

Implementing a new method to measure $\delta^{34}\text{S}_{\text{SO}_4}$ in ice cores to assess sulfate sources in West Antarctica

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This thesis is submitted for the degree of
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Declaration

This thesis is the result of my own work and includes nothing which is the outcome of work done in collaboration except as declared in the Acknowledgments and specified in the text. I further state that no substantial part of my thesis has already been submitted, or, is being concurrently submitted for any such degree, diploma or other qualification at the University of Cambridge or any other University or similar institution except as declared in the Acknowledgments and specified in the text. It does not exceed the 275 numbered page limit for the Degree Committee of Earth Sciences, including 225 pages of text, appendices, bibliography, footnotes, tables and equations.

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Abstract

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Sulfate sources in Antarctica can reveal information about the interconnection of climate systems and past climate events. The major sulfate sources in Antarctica are sea salt, biogenic activity, and volcanic activity, though volcanic events have a limited $\sim 1\text{--}2$ year deposition period. Each source can be identified by its unique sulfur isotopic composition of sulfate ($\delta^{34}\text{S}_{\text{SO}_4}$). However, $\delta^{34}\text{S}_{\text{SO}_4}$ measurements in Antarctic ice cores are scarce and have poor temporal resolution due to the large sample volume required for isotopic analysis.

For this thesis, I established a new method to measure $\delta^{34}\text{S}_{\text{SO}_4}$ in ice cores via multicollector inductively coupled mass spectrometry (MC-ICP-MS) at the University of Cambridge. This technique requires < 30 nmol of sulfur compared to the ~ 1 μmol previously required for analysis with gas source mass spectrometry (GS-MS). Using this method, I produced the first seasonal record of $\delta^{34}\text{S}_{\text{SO}_4}$ in an ice core to reconstruct sub-annual changes in sulfate sources at Dyer Plateau in West Antarctica. I also confirmed the $\delta^{34}\text{S}_{\text{SO}_4}$ signature of sea salt from the sea ice surface and further constrained the sulfur isotopic composition of biogenic sulfate. However, I was unable to reconstruct short-term changes in sea ice extent, which was the original aim of this research, because of the presence of an additional unknown sulfate source. This source has a low $\delta^{34}\text{S}_{\text{SO}_4}$ signature and increased winter deposition, suggesting that it is likely of volcanic and/or stratospheric origin.

I then measured $\delta^{34}\text{S}_{\text{SO}_4}$ in two additional West Antarctic ice cores to explore potential spatial variability in the third sulfate source. Sherman Island and Skytrain Ice Rise ice cores both showed the same unknown sulfate source with a low sulfur isotopic composition that I had found in the Dyer Plateau ice core. A similar source has been reported for numerous ice cores in East and West Antarctica, but the source was $\sim 3\times$ greater in the West Antarctica study. My results were similar to the East Antarctica findings, suggesting that there is no

clear distinction in the third sulfate source between East and West Antarctica, but instead significant variability on a smaller spatial scale.

Lastly, I considered long-term changes in sulfate sources in Antarctica. I found a significant increase in sea salt and biogenic sulfate emissions at Skytrain Ice Rise between the early and late Holocene, supporting the proposed retreat of the Ronne Ice Shelf $\sim 8,000$ years ago. I also measured $\delta^{34}\text{S}_{\text{SO}_4}$ in glacial and Holocene samples to explore the possibility of a large terrestrial sulfate source during the Last Glacial Maximum. Glacial $\delta^{34}\text{S}_{\text{SO}_4}$ values were 3–5‰ lower than in Holocene samples, which could be explained by a sulfate-rich terrestrial dust source that was $\sim 50\%$ of total sulfate. However, the origin of such a source with the required low $\delta^{34}\text{S}_{\text{SO}_4}$ signature is unclear.

This thesis highlights the importance of additional $\delta^{34}\text{S}_{\text{SO}_4}$ measurements in Antarctic ice cores. My results show that sulfur isotope ratios can be used to reconstruct past climate events, but background sulfate sources must be better characterized before we can use $\delta^{34}\text{S}_{\text{SO}_4}$ to reconstruct short-term climate processes.

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Chapter 1

Introduction

1.1 Understanding Climate

Earth's climate comprises many different systems, such as ocean currents, atmospheric composition, ice sheet melt, and the many feedback processes that link them. How these components interact creates a global system that affects all aspects of life. For example, agriculture, biodiversity, and human migration are all impacted by climate. Understanding these connections is essential to diagnose the short and long-term consequences of climate change. Current climate behavior can reveal short-term responses to a shifting global environment. To fully understand the climate system, however, today's climate must be viewed in the context of a longer climate record. Climate models are a valuable tool to study and predict climate behavior, but they must be based on ground truth from paleo data. For these reasons, paleoclimate reconstructions are an essential component of climate research.

1.2 Paleoclimate

Paleoclimate reconstructions reveal how climate subsystems interacted in the past. Climate models can then extrapolate from this data and predict how the climate may change in the future. Without direct observations, e.g., satellites, paleoclimate conditions are reconstructed using proxies. A proxy is preserved, measurable data that has recorded characteristics of past climates. For example, tree ring width is a proxy for temperature and precipitation. Trees thrive in favorable growing conditions, so narrower tree rings suggest a colder, drier climate. Narrow tree rings can also reflect large climate events like volcanic eruptions, which can cause significant climate shifts like the Little Ice Age (Briffa, 2000). In another example, carbon and oxygen isotopes in foraminifera can be used to reconstruct past ocean temperature,

salinity, and ocean circulation patterns (Bahr et al., 2017; Mackensen and Bickert, 1999; Röthlisberger et al., 2010).

Paleoclimate reconstructions highlight the cause and effect of many climate processes. Therefore, changes in paleoclimate not only provide context for today's climate, but also suggest how the climate may change on a longer timescale.

1.2.1 Reconstructing sulfate sources in Antarctica—Research aim

Ice sheets are a valuable tool in paleoclimate reconstructions because they contain a chemical and physical archive of past climate conditions. One such archive is a chronological record of sulfate (SO_4^{2-}) deposition, which contains information about numerous past climate events such as volcanic eruptions (Sigl et al., 2013). In another example, the sulfur isotopic composition of sulfate ($\delta^{34}\text{S}_{\text{SO}_4}$) can be used to identify sulfate sources (e.g., Patris et al., 2000) and may reveal past changes in sea ice extent, both of which are the focus of my research.

To examine sulfate sources in Antarctica, I established a new method to measure $\delta^{34}\text{S}_{\text{SO}_4}$ in small ice samples. I then used this technique to look for spatial variability of sulfate sources as well as any changes in the sulfate signal on glacial/interglacial timescales. In addition to sulfur isotope analysis, I also measured the concentration of major ion species in the ice cores and used these data conjointly to assess their use as a new sea ice proxy. Overall, I analyzed three ice cores from West Antarctica. The number of Antarctic sulfur isotope studies is extremely limited (e.g., Alexander et al., 2003; Kunasek et al., 2010; Uemura et al., 2016), and my work is a valuable contribution to the current literature.

1.3 Ice sheets as archives of paleo data

1.3.1 Ice sheet dynamics

There are many sources of paleo data used for climate reconstructions and models, including corals, stalagmites, and marine sediments. Another valuable archive for paleoclimate data is ice sheets in Greenland and Antarctica, which contain histories of temperature, atmospheric composition, and other climate factors (e.g., Jouzel et al., 2007; Simpson et al., 2007). An ice sheet is a permanent mass of glacial ice overlaying a continent. Ice sheets are formed when the net snow accumulation is positive, i.e., the amount of ice gained is greater than the amount of ice lost. As long as this mass balance remains equal, the ice sheet is stable. Ice mass is gained by precipitation. Snow that falls on an ice sheet is buried and compacted over time, creating a chronological archive of climate data. The longest recovered record spans

the past 800 thousand years (kyr), but older records may exist (EPICA community members, 2004; Parrenin et al., 2017). Ice mass is primarily lost by 1) surface melting, 2) basal melting under floating ice shelves, and 3) iceberg calving (Benn et al., 2017; Depoorter et al., 2013; Rignot et al., 2013). An ice sheet is constantly spreading under its own weight, and the base of the sheet is often lubricated by a thin layer of meltwater from contact with the warmer continent (Figure 1.1).

Ice sheet dynamics affect how climate signals are archived in the ice. For example, annual layer thickness and, therefore, the temporal resolution depend on numerous factors like the accumulation rate and depth of the ice sheet. Deeper layers are thinner because of increased compaction and ice sheet spreading. Therefore, shallow ice records from high-accumulation areas have the greatest resolution, but they are spatially limited and have relatively short timespans. Ice sheet data is recovered by drilling an ice core from the surface of the ice sheet to the bedrock. During the drilling process, the core is retrieved from the borehole several meters at a time and then transported to a lab for analysis.

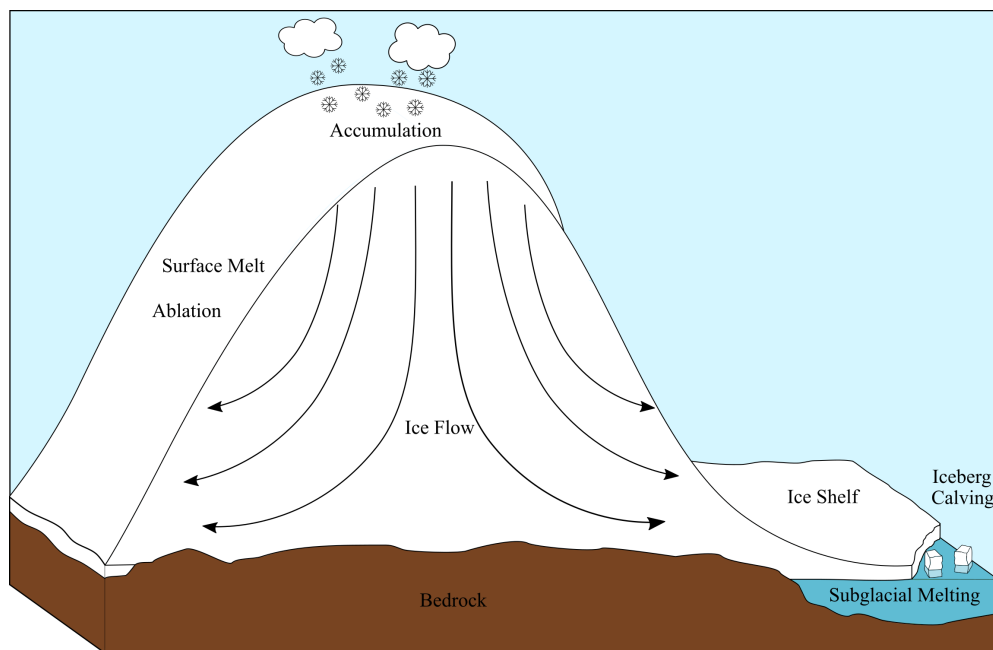


Fig. 1.1 *Diagram of ice sheet mechanics showing ice sheet spreading, ice mass gain by precipitation, and ice mass loss by surface melt, basal melt, and iceberg calving.*

1.3.2 Climate signals in ice sheets

Ice sheets record numerous environmental signals that are used for climate reconstructions. For example, air bubbles in the ice contain direct samples of ancient atmospheres (e.g.,

Chappellaz, 1994; Staffelbach et al., 1991), dust records can reveal when ice sheets advanced or retreated (Simonsen et al., 2019), and black carbon is a proxy for biomass burning (Legrand et al., 2016). Ice sheets can record some signals at up to seasonal resolution and have clear winter and summer depositional layers. These layers can sometimes be identifiable by sight if, for example, winter layers are darker than summer layers due to increased dust content and compaction. Another technique is to reconstruct seasonal signals of temperature or chemical content during the deposition period (Rasmussen et al., 2006; Sommer et al., 2000). Sea salt aerosols, for example, have a clear seasonal signal with high sodium (Na^+) concentrations in the winter (Minikin et al., 1994; Wagenbach et al., 1998), and oxygen isotopes can be used to construct a temperature history (Jouzel et al., 2007).

1.3.3 Overview of isotope systems

Ice sheets record isotope data that can be used to reconstruct various paleoclimate properties, such as temperature and biogenic activity in the ocean (Jouzel et al., 2007; Legrand and Pasteur, 1998; Minikin et al., 1998). Isotopes are variants of an element that have the same number of protons but a different number of neutrons and, therefore, a different molecular mass. For example, sulfur has four stable isotopes: ^{32}S , ^{33}S , ^{34}S , and ^{36}S , with natural abundances of 95.02%, 0.75%, 4.32%, and 0.02%, respectively. Isotopes are expressed as ratios relative to the major isotope, e.g., $^{34}\text{S}/^{32}\text{S}$. This ratio is then normalized to the isotope ratio of a reference standard and reported as a delta value (δ) in permil (‰). The equation is as follows:

$$\delta^b X_{\text{sample}} = \left(\frac{\left(\frac{bX}{aX} \right)_{\text{Sample}}}{\left(\frac{bX}{aX} \right)_{\text{Standard}}} - 1 \right) \cdot 1000 \quad (1.1)$$

where X is the measured element, a is the major isotope, and b is the minor isotope. The isotope ratio of an element ($^b\text{X}/^a\text{X}$) is also referred to as R. The reference standard for all sulfur isotope measurements is Vienna-Canyon Diablo Troilite (VCDT).

Elements have distinct R values because of different variables that favor one isotope over another. For example, the oxygen isotope ratio ($^{18}\text{O}/^{16}\text{O}$) of water in ice sheets is lower than that of seawater because of evaporation and transport. Lighter water molecules ($^1\text{H}^1\text{H}^{16}\text{O}$) evaporate from the ocean surface more easily than heavier water molecules ($^1\text{H}^1\text{H}^{18}\text{O}$), and they condense less easily. Therefore, the water vapor is depleted in ^{18}O relative to seawater and has a lower R value. This difference increases as the moist air is transported toward the pole, and heavier water molecules are preferentially lost by precipitation as the air cools.

This alteration of isotope ratios is called isotope fractionation and is reflected in the isotope signature of a material. In the above example, the lower R value of precipitation at the poles means that ice sheets have lower $\delta^{18}\text{O}_{\text{H}_2\text{O}}$ values than seawater. In addition to external forces like transportation, the type and degree of isotope fractionation depend on the element source and processes during formation. For example, the sulfur isotopic composition of sulfate deposited on an ice sheet can range between -10–21‰ based on its source (e.g., Baroni et al., 2008; Castleman et al., 1973; Nielsen et al., 1991; Rees, 1978).

1.4 Sulfate in ice sheets

Sulfate is another significant chemical signal recorded by ice sheets and has five major sources: sea salt, anthropogenic activity, biogenic activity, volcanic activity, and terrestrial input (Figure 1.2) (Rankin et al., 2002; Röthlisberger et al., 2002; Seguin et al., 2014). Source emissions vary in strength and are temporally and spatially dependent.

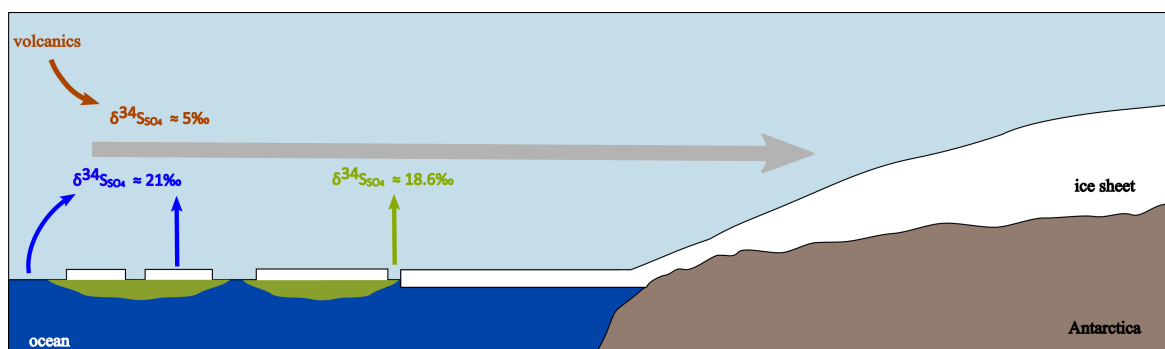


Fig. 1.2 Diagram showing the three primary sources of sulfate in Antarctica: sea salt (blue), marine biogenic activity (green), and volcanic emissions (orange). Because of Antarctica's remote location, anthropogenic and terrestrial sulfate does not reach Antarctica in significant quantities.

1.4.1 Sea salt sulfate

Sea salt is emitted from both the sea ice surface and the open ocean. The transport mechanism of sea salt to the ice sheet is much debated. The $\delta^{34}\text{S}_{\text{SO}_4}$ of sea salt is $21.0 \pm 0.1\text{‰}$, derived from global ocean values (Rees, 1978).

1.4.2 Anthropogenic sulfate

Anthropogenic sulfate does not reach Antarctica in significant quantities because the continent is so remote. This conclusion is supported by stable sulfate concentrations recorded in the Antarctic ice sheet over the last ~ 150 years (Graf et al., 2010; Legrand, 1995). In contrast, anthropogenic sulfate does reach Greenland because the majority of emissions are in the Northern Hemisphere; therefore, sulfate concentrations in the Greenland ice sheet increase sharply after the mid-19th century (Goto-Azuma and Koerner, 2001). Multiple studies have found that the $\delta^{34}\text{S}$ of anthropogenic sulfate ranges between $\sim 4.4\text{--}7\text{‰}$ (e.g., Patris et al., 2000; Seguin et al., 2014).

1.4.3 Biogenic sulfate

Sulfate is also produced by biogenic activity in the open ocean and around the sea ice edge (Curran and Jones, 2000; Trevena et al., 2000; Turner et al., 1995). Marine phytoplankton produce dimethylsulfide (DMS), which is oxidized to sulfate and methanesulfonic acid (MSA). These aerosols are then transported to and deposited on the ice sheet surface. Biogenic sulfate has a strong seasonal signal, with low emissions in the winter when there is maximum sea ice extent and peak emissions in the summer when there are warmer temperatures and prolonged sunlight (Oduro et al., 2011). The $\delta^{34}\text{S}$ of biogenic sulfate has often been cited as $\sim 18\text{‰}$ (Patris et al., 2000), although values as low as $15.6 \pm 3.1\text{‰}$ have been reported (Calhoun et al., 1991).

1.4.4 Volcanic sulfate

Volcanic eruptions emit large volumes of sulfur dioxide (SO_2) into the atmosphere, which is oxidized to SO_4^{2-} and then deposited on the ice sheet surface (Alexander et al., 2002; Savarino et al., 2003; Sigl et al., 2013). These spikes in sulfate concentration typically span 1–2 years (Legrand and Pasteur, 1998; Robock, 2000) and swamp all other sulfate sources. A wide range of volcanic $\delta^{34}\text{S}_{\text{SO}_4}$ values has been reported (Baroni et al., 2008); however, average values range between $\sim 0\text{--}5\text{‰}$ (Alexander et al., 2003; Burke et al., 2019; Nielsen et al., 1991; Patris et al., 2000).

Sulfur dioxide from large, tropical eruptions can enter the stratosphere, where it is exposed to ultraviolet light and undergoes mass-independent fractionation (MIF). Mass-independent fractionation occurs when the separation of isotopes by a physical or chemical process is not proportional to their difference in mass. This process is marked by a non-zero $\Delta^{33}\text{S}_{\text{SO}_4}$ signature (Burke et al., 2019), as calculated below:

$$\Delta^{33}S_{SO_4} = \delta^{33}S_{SO_4} - \left(\left(\frac{\delta^{34}S_{SO_4}}{1000} + 1 \right)^{0.515} - 1 \right) \quad (1.2)$$

Sulfate from stratospheric eruptions can be deposited on both the Greenland and Antarctic ice sheet. However, sulfate from smaller, tropospheric eruptions reaches only one polar ice sheet or may not be recorded at all (Sigl et al., 2013). These eruptions do not carry a MIF-derived $\Delta^{33}S_{SO_4}$ signal. Taken together, the $\delta^{34}S_{SO_4}$ and $\delta^{33}S_{SO_4}$ values of ice sheets can be used to identify the size and timing of a volcanic eruption and determine how that event affected the climate.

1.4.5 Terrestrial Sulfate

Sulfate in ice sheets can also derive from terrestrial sources, primarily dust that contains sulfate-bearing minerals (Goto-Azuma et al., 2019; Kaufmann et al., 2010; Wolff et al., 2006). Terrestrial biogenic activity has also been considered but does not contribute a significant amount of sulfate to the Antarctic ice sheet (Jonsell et al., 2005; Wolff et al., 2010). The dust source derives primarily from the Patagonia region of South America, where terrigenous material is uplifted by winds and transported to Antarctica (Kohfeld and Harrison, 2001; Oyabu et al., 2020; Wolff et al., 2010). Continental dust has a wide range of $\delta^{34}S_{SO_4}$ between 0–20‰ depending on its source, which makes it difficult to isolate the terrestrial component from other sulfate sources (Nielsen et al., 1991). The primary sulfate mineral in continental dust is gypsum ($CaSO_4$), which is a major component of evaporites (Babel and Schreiber, 2014). Gypsum can also form from the reaction of terrigenous calcium carbonate ($CaCO_3$) with marine sulfate emissions during transport (Angelis et al., 2012; Usher et al., 2003). This secondary gypsum has the same $\delta^{34}S_{SO_4}$ as marine biogenic sulfate, further complicating the quantification of the terrestrial source. However, the terrestrial sulfate source is minimal because of the long transport distance between the source origin and final deposition. As such, the terrestrial sulfate component is often considered negligible (e.g., Alexander et al., 2003; Kunasek et al., 2010).

Both the soluble and insoluble components of terrestrial input are measured to quantify the terrestrial sulfate source. Insoluble dust particles are measured to calculate the dust flux, but they are primarily silicon and do not contain sulfur (Iizuka et al., 2009; Kohfeld and Harrison, 2001; Oyabu et al., 2020; Wolff et al., 2010). Terrestrial input can also be determined by measuring the concentration of soluble terrestrial-derived species, such as aluminium, calcium, and iron (e.g., Kunasek et al., 2010; Legrand et al., 1988a; Palais and Legrand, 1985), and studies report good agreement in terrestrial input calculated with

both insoluble and soluble measurements (Iizuka et al., 2009). Because terrestrial sulfate derives primarily from soluble CaSO_4 , it can be quantified using calcium concentration measurements (Goto-Azuma et al., 2019; Röthlisberger et al., 2002).

1.5 Background sulfate in Antarctica

1.5.1 Spatial patterns in sulfur isotope ratios

Sulfur isotope data from Antarctica is limited, and most studies have focused on East Antarctica (Figure 1.3, Table 1.1). Results have shown a distinct difference in background sulfate in East and West Antarctica, although this finding is only supported by two studies in West Antarctica. Further research is needed to better characterize this spatial variation and how it relates to the overall sulfate system in Antarctica.

1.5.1.1 West Antarctica

Kunasek et al. (2010) and Pruett et al. (2004) both measured sulfur isotope ratios on the West Antarctic Ice Sheet (WAIS), and their results showed $\delta^{34}\text{S}_{\text{SO}_4}$ values up to $\sim 10\text{‰}$ lower than values in East Antarctica (Table 1.1 and the references therein). These low $\delta^{34}\text{S}_{\text{SO}_4}$ values suggested a large sulfate source with a low sulfur isotopic composition in addition to sea salt and biogenic sulfate. Both studies proposed a significant volcanic contribution from known regional volcanoes or a large stratospheric sulfate input due to increased cyclonic activity and lower elevation in West Antarctica compared to East Antarctica. Kunasek et al. (2010) also suggested sulfate input from volcanic activity in the southern Andes.

However, these hypotheses are not fully supported by other studies. A modeling study by Stohl and Sodemann (2010) showed no significant difference in stratospheric sulfate between West and East Antarctica, suggesting the third sulfate source was solely volcanic. The bordering volcanoes considered by Kunasek et al. (2010) are inactive and likely provide little sulfate input. However, an atmospheric model by Graf et al. (2010) suggested that Mount Erebus could be a significant sulfate source in West Antarctica because of the high elevation of its summit (3794 m). These findings are limited by the dearth of sulfur isotope data from West Antarctica, and additional studies are necessary to further constrain the spatial extent of the area with low $\delta^{34}\text{S}_{\text{SO}_4}$ values.

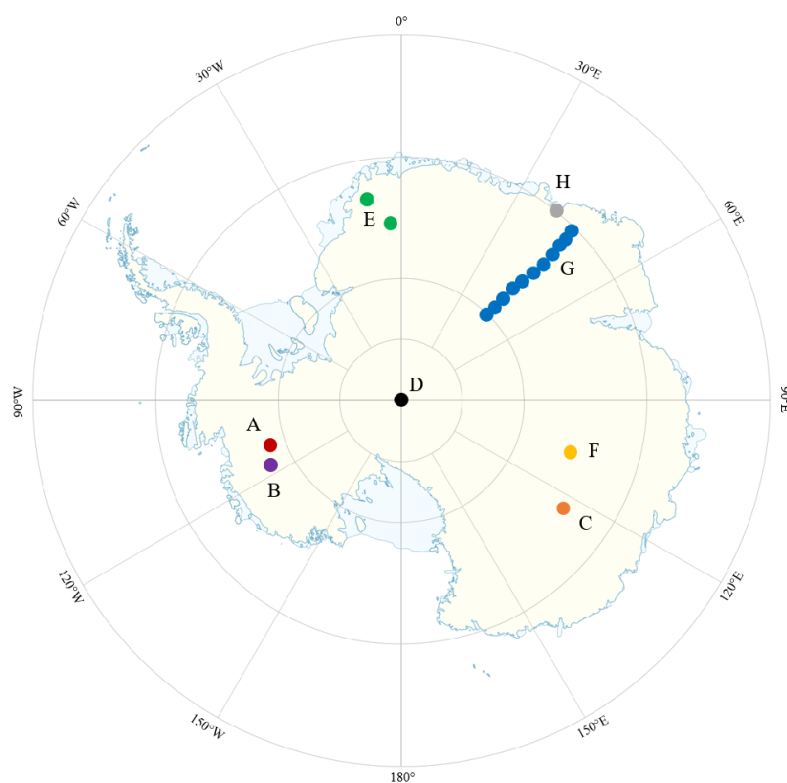
1.5.1.2 East Antarctica

Although $\delta^{34}\text{S}_{\text{SO}_4}$ values are higher in East Antarctica than West Antarctica, they are still lower than expected based on the assumed sulfate sources and their respective $\delta^{34}\text{S}_{\text{SO}_4}$ signatures (Table 1.1 and the references therein). Patris et al. (2000) and Akata et al. (2011) are the only two studies that produced sulfur isotope data consistent with the generally accepted $\delta^{34}\text{S}_{\text{SO}_4}$ signatures for sea salt, biogenic, and volcanic sulfate. Alexander et al. (2003) proposed that their low $\delta^{34}\text{S}_{\text{SO}_4}$ values resulted from the isotopic fractionation of sulfate during chemical transformation and transport. They invoked this argument to explain lower $\delta^{34}\text{S}_{\text{SO}_4}$ values in glacial periods because the larger ice sheets increased the transport time before deposition. Changes in the atmospheric composition and, therefore, sulfate oxidation pathways, were also proposed to explain the $\sim 4\%$ difference between glacial and interglacial samples.

However, sulfur isotope fractionation was not observed by Uemura et al. (2016), who measured $\delta^{34}\text{S}_{\text{SO}_4}$ in a latitudinal transect of shallow cores in Dronning Maud Land. Similarly, Jonsell et al. (2005) compared $\delta^{34}\text{S}_{\text{SO}_4}$ measurements in a coastal core to one further inland on the Antarctic Plateau. Both studies reported spatially and temporally consistent $\delta^{34}\text{S}_{\text{SO}_4}$ values with no significant altitudinal effects. As in the West Antarctica studies, Jonsell et al. (2005) suggested sustained volcano outgassing as an explanation for low $\delta^{34}\text{S}_{\text{SO}_4}$ values. They also suggested, however, that the accepted marine biogenic $\delta^{34}\text{S}_{\text{SO}_4}$ signature of $\sim 18\%$ was too high. This idea was further developed by Uemura et al. (2016), who used a range of biogenic $\delta^{34}\text{S}_{\text{SO}_4}$ values between 12.5–20.3‰ in their source reconstructions, based on additional previously reported biogenic $\delta^{34}\text{S}_{\text{SO}_4}$ values (Amrani et al., 2013; Oduro et al., 2012). A lower marine biogenic $\delta^{34}\text{S}_{\text{SO}_4}$ signature was also supported by direct sulfate aerosol measurements above the Southern Ocean that recorded a $\delta^{34}\text{S}_{\text{SO}_4}$ value of $15.6 \pm 3.1\%$ (Calhoun et al., 1991), perhaps caused by sulfate oxidation in the marine boundary layer (Uemura et al., 2016). Using this lower biogenic $\delta^{34}\text{S}_{\text{SO}_4}$ signature, Uemura et al. (2016) calculated that $84 \pm 16\%$ of sulfate in East Antarctica was of biogenic origin.

1.5.2 Background sulfate in sea ice extent reconstructions

Sulfate in ice cores may also be helpful in sea ice extent reconstructions. Sea salt is a major source of sulfate, and the strength of the sea salt source depends on the ratio of sea ice to open ocean. If this relationship could be quantified, sea salt would be a valuable sea ice proxy. The success of this proxy depends not only on interpreting sulfate sources in Antarctica, but also on understanding the sea ice system.



Holocene: 4.0–9.3‰

Holocene: 3.1–9.9‰

Holocene: 10.98–14.43‰

Holocene: 17.7–18.1‰

Holocene: 14.6‰

Holocene: 9.5–14.3‰

Glacial: 12.0–12.6‰

Eemian: 13.6–15.4‰

Holocene: 14.8–16.9‰

Holocene: ~17–20‰

Holocene: 11.45–15.30‰

Holocene: 12.0–13.4‰

Transition: 12.1‰

Glacial: 10.1–12.7‰

Fig. 1.3 Map of ice core sites used in Antarctic sulfur isotope studies and the reported $\delta^{34}\text{S}_{\text{SO}_4}$ values at each site. See Table 1.1 for corresponding location names, sample dates, and references.

Table 1.1 Sulfur isotope studies in East and West Antarctica

Map marker ¹	Location	Time period	Age	$\delta^{34}\text{S}_{\text{SO}_4}$ (‰)	Reference
<i>West Antarctica</i>					
A	WAIS	Holocene	1809–1978	4.0–9.3	Kunasek et al., 2010
B	RIDSA	Holocene	1935–1976	3.1–9.9	Pruett et al., 2004
<i>East Antarctica</i>					
C	Dome C	Holocene	~1450–2000	11.45–15.30	Baroni et al., 2008
D	South Pole	Holocene	~1450–1820	10.98–14.43	Baroni et al., 2008
D	Firn core, South Pole	Holocene	1930–1950	17.7–18.1	Patris et al., 2000
E	Dronning Maud Land	Holocene	~900–1990	14.6	Jonsell et al., 2005
F	Vostok	Holocene	11.2–5.7 ka ²	9.5–14.3	Alexander et al., 2003
		Glacial	109.9–14.3 ka	12.0–12.6	
		Eemian	130.2–121.9 ka	13.6–15.4	
C	Dome C	Holocene	9.5–2.5 ka	12.0–13.4	Alexander et al., 2003
		Transition	13.9 ka	12.1	
		Glacial	36.4–30.7 ka	10.1–12.7	
G	Dronning Maud Land	Holocene	surface samples	14.8–16.9	Uemura et al., 2016
H	Syowa Station	Holocene	surface samples	~17–20	Akata et al., 2011

¹See Figure 1.3² thousand years ago

1.6 The sea ice system

1.6.1 Formation and seasonal cycle

Sea ice forms on the ocean surface when seawater freezes, unlike icebergs that originate on land and are made from freshwater snow. Sea ice extent fluctuates throughout the year: ice begins to form in fall, reaches a maximum in winter, breaks up in spring, and reaches a minimum in summer. There are four stages to sea ice formation: nilas, young ice, first-year ice, and multiyear ice. Multiyear ice occurs less in Antarctica than in the Arctic because Antarctica is surrounded by large, open areas of ocean with relatively warm temperatures, and so most Antarctic sea ice melts in the summer (Abram et al., 2010; Curran, 2003). Because of this strong seasonality, Antarctica is an excellent site for short-term, seasonal reconstructions of sea ice extent. However, not all Antarctic sea ice melts in the summer. The majority of this multiyear ice is found in the Weddell Sea, where it is constrained by ocean currents (Abram et al., 2007). As a result, it may be more difficult to detect seasonal fluctuations in sea ice extent in this region.

1.6.2 Seawater fractionation during sea ice formation

Sea ice formation fractionates seawater and results in sulfate-depleted salt on the sea ice surface (Frey et al., 2020; Rankin et al., 2002; Wagenbach et al., 1998). This process depends on the temperature gradient between the ocean, sea ice, and atmosphere. Seawater freezes at -1.8°C . As sea ice forms, salty brine is excluded between the ice crystals and forms pockets and channels within the ice (Butler and Kennedy, 2015; Perovich and Richter-Menge, 1994). The brine is carried to the sea ice surface by a thermomolecular pressure gradient between the sea ice and the colder atmosphere (Martin et al., 1996; Rankin et al., 2002). As the brine cools, salts begin to precipitate out into the ice structure, including mirabilite ($\text{Na}_2\text{SO}_4 \cdot 10\text{H}_2\text{O}$) at -8°C (Butler and Kennedy, 2015). Other salts precipitate at colder temperatures, such as sodium chloride (NaCl) at -22°C . However, because of the temperature gradient between the cold atmosphere and the relatively warm ocean surface, such low temperatures are only reached at the top of thick, multiyear ice (Rankin et al., 2002).

