr prior to each analytical session to reduce any possible memory effect from previous user's samples.

Table 4.4: Operating conditions of the ICP-MS and data acquisition parameters for the determination of selected elements in Mt Erebus Saddle ice core samples.

Parameter	Setting
Forward power	1500 W
RF matching	1.75-1.84 V
Carrier gas	1.04 -1.10 L min ⁻¹
Makeup gas	0 L min ⁻¹
Nebulizer pump	0.12-0.16 rps
Spray chamber temperature	2°C
Sampling depth	7 mm
Torch position	Optimised daily to maximise sensitivity
Ion lenses voltages	Optimised daily to maximise sensitivity and signal stability across mass range
Isotopes measured	²³ Na, ²⁴ Mg, ²⁷ Al, ⁴³ Ca, ⁴⁷ Ti, ⁵¹ V, ⁵⁵ Mn, ⁷⁵ As, ⁸⁵ Rb, ⁸⁸ Sr, ⁸⁹ Y, ⁹⁰ Zr, ¹³³ Cs, ¹³⁸ Ba, ¹³⁹ La, ¹⁴⁰ Ce, ¹⁴¹ Pr, ²⁰⁵ Tl, ²⁰⁸ Pb, ²⁰⁹ Bi, ²³² Th, ²³⁸ U
Uptake and stabilization time	50 s and 60 s
Washing time between samples	10 s H ₂ O, 200 s 5 wt.% HNO ₃ , 220 s 1 wt.% HNO ₃ (total 430 s)
Integration time	0.10 s or 0.15 s depending on element
No. of runs and scan passes	3 x 26

4.2.3.2 Calibration and external standards

Two calibration standards were required to incorporate the large concentration range across all the elements measured in the samples. The first standard contained major and minor elements (Na, Mg, Al, Mn and Ba) and the second standard contained lithophile trace elements (Ti, V, As, Rb, Sr, Y, Zr, Cs, La, Ce, Pr, Tl, Pb, Bi, Th, U). The relative concentrations of the various elements in the calibration standards were chosen to reflect the ratio of element concentrations expected in the ice core samples. Stock calibration standards were made up in 5 wt.% HNO₃ from mono-elemental 1000 ppm standards. Daily calibration standards were gravimetrically diluted from the stock standards (Table 4.5). P/A factor tuning calibrates measurements made by the two modes of detection (pulse and analog) of a quadrupole-based ICP-MS. P/A factors were tuned for elements which recorded > 1,000,000 counts s⁻¹ (Na, Mg and Al) every three days or when the sensitivity changed markedly.

Table 4.5: Concentrations of elements in ICP-MS daily calibration standards.

	Element(s)	Concentration	
Calibration Std. 1	Na, Ca	10	ppb
	Mg	1	ppb
	Al, Mn, Ba	100	ppt
Calibration Std. 2	Ti, Sr	100	ppt
	As, Rb, Pb	20	ppt
	V, Zr	10	ppt
	Y, Cs, La, Ce, Tl, Bi, Th, U	1	ppt

Samples were stored frozen prior to analysis to minimise leaching of elements from the interior walls of the vials. Samples were defrosted and acidified to 1 wt.% HNO₃ with 68 wt.% HNO₃ (Seastar) in a Class 100 clean room at least 12 hr prior to analysis. 1 wt.% HNO₃ blanks were run every 6 samples and counts recorded on the blanks were subtracted from those recorded on samples and standards to correct for background. Both calibration standards were run as bracketing standards every 12 samples to correct for instrumental drift. An external reference material, SLRS-4 (river water, National Research Council, Canada), was run at 10 times dilution with each batch of samples to test the accuracy and reproducibility of the measurements. All data processing including calibration and blank correction was performed offline.

4.2.3.3 Precision, accuracy and detection limits of ICP-MS measurements

The precision and accuracy of the MES ice core ICP-MS analyses are displayed in Tables 4.6 and 4.7. With the exception of only 3 elements, the concentrations determined in the external reference material are within error of the certified values. For several of these elements, notably Ti, As, Sr and Th, the % difference between the concentrations determined in this study and the certified values is greater than the precision of the measurements in this study. Ti, As, Sr and Th were consistently determined to be at higher concentrations than the certified values, suggesting that either poly-molecular interferences were consistently augmenting the signal or that the certified values are under-estimated. The certified values are determined by more than one independent analytical technique, although this does not always include ICP-MS. The

concentrations of V, Cs and Pr determined in this study are not within error of the certified values. The Pr concentration determined deviates from the certified value because Pr was not present in the calibration standard and Pr concentrations were determined using the sensitivity recorded on Ce. The V certified value is the product of 4 independent analytical techniques and the Cs is compiled from > 3 ICP-MS studies so it is likely that the measurements in this study are inaccurate. This could be the result of poly-atomic interferences (on V only) or an error made when adding monoelemental solutions to the calibration standard.

Detection limits are presented in Table 4.8 and demonstrate considerable improvement through the course of the analytical work undertaken for this study. The mean detection limits of all the analysis undertaken are consistently lower than achieved for other studies using quadrupole ICP-MS instruments and, for many elements, are comparable with those achieved with sector-field or double-focusing instruments.

Table 4.6: Major element concentrations (ppb) determined by repeated ICP-MS measurement of SLRS-4 riverine water standard for each analytical session with precision and accuracy of measurements.

Analytical session	n	Na	Mg	Al	Ca	Mn	Ba
Nov-08	10	2362	1668	60.3	6363	3.66	12.7
Feb-09	11	2285	1426	55.1	5933	3.60	13.2
Mar-09	6	2263	1554	54.7	6068	3.48	13.0
Apr-09	6	2232	1505	54.3	5874	3.46	12.7
Jun-09	11	2295	1618	57.5	6149	3.55	13.2
Aug-09	3	2288	1608	55.1	5952	3.63	13.3
Oct-09	6	2265	1613	57.0	6111	3.52	13.0
Dec-09	3	2340	1644	56.6	6747	3.60	13.1
Jul, Aug-10	26	2270	1518	55.0	5986	3.49	12.8
Long-term mean	82	2289	1573	56	6132	3.56	13.0
2 SD		80	156	4	546	0.14	0.44
Certified values		2400	1600	54	6200	3.37	12.22
2 SD		200	100	4	200	0.18	0.6
Precision 2RSD (%)		3.5	9.9	6.8	8.9	4.0	3.4
Accuracy (% difference)		4.6	1.7	4.0	1.1	5.5	6.4

Certified values for SLRS-4 are GeoREM preferred values obtained from <http://georem.mpch-mainz.gwdg.de>.

n = number of SLRS-4 determinations in each analysis batch.

Table 4.7: Trace element concentrations (ppt) determined by repeated ICP-MS measurement of SLRS-4 riverine water standard for each analytical session with precision and accuracy of measurements.

Analytical session	n	Ti	V	As	Rb	Sr	Y	Zr	Cs	La	Ce	Pr	Tl	Pb	Bi	Th	U
Nov-08	10	1564	380	774	1570	28630	139	135	6.83	285	347	70.6	6.98	76.7	2.55	20.0	45.9
Feb-09	11	1706	384	750	1640	30128	142	160	6.93	306	387	85.7	6.48	83.7	2.39	23.2	51.7
Mar-09	6	1696	401	763	1617	29806	146	120	6.77	308	379	83.9	7.21	82.6	2.40	22.2	54.0
Apr-09	6	1600	374	766	1590	29315	141	130	6.58	292	366	80.1	16.28 ^a	80.2	2.06	21.7	53.9
Jun-09	11	1559	385	757	1659	30701	146	121	6.90	306	384	85.8	9.49	83.2	2.58	22.0	52.3
Aug-09	3	1529	373	745	1653	30512	147	127	6.94	299	392	87.5	8.86	83.4	2.29	21.5	51.9
Oct-09	6	1491	371	758	1607	29628	144	125	6.70	295	378	86.9	8.99	82.0	2.52	20.5	50.1
Dec-09	3	1620	391	745	1616	29915	141	146	6.79	296	365	85.3	13.67 ^a	86.5	38.79 ^a	20.9	50.3
Jul, Aug-10	26	1515	378	-	1597	29414	141	188	6.75	296	374	85.2	7.69	79.5	2.43	21.9	50.2
Long-term mean	82	1587	382	757	1616	29783	143	139	6.80	298	375	83.4	7.96	82.0	2.40	21.5	51.1
2 SD		152	19	21	59	1269	6	45	0.23	15	27	10.6	2.31	5.7	0.34	1.9	4.9
Certified values		1460	320	680	1530	26300	146	120	9	287	360	69.3	6.8	86	2.1	18	50
2 SD		80	30	60	50	3200	8	15	2	8	12	1.8	1.3	7	0.1	3	3
Precision 2 RSD (%)		9.6	5.1	2.7	3.7	4.3	4.0	32.2	3.4	5.1	7.3	12.6	29.0	6.9	14.0	9.1	9.6
Accuracy (% difference)		8.7	19.3	11.3	5.6	13.2	2.0	15.9	24.5	3.9	4.1	20.4	17.0	4.7	14.4	19.6	2.3

^a Anomalous values excluded from long-term mean.

Certified values for SLRS-4 are GeoREM preferred values obtained from <http://georem.mpch-mainz.gwdg.de>.

n = number of SLRS-4 determinations in each analysis batch.

Table 4.8: Detection limits (ppt) for elements determined in each analytical session of ICP-MS analyses of the MES ice core.

Analytical session	n	Na	Mg	Al	Ca	Ti	V	Mn	As	Rb	Sr	Y	Zr	Cs	Ba	La	Ce	Pr	Tl	Pb	Bi	Th	U
Nov-08	11	107	3.8	12.1	3581	23	0.66	3.7	8.9	0.40	8.79 ^d	0.14	0.52	0.25	0.46	0.19	0.26	0.22	0.60	1.04	0.69	0.58	0.53
Feb-09	13	185	5.2	11.1	1224	23	0.91	3.5	8.8	0.36	0.33	0.13	0.57	0.24	0.36	0.20	0.27	0.22	0.66	1.02	0.64	0.80	0.64
Mar-09	5	317	3.4	11.6	1265	20	1.03	3.9	9.5	0.39	0.30	0.12	0.49	0.24	0.28	0.18	0.23	0.22	0.54	0.85	0.55	0.53	0.53
Apr-09	7	209	6.2	11.4	812	22	0.76	3.4	13.5	0.31	0.25	0.09	0.39	0.20	0.29	0.16	0.22	0.18	0.60	0.98	0.57	0.62	0.61
Jun-09	12	310	6.3	9.2	755	26	0.88	3.1	1.8	0.29	0.28	0.07	0.80	0.13	0.25	0.09	0.13	0.27	0.27	0.46	0.25	0.23	0.25
Aug-09	3	201	5.7	8.4	815	24	0.77	2.1	1.5	0.32	0.44	0.08	0.36	0.16	0.26	0.10	0.13	0.11	0.30	0.52	0.28	0.27	0.26
Oct-09	5	42	2.5	8.5	446	24	0.85	2.1	2.1	0.20	0.42	0.07	0.40	0.11	0.18	0.09	0.10	0.09	0.23	0.45	0.21	0.18	0.18
Dec-09	3	57	5.7	5.1	647	23	1.04	3.2	1.8	0.20	0.74	0.07	0.39	0.09	0.44	0.08	0.09	0.08	0.21	0.49	0.17	0.11	0.11
Jul, Aug-10	13	52	5.3	6.9	655	18	0.78	3.1	-	0.21	0.25	0.09	0.72	0.13	0.28	0.11	0.12	0.11	0.25	0.42	0.24	0.25	0.21
Mean																							
detection limit	72	167	5.0	9.7	1271	22	0.83	3.2	6.7	0.31	0.31	0.10	0.58	0.18	0.32	0.14	0.19	0.19	0.44	0.72	0.43	0.45	0.40
1 σ		116	2.8	5.9	1955	6	0.19	0.8	4.8	0.10	0.18	0.03	0.74	0.06	0.13	0.05	0.08	0.23	0.22	0.34	0.23	0.27	0.22
Previous studies																							
<i>Grotti et al.</i> [2008] ^a	60						4.6	8.9											5.9				
<i>Barbante et al.</i> [1999] ^b	5					63	3	1.8							1.8					0.6	0.09		0.03
<i>Osterberg et al.</i> 2006 ^b	10			40	110	0.7	0.1	1			0.3		0.00 7		0.33	0.01	0.01	0.00 2	0.03	0.2	0.03		0.00 6
<i>Krachler et al.</i> [2005] ^b	15			93			0.14	0.28		0.14	0.65				0.38				0.00 3	0.06	0.01		0.00 5
<i>Correia et al.</i> [2003] ^c		160	39	56	6600	23	9.5	5.2	28	1.6	1.5	0.37	5	0.89	5.2	0.57	0.66	0.26	1.1	2.1		1.5	0.39

^a Determined by quadrupole ICP-MS using collision cell; ^b Determined by sector-field or double focusing ICP-MS; ^c Determined by quadrupole ICP-MS; sample introduced via a desolvation unit; ^d ⁸⁶Sr measured instead of ⁸⁸Sr - result excluded from mean.

n = number of runs in analysis batch.

Chapter 5: Dating the ice core record

The Mt Erebus Saddle ice core age model was developed by annual layer counting, using thermonuclear bomb tritium fallout, and volcanic trace element deposition events as age tie points, and further constrained by a glacial flow model.

5.1 Annual layer counting

For Antarctic ice cores, the term ‘annual layer counting’ refers to the process of identifying annual peaks in measured parameters [Steig *et al.*, 2005]; there are no annual dust horizons visible to the naked eye, as are found in Greenland ice cores [Alley *et al.*, 1997]. In the case of the Mt Erebus Saddle core, stable isotope ratios and soluble chemistry measurements were available for annual layer counting. As $\delta^{18}\text{O}$ and δD are controlled by site temperature (Section 2.5.1), it is assumed that values peak in summer (January 1st) and trough in winter. Dating of the record from the 2 m snow pit from Mt Erebus Saddle (Section 3.4) was conducted by counting peaks in $\delta^{18}\text{O}$ and the $\delta^{18}\text{O}$ record of the ice core was ‘wiggle-matched’ to it (Fig. 5.1). The derived isotopic parameter d-excess also exhibits an annual cycle with summer maxima in the Mt Erebus Saddle ice core record. In addition, the NO_3^- record was useful for annual layer counting because peaks regularly occurred in winter to spring (Fig. 5.2). This signal is preliminarily interpreted as originating from NO_3^- production in stratospheric clouds [Michalski *et al.*, 2005].

Figure 5.1: $\delta^{18}\text{O}$ records from the Mt Erebus Saddle ice core (drilled summer 2006/07) and snow pit (sampled in 2004/05) on same age scale.

Figure 5.2: $\delta^{18}\text{O}$ and NO_3^- profiles of a selected ice core section which display summer $\delta^{18}\text{O}$ peaks and winter NO_3^- peaks.

As the isotope record extended deeper down the core, the identification of annual peaks in the $\delta^{18}\text{O}$ and δD records became more challenging. Diffusion of water molecules through the firn pore space, effectively smooths the annual $\delta^{18}\text{O}$ and δD

peaks and causing loss of amplitude with depth. This phenomenon is well documented in both Antarctic and Greenland ice cores [Jouzel *et al.*, 1989; Rasmussen *et al.*, 2006; Steen-Larsen *et al.*, 2011] and the diffusion coefficients of each of the isotopes involved have been calculated. The $\delta^{18}\text{O}$ and δD signals can therefore be deconvolved or back-diffused in order to reconstruct the original signal [Johnsen, 1977; Johnsen *et al.*, 2000]. Back-diffusion of the Mt Erebus Saddle stable isotopic record was performed to 108 m depth. A description of the method used and the back-diffused time series of $\delta^{18}\text{O}$ and δD are provided in Appendix VI. The back-diffused time series of $\delta^{18}\text{O}$ and δD display well-defined annual peaks of a larger amplitude than the raw data. Therefore, a combination of these back-diffused time series and raw d-excess data was used to pick annual layers in the ice core to 108 m depth (Fig. 5.3).

Figure 5.3: Stable isotope data for 50-60 m section of the Mt Erebus Saddle core. Both the raw δD data (light green) and back-diffused δD record (dark green) are displayed. Annual layers were identified at peaks in the back-diffused δD record and corresponding peaks in the raw d-excess record (brown) were also identified to ensure peaks in the back-diffused δD record were not artifacts of processing.

Due to time constraints back-diffused stable isotopic series were not available for annual layer counting between 108 and 120 m depth. Therefore, in order to date this section, a polynomial fit applied to the age model developed by annual layer counting was extrapolated to 120 m.

5.2 Bomb tritium peak

Thermonuclear atmospheric bomb testing in the 1950s and 1960s emitted large quantities of short-lived radionuclides into Earth's atmosphere, including the radioactive hydrogen isotope, tritium ^3H . ^3H was deposited worldwide and a peak in tritium levels characterises the 1964-1969 time period in Antarctic ice cores, providing a useful age marker [Oerter *et al.*, 1999].

After the development of an initial age model via annual counting, determination of tritium contents of selected samples allowed independent verification of the annual layer counting method. Samples were taken from six sections of ice core from depths hypothesized to span the time characterised by the ^3H bomb peak. Tritium levels in Antarctic ice usually display a seasonal cycle that peaks in the austral winter (June to August) due to the incursion of stratospheric air masses [Jouzel *et al.*, 1979]. Given this, each sample was taken over a depth range intended to include all four seasons of the year to remove seasonal bias. Direct measurement of ^3H content was conducted at the GNS Science Tritium and Water Dating Laboratory, Lower Hutt, New Zealand by ultra-low level liquid scintillation spectrometry (QuantulusTM) in a monitored tritium-free environment [Morgenstern and Taylor, 2009]. The results of tritium analysis display a clear ^3H peak (Fig. 5.4) which coincides with the ^3H peak measured in Antarctic and New Zealand precipitation. This validates the strategy of annual layer counting and provides an age tie point for the ice core age model.

Figure 5.4: Tritium contents of six Mt Erebus Saddle ice core samples analysed (black circles) plotted with tritium contents of precipitation from the Ross Ice Shelf, Halley Bay on the Antarctic Peninsula, and Kaitoke, New Zealand, decay-corrected to December 2006 (*U. Morgenstern, GNS Science, Personal communication*). One tritium unit (TU) is defined as one atom of tritium per 10^{18} atoms of hydrogen, equivalent to 0.118 becquerels (Bq) per litre of water. Error bars are 1σ . Raw data are provided in Appendix VII.

5.3 Volcanic eruption markers

The soluble chemistry of ice cores from Antarctica and Greenland can record the occurrence of historic volcanic eruptions which ejected large volumes of fine ash and gas into the stratosphere, providing useful age markers [e.g. *Traufetter et al.*, 2004]. Sulphur dioxide that is emitted is oxidized to sulphate [*Robock*, 2000] and large amplitude peaks in ice core nssSO_4^{2-} (Section 2.5.2) are therefore typically identified as volcanic eruption markers. However, for the Mt Erebus Saddle ice core, positive identification of nssSO_4^{2-} deposition from volcanic sources is difficult. Mt Erebus Saddle is located within 15 km of seasonally open water causing the nssSO_4^{2-} signal to

be dominated by biogenic nssSO_4^{2-} . As a result, the nssSO_4^{2-} record does not exhibit isolated large amplitude peaks that can be attributed to volcanic eruptions (Fig. 5.5). This problem has been encountered in studies of other near-coastal ice cores, notably Siple Dome [Dixon *et al.*, 2004].

Figure 5.5: The nssSO_4^{2-} concentration record and concentration ratios of Pb, Bi and Tl to Al for the period 1800 to 2007 AD (65.5 m depth to surface). The pale green bars indicate positively identified volcanic eruptions: 1) 1809 AD $\pm$ 2 yr unknown eruption [Traufetter *et al.*, 2004], VEI (volcanic explosivity index) undefined, deposition year 1807 AD; 2) Tambora, Indonesia, VEI 7, eruption year 1815 AD [Simkin and Siebert, 1994]. The grey bar indicates a further possible volcanic eruption: 3) Coseguina, Nicaragua, VEI 5, eruption year 1835 AD [Simkin and Siebert, 1994].

Volcanoes may also emit heavy, volatile trace elements, such as Pb, Tl and Bi, in the vapour phase [Hinkley *et al.*, 1994]. Concentrations of Bi [Kaspari *et al.*, 2007] and Tl [Kellerhals *et al.*, 2010] enriched relative to terrestrial tracers in ice core samples have previously been used as indicators of stratospheric eruptions. Pb, Bi and Tl

concentrations in the Mt Erebus Saddle ice core were determined by ICP-MS and are plotted in Figure 5.5 adjacent to the nssSO_4^{2-} record for comparison. Between 60.52 and 61.14 m depth, concentrations of Pb, Bi and Tl are all strongly enriched relative to terrestrial element concentrations in at least 8 consecutive samples (Fig. 5.5, number 2). The annual layer count identifies this peak as deposition from the eruption of Mt Tambora of April 1815 AD. The deposition peak begins in mid-1816 AD, a similar timing to nssSO_4^{2-} deposition from the eruption detected in other Antarctic ice cores [Dixon *et al.*, 2004; Palmer *et al.*, 2001; Stenni *et al.*, 2002; Traufetter *et al.*, 2004]. Furthermore, if this peak is tied to the Tambora eruption then the timing of another Pb, Bi and Tl peak (Fig. 5.5, number 1) coincides with the 1809 ± 2 AD eruption of an unknown volcano, which is detected in the nssSO_4^{2-} record of several Antarctic ice cores [Dixon *et al.*, 2004; Palmer *et al.*, 2001; Stenni *et al.*, 2002; Traufetter *et al.*, 2004]. The attribution of another trace element peak (Fig. 5.5 number 3) to the eruption of Coseguina is more uncertain because Pb, Bi and Tl do not show the same enrichment pattern as each other and fewer samples are affected. This makes it less certain that the enrichments observed are due to volcanic activity. For this reason, this trace element peak is not used as a tie point in the ice core age model.

A detailed study of Pb isotopes and Bi and Pb concentrations across the nssSO_4^{2-} peak attributed to Tambora in the Law Dome ice core found that although Pb and Bi were enriched relative to the terrestrial reference element across the nssSO_4^{2-} peak, the Pb isotopic signatures measured were closer to that of Mt Erebus rather an Indonesian Arc volcano such as Tambora [Vallelonga *et al.*, 2003]. As Mt Erebus Saddle is located adjacent to Mt Erebus it is plausible that the trace element record of the Mt Erebus Saddle ice core may record the eruption history of Mt Erebus rather than that of global-scale stratospheric eruptions. In order to test this hypothesis, trace element ratios measured across the suspected volcanic Pb, Tl and Bi peaks were compared to trace element ratios measured in the plume of Mt Erebus (Fig. 5.6). None of the trace element ratios exhibit any marked deviation from the median value of the ice core record during the proposed 1809 and Tambora eruptions. The only possible exception is Cs/V but this deviates away from the Erebus plume value. This lends support to attribution of the Bi, Pb and Tl peaks at 63.2 m and 60.8 m to the 1809 eruption and

Tambora respectively, and as a result, these peaks are used as age tie points in the age model. The most likely reason for the negligible contribution to the ice core trace element budget from Mt Erebus is the prevalence of southerly or northerly winds, which have been observed to transport the Erebus plume at altitudes >3000 m for several km distance away from the crater [Oppenheimer *et al.*, 2010]. Only one 2 mm thick tephra layer was observed in the 120 m of ice core at 90.2 m depth (1666 AD).

Figure 5.6: Selected trace element ratio records for the time period including the proposed 1809 AD and Tambora eruption markers in Bi, Pb and Ti. The trace element ratios of the Mt Erebus plume are plotted where available [Zreda-Gostynska *et al.*, 1997] and the median values for the entire Mt Erebus Saddle record are shown. Breaks in the record occur where the concentration of an element is below the ICP-MS detection limit.

5.4 Density and accumulation rate

Density is an important parameter measured in ice cores because it allows sample depth to be related to snow accumulation. The density of each metre-length core section was calculated by assuming a core radius of 5 cm and a core length of 100 cm according to the equation:

$$\text{Density (g cm}^{-3}\text{)} = \text{mass of core section (g)} / (\text{core radius (cm)}^2 * \pi * \text{core length (cm)})$$

Figure 5.7: Density profile of the Mt Erebus Saddle ice core. Grey bar indicates the density range of the firn-ice transition (0.81-0.84 g cm⁻³), as defined by *Bender et al.* [1997]. The apparent decrease in density after 120 m depth is the result of poor core quality which reduces the actual core volume. Data are provided in Appendix VIII.

Density increases with depth, reflecting the compaction of snow into firn and then into ice (Fig. 5.7). The firn-ice transition, the depth at which air bubbles are closed off to the atmosphere, is located around 60-67 m depth.

Figure 5.8: Annual accumulation rates of the Mt Erebus Saddle ice core (grey line) between 1950 and 2006 AD. Thick black line is the 5-year moving average.

Density is used to calculate accumulation rates in $\text{m (H}_2\text{O equivalent) yr}^{-1}$ which allows accumulation rates from sections of core with different densities to be compared. A 1 m depth section of 10 cm diameter ice core with a density of 0.42 g cm^{-3} is equivalent to a 10 cm diameter cylinder of water that has a depth of 0.42 m. The annual accumulation rates calculated for 1950 to 2006 AD are displayed in Figure 5.8. The density profile and accumulation rate are parameters that must be included in the back-diffusion model (Appendix VI) and glacial flow model (Appendix V) used to model the age-depth profile of the core. The annual accumulation profile prior to 1950 AD

has not yet been established as the layer thickness needs to be corrected for layer thinning caused by ice flow.

Figure 5.9: Relationship between annual layer thickness and core depth for the age models produced by annual layer counting and the glacial flow model.

5.5 Assessment of dating error

A total of 561 annual layers are identified in the 120 m of core analysed. The incremental error on the dating of individual years or the duration of discrete time periods is ± 1 yr between the surface and 61.1 m (1816 AD), the depth of the Mt Tambora eruption marker. The cumulative dating error, which is the difference between the age of the reference marker and the initial age indicated by the annual layer count is ± 1 yr at 1964 AD (^3H peak) and ± 9 yr at 61.1 m (Mt Tambora). The dating uncertainty on the record below 61.1 m depth is difficult to constrain because no further age reference markers are identifiable.

A glacial flow model, developed by *Dansgaard and Johnsen* [1969], was used to model the age of the ice core as a function of depth (Appendix V). Outputs from the model are used in the back-diffusion of stable isotopic data (Appendix VI) so the flow model and the annual layer count are not independent assessments of the age-depth evolution. However, it is encouraging that the age model produced by annual layer counting shows excellent agreement with the glacial flow model (Fig. 5.10).

Figure 5.10: Age-depth relationship of the Mt Erebus Saddle ice core age model compared to the glacial flow model output. Age tie points used in the development of the age model are shown (dark grey bars). The section of core below 108 m depth (pale grey shading) was dated by extrapolation of the age model.

Chapter 6: Experimental investigation of the effects of mineral dust on the reproducibility and accuracy of ice core trace element analyses

This chapter constitutes a paper accepted for publication in Chemical Geology (Section 1.6). Supplementary data tables are located in Appendix IX.

Abstract

Determination of trace element concentrations by inductively coupled plasma mass spectrometry (ICP-MS) can yield valuable information about paleoclimate from ice core records. Typically, ICP-MS analyses are performed on melted and acidified ice core samples which contain particulate material i.e., mineral dust. This particulate material is usually enriched in trace elements relative to ice core samples. Consequently, it is important to constrain the effect of acidification on mineral dust present in ice core samples and to assess the contribution of dust leaching to the trace element budget of ice cores.

We have conducted a systematic experimental investigation designed to replicate the conditions of conventional ice core trace element analyses. Powdered rock standards of various lithologies were leached in 1 wt.% HNO₃ and the leachates were sampled at regular time intervals. Oxides and sheet silicate minerals, in the ferromanganese nodule (Nod-P-1) and granite (JG-2) leachates respectively, released available trace elements into solution relatively quickly; trace element recovery reached 57% for Mg and 42% for Mn in the granite leachate and recoveries between 60 and 80% were reached for most elements in the ferromanganese nodule leachate after only 12 hr of leaching. In contrast, mafic minerals in the basalt (BHVO-2) and dolerite (W-2) released trace elements slowly, achieving recoveries of < 20% for elements from Li to Mn after 12 hr of leaching. The mafic minerals continued to release trace elements into solution over several weeks causing Al and Ti concentration increases > 4000%.

These results demonstrate that acidification of ice core samples containing mineral dust will cause time- and mineral-dependent leaching of trace elements. Leaching behaviour of trace elements remained constant with varying mineral dust concentration but freezing pre-acidified samples was found to promote leaching of some trace elements. Ideally, all ice core samples would be fully digested or filtered to eliminate the error introduced by partial dissolution of dust but this is time-consuming and impractical. We therefore recommend acidifying samples for as long as practical to reach a maximum leachable concentration. For datasets obtained by conventional methods, Al is identified as the most suitable element to use as a terrestrial tracer because it is leached to a uniform extent across all lithologies. Fundamental flaws are identified in the calculation of crustal enrichment factors which are likely to cause some elements to appear enriched as a result of incongruent leaching. Ratios of trace elements, in particular rare earth elements (REEs), leached from mineral dust will not reflect those of the dust and are not suitable as tracers of dust provenance.

6.1 Introduction

Ice cores provide continuous, high-resolution records of past atmospheric and environmental conditions [e.g., *Fischer et al.*, 2007]. Increasingly, conventional stable isotope and major ion analyses of ice cores are being complimented by determination of trace elements by inductively coupled plasma mass spectrometry (ICP-MS) [*Barbante et al.*, 1997; *Gabrielli et al.*, 2006; *Planchon et al.*, 2001; *Purdie et al.*, 2010]. The typical method of ICP-MS analysis involves analysing melted, acidified, ice core samples that have not been filtered or centrifuged to remove particulates [e.g. *Barbante et al.*, 1997].

Sample acidification is a prerequisite for ICP-MS analysis of solutions but when particulates are present in the sample solution, acidification can cause particulate dissolution. The principal inorganic constituents of ice core samples are marine salts, and mineral dusts and whilst marine salts are readily soluble, mineral dusts are relatively insoluble. However, once the sample is acidified, typically to 1 wt.% HNO₃, trace elements can be leached, at least partially, from the mineral dust particles into solution. ICP-MS determinations of trace elements in ice core samples therefore do not solely measure the soluble chemical constituents but also an additional component resulting from the partial dissolution of mineral dust.

This has implications for understanding the trace element budget of ice cores because the contribution of mineral dust leaching to measured trace element concentrations in ice core samples has not been quantified previously and very little is known about how the leaching process varies for different trace elements, minerals or lithologies [*Snäll and Liljefors*, 2000]. Silicate minerals such as feldspars, clays and pyroxenes, which are commonly found in ice cores [*Ayling and McGowan*, 2006; *Gaudichet et al.*, 1988], will only undergo partial dissolution because silicate mineral lattices can withstand 1 wt.% HNO₃ solutions [*Günzler and Williams*, 2001]. Therefore, interpretation of ICP-MS data would be aided by an understanding of incongruent leaching i.e., which elements are leached in preference to others and whether the pattern is consistent between dust with different mineralogies.

There are several further factors which may affect the extent and rate of mineral dust dissolution in an acidified ice core sample, thereby introducing uncertainty concerning the reproducibility and accuracy of trace element concentrations determined by ICP-MS. The most important of these factors is the length of time that samples are acidified prior to analysis. Previous ICP-MS analysis of snow pit samples has shown that replicate analyses of the same sample measured at different time intervals can lead to trace element concentration increases of greater than 100% [Bull, 2009].

A further source of uncertainty in ice core trace element determinations lies in the uptake and incomplete ionisation of dust particles from within unfiltered ice core samples [Bull, 2009; Vallelonga *et al.*, 2004]. The extent to which this occurs and its effect on signal intensity [Hobbs and Olesik, 1993] requires further investigation that is beyond the scope of this paper.

This study presents a systematic experimental investigation into the influence of partial dissolution of mineral dust particles on the reproducibility of trace element determinations in ice core samples. Leaching experiments were carried out on geochemically well-characterised, powdered international rock standards in 1 wt.% HNO₃ to examine how trace element measurements vary depending on the length of the acidification time, whether samples were frozen after acidification or not and variable dust lithologies and concentrations. These findings allow us make several recommendations for future ice core ICP-MS trace element studies and interpretation of ice core trace element data.

6.2 ICP-MS trace element analysis of ice cores

The length of time that ice core samples are acidified prior to analysis varies widely between published studies of conventional ICP-MS trace element analyses (Table 6.1). It is typically 24 hr, but in many cases the length of time is not stated by the authors. The effects that resulting variable levels of mineral dust dissolution may have on the reproducibility of ICP-MS measurements ultimately limits the comparability of trace element records from different ice cores. Even if one specific acidification time is chosen, implemented and reported, the nature of ICP-MS analysis requires samples to be analysed in runs that can be > 12 hr in length, causing the first sample to have experienced a considerably shorter acidification time than the final sample. An acidification time of > 3 months was adopted by *Townsend and Edwards* [1998] because unpublished tests on ice core samples found the maximum leachable concentration of Fe was reached at this time, allowing all samples measured to be free of time-dependent leaching effects.

Trace element concentrations in ice cores can also be determined using coupled ice core melter and ICP-MS analysis systems where acidification occurs directly prior to analysis [*Knusel et al.*, 2003; *McConnell et al.*, 2002]. Many lithophile elements (e.g. Al and REEs) record significantly lower concentrations when analysed in this way compared to conventional methods [*Knusel et al.*, 2003]. This is presumably because any mineral dust present in the sample is only exposed to acid for a short length of time, thereby minimising trace element leaching.

The type and molarity of acid used to acidify samples is also likely to affect the rate of which leaching occurs and also varies between published studies (Table 6.1). In some cases, samples from the same location were acidified to different strengths [*Krachler et al.*, 2004; *Krachler et al.*, 2005; *Tao et al.*, 2001], creating a source of uncertainty for comparison of ice core trace element records.

Table 6.1: Summary of sample preparation and storage procedures utilised in previously published ice core ICP-MS trace element studies.

Reference	Sampling location	Targeted species	Refrozen after acid addition?	Acidification used	Acidification time
<i>Barbante et al.</i> [1997]	Greenland and Victoria Land, Law Dome;	Heavy metals	Y	0.34 wt.% HNO ₃	Not stated
<i>Townsend and Edwards</i> [1998]		Trace elements	N	0.1 M HCl ^a	> 3 months
<i>Barbante et al.</i> [1999] ^b	European Alps	Trace elements	N	0.34 wt.% HNO ₃	Measured 'just after' acidification
<i>Planchon et al.</i> [2001] ^b	Coats Land, Antarctica	Heavy metals	Y	1 wt.% HNO ₃	Not stated
<i>Tao et al.</i> [2001]	Devon Ice Cap, Canadian Arctic	Heavy metals	Y	pH 1.6 HNO ₃	Not stated
<i>Krachler et al.</i> [2004]	Devon Ice Cap, Canadian Arctic	Trace elements	Y	pH 1.2 HNO ₃	Not stated
<i>Gabrielli et al.</i> [2005a]	EPICA Dome C, Antarctica	Trace elements	Y	pH 1 HNO ₃	Not stated
<i>Gabrielli et al.</i> [2005b]	Vostok, Antarctica	Trace elements	N	pH 1 HNO ₃	> 24 hr
<i>Krachler et al.</i> [2005]	Devon Ice Cap, Canadian Arctic	Trace elements	Y	0.5 wt.% HNO ₃	~ 24 hr
<i>Gabrielli et al.</i> [2006]	European Alps	Trace elements	Not stated	2 wt.% HNO ₃	Not stated
<i>Gaspari et al.</i> [2006] ^b	EPICA Dome C, Antarctica	Fe	N	pH 1 HNO ₃	> 24 hr
<i>Osterberg et al.</i> [2006] ^b	Mt Logan, Yukon, Canada	Trace elements	Y	1 wt.% HNO ₃	24 hr before freezing.
<i>Marteel et al.</i> [2008]	EPICA Dome C, Antarctica	Heavy metals	Y	1 wt.% HNO ₃	Not stated
<i>Marteel et al.</i> [2009]	EPICA Dome C, Antarctica	Trace elements	Y	Not stated	Not stated
<i>Kaspari et al.</i> [2009]	Mt Everest, Himalayas	Bi, U, Cs, S, Ca	Y	1 wt.% HNO ₃	7 d before freezing; time after defrosting not stated
<i>Gabrielli et al.</i> [2010]	EPICA Dome C, Antarctica	REEs	Not stated	pH 1 HNO ₃	Not stated
<i>Purdie et al.</i> [2010]	Southern Alps,	Trace elements	N	1 wt.% HNO ₃	Not stated

^a Samples were also measured by flow injection analysis, hence HCl use. ^b Method was adopted in subsequent studies.

The studies listed in Table 6.1 also vary widely in their approach to sample storage. It is generally accepted that ice core samples should be stored frozen prior to analysis, however samples were acidified before being refrozen in several studies. This could cause increased leaching of the mineral dust because when freezing takes place, dense acid sinks to the bottom of the vial where mineral dust is also located, causing the mineral dust to be exposed to more concentrated acid whilst freezing takes place.

6.3 Experiment design

6.3.1 Overview

In order to replicate the partial dissolution of mineral dust in acidified ice core samples, small amounts of powdered international rock standards were leached in 1 wt.% HNO₃. Leachates were removed at selected times, and are considered to be analogous to ice core samples containing mineral dust which are acidified for different lengths of time prior to analysis. The use of rock standards for which bulk trace element concentrations are well characterised facilitates accurate measurement of the degree to which elements are leached from these standards as analogues of mineral dust.

Two experiments were conducted. The first tested how leachate composition changed with acidification time, dust lithology (rock standard type) and dust concentration. The second examined whether freezing samples after acidification affected leachate compositions.

