A Paleoclimate Reconstruction of the Little Ice Age to
Modern Era Climate Conditions in the Eastern Ross Sea,
Antarctica as captured in the RICE Ice Core

By

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Abstract

The Little Ice Age (LIA) (1400-1850 AD) represents one of the most significant climatic shifts over the past 5000 years. Previous studies from Antarctica indicate generally cooler and stormier conditions during this period, but this pattern shows distinct spatial and temporal variability. The Roosevelt Island Climate Evolution (RICE) ice core provides a new opportunity to study the drivers behind this variability at annual/seasonal resolution, in a relatively under-sampled and climatically sensitive region in the eastern Ross Sea. Contrary to previous studies, isotope measurements suggest warm conditions during the LIA at Roosevelt Island.

This study presents analysis of eight major ions (Na^+ , Mg^{2+} , Ca^{2+} , K^+ , MS^- , Cl^- , NO_3^- , SO_4^{2-}) using both Ion Chromatograph and ICP-MS data, in order to reconstruct the atmospheric circulation pattern, sea ice extent and marine primary productivity across this LIA to Modern Era (ME) at Roosevelt Island. The dataset is tied to a robust age model allowing annual dating and the opportunity to accurately reconstruct rates of change during this ME-LIA. Challenges revolving around the calibration of the Ion Chromatograph are also discussed. The major ion record determines whether the lack of cooling in the Roosevelt Island core implied by the stable isotopes represents a true temperature anomaly or whether the atmospheric circulation pattern caused an isotopic enrichment that masks an underlying cooling.

It was determined that Roosevelt Island experienced during the LIA (i) an increase in marine air mass intrusions along with weaker katabatic winds compared to the 200 years prior, (ii) decreased biological productivity and (iii) increased sea ice. From the 1850-1880s to 1992 AD, there is a shift to reduced marine winds, increased katabatics, increased biological productivity and decreased sea ice until 1992. In the wider Ross Sea context, this suggests an east-west divide in terms of the dominance of katabatics versus marine wind influence. This divide is attributed with the warming signal seen in the RICE record in the Eastern Ross Sea and the cooling in the Western Ross Sea records. It is also likely linked to the influence of climate indices on the depth/position of the Amundsen Sea Low.

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List of Abbreviations

ASL : Amundsen Sea Low

CFA: Continuous Flow Analysis

DEM: Digital Elevation Model

ENSO : El Niño Southern Oscillation

IC : Ion Chromatograph

ICP-MS : Induced Coupled Plasma Mass Spectrometry

LIA : Little Ice Age (~1400-1850 AD)

ME : Modern Era (~1850-1992 AD)

MES : Mount Erebus Saddle (ice core)

MSLP: Mean Sea Level Pressure

PC: Principal Component (from Principal Component Analysis)

PPB: parts per billion

PDO : Pacific Decadal Oscillation

QC: Quality Control standard

RICE : Roosevelt Island Climate Evolution (ice core)

SAM : Southern Annular Mode

SIE : Sea ice extent

SOI : Southern Oscillation Index

VLG : Victoria Lower Glacier (ice core)

WAIS: West Antarctic Ice Sheet (ice core)

Chapter 1: Introduction

1.1 Thesis Context

With carbon dioxide concentrations continuing to rise, the importance of determining Antarctica's atmospheric and oceanic behaviour in a warming world is imperative. In order to assess that behaviour we consult paleoclimate records. The past 2000 years allow records of rapid climate change in the recent past to be studied at high resolution and thus track change through the transition from a natural to a human influenced climate. However, Antarctica's record of climate change and the impact on the atmospheric/oceanic conditions over the last 2000 years is relatively sparse, due to poor spatial and temporal coverage of high (annual/seasonal) resolution paleoclimate records (Rahaman et al., 2016).

The Little Ice Age (LIA) is of particular significance as current atmospheric and oceanic conditions observed in Antarctica may have been occurring in a similar way in the LIA, despite warmer temperatures (Bertler et al., 2011). Clear spatial variability exists in the temperature signal of the LIA, with the majority of records indicating a cooling (Bertler et al., 2011; Kreutz et al., 2000; Orsi et al., 2012; Rhodes et al., 2012), whereas Siple Station records a warming (Mosley-Thompson & Thompson, 1990). The eastern Ross Sea is relatively under sampled during this time and is located in a sensitive region that could contribute to better understanding this spatial variability and the causal processes occurring in the Ross Sea region.

1.2 Study location

*Figure 1.1 (left): Photo of RICE ice core.
Figure 1.2. (right): Photo of RICE ice core
preparation in Antarctica.
Photos courtesy of Nancy Bertler.*

The highly resolved Roosevelt Island Climate Evolution (RICE) ice core provides a new opportunity to study this relatively under sampled area in the eastern Ross Sea during the LIA. The RICE project is an international collaboration comprising 9 nations and 21 institutions, aimed at determining the stability of the Ross Ice Shelf in a warmer world. The RICE ice core is a 763 m core and was recovered from Roosevelt Island over the 2011/2012 and 2012/2013 field seasons (Figures 1.2 & 1.2).

Figure 1.3: Location of Roosevelt Island.

Roosevelt Island is an independent ice rise located on the north-eastern edge of the Ross Ice Shelf (79.36398°S, 161.70645°W, 550 m above sea level) (Figures 1.3). The RICE ice core provides an excellent opportunity to assess the atmospheric and oceanic processes occurring in Antarctica during the Little Ice Age to Modern Era (ME) transition, as it sits in a region that is known to be very sensitive to changes in climate drivers (Emanuelson, 2016). These drivers include the El Niño-Southern Oscillation (ENSO), Southern Annular Mode (SAM) and Pacific Decadal Oscillation (PDO), which interact with teleconnections in the tropics through the Amundsen Sea Low (ASL) and with the mid-latitudes through the position and strength of the Westerly winds.

1.3 Research Questions

This thesis will further our knowledge of the Little Ice Age-Modern Era conditions in Antarctica, as well as contribute to the wider Roosevelt Island Climate Evolution (RICE) project database. The thesis presented here focuses on 3 research questions:

- 1) What were the atmospheric and climatic conditions experienced at Roosevelt Island during the LIA/ME and over this transition?
- 2) What climate drivers can be linked to the processes we observe at Roosevelt Island during the LIA/ME and over this transition?
- 3) How do the climate conditions at Roosevelt Island fit in the context of the wider Ross Sea setting during the LIA/ME and over this transition?

1.4 Outline

This thesis comprises six chapters. Chapter 1 describes the context behind this research and the three research questions. Chapter 2 provides a background to the Little Ice Age, the Antarctic and the Ross Sea climatic/atmospheric setting and how major ion analyses in ice cores are used to reconstruct past environmental conditions. Chapter 3 will describe the methodology undertaken to analyse the major ion

chemistry of the RICE ice core. Chapter 4 presents the results of time series and the associated statistical analyses. Chapter 5 provides a discussion on the 3 research questions. Finally, Chapter 6 details the main conclusions and the implications for future work.

1.5 Candidate's Involvement

This thesis contributes to the large amount of work that has already been conducted on the RICE ice core by the international RICE team. My contribution involved independently (following an induction) analysing 1020 ice core samples for 8 major ions during July 2016 on the Ion Chromatograph at the NZ National Ice Core Laboratory. Aided by Nancy Bertler and Rebecca Pyne, I developed a calibration for this data set which allowed the analysis of both ultra low and high ion concentrations required for studying a coastal ice core site. I subsequently processed previously run data from June/October 2013 and November 2015, that used alternative calibrations and in the former's case, a different IC machine. I pieced this older data with my data to form a longer IC timeseries (1558-1991 AD). This time series was then compared to the longer ICP-MS record measured by Andrea Tuohy and Peter Neff (1202-2011 AD). I was then guided on the data analysis techniques, but was responsible for their implementation. I completed the data interpretation and implications for past climate with the help of Nancy Bertler and Lionel Carter.

Chapter 2: Background

2.1 Little Ice Age Patterns

The LIA represents one of the most significant climatic shifts over the past 5000 years (Kreutz et al., 1997; Mayewski & Maasch, 2006). The LIA phenomenon was initially used to describe the period between approximately 1400-1850s, when the Northern Hemisphere experienced exceptionally cold temperatures, subsequent glacial advances and mountain snow lines dropped to approximately 100 m below their current position (Figure 2.1) (Bond et al., 1999; Broecker et al., 1999; Grove, 1988). Broecker et al. (1999) reported that European summertime temperatures were relatively cold during the 17th and early 19th century (Figure 2.1). In North America, low summer temperatures were recorded from ~1580 to ~1730 AD and ~1815 to 1870 AD (Broecker et al., 1999). However, the cooling was not synchronous across the whole of the Northern Hemisphere, with many regions recording warm temperatures similar to today, including areas in the Middle East, central North Atlantic, Africa, parts of the United States, tropical Eurasia and the extratropical Pacific Ocean (Mann et al., 2009).

Figure 2.1: Summary of LIA cold signatures and their timing. Europe (Grove, 1988), North America (Broecker et al., 1999), Gran Campo Nevado (Koch & Kilian, 2005), North Patagonia glacial advances (Villalba, 1994), Mueller Glacier, NZ (Schaefer et al., 2009). Victoria Lower Glacier (Bertler et al., 2011), Mt. Erebus Saddle (Rhodes et al., 2012), Princess Elizabeth Land (Li et al., 2009), Law Dome (Morgan, 1997), WAIS (Orsi et al., 2012).

However, contrary to previous understanding, the LIA signature has also been recorded in the Southern Hemisphere (Figure 2.1). Records from South America,

including Chile and Patagonia, also show a cooler, wetter interval with glacial advances that coincide with the LIA (Koch & Kilian, 2005; Villalba, 1994).

Mount Cook glacial records (^{10}Be) in New Zealand show broad similarities with the Northern Hemisphere over the past 700 years, with several advances followed by a termination during the mid to late 19th century (Schaefer et al., 2009). However, Northern hemisphere glacier terminal moraine records show a LIA-maximum less than 400 years old, whereas Mueller Glacier's (Mt. Cook region) most prominent moraine from the past millennium is older, at ~570 years old (Schaefer et al., 2009). Putnam et al. (2012) linked the difference in timing to a southward shift in the Intertropical Convergence Zone (ITCZ) ~500-400 years ago, which coincided with the Northern Hemisphere's (New Zealand) glacial advance (retreat).

Previous research has also confirmed a coincidence between the timing of the LIA and a generally cooler signature in Antarctic ice core and borehole records (Bertler et al., 2011; Li et al., 2009; Morgan, 1997; Orsi et al., 2012; Rhodes et al., 2012).

Figure 2.2: Summary of the suggested causes of the LIA and their respective estimated timings. Green shows solar irradiance impacts (Orsi et al., 2012). Red represents volcanic impacts (Crowley, 2000; Miller et al., 2012). Orange refers to climatological impacts (Sachs et al., 2009). Blue relates to oceanic/climate impacts (Broecker et al., 1999; Mann et al., 2009; Rustic et al., 2015).

Causes of this climatic phenomenon have ranged (Figure 2.2) from differences in deep-water formation in the Arctic vs. Antarctic (Broecker, 2000), decreased solar irradiance (Bard et al., 2000; Orsi et al., 2012), volcanism (Crowley, 2000; Miller et al., 2012; Orsi et al., 2012), changes in the North Atlantic Oscillation (NAO) (Bradwell et al., 2006;

Mann et al., 2009; Trouet et al., 2009) and El Niño Southern Oscillation (ENSO) (Oppo et al., 2009; Rustic et al., 2015) or movements in the Intertropical Convergence Zone (Haug et al., 2001; Newton et al., 2006; Putnam et al., 2012; Rouillard et al., 2016; Rustic et al., 2015; Sachs et al., 2009).

2.2 Antarctic Setting

2.2.1 General Antarctic circulation

Antarctica is the highest, driest, coldest and windiest place on Earth (Bertler & Barrett, 2010). The continent is comprised of the $10.35 \times 10^6 \text{ km}^2$ East Antarctic Ice sheet (EAIS) and the smaller West Antarctic Ice Sheet (WAIS) ($1.97 \times 10^6 \text{ km}^2$), which are separated by the Transantarctic Mountains that stretch 3,500 km from the Ross to the Weddell Sea (Bertler & Barrett, 2010; King & Turner, 1997). Antarctica's thermal isolation is mainly due to the eastwards-flowing Antarctic Circumpolar Current (ACC), stretching between 40-65° latitude. The ACC is the largest current in the world, the only current to connect all ocean basins, and is driven by the strong mid-latitude westerly winds (King & Turner, 1997) .

Antarctica is surrounded by a belt of sea ice. During winter the sea ice covers up to $18 \times 10^6 \text{ km}^2$ of ocean but by the end of summer, it reduces to approximately $3 \times 10^6 \text{ km}^2$ (NSIDC, 2016). Unlike in the Arctic, the majority of Antarctic sea ice melts each summer, resulting in most sea ice being thin 1st year ice.

The Antarctic atmospheric circulation is comprised of three main features; a weak surface anticyclone over the continent, the circumpolar trough and three climatologically low pressure centres (King & Turner, 1997). The weak anti-cyclonic vortex over the continent is observed at the 500 hPa pressure surface, and is displaced slightly off the South Pole towards the Ross Ice Shelf (King & Turner, 1997). Whereas at the 300 hPa surface the vortex is stronger and more symmetrical about the South Pole (King & Turner, 1997). The circumpolar trough is a belt of low pressure that extends around Antarctica at roughly 66°S, driven by a high concentration of cyclonic activity

around the continent. Due to the asymmetry in the Antarctic continent three distinct climatological low-pressure centres occur within the Antarctic Circumpolar Trough. The most significant of these low pressures is the Amundsen Sea Low (ASL).

On average the ASL exists roughly between 60-70°S, 170-290°E, just north of Marie Byrd Land in the Ross/Amundsen Seas. From this location it controls much of the meridional precipitation that reaches the Ross Sea through the formation of synoptic scale cyclones (Bertler et al., 2006; Neff & Bertler, 2015). The ASL's depth shows a semi-annual oscillation, experiencing its lowest pressures in autumn and spring and its highest in summer and winter (Turner et al., 2013). It also exhibits a zonal and meridional climatological seasonal progression, often reaching its farthest easterly position in summer and farthest westerly (and southerly) position in winter (Fogt et al., 2012; Turner et al., 2013). The ASL is sensitive to the influence of the El Niño Southern Oscillation (ENSO), Pacific Decadal Oscillation (PDO) and the Southern Annular Mode (SAM).