The seawater freezing process results in a salty, sulfate-depleted slush layer on the sea ice surface. Because of the precipitation of mirabilite, this layer has a $\text{SO}_4^{2-}/\text{Na}^+$ mass ratio of $\sim 0.05\text{--}0.1$ compared to the 0.25 ratio in seawater (Hall and Wolff, 1998; Rankin et al., 2000, 2002; Roscoe et al., 2011; Seguin et al., 2014; Wagenbach et al., 1998). This low $\text{SO}_4^{2-}/\text{Na}^+$ ratio may be useful in sea ice extent proxies to separate sea salt from the sea ice surface from sea salt from the open ocean.

1.6.3 Frost flowers and blowing snow

Frost flowers are dendritic ice crystal structures that grow on the surface of newly-formed sea ice (Figure 1.4). Frost flowers form on protrusions on the ice surface and appear because of the temperature gradient between the ice and the atmosphere (Martin et al., 1996; Perovich and Richter-Menge, 1994; Rankin et al., 2002). Air temperature rapidly decreases above the sea ice surface, creating a supersaturated boundary layer as the brine evaporates (Alvarez-Aviles et al., 2008; Martin et al., 1996; Rankin et al., 2002). Water vapor condenses out of this layer between -12°C and -16°C , forming frost flowers that are typically 10–20 mm tall (Martin et al., 1995, 1996). Sulfate-depleted brine from the ice surface is then wicked into the flowers by surface tension (Perovich and Richter-Menge, 1994; Roscoe et al., 2011). Frost flowers do not form on multiyear ice, and the surface snow is less saline than snow on first-year sea ice because brine production and salinity decrease over time (Cox and Weeks, 1974; Rankin et al., 2002; Rhodes et al., 2018). The $\delta^{34}\text{S}_{\text{SO}_4}$ of frost flowers does not differ significantly from that of sea salt, at $20.8 \pm 0.4\text{‰}$ (Seguin et al., 2014), and they have the same $\text{SO}_4^{2-}/\text{Na}^+$ mass ratio as the surface brine (Rankin et al., 2002).

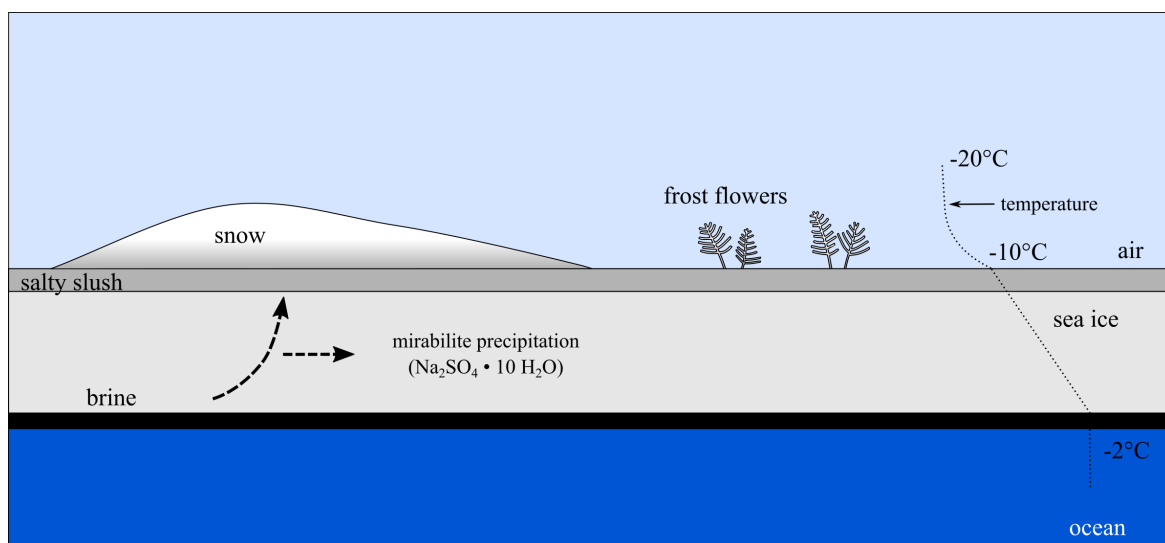


Fig. 1.4 Diagram showing frost flower formation on the surface of first-year sea ice and a typical temperature gradient between the ocean, ice, and atmosphere.

Frost flowers can have a salinity 3x that of seawater (Roscoe et al., 2011), and they were previously considered a major source of sea salt aerosols (SSA). Because of their dendritic shape, it was assumed that frost flowers could be easily lifted and blown inland from the sea ice surface (Hall and Wolff, 1998; Rankin et al., 2000; Rankin and Wolff, 2003). However, laboratory studies found that frost flowers have a relatively strong mechanical structure and

can withstand winds up to 12 m/s (Obbard et al., 2009; Roscoe et al., 2011; Yang et al., 2017). Furthermore, when frost flowers did break, they were primarily reincorporated into the brine (Roscoe et al., 2011). Based on these results, frost flowers are now considered to play a minimal role in SSA production (Huang and Jaeglé, 2017; Yang et al., 2019, 2017).

Frost flowers are typically covered by snow within several days of formation (Rankin et al., 2002). This snow accumulation is relatively low closer to the coast but increases with distance offshore and has been measured at 1.65 m deep (Massom et al., 2001). Brine on the sea ice surface is carried upward via capillary action and can penetrate ~ 10 cm into the snow column; however, the bulk of the salinity is in the bottom 0–5 cm (Massom et al., 2001; Yang et al., 2008). When the snow is thick enough to push the ice beneath the ocean surface, the sea ice is flooded with seawater that can migrate up to ~ 20 cm into the snow column (Domine et al., 2004; Massom et al., 2001). Flooding is less common for thicker, more stable multiyear ice, which further contributes to the relatively low salinity of its surface snow (Massom et al., 2001).

Sublimated blowing snow from the sea ice surface has also been proposed as a potential source of sea salt aerosols (Yang et al., 2008). The rate of sublimation depends primarily on wind speed, with a threshold velocity of ~ 7 m/s (Hara et al., 2014; Yang et al., 2019). Snow age and salinity also affect sublimation, with increased SSA production above young snow on first-year sea ice (Box et al., 2004; Frey et al., 2020; Yang et al., 2019). The blowing snow hypothesis is supported by both climate models and direct observations, which show high SSA production even with relatively low snow salinity (Frey et al., 2020; Nishimura and Nemoto, 2005; Rhodes et al., 2017; Yang et al., 2019).

1.7 Sea ice extent reconstructions using marine and ice core proxies

Sea ice is a major component of the global climate system. For example, sea ice reflects solar radiation, which has a cooling effect on the climate called the albedo effect. If the amount of sea ice decreases, more radiation is absorbed, and the climate warms. These processes create a positive feedback loop that leads to continuously rising temperatures. Since the 1970's, satellites have provided direct observations of sea ice cover, showing a drastic decrease in Arctic sea ice (Serreze and Barry, 2011) but a more regional pattern in Antarctica. Sea ice extent has been increasing in the Weddell and Ross Sea sectors (e.g., Parkinson and Cavalieri, 2012) but decreasing in the Bellingshausen Sea (e.g., Hobbs et al., 2016). Numerous proxies have been used to reconstruct Antarctic sea ice extent prior to the satellite-era. However,

most of these proxies are qualitative, do not extend beyond 1700 CE, and are from shallow, coastal ice cores (Abram et al., 2013; Thomas et al., 2019). Additional studies and improved proxies are necessary to gain a better understanding of regional, sub-annual, and long-term changes in Antarctic sea ice extent.

1.7.1 Marine sediment core proxies

Many sea ice reconstructions are based on paleo data from marine sediment cores. Over time, dead organisms, fecal matter, and other inorganic particles in the ocean fall to the sea floor and create a record of past ocean conditions. Using these archives, sea ice extent has been reconstructed based on past fossil assemblages, including sea ice related diatoms and dinoflagellates (e.g., de Vernal et al., 2005; Gersonde et al., 2005; Turner et al., 2015). Other geochemical markers such as the lipid IP25 have also been used to reconstruct changes in sea ice extent (Belt and Müller, 2013; de Vernal et al., 2013). Marine sediment core records extend into the Last Glacial Maximum (LGM) and provide valuable data about long-term changes in sea ice cover that serve as constraints in modeling exercises (Bracegirdle et al., 2015). However, the low temporal resolution and spatial scarcity of marine sediment cores limit their use in continuous, high-resolution sea ice extent reconstructions. For more complete sea ice records, marine core data is often combined with other ice core proxies like sea salt and halogens in ice cores (Thomas et al., 2019).

1.7.2 Ice core proxies

Numerous physical and geochemical markers in ice cores have been used as proxies in sea ice extent reconstructions. For example, bromine chemistry is affected by the salt-rich snow cover on sea ice, leading to “bromine explosions” in the summer/spring (Impey et al., 1997). The ratio of bromine to sodium can also be used to calculate a bromine enrichment factor that may correlate with the production of first-year sea ice (Vallelonga et al., 2017). Other proxies include organic compounds such as fatty acids (O’Dowd et al., 2004), water isotopes (Holloway et al., 2016), and snow accumulation (Thomas et al., 2015). Two of the most-used sea ice proxies are MSA from marine biogenic activity and sea salt.

1.7.2.1 MSA

One of the most-used proxies for sea ice extent is MSA, which derives from the oxidation of DMS produced by marine biogenic activity. Multiple studies have shown increased MSA concentrations in the sea ice zone relative to the open ocean because of increased

phytoplankton DMS production around the sea ice edge (Curran and Jones, 2000; Turner et al., 1995). As previously discussed, biogenic activity increases as winter sea ice begins to break up, causing a summer peak and a winter trough in MSA concentrations (Curran and Jones, 2000; Thomas and Abram, 2016; Turner et al., 1995). The oxidation of DMS to MSA also produces sulfate that could potentially be used to track sea ice extent. However, sulfate also derives from other sources such as sea salt. Biogenic activity is the sole producer of MSA, making it a preferable proxy for sea ice extent. The MSA proxy has been used in many sea ice studies with varying success (e.g., Criscitiello et al., 2013; Rhodes et al., 2009; Xiao et al., 2015). MSA concentrations are best used for regional sea ice extent reconstructions and must be considered in the context of longer records of environmental variables that can affect MSA production.

1.7.2.2 Sea salt

Another major proxy for sea ice extent is sea salt in ice cores. Sea salt is quantified by the sodium concentration in the ice because the reactivity of chloride makes it an unreliable tracer (Röthlisberger, 2003). Sea salt was originally believed to primarily come from bubble bursting in the open ocean (Petit et al., 1999; Wagenbach et al., 1998). By this theory, sea salt would be negatively correlated with sea ice extent. However, the reverse was observed, with sodium peaks in the winter, lows in the summer, and higher overall sea salt concentrations in glacial periods relative to interglacials (e.g., Minikin et al., 1994; Mulvaney and Wolff, 1994). Numerous mechanisms were proposed to explain this result, including increased storminess in the winter and/or glacial period (Petit et al., 1999) and changes in circulation patterns (Goodwin et al., 2004; Peel and Mulvaney, 1992). However, these hypotheses were not supported by climate models (Genthon, 1992; Mahowald et al., 2006; Reader and McFarlane, 2003).

Numerous studies discovered that sea salt in ice cores was significantly depleted in sulfate, with $\text{SO}_4^{2-}/\text{Na}^+$ mass ratios of $\sim 0.05\text{--}0.1$ instead of the expected 0.25 (e.g., Gjessing, 1989; Hall and Wolff, 1998; Rankin et al., 2000; Wagenbach et al., 1998). These results suggested sea ice as the primary source of sea salt because of seawater fractionation during ice formation (Rankin et al., 2002; Wagenbach et al., 1998). As discussed previously, blowing snow from the ice surface is a major source of sea salt aerosols. Also, Frey et al. (2020) found that sea salt aerosol production is significantly greater above the sea ice zone than the open ocean, further supporting the use of sea salt as a sea ice proxy.

The sea salt sea ice proxy has shown mixed results when applied to various Antarctic ice cores. Multiple cores in East Antarctica and Dronning Maud Land showed a correlation between sea salt and atmospheric circulation patterns rather than sea ice extent (Fischer,

2004; Udisti et al., 2012). Sea salt proxies also risk underrepresenting multiyear sea ice because of its lower salinity (Rhodes et al., 2017). However, some West Antarctic ice cores were more promising, such as the positive correlation between sea salt in the Siple Dome core and sea ice extent in the Amundsen Sea (Kreutz et al., 2000). Numerous factors other than sea ice extent can affect the sea salt concentration in ice cores, such as transport distance, changes in atmospheric circulation patterns, and polynyas (Criscitiello et al., 2013; Kaspari et al., 2005). Therefore, the sea salt proxy may be optimal for longer timescales to eliminate any potential influence from short-term processes. This hypothesis is supported by 6 kyr sea ice extent reconstructions in the Ross and Weddell Seas and the measured increase in sodium concentrations during the LGM, all of which are well-documented in marine sediment core data (Gersonde et al., 2005; Hodell et al., 2001; Steig et al., 1998).

A limitation of the sodium sea salt proxy is its inability to separate sea salt from sea ice and sea salt from the open ocean. This distinction could be accomplished by analyzing the $\text{SO}_4^{2-}/\text{Na}^+$ mass ratio of the salt; however, sulfate from sea salt must first be isolated from other sulfate sources. This suggests the possibility of developing a new sea ice proxy that combines elemental and sulfur isotope analysis.

1.7.3 A new sea ice proxy: Combining elemental and sulfur isotope analysis

A new, two-step sea ice proxy can be developed based on sodium and sulfate concentrations and sulfur isotope analysis. This proxy is predicated on the assumption of two sulfate sources: sea salt and marine biogenic activity. Because Antarctica is so remote, anthropogenic sulfate can be considered negligible, and volcanic sulfate can be avoided by analyzing only background sulfate, determined by total sulfate concentration measurements. Total sea salt sulfate can be isolated using an isotope mixing equation, and the sea ice and open ocean proportion of the sea salt component can then be quantified based on its $\text{SO}_4^{2-}/\text{Na}^+$ ratio. The viability of this proxy depends on the background sulfate sources in the region and the validity of the two-source assumption, as well as the accuracy of the known sea salt and biogenic $\delta^{34}\text{S}_{\text{SO}_4}$ signatures. As I will show, background sulfate sources are less understood than generally assumed. This finding shifted the focus of my research toward greater consideration of spatial variability in sulfate sources.

1.8 Research Objectives

To enable high-resolution sulfur isotope measurements, I implemented a new method at the University of Cambridge to measure $\delta^{34}\text{S}_{\text{SO}_4}$ in ice cores. Sulfur isotope ratios have traditionally been measured with gas source mass spectrometry (GS-MS), which requires a $\sim 1\text{--}2$ kg ice sample (e.g., Alexander et al., 2003; Jonsell et al., 2005). Based on work by Paris et al. (2013), I established a method to measure < 30 nmol of sulfur using multi-collector inductively coupled mass spectrometry (MC-ICP-MS). This technique requires only milliliters of sample, enabling up-to seasonal resolution of $\delta^{34}\text{S}_{\text{SO}_4}$ in ice cores. I used this technique to measure $\delta^{34}\text{S}_{\text{SO}_4}$ in multiple Antarctic ice cores to examine sulfate sources in West Antarctica and assess the potential of a new sea ice proxy. By focusing on West Antarctica, I greatly expanded the current literature and facilitated further comparisons with East Antarctica. Overall, my research increases our knowledge of sulfate sources in Antarctica and what they may reveal about other climate subsystems.

1.8.1 Thesis roadmap

Chapter 1—Introduction Chapter 1 provides a brief overview of ice sheet dynamics, sulfate sources in Antarctica, and the sea ice system. Existing proxies for sea ice extent are reviewed, and a new potential sea ice extent proxy is introduced.

Chapter 2—Developing an analytical method to measure $\delta^{34}\text{S}_{\text{SO}_4}$ in ice cores using multicollector inductively coupled mass spectrometry Chapter 2 introduces the analytical method used for all isotope measurements. This chapter describes the development process for both sample preparation via column chromatography, as well as the final $\delta^{34}\text{S}_{\text{SO}_4}$ measurement via MC-ICP-MS.

Chapter 3—Seasonality of sulfate sources in West Antarctica and a potential new sea ice proxy Chapter 3 includes the first seasonal record of $\delta^{34}\text{S}_{\text{SO}_4}$ in ice cores. Fluctuations in $\delta^{34}\text{S}_{\text{SO}_4}$ are initially explored in an attempt to reconstruction sea ice extent around the Antarctic Peninsula. Unexpected results lead to a re-examination of sulfate sources in West Antarctica as well as previously-established $\delta^{34}\text{S}_{\text{SO}_4}$ signatures of major sulfate sources.

Chapter 4—Spatial variability in sulfate sources in West Antarctica and implications for the past retreat of the Ronne Ice Shelf Chapter 4 examines $\delta^{34}\text{S}_{\text{SO}_4}$ records of two additional ice cores from West Antarctica. This data and the results from Chapter 3 are then integrated with previous sulfur isotope studies to present a spatial map of sulfate sources in West and East Antarctica. Both early and late Holocene samples are analyzed to

explore changes in the extent of the Ronne Ice Shelf $\sim 8,000$ years ago. Finally, $\delta^{34}\text{S}_{\text{SO}_4}$ measurements of several samples at each site are evaluated to identify volcanic eruptions that can be used to refine the ice core age scale.

Chapter 5—Changes in sulfate sources in West Antarctica from the Last Glacial Maximum to the Holocene Chapter 5 examines $\delta^{34}\text{S}_{\text{SO}_4}$ measurements from LGM and Holocene sections of the Skytrain Ice Rise ice core in West Antarctica. A large terrestrial dust source during the LGM is explored as a potential explanation for 3–5‰ lower $\delta^{34}\text{S}_{\text{SO}_4}$ values in glacial periods.

Chapter 6—Conclusion Chapter 6 concludes this thesis by summarizing the developments in our understanding of sulfate sources in Antarctica on a seasonal, spatial, and glacial/interglacial scale.

Chapter 2

Developing an analytical method to measure $\delta^{34}\text{S}_{\text{SO}_4}$ in ice cores using multicollector inductively coupled mass spectrometry

2.1 Introduction

A primary component of this research was to establish a new analytical method for the determination of sulfur isotope ratios in ice cores at the University of Cambridge. This technique could then be used to develop proxies for Antarctic sea ice extent. Column chromatography was used to separate sulfate (SO_4^{2-}) from ice samples, followed by isotope analysis via multicollector inductively coupled mass spectrometry (MC-ICP-MS) to measure the sulfur isotopic composition of sulfate ($\delta^{34}\text{S}_{\text{SO}_4}$). An MC-ICP-MS can measure < 30 nmol of sulfur compared to the ~ 1 μmol required for gas source mass spectrometry (GS-MS), a prevalent technique for sulfur isotope analysis (e.g., Alexander et al., 2003; Jonsell et al., 2005). Therefore, MC-ICP-MS is the ideal instrument to measure sulfur isotope ratios in dilute ice samples. Only two labs in the world conduct these ice measurements, St. Andrew's University and the Institut des Géosciences de l'Environnement, so it was valuable to establish this technique at the University of Cambridge.

2.2 Developing a column chromatography method to separate sulfate in ice cores

2.2.1 Introduction to column chromatography

Column chromatography is used to separate a liquid sample into its individual components, often to isolate a particular analyte. The column is packed with a polymer ion-exchange resin, and the sample is loaded onto the resin bed. A series of solutions, called eluents, are then run through the column, and different components of the sample are eluted at different times. The desired sample fraction is collected for analysis when it leaves the column. A diagram of a chromatography column is shown in Figure 2.1. For this research, I developed a column chromatography method to isolate sulfate in ice cores, with a goal sample size of 30 nmol. Details of column development, resin selection, and the elution method follow below.

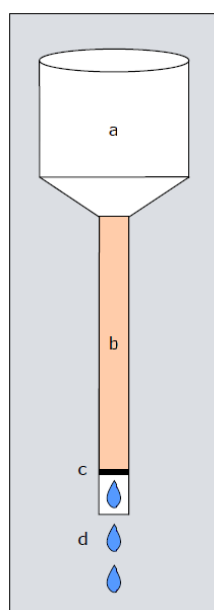


Fig. 2.1 Diagram of a chromatography column showing the column reservoir (a), resin column (b), frit (c), and eluate (d). The sample is loaded on top of the resin column, which is supported by a permeable frit. Eluent is introduced into the reservoir, and it carries the sample into the resin column. As the sample flows through the column, certain sample ions exchange with the resin, and others are eluted at the column base.

2.2.2 Column selection and set up

The first columns were made by hand from heat-shrink Teflon tubing. Two different sizes of tubing were used: one with an inner diameter (ID) of 3.2 mm after heating, and one with an ID of 1.6 mm after heating. The final columns were similar in shape but not perfectly straight due to slight variations in heat strength or rotation during the shrinking process. It was particularly difficult to achieve a smooth, even transition from the reservoir to the column. More importantly, these imperfections varied by column, which would cause inconsistencies across samples. To eliminate this potential error, I decided to use Savillex columns with a 2 mL reservoir and a 1.5 mm ID (Figure 2.2).

The small column ID caused frequent air bubbles that prevented flow during the elution process. To maintain flow and enable optimal separation, it was essential that there was no space between the top of the resin column and the reservoir. This issue supported the use of Savillex columns because small inconsistencies at the top of the handmade columns caused gaps between the resin and the reservoir and frequently led to air bubbles. The small column diameter also made it difficult to introduce eluent without disturbing the resin, which could blur the separation of different sample fractions. I discovered that gel-electrophoresis pipette tips minimized this issue by reducing the injection pressure. The columns were fit with polyethylene frits and stored in 10% HCl when not in use.

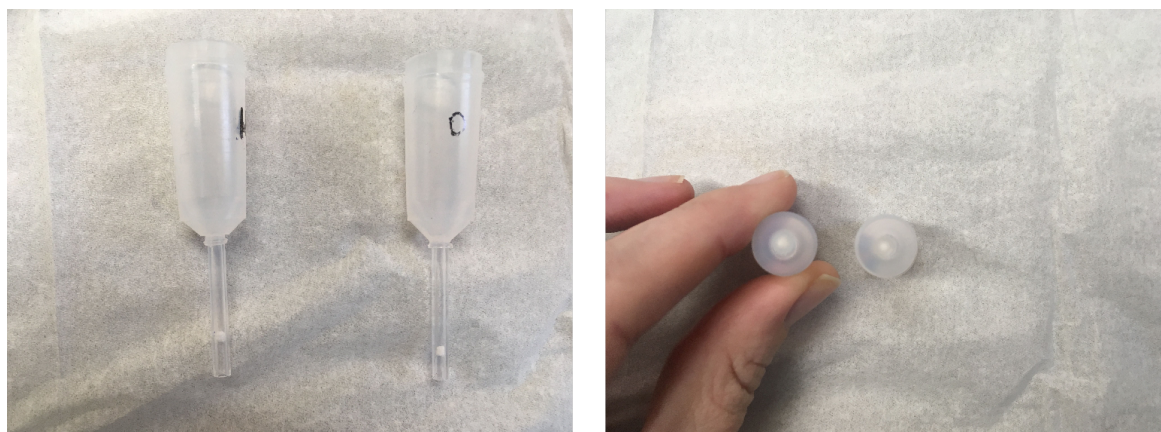


Fig. 2.2 *Left: Savillex columns with a 2 mL reservoir and a 1.5 mm ID. Right: Comparison of a 3.2 mm ID column and a 1.5 mm ID column.*

2.2.3 Introduction to ion-exchange resin

Ion-exchange resin is used to isolate specific ions in liquid samples such as ice cores. Functional groups are attached to the polymer resin and act as exchange sites for sample

Table 2.1 *Relative selectivities of counterions in anion and cation exchange resin*

Counterion	Relative Selectivity for AG 1-X8 Anion Resin	Counterion	Relative Selectivity for AG 50W-X8 Cation Resin
OH^-	1.0	H^+	1.0
HSO_4^-	85	Na^+	1.5
ClO_3^-	74	NH_4^+	1.95
NO_3^-	65	K^+	2.5
Br^-	50	Ag^+	7.6
HSO_3^-	27	Fe^{2+}	2.55
NO_2^-	24	Ni^{2+}	3.0
Cl^-	22	Ca^{2+}	3.9
HCO_3^-	6.0	Pb^{2+}	7.5
F^-	1.6	Ca^{2+}	8.7

ions. Each functional group holds a counterion that exchanges with a same-charged ion in the sample solution. For this exchange to take place, the sample ion must have a higher selectivity than the resin counterion, i.e., it must have a higher affinity for the functional group. If the ion has a lower selectivity, it will pass through the column without exchanging. The relative selectivities of major counterions are listed in Table 2.1.

Ion-exchange resin comes in anion or cation form; anion resin exchanges with anions, and cation resin exchanges with cations. Resin cannot be converted between these types. However, the counterion can be changed by rinsing the resin with 2–5 column volumes (CV) of a 1 M solution with a more selective ion. For example, AG 1-X8 anion resin (Bio-Rad) has chloride (Cl^-) counterions with a relative selectivity of 22. However, nitric acid can be used to convert the resin to nitrate (NO_3^-) form, which has a relative selectivity of 65. Resin can also be converted to a less selective form if it is rinsed with an excess of the new ion. Changing the ionic form of the resin increases or decreases the amount and type of ions that are retained in the column. This affects the overall separation method and can narrow the sample separation to the desired analyte.

2.2.4 Resin selection

I chose to use anion exchange resin AG 1-X8 to perform the sulfate separation rather than cation exchange resin. AG 1-X8 resin has quaternary ammonium functional groups, while the standard cation exchange resin, AG 50W-X8 (Bio-rad), has sulfonic acid groups. Therefore, anion resin was preferable to minimize the sulfur blank. Using anion exchange resin required

a two-step elution method: 1) a first eluent eluted cations and less-selective anions from the column while sulfate was retained on the resin, and 2) a second, more-selective eluent eluted sulfate from the column for collection and analysis. The development of the elution technique is discussed in the following section.

The resin was first batch cleaned as follows:

1. Rinsed five times with MilliQ water (MQ) to remove any small particles
2. Rinsed once with 8 M distilled (Δ) HNO_3
3. Rinsed five times with MQ
4. Rinsed once with 6 M ΔHCl
5. Rinsed five times with MQ

The clean resin was then made into a 50% v/v slurry with MQ for a known injection volume when packing the column.

To maximize the separation of sulfate from other anions, the resin was converted from chloride form to the more-selective nitrate form after it had been packed in the column. Therefore, non-sulfate anions that would have exchanged with the chloride resin were instead removed by the first eluent and not eluted with the sulfate fraction. To pack the resin, the columns were first rinsed with 20 CV of MQ to remove any remaining HCl. Another 20 CV of MQ were added, and 35 μL of resin were immediately injected into the reservoir to settle as the MQ ran through the column. Once packed, the resin was rinsed with 10 CV of 1 M ΔHNO_3 to replace all chloride counterions with nitrate. I determined the necessary volume of 1 M ΔHNO_3 by adding 1% AgNO_3 solution to the subsequent eluate, which formed a white precipitate if chloride was still present. This 10 CV volume was greater than the 2–5 CV dictated in the Bio-Rad manual, perhaps due to the small column size. However, the greater volume ensured a complete conversion. The resin was then rinsed with 20 CV of MQ to flush out all HNO_3 and return the column to a neutral state.

Anionic AG 1-X8 resin has an ion exchange capacity of 1.2 meq/mL. Assuming a 10% operating capacity, the effective ion exchange capacity is 0.12 meq/mL, so an ice sample with 30 nmol of sulfate would require less than 3 μL of resin (accounting for non-sulfate anions). A 3 μL resin volume was too small to build a viable column. Therefore, I chose a 35 μL resin volume (operating capacity of $\sim 1\%$) based on an established separation method at St. Andrew's University (A. Burke, personal communication, 2018).

2.2.5 Optimizing the elution technique for column separation of sulfate in ice samples

Once the column design and resin were established, I considered three primary variables when developing the elution method: sample volume and the first and second eluent. Each variable and its effects on the elution process are described below.

Sample Volume—A smaller sample volume produced a sharper elution peak because the sample remained in a narrow band at the top of the resin column before the eluent was introduced. This resulted in a clean separation with a well-defined sample peak. A larger sample volume began to flow through the resin before the eluent was introduced, which caused a broadening of the sample peak.

Eluent #1—The first eluent removed from the column any ions that did not exchange with the resin. This included both cations and anions that are less selective than nitrate, the resin counterion. For this method, the eluent had to be less selective than sulfate, or sulfate would not be retained on the resin and would be eluted prematurely.

Eluent #2—The counterion of the second eluent exchanged with the sulfate analyte that was retained on the resin after the first eluent. As previously described, the eluent counterion needs to have a higher selectivity than sulfate for this exchange to occur. However, a counterion with equal selectivity would also exchange with sulfate if supplied in excess. Therefore, the second eluent needed to have a sufficiently high selectivity and/or concentration to elute 100% of sulfate from the column. These factors also affected both the timing and sharpness of the sample peak.

Prior to each elution test, the same method was used to clean the column and pack/convert the ion exchange resin. The standard elution method then proceeded as follows:

1. Clean resin with 3 x 5 CV of Eluent #2 to remove any sulfate blank
2. Equilibrate resin with 5 x 5 CV of MQ to facilitate counterion exchange with sulfate
3. Load sample in desired volume
4. Elute cations and less selective anions with 3 x 5 CV of Eluent #1
5. Elute sulfate with 3 x 5 CV of Eluent #2

2.2.6 Testing method for different elution techniques

I tested different eluents and sample volumes using an iterative process of running columns, checking for the recovery and separation of sulfate, and altering the method as necessary.

Because of the small sample size, total recovery of sulfate was essential. It was also crucial to remove all cations from the sample to optimize sulfur isotope measurements (Paris et al., 2013). To check for sulfate separation and recovery, the six fractions from steps four and five were individually collected and dried at 80°C. They were then diluted with MQ and analyzed for anion and cation concentrations on a Thermo Scientific Dionex HPIC system with the assistance of Dr Harold Bradbury at the University of Cambridge. In early tests, four fractions were collected in step five to confirm that all sulfate had been eluted in the previous three fractions.

Two standards were tested during the method development process. First, sodium sulfate (Na_2SO_4) was used to assess column mechanics and separation properties of the resin. Second, a seawater standard from the International Association for Physical Sciences of the Ocean (IAPSO) was used to simulate ice core samples. The seawater standard was prepared in two ways: 1) It was diluted to a 85.7 ppm sulfate concentration, and 35 μL with 30 nmol of sulfate were loaded directly onto the column, and 2) it was diluted to an approximate ice concentration of 290 ppb sulfate, 10 mL were dried at 80°C, and the resulting 30 nmol of sulfate were rediluted in 35 μL of MQ and loaded onto the column. The first method tested strictly column performance, while the second method included sample preparation. Assuming no sulfate loss during the dry down process, the dry down method (DD) and the direct load method (DL) should perform equally. To test this hypothesis, I dried six 10 mL vials of the diluted seawater standard, rediluted them in MQ, and analyzed them on the Dionex HPIC. The average sulfate recovery was $100 \pm 3\%$, showing no sulfate loss. All uncertainties are reported as two standard deviations (2σ).

2.2.7 Results of elution method tests

Na_2SO_4 standard tests

Two of the Na_2SO_4 column tests were completed before a 30 nmol sulfate sample size had been chosen. The amount of sulfate necessary for isotope analysis was not yet known, so ~ 50 nmol of sulfate were used to ensure sufficient sample for replicate $\delta^{34}\text{S}_{\text{SO}_4}$ measurements. However, the exact amount of sulfate loaded onto the column was not quantified, and the sodium (Na^+) eluate concentrations were not measured due to instrument limitations. Therefore, these tests were a qualitative assessment of sulfate elution throughout the run. Test parameters and results are shown in Table 2.2. An elution method was deemed successful if sulfate recovery was $> 95\%$ in fractions 4–6.

In the initial Na_2SO_4 test, Eluent #1 was MQ because only cations needed to be eluted from the column, with no chance of less selective anions sticking to the resin. Eluent #2 was nitric acid because nitrate has the highest relative selectivity of possible eluents.

Table 2.2 *Na₂SO₄ elution test parameters and sulfate recovery¹*

Test	SO ₄ ²⁻ (nmol)	Sample (μL)	Eluent #1	Eluent #2	Fractions 1–3	Fractions 4–6	Fraction 7
1	~50	70	MQ	3% HNO ₃	3.0 ± 4.1	95.6 ± 5.0	1.4 ± 1.2
2	~50	70	0.25% HNO ₃	5% HNO ₃	1.6 ± 0.3	98.3 ± 0.4	0.1 ± 0.2

¹ Recovery is reported as percent of the total amount of eluted sulfate

However, nitrate still has a lower selectivity than sulfate, so the eluent had to have a sufficient concentration to recover all sulfate from the column. The sample volume was 2 CV, based on personal communications with Dr Paris Gautier (2018). Each Na₂SO₄ test was repeated five times.