6.3.2 Rock standards

The following four rock standards were selected to compare the leaching behaviour of different lithologies: BHVO-2 (Hawaiian Basalt, USGS); W-2 (Centerville Diabase, USGS); Nod-P-1 (Manganese Nodule, USGS) and JG-2 (Granite, Geological Survey of Japan). BHVO-2 is basalt comprised of clinopyroxene and plagioclase feldspar with minor amounts of magnetite. W-2 is a diabase or a dolerite, comprised of plagioclase feldspar, clinopyroxene with minor amounts of muscovite mica, quartz, and opaque minerals (S. A. Wilson, USGS, Personal communication). JG-2 is a biotite-rich granite [Ando *et al.*, 1989] and Nod-P-1 is a Pacific Ocean ferromanganese nodule which is ~ 70% Fe-Mn oxyhydroxide mineral phases and 30% quartz and plagioclase feldspar (S. A. Wilson, USGS, Personal communication).

Figure 6.1: A) Grain size distributions of BHVO-2, JG-2, W-2 and Nod-P-1 measured by laser particle counter. B) Horizontal bars indicate grain size ranges recorded at various Antarctic sites:
a) EPICA Dome C [Delmonte *et al.*, 2004] is located in East Antarctica, **b) James Ross Island** [McConnell *et al.*, 2007] is near the Antarctic Peninsula, **c) Windless Bight** [Dunbar *et al.*, 2009] is directly south of Ross Island, **d) Victoria Lower Glacier** and **e) Wilson Piedmont Glacier** [Ayling and McGowan, 2006] are both in the McMurdo Dry Valleys.

These rock standards encompass a range of textures and mineralogies and contain minerals commonly found in ice core dust [Ayling and McGowan, 2006; Gaudichet *et al.*, 1988]. The rock standard lithologies are also comparable to those exposed in the McMurdo Dry Valleys, Antarctica, where the New Zealand contribution to the International Trans-Antarctic Scientific Expedition focuses its snow pit and ice core sampling [Mayewski *et al.*, 2005]. Nod-P-1 was selected because its predominantly Fe-Mn oxyhydroxide mineralogy is similar to Fe-Mn oxides coatings on many aeolian particles [Post, 1999] and to desert varnish [Bauman, 1976], which coats the surface of

a significant proportion of exposed rocks in the McMurdo Dry Valleys region [Bockheim, 2010].

The grain size distributions of the four rock standards, measured by laser particle counter (Beckman Coulter LS13 320), encompass the grain size range between $<1\ \mu\text{m}$ to $>80\ \mu\text{m}$ measured on ice core dust material (Fig. 6.1). As the grain size distributions vary between the four rock standards, the influence of grain size on the leaching process [Snäll and Liljefors, 2000] is also considered in the interpretation of our results.

6.3.3 Dust concentrations

Construction of a representative experiment necessitated that the powdered rock standards were leached at dust concentrations equivalent to those reported in ice core samples. The dust concentration of ice cores varies widely depending on geographical location and proximity to local dust sources. Ice cores from the interior of the Antarctic continent have dust concentrations as low as 0.015 ppm in the Holocene and 0.65 ppm in the last glacial period [Delmonte *et al.*, 2004]. Where sources of aeolian dust are proximal, such as at ice core sites adjacent to the McMurdo Dry Valleys, Antarctica, maximum dust concentrations of between 470 ppm and 1900 ppm have been recorded [Ayling and McGowan, 2006]. Dust concentrations in South American ice cores range from 0.16 ppm [Thompson *et al.*, 1995] to 8.5 ppm [Ramirez *et al.*, 2003] and values as high as 243 ppm have been reported in northern China [Wu *et al.*, 2009]. A dust concentration of 10 ppm, equivalent to that of Greenland ice cores from the Last Glacial Maximum [Ruth *et al.*, 2003] was selected for this investigation because this mass of rock standard (5 mg) could be weighed precisely.

To test the effect of varying the starting dust concentration on leachate composition, rock standard W-2 was also leached at concentrations of 50 ppm and 500 ppm. W-2 was selected because it has a broad grain size distribution (Fig. 6.1) and, unlike Nod-P-1, has a predominantly silicate mineralogy.

6.3.4 *Leachate sampling*

Each of the four rock standards at dust concentrations of 10 ppm and the two additional dust concentrations of W-2 were leached with 1 wt.% HNO₃ (Seastar) in pre-cleaned Teflon (PFA) bottles in a temperature-controlled, Class 100 clean room. The required mass of each rock standard was weighed precisely using an ultra micro-balance (Mettler Toledo UMX2) and carefully added to each bottle. The actual dust concentration in the experiments was accurate to $\pm 1\%$. The time at which the weighed rock powder was added to each bottle was recorded and each bottle was immediately shaken for 30 s to mix the rock standard and acid.

Samples of the leachate were extracted at the following times after addition of the rock standard: 10 min, 1 hr, 2 hr, 4 hr, 8 hr, 12 hr, 24 hr, 36 hr, 48 hr, 72 hr, 3 d, 5 d, and 7 d, followed by weekly to fortnightly sampling. Ten minutes prior to sampling, each bottle was shaken for 10 s to redistribute elements within solution. 7 mL of leachate was then pipetted from the top of each bottle into acid-cleaned vials. These leachate samples were then centrifuged for 5 min at 1000 rpm to remove any remaining particles of rock standard and 5 mL of supernatant was pipetted off each into further acid-cleaned vials. After sampling, 7 mL of 1 wt.% HNO₃ was added to each bottle to replace the volume of leachate extracted, thus keeping the dust concentration effectively constant. All leachate samples were stored at room temperature before analysis to avoid any effects of freezing. Duplicate leachate samples taken at several sampling times showed a median concentration difference of 1.4% across all elements and confirm the reproducibility of the leachate sampling method (Appendix IX, Tables A18 to A22).

6.3.5 *Freezing test*

To quantify the effect of freezing pre-acidified samples on leachate composition, small amounts of rock standard powder were frozen in either 1 wt.% HNO₃ or ultra-pure water (> 18.2 MΩ). Solutions were frozen in acid-cleaned vials and stored upright to replicate the conditions in which ice core samples are normally refrozen. 0.5 mg of BHVO-2 was added to three vials containing 8 mL of 1 wt.% HNO₃ and three vials containing 8 mL of ultra-pure water. This experiment was repeated for JG-2. All 12 vials were then shaken and frozen for at least 48 hr. Once thawed, the ultra-pure water samples were acidified to 1 wt.% HNO₃ and all the vials were shaken to homogenise the sample again. Simultaneously, six fresh vials were made up containing the same concentration of BHVO-2 (3 vials) or JG-2 (3 vials) in 1 wt.% HNO₃. These vials acted as control samples and provided a means of testing whether the physical process of freezing itself had any effect on the concentrations leached from the mineral dust. The masses of both of the rock standard and the solution in each of the vials were weighed precisely and dust concentrations in the 18 sample vials ranged between 62 ppm and 65 ppm. All samples were allowed to undergo dissolution for 12 hr at room temperature and then centrifuged and sampled as previously described (Section 6.3.4). Several additional vials containing only ultra-pure water or 1 wt.% HNO₃ were frozen and sampled in the same manner to act as procedural blanks (Appendix IX, Table A26).

6.4 Analytical procedures

6.4.1 Hardware and operating conditions

The leachate samples were analysed for concentrations of 29 elements (Li, Na, Mg, Al, Ca, Ti, V, Cr, Mn, Cu, Zn, As, Rb, Sr, Y, Zr, Cs, Ba, La, Ce, Pr, Gd, Er, Yb, Tl, Pb, Bi, Th, U) by ICP-MS (Agilent 7500cs Series). An ASX-520 micro-volume autosampler linked to the ICP-MS was used to introduce samples into the Teflon (PFA) nebuliser (0.1 mL/min flow rate) via a peristaltic pump. The ICP-MS operating conditions are given in Table 6.2. Tuning parameters were optimised to obtain high sensitivity across the mass range. The mass ratio $^{156}\text{CeO}/^{140}\text{Ce}$ was monitored and tuning parameters adjusted to maintain a level of cerium oxide formation below 2%. Prior to analysis, the Ni sampling and skimmer cones were cleaned and the sample introduction system was aspirated with 5 wt.% HNO_3 for 1 hr to reduce any possible memory effects from previous sample media.

Table 6.2: ICP-MS operating conditions and data acquisition parameters.

Parameter	Setting
Forward power	1500 W
RF matching	1.75-1.84 V
Carrier gas	1.04-1.09 L.min ⁻¹
Makeup gas	0 L.min ⁻¹
Nebulizer pump	0.11-0.14 rps
Spray chamber temperature	2 °C
Sampling depth	7 mm
Torch position	Optimised daily
Ion lenses voltages	Optimised daily
Uptake and stabilisation time	50 s, 60 s
Wash time	10 s H ₂ O, 200 s 5 wt.% HNO ₃ , 220 s 1 wt.% HNO ₃ , total 430 s
Integration time per mass	0.15 s
No. of runs and scan passes	3 x 23

6.4.2 Calibration and blank correction

Dilutions of fully-digested BHVO-2, W-2, Nod-P-1 and JG-2 rock standards were run as calibration standards during ICP-MS analysis of the leachate samples. 50 mg of each of the four rock standards were digested in ca. 2 mL 29M HF (Seastar) and ca. 0.5 mL 16M HNO₃ (Seastar) in pre-cleaned Savillex beakers heated to 120°C on a hotplate for 4 d. The solution was then evaporated and the remaining sample was twice refluxed in 16M HNO₃, followed by reflux in 6M HCl (Seastar). After checking that the rock standard powder had completely digested, the sample was dried down and brought back into solution with 1M HNO₃. Gravimetric dilutions of the fully-digested rock standard solutions were made prior to each ICP-MS analytical session to produce calibration standards close to the expected leachate trace element concentrations (Table 6.3). Furthermore, the use of fully-digested rock standards as calibration standards enabled the accurate assessment of the proportion of elements leached from the rock standard dust into the leachate.

Two W-2 calibration standards of different dilutions (Table 6.3) were made to bracket the concentration range of samples from the 10 ppm, 50 ppm and 500 ppm dust concentration tests. Samples of the leachate from the W-2 500 ppm dust concentration test were diluted by a factor of 10 before analysis.

1 wt.% HNO₃ blanks were run every 6-10 samples. Counts recorded on the blanks were subtracted from those measured on samples and standards to correct for background levels. Detection limits, defined as 3 σ of blank measurements, are presented in Table 6.4.

Table 6.3: Element concentrations (ppm) for BHVO-2, W-2, Nod-P-1 and JG-2 and dilution factors used to make up calibration standards from fully-digested rock standard powders.

Element	BHVO-2	W-2	Nod-P-1	JG-2
Li	4.8 ± 0.2	9.3 ± 0.4	140 ± 1	41.1 ± 2.55 ^a
Na	16471 ± 594	16323 ± 275	17100 ± 240	26200 ± 3
Mg	43380 ± 720	38220 ± 348	20300 ± 700	480 ± 208 ^a
Al	71470 ± 1059	81794 ± 847	24600 ± 1000	65400 ± 1191 ^a
Ca	76000 ± 1333	72400 ± 520	22400 ± 100	4900 ± 30
Ti	16300 ± 2000	6353 ± 60	2720 ± 40	240 ± 60 ^a
V	317 ± 11	268 ± 10	510 ± 3	2.86 ± 0.0778 ^a
Cr	280 ± 19	93 ± 6	13.3 ± 0.01	7.1 ± 2.31 ^a
Mn	1317 ± 39	1294 ± 31	296000 ± 13000	129 ± 45 ^a
Cu	127 ± 7	105 ± 3	11350 ± 212 ^a	0.53 ± 0.13 ^a
Zn	103 ± 6	77 ± 6	1808 ± 301 ^a	13.5 ± 1.56 ^a
As	nd	1.1 ± 0.1	88.5 ± 3.9	0.75 ± 0.03
Rb	9.11 ± 0.04	21 ± 1	660 ± 14.8 ^a	16.73 ± 1.009 ^a
Sr	396 ± 1	196 ± 5	24.1 ± 0.57 ^a	299.3 ± 7.869 ^a
Y	26 ± 2	22 ± 1	90.5 ± 0.707 ^a	88.6 ± 9.12 ^a
Zr	172 ± 11	92 ± 4	289 ± 12.7 ^a	109.9 ± 4.146 ^a
Cs	0.1 ± 0.01	0.92 ± 0.07	1.78 ± 0.035 ^a	7.4 ± 0.53 ^a
Ba	131 ± 1	172 ± 7	2572 ± 167.6 ^a	62.6 ± 7.22 ^a
La	15.2 ± 0.1	10.8 ± 0.5	108 ± 3.54 ^a	20.9 ± 2.41 ^a
Ce	37.5 ± 0.2	23.4 ± 0.7	317 ± 17 ^a	49.7 ± 3.65 ^a
Pr	5.35 ± 0.17	3 ± 0.1	32 ± 1.4 ^a	6.3 ± 0.26 ^a
Gd	6.24 ± 0.03	3.66 ± 0.12	31.1 ± 0.919 ^a	8.7 ± 1.1 ^a
Er	2.54 ± 0.01	2.22 ± 0.1	13.9 ± 0.389 ^a	7.13 ± 1.72 ^a
Yb	2 ± 0.01	2.05 ± 0.04	13.1 ± 0.283 ^a	8.79 ± 2.01 ^a
Tl	na	0.132 ± 0.002	178 ± 45.3 ^a	1.56 ± 5
Pb	1.6 ± 0.3	7.7 ± 0.6	494 ± 54.5 ^a	31.27 ± 1.704 ^a
Bi	nd	0.03 ±	5.8 ± 0.4	0.81 ± 0.31 ^a
Th	1.22 ± 0.06	2.17 ± 0.09	16.7 ± 0.07 ^a	30.58 ± 2.173 ^a
U	0.403 ± 0.001	0.51 ± 0.02	4.11 ± 0.148 ^a	11.44 ± 1.45 ^a
Dilution factor(s) of calibration standard(s)	x 682205	x 501957 x 98013	x 984011 x 1261230 ^b	x 948716

Data for BHVO-2 and W-2 are GeoREM preferred values ± 1 standard deviation (<http://georem.mpch-mainz.gwdg.de/> [Jochum *et al.*, 2005]). Data for Nod-P-1 and JG-2 are GeoREM published values ± 1 standard deviation.

na = data not available; nd = not detectable

^a Mean of GeoREM published values ± 1 standard deviation of GeoREM published values

^b Second dilution of Nod-P-1 (see Section 6.4.3)

6.4.3 Reproducibility and accuracy of data

Accuracy and precision of the ICP-MS trace element analyses of the leachate samples were assessed by calibrating the measurements on one fully-digested rock standard solution using another fully-digested rock standard solution, e.g., BHVO-2 measured

using JG-2 as calibration standard. As the Nod-P-1 standard is widely different to the other three in terms of its mineral assemblage and element concentrations, a second dilution (Nod-P-1') was calibrated using the original dilution of the Nod-P-1 fully-digested standard. Reproducibility and accuracy of the ICP-MS analyses are reported in Table 5.4. All error bars displayed on figures referred to in Sections 6.5.1, 6.5.2, 6.6.1 and 6.6.2 represent 2σ analytical precision.

Table 6.4: Accuracy, precision and detection limits for ICP-MS analyses of rock standards.

Element	Accuracy (% error)				Precision (2*RSD (%))				Detection limit (ppt)
Li	2.6	3.5	2.1	4.4	1.2	6.1	4.2	2.6	0.6
Na	2.2	3.3	1.0	2.5	2.0	1.5	2.9	2.1	763.0
Mg	0.8	56.0	1.6	1.5	1.4	6.9	4.0	0.8	49.1
Al	0.8	1.7	1.2	0.8	2.3	0.7	3.2	0.9	48.6
Ca	1.1	11.5	4.2	3.1	2.4	7.3	6.5	3.1	874.0
Ti	2.5	2.6	1.1	3.1	1.0	6.1	2.4	3.7	23.5
V	0.8	75.2	0.6	2.0	2.3	12.9	1.7	3.7	1.60
Cr	nd	nd	3.4	4.0	nd	nd	12.1	4.4	8.8
Mn	1.2	0.6	0.8	7.2	2.0	2.95	2.1	6.6	15.1
Cu	0.4	nd	0.4	12.2	1.0	nd	1.2	13.5	37.7
Zn	0.4	nd	0.8	2.0	0.8	nd	2.2	2.3	35.7
As	ndS	ndS	1.6	ndS	ndS	ndS	3.2	ndS	1.2
Rb	5.5	1.4	0.2	1.5	1.9	4.9	1.5	4.9	0.3
Sr	1.1	1.0	0.3	4.2	1.8	5.4	0.7	5.2	0.9
Y	1.4	9.1	0.7	1.7	2.6	4.3	1.3	5.2	0.1
Zr	1.9	34.2	2.0	3.5	1.9	5.9	4.9	5.0	1.0
Cs	1.4	0.4	2.8	9.0	2.1	31.0	6.6	6.7	0.1
Ba	0.8	1.4	0.8	2.6	2.2	3.0	1.4	3.8	3.3
La	1.8	5.9	1.1	0.0	2.3	2.1	2.1	3.9	0.1
Ce	0.8	2.8	0.7	2.1	1.7	1.8	1.1	2.9	0.2
Pr	1.2	0.5	0.4	2.5	1.3	3.4	1.1	3.1	0.1
Gd	2.4	5.9	1.4	5.0	2.3	2.9	1.4	2.2	0.6
Er	1.6	nm	1.4	4.5	3.3	nm	2.8	6.2	1.0
Yb	0.6	nm	1.5	4.2	2.0	nm	4.0	10.8	0.5
Tl	ndS	ndS	0.3	ndS	ndS	ndS	0.5	ndS	0.3
Pb	14.8	nd	1.0	12.6	3.8	nd	1.8	11.0	14.7
Bi	ndS	ndS	1.1	ndS	ndS	ndS	4.0	ndS	0.3
Th	1.0	7.0	0.8	4.7	2.7	6.1	2.0	6.5	0.2
U	4.8	17.9	1.9	6.4	5.8	7.7	3.7	7.0	0.2
Standard measured	BHVO-2	JG-2	Nod-P-1	W-2	BHVO-2	JG-2	Nod-P-1	W-2	Standard measured
Calibration standard	W-2	BHVO-2	Nod-P-1'	BHVO-2	W-2	BHVO-2	Nod-P-1'	BHVO-2	Calibration standard

RSD = relative standard deviation; ndS = not detectable/not certified in BHVO-2 standard; nd = below detection limit; nm = not measured

Nod-P-1' is a second dilution of the Nod-P-1 standard (see Section 6.4.3).

6.5 Results

6.5.1 *Effect of acidification time on trace element leachate concentration*

Similar trends in concentration increase over time were exhibited by many trace elements in the BHVO-2 and W-2 leachates (Fig. 6.2; Appendix IX, Tables A18 to A19). Large increases in leachate concentrations relative to the first sample, taken after 10 min of leaching, of >80% after 12 hr and >200% after 7 wk of leaching were recorded for elements from Li to Mn, Sr and Ba. The Al leachate concentration increased by 193% and 154% in BHVO-2 and W-2, respectively, over the first 12 hr of leaching and did not stop increasing after 12 weeks (Fig. 6.3). REE and Y concentration increases in both the BHVO-2 and W-2 leachates occurred during the first 2 hr of leaching but larger increases over time were measured in the BHVO-2 leachate (Fig. 6.2 and 6.3).

The JG-2 leachates showed different trends in trace element concentrations as compared to the other silicate rock standards (Fig. 6.2; Appendix IX, Table A21). Only Na, Al and As showed sustained increases in leachate concentration of a similar magnitude to those recorded in the BHVO-2 and W-2 leachates (Fig. 6.4). Aside from these elements, leachate concentration increases after 12 hr of leaching were generally below 50% and after 7 wk the concentration increase ranged from only 50% to 210%. The Mn concentration rose only slightly in the first 48 hr of the leaching test and then maintained a relatively constant leachate concentration over the longer-term, whereas the light REEs (La, Ce and Pr) showed a sustained increase in leachate concentration over the longer-term (Fig. 6.4).

In the Nod-P-1 leachates, Na, Li, Ca and Sr were at their highest concentrations after just 10 min of leaching and subsequent samples showed a slight (7 to 26%), gradual decrease in concentration over time rather than an increase (Fig. 6.5). All other elements, excepting Mn, showed a similar trend to Al which increased in concentration by 240% in the first 24 hr but then remained relatively constant over time (Figs. 6.2 and 6.5; Appendix IX, Table A21). Mn was the only element which continued to increase in concentration in the Nod-P-1 leachates over the entire sampling period.

Figure 6.2: Relative concentration increases of trace elements in the leachates of W-2, BHVO-2, JG-2 and Nod-P-1 at selected acidification times.

Figure 6.3: Concentrations of Al and La in BHVO-2 leachates plotted versus acidification time in hr (top panel) and weeks (bottom panel)

Figure 6.4: Concentrations of Al, Mn and La in JG-2 leachates plotted versus acidification time in hr (top panel) and weeks (bottom panel).

Figure 6.5: Concentrations of Na, Al and La in Nod-P-1 leachates plotted versus acidification time in hr (top panel) and weeks (bottom panel).

6.5.2 Variation in leaching characteristics between dust lithologies

The relative amounts of each element leached from the rock standard dust into the leachate solution varied between elements and between dust lithologies (Fig. 6.6). The recovery of each element by mass was calculated according to the following equation:

$$\% \text{ recovery of element E} = (\text{mass of E in leachate} / \text{mass of E in dust added}) * 100$$

BHVO-2 and W-2 showed some similar trends in element recovery, which contrast with those exhibited by JG-2 and Nod-P-1. After 12 hr of leaching, recovery of lighter elements from Li to Mn was consistently < 20% for both BHVO-2 and W-2, whereas for JG-2, recovery was 58% for Mg, 38% for Ti and 42% for Mn. Light REEs showed some of the highest recoveries (31 to 33%) in the BHVO-2 and W-2 leachates, whereas in the JG-2 leachate, recoveries of only 11 to 12% were reached. Additionally, Y, which displayed similar time-dependent leaching trends to the REEs, showed different recovery values. Y recovery was highest (52%) in the JG-2 leachate, which had the

lowest recovery of light REEs after 12 hr leaching, and Y recovery was lowest (12%) in the W-2 leachate, which exhibited relatively high recoveries of light REEs. Zr was the only element which had a consistently low recovery (~ 10%) across all four rock standards.

Recovery was higher for the majority of elements in the Nod-P-1 leachate compared to the silicate rock standards (Fig. 6.6). Typical recoveries ranged between 57% and 79% after 12 hr of leaching. However, Mn which is the most abundant element in Nod-P-1, showed a recovery of only 4% after 12 hr and 6% after 10 weeks (Appendix IX, Table A21).

Figure 6.6: Proportion of each element leached from BHVO-2, JG-2, W-2 and Nod-P-1 into leachate after 12 hr acidification, expressed as % recovery. Elements which recorded concentrations below the detection limit are assumed to have 0% recovery.

Figure 6.7: Linear relationship between dust (W-2) concentration (10, 50, 500 ppm) and concentrations of Sr and Ce measured in the leachates after 12 hr.

6.5.3 *Effect of dust concentration*

Results obtained by leaching W-2 at three different dust concentrations (10 ppm, 50 ppm and 500 ppm) demonstrate that a linear relationship exists between dust concentration and the leachate concentration of any element in the leachate (Appendix IX, Tables A19, A22, A23). Correlation coefficients ranging between 0.98 and 1.0 describe the linear relationship between dust concentration and leachate concentration of all the elements measured after 12 hr of leaching (Fig. 6.7). The leachate did not become oversaturated even when 500 ppm of dust was leached for more than 6 weeks. The % recovery of trace elements from the dust into the leachate was therefore consistent across all dust concentrations at any given acidification time.

6.5.4 *Effect of freezing*

Several elements (highlighted in Table 6.5) appear to have been more aggressively leached in the BHVO-2 or JG-2 mock ice core samples that were acidified to 1 wt.% HNO_3 prior to freezing compared to those which were acidified after freezing and thawing, and those which were not frozen prior to 12 hr of leaching in 1 wt.% HNO_3 . For those elements highlighted in Table 6.5, the 2σ of the leachate concentrations from acidified, frozen samples and the un-acidified, frozen samples do not overlap, which suggests that the two populations are different. This is illustrated in Figure 6.8

which shows that recovery of Ti and Zr was increased in both the BHVO-2 and JG-2 mock ice core samples that were acidified before freezing. The difference in recovery between the acidified, frozen and un-acidified, frozen samples is acknowledged to be subtle but respective concentration increases in BHVO-2 and JG-2 samples of 23% and 31% for Ti and 34% and 71% for Zr, are substantially higher than the limit of analytical precision (Table 6.4). Recovery was not significantly higher for any element in the samples that were frozen, un-acidified compared to those which were not frozen.

Table 6.5: Mean recovery (%) (n=3) of trace elements from BHVO-2 and JG-2 leached at a dust concentration of 63 ppm for 12 hr after either being frozen acidified, frozen un-acidified or not frozen. Grey shading and bold type indicates that the 2σ of the acidified and un-acidified frozen samples do not overlap. Leachate concentrations have been scaled to a dust concentration of 63 ppm across all samples. Raw data are given in Appendix IX (Tables A24 and A25).

	BHVO-2			JG-2		
	Acidified Frozen	Un-acidified Frozen	Not frozen	Acidified Frozen	Un-acidified Frozen	Not frozen
Li	4.9	5.2	5.4	50.6	38.6	44.0
Na	2.9	4.0	3.7	1.8	1.6	1.7
Mg	5.3	3.6	4.0	2.8	3.8	16.8
Al	2.5	2.6	2.9	4.0	3.1	3.3
Ca	2.5	2.6	2.8	9.3	11.0	14.6
Ti	0.6	0.5	0.6	45.6	34.8	44.5
V	0.6	0.5	0.6	66.9	61.2	61.0
Cr	1.3	1.1	1.2	nd	nd	nd
Mn	3.5	2.8	3.1	38.9	32.0	40.4
Cu	20.4	18.8	20.0	nd	nd	Nd
Rb	0.9	1.1	1.1	8.4	7.3	8.0
Sr	3.1	3.2	3.5	14.1	12.8	13.3
Y	20.4	20.3	21.7	67.9	52.9	56.3
Zr	1.6	1.2	1.1	2.0	1.2	1.1
Cs	nd	nd	nd	46.5	40.1	40.8
Ba	2.1	2.2	2.3	38.0	33.5	34.3
La	33.4	33.3	35.4	14.3	11.3	11.5
Ce	32.4	32.3	34.6	14.1	11.1	11.4
Pr	31.3	31.1	33.2	16.3	12.8	13.3
Gd	23.5	23.3	24.4	42.0	34.5	36.8
Er	19.5	19.4	20.5	43.3	33.1	34.5
Yb	17.9	17.8	18.8	56.9	44.6	47.4
Th	20.3	21.0	22.0	83.5	35.6	33.1
U	19.2	19.1	20.3	57.9	42.0	47.1

Figure 6.8: Recovery of Zr versus recovery of Ti for acid-leached JG-2 and BHVO-2 samples that were either acidified and frozen, un-acidified and frozen, or not frozen prior to 12 hr of acid-leaching at room temperature. Smaller symbols represent the 3 samples stored under each condition. Larger symbols represent the mean of 3 samples stored under each condition. Ellipses define 2σ about the mean of each population. Analytical errors are within the extent of the ellipses.

6.6 Discussion

6.6.1 *Implications for interpretation of trace element concentrations in ice core samples*

Trace element concentrations leached from mineral dust present in ice core samples will vary considerably (by more than an order of magnitude) depending on the length of acidification time prior to ICP-MS analysis. The rate of leaching differs widely between different elements in the same dust lithology and, in many cases, the same element leached from different lithologies (Fig. 6.2).

Leaching of trace elements from mineral dust is not only time-dependent but also dependent on the mineral constituents of the dust. The rock standards JG-2 (biotite granite) and W-2 (diabase/dolerite) have contrasting mineralogies and showed different patterns of trace element recovery or 'leachability' as a result. A major mineral constituent of JG-2 is biotite mica which is a sheet silicate, similar in structure to clay minerals common in ice cores [Gaudichet *et al.*, 1988]. K^+ ions bond the silicate sheets together and trace elements, particularly mono- and di-valent cations, can substitute for the K^+ ions [Deer *et al.*, 1966]. As the bonds holding the cations between the silicate sheets are relatively weak, trace elements were rapidly leached from the biotite mica of the JG-2 standard. The other dominant mineral constituent of JG-2 is quartz which contains very few trace element impurities and is unlikely to contribute to the leachate trace element budget. In contrast to JG-2, W-2 contains <1% muscovite mica and its mineralogy is dominated by plagioclase feldspar and clinopyroxene (S. A. Wilson, USGS, Personal communication). Trace element impurities are held relatively tightly within the complex silicate structures of these minerals [Deer *et al.*, 1966]. We interpret this contrast in mineralogy as the cause for the higher recovery values after 12 hr of leaching and the reduced rates of leachate concentration increase with acidification time in the JG-2 leachates compared to the W-2 leachates. Rock standards W-2 and JG-2 have very similar grain size distributions (Fig. 6.1) so the differences in recovery cannot be attributed to a grain size effect.

The BHVO-2 and W-2 leaching tests produced relatively similar trace element recovery profiles because both rock standards are mafic igneous rocks. The somewhat higher trace element recoveries of W-2 could be the result of the lower modal grain size and broader grain size distribution of W-2 compared to BHVO-2 (Fig. 6.1). An increased relative surface area on which leaching can act is likely to result in an increased recovery of trace elements [Snäll and Liljefors, 2000]. This suggests that the reproducibility of ICP-MS trace element concentrations of ice cores with very low dust concentrations, such as EPICA Dome C, will still be affected by mineral dust dissolution because the mean grain size is low (2 μm , Delmonte *et al.* [2004]) and provides a large relative surface area for leaching.

In contrast to silicate mineral lattices, which are relatively resistant to HNO_3 attack, bonds in oxyhydroxide minerals, like those predominant in Nod-P-1 (Fe-Mn nodule), are easily broken down by HNO_3 . This explains the high proportions of trace elements released rapidly into solution in the Nod-P-1 leaching test. 100% recovery of trace elements was not achieved in the Nod-P-1 test because silicate minerals are present in the nodule. Recovery of Mn is anomalously low compared to other elements because it is present in some Mn-oxyhydroxides as Mn^{4+} and Mn^{3+} ions [Post, 1999], which are more difficult to leach than Mn^{2+} ions [Zhang *et al.*, 2001]. Cr and As may also be oxidised by Mn oxides to Cr^{4+} and As^{5+} [Post, 1999], which could explain the relatively low recovery of As and Cr in the Nod-P-1 leachates (Fig. 6.6). Significant decreases in the leachate concentration of trace elements relative to the first sample were only recorded in Nod-P-1 leachates and could be the result of re-adsorption onto the mineral structure.

If the leachate samples taken 10 min after acidification are considered analogous to ice core samples measured by coupled continuous melter and ICP-MS analysis systems then our results suggest that considerable trace element leaching from mineral dust occurs within the short acidification time of these systems (~ 4.5 min, Knusel *et al.* (2003)). Consequently, the reproducibility of trace element determinations will be poor. Furthermore, we suggest that not only lithophile elements [Knusel *et al.*, 2003],

but all trace elements will record lower concentrations on coupled continuous melter and ICP-MS analysis systems relative to conventional ICP-MS analysis methods.

6.6.2 *Implications for the interpretation of trace element ratios*

Trace element ratios are also affected by the time- and mineral-dependent leaching of trace elements from mineral dust which can influence how effective they are as tools for interpretation of ICP-MS data. Marine to terrestrial element ratios of ice core samples can be used to ascertain the relative contributions of marine and terrestrial sources [Bull, 2009], which may vary seasonally or in response to climate. This requires the choice of a conservative marine and conservative terrestrial tracer. Na is the standard choice for a marine tracer and is used here to investigate whether variability in mineral dust leaching can affect marine/terrestrial element ratios. Incidentally, if Mg or Sr are substituted for Na as marine tracers the results displayed here alter very little. Popular choices for terrestrial tracers are Al [Gabrielli *et al.*, 2005b; Planchon *et al.*, 2002a; Townsend and Edwards, 1998], Mn [Gabrielli *et al.*, 2005a] and La [Wei *et al.*, 2008], which we have shown to have variable leaching characteristics. The choice of terrestrial tracer therefore causes very different trends in the evolution of marine/terrestrial ratios (Fig. 6.9). The Na/La ratio of BHVO-2 leachate varied between 185 and 825 over 48 hr and never achieved a constant value. La is identified as an unsuitable terrestrial tracer for the silicate rock standards (BHVO-2, W-2 and JG-2) as La and Na show strikingly different leaching behaviour in all three standards (Fig. 6.2). The Na/Mn value also varied considerably with acidification time whereas the Na/Al ratio in BHVO-2 leachate remained relatively constant after 2 hr of leaching at a value close to that of the whole rock (Fig. 6.9). Therefore ice core samples analysed at acidification times > 2 hr would not exhibit variation in the value of Na/Al resulting from differential leaching rates of Na and Al. As Al displayed similar leaching behaviour to Na in all four of the rock types tested, the Na/Al quickly (after ~ 12 hr) reached a constant value in each of the leachates (Fig. 6.10) and is therefore identified as the most suitable terrestrial tracer to be employed in a marine/terrestrial ratio. However, Na/Al ratios vary between dust lithologies (Fig. 6.10) and, therefore, if the

dominant mineral dust lithology in an ice core changed then the value of the marine/terrestrial ratio would also change. Any major shift in the Na/Al ratio should be interpreted with care because the relative marine and terrestrial input could be unchanged.

Figure 6.9: Variation in the marine/terrestrial ratio with acidification time in BHVO-2 leachates using three different terrestrial tracers: Mn, La and Al. Dashed lines indicate BHVO-2 whole rock ratio.

Figure 6.10: Variation in Na/Al ratio of BHVO-2, JG-2, W-2 and Nod-P-1 leachates versus acidification time. Actual Na/Al ratios of the rock standards are BHVO-2 (0.23), JG-2 (0.40), W-2 (0.20) and Nod-P-1 (0.70).

Figure 6.11: Variation in Al/La ratio of BHVO-2, JG-2, W-2 and Nod-P-1 leachate samples with acidification time. Actual Al/La ratios of the rock standards are BHVO-2 (4702), JG-2 (3132), W-2 (7574) and Nod-P-1 (229).

The Al/La ratio, the ratio of two potential conservative terrestrial tracers, varied with acidification time and dust lithology in our tests (Fig. 6.11). The Al/La ratio could potentially show changes between a predominantly silicate mineral assemblage with a high Al/La ratio and an oxide-based mineral assemblage with a low Al/La ratio.

However, the Al/La ratio values in the four leachates of our tests did not reflect those of the rock standards and the use of terrestrial trace elements ratios as tracers of the provenance of mineral dust sources should also be treated with caution.. For example, the Al/La ratio measured in the Nod-P-1 leachate was akin to that of the W-2 leachate whereas their whole rock Al/La ratios are 7574 and 229 respectively.

Element ratios are the basis of the calculation of enrichment factors, which are calculated by the following equation:

$$\text{Crustal Enrichment Factor } E = \left(\frac{[E_{\text{sample}}]}{[X_{\text{sample}}]} \right) / \left(\frac{[E_{\text{crust}}]}{[X_{\text{crust}}]} \right)$$

Ratios of element concentrations measured in the sample are divided through by element ratios reported for the continental crust. Any relative contribution from element E above that of the conservative terrestrial element X is classed as being enriched (from a source other than the crust) and any lower relative contribution from element E means that it is depleted relative to the crust. Crustal enrichment factors are used as a means of classifying trace elements in terms of their origin, usually defined as marine, terrestrial, anthropogenic or volcanic [Hur et al., 2007; Planchon et al., 2002b; Vallelonga et al., 2004]. As the calculation involves a ratio of two elements measured in the sample which may be leached incongruently from mineral dust the same caveats discussed above apply here too.

To test the sensitivity of crustal enrichment factors to incongruent mineral dust leaching crustal enrichment factors were calculated for Cu, V and U, which have been previously identified as having anthropogenic or volcanic inputs in some ice core samples [Hur et al., 2007; Planchon et al., 2002b; Vallelonga et al., 2004]. The calculations were conducted on leachate concentrations of an artificial ice core dust lithology comprising 50% JG-2, 24.5% BHVO-2, 24.5% W-2 and 1% Nod-P-1, leached at 10 ppm dust concentration, using three different crustal reference elements, Al, Mn and La (Fig. 6.12). Time-dependent trace element leaching causes the EF_c values to vary with acidification time meaning values obtained for different samples or ice cores should only be compared with caution. This is especially applicable for calculations made using Al as a crustal reference element because Al is leached continuously and

slowly over time, which causes the EF_c values to decrease by more than 100% over the first week of leaching. Using Al as the crustal reference element produces the highest EF_c values for Cu, V and U because Al is more difficult to leach than Mn or La. In the case of Cu and U, the EF_c values are greater than 10 throughout the first week of leaching and this could be used to infer that Cu and U have anthropogenic or volcanic inputs, which is clearly not the case here. Ice core dust is rich in easily-transportable clay minerals which, as our JG-2 (biotite granite) test demonstrated, which quickly release many mono- and di-valent cations under leaching but release Al more slowly. Therefore, calculation of a crustal enrichment factor for an ice core sample using Al as the conservative terrestrial tracer could easily produce a misleading result which identifies cations, such as Cu, U or other metals, as being enriched relative to the crust and therefore originating from another source, such as anthropogenic pollution.

Figure 6.12: Crustal enrichment factors for Cu, V, and U calculated for a dust lithology comprising 50% JG-2, 24.5% BHVO-2, 24.5% W-2 and 1% Nod-P-1 using Al, Mn and La as crustal reference elements. Element ratios of the upper continental crust are from Wedepohl [1995].

Our tests have highlighted that the recovery of leached elements is dependent on the mineralogy of the dust present and that consequently, the leached concentrations rarely reflect those of the source dust. Yet, the crustal enrichment factor calculation normalises the element ratio measured in the ice core sample, which includes a component of partially dissolved mineral dust, to the element ratio of continental

crust, which is derived from analysis of fully-digested rock [Reimann and De Caritat, 2000]. A more suitable approach towards the identification of Cu anthropogenic pollution, for example, would be to simply examine the evolution of the ice core Cu/Al, where Al could be replaced by any other terrestrial tracer. Providing that the sample acidification time allows a maximum leachable concentration to be reached, and that no major dust lithology change occurs, then an increase in Cu/Al would suggest a contribution from anthropogenic pollution.