2.2.2 El Niño Southern Oscillation

ENSO is the Earth's dominant mode of inter-annual variability. It describes the interaction between the ocean and atmosphere in the central Pacific (Walker Circulation) that oscillates on 2-7 year periodicity between the anomalously cold (La Niña) and anomalously warm (El Niño) sea surface temperatures off South America (Figure 2.3) (Collins et al., 2010). It is responsible for temperature and precipitation changes across the Pacific and other parts of the world including Antarctica through teleconnections (Liu et al., 2014). The Southern Oscillation Index (SOI) measures the difference in observed sea level pressure between Tahiti and Darwin; this can be used to reflect shifts from the La Niña (positive SOI) to El Niño (negative SOI) to normal phases (neutral SOI).

It also has been suggested that ENSO influences the zonal position of the ASL; during an El Niño the ASL moved 1400 km to the east off Marie Byrd Land between 1980-1990 AD (Bromwich et al., 2000; Cullather et al., 1996). However, it has been suggested that although the ASL does occupy a slightly westerly (easterly) position during La Niña (El

Niño) this difference in position is not statistically significant (Turner et al., 2013). Despite this, ENSO does show a statistically significant relationship in affecting the ASL's intensity, with an El Niño (La Niña) seeing higher (lower) mean sea level pressure (MSLP) (Turner et al., 2013). This impact on the ASL is greatest during winter (Turner et al., 2013).

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Figure 2.3: the oceanic and atmospheric patterns associated with the Walker circulation cell during normal conditions (La Niña conditions are just these patterns accelerated) and El Niño. Taken from Collins et al. (2010).

2.2.3 Pacific Decadal Oscillation

The Pacific Decadal Oscillation (PDO) is one of the main drivers of multi-decadal variability in sea surface temperatures in the extratropical North Pacific (MacDonald, 2005). It is often described as a long-lived El Niño-like pattern in terms of the Pacific climate variability (NOAA-NCDC, 2016). Like the ENSO pattern, the phases of the PDO are marked by either warm or cool phases, based on the ocean temperature anomalies in the northeast and tropical Pacific Ocean (NOAA-NCDC, 2016). For the 20th century, the PDO appears to fluctuate on two general periodicities; 15-to-25 years and 50-to-70 years (Mantua & Hare, 2002). Over the past century, two full PDO cycles have occurred; a “cool” phase between 1890 to 1924 and 1947-1976 and a “warm” phase between 1925-1946 and 1977 until the mid-1990s (at least)(Mantua & Hare, 2002). This periodicity appears to fluctuate through time, between 1600 and 1800 AD there is very little variability within the 50 to 100 year frequency range and yet this reemerges between 1300 and 1500 AD and 1000 to 1200 AD(MacDonald, 2005). The PDO's influence has been recorded in Antarctica. The Vostok ice core's (central Antarctica) δD

and snow accumulation records show a 50-year cycle that significantly correlates with the PDO, suggesting a climatic teleconnection between central Antarctica and the tropical Pacific on a decadal scale (Ekaykin et al., 2004)

2.2.4 Southern Annular Mode

The SAM is the dominant mode of climatic variability in the Southern Hemisphere (Marshall, 2003). It describes a zonally symmetric pattern of opposing geopotential height perturbations, with one node over Antarctica and the other over the mid-latitudes around 45°S (Gillett et al., 2006). The 'sign' of the SAM oscillates between a positive phase and negative phase. In the positive phase, a geopotential low anomaly develops over Antarctica as the pressure increases over the mid-latitudes (Figure 2.4), which strengthens the storm track and forces it polewards (Gillett et al., 2006). In the negative phase, the opposite is observed. This process represents the shift in the position and intensity of the westerly winds (Meredith et al., 2008). The poleward shift of the storm tracks is strongest in the austral summer, when the Southern Hemisphere jet is further towards Antarctica and relatively separated from the Hadley cell (Kushner et al., 2001). The SAM changes state on a week by week basis, however since the 15th century it has seen a gradual shift to its positive phase, causing a cooling over the Antarctic continent, but a warming on the Antarctic Peninsula (Abram et al., 2014; Renwick & Thompson, 2006)

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Figure 2.4: Diagram showing the position of the geopotential high (red) over the mid-latitudes and the geopotential low (blue) over Antarctica, during a positive SAM event. The opposite pattern occurs in the negative phase (Renwick & Thompson, 2006).

The phase of SAM exerts a strong control on the meridional position of the ASL. During the negative phase of SAM, the ASL mean position occurs at roughly $68.72^{\circ}\text{S} \pm 6.67^{\circ}$ and in positive mode the ASL is situated at $70.43^{\circ}\text{S} \pm 6.10^{\circ}$ (Turner et al., 2013).

However, the SAM appears to show no statistically significant relationship to the ASL's zonal location, with its mean longitudinal position in the positive phase recording $128.76^{\circ}\text{W} \pm 58.53^{\circ}$ and the negative phase occurring at $130.94^{\circ}\text{W} \pm 66.20^{\circ}$ (Turner et al., 2013). The SAM positive phase also tends to lead to an overall lower circumpolar trough MSLP including the ASL, intensifying its circulation (Turner et al., 2013).

According to Fogt and Bromwich (2011) the expression of the ENSO in the South Pacific teleconnection is detectable when they occur with a weak SAM or when an El Niño (La Niña) events occur with a negative (positive) SAM phase.

Past occurrences of these climate modes can be recorded in paleoclimate records including ice cores.

2.3 Ice core paleoclimatology and major ion analysis

2.3.1 Ice Core Paleoclimatology

Ice cores are an invaluable paleoenvironmental proxy, providing a near instrumental-quality record of past temperature, changes in atmospheric circulation, dust loading, volcanic eruptions, biological processes and human influence on the environment as evinced by isotopic, major ion and trace element proxies (Brook, 2007). At sites with high snow accumulation rates, they allow continuous reconstructions as far back as 850,000 years ago, with some seasonally resolving the past ~30,000-40,000 years (Bertler & Barrett, 2010). This is particularly important in areas in Antarctica as instrumental data are sparse and short in duration (Jouzel & Merlivat, 1984). Major ion analysis can track the input of elements from sources including continental dust, volcanic eruptions, sea salt and biological processes (Brook, 2007). These records can be used to reconstruct past atmospheric circulation processes, sea ice extent, wind direction, primary productivity and aridity across the globe.

2.3.2 Major Ion Analysis

This study presents eight major ions; four cations; Na^+ , Ca^{2+} , K^+ , Mg^{2+} , and three anions; NO_3^- , MS^- , SO_4^{2-} , as well as non-sea salt sulphate (nssSO_4^{2-}), which is calculated using the Na^+ and SO_4^{2-} . Together, these ions are used to reconstruct the marine/katabatic wind influence, primary productivity and sea ice extent at Roosevelt Island and surrounding region.

Na^+ & Cl^-

Na^+ provides an indicator of sea salt and can therefore act as a sensitive recorder of marine-sourced winds (Kreutz et al., 2000; Legrand & Mayewski, 1997). Legrand and Mayewski (1997) confirm the use of Na^+ and Cl^- as a proxy for marine air masses as their molar ratios show a similar value to the bulk seawater reference value (1.17).

SO_4^{2-} and nssSO_4^{2-}

Sea salt SO_4^{2-} (ss SO_4^{2-}) tends to be sourced from polynyas, cyclonic activity, bubble bursting and frost flowers, which generally reach Antarctica almost exclusively through the lower troposphere (Dixon et al., 2005). Typically SO_4^{2-} peaks in summer and reaches its minimum during winter (Legrand & Delmas, 1984).

Non-sea salt sulfate (nss SO_4^{2-}) is calculated by subtracting the proportional sea salt sulfate (ss SO_4^{2-}) from total sulphate. Non-sea salt SO_4^{2-} (nss SO_4^{2-}) can reach sites from volcanic eruptions (minor apart from large eruptions) and biological reactions occurring in local polynyas (Dixon et al., 2005). Phytoplankton produce non-sea salt sulphate when dimethylsulphoniopropionate (DMSP) is converted to dimethyl-sulfide (DMS), which becomes oxidised to form MS^- and sulphate (Abram et al., 2013; Sinclair et al., 2014).

Ca^{2+}

Most studies use Ca^{2+} as evidence of terrestrial dust, sourced from fine-grained calcium carbonate, dolomite and gypsum deposits (Laj et al., 1997; Markle et al., 2012; McConnell et al., 2007; Wolff et al., 2006). In the Greenland Ice Core Project (GRIP), calcium was used as a proxy for continental dust, as it was assumed to be sourced

from soluble carbonates from soils in the region (Delmonte et al., 2002). However, previous studies including McConnell et al. (2007) have hinted at the lack of reliability in using Ca^{2+} as a proxy for a terrestrial source because (particularly at coastal locations) up to 90% of total soluble calcium can come from seawater and could therefore reflect a marine influence. Sommer et al. (2000) has suggested that more than 60% of the calcium concentration between their three East Antarctic cores was likely derived from an ocean source. Recent research from the Danish group of the RICE team has confirmed this, as they determine the Ca^{2+} source at Roosevelt Island is likely to be marine (P.Vallelonga, pers. comms).

K^+

Bertler (2004) highlighted that potassium has both marine and terrestrial sources. The marine influence is supported by Bertler et al. (2005), which shows the ion having a statistically significant inverse relationship with increasing altitude.

Mg^{2+}

Legrand and Mayewski (1997) highlight the use of Mg^{2+} as evidence of terrestrial salts, which can therefore act as a proxy for the katabatic winds (Markle et al., 2012). Mg can also be used as a sea salt indicator (Legrand & Delmas, 1984; Li et al., 2009). Rhodes et al. (2012) showed how Na^+ , Mg^{2+} and Sr were strongly correlated ($R^2 > 0.92$) and their concentration ratios correspond to seawater concentration ratios, indicating a marine source.

NO_3^-

NO_3^- is thought to form in the tropics through lightning and soil exhalation and then transported to Antarctica through the upper troposphere/lower stratosphere (Legrand & Delmas, 1986). Following deposition on the polar plateaus, the NO_3^- signature can be transported to coastal sites through katabatic winds (Legrand & Mayewski, 1997). Therefore NO_3^- is used as an indicator of polar stratospheric clouds and hence provides evidence of a stratospheric air mass contribution (Legrand & Mayewski, 1997).

MSA

Methanesulphonic acid (MSA) is another by product of the conversion of dimethylsulphoniopropionate (a gas produced by species of phytoplankton in the ocean) to dimethyl-sulfide (DMS), which becomes oxidised to form MS^- and sulphate (Abram et al., 2013; Sinclair et al., 2014). In the ice core geochemistry we analyse MS^- , the ion form of MSA. As primary productivity is closely linked to sea ice in the Antarctic, the MS^- record can be used as a proxy for sea ice, however this relationship varies across Antarctica. At Newall Glacier and Law Dome, MS^- shows a positive correlation with sea ice and is therefore used as a sea ice proxy (Curran et al., 2003; Welch et al., 1993). A positive correlation in the Indian Ocean sector of the East Antarctic coastline is supposedly due to MSA forming from sea-ice algae (Sinclair et al., 2014). Whereas MS^- records from the Weddell Sea, Dolleman Island and Lambert Glacier, all showed a negative correlation with sea ice, with a decrease in MSA concentration occurring following a winter with increased sea ice (Abram et al., 2007; Pasteur et al., 1994; Sun et al., 2002). In the Ross Sea, Sinclair et al. (2014) and Rhodes et al. (2009) determined that MSA concentration shows a negative correlation with sea ice and therefore reflects the amount of open-ocean area in the Ross Sea Polynya ($R^2=0.903$).

$\text{SO}_4^{2-}/\text{Na}^+$ ratio indicator of frost flowers

It was originally thought that bubble bursting and sea spray were the only source of marine aerosols/sea salts in ice core records. However, sea salt concentration peaks in winter, despite having to travel further from the ocean across expansive sea ice (Abram et al., 2007; Rankin et al., 2000; Rankin et al., 2004). Two hypotheses were put forward – that either more efficient transport occurred during winter or that Na^+ was formed locally on sea ice through frost flower formation. It was shown that samples depleted in nss SO_4^{2-} in relation to Na^+ indicate fractionation to frost flowers (Rankin et al., 2000), while enriched ratios suggest a more vigorous transport (Wolff et al., 2003). Frost flowers occur when sea ice forms rapidly under cold conditions, when the conditions are below -8°C sodium sulphate in the form of mirabilite will precipitate from the developing brine (Kaspari et al., 2005). This process removes most of the sulphate and approximately 13% of the sodium from the solution, resulting in a fractionation between the two ions (Rankin et al., 2002). Following this, the surface

brine evaporates and creates a water vapour layer in which enhanced crystal growth forms frost flowers (Martin et al., 1996). The onshore winds and synoptic cyclones subsequently transport this signature to the coastal sites. These winds need to be strong enough to incorporate the salt from the flowers, but not so powerful that the flowers are destroyed (Rankin et al., 2000). Frost flowers have been shown to contribute 40% to the Na^+ budget in Antarctic ice cores, and in locations where there is at least 300 km of sea ice they dominate over open-water production at coastal sites (Kaspari et al., 2005; Rankin et al., 2000). As a result $\text{nss SO}_4^{2-} / \text{Na}^+$ can be used to reconstruct sea ice extent through the ratio typical of frost flowers, thus providing an additional proxy for sea ice extent (Dixon et al., 2005; Rankin et al., 2000).

Fe

Bertler (2004) highlight the use of Fe as a terrestrial dust source.

2.4 Previous Research

Figure 2.5: Map of Antarctica showing location of LIA ice core/borehole site locations (blue and red dots). ASL is the nominal location of the Amundsen Sea Low.

As previously mentioned, a LIA signature has been observed in several Antarctic ice core/bore hold records from across the continent (Figure 2.5). These records generally describe a period of colder temperatures, for instance, Bertler et al. (2011) reconstructed a 2 °C colder summer temperature from the Victoria Lower Glacier (VLG)

ice core during the LIA time period. They determined Antarctica to be generally cooler, drier and stormier with stronger katabatic winds and snow accumulation decreasing by 67%, which likely resulted in an increased sea-ice extent in the Ross Sea (Bertler et al., 2011). Rhodes et al. (2012) calculated a similar cooling in the Ross Sea Region of $1.6^{\circ}\text{C} \pm 1.4^{\circ}\text{C}$ between 1500 and 1800 AD from the Mt. Erebus Saddle ice core. They estimated that katabatic winds exceeded 57 ms^{-1} , resulting in an enlarged Ross Sea polynya and a subsequent 80% increase in biological productivity in 1600-1875 AD. Li et al. (2009) also recorded colder, drier and reduced snow accumulation conditions in Princess Elizabeth Land (DT263), East Antarctica between 1450-1850 AD, coinciding with the LIA, conditions which they believe hold for the eastern Indian Ocean sector of East Antarctica. Morgan (1997) also suggested that summer month temperatures were relatively stable over the last 700 years at Law Dome (Dome Summit South ice core), however, the winters showed a cold period centred in the early 1800s. And most recently, Orsi et al. (2012) reconstructed that temperatures between 1300-1800 CE were $0.52^{\circ}\text{C} \pm 0.28^{\circ}\text{C}$ colder than the last 100 year average from the West Antarctic Ice Sheet (WAIS) Divide borehole temperature reconstruction.