The results of the first Na₂SO₄ test showed that sulfate was eluted both early (fractions 1–3) and late (fraction 7) (Figure 2.3). There were two possible reasons why sulfate eluted early: overloading the column or a column equilibration error. A column is overloaded when an excess of sample ions cannot exchange with the resin. This was extremely unlikely because of the large resin excess. Instead, sulfate was probably eluted early because the resin was accidentally not equilibrated after it was cleaned. As a result, the sample was loaded onto an acidic medium that inhibited sulfate's ability to bind to the resin. Sulfate was eluted late because 3% HNO₃ was too dilute to efficiently remove sulfate from the resin, as evident by the shallow slope of the right side of the elution peak.

Based on the results of the first Na₂SO₄ test, I increased the concentration of Eluent #2 from 3% to 5% HNO₃ and equilibrated the column with MQ prior to loading the sample. The new elution profile showed the expected changes: sulfate no longer eluted late, and the amount of sulfate eluted early decreased by half (Figure 2.3). Most importantly, sulfate recovery in fractions 4–6 was more consistent and increased from 95.5 ± 5.0% to 98.3 ± 0.4%. Sulfate recovery may have improved even further, except Eluent #1 was also changed from MQ to 0.25% HNO₃. In hindsight, my reason for this change is unclear; however, it may have increased early elution of sulfate. I returned Eluent #1 to MQ for future elution tests.

IAPSO seawater standard tests

I next conducted two sets of seawater elution tests. The first group of elution tests used the second Na₂SO₄ elution method described above, with MQ as Eluent #1 and 5% HNO₃ as Eluent #2. The ion concentrations of the 85.7 ppm and 290 ppb seawater dilutions were verified with a Dionex HPIC for a quantitative assessment of sulfate separation and recovery. Nine elution tests were completed with the DD method, and six tests were completed

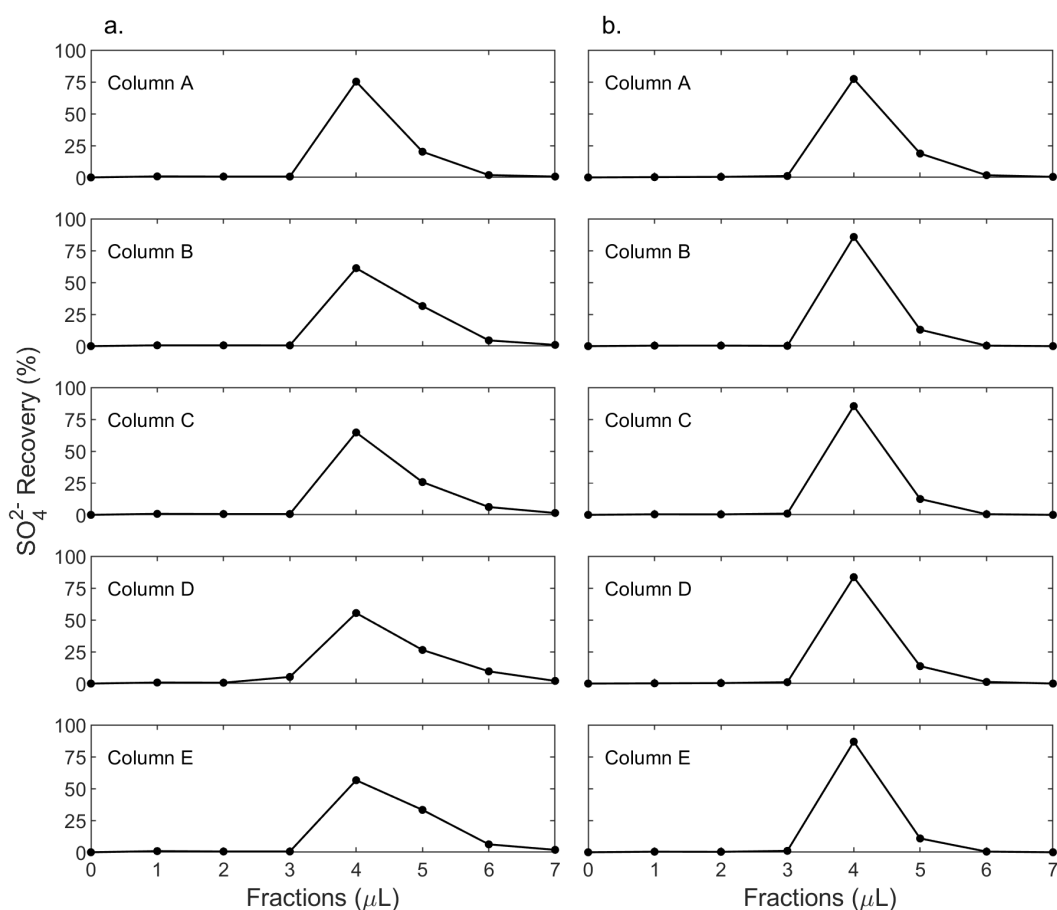


Fig. 2.3 Elution profiles for the first (a) and second (b) Na_2SO_4 elution tests with five Savillex columns. The first test used MQ and 3% HNO_3 as Eluent #1 and Eluent #2, respectively. The second test used 0.25% HNO_3 and 5% HNO_3 as Eluent #1 and Eluent #2, respectively. Sulfate is reported as the percent of total eluted sulfate. In the first test, sulfate eluted early in fractions 1–3, gradually through fractions 4–6, and it tailed into fraction 7. In the second test, the amount of sulfate eluted in fractions 1–3 decreased by half, and no sulfate was eluted in fraction 7. The sharper elution peak in the second test is a result of the increased concentration of the second eluent.

Table 2.3 *Seawater standard elution test parameters and sulfate recovery¹*

Test	SO_4^{2-} (nmol)	Sample (μL)	Eluent #1	Eluent #2	Fractions 1–3	Fractions 4–6
1	30	35	MQ	5% HNO_3	0.4 ± 1.1	96.6 ± 8.1
2	30	35	MQ	1 M HNO_3	-	99.4 ± 4.4

¹ Recovery is reported as percent of the total sulfate loaded into the column

with the DL method. Tests were performed using three different columns. There was no significant difference in sulfate recovery between DD and DL samples, which agreed with the evaporation tests described earlier. As such, DD and DL results are consolidated in future discussions of the first seawater tests and under Test 1 in Table 2.3 for a total of 15 replicate column runs.

In the first elution tests, $0.4 \pm 1.1\%$ of sulfate was eluted in fractions 1–3, and $96.6 \pm 8.1\%$ of sulfate was eluted in fractions 4–6. The decrease in early elution supported my hypothesis from the second Na_2SO_4 test that the 0.25% HNO_3 eluent had eluted some sulfate from the column. In the first three of the fifteen column runs included in Test 1, $0.0 \pm 0.0\%$ of sulfate was eluted in fraction 7, so the additional fraction was no longer collected. Because of the clean separation of sulfate from cations (Figure 2.4), fractions 1–6 were no longer collected individually. Instead, fractions 1–3 were combined for the first elution, and fractions 4–6 were combined for the second elution. Interestingly, only $0.2 \pm 0.6\%$ of chloride was collected across all fractions, suggesting that it evaporated as HCl when the samples were dried down. This benefited sulfur isotope analysis because it minimized potential matrix effects, discussed later in this chapter.

The average recovery of the first seawater tests was lower and less consistent than desired. Therefore, I increased the concentration of Eluent #2 from 5% to 1 M HNO_3 for a second iteration of seawater tests. The new average sulfate recovery was $99.4 \pm 4.5\%$, so I permanently changed the second eluent to 1 M HNO_3 (Table 2.3). Blank measurements for this method were below the detection limit at < 0.1 nmol sulfate ($n = 12$), which was similar to the 0.1–0.3 nmol reported by Paris et al. (2013). They had used cation resin with sulfonic acid functional groups, which could have attributed to their slightly higher blank measurement.

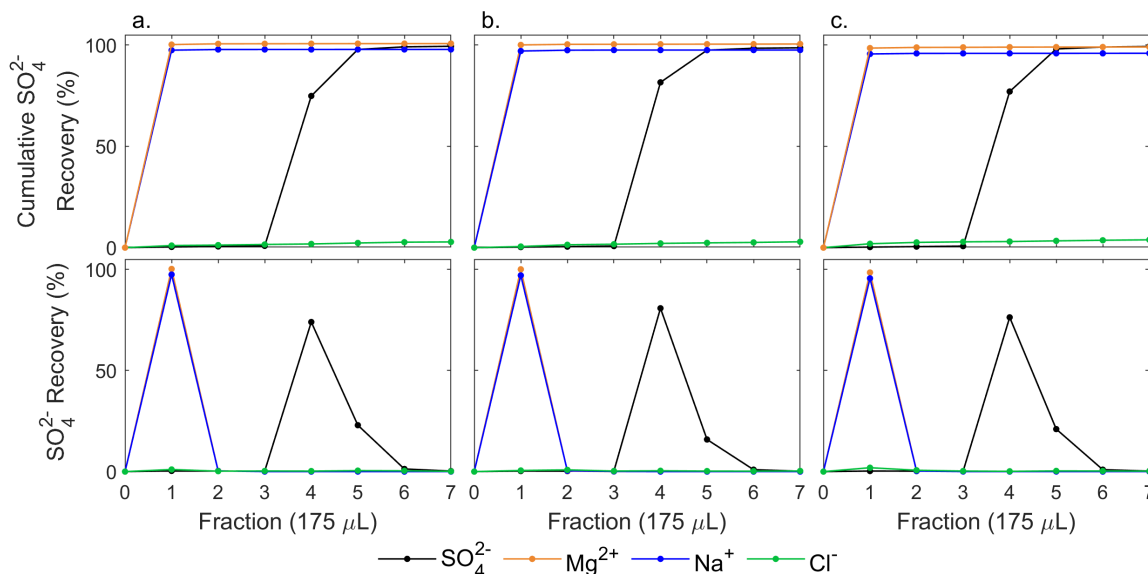


Fig. 2.4 Elution profiles for three columns in the first IAPSO seawater standard test. The top panels show cumulative sulfate recovery, and the bottom panels show sulfate recovery in each fraction. Total sulfate recovery in all columns was $\sim 99\%$, and there was a clean separation of sulfate from all cations. Sulfate was completely eluted in fractions 4–6, so fraction 7 was not collected in future column tests. An average $3.2 \pm 1.2\%$ of chloride was recovered in each run likely due to HCl evaporation during the drying stage. This chloride recovery was higher than the average value of $0.2 \pm 0.6\%$ in other column runs. These higher recoveries did not appear in other tests.

2.2.8 Final column chromatography method

The final elution method showed almost 100% sulfate recovery and the complete separation of sulfate from other ions. Therefore, the final prepared sample was ideal for isotope analysis, which depended on precise sulfate concentrations and ion ratios. The final column method is as follows:

1. **Clean columns**—Rinse with 20 CV MQ
2. **Pack resin**—Fill column with 20 CV MQ and inject 35 μL resin to settle
3. **Convert resin to nitrate form**—Rinse with 10 CV 1 M ΔHNO_3 then 20 CV MQ
4. **Clean resin**—Rinse with 3 x 3 CV 1 M ΔHNO_3
5. **Equilibrate resin**—Rinse with 5 x 5 CV MQ
6. **Load sample**—35 μL sample volume
7. **Elute cations and less selective anions**—Rinse with 3 x 5 CV MQ
8. **Elute sulfate for analysis**—Elute with 3 x 5 CV 1 M ΔHNO_3

2.3 Developing an MC-ICP-MS method to analyze $\delta^{34}\text{S}_{\text{SO}_4}$ in ice cores

2.3.1 Introduction to mass spectrometry

A mass spectrometer separates isotopes by their mass/charge (m/z) ratios. Individual isotope beams are then measured to calculate the desired isotope ratio in an element, as described in Chapter 1. The certified reference standards used in isotope calculations can be rare, expensive, or difficult to prepare for the desired analysis. Therefore, isotope measurements are often made with a secondary standard and then converted to the desired reference scale. For example, sulfur is divided into four isotope beams, ^{32}S , ^{33}S , ^{34}S , and ^{36}S . The mass 32 and 34 beams can be measured individually to determine the $^{34}\text{S}/^{32}\text{S}$ ratio of a sample and then calculate its $\delta^{34}\text{S}$ value. Sulfur isotope compositions are reported on the VCDT scale. In this research, however, measurements were made with a Na_2SO_4 secondary standard with a known $\delta^{34}\text{S}_{\text{VCDT}}$ value and then converted to the VCDT scale. This conversion is discussed later in this chapter.

There are several types of mass spectrometers that use different techniques to separate an element into its individual isotopes. For example, a quadrupole mass spectrometer creates an oscillating electric field through which only specific m/z ratios can pass to reach the detector. For my research, I used a time-of-flight (TOF) mass spectrometer to measure $\delta^{34}\text{S}_{\text{SO}_4}$ of ice core samples (Figure 2.5). In a TOF mass spectrometer, the ionized sample passes through an electromagnetic field that bends the different components of the ion beam based on their m/z ratios. Isotopes with low m/z ratios bend more than those with high m/z ratios, and the designated isotope beams are then collected to calculate the isotope signature of the sample.

Mass spectrometers are components of multiple instruments, such as gas source mass spectrometers and multicollector inductively coupled mass spectrometers. Different instruments are specialized for different types of samples and have different analytical capabilities. Sulfur isotopes have traditionally been measured by GS-MS, which converts the sample to SO_2 or SF_6 gas for analysis. A more novel analytical technique to measure sulfur isotopes is MC-ICP-MS, which directly measures sulfate aerosol. In the following sections, I compare GS-MS versus MC-ICP-MS analysis and detail why MC-ICP-MS is the optimal instrument for my research.

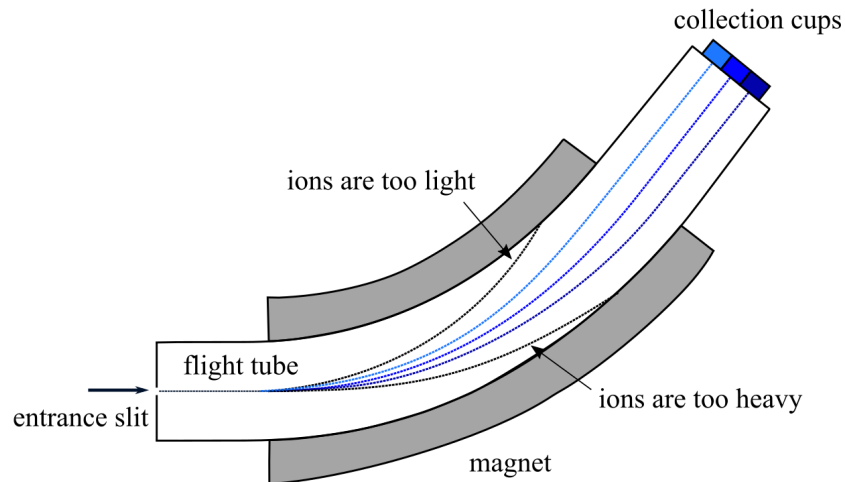


Fig. 2.5 Diagram of a time-of-flight mass spectrometer. The ionized sample enters the magnet through the entrance slit, and the magnetic field acts as a mass filter. The magnet deflects light masses more than heavy masses, so the sample beam is split into its individual isotope components. If an isotope is too light or too heavy, it collides with the flight tube and does not exit the magnet. Cups are positioned to collect and measure the desired isotopes to determine sample isotope ratios.

2.3.2 Gas source mass spectrometry vs Multicollector inductively coupled mass spectrometry: Sample preparation and introduction

For both GS-MS and MC-ICP-MS analysis, the sample must be in the required phase, ionized, and accelerated and focused into an ion beam before entering the mass spectrometer. However, GS-MS and MC-ICP-MS use different methods to accomplish each step, as described below:

Step 1: Achieving the required sample phase

GS-MS requires the sample to be in gas form, which can be accomplished by several methods. The sample can be precipitated as BaSO_4 and then combusted to SO_2 (Thode et al., 1961), or it can be converted to SF_6 using a fluorination vacuum line (e.g., Gautier et al., 2018; Ono et al., 2006). The gas analytes are then purified on a gas chromatography column before ionization. However, there are potential issues with each preparation method. The SO_2 technique requires a relatively large sample of $\sim 1\mu\text{mol}$ sulfur, only 90% of which is successfully combusted (Thode et al., 1961). Furthermore, isotope ratios must be corrected for oxygen interferences, which limits the accuracy and precision of the measurements (Fry et al., 2002), although interferences can be minimized by keeping the GS-MS under a constant flow of helium to eliminate atmosphere in the combustion chamber (Ono et al.,

2006). The SF_6 technique avoids these interferences; however, fluorination vacuum lines are difficult to construct and not available in most labs.

For MC-ICP-MS analysis, the sample is introduced as an aerosol. The sample is first dissolved in a solvent (usually a weak acid), then nebulized and carried into the instrument with a carrier gas.

Step 2: Sample ionization

GS-MS and MC-ICP-MS use different ion sources: electron ionization (EI) and an ICP torch, respectively. In electron ionization, the vaporized sample is bombarded with high-energy electrons to form ions. The electrons are produced from a heated wire filament and captured by a positively-charged trap on the other side of the collision chamber. The ionized sample is then propelled into the mass spectrometer by a positively-charged repeller plate (Figure 2.6).

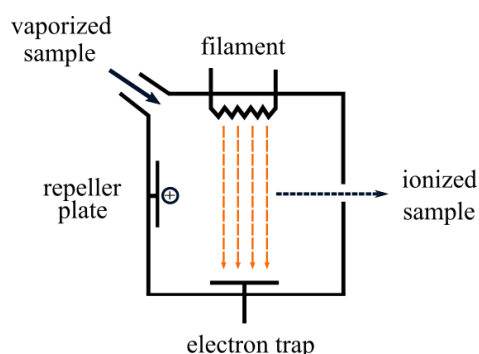


Fig. 2.6 *Diagram of an electron ionization collision cell. The gas sample enters the cell and is bombarded by high-energy electrons that are generated from a heated filament. The positively-charged sample ions are then repelled by a charged plate that forces them out of the collision cell and further into the mass spectrometer.*

An MC-ICP-MS ionizes the sample using inductively coupled plasma that comprises argon gas ions with a high electron density (Figure 2.7). The plasma is generated by running an electric current through an induction coil to produce a magnetic field. This rapidly oscillating magnetic field ionizes argon gas in the torch, which rapidly increases the electron density and raises the temperature to 6,000–10,000 K. The high electron density then ionizes the sample when it enters the torch. Inductively coupled plasma has a greater ionization efficiency (IE) than electron ionization, meaning it produces more ions per unit sample. Therefore, MC-ICP-MS is preferable to measure sulfur isotopes in dilute ice core samples, where the average background sulfate concentration is 20–100 ppb (Dai et al., 1995; Dixon et al., 2005; Li et al., 2014; Patris et al., 2000; Pruett et al., 2004).

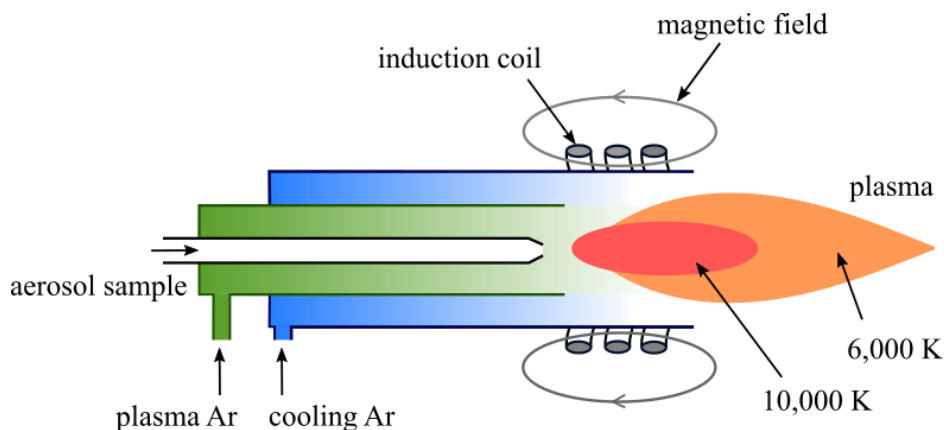


Fig. 2.7 *Diagram of an inductively coupled plasma torch. Plasma is generated by running an electric current through an induction coil to generate an oscillating magnetic field. This field ionizes the argon gas flowing into the torch and rapidly increases the electron density. The aerosol sample is carried into the torch with argon gas, where it is ionized before continuing into the accelerating and focusing sector of the mass spectrometer.*

Step 3: Accelerating and focusing the sample beam

GS-MS and MC-ICP-MS use similar techniques to accelerate and focus sample ions. After leaving the ion source, ions are accelerated using a voltage potential difference across a series of charged plates (Figure 2.8). Simultaneously, the ion beam passes through several slits and is shaped and focused by a series of lenses. The beam then goes through the entrance slit, which determines the instrument resolution. In GS-MS analysis, the ionized sample goes from the EI collision cell directly through the accelerating and focusing plates. In MC-ICP-MS, however, the sample first passes through a sample and skimmer cone that maintain a high vacuum within the mass spectrometer and further focus the sample ions.

In GS-MS, the sample then continues into the mass spectrometer. However, ions from an ICP source have a wider distribution of kinetic energy (KE) that can lead to mass bias, so an energy filter is used to minimize the spread in KE across ions. Therefore, when the ion beam enters the mass spectrometer, isotopes are separated solely by their relative masses.

2.3.3 Instrument resolution and isobaric interferences

Both GS-MS and MC-ICP-MS can collect and measure multiple isotopes simultaneously to minimize the effects of any instability in the instrument between measurements. Isotope ratios are determined by scanning across the desired mass range to produce a flat-topped signal peak and then taking the measurement at a stipulated mass, frequently the center of the peak. The designated mass must not overlap with other peaks of the same or a similar mass. Such overlap is called an isobaric interference, and it falsely increases the isotope signal.

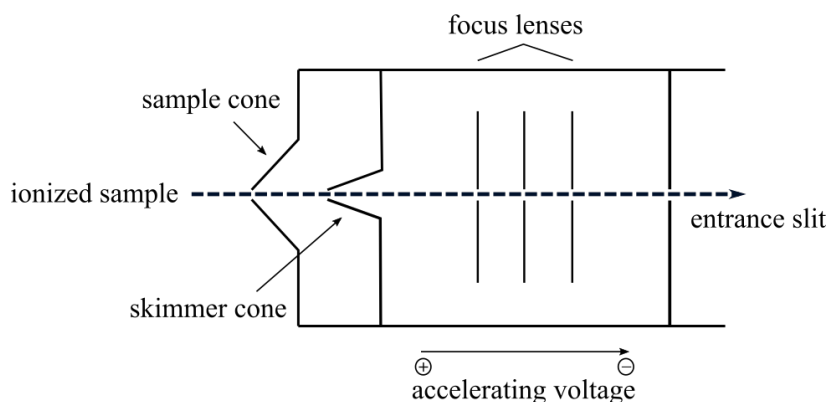


Fig. 2.8 Diagram of the accelerating and focusing sector of an MC-ICP-MS. The sample flows from the torch through a sample and skimmer cone that focus the sample beam and maintain a high vacuum in the instrument. The sample is then accelerated through a voltage potential and focused by a series of lenses before passing through the entrance slit and into the mass spectrometer. A GS-MS uses a similar technique, but the sample enters directly from the electron ionization source without passing through a sample or skimmer cone.

Isobaric interferences can arise from isotopes of a different element or from molecules with a similar mass. For example, major isobaric interferences affect MC-ICP-MS sulfur isotope measurements because the solvent forms hydrides in the torch.

Because of the small mass difference between isotopes and potential interferences, a successful measurement requires sharp, well-defined peaks that can be distinguished from other signals. The ability to distinguish between signal peaks is called the instrument mass resolution and is defined as follows:

$$M = \frac{M}{\Delta M} \quad (2.1)$$

where M is the measurement mass, and ΔM is the difference between the mass at 95% and 5% of the signal at mass M . The resolving power of MC-ICP-MS is greater than that of GS-MS, and MC-ICP-MS measurements can have a resolution of 8,000–10,000. This high resolution increases the ability to separate isobaric interferences in MC-ICP-MS measurements. However, they are still too great to complete sulfur isotope analysis and must be addressed.

Isobaric interferences in MC-ICP-MS analysis affect all masses of sulfur and, therefore, impact all sulfur isotope measurements (Paris et al., 2013). These interferences are caused by isotopologues of O_2 and other molecular hybrids found in or formed by the solvent used to

Table 2.4 *Isobaric interferences on ^{32}S , ^{33}S , and ^{34}S*

Isotope	Interference	ΔM^1 (mDa)	$m/\Delta M^2$
^{32}S	$^{16}\text{O}^{16}\text{O}$	17.8	1801
^{33}S	$^{32}\text{S}^1\text{H}$	8.4	3908
	$^{16}\text{O}^{16}\text{O}^1\text{H}$	26.2	1260
^{34}S	$^{18}\text{O}^{16}\text{O}$	26.2	1297

¹ ΔM refers to the mass difference between the interference and the isotope of interest. It is not the value used to calculate instrument resolution.

² $m/\Delta M$ is the resolution necessary to identify the interference peak.

dissolve the sample. Isotopologues are molecules of the same composition but with different masses. The largest interferences on sulfur measurements are $^{16}\text{O}^{16}\text{O}$ and $^{16}\text{O}^{18}\text{O}$, which impact ^{32}S and ^{34}S , respectively. Interferences on ^{33}S arise from sulfur and oxygen hydrides. However, isobaric interferences in sulfur MC-ICP-MS measurements can be minimized by desolvating the sample prior to analysis (e.g., Clough et al., 2006; Paris et al., 2013; Yu et al., 2017). Accurate isotope measurements can then be taken on a small interference-free plateau on the left side of the sample peak, making MC-ICP-MS a viable technique to measure sulfur isotopes in ice cores. The origin, mass, and resolution of each isobaric interference are shown in Table 2.4.

2.3.4 Previous work in MC-ICP-MS sulfur isotope analysis

Past research has used MC-ICP-MS to measure sulfur isotope ratios in multiple mediums, including marine sediment pore water (Yu et al., 2017), uranium ore (Han et al., 2013), and human serum (Albalat et al., 2016). Paris et al. (2013) measured the sulfur isotopic composition of seawater and detailed the effects of isobaric interferences on their analysis. These effects were clear when they observed that the ^{32}S signal of 20 μM Na_2SO_4 was < 1 V compared to the > 100 V interference signal (Figure 2.9). They concluded that the sample must be desolvated prior to isotope analysis. After desolvation, however, it was necessary to add sodium to the sample as a counteraction to optimize ionization efficiency. Other cations have since been used successfully, including calcium (Clough et al., 2006) and ammonium (Albalat et al., 2016).

Paris et al. (2013) was my primary reference while establishing an MC-ICP-MS method for sulfur isotope analysis at the University of Cambridge. I needed to consider multiple variables during method development, primarily sample preparation and introduction to the mass spectrometer. I also needed to establish the final measurement technique, such as how to designate the measurement mass.

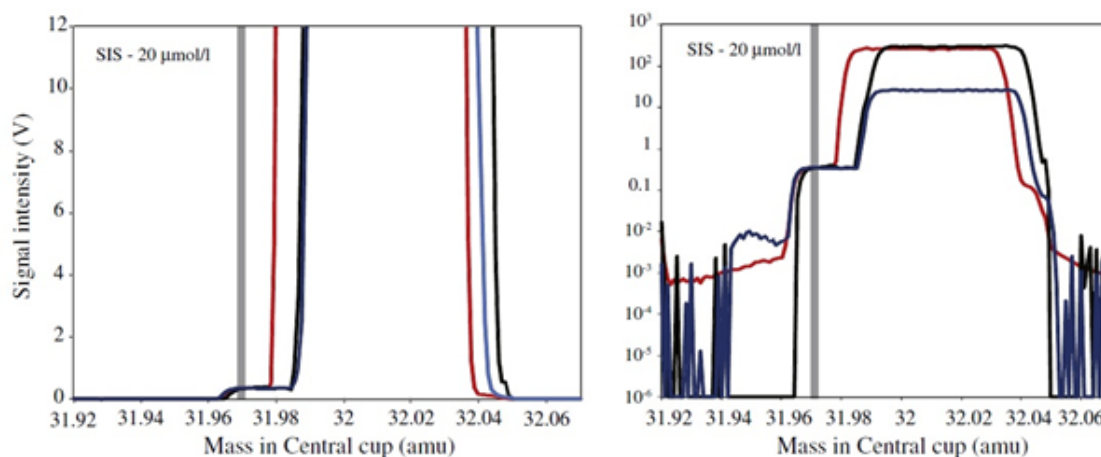


Fig. 2.9 Signal peaks of ^{32}S (red), ^{33}S (black), and ^{34}S (blue) for $20\ \mu\text{M}\ \text{Na}_2\text{SO}_4$ with a standard introduction system in linear (left) and logarithmic (right) scale. Interferences on ^{32}S are $\sim 200\times$ larger than the $< 1\ \text{V}\ ^{32}\text{S}$ signal, which is too little for accurate measurements. To avoid interferences, isotope measurements are taken on the small interference-free plateau on the left side of the peak (grey bar). Figure taken from Paris et al. (2013)

2.3.5 Choosing a desolvating introduction system: Aridus vs Apex

My first step in MC-ICP-MS method development was to choose a desolvating introduction system. By preventing excess solvent from entering the mass spectrometer, the optimal introduction system would minimize isobaric interferences (Han et al., 2013; Paris et al., 2013; Prohaska et al., 1999). However, the majority of desolvating introduction systems use a desolvating membrane, which reduces ion yield and causes an almost complete loss of the sulfur signal. The reason for this loss is unknown, but it is well documented throughout the literature (Burke et al., 2019; Han et al., 2013; Paris et al., 2013). The sulfur signal can be recovered by spiking the sample with a counteranion, e.g., sodium, but this step introduces other issues such as matrix effects, which are discussed later in this chapter (Albalat et al., 2016; Han et al., 2013). Therefore, a desolvating introduction system without a desolvating membrane would be ideal for sulfur isotope analysis.

With this in mind, I considered two introduction systems for my research, the Aridus (Figure 2.10) and the Apex (Figure 2.11). The Aridus uses a desolvating membrane (Figure 2.12), but the Apex can operate with or without one. The Apex first uses a Peltier-cooled condenser to desolvate the sample, and an optional desolvating membrane can be added if necessary. The first Apex configuration would be ideal to prevent signal loss, but it was uncertain that a Peltier-cooled condenser would adequately reduce isobaric interferences.

There was also the question of membrane type. The Aridus uses a heated PTFE membrane, and the Apex uses a cooled nafion, or ACM, membrane. Research has shown that a PTFE membrane causes signal loss (e.g., Paris et al., 2013); however, the effect of an ACM membrane on sulfur isotope analysis has not been reported.

To choose the best introduction system for sulfur isotope analysis, I needed to address the following questions:

1. What is the efficiency of a Peltier-cooled condenser relative to a desolvating membrane?
2. Do both PTFE and ACM membranes cause signal loss? Is there any difference in desolvating efficiency?
3. If it is necessary to spike samples with a counteraction to recover the sulfur signal, how does each introduction system respond, and is there any impact on the final isotope measurement?

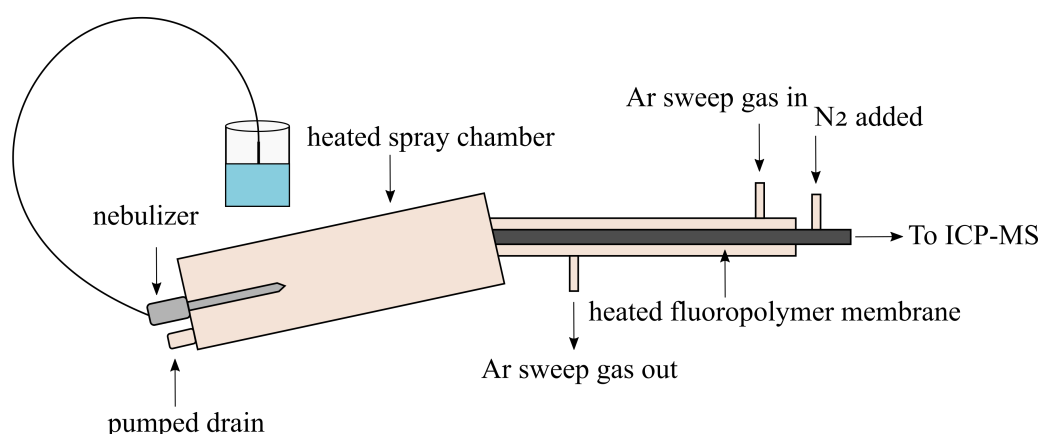


Fig. 2.10 Diagram of the Aridus desolvating introduction system. The sample is aspirated through a nebulizer and enters a heated spray chamber to create a sample aerosol-vapor mixture. Argon gas then carries the sample through a heated PTFE desolvating membrane towards the MC-ICP-MS. The volatile solvent evaporates through the permeable membrane and is removed from the system by counter-flowing argon sweep gas, which can also pass through the porous membrane. Nitrogen gas is added to further increase sensitivity by improving ionization in the plasma and reducing polyatomic interferences from the argon carrier gas. The dry sample then enters the MC-ICP-MS for sulfur isotope analysis.