6.6.3 REEs as dust source tracers

Leaching the W-2 (diabase/dolerite) rock standard produced a REE concentration pattern in the W-2 leachate that is significantly different to that of the W-2 rock standard itself (Fig. 6.13). The W-2 leachates are enriched in light REEs (LREEs, La, Ce and Pr) relative to middle REEs (MREEs, Gd) and heavy REEs (HREEs, Er and Yb). The LREE/HREE ratio of the leachate is 11.7 compared to a ratio of 2.5 for the W-2 rock standard. The magnitude of this enrichment remains constant with increasing acidification time causing the REE concentration pattern to not reflect that of the W-2 rock standard at any point in time. A similar pattern of LREE enrichment is seen in the BHVO-2 leachates (Appendix IX, Table A27) and was also identified as an artefact of ice core sample acidification by Gabrielli *et al.* [2010] in samples from EPICA Dome C, which have mineral dust concentrations several orders of magnitude lower than those used here (Section 6.3.3). In contrast, the JG-2 leachate is enriched in HREEs and MREEs relative to LREEs (Appendix IX, Table A27) because HREEs and MREEs are preferentially incorporated into biotite mica [Bea *et al.*, 1994]. The geochemical characteristics of REEs mean they have the potential to be excellent tracers of mineral dust source region [Henderson, 1984] but REE concentration patterns derived by conventional ICP-MS analysis of ice core samples containing mineral dust will fractionate LREE/HREE and LREE/MREE ratios and will therefore not be representative of dust source region. A more robust approach would be to isolate and fully-digest mineral dust from ice core samples for analysis of REE concentrations.

Figure 6.13: Chondrite-normalised plot of REE concentrations in W-2 rock standard and REE concentrations in leachates of W-2 leached at a concentration of 500 ppm. Leachate results from three different acidification times are displayed. Composition of CI carbonaceous chondrite was taken from *McDonough and Sun [1995]*.

6.6.4 Redox-sensitive elements

The Nod-P-1 rock standard has a Ce anomaly of 1.28 because Fe-Mn nodules are formed in an oxidised environment and incorporate Ce^{4+} scavenged from seawater, as well as Ce^{3+} . In contrast, silicate rocks (BHVO-2, W-2 and JG-2) are formed in less oxidising magmatic environments and Ce is only present as Ce^{3+} resulting in no Ce anomaly. The Ce anomaly of the Nod-P-1 leachate was different to that of the Nod-P-1 rock standard throughout the leaching test (Fig. 6.14) because Ce^{3+} was leached in preference to Ce^{4+} . This explains why the recovery of Ce after 12 hr of leaching was significantly lower than that of the other LREEs (Fig. 6.6), which are only present as trivalent cations. As Ce^{3+} was leached, the Ce anomaly of the leachate progressively increased until a value of 1 was reached when all the Ce^{3+} present had been recovered. The Ce anomaly remained at 1 because Ce^{4+} was not leached into solution and the Ce anomaly did not therefore reflect the oxidised state of Fe-Mn nodule at any point

during the leaching test. Ice core samples should be filtered to recover dust in order to provide useful information about the redox state of the environment.

Figure 6.14: Ce anomaly (Ce/Ce^*) of Nod-P-1 rock standard and variation in Ce/Ce^* of Nod-P-1 leachate with acidification time. $Ce/Ce^* = [Ce]_{chondrite} / (0.5 * [La]_{chondrite}^2 + 0.5 * [Pr]_{chondrite}^2)$. Ce recovery versus acidification time is also displayed (grey line).

Fe and Mn are other redox-sensitive elements that are present at different oxidation states in Fe-Mn oxyhydroxide minerals. There is considerable scientific interest in determining the oxidation state of Fe in mineral dust that is a source of Fe to the surface ocean because Fe^{2+} is soluble in the ocean and therefore considered more bio-available than Fe^{3+} [Schroth *et al.*, 2009]. Our findings suggest that leaching of dust samples in 1 wt.% HNO_3 may yield a good first approximation of the concentration of Fe present as Fe^{2+} .

6.7 Recommendations for future ice core trace element studies

Based on the findings of this study a number of recommendations can be made regarding ICP-MS trace element analysis and the interpretation of ice core trace element data.

6.7.1 Ice core ICP-MS analysis

In order to eliminate the issue of partial dissolution of mineral dust, ice core samples could be fully-digested prior to ICP-MS analysis following the method of *Correia et al.* [2003]. Alternatively, samples could be filtered or centrifuged to remove the particulate phase and the soluble trace element budget could be accurately determined by ICP-MS. Complete digestion of the extracted dust would then allow determination of the partitioning of the ice core trace element budget between soluble and insoluble phases.

However, the process of dust separation and complete digestion is time-consuming and somewhat impractical for ice core projects involving large numbers of samples. In which case, unfiltered samples should be acidified and stored at room temperature for several months, prior to ICP-MS analysis in order to obtain the trace element concentrations of the maximum acid-leachable fraction. This longer acidification time will also significantly reduce any difference in leaching between the first and last sample an analytical session. Although our results indicate that refreezing samples after acidification promotes leaching of some elements, if samples are then allowed to leach for several months, as recommended, the freezing-enhanced leaching contribution will become negligible.

6.7.2 *Ice core trace element data interpretation*

Trace element concentrations measured on samples acidified for varying lengths of time should not be directly compared without some assessment of the degree of uncertainty associated with incongruent mineral dust leaching.

Trace element concentrations originating from the partial dissolution of mineral dust will not reflect the composition of the dust itself and are not useful geochemical fingerprints of dust lithology. Assuming a uniform dust lithology, the trace element concentrations leached into solution will increase linearly with dust concentration. However, a change in the mineralogy of the source dust can cause considerable changes in the relative leaching of many mono- and di-valent trace elements.

Al is the most suitable element to use to assess the contribution of mineral dust partial dissolution because its rate of recovery from mineral dust tends not to vary between different dust lithologies. Na/Al is identified as the marine/terrestrial ratio least affected by partial dissolution of mineral dust and therefore most likely to record changes in relative contributions of marine and terrestrial air masses. However, a change in dust lithology will alter the Na/Al ratio of the ice core sample so other trace element ratios should be also examined to decipher the cause of any change.

In general, calculation of crustal enrichment factors should be carried out with caution because it normalises dust-leached concentrations to concentrations of bulk continental crust. If Al is used as a conservative terrestrial tracer in the calculation of crustal enrichment factors many elements will appear enriched purely as a result of incongruent leaching. This could lead to misleading conclusions regarding the input of trace elements from non-terrestrial sources such as volcanic degassing or anthropogenic pollution. REE concentration patterns obtained from samples containing leached mineral dust have fractionated LREE/MREE and LREE/HREE ratios and are therefore not suitable as tracers of dust source.

6.8 Conclusions

We have conducted experiments to systematically assess the effects of mineral dust partial dissolution resulting from sample acidification on the trace element budget of ice core samples. The main conclusions of this investigation are:

- Leaching of trace elements from mineral dust in acidified samples is both time- and mineral-dependent.
- Oxide and sheet silicate minerals, such as micas and clays, release trace elements into solution relatively quickly whereas mafic minerals continue to release trace elements into solution over several weeks causing concentration increases of several orders of magnitude.
- The concentration of trace elements leached from mineral dust is proportional to the mineral dust concentration in the sample.
- We recommend acidifying samples for as long as practical to reach a maximum leachable concentration.
- Incongruent leaching of trace elements from mineral dust is likely to produce misleading crustal enrichment factor values.
- Ratios of trace elements, in particular REEs, leached from mineral dust will not reflect those of the dust and are not suitable as tracers of dust provenance.

Chapter 7: Increased katabatic wind speeds and greater polynya extent in the Ross Sea region during the Little Ice Age

This chapter constitutes a paper prepared for submission to Climate of the Past (Section 1.6). Supplementary information is provided in appendices, which are located in Sections 7.7 and 7.8 of this chapter.

Abstract

Processes of bottom water formation and primary production in the Ross Sea region of Antarctica have the potential to create feedbacks in the global climate system. We present an ice core stable isotopic and soluble chemistry record, which captures the climate of the Little Ice Age (LIA), the most recent abrupt climate change, in this key region of Antarctica. Lithophile elements (e.g., Al), sourced from mineral dust are developed as proxies for katabatic wind speed, whilst deuterium excess (d-excess) and marine elements (e.g., Na) are related to the incursion of cyclonic systems into the Ross Sea. The LIA record is characterised by relatively low δD values and high concentrations of lithophile elements, compared to the ensuing time, suggesting that temperatures were ~ 1.6 °C colder and that strong ($> 57 \text{ m s}^{-1}$) katabatic winds prevailed. Al, Ti and Pb concentration increases of an order of magnitude ($> 120 \text{ ppb Al}$) mark the strongest wind events of the LIA and a $> 50\%$ decrease in mean concentrations signals the LIA termination. Furthermore, an abrupt 5‰ d-excess increase at 1625 AD suggests that cyclonic activity was enhanced between 1625 and 1875 AD. Methylsulphonate (MS^-) concentrations indicate that the Ross Sea Polynya was larger and more productive prior to 1875 AD, relative to the subsequent time. We suggest that a more extensive Ross Sea Polynya, maintained by strong katabatic winds, resulted in increased sea ice formation driving higher rates of bottom water formation during the LIA.

7.1 Introduction

The Little Ice Age (LIA) terminated only ca. 150 yr ago and is the most recent of several cooling events that punctuated the Holocene [Domack and Mayewski, 1999; Masson *et al.*, 2000]. The cause of the LIA has been widely speculated upon [e.g., Ammann *et al.*, 2007; Broecker, 2000; Crowley, 2000], but no consensus has been reached despite the multitude of meteorological instrumental and proxy records available from the Northern Hemisphere [Jones *et al.*, 2009]. Considerable variability exists globally in the timing, magnitude and character of the regional climate response [Matthews and Briffa, 2005]. In particular, it is unclear whether or not the two hemispheres experienced synchronous climate perturbations and what role the thermohaline circulation of the world's oceans may have played in instigating or amplifying the climate response [Broecker, 2000]. One vital aspect to understanding this event is the interpretation of Southern Hemisphere paleoclimate records, but few are currently available [Jones and Mann, 2004].

Antarctic ice cores are important archives of past climate and recently several have been obtained with sufficient temporal resolution to record the LIA [Bertler *et al.*, in press; Stenni *et al.*, 2002]. Whilst significant spatial and temporal variability exists [Masson *et al.*, 2000; Morgan and van Ommen, 1997; Mosley-Thompson and Thompson, 1990; Stenni *et al.*, 2002], Antarctica appears to have experienced cooler conditions during the LIA, synchronous with the Northern Hemisphere [Bertler *et al.*, in press]. This suggests that reorganisation of the thermohaline circulation was not the driver of the LIA climate change and that further investigation is required.

In this study, we examine ice core glaciochemical records to reconstruct LIA climate in a key region of Antarctica – the Ross Sea region. The Ross Sea, in particular the Ross Sea Polynya, located along the edge of the Ross Ice Shelf, is a major site of Southern Ocean sea ice generation [Tamura *et al.*, 2008], which drives bottom water formation [Jacobs and Giulivi, 1998]. Additionally, the region is the most biologically productive area of the Southern Ocean [Arrigo and van Dijken, 2003b]. Consequently, climatic changes occurring here have the potential to produce feedbacks, which influence both regional conditions and the global climate system [Turner *et al.*, 2009].

A sub-annual resolution ice core record was retrieved from Mt Erebus Saddle (MES) on Ross Island, south-western Ross Sea (Fig. 7.1). The MES ice core site is located at the edge of the Ross Ice Shelf, at a boundary between the influences of two dominant meteorological regimes. Air masses originate from both the Southern Ocean, in the form of cyclones [Sinclair *et al.*, 2010], and the interior of Antarctica, in the form of katabatic flow [Bromwich *et al.*, 1992; Sinclair *et al.*, 2010]. The two dominant air masses have different geochemical characteristics that allow them to be identified [Bertler *et al.*, 2004a]. Thus, the location of the MES ice core site allows the meteorological regimes of the interior of Antarctica and the Ross Sea region to be traced back through time in the same ice core record.

Figure 7.1: A) Map of the Antarctic continent. Locations of ice core sites referred to in the text are marked by solid black circles and are labeled as follows: DC = EPICA Dome C, DM = EPICA Dronning Maud Land, LD = Law Dome, SD = Siple Dome, SP = South Pole, SS = Siple Station, TD = Talos Dome, TY = Taylor Dome. The dashed rectangle defines the area of map B. B) Map of the Ross Sea region bound by the East Antarctic Ice Sheet (EAIS) and the West Antarctic Ice Sheet (WAIS). Approximate katabatic flow paths are indicated by grey arrows (modified after Parish [1988]). The dashed rectangle defines the area of map C. C) Map of McMurdo Sound area. The location of Mt Erebus Saddle (MES) is shown. Dark grey shading indicates areas of exposed rock outcrop.

A 550 yr continuous record of ice core lithophile element concentrations from this site provides a proxy for katabatic wind speeds, which were stronger prior to 1850 AD than at any ensuing time. A substantial decrease in katabatic flow speeds is identified at the LIA termination. Furthermore, by linking the katabatic wind proxy to δ -excess, which is associated with the incursion of cyclonic systems, and methylsulphonate (MS^-), a proxy for primary productivity, we demonstrate that stronger offshore winds caused a larger or more persistent Ross Sea Polynya between 1625 and 1875 AD.

7.2 Study site, core processing and analytical methods

MES is a local snow accumulation zone situated at an altitude of 1600 m between Mt Erebus and Mt Terra Nova on Ross Island (Fig. 7.1) (77°30.90'S, 167°40.59'E). Ice flows off the saddle in NNW and SSE directions. Ground penetrating radar indicated a depth to bedrock of 220 m and imaged parallel isochrones, suggesting favourable glaciological conditions for the preservation of a continuous, annually-resolved ice core record. A 168 m deep ice core was drilled at the centre of the ridge, in the zone of minimum ice flow, in December 2006. Annual temperature at the site, ascertained from firn temperature logging, is -25.6 °C and the accumulation rate calculated from the annual layer count is 0.22 m (H₂O equivalent) yr⁻¹.

A brief summary of the processing and analysis of the ice core is only provided here, with full details of the analytical methods including precision, accuracy and detection limits given in Appendix I (Section 7.7). Here, we present data from the uppermost 120 m of the ice core, which was processed for chemical analysis using a continuous melter-discrete sampling system [Osterberg *et al.*, 2006]. Pristine samples from the interior of the core were analysed by ion chromatography (IC) for major ions and by inductively coupled plasma mass spectrometry (ICP-MS) for 22 major, minor and trace elements. Stable isotope ratios $\delta^{18}\text{O}$ and δD were determined on samples from corresponding depths obtained from the outer section of core. In addition, the tritium (³H) contents of six samples were measured.

7.3 Dating

The MES ice core was dated by annual layer counting of stable isotopic and soluble chemistry signals, using key reference horizons as age tie points. A back-diffusion model [Johnsen, 1977; Johnsen *et al.*, 2000] was applied to the stable isotope ratio profiles to recover the annual signal at depth, facilitating annual layer counting. A glacial flow model provided further constraint on the evolution of the age model [Dansgaard and Johnsen, 1969]. Detailed description of the parameters used for annual layer counting is provided in Appendix II (Section 7.8).

A peak in levels of ^3H , relating to thermonuclear bomb testing, provides an age tie point for the age model and confirms reliability of the annual layer counting technique. Elevated tritium contents were determined in the MES ice core between 1964 and 1972 AD, in line with measurements reported in Antarctic and New Zealand precipitation (Appendix II (Section 7.8)) and other Antarctic ice core records [Jouzel *et al.*, 1979; Oerter *et al.*, 1999; Stenni *et al.*, 2002].

Large amplitude peaks in non-sea salt (nss) SO_4^{2-} determined in ice core records are typically attributed to major volcanic eruptions and are often used as age tie points in age model development [Dixon *et al.*, 2004; Legrand and Delmas, 1987; Palmer *et al.*, 2001; Stenni *et al.*, 2002; Traufetter *et al.*, 2004]. However, positive identification of volcanic nss SO_4^{2-} deposition in the MES ice core is difficult because the nss SO_4^{2-} signal is dominated by biogenic nss SO_4^{2-} from the seasonally open ocean (Section 7.5.1).

As an alternative, we examined the deposition history of heavy, volatile trace elements, which are emitted by volcanoes [Hinkley *et al.*, 1994] and can be deposited on ice sheets [Kaspari *et al.*, 2007; Kellerhals *et al.*, 2010]. In the MES ice core, Pb, Bi and Tl are all strongly enriched relative to terrestrial element concentrations in at least 8 consecutive samples between 60.5 and 61.1 m depth (Fig. 7.2). The annual layer count suggests this signal is deposition from the eruption of Mt Tambora, Indonesia in April 1815 AD [Simkin and Siebert, 1994]. However, Vallelonga *et al.* [2003] attributed elevated Pb and Bi concentrations in a Law Dome (Fig. 1A) ice core at this time to emissions from Mt Erebus, on the basis of Pb isotopic signatures. As MES is located

adjacent to Mt Erebus it is plausible that the trace element record of the MES ice core may record the eruption history of Mt Erebus rather than that of global-scale stratospheric eruptions. To test this hypothesis, trace element ratios measured across the Pb, Tl and Bi peaks were compared to trace element ratios measured in the plume of Mt Erebus (Fig. 7.2). None of the trace element ratios exhibit any marked deviation from the median value of the ice core record (green line) during the proposed Mt Tambora eruption. This lends support to attribution of the Bi, Pb and Tl peaks at 61.1 m to the Mt Tambora eruption. Moreover, the median values (Fig. 7.2, green line) of the MES ice core trace element ratios are different from those of the Mt Erebus plume (Fig. 7.2, purple line) providing evidence that the ice core trace element budget is predominantly influenced by input from other sources.

Figure 7.2: Bi, Pb and Ti concentrations normalised to Al and selected trace element ratio records for the time period including the Mt Tambora eruption marker. The trace element ratios of the Mt Erebus plume are plotted where available [Zreda-Gostynska *et al.*, 1997] and the median values for the entire MES ice core record are shown. Breaks in the record occur where the concentration of an element is below the ICP-MS detection limit.

Further support for the accuracy of the age model can be drawn from comparison of Pb concentrations determined in the MES ice core with the history of anthropogenic Pb contamination recorded in an ice core from Law Dome (Fig. 7.3). A rise in Pb/Al is seen at 1893 AD in the MES record, within 9 yr of the increase in Pb concentrations at Law Dome, which is attributed to anthropogenic activity [Vallelonga *et al.*, 2002].

Figure 7.3: Anthropogenic influence on Pb deposition at MES since 1840 AD. All MES data plotted are annual means to remove seasonal variability. A 5 yr running mean is plotted through the MES Pb concentration data (dash line). MES Pb concentrations are also shown normalised to Al to remove the influence of variable mineral dust contributions. Pb concentrations determined at Law Dome are plotted for comparison [Vallelonga *et al.*, 2002]. Grey arrow indicates onset of anthropogenic Pb pollution determined at Law Dome. All error bars are $\pm 2\sigma$.

A total of 561 annual layers are identified in the 120 m of core analysed. A sub-annual sampling resolution is maintained throughout the core; in the deepest 10 m section of core 84 yr are preserved and each year has ≥ 4 stable isotope samples and ≥ 2 ICP-MS samples. The incremental error on the dating of individual years or the duration of discrete time periods is ± 1 yr between the surface and 61.1 m (1816 AD), the depth of the Mt Tambora eruption marker. The cumulative dating error, which is the difference between the age of the reference marker and the initial age indicated by the annual layer count is ± 1 yr at 1964 AD (^3H peak) and ± 9 yr at 61.1 m (Mt Tambora). The dating uncertainty on the record below 61.1 m depth is difficult to constrain because no further age reference markers are identifiable.

7.4 Results

7.4.1 *Stable isotopes*

The MES ice core δD record displays well-developed seasonal cycles between a mean summer (Jan 1st, fixed by dating) maximum of -202‰ and a mean winter (July 1st) minimum of -221‰ in the 1970-2006 AD time period (Fig. 7.4). Only the δD record will be referred to in the following sections because the $\delta^{18}O$ displays essentially the same variability. The second order stable isotopic parameter d-excess also shows a well-developed seasonal cycle with early-summer maxima and a mean annual oscillation of 2.1‰ between summer and winter values (Fig. 7.4). Although δD and d-excess show similar seasonality, by plotting both time series about their respective long term means, it is demonstrated that they have different interannual variability (Fig. 7.5). Regression of δD and d-excess annual mean or maximum values produces no significant correlation.

The long term δD record of MES ice core is characterised by frequent oscillations about the 1950-2006 AD mean (Fig. 7.7). The only deviations in δD below this mean of > 4 yr duration occur prior to 1850 AD. The most notable of these low δD periods are 1470-1535 AD, 1560-1580 AD, 1605-1630 AD, 1670-1700 AD, 1760-1780 AD and 1835-1850 AD. The mean δD of the pre-1850 AD period is 5.6‰ lower than that of the post-1850 AD period (Table 7.1). In contrast, the d-excess record of the MES ice core is dominated by an abrupt shift towards a consistently elevated d-excess state at 1625 AD. The preceeding time period (1446-1625 AD) is characterised by d-excess values 3.1‰ lower than the 1950-2006 mean. Between 1625 and 1875 AD the d-excess 5 yr running mean only deviates below the 1950-2006 mean once, at ca. 1800 AD. The mean d-excess value of the 1625-1875 AD time period is 5.1‰ higher than that of the preceeding time and 1.5‰ higher than the following time (Table 7.1).

Figure 7.4: Mean seasonal cycles of δD , d-excess, marine aerosol (Na) and lithophile elements (Al and Mn) for 1970-2005 AD. Two cycles are plotted to aid viewing. Data points are plotted at the end of each month, i.e., peak δD is plotted at end of December, equivalent to January 1st. δD and d-excess are back-diffused to correct for changes in amplitude and phasing of seasonal cycles resulting from molecular diffusion (Appendix II, Section 7.8).

Table 7.1: Mean and range (in parentheses) of selected stable isotopic and soluble chemistry parameters within specified time intervals of the MES ice core record.

	δD (‰)	d-excess (‰)	Na (ppb)	Al (ppb)	Mn (ppt)	Ce (ppt)
1950-2006	-211.6 (-254.1 to -130.4)	7.0 (0.2 to 21.8)	76.5 (2.15 to 506)	1.33 (0.09 to 7.06)	61.9 (0 to 301)	3.95 (0 to 24.3)
1850-2006 (post-LIA)	-209 (-255 to -130.4)	7.7 (0.2 to 21.8)	95.7 (2.15 to 853)	1.64 (2.02 to 18.9)	55.7 (0 to 472)	4.1 (0 to 26.6)
1446-1850 (LIA)	-215.4 (-266.5 to -147.2)	6.81 (-3.66 to 20.5)	89.5 (2.48 to 1111)	3.45 (0.20-125)	90.5 (0 to 940)	15.7 (0.25-294)
1625-1875	-213.7 (-266.5 to -157.6)	9.1 (1.6 to 20.5)	97.1 (2.48 to 1110)	5.02 (0.20 to 125)	85.3 (0 to 940)	15.3 (0.10 to 294)
1446-1625	-216.5 (-253.9 to -147.2)	3.9 (-3.7 to 13.4)	89.5 (8.23 to 544)	3.45 (0.288 to 38.6)	90.5 (8.8 to 538)	15.7 (0.6 to 252)

7.4.2 Soluble chemistry

A Pearson's correlation shows the degree of co-variability between the concentrations of the elements determined by ICP-MS (Table 7.2). Na, Mg and Sr are highly correlated ($R^2 > 0.86$, $p < 0.01$) in the MES ice core record. Bivariate plots place the samples onto straight lines corresponding to seawater concentration ratios, indicating a marine source for these elements. We focus on the Na record but consideration of the Mg or Sr record would produce similar results. Annual maximum Na concentrations (92 ppb mean) generally occur in summer, coincident with the annual peaks in δD (Fig. 7.4) between 1970 and 2006 AD. The Na record exhibits significant interannual variability (Fig. 7.5) and concentrations range from 2 to 506 ppb in the 1950-2006 AD record (Table 7.1). Na concentrations remain relatively constant with no abrupt changes over the long term record (Fig. 7.6). However, the mean Na concentration increased by 8.5% (Table 7.1) after the abrupt positive shift in d-excess observed at 1625 AD.

Table 7.2: Correlation coefficients for major, minor and trace element concentrations (12 samples yr⁻¹) during the 1970-2006 AD time period in the MES ice core. All values shown are significant at the 99% level, n = 439.

R ²	Na	Mg	Al	Ti	V	Mn	Rb	Sr	Y	Ba	La	Ce	Pb
Na	1												
Mg	0.86	1											
Al	-	0.02	1										
Ti	-	-	0.51	1									
V	0.36	0.38	0.44	0.52	1								
Mn	-	0.02	0.75	0.55	0.39	1							
Rb	0.15	0.15	0.61	0.58	0.73	0.47	1						
Sr	0.90	0.90	0.06	0.06	0.50	0.06	0.27	1					
Y	-	-	0.42	0.43	0.29	0.44	0.46	0.02	1				
Ba	-	-	0.12	0.18	0.08	0.13	0.13	0.03	0.12	1			
La	-	-	0.75	0.69	0.53	0.62	0.71	0.05	0.52	0.10	1		
Ce	-	-	0.74	0.68	0.51	0.64	0.68	0.05	0.54	0.09	0.97	1	
Pb	-	-	0.11	0.21	0.06	0.16	0.13	0.03	0.13	0.49	0.10	0.09	1

Al, Ti, Mn, Rb, Y, La and Ce concentrations all correlate at $R^2 > 0.5$ ($p < 0.01$) and display similar temporal variability between 1970 and 2006 AD (Fig. 7.5). This group of elements is hereafter referred to as ‘lithophile elements’. Cs, Pr, Tl, Bi, Th and U were excluded from the correlation because they frequently registered at below the ICP-MS detection limit. In addition, Ca and Zr were excluded due to evidence of contamination from ceramic tools used in processing of the ice core. Pb is only weakly correlated ($R^2 < 0.2$) with the lithophile elements because substantial anthropogenic input occurs during the time period considered (Fig. 7.3). Maximum concentrations of lithophile elements in the MES ice core occur during autumn and winter months (Fig. 7.4, Al and Mn shown), the opposite to the seasonal cycles of Na, δD and d-excess. The Al mean seasonal cycle of 1970-2006 AD shows a 45% concentration increase in winter relative to summer.

The long term ice core record reveals that lithophile element concentrations decreased significantly around 1850 AD (Fig. 7.6). The mean concentrations of Al, Mn and Ce are all > 60% higher in the period prior to 1850 AD compared to post-1850 AD (Table 7.1). Furthermore, significant variability between the behaviour of different lithophile elements, not observable in the record of the last 35 yr (Figure 7.5), can be discerned

in the long term record (Figure 7.6). For example, the mean Mn concentration decreased by 38% after 1850 AD, whereas the Ce mean concentrations decreased by 74%. The lithophile elements can be categorised by the extent of inter-correlation in the pre-1850 AD period (Table 7.3). Three discrete groups are identifiable: correlation coefficients of $R^2 > 0.52$ are produced between Al, Ti and Pb, $R^2 > 0.63$ between Mn and Rb, and $R^2 > 0.92$ between Y, La, and Ce. Figures 7.5 and 7.6 both display the concentration record of one element from each of these groups.

MS^- concentrations vary between 1 and 187 ppb about a mean of 54 ppb (Fig. 7.7). A period of significantly higher concentrations, equating to a 81% increase in mean concentration, is identifiable between 1825 and 1875 AD. MS^- data are only available for the section of MES core dating from 1797 to 2006 AD.

Table 7.3: Correlation coefficients for lithophile element concentrations (2 samples yr^{-1}) during the LIA recorded in MES ice core (1446-1850 AD).

All values shown are significant at the 99% level, $n = 809$.

R^2	<i>Al</i>	<i>Ti</i>	<i>Mn</i>	<i>Rb</i>	<i>Y</i>	<i>La</i>	<i>Ce</i>	<i>Pb</i>
Al	1							
Ti	0.81	1						
Mn	0.13	0.12	1					
Rb	0.07	0.06	0.63	1				
Y	0.08	0.06	0.52	0.43	1			
La	0.06	0.05	0.45	0.38	0.92	1		
Ce	0.10	0.08	0.45	0.36	0.94	0.98	1	
Pb	0.59	0.52	-	-	-	-	-	1

Figure 7.5: Stable isotope and soluble chemistry data for the period 1970-2006 AD of the MES ice core. All the time series have been re-sampled to monthly resolution and a 3 month running mean has then been applied to the soluble chemistry time series. δD and d-excess are plotted around 1970-2006 mean values. Representative analytical error bars ($\pm 2\sigma$) are displayed on selected points. δD analytical error bars are too small to plot and the d-excess analytical error is indicated. Shaded bars highlight d-excess values exceeding the 1970-2006 mean with associated Na peaks (grey shading) or without associated Na peaks (green shading).

Figure 7.7: Deuterium excess and MS^- time series from MES ice core. MS^- is raw data smoothed by 5-point running mean. Deuterium excess time series re-sampled to $2 \text{ samples yr}^{-1}$ and smoothed by 5 yr running mean (as Fig. 7.6). Timing of a diatom bloom reported by *Leventer and Dunbar* [1988] in two sediment core records from the west of Ross Island in McMurdo Sound is indicated. Representative analytical error bars ($\pm 2\sigma$) are displayed on selected points. The gap in MS^- time series exists because some samples have not been analysed for MS^- concentration.

7.5 Discussion

7.5.1 Linking the ice core record to climate parameters

Stable isotopic ratios (δD and $\delta^{18}\text{O}$) in ice cores are well-established proxies of Antarctic air temperature [Craig, 1961; Dansgaard, 1964]. However, for the MES ice core record direct calibration of the stable isotopic paleothermometer is challenging. No statistically significant relationship can be established with air temperature recorded at Scott Base (Fig. 7.1C) or gridded reanalysis data, most likely because neither data set provides an accurate representation of conditions at MES. The effects of the extreme topography of Ross Island are not well represented in the gridded dataset, and MES experiences significantly different weather conditions to Scott Base (N. A. Bertler, Personal communication).

Two different mechanisms of aerosol generation are advocated for marine chemistry in ice core records: aerosol generated via bubble bursting over the open ocean [Curran *et al.*, 1998; Legrand and Mayewski, 1997] and the entrainment of frost flowers from the sea ice surface [Rankin *et al.*, 2002]. The growth of frost flowers on the sea ice surface involves precipitation of mirabilite ($\text{Na}_2\text{SO}_4 \cdot 10\text{H}_2\text{O}$), which is depleted in SO_4^{2-} relative to Na^+ [Rankin *et al.*, 2000]. This leads to a fractionated $\text{Na}^+/\text{SO}_4^{2-}$ ratio in ice core marine aerosol records with a frost flower source [Kaspari *et al.*, 2005; Rankin *et al.*, 2004]. However, the $\text{Na}^+/\text{SO}_4^{2-}$ ratio of MES ice core samples exhibits no depletion in SO_4^{2-} (Fig. 7.8). SO_4^{2-} concentrations are actually enriched relative to seawater concentrations due to additional input from biogenic SO_4^{2-} . The absence of $\text{Na}^+/\text{SO}_4^{2-}$ values higher than the seawater value, together with the predominance of summer maxima in Na concentrations (Fig. 7.5), is indicative of an open water source for marine aerosol at MES [Rankin *et al.*, 2004].

Figure 7.8: Scatterplot of Na⁺ versus SO₄²⁻ concentrations of all MES samples measured by IC (surface-65.8 m; 1797-2006 AD). ICP-MS Na concentrations are plotted for 59.6-65.8 m because IC cation data is not available. Black line is the Na⁺/SO₄²⁻ of seawater and all samples, except one, plot below this line. Na⁺/SO₄²⁻ values indicate Na⁺ is sourced from the open ocean.

The d-excess and marine element records show similar interannual trends; in the 1970-2006 AD record, 90% of d-excess peaks greater than the long term mean have corresponding peaks in marine element concentrations (Fig. 7.5, grey shaded bars). Furthermore, the maximum summer values of Na and d-excess between 1970 and 2006 AD are significantly correlated ($R^2 = 0.58$, $p < 0.01$), suggesting a common forcing.

Deuterium excess is primarily controlled by factors associated with the moisture source, principally relative humidity [Merlivat and Jouzel, 1979; Petit *et al.*, 1991]. We speculate that high d-excess values in the MES record are related to the advection of air masses from low latitude source regions, of low relative humidity, by cyclonic activity. Synoptic-scale cyclones are known to provide precipitation to the southwestern Ross Sea by either remaining stationary to the north of the Ross Sea and promoting the incursion of marine air or by tracking around the interior of the Ross Ice Shelf [Sinclair *et al.*, 2010]. Either mechanism would cause the entrainment of Na from

the seasonally open water of the Ross Sea, leading to the relationship between d-excess and Na observed.

Seasonal cycles in d-excess, as observed in the MES core, have also been reported in Antarctic ice core records from Law Dome [Delmotte *et al.*, 2000], South Pole and Adelie Land [Ciais *et al.*, 1995]. Detailed delineation of potential oceanic moisture source regions, coupled with isotopic modelling, is required to understand the origin of the seasonality in the MES d-excess signal.

Lithophile elements are tracers of mineral dust transport to an ice core site [Rhodes *et al.*, 2011]. Several areas of outcropping rock are located within 160 km of MES in the Dry Valleys and along the Transantarctic Mountains (Fig. 7.1), and these are likely source areas for mineral dust in the ice core. Furthermore, with such abundant local dust sources it can be assumed that the variability of lithophile element concentrations in the MES ice core is primarily controlled by input from these local (100s of km distance away), rather than global (1000s of km distance away) dust sources. Previous studies of dust transport and deposition in the south-western Ross Sea region support this conclusion [Ayling and McGowan, 2006; Dunbar *et al.*, 2009]. We do not attempt to relate the lithophile element signatures recorded in the ice core to the various dust lithologies of the region as previous work [Rhodes *et al.*, 2011] has shown that no reliable indication of provenance would be produced (Section 6.6.2). Rather, the lack of perfect positive correlation between Al, Ti, Mn, Rb, Y, La and Ce is likely to reflect mineral-specific differential rates of weathering and transport efficiency [Caquineau *et al.*, 1998; Reimann and De Caritat, 2000], and incongruent leaching of trace elements from mineral dust in acidified samples [Rhodes *et al.*, 2011].

Increased lithophile element concentrations during autumn and winter months (Fig. 7.4) indicate that strong ($> 35 \text{ m s}^{-1}$) southerly winds, which are recorded at Scott Base (data available at www.cliflo.co.nz), are required to transport sufficient mineral dust material to MES to produce the concentration maxima. The strong southerly flows recorded at Scott Base result from katabatic winds, which originate from the West and East Antarctic Ice Sheets [Parish, 1988] and propagate across the Ross Ice Shelf [Bromwich *et al.*, 1992]. It is also important to note that the opposite seasonal cycle of lithophile and marine element concentrations at MES (Fig. 7.4) supports the

assignment of two different meteorological systems, katabatic winds and marine cyclones respectively, as transport mechanisms for these chemical species.

Figure 7.9: A) NCEP/NCAR reanalysis 850 mb meridional wind composite mean for the winter months (JJA) of 1979-2006 AD across the Ross Sea region (90-70°S, 150-220°E). White dashed line defines the source region of meridional winds arriving at MES. B) Spatial correlation pattern between meridional wind (850mb) and MES Al concentration record for the winter months (JJA) of 1990-2000 AD across the Ross Sea region. White dashes outline region of significant correlation ($p < 0.025$, $n = 10$).

To further investigate the relationship between lithophile element concentrations and katabatic winds, we correlate MES ice core data with NCEP/NCAR reanalysis meridional wind strength [Kalnay *et al.*, 1996]. In this region of Antarctica, the meridional (south to north) component of the wind field is an approximation of katabatic wind flow (Fig. 7.9). No significant correlation between wind speed and lithophile element concentration could be achieved for the entire time period for which reliable Antarctic NCEP/NCAR data are available (1979-2006 AD). However, when individual decades are studied, a significant correlation with Al concentration is observed between 1990 and 2000 AD (Fig. 7.9). In contrast to the 1980s, the 1990s were characterised by a relatively strong teleconnection between the El Niño Southern Oscillation and

Antarctica [Fogt and Bromwich, 2006]. This led to enhanced katabatic flow speeds in the Ross Sea region [Bertler *et al.*, 2004b], and a stronger signal in the MES katabatic wind proxy. The area of significant correlation includes the Transantarctic Mountains to the south of MES, a source region for katabatic winds to the site, which further confirms katabatic flow as the mechanism for mineral dust transport to MES.

7.5.2 Little Ice Age climate

The portion of the LIA captured in the MES ice core (1446-1850 AD) is characterised by elevated lithophile element concentrations (Fig. 7.6, Table 7.1) and the rapid decrease in lithophile element concentrations between 1848 and 1850 AD marks the termination of the LIA. The ice core record currently dates back to 1446 AD and there is no indication that the onset of the LIA is captured. A frequently cited date for the onset of the LIA in the Northern Hemisphere is 1450 AD [Grove, 1988] but estimates vary; an ice core record from the Antarctic Dry Valleys [Bertler *et al.*, in press], and a tree ring climate reconstruction from South America [Villalba, 1994], have suggested the onset was ca. 150 yr earlier in the Southern Hemisphere.

As lithophile element concentrations in the MES ice core are proxies for katabatic wind strength, the elevated concentrations suggest that katabatic wind speeds were considerably stronger during the LIA. As a threshold wind velocity must be exceeded to transport particles in suspension [Bagnold, 1941], it is likely that increased maximum wind speed, as opposed to relatively prolonged katabatic flow events, led to the increased transport of mineral dust revealed by higher lithophile element concentrations during the LIA. Formulating an approximation of how much stronger katabatic winds were is challenging, principally because the relationship between dust entrainment and wind speed is not linear [Bagnold, 1941; Pye, 1987; Schulz *et al.*, 1998]. However, as the elevated lithophile element concentrations of the LIA are not repeated in the post-1850 AD ice core record, we can assume that wind speeds did not reach such strength again. At Scott Base the maximum daily gust speed recorded since 1972 was 57.7 ms^{-1} from due south, so LIA maximum wind speeds must have exceeded this value.