Kreutz et al. (2000) recorded an increase in sea salt concentrations at Siple Dome from 1400 AD until the 20th century. They attributed this to a possible intensification and enhanced decadal variability in sea level pressure of the ASL. Thompson and Mosley-Thompson (1981) determined that concentrations of insoluble particles dramatically increased between 1450 and 1850 AD at the South Pole ice core, a nearly two-fold increase in total particle concentration. This could potentially be attributed to a poleward shift in the westerlies, causing more meridional flow (Shulmeister et al., 2004). However, for the past 600 years there has been a negative correlation between the Law and Siple Dome ice core records, which is indicative of a more zonal westerly circulation in the southern Indian Ocean and southwest Pacific sectors during the LIA (Mayewski et al., 2004).

However, the LIA signature in Antarctica is temporally and spatially variable (Bertler et al., 2011). For example, Mosley-Thompson and Thompson (1990) reconstructed warmer and less dusty atmospheric conditions between 1600 and 1830 AD at Siple Station. The record suggests that it was not uncommon to observe a warming in the

Ross Sea and a cooling in the Antarctic interior when the stronger zonal westerlies prevailed, highlighting the importance of understanding regional climate dynamics and feedbacks. These warmer conditions are potentially due to the influence of warm marine air masses travelling across West Antarctica during the LIA (Kreutz et al., 1997).

During this time period, CO₂ levels also dropped by 6 and 10 ppmv between 1550 and 1880 AD as recorded in the Law and Taylor Dome ice core records, respectively (Etheridge et al., 1996; Indermuhle et al., 1999).

2.5 Roosevelt Island Setting

As a coastal location, Roosevelt Island sits at the confluence of the warm, meridional marine winds and the cold, dense katabatic winds (Figure 2.6). These are largely driven by the position of the ASL.

Figure 2.6: Schematic diagram showing oceanic and atmospheric processes affecting Roosevelt Island (orange) and Ross Ice Shelf (blue). ASL is the nominal location of the Amundsen Sea Low.

The marine winds arrive via the mesoscale and synoptic scale cyclones derived from the Ross/Amundsen Seas (Sinclair et al., 2010; Tuohy et al., 2015). Cyclones reaching

Antarctica are mainly formed at the Polar Front, where the warm winds from the mid-latitudes meet the cooler air bodies from the continent creating a major meridional temperature change in the troposphere (King & Turner, 1997). Significant temperature gradients can also occur along Antarctica's coast, where cold continental air meets warm maritime air masses. This gradient can form mesoscale cyclones or small synoptic scale disturbances, which travel eastwards along the coast or north towards the Southern Ocean (King & Turner, 1997). Mesoscale cyclones are typically less than 1000 km in horizontal diameter, averaging at approximately 100-500 km, with surface speeds of over 15 ms^{-1} , bringing strong winds and low surface pressures to the continent (Carrasco et al., 2003; King & Turner, 1997). They are often located over ice-free areas of ocean in southern airstreams to the west of synoptic lows (King & Turner, 1997). Synoptic scale cyclones are those that exceed 1000 km diameter and travel in the circumpolar westerly flow around Antarctica providing high volumes of precipitation (Sinclair et al., 2010). It is the eastern branch of these low-pressure systems which bring warm, moist maritime air to the continent leading to precipitation (King & Turner, 1997). The Ross Sea region's low elevation and proximity to the circumpolar trough makes it susceptible to frequent and intense cyclonic activity along the coast, causing stark contrasts with the inner plateau, which does not receive the same amount of accumulation (Sinclair et al., 2012).

The katabatic winds are gravity-driven atmospheric currents (Shulmeister et al., 2004). They form high on the Antarctic plateau, where net long-wave radiation losses cool the near-surface air. This dense air then drains outwards and downwards towards the coast (King & Turner, 1997; Nylén & Fountain, 2004). Katabatic winds are relatively slow in the continental interior due to the flat topography, however near the steep coastline their speeds increase (Nylén & Fountain, 2004). These winds can also be enhanced by the movement of the aforementioned depressions moving eastwards along the coast, causing the cold katabatic air to travel far out over the ocean (Murphy & Simmonds, 1993).

Roosevelt Island is also in the vicinity of the Ross Sea Polynya and a smaller polynya off its coast (N. Bertler, pers. comms). Polynyas are areas of reduced sea ice within the ice pack; their surface waters sustain high levels of biological productivity in spring and

summer (Arrigo & van Dijken, 2003). The Ross Sea Polynya is the largest consistently forming polynya on Earth and is the most biologically productive region in the Southern Ocean (Arrigo et al., 2008). The MS^- and nss SO_4^{2-} concentrations recorded in the Roosevelt Island record are likely to reflect the dimethylsulphonionpropionate produced by the phytoplankton in this polynya. Both polynya are maintained through mechanical processes, therefore their sizes are largely dependent on the strength of the southerly winds, the ASL and the katabatic winds off the continent (Drucker et al., 2011).

2.6 RICE Isotope Record

Stable isotope records of δO and δD have been used in several ice core studies for paleothermometry (Barlow et al., 1993; Jouzel et al., 1996). The use of δD as a paleoclimate indicator is based on the temperature-dependent fractionation of the two hydrogen isotopes during their movement through the hydrological cycle from the lower latitudes to the poles (Dansgaard, 1964). Due to the complex processes that affect the fractionation of these isotopes from the low latitudes to poles, δD is not a direct link to surface temperature at an ice core site. Instead, δD is determined by the difference in temperature between the site and its moisture source. According to Brook (2007), because the temperature changes at high latitudes are greater than at low latitudes, a relationship between δD and surface temperature at the ice core site are assumed. Based on this proxy, the University of Copenhagen RICE team reconstructed the temperature at RICE for the last 2000 years using δD as a proxy. However, contrary to previous Antarctic measurements during the LIA, the RICE deuterium isotope record shows an overall warming during this period (Figure 2.7). This could be attributed to a seasonal precipitation bias or the atmospheric circulation pattern has caused an isotopic enrichment which masks the underlying cooling.

Figure 2.7: RICE δD isotope record from 1200-2012 AD. Grey box denotes Little Ice Age period.

3.0 Methodology

3.1 Ice core preparation

Figure 3.1: Photo showing continuous melter system.

Photo courtesy of Nancy Bertler.

The RICE ice core was collected from Roosevelt Island (79° 21' 46" S, 161° 42' 3" W, 560 m a.s.l) during the 2011/12 and 2012/13 Antarctic field seasons by the RICE team. Following collection, the core was processed and melted over two core processing campaigns using a continuous melter system based on the design in Bigler et al. (2011) at the New Zealand Ice Core Laboratory, GNS Science in 2013 and 2014 (Figure 3.1). The stable isotope Continuous Flow Analysis (CFA) experimental setup is detailed in Emanuelsson et al. (2015). In addition to CFA analysis, 11,000 discrete ice core samples were collected in ultra-clean vials to cover the past 2000 years. These discrete samples were used for the ion analysis described in this thesis.

3.2 Age model

Roosevelt Island's coastal location and high snow accumulation allowed for sub-annual resolution through the LIA-ME section of the RICE IC data. The core was dated by the RICE team prior to the candidate's involvement (Figure 3.2) (Winstrup et al., In prep). The following techniques were used: annual layer counting of seasonally resolved proxies, methane concentration matched to the WAIS Divide ice core, tritium decay measurements, and volcanic eruptions as identified by tephra (N.Bertler, pers. comms). The 0-40 m section of the core was dated using a manual layer count (2012-1891 AD), whereas the 40-300 m (1891-0 AD) section was counted using an automated system. The counting made use of black carbon, calcium, conductivity, pH and stable isotopes. Thirteen geochemical signals of volcanic eruptions linked to the WAIS divide volcanic record and one tephra layer were used as discrete age benchmarks to constrain the age model.

Ages for all samples in this thesis were determined using linearly interpolation of the age model at the sample mean depth.

Figure 3.2: Age/depth plot for the last 2000 years for the RICE ice core. Blue line shows the age model-age, black shows the age uncertainty (Winstrup et al., In prep).

3.3 Ion Chromatograph Analysis

Samples spanning the LIA-ME time period were measured at the NZ Ice Core Laboratory, GNS Science for 8 major ions: Na^+ , Mg^{2+} , Ca^{2+} , K^+ , MS^- , Cl^- , NO_3^- and SO_4^{2-} . This data was analysed over four different processing runs, using four different calibrations and on two different machines, detailed in Table 1. The bulk of the samples (1020) were measured by the candidate during the July 2016 processing run/calibration.

Calibration	Time period	Machine
Jun-13	1585-1613, 1729-1755 & 1959-1991 AD	Capillary
Oct-13	1900-1959 AD	Capillary
Nov-15	1558-1571 & 1893-1900 AD	2 mm Analytical
Jul-16	1571-1585 & 1755-1893 AD	2 mm Analytical

Table 1: four calibrations used to measure major ion chromatograph data and the type of Ion Chromatograph system used and the time period (years AD) this spanned, either the Capillary System or the 2 mm Analytical System.

3.3.1 Dionex Ion Chromatograph ICS-5000 Capillary System Methodology

The June and October 2013 data was measured using the Dionex Ion Chromatograph ICS-5000 Capillary System. Anions were measured using a Dionex IonPac AS-19 0.4 x 250 mm column with a Dionex IonPac AG19 0.4 X 50 mm guard column with a KOH eluent gradient concentration of 20-40 mM. Cations were measured using a Dionex IonPac CS-12A 0.4 x 250 mm column with a Dionex IonPac CG12A 0.4 x 50 mm guard column with a 20 mM isocratic methane sulphonic acid eluent. Both cation and anion sides were fitted with a CCES 500 2 ml and ACES 500 2 ml anion suppressors, respectively.

This capillary system produced very broad peaks, which made it difficult to accurately determine ion concentrations (this will be further discussed in section 3.4.1). The system also had issues with carry over (when solution from the previous sample is included in second sample's measurement), therefore in 2015/2016 a new 2 mm Analytical System was used.

3.3.2 Dionex Ion Chromatograph ICS-5000 2mm Analytical System Methodology

The November 2015 and July 2016 data was measured using the Dionex Ion Chromatograph ICS-5000 2 mm Analytical System. Anions were measured using a Dionex IonPac AS-18 2 x 250 mm column with a Dionex IonPac AG18 2X 50 mm guard column and 250 µl sample loop with a KOH eluent gradient concentration of 20-40 mM. Cations were measured using a Dionex IonPac CS-12A 2 x 250 mm column with a Dionex IonPac CG12A 2 x 50 mm guard column and a 100 µl sample loop with 20mM isocratic methane sulphonic acid eluent. Both cation and anion sides were fitted with a CERS 500 2 ml and AERS 500 2 ml anion suppressors, respectively.

The sampling system was automated using an AS-HV autosampler. During preliminary tests, the autosampler was set to load 1 ml of sample into the sample loop; however, this was insufficient to accurately measure the very low concentrations of ions. The loading method was then changed to load 2 ml and this improved the results. The samples were introduced into the two sample loops through the separate isocratic

pumps.

3.4 Calibration

As listed in section 3.3 / Table 1, four calibrations were used to resolve the concentration of major ions in the samples during the LIA-ME time period. All ion chromatography (IC) data was analyzed using the Chromeleon software (version 7.2) ("Chromeleon 7.2 Chromatography Data System (CDS) Software," 2016). Every peak was manually checked to determine if the software had identified the correct peak and the area under the curve. If the software did not accurately select the peak, then the individual peak was manually integrated.

3.4.1 June/Oct 2013

During June and October 2013, a 9-point calibration was used (Tables 2 & 3). Issues with the Capillary machine meant that several manual manipulations in Chromeleon were required to produce meaningful results. The Ca^{2+} and Mg^{2+} peaks were flat, broad and close together, making it harder to decipher where they start and end. The NO_3^- , K^+ and MS^- peaks were also flat, broad peaks and hard to resolve. However, the Na^+ , Cl^- and SO_4^{2-} analysis produced narrow and well-defined peaks. All ions were fitted with a linear calibration, apart from magnesium where a cubic curve was used (Table 2 & 3).

Peak	Calibration Type	No. points	R ²	Range (ppb)
Na⁺	Linear with offset	9	0.99986	10-2000
K⁺	Linear	7	0.99969	10-750
Mg²⁺	Cubic with offset	6	0.99876	5-250
Ca²⁺	Linear with offset	6	0.99964	2.5-375
MS⁻	Linear with offset	8	0.99979	2.5-375
Cl⁻	Linear	8	0.9999	10-1500
NO₃⁻	Linear with offset	6	0.99942	5-250
SO₄²⁻	Linear with offset	8	0.99967	5-500

Table 2: Chromeleon calibration information for June 2013 calibration

Peak	Calibration Type	No. points	R ²	Range (ppb)
Na ⁺	Linear with offset	9	0.99994	2-400
K ⁺	Linear with offset	9	0.99859	5-1000
Mg ²⁺	Cubic with offset	5	0.99947	12.5-250
Ca ²⁺	Linear with offset	5	0.96779	5-100
MS ⁻	Linear with offset	7	0.99947	1.25-50
Cl ⁻	Linear with offset	9	0.99968	2.5-500
NO ₃ ⁻	Linear with offset	5	0.9959	2.5-50
SO ₄ ²⁻	Linear with offset	9	0.99978	2.5-500

Tables 3: Chromeleon calibration information for October 2013 calibration.

3.4.2 November 2015

The November 2015 data used a 13-point anion and cation calibration (Table 4). All ions were fitted with a linear calibration, except potassium which was fitted with a quadratic (Table 4). The peaks were relatively well defined in this calibration, and therefore minimal manual manipulations were necessary. Na⁺, Mg²⁺, Ca²⁺, MS⁻, Cl⁻, and SO₄²⁻ all report R² values exceeding 0.9999, with NO₃⁻ and K⁺ recording values >0.999. To obtain a good linear/quadratic fit for NO₃⁻ and K⁺, respectively, required limiting the concentration range at which these ions could be calibrated. This could result in samples with values above/below this range being reported higher/lower than the accurate reading.

Peak	Calibration Type	No. points	R ²	Range (ppb)
Na ⁺	Linear with offset	11	0.99996	7.9-1479.0
K ⁺	Quadratic with offset	7	0.9995	7.4-37.4
Mg ²⁺	Linear with offset	11	0.99995	2-371
Ca ²⁺	Linear with offset	9	0.99991	3.8-300
MS ⁻	Linear with offset	11	0.99991	2.0-370.0
Cl ⁻	Linear with offset	13	0.99997	4.9-1903.0
NO ₃ ⁻	Linear with offset	9	0.9998	4.7-92.0
SO ₄ ²⁻	Linear with offset	10	0.99993	4.9-745.0

Table 4: Chromeleon calibration information for November 2015 calibration

3.4.3 July 2016

The July 2016 IC samples were initially processed using a 13-point calibration for both the anions and cations; however this resulted in a weak fit/low R², as they did not

capture the full range of the data, particularly in the low ppb. Consequently, more calibration points were added and resulted in a 32-point calibration for the cations and a 22-point calibration for the anions (Table 5). Higher concentration calibration points were added for Cl^- (up to ~12,000 ppb), SO_4^{2-} (up to 2800 ppb), K^+ (up to 90 ppb) and Na^+ (up to 7900 ppb). These were only “turned on” if a spike was present.