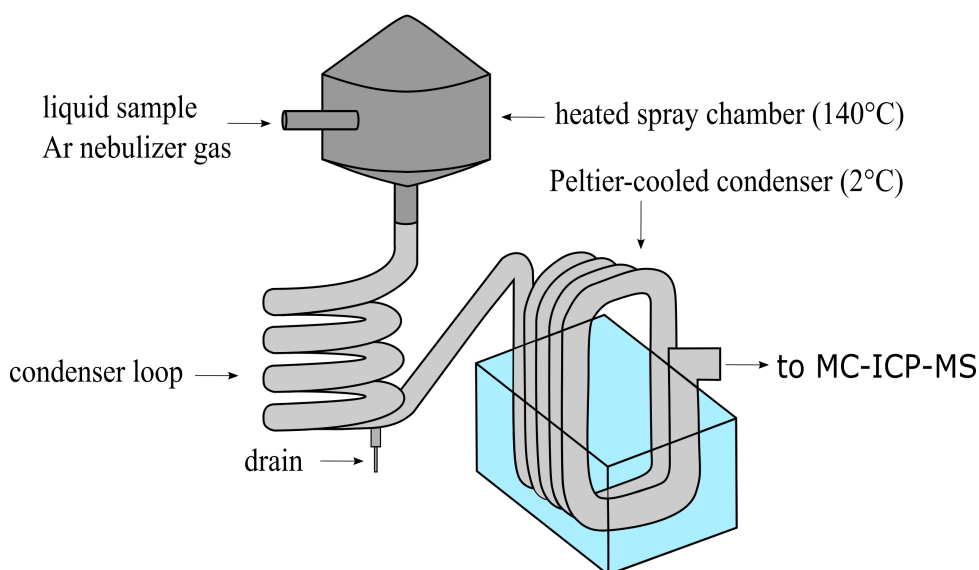


Fig. 2.11 Diagram of the Apex desolvating introduction system. The sample is aspirated through a nebulizer and enters a heated cyclonic spray chamber. Argon gas then carries the sample aerosol-vapor mixture through a condenser loop and a 2°C Peltier-cooled condenser, where most evaporated solvent is removed from the system. Nitrogen gas is then added to further increase sensitivity before the dry sample aerosol continues to the MC-ICP-MS. An ACM membrane can be added after the Peltier-cooled condenser to further desolvate the sample. As the sample flows through the membrane, remaining evaporated solvent condenses, passes through the permeable membrane, and is removed from the system with counter-flowing argon sweep gas. Unlike a PTFE membrane, the sweep gas cannot pass through the ACM membrane. This reduces potential argon interferences and stabilizes the sulfur signal.

2.3.6 Comparing Apex functionality with and without a desolvating membrane

My first test compared the Apex's desolvating efficiency both with and without the ACM membrane (designated configuration one and two, respectively). A 30 μM $(\text{NH}_4)_2\text{SO}_4$ ICP standard was used for all tests in case a counteraction was necessary to retain the sulfur signal. Initial measurements used standard skimmer and sample cones. However, Jet X cones increased the sulfur signal ~ 5 -fold and, thus, were used for all future analyses (Figure 2.13).

The first Apex configuration reduced isobaric interferences, but they were still significantly larger than the ~ 6 V ^{32}S signal. The second Apex configuration increased the ^{32}S signal to ~ 8.5 V and decreased isobaric interferences to $\sim 3\%$ of the signal (Figure 2.14). These results confirmed that a desolvating membrane was necessary to minimize isobaric

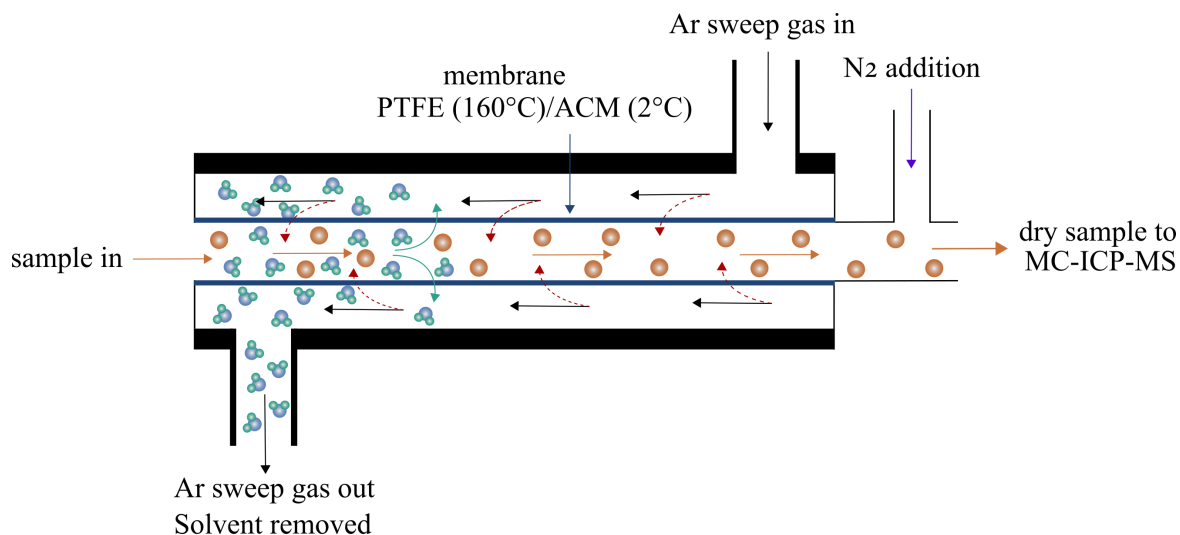


Fig. 2.12 Diagram of a PTFE and nafion/ACM desolvating membrane. Both membranes have argon sweep gas (black) flowing counter to the sample (orange) to remove excess solvent (green). In the Aridus system, the argon sweep gas can also pass through the porous membrane (red). Nitrogen gas (purple) is added to increase sensitivity.

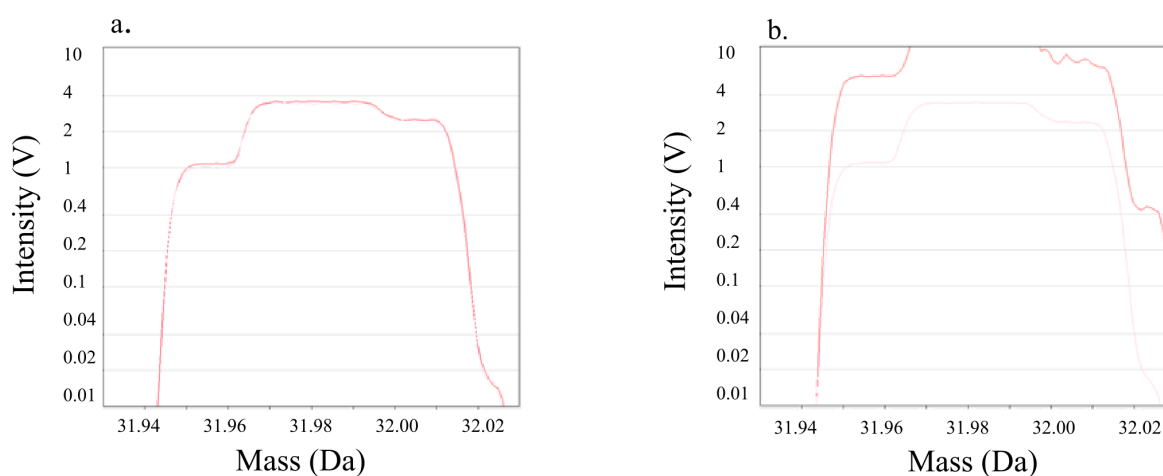


Fig. 2.13 Mass scans of ^{32}S of a $30\ \mu\text{M}$ $(\text{NH}_4)_2\text{SO}_4$ standard. The standard was introduced to the MC-ICP-MS using the first Apex configuration, and measurements were made with standard (a) and Jet X (b) skimmer and sample cones. Jet X cones increased the ^{32}S signal ~ 5 -fold.

interferences and optimize the intensity of the sulfur signal for MC-ICP-MS analysis. Thus, I eliminated the first Apex configuration as a potential introduction system. I originally planned to test the first Apex configuration with dilute sulfuric acid (H_2SO_4) to determine if a counteraction was necessary when a desolvating membrane was not used. However, because a membrane proved necessary to adequately reduce isobaric interferences, this step was not taken. For the remaining discussion, Apex will always refer to the second configuration.

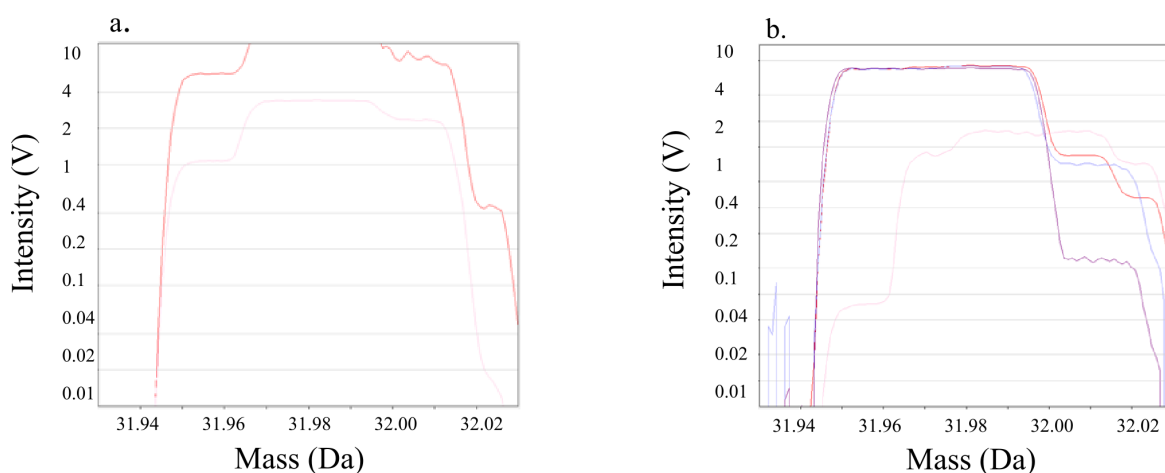


Fig. 2.14 Mass scan of ^{32}S of a $30\ \mu\text{M}$ $(\text{NH}_4)_2\text{SO}_4$ standard introduced to the MC-ICP-MS using the first (a) and second (b) Apex configuration. The addition of the ACM membrane in configuration two significantly reduced isobaric interferences from the solvent, showing that a desolvating membrane was necessary to optimize sulfur isotope measurements. Plot (b) also shows measurements for ^{33}S (blue) and ^{34}S (purple), but they were not considered in this evaluation.

2.3.7 Desolvating membrane comparison: PTFE vs ACM

To compare PTFE and ACM membranes, I measured the ^{32}S signal of $10\ \mu\text{M}$ and $20\ \mu\text{M}$ H_2SO_4 on the MC-ICP-MS using both the Aridus and Apex introduction systems (Figure 2.15). The signal was $< 0.6\ \text{V}$ for both systems at both concentrations, showing an almost complete signal loss regardless of membrane type. These results confirmed that a counteraction was necessary to prevent signal loss in MC-ICP-MS sulfur isotope analysis regardless of the introduction system.

I then compared the relative sensitivities of the Apex and the Aridus by measuring the ^{32}S signal of a $30\ \mu\text{M}$ $(\text{NH}_4)_2\text{SO}_4$ standard (Figure 2.16). The Aridus showed slightly higher sensitivity, but these measurements were done on different days, so the difference could be explained by instrument drift or changes in tuning. However, there was a significant difference in isobaric interferences between the two systems. Interferences in Aridus measurements

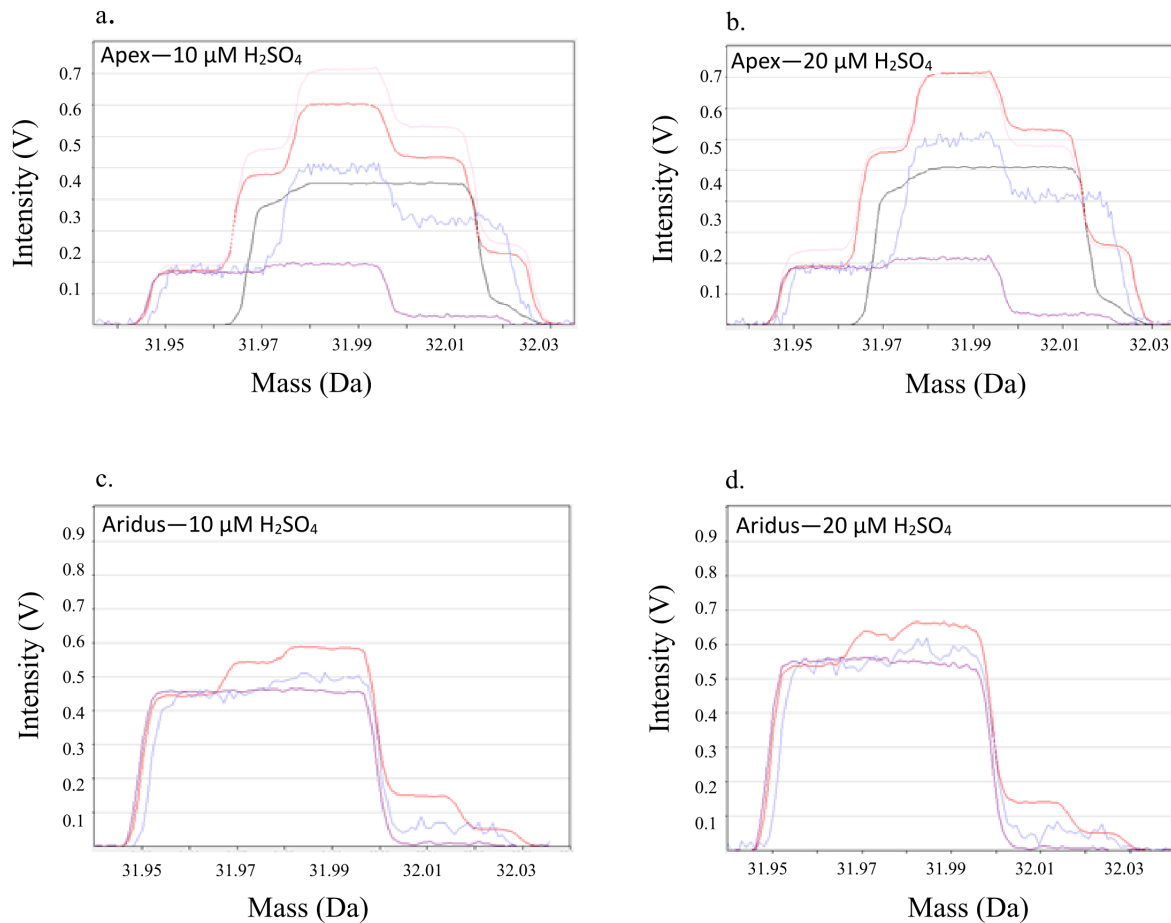


Fig. 2.15 Mass scans of ^{32}S (red), ^{33}S (blue), and ^{34}S (purple) of 10 μM and 20 μM H_2SO_4 measured with an Apex (a, b) or Aridus (c, d) sample introduction system. The phosphorous signal (black) is also shown in the Apex plots but can be disregarded for this study. All plots show an almost complete loss of the sulfur signal during MC-ICP-MS analysis regardless of the H_2SO_4 concentration. The Aridus and Apex measurements were completed on different days, likely explaining the different signal intensities of the two systems. All plots show the expected isobaric interferences on each sulfur mass and the interference-free plateau on the left shoulder of each peak.

were an order of magnitude lower than those in Apex measurements, showing greater desolvation of the sample. Therefore, the Aridus appeared the preferable desolvating system for sulfur measurements on an MC-ICP-MS.

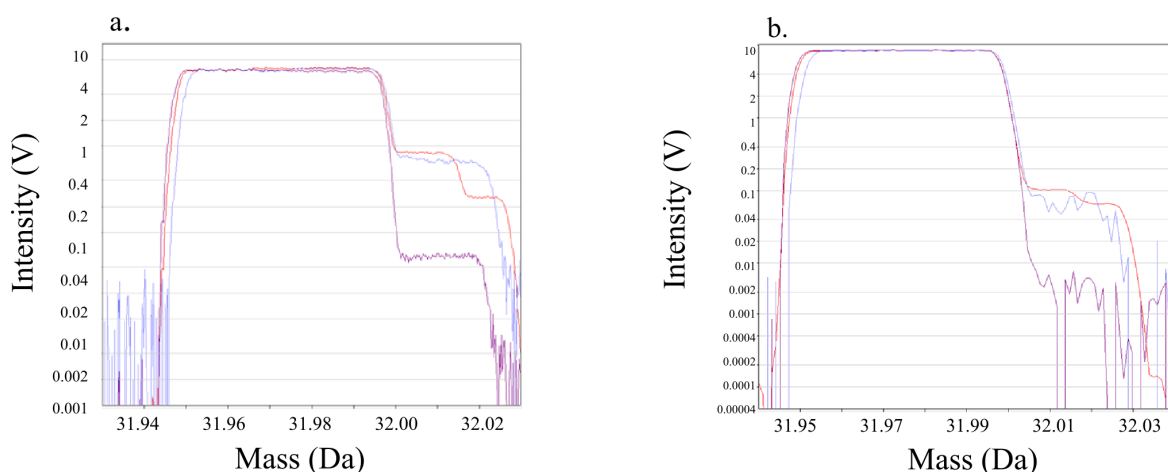


Fig. 2.16 Mass scans of ^{32}S (red), ^{33}S (blue), and ^{34}S (purple) of a $30\ \mu\text{M}$ $(\text{NH}_4)_2\text{SO}_4$ standard measured using the Apex (a) and the Aridus (b) sample introduction system. The Aridus shows slightly higher sensitivity than the Apex, and the ^{32}S interferences with the Aridus are almost an order of magnitude less than with the Apex, at ~ 0.1 and ~ 0.8 V, respectively.

2.3.8 Sulfur signal loss and recovery when using desolvating membranes

There are two hypotheses for the cause of sulfur loss in MC-ICP-MS measurements: 1) sulfate is retained in the membrane, and 2) sulfur volatilizes before entering the mass spectrometer. To test these theories, I introduced dilute H_2SO_4 and a counteraction solution to the Aridus separately. First, a $20\ \mu\text{M}$ H_2SO_4 standard was introduced through the Aridus and, as expected, no sulfur signal was produced. Second, a $40\ \mu\text{M}$ sodium ICP standard (NaOH) was run through the Aridus to act as a counteraction. If sulfate was retained in the membrane, it may have been released by the sodium addition and carried to the MC-ICP-MS for analysis. If sulfate had volatilized, however, it would not be recovered by running sodium through the system. As per Paris et al. (2013), the standards were introduced in a 2:1 molar ratio of sodium to sulfate to achieve the maximum ^{32}S signal.

The proposed wash-out effect was observed, and the ^{32}S signal increased from ~ 0.6 V to ~ 2 V after the sodium standard was introduced (Figure 2.17). The signal then gradually decreased before returning to background values after 5–10 minutes. This result supported

the hypothesis that sulfate is trapped in the membrane and not lost through volatilization. However, the low signal recovery and the protracted nature of the wash-out effect reinforced the need to spike samples with a counteraction prior to analysis.

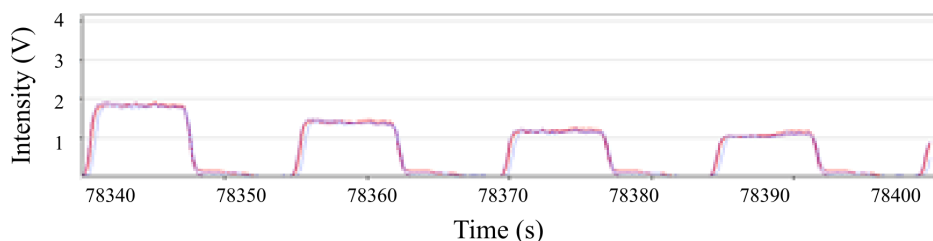


Fig. 2.17 Time series of ^{32}S (red), ^{33}S (blue), and ^{34}S (purple) signals measured after $20\ \mu\text{M}$ H_2SO_4 was introduced to the MC-ICP-MS through the Aridus followed by a $40\ \mu\text{M}$ NaOH ICP standard. Sodium mixed with sulfate in the membrane and caused a gradual wash out effect that lasted 5–10 minutes.

Previous studies have primarily used sodium as a counteraction, although silver and ammonium have also been used (Albalat et al., 2016; Han et al., 2013). Paris et al. (2013) reported that sensitivity increased as the sodium-to-sulfate molar ratio increased, and the signal plateaued once a 2:1 ratio was reached. To further evaluate the two introduction systems, I measured the sulfur signal of standards with different sodium-to-sulfate ratios. Standards for these experiments were prepared as follows:

1. Sulfur ICP standard (H_2SO_4) was dried at 80°C to obtain the desired amount of sulfate
2. Sodium ICP standard (NaOH) was added to achieve a specific sodium-to-sulfate molar ratio.
3. The standard was then diluted with 2% HNO_3 to the desired concentration.

Two concentrations of sulfate standards ($10\ \mu\text{M}$ and $20\ \mu\text{M}$) were prepared with 1:1, 2:1, 3:1, and 4:1 sodium-to-sulfate ratios. As expected, the $20\ \mu\text{M}$ standard showed that the ^{32}S signal peaked at a 2:1 ratio and then plateaued, although the signal slightly decreased as additional sodium was added (Figure 2.18). This decrease was likely due to increased charge density in the torch and, therefore, decreased sensitivity. As previously observed, the Aridus produced a slightly higher ^{32}S signal than the Apex system, and the signal peak and plateau were also more distinct.

In contrast, the $10\ \mu\text{M}$ H_2SO_4 test showed the Apex with a slightly higher ^{32}S signal at a 2:1 sodium-to-sulfate ratio, and the Aridus showed a less-defined signal peak and plateau. I attributed this result to the quick nature of these tests, where the signal voltage was determined from 3–4 mass scans with no background correction. Furthermore, the expected signal peak and the subsequent signal decrease would be less visible for the $10\ \mu\text{M}$ standard than the $20\ \mu\text{M}$

μM standard. Because of the lower ion density in the torch, additional sodium ions would have less impact on signal sensitivity compared to higher concentrations standards. Lastly, these slight signal anomalies were also observed by Paris et al. (2013). Therefore, I still considered 2:1 as the optimal sodium-to-sulfate ratio and selected the Aridus as the final sample introduction system. The final Aridus settings are shown in Table 2.5.

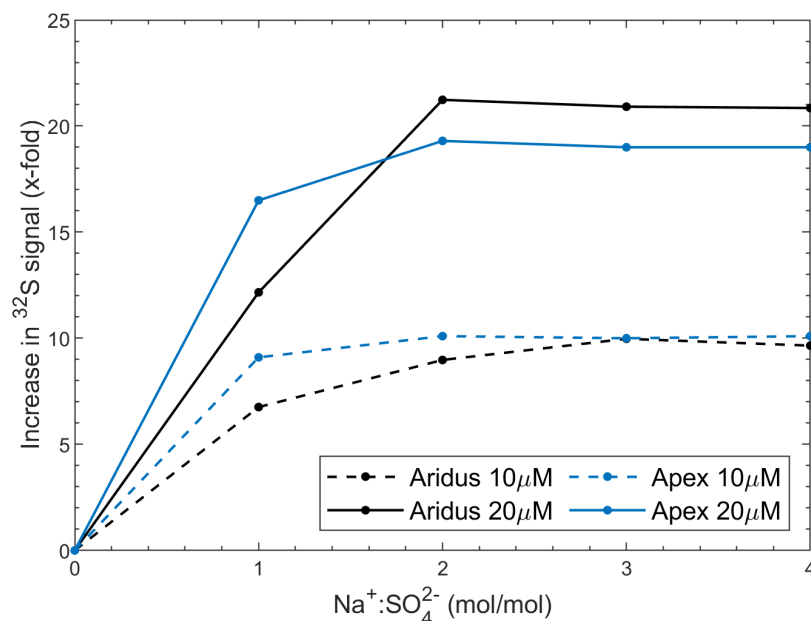


Fig. 2.18 Relative intensities of ^{32}S in $10 \mu\text{M}$ and $20 \mu\text{M}$ H_2SO_4 with an increasing molar ratio of sodium-to-sulfate, measured with the Aridus and Apex introduction systems. Results showed the expected signal peak at a 2:1 molar ratio of sodium-to-sulfate. The signal then reached a near plateau but decreased slightly as additional sodium ions increased the charge density in the torch.

Table 2.5 Aridus settings for $\delta^{34}\text{S}_{\text{SO}_4}$ MC-ICP-MS measurements

Spray chamber temperature	110°C
Desolvating membrane temperature	160°C
Nebulizer	ESI PFA-60
Flow rate	58 $\mu\text{L}/\text{second}$
Argon sweep gas	5–6 L/minute
Nitrogen flow	0.04–0.06 L/min
Cones	Jet X

2.3.9 Choosing a counteraction for MC-ICP-MS analysis

There is little literature exploring counteractions other than sodium. Therefore, I tested various counteractions by adding different ratios of Na^+ , ammonium (NH_4^+), calcium (Ca^{2+}), and barium (Ba^{2+}) to $20\ \mu\text{M}\ \text{H}_2\text{SO}_4$. For single-charged cations, a 2:1 molar ratio with sulfate produced the maximum signal, agreeing with previous results. For double-charged cations, a 1:1 molar ratio produced the maximum signal. Therefore, charge balance was the key to optimizing sensitivity for sulfur isotope measurements (Figure 2.19).

Different counteractions had varying effects on instrument sensitivity and stability. For example, sodium and calcium improved sensitivity more than barium. Also, double-charged counteractions caused a larger signal drop than single-charged counteractions after surpassing the optimal molar ratio. I attributed this finding to the faster accumulation of charge in the torch, leading to increased interference and decreased sensitivity. Double-charged cations also took longer to wash out of the Aridus membrane than single-charged cations, which led to signal drift across a run. Based on these results, a single-charged counteraction was preferable to a double-charged counteraction. It was difficult to obtain a 2:1 ratio of ammonium-to-sulfate because of the strong dissociation of NH_3 . Therefore, I chose sodium as the counteraction for all analyses.

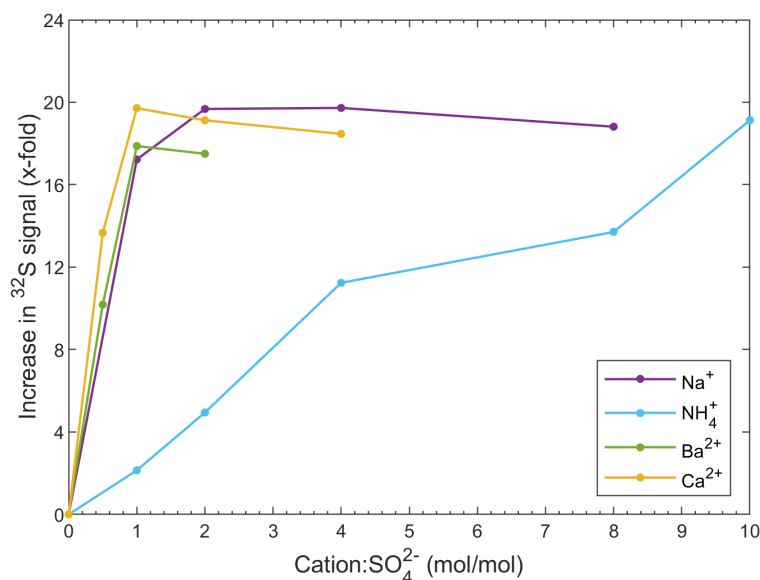


Fig. 2.19 Measured ^{32}S signal for $20\ \mu\text{M}\ \text{H}_2\text{SO}_4$ with increasing ratios for various counteractions. Charge balance was essential to maximize the ^{32}S signal. Single-charged counteractions reached the maximum ^{32}S signal at a 2:1 molar ratio with sulfate, and double-charged counteractions reached the maximum ^{32}S signal at a 1:1 molar ratio with sulfate. Because of the strong dissociation of NH_3 , it was difficult to achieve the proper ammonium-to-sulfate ratio.

2.3.10 Resolving matrix effects caused by counteraction addition

High sodium concentrations in samples may affect sulfur isotope measurements; this is called a matrix effect. To assess potential matrix effects, I needed to select an interim secondary standard to conduct sulfur isotope measurements. In MC-ICP-MS analysis, standards are alternated with samples throughout the run, and the sample $\delta^{34}\text{S}_{\text{SO}_4}$ value is calculated using the average isotope ratios of the surrounding standards. This technique, called sample bracketing, also corrects for any instrument fractionation throughout the run, which is assumed to affect samples and standards equally (Carter et al., 2018). For these matrix tests, an initial secondary bracketing standard was prepared from sulfur and sodium ICP standards with a 2:1 sodium-to-sulfate ratio. The standard concentration was always matched to the concentrations of the sample. My selection of the final secondary standard is described in the following section.

To quantify potential sodium matrix effects, different amounts of sodium were added to 8 μM and 20 μM H_2SO_4 standards, which served as mock samples. The 8 μM standard was prepared with sodium-to-sulfate ratios of 2:1 up to 8:1. The 20 μM standard was prepared with sodium-to-sulfate ratios from 0.5:1 up to 8:1. If there were no matrix effects from the sodium in the samples, $\delta^{34}\text{S}_{\text{SO}_4}$ would be the same for all measurements. Because the bracketing standard and the mock samples were made from the same sulfur ICP standard, $\delta^{34}\text{S}_{\text{SO}_4}$ should have been 0‰ for all measurements.

There were clear matrix effects for both the 8 μM and 20 μM H_2SO_4 standard (Figure 2.20). Both concentrations showed a negative, linear correlation between $\delta^{34}\text{S}_{\text{SO}_4}$ and sodium concentration, with $\delta^{34}\text{S}_{\text{SO}_4} = 0‰$ at a 2:1 sodium-to-sulfate ratio. The 8 μM standard had a steeper line of best fit than the 20 μM standard, indicating greater matrix effects. Likely, the lower charge density in the torch was more easily ‘diluted’ and impacted by additional sodium ions. The linear correlation between $\delta^{34}\text{S}_{\text{SO}_4}$ and sodium concentration did not hold for sodium-to-sulfate ratios below 1:1. For the 20 μM standard, $\delta^{34}\text{S}_{\text{SO}_4}$ for the 0.5:1 sulfate-to-sodium ratio was 6‰ higher than the 1:1 sodium-to-sulfate ratio. Similar results were seen by Paris et al. (2013).

Overall, results showed that a 2:1 sodium-to-sulfate molar ratio eliminated or minimized sodium matrix effects in sulfur isotope measurements. However, for a 20 μM standard, the sodium-to-sulfate ratio could range from 1.8:2 to 2.2:2, and $\delta^{34}\text{S}_{\text{SO}_4}$ values would remain within measurement uncertainty (2σ). My findings agreed with the advice of Dr Andrea Burke at St. Andrew’s University (personal communication, 2018). In her experience, slight variations in the sodium-to-sulfate ratio are acceptable as long as the sodium matrix of the sample is exactly matched to that of the standard.

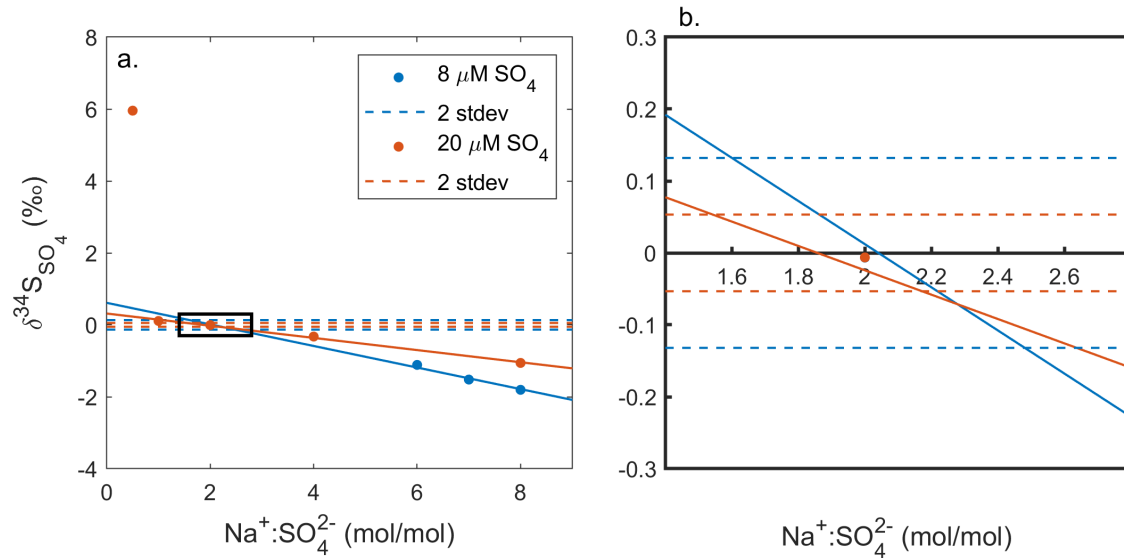


Fig. 2.20 Matrix effects from sodium addition to 8 μM (blue) and 20 μM (orange) H_2SO_4 ICP standard (a), with a close-up of the $\delta^{34}\text{S}_{\text{SO}_4} = 0$ ‰ intercept (b). Each standard was run against an ICP bracketing standard of the same concentration with a 2:1 sodium-to-sulfate ratio. Both standards measured $\delta^{34}\text{S}_{\text{SO}_4} = 0$ ‰ at a 2:1 sodium-to-sulfate ratio, showing minimal matrix effects.