By examining the behaviour of the three groups of lithophile elements identified in Section 6.4.2 and their links to mineralogy and wind speed, considerable climate variability within the LIA is revealed. Al, Ti and Pb show increased mean concentrations (Table 7.1, Al shown), coupled with discrete periods of dramatic concentration increases of several orders of magnitude, during the LIA (Fig. 7.6, Al shown). These elements are predominantly sourced from complex silicate minerals, such as feldspars, which have relatively high densities and large grain sizes, causing the threshold wind velocity required to transport them in suspension to be high [Bagnold, 1941]. The discrete periods of increased Al, Ti and Pb concentrations (1760-1805 AD and 1838-1850) represent the most extreme wind speeds of the LIA period. In contrast, the lithophile elements of the second group, Mn and Rb, which show more muted concentration increases during the LIA, are common in Fe-Mn oxyhydroxides and sheet silicate minerals such as clays and micas, respectively. All of these minerals have relatively low densities and are easily weathered, forming flake-like particles of a low, uniform grain size, which require a lower threshold wind velocity to initiate transport in suspension [Bagnold, 1941]. Thus, Mn and Rb concentrations are not a reflection maximum wind strength. The third group of lithophile elements, consisting of La, Ce and Y, show characteristics of both the other two groups. Similarly to Mn, La, Ce and Y are abundant in oxyhydroxide minerals but they are also common impurities in silicate minerals, particularly apatite. During discrete time periods of the LIA, concentrations increase by an order of magnitude but the timing of these extreme events does not always match that of the large increases in Al and Ti (Fig. 7.6).

The MES δD record suggests that colder temperatures, as well as stronger winds, than those experienced in the past 50 yr prevailed during the LIA. The significant negative deviations in δD from the 1950 to 2006 AD mean identified in Section 7.4.1 all date from the LIA. In the absence of representative weather station data with which to calculate a local δ -temperature slope, we employ the Taylor Dome δ – temperature calibration of 4‰ δD / °C [Steig *et al.*, 1998] to estimate the degree of cooling experienced at MES during the LIA. Taylor Dome, located in the Ross Sea region (Fig. 7.1A), is the most proximal ice core for which a local δ – temperature slope has been established. The difference between the mean δD of the LIA and the post-LIA period is

6.4‰ (Table 7.1), which equates to a mean cooling of 1.6 °C during the LIA. The difference in the minimum δD values suggests that temperatures could have been 2.5 °C colder during discrete time periods of the LIA.

Furthermore, the increase in d-excess at 1625 AD suggests that either a change occurred at the oceanic moisture source to reduce relative humidity or the moisture source switched to one of a lower relative humidity [Petit *et al.*, 1991]. The abrupt nature of the transition seems to make a moisture source change the more likely explanation. The elevated d-excess values between 1625 and 1875 AD could indicate that intrusion of marine cyclones from lower latitude (low relative humidity) oceanic moisture source regions was more frequent during this time. An increased level of storminess during this time period is also supported by the presence of higher marine aerosol concentrations in the post-1625 AD MES ice core record.

7.5.3 Ross Sea Polynya in the Little Ice Age

Although the MS^- record has limited temporal coverage, it indicates that primary productivity and polynya area, were greater prior to 1875 AD than in the following years (Fig. 7.7). The effectiveness of the biogenic sulphur species MS^- as a primary productivity proxy relating to the area of the Ross Sea Polynya has been demonstrated previously [Rhodes *et al.*, 2009]. Polynya size exerts a direct influence on rates of marine primary productivity [Arrigo and van Dijken, 2004] because primary productivity is stimulated by increased the sunlight availability when polynya size is enhanced [Arrigo and McClain, 1994]. By extrapolating the linear relationship between MS^- concentration (x) and primary production (y) established by Rhodes *et al.* [2009] ($y = 1.35x - 3.41$), we calculate that between 1825 and 1875 AD primary productivity rates were approximately 80% higher than post-1875 AD levels.

Independent evidence for heightened primary productivity in the Ross Sea at this time is found in increased diatom abundances in sediment cores from McMurdo Sound [Leventer and Dunbar, 1988]. Records of diatom abundance from two sediment cores from the west of Ross Island reveal a period of increased primary productivity between

1825 and 1880 AD [Leventer and Dunbar, 1988] corresponding almost precisely to the interval of higher MS^- concentrations observable in the MES record (Fig. 7.7). A further prolonged time period (1600-1875 AD) of increased open water diatom populations is identified in a four sediment cores retrieved from the north and northwest of Ross Island. Taking into account dating errors, this corresponds remarkably well to the period of high d-excess values recorded in the MES ice core (1652-1875 AD) (Fig. 7.6).

Heightened primary productivity, and therefore greater polynya extent, appears to be linked to increased cyclonic activity. This can be explained by considering the controls on polynya formation and size. The Ross Sea Polynya (and other minor polynyas in the Ross Sea region) are mechanically-driven and are maintained by strong offshore katabatic winds [Bromwich *et al.*, 1998; Morales Maqueda *et al.*, 2004]. For katabatic winds to propagate across the relatively flat Ross Ice Shelf a strong pressure gradient is required and this is created by the presence of cyclonic (low pressure) systems [Bromwich *et al.*, 1992; Bromwich *et al.*, 1993]. As variability in the size of the Ross Sea Polynya over recent decades has been linked to katabatic wind strength [Morales Maqueda *et al.*, 2004], we propose that the combination of colder temperatures and increased cyclonic activity in the Ross Sea region led to stronger katabatic flows, which maintained a spatially larger and/or more temporally persistent polynya between 1625 and 1875 AD. Supporting evidence for stronger katabatic winds across East Antarctica during this interval of the LIA is found in an ice core micro-particle record from South Pole [Mosley-Thompson, 1995].

As the MES ice core provides evidence for a greater polynya extent between 1625 and 1875 AD, we now consider that greater polynya size led not only to increased primary productivity but also to increased rates of sea ice production [Morales Maqueda *et al.*, 2004]. Sea ice formation drives the formation of deep water masses by ejecting dense, saline brine which sinks to depth. In the Ross Sea, an intermediate water mass called High Salinity Shelf Water (HSSW) is formed, which contributes to Antarctic Bottom Water [Jacobs and Giulivi, 1998]. Therefore, it is feasible that increased sea ice production in the polynya amplified bottom water formation rates during the 1625-1875 AD period. Furthermore, it is conceivable that the increased katabatic wind

strength recorded in the MES and South Pole ice cores affected the other wind-driven polynyas around the Antarctic continent [*Morales Maqueda et al.*, 2004]. Increased bottom water formation in Antarctic coastal polynyas may have driven the increase in Southern Hemisphere bottom water formation during in the LIA, identified by *Broecker et al.* [1999]. Combined with enhanced primary productivity, this could have resulted in stronger drawdown of atmospheric CO₂ into the ocean, contributing to the 6-8 ppm decrease in atmospheric CO₂ concentration observed in other Antarctic ice cores, which occurred ca. 1600 AD and persisted until ca. 1800 AD [*Etheridge et al.*, 1996; *Indermuhle et al.*, 1999].

7.6 Conclusions

Ice core stable isotope and soluble chemistry document the last 550 yr of climate in the south-western Ross Sea region of Antarctica at sub-annual resolution. Dating of the record is accomplished by a combination of annual layer counting and a glacial flow model, with the timing of anthropogenic Pb deposition in Antarctica providing support for accuracy of the age model. Examination of the monthly resolution record of the last 35 yr allowed climate proxies to be developed. Lithophile elements concentrations are related to mineral dust transport by katabatic winds whilst more positive d-excess values appear to be linked to the incursion of marine cyclones into the Ross Sea.

The MES ice core record suggests that the Ross Sea region experienced colder temperatures (by ~ 1.6 °C) and stronger ($> 57 \text{ m s}^{-1}$) katabatic winds during the LIA. The termination of the LIA between 1848 and 1850 AD is marked by a decrease in lithophile elements concentrations indicating a substantial reduction in katabatic wind speed. Furthermore, the d-excess record suggests incursion of marine cyclones into the Ross Sea was more frequent between 1625 and 1875 AD. The MS⁻ record demonstrates that marine primary productivity increased during this time and suggests that polynya area was greater. The occurrence of diatom blooms recorded in sediment cores [Leventer and Dunbar, 1988] support this interpretation. It is hypothesised that colder temperatures and increased cyclonic activity promoted stronger katabatic winds across the Ross Ice Shelf, causing sea ice divergence and creating a greater polynya area in the Ross Sea.

We suggest that increased sea ice formation resulting from greater polynya extent caused enhanced rates of bottom water formation at this time. Change in the thermohaline circulation of the oceans could therefore be a response to, rather than the initial driver of, climate change at the LIA [cf. Broecker, 2000].

7.7 Appendix I: Analytical methods

7.7.1 Core processing

The continuous-melter-discrete sampling system [Osterberg *et al.*, 2006] allowed the pristine ice of the inner core to be continuously sampled for chemical analysis (IC and ICP-MS). From the surface to 66 m depth the mean sampling resolution was 43 samples m^{-1} and between 66 m and 120 m depth the mean sampling resolution was increased to 61 samples m^{-1} . Between 77 m and 120 m depth, an alteration to the continuous-melter-discrete sampling system enabled material for ICP-MS to be sampled at half the depth resolution relative to the stable isotope and IC samples to improve processing efficiency.

All vials used to sample material intended for IC or ICP-MS analysis were rigorously cleaned to prevent chemical contamination. Polypropylene vials used for IC samples were triple-rinsed with ultra-pure water ($> 18.2 \text{ M}\Omega$), soaked for > 3 days and triple-rinsed again. Polypropylene vials used for ICP-MS samples were first triple-rinsed with ultra-pure water then soaked in 5 wt.% analytical reagent grade HNO_3 for > 10 days, triple-rinsed, soaked in ultra-pure water for > 5 days and triple-rinsed with ultra-pure water. Vial cleaning was conducted under HEPA Class 100 clean room conditions whilst wearing Tyvek® clean suits with hoods and powder-free polyethene gloves.

Procedural blanks monitor the potential contribution of the processing and sampling procedure to the concentrations of chemical species measured. Fabricated ice cores of frozen ultra-pure water ($> 18.2 \text{ M}\Omega$) were processed, melted and sampled daily by the methods described above to provide procedural blanks. Chemical concentrations recorded in the procedural blanks are summarized in Table 7.4. The procedural blank concentrations equate to: $< 10\%$ of the mean ice core concentrations of Na, Mg, As, Rb, Sr, Tl, Bi Th, K^+ and SO_4^{2-} ; $< 15\%$ of the mean ice core concentrations of Al, V, Mn, Cs, Ce, La and Pr; $< 20\%$ of the mean ice core concentrations of Y, Zr, U, NO_3^- and Cl^- ; $< 25\%$ of the mean ice core concentrations of Ti and Ba, and $< 30\%$ of the mean ice core concentration of Pb. Contamination of Ca was a problem as the procedural blank

accounts for 70% of the mean concentration. The Ca and Zr in the procedural blanks likely originate from ceramic knives used to prepare the ice core for melting.

Table 7.4: Concentrations of elements and major ions determined by ICP-MS and IC in the procedural blanks sampled during processing of the MES ice core.

Element	Concentration	Major ion	Concentration
	(ppt)		(ppb)
Na	1120	Na ⁺	0.34
Mg	290	Mg ²⁺	0.66
Al	560	K ⁺	0.10
Ca	6890	Ca ²⁺	20.3
Ti	78.5	MS ⁻	0.00
V	0.70	Cl ⁻	26.6
Mn	10.9	SO ₄ ²⁻	4.50
As	0.29	NO ₃ ⁻	6.27
Rb	0.47		
Sr	4.50		
Y	0.50		
Zr	3.05		
Cs	0.05		
Ba	5.28		
La	0.66		
Ce	1.42		
Pr	0.17		
Tl	0.00		
Pb	4.67		
Bi	0.09		
Th	0.07		
U	0.04		

7.7.2 Stable isotope ratios

The stable isotope ratios $\delta^{18}\text{O}$ and δD (where $\delta^{18}\text{O} = ([(^{18}\text{O}/^{16}\text{O})_{\text{sample}} / (^{18}\text{O}/^{16}\text{O})_{\text{V-SMOW}}] - 1) * 1000$) were measured at the Stable Isotope Laboratory, GNS Science using both traditional mass spectrometry and laser absorption spectroscopy. Samples from the first 91 m depth of ice core were analysed by a conventional isotope ratio mass spectrometer instrument. $\delta^{18}\text{O}$ measurements were conducted using a GVI AquaPrep system linked to a dual inlet GVI mass spectrometer. 400 μL of sample was equilibrated with 300 μL of CO_2 for 24 hr at 25.5 °C. The CO_2 was then extracted and transferred to the mass spectrometer for analysis. δD analyses were performed by directly reducing 100 μL of sample to H_2 gas in a PyrOH reaction column and measuring the gas on the same dual inlet GVI mass spectrometer. $\delta^{18}\text{O}$ and δD are reported with respect to V-SMOW and normalized to internal standards: INS9 with reported values of -17.4‰ for $\delta^{18}\text{O}$ and, -131.0‰ for δD , and INS11 with reported values of -0.4‰ for $\delta^{18}\text{O}$ and, -4.6‰ for δD . The analytical precision of this instrument is $\pm 0.1\text{‰}$ for $\delta^{18}\text{O}$ and $\pm 1.0\text{‰}$ for δD , resulting in an uncertainty of $\pm 1.3\text{‰}$ on the second order parameter d-excess [Dansgaard, 1954].

Samples from 92 m to 120 m depth (1655-1446 AD) were analysed using a LGR Liquid-Water Isotope Analyser which measures $\delta^{18}\text{O}$ and δD simultaneously by laser absorption. Path lengths of several km are generated within a mirrored-cavity resulting in clear separation of laser absorption lines of different water molecules. $\delta^{18}\text{O}$ and δD are normalized to the internal standards stated above. The analytical precision for this instrument is $\pm 0.2\text{‰}$ for $\delta^{18}\text{O}$ and $\pm 0.6\text{‰}$ for δD , resulting in an uncertainty of $\pm 1.7\text{‰}$ on d-excess.

To test the comparability of measurements conducted on the two instruments a batch of samples ($n = 187$) was analysed by both instruments. Comparison of the stable isotope ratios measured on the two instruments identifies offsets between the datasets (Fig. 7.10). The offsets between the δD and $\delta^{18}\text{O}$ values produced a significant offset between the calculated values of d-excess (Fig. 7.11). Therefore, the δD and $\delta^{18}\text{O}$ values measured on the LGR Liquid-Water Isotope Analyser ($\delta\text{D}_{\text{laser}}$) were corrected to make them comparable to the GVI mass spectrometer values ($\delta\text{D}_{\text{mass spec.}}$).

equiv.) using the linear relationships established by analysing samples on both instruments (e.g., Fig. 7.10).

$$\delta D_{\text{mass spec. equiv.}} = (\delta D_{\text{laser}} + 1.6576) / 0.9809$$

$$\delta^{18}\text{O}_{\text{mass spec. equiv.}} = (\delta^{18}\text{O}_{\text{laser}} - 0.1577) / 0.1.0034)$$

Deuterium excess values were then calculated from the corrected δD and $\delta^{18}\text{O}$ datasets. A revised analytical uncertainty (u) for d-excess, which takes into account the errors on both instruments, is calculated as: $\sqrt{1.3^2 + 1.7^2} = 2.14\text{‰}$. This value is applied when the entire record encompassing stable isotope ratios measured by both instruments is considered.

Figure 7.10: δD measured on GVI mass spectrometer and LGR Liquid-Water Isotope Analyser (Laser). Error bars are 2σ .

Figure 7.11: Deuterium excess derived from $\delta^{18}\text{O}$ and δD values measured on GVI mass spectrometer and LGR Liquid-Water Isotope Analyser (Laser). Error bars are analytical uncertainty (u) ($u = \sqrt{a^2 + (8 \cdot b^2)}$), where a = precision on $\delta^{18}\text{O}$ and b = precision on δD).

7.7.3 Ion chromatography

Ion chromatography analysis for major ions (Na^+ , K^+ , Mg^{2+} , Ca^{2+} , MS^- , Cl^- , NO_3^- , SO_4^{2-}) was conducted at the Climate Change Institute, University of Maine using Dionex ion chromatographs with chemical suppression and conductivity detectors paired to a Gilson 215 Liquid Handler autosampler. Anions were measured using an AS-18 column, 400 μL sample loop, and a Dionex Reagent Free Controller producing a KOH eluent concentration of 35 mM. Cations were measured using a CS-12A column and a 500 μL loop with 25 mM methanesulphonic acid eluent. Calibration using five calibration standards bracketing the anticipated concentration range routinely achieved correlation coefficients of $R^2 > 0.99$ for all major ions. The external reference material ION-92 (National Water Research Institute, Canada) was analysed at dilutions of 100 and 1000 times to verify the calibration and to calculate the accuracy and precision of the measurements. Na^+ , Mg^{2+} , Ca^{2+} , MS^- , Cl^- and SO_4^{2-} measurements are accurate to within 5%. The reproducibility, calculated as $2 \cdot \text{RSD}$ (relative standard deviation), of

Na⁺, Mg²⁺, Ca²⁺ and MS⁻ measurements is $< \pm 11\%$ and $< \pm 4\%$ for Cl⁻ and SO₄²⁻. NO₃⁻ is not detectable in ION-92 and K⁺ measurements were not reproducible.

7.7.4 *Inductively coupled plasma mass spectrometry*

Ice core samples were analysed for concentrations of 22 major, minor and trace elements (Na, Mg, Al, Ca, Ti, V, Mn, As, Rb, Sr, Y, Zr, Cs, Ba, La, Ce, Pr, Tl, Pb, Bi, Th, U) by ICP-MS (Agilent 7500cs Series) at the Geochemistry Laboratory of the School of Geography, Environment and Earth Sciences, Victoria University of Wellington. The operating conditions adopted for ICP-MS analysis are displayed in Table 7.5. An ASX-520 micro-volume autosampler linked to the ICP-MS introduced sample to the PFA Teflon nebuliser (0.2 mL min⁻¹ flow rate) via a peristaltic pump. The formation of oxides in the plasma was monitored by aspirating a 1 ppb solution of Ce and tuning parameters were adjusted to maintain the proportion of the ¹⁴⁰Ce converted to ¹⁴⁰Ce¹⁶O at below 2%. Nickel sampling and skimmer cones were cleaned, and the sample introduction system was circulated with 5 wt.% HNO₃ (Seastar) for 1 hr prior to each analytical session to reduce any possible memory effect from the samples of previous users.

Calibration standards were gravimetrically diluted daily from stock multi-element standards made up from mono-elemental 1000 ppm standards. The element concentrations in the calibration standards varied between elements according to the relative concentrations expected in the ice core samples. P/A factor tuning was required to calibrate measurements conducted by the two different mass detectors (pulse and analogue) on elements which recorded $> 1,000,000$ counts s⁻¹ (Na, Mg and Al).

Table 7.5: Operating conditions of the ICP-MS and data acquisition parameters for the determination of selected elements in MES ice core samples

Parameter	Setting
Forward power	1500 W
RF matching	1.75-1.84 V
Carrier gas	1.04 – 1.10 L min ⁻¹
Makeup gas	0 L min ⁻¹
Nebulizer pump	0.12-0.16 rps
Spray chamber temperature	2°C
Sampling depth	7 mm
Torch position	Optimised daily to maximise sensitivity
Ion lenses voltages	Optimised daily to maximise sensitivity and signal stability across mass range
Isotopes measured	²³ Na, ²⁴ Mg, ²⁷ Al, ⁴³ Ca, ⁴⁷ Ti, ⁵¹ V, ⁵⁵ Mn, ⁷⁵ As, ⁸⁵ Rb, ⁸⁸ Sr, ⁸⁹ Y, ⁹⁰ Zr, ¹³³ Cs, ¹³⁸ Ba, ¹³⁹ La, ¹⁴⁰ Ce, ¹⁴¹ Pr, ²⁰⁵ Tl, ²⁰⁸ Pb, ²⁰⁹ Bi, ²³² Th, ²³⁸ U
Uptake and stabilization time	50 s and 60 s
Washing time between samples	10 s H ₂ O, 200 s 5 wt.% HNO ₃ (Seastar), 220 s 1 wt.% HNO ₃ (total 430 s)
Integration time	0.10 s or 0.15 s depending on element
No. of runs and scan passes	3 x 26

Table 7.6: Detection limits (ppt) for elements determined by ICP-MS analysis.

Element	Detection limit
Na	167
Mg	5.0
Al	9.7
Ca	1271
Ti	22
V	0.83
Mn	3.2
As	6.7
Rb	0.31
Sr	0.31
Y	0.1
Zr	0.58
Cs	0.18
Ba	0.32
La	0.14
Ce	0.19
Pr	0.19
Tl	0.44
Pb	0.72
Bi	0.43
Th	0.45
U	0.4

Samples were stored frozen prior to analysis then thawed and acidified to 1 wt.% HNO₃ with 68 wt.% HNO₃ (Seastar) at least 12 hr prior to analysis. Counts recorded on 1 wt.% HNO₃ blanks were subtracted from those recorded on samples and standards to correct for background. Detection limits are calculated as 3 σ on the blank measurements (Table 7.6). The calibration standards were run as bracketing standards every 12 samples to correct for instrumental drift. An external reference material, SLRS-4 (river water, National Research Council, Canada), was run at 10 times dilution during each analytical session to test the accuracy and reproducibility of the measurements (Table 7.7).

Table 7.7: Element concentrations (ppt) determined by repeated measurement of SLRS-4 riverine water standard (n = 82) with precision and accuracy of measurements.

Element	This study	Certified values	Precision 2 RSD (%)	Accuracy (% difference)
Na ^a	2289 ± 80	2400 ± 200	3.5	4.6
Mg ^a	1573 ± 156	1600 ± 100	9.9	1.7
Al ^a	56 ± 4	54 ± 4	6.8	4.0
Ca ^a	6132 ± 546	6200 ± 200	8.9	1.1
Mn ^a	3.56 ± 0.14	3.37 ± 0.18	4.0	5.5
Ba ^a	13 ± 0.44	12.22 ± 0.6	3.4	6.4
Ti	1587 ± 152	1460 ± 80	9.6	8.7
V	382 ± 19	320 ± 30	5.1	19.3
As	757 ± 21	680 ± 60	2.7	11.3
Rb	1616 ± 59	1530 ± 50	3.7	5.6
Sr	29.8 ± 1.27	26300 ± 3200	4.3	13.2
Y	143 ± 6	146 ± 8	4.0	2.0
Zr	139 ± 45	120 ± 15	32.2	15.9
Cs	6.8 ± 0.23	9 ± 1	3.4	24.5
La	298 ± 15	287 ± 8	5.1	3.9
Ce	375 ± 27	360 ± 12	7.3	4.1
Pr	83.4 ± 10.6	69.3 ± 1.8	12.6	20.4
Tl	7.96 ± 2.31	6.8 ± 1.3	29.0	17.0
Pb	82 ± 5.7	86 ± 7	6.9	4.7
Bi	2.4 ± 0.34	2.1 ± 0.1	14.0	14.4
Th	21.5 ± 1.9	18 ± 3	9.1	19.6
U	51.1 ± 4.9	50 ± 3	9.6	2.3

^aConcentrations in ppb

Certified values for SLRS-4 are GeoREM [Jochum *et al.*, 2005] preferred values obtained from <http://georem.mpch-mainz.gwdg.de>.

7.7.5 Tritium analysis

Tritium (^3H) content was measured at the GNS Science Tritium and Water Dating Laboratory, Lower Hutt, New Zealand by ultra-low-level liquid scintillation spectrometry (QuantulusTM). Measurements were conducted on six samples from a depth range of 11 m to 21.3 m which were sampled from the ice core in the cold laboratory (-20 °C) using a band saw. The water samples were purified in a vacuum distillation system to exclude tritium contamination and measured without prior tritium enrichment in a monitored tritium-free environment. Details of the tritium analysis procedure are described in [Morgenstern and Taylor, 2009].

7.8 Appendix II: Dating methods

7.8.1 Annual layer counting

A snow pit sampled at Mt Erebus Saddle 2 yr prior to drilling of the ice core was dated by identifying annual peaks in $\delta^{18}\text{O}$ for the time period 2000 to 2005 AD [Rhodes *et al.*, 2009]. The equivalent section of the $\delta^{18}\text{O}$ record was located in the ice core to facilitate dating of the uppermost section. The annual signals of $\delta^{18}\text{O}$, δD and d-excess were well-preserved in the top 25 m of the ice core and maximum values were identified as mid-summer (Jan 1st). NO_3^- displayed a well-defined annual signal with maximum values in winter-spring. This NO_3^- signal is preliminarily interpreted as originating from production in stratospheric clouds [Michalski *et al.*, 2005]. A combination of $\delta^{18}\text{O}$, δD , d-excess and NO_3^- were utilised for annual layer counting.

7.8.2 Back-diffusion of stable isotopes

$\delta^{18}\text{O}$ and δD peaks were difficult to identify deeper down the core because molecular diffusion in the firn pore space effectively blurs the annual $\delta^{18}\text{O}$ and δD cycles into each other and removes the high frequency annual signal [Steen-Larsen *et al.*, 2011]. The $\delta^{18}\text{O}$ and δD signals can be deconvolved or back-diffused in order to obtain the original signal using calculated diffusion coefficients of each of the isotopes involved [Johnsen, 1977; Johnsen *et al.*, 2000]. Back-diffusion of the Mt Erebus Saddle stable isotopic record was performed to 108 m depth. The back-diffused time series of $\delta^{18}\text{O}$ and δD display well-defined annual signals of a larger amplitude than in the raw data. Therefore, a combination of these back-diffused time series and the raw d-excess signal, which appears to remain sensitive to seasonality, was used to identify annual layers in the ice core to 108 m depth (1545 AD). As back-diffused stable isotope series were not available for annual layer counting between 108 and 120 m depth, a polynomial fit applied to the age model developed by annual layer counting was extrapolated to 120 m depth.

7.8.3 Tritium peak

Elevated tritium content is observed between 1964 and 1972 AD, in line with that observed in Antarctic and New Zealand precipitation (Fig. 7.12).

Figure 7.12: Tritium contents of six MES ice core samples analysed (black circles) plotted with tritium contents of precipitation from the Ross Ice Shelf, Halley Bay on the Antarctic Peninsula, and Kaitoke, New Zealand, decay-corrected to December 2006. One tritium unit (TU) is defined as one atom of tritium per 10^{18} atoms of hydrogen, equivalent to 0.118 becquerels (Bq) per litre of water. Error bars are 1σ .

Chapter 8: Conclusions

The principal aim of this thesis was to construct a paleoclimate record of the Late Holocene in the Ross Sea region, Antarctica, utilising climate proxies developed from ice core stable isotopic and soluble chemistry records of the Mt Erebus Saddle snow pit and ice core.

8.1 Interpretation of snow pit stable isotope and major ion data

A 2 m snow pit record of stable isotope ratios and major ion concentrations demonstrated that the glaciochemical records preserved in the snow and ice at Mt Erebus Saddle held seasonally resolvable signals related to climatic and environmental factors. $\delta^{18}\text{O}$ was utilised for annual layer counting of the 5 yr record. MS^- , a biogenic sulphur species, displayed an annual signal related to the area of open water available for primary production during summer in the south-western Ross Sea (Fig. 8.1). Interannual variability in the annual MS^- concentration was shown to be the result of large icebergs, which carved from the Ross Ice Shelf and restricted the area of the Ross Sea Polynya for several years of the record. MS^- was developed as a proxy for both open water area and the rate of primary productivity in the Ross Sea. This is the only study to-date to statistically link the level of primary productivity, and hence MS^- production, to the concentration of MS^- recorded in a snow pit or ice core record. Furthermore, this work demonstrates the sensitivity of coastal ice core chemistry records to local marine biogenic processes.

8.2 Core processing and ICP-MS method development

The MES ice core was processed at the New Zealand Ice Core Laboratory at GNS Science using a continuous melter system to produce samples suitable for analysis of ultra-low concentrations of trace elements. An accurate, precise and efficient method

for ICP-MS analysis of major, minor and trace element concentrations was refined over the course of the analytical work involved in this thesis.

Figure 8.1: Summary of the relationships between MS^- concentration, sea ice cover and primary productivity. High MS^- concentrations result from extensive open water and high primary productivity (high chlorophyll a concentrations). Low MS^- concentrations result from restricted open water and low primary productivity (low chlorophyll a concentrations).

8.3 Dating the ice core

The ice core was dated by annual layer counting, predominantly of stable isotope ratios δD and $\delta^{18}O$, as for the snow pit record. The relatively high accumulation rate at MES (23 cm water equivalent yr^{-1}) and mean annual temperature of $-28^\circ C$ preserved an annual signal in stable isotope ratios and other geochemical parameters measured in the ice core. Back-diffusion modelling of the stable isotopic records was used to

correct for molecular diffusion, which dampened the annual signal below 25 m depth in the ice core. Age tie points in the form of thermonuclear bomb tritium fallout (1964 AD) and heavy, volatile element deposition from the eruption of Mt Tambora (1816 AD) helped to constrain the age model. Additional support for the dating method was identified in the anthropogenic Pb deposition history recorded in the MES ice core, which was similar in timing to that recorded at Law Dome, East Antarctica [Vallelonga *et al.*, 2002]. Finally, a Dansgaard-Johnsen glacial flow model provided further confidence in the age-depth relationship produced by the annual layer counting technique. The maximum age uncertainty of the MES ice core age model is ± 1 yr between 2006 and 1964 AD, ± 9 yr between 1964 and 1816 AD, ± 1 yr at 1816 AD and ± 18 yr between 1816 and 1446 AD.

8.4 Dust leaching experiment

A systematic experiment was designed and implemented to assess the contribution of acid-leaching of mineral dust particles to trace element concentrations measured in ice core samples by ICP-MS. Before ICP-MS analysis ice core samples must be acidified and mineral dust particulates are generally not removed prior to this. The contribution of dust leaching to soluble ice core chemistry and the factors which could affect the magnitude of this contribution had not previously been considered in detail. The experiment involved leaching powdered international rock standards of different lithologies and concentrations in 1 wt.% HNO₃ for variable lengths of time. The leachates were periodically sampled and analysed by ICP-MS to ascertain the extent of leaching that had occurred.

The results showed that leaching of trace elements from mineral dust in acidified samples is both time- and mineral-dependent (Fig. 8.2A). Oxide and sheet silicate minerals, such as micas and clays, released trace elements into solution relatively quickly, whereas mafic minerals continued to release trace elements into solution over several weeks causing concentration increases of several orders of magnitude in the

leachates. Additionally, the concentration of trace elements leached from mineral dust was found to be proportional to the mineral dust concentration in the sample.

Figure 8.2: Summary of time- and mineral-dependent leaching effects on A) trace element concentrations, B) crustal enrichment factors and C) terrestrial element ratios.

The findings of this study have important implications, both for the methods by which ICP-MS analyses of ice core samples are conducted, and the assumptions made during interpretation. To minimise the effects of time-dependent leaching, it is recommended to acidify samples for as long as practical or to use a system of continuous melting and immediate analysis. It also is demonstrated that incongruent leaching of trace elements from mineral dust is likely to produce misleading crustal enrichment factor values that may cause contributions of some trace elements to the ice core chemistry budget to be incorrectly attributed to anthropogenic or volcanic sources (Fig. 8.2B). Furthermore, it is evident that some ratios of trace elements, in particular REEs, leached from mineral dust will not reflect those of the dust and are therefore not suitable as tracers of dust provenance (Fig. 8.2C).

8.5 Reconstruction of Late Holocene climate in the Ross Sea region

The MES ice core record dates from 1446 to 2006 AD and therefore captures much of the Little Ice Age (LIA) climate event. To develop climate proxies to apply to the LIA climate record, the monthly resolution record of the last 30 yr was compared to gridded reanalysis data [Kalnay *et al.*, 1996]. Lithophile element concentrations were found to reflect mineral dust transport from local sources by katabatic winds. A significant positive correlation ($R^2 > 0.6$, $p < 0.025$) between Al concentration and wind speed in a katabatic source region was found for the 1990s decade, when katabatic winds were particularly strong [Bertler *et al.*, 2004b]. The lithophile elements showed some contrasting trends further back in time, suggestive of a change in dust source region or transport mechanism. However, results from the dust leaching experiment had demonstrated that element ratios were not likely to be diagnostic of dust source region. The variability between the elements was instead related to the weathering, transport and leaching characteristics of the dominant minerals in which the elements occur.

The MES ice core paleoclimate record is summarised in Figure 8.3. The δD record suggests that the Ross Sea region experienced colder temperatures, and elevated

lithophile element concentrations indicate greater transport of mineral dust resulting from stronger katabatic winds, during the LIA. Al, Ti and Pb concentration increases of an order of magnitude mark the strongest wind events of the LIA, where wind speed exceeded the threshold velocity required to transport relatively dense silicate minerals of relatively large grain size to MES. The termination of the LIA between 1848 and 1850 AD is marked by an abrupt decrease in the lithophile element concentrations, equivalent to > 50% reduction in mean Al concentration, indicating a reduction in katabatic wind speed. Furthermore, d-excess values consistently higher than the 1950-2006 AD mean provide evidence for enhanced cyclonic activity, which advected moisture sourced from lower latitudes, over the Ross Sea region between 1625 and 1875 AD.

Figure 8.3: Summary of the climatic and environmental changes recorded in the δD , d-excess, lithophile element (Al) and MS^- records of the MES ice core and diatom blooms of sediment cores [Leventer and Dunbar, 1988].

The snow pit study of MS^- demonstrated that the MS^- record preserved at MES was an effective proxy for primary productivity and the summer area of the Ross Sea Polynya.

This allowed the identification of the 1820 and 1875 AD period as one of greater polynya area and 80% higher primary productivity (Fig. 8.3). Independent evidence for heightened primary productivity between 1825 and 1880 AD is found in sediment core diatom abundances [Leventer and Dunbar, 1988]. The timing of a more prolonged period (1600-1875 AD) of increased open water diatom populations identified in a further four sediment cores to the north and northwest of Ross Island [Leventer and Dunbar, 1988] corresponds with the period of increased cyclonicity recorded in the δ -excess of the MES ice core.

It is proposed that the combination of colder temperatures and increased cyclonic activity in the Ross Sea region led to stronger katabatic flows which maintained a spatially larger and/or more temporally persistent polynya between 1625 and 1875 AD. Moreover, it is likely that larger polynya area led to increased sea ice formation, driving increased rates of bottom water formation. Combined with enhanced primary productivity, this could have resulted in stronger drawdown of atmospheric CO₂ into the ocean, contributing to the atmospheric CO₂ concentration reduction observed in other Antarctic ice cores [Etheridge *et al.*, 1996; Indermuhle *et al.*, 1999] between 1600 and 1800 AD.

This paleoclimate record is significant because a reorganisation of the thermohaline circulation of the oceans has been proposed as a driver of the LIA [Broecker, 2000]. Alternatively, the MES ice core record suggests that increased bottom water formation, at least in the Ross Sea region, resulted from the stronger atmospheric circulation of the LIA, and was therefore a response to, rather than the initial driver, of LIA climate change.

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Appendices

Appendix I: Mt Erebus Saddle 2004/05 snow pit data

Major ion concentrations were determined by ion chromatography (IC) at the University of Maine on samples from the Mt Erebus Saddle (MES) 2 m snow pit (Table A1). $\delta^{18}\text{O}$ values were determined at the Alfred Wegener Institute. The $\delta^{18}\text{O}$ and MS^- data formed the basis of a *Geophysical Research Letters* paper presented in Chapter 3. The annual mean MS^- concentrations of the five complete years incorporated by the snow pit record were regressed against both open water area and annual primary production (Fig. A1).

Table A1: Stable isotope ratios ($\delta^{18}\text{O}$) and major ion concentrations for MES 04/05 snow pit.

Concentrations given in ppb.