Peak	Calibration Type	No. points	R ²	Range (ppb)
Na⁺	Linear with offset	30	0.99987	11.6-2574.5
K⁺	Quadratic with offset	16	0.99946	2.7-27.4
Mg²⁺	Quadratic with offset	17	0.9999	9.9-186.0
Ca²⁺	Quadratic with offset	16	0.99987	9.8-164.1
MS⁻	Quadratic with offset	19	0.99961	1.3-91.1
Cl⁻	Linear with offset	30	0.99995	5.4-3842.9
NO₃⁻	Linear with offset	10	0.99893	12.1-66.5
SO₄²⁻	Linear with offset	21	0.9999	22.7-915.3

Table 5: Chromeleon calibration information for July 2016 calibration.

Anion calibration points were created by diluting the anion “L0” single standard mix solution (see Appendix A for concentration data) with water to 22 different solution/water ratios via pipette, making a total volume of 4 ml. The cation calibration points/levels were created by diluting the cation “L0” single standard mix solution (see Appendix A for concentration data) with water to 32 different solution/water ratios via pipette to a total volume of 4 ml. The true concentrations of these points/levels were determined by weighing the vial, the vial+standard, then the vial+standard+water on a Metler 5-point scale. The weight of the water (m_{water}) was calculated by subtracting the weight of the vial+standard from the vial +standard+water. The weight of the standard (m_{std}) was calculated by subtracting the weight of the vial from the vial+standard. The concentration of each level was then calculated using the equation below:

$$\text{Level concentration} = \text{L0 conc (ion)} \times \frac{(m_{\text{water}}) / \text{density of water}}{(m_{\text{std}} + m_{\text{water}}) / \text{density of standard}}$$

where the density of water and the standard both equal 0.9982, as the standard was assumed to have approximately the same density as water for the lab temperature, which is maintained between 18-21 °C.

The additional higher calibration points for Cl^- , SO_4^{2-} , K^+ and Na^+ were made by pipetting the approximate volume of “L0” solution in order to give the desired higher concentration and diluting this with water to 4 ml. The same weight and calculation method were applied as above to determine the true concentration.

The larger number of calibration points confirmed that for lower concentrations (see Appendix A), a curve/quadratic calibration is a more suitable fit, whereas the higher concentrations better fitted a linear calibration. A linear calibration was used for Cl^- , NO_3^- , SO_4^{2-} and Na^+ , whereas K^+ , Mg^{2+} , Ca^{2+} , MS^- were fitted with a quadratic calibration (Table 5). For each ion, some levels were excluded from the calibration in order to improve the calibration fit in the regions where the data was most concentrated. For example, the median concentration for Ca^{2+} is 18 ppb, with 25-75% percentile of the data concentrated between 13-27 ppb. As Figure 3.3 shows, in this range the calibration data is curved, and therefore a quadratic calibration is used. In order to improve the fit and the accuracy of measuring this range in the Ca^{2+} data, points above 164 ppb and below 9.8 ppb were disabled. This was done for each ion (see Appendix A).

Figure 3.3: Schematic of calcium calibration on Chromeleon Software. $\mu\text{S} \cdot \text{min}$ is the measure of conductivity.

All ion calibrations report an R^2 value of at least 0.999, except NO_3^- , K^+ and MS^- . These three ions also have very narrow resolvable ranges, which limited our ability to analyze the sample data.

3.5 Quality control

The table below summarises the decisions made on whether each calibrations data could be used based on its quality (Table 6). These decisions were largely based on the ability of the machine to accurately measure the Quality Control standards (QCs)

Ion	Jun-13	Oct-13	Nov-15	Jul-16	ICP-MS
Na^+	✓	✓	✓	✓	✓
Ca^{2+}	✓	✓	✓	✓	✓
Mg^{2+}			✓	✓	✓
K^+					✓
Cl^-	✓	✓	✓	✓	
SO_4^{2-}	✓	✓	✓	✓	✓
NO_3^-					
MS^-				✓	
nssSO_4^{2-}	✓	✓	✓	✓	✓
Fe					✓

Table 6: IC major ions that can be used based on confidence in calibration along with available ICP-MS major ion data (and Fe). Blue shows Capillary IC system, purple indicates the 2 mm Analytical System and orange indicates the ICP-MS data.

A set of internal and external QC standards with known concentrations were analysed during sample processing. The external quality control mixed standards, AES and Big-Moose, came with known manufacturer certified values, which were compared to the IC measured value. The internal quality controls were made by varying the dilution factors of the single standard mix solution “L0” for both anions and cations (see Appendix A for concentration data). The levels included L1.5 (ultra-low concentration- ~0.06% of L0), L3 (low concentration- ~0.5% of L0), L7 (medium concentration ~5% of L0) and L11 (high concentration- ~10% of L0). The June and October 2013 calibrations both only used the external quality control, Big-Moose. The November 2015 calibration used both external quality controls, Big-Moose and AES, as well as three internal quality controls: L3, L7 and L11. The July 2016 calibration used AES and four internal quality controls: L1.5, L3, L7, L11. During the July calibration the L7 and L1.5 were alternated every 10 samples following the AES, switching between the anion and cation solutions so as to minimize the effects of consistent carry over. Every 50 samples, a whole set of L1.5, L3, L7 and L11 was run for both the cation and anion sides, ending with a blank water sample.

Table 7 summarizes the range of the RICE sample data in order to indicate the important range of concentrations for each ion and, based on this, which quality controls provide a good estimate of the uncertainty of the samples.

	MS ⁻	Cl ⁻	NO ₃ ⁻	SO ₄ ²⁻	Na ⁺	K ⁺	Mg ²⁺	Ca ²⁺
Upper Percentile (95%)	69.9	1717.2	43.6	361.5	1004.4	29.0	174.3	49.5
Median	21.4	635.9	19.3	116.1	321.7	8.1	62.0	18.8
Lower Percentile (5%)	5.3	227.7	5.0	41.4	99.4	3.0	23.1	8.2
Relevant Internal QC	L3 (~16)	L7 (~462)	L3 (~4.3)/L7(~43)	L3 (~45)/L7(~450)		L3 (~1.8)/L7(~19)		L3 (~18)
Relevant External QC		Big-Moose (~463)			AES (~224)		AES (~48)	

Table 7: summarizes median values of the total RICE sample range and the central 90% of the data. Internal/External quality controls, which show similar concentrations to this range, are highlighted.

Internal quality control concentrations quoted are averages of November/July calibrations. All values are in ppb.

3.5.1 June/Oct 2013

When we compare the Big-Moose certified values (from the manufacturer) (Table 8) with the median/range of the RICE sample data (Table 7), all of the values exceed those of the samples (apart from Cl^- and Na^+). Big-Moose therefore has relatively limited use as an uncertainty indicator for our samples, but this was the best available external quality control at the time. When we compare the certified values to the IC measured Big-Moose, Ca^{2+} and Mg^{2+} are 25% and 16% lower than expected, respectively, in the June 13 calibration and 55% and 11% lower, respectively, in the October calibration (Table 8 & 9). This is because Big-Moose values are significantly higher than the range for which the calibration can resolve for Mg^{2+} (up to 250 ppb in both June/Oct) and Ca^{2+} (up to 375 ppb and 100 ppb in June/Oct, respectively). Despite Big-Moose's high values, Na^+ , K^+ , Cl^- , SO_4^{2-} are still within 7% of the certified values (Tables 8 & 9), even though for Na^+ and SO_4^{2-} these exceed their calibration range. This highlights that for these ions, despite the smaller calibration range, the IC can still resolve higher concentrations accurately.

Big MOOSE	Na^+	K^+	Mg^{2+}	Ca^{2+}	Cl^-	SO_4^{2-}
Measured	768 ± 5	303 ± 49	275 ± 6	1503 ± 92	468 ± 9	5287 ± 14
RSD	0.7	16.2	2.3	6.1	1.9	0.3
Certified value	731 ± 58	326 ± 35	327 ± 27	2000 ± 200	463 ± 53	5080 ± 280
Accuracy (% dif)	5	-7	-16	-25	1.1	4.1

Big MOOSE	Na^+	K^+	Mg^{2+}	Ca^{2+}	Cl^-	SO_4^{2-}
Measured	743 ± 3	341 ± 15	291 ± 4	903 ± 36	488 ± 5	5408 ± 76
RSD	0.4	4.3	1.4	4.0	1.0	1.4
Certified value	731 ± 58	326 ± 35	327 ± 27	2000 ± 200	463 ± 53	5080 ± 280
Accuracy (% dif)	2	4	-11	-55	5	6

Tables 8-9: Comparison of the external quality control Big Moose's certified values from the manufacturer with the concentrations measured on the IC during the June 2013 (upper table) and October 2013 (lower table) run. Concentrations are reported in parts per billion (ppb) and standard deviation is 1σ measured from replicates (except Big Moose which reports in 2 σ). RSD=relative standard deviation. Accuracy (%dif) is the percentage difference between the average measured value and the certified value, therefore a lower value indicates a better accuracy. Red numbers indicate when values are outside the range of the calibration, therefore we expect these to show reduced accuracy/higher % difference. Blue column denotes cations and orange, anions.

3.5.2 November 2015

Tables 10 and 11 compare the measured IC values for the two external quality controls, Big-Moose and AES. AES is a more useful external QC compared to Big-Moose as the certified values are closer to our sample ranges (Table 10), particularly for Na^+ and Mg^{2+} . All measured ions are within the range of the certified values of the external quality controls AES and Big Moose, apart from K^+ , which is outside the range of Big Moose because it exceeds K^+ 's calibration range (Table 11). However, this is not a concern as 326 ppb far exceeds 95% of the RICE sample range for K^+ (Table 7).

AES	Na^+	K^+	Mg^{2+}	Ca^{2+}	Cl^-	SO_4^{2-}
Measured	228 ± 3	47 ± 2	43 ± 0.6	228 ± 6	284 ± 2	1102 ± 7
RSD	1.4	3.7	1.3	2.5	0.8	0.6
Certified value	224 ± 31	41 ± 11	48 ± 7	222 ± 40	283 ± 39	1110 ± 90
Accuracy (% dif)	2	16	-10	3	0.4	-0.7

Big MOOSE	Na^+	K^+	Mg^{2+}	Ca^{2+}	Cl^-	SO_4^{2-}
Average	730 ± 10	221 ± 2	320 ± 4	2002 ± 27	465 ± 3	5022 ± 17
RSD	1.4	0.9	1.3	1.3	0.6	0.3
Certified value	731 ± 58	326 ± 35	327 ± 27	2000 ± 200	463 ± 53	5080 ± 280
Accuracy (% dif)	-0.1	-32	-2	0.1	0.5	-1

Tables 10-11: Comparison of the external quality controls AES and Big Moose's certified values from the manufacturer with the concentrations measured on the IC during the November 2015 run. See description in Tables 8-9 above.

When the internal QC weight calculated estimates are compared to the measured values, Na^+ , Mg^{2+} , Ca^{2+} , MS^- , Cl^- and SO_4^{2-} are accurate to within 9% (Tables 12-14). The accuracy of K^+ and NO_3^- ranges from 4-91% and 8-60%, respectively. Both of these large differences occur when compared to Level 3, because they fall outside the range of K^+ and NO_3^- 's calibrations.

L3	Na ⁺	K ⁺	Mg ²⁺	Ca ²⁺	MS ⁻	Cl ⁻	NO ₃ ⁻	SO ₄ ²⁻
Measured	71 ± 0.6	4 ± 0.1	17 ± 0.4	17 ± 0.8	20 ± 2	43 ± 0.3	7 ± 0.7	45 ± 0.5
RSD	0.9	3.0	2.4	4.5	8.2	0.6	11.5	1.0
Weight estimate	72.9 ± 0.4	1.8 ± 0.02	18.3 ± 0.1	18.5 ± 0.1	18.1 ± 0.05	45.1 ± 0.3	4.5 ± 0.04	45.6 ± 0.3
Accuracy (% dif)	-2	91	-4	-6	8	-5	60	-1

L7	Na ⁺	K ⁺	Mg ²⁺	Ca ²⁺	MS ⁻	Cl ⁻	NO ₃ ⁻	SO ₄ ²⁻
Measured	729 ± 6	17 ± 1	183 ± 2	186 ± 2	185 ± 1	457 ± 2	48 ± 1	458 ± 2
RSD	0.8	6.0	1.0	1.1	0.6	0.4	2.0	0.4
Weight estimate	713.62 ± 4	18.03 ± 0.2	178.93 ± 1	180.66 ± 1	176.19 ± 0.4	439.31 ± 3	43.89 ± 0.4	443.44 ± 3
Accuracy (% dif)	2	-5	2	3	5	4	9	3

L11	Na ⁺	K ⁺	Mg ²⁺	Ca ²⁺	MS ⁻	Cl ⁻	NO ₃ ⁻	SO ₄ ²⁻
Measured	1489 ± 6	37 ± 0.7	375 ± 2	374 ± 2	368 ± 3	915 ± 3	91 ± 1	917 ± 2
RSD	0.4	1.9	0.6	0.5	0.9	0.3	1.3	0.2
Weight estimate	1420.5 ± 8	35.9 ± 0.4	356.2 ± 2	359.6 ± 2	336.7 ± 1	839.4 ± 6	83.9 ± 0.9	847.3 ± 6
Accuracy (% dif)	5	4	6	4	9	9	8	8

Tables 12-14: Comparison of the averaged weight estimated concentrations of the three internal quality controls (Level 3, 7, 11) with the corresponding average concentrations measured on the IC during the November 2015 run. As two bottles of each solution were made the data represents an average of these solutions. See description in Tables 8-9 above.

3.5.3 July 2016

The IC averaged measurements for the AES solution compared to the expected value for the ions is summarized in Table 15 below. As shown, all the measured ions are within the range of the certified values of the external quality control AES.

AES	Na ⁺	K ⁺	Mg ²⁺	Ca ²⁺	Cl ⁻	SO ₄ ²⁻
Average	231 ± 1	45 ± 1	48.39 ± 0.6	206.20 ± 1	285.16 ± 2	1131.17 ± 15
RSD	0.5	2.9	1.3	1.5	0.80	1.3
Certified value	224 ± 31	41 ± 11	48 ± 7	222 ± 40	283 ± 39	1110 ± 90
Accuracy (% dif)	3	11	0.8	-7	0.8	1.9

Table 15: Comparison of the external quality control AES certified values with the concentrations measured on the IC during the July 2016 run. As two bottles of L3/L11 and three bottles of L1.5/L7 were made the data represents an average of these solutions. See description in Tables 8-9 above.