2.3.11 Choosing a bracketing standard for sulfur isotope analysis

Before further tests could be conducted, I needed to choose a final bracketing standard for all $\delta^{34}\text{S}_{\text{SO}_4}$ measurements. As shown above, the bracketing standard needed to have a 2:1 sodium-to-sulfate ratio, but it could be prepared from different starting materials and by different methods. I evaluated three potential standards: Na_2SO_4 made from sulfur and sodium ICP standards, reagent grade Na_2SO_4 that was purified on a chromatography column, and unpurified reagent grade Na_2SO_4 . The initial standard test evaluated the precision of replicate standard measurements. Each potential bracketing standard was run against itself five times, which should have produced $\delta^{34}\text{S}_{\text{SO}_4} = 0$ ‰ with a minimal uncertainty (Figure 2.21).

Standard one: Na_2SO_4 prepared from sulfur ICP standard

The bracketing standard was prepared by drying down 100 ppb sulfur ICP standard. Initial tests showed that individually spiking the standard with sodium (NaOH) led to poor precision, so this technique was quickly abandoned. Instead, the dried standard was rediluted with sodium-spiked acid. To prepare a 15 μM bracketing standard, 0.48 mL of sulfur ICP standard was dried down at 80°C and rediluted with 100 mL of 30 μM sodium in 2% HNO_3 ,

prepared from an NaOH ICP standard. This method ensured a 2:1 sodium-to-sulfate ratio in the bracketing standard, assuming no sulfate loss via evaporation. The final result of the 5x bracketing test was $\delta^{34}\text{S}_{\text{SO}_4} = 0.01 \pm 0.02\text{‰}$.

Standard two: Reagent grade Na_2SO_4 purified on a chromatography column

For a $15\text{ }\mu\text{M}$ purified Na_2SO_4 bracketing standard, 30 nmol of sulfur were loaded directly onto the column as $35\text{ }\mu\text{L}$ of 0.86 mM reagent grade Na_2SO_4 ; no dry down step was necessary. The standard column procedure was then followed. The sulfate fraction was collected, dried down at 80°C , and rediluted with 2 mL of $30\text{ }\mu\text{M}$ sodium-spiked acid. The final result of the 5x bracketing test was $\delta^{34}\text{S}_{\text{SO}_4} = 0.05 \pm 0.35\text{‰}$.

Standard three: Unpurified reagent grade Na_2SO_4

Reagent grade Na_2SO_4 was dissolved in 2% HNO_3 for a $15\text{ }\mu\text{M}$ bracketing standard. The final result of the 5x bracketing test was $\delta^{34}\text{S}_{\text{SO}_4} = 0.01 \pm 0.13\text{‰}$.

Each bracketing standard had a slightly different matrix and sodium-to-sulfate ratio based on the preparation technique, as shown in Table 2.6.

The bracketing standard tests showed the importance of a 2:1 sodium-to-sulfate ratio. As expected, the ICP standard replicate measurements had the greatest precision because of its high purity grade. Following this argument, the purified Na_2SO_4 standard should have had greater precision than the reagent grade Na_2SO_4 ; however, the opposite was observed. This result was likely due to the exact 2:1 sodium-to-sulfate ratio in the reagent grade standard. To further evaluate the optimal bracketing standard, I included all standards in the continued method testing.

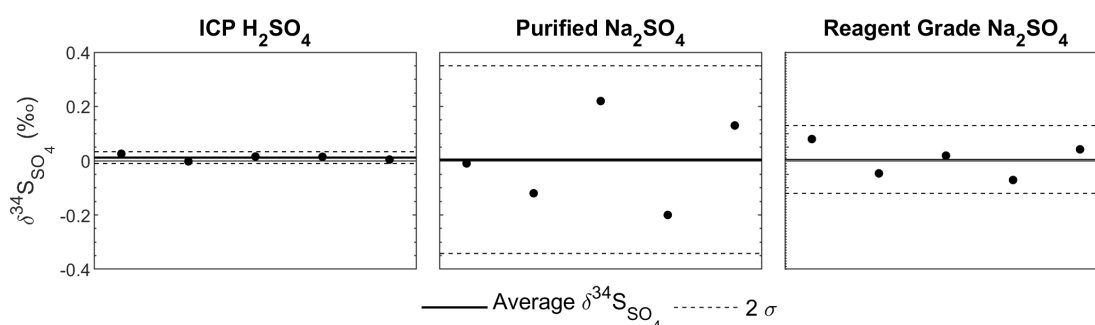


Fig. 2.21 Five replicate measurements of three potential sulfur bracketing standards. For reference-grade ICP standard, purified Na_2SO_4 , and reagent grade Na_2SO_4 , $\delta^{34}\text{S}_{\text{SO}_4} = 0.01 \pm 0.02\text{‰}$, $0.05 \pm 0.35\text{‰}$, and $0.01 \pm 0.13\text{‰}$, respectively.

Table 2.6 *Bracketing standard properties for three potential sulfur standards*

Bracketing standard	Matrix match with sample?	Exact 2:1 sodium-to-sulfate ratio?
ICP standard	YES Diluted with same sodium-spiked acid as the sample	NO Potential sulfate loss during evaporation or a slight dilution error
Purified Na_2SO_4	YES Diluted with same sodium-spiked acid as the sample	NO Potential sulfate loss during evaporation or a slight dilution error
Reagent grade Na_2SO_4	NO Diluted with 2% HNO_3	YES Simple dilution

2.3.12 Determining the optimal sodium addition technique

Sodium was added to the dried sample after the column separation. However, it could be added either before or after the sample was rediluted for analysis, and the introduction technique could vary. To determine the optimal spiking method, I considered the following objectives: 1) obtaining an exact 2:1 ratio of sodium-to-sulfate in the sample, 2) matching the matrix of the sample to that of the bracketing standard, and 3) matching the sulfate concentration of the sample to that of the bracketing standard. It was not possible to achieve all three goals because accomplishing one precluded another. For example, a sample and standard could have both a 2:1 sodium-to-sulfate ratio and matching matrices. To achieve a concentration match, however, either the sample or the standard would have to be diluted, which would reverse the first two points.

I tested three spiking methods to assess the relative importance of each factor: 1) NaOH was added to the dried samples individually before they were rediluted with 2% HNO_3 , 2) NaOH was added to the 2% HNO_3 used to redilute the samples, and 3) the sample's sulfur signal was continuously measured, and sodium-spiked 2% HNO_3 was added until it reached peak intensity, signaling a 2:1 sodium-to-sulfate ratio in the sample. The first two tests assumed 100% sulfate recovery during column separation. The third test assumed some sulfate loss during column separation.

To conduct these tests, mock ice samples were made from IAPSO seawater standard. Samples were prepared with 84 ppm sulfate, so 30 nmol of sulfur were directly loaded onto the column in 35 μL . The $\delta^{34}\text{S}_{\text{SO}_4}$ of the seawater and all potential bracketing standards

Table 2.7 *The sulfur isotopic composition of three sulfur standards measured by GS-MS*

	$\delta^{34}\text{S}_{\text{SO}_4}$ (‰)	2 σ
IAPSO seawater	21.16	0.11 (n = 10)
ICP standard	3.24	0.22 (n = 9)
Na_2SO_4	3.55	0.12 (n = 8)

were first measured on a Thermo Delta V GS-MS as a reference for MC-ICP-MS test values (Table 2.7). These measurements were made with the assistance of Dr Sasha Turchyn at the University of Cambridge. Another seawater standard and bracketing standard with known isotope compositions were provided by Dr Guillaume Paris for additional testing. All bracketing samples were prepared at a 15 μM concentration. Unless stipulated otherwise, all samples were run in triplicate.

Sodium addition test #1: Individual sample spiking

For the first spiking test, sodium was individually added to each sample. After the sample was dried down, 60 nmol of sodium (NaOH) were added to the 30 nmol sulfur sample for a 2:1 sodium-to-sulfate ratio. The sample was then diluted with 2 mL of 2% HNO_3 for a final 15 μM sulfate concentration. A concentration match was not conducted before isotope analysis. To minimize additional volume, sodium was added as a small amount of concentrated NaOH, and it was difficult to add exactly 60 nmol of sodium across all samples. This test was only conducted with the ICP bracketing standard because initial results had very poor precision.

Sodium addition test #2: Dilution with sodium-spiked 2% HNO_3

In the second addition test, the dried 30 nmol sample was diluted with 2 mL of 30 μM sodium-spiked acid. The resulting 15 μM sample had a 2:1 sodium-to-sulfate ratio assuming 100% column recovery. As in the first test, no concentration match was performed before sulfur isotope analysis.

This sodium addition technique had different results based on the bracketing standard that was used. The ICP standard was prepared first and used to conduct multiple seawater measurements. Each seawater sample was run in triplicate, and the resulting $\delta^{34}\text{S}_{\text{SO}_4}$ values had good accuracy but worse reproducibility than expected (Table 2.8). However, the reproducibility was not too far from the values reported by Paris et al. (2013), at $\sim 0.20\text{‰}$ and $\sim 0.15\text{‰}$, respectively. Because these initial results were promising, the seawater and bracketing standard provided by Dr Guillaume Paris were then analyzed. The sample had already been purified on a column, and the bracketing standard was reagent grade Na_2SO_4 in

Table 2.8 *The sulfur isotopic composition of IAPSO seawater samples measured against three sulfur bracketing standards via MC-ICP-MS*

	ICP		Purified Na_2SO_4		Reagent grade Na_2SO_4	
	$\delta^{34}\text{S}_{\text{SO}_4}$ (‰)	2 σ (n = 3)	$\delta^{34}\text{S}_{\text{SO}_4}$ (‰)	2 σ (n = 3)	$\delta^{34}\text{S}_{\text{SO}_4}$ (‰)	2 σ (n = 3)
	21.18	0.24	21.31	0.23	21.18	0.11
	21.37	0.13	21.25	0.47	21.31	0.07
	21.45	0.26	21.34	0.30	21.26	0.10
	21.22	0.16	21.11	0.48		
	21.23	0.18	21.22	0.16		
	21.33	0.22	21.28	0.26		
	21.09	0.28				
	21.32	0.24				
	21.36	0.13				
	21.29	0.07				
	21.22	0.05				
Mean	21.28	0.20	21.25	0.16	21.25	0.12

5% HNO_3 . The sample was dried down and rediluted with sodium-spiked acid as previously described, and the bracketing standard was diluted to 15 μM with 2% HNO_3 . The measured $\delta^{34}\text{S}_{\text{SO}_4}$ values agreed with the known ratios, at $16.56 \pm 0.17\text{‰}$ and $16.60 \pm 0.25\text{‰}$, respectively, showing that reagent grade Na_2SO_4 was a viable bracketing standard.

Following the successful results with the Paris samples, tests were continued with the mock ice samples with purified and reagent grade Na_2SO_4 as the bracketing standard. Unexpectedly, reagent grade Na_2SO_4 achieved better precision than purified Na_2SO_4 and ICP standard (Table 2.8). This suggested that the exact 2:1 sodium-to-sulfate ratio in the standard had a greater effect on isotope measurements than an exact matrix match between the sample and standard. Therefore, I chose reagent grade Na_2SO_4 as the bracketing standard.

Sodium addition test #3: Gradual addition of sodium-spiked 2% HNO_3

The third addition test did not assume 100% column recovery, and the entire 2 mL of sodium-spiked acid were not added at once. Instead, the sample was diluted with 1.5 mL of the spiked acid, and the sulfur signal was measured on the MC-ICP-MS. In theory, additional sodium-spiked acid would then be added while monitoring the sulfur signal, which would peak at a 2:1 sodium-to-sulfate ratio. The sample would then be diluted with 2% HNO_3 to match the standard concentration.

I encountered several issues with the technique. First, the continued concentration measurements used a significant volume of the sample. This also made it difficult to

determine the proper sodium addition because sulfate was constantly being removed from the sample. Most importantly, it was not possible to identify the signal plateau without going over the 2:1 sodium-to-sulfate ratio. Overall, this method introduced more uncertainty than assuming 100% column sulfate recovery. Therefore, I chose the second technique as the optimal sodium addition method for all future isotope analyses.

2.3.13 Final method check

Until this point, I had only analyzed standards to evaluate method performance. For a final method check, I measured lake samples from Lake Baikal to confirm that the developed MC-ICP-MS method worked for true samples. Lake Baikal is a large, freshwater lake in southern Siberia. Samples were collected by Dr Sasha Turchyn, who analyzed nine surface samples with a Thermo Delta V GS-MS at the University of Cambridge. The average $\delta^{34}\text{S}_{\text{SO}_4}$ of the nine samples was $7.95 \pm 0.20\text{‰}$ (1 σ).

I analyzed thirteen lake samples that ranged from the surface to the deep lake and compared my results to the lake value described above. The average $\delta^{34}\text{S}_{\text{SO}_4}$ of the thirteen lake samples was $7.85 \pm 0.24\text{‰}$ (2 σ). Results showed isotopic heterogeneity with depth and agreed with the GS-MS value, showing that the MC-ICP-MS method was accurate. IAPSO seawater was measured as an internal standard throughout the run to further assess the accuracy and reproducibility of the $\delta^{34}\text{S}_{\text{SO}_4}$ measurements. The determined $\delta^{34}\text{S}_{\text{SO}_4}$ of $21.22 \pm 0.14\text{‰}$ (2 σ , $n = 6$) agreed with the known IAPSO seawater value ($21.16 \pm 0.11\text{‰}$). Results are shown in Table 2.9, with samples LB10–LB66 going from shallow to deep samples.

2.3.14 Conducting sulfur isotope measurements with the established MC-ICP-MS method

Instrument parameters

I made all sulfur isotope measurements with a Neptune Plus MC-ICP-MS. Analytical resolution was $\sim 8,000$ – $9,000$, and the average sensitivity was 10–12 V for a $15\text{ }\mu\text{M}$ sulfate sample. Instrument settings are shown in Table 2.10.

Designating the measurement mass

The signal for each sulfur isotope was a flat peak over a mass range of $\sim 70\text{ mDa}$, and the peak location could shift slightly with changes in instrument tuning. Therefore, a specific measurement mass had to be stipulated for each analytical session. The ideal measurement

Table 2.9 *The sulfur isotopic composition of Lake Baikal samples measured via MC-ICP-MS*

Sample	$\delta^{34}\text{S}_{\text{SO}_4}$ (‰)	2 σ (n = 3) ¹
LB10	7.90	0.14 ²
LB11	7.99	0.02
LB25	7.99	0.12
LB27	7.81	0.20
LB29	7.93	0.29
LB31	7.68	0.13
LB44	7.89	0.01
LB45	7.85	0.13
LB59	7.82	0.04
LB61	8.00	0.36
LB63	7.64	0.06
LB65	7.89	0.13
LB66	7.75	0.10

¹ Sample reproducibility, independent of $\pm 0.14\text{‰}$ external error determined from replicate internal standard measurements

² Only one measurement performed due to limited sample volume— external error of internal standard reported

Table 2.10 *Neptune parameters for $\delta^{34}\text{S}_{\text{SO}_4}$ analysis*

Sample/Standard measurements	50 blocks
Blank measurements	10 blocks
Integration time	4.194 sec
Uptake time	60 sec
Wash (post sample/standard)	80 sec

mass depended on numerous factors such as isobaric interferences, peak alignment, resolution, and magnet stability.

All isobaric interferences for sulfur were heavier than the affected mass, resulting in an interference-free plateau on the left side of each peak (Figure 2.22). The calculated widths of these plateaus were approximately 18 mDa, 8 mDa, and 26 mDa for ^{32}S , ^{33}S , and ^{34}S , respectively, but rounded peak shoulders further reduced the width of the plateau that was viable for measurements. Working at a high resolution allowed sharper peaks and, therefore, a wider plateau for isotope measurements. For accurate ratio measurements, all isotope peaks needed to be aligned so that a single measurement could be taken at the center of all interference-free plateaus.

To determine the optimal alignment technique, I performed a mass scan with 1 mDa resolution across the sulfur peak, and $^{34}\text{S}/^{32}\text{S}$ and $^{33}\text{S}/^{32}\text{S}$ ratios were calculated at each mass (Figure 2.23). Results showed that the ^{32}S and ^{34}S peaks should be aligned along the left shoulder, to create a stable ~ 7 mDa plateau for $^{34}\text{S}/^{32}\text{S}$ measurements. Final $^{34}\text{S}/^{32}\text{S}$ ratios were measured in the center of this plateau, which was approximately +10 mDa from the left shoulder of the peak. The center mass was then chosen by eye after scanning the ^{32}S and ^{34}S sulfur peaks of 2% HNO_3 . Blank acid showed the plateaus more clearly than a standard because the lower ^{32}S signal showed greater interference effects.

The interference-free plateau for the ^{33}S signal was only ~ 5 mDa. This suggested that the peak should be offset from the ^{32}S and ^{34}S peaks by approximately +7 mDa to be included in the +10 mDa measurement described above. However, the mass scan was unable to resolve a stable $^{33}\text{S}/^{34}\text{S}$ plateau, which must be ≤ 2 mDa. Because my research did not focus on $\delta^{33}\text{S}_{\text{SO}_4}$ measurements, I did not perfect this alignment technique.

One measurement mass was stipulated for an entire analytical run. A common measurement technique is to conduct a peak center for every sample, to correct for any drift in the magnet that could cause the peak to shift throughout the run. However, this step was not necessary because the stable magnet led to negligible drift in peak position. The ~ 7 mDa $^{34}\text{S}/^{32}\text{S}$ plateau was sufficiently wide that there was minimal chance of falling off the signal shoulder during the run.

Taking the final isotope measurement

Before analyzing samples, the bracketing standard was measured five times to allow the instrument to stabilize before conducting at least one triplicate measurement of IAPSO seawater standard. If the external error of the standard $\delta^{34}\text{S}_{\text{SO}_4}$ values was $\leq 0.15\text{‰}$, the sample run continued; if the error was $> 0.15\text{‰}$, the instrument tuning was readjusted as needed. Blanks of sodium-spiked 2% HNO_3 were measured before and after each sample

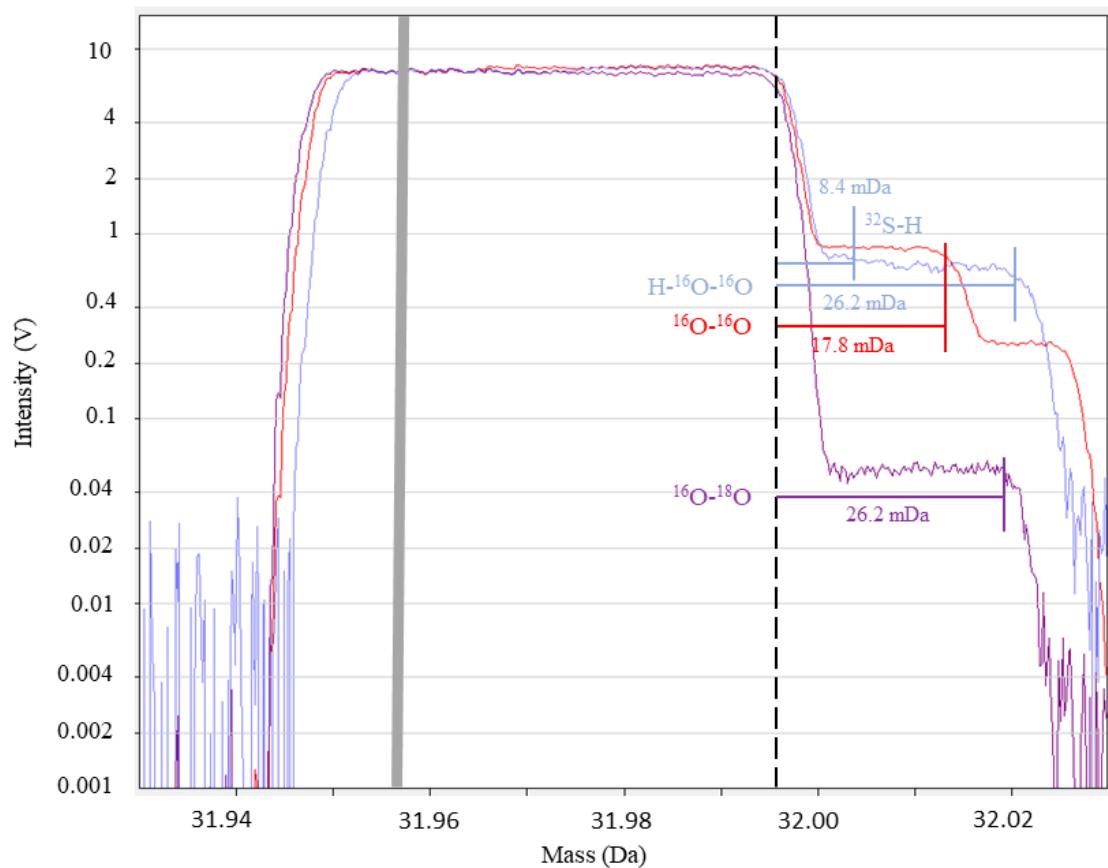


Fig. 2.22 Mass scan of ^{32}S (red), ^{33}S (blue), and ^{34}S (purple) for a $30\ \mu\text{M}$ $(\text{NH}_4)_2\text{SO}_4$ standard measured on the MC-ICP-MS with an Apex desolvating introduction system prior to Aridus selection. Isobaric interferences are visible for all sulfur isotope masses, although the $^{32}\text{S}^1\text{H}$ interference on ^{33}S is not well resolved in this scan. Peaks ^{32}S and ^{34}S were aligned on the left shoulder to create a $\sim 7\ \text{mDa}$ interference-free plateau, and the $^{34}\text{S}/^{32}\text{S}$ ratio was measured at the center of the plateau (grey bar). The ^{33}S peak was offset from the ^{32}S and ^{34}S peaks by $+7\ \text{mDa}$ to align with the interference-free plateau.

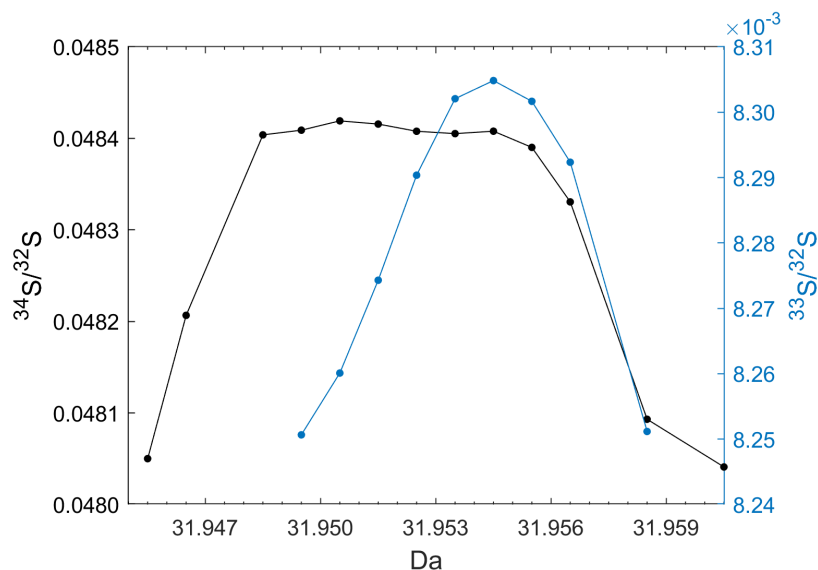


Fig. 2.23 Mass scan with 1 mDa resolution showing $^{34}\text{S}/^{32}\text{S}$ (black) and $^{33}\text{S}/^{32}\text{S}$ (blue) measured across the sulfur peak. The $^{34}\text{S}/^{32}\text{S}$ ratio was stable across a ~ 7 mDa plateau. The $^{33}\text{S}/^{32}\text{S}$ plateau was ≤ 2 mDa and not resolved in this scan.

and standard. A blank correction was then applied to ^{32}S and ^{34}S to subtract any background sulfate signal. The correction was as follows:

$$\delta^{32}\text{S}_{\text{corrected}(i)} = \delta^{32}\text{S}_{\text{measured}(i)} - \left(\frac{\delta^{32}\text{S}_{\text{blank}(i+1)} + \delta^{32}\text{S}_{\text{blank}(i-1)}}{2} \right) \quad (2.2)$$

where i is the number of the sample or standard in the measurement sequence. The sample or standard isotope ratio was then calculated using the corrected ^{32}S and ^{34}S measurements. A total procedural blank was run at the start of each analytical session to monitor the blank contribution from sample preparation. The gloves used throughout the analysis had a small sulfur blank, so special care was taken when handling Teflon sample vials. Neptune vials were washed in 10% HCl before loading the sample.

Each replicate of every sample was alternated with reagent grade Na_2SO_4 bracketing standard to account for any drift throughout the run. I attempted less frequent bracketing, but it resulted in decreased accuracy and precision. Sample $\delta^{34}\text{S}_{\text{SO}_4}$ values were calculated using the bracketing standards immediately before and after the sample. The calculation was as follows:

$$\delta^{34}\text{S}_{\text{sample}(i)} = \left(\frac{\left(\frac{^{34}\text{S}}{^{32}\text{S}} \right)_{\text{sample}(i)}}{\left(\frac{\left(\frac{^{34}\text{S}}{^{32}\text{S}} \right)_{\text{standard}(i+2)} + \left(\frac{^{34}\text{S}}{^{32}\text{S}} \right)_{\text{standard}(i-2)}}{2} \right)} - 1 \right) \cdot 1000 \quad (2.3)$$

where i is the number of the sample in the measurement sequence, and $^{34}\text{S}/^{32}\text{S}$ is the blank corrected sulfur isotope ratio. The calculated $\delta^{34}\text{S}_{\text{SO}_4}$ value was then converted to the VCDT scale as follows:

$$\delta^{34}\text{S}_{\text{VCDT}} = \delta^{34}\text{S}_{\left(\frac{\text{SA}}{\text{BS}}\right)} + \delta^{34}\text{S}_{\left(\frac{\text{BS}}{\text{VCDT}}\right)} + \delta^{34}\text{S}_{\left(\frac{\text{SA}}{\text{BS}}\right)} \cdot \delta^{34}\text{S}_{\left(\frac{\text{BS}}{\text{VCDT}}\right)} \cdot 0.01 \quad (2.4)$$

where (SA/BS) is the sample run against the secondary Na_2SO_4 bracketing standard, and (BS/VCDT) is the secondary bracketing standard on the VCDT scale. Samples were run in triplicate and averaged for the final isotope value.

Measurement uncertainty: Interval vs external error

Uncertainty in measured isotope values includes internal and external error. Internal error is the error of the 50 blocks measured for each sample. Internal error was determined as described in Paris et al. (2013). First, the standard error was calculated for each sample, standard, and blank $^{34}\text{S}/^{32}\text{S}$ ratio. This error was then propagated through the blank correction and $\delta^{34}\text{S}_{\text{SO}_4}$ calculation for each sample. The typical internal error was $\sim 0.02\text{‰}$ (2σ).

The external error is the reproducibility of an internal standard analyzed alongside the samples. IAPSO seawater was used as an internal standard and measured every five samples throughout each MC-ICP-MS run. External error ranged between $\sim 0.10\text{--}0.15\text{‰}$ (2σ). Because the internal error is very small, only external error is reported unless stipulated otherwise. However, the internal error should be acknowledged as another source of uncertainty.

In addition to the external error, the reproducibility of replicate sample measurements is also reported. Because the internal standards and samples are prepared and analyzed with the same method and in the same run, the external error and sample reproducibility should be the same. Although some differences in error were seen for specific samples, the reproducibility of the internal standards was considered the basis for defining external error. When no replicate sample measurements were made, only the external error was reported.

2.4 Conclusion

I have established a method to measure the sulfur isotopic composition of sulfate via MC-ICP-MS analysis at the University of Cambridge. An MC-ICP-MS can measure < 30 nmol of sulfur compared to the $\sim 1 \mu\text{mol}$ required for GS-MS analysis, so this method was ideal for $\delta^{34}\text{S}_{\text{SO}_4}$ measurements in ice cores, which have an average sulfate concentration of $\sim 20\text{--}100$ ppb. A desolvating introduction system was used to minimize isobaric interferences from the solvent, which is a primary concern during MC-ICP-MS analysis. The final MC-ICP-MS method measured $\delta^{34}\text{S}_{\text{SO}_4}$ with an average precision of $\sim 0.11\text{‰}$ (2σ) for triplicate measurements, and the smaller sample size allowed increased depth resolution of $\delta^{34}\text{S}_{\text{SO}_4}$ measurements in ice cores. I have used this technique to produce the first seasonal record of $\delta^{34}\text{S}_{\text{SO}_4}$ in ice cores as well as examine sulfate source in Antarctica on a spatial and glacial/interglacial scale, which I will discuss in the following chapters.

Chapter 3

Seasonality of sulfate sources in West Antarctica and a potential new sea ice proxy

3.1 Introduction

3.1.1 Chapter outline

The first part of this chapter focuses on identifying seasonal signals in two ice cores from West Antarctica using ion chromatography (IC) analysis. In the second section, I present the first record of seasonal changes in the sulfur isotopic composition of sulfate ($\delta^{34}\text{S}_{\text{SO}_4}$) in an ice core, produced with the new method described in Chapter 2. Although I originally intended to use these data conjointly in a new sea ice proxy, my results suggested that the background sulfate signal was too complex to assume that sea salt and marine biogenic activity are the only significant sulfate sources. As such, the third part of this chapter discusses my reassessment of potential sulfate sources in West Antarctica, as well as the validity of the generally accepted sulfur isotopic composition of marine biogenic sulfate. I also present the first direct $\delta^{34}\text{S}_{\text{SO}_4}$ measurements from the sea ice surface in Antarctica and confirm the widely used 21‰ sulfur isotopic signature of sea salt sulfate. Finally, I assess the potential use of $\delta^{34}\text{S}_{\text{SO}_4}$ as a sea ice proxy in light of my earlier characterization of background sulfate sources.

3.1.2 Sulfate sources in West Antarctica and seasonality in the sulfate signal

The two primary sources of sulfate in West Antarctica are sea salt and marine biogenic activity, excluding volcanic deposition during eruption events (Legrand and Delmas, 1984; Minikin et al., 1998). The emission strength of sea salt sulfate (SO_{4ss}^{2-}) and biogenic sulfate (SO_{4bio}^{2-}) fluctuates with seasonal changes in sea ice extent. Sea salt is positively correlated with sea ice extent, with maximum sea salt concentrations in the winter and minimum concentrations in the summer (Hara, 2004; Rankin and Wolff, 2003; Wagenbach et al., 1998). A negative correlation has been observed at sites with little sea ice or close proximity to polynyas and other open ocean sources (Minikin et al., 1994), but such sites were not used in this research.

Biogenic sulfate derives from dimethylsulfide (DMS) produced by phytoplankton in the sea ice zone, and biogenic emissions are negatively correlated with sea ice extent (Abram et al., 2013). Once emitted, DMS oxidizes to form sulfate and methanesulfonic acid (MSA), which is transported to and deposited on the ice sheet (Curran and Jones, 2000; Thomas and Abram, 2016; Turner et al., 1995). Biogenic emissions are lowest in the winter and increase as sea ice starts to retreat in the spring (Legrand and Pasteur, 1998; Sharma et al., 2012). Emissions peak in the summer when there are warm temperatures, prolonged sunlight, and minimal sea ice extent (Legrand et al., 1992; Oduro et al., 2011; Thomas and Abram, 2016). This results in an ice core summer signal with high concentrations of sulfate and MSA and low concentrations of sodium (Na^+) from sea salt. In the winter, ice cores record low concentrations of sulfate and MSA and high sodium concentrations. The $\text{SO}_4^{2-}/\text{Na}^+$ mass ratio also peaks in the summer due to high biogenic emissions and a small sea salt source. At coastal sites, sulfate is deposited predominantly by wet deposition, so there is a possibility of source bias based on seasonal differences in precipitation. For example, greater precipitation in the summer could record a strong biogenic sulfate signal, while less precipitation in the winter could lead to an underrepresentation of sea salt sulfate. However, this issue is difficult to resolve and is not addressed in this research.

A seasonal signal may also be reflected in the sulfur isotopic composition. Sea salt and biogenic sulfate have different $\delta^{34}\text{S}$ signatures, so the relative amount of SO_{4ss}^{2-} and SO_{4bio}^{2-} determines the bulk $\delta^{34}\text{S}_{\text{SO}_4}$ in an ice core. The generally accepted $\delta^{34}\text{S}$ signatures of sea salt and biogenic sulfate are 21.1‰ (Rees, 1978) and $18.6 \pm 0.9\text{‰}$ (Patris et al., 2000), respectively. Assuming that sea salt and marine biogenic activity are the only significant sulfate sources and that these $\delta^{34}\text{S}_{\text{SO}_4}$ signatures are correct, the bulk $\delta^{34}\text{S}_{\text{SO}_4}$ in an ice core should approach $\sim 21.1\text{‰}$ in the winter and $\sim 18.6\text{‰}$ in the summer. However, several studies have proposed a lower biogenic signature (Calhoun et al., 1991; Jonsell et al., 2005;

Uemura et al., 2016), and direct $\delta^{34}\text{S}_{\text{SO}_4}$ measurements of the sea ice surface in Antarctica have never been made.

If the $\delta^{34}\text{S}_{\text{SO}_4}$ value in an ice core is determined by the ratio of sea salt to biogenic sulfate, $\delta^{34}\text{S}_{\text{SO}_4}$ could theoretically be used to reconstruct changes in sea ice extent. However, because of instrument limitations due to the required sample size, earlier studies have been unable to resolve seasonal changes in $\delta^{34}\text{S}_{\text{SO}_4}$. Furthermore, two studies have suggested a background volcanic and/or stratospheric source in West Antarctica with a very low $\delta^{34}\text{S}_{\text{SO}_4}$ signature (Kunasek et al., 2010; Pruett et al., 2004). The addition of a third, unknown source could preclude the use of $\delta^{34}\text{S}_{\text{SO}_4}$ to reconstruct sea ice extent.