Sample ID	Age Model	Depth (cm)	Na ⁺	K ⁺	Mg ²⁺	Ca ²⁺	MS ⁻	Cl ⁻	NO ₃ ⁻	SO ₄ ²⁻	$\delta^{18}\text{O}$ (‰)
MES-04-05-001	1999.58	210	33.1	4.6	6.5	16.5	11.3	61.4	7.0	79.6	-32.78
MES-04-05-002	1999.61	209	28.0	3.2	5.7	9.3	7.7	53.5	53.9	87.5	-32.84
MES-04-05-003	1999.63	208	32.9	3.9	5.5	5.3	10.8	58.9	5.9	93.8	-32.81
MES-04-05-004	1999.64	207	32.3	2.8	5.9	6.4	5.3	52.3	49.5	99.0	-32.75
MES-04-05-005	1999.66	206	32.0	3.1	5.7	3.7	7.7	55.3	53.2	105.0	-32.74
MES-04-05-006	1999.67	205	35.1	3.5	5.9	3.4	9.0	55.4	51.5	108.7	-32.46
MES-04-05-007	1999.69	204	33.1	3.1	5.9	3.2	9.7	56.6	54.1	105.6	-32.55
MES-04-05-008	1999.70	203	34.9	2.5	5.8	2.4	18.8	65.6	6.7	103.7	-32.29
MES-04-05-009	1999.72	202	37.1	2.2	6.2	3.6	19.7	66.1	5.6	96.6	-32.11
MES-04-05-010	1999.74	201	38.8	3.1	6.5	5.5	19.4	75.7	64.6	118.6	-31.95
MES-04-05-011	1999.75	200	37.2	3.3	6.2	3.7	15.7	59.3	51.6	97.1	-31.91
MES-04-05-012	1999.77	199	308.9	212.5	8.4	27.5	22.7	449.4	51.9	128.1	-31.44
MES-04-05-013	1999.78	198	32.1	4.8	7.1	8.8	21.2	59.4	61.5	139.5	-31.50
MES-04-05-014	1999.80	197	26.7	3.9	5.5	4.8	23.3	53.9	6.2	141.9	-31.28
MES-04-05-015	1999.81	196	25.6	4.2	5.3	4.2	34.0	72.7	102.1	214.5	-31.17
MES-04-05-016	1999.83	195	23.6	3.9	4.9	3.6	36.5	70.6	101.4	228.3	-30.78
MES-04-05-017	1999.84	194	22.7	3.2	4.7	3.2	41.0	69.4	117.0	231.2	-30.63
MES-04-05-018	1999.86	193	23.8	3.6	4.8	3.2	45.3	71.2	110.4	243.3	-30.62
MES-04-05-019	1999.88	192	25.2	3.3	4.9	3.2	45.5	76.3	121.9	251.7	-30.29
MES-04-05-020	1999.89	191	26.5	2.6	4.8	3.4	55.8	81.4	13.9	238.0	-29.99
MES-04-05-021	1999.91	190	27.0	3.4	5.1	4.4	25.7	60.8	87.1	157.1	-29.89
MES-04-05-022	1999.92	189	25.6	3.1	4.9	3.6	31.8	64.0	93.7	172.9	-29.74
MES-04-05-023	1999.94	188	23.1	2.6	4.6	3.0	46.1	70.7	8.5	190.3	-29.50
MES-04-05-024	1999.95	187	21.4	2.4	4.5	2.9	60.7	88.2	28.5	224.9	-29.22
MES-04-05-025	1999.97	186	57.8	3.4	8.3	3.5	39.8	147.4	87.2	192.8	-28.99
MES-04-05-026	1999.98	185	171.3	6.0	21.0	6.9	40.0	310.2	67.7	246.3	-29.01
MES-04-05-027	2000.00	184	239.1	6.6	29.9	11.2	38.8	389.6	22.1	230.0	-28.67
MES-04-05-028	2000.08	183	377.2	11.3	47.1	14.3	48.3	750.1	40.5	379.4	-28.59
MES-04-05-029	2000.17	182	248.3	8.6	32.1	11.0	50.3	533.8	43.5	291.4	-28.97
MES-04-05-030	2000.17	181	131.8	4.7	16.9	6.5	57.9	312.7	5.0	177.7	-29.02
MES-04-05-031	2000.25	180	81.5	4.6	10.3	5.6	50.1	180.0	4.7	124.4	-29.33
MES-04-05-032	2000.33	179	69.5	4.1	8.6	4.8	44.4	157.5	5.1	109.0	-29.79
MES-04-05-033	2000.41	178	61.6	4.0	8.1	4.3	32.9	148.5	29.2	110.5	-30.06
MES-04-05-034	2000.50	177	46.0	3.3	6.5	3.0	20.7	82.3	16.7	69.0	-30.63
MES-04-05-035	2000.58	176	48.2	4.0	6.7	3.2	21.3	86.8	17.7	71.9	-30.28
MES-04-05-036	2000.60	175	73.2	4.4	8.0	4.4	20.4	125.3	21.3	78.7	-30.63
MES-04-05-037	2000.61	174	123.7	5.1	11.7	6.5	15.4	210.5	21.8	96.7	-30.47
MES-04-05-038	2000.63	173	167.4	5.5	13.9	12.0	15.2	315.7	23.0	123.6	-29.74
MES-04-05-039	2000.64	172	102.8	4.2	10.0	6.5	9.3	192.9	29.2	105.2	-28.72
MES-04-05-040	2000.66	171	79.6	3.6	8.1	4.7	10.5	138.6	5.6	84.0	-28.51
MES-04-05-041	2000.68	170	17.9	4.4	3.1	7.3	7.5	26.6	31.2	59.2	-28.36
MES-04-05-042	2000.69	169	16.0	3.7	2.8	4.6	6.5	24.8	32.3	59.0	-28.08
MES-04-05-043	2000.71	168	15.4	3.7	2.7	2.7	n.a.	24.3	34.0	56.6	-28.25
MES-04-05-044	2000.73	167	19.3	4.0	3.0	4.0	n.a.	29.9	33.2	57.7	-28.03
MES-04-05-045	2000.74	166	24.9	3.7	3.5	3.0	n.a.	37.5	30.1	55.5	-28.18
MES-04-05-046	2000.76	165	33.9	3.8	4.6	5.3	5.9	49.4	25.4	50.0	-28.03
MES-04-05-047	2000.77	164	35.5	3.8	4.6	3.4	8.2	53.1	n.a.	53.8	-27.76
MES-04-05-048	2000.79	163	34.2	3.7	4.6	3.8	7.1	49.2	26.8	50.9	-27.88
MES-04-05-049	2000.81	162	31.8	3.7	4.3	2.6	7.5	46.5	27.1	56.8	-27.85
MES-04-05-050	2000.82	161	30.6	3.7	4.3	3.9	6.7	45.1	30.8	66.7	-27.69
MES-04-05-051	2000.84	160	29.3	3.8	4.0	2.5	8.7	42.9	32.6	74.2	-27.29
MES-04-05-052	2000.85	159	26.7	3.6	3.6	3.8	9.9	42.4	6.0	93.4	-27.42
MES-04-05-053	2000.87	158	23.7	3.6	3.2	2.9	10.6	35.6	5.0	90.3	-27.03
MES-04-05-054	2000.89	157	19.1	3.4	2.8	3.0	11.2	30.1	n.a.	85.6	-26.92

Sample ID	Age Model	Depth (cm)	Na ⁺	K ⁺	Mg ²⁺	Ca ²⁺	MS ⁻	Cl ⁻	NO ₃ ⁻	SO ₄ ²⁻	δ ¹⁸ O (‰)
MES-04-05-055	2000.90	156	17.0	3.6	2.6	3.2	10.2	26.6	39.5	74.4	-26.62
MES-04-05-056	2000.92	155	16.4	3.5	2.6	3.2	11.1	26.8	41.4	76.2	-26.45
MES-04-05-057	2000.94	154	16.8	3.4	2.4	2.7	14.7	29.0	6.2	87.5	-26.40
MES-04-05-058	2000.95	153	19.3	3.6	2.8	3.2	14.2	38.4	51.2	80.5	-26.17
MES-04-05-059	2000.97	152	50.4	4.1	5.6	4.6	16.4	90.8	45.8	102.1	-26.05
MES-04-05-060	2000.98	151	108.6	4.0	12.7	6.1	21.6	183.0	n.a.	146.8	-25.72
MES-04-05-061	2001.00	150	206.5	6.7	26.0	8.4	25.6	340.6	36.5	169.9	-25.93
MES-04-05-062	2001.03	149	544.1	15.5	64.3	21.5	37.3	851.0	43.9	309.7	-25.79
MES-04-05-063	2001.06	148	239.3	7.0	29.8	11.9	34.0	442.1	n.a.	179.9	-25.76
MES-04-05-064	2001.09	147	53.9	4.7	8.0	5.0	28.0	150.3	50.9	133.9	-26.01
MES-04-05-065	2001.12	146	79.7	4.1	8.6	5.7	35.3	145.9	6.8	170.0	-26.06
MES-04-05-066	2001.15	145	89.2	5.5	9.8	6.5	32.7	150.6	55.6	171.5	-25.92
MES-04-05-067	2001.18	144	97.6	6.8	12.2	8.9	30.7	157.5	52.5	187.7	-26.57
MES-04-05-068	2001.21	143	24.2	4.2	3.8	4.6	33.1	64.8	71.2	104.0	-27.03
MES-04-05-069	2001.24	142	44.7	4.2	5.4	4.1	34.2	83.4	65.7	129.4	-26.62
MES-04-05-070	2001.27	141	83.6	4.5	9.9	5.8	38.2	135.8	59.8	162.7	-26.71
MES-04-05-071	2001.31	140	134.9	6.3	16.3	8.2	38.0	215.7	45.3	200.6	-26.59
MES-04-05-072	2001.34	139	149.2	5.3	18.3	7.5	43.7	244.5	5.0	224.4	-26.77
MES-04-05-073	2001.37	138	139.5	5.3	17.0	8.0	40.2	223.4	15.3	214.6	-27.45
MES-04-05-074	2001.40	137	195.1	7.4	23.1	9.1	39.8	305.9	39.9	252.9	-26.72
MES-04-05-075	2001.43	136	159.0	5.7	19.1	8.0	33.5	257.9	45.3	222.9	-27.26
MES-04-05-076	2001.46	135	144.8	5.0	16.6	7.5	32.8	230.6	4.9	223.8	-28.00
MES-04-05-077	2001.49	134	112.8	4.6	13.3	8.4	30.3	176.8	6.2	197.6	-28.47
MES-04-05-078	2001.52	133	61.0	4.6	7.7	5.3	23.2	101.0	57.8	130.7	-28.99
MES-04-05-079	2001.55	132	26.4	3.8	4.2	4.0	26.4	47.1	8.3	97.7	-28.85
MES-04-05-080	2001.58	131	23.9	3.9	4.1	4.5	21.8	42.2	57.4	87.0	-29.44
MES-04-05-081	2001.64	130	25.8	4.0	4.4	9.1	20.0	45.1	49.1	89.5	-29.25
MES-04-05-082	2001.70	129	39.1	4.2	5.5	6.3	20.4	64.4	48.1	93.2	-29.08
MES-04-05-083	2001.76	128	87.5	4.4	10.3	6.5	19.9	139.1	43.3	105.2	-28.67
MES-04-05-084	2001.82	127	122.3	5.0	15.0	6.9	23.0	197.0	39.8	117.0	-28.49
MES-04-05-085	2001.88	126	136.0	5.1	16.8	7.9	25.9	216.3	38.1	118.9	-28.16
MES-04-05-086	2001.94	125	111.7	5.1	14.4	7.3	26.4	180.9	41.8	110.2	-27.92
MES-04-05-087	2002.00	124	99.6	4.8	12.8	6.6	31.5	165.0	41.1	110.2	-28.20
MES-04-05-088	2002.03	123	115.0	4.9	13.9	12.1	41.4	192.0	n.a.	113.0	-28.07
MES-04-05-089	2002.05	122	120.9	4.9	14.7	7.5	48.7	202.9	n.a.	103.0	-28.49
MES-04-05-090	2002.08	121	112.4	5.3	14.0	6.8	49.2	184.3	20.3	92.7	-28.64
MES-04-05-091	2002.11	120	97.8	4.9	12.4	5.7	55.9	151.5	13.4	119.5	-28.96
MES-04-05-092	2002.13	119	89.4	4.2	10.3	5.4	67.7	131.4	n.a.	148.1	-29.32
MES-04-05-093	2002.16	118	83.8	4.8	10.2	5.6	67.9	118.3	n.a.	154.4	-29.49
MES-04-05-094	2002.18	117	73.8	4.5	9.0	6.0	63.8	102.1	11.4	135.2	-29.79
MES-04-05-095	2002.21	116	78.5	5.5	9.5	8.6	61.2	105.7	13.1	136.3	-29.59
MES-04-05-096	2002.24	115	80.3	5.1	9.8	8.1	59.0	111.2	11.2	127.0	-30.09
MES-04-05-097	2002.26	114	86.0	5.4	9.9	6.8	50.2	127.6	12.3	105.2	-30.43
MES-04-05-098	2002.29	113	94.9	4.3	10.0	6.6	57.5	145.3	n.a.	100.9	-30.43
MES-04-05-099	2002.32	112	94.8	5.2	11.0	6.5	42.4	151.9	13.2	81.9	-30.83
MES-04-05-100	2002.34	111	97.2	4.2	10.1	5.1	46.7	153.2	n.a.	91.8	-31.05
MES-04-05-101	2002.37	110	94.4	4.7	10.9	7.0	37.4	150.6	10.6	82.7	-31.26
MES-04-05-102	2002.40	109	93.9	4.7	10.7	7.0	31.2	150.1	12.8	83.4	-31.60
MES-04-05-103	2002.42	108	100.6	4.8	11.6	6.1	30.1	156.0	10.9	85.8	-32.12
MES-04-05-104	2002.45	107	121.6	5.3	15.0	8.9	23.2	190.0	13.3	104.9	-32.84
MES-04-05-105	2002.47	106	115.4	5.4	15.0	10.1	19.7	178.0	15.5	97.5	-33.66
MES-04-05-106	2002.50	105	100.9	5.1	13.8	9.2	13.1	158.0	20.1	83.1	-34.42
MES-04-05-107	2002.53	104	76.0	4.8	10.3	7.4	12.0	116.8	21.8	62.1	-34.85
MES-04-05-108	2002.55	103	66.7	4.3	8.4	5.6	11.5	104.4	n.a.	61.0	-35.32
MES-04-05-109	2002.58	102	69.9	4.5	9.7	6.4	7.6	106.5	23.9	55.0	-35.28
MES-04-05-110	2002.61	101	65.5	4.3	8.9	5.8	4.8	99.9	27.7	51.3	-35.08
MES-04-05-111	2002.63	100	58.0	4.2	7.9	5.5	5.0	89.9	28.0	51.9	-34.54
MES-04-05-112	2002.66	99	53.5	4.2	7.3	5.1	n.a.	84.3	29.8	50.6	-34.05
MES-04-05-113	2002.69	98	50.9	4.2	7.2	4.5	6.2	82.4	30.3	52.3	-33.27

Sample ID	Age Model	Depth (cm)	Na ⁺	K ⁺	Mg ²⁺	Ca ²⁺	MS ⁻	Cl ⁻	NO ₃ ⁻	SO ₄ ²⁻	δ ¹⁸ O (‰)
MES-04-05-114	2002.71	97	47.7	4.2	6.4	4.2	6.9	73.6	29.9	65.8	-32.48
MES-04-05-115	2002.74	96	38.4	4.2	5.5	4.3	7.1	59.7	32.0	87.9	-31.49
MES-04-05-116	2002.76	95	33.9	4.4	4.8	4.5	7.8	53.2	27.6	91.4	-30.87
MES-04-05-117	2002.79	94	25.0	4.0	3.9	3.6	8.6	38.1	22.6	90.4	-30.26
MES-04-05-118	2002.82	93	15.2	4.0	3.1	3.9	10.0	24.0	18.0	73.4	-29.77
MES-04-05-119	2002.84	92	11.9	3.7	2.3	2.0	9.8	19.6	14.0	68.1	-29.32
MES-04-05-120	2002.87	91	12.7	3.7	2.2	2.7	9.3	19.9	13.9	70.9	-28.94
MES-04-05-121	2002.90	90	13.1	4.2	2.7	8.6	10.1	17.8	11.5	77.9	-28.71
MES-04-05-122	2002.92	89	14.0	3.8	2.7	5.6	10.1	18.7	9.2	79.3	-28.79
MES-04-05-123	2002.95	88	18.5	3.9	2.7	3.7	10.4	21.8	9.7	81.4	-28.29
MES-04-05-124	2002.97	87	17.8	3.7	2.9	4.0	10.6	25.1	12.5	80.7	-28.09
MES-04-05-125	2003.00	86	18.5	3.7	3.0	3.4	11.1	25.5	11.0	77.8	-28.16
MES-04-05-126	2003.03	85	18.9	3.6	3.0	3.6	12.1	27.2	n.a.	83.6	-28.04
MES-04-05-127	2003.05	84	24.2	7.5	3.2	4.5	10.4	34.6	20.1	82.1	-28.20
MES-04-05-128	2003.08	83	18.0	4.1	2.9	3.5	11.0	29.0	25.5	82.1	-28.16
MES-04-05-129	2003.10	82	18.0	4.8	2.8	3.8	9.4	30.6	29.0	79.5	-28.34
MES-04-05-130	2003.13	81	16.6	4.1	2.6	2.9	10.1	28.5	32.5	76.8	-28.39
MES-04-05-131	2003.15	80	18.2	4.6	2.7	3.4	9.8	31.2	31.3	79.6	-28.56
MES-04-05-132	2003.18	79	17.7	4.2	2.7	2.5	9.2	31.0	29.9	79.2	-28.31
MES-04-05-133	2003.20	78	17.5	3.8	2.6	2.5	9.9	32.0	29.6	81.9	-28.65
MES-04-05-134	2003.23	77	16.8	4.6	2.6	3.4	9.0	31.8	45.5	79.3	-28.77
MES-04-05-135	2003.25	76	17.3	3.9	2.5	2.9	8.9	34.3	18.2	91.9	-28.86
MES-04-05-136	2003.28	75	14.5	4.5	2.4	2.6	8.9	32.7	52.3	85.2	-28.94
MES-04-05-137	2003.30	74	13.2	4.5	2.2	3.3	9.7	31.7	56.7	86.3	-28.84
MES-04-05-138	2003.33	73	13.3	4.8	2.2	2.6	11.1	31.1	57.6	87.8	-28.95
MES-04-05-139	2003.35	72	10.9	4.4	2.1	2.7	12.5	22.0	42.3	86.5	-29.03
MES-04-05-140	2003.38	71	12.8	5.5	2.1	3.3	13.0	22.5	49.6	86.2	-29.03
MES-04-05-141	2003.40	70	11.2	4.6	2.0	2.8	13.2	20.7	32.2	80.6	-29.11
MES-04-05-142	2003.43	69	12.1	4.5	2.1	2.4	12.8	21.7	20.1	76.4	-29.15
MES-04-05-143	2003.45	68	12.6	4.5	2.4	2.6	12.1	22.2	25.8	79.1	-29.01
MES-04-05-144	2003.48	67	12.3	4.4	2.3	3.5	11.6	21.6	24.4	74.9	-29.07
MES-04-05-145	2003.50	66	12.6	4.7	2.8	3.8	11.3	21.9	24.2	76.9	-29.23
MES-04-05-146	2003.53	65	12.6	4.7	2.2	2.9	13.1	21.7	24.8	80.8	-29.19
MES-04-05-147	2003.55	64	12.4	3.9	2.2	2.7	14.6	22.9	5.1	88.3	-29.09
MES-04-05-148	2003.58	63	15.3	5.7	2.7	2.6	18.1	23.6	21.9	118.2	-29.24
MES-04-05-149	2003.60	62	16.7	4.7	3.1	3.2	18.4	24.3	20.6	140.3	-29.05
MES-04-05-150	2003.63	61	16.8	5.1	3.0	3.6	18.7	28.4	41.4	136.5	-28.93
MES-04-05-151	2003.65	60	15.3	5.3	2.7	3.6	18.9	32.5	57.7	120.5	-28.98
MES-04-05-152	2003.67	59	11.9	4.9	2.6	5.1	13.2	29.3	38.3	93.8	-28.62
MES-04-05-153	2003.70	58	15.1	5.3	2.8	4.1	20.5	32.6	62.4	134.0	-28.63
MES-04-05-154	2003.72	57	14.3	5.2	2.6	4.0	20.9	28.8	71.0	141.1	-28.33
MES-04-05-155	2003.74	56	15.1	5.5	2.8	3.9	22.4	29.7	74.3	153.3	-28.34
MES-04-05-156	2003.77	55	16.2	5.0	2.8	3.3	22.4	31.0	74.2	157.5	-28.21
MES-04-05-157	2003.79	54	16.6	5.1	2.8	4.3	22.5	32.3	70.0	156.8	-28.29
MES-04-05-158	2003.81	53	15.0	5.1	2.6	3.5	22.9	33.8	77.8	157.7	-28.06
MES-04-05-159	2003.84	52	12.9	4.9	2.4	3.3	22.3	32.1	88.0	153.5	-28.11
MES-04-05-160	2003.86	51	14.6	5.3	2.7	4.4	21.8	33.1	85.5	167.5	-27.98
MES-04-05-161	2003.88	50	15.0	5.3	2.8	3.8	21.6	33.5	81.9	183.3	-27.67
MES-04-05-162	2003.91	49	15.6	5.4	2.9	4.5	21.1	35.0	89.4	192.3	-27.37
MES-04-05-163	2003.93	48	15.6	5.6	2.8	3.4	22.2	33.8	91.8	202.9	-27.31
MES-04-05-164	2003.95	47	16.6	5.8	3.0	3.2	20.0	33.7	94.8	214.0	-27.21
MES-04-05-165	2003.98	46	16.8	6.0	3.5	8.5	21.2	34.1	92.6	221.5	-27.13
MES-04-05-166	2004.00	45	16.3	5.8	3.2	4.7	19.8	32.0	90.8	218.9	-27.04
MES-04-05-167	2004.06	44	17.5	5.8	8.9	14.5	19.8	35.8	100.4	227.3	-27.14
MES-04-05-168	2004.13	43	19.5	7.0	3.6	4.9	18.8	38.1	94.4	230.9	-27.56
MES-04-05-169	2004.19	42	9.1	5.3	2.0	3.7	5.9	35.4	64.6	95.3	-27.75
MES-04-05-170	2004.26	41	17.9	5.8	3.1	4.1	16.2	38.5	83.6	198.1	-28.34
MES-04-05-171	2004.32	40	21.5	5.9	3.4	3.9	14.1	41.8	61.9	186.0	-29.08

Sample ID	Age Model	Depth (cm)	Na ⁺	K ⁺	Mg ²⁺	Ca ²⁺	MS ⁻	Cl ⁻	NO ₃ ⁻	SO ₄ ²⁻	δ ¹⁸ O (‰)
MES-04-05-172	2004.39	39	14.8	5.9	2.8	4.1	12.8	28.4	54.5	166.3	-29.41
MES-04-05-173	2004.45	38	10.3	5.0	2.1	2.5	13.0	20.1	7.8	150.4	-29.92
MES-04-05-174	2004.52	37	9.2	5.2	2.1	2.5	10.5	20.6	18.4	141.9	-30.44
MES-04-05-175	2004.58	36	9.3	5.4	2.8	2.6	9.0	21.5	18.9	132.7	-30.53
MES-04-05-176	2004.59	35	9.2	5.7	2.0	3.6	7.8	20.4	17.7	112.1	-30.50
MES-04-05-177	2004.60	34	7.5	5.1	1.7	2.8	6.8	15.8	10.0	78.5	-30.17
MES-04-05-178	2004.61	33	5.1	4.8	1.5	2.6	6.3	12.7	5.4	60.9	-30.13
MES-04-05-179	2004.63	32	4.1	3.9	1.3	2.3	4.3	10.8	n.a.	52.0	-29.47
MES-04-05-180	2004.64	31	4.3	4.7	1.4	3.0	4.3	12.0	7.1	52.2	-29.01
MES-04-05-181	2004.65	30	5.1	4.7	1.4	2.5	4.6	12.6	7.2	54.4	-28.63
MES-04-05-182	2004.66	29	5.1	4.9	26.0	1.9	4.2	13.1	5.4	57.0	-28.17
MES-04-05-183	2004.67	28	4.2	4.8	3.2	2.4	5.3	11.5	n.a.	53.7	-27.74
MES-04-05-184	2004.68	27	3.0	4.8	1.5	1.7	4.9	9.5	6.8	47.5	-27.46
MES-04-05-185	2004.69	26	2.8	5.0	1.2	2.4	5.6	9.5	5.6	48.2	-27.11
MES-04-05-186	2004.70	25	2.3	4.8	1.2	1.8	6.1	8.8	5.8	46.4	-26.94
MES-04-05-187	2004.72	24	2.4	4.5	1.2	1.6	6.5	8.8	5.2	49.8	-26.58
MES-04-05-188	2004.73	23	8.1	4.8	1.6	1.7	7.2	25.1	7.1	68.4	-26.43
MES-04-05-189	2004.74	22	9.1	4.9	1.8	2.7	7.4	28.9	10.4	74.3	-26.58
MES-04-05-190	2004.75	21	16.5	5.2	2.5	2.6	6.8	47.7	8.8	76.1	-26.38
MES-04-05-191	2004.76	20	11.7	5.1	2.4	3.4	5.6	21.9	6.0	47.4	-24.99
MES-04-05-192	2004.77	19	13.6	5.7	2.1	2.2	8.0	22.0	5.7	38.4	-24.25
MES-04-05-193	2004.78	18	44.7	11.5	3.0	3.7	11.9	65.9	5.7	44.3	-23.49
MES-04-05-194	2004.79	17	48.4	7.7	5.0	3.9	18.4	68.1	5.3	64.3	-22.82
MES-04-05-195	2004.81	16	54.4	6.0	5.8	3.5	22.1	73.5	4.9	76.3	-22.41
MES-04-05-196	2004.82	15	44.5	5.9	5.8	3.7	23.6	59.2	5.4	69.9	-21.87
MES-04-05-197	2004.83	14	42.9	5.8	5.5	4.0	22.3	56.3	5.3	66.8	-21.46
MES-04-05-198	2004.84	13	33.4	5.5	4.5	3.5	24.0	46.0	5.2	60.0	-21.50
MES-04-05-199	2004.85	12	31.2	5.7	4.3	2.8	27.5	44.5	5.3	68.1	-21.67
MES-04-05-200	2004.86	11	42.9	5.9	5.3	4.1	31.1	65.4	8.4	79.4	-21.94
MES-04-05-201	2004.87	10	50.0	5.9	6.2	3.7	37.6	75.3	16.0	87.5	-22.62
MES-04-05-202	2004.88	9	62.9	6.4	7.7	4.1	36.5	99.0	27.1	104.9	-23.27
MES-04-05-203	2004.90	8	100.9	10.2	15.2	17.4	39.6	117.7	79.1	223.2	-31.32
MES-04-05-204	2004.91	7	78.3	23.3	11.0	17.9	11.0	104.5	80.4	134.6	-31.17
MES-04-05-205	2004.92	6	74.6	8.0	10.1	7.7	42.3	80.3	18.2	190.8	-32.01
MES-04-05-206	2004.93	5	65.9	7.4	9.0	7.0	32.1	70.4	38.2	158.7	-31.57
MES-04-05-207	2004.94	4	80.6	9.3	11.1	8.3	44.9	83.9	44.3	203.4	-31.61

n.a. = not available

Figure A1: Scatterplots of annual mean MS^- values against A) annual mean open water area and B) annual production. The equations of the linear trendlines are displayed. Correlations are significant at 95% (A) and 99% (B) levels. Using Isoplot software (version 3.0, K. R. Ludwig, Berkeley Geochronology Centre, (2003)) errors on the slope and intercept of each linear trendline at 95% confidence level are: A) slope ± 0.0018 , intercept ± 0.046 ; B) slope ± 0.70 , intercept ± 18 .

Appendix II: Procedural blanks for Mt Erebus Saddle ice core processing and sampling.

Ultra-pure water ($> 18.2 \text{ M}\Omega$) was frozen in 500 mL Nalgene jars to create mock ice core. This core was then cut in the cold laboratory and sampled using the continuous melter system following the same procedure as for the MES ice core. The procedural blanks were treated as ice core samples during analysis and data processing. Any background contribution from the analytical instrument, ultra-pure water or acid added to the procedural blanks has therefore been corrected for. Blanks for ICP-MS and IC were sampled concurrently from the same section of mock ice core so ICP-MS and IC blanks with the same blank I.D. are directly comparable. Concentrations of trace elements in the procedural blanks determined by ICP-MS are provided in Table A2 and major ion concentrations determined by ion chromatography are provided in Table A3. Due to time constraints not all procedural blanks were analysed by ICP-MS and only blanks 1 to 34 have been analysed by IC to date. Procedural blanks were sampled at the beginning of each day the melter system was used.

Table A2: Concentrations of trace elements determined by ICP-MS in the procedural blanks. Blanks that are in bold and italicised had problems that were noted down in melting log book which adversely affected chemical concentrations (see footnotes pg. 192). Concentrations are given in ppt.

Blank I.D.	Date melted	Na	Mg	Al	Ca	Ti	V	Mn	As	Rb	Sr	Y	Zr	Cs	Ba	La	Ce	Pr	Tl	Pb	Bi	Th	U
MES Blk 1	16/10/2007	4499	1967	1758	170913	35.49	2.20	74.73	-1.32	-0.52	-0.11	1.24	-0.15	-0.17	78.98	0.33	0.37	0.14	0.03	12.94	0.03	0.00	0.09
MES Blk 3	16/10/2007	231	261	170	45937	9.00	0.88	11.01	0.63	0.58	21.68	0.31	0.08	-0.01	7.48	0.09	0.07	0.02	-0.04	2.05	0.17	0.03	0.08
MES Blk 4	16/10/2007	-42	126	184	14990	5.20	0.98	6.46	0.05	0.23	5.35	0.10	0.11	0.02	3.92	0.05	0.06	0.01	-0.03	1.78	0.10	-0.12	0.22
MES Blk 6	17/10/2007	2000	650	693	23792	55.87	1.68	28.94	3.16	1.98	17.08	0.63	0.51	0.12	68.47	0.34	0.54	0.16	0.01	18.35	0.03	0.21	0.06
MES Blk 8	18/10/2007	204	118	109	642	-6.39	0.31	0.06	0.15	0.17	1.17	0.03	0.22	0.01	1.29	0.04	0.06	0.01	-0.01	1.23	-0.01	0.00	0.01
MES Blk 10	18/10/2007	62	236	324	96457	7.90	0.80	15.98	0.04	0.20	22.15	0.69	0.02	0.00	4.09	0.20	0.11	0.04	-0.06	0.60	0.01	-0.04	0.12
MES Blk 12	18/10/2007	157	263	307	9647	16.07	1.82	7.24	1.22	0.38	8.61	0.10	0.29	0.02	15.68	0.26	0.42	0.04	0.03	2.22	0.08	0.06	0.04
MES Blk 14	5/02/2008	-86	156	193	13575	7.87	0.53	17.38	-0.27	0.25	7.75	0.08	0.14	0.02	11.15	0.03	0.04	-0.03	-0.01	2.29	0.04	0.08	0.01
MES Blk 15	5/02/2008	-190	78	105	2603	9.14	0.30	6.49	-0.56	0.22	3.33	0.03	-0.01	0.02	6.32	0.04	0.02	0.01	0.06	1.32	0.08	-0.04	0.02
MES Blk 16	5/02/2008	88	116	556	11214	28.53	0.21	6.59	-0.72	0.14	6.90	0.11	0.06	0.02	7.55	0.03	0.02	0.00	0.03	1.73	-0.01	0.06	0.04
MES Blk 17	5/02/2008	139	132	127	15123	15.00	0.63	12.28	2.32	0.28	7.03	0.12	0.06	0.05	11.66	0.09	0.10	0.02	0.05	5.34	0.15	-0.01	-0.02
MES Blk 18	5/02/2008	367	151	150	17992	13.87	0.64	14.46	2.99	0.44	8.26	0.19	-0.02	0.05	13.57	0.10	0.22	0.03	0.08	6.41	0.02	-0.01	0.01
MES Blk 20	8/02/2007	37	142	109	49755	13.56	0.59	11.38	0.40	0.16	12.73	0.31	0.12	0.02	4.28	0.07	0.03	0.02	-0.04	1.61	0.04	0.00	-0.03
MES Blk 21	8/02/2007	-150	65	124	6543	19.91	0.74	5.79	-0.41	0.12	2.96	0.04	0.13	0.01	4.82	0.03	0.05	0.00	0.07	1.42	0.12	0.00	0.05
MES Blk 23	13/02/2008	157	88	101	3975	13.13	0.30	8.40	-0.54	0.23	5.86	0.09	0.20	-0.01	4.31	0.07	0.06	0.00	0.00	0.88	0.08	0.06	0.13
MES Blk 24	13/02/2008	210	40	72	1468	7.88	0.25	3.71	-0.75	0.14	3.09	0.04	0.04	0.00	2.79	0.08	0.05	0.00	0.05	1.33	0.09	0.01	0.13
MES Blk 25	13/02/2008	4635	597	85	17375	18.17	0.68	10.39	0.63	1.83	9.98	0.11	0.50	0.01	6.27	2.53	0.75	0.00	0.09	2.84	0.10	0.06	0.10
MES Blk 26	18/02/2008	289	57	53	1667	4.77	0.22	9.03	-0.17	0.27	4.47	0.05	0.26	0.00	8.70	0.05	0.09	0.00	0.09	1.51	0.03	-0.02	0.02
MES Blk 27	18/02/2008	821	112	97	2412	6.81	0.19	6.50	-0.62	0.33	4.83	0.05	0.21	-0.01	5.70	0.54	0.17	0.00	0.04	2.07	0.07	0.01	0.06
MES Blk 28	18/02/2008	1856	180	136	2308	2.40	0.25	5.50	-1.14	1.26	5.38	0.05	0.24	-0.02	4.53	1.09	0.35	0.00	-0.04	2.25	-0.01	-0.05	-0.03
MES Blk 29	18/03/2008	243	94	506	3676	1.43	0.22	3.31	2.04	0.31	6.81	0.03	0.33	0.03	1.48	0.17	0.29	0.00	0.02	2.73	-0.02	-0.03	0.02
MES Blk 30	18/03/2008	119	14	405	493	-0.48	0.11	-0.35	0.00	0.08	2.02	0.02	-0.01	0.00	0.69	0.05	0.10	0.00	0.01	1.27	0.03	-0.02	0.00
MES Blk 31	18/03/2008	76	29	460	2754	0.95	0.12	0.50	1.46	0.07	3.32	0.02	0.07	0.01	0.65	0.05	0.09	0.00	0.04	1.03	-0.01	-0.02	0.02
MES Blk 32	19/03/2008	91	29	134	492	8.80	0.15	4.16	0.14	0.23	2.61	0.05	0.19	0.03	3.17	0.08	0.14	0.00	0.00	1.56	0.05	-0.04	0.01
MES Blk 33	19/03/2008	165	761	487	2376	3.09	0.19	22.00	2.07	0.19	3.61	0.08	0.24	0.03	3.67	0.30	0.50	0.00	-0.01	3.12	-0.06	-0.05	-0.05
MES Blk 34	19/03/2008	4	33	169	552	-0.66	0.04	1.42	0.21	0.05	3.38	0.02	-0.03	0.03	3.66	0.05	0.09	0.00	0.03	1.00	0.00	-0.04	-0.03
MES Blk 35	26/03/2008	103	43	93	647	13.55	0.07	3.35	1.45	0.05	3.56	0.04	-0.02	0.01	1.03	0.04	0.09	0.00	0.03	0.49	0.01	-0.07	-0.03
MES Blk 36	26/03/2008	107	163	573	4178	-0.34	0.10	4.38	0.27	0.10	4.26	0.05	0.04	0.02	2.33	0.05	0.08	0.00	0.01	3.37	0.01	-0.03	-0.06
MES Blk 37	26/03/2008	54	50	38	261	0.04	0.15	1.41	0.32	0.05	3.05	0.02	-0.02	0.01	0.66	0.04	0.07	0.00	0.00	0.26	0.00	-0.05	0.03
MES Blk 38	2/04/2008	4105	2720	39171	90884	193.16	1.90	45.58	0.74	1.48	66.56	1.17	25.78	0.14	46.18	0.70	1.32	0.14	0.03	98.25	0.54	0.02	0.15
MES Blk 39	2/04/2008	64	109	134	1126	4.27	0.48	2.22	0.35	0.17	1.26	0.04	0.23	0.03	1.92	0.07	0.14	0.03	0.12	1.66	0.05	0.00	0.07
MES Blk 40	2/04/2008	-117	123	217	2451	11.89	0.21	4.30	0.00	0.16	1.69	0.04	0.10	0.03	1.94	0.08	0.10	0.00	-0.08	4.24	0.02	0.05	0.09
MES Blk 41	9/04/2008	217	86	120	1458	12.55	0.43	6.97	1.40	0.20	2.33	0.03	0.10	0.03	3.51	0.12	0.12	0.00	-0.06	2.30	0.04	0.09	0.05
MES Blk 42	9/04/2008	279	81	100	2967	6.79	0.31	6.57	-0.53	0.12	2.71	0.10	0.30	0.02	2.27	0.05	0.09	0.01	0.00	1.76	0.00	0.08	0.07
MES Blk 43	9/04/2008	448	87	119	2133	6.09	0.26	2.97	-0.23	0.25	2.74	0.01	0.14	0.00	3.14	0.10	0.12	0.00	-0.07	1.55	-0.12	0.08	0.02