When the internal quality controls are compared to their measured values, all the ions show low levels of accuracy at L1.5, because either the calibration range does not resolve concentrations this low or it is at the very low end of the range, as is the case for MS⁻ and Cl⁻ (Table 16). This is not of concern because none of the L1.5 concentrations are within the range of 90% of the sample data. While it is not a relevant uncertainty measure for the samples, L1.5 does demonstrate that the current IC set up cannot resolve these low concentrations accurately.

When the expected and measured values are compared (excluding L1.5), Na, Cl and SO₄ are accurate to within 3% for all levels (Tables 17-19). Ca²⁺, Mg²⁺, MS⁻ and K⁺ are accurate to within 18% compared to the weighted estimates. Particularly low levels of accuracy are seen in L11 due to the concentrations exceeding the calibration range (Table 5). Nitrate is accurate to within 3% for Level 7 and Level 11, but measures poorly when compared to Level 3, because this is below the calibration range. As this is below the 5% percentile of the sample NO₃⁻ concentrations, this is not of concern.

L1.5	Na ⁺	K ⁺	Mg ²⁺	Ca ²⁺	MS ⁻	Cl ⁻	NO ₃ ⁻	SO ₄ ²⁻
Average	11 ± 0.06	2 ± 0.01	7.42 ± 0.2	9 ± 0.6	6 ± 1	7 ± 0.4	5 ± 0.5	13 ± 0.3
RSD	0.5	0.7	2.6	7.0	25.1	5.8	8.7	2.1
Weight estimate	10.2 ± 0.1	0.3 ± 0.004	2.5 ± 0.03	2.5 ± 0.03	2.1 ± 0.01	6.2 ± 0.06	0.6 ± 0.006	6.2 ± 0.06
Accuracy (% dif)	11	654	192	238	163	14	726	115

L3	Na ⁺	K ⁺	Mg ²⁺	Ca ²⁺	MS ⁻	Cl ⁻	NO ₃ ⁻	SO ₄ ²⁻
Average	72 ± 2	2 ± 0.2	19 ± 0.6	20 ± 1	18 ± 2	44 ± 0.5	6 ± 0.5	47 ± 0.7
RSD	3.0	6.6	3.4	6.8	9.4	1.1	7.5	1.4
Weight estimate	73.4 ± 0.4	1.9 ± 0.02	18.4 ± 0.1	18.3 ± 0.1	15.4 ± 0.03	45.4 ± 0.3	4.1 ± 0.03	45.4 ± 0.3
Accuracy (% dif)	-1	18	2	9	14	-3	53	3

L7	Na ⁺	K ⁺	Mg ²⁺	Ca ²⁺	MS ⁻	Cl ⁻	NO ₃ ⁻	SO ₄ ²⁻
Average	747 ± 3	19 ± 1	185 ± 1	183 ± 1	149 ± 2	459 ± 3	43 ± 2	461 ± 5
RSD	0.4	6.1	0.6	0.7	1.3	0.7	5.2	1.1
Weight estimate	745.0 ± 4	19.6 ± 0.2	186.3 ± 1	186.1 ± 1	155.6 ± 0.2	458.1 ± 3	41.6 ± 0.3	458.0 ± 3
Accuracy (% dif)	0.3	-2	-0.4	-2	-4	0.1	3	0.6

L11	Na ⁺	K ⁺	Mg ²⁺	Ca ²⁺	MS ⁻	Cl ⁻	NO ₃ ⁻	SO ₄ ²⁻
Average	1481 ± 3	36 ± 0.5	348 ± 0.8	325 ± 0.8	260 ± 4	913 ± 11	85 ± 2	919 ± 16
RSD	0.9	1.5	0.2	0.2	1.5	1.2	2.0	1.8
Weight estimate	1477.6 ± 9	38.9 ± 0.3	369.5 ± 2	369.0 ± 2	308.9 ± 0.5	909.2 ± 5	82.6 ± 0.7	909.0 ± 5
Accuracy (% dif)	0.3	-7	-6	-12	-16	0.5	2.7	1.1

Tables 16-19: Comparison of the averaged weight estimated concentrations of the four internal quality controls (Level 1.5, 3, 7, 11) with the corresponding average concentrations measured on the IC during the July 2016 run. As two/three bottles of each solution were made the data represents an average of these solutions. See description in Tables 8-9 above.

3.5.4 Data Quality Summary

The previous sections (3.4 & 3.5) detail the confidence/issues surrounding the four calibrations based on the calibration method and comparison to quality controls. Figures 3.3 and 3.4 below show all four calibrations plotted against time, representing the full set of IC data available for this study.

Figure 3.4: Cation stacked time series comparing all four calibrations spanning part of the Little Ice Age and Modern Era. Numbers 1-4 reflect areas of concern in the calibrations.

Figure 3.5: Anion stacked plot comparing all four calibrations spanning part of the Little Ice Age and Modern Era. Numbers 5-8 indicate areas of concern in the calibration.

Figures 3.4 and 3.5 highlight regions of concern when the four calibrations are pieced together. Circle 1 indicates where the July 2016 and June 2013 K^+ calibration records do not align. Arrow 2 highlights where a dramatic change in amplitude and frequency of the K^+ records occurs between the Nov 2015/Oct 2013 data. This is supported by both the November 2015 and Oct/June 2013 calibrations having difficulties resolving the K^+ peaks. As we cannot be confident in this data, none of the K^+ calibrations results will be included in this study and only the ICP-MS concentrations will be used (Table 6). The Mg^{2+} time series also shows large issues in the June/Oct 2013 calibration sections, with a step change compared to the July and November calibrations (Circle 3 and 4). This is likely due to issues arising from distinguishing the Ca^{2+}/Mg^{2+} peaks described in section 3.4.1. As a result, the Oct/June 2013 Mg^{2+} data will not be used in this study (Table 6). The MS^- record also shows problems, particularly with the November 2015 data showing a step change at Circle 5 and the Oct 2013 method not recording any data at Circle 6. This is not surprising as both the June/Oct and November calibrations had issues with resolving the MS^- peaks. Therefore only the July 2016 calibration will be used for MS^- , this is disappointing, as it has been shown to be an accurate recorder of changes in sea ice and its inter-annual variability (Abram et al., 2013). The NO_3^- time series shows clear issues between calibrations, with a baseline shift between July/June calibrations at Circle 7 and Circle 8 indicates where the November 2015 method was unable to identify the peaks. Therefore none of the NO_3^- data will be analysed in this study (Table 6).

The Na^+ , Ca^{2+} , Cl^- and SO_4^{2-} time series show no apparent issues when the calibrations are matched together in the time series above. Therefore the Na^+ , Ca^{2+} , Cl^- and SO_4^{2-} data from all four calibrations will be used (Table 6).

3.6 nss SO_4^{2-} calculation:

Non-sea salt sulfate (nss SO_4^{2-}) concentration was calculated by subtracting the proportional sea salt sulfate (ss SO_4^{2-}), (which was calculated based on the estimate from the SO_4^{2-}/Na^+ marine ratio of 0.252 (in ng/g)) from total SO_4^{2-} (Legrand and Delmas, 1984). As both the SO_4^{2-} and Na^+ data was deemed usable in section 3.5, the nss SO_4^{2-} data will be used from all four calibrations.

3.7 Additional Data

3.7.1 ICP-MS

Induced Coupled Mass Spectrometry (ICP-MS) Na^+ , Mg^{2+} , Ca^{2+} and Fe data spanning 1204-1992 AD was used to compare to the IC data and to extend the time series to before the start of the LIA. SO_4^{2-} was calculated by multiplying the Sulfur concentrations by 3. These were processed by two previous PhD students at Victoria University; Peter Neff and Andrea Tuohy in 2014 (Tuohy et al., 2015). As part of ICP-MS analysis samples are acidified, which often leads to higher concentrations than the corresponding IC measurements. This is thought to be because of acidification occurring as a result of dust particles present in the solution (N.Bertler, pers. comms). Data from the period between 1894-2011 AD can be resolved sub-annually/seasonal (average spacing= 0.1259 yrs). Whereas samples between 1204-1893 AD were combined to get a four year resolution.

3.7.2 Stable Isotope Data

The deuterium stable isotope record was measured using a continuous-flow laser spectroscopy system with an off-axis integrated cavity output spectroscopy (OA-ICOS) analyser, manufactured by Los Gatos Research (LGR). The water was derived from the inner section of the continuous flow analysis (CFA) section. Water from the outside of the CFA piece was collected for discrete samples. A detailed description of this set up and a quality assessment is provided by Emanuelsson et al. (2015). The combined uncertainty for Deuterium (δD) at 2 cm resolution is $\pm 0.85\text{‰}$. A detailed description of the isotope calibration, the calculation of cumulative uncertainties, and the assignment of depth is provided by Keller et al. (Submitted).

Chapter 4: Results

4.1 Time series data

The IC data and modern ICP-MS (1894-2011 AD) samples were annually resolved by applying a MATLAB linear interpolation function to the age model resolved age, the respective ion concentration and the desired sampling interval; 1 year. The long term ICP-MS samples (1200-1992 AD) were interpolated to 4 years via the same method. These data are plotted as time series below.

4.1.1 Long-term trend (1200-1992 AD) of 4 yearly resolved ICP-MS data

The ICP-MS 4 year resolved data were initially analysed to determine the long-term trend in the major ion data over the LIA and ME (Figure 4.1).

Na⁺ shows a step-function increase in concentrations mid 15th century from an average of 197 ppb in 1204-1444 AD to 335 ppb between 1448-1848 AD (Figure 4.1). A two-sample Student t-test was used on Na⁺ and the subsequent ions to test the significance of this shift (Table 20). This confirmed the 70% increase in sodium to be statistically significant. Following ~1880 AD a decline in Na⁺ concentrations towards 1992 AD is observed. This will be discussed further in section 4.1.2

	Na ⁺	Ca ²⁺	K ⁺	Mg ²⁺	SO ₄	nssSO ₄ ²⁻
p-value	p<0.01	p<0.01	p<0.01	p<0.01	p<0.01*	P<0.01
% Difference in means	70%	43%	45%	52%	19%	-18%

*Table 20: Two sample t-test between ICP-MS 4 yr resolved 1204-1444 AD data and 1448-1848 AD data to test for step function. *Could be due to increasing trend not step function*

Ca²⁺, like sodium also shows a statistically significant mid 15th century 43% increase from a mean of 13 ppb between 1204-1444 AD to 18 ppb between 1448-1848 AD (Figure 4.1) (Table 20). Ca²⁺ also shows a decline from ~1880s-1992 AD.

Figure 4.1: ICP-MS 4 yr resolved time series 1204-1992 AD.
Blue lines and arrows show schematically trends in data discussed in text.

K^+ , shows a statistically significant 45% increase in concentration from a mean of 10 ppb in 1204-1444 AD to 15 ppb between 1448-1848 AD (Figure 4.1). From ~1880 AD a decline is also observed until 1992 AD.

Mg^{2+} , showed a significant 52% shift mid 15th century from a mean of 31 ppb in 1204-1444 AD to 48 ppb between 1448-1848 AD (Figure 4.1). Consistent with the aforementioned ions, Mg^{2+} also records a decrease from ~1880-1992 AD. As shown, Na^+ , Mg^{2+} , Ca^{2+} and K^+ all exhibit very similar trends in the 4yr resolved ICP-MS data.

The SO_4^{2-} two sample t-test shows a smaller increase compared to previous species of only 14% from a mean of 118 ppb in 1204-1444 AD to 140 ppb between 1448-1848 AD (Table 20). This increase was deemed statistically significant at the 99% level (Figure 4.1). SO_4^{2-} subsequently shows a steady incline until 1992 AD.

$nssSO_4^{2-}$ is the only ion which showed a statistically significant decrease between 1204-1444 AD and 1448-1848 AD of 18% (Figure 4.1). This shift appears to occur later than the aforementioned ions, decreasing in the late 16th century. From the late 19th century an increasing trend is observed until 1992 AD.

In addition, the ICP-MS measured trace element Fe (a dust indicator) was analysed (Figure 4.1). Fe appears to remain consistent from 1200-1850 AD, however there appears to be a long term cyclicity peaking mid 13th century and in late 16th century. Following 1850 AD, Fe shows a dramatic increase in concentration to 1992. Fe shows a statistically significant increase of 0.0088 ppb per year between 1850-1992 AD (Table 21).

4.1.2 Modern Era Trends of IC and ICP-MS annually resolved data (1850-2011 AD)

In order to analyse the trends during the Modern Era (ME) transition, the annually resolved ICP-MS and IC measurements were compared between 1850-2011 AD (Figure 4.2). Statistical analysis was carried out on both the annual IC data and the 4 year resolved ICP-MS data in order to determine the significance of the trends (Tables 19

and 20). This was not carried out on the annual ICP-MS data as this only extends back to 1894 AD, this record was therefore deemed too short to capture any ME trend.

Figure 4.2: ICP-MS (shown in orange) and IC (shown in blue) annually resolved major ion time series 1850-2011 AD.

ICP-MS annual data, only stretches between 1893-2011 AD.

October and June 2013 calibrations were removed for Mg^{2+} .

Low confidence in the K^+ IC data prevents it from being compared with ICP-MS data.

No ICP-MS record exists for Cl^- or MS . No IC record exists for Fe .

Na⁺, Mg²⁺, Ca²⁺ and K⁺ show similar trends since 1850 AD (Figure 4.2). Na⁺ shows a statistically significant decline (p-value <0.01) of 2-3 ppb per year from the mid 19th century to 1992. Ca²⁺ also shows a significant decline (p-value<0.01), but with a decrease of 0.13 ppb per year (Table 21). K⁺ and Mg²⁺ also show a statistically significant decline (p-value <0.01) of 0.1 ppb and 0.3 ppb, respectively between 1850-1992 AD (Table 21). 1

	Na ⁺		Ca ²⁺	K ⁺	Mg ²⁺
p-value	<0.01	<0.01	<0.01	<0.01	<0.01
R ²	0.21761	0.049	0.26307	0.299909	0.38275
ppb/yr	-2.2399	-3.002	-0.1301	-0.1064	-0.3322

	SO ₄ ²⁻		nssSO ₄ ²⁻		Cl ⁻	Fe
p-value	>0.1	>0.1	<0.01	<0.01	<0.01	<0.01
R ²	0.01626	0.00158	0.2077	0.18	0.068	0.22301
ppb/yr	0.2003	0.15	0.7647	0.91	-5.3	0.0088

Tables 21 (upper) and 22 (lower): Modern era trend analysis. Where available IC annual (1850-1991 AD) and ICP-MS 4 yr (1852-1992 AD) data is tested for significance of a trend. Orange columns are ICP-MS data and Blue are IC data. Some ions don't have both due to no ICP-MS being available or the quality of the IC data prevents it from being analysed. Bold indicates where the trend is significant.