Both previous sulfur isotope studies from West Antarctica were conducted on the West Antarctic Ice Sheet (WAIS), and the sites were separated by < 30 miles. Therefore, it is unclear if their results are specific to that one location or ubiquitous across West Antarctica. For this research, I measured $\delta^{34}\text{S}_{\text{SO}_4}$ in an ice core from the Antarctic Peninsula. Sulfur isotope ratios had not previously been studied in this region, and the site varies greatly from WAIS. As such, it was possible that cores from the Antarctic Peninsula would not see the same third sulfate source that had been observed at WAIS, which could enable the use of $\delta^{34}\text{S}_{\text{SO}_4}$ as a sea ice proxy.

3.1.3 Foundation for a new sea ice proxy

The potential new proxy for sea ice extent depends on a sulfate system with only two end members: sea salt and biogenic emissions. This assumption is considered valid because anthropogenic sulfate does not reach Antarctica in significant quantities (Legrand, 1995), and terrestrial input is minimal (Kunasek et al., 2010). Volcanic deposition can also be avoided by measuring sulfate concentrations along the core and analyzing a section with overall lower sulfate concentrations and, therefore, only a background sulfate input. These omissions leave sea salt and marine biogenic activity as likely the sole sources of sulfate.

The proposed proxy comprises two steps: 1) isolate the sea salt source using a two-source isotope mixing equation, and 2) quantify the amount of sea salt derived from the sea ice surface based on its sulfate-to-sodium ratio, as described in Chapter 1.

Step One

First, sea salt and biogenic sulfate are calculated with the following equations:

$$\delta^{34}\text{S}_{\text{SO}_{4\text{tot}}} = \delta^{34}\text{S}_{\text{SO}_{4\text{ss}}} \cdot f_{\text{ss}} + \delta^{34}\text{S}_{\text{SO}_{4\text{bio}}} \cdot f_{\text{bio}} \quad (3.1)$$

$$f_{\text{bio}} = 1 - f_{\text{ss}} \quad (3.2)$$

$$[SO_4^{2-}]_{ss} = f_{ss} \cdot [SO_4^{2-}]_{tot} \quad (3.3)$$

$$[SO_4^{2-}]_{bio} = f_{bio} \cdot [SO_4^{2-}]_{tot} \quad (3.4)$$

where the *tot* subscript indicates the total sample, and f_{ss} and f_{bio} are the fraction of total sulfate from sea salt and marine biogenic activity, respectively.

Step Two

Once the SO_4^{2-} concentration has been quantified, the SO_4^{2-}/Na^+ mass ratio of the sample can be used to differentiate between sea salt from the sea ice surface and sea salt from the open ocean. The sulfate-to-sodium mass ratio of sea salt from seawater (ss_{ocean}) is 0.251 (Wilson, 1975). Therefore, assuming that all the sodium originates from sea salt, the expected SO_4^{2-}/Na^+ mass ratio in an ice core is ~ 0.25 . However, numerous ice cores studies have found values closer to ~ 0.1 (Table 3.1 and the references therein). This low ratio is caused by seawater fractionation during ice formation that results in sulfate-depleted sea salt on the ice surface (ss_{ice}), as detailed in Chapter 1. As a result, ss_{ocean} and ss_{ice} have different SO_4^{2-}/Na^+ ratios, also called k-values. Therefore, the total SO_4^{2-}/Na^+ in an ice core can be used to quantify the sulfate contribution of each sea salt source using the following equations:

$$k_{sam} = \frac{[SO_4^{2-}]_{ss}}{[Na^+]} \quad (3.5)$$

$$k_{sam} = k_{ice} \cdot f_{ice} + k_{ocean} \cdot f_{ocean} \quad (3.6)$$

where f_{ice} and f_{ocean} are the fraction of SO_4^{2-} from sea ice and the open ocean, respectively. For this study, k_{ice} was set at 0.1, and k_{ocean} was set at 0.25.

Equations 4 and 5 can then be combined into:

$$[SO_4^{2-}]_{ice} = f_{ice} \cdot [SO_4^{2-}]_{ss} \quad (3.7)$$

$$[SO_4^{2-}]_{ocean} = f_{ocean} \cdot [SO_4^{2-}]_{ss} \quad (3.8)$$

where $[SO_4^{2-}]_{ice}$ and $[SO_4^{2-}]_{ocean}$ are the concentration of sulfate from sea ice and the open ocean, respectively. The resulting record of $[SO_4^{2-}]_{ice}$ would reflect changes in sea ice extent. Seasonal changes in Antarctic sea ice are very large, with almost all ice fully retreating in the

Table 3.1 *Previously reported k-values in Antarctica*

Sample type	k-value	Citation
Sea ice scrapings: Weddell Sea	FYI ¹ : 0.20 ± 0.15 MYI ² : 0.17 ± 0.14 Surface snow: 0.18 ± 0.15	Frey et al., 2020
Sea ice scraping: Brunt Ice Shelf	0.0853	Rankin et al., 2000
Bulk aerosol: Halley Station	0.107	Hall and Wolff, 1998
Bulk aerosol: Halley Station, Durmont d'Urville Station, Neumayer Station	0.07	Wagenbach et al., 1998
Shallow firn: Filchner-Ronne Ice Shelf	0.049	Minikin et al., 1994

¹First-year sea ice²Multiyear sea ice

summer before reforming in the winter (Figure 3.1) (Abram et al., 2010; Curran, 2003). This large oscillation in sea ice cover provides an excellent opportunity to test the viability of this potential new sea ice proxy.

3.2 Methods

3.2.1 Description of ice core sites and sea ice samples

The Antarctic Peninsula is a promising research area because coastal ice cores most effectively record changes in the sea ice signal. Their close proximity to the ocean and relatively low elevation ensures that fewer sea salt aerosols are lost in transport, so the magnitude of the source signal is greater than in inland cores (Guelle et al., 2001; Minikin et al., 1998; Seguin et al., 2014). The seasonal signal is also stronger in coastal cores because they record local changes in sea salt aerosol emissions from the open ocean and sea ice, whereas inland cores see a wider source area (Rankin et al., 2002). Coastal cores also have higher accumulation rates that make it easier to detect and measure sub-annual fluctuations in the sea ice signal.

Multiple ice cores from the Antarctic Peninsula were available at the British Antarctic Survey (BAS), including the Bryan Coast core, Dyer Plateau core, Jurassic core, and Ferrigno

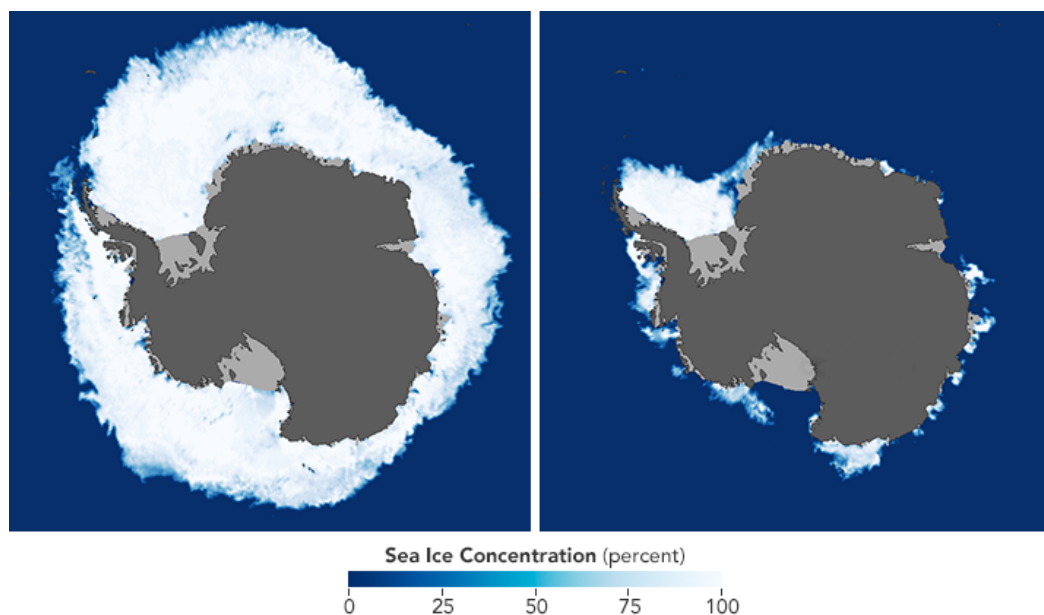


Fig. 3.1 Map showing the maximum winter (left) and minimum summer (right) Antarctic sea ice extent in the year 2015/2016. Image from *nasa.gov*.

core (Figure 3.2). The main factors when selecting a core was its proximity to the ocean and the elevation of the core site. The accumulation rate at all sites was sufficient for a high-resolution $\delta^{34}\text{S}_{\text{SO}_4}$ record, so it was not considered when selecting a core for analysis (Table 3.2).

Table 3.2 Ice cores from the Antarctic Peninsula

Core	Depth (m)	Years (CE)	Elevation (m)	Accumulation (m weq/yr)
Bryan Coast ¹	140	1712–2010	1177	0.52
Dyer Plateau ²	233	1505–1989	2002	0.44
Jurassic ³	140	1872–2011	1139	1.00
Ferrigno ¹	136	1712–2010	1354	0.46
Bruce Plateau ⁴	448	1900–2009	1976	1.84
James Ross Island ⁵	364	~14 ka ⁷ –2008	1542	0.63
Gomez ⁶	136	1855–2006	1400	1.10

¹Thomas and Abram (2016); accumulation rate averaged from 2000–2009

²E. Thomas, personal communication, 2019

³E. Thomas, personal communication, 2019; accumulation rate averaged from 2000–2001

⁴Porter et al. (2016); accumulation rate averaged from 1900–2009

⁵R. Mulvaney, personal communication, 2020; accumulation rate averaged from ~1968–2008

⁶Thomas et al. (2008); accumulation rate averaged from 1997–2006

⁷Thousand years ago

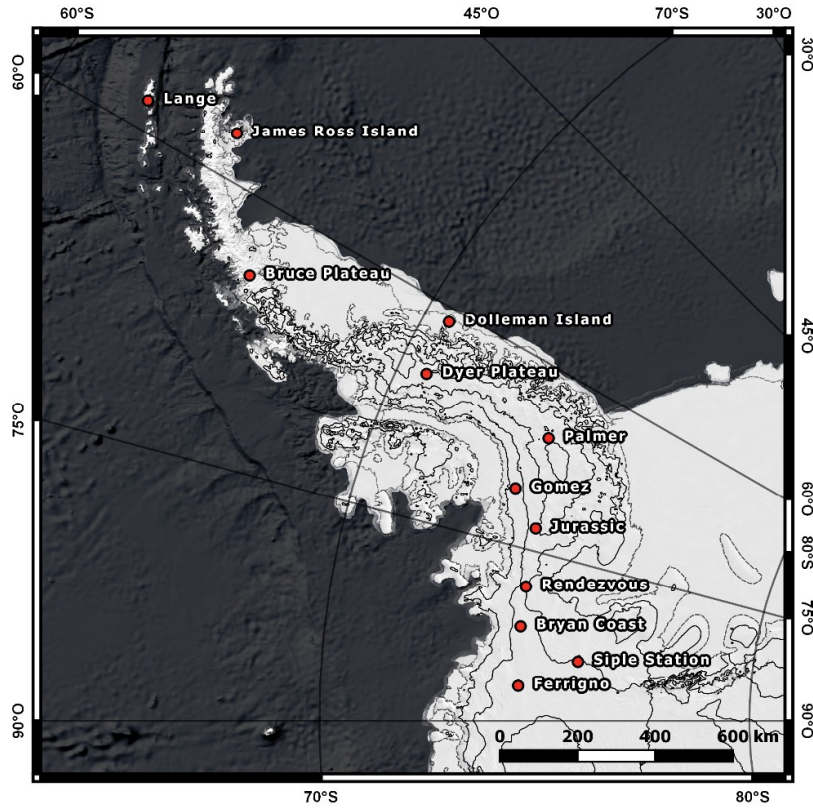


Fig. 3.2 Map of ice cores from the Antarctic Peninsula with 500 m elevation contours (D. Tetzner, personal communication, 2020). The Bryan Coast, Dyer Plateau, Jurassic, and Ferrigno cores were available for analysis at the British Antarctic Survey.

3.2.1.1 The Bryan Coast ice core

The Bryan Coast location ($74^{\circ}50'S$, $81^{\circ}68'W$) is ~ 75 km from the coast. The site has an elevation of 1177 m and an accumulation rate of 0.52 m weq/yr (meters water equivalent per year). An age scale was already complete, showing that the 140 m core spans from 1712–2010 CE.

3.2.1.2 The Dyer Plateau ice core

Dyer Plateau ($70^{\circ}39'S$, $64^{\circ}53'W$) is ~ 75 km further from the coast than the Bryan Coast site. Dyer Plateau has an elevation of 2000 m and an accumulation rate of 0.44 m weq/yr. Three meters of the Dyer Plateau ice core were available for analysis, comprising three consecutive ~ 1 m cores. The exact depth and age of the 3 m section was unknown but ranged between 35–40 m and 1937–1944 CE, respectively. Henceforth, I will refer to cores by their storage bag number: 37, 38, or 39, with numbers going from the shallowest to deepest core section. Only the bottom 22 cm of core 37 were analyzed because of time constraints.

3.2.1.3 Sea ice and frost flower samples

Samples of the sea ice surface and frost flowers were collected from various locations in the Weddell Sea by Dr Marcus Frey in 2013. If the ice was covered by snowpack, a pit was dug and sampled at 2 cm resolution, with the bottom sample scraping the sea ice surface.

3.2.2 Sample preparation

3.2.2.1 The Bryan Coast ice core

Ion chromatography of the Bryan Coast ice core had already been completed at BAS for discrete, 10 cm samples. Based on these data, two ~20-year core sections were chosen for isotope analysis, spanning 1720–1740 and 1970–1990. The chosen sections were cut from Archive 2 of the core at 10 cm resolution to correspond with the given IC data (Figure 3.3). Samples were placed in pots made of polyphenylene ether (PPE) plastic that had been cleaned in 10% HCl for 24 hours and then stored at room temperature. The samples were then weighed out into Teflon vials to obtain 30 nmol of sulfur and dried down at 80°C for column separation.

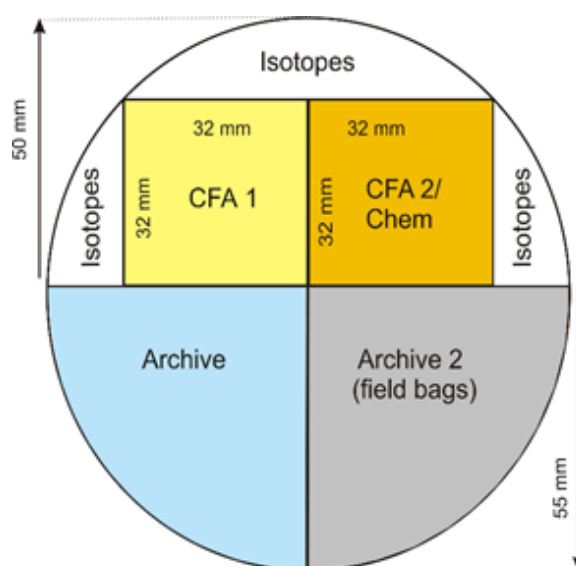


Fig. 3.3 Cross section of an ice core showing the cut plan for various analyses. Archive 2 was used for this research.

3.2.2.2 The Dyer Plateau ice core

Dyer Plateau samples were cut at 2 cm resolution from the Archive 2 section of the ice core (Figure 3.3). Samples were stored in PPE pots that had been cleaned in 10% HCl for 24 hours, and they were kept frozen until analysis. When ready, each sample was melted at room temperature and weighed to determine its exact volume. A 2 mL aliquot was taken for IC analysis, and the remaining sample was refrozen until further processing. The IC sulfate concentration data were used to calculate how many nmol of sulfate were in each sample. They were then melted at room temperature and combined as necessary to ensure enough sulfate per sample for isotope analysis. The final samples were weighed into Teflon vials to obtain 30 nmol of sulfur and dried down at 80°C for column separation. Vials had to be refilled multiple times to dry the complete volume, and all samples were kept refrigerated until the complete volume had been dried.

I preserved any seasonal sulfate signals by grouping samples in a peak or on a plateau. An example of a peak sampling pattern is shown in Figure 3.4. As a result, some samples had less than 30 nmol sulfur, and the redilution step of the column method had to be adjusted accordingly. Although not ideal, analyzing smaller samples was preferable to combining winter and summer samples and losing the seasonal signal. Some high-concentration samples had more than 30 nmol of sulfur, allowing for replicate analyses if necessary. The average sample volume was 50–60 mL, although samples from low-concentration plateaus ranged between 150–200 mL. Once combined, there were 23 Dyer Plateau samples for isotope analysis.

3.2.2.3 Sea ice and frost flower samples

Sea ice and frost flower samples had very high sulfate concentrations, and only several μL s of sample were necessary for a single measurement (Table 3.6). Each sample was diluted to ~ 800 ppb and reanalyzed via IC to confirm the sulfate concentration. Due to the high sample concentration, a direct ~ 35 μL aliquot could be taken for column separation.

3.2.3 Analytical methods

3.2.3.1 Ion chromatography

All IC analyses were completed at the British Antarctic Survey in Cambridge, England. Measurements were made with a Dionex ICS-4000 Integrion and were performed by lab technicians Jack Humby and Shaun Miller or by Isobel Rowell, a PhD student at the University of Cambridge.

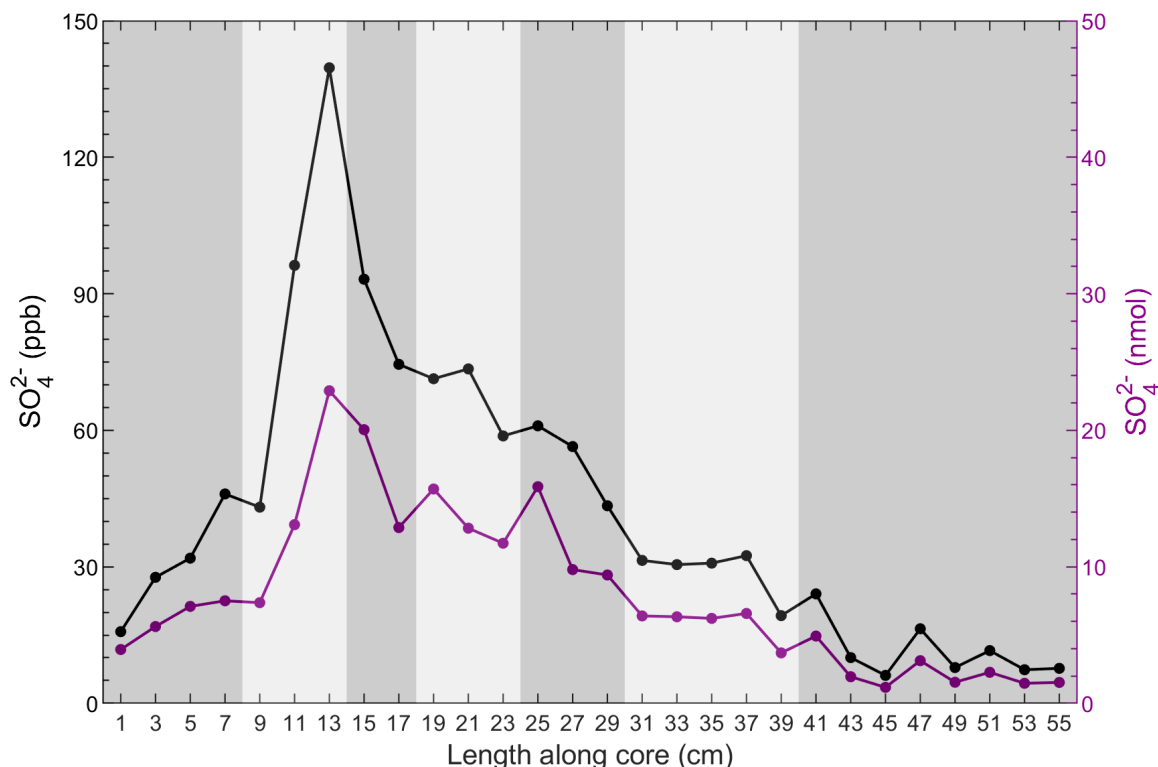


Fig. 3.4 Sampling pattern of a Dyer Plateau sulfate peak for final isotope measurements showing the sulfate concentration and calculated nmol of sulfur in each sample. Each data point is the center of a 2 cm sample that had been analyzed via IC. These samples were then combined as necessary to obtain ~ 30 nmol of sulfur per isotope sample. Grouped IC samples are designated by alternating shading.

3.2.3.2 Isotope analysis

I conducted all isotope measurements via multicollector inductively coupled mass spectrometry (MC-ICP-MS) at the University of Cambridge as outlined in Chapter 2. All measurement uncertainties are reported as 2 standard deviations (2σ).

3.3 Results: Ion chromatography

3.3.1 The Bryan Coast ice core

The Bryan Coast ice core had background SO_4^{2-} , Na^+ , and MSA concentrations of 32.9 ± 19.6 ppb, 57.3 ± 46.8 ppb, and 7.5 ± 5.0 ppb, respectively. There was no significant trend in concentrations throughout the 250-year record. In both the pre-industrial and post-industrial core sections, aligned peaks of SO_4^{2-} , MSA, and the $\text{SO}_4^{2-}/\text{Na}^+$ ratio were consistent with

a summer signal. Troughs in SO_4^{2-} , MSA, and $\text{SO}_4^{2-}/\text{Na}^+$ frequently aligned with Na^+ peaks, consistent with a winter signal (Figure 3.5). Concentration data for mid-winter and mid-summer samples are shown in Table 3.3 for both core sections.

Table 3.3 Winter and summer major ion concentrations in two sections of the Bryan Coast ice core¹

	Winter	Summer
<i>Pre-industrial core</i>		
$[\text{SO}_4^{2-}]$	13.5 ± 6.6	53.3 ± 19.4
$[\text{Na}^+]$	127.1 ± 45.7	22.0 ± 23.4
$[\text{MSA}]^2$	6.4 ± 14.3 (3.4 ± 6.62)	12.1 ± 4.9
$[\text{SO}_4^{2-}]/[\text{Na}^+]$	0.4 ± 0.2	1.9 ± 1.9
<i>Post-industrial core</i>		
$[\text{SO}_4^{2-}]$	15.9 ± 5.3	56.2 ± 19.3
$[\text{Na}^+]$	114.8 ± 60.5	34.1 ± 24.4
$[\text{MSA}]$	2.0 ± 0.9	13.0 ± 4.1
$[\text{SO}_4^{2-}]/[\text{Na}^+]$	0.3 ± 0.2	1.4 ± 1.1

¹ All concentrations reported in ppb

² Parenthetical values omit the 67.0 ppb spike in 1728 resulting from MSA migration

3.3.2 The Dyer Plateau ice core

3.3.2.1 High-resolution record with 2 cm discrete samples

The background SO_4^{2-} concentration of the Dyer Plateau ice core ranged between 12.3–130.5 ppb, with an average of 45.2 ± 54.5 ppb. The average Na^+ and MSA concentrations were 30.8 ± 43.0 ppb and 7.4 ± 5.0 ppb, respectively. There was no significant trend in the concentration data. Aligned peaks in SO_4^{2-} , MSA, and $\text{SO}_4^{2-}/\text{Na}^+$ were consistent with a summer signal, and $\text{SO}_4^{2-}/\text{Na}^+$ reached ~ 47.5 . Peaks in Na^+ showed a winter signal, but some high Na^+ concentrations also occurred during the summer. Because of the high-resolution record, peaks were detailed and variable. There were four large summer SO_4^{2-} peaks spaced every ~ 40 samples that had similar widths and ranged between 55.2–130.5 ppb. However, small SO_4^{2-} and MSA peaks were also visible during the winter (Figure 3.6). Seasonal concentration data for the Dyer Plateau core are shown in Table 3.4.

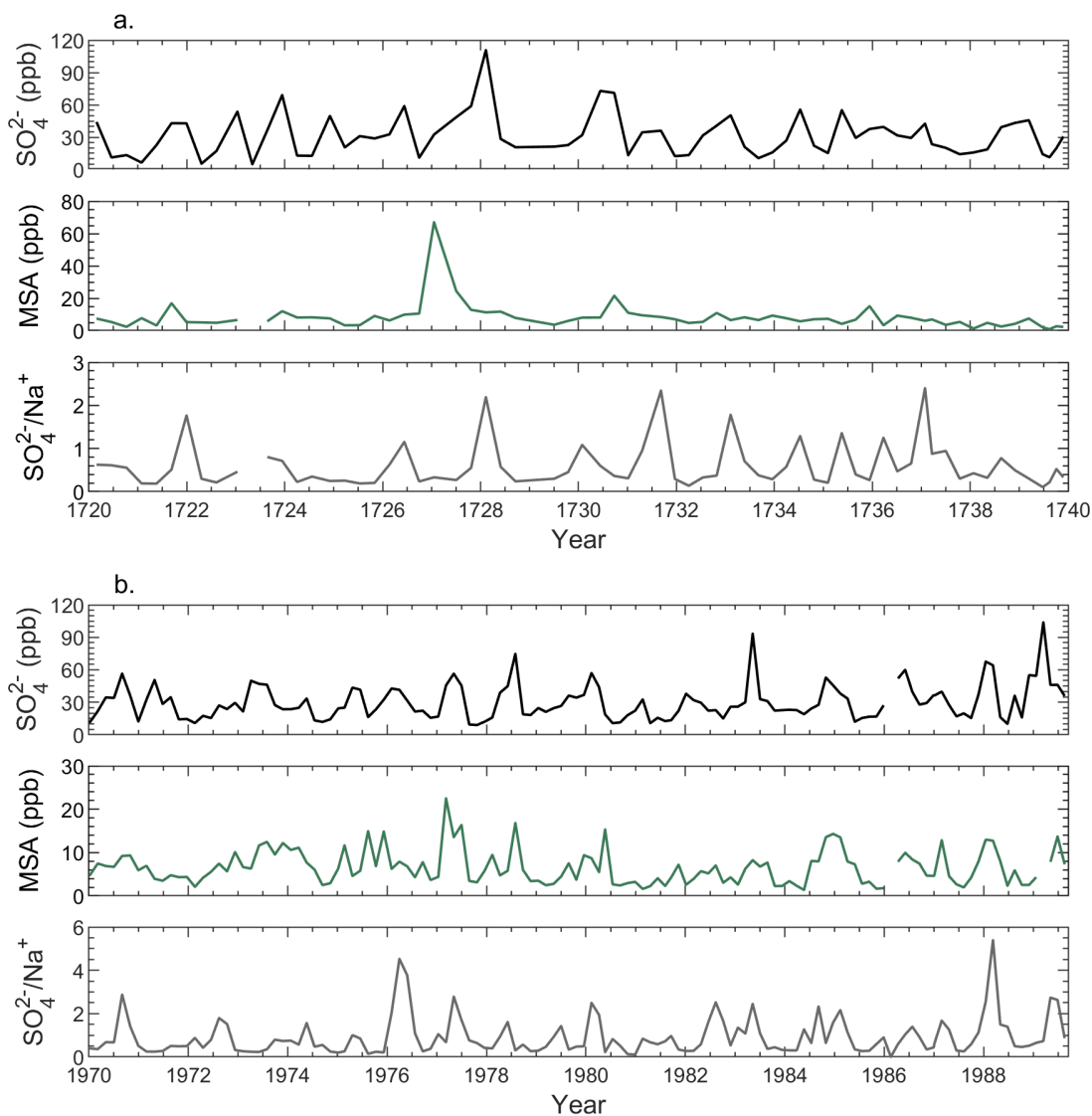


Fig. 3.5 A 20-year pre-industrial (a) and post-industrial (b) record of sulfate and MSA concentrations alongside $\text{SO}_4^{2-}/\text{Na}^+$ ratios from the Bryan Coast ice core. Peak alignment of all species shows a summer signal in both cores. In the pre-industrial core, a large MSA peak in 1728 has migrated to the lower, adjacent winter layer because of increased salt content (Osman et al., 2017).

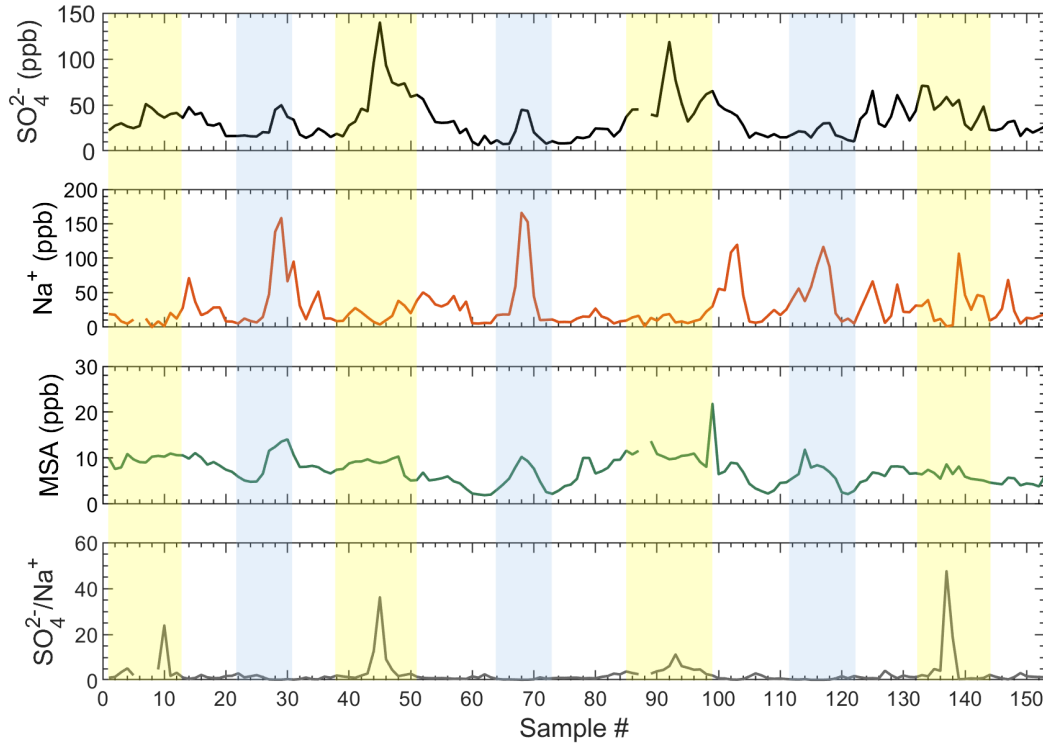


Fig. 3.6 Sulfate, sodium, and MSA concentrations alongside $\text{SO}_4^{2-}/\text{Na}^+$ ratios for a ~ 3 -meter section of the Dyer Plateau ice core. Summer and winter samples are marked with yellow and blue bars, respectively, and average seasonal values are calculated from these samples (Table 3.4). Data are plotted versus sample number and include all IC measurements, including the complete 37 core. Sample one refers to the shallowest sample, which is the first sample of core 37.

Table 3.4 Winter and summer major ion concentrations in the Dyer Plateau ice core¹

	Winter	Summer
$[\text{SO}_4^{2-}]$	15.6 ± 5.71	64.9 ± 24.5
$[\text{Na}^+]$	22.3 ± 23.1	30.7 ± 26.5
$[\text{MSA}]$	5.3 ± 2.71	9.1 ± 3.3
$[\text{SO}_4^{2-}]/[\text{Na}^+]$	1.2 ± 0.7	10.0 ± 11.7

¹All concentrations reported in ppb and calculated for winter and summer samples as shown in Figure 3.6.