Blank I.D.	Date melted	Na	Mg	Al	Ca	Ti	V	Mn	As	Rb	Sr	Y	Zr	Cs	Ba	La	Ce	Pr	Tl	Pb	Bi	Th	U
MES Blk 49	29/05/2008	356	206	303	50325	2.02	1.44	40.21	0.76	0.41	15.01	0.44	0.10	0.02	8.06	0.12	0.11	0.01	0.02	2.41	0.01	-0.02	0.02
MES Blk 51	4/06/2008	16	34	55	718	-2.41	0.18	-0.79	-0.02	0.12	0.77	0.04	0.24	0.01	0.98	0.01	0.03	0.01	-0.03	0.95	0.02	-0.01	0.01
MES Blk 52	4/06/2008	265	177	335	4172	23.47	1.04	89.28	3.28	0.25	2.54	0.09	1.06	0.05	3.57	0.09	0.18	0.03	0.03	1.41	0.01	0.01	0.01
MES Blk 54	17/09/2008	362	332	1666	21466	22.16	0.45	13.47	0.49	0.39	9.17	0.28	4.35	0.01	5.45	0.12	0.16	0.01	-0.01	3.93	0.03	0.01	0.02
MES Blk 55	17/09/2008	90	195	143	10057	-5.34	0.06	3.73	0.14	0.22	3.74	0.40	2.20	0.01	1.37	0.13	0.13	0.03	-0.01	6.70	0.01	0.00	0.02
MES Blk 57	25/09/2008	202	111	348	1818	-4.67	0.18	1.18	0.22	0.12	1.00	0.31	12.32	0.02	2.79	0.11	0.10	0.02	0.03	0.47	0.05	-0.01	-0.02
MES Blk 58	25/09/2008	51	26	220	169	2.57	0.00	-1.01	0.02	0.09	0.45	0.29	3.23	0.01	2.82	0.01	0.03	0.01	-0.02	0.34	0.00	-0.03	-0.03
MES Blk 60	25/09/2008	122	181	162	2035	-1.42	0.10	5.13	0.35	0.10	1.75	0.05	1.36	0.01	2.74	0.15	0.18	0.02	-0.03	0.38	-0.01	0.00	-0.02
MES Blk 60A	1/10/2008	52	31	45	804	-1.49	0.07	0.01	0.26	0.28	1.23	0.01	0.06	0.02	1.38	0.01	0.03	0.01	0.02	0.69	-0.01	0.00	-0.03
MES Blk 63	6/10/2008	82	25	40	393	-5.14	0.06	-1.61	0.22	0.10	0.56	0.02	0.59	0.01	0.73	0.00	0.01	0.00	-0.01	0.28	0.01	-0.01	-0.02
MES Blk 64	6/10/2008	9	55	56	1267	18.16	0.04	-0.65	0.22	0.11	0.73	0.46	0.40	0.01	1.04	0.00	0.02	0.01	0.02	0.38	0.01	0.00	-0.02
MES Blk 66	7/10/2008	60	30	68	400	-0.99	0.17	-2.17	0.03	0.08	0.60	0.03	0.01	0.00	0.64	0.02	0.02	0.00	-0.04	0.19	-0.02	0.02	0.00
MES Blk 67	13/10/2008	12050	357	209	1466	123.64	0.19	29.30	1.76	1.43	5.61	0.31	2.02	0.07	18.29	0.75	1.67	0.18	-0.04	4.69	-0.05	0.15	0.06
MES Blk 68	13/10/2008	4719	3601	36584	22761	3674.94	6.60	1112.01	0.26	1.44	81.93	0.67	11.87	0.42	116.32	0.98	11.02	0.30	0.04	112.12	0.11	0.83	0.84
MES Blk 69	16/10/2008	183	320	183	1319	62.39	0.21	20.49	0.30	0.13	6.62	0.21	0.49	0.04	6.24	0.05	0.39	0.02	-0.06	3.93	-0.07	0.03	0.00
MES Blk 70	16/10/2008	248	151	1261	1169	13.84	0.16	0.28	0.40	0.12	1.20	0.40	1.49	0.03	2.73	0.05	0.37	0.02	-0.01	3.35	-0.02	0.09	0.01
MES Blk 72	20/10/2008	235	37	68	648	-5.53	0.32	0.03	0.15	0.16	0.57	0.05	0.89	0.02	1.27	0.06	0.08	0.02	-0.02	0.56	-0.03	0.04	0.00
MES Blk 75	13/11/2008	14271	66	358	2797	7.98	0.15	8.67	0.20	0.30	3.04	0.05	0.49	0.16	3.64	0.05	0.09	0.03	-0.02	1.66	0.00	0.03	-0.01
MES Blk 76	13/11/2008	-440	105	137	6836	16.21	0.14	10.02	0.34	0.45	5.22	0.04	1.39	0.02	4.70	0.05	0.09	0.01	-0.01	5.55	0.07	0.10	0.00
MES Blk 77	18/11/2008	-312	104	139	3145	12.30	0.16	8.60	0.06	0.23	2.75	0.10	0.33	0.02	3.10	0.04	0.08	0.01	0.00	1.22	-0.01	0.02	0.01
MES Blk 78	18/11/2008	39597	2948	4961	13907	2675.44	5.71	25.36	0.37	0.83	14.46	1.07	47.10	0.43	42.15	0.78	9.97	0.26	0.05	107.67	0.11	0.71	0.71
MES Blk 80	20/11/2008	3734	65	105	1875	8.52	0.13	15.02	-0.40	0.18	2.59	0.04	0.09	0.03	3.01	0.05	0.07	0.02	0.04	1.47	0.00	0.01	0.01
MES Blk 81	16/07/2009	9730	10805	69361	73365	9580.48	17.96	74.29	-0.23	1.77	495.91	2.13	36.18	0.96	161.69	3.20	23.27	1.11	0.13	216.08	2.13	1.85	2.43
MES Blk 82	16/07/2009	23	32	135	1939	11.06	0.00	4.94	-0.33	0.11	1.39	0.02	2.71	0.01	2.08	0.03	0.05	0.01	-0.02	3.07	0.03	0.02	0.02
MES Blk 83	16/07/2009	105	161	2710	2736	263.86	0.60	4.44	-0.51	0.15	3.98	0.05	0.81	0.03	4.15	0.10	0.86	0.02	-0.08	11.09	-0.01	0.04	0.07
MES Blk 84	20/07/2009	623	189	1647	3899	317.38	0.76	26.02	0.13	0.42	4.92	0.06	1.81	0.07	7.86	0.11	0.61	0.04	-0.06	9.83	0.01	0.26	0.07
MES Blk 85	20/07/2009	47	40	93	1691	4.89	0.14	4.43	-0.40	0.12	1.36	0.02	0.55	0.01	3.62	0.04	0.07	0.01	-0.11	2.55	-0.01	0.03	0.02
MES Blk 86	20/07/2009	-28	23	181	1014	25.44	0.24	4.38	0.06	0.10	1.39	0.01	2.19	0.02	23.91	0.03	0.07	0.01	0.00	2.16	-0.06	0.24	0.01
MES Blk 87	28/07/2009	300	91	134	2721	102.52	0.49	23.66	0.70	0.52	3.58	0.09	1.61	0.03	4.71	0.09	0.21	0.03	-0.03	4.91	0.02	0.02	0.02
MES Blk 88	28/07/2009	723	167	235	3985	86.78	1.27	78.99	1.92	0.80	5.05	0.15	2.46	0.03	8.25	0.13	0.20	0.03	-0.03	7.36	0.01	0.12	0.02
MES Blk 89	28/07/2009	1198	1097	9831	13212	837.54	2.88	30.76	0.59	0.81	12.59	0.49	3.90	0.38	11.26	0.59	3.87	0.10	0.00	22.96	0.21	0.17	0.24
MES Blk 90	30/07/2009	842	621	5319	5224	1224.32	2.40	13.95	0.44	0.59	5.25	0.18	1.52	0.10	6.69	0.31	3.36	0.06	0.05	27.16	0.06	0.19	0.33
MES Blk 91	30/07/2009	156	64	126	774	2.51	0.31	5.80	0.25	0.31	1.09	0.05	0.10	0.03	3.39	0.10	0.22	0.02	0.03	2.28	0.06	0.03	0.01
MES Blk 92	30/07/2009	14442	4592	2820	8772	94.17	20.23	88.11	1.60	8.15	7.36	26.76	11.05	1.25	20.79	42.53	89.51	12.48	0.13	6.00	0.02	3.93	0.65
MES Blk 93	31/07/2009	669	308	644	11058	134.48	0.95	41.21	1.08	1.60	13.64	0.19	0.88	0.08	11.07	0.36	0.69	0.69	-0.07	9.70	0.03	0.05	0.09
MES Blk 94	31/07/2009	685	262	978	11737	162.82	1.55	65.30	1.46	1.62	14.88	0.31	3.23	0.11	24.35	0.39	0.84	0.10	-0.06	11.40	0.59	0.08	0.11
MES Blk 95	31/07/2009	1066	240	99	5952	55.22	0.62	26.41	0.91	1.09	8.89	0.54	16.98	0.06	11.63	0.14	0.29	0.03	0.03	5.47	-0.02	0.02	0.01
MES Blk 96	2/06/2010	3843	1637	329	8102	53.67	0.26	25.17	-1.83	-0.30	-0.29	0.11	-0.46	-0.12	14.19	0.12	0.19	0.00	0.01	6.61	1.32	-0.19	0.02

Blank I.D.	Date melted	Na	Mg	Al	Ca	Ti	V	Mn	As	Rb	Sr	Y	Zr	Cs	Ba	La	Ce	Pr	Tl	Pb	Bi	Th	U
MES Blk 97	2/06/2010	5380	933	495	11518	130.37	0.73	29.90	-1.74	-0.32	-0.24	0.84	-0.48	-0.12	27.93	0.19	0.38	0.00	0.00	16.33	0.47	-0.18	0.03
MES Blk 98	2/06/2010	7114	859	304	12183	44.28	0.43	17.65	1.05	3.61	13.13	0.35	2.17	0.18	17.86	0.11	0.26	0.00	0.00	9.99	0.23	0.03	0.01
MES Blk 101	3/06/2010	1091	537	937	10498	86.28	1.82	12.52	nm	1.41	12.16	0.17	3.36	0.20	7.47	0.08	0.12	0.02	0.00	20.31	0.14	0.03	0.00
MES Blk 102	3/06/2010	497	128	277	3264	71.63	0.35	11.58	nm	1.22	3.56	0.06	0.65	0.05	6.91	0.10	0.29	0.03	0.01	5.51	0.10	0.03	-0.01
MES Blk 104	4/06/2010	735	145	541	2894	39.96	0.60	14.61	nm	1.65	4.06	0.21	1.43	0.07	9.48	0.45	0.90	0.11	0.00	7.16	3.25	0.13	0.04
MES Blk 105	4/06/2010	655	395	208	3237	33.09	0.40	13.75	nm	0.91	5.60	0.04	0.68	0.04	7.50	0.34	0.13	0.01	0.03	4.42	0.54	0.00	-0.01
MES Blk 106	8/06/2010	141	164	681	5418	38.45	0.15	5.53	nm	0.48	3.89	0.06	0.35	0.03	3.80	0.07	0.12	0.02	-0.01	2.67	0.10	-0.01	0.00
MES Blk 108	8/06/2010	33	117	265	3896	1.96	0.14	4.50	nm	nm	nm	0.04	nm	nm	2.17	0.06	0.15	0.02	-0.02	1.96	0.00	0.00	0.00
MES Blk 110	11/06/2010	35	683	132	10521	3.78	0.19	10.87	nm	1.16	4.66	0.13	24.05	0.02	0.63	0.03	0.07	0.00	0.02	0.23	0.03	0.00	0.02
MES Blk 111	11/06/2010	5	35	100	286	6.99	0.05	4.74	nm	0.06	0.16	0.00	0.17	0.01	0.24	-0.01	0.01	-0.01	0.02	0.10	0.03	0.01	0.01
MES Blk 112	14/06/2010	7	1277	190	2972	12.52	0.05	17.45	nm	nm	nm	3.14	72.60	nm	1.12	nm	0.04	-0.01	0.00	0.74	0.00	0.00	0.01
MES Blk 114	14/06/2010	9	49	860	1046	5.15	0.25	4.19	nm	nm	nm	1.30	31.45	nm	2.33	nm	0.22	0.03	0.03	2.17	0.00	0.00	0.00
MES Blk 116	15/06/2010	49	25	169	1058	1.75	0.04	-0.74	nm	nm	nm	0.03	3.40	nm	2.78	0.00	0.02	0.01	0.00	0.46	0.00	0.00	0.02
MES Blk 117	15/06/2010	24	26	148	986	-1.18	0.15	1.06	nm	nm	nm	0.01	0.52	nm	0.45	0.02	0.05	0.01	-0.02	1.26	0.00	0.00	0.01
MES Blk 118	16/06/2010	106	33	132	1121	3.80	0.02	-0.39	nm	nm	nm	0.01	1.53	nm	0.71	0.01	0.02	0.00	0.00	0.19	0.00	0.00	-0.02
MES Blk 119	16/06/2010	29	20	118	696	1.16	0.12	0.38	nm	0.06	0.44	0.01	0.40	-0.01	0.41	0.05	0.10	0.00	-0.02	0.46	0.02	-0.01	0.02
MES Blk 121	21/06/2010	66	38	240	1487	2.99	0.11	0.55	nm	0.21	0.87	0.05	-0.02	0.01	0.82	0.08	0.20	0.03	-0.03	1.66	0.04	-0.01	0.01
MES Blk 122	22/06/2010	82	-18	141	1181	5.27	0.11	2.13	nm	0.25	0.85	0.05	0.16	0.02	1.21	0.10	0.17	0.02	0.00	1.40	0.04	-0.02	0.01
MES Blk 123	22/06/2010	68	-4	146	1474	3.87	0.11	6.22	nm	0.27	1.10	0.03	0.12	0.02	1.14	0.07	0.11	0.02	0.01	2.01	0.00	0.01	0.01
MES Blk 125	23/06/2010	210	429	515	3567	1.18	-0.06	8.21	nm	nm	nm	0.04	0.13	nm	2.15	0.08	0.14	0.04	0.01	6.38	0.00	0.00	0.02
MES Blk 126	28/06/2010	26	-35	141	348	1.79	-0.06	0.01	nm	0.04	0.24	0.01	0.11	0.00	0.16	0.02	0.03	0.01	0.00	0.05	-0.01	-0.02	0.00
MES Blk 127	28/06/2010	22	127	144	1451	0.28	-0.06	1.97	nm	0.05	0.61	0.02	0.09	0.01	0.23	0.02	0.01	0.01	0.00	0.10	0.01	-0.01	0.03
Mean procedural blank		1558	478	2075	10649	217.20	0.98	25.60	0.39	0.55	12.07	0.52	3.73	0.06	10.51	0.66	1.68	0.18	0.00	9.36	0.12	0.10	0.08
Mean procedural blank (excl. bold, italicised values)		1127	290	561	7025	78.50	0.70	10.90	0.33	0.47	4.54	0.50	3.03	0.05	5.39	0.66	1.42	0.17	0.00	4.68	0.09	0.07	0.04

nm = element not measured. Values in grey are below the detection limit.

Problems noted down in melting log book for bold, italicised blanks:

MES Blank 1 = 1st blank to be sampled on continuous melter at New Zealand Ice Core Laboratory.

MES Blank 6 = Pump for outer line suction was not working so blank would have received material from outer section of mock core.

MES Blank 38 = Pump for outer line suction was not working so blank would have received material from outer section of mock core.

MES Blanks 67, 68 = Mock ice core cut too narrow so that it barely covered the inner circle of melt disk.

MES Blanks 75, 76 = New melter head used for first time.

MES Blank 81 = 1st blank to be run through melter head after it was anodised.

MES Blanks 93, 94, 95 = Small piece of mock ice did not sit well over inner circle of melt disk.

Table A3: Concentrations of major ions (ppb) determined by IC in the procedural blanks.

Blank I.D.	Na ⁺	K ⁺	Mg ²⁺	Ca ²⁺	MS ⁻	Cl ⁻	SO ₄ ²⁻	NO ₃ ⁻
MES Blk 1	1.05	0.17	1.99	41.9	n.a.	29.0	12.7	9.55
MES Blk 2	0.16	0.10	1.32	22.8	n.a.	26.2	n.a.	5.80
MES Blk 3	0.15	0.07	1.10	19.0	n.a.	26.0	n.a.	6.17
MES Blk 4	0.11	0.04	0.78	12.0	n.a.	25.5	n.a.	6.05
MES Blk 5	0.16	0.06	0.70	18.8	n.a.	25.7	n.a.	5.72
MES Blk 6	1.00	0.10	0.90	34.9	n.a.	27.5	12.2	7.99
MES Blk 7	0.82	0.10	0.85	30.3	n.a.	26.6	12.2	6.24
MES Blk 8	0.20	0.07	0.62	21.5	n.a.	25.5	n.a.	6.08
MES Blk 9	0.08	0.07	0.57	12.9	n.a.	25.4	n.a.	5.69
MES Blk 10	0.09	0.07	0.51	9.8	n.a.	25.7	n.a.	6.06
MES Blk 11	0.29	0.06	0.67	12.6	n.a.	25.9	13.4	6.08
MES Blk 12	0.19	0.34	0.54	10.6	n.a.	25.9	12.4	5.72
MES Blk 13	0.12	0.05	0.48	7.7	n.a.	25.6	12.1	5.76
MES Blk 14	0.42	0.09	0.61	25.3	n.a.	26.6	n.a.	7.78
MES Blk 15	0.11	n.a.	0.54	17.0	n.a.	27.0	n.a.	5.65
MES Blk 16	0.12	n.a.	0.53	15.5	n.a.	26.7	n.a.	5.93
MES Blk 17	0.24	0.20	0.55	19.1	n.a.	27.6	n.a.	6.40
MES Blk 18	0.31	0.10	0.51	17.5	n.a.	26.9	n.a.	6.46
MES Blk 19	2.53	0.07	0.59	19.4	n.a.	26.4	14.2	7.08
MES Blk 20	0.30	0.07	0.57	21.8	n.a.	26.7	n.a.	5.94
MES Blk 21	0.16	0.12	0.54	21.3	n.a.	26.1	n.a.	6.29
MES Blk 22	0.09	0.15	0.47	19.0	n.a.	26.7	n.a.	5.65
MES Blk 23	0.11	0.17	0.48	25.1	n.a.	27.4	n.a.	5.84
MES Blk 24	0.09	0.10	0.52	19.3	n.a.	26.7	n.a.	5.89
MES Blk 25	0.16	0.07	n.a.	13.3	n.a.	27.3	n.a.	5.66
MES Blk 26	0.44	0.08	0.51	29.0	n.a.	26.9	15.4	5.69
MES Blk 27	0.12	0.07	0.49	27.1	n.a.	25.8	n.a.	5.72
MES Blk 28	0.09	0.08	0.47	21.0	n.a.	26.0	n.a.	6.07
MES Blk 29	1.03	0.19	0.69	27.1	n.a.	28.3	12.2	8.10
MES Blk 30	0.14	0.08	0.61	23.5	n.a.	26.3	n.a.	5.65
MES Blk 31	0.10	0.08	0.52	12.2	n.a.	26.0	n.a.	5.88
MES Blk 32	0.09	0.09	0.47	19.2	n.a.	26.1	12.3	6.02
MES Blk 33	0.22	0.09	0.66	26.8	n.a.	28.6	11.9	5.67
MES Blk 34	0.42	0.08	0.58	16.6	n.a.	26.6	12.2	7.00
Mean procedural blank	0.34	0.10	0.66	20.3	0.00	26.6	4.5	6.27

n.a. = not available

Appendix III: Accuracy, precision and detection limits of major ion concentration measurements

The detection limits of the ion chromatography method are displayed in Table A4. Table A5 displays the accuracy and precision of major ion determinations made by myself during a visit to the University of Maine in late February to March 2010. These are the only analytical sessions for which external standard data has been made available. The external standard is ION-92 (Environment Canada). As the concentrations of major ions vary by several orders of magnitude in the ice core samples, ION-92 was measured at two dilutions (x100 and x1000) during each analytical session.

Table A4: Detection limits (ppb) of major ions determined by IC. Data courtesy of Sharon Sneed, University of Maine.

Na^+	K^+	Mg^{2+}	Ca^{2+}	MS^-	NO_3^-	Cl^-	SO_4^{2-}
0.16	0.33	0.51	0.08	0.32	0.35	0.76	0.43

Table A5: Concentrations of major ions (ppb) determined in two dilutions of the external standard ION-92 and the accuracy and precision of measurements. NO_3^- is not detectable in external standard.

Analysis date (ddmmyy)	Na^+	Na^+	K^+	K^+	Mg^{2+}	Mg^{2+}	Ca^{2+}	Ca^{2+}	MS^-	MS^-	Cl^-	Cl^-	SO_4^{2-}	SO_4^{2-}
240210	25.6	208	1.41	4.33	10.3	97.3	45.8	434	17.5	38.7	107	1048	34.3	351
240210	27.5	220	1.21	5.04	13.6	104	49.6	459	20.1	36.7	110	1051	39.9	353
250210	27.7	221	1.17	5.04	11.5	104	46.8	459	17.8	42.2	109	1063	33.9	345
250210	29.8	226	1.67	6.27	12.1	106	49.3	469	22.5	51.2	117	1098	40.4	365
260210	29.0	227	1.20	4.97	11.3	105	47.1	469	22.1	46.7	115	1100	36.4	360
260210	29.0	227	1.20	4.97	11.3	105	47.1	469	22.1	46.7	115	1100	36.4	360
270210	14.0	185	0.85	3.61	9.50	90.8	41.0	407	29.4	50.6	112	1088	41.2	362
270210	15.8	193	0.94	4.43	8.79	93.0	46.3	421	21.3	49.2	117	1126	43.4	370
010310	14.0	185	0.85	3.61	9.50	90.8	41.0	407	29.4	50.6	112	1088	41.2	362
010310	15.8	193	0.94	4.43	8.79	93.0	46.3	421	21.3	49.2	117	1126	43.4	370
020310	6.85	182	n.a.	n.a.	9.29	92.4	35.0	420	19.9	43.7	110	1078	40.6	361
020310	7.40	188	n.a.	n.a.	8.47	94.7	40.5	436	28.8	48.1	112	1105	42.9	372
030310	8.97	185	n.a.	n.a.	8.49	93.8	34.2	430	24.5	49.9	126	1149	47.4	379
030310	9.04	189	n.a.	n.a.	9.11	95.1	44.6	442	28.7	57.2	121	1195	46.7	387
040310	5.99	178	n.a.	n.a.	8.25	87.1	35.0	408	25.8	57.0	114	1082	41.2	367
040310	7.07	185	n.a.	n.a.	8.66	90.6	40.7	424	35.2	74.1	121	1158	45.3	379
110310	17.5	180	0.38	1.84	8.98	86.0	41.0	393	n.a.	42.3	n.a.	1018	38.5	341
110310	19.4	181	0.92	2.99	10.0	81.0	n.a.	356	42.1	70.3	114	1072	41.8	358
090310	18.3	183	0.63	2.64	9.39	88.2	n.a.	n.a.	28.0	50.5	113	1003	42.9	343
090310	17.4	188	0.56	3.17	8.71	87.0	n.a.	n.a.	24.8	58.4	107	1059	39.8	361
100310	17.0	178	0.37	2.26	8.83	86.2	39.7	384	16.9	44.1	106	1005	37.9	343
100310	17.7	181	0.39	2.49	9.12	87.7	44.8	399	20.2	49.3	107	1026	42.6	349
160310	16.6	182	0.43	2.59	9.69	88.5	41.7	398	28.7	51.4	110	1060	39.6	352
160310	17.9	187	1.10	4.26	8.76	91.2	45.5	432	38.0	66.1	117	1115	44.3	364
180310	16.8	181	1.36	5.95	9.21	88.3	41.2	400	28.0	46.9	112	1056	39.8	356
180310	17.1	183	1.93	7.29	8.96	89.5	43.0	406	24.3	41.8	111	1040	42.5	356
230310	18.8	186	18.8	n.a.	1.48	n.a.	10.1	n.a.	19.2	51.3	115	1113	40.8	361

Analysis date (ddmmyy)	Na ⁺	Na ⁺	K ⁺	K ⁺	Mg ²⁺	Mg ²⁺	Ca ²⁺	Ca ²⁺	MS ⁻	MS ⁻	Cl ⁻	Cl ⁻	SO ₄ ²⁻	SO ₄ ²⁻
230310	19.5	189	19.5	n.a.	2.13	n.a.	10.6	n.a.	28.5	53.4	118	1164	45.8	376
240310	18.2	185	0.94	3.51	9.30	89.5	40.5	404	22.6	46.6	113	1141	40.9	363
240310	19.2	191	1.30	4.80	10.8	89.2	46.8	395	15.4	46.1	119	1185	48.6	383
300310	21.2	192	1.85	5.09	10.4	92.6	42.1	413	24.8	54.8	113	1063	38.3	356
300310	25.4	220	2.40	6.26	13.3	108	53.7	475	24.4	55.9	118	1104	46.0	373
010410	24.4	216	1.63	4.85	12.2	108	50.2	468	30.8	50.2	113	1071	37.5	353
010410	26.8	221	2.58	7.41	21.1	112	78.7	490	41.6	62.3	116	1094	62.1	367
Long-term mean	18.3	195	2.45	4.4	9.74	94.2	42.6	426	25.6	51.0	114	1089	41.9	362
2 SD	13.6	33.1	9.52	3.0	6.20	15.8	23.1	63.8	13.3	16.5	9.34	95.94	10.1	22.9
Certified	19.3	193	0.90	9.00	9.60	96.0	42.8	428	20.0	50.0	106	1055	37.0	370
2 SD	4.80	48.0	0.40	4.00	2.20	22.0	8.0	80.0			24.6	246.0	9.80	98.0
Precision 2 RSD (%)	37.0	8.50	194	34.1	31.8	8.40	27.1	7.5	25.9	11.2	4.10	4.40	12.0	3.17
Accuracy (% error)	5.12	0.84	172	51.2	1.51	1.85	0.5	0.39	28.0	2.0	7.96	3.27	13.2	2.24

Appendix IV: Stable isotope data for Mt Erebus Saddle 2006/07 ice core

All stable isotope ratios of oxygen and hydrogen and the derived d-excess values are provided in Table A6. The stable isotope ratios of a small number of samples had to be removed from analysis because they were anomalously heavy (Table A7). This was the result of ethanol or ultra-pure water contamination within the melter system.

The instrument used for stable isotope ratio determination changed from a GVI mass spectrometer to a LGR Liquid-Water Isotope Analyser at 92 m depth in the ice core. To ascertain whether comparable measurements were produced, a batch of samples (MES06/07_ISO_3783 to MES06/07_ISO_3921 and MES06/07_ISO_4858 to MES06/07_ISO_4905) was measured using both instruments (Table A8). Comparisons of the stable isotope ratios measured on the two instruments show offsets (Figs. A2 and A3), most notably for δD , which for only the lightest (most negative) values, are greater than the combined analytical error of both instruments. The mean difference between measurements on the GVI mass spectrometer and LGR Liquid-Water Isotope Analyser was -0.14‰ for $\delta^{18}O$ and -2.86‰ for δD , which resulted in a mean difference of -1.84‰ for d-excess. For several samples tested, the difference between the d-excess derived from the GVI mass spectrometer and the LGR Liquid-Water Isotope Analyser data is greater than the analytical uncertainty (Fig. A4). Therefore, the δD and $\delta^{18}O$ values measured on the LGR Liquid-Water Isotope Analyser were corrected to make them comparable to the GVI mass spectrometer values using the linear relationships established by analysing samples on both instruments (Figs. A2 and A3).

$$\delta D_{\text{mass spec. equiv.}} = (\delta D_{\text{laser}} + 1.6576) / 0.9809$$

$$\delta^{18}O_{\text{mass spec. equiv.}} = (\delta^{18}O_{\text{laser}} - 0.1577) / 1.0034$$

Deuterium excess values were then calculated from the corrected δD and $\delta^{18}O$ datasets. A revised analytical uncertainty (u) for d-excess, which takes into account the errors on both instruments, is calculated as: $\sqrt{1.3^2 + 1.7^2} = 2.14\text{‰}$. The δD and d-excess records of the MES ice core before and after the above corrections were applied are displayed in Figure A5.

Tables A6 and A7 are located on the enclosed data disk

Table A8: Comparison of the stable isotope ratios ($\delta^{18}\text{O}$ and δD) of selected MES ice core samples determined by GVI mass spectrometer (Mass spec.) and LGR Liquid-Water Isotope Analyser (Laser). Difference between mass spec. and laser measurements (Δ) and analytical precision (σ = 1 standard deviation) of samples is provided.

Internal sample I.D.	Depth (m)	δ ¹⁸ O (‰)				δD (‰)					
		Mass spec.	σ	Laser	σ	Δ	Mass spec.	σ	Laser	σ	Δ
MES0607_ISO_3783	77.02	-26.95		-26.64	0.06	-0.31	-210.37	0.43	-205.77	0.24	-4.60
MES0607_ISO_3784	77.03	-28.60		-28.27	0.05	-0.33	-225.37	0.41	-220.07	0.39	-5.30
MES0607_ISO_3785	77.04	-29.18		-28.95	0.11	-0.23	-230.77	0.07	-225.51	0.47	-5.26
MES0607_ISO_3786	77.06	-26.41		-26.32	0.05	-0.09	-206.83	0.04	-202.90	0.09	-3.93
MES0607_ISO_3787	77.07	-27.20		-27.13	0.08	-0.07	-213.64	0.72	-209.06	0.24	-4.58
MES0607_ISO_3788	77.08	-28.70		-28.73	0.08	0.03	-226.23	0.03	-221.37	0.17	-4.86
MES0607_ISO_3789	77.09	-29.15		-29.19	0.09	0.04	-229.79	0.54	-224.53	0.28	-5.26
MES0607_ISO_3790	77.10	-27.64		-27.73	0.04	0.10	-214.15	0.81	-210.26	0.17	-3.88
MES0607_ISO_3791	77.11	-26.19		-26.21	0.04	0.02	-200.29	0.60	-196.42	0.14	-3.87
MES0607_ISO_3792	77.12	-26.14		-25.99	0.12	-0.16	-198.57	0.64	-195.11	1.19	-3.46
MES0607_ISO_3793	77.13	-26.10		-26.13	0.09	0.03	-199.46	0.26	-195.86	0.25	-3.60
MES0607_ISO_3794	77.15	-26.44		-26.43	0.03	-0.01	-202.67	0.26	-199.31	0.26	-3.36
MES0607_ISO_3795	77.16	-26.76		-26.80	0.07	0.03	-206.98	0.40	-202.88	0.13	-4.09
MES0607_ISO_3796	77.17	-26.94		-26.94	0.05	-0.01	-208.08	0.38	-204.47	0.09	-3.60
MES0607_ISO_3797	77.18	-27.45		-27.42	0.07	-0.03	-213.61	0.40	-210.04	0.09	-3.57
MES0607_ISO_3798	77.19	-27.96		-27.91	0.05	-0.05	-218.06	0.30	-215.13	0.19	-2.93
MES0607_ISO_3799	77.20	-28.39		-28.47	0.07	0.08	-223.11	0.51	-219.43	0.11	-3.68
MES0607_ISO_3800	77.21	-28.71		-28.78	0.10	0.07	-226.11	0.34	-222.36	0.06	-3.75
MES0607_ISO_3801	77.22	-29.03		-29.05	0.04	0.02	-228.77	1.03	-225.90	0.11	-2.88
MES0607_ISO_3802	77.24	-29.37		-29.23	0.01	-0.14	-231.76	0.04	-227.79	0.12	-3.97
MES0607_ISO_3803	77.25	-29.47		-29.38	0.03	-0.09	-231.90	0.13	-228.42	0.16	-3.48
MES0607_ISO_3804	77.26	-29.47	0.02	-29.19	0.06	-0.27	-231.63	0.12	-227.96	0.06	-3.67
MES0607_ISO_3805	77.27	-29.45		-29.17	0.08	-0.29	-229.75	0.45	-227.17	0.12	-2.59
MES0607_ISO_3806	77.28	-28.57		-28.26	0.07	-0.31	-220.80	0.65	-217.47	0.09	-3.33
MES0607_ISO_3807	77.29	-27.43		-27.26	0.02	-0.16	-208.47	0.54	-205.50	0.09	-2.97
MES0607_ISO_3808	77.30	-26.99		-26.78	0.07	-0.21	-201.62	0.37	-199.71	0.19	-1.91
MES0607_ISO_3809	77.31	-26.72		-26.61	0.02	-0.10	-199.76	0.28	-197.12	0.11	-2.64
MES0607_ISO_3810	77.33	-26.50		-26.20	0.11	-0.30	-198.46	0.11	-195.34	0.11	-3.12
MES0607_ISO_3811	77.34	-25.93		-25.58	0.05	-0.35	-193.42	0.60	-189.34	0.22	-4.08
MES0607_ISO_3812	77.35	-25.76		-25.57	0.12	-0.19	-190.99	0.06	-187.09	0.97	-3.90
MES0607_ISO_3813	77.36	-25.79		-25.66	0.08	-0.13	-191.05	0.37	-188.03	0.10	-3.02
MES0607_ISO_3814	77.37	-25.98		-25.80	0.04	-0.18	-193.51	0.46	-190.54	0.16	-2.97
MES0607_ISO_3815	77.38	-26.25		-26.10	0.07	-0.15	-196.64	0.49	-193.48	0.07	-3.16
MES0607_ISO_3816	77.39	-26.45		-26.20	0.08	-0.25	-199.42	0.29	-195.83	0.13	-3.59
MES0607_ISO_3817	77.40	-26.88		-26.64	0.06	-0.25	-203.99	0.41	-200.83	0.02	-3.17
MES0607_ISO_3818	77.42	-27.24		-26.96	0.09	-0.28	-207.90	0.18	-204.39	0.12	-3.50
MES0607_ISO_3819	77.43	-27.63		-27.40	0.02	-0.23	-211.57	0.18	-208.45	0.07	-3.12
MES0607_ISO_3820	77.44	-27.98		-27.78	0.08	-0.20	-214.95	0.06	-212.29	0.23	-2.66
MES0607_ISO_3821	77.45	-28.32		-28.25	0.10	-0.07	-218.76	0.66	-216.33	0.13	-2.43
MES0607_ISO_3822	77.46	-28.84		-28.88	0.04	0.04	-224.14	0.14	-220.53	0.23	-3.61
MES0607_ISO_3823	77.47	-29.15		-29.30	0.09	0.15	-227.26	0.22	-223.91	0.11	-3.34
MES0607_ISO_3824	77.48	-29.50		-29.55	0.06	0.05	-229.59	0.14	-227.15	0.02	-2.44
MES0607_ISO_3825	77.49	-29.85		-29.96	0.03	0.12	-232.84	0.44	-230.27	0.16	-2.56
MES0607_ISO_3826	77.51	-30.14		-30.23	0.01	0.09	-236.19	0.08	-233.01	0.10	-3.19
MES0607_ISO_3827	77.52	-30.44		-30.45	0.03	0.01	-238.09	1.06	-235.37	0.26	-2.72
MES0607_ISO_3828	77.53	-30.68		-30.66	0.03	-0.02	-238.52	0.92	-237.09	0.22	-1.43
MES0607_ISO_3829	77.54	-30.91		-30.86	0.03	-0.05	-242.49	0.08	-239.10	0.23	-3.39
MES0607_ISO_3830	77.55	-31.19	0.01	-31.00	0.05	-0.19	-244.70	0.06	-240.66	0.10	-4.04
MES0607_ISO_3831	77.56	-31.30		-31.15	0.08	-0.15	-245.83	0.16	-242.05	0.14	-3.78
MES0607_ISO_3832	77.57	-31.37		-31.16	0.10	-0.22	-245.77	0.14	-242.09	0.96	-3.68
MES0607_ISO_3833	77.58	-31.48		-31.28	0.03	-0.19	-247.08	0.72	-242.58	0.17	-4.50

Internal sample I.D.	Depth (m)	Mass spec.	$\delta^{18}\text{O}$ (‰)				Mass spec.	δD (‰)			
			σ	Laser	σ	Δ		σ	Laser	σ	Δ
MES0607_ISO_3834	77.60	-31.52		-31.31	0.03	-0.20	-246.95	0.57	-242.75	0.22	-4.20
MES0607_ISO_3835	77.61	-31.38		-31.31	0.10	-0.06	-246.60	0.29	-242.15	0.13	-4.45
MES0607_ISO_3836	77.62	-31.28		-31.15	0.05	-0.13	-244.96	0.34	-241.45	0.15	-3.51
MES0607_ISO_3837	77.63	-30.82		-30.73	0.01	-0.09	-242.19	0.67	-238.00	0.24	-4.19
MES0607_ISO_3838	77.64	-27.50		-27.32	0.06	-0.18	-214.57	0.25	-211.46	0.05	-3.11
MES0607_ISO_3839	77.65	-25.09		-25.06	0.09	-0.02	-194.20	1.14	-192.07	0.18	-2.13
MES0607_ISO_3840	77.66	-24.70		-24.63	0.05	-0.07	-190.54	0.74	-188.81	0.10	-1.73
MES0607_ISO_3841	77.67	-24.58		-24.54	0.01	-0.04	-189.59	0.54	-187.84	0.15	-1.75
MES0607_ISO_3842	77.69	-24.51		-24.56	0.03	0.05	-189.21	0.64	-187.34	0.22	-1.87
MES0607_ISO_3843	77.70	-24.40		-24.49	0.07	0.09	-188.71	0.92	-186.24	0.19	-2.47
MES0607_ISO_3844	77.71	-23.94		-24.10	0.08	0.16	-183.85	0.17	-182.00	0.17	-1.85
MES0607_ISO_3845	77.72	-23.76		-23.89	0.07	0.13	-181.95	0.60	-180.22	0.16	-1.73
MES0607_ISO_3846	77.73	-23.79		-23.88	0.04	0.09	-181.99	0.04	-179.96	0.14	-2.03
MES0607_ISO_3847	77.74	-23.78		-23.84	0.08	0.06	-181.75	0.36	-180.09	0.02	-1.65
MES0607_ISO_3848	77.75	-23.89		-23.95	0.11	0.06	-181.70	0.46	-180.73	0.14	-0.96
MES0607_ISO_3849	77.76	-23.93		-23.95	0.05	0.02	-183.03	0.28	-181.33	0.03	-1.70
MES0607_ISO_3850	77.78	-23.99		-23.94	0.10	-0.04	-184.31	0.19	-182.03	0.11	-2.28
MES0607_ISO_3851	77.79	-24.12		-24.00	0.05	-0.12	-185.69	1.14	-182.86	0.22	-2.83
MES0607_ISO_3852	77.80	-24.27	0.01	-24.05	0.06	-0.22	-187.25	0.03	-183.58	0.87	-3.67
MES0607_ISO_3853	77.81	-24.41		-24.27	0.06	-0.14	-188.36	0.88	-185.50	0.12	-2.86
MES0607_ISO_3854	77.82	-24.59		-24.48	0.06	-0.11	-189.40	1.03	-187.44	0.06	-1.96
MES0607_ISO_3855	77.83	-24.76		-24.55	0.11	-0.21	-191.43	0.27	-188.87	0.09	-2.56
MES0607_ISO_3856	77.84	-24.84		-24.60	0.07	-0.23	-192.66	0.99	-189.91	0.28	-2.75
MES0607_ISO_3857	77.85	-25.05		-24.84	0.10	-0.21	-194.38	0.21	-191.58	0.11	-2.80
MES0607_ISO_3858	77.87	-25.17		-24.93	0.06	-0.24	-194.54	0.17	-192.67	0.15	-1.87
MES0607_ISO_3859	77.88	-25.18		-25.03	0.06	-0.16	-195.63	0.23	-193.07	0.29	-2.56
MES0607_ISO_3860	77.89	-25.31		-25.26	0.09	-0.05	-196.12	0.09	-194.05	0.15	-2.07
MES0607_ISO_3861	77.90	-25.39		-25.22	0.05	-0.17	-197.26	0.68	-194.73	0.17	-2.54
MES0607_ISO_3862	77.91	-25.47		-25.37	0.05	-0.10	-197.95	0.85	-195.23	0.17	-2.72
MES0607_ISO_3863	77.92	-25.53		-25.51	0.06	-0.02	-197.24	0.22	-195.76	0.14	-1.48
MES0607_ISO_3864	77.93	-25.56		-25.40	0.05	-0.15	-198.30	0.01	-195.75	0.11	-2.55
MES0607_ISO_3865	77.94	-25.58		-25.46	0.04	-0.12	-197.82	0.59	-195.71	0.15	-2.11
MES0607_ISO_3866	77.96	-25.59		-25.39	0.07	-0.21	-197.79	0.02	-195.16	0.25	-2.64
MES0607_ISO_3867	77.97	-26.07		-26.01	0.05	-0.06	-198.83	0.07	-196.74	0.36	-2.09
MES0607_ISO_3868	77.98	-26.18		-26.07	0.07	-0.10	-198.81	0.54	-197.08	0.14	-1.74
MES0607_ISO_3869	77.99	-26.37		-26.28	0.05	-0.10	-200.98	0.13	-198.55	0.20	-2.43
MES0607_ISO_3870	78.00	-26.67		-26.53	0.03	-0.14	-203.51	0.02	-200.90	0.13	-2.62
MES0607_ISO_3871	78.01	-26.83		-26.67	0.06	-0.16	-206.19	0.86	-202.70	0.23	-3.49
MES0607_ISO_3872	78.02	-27.08		-26.84	0.05	-0.24	-207.54	0.62	-204.31	0.99	-3.23
MES0607_ISO_3873	78.04	-27.17		-26.90	0.03	-0.27	-208.80	0.40	-205.94	0.23	-2.86
MES0607_ISO_3874	78.05	-27.53		-27.30	0.08	-0.23	-212.32	0.23	-209.21	0.26	-3.11
MES0607_ISO_3875	78.06	-27.90		-27.77	0.06	-0.13	-216.18	0.47	-213.18	0.03	-3.01
MES0607_ISO_3876	78.07	-28.26		-28.05	0.04	-0.21	-219.53	0.23	-216.17	0.38	-3.35
MES0607_ISO_3877	78.08	-28.43		-28.41	0.05	-0.02	-220.80	0.37	-218.60	0.28	-2.20
MES0607_ISO_3878	78.09	-28.55	0.01	-28.47	0.06	-0.08	-221.59	0.41	-219.85	0.27	-1.74
MES0607_ISO_3879	78.11	-28.82		-28.66	0.06	-0.16	-225.00	0.65	-222.43	0.33	-2.57
MES0607_ISO_3880	78.12	-29.06		-28.84	0.08	-0.23	-227.43	0.33	-224.69	0.21	-2.74
MES0607_ISO_3881	78.13	-29.43		-29.17	0.07	-0.26	-229.65	0.39	-227.77	0.38	-1.88
MES0607_ISO_3882	78.14	-29.66		-29.57	0.09	-0.09	-231.81	0.60	-228.78	0.25	-3.02
MES0607_ISO_3883	78.15	-29.68		-29.61	0.04	-0.07	-232.21	0.34	-229.07	0.07	-3.14
MES0607_ISO_3884	78.16	-29.71		-29.68	0.10	-0.03	-232.51	0.46	-229.64	0.21	-2.86
MES0607_ISO_3885	78.18	-29.65		-29.58	0.10	-0.07	-230.73	0.06	-228.39	0.18	-2.34
MES0607_ISO_3886	78.19	-29.57		-29.55	0.03	-0.02	-230.28	0.71	-227.63	0.38	-2.65
MES0607_ISO_3887	78.20	-29.42		-29.31	0.06	-0.11	-226.72	0.38	-225.72	0.28	-1.00
MES0607_ISO_3888	78.21	-28.48		-28.44	0.10	-0.04	-216.71	0.12	-216.04	0.09	-0.66
MES0607_ISO_3889	78.22	-27.83		-27.73	0.07	-0.10	-211.14	0.52	-208.70	0.25	-2.43
MES0607_ISO_3890	78.24	-27.33		-27.28	0.06	-0.04	-205.77	0.20	-203.13	0.20	-2.63
MES0607_ISO_3891	78.25	-26.86		-26.75	0.05	-0.11	-201.15	0.37	-198.47	0.25	-2.67
MES0607_ISO_3892	78.26	-26.29		-26.27	0.06	-0.02	-195.64	0.03	-191.32	0.80	-4.32