SO₄²⁻ does not show a statistically significant trend. In contrast, non-sea salt sulphate exhibits a statistically significant (p-value< 0.01) increase of ~0.8 ppb per year from 1850-1992 AD (Table 22).

As Cl⁻ cannot be analysed via ICP-MS we only have the IC data spanning 1557-1613 AD and 1728-1991 AD. The 5.3 ppb per year decline in concentration between 1850-1991 AD, is statistically significant (p-value< 0.01) (Table 22).

As MS⁻ cannot be analysed by the ICP-MS, we only have the IC data and only the July 2016 calibration spanning 1585-1613 AD and 1755-1893 AD, due to issues arising from the other calibrations. This time series does appear to decrease from mid 19th century to the late 19th century, however as there is not sufficient data to test its modern era (1850-1992 AD) decline this is not included in Table 22.

4.2 Major ion source regions

4.2.1 Molar ratios

The background chapter highlighted the common sources of the major ions used in this study. However, in order to test whether the RICE concentrations reflect these sources at Roosevelt Island, we can compare the RICE molar ratios with the molar ratios expected in seawater (Table 23).

	Cl^-/Na^+	$\text{Mg}^{2+}/\text{Na}^+$	$\text{SO}_4^{2-}/\text{Na}^+$	$\text{Ca}^{2+}/\text{Na}^+$
Expected	1.8	0.12	0.25	0.038
Observed	1.86	0.126	0.383	0.048

Table 23: Comparison of expected molar ratios in seawater (Pilson, 1998) with observed IC annual average molar ratios. Using the July 2016 data (1755-1893 AD) data.

We find our observed Cl^-/Na^+ molar ratios to fall within the expected molar ratios of seawater (Table 23), confirming these ions as a sea salt indicator for RICE.

As previously noted, the Danish RICE team determined the Roosevelt Island Ca^{2+} record as an indicator of sea salt (P.Vallelonga, pers. comms). Our analysis confirms this suggestion. However, the $\text{Ca}^{2+}/\text{Na}^+$ ratio is a little high, suggesting an additional source (Table 23). We propose that this could indicate a terrestrial source.

As previously noted, Mg^{2+} has been used as both a sea salt and terrestrial indicator in the past. However, the similarity of our Mg^{2+} time-series record to that of the other sea salt species e.g. Na^+ , suggests this could represent a sea salt signature. This is confirmed by the similarity of the IC data's $\text{Mg}^{2+}/\text{Na}^+$ ratio to that expected from seawater (Table 23).

Total SO_4^{2-} shows a steady increase in concentration from the mid 15th century, which carries through until 1992. However, the $\text{SO}_4^{2-}/\text{Na}^+$ ratio is much higher than can be expected from wholly a sea salt source, highlighting the influence of nss SO_4^{2-} (Table 23).

4.2.2 Spatial Correlations

To further understanding of dominant major ion and Fe sources and transport mechanisms, we compare their modern concentrations to the European Reanalysis Interim (ERA-interim) (1979-2015 AD) surface meridional and zonal wind strength and sea ice concentration. The annual major ion concentrations (ICP-MS 1979-2011 AD) were compared to the summer time ERA-interim meridional and zonal wind strength as we see the strongest correlations during this period due to the connection with the ENSO and SAM.

Figure 4.3: The ERA-interim 1979-2015 AD summer (DJF) meridional surface (10 m) winds (V winds) data set correlated with the ICP-MS 1979-2011 AD ions at the 95% confidence level. Positive (negative) correlation indicates a poleward (equatorward) flow with increased major ion concentration. Pearson product-moment correlation coefficient calculated using the 'escorc' function is used. Obtained using Climate Reanalyzer (UMaine, 2016). Red circle denotes RICE location.

Figure 4.3 shows that our sea salt species Ca^{2+} , K^+ , Mg^{2+} , Na^+ exhibit a negative correlation with the meridional wind off West Antarctica/Marie Byrd Land. As this region is intrinsically linked to the Amundsen Sea Low, we suggest that the sea salt species are transported to Roosevelt Island by the northerly winds linked to the eastern branch of the ASL (Figure 2.6). This is supported by the positive correlation off

the western Ross Ice Shelf, linked to the southerly flow that could be associated with the western branch of the ASL.

SO_4^{2-} and Fe do not appear to show any significant links to the meridional winds which could affect transport to Roosevelt Island (Figure 4.3).

Figure 4.4: ERA-interim summer (DJF) zonal (u) surface (10 m) wind correlation with ICP-MS annual 1979-2011 AD ions. Positive (negative) correlation indicates a westerly (easterly) flow with increased major ion concentration. Pearson product-moment correlation coefficient calculated using the 'escor' function is used. Obtained using Climate Reanalyzer (UMaine, 2016). Red circle denotes RICE location.

Figure 4.4 shows the correlation of the ICP-MS ions with the ERA-interim summer zonal winds. Ca^{2+} particularly shows a strong positive correlation with the westerlies, which is not surprising as a sea salt species. K^+ and Mg^{2+} also show similar links to the westerly wind belt but not as well defined as Ca^{2+} . Somewhat surprising is the lack of a significant pattern with the zonal winds and sodium. It was initially thought a more significant trend in Ca^{2+} , K^+ data might have correlated with the increasing SAM trend, however this data was run again detrended and the same pattern arose. SO_4^{2-} and Fe show a strong correlation with the westerly winds to the east of the Drake Passage, which likely reflects the relationship of the well-known Antarctic Dipole between the Ross/Amundsen and Weddell Seas (Yuan & Martinson, 2001).

Figure 4.5: ERA-interim summer (DJF) mean sea level pressure correlation with ICP-MS annual 1979-2011 AD ions. Positive (negative) correlation indicates a high (low) MSLP with increased major ion concentration. Pearson product-moment correlation coefficient calculated using the 'escorc' function is used. Obtained using Climate Reanalyzer (UMaine, 2016). Red circle denotes RICE location.

When the ions are compared with the mean sea level pressure (Figure 4.5), Ca^{2+} and K^+ show a strong correlation with the Amundsen Sea Low (ASL). Na^+ and Mg^{2+} also show a strong correlation to an area of low pressure off the Marie Byrd Land, however it is not to the same extent as the Ca^{2+} and K^+ pattern (Figure 4.5). Again, SO_4^{2-} and Fe do not appear to show a statistically significant correlation with any region that would likely affect the Roosevelt Island region.

Figure 4.6: ICP-MS annual nssSO4 1979-2011 AD record correlation with ERA-interim annual sea ice concentration. Pearson product-moment correlation coefficient calculated using the 'escorc' function is used. Obtained using Climate Reanalyzer (UMaine, 2016). Orange circle indicates likely Ross Sea Polynya correlation. Red circle denotes RICE location.

The correlation between nssSO_4^{2-} and ERA-interim sea ice concentration shows small regions of statistically significant correlations in the Ross Sea (Figure 4.6). The largest negative correlation in the Ross Sea (circled) falls in the region of the Ross Sea/Terra Nova polynya and could therefore link to the winter open ocean extent of the polynya. The negative correlation is expected between nssSO_4^{2-} and sea ice as in the Ross Sea as more open ocean is more conducive to biological productivity.

4.2.3 Sea salt source and timing

Na has been demonstrated to be derived from a marine source. The $\text{SO}_4^{2-}/\text{Na}^+$ ratio is used to differentiate between an open water source via bubble bursting or frost flowers during sea ice extent (Rankin et al., 2000; Wolff et al., 2003). As evinced by Table 24, the $\text{SO}_4^{2-}/\text{Na}^+$ ratio exceed that expected from frost flowers. Therefore, we assume the majority of sea salt is brought to the site directly from the sea water via bubble bursting.

	Seawater ratio expected	Frost flower expected	Observed
$\text{SO}_4^{2-}/\text{Na}^+$	0.25	0.11	0.38

Table 24: Comparing $\text{SO}_4^{2-}/\text{Na}^+$ molar ratios in order to determine likely sea salt source. Seawater ratio expected is reported in Pilson (1998). Frost flower ratio expected is reported by Wolff et al., 2003.

By comparing the MS^- and Na^+ record we can determine when this snow precipitation occurs (Figure 4.7). As MS^- is an indicator of biological activity (as described in section 2.3.2) and has shown a negative relationship with sea ice in the Ross Sea, peaks in MS^- indicate more open ocean, which occurs during summer, hence it is a summer indicator. Previous analysis of the RICE core has exhibited MS^- aligning with Na^+ in deep sections of the core due to post depositional processes (N. Bertler, pers. comms.). However, when Na^+/MS^- data from close to the surface is compared, the ions are also in phase. Therefore it is assumed post-depositional processes are not causing this relationship between 1840-1860 AD. Figure 4.7 shows the comparison of Na^+ and MS^- over a 20 year section of the July 2016 data (section where there is confidence in MS^- data). The graph shows that the peaks in Na^+ generally coincide with the peaks in

MS⁻ (occur in summer), therefore indicating that snow precipitation occurs in summer. If the peaks were opposing, this would suggest a winter signature and the significant sea salt signature would be due to increased transport of air masses. Instead, summer precipitation confirms that the sea salt signature is due to proximity to the open ocean, continually supplying the site, through periods of reduced storm activity (summer).

Figure 4.7: Segment of July 2016 data comparing MS⁻ and Na⁺ concentration peaks. Indicates that MS⁻ and Na⁺ coincide, indicating summer snow deposition.

4.2.4 Non-sea salt source

Generally, nssSO₄²⁻ data are used as evidence for biological activity or volcanic eruptions. Biological activity is closely related to sea ice production, with an increase coinciding with a decrease in sea ice in the Ross Sea (Rhodes et al., 2009). Figure 4.8 shows the correlation between the nssSO₄²⁻ annual record over 1979-1991 AD to the sea ice extent in the Ross Sea from (Raymond, 2009, 2014). Between 1979 and 1987 AD this relationship is opposing, which is to be expected based on the negative correlation between sea ice and biological productivity in the Ross Sea with regards to MS⁻ (Figure 4.8) (Rhodes et al., 2009; Sinclair et al., 2014). Following 1987 AD there is a shift to a statistically significant positive correlation (p-value <0.1) between the two records. This could represent a shift in source region for nssSO₄²⁻ from a Ross Sea to another source, which could link to the position of the Amundsen Sea Low.

Figure 4.8: IC nssSO₄²⁻ record compared to (Raymond, 2009, 2014) sea ice extent data from 160° longitude (roughly Ross Sea region).

To investigate the influence of volcanic eruptions on the sulphate record, we compare the RICE nssSO₄²⁻ record with the Victoria Lower Glacier (Bertler et al., 2011) and EPICA Dronning Maud Land nssSO₄²⁻ record. In Bertler et al. (2011) 5 volcanic peaks are resolved by both the EPICA and VLG cores (Figure 4.9) (Traufetter et al., 2004). According to Bertler et al. (2011) the EDML record is an exceptional record to decipher volcanic eruptions due to its high resolution, suitable age control and was drilled at an elevation of 3233 m and ~500 m inland from the coast, which reduces the influence of ss SO₄²⁻ compared to coastal sites like RICE and VLG. Only two coinciding major peaks are observed in RICE; the Samalas (Indonesia) eruption (Lavigne et al., 2013) at ~1257 AD and the Agung eruption at 1963 AD. There may be a modest signals of the Tambora, Krakatau and Huayanaputina eruptions, but the background biological record at RICE appears to mask those signals. The RICE age model does use the Agung 1965 AD eruption and the Kuwae eruption in 1453 AD, which have been noted in conductivity and Ca²⁺ data, the latter cannot be identified in our nssSO₄²⁻ record. Therefore it is argued that the nssSO₄²⁻ record represents mainly a biological indicator.

Figure 4.9: Comparison of the Victoria Lower Glacier (Bertler et al., 2011), EPICA Dronning Maud Land (EDML) and RICE ICP-MS nssSO_4^{2-} record for the past 900 years. Shaded areas indicate eruptions that are shown in both the EDML and VLG nssSO_4^{2-} as dated in the EDML record. Figure modified from Bertler et al. (2011), EDML data from Traufetter et al. (2004). RICE data is set to 4 year resolution.

4.3 Principal Component Analysis

A principal component analysis was conducted on two data sets; the long term (1204-1992 AD) 4 year resolved ICP-MS data set (Appendix C) and the annually resolved middle continuous IC section (1729-1991 AD) (Appendix B). The IC annual principal component analysis was conducted using Na^+ , Cl^- , Ca^{2+} , SO_4^{2-} and nssSO_4^{2-} (Table 25). Magnesium was not used due to the lack of confidence in the 1900-1991 AD (Oct/June 13) data (section 3.6), if we did use it then the time period in the PCA would be substantially reduced. The PCA was conducted using PAST software (Hammer, 2016).

	PC1
Eigenvalue	3.4653
% Variance	63

	PC2
Eigenvalue	1.4
% Variance	25

	PC3
Eigenvalue	0.71
% Variance	13

Table 25: Principal component analysis on IC 1729-1991 AD annual data.

Table 25 shows the results of the PCA on the IC 1729-1991 AD annual data (Appendix B). The first principal component (PC1), explains 63% of the variability. This shows a high level of contribution from Na^+ , Cl^- , Ca^{2+} and SO_4^{2-} , with a negative relationship with nssSO_4^{2-} . PC2, which explains 25% of the variance, shows high levels of contribution from nssSO_4^{2-} and SO_4^{2-} , with negative relationships with Na^+ , Cl^- and Ca^{2+} . Finally, PC3 explains 13% of the variance with high levels of Ca^{2+} . However, when plotting the scores against time there appears to be a correlation between the areas of higher concentration in PC3 and the outliers in the Oct/June 13 calibration for Ca^{2+} (Figure 3.3), therefore this principal component will not be used. PC4 and 5 explain too little (defined as <5%) of the overall variability to be considered.

	PC1
Eigenvalue	3.8
% Variance	62

	PC2
Eigenvalue	1.7
% Variance	28

	PC3
Eigenvalue	0.3
% Variance	6

Table 26: Principal component analysis on ICP-MS 4yr 1204-1992 AD resolved data.

Table 26 show the principal component analysis on the 4 year resolved ICP-MS data spanning 1204-1992 AD (Appendix C). Iron was not included in the PCA due to very high values in the last 4 years that would have dominated the analysis. PC1, explains 62% of the variance, with a large contribution from Na^+ , K^+ , Ca^{2+} , Mg^{2+} and SO_4^{2-} as well as the negative contribution from nssSO_4^{2-} (Table 26). PC2, explains 28% of the variance with a large contribution from non-sea salt sulphate and sulphate (Table 26). PC3 only explains 6% of the variance, but appears to capture a complex contribution, dominated by Ca^{2+} and nssSO_4^{2-} components. PC4, 5 and 6 explain too little (defined as <5%) of the overall variability to be considered.