3.3.2.2 Combined isotope samples

The IC record for the combined isotope samples retained the major features of the original IC record but lost a lot of detail due to the lower resolution (Figure 3.7). On average, the smoothed peaks were wider and had a lower maximum concentration. Because only the bottom 22 cm of core 37 were used for isotope analysis, the isotope IC record only shows three summer SO_4^{2-} peaks. A significant difference in the combined record was the $\sim 5\times$ decrease in the largest $\text{SO}_4^{2-}/\text{Na}^+$ values. One small winter SO_4^{2-} peak was still visible in the shallow section of the core, but the other small peak was lost. Each isotope sample was assigned a season for future analysis based on the alignment of the SO_4^{2-} , Na^+ , MSA, and $\text{SO}_4^{2-}/\text{Na}^+$ data. The spacing of the SO_4^{2-} peaks was also considered. Seasonal concentration data for the combined Dyer Plateau isotope samples are shown in Table 3.5, and individual sample data are shown in Table 3.7

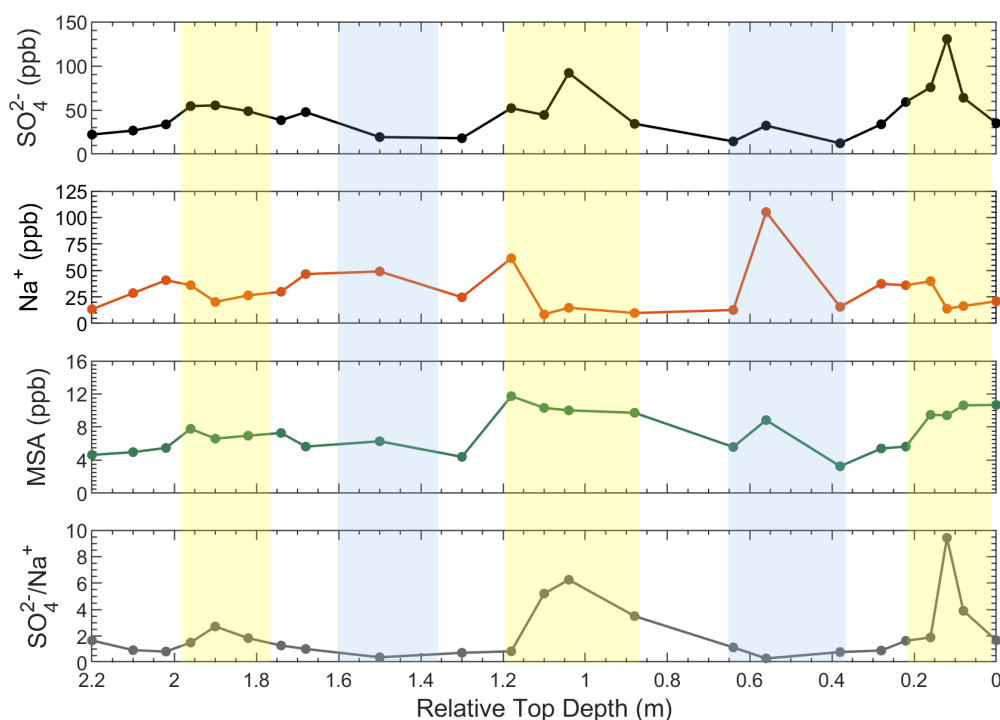


Fig. 3.7 Sulfate, sodium, and MSA concentrations alongside $\text{SO}_4^{2-}/\text{Na}^+$ ratios for the combined Dyer Plateau isotope samples. Approximate summer and winter samples are marked with yellow and blue bars, respectively. Samples are plotted against the relative top depth, defined as the distance from the top of the first core section to the top of the sample.

Table 3.5 *Winter and summer major ion concentrations of the combined Dyer Plateau isotope samples¹*

	Winter	Summer
[SO ₄ ²⁻]	22.4 ± 10.1	60.0 ± 28.2
[Na ⁺]	44.0 ± 37.4	25.8 ± 15.9
[MSA]	5.9 ± 2.0	9.1 ± 1.9
[SO ₄ ²⁻]/[Na ⁺]	0.7 ± 0.4	3.3 ± 2.6

¹All concentrations reported in ppb and calculated for designated winter and summer samples as shown in Figure 3.7.

3.3.3 Sea ice and frost flower samples

Concentration data for the sea ice and frost flower samples are shown in Table 3.6. All samples were depleted in sulfate due to seawater fractionation during ice formation, with k-values ≤ 0.15.

Table 3.6 *Major ion concentrations and k-values for sea ice and frost flower samples*

Sample	Type	SO ₄ ²⁻ (ppm) ¹	Na ⁺ (ppm) ¹	k-value
P145	Ice surface	1086.6	7077.5	0.15
P157	Ice surface	690.1	5179.0	0.13
P169	Bottom of snow pit	825.6	5751.0	0.14
P375	Frost flowers	3334.1	23233.3	0.14
P380	Frost flowers	3345.4	25856.4	0.13
P382	Frost flowers	1824.3	23053.5	0.08

¹Undiluted

3.4 Discussion: Ion chromatography

3.4.1 The Bryan Coast ice core

Overall, the Bryan Coast IC data showed the expected seasonal signals that indicated a large biogenic and low sea salt source in the summer, and a high sea salt and low biogenic source in the winter. Although significant seasonal patterns were observed in the ice core record, the winter alignment of the Na⁺ peak was not always clear. This inconsistency was likely caused by varying storm activity throughout the year because Na⁺ peaks also aligned with high chloride (Cl⁻) concentrations, confirming a sea salt source. Interestingly, an MSA peak in 1727 appeared in the winter layer because of MSA migration, which has been observed

particularly in coastal, high-accumulation ice cores (Osman et al., 2017). The mechanism of MSA migration is not fully understood but likely results from the diffusion of MSA from a high-concentration summer layer to a low-concentration winter layer, as well as the stabilization of MSA by high Na^+ concentrations in the winter layer (Mulvaney et al., 1992).

3.4.2 The Dyer Plateau ice core

3.4.2.1 Annual layer thickness

The similar width but different magnitude of the four summer SO_4^{2-} peaks suggested a different source strength but the same depositional period/season length. The summer peaks were spaced ~ 20 samples apart, indicating an annual layer thickness of ~ 80 cm and a total record of ~ 4 years. Accumulation data from 1930–1950 (R. Mulvaney, personal communication, 2020) showed that the annual layer thickness ranged from 41.0–92.5 cm and averaged 60.3 ± 13.3 cm, demonstrating that the determined layer thickness was consistent with the accumulation data.

3.4.2.2 Comparison with the Bryan Coast ice core

The higher-resolution Dyer Plateau IC records were more detailed than those of Bryan Coast. Peak shapes were more defined because narrow, high-concentration peaks were not diluted by large sample volumes. The Dyer core had a slightly greater range in SO_4^{2-} concentrations than the Bryan Coast core, at 12.3–130.5 ppb and 9.0–103.8 ppb, respectively. Also, both the average and peak SO_4^{2-} concentrations of the Dyer Plateau core were slightly higher than the Bryan Coast ice core, which was unexpected because Dyer Plateau is further from the ocean/sea ice source and at a higher altitude. However, the higher-resolution and less-smoothed Dyer record likely explains these findings.

Sodium and MSA concentrations were lower than in the Bryan Coast core, consistent with the increasing loss of MSA aerosols over long transport distances and rising elevation (Becagli et al., 2005; Savoie et al., 1992). Furthermore, MSA is depleted faster than SO_4^{2-} , which explains the low MSA but similar SO_4^{2-} concentrations in the Dyer Plateau core relative to Bryan Coast (Minikin et al., 1994). The elevation effect could also explain the higher $\text{SO}_4^{2-}/\text{Na}^+$ ratios at Dyer Plateau relative to Bryan Coast. Sea salt sulfate is depleted with increasing elevation more quickly than smaller, biogenic sulfate aerosols (Minikin et al., 1994). Therefore, in the summer, a smaller ratio of sulfate to sodium is lost during transport to Dyer Plateau than to Bryan Coast, resulting in $\text{SO}_4^{2-}/\text{Na}^+$ ratios up to $\sim 10\times$ higher.

3.4.2.3 Seasonal signals and sulfate sources

The alignment pattern of SO_4^{2-} , Na^+ , MSA, and the $\text{SO}_4^{2-}/\text{Na}^+$ ratio in the Dyer Plateau ice core showed the expected seasonality, with high biogenic and low sea salt emissions in the summer, and low biogenic and high sea salt emissions in the winter. However, the small winter SO_4^{2-} and MSA peaks were unexpected. There are two possible explanations for this observation: 1) A rise in biogenic activity resulted in increased emissions of MSA and biogenic sulfate, or 2) winter storm activity led to increased sea salt deposition in the winter, followed by MSA migration from the adjacent summer layer. The concurrent Na^+ peak and low $\text{SO}_4^{2-}/\text{Na}^+$ ratio ruled out increased biogenic emissions, supporting the second argument.

The relatively large winter $\text{SO}_4^{2-}/\text{Na}^+$ ratios suggested that sea salt may not be as dominant a source as initially thought. In the 2 cm resolution record, several winter samples had $\text{SO}_4^{2-}/\text{Na}^+$ ratios around 0.25, suggesting a predominantly sea salt source. However, each sample represented a short timespan that likely showed a single deposition event and was not representative of typical winter $\text{SO}_4^{2-}/\text{Na}^+$ values. This low sea salt source strength could result from the higher altitude of the ice core site or perhaps meteorological conditions such as wind strength and the source of the air masses that reach the plateau. Furthermore, numerous winter samples had to be combined for a single isotope measurement because of their low sulfate concentrations. As a result, the lowest $\text{SO}_4^{2-}/\text{Na}^+$ ratio in the combined isotope samples was 0.39, which could make it difficult to detect a seasonal sea ice signal.

3.5 Problems with the Bryan Coast ice core

I observed a significant number of particulates in the Bryan Coast samples after they had melted. This issue was unforeseen because ice core samples are not typically filtered, and it had not been reported in the literature (Burke et al., 2019). Personal communication with Laura Crick, a PhD student at St. Andrews University, confirmed that they do not encounter this problem when performing a similar analysis. However, research at St. Andrews focuses on high sulfate concentration volcanic signals in deep, inland ice cores. Particulates in the Bryan Coast core were likely due to its proximity to the coast. Bryan Coast samples were also frequently $> 5\times$ the volume of the volcanic samples typically used at St. Andrews, so any particulate matter became concentrated as the sample dried down. Particulates in the samples caused two problems: 1) they may have released sulfur into the samples when they were drying, and 2) the rediluted sample stuck to particulates in the dried vial, resulting in sample loss prior to column separation. Without knowing exactly how much sulfate was in the final sample, it was impossible to add the correct amount of sodium to achieve a 2:1

molar ratio of sodium-to-sulfate as described in Chapter 2. As a result, it felt too risky to use the Bryan Coast samples, and I discarded them.

These findings suggested that coastal ice cores such as Bryan Coast must be filtered prior to analysis. However, I conducted blank tests that showed a too-high sulfate contribution from the filters, so specialized pre-cleaned Teflon filters would likely have been required. I considered centrifuging as an alternative technique, but it would have been a lengthy process, and the sample would be transferred between numerous containers, creating additional opportunities for contamination. The best option was to select an ice core that was further from the coast but still recorded seasonal fluctuations in sea ice extent, such as the Dyer Plateau ice core.

3.6 Results: Isotope analysis

3.6.1 The Dyer Plateau ice core

An IAPSO seawater internal standard was analyzed every five samples during the MC-ICP-MS run to assess the accuracy of the Dyer Plateau $\delta^{34}\text{S}_{\text{SO}_4}$ measurements. The known $\delta^{34}\text{S}_{\text{SO}_4}$ of the standard was $21.16 \pm 0.11\text{‰}$ ($n = 10$), measured with the assistance of Dr Alexandra Turchyn with a Thermo Delta V gas source mass spectrometer at the University of Cambridge. The measured $\delta^{34}\text{S}_{\text{SO}_4}$ of the IAPSO seawater standard throughout the MC-ICP-MS run was 21.13‰ with an external error of $\pm 0.13\text{‰}$ ($n = 15$), agreeing with the known standard value. A procedural blank measured at the start of the run was $\sim 1\%$ of the ^{32}S signal, which was not significantly different than the solvent blank.

All $\delta^{34}\text{S}_{\text{SO}_4}$ data for the Dyer Plateau samples are shown in Table 3.7. Due to a problem during column separation and subsequent sulfate loss, several samples were only analyzed 1–2 times instead of the standard triplicate measurement. Samples 12, 13, and 21 were initially measured only once, but enough sample was left over for another measurement that was completed approximately one week after the first analysis. The reproducibility of sample measurements averaged $\pm 0.09\text{‰}$, excluding sample 9, which had an anomalously poor reproducibility of $\pm 0.35\text{‰}$.

3.6.2 Sea ice and frost flower samples

An IAPSO seawater internal standard was analyzed at the start and end of the MC-ICP-MS run. The measured $\delta^{34}\text{S}_{\text{SO}_4}$ of the standard throughout the run was 21.10‰ with an external error of $\pm 0.08\text{‰}$ ($n = 6$). Most samples were measured in triplicate, but a nebulizer clog partway through the run resulted in fewer measurements for the last two samples.

Table 3.7 Major ion concentrations and sulfur isotope data for the Dyer Plateau ice core¹

Sample	n	Relative top depth (m)	[SO ₄ ²⁻]	[Na ⁺]	[MSA]	[SO ₄ ²⁻]/[Na ⁺]	$\delta^{34}\text{S}_{\text{SO}_4}$ (‰)	2 σ^2
1	3	0	35.0	20.9	10.7	1.67	16.31	0.04
2	2	0.08	63.9	16.4	10.6	3.91	14.33	0.04
3	3	0.12	130.5	13.9	9.4	9.42	13.15	0.02
4	3	0.16	75.7	39.9	9.5	1.90	16.91	0.03
5	2	0.22	59.0	36.0	5.6	1.64	15.48	0.09
6	2	0.28	33.8	37.4	5.4	0.90	14.34	0.16
7	3	0.38	12.3	15.6	3.3	0.79	12.76	0.12
8	2	0.56	32.3	105.2	8.8	0.31	18.55	0.06
9	3	0.64	14.4	12.6	5.6	1.14	15.91	0.35
10	2	0.88	34.3	9.8	9.7	3.50	18.35	0.20
11	3	1.04	92.0	14.7	10.0	6.25	15.39	0.13
12	2 ³	1.10	44.4	8.5	10.3	5.21	17.73	0.05
13	2 ³	1.18	52.1	61.5	11.7	0.85	16.57	0.22
14	3	1.30	18.0	24.6	4.4	0.73	15.20	0.05
15	3	1.50	19.3	49.0	6.3	0.39	15.35	0.24
16	1	1.68	47.6	46.6	5.6	1.02	13.74	0.13 ⁴
17	2	1.74	38.4	29.9	7.3	1.29	16.96	0.08
18	3	1.82	48.7	26.5	7.0	1.84	18.10	0.07
19	2	1.90	55.2	20.3	6.6	2.72	17.73	0.09
20	2	1.96	54.5	36.1	7.8	1.51	16.83	0.13
21	2 ³	2.02	33.7	40.8	5.5	0.83	16.84	0.11
22	2	2.10	26.7	28.6	5.0	0.93	15.92	0.05
23	1	2.20	22.2	13.3	4.6	1.66	14.74	0.13 ⁴

¹All concentrations reported in ppb²Sample reproducibility, independent of $\pm 0.13\text{‰}$ external error³Two measurements made approximately one week apart⁴Only one measurement performed due to sample loss— external error from internal standard reported

The reproducibility of sample measurements averaged $\pm 0.13\text{‰}$, though there was more variability than expected. All isotope data are shown in Table 3.8.

Table 3.8 *Sulfur isotope data for sea ice surface and frost flower samples*

Sample	n	Type	$\delta^{34}\text{S}_{\text{SO}_4}$ (‰)	$2\sigma^1$
P145	3	Sea ice	21.10	0.05
P157	3	Sea ice	21.16	0.22
P169	3	Sea ice	21.26	0.14
P375	3	Frost flowers	21.11	0.21
P380	2	Frost flowers	21.12	0.08 ²
P382	1	Frost flowers	21.07	0.08 ³

¹Sample reproducibility, independent of $\pm 0.08\text{‰}$ external error

²Result of $2\sigma = 0.00\text{‰}$ — external error of internal standard reported

³Only one measurement performed due to nebulizer clog— external error of internal standard reported

3.7 Discussion

3.7.1 Initial assessment of sulfur isotope data

Measured $\delta^{34}\text{S}_{\text{SO}_4}$ values for the Dyer Plateau samples were lower and more variable than expected, ranging from 12.76–18.55‰. There was no strong seasonal signal, but the lowest $\delta^{34}\text{S}_{\text{SO}_4}$ values mostly occurred during the winter/spring (Figure 3.8). Assuming that sea salt and marine biogenic activity were the only significant sulfate sources, $\delta^{34}\text{S}_{\text{SO}_4}$ should have ranged between ~ 18.6 – 21.1‰ (Patris et al., 2000; Rees, 1978). The low measured $\delta^{34}\text{S}_{\text{SO}_4}$ values suggested either 1) a different sulfur isotopic composition of biogenic and/or sea salt sulfate, 2) an additional sulfate source other than sea salt and biogenic activity, or 3) some combination of the two.

3.7.2 Confirmation of sea ice and frost flower $\delta^{34}\text{S}_{\text{SO}_4}$ signatures

To confirm the sulfur isotopic composition of sea salt in ice cores, I made the first direct measurements of sea salt $\delta^{34}\text{S}_{\text{SO}_4}$ on the surface of Antarctic sea ice. The standard sea salt $\delta^{34}\text{S}_{\text{SO}_4}$ signature used in research is 21.1‰, which was determined in a laboratory study by Rees (1978). However, it was not certain that sea ice and frost flower formation did not cause fractionation of sulfur isotopes. Seguin et al. (2014) previously reported a $\delta^{34}\text{S}_{\text{SO}_4}$ value of $20.8 \pm 0.4\text{‰}$ for frost flowers in the Canadian Arctic, which was not significantly different than the $\delta^{34}\text{S}_{\text{SO}_4}$ value for sea salt found by Rees (1978). As such, it has been assumed that

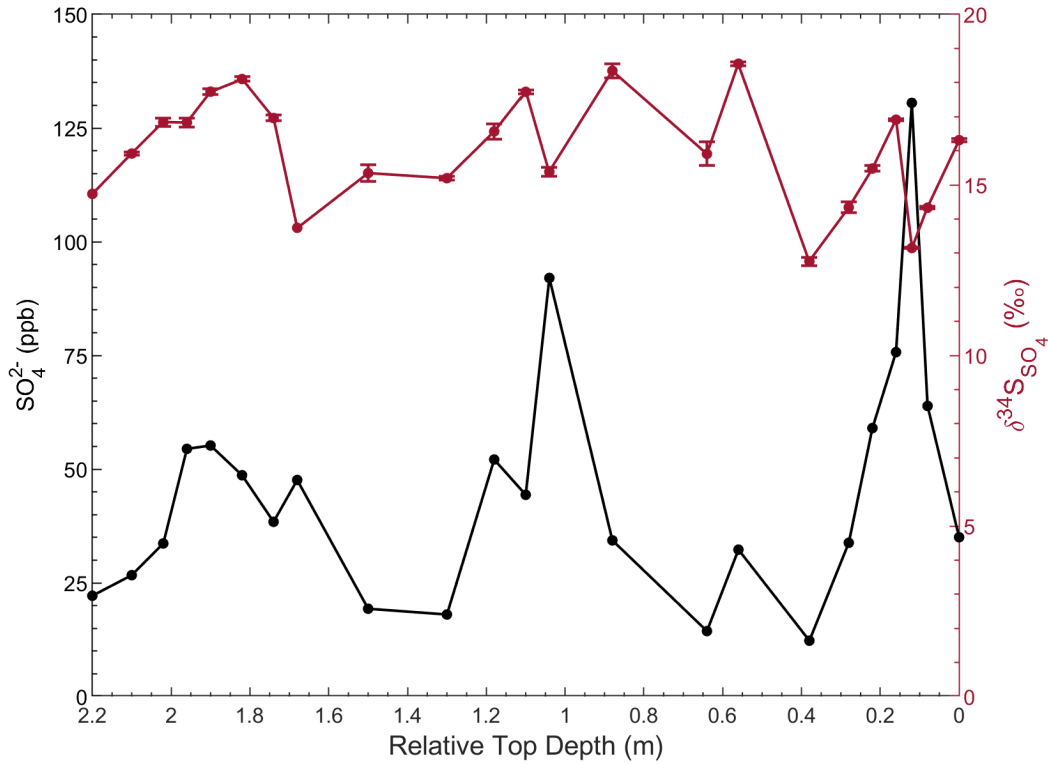


Fig. 3.8 Sulfate concentrations and $\delta^{34}\text{S}_{\text{SO}_4}$ values in the Dyer Plateau ice core. There was more variability in $\delta^{34}\text{S}_{\text{SO}_4}$ than expected, suggesting short-term deposition events. No strong seasonality in $\delta^{34}\text{S}_{\text{SO}_4}$ was clear, but lower $\delta^{34}\text{S}_{\text{SO}_4}$ values seemed to occur more in the winter/spring than in the summer.

isotopic fractionation also does not occur on Antarctic sea ice. My results confirmed that that is a valid assumption. The measured $\delta^{34}\text{S}_{\text{SO}_4}$ of frost flowers was $21.10 \pm 0.05\text{‰}$, and the measured $\delta^{34}\text{S}_{\text{SO}_4}$ of sea salt from the ice surface was $21.17 \pm 0.17\text{‰}$, both within error of the measurements by Seguin et al. (2014) and Rees (1978). Therefore, I used a sea salt $\delta^{34}\text{S}_{\text{SO}_4}$ signature of 21.1‰ for all model studies discussed in this chapter.

3.7.3 Possible scenarios to explain low $\delta^{34}\text{S}_{\text{SO}_4}$ values in the Dyer Plateau ice core

3.7.3.1 Scenario #1: A different sulfur isotopic composition of biogenic sulfate

Although the sea salt sulfate isotopic composition was confirmed, a lower sulfur isotopic composition of biogenic sulfate was still a possibility. To explore this scenario, I used a two-source isotope mixing model (Figure 3.9). Source fractions below zero or above 1 are physically impossible and arise when the measured $\delta^{34}\text{S}_{\text{SO}_4}$ is lower than the assigned

$\delta^{34}\text{S}_{\text{SO}_4}$ values of the sea salt and biogenic source. In the summer, $\delta^{34}\text{S}_{\text{SO}_4\text{bio}}$ values between 10–16‰ led to realistic solutions, but in the winter, only values between 10–13‰ produced realistic results. Based on previous studies, $\delta^{34}\text{S}_{\text{SO}_4\text{bio}}$ was unlikely to be that low, so a third sulfate source with a low sulfur isotopic composition (SO_4^{2-}) seemed more probable (Patris et al., 2000). This assumption led to two possible explanations for these results: 1) the accepted $\delta^{34}\text{S}_{\text{SO}_4\text{bio}}$ signature of 18.6‰ with a constant third source input or 2) a $\delta^{34}\text{S}_{\text{SO}_4\text{bio}}$ signature of ~ 15 –16‰ with a seasonal third source input.

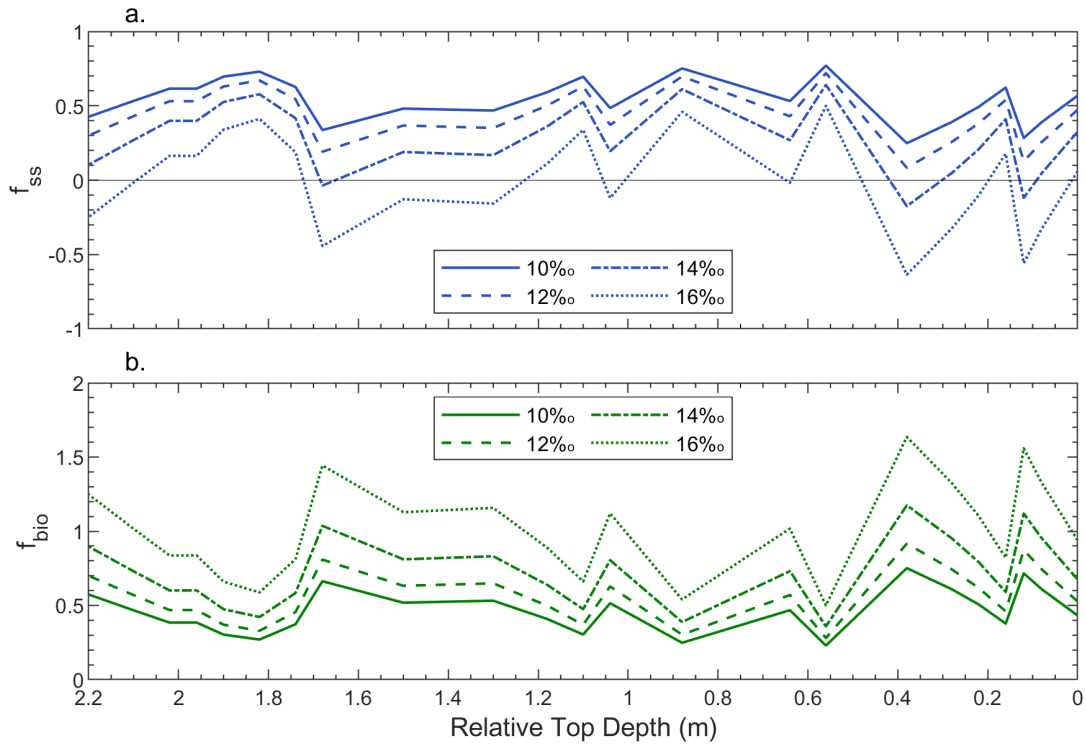


Fig. 3.9 Possible sulfate source fractions of sea salt sulfate (a) and biogenic sulfate (b) in the Dyer Plateau ice core using a two-source isotope mixing model. The plot shows results for $\delta^{34}\text{S}_{\text{SO}_4\text{bio}}$ values between 10–16‰. Biogenic $\delta^{34}\text{S}_{\text{SO}_4}$ values above ~ 13 ‰ produced negative source fractions.

3.7.3.2 Scenario #2: Constant input of a third sulfate source with a low sulfur isotopic composition

With the addition of a third, unknown sulfate source, the isotope mixing model became underconstrained, and it was not possible to quantify the three sulfate sources. Instead, I first quantified SO_4^{2-} using the Na^+ concentration and an assigned k-value and then determined f_{ss} as follows:

$$[SO_4^{2-}]_{ss} = k \cdot [Na^+] \quad (3.9)$$

$$f_{ss} = \frac{[SO_4^{2-}]_{ss}}{[SO_4^{2-}]_{tot}} \quad (3.10)$$

The biogenic and unknown source were then combined into a single, non-sea salt term (SO_{4nss}^{2-}), and the sulfur isotopic composition of SO_{4nss}^{2-} was quantified by combining and rearranging Equations 3.9 and 3.10 in a two-source isotope mixing model as below:

$$\delta^{34}S_{SO_{4nss}} = \frac{\delta^{34}S_{SO_{4tot}} \cdot [SO_4^{2-}]_{tot} - \delta^{34}S_{SO_{4ss}} \cdot k \cdot [Na^+]}{[SO_4^{2-}]_{tot} - k \cdot [Na^+]} \quad (3.11)$$

For the initial calculation of $[SO_4^{2-}]_{ss}$ and f_{ss} , the k -value was set between 0.1–0.25 (Figure 3.10). As expected, the k -value greatly affected the fraction attributed to the sea salt source, resulting in a $\sim 50\%$ spread in f_{ss} values. In the subsequent calculation of $\delta^{34}S_{SO_{4nss}}$, the k -value had minimal impact in the summer but could change the winter $\delta^{34}S_{SO_{4nss}}$ value by $\sim 10\%$. This result suggested a potential seasonality in the k -value, which would be consistent with the different SO_4^{2-}/Na^+ ratios of sea salt from the open ocean and sea salt from sea ice. As such, I needed to impose seasonality on the k -value instead assuming that it was constant.

3.7.3.3 Implementing a seasonal k -value based on the p-TOMCAT chemical transport model

I determined a seasonal k -value using the p-TOMCAT chemical transport model, which is detailed in Rhodes et al. (2018). The model was run with the assistance of Dr Mackenzie Grieman, a postdoctoral researcher at the University of Cambridge. The p-TOMCAT model determined the amount of ss_{ice} and ss_{ocean} that reached Dyer Plateau. The model was run for the years 1998–2000 with monthly resolution. I then determined a seasonal k -value by assigning a value of 0.25 and 0.1 to ss_{ocean} and ss_{ice} , respectively, and calculating the weighted average based on the model output. Results were grouped by season, with summer defined as December, January, and February; fall defined as March, April, and May; winter defined as June, July, August; and spring defined as September, October, and November. The parameterizations used for the sea salt source strengths have been validated by field experiments (Frey et al., 2020), and the model does a reasonable job of replicating the

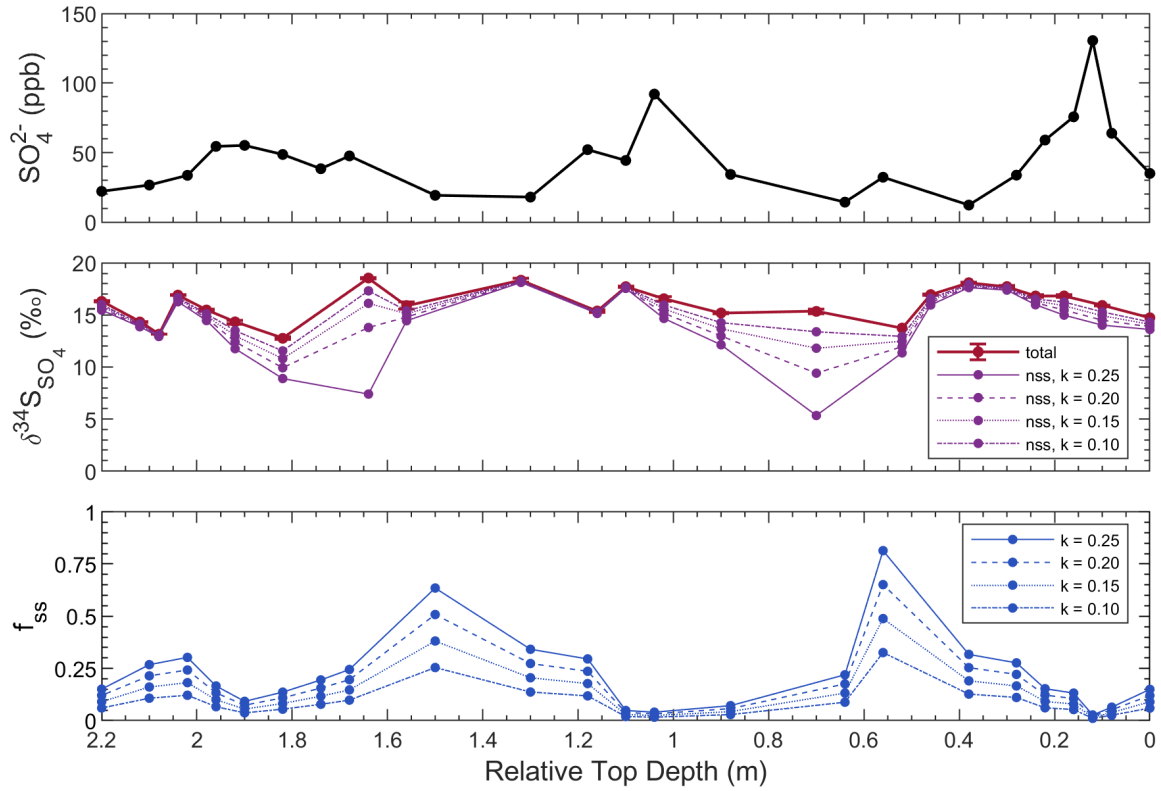


Fig. 3.10 Sulfate concentrations and total $\delta^{34}\text{S}_{\text{SO}_4}$ values in the Dyer Plateau isotope samples. The sea salt source fraction was calculated with k -values ranging between 0.10–0.25, and $\delta^{34}\text{S}_{\text{SO}_4\text{nss}}$ was then calculated using a two-source isotope mixing model. The k -value had a significant effect on winter f_{ss} and $\delta^{34}\text{S}_{\text{SO}_4\text{nss}}$ values but a minimal effect in the summer, suggesting seasonality in the k -value.

concentrations and seasonality of sea salt aerosols at Antarctic sampling sites (Levine et al., 2014; Yang et al., 2019).

Another method to determine the seasonal k -value was to calculate back trajectories and determine the source of air masses reaching Dyer Plateau. These trajectories could then be superimposed on maps showing the sea ice extent at that time to determine how long the air mass travelled over the open ocean compared to sea ice. Based on this ratio, each trajectory would be assigned a k -value between 0.1 and 0.25. A total k -value for Dyer Plateau would then be calculated as the weighted average based on the relative strength of each trajectory.

I initially attempted this technique using the HYSPLIT atmospheric model from the National Oceanic and Atmospheric Administration (NOAA) (Figure 3.11). Back trajectories were clustered by season and compared to satellite images of Antarctic sea ice extent. For a rough estimate, k -values were assigned to each cluster instead of individual trajectories.

A seasonal k-value for Dyer Plateau was then calculated as described in the preceding paragraph.

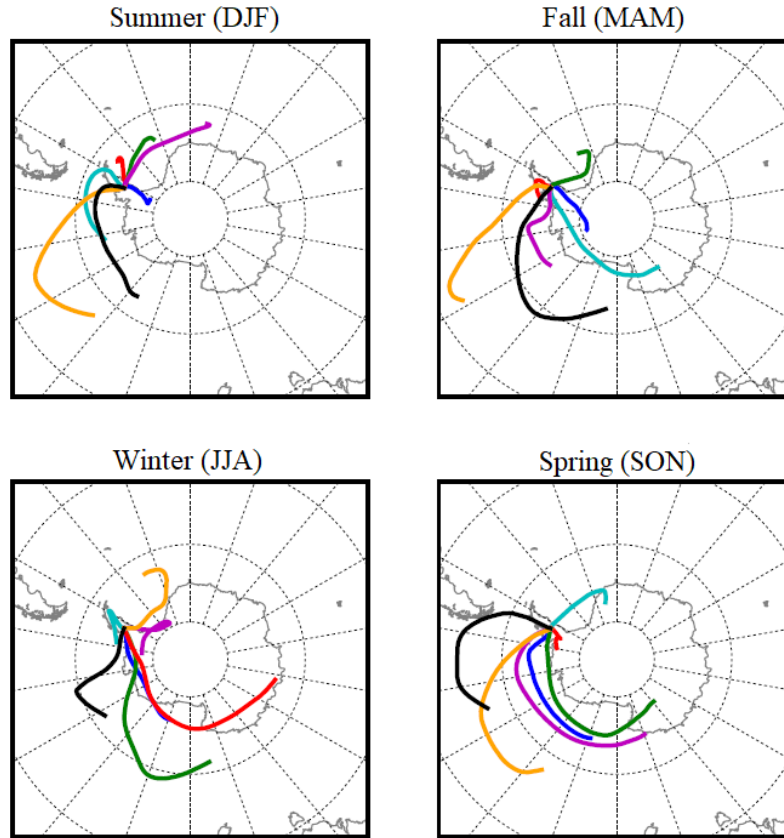


Fig. 3.11 Ten-day back trajectories for the Dyer Plateau ice core determined using the HYSPLIT model and clustered by season. Colors are randomly assigned.