Internal sample I.D.	Depth (m)	Mass spec.	$\delta^{18}\text{O}$ (‰)				Mass spec.	δD (‰)			
			σ	Laser	σ	Δ		σ	Laser	σ	Δ
MES0607_ISO_3893	78.27	-25.54		-25.45	0.09	-0.10	-188.24	0.21	-184.59	0.24	-3.65
MES0607_ISO_3894	78.28	-24.97		-24.88	0.09	-0.09	-182.47	0.06	-179.72	0.25	-2.75
MES0607_ISO_3895	78.29	-24.42		-24.11	0.10	-0.31	-176.93	0.01	-174.07	0.25	-2.86
MES0607_ISO_3896	78.31	-24.04		-23.83	0.02	-0.21	-174.01	0.96	-171.22	0.18	-2.80
MES0607_ISO_3897	78.32	-23.84		-23.80	0.03	-0.04	-173.17	0.79	-170.53	0.39	-2.64
MES0607_ISO_3898	78.33	-23.80		-23.63	0.11	-0.18	-174.20	0.43	-171.20	0.27	-3.01
MES0607_ISO_3899	78.34	-23.89		-23.69	0.03	-0.20	-175.41	0.10	-173.11	0.34	-2.30
MES0607_ISO_3900	78.35	-24.16	0.04	-23.96	0.07	-0.20	-179.24	0.27	-176.39	0.28	-2.85
MES0607_ISO_3901	78.36	-24.77		-24.62	0.10	-0.15	-185.86	0.59	-183.96	0.29	-1.90
MES0607_ISO_3902	78.38	-25.20		-25.06	0.07	-0.14	-190.93	0.15	-190.33	0.11	-0.60
MES0607_ISO_3903	78.39	-25.71		-25.23	0.13	-0.48	-197.05	0.20	-195.51	0.14	-1.53
MES0607_ISO_3904	78.40	-26.23		-25.84	0.10	-0.38	-202.69	0.01	-201.13	0.16	-1.55
MES0607_ISO_3905	78.41	-26.80		-26.37	0.01	-0.43	-208.31	0.32	-206.93	0.09	-1.38
MES0607_ISO_3906	78.42	-27.37		-26.85	0.10	-0.52	-214.15	0.47	-212.24	0.13	-1.91
MES0607_ISO_3907	78.44	-27.83		-27.60	0.08	-0.23	-219.10	0.00	-216.49	0.13	-2.61
MES0607_ISO_3908	78.45	-28.43		-28.01	0.05	-0.41	-224.37	0.13	-221.07	0.21	-3.31
MES0607_ISO_3909	78.46	-28.95		-28.42	0.07	-0.53	-228.14	0.77	-224.76	0.18	-3.37
MES0607_ISO_3910	78.47	-29.14		-28.69	0.03	-0.45	-229.49	0.61	-226.10	0.06	-3.39
MES0607_ISO_3911	78.48	-29.29		-29.14	0.05	-0.15	-230.44	1.24	-227.12	0.20	-3.32
MES0607_ISO_3912	78.49	-29.31		-29.22	0.11	-0.09	-230.31	0.39	-225.96	1.09	-4.36
MES0607_ISO_3913	78.51	-29.11		-28.96	0.02	-0.15	-227.33	0.64	-223.56	0.28	-3.78
MES0607_ISO_3914	78.52	-28.80		-28.67	0.07	-0.13	-222.16	0.25	-219.02	0.24	-3.14
MES0607_ISO_3915	78.53	-28.68		-28.41	0.08	-0.27	-220.49	0.48	-218.02	0.22	-2.46
MES0607_ISO_3916	78.54	-28.62		-28.36	0.05	-0.26	-219.13	0.20	-217.26	0.16	-1.87
MES0607_ISO_3917	78.55	-28.39		-27.85	0.10	-0.54	-216.46	0.10	-213.72	0.38	-2.74
MES0607_ISO_3918	78.56	-28.17		-27.65	0.06	-0.52	-213.39	0.32	-211.85	0.16	-1.54
MES0607_ISO_3919	78.58	-28.01		-27.50	0.06	-0.50	-212.01	0.19	-210.31	0.21	-1.70
MES0607_ISO_3920	78.59	-27.92		-27.66	0.03	-0.27	-210.61	1.33	-210.04	0.16	-0.57
MES0607_ISO_3921	78.60	-27.89		-27.68	0.02	-0.20	-211.70	0.15	-210.56	0.26	-1.14
MES0607_ISO_4858	91.95	-26.92	0.01	-27.27	0.07	0.35	-203.66	0.19	-204.17	0.12	0.51
MES0607_ISO_4859	91.96	-26.99		-27.32	0.07	0.33	-205.79	0.98	-205.21	0.17	-0.59
MES0607_ISO_4860	91.97	-26.99		-27.30	0.05	0.32	-205.38	0.18	-205.70	0.23	0.32
MES0607_ISO_4861	91.99	-25.64		-25.96	0.10	0.32	-195.66	0.52	-195.38	0.16	-0.28
MES0607_ISO_4862	92.03	-26.08		-26.32	0.07	0.24	-199.06	0.39	-198.85	0.20	-0.21
MES0607_ISO_4863	92.04	-26.95		-27.00	0.13	0.05	-206.60	0.35	-205.83	0.20	-0.78
MES0607_ISO_4864	92.05	-26.94		-27.05	0.04	0.11	-206.38	0.16	-205.90	0.10	-0.48
MES0607_ISO_4865	92.06	-26.85		-27.03	0.12	0.18	-205.74	0.19	-205.79	0.25	0.05
MES0607_ISO_4866	92.08	-26.72		-26.80	0.07	0.07	-205.14	0.62	-204.22	0.18	-0.92
MES0607_ISO_4867	92.09	-25.52		-25.61	0.01	0.09	-193.12	0.42	-192.49	0.14	-0.63
MES0607_ISO_4868	92.10	-24.97		-24.89	0.12	-0.08	-185.72	0.62	-185.54	0.76	-0.19
MES0607_ISO_4869	92.12	-24.56		-24.60	0.09	0.04	-183.02	0.92	-181.97	0.17	-1.04
MES0607_ISO_4870	92.13	-24.34		-24.38	0.11	0.04	-180.28	0.24	-179.86	0.18	-0.42
MES0607_ISO_4871	92.14	-24.14		-24.03	0.08	-0.11	-178.93	0.12	-177.98	0.23	-0.95
MES0607_ISO_4872	92.16	-23.90		-23.83	0.07	-0.07	-177.02	0.89	-176.07	0.27	-0.94
MES0607_ISO_4873	92.17	-23.85		-23.91	0.09	0.06	-178.33	0.28	-177.10	0.38	-1.23
MES0607_ISO_4874	92.18	-23.97		-23.90	0.05	-0.07	-180.32	0.49	-178.92	0.31	-1.40
MES0607_ISO_4875	92.19	-24.11		-24.08	0.04	-0.03	-181.52	0.36	-180.71	0.31	-0.81
MES0607_ISO_4876	92.21	-24.37		-24.47	0.11	0.10	-184.82	0.30	-184.19	0.40	-0.63
MES0607_ISO_4877	92.22	-24.73		-24.74	0.06	0.00	-188.85	0.46	-187.77	0.44	-1.08
MES0607_ISO_4878	92.23	-25.11		-25.21	0.06	0.11	-192.18	0.69	-191.41	0.15	-0.77
MES0607_ISO_4879	92.25	-25.70		-25.70	0.03	0.00	-197.99	0.19	-197.03	0.09	-0.96
MES0607_ISO_4880	92.26	-26.21	0.01	-26.26	0.06	0.05	-201.99	0.17	-201.51	0.03	-0.49
MES0607_ISO_4881	92.27	-26.47		-26.57	0.08	0.09	-204.32	0.21	-203.32	0.25	-1.00
MES0607_ISO_4882	92.29	-26.61		-26.64	0.08	0.03	-204.92	0.44	-204.29	0.11	-0.63
MES0607_ISO_4883	92.30	-26.78		-26.85	0.10	0.06	-206.06	0.09	-205.35	0.38	-0.71
MES0607_ISO_4884	92.31	-26.75		-26.94	0.09	0.19	-206.77	0.25	-205.69	0.38	-1.08
MES0607_ISO_4885	92.32	-27.18		-27.29	0.06	0.11	-206.52	0.44	-206.04	0.32	-0.48
MES0607_ISO_4886	92.34	-27.28		-27.29	0.14	0.01	-206.61	0.26	-205.69	0.18	-0.91
MES0607_ISO_4887	92.35	-27.38		-27.47	0.03	0.10	-207.53	0.18	-206.75	0.25	-0.78

Internal sample I.D.	Depth (m)	Mass spec.	$\delta^{18}\text{O}$ (‰)				Mass spec.	δD (‰)			
			σ	Laser	σ	Δ		σ	Laser	σ	Δ
MES0607_ISO_4888	92.36	-27.46		-27.50	0.07	0.04	-206.94	0.33	-206.66	0.83	-0.28
MES0607_ISO_4889	92.38	-27.62		-27.94	0.02	0.32	-209.30	0.00	-208.31	0.16	-1.00
MES0607_ISO_4890	92.39	-27.79		-28.15	0.02	0.36	-211.45	0.45	-210.18	0.15	-1.27
MES0607_ISO_4891	92.40	-27.95		-28.50	0.08	0.55	-213.08	0.35	-212.11	0.17	-0.96
MES0607_ISO_4892	92.42	-28.21		-28.71	0.07	0.50	-215.40	0.77	-214.41	0.15	-0.99
MES0607_ISO_4893	92.43	-28.47		-28.98	0.08	0.51	-217.90	0.63	-217.01	0.19	-0.89
MES0607_ISO_4894	92.44	-28.88		-29.27	0.08	0.39	-221.86	0.05	-221.05	0.18	-0.81
MES0607_ISO_4895	92.45	-29.21		-29.65	0.05	0.44	-225.54	0.02	-224.36	0.19	-1.18
MES0607_ISO_4896	92.47	-29.95		-30.30	0.08	0.35	-232.42	0.52	-231.44	0.42	-0.99
MES0607_ISO_4897	92.48	-30.55		-30.83	0.06	0.28	-238.10	0.33	-237.66	0.19	-0.43
MES0607_ISO_4898	92.49	-30.84		-30.85	0.11	0.01	-240.33	0.39	-239.12	0.17	-1.22
MES0607_ISO_4899	92.51	-31.18		-31.19	0.08	0.00	-244.14	0.28	-242.29	0.16	-1.84
MES0607_ISO_4900	92.52	-31.38		-31.48	0.07	0.10	-246.81	0.60	-244.66	0.13	-2.15
MES0607_ISO_4901	92.53	-31.50		-31.69	0.14	0.20	-247.19	0.48	-245.77	0.21	-1.43
MES0607_ISO_4902	92.55	-31.51		-31.62	0.05	0.11	-247.54	0.24	-245.70	0.12	-1.84
MES0607_ISO_4903	92.56	-31.06		-31.21	0.10	0.15	-243.74	0.62	-241.64	0.09	-2.10
MES0607_ISO_4904	92.57	-29.59		-29.80	0.15	0.21	-228.95	0.40	-227.62	0.17	-1.33
MES0607_ISO_4905	92.58	-29.09		-29.04	0.09	-0.05	-224.07	0.55	-222.58	0.29	-1.50
Average =		-27.25	0.01	-27.18	0.07	-0.06	-209.54	0.40	-207.19	0.23	-2.35

Figure A2: $\delta^{18}\text{O}$ measured on GVI mass spectrometer and LGR Liquid-Water Isotope Analyser (Laser). Error bars are 2σ .

Figure A3: δD measured on GVI mass spectrometer and LGR Liquid-Water Isotope Analyser (Laser). Error bars are 2σ .

Figure A4: Deuterium excess calculated from $\delta^{18}\text{O}$ and δD values measured on GVI mass spectrometer and LGR Liquid-Water Isotope Analyser (Laser). Error bars are u (u = analytical uncertainty (Section 4.2.1)).

Figure A5: Stable isotope (δD and d-excess) records of the MES ice core A) before, and B) after, a correction was applied to laser-measured data to account for the calibration difference between the mass spectrometer and laser instruments.

Appendix V: Dansgaard-Johnsen glacial flow model

A Dansgaard-Johnsen glacial flow model was applied to the MES ice core by Hans-Christian Steen Larsen from the Center for Ice and Climate, University of Copenhagen. This glacial flow model assumes that the horizontal velocity of the ice at the drill site is constant down to a specified depth. After this depth is exceeded the horizontal velocity decreases linearly with depth because it is attenuated by friction with the bedrock. This makes the Dansgaard-Johnsen glacial model suitable for use on cold-based glaciers which have little basal sliding [*Dansgaard and Johnsen, 1969*].

The following parameters were input into the model:

Density-depth profile of ice core: Table A15

Site annual temperature: -25.6°C

Site elevation: *1600 m above sea level*

Depth to bedrock: *220 m*

Annual accumulation rate: *$0.252\text{ m (H}_2\text{O equivalent) yr}^{-1}$ (1950-2000 mean)*

The profile of the annual layer thickness produced takes into account the compression of layers resulting from densification and thinning due to strain (Table A9). The modelled depth-age profile of the MES ice core is provided in Table A10.

Tables A9 and A10 are located on the enclosed data disk.

Appendix VI: Back-diffusion of Mt Erebus Saddle 2006/07 ice core stable isotope ratios

Ice core stable isotopic records are affected by diffusion of water molecules in the firn layer and below the firn-ice transition [Johnsen *et al.*, 2000]. This effectively smoothes the record by filtering out high frequency signals, making annual cycles difficult to identify [Dansgaard *et al.*, 1973]. However, an estimation of the original signal, including high frequencies, can be obtained by back-diffusion or deconvolution, which is the inverse of filtering.

The back-diffusion method of Johnsen *et al.* [2000] was employed by Hans-Christian Steen Larsen from the Center for Ice and Climate, University of Copenhagen on the MES ice core stable isotopic record. This method takes into account diffusion during the post-depositional processes of densification of snow into firn then ice and also thinning of glacial ice due to strain. It differs from other models because diffusion is assumed to take place in a porous media, as opposed to only the vapour phase, meaning that molecules can diffuse and be re-adsorbed in the pore space. The main effect of this is that diffusion has a greater relative effect on $\delta^{18}\text{O}$ profiles than δD profiles, which is in agreement with ice core stable isotope profiles (Johnsen *et al.*, 2000).

Back-diffusion must be performed on evenly spaced data so the raw $\delta^{18}\text{O}$ and δD records were re-sampled (Table A11). The diffusion lengths of $\delta^{18}\text{O}$ and δD (Table A12) were calculated using the results of the Dansgaard-Johnsen flow model (Appendix V) [Dansgaard and Johnsen, 1969], because diffusion is temperature sensitive [Johnsen *et al.* 2000], and a Herron-Langway densification model [Herron and Langway, 1980] (Table A13). The densification model used an initial density of 0.370 g cm^{-3} and a critical density of 550 g cm^{-3} , and the parameters f_0 and f_1 were respectively scaled by the factors 0.95 and 1.00. The back-diffused $\delta^{18}\text{O}$ and δD profiles produced are provided in Table A14. An additional set of stable isotopic profiles was produced using the same back-diffusion method but with increased diffusion lengths to aid in the identification of annual layers (Table A15).

Table A11 to A15 are located on the enclosed data disk.

Appendix VII: Mt Erebus Saddle tritium (^3H) measurements

^3H measurements were carried out at the GNS Science Tritium and Water Dating Laboratory, Lower Hutt, New Zealand (Table A16). Sample depths for ^3H analysis were selected according to an early ice core age model based on annual layer counting of raw $\delta^{18}\text{O}$ and δD time series. Once a back-diffused stable isotope time series had been produced the accuracy of the age model improved significantly. For this reason, although the intention was to sample an entire year, often the samples did not incorporate all four seasons. As tritium content is known to show a seasonal cycle in Antarctic ice, with a peak during winter [Jouzel *et al.*, 1979], the bias towards summer-time sampling which is shown here could cause the tritium content measured to be depleted relative to the annual average.

Table A16: Six tritium content measurements conducted on samples from selected depths in the ice core.

Drill Date	Tritium content (TU)	σ (TU)	Start depth (m)	End depth (m)	Start year	End year	Months sampled
20/12/2006	1.87	1.86	11.0	11.2	1983.15	1983.51	February to June
20/12/2006	7.91	1.94	16.0	16.1	1971.98	1972.18	December to March
20/12/2006	8.80	1.95	17.0	17.4	1968.89	1969.54	November to July
20/12/2006	13.21	2.01	17.9	18.2	1966.40	1967.09	May to February
20/12/2006	15.59	2.04	19.0	19.1	1964.09	1964.36	February to May
20/12/2006	3.20	1.82	21.1	21.3	1958.90	1959.39	November to May

TU = tritium units; σ = 1 standard deviation

Appendix VIII: Mt Erebus Saddle 2006/07 ice core density measurements

Density values for each metre-length of core calculated by weighing each section in the field are presented in Table A17. A mean density of 0.382 g cm^{-3} is used in this study for the top metre of snow. This value was produced by dual-energy x-ray (DEXA) scanning of the core.

Table A17: Field density measurements for the MES ice core. Bag number refers to the depth of each metre-length section i.e., Bag number 3 refers to the section of core between 2 and 3 m core depth.

Bag number	Density (g/cm ³)	Bag number	Density (g/cm ³)	Bag number	Density (g/cm ³)
3	0.413	55	0.796	107	0.877
4	0.442	56	0.803	108	0.884
5	0.460	57	0.781	109	0.868
6	0.468	58	0.823	110	0.874
7	0.496	59	0.809	111	0.863
8	0.505	60	0.814	112	0.887
9	0.524	61	0.772	113	0.877
10	0.523	62	0.814	114	0.868
11	0.532	63	0.841	115	0.872
12	0.534	64	0.839	116	nm
13	0.549	65	0.791	117	0.887
14	0.549	66	0.846	118	0.865
15	0.565	67	0.852	119	0.851
16	0.576	68	0.845	120	0.861
17	0.582	69	0.829	121	0.879
18	0.586	70	0.847	122	0.853
19	0.597	71	nm	123	0.875
20	0.611	72	0.852	124	0.839
21	nm	73	0.813	125	nm
22	0.614	74	0.819	126	0.863
23	0.623	75	0.866	127	0.864
24	0.612	76	0.845	128	0.870
25	0.652	77	0.858	129	0.875
26	0.637	78	0.840	130	0.868
27	0.635	79	0.849	131	0.868
28	0.644	80	0.860	132	0.873
29	0.654	81	0.840	133	0.870
30	nm	82	0.871	134	0.842
31	0.652	83	0.853	135	0.859
32	0.667	84	0.872	136	0.863
33	0.673	85	0.872	137	0.852
34	0.679	86	0.865	138	0.852
35	0.681	87	0.866	139	0.869
36	0.690	88	0.861	140	0.858
37	0.698	89	0.846	141	0.844
38	0.701	90	0.867	142	0.862
39	0.711	91	0.856	143	0.862
40	0.696	92	0.821	144	0.834
41	0.716	93	0.872	145	0.828
42	0.724	94	0.870	146	0.841
43	0.724	95	0.863	147	0.787
44	0.730	96	0.865	148	0.799
45	0.732	97	0.877	149	0.843
46	0.724	98	0.859	150	0.811
47	0.745	99	0.890	151	0.873
48	0.765	100	0.859	152	0.829
49	0.756	101	0.882	153	0.829
50	0.764	102	0.876	154	0.716
51	0.765	103	0.883	155	0.778
52	0.793	104	0.874	156	0.710
53	0.787	105	0.873		
54	0.788	106	0.839		

nm = not measured

Appendix IX: Supplementary data tables for dust leaching investigation

Tables A18 to A27 were included as a Supplementary Information section in the submission of the paper “Experimental investigation of the effects of mineral dust on the reproducibility and accuracy of ice core trace element analysis” to *Chemical Geology* (Chapter 6). Tables A18 to A25 present the trace element concentrations measured in the mineral dust leachates. Tables A18 to A24 include some duplicate leachates measurements. Table A26 contains data relating to procedural blanks and Table A27 contains REE ratios of the leachates.

Table A18: Concentrations of trace elements (ppt) in leachates of BHVO-2 at 10 ppm dust concentration.

Acidi- fication time (hr)	Li	Na	Mg	Al	Ca	Ti	V	Cr	Mn	Cu	Zn	As	Rb	Sr	Y	Zr	Cs	Ba	La	Ce	Pr	Gd	Er	Yb	Tl	Pb	Bi	Th	U
0.167	2.6	2000	1869	6670	8539	266	7.7	17.7	125.4	121.4	nd	ndS	0.5	52.4	32.9	13.0	nd	15.3	31.7	75.5	10.3	8.9	nm	nm	ndS	nd	ndS	1.8	0.4
1	4.0	2443	3779	8936	14089	378	9.6	20.4	187.2	169.5	nd	ndS	0.6	70.4	50.1	22.3	nd	18.9	48.2	115	15.8	14.1	nm	nm	ndS	nd	ndS	2.8	0.7
2	1.3	2887	5240	11553	14397	495	11.5	22.7	221.3	228.6	nd	ndS	0.6	84.3	52.9	26.2	nd	21.2	50.6	122	16.5	14.9	nm	nm	ndS	nd	ndS	3.0	0.8
4	2.2	2874	7670	12928	14566	599	12.2	25.5	265.5	214.2	nd	ndS	0.6	91.5	54.2	28.2	nd	22.3	52.0	125	16.9	14.6	nm	nm	ndS	nd	ndS	3.0	0.8
8	5.2	4590	12598	17262	18829	771	15.4	31.2	349.5	249.9	nd	ndS	0.8	115	54.4	32.5	nd	27.1	51.3	124	16.8	15.2	nm	nm	ndS	nd	ndS	3.0	0.9
12	3.3	4950	15194	19538	19712	868	16.4	32.1	383.9	258.5	nd	ndS	0.8	125	53.2	33.3	nd	27.8	50.8	122	16.6	14.3	nm	nm	ndS	nd	ndS	3.1	0.8
24	3.0	6867	21797	28411	25342	1176	20.0	36.7	462.9	341.9	nd	ndS	0.9	173	52.6	38.2	nd	34.6	50.5	121	16.5	14.5	nm	nm	ndS	nd	ndS	3.1	0.8
36	3.7	7947	26693	35022	29177	1384	22.2	40.3	511.7	745.5	nd	ndS	0.9	208	52.2	40.2	nd	38.7	49.9	120	16.5	14.3	nm	nm	ndS	nd	ndS	3.1	0.9
48	4.2	9489	29747	41219	33255	1622	25.0	46.4	549.9	313.4	nd	ndS	1.0	250	52.9	41.7	nd	43.2	50.0	120	16.4	14.9	nm	nm	ndS	nd	ndS	3.2	0.8
72	3.9	11910	33673	53817	39040	1979	28.6	50.6	587.3	315.7	nd	ndS	1.1	317	52.1	44.1	nd	52.0	49.4	119	16.1	14.7	nm	nm	ndS	nd	ndS	3.0	0.8
120	4.3	16726	38095	76806	52059	2700	35.4	53.9	646.1	346.2	nd	ndS	1.2	445	51.9	48.3	nd	69.3	50.1	120	16.3	14.9	nm	nm	ndS	nd	ndS	3.1	0.8
168	4.9	19558	38817	91562	59598	3177	39.3	56.5	660.8	346.4	nd	ndS	1.2	529	51.4	49.5	nd	78.9	49.5	118	16.2	15.0	nm	nm	ndS	nd	ndS	3.2	0.8
336	10.0	27818	41066	147185	89880	4921	59.0	nm	773.5	406.8	nd	ndS	1.5	834	51.8	59.4	nd	119.6	50.1	120	16.4	14.5	nm	nm	ndS	nd	ndS	3.2	0.9
528	5.7	42536	42005	199299	118901	7460	82	75	841	425	nd	ndS	2.0	1161	55.6	54.2	nd	163	53.3	128	17.5	15.1	nm	nd	ndS	nd	ndS	3.4	1.0
672	9.4	47737	42142	222249	132413	8720	95	78	883	433	nd	ndS	2.3	1304	55.6	59.1	nd	185	53.8	128	17.5	14.9	nm	nd	ndS	nd	ndS	3.3	1.0
1296	8.7	65953	44145	295276	175479	13869	146	95	1117	485	nd	ndS	2.9	1760	59.1	67.9	nd	259	57.1	135	18.3	16.8	nm	nd	ndS	nd	ndS	3.2	0.9
1848	11.3	77118	46190	341658	201681	18157	191	110	1291	506	nd	ndS	3.5	2056	62.1	88.1	nd	309	60.2	143	19.1	17.5	nm	nd	ndS	nd	ndS	3.3	1.0
12	2.60	4924	15124	19690	19424	862	16.2	29.9	378	257	nd	ndS	0.75	125	52.3	33.3	nd	28.2	50.2	120	16.5	14.5	nm	nm	ndS	nd	ndS	3.1	0.8
120	4.15	16705	38075	77189	52051	2671	35.5	55.5	643	398	nd	ndS	1.16	446	51.9	49.0	nd	69.2	50.0	120	16.5	14.4	nm	nm	ndS	nd	ndS	3.3	0.8

nd = not detected; ndS = not detectable in rock standard; nm = not measured

Table A19: Concentrations of trace elements (ppt) in leachates of W-2 at 10 ppm dust concentration.

Acidi- fication time(hr)	Li	Na	Mg	Al	Ca	Ti	V	Cr	Mn	Cu	Zn	As	Rb	Sr	Y	Zr	Cs	Ba	La	Ce	Pr	Gd	Er	Yb	Tl	Pb	Bi	Th	U
0.167	8.7	6408	8288	8424	31560	827	46.8	9.7	179	340	nd	nd	36.2	80.1	26.1	2.47	4.13	135	39.4	80.3	9.27	7.12	2.17	1.39	nd	35.4	nd	4.25	0.65
1	11.3	6591	10726	10428	32730	1106	57.9	12.2	192	248	nd	nd	41.3	92.2	26.6	2.52	4.58	152	40.4	82.4	9.50	7.03	2.19	1.40	nd	36.8	nd	5.40	0.71
2	14.0	7064	11953	11653	34962	1191	61.6	12.9	238	255	nd	nd	42.3	101	26.5	3.03	4.97	163	40.4	82.0	9.53	7.17	2.31	1.52	nd	37.3	nd	5.79	0.71
4	13.8	8843	13081	14270	40849	1225	65.3	12.6	242	272	nd	nd	42.9	124	26.5	3.23	4.77	179	40.2	81.2	9.31	7.43	2.31	1.45	nd	38.9	nd	6.08	0.80
8	15.5	11172	14611	17587	48435	1368	73.0	17.4	355	323	nd	nd	45.0	158	27.1	4.18	5.11	201	41.1	83.2	9.61	7.17	2.20	1.33	0.36	38.2	nd	6.54	0.82
12	16.9	13500	16042	21434	55553	1474	77.3	16.8	370	320	nd	nd	44.6	188	26.5	3.91	5.05	216	40.8	82.3	9.40	7.25	2.10	1.51	0.28	38.5	nd	6.72	0.88
24	19.9	18377	18472	29241	70760	1719	85.7	18.4	383	323	nd	nd	44.2	253	25.8	4.17	4.97	244	40.2	80.3	9.14	6.89	2.12	1.34	nd	39.1	nd	6.98	0.91
36	23.1	21367	20279	33798	80563	1866	92.4	19.8	403	328	nd	nd	44.1	294	25.4	4.27	4.96	261	39.8	79.6	9.07	6.79	2.17	1.39	nd	38.3	nd	6.93	0.95
48	28.1	23741	21483	37537	88609	2051	99.6	24.3	431	341	nd	nd	45.5	334	26.2	5.75	4.99	276	40.1	79.5	9.10	6.98	2.16	1.38	0.31	37.0	nd	6.78	0.93
72	33.5	29326	24623	46224	107030	2333	108.7	25.9	470	347	nd	nd	45.2	403	25.7	5.80	4.93	307	40.3	80.7	9.09	6.96	2.21	1.45	nd	38.6	nd	7.07	1.02
120	34.2	37141	26969	57599	128250	2786	124.2	29.4	527	370	nd	nd	46.8	505	26.2	6.47	5.08	357	41.6	82.4	9.42	6.97	2.22	1.42	nd	39.9	nd	7.43	1.03
168	38.3	43212	28278	64399	145117	3165	139.5	33.1	539	406	nd	nd	49.7	592	27.5	7.86	5.17	399	43.3	85.1	9.69	6.93	2.38	1.69	nd	40.6	nd	7.24	1.10
384	22.4	62347	28781	349374	188604	4106	164.7	37.6	570	440	nd	nd	53.9	805	29.4	8.43	5.28	510	46.3	89.1	10.19	7.35	2.51	1.66	0.31	41.3	nd	7.27	1.34
528	24.7	69483	29790	385505	208959	4516	179.5	39.5	609	456	nd	nd	56.3	896	30.0	9.36	5.34	560	47.8	91.1	10.51	7.70	2.61	1.91	0.39	42.0	nd	7.34	1.35
672	37.9	82571	31508	445465	256383	5291	215.3	48.0	718	487	nd	nd	61.8	1091	31.8	13.38	5.21	679	51.1	95.0	10.66	8.31	2.83	2.12	0.41	44.7	nd	6.89	1.31
1128	39.4	91016	33020	481133	276823	5701	243.3	56.3	798	503	nd	nd	64.6	1186	33.1	15.66	5.01	742	52.5	96.9	10.95	8.89	2.99	2.28	0.44	46.8	nd	7.47	1.46
1680	37.7	70991	29887	393223	226498	4672	187.3	42.1	630	463	nd	nd	58.1	966	30.2	10.72	5.36	600	48.5	93.0	10.43	8.16	2.45	2.02	0.36	44.4	nd	7.00	1.22
0.167	7.6	4544	7597	28239	28168	733	43.3	8.74	200	240	nd	nd	35.3	66.7	25.8	2.23	4.01	126	38.8	79.1	9.19	6.92	2.24	1.36	0.17	35.0	nd	4.10	0.6
4	14.5	9004	13188	58001	42176	1254	66.3	12.5	235	270	nd	nd	43.2	128	26.5	2.82	4.86	180	40.0	81.5	9.37	7.34	2.27	1.33	0.20	38.4	nd	6.01	0.75
12	18.7	13594	15952	86192	55891	1457	76.2	15.5	340	313	nd	nd	43.8	188	26.0	3.57	4.99	215	40.0	80.6	9.35	7.28	2.14	1.46	0.26	38.4	nd	6.50	0.86
120	33.2	38276	26865	230806	132434	2829	125	27.5	521	377	nd	nd	47.9	520	27.0	6.64	5.12	366	42.5	83.6	9.43	7.12	2.30	1.57	0.24	40.0	nd	7.02	1.07

nd=not detected

Table A20: Concentrations of trace elements (ppt) in leachates of JG-2 at 10 ppm dust concentration.

Acidi- fication time (hr)	Li	Na	Mg	Al	Ca	Ti	V	Cr	Mn	Cu	Zn	As	Rb	Sr	Y	Zr	Cs	Ba	La	Ce	Pr	Gd	Er	Yb	Tl	Pb	Bi	Th	U
0.167	106	4205	2011	15424	7325	647	9.7	nd	388	nd	39.0	nd	189	21.0	345	9.2	20.7	144	17.0	40.1	5.7	22.1	nm	nm	1.1	44.4	7.6	50.9	33.2
1	131	5145	2524	17638	9096	764	11.8	nd	468	nd	117.2	nd	213	23.5	417	11.9	24.8	167	21.1	48.9	7.0	27.1	nm	nm	1.3	68.6	8.0	60.0	36.4
2	141	5128	2487	18221	7853	806	10.2	nd	478	nd	nd	nd	216	20.8	435	9.5	25.4	165	21.7	50.6	7.3	27.7	nm	nm	1.3	38.6	7.4	63.0	37.7
4	147	3681	2331	18654	7870	841	10.9	nd	499	nd	nd	nd	220	20.0	454	9.5	26.8	169	22.6	52.3	7.4	28.2	nm	nm	1.3	39.7	7.3	68.0	39.7
8	155	3754	2492	19653	7776	880	10.5	nd	526	nd	nd	1.15	224	20.4	455	10.3	28.0	177	22.9	53.2	7.5	28.8	nm	nm	1.3	39.8	7.0	72.3	42.1
12	157	4184	2763	20219	8711	901	11.7	nd	546	nd	44.3	1.57	230	21.7	458	11.4	28.7	181	22.8	53.7	7.6	28.5	nm	nm	1.2	38.2	6.4	73.9	41.9
24	170	4404	2814	22014	8345	932	12.6	nd	590	nd	26.7	1.43	234	21.5	447	11.6	29.3	188	23.1	53.9	7.6	28.6	nm	nm	1.2	39.4	6.4	81.0	45.6
36	180	4418	3011	22998	8056	963	13.1	nd	623	nd	25.9	1.56	235	21.7	442	11.1	29.5	191	23.2	54.0	7.6	28.3	nm	nm	1.3	38.4	6.3	84.6	46.7
48	184	4919	3586	23961	9369	890	14.5	nd	657	nd	35.5	1.43	241	23.5	440	12.6	29.5	192	23.3	54.2	7.5	28.9	nm	nm	1.3	41.2	6.2	86.0	46.4
72	187	5434	3197	26194	7954	921	14.6	nd	701	nd	nd	1.58	247	22.8	438	12.0	29.6	197	23.6	55.1	7.6	28.3	nm	nm	1.3	39.5	6.3	92.1	48.6
120	197	10095	5850	31069	15420	935	15.5	nd	752	nd	200.8	1.68	265	30.7	440	20.3	29.7	208	24.9	58.1	8.0	28.8	nm	nm	1.5	43.7	6.6	102.6	52.4
168	199	7661	3570	33109	7954	929	14.7	nd	757	nd	26.7	1.59	267	23.7	432	13.0	29.3	200	25.0	58.4	8.0	28.7	nm	nm	1.5	41.0	6.3	105.2	53.0
336	211	3302	3978	43467	10329	1097	17.7	nd	816	nd	70.9	2.43	317	28.0	461	16.9	30.9	214	29.1	67.6	9.2	29.8	29.7	37.0	1.7	46.5	6.6	122.9	55.8
1296	218	25949	1398	80209	10744	1220	19.7	nd	827	nd	26.5	4.77	496	38.5	475	21.4	33.8	243	37.6	87.1	11.5	31.9	31.5	40.9	2.7	64.0	6.9	157.8	61.6
1848	216	32164	2381	94719	15552	1272	18.0	nd	822	nd	143.3	4.12	560	45.5	466	24.7	35.1	256	39.5	92.0	12.3	30.7	32.5	40.3	3.3	70.0	8.2	155.7	59.3
12	158	4264	2408	20488	7898	891	11.7	nd	542	nd	21.6	1.65	228	20.8	454	11.0	28.6	180	22.8	53.6	7.5	28.2	nm	nm	1.28	38.60	6.22	75.42	43.11
36	176	4621	2885	23444	8051	977	13.4	nd	630	nd	27.2	1.81	238	21.7	446	11.6	29.8	193	23.2	54.8	7.67	28.3	nm	nm	1.28	39.6	6.41	85.4	46.8

nd = not detected; nm = not measured

Table A21: Concentrations of trace elements (ppt) in leachates of Nod-P-1 at 10 ppm dust concentration.