4.4 Investigation of Important Climate Indices

Decadal scale climate drivers including the ENSO, SAM and the PDO influence the Ross Sea (Emanuelson, 2016). Therefore it is essential to assess how much of the variability seen in the major ion record can be explained by individual drivers.

4.4.1 1ST Principal Component

When the annual PC1 data is correlated with the ENSO, SAM and PDO indexes no statistically significant relationships are identified (Table 27).

	SAM	SOI	PDO
P-value	0.058	0.891	0.359
R ²	0.01378	0.00015	0.00618

Table 27: Statistical relationship between the IC annually resolved PC1 and the annual averaged SAM index (Abram et al., 2011), SOI index (NCAR), PDO index (NOAA).

Figure 4.10: Time series comparing the average annual Southern Oscillation Index (SOI) (NCAR) and the IC PC1 between 1866-1991 AD.

The comparison with the SOI shows similar frequencies between the SOI index and PC1, but peaks are as much antiphase as in phase (Figure 4.10). However the decline in the SOI index since ~1950s does coincide with a decline in PC1 .

Figure 4.11: Time series comparing the SAM reconstructed index (Abram et al., 2014) with the IC annual PC1 between 1729-1991 AD. 1861AD peak removed from PC1.

The SAM comparison, shows peaks in PC1 coinciding roughly with the positive SAM (Figure 4.11). However, peak amplitude and ~50 year trends are random.

Figure 4.12: time series comparing the average annual PDO index (NOAA) and the IC PC1 between 1854-1992AD. Removed peak at 1861.

The PDO comparison with PC1 shows few similarities in the frequencies or trends (Figure 4.12).

Figure 4.13: Time series comparing the Southern Annular Mode (SAM) reconstruction (Abram et al., 2014) and the ICP-MS PC1 between 1200-1992 AD.

The ICP-MS PC1 was also compared to the Abram et al. (2014) SAM reconstruction back to 1200 AD, to determine any correlations over the longer timescale (Figure 4.13). The mid 15th century rise in PC1 appears to coincide with the shift towards the positive phase SAM, which continues until 1800 AD. PC1's decline in the late 19th century shortly follows a shift in the SAM to a negative phase in 1800 AD. In the 20th century the two patterns diverge with the sea salt continuing on a downward trajectory and the SAM shifting back to a positive phase. However, no statistically significant correlation was found (Table 28).

	SAM
P-value	0.64
R ²	0.00112

Table 28: Statistical relationship between the ICP-MS 4 year resolved PC1 and the SAM index interpolated to 4 year resolution (Abram et al., 2011).

4.4.2 2nd Principal Component

The annual second principal component was then correlated with the SAM, SOI and PDO indexes. Once again, no statistically significant relationship was determined (Table 29).

	SAM	SOI	PDO
P-value	0.137	0.835	0.608
R²	0.0085	0.00035	0.00194

Table 29: Statistical relationship between the IC annually resolved PC2 and the annual averaged SAM index (Abram et al., 2014), SOI index (NCAR), PDO index (NOAA)

The SOI comparison shows that until ~1920 AD the time series experienced sections of in phase and out of phase behaviour (Figure 4.14). However, since 1920 AD they appear to be in phase and both decline from the mid 20th century.

Figure 4.14: Time series comparing the average annual SOI index (NCAR) and the IC annual PC2 between 1866-1991 AD.

The correlation between the PDO and the annual PC2 show that since ~1920 AD the records are in phase, however prior to this, the relationship switches (Figure 4.15).

Figure 4.15: Time series comparing the average annual PDO index (NOAA) and the IC PC2 between 1854-1992 AD.

Figure 4.16: Time series comparing the annual SAM reconstruction (Abram et al., 2014) and the ICP-MS PC2 (red) between 1200-1992 AD.

The comparison between the long term PC2 time series and the SAM index between 1200-2000 AD confirms the lack of significant relationship (Figure 4.16) (Table 30).

	SAM
P-value	0.279
R ²	0.00597

Table 30: Statistical relationship between the ICP-MS 4yr resolved PC2 and the SAM index (Abram et al., 2011).

4.4.3 Summary of PC/Climate Index Comparison

As described, no statistically significant correlations are observed between the RICE principal components and the climate indices. However similarities do occur between the frequencies and trends, which will be addressed further in the following sections.

4.4.4 Climate vs. PC Spatial Trends

In order to further assess any relationship between the discussed climate indices and our two principal components, we compared the spatial correlation patterns when plotted against ERA-interim (1979-2015 AD) meridional winds, zonal winds and mean sea level pressure.

Figure 4.17: The ERA-interim 1979-2015 annual meridional winds (V winds) data set correlated with the annual SOI record (1979-2015)(NCAR) and the SAM record (1979-2007 AD) (Abram et al., 2014) compared with the ERA-interim 1979-2015 AD summer (DJF) meridional winds (V winds) dataset correlation with the annual IC principal components for 1979-1991 AD at the 95% confidence level. Positive (negative) correlation indicates a southerly (northerly). Pearson product-moment correlation coefficient calculated using the 'escorc' function is used. Obtained using Climate Reanalyzer (UMaine, 2016). Red circle denotes RICE location.

The first principal component appears to show a similar pattern to ENSO/SOI, with meridional northerly winds associated with West Antarctica and then Southerly/offshore winds coming from the western Ross Sea (Figure 4.17). PC2 shows a small negative correlation over Roosevelt Island, which suggests southerly flow coincides with increased biological activity perhaps influencing the local Roosevelt Island polynya.

Figure 4.18: The ERA-interim 1979-2015 AD annual zonal winds (u winds) data set correlated with the annual SOI record (1979-2015)(NCAR) and the SAM record (1979-2007 AD) (Abram et al., 2014) compared with the ERA-interim 1979-2015 summer (DJF) zonal winds (u winds) data set correlation with the annual IC principal components for 1979-1991 AD at the 95% confidence level. Positive (negative) correlation indicates a westerly (easterly) flow. Pearson product-moment correlation coefficient calculated using the 'escorc' function is used. Obtained using Climate Reanalyzer (UMaine, 2016). Red circle denotes RICE location.

The correlation of zonal wind, PC1 and 2 shows little resemblance to the ENSO/SAM pattern (Figure 4.18). However, when we compare to the patterns of individual ions (Figure 4.4), PC1 does not appear to capture the zonal wind signal shown in Ca^{2+} and K^+ , which is very similar to the SAM zonal wind pattern.

Figure 4.19: The ERA-interim 1979-2015 AD annual MSLP data set correlated with the annual SOI record (1979-2015)(NCAR) and the SAM record (1979-2007 AD)(Abram et al., 2014) compared with the ERA-interim 1979-2015 AD summer (DJF) MSLP data set correlation with the annual IC principal components for 1979-1991 AD at the 95% confidence level. Pearson product-moment correlation coefficient calculated using the 'escorc' function is used. Obtained using Climate Reanalyzer (UMaine, 2016). Red circle denotes RICE location.

The correlation of PC1 with MSLP shows an area of strong negative correlation which likely represents the ASL, which coincides with an area of low pressure in the ENSO pattern (Figure 4.19). The PC2 shows no similarity to the ENSO or SAM pattern.

4.5 Time Series Cyclicality/Spectral Analysis:

Spectral analysis of the PCA data was made to test if the records share frequencies with ENSO, SAM and the PDO. A white noise and redfit filter were applied to determine which peaks are significant with respect to white (random) and red

(frequency dependent) noise, using a rectangular window, oversampling two times and in two segments. A wavelet analysis was also undertaken to test the temporal extent of observed frequencies. A Morelet function was applied with a lag of 0 and sample interval of 1. The cone of influence was plotted to indicate that the regions outside of this zone could be impacted by the padding effects of the analysis. The analysis was conducted on PAST software (Hammer, 2016).

4.5.1 1ST Principal Component

Figure 4.20 shows the spectral analysis of annually resolved IC PC1 between 1729-1991 AD. The large peak at 1861 AD (Figure 4.2) was removed from the wavelet analysis as it obstructed the other signals (Figure 4.21). The spectral analysis shows a significant peak (99% CI) at 58 years, which is present in the wavelet analysis as a band from around 42-78 years, across the entire time series. Before the mid 19th century the band ranges from 42-78 years, following this it becomes more constrained to 42-60 years. However, the more recent section of this wavelet cycle goes beyond the cone of influence, therefore this loss in significance could be caused by the extremes of the wavelet. Signals of 2.8-4 years are also picked up by the spectral analysis, which can be seen in frequent but somewhat irregular spacing throughout the whole record. These frequencies coincide with the ENSO 2-7 year periodicity, suggesting the influence of ENSO at Roosevelt Island during this time period.

Figure 4.20: Spectral Analysis with REDFIT of the annual PC1 1729-1991 AD data. The lower and upper green lines represent the 90% and 95% levels confidence intervals of the REDFIT analysis, respectively.

Figure 4.21: Wavelet analysis on IC annual 1729-1991 AD PC1 data. Without peak at 1861. Line is cone of significance and circles around red is the $p=0.05$ significance level. Black numbers indicate period of cycles.

4.5.2 2nd Principal Component

The spectral analysis on the IC annual PC2 data shows 7 significant peaks, at the 95% confidence level (87, 8.5, 4.7, 3.4, 2.4, 2.2, 2 years) (Figure 4.22). The 87 year cycle can be seen in the wavelet analysis as a 64-97 year cycle. However, it is only inside the cone of influence in the middle period as the moving window at this frequency quickly reaches outside the time series (Figure 4.23). The 2-4 year cycles appear to occur throughout the time period, with not all recording at the 95% significance level. These periodicities, like in PC1, are likely associated with the ENSO influence on the record.

Figure 4.22: REDFIT analysis of IC PC2 annual 1729-1991 AD data. The lower and upper green lines represent the 90% and 95% levels confidence intervals, respectively.

Figure 4.23: Wavelet analysis on IC annual 1729-1991 AD PC2 data. Line is cone of significance and circles around red is the $p=0.05$ significance level. Black numbers indicate period of cycles.

4.5.3 Fe Record

Spectral analysis was also conducted on the Fe ICP-MS record. The data show 4 significant peaks, at the 95% confidence level (519, 207, 12, 9 years) (Figure 4.24). As the data is resolved at a 4 year resolution, cycles with a periodicity of less than 8 years cannot be resolved, therefore any ENSO signature cannot be observed.

Figure 4.24: REDFIT analysis of ICP-MS 4yr 1204-1984 AD Fe record data. 1992 AD and 1988 AD peak removed as they were obstructing spectral frequencies. The lower and upper green lines represent the 90% and 95% levels confidence intervals, respectively.

Chapter 5: Discussion

Three research questions were set out at the beginning of this thesis to determine the conditions experienced at Roosevelt Island during the LIA/ME and how this is placed in the context of the wider Ross Sea region. Answering these questions will therefore contribute to our understanding of the atmospheric and oceanic circulation in the Ross Sea.

5.1 Research Question 1: What were the atmospheric and climatic conditions experienced at Roosevelt Island during the Little Ice Age/ Modern Era transition?

During the Little Ice Age (LIA) (~1400-1850 AD), the RICE records received more enriched isotopes, suggesting warmer conditions at Roosevelt Island (Figure 5.1) (Bertler et al., in prep). This period coincided with a decrease in snow accumulation rate (Figure 5.1) (Winstrup et al., In prep). Entering into the modern era (~1850 AD), a dominance of more enriched isotopes occurs, suggesting warmer conditions, coinciding with the 0.2°C increase in temperature recorded on average throughout Antarctica (Schneider et al., 2006). This shift in temperature was also met with an additional decrease in accumulation rate (compared to the LIA time period) (Figure 5.1).

Figure 5.1: RICE deuterium isotope record and accumulation rate (m water equivalent per year) over the Little Ice Age/Modern Era period (1200-2000 AD) (Bertler et al., in prep). Grey box indicates the generally accepted Little Ice Age period. Method of isotope preparation is detailed in Emanuelsson et al. (2016). Method of accumulation rate detailed in Winstrup et al. (in prep). Smoothed by a factor of 50.

The causes for these changes are potentially linked to the changes in atmospheric/oceanic circulation, which can be assessed by analysis of the RICE major ion record.

The principal component analysis indicated two main sources of major ions (Chapter 4.3) (Appendices B & C). The large contribution of identified sea salt species; Na^+ , Cl^- , Ca^{2+} and SO_4^{2-} in the IC PCA and Na^+ , Ca^{2+} , K^+ , Mg^{2+} , SO_4^{2-} in the ICP-MS PCA, confirms in both cases that the first principal component represents marine sourced winds. When ICP-MS PC1 is plotted as a proxy for marine air mass intrusions against time, we find that marine winds increased in the mid 15th century continuing in a roughly steady state through the LIA until the mid-late 19th century when greater variability occurs superimposed on a declining trend until 1992 AD (Figure 5.2).

Figure 5.2: ICP-MS 4 yr resolved PC1: sea salt/marine influence proxy. Blue lines indicate schematically changes in trend.

PC2 shows a significant contribution from nssSO_4^{2-} and sulphate in the IC and ICP-MS PC2. As evinced, nssSO_4^{2-} is largely linked to biological productivity near Roosevelt Island, therefore PC2 is assumed to indicate a biological influence. When the ICP-MS PC2/our biological proxy is plotted against time, biological productivity is shown to decline mid 16th century until a sharp increase in the late 19th century that on to 1992 AD (Figure 5.3). This record also shows the nssSO_4 – related spikes of the two volcanic events; the Samalas eruption at 1257 AD and Agung at 1963 AD.

Figure 5.3: ICP-MS 4 yr resolved PC2: biological proxy. Blue lines indicate schematically changes in trend.

Fe is a terrestrial/dust indicator (Bertler, 2004). However, determining the source of dust to West Antarctic ice cores is difficult as there are three main sources as highlighted by Neff and Bertler (2015). Firstly, a small component comes from exposures on the mountain ranges from West Antarctica. Secondly, dust is derived from rock outcrops in the Transantarctic Mountains e.g. Executive Committee Range and Ford Ranges. However, the atmospheric patterns that bring this dust to Roosevelt Island are considered unusual (Neff and Bertler, 2015; Bertler, pers comm.). Finally, a large component of dust may be derived from New Zealand, South America (in particular Patagonia), Australia and South Africa (Neff & Bertler, 2015). As the principal source of dust to Roosevelt Island is not yet identified, the Fe record could indicate a change in source in addition to changes in transport strength. The decrease in marine air mass intrusions during elevated Fe concentrations, does not support a strong marine source. Therefore it is proposed that the Fe record can be used as a proxy for katabatic winds derived from West Antarctic sources. This would suggest that katabatic winds were weaker through the LIA, but during the late 19th century, and increased again into the 20th century (Figure 5.4).