Acidi- fication time (hr)	Li	Na	Mg	Al	Ca	Ti	V	Cr	Mn	Cu	Zn	As	Rb	Sr	Y	Zr	Cs	Ba	La	Ce	Pr	Gd	Er	Yb	Tl	Pb	Bi	Th	U
0.166667	954	130367	56799	20606	174190	2835	1147	5.9	84554	45314	9095	120	36.3	4611	501	136	1.8	6863	555	612	171	164	67.2	59.9	2.2	200	0.21	14.6	24.9
1	1033	129215	81243	32894	180640	4444	1522	8.0	95960	60989	11234	144	44.1	4995	579	179	2.3	9772	668	856	205	195	81.0	72.5	3.3	248	0.28	19.8	28.3
2	1054	127882	92376	40381	178997	5273	1688	8.7	103987	66238	11819	155	47.0	5044	598	209	2.6	10898	695	949	214	203	84.6	76.1	4.1	245	0.31	22.4	28.8
4	1068	126251	103137	48923	178817	6319	1866	10.0	103169	71602	12509	156	51.2	5112	627	226	2.8	12251	732	1074	224	212	89.2	81.2	3.8	256	0.27	26.6	29.9
8	1083	123758	112995	57904	178488	7499	2058	12.0	100596	76282	13125	153	56.7	5204	657	236	3.4	13845	771	1222	237	223	95.0	85.8	3.1	275	0.30	32.9	30.4
12	1086	123334	118832	63683	177539	8318	2184	13.4	107790	78619	13454	154	60.7	5200	670	249	3.7	14754	787	1318	242	228	97.6	89.2	4.1	303	0.32	40.0	30.6
24	1066	119363	122567	70077	173295	9316	2307	15.6	97766	79557	13428	145	62.7	5079	670	257	3.9	15444	788	1407	242	228	99.0	89.9	4.4	287	0.26	49.6	29.9
36	1040	115504	123262	73310	169907	9877	2339	17.7	105609	78418	13367	144	64.5	4917	655	262	4.3	15636	773	1451	237	225	97.1	88.4	6.6	323	0.38	56.4	29.0
48	997	111106	118220	71820	161385	9859	2319	18.9	98417	76521	12752	143	64.2	4768	638	260	4.2	15382	751	1439	230	218	96.9	88.4	5.4	303	0.42	59.3	28.3
72	982	109738	119586	75139	163107	10458	2383	20.5	98560	76785	12760	143	67.5	4738	637	264	4.5	15653	753	1492	229	218	96.2	88.4	5.6	311	0.48	65.1	27.6
120	983	108159	121276	79866	159055	11168	2442	24.2	96349	77265	12732	147	73.5	4692	633	267	5.0	15979	751	1551	228	219	96.4	89.2	8.6	323	0.41	71.8	27.7
168	961	106165	120680	81546	155838	11398	2450	27.0	101591	76723	12633	153	76.8	4634	627	283	5.3	16004	746	1563	226	215	96.3	89.6	17.6	322	0.75	74.3	27.4
384	1054	108187	130294	95021	156317	12334	2518	32.6	121926	77405	12713	162	88.5	4654	630	324	6.3	17282	794	1730	240	233	103.1	99.3	11.9	385	0.50	94.9	31.6
528	1055	107917	129451	96720	155067	12270	2487	33.8	111734	76820	12613	158	90.6	4631	629	320	6.7	17436	799	1762	243	234	103.0	100.7	7.4	362	0.38	98.1	33.0
672	912	98147	118418	91726	147439	11771	2374	33.4	139041	71773	11585	159	84.3	4234	576	314	5.8	14753	689	1530	209	206	88.3	83.5	32.8	324	1.28	78.4	25.0
1128	890	96813	116853	96036	143871	11754	2351	35.3	165479	70604	11320	169	87.7	4134	559	348	6.2	14483	672	1519	203	199	87.0	82.4	32.2	354	1.81	78.0	24.3
1680	901	98307	118188	101623	144467	12012	2381	39.2	168812	70819	11342	171	91.4	4140	559	397	6.0	14507	667	1524	203	200	85.4	82.8	5.6	323	1.10	79.2	23.6
4	1060	125933	103210	49031	179333	6359	1869	11.0	111308	71585	12511	157	51.4	5117	626	235	2.87	12218	730	1078	224	212	89.3	80.6	3.98	271	0.3	26.6	29.3
12	1091	124167	119208	63647	179852	8345	2198	13.3	103853	79284	13569	154	60.1	5243	673	250	3.7	14776	790	1317	243	229	98.4	88.9	4.38	292	0.29	38.9	30.5
120	972	107623	120941	79467	158871	11209	2436	24.1	94471	76821	12713	147	72.9	4667	633	266	5.1	15914	747	1542	227	216	96.2	88.8	8.85	318	0.44	71.7	27.5

Table A22: Concentrations of trace elements (ppt) in leachates of W-2 at 50 ppm dust concentration.

Acidi- fication time(hr)	Li	Na	Mg	Al	Ca	Ti	V	Cr	Mn	Cu	Zn	As	Rb	Sr	Y	Zr	Cs	Ba	La	Ce	Pr	Gd	Er	Yb	Tl	Pb	Bi	Th	U
0.167	59.0	43002	47053	249328	194228	4856	265	nm	1025	1251	154	12.8	188	575	136	9.0	20.6	780	210	423	48.8	37.7	11.3	7.2	1.23	199	0.67	23.0	3.42
1	66.3	40234	61154	271454	203206	5982	324	nm	1191	1418	203	13.5	218	608	141	9.7	23.2	887	219	440	51.1	39.0	11.9	7.5	1.38	214	0.75	28.4	3.81
2	69.2	38757	64611	281270	207949	6227	339	nm	1217	1482	218	14.5	230	627	143	9.4	24.6	923	219	443	51.5	38.7	12.0	7.5	1.38	216	1.31	30.6	3.90
4	72.7	45207	70626	334421	232960	6647	364	nm	1328	1535	230	14.9	234	733	142	9.4	25.3	995	218	441	51.0	38.8	11.8	7.5	1.44	217	0.86	31.4	4.06
8	82.2	65342	78425	422780	282863	7289	398	nm	1464	1644	270	16.7	241	946	143	9.4	26.3	1120	221	444	51.3	39.1	11.9	7.7	1.44	220	1.03	32.7	4.22
12	87.3	72366	82417	475295	305220	7552	411	nm	1525	1656	285	17.1	241	1050	142	9.5	26.3	1172	221	445	51.0	39.4	12.0	7.9	1.42	223	1.01	33.5	4.25
24	101	91413	92726	596321	367387	8474	455	nm	1709	1722	309	18.2	248	1310	144	9.8	27.0	1310	226	453	52.0	39.7	12.3	8.0	1.54	229	1.05	34.7	4.41
36	115	110850	102612	716683	432924	9318	496	nm	1886	1792	350	19.3	253	1581	146	9.2	27.4	1439	229	459	52.4	40.0	12.5	8.1	1.53	231	1.05	35.3	4.64
48	127	126782	110105	812093	485329	10184	529	nm	2043	1885	672	19.9	257	1799	148	10.3	27.4	1552	232	464	52.8	40.1	12.6	8.3	1.63	237	1.26	35.8	4.85
72	148	156134	124030	970877	562312	11520	579	nm	2252	1931	440	20.7	260	2136	149	10.4	27.4	1687	236	471	53.6	39.9	12.8	8.3	1.72	237	0.82	36.4	5.14
120	179	200621	141060	1227617	698976	14107	670	nm	2607	2049	464	21.1	271	2718	154	11.9	28.0	1969	245	487	55.3	40.7	13.6	9.1	1.70	244	0.89	37.9	5.44
168	187	230136	149055	1400123	787942	15747	736	nm	2849	2107	482	22.6	278	3082	157	15.5	28.1	2148	250	494	56.2	41.2	13.6	8.8	1.76	247	0.89	38.5	5.81
336	214	326756	163602	1865842	1064413	19771	919	206	3298	2422	548	27.4	312	4411	175	12.1	30.8	2874	283	552	62.4	47.7	15.0	9.7	1.92	285	1.81	43.5	6.90
504	227	368008	170948	2082679	1186039	21815	1001	224	3550	2514	586	27.0	324	4850	178	15.6	30.7	3115	289	560	63.9	47.0	15.8	10.1	2.01	284	2.15	42.9	7.15
672	218	390678	169775	2165124	1229036	24848	1057	237	3619	2571	489	25.7	326	5145	177	17.1	29.2	3192	281	544	61.2	46.5	15.3	10.3	2.12	276	1.20	37.4	6.97
1104	221	447514	177957	2423672	1375383	28146	1214	269	4041	2679	496	28.7	350	5872	186	22.2	30.1	3648	298	571	64.1	48.4	16.8	11.9	2.47	285	1.27	40.4	7.44
1656	223	492314	185689	2610496	1485990	30774	1366	306	4490	2776	513	28.4	364	6384	195	32.7	30.6	4017	308	587	65.6	50.9	17.8	12.4	2.40	296	1.24	40.9	8.07
4	76.6	47640	71451	89026	241493	6864	370	nm	1357	1550	248	15.5	236	785	142	9.23	25.4	1023	220	443	50.9	38.6	11.7	7.61	1.39	219	0.83	31.9	4.11
12	86.3	70599	81315	116163	294525	7546	410	nm	1511	1639	272	17.3	239	1035	142	9.19	26.1	1166	220	443	50.9	38.6	12.0	7.73	1.44	221	0.97	33.2	4.32
168	191	232083	150694	353716	782176	15951	740	nm	2830	2132	492	22.8	279	3091	157	14.4	28.3	2155	250	494	56.2	42.1	13.3	9.06	1.88	249	0.91	38.5	6.17

nm = not measured

Table A23: Concentrations of trace elements (ppt) in leachates of W-2 at 500 ppm dust concentration.

Acidi- fication time (hr)	Li	Na	Mg	Al	Ca	Ti	V	Cr	Mn	Cu	Zn	As	Rb	Sr	Y	Zr	Cs	Ba	La	Ce	Pr	Gd	Er	Yb	Tl	Pb	Bi	Th	U
0.167	403	241361	364062	1486963	1397446	33958	2076	nm	7927	10845	1364	111	1584	3558	1249	34.8	162	6237	1919	3896	451	346	104	64.5	10.4	1944	6.4	208	30.6
1	547	299339	518381	1980345	1652616	46808	2786	nm	10974	12790	1862	138	1928	4456	1371	33.8	186	7661	2110	4284	496	377	115	74.8	11.6	2444	7.5	276	36.1
2	615	386816	589144	2554579	1944614	53165	3093	nm	12453	13629	2480	149	2040	5716	1392	35.3	195	8633	2143	4354	501	384	118	74.6	12.6	2511	8.5	293	37.4
4	679	471838	662021	3101405	2224540	58407	3421	nm	14431	14321	2260	156	2131	6923	1415	40.5	203	9607	2178	4420	506	386	121	75.9	12.7	2555	8.5	309	38.9
8	754	563168	730261	3767238	2572730	61489	3664	nm	16204	14976	2513	164	2150	8385	1424	32.2	206	10485	2192	4439	511	389	120	77.4	13.1	2591	8.3	321	40.0
12	798	655977	784569	4307035	2842003	65072	3938	nm	17896	15408	2618	173	2183	9579	1429	34.2	209	11072	2193	4420	507	384	121	76.6	13.1	2552	7.9	318	40.8
24	935	864179	924658	5623643	3543918	78614	4535	nm	21158	16228	3015	192	2264	12313	1443	73.5	217	12650	2233	4484	515	388	123	80.1	14.0	2643	7.6	336	43.6
36	1057	1046366	988728	6791888	4138624	83210	4803	nm	21845	16813	3278	226	2297	14768	1457	62.6	219	13696	2258	4555	520	390	122	79.8	14.0	2680	8.0	343	46.0
48	1129	1150771	1038098	7440062	4456695	88236	5055	nm	22855	17090	3368	213	2328	16184	1468	50.9	221	14390	2283	4584	525	397	125	80.9	14.4	2700	8.0	352	47.6
72	1301	1383878	1129610	8874845	5199137	94111	5343	nm	24336	17515	3750	219	2328	19498	1463	26.3	221	15713	2306	4626	530	397	127	82.2	14.0	2755	8.4	354	49.7
120	1618	1818801	1351232	11435366	6584822	120778	6489	nm	28845	18920	4379	229	2457	24932	1527	53.2	227	18332	2403	4797	549	410	131	87.1	15.8	2808	7.9	367	54.0
168	1766	2073927	1412452	12895095	7314193	131249	6864	nm	30119	19164	4579	234	2457	28093	1526	50.1	226	19657	2423	4809	549	408	132	86.2	15.8	2823	8.1	374	55.4
336	2109	2991356	1667826	17409733	10561986	170567	9089	2330	36810	22531	5564	271	2784	39615	1698	83.6	246	26054	2726	5349	608	454	152	97.7	17.5	3142	18.7	408	65.0
504	2206	3379704	1722474	19410920	11842108	207854	10123	2551	38924	23830	5516	277	2935	44735	1766	97.7	252	28798	2828	5528	626	467	158	103.3	18.4	3242	20.2	421	69.3
672	2044	3402770	1589608	19295224	11029783	200642	9853	2392	36550	23362	4904	263	2724	45530	1672	57.6	235	27871	2681	5208	585	447	149	99.1	18.3	3023	12.6	366	65.6
1104	2120	3926980	1667805	21797024	12492536	229596	11400	2733	39424	24999	5079	262	2847	51620	1745	55.2	238	31269	2799	5410	607	468	157	107.7	20.0	3143	12.5	386	72.3
1656	2135	4323404	1727528	23536276	13523269	250931	12891	3026	42579	26241	5207	272	2934	56487	1824	61.5	241	34199	2883	5550	628	477	166	117.5	19.2	3194	11.8	395	76.3
4	698	502631	688233	823696	2299170	63158	3608	nm	15055	14420	2309	158	2150	7378	1419	52.5	205	9898	2185	4423	513	388	120	77.4	13.2	2573	8.28	311	38.4
12	827	702096	819051	1138137	2950371	69869	4152	nm	18670	15633	2673	174	2222	10079	1446	92.4	213	11453	2219	4489	515	391	120	78.2	13.5	2617	8.23	327	40.6

nm = not measured

Table A24: Concentrations of trace elements (ppt) in leachate of BHVO-2 after 12 hr acidification following storage under different conditions.

Dust concentration (ppm)	Storage option	Li	Na	Mg	Al	Ca	Ti	V	Cr	Mn	Cu	As	Rb	Sr	Y	Zr	Cs	Ba	La	Ce	Pr	Gd	Er	Yb	Tl	Pb	Bi	Th	U
63.132	AF	14.8	27978	143363	114921	118452	6219	116	240	2849	1638	ndS	4.73	757	322	159	nd	169	307	735	101	89.0	29.8	21.4	ndS	nd	ndS	14.4	4.42
62.055	AF	14.9	33269	141415	119642	123000	6468	120	215	2769	1569	ndS	5.46	790	342	172	nd	174	327	785	108	94.5	31.8	22.8	ndS	nd	ndS	16.0	5.18
62.750	AF	14.3	27365	150301	109814	114535	6155	117	243	3040	1660	ndS	4.93	734	333	172	nd	166	319	766	105	91.9	31.2	23.0	ndS	nd	ndS	16.0	4.90
64.757	UF	14.4	36004	101391	127462	128547	5664	114	184	2296	1572	ndS	6.36	845	351	135	nd	189	337	806	111	96.3	33.1	23.8	ndS	nd	ndS	16.9	5.05
64.726	UF	15.6	45822	102258	118838	135631	5128	103	179	2463	1495	ndS	6.81	819	338	128	nd	181	326	779	107	94.1	31.6	22.7	ndS	nd	ndS	16.5	4.97
63.092	UF	17.5	43324	98652	117419	121154	4909	103	211	2360	1529	ndS	6.71	787	328	119	nd	173	314	751	103	90.0	30.4	22.0	ndS	nd	ndS	15.8	4.82
63.664	NF	19.0	43318	114036	136736	140444	5996	116	221	2583	1623	ndS	6.50	901	367	115	nd	196	349	841	115	98.8	33.8	24.2	ndS	nd	ndS	17.2	5.37
63.080	NF	15.6	39749	105888	128810	132560	5532	107	194	2467	1495	ndS	6.14	849	346	113	nd	188	331	798	109	93.4	32.3	23.2	ndS	nd	ndS	16.1	5.04
61.906	NF	14.3	32392	110562	129515	131952	5562	113	227	2755	1680	ndS	5.70	860	350	123	nd	190	335	808	111	94.8	32.3	23.3	ndS	nd	ndS	17.1	5.02

AF=Acidified, frozen; UF = Un-acidified, frozen; NF = Not frozen; nd = not detected; ndS = not detectable in rock standard

Table A25: Concentrations of trace elements (ppt) in leachate of JG-2 after 12 hr acidification following storage under different conditions.

Dust concen- tration	Storage option	Li	Na	Mg	Al	Ca	Ti	V	Cr	Mn	Cu	Zn	As	Rb	Sr	Y	Zr	Cs	Ba	La	Ce	Pr	Gd	Er	Yb	Tl	Pb	Bi	Th	U
63.132	AF	1272	35054	980	174245	27917	6582	100	nd	3366	nd	74.5	11.7	1568	156	3739	163.6	196	1487	192	446	61.8	224.1	244.0	299	nd	261	46.5	953	384
62.055	AF	1296	26899	973	157196	23620	7018	103	nd	3498	nd	74.5	10.9	1694	139	3326	133.9	225	1370	181	427	59.6	206.3	224.1	276	nd	281	21.5	1467	459
62.750	AF	1404	28916	1018	167747	34949	7300	104	nd	3773	nd	75.3	21.1	1721	146	4509	180.4	229	1452	207	476	66.3	260.2	286.3	351	nd	273	24.7	2143	428
64.757	UF	931	24650	1417	118643	28797	5107	74	nd	2720	nd	84.2	8.7	1362	121	2621	81.9	170	1188	137	316	44.1	166.3	168.4	210	nd	265	19.9	648	287
64.726	UF	1034	25743	1347	127947	38840	5214	129	nd	2946	nd	86.6	9.6	1432	131	3417	100.8	184	1250	164	381	53.7	210.2	218.0	277	nd	326	26.0	624	309
63.092	UF	1073	28804	1190	138679	35313	5664	78	nd	3115	nd	512.3	9.7	1532	149	3017	97.4	207	1382	159	367	51.0	191.9	192.1	242	nd	268	28.1	676	329
63.664	NF	983	31224	1575	132273	30997	5397	74	nd	2895	nd	87.6	10.9	1411	142	3242	84.4	184	1364	161	375	52.4	204.8	208.1	262	nd	232	24.6	658	391
63.080	NF	1223	27857	8826	143995	53659	7056	102	nd	4089	nd	261.4	24.5	1713	142	2951	91.3	204	1309	155	363	51.6	194.2	186.7	239	nd	360	21.9	599	320
61.906	NF	1196	24147	6937	131116	50193	7647	99	nd	3925	nd	232.2	13.7	1510	125	3278	84.4	172	1157	144	334	47.2	196.0	197.6	259	nd	228	18.6	523	308

AF=Acidified, frozen; UF = Un-acidified, frozen; NF = Not frozen; nd = not detected

Table A26: Concentrations of trace elements recorded in freezing experiment procedural blanks (vials containing 8 mL of ultra-pure water or 1% HNO₃ (Seastar) which were treated as samples).

	H ₂ O	H ₂ O	H ₂ O	HNO ₃	HNO ₃	HNO ₃
Li	0.95	0.32	0.33	-0.04	-0.06	-0.03
Na	-216.87	-127.21	2878.78	-319.96	-326.02	-335.10
Mg	503.48	315.11	569.47	442.95	262.04	-62.85
Al	90.02	42.48	15.75	100.19	67.66	66.56
Ca	696.91	275.42	2466.22	731.32	-284.79	25.04
Ti	34.43	-5.77	55.81	8.43	-13.60	-8.06
V	-0.48	-0.52	-0.11	-0.91	-1.06	-0.64
Cr	2.50	0.94	3.31	-1.07	-1.84	1.37
Mn	38.50	24.43	11.84	12.82	5.03	-5.92
Cu	-0.35	-0.46	20.13	-4.51	-4.92	-2.24
As	ndS	ndS	ndS	ndS	ndS	ndS
Rb	-0.20	-0.07	1.71	-0.10	-0.10	-0.19
Sr	-0.25	-0.09	6.49	0.94	-0.23	-0.07
Y	0.00	-0.02	-0.01	0.10	0.04	0.06
Zr	0.32	0.05	0.01	-0.13	-0.21	-0.28
Cs	-0.01	-0.04	0.00	-0.01	0.01	-0.01
Ba	0.22	1.94	-1.19	-1.40	-2.41	-2.12
La	-0.04	-0.03	0.01	-0.04	-0.01	0.00
Ce	-0.06	-0.05	-0.05	-0.03	-0.02	-0.04
Pr	0.00	0.00	0.02	0.01	0.00	-0.01
Gd	0.00	0.06	-0.09	-0.09	-0.11	0.03
Er	0.01	0.04	0.08	-0.08	-0.01	0.02
Yb	-0.05	0.09	0.07	0.18	0.04	0.08
Tl	ndS	ndS	ndS	ndS	ndS	ndS
Pb	-1.23	-1.21	142.50	0.25	0.18	-0.07
Bi	ndS	ndS	ndS	ndS	ndS	ndS
Th	-0.07	-0.06	-0.14	-0.16	-0.16	-0.12
U	-0.01	-0.04	0.04	-0.01	-0.04	0.02

Values in grey are below the detection limit; ndS = not detected/certified in BHVO-2 standard

Table A27: LREE/MREE and LREE/HREE ratios of BHVO-2, JG-2 and W-2 leachates and rock standards.

**Ratios are of chondrite-normalised concentrations. (LREE= light rare earth elements La, Ce, Pr;
MREE= medium rare earth elements Gd); HREE= heavy rare earth elements Er, Gd).**

Acidification time (hr)	BHVO-2	JG-2	JG-2	W-2	W-2
	LREE/MREE	LREE/MREE	LREE/HREE	LREE/MREE	LREE/HREE
0.167	2.74	0.60	nm	3.70	12.3
1	2.65	0.60	nm	3.74	11.9
2	2.62	0.60	nm	3.72	11.9
4	2.75	0.61	nm	3.75	11.9
8	2.62	0.61	nm	3.75	11.9
12	2.76	0.62	nm	3.78	11.9
24	2.69	0.62	nm	3.81	11.8
36	2.71	0.63	nm	3.84	12.0
48	2.61	0.61	nm	3.81	11.8
72	2.60	0.64	nm	3.85	11.7
120	2.59	0.66	nm	3.86	11.7
168	2.55	0.66	nm	3.90	11.7
336	2.67	0.74	0.53	3.91	11.5
528	2.74	nm	nm	3.94	11.3
672	2.77	nm	nm	3.88	11.3
1104	nm	nm	nm	3.85	11.0
1296	2.60	0.88	0.63	nm	nm
1656	nm	nm	nm	3.89	10.6
1848	2.62	0.97	0.66	nm	nm
Rock standard	1.94	1.81	1.59	1.79	2.48

nm = not measured.

Appendix X: Antarctic Little Ice Age climate

In order to rapidly consider the Little Ice Age climate record, developed from the MES ice core, in the context of that of the entire Antarctic continent, a graphical summary of the available paleoclimate data is displayed (Fig. A6).

Figure A6: Summary of conditions across Antarctica during the Little Ice Age (modified after Bertler *et al.* [in press]). Datasets included are: McMurdo Dry Valleys temperature, Ross Sea sea surface temperature (SST), humidity, and sea-ice extent from ice core records [Bertler *et al.*, in press]; temperature data for Law Dome, Dome C, Vostok, Dominion Range, Byrd, and Plateau Remote from stable isotopic records [Masson *et al.*, 2000]; temperature data for Talos Dome, EPICA Dome C, South Pole, and Taylor Dome from stable isotopic records and snow accumulation data for Talos Dome [Stenni *et al.*, 2002]; temperature data from Taylor Dome borehole measurements referred to by Broecker [2000]; Antarctic Bottom Water formation rates [Broecker, 2000]; katabatic flow, diatom plume, polyna size, and sea ice from diatom data [Leventer and Dunbar, 1988]; Amundsen Sea Low strength from geochemical ice core data [Kreutz *et al.*, 2000]; East Antarctic High from geochemical ice core data [Mayewski *et al.*, 2004]; Southern Hemisphere Westerlies from geochemical ice core data [Yan *et al.*, 2005]; SST from magnetic susceptibility at Palmer Deep [Domack and Mayewski, 1999]; snow accumulation data for Dronning Maud Land [Karlöf *et al.*, 2000]; and atmospheric CO₂ concentration [Etheridge *et al.*, 1996; Indermuhle *et al.*, 1999].

Appendix XI: Mt Erebus Saddle 2006/07 soluble chemistry data

Concentration data for the elements Na, Mg, Al, Ca, Ti, V, Mn, As, Rb, Sr, Y, Zr, Cs, Ba, La, Ce, Pr, Tl, Pb, Bi, Th and U for all the ice core samples analysed by ICP-MS are provided in Table A28. A small batch of samples were analysed by ICP-MS in collision cell mode using a hydrogen-flushed collision cell to remove polyatomic interferences. Concentration data for the elements Na, Mg, Al, Ca, Mn, Fe and Ba for these samples are provided in Table A29.

The major ion data for all ice core samples analysed by IC at the University of Maine are provided in Table A30. Concentrations of Na^+ and Mg^{2+} determined by IC were compared to the Na and Mg concentrations determined in corresponding samples by ICP-MS and significant discrepancies were found. Approximately 5% of the samples analysed by IC showed anomalously high concentrations of Na^+ and Mg^{2+} and were also characterised by high concentrations of all the other cations and anions measured (Figure A7A). One possible cause of these anomalous data points is that air may have been drawn into the chromatograph during sample uptake. Once these data points were removed, the Na^+ record determined by IC and the Na record determined by ICP-MS corresponded well (Figure A7B) and showed a strong positive correlation ($R^2 = 0.69$). The major ion dataset with the anomalous values removed is displayed in Table A31.

Tables A28 to A31 are located on the enclosed data disk.

Figure A7: Identification and removal of anomalous IC data points. (A) Data for all cations (Na^+ and K^+ shown) and anions (SO_4^{2-} and MS^- shown) exhibit anomalously high concentrations determined by IC on several samples throughout the MES record. The segment from 12 to 20 m depth is displayed here to illustrate this. Comparison of the Na record determined by IC (light blue) with that determined by ICP-MS (dark blue) suggests that the concentrations determined by IC on these samples are unreliable. **(B)** Removal of the IC data for these samples results in an IC Na record similar to the ICP-MS Na record.

Appendix XII: Mt Erebus Saddle ice core age model

The results of the annual layer count are provided here in Table A32. The depth at which δD occurs in each annual cycle dates to January 1st. Below 110 m depth the age-depth relationship produced by the polynomial extrapolation of the annual layer count is given. This age model can be applied to any of the stable isotope or soluble chemistry parameters displayed in Tables A6, A14 and A28 to A21 by using an interpolation function. As the ice core age model could be subject to improvement in the future, age is not included in the raw data tables.

Table A32: MES ice core age model.

Age (yr)	Depth (m)	Age (yr)	Depth (m)	Age (yr)	Depth (m)	Age (yr)	Depth (m)
2007	0.00	1964	19.14	1921	33.42	1878	45.66
2006	0.40	1963	19.48	1920	33.83	1877	46.00
2005	0.96	1962	20.02	1919	34.19	1876	46.20
2004	1.73	1961	20.48	1918	34.48	1875	46.48
2003	2.21	1960	20.86	1917	34.88	1874	46.72
2002	2.91	1959	21.27	1916	35.15	1873	46.98
2001	3.23	1958	21.63	1915	35.52	1872	47.15
2000	3.69	1957	21.97	1914	35.84	1871	47.44
1999	4.12	1956	22.20	1913	36.10	1870	47.67
1998	4.59	1955	22.56	1912	36.43	1869	47.97
1997	5.00	1954	23.05	1911	36.71	1868	48.22
1996	5.48	1953	23.30	1910	37.01	1867	48.48
1995	5.98	1952	23.57	1909	37.41	1866	48.87
1994	6.64	1951	23.90	1908	37.63	1865	49.11
1993	7.16	1950	24.23	1907	37.92	1864	49.51
1992	7.63	1949	24.65	1906	38.25	1863	49.78
1991	7.93	1948	24.98	1905	38.52	1862	50.08
1990	8.22	1947	25.23	1904	38.81	1861	50.24
1989	8.79	1946	25.59	1903	39.03	1860	50.61
1988	9.11	1945	25.98	1902	39.25	1859	50.88
1987	9.47	1944	26.21	1901	39.45	1858	51.23
1986	9.99	1943	26.43	1900	39.79	1857	51.44
1985	10.38	1942	26.72	1899	40.06	1856	51.67
1984	10.72	1941	26.97	1898	40.48	1855	51.99
1983	11.29	1940	27.27	1897	40.76	1854	52.27
1982	11.74	1939	27.72	1896	40.99	1853	52.61
1981	12.18	1938	28.03	1895	41.26	1852	52.84
1980	12.88	1937	28.30	1894	41.51	1851	53.05
1979	13.19	1936	28.69	1893	41.81	1850	53.30
1978	13.62	1935	28.90	1892	42.03	1849	53.55
1977	13.94	1934	29.33	1891	42.34	1848	53.71
1976	14.46	1933	29.64	1890	42.74	1847	53.96
1975	14.80	1932	30.00	1889	42.90	1846	54.13
1974	15.14	1931	30.27	1888	43.20	1845	54.33
1973	15.55	1930	30.60	1887	43.42	1844	54.51
1972	16.10	1929	30.94	1886	43.68	1843	54.75
1971	16.49	1928	31.25	1885	43.95	1842	54.95
1970	16.76	1927	31.58	1884	44.23	1841	55.20
1969	17.37	1926	31.99	1883	44.44	1840	55.40
1968	17.65	1925	32.30	1882	44.77	1839	55.69
1967	17.94	1924	32.72	1881	45.04	1838	55.91
1966	18.39	1923	32.90	1880	45.19	1837	56.18
1965	18.75	1922	33.13	1879	45.46	1836	56.39

Age (yr)	Depth (m)	Age (yr)	Depth (m)	Age (yr)	Depth (m)	Age (yr)	Depth (m)
1835	56.60	1790	67.32	1745	75.74	1700	84.66
1834	56.97	1789	67.49	1744	75.96	1699	84.85
1833	57.16	1788	67.72	1743	76.14	1698	85.01
1832	57.41	1787	67.90	1742	76.28	1697	85.22
1831	57.64	1786	68.13	1741	76.44	1696	85.39
1830	57.84	1785	68.26	1740	76.65	1695	85.61
1829	58.11	1784	68.56	1739	76.83	1694	85.75
1828	58.37	1783	68.77	1738	76.94	1693	85.95
1827	58.60	1782	68.98	1737	77.13	1692	86.09
1826	58.82	1781	69.19	1736	77.34	1691	86.26
1825	59.09	1780	69.38	1735	77.49	1690	86.50
1824	59.28	1779	69.52	1734	77.68	1689	86.60
1823	59.54	1778	69.71	1733	77.85	1688	86.79
1822	59.79	1777	69.91	1732	78.02	1687	86.95
1821	60.00	1776	70.06	1731	78.31	1686	87.09
1820	60.27	1775	70.28	1730	78.58	1685	87.23
1819	60.46	1774	70.50	1729	78.78	1684	87.43
1818	60.70	1773	70.70	1728	78.96	1683	87.53
1817	60.96	1772	70.83	1727	79.14	1682	87.74
1816	61.23	1771	70.99	1726	79.35	1681	87.87
1815	61.49	1770	71.13	1725	79.52	1680	88.16
1814	61.69	1769	71.37	1724	79.69	1679	88.33
1813	61.87	1768	71.59	1723	79.83	1678	88.50
1812	62.09	1767	71.77	1722	80.05	1677	88.57
1811	62.24	1766	71.99	1721	80.34	1676	88.75
1810	62.50	1765	72.15	1720	80.48	1675	88.93
1809	62.67	1764	72.38	1719	80.72	1674	89.06
1808	62.93	1763	72.57	1718	80.98	1673	89.24
1807	63.19	1762	72.74	1717	81.08	1672	89.39
1806	63.45	1761	72.92	1716	81.32	1671	89.54
1805	63.63	1760	73.08	1715	81.62	1670	89.72
1804	64.05	1759	73.27	1714	81.88	1669	89.87
1803	64.37	1758	73.49	1713	82.15	1668	90.05
1802	64.65	1757	73.66	1712	82.28	1667	90.20
1801	64.82	1756	73.83	1711	82.53	1666	90.37
1800	65.04	1755	74.04	1710	82.68	1665	90.56
1799	65.24	1754	74.21	1709	82.89	1664	90.69
1798	65.48	1753	74.41	1708	83.09	1663	90.81
1797	65.82	1752	74.54	1707	83.26	1662	90.99
1796	66.16	1751	74.82	1706	83.41	1661	91.14
1795	66.41	1750	74.98	1705	83.61	1660	91.33
1794	66.56	1749	75.08	1704	83.79	1659	91.49
1793	66.76	1748	75.22	1703	84.05	1658	91.64
1792	66.92	1747	75.38	1702	84.18	1657	91.79
1791	67.14	1746	75.56	1701	84.35	1656	91.93

Age (yr)	Depth (m)	Age (yr)	Depth (m)	Age (yr)	Depth (m)	Age (yr)	Depth (m)
1655	92.13	1610	98.90	1565	105.39	1520	111.24
1654	92.28	1609	99.03	1564	105.53	1519	111.36
1653	92.40	1608	99.18	1563	105.64	1518	111.49
1652	92.59	1607	99.32	1562	105.79	1517	111.61
1651	92.72	1606	99.47	1561	105.92	1516	111.74
1650	92.89	1605	99.65	1560	106.03	1515	111.86
1649	93.13	1604	99.86	1559	106.23	1514	111.99
1648	93.27	1603	100.09	1558	106.36	1513	112.11
1647	93.42	1602	100.28	1557	106.48	1512	112.24
1646	93.61	1601	100.41	1556	106.61	1511	112.36
1645	93.77	1600	100.56	1555	106.72	1510	112.48
1644	93.91	1599	100.68	1554	106.84	1509	112.61
1643	94.08	1598	100.81	1553	107.01	1508	112.73
1642	94.25	1597	100.93	1552	107.11	1507	112.85
1641	94.37	1596	101.07	1551	107.26	1506	112.98
1640	94.48	1595	101.21	1550	107.34	1505	113.10
1639	94.62	1594	101.32	1549	107.45	1504	113.22
1638	94.83	1593	101.44	1548	107.55	1503	113.34
1637	94.94	1592	101.56	1547	107.72	1502	113.47
1636	95.11	1591	101.72	1546	107.85	1501	113.59
1635	95.22	1590	101.87	1545	108.02	1500	113.71
1634	95.38	1589	101.97	1544	108.16	1499	113.83
1633	95.52	1588	102.12	1543	108.32	1498	113.95
1632	95.64	1587	102.22	1542	108.47	1497	114.07
1631	95.81	1586	102.38	1541	108.59	1496	114.20
1630	95.92	1585	102.51	1540	108.73	1495	114.32
1629	96.05	1584	102.67	1539	108.81	1494	114.44
1628	96.22	1583	102.77	1538	108.94	1493	114.56
1627	96.36	1582	102.93	1537	109.07	1492	114.68
1626	96.51	1581	103.12	1536	109.20	1491	114.80
1625	96.62	1580	103.25	1535	109.32	1490	114.92
1624	96.77	1579	103.37	1534	109.45	1489	115.04
1623	96.91	1578	103.50	1533	109.58	1488	115.16
1622	97.03	1577	103.62	1532	109.71	1487	115.28
1621	97.19	1576	103.76	1531	109.84	1486	115.39
1620	97.30	1575	103.87	1530	109.97	1485	115.51
1619	97.44	1574	103.98	1529	110.10	1484	115.63
1618	97.60	1573	104.12	1528	110.22	1483	115.75
1617	97.70	1572	104.32	1527	110.35	1482	115.87
1616	97.96	1571	104.48	1526	110.48	1481	115.99
1615	98.17	1570	104.62	1525	110.60	1480	116.10
1614	98.33	1569	104.75	1524	110.73	1479	116.22
1613	98.50	1568	104.96	1523	110.86	1478	116.34
1612	98.61	1567	105.13	1522	110.98	1477	116.46
1611	98.76	1566	105.28	1521	111.11	1476	116.57

Age (yr)	Depth (m)
1475	116.69
1474	116.81
1473	116.92
1472	117.04
1471	117.16
1470	117.27
1469	117.39
1468	117.50
1467	117.62
1466	117.73
1465	117.85
1464	117.96
1463	118.08
1462	118.19
1461	118.31
1460	118.42
1459	118.54
1458	118.65
1457	118.76
1456	118.88
1455	118.99
1454	119.10
1453	119.22
1452	119.33
1451	119.44
1450	119.56
1449	119.67
1448	119.78
1447	119.89
1446	120.00

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