Figure 5.4: ICP-MS 4 yr resolved Fe time series for 1204-1992 AD. Large peak in 1992 AD was cut off to see more variability at lower concentrations. Blue lines indicate schematically changes in trend.

5.2 Research Question 2: What climate drivers can be linked to the processes observed at Roosevelt Island during the Little Ice Age/Modern Era transition?

Emanuelsson (2016) identified the influence of climate modes including El Niño Southern Oscillation (ENSO) and the Southern Annular Mode (SAM) at Roosevelt Island. These climate modes, as well as the Pacific Decadal Oscillation (PDO) time series are compared with the marine/biological record, but there is no statistically significant relationship. This result is not surprising, as the influence of these drivers are: (i) cumulative, (ii) seasonally variable, and (iii) not independent (Bertler, 2004; Fogt & Bromwich, 2011; Stammerjohn et al., 2012; Turner et al., 2013). However, spectral analyses suggest a measurable influence of ENSO at Roosevelt Island, with 2-5 year frequencies observed in both the marine influence record (PC1) and the biological record (PC2). The PDO might also affect the biological record with a 39 year cyclicity. The 9 year cycle could also indicate either a sunspot cycle (nominally 11 year cyclicity), which has been shown to influence local atmospheric circulation patterns (Bertler et al., 2005). The 40-90 year long trend seen in both the marine and biological records cannot be explained by a single climate driver alone, but could be the manifestation of the interaction between multiple drivers or the long term solar cycle.

The iron spectral analysis has a 519 long cycle. When the SAM reconstruction is run through a spectral analysis a 528 year cycle arises at the 95% significance level, which could explain the frequency in the Fe record.

The lack of statistically significant relationships between the PC1/marine influence and biological (PC2) records with either ENSO, SAM or the PDO, does not suggest that these climate drivers do not affect the records, but rather that the relationships are complex. This can be seen when the ENSO/ERA-interim meridional winds were compared with PC1 (Figure 4.17), which showed a similar region of correlation off the West Antarctic coast. In addition, several sea salt species also showed statistically significant correlations in the zonal wind pattern coinciding with the SAM. This highlights the complexity of the relationship with both climate patterns clearly having an impact on the marine winds.

5.3 Research Question 3: How do the climatic conditions at Roosevelt Island fit in the context of the wider Ross Sea setting during the LIA/ME transition?

Figure 5.5: Comparison of deuterium isotopes from the Victoria Lower Glacier (VLG) core (Bertler et al., 2011), Mt. Erebus Saddle (MES) (Rhodes et al., 2012) and RICE (this study). Grey box marks Little Ice Age cooling, RICE and MES show the generally accepted LIA period and VLG shows site-specific period described by Bertler et al. (2011). Smoothed by a factor of 50.

5.3.1 Little Ice Age

Based on the RICE deuterium isotope data, the LIA extends from 1450 to 1850 AD (Figure 5.5). Roosevelt Island experienced increased marine air mass intrusions during the LIA and probably decreased biological activity, with weaker katabatic winds. This is also supported by the near-by Siple Dome site, which recorded higher sea salt

concentrations from 1400 AD until the 20th century (Kreutz et al., 2000). However, this pattern, was not synchronous across the entire Ross Sea region. The Victoria Lower Glacier record, located in the western Ross Sea, recorded higher Fe concentrations and reduced sodium (Bertler et al., 2011). This was interpreted to reflect stronger katabatic winds and increased sea ice extent and/or a shorter sea ice break-out season between 1300-1850 AD. Bertler et al. (2011) also recorded 67% decrease in snow accumulation in the LIA compared to the Medieval Warm Period (1140-1287 AD), whereas RICE experienced only an 8% decrease compared to the previous 200 years (1200-1400 AD) (Figure 5.1).

Another southwestern Ross Sea record, the Mount Erebus Saddle (MES) ice core, indicates strong prevailing katabatic winds between 1500-1800 AD and that the biological productivity in the Ross Sea polynya was ~80% higher prior to 1875 AD than at any subsequent time (Rhodes et al., 2012).

Figure 5.6: Little Ice Age (1450-1850 AD) conditions in the Ross Sea. 1) RICE 2) Victoria Lower Glacier (Bertler et al., 2011) 3) Mt. Erebus Saddle (Rhodes et al., 2012) 4) Siple Dome (Kreutz et al., 2000).

These records suggest an east-west divide in the Ross Sea in the LIA (Figure 5.6).

Whereby the western Ross Sea records (Victoria Lower Glacier (2 in Fig. 5.6) and Mount Erebus Saddle (3 in diagram) show a cooling during the LIA, which can likely be explained by the dominance of cold katabatic winds flowing off the continent.

Whereas, the RICE record shows a dominance of the marine sourced winds, warmer,

more moist air masses to Roosevelt Island. Sinclair et al. (2010) revealed that in the McMurdo Sound 90% of snow precipitation was derived from cyclones from the Ross Sea and further afield, whereas only 10% occurred during katabatic events, this could account for the greater in snow accumulation at RICE (compared to Modern Era) and the decrease at VLG.

We also see this divide in biological productivity, with the west experiencing an increase in the marine productivity and size of the Ross Sea polynya and RICE recording a decrease in biological productivity. This could potentially be due to RICE picking up a signal from the smaller polynya off its coast, which could have seen a decrease in biological productivity. However, both regions record an increase in sea ice during the LIA.

5.3.2 Modern Era (1850-1992AD)

Figure 5.7: Modern era (1850-1992 AD) conditions in the Ross Sea. 1) RICE 2) Victoria Lower Glacier (Bertler et al., 2011) 3) Mt. Erebus Saddle (Rhodes et al., 2012).

In the modern era (1850-1992 AD), the records appear to align more, with both VLG and RICE recording more enriched isotopes/warming following ~1850 AD (Figure 5.5). Both records show a dominance of katabatic winds and a reduction in sea ice (Figure

5.7). MES also indicates the Ross Sea polynya size decreased (Rhodes et al., 2012). However, the RICE record shows an increase in biological productivity during this period, whereas VLG data show a reduction. Our data suggest that RICE might be sensitive to air masses that travelled over the local polynya off its coast, and not the much larger Ross Sea Polynya.

5.3.3 Explanation for trends in LIA

These opposing differences in the Ross Sea can be explained by two hypotheses:

1) Roosevelt Island location

The VLG and MES sites are located in regions dominated by katabatic flow from the Transantarctic Mountains and katabatic surges derived from the West Antarctic ice streams. In contrast, Roosevelt Island is influenced by katabatics off Marie Byrd Land (Figure 5.8). The differences in the marine record are partly accounted for by Roosevelt Island's position in the path of the mesoscale and synoptic scale cyclones that enter the Ross Sea, bringing warm, moist air, laden with sea salts (Sinclair et al., 2010).

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Figure 5.8: Reconstruction of simulated streamlines of time average katabatic winds over Antarctica, as taken from Parish and Bromwich (1987). Image taken from Carrasco and Bromwich (1994). 1) Roosevelt Island. 2) Victoria Lower Glacier (Bertler et al., 2011), 3) Mount Erebus Saddle (Rhodes et al., 2012).

2) Ross Sea Low Pressure system/potential shift in ASL

The proposed east-west divide could be explained by a deep low pressure system shifting into the Ross Sea, with the eastern branch bringing warm marine winds to RICE and the western branch prompting more katabatic winds off the continent at VLG/MES. Kreutz et al. (2000) and Bertler et al. (2011) suggest that during the LIA the ASL probably deepened and previous research has also suggested that zonal shifts in the ASL outside its usual seasonal progression could occur (Cullather et al., 1996; Kreutz et al., 2000).

According to Cullather et al. (1996) and Kreutz et al. (2000) these zonal shifts can affect the amount of precipitation the Ross Ice Shelf receives. During normal net precipitation conditions, the ASL on average sits near the eastern Ross Ice Shelf. In this instance, moisture is brought to the eastern Ross Sea directly from the north. In this position, the eastern branch brings warmer surface air temperatures and higher precipitation to West Antarctica (Hosking et al., 2013; Schneider et al., 2006; Vaughan et al., 1999). The increased western flank of the ASL will also intensify, causing cold, southerly air to flow off the continent, which has been associated with an increase sea ice extent (SIE) in the western Amundsen and Ross Sea (Massom et al., 2008). We observe very similar conditions during the LIA at RICE. However, in low precipitation events, the ASL moves to the east and closer to the Antarctic Peninsula. The majority of the marine air that reaches the eastern Ross Sea during these conditions travels over West Antarctica, delivering colder, drier air (Cullather et al., 1996).

As previously discussed, the ENSO and SAM phases have a large impact on the ASL. Despite neither climate modes showing a statistically significant effect on the zonal position, evidence has shown an impact on ASL intensity (Turner et al., 2013). The positive SAM phase intensifies the circulation of the ASL and the ENSO has been shown to have a significant influence on the frequency of the marine air mass trajectories from the Ross Sea and Amundsen Seas (Turner et al., 2013; Markle et al., 2012). Emanuelsson et al. (2016) highlights that during El Niño events and negative SAM there is an increased frequency of anticyclone formation in the Amundsen-Bellinghousen Sea, which results in air masses travelling over western Marie Byrd Land

and the eastern Ross Sea. During these periods, high precipitation rates and more enriched isotopes are said to occur at Roosevelt Island, as observed at RICE during the LIA. Whereas during La Niña and positive SAM, increased cyclonic activity occurs in the Amundsen-Bellingshausen Sea and anti-cyclonic activity occurs farther northeast over South America, thus air mass intrusion decreases over western Marie Byrd Land/eastern Ross Sea. This leads to a reduced snow accumulation and depletion in the isotope signal at Roosevelt Island (Emanuelsson et al., 2016). According to Emanuelsson et al. (2016) these large differences in precipitation at RICE are due to Roosevelt Island being sheltered from direct moisture from La Niña cyclones due to the West Antarctic orography.

Our records support an association between a westward shift of the ASL and its deepening and/or more El Niño/negative SAM conditions during the LIA. However, we cannot fully determine the behaviour of the ENSO/SAM during the Little Ice Age. Although zonal shifts/deepening in the ASL can occur, the RICE data do not provide evidence of the behaviour of SAM and ENSO during the LIA.

Chapter 6: Conclusions and Future Work

6.1 Conclusions

The Little Ice Age (LIA) is an important climatic interval to study as it is an historically recent event, which is captured in a growing number of records and sites, enabling analysis at relatively high spatial and temporal resolution. The LIA ended with the rise of industrialisation. It has been suggested that the termination might have been premature due to anthropogenic forcing (Painter et al., 2013). Previous work on Antarctic records has indicated an overall cooling during the LIA, however with significant spatial and temporal variability, e.g. sites such as Siple Station recording a distinct warming period (Bertler et al. 2011). The RICE record provides a new opportunity to improve our understanding of the regional expression of the LIA, providing a record for a relatively undersampled region. Moreover, the eastern Ross Sea is a region that is particularly sensitive to changes in the mid-latitudes and tropics and thus can evaluate not only local conditions but the influence of teleconnections through time (Emanuelson, 2016).

For this work, 1020 ice core samples were analysed for eight major ions; Na^+ , Mg^{2+} , Ca^{2+} , K^+ , MS^- , Cl^- , NO_3^- and SO_4^{2-} on an ion chromatograph spanning the LIA to ME transition. Na^+ , Cl^- , Mg^{2+} , Ca^{2+} and K^+ , were identified as sea salt species, mainly sourced from the open ocean. nssSO_4^{2-} was determined to capture primary productivity with contributions from volcanic eruptions. Sea salt species show a close relationship to sea ice concentration and evidence of two main volcanic eruptions. A Principal Component Analysis (PCA) identified two main major ion sources; one associated with marine sourced winds (oceanic) and one linked to primary productivity (biological). Fe was used as a proxy for the katabatic winds (inland). Trends in the marine sourced winds/biological record show a complex relationship with climate modes including the El Niño Southern Oscillation, the Southern Annular Mode and the Pacific Decadal Oscillation.

The RICE record indicates Roosevelt Island experienced warmer conditions with increased snow accumulation (compared to the ME), increased marine air mass intrusions, reduced katabatics, increased sea ice and decreased biological productivity. Whereas during the modern era, katabatic winds dominated, along with decreased snow accumulation, decreased sea ice and increased biological activity.

We find that the Ross Sea is characterised by an east-west divide during the LIA, with the western Ross Sea being dominated by katabatic winds and the eastern region by marine sourced winds. This is hypothesised to be due to a low-pressure system sitting in the Ross Sea region, which could be associated with the Amundsen Sea Low.

6.2 Limitations and Implications for Future Work

6.2.1 Ion Chromatograph Calibration improvements

This study demonstrated that in order to determine the concentrations of MS^- , K^+ , Mg^{2+} and Ca^{2+} in the low ppb range, a quadratic/curve function must be applied to the calibration, whereas a linear function could be used at higher concentrations. Due to time constraints, this study fitted either a linear or quadratic calibration to each major ion depending on the relevant concentration range. Further work could test the capability of the ion chromatograph to resolve these low concentrations and then subsequently fit these with a quadratic calibration, while still using a linear calibration for the higher values of that ion.

6.2.1 Iron source

Assigning a source to dust (i.e. by the use of iron concentration) remains challenging. There are three possible source regions; the West Antarctic ice sheet (WAIS), the Transantarctic Mountains and arid regions of the Southern Hemisphere continents, e.g. Patagonia, South Africa and New Zealand (Neff, 2016). The RICE rare earth element record for this time period could be analysed to identify the dust provenance. Alternatively, assessing another West Antarctic ice core e.g. Siple Dome's iron source

could also confirm whether our Fe record is sourced from WAIS and hence determine whether it does represent a katabatic wind proxy.

6.2.3 Climatology

The patterns we observe during the LIA are consistent with a low-pressure system located in the Ross Sea region and a likely a shift in ASL. Further work could model the climatology in the region to determine its sensitivity to changes in the position and intensity of the ASL, thus confirming whether the trends observed in the LIA could be attributed to this. Analysis of deuterium excess could also help determine the source of the winds.

Further analysis could be undertaken into the complex relationship between the RICE major ion signal and the El Niño Southern Oscillation, Southern Annular Mode and Pacific Decadal Oscillation. Correlating these climate indices (along with their interactions) with the RICE record at seasonal resolution could further our understanding of their impact on Roosevelt Island. A preliminary assessment has been carried out here with the recent finalisations of the annually resolved age model for the RICE record for the past 2,000 years.

Appendices

The following appendices are attached on Disc 1:

Appendix A: Ion chromatograph calibration and Quality Control standard data

Appendix B: IC July 2016 Raw Data and Annual Principal Component Analysis

Appendix C: 4 year ICP-MS Principal Component Analysis

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