Each method had its own advantages and drawbacks. For example, the p-TOMCAT model has poor spatial resolution when determining the source region of the sea salt and the deposition location. Also, the model does not resolve the mountainous topography of the Antarctic Peninsula, which could result in significant loss of sea salt before the air mass reaches Dyer Plateau due to increased precipitation as the air mass rises. However, the model explicitly calculates sea salt emission fluxes and gives greater weight to local, short-term transport that would have the greatest impact on sea salt deposition. This approach likely provided a better estimate of ss_{ice}/ss_{ocean} than back trajectories, which are more certain about the source of the air masses reaching Dyer Plateau but do not contain any information about their sea salt content. Therefore, I had to make a qualitative estimate of the sea salt content based on the path of each trajectory. However, this estimate did not account for the height of the air mass relative to the ocean or sea ice surface, nor for the distance from the source to

Table 3.9 *Calculated seasonal k-values for the Dyer Plateau ice core*

	Winter	Spring	Summer	Fall
p-TOMCAT	0.16	0.14	0.23	0.22
Back trajectories	0.13	0.12	0.20	0.19

the deposition site, both of which would impact how much sea salt is lifted and transported to Dyer Plateau. Lastly, back trajectories and the p-TOMCAT model are both limited by their dependence on modern data to reconstruct past scenarios. For my research, the source of the air mass reaching Dyer Plateau was less important than the ratio of ss_{ice}/ss_{ocean} , so the p-TOMCAT model was the preferable choice. The final seasonal k-values from each method are shown in Table 3.9.

Although I used the p-TOMCAT result in my research, I also evaluated the back trajectory k-values to quantify the differences between these approaches. The back trajectory results led to a 20% increase in total sea ice cover compared to the p-TOMCAT model. I also evaluated both k-values in a three-source model to quantify sea salt sulfate, biogenic sulfate, and the third sulfate source. The sulfur isotopic composition of SO_{4other}^{2-} ranged between 0–5‰ based on the average sulfur isotopic composition of volcanic/stratospheric sulfate (Burke et al., 2019; Castleman et al., 1974; Patris et al., 2000).

The greatest difference in the source output occurred in winter, when the back trajectory method led f_{ss} to decrease $\sim 5\%$, f_{bio} to increase $\sim 6\%$, and f_{other} to decrease $\sim 1\%$. The details of this mixing model and the selection of the $\delta^{34}S_{SO_{4other}}$ values are discussed at length in the following sections. The general takeaway of this comparison was that, although the p-TOMCAT results were preferable, using the back trajectory k-values did not significantly alter my final interpretation. However, these findings highlighted the uncertainty in the final source partitioning caused by the uncertainty in the seasonal k-value.

When calculated with seasonal k-values, $\delta^{34}S_{SO_{4nss}}$ averaged $14.87 \pm 2.0\%$, ranging between 10.64–18.23‰. These $\delta^{34}S_{SO_{4nss}}$ values were similar to the total $\delta^{34}S_{SO_4}$ in the summer but were 0.85–3.94‰ lower than total $\delta^{34}S_{SO_4}$ in winter (Figure 3.12).

Once $\delta^{34}S_{SO_{4nss}}$ had been determined, biogenic sulfate and the third sulfate source needed to be separated and quantified. Based on the minimal terrestrial input in West Antarctica (Kunasek et al., 2010) and the findings of previous sulfate source studies (Patris et al., 2000; Pruetz et al., 2004; Uemura et al., 2016), I considered SO_{4other}^{2-} to be likely volcanic and/or stratospheric in origin. However, Alexander et al. (2003) has asserted that the third sulfate source cannot be stratospheric based on the lack of mass-independent fractionation (MIF) in $\delta^{33}S_{SO_4}$ measurements in the Dome C ice core. The MIF signal may have been lost because

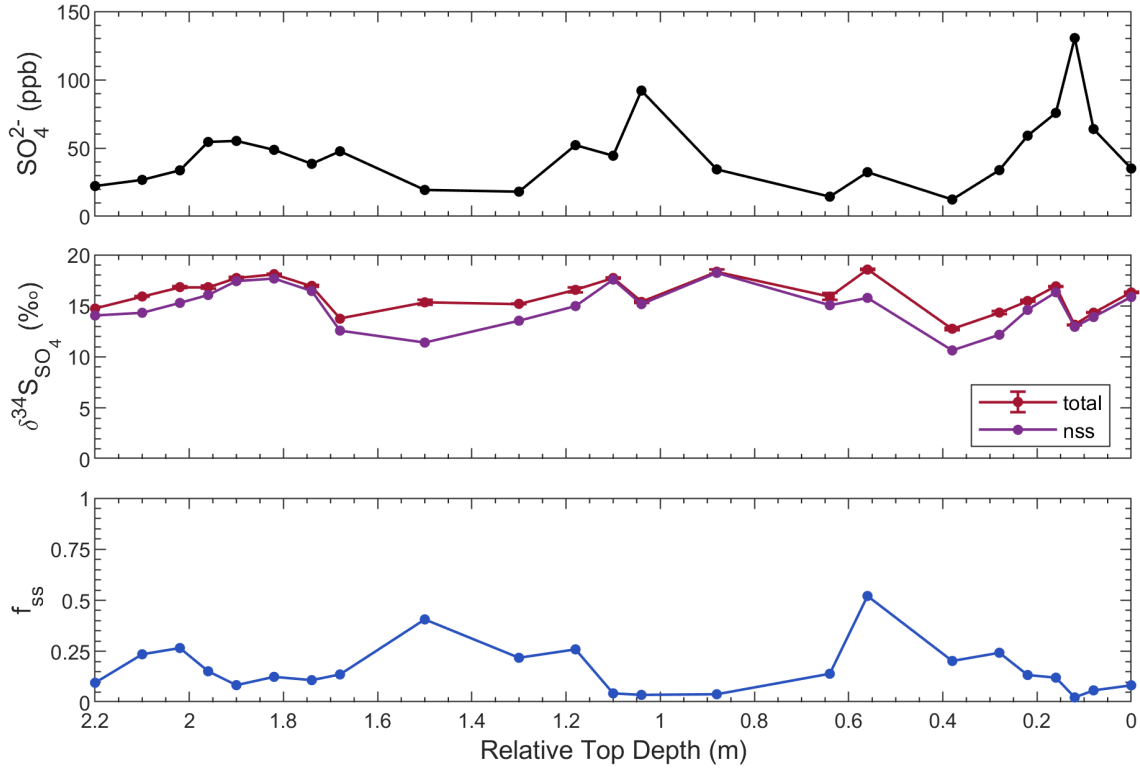


Fig. 3.12 Sulfate concentrations and $\delta^{34}S_{SO_4}$ values of the Dyer Plateau isotope samples. The sea salt source fraction was calculated with seasonal k -values, and $\delta^{34}S_{SO_{4nss}}$ was then calculated using a two-source isotope mixing model.

the large sample volume caused negative and positive MIF values to cancel each other out (e.g., Burke et al., 2019). However, the possibility of a non-volcanic/stratospheric origin could not be ruled out.

The biogenic and third sulfate source were isolated by adapting Equations 3.1–3.4 as follows:

$$\delta^{34}S_{SO_{4nss}} = \delta^{34}S_{SO_{4bio}} \cdot fnss_{bio} + \delta^{34}S_{SO_{4other}} \cdot fnss_{other} \quad (3.12)$$

$$fnss_{bio} = 1 - fnss_{other} \quad (3.13)$$

$$[SO_4^{2-}]_{bio} = fnss_{bio} \cdot [SO_4^{2-}]_{nss} \quad (3.14)$$

$$[SO_4^{2-}]_{other} = fnss_{other} \cdot [SO_4^{2-}]_{nss} \quad (3.15)$$

where f_{nss} represents the fraction of non-sea salt sulfate rather than total sulfate.

To solve Equations 3.12–3.15, a two-source isotope mixing model was run over a range of $\delta^{34}\text{S}_{\text{SO}_4\text{other}}$ values. For the first model attempt, $\delta^{34}\text{S}_{\text{SO}_4\text{other}}$ ranged between -5 – 10 ‰ based on the range of literature values for the sulfur isotopic composition of volcanic sulfate (Nielsen et al., 1991). Despite this large range, average volcanic $\delta^{34}\text{S}_{\text{SO}_4}$ values are between 0 – 5 ‰ (Burke et al., 2019; Patris et al., 2000), and stratospheric sulfate has a $\delta^{34}\text{S}_{\text{SO}_4}$ signature of 2.6 ‰ (Castleman et al., 1974). However, I initially evaluated a wider range of isotopic compositions to observe all possible outcomes for source partitioning. Although the primary goal was to assess f_{other} with a $\delta^{34}\text{S}_{\text{SO}_4\text{bio}}$ signature of 18.6 ‰, the model was also run for $\delta^{34}\text{S}_{\text{SO}_4\text{bio}}$ values between 15 – 20 ‰ to explore a potentially different biogenic signature (Figure 3.13).

The model showed that a $\delta^{34}\text{S}_{\text{SO}_4\text{bio}}$ signature < 18.3 ‰ produced negative f_{other} values. A $\delta^{34}\text{S}_{\text{SO}_4\text{bio}}$ signature of 18.6 ‰ produced realistic f_{other} values between 0 – 1 ; however, this scenario required a large input of SO_4^{2-} in the winter. For example, when $\delta^{34}\text{S}_{\text{SO}_4\text{other}}$ was -5 ‰ and 10 ‰, the minimum winter f_{other} value was 22.0% and 60.5% , respectively. In summer, f_{other} decreased dramatically to $< 5\%$. One possible explanation for this overall large third sulfate source was local volcanic emissions. However, regional volcanic activity is limited, with only two known active volcanoes in Antarctica: Mt. Erebus and Deception Island. It seemed unlikely that these sources could be solely responsible for such a large background sulfate concentration.

Another argument against local volcanism was the seasonality in third source deposition, which is consistent with a stratospheric source. Modeling studies and direct measurements in Antarctica have shown increased stratospheric input in the winter (Fourre et al., 2006; Walters et al., 2019). Stratospheric sulfate can come from large, primarily tropical volcanic eruptions that distribute sulfate globally (Burke et al., 2019; McConnell et al., 2017; Sigl et al., 2013). However, the lifetime of stratospheric volcanic sulfate is ~ 1 – 2 years, so the background stratospheric volcanic contribution would be limited (Burke et al., 2019; Toohey et al., 2019).

Another significant source of stratospheric sulfate is carbonyl sulfide (COS), which is the most abundant sulfur gas in the atmosphere (Barkley et al., 2008; Brühl et al., 2012; Mihalopoulos et al., 1991). Carbonyl sulfide is emitted primarily from the ocean as well as volcanoes and wetland regions (Kettle et al., 2002; Kuai et al., 2014)). This compound is transported to the stratosphere where it is exposed to ultraviolet light and undergoes photodissociation to form sulfate (Crutzen, 1976). Stratospheric sulfate also arises from homogenous nucleation near the tropical tropopause, where it then enters the stratosphere and

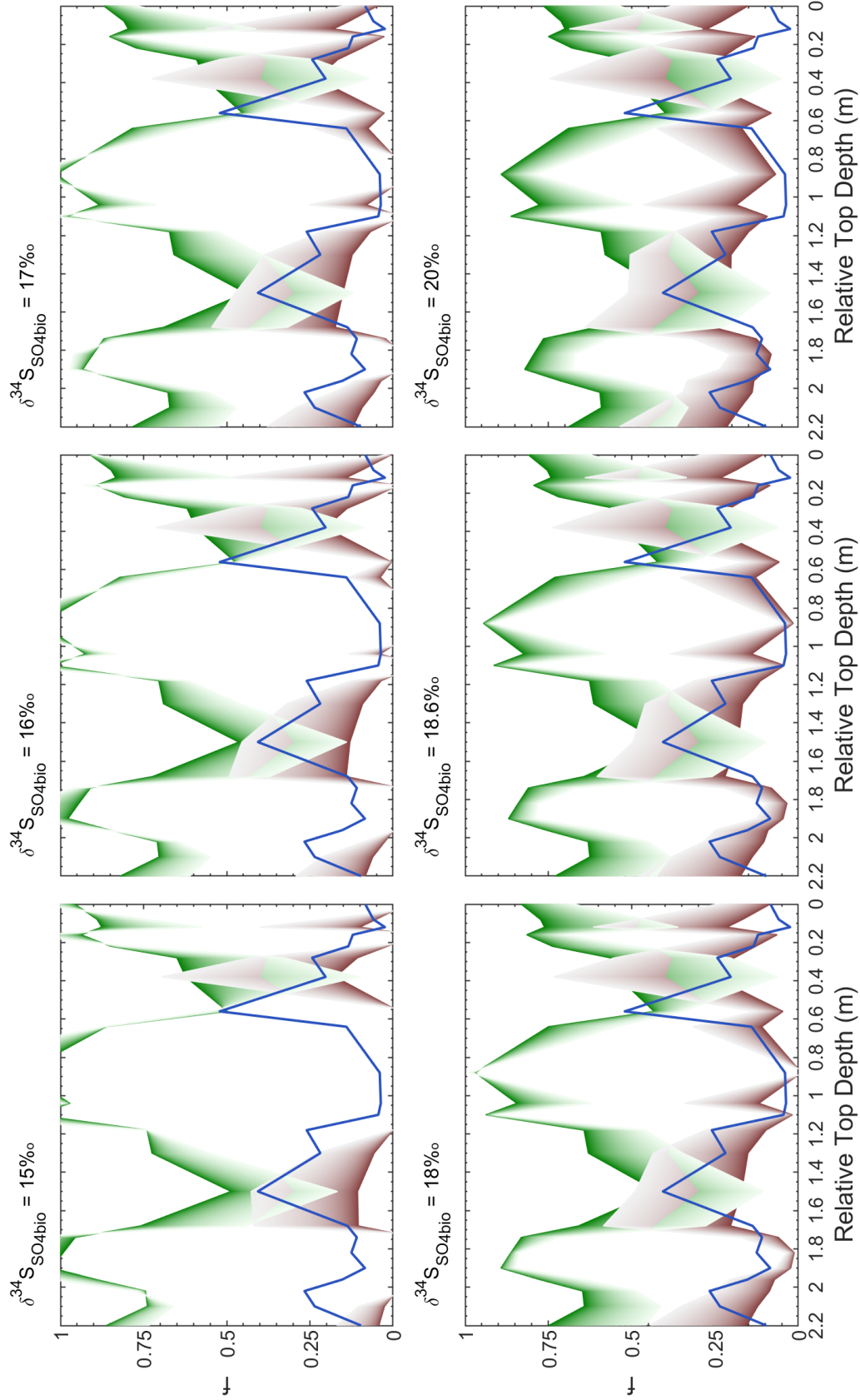


Fig. 3.13 Possible sulfate source fractions of sea salt sulfate (blue), biogenic sulfate (green), and a third sulfate source (brown). The sea salt fraction was calculated with seasonal k -values, and f_{bio} and f_{other} were then quantified with a two-source isotope mixing model. Values for $\delta^{34}\text{S}_{\text{SO}_4\text{other}}$ ranged between -5 – 10 ‰, and the model was run for $\delta^{34}\text{S}_{\text{SO}_4\text{bio}}$ values between 15 – 20 ‰. Model output colors go from dark to light for low to high $\delta^{34}\text{S}_{\text{SO}_4\text{other}}$ values.

disperses towards the high latitudes (Brock et al., 1995; Hamill et al., 1997). In Antarctica, stratospheric sulfate is preferentially deposited in the winter because of the strong polar vortex (Hamill et al., 1997), which could explain the larger third sulfate source in the winter. Overall, the most likely origin of $\text{SO}_{4\text{other}}^{2-}$ is a combination of these processes. Local volcanism could explain the low, year-round background sulfate, with an overlaying winter input of stratospheric sulfate aerosols. Even with this consideration, given the model suggested that this source would be 22.0–60.5% of total sulfate, this seemed rather high.

Various percentages of volcanic/stratospheric sulfate have been reported in East and West Antarctica. In East Antarctica, numerous studies found a volcanic/stratospheric sulfate source of ~10–30% total sulfate based on a stratospheric and volcanic $\delta^{34}\text{S}_{\text{SO}_4}$ signature of ~2‰ and 0–5‰, respectively (Jonsell et al., 2005; Uemura et al., 2016). In West Antarctica, Kunasek et al. (2010) proposed a 72–90% volcanic/stratospheric sulfate source based on a combined volcanic/stratospheric $\delta^{34}\text{S}_{\text{SO}_4}$ signature of -2–2‰.

Overall, the third sulfate source at Dyer Plateau was more similar to the proposed volcanic/stratospheric source in East Antarctica, although the West Antarctica results are based on a single location. These previous studies offered some validation for the higher-than-expected f_{other} values calculated over the lower range of $\delta^{34}\text{S}_{\text{SO}_{4\text{other}}}$ values. However, the large f_{other} values for higher $\delta^{34}\text{S}_{\text{SO}_{4\text{other}}}$ values did not seem realistic. Furthermore, because the seasonality of the source suggested stratospheric input, a $\delta^{34}\text{S}_{\text{SO}_{4\text{other}}}$ signature closer to ~2.6‰ was probable. Therefore, I constrained $\delta^{34}\text{S}_{\text{SO}_{4\text{other}}}$ to 0–5‰ for subsequent model runs, based on the common sulfur isotopic composition of volcanic/stratospheric sulfate. This narrower range also enabled a better comparison with earlier studies, which used similar values. A $\delta^{34}\text{S}_{\text{SO}_{4\text{other}}}$ value of 5‰ still required a large winter $\text{SO}_{4\text{other}}^{2-}$ contribution of 38.2% of total sulfate. However, these findings were based on a $\delta^{34}\text{S}_{\text{SO}_{4\text{bio}}}$ signature of ~18‰, and a lower $\delta^{34}\text{S}_{\text{SO}_{4\text{bio}}}$ signature would require less $\text{SO}_{4\text{other}}^{2-}$ input.

3.7.3.4 Scenario #3: A lower sulfur isotopic composition of biogenic sulfate and a seasonal third sulfate source

The initial model showed strong seasonality in the third sulfate source, with a large contribution in the winter and a small contribution in the summer. Because of the low sulfur isotopic composition of the third source, $\delta^{34}\text{S}_{\text{SO}_{4\text{bio}}}$ would have to be $\geq 18.3\text{‰}$ to avoid a negative input of $\text{SO}_{4\text{other}}^{2-}$ in the summer. However, this high $\delta^{34}\text{S}_{\text{SO}_{4\text{bio}}}$ value then required a large input of $\text{SO}_{4\text{other}}^{2-}$ in the winter and early spring. Based on this observation, a lower $\delta^{34}\text{S}_{\text{SO}_{4\text{bio}}}$ signature could be possible if the summer input of $\text{SO}_{4\text{other}}^{2-}$ was set to zero. The lower $\delta^{34}\text{S}_{\text{SO}_{4\text{bio}}}$ signature would then decrease the necessary winter input of $\text{SO}_{4\text{other}}^{2-}$ to a more moderate value.

I tested this hypothesis by establishing different three-source models for winter/spring samples and summer/fall samples. In the summer/fall, a two-source isotope mixing model was used to quantify sea salt and biogenic sulfate. In the winter/spring, sea salt sulfate was first calculated with seasonal k-values, and biogenic sulfate and the third sulfate source were then quantified using a two-source isotope mixing model. The model $\delta^{34}\text{S}_{\text{SO}_4\text{other}}$ values now ranged between 0–5‰, and the model was run for $\delta^{34}\text{S}_{\text{SO}_4\text{bio}}$ values between 15–17‰ (Figure 3.14).

Results showed that it was not possible to use a two-source isotope mixing model for the summer/fall samples because it caused a large sea salt peak in the summer. This result made sense considering the originally measured summer $\delta^{34}\text{S}_{\text{SO}_4}$ values at those points were higher than the assigned $\delta^{34}\text{S}_{\text{SO}_4\text{bio}}$ value. Interestingly, the summer sample at 1.09 m did roughly match the calculated f_{ss} value, suggesting strictly a biogenic and sea salt sulfate source. This result could be due to short-term deposition of SO_4^{2-} in the summer that does not affect all samples. Another way to approach the summer samples was to calculate f_{ss} and f_{bio} using seasonal k-values instead of a two-source isotope mixing model (Figure 3.15). As expected, these results did not have the winter sea salt peaks and showed a clear seasonal signal in all sources. With this method, however, the summer source contributions were not an accurate reconstruction because they did not satisfy the isotope data, so there was clearly a third source affecting the summer/fall samples.

3.7.4 Final characterization of sulfate sources at Dyer Plateau

All model results suggested that there is a third sulfate source at Dyer Plateau that has a low sulfur isotopic composition and may be of volcanic/stratospheric origin. Calculated $\delta^{34}\text{S}_{\text{SO}_4\text{bio}}$ values agreed with the $\delta^{34}\text{S}_{\text{SO}_4\text{bio}}$ signature of $18.6 \pm 0.9\text{‰}$ reported by Patris et al. (2000). Although higher $\delta^{34}\text{S}_{\text{SO}_4\text{bio}}$ values also produced realistic model results, they required an even larger input of SO_4^{2-} , which seemed unlikely. Furthermore, the $\sim 18\text{‰}$ $\delta^{34}\text{S}_{\text{SO}_4\text{bio}}$ signature agreed with the sulfur isotopic composition of MSA, which has been measured at $17.4 \pm 0.4\text{‰}$ (Sanusi et al., 2006). Both MSA and SO_4^{2-} are produced by the oxidation of DMS. If there is no isotopic fractionation during formation, the $17.4 \pm 0.4\text{‰}$ $\delta^{34}\text{S}$ of MSA could serve as an additional constraint on the sulfur isotopic composition of biogenic sulfate. Based on these considerations, a final three-source model was run with $\delta^{34}\text{S}_{\text{SO}_4\text{bio}}$ set to 18.6‰ (Figure 3.16).

Final model results showed realistic source fractions between 0–1 for all sources. Average seasonal source inputs are shown in Table 3.10. Biogenic activity was the primary source of sulfate to the ice in both summer and winter. The sea salt sulfate fraction was greater than the biogenic fraction for two late-winter/early-spring samples (0.56 m and 1.5 m); however, the

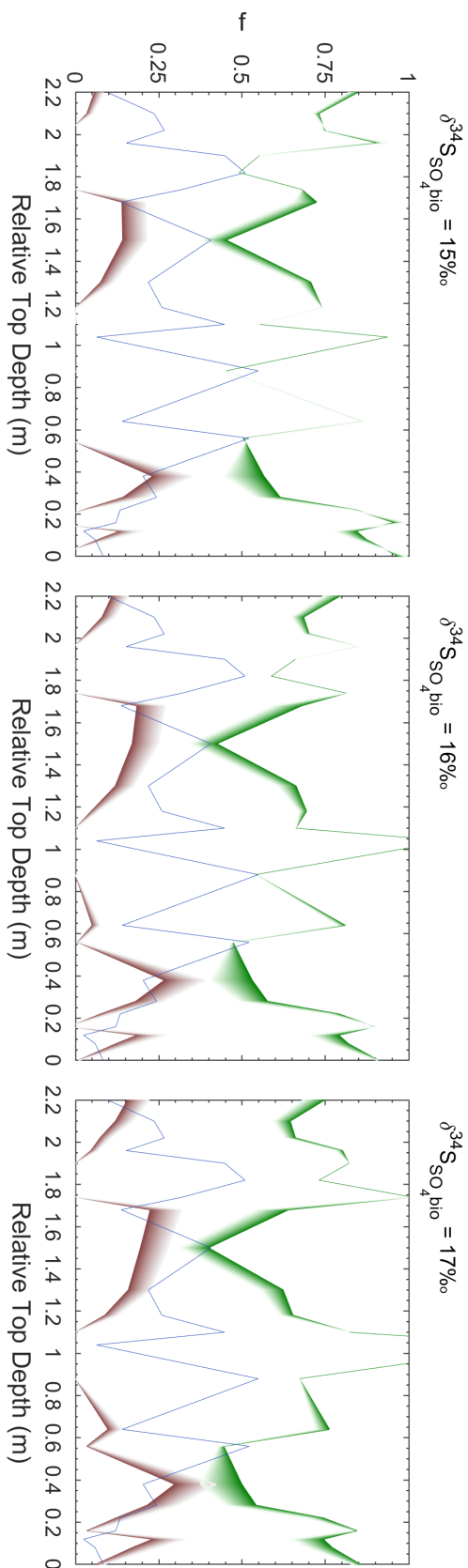


Fig. 3.14 Possible sulfate source fractions of sea salt sulfate (blue), biogenic sulfate (green), and the third sulfate source (brown). Third source input was limited to winter/spring samples. For summer samples, f_{ss} and f_{bio} were quantified using a two-source isotope mixing model. For winter samples, f_{ss} was quantified using seasonal k -values, and f_{bio} and f_{other} were then quantified using a two-source isotope mixing model. Values for $\delta^{34}\text{S}_{\text{SO}_4 \text{ other}}$ ranged between 0–5‰, and the model was run for $\delta^{34}\text{S}_{\text{SO}_4 \text{ bio}}$ values between 15–17‰. Model output colors go from dark to light for low to high $\delta^{34}\text{S}_{\text{SO}_4 \text{ other}}$ values.

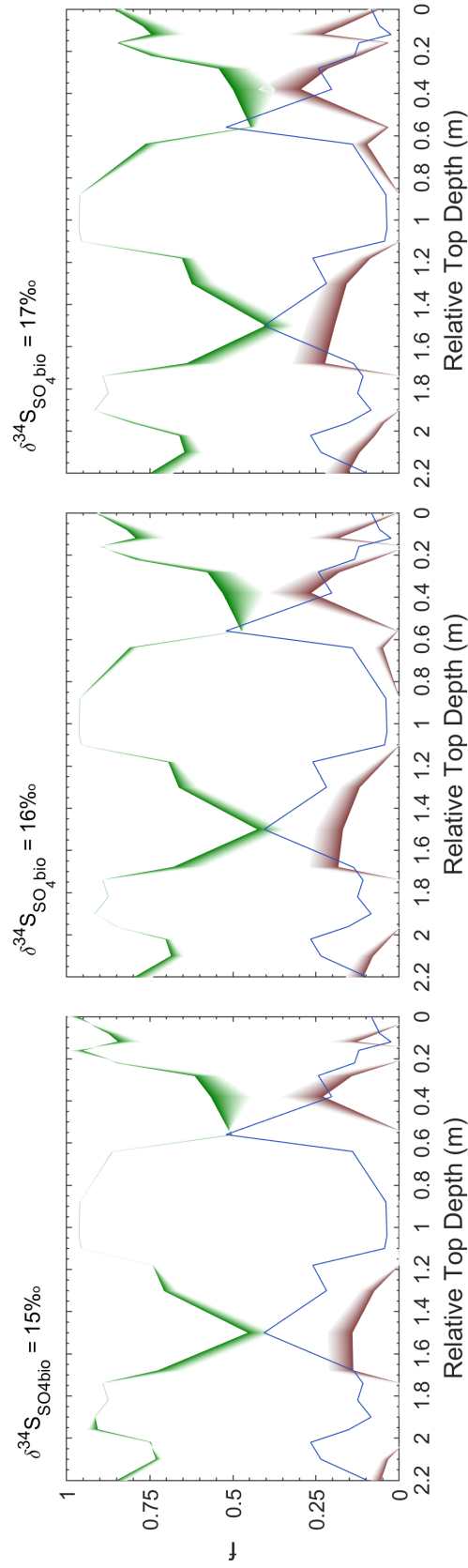


Fig. 3.15 Possible sulfate source fractions of sea salt sulfate (blue), biogenic sulfate (green), and the third sulfate source (brown). Third source input was limited to winter/spring samples. The sea salt sulfate fraction was calculated using seasonal k -values for the entire ice core record. For winter samples, f_{bio} and f_{other} were then quantified using a two-source isotope mixing model. Values for $\delta^{34}\text{S}_{\text{SO}_4\text{other}}$ ranged between 0–5‰, and the model was run for a $\delta^{34}\text{S}_{\text{SO}_4\text{bio}}$ signature of 18.6‰. Model output colors go from dark to light for low to high $\delta^{34}\text{S}_{\text{SO}_4\text{other}}$ values.

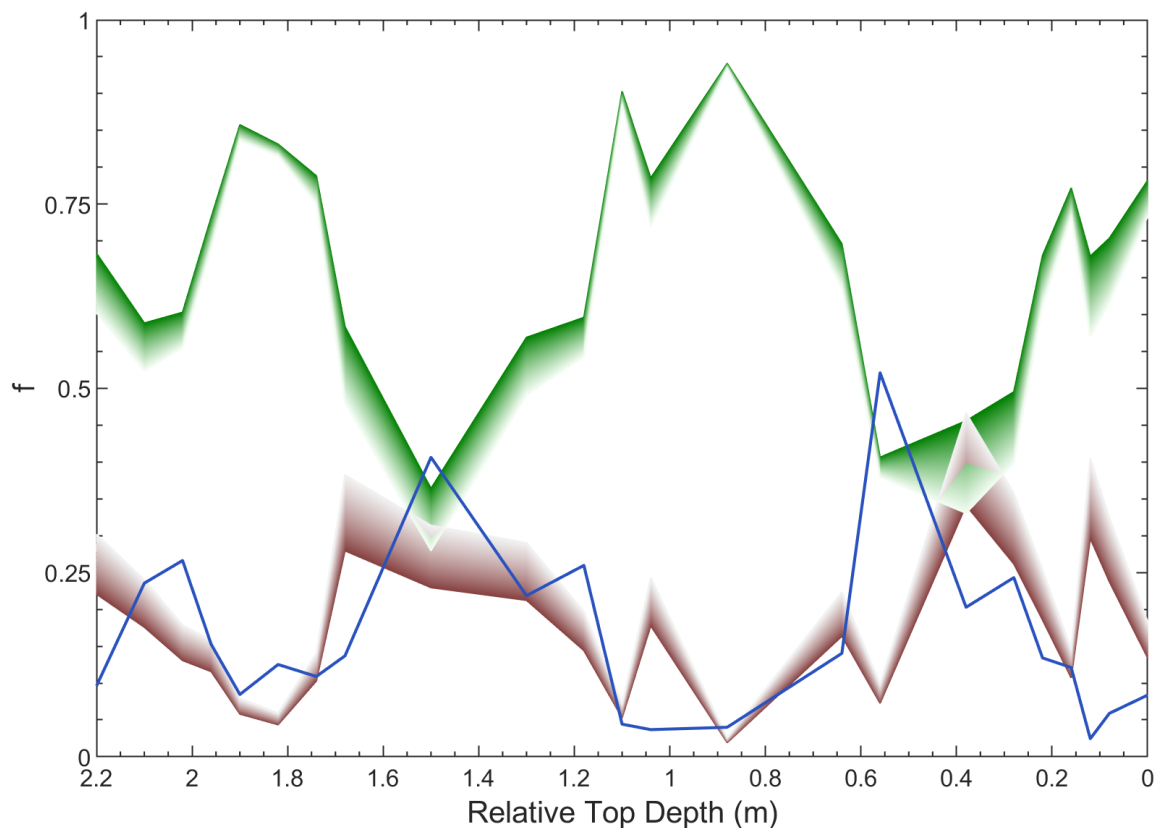


Fig. 3.16 Possible sulfate source fractions of sea salt sulfate (blue), biogenic sulfate (green), and a third sulfate source (brown) at Dyer Plateau. The sea salt fraction was calculated using seasonal k -values, and f_{bio} and f_{other} were then quantified using a two-source isotope mixing model. The biogenic $\delta^{34}S_{SO_4}$ signature was set to 18.6‰, and $\delta^{34}S_{SO_4 other}$ ranged between 0–5‰. Model output colors go from dark to light for low to high $\delta^{34}S_{SO_4 other}$ values.

average winter sea salt fraction did not exceed 27%. The average winter and summer third source sulfate fraction ranged between 20.7–28.3% and 14.0–19.2%, respectively. This result was similar to reported source fractions of volcanic/stratospheric sulfate in East Antarctica, but it was significantly less than the 72–90% fraction reported by Kunasek et al. (2010) for the WAIS ice core in West Antarctica. The reason for this difference is unclear due to the dearth of sulfur isotope studies in West Antarctica. Additional sites must be analyzed to place these results in context.

3.8 Future work

Sulfur isotope ratios cannot be used as a robust sea ice proxy until sulfate sources in Antarctica are more fully understood. To further constrain the sulfur isotopic composition of

Table 3.10 *Winter and summer sulfate source fractions for the Dyer Plateau ice core*

	Winter fraction (%)	Summer fraction (%)
Sea salt sulfate	26.4 ¹	7.5 ¹
Biogenic sulfate	45.3–52.9	73.3–78.5
Third sulfate source	20.7–28.3	14.0–19.2

¹No range because sea salt sulfate was calculated with a k-value and did not depend on the $\delta^{34}\text{S}_{\text{SO}_4\text{other}}$ value.

biogenic sulfate, direct marine aerosol measurements should be made throughout the year for various locations around Antarctica. Such research would also explore the possibility of seasonality or regional variability in the $\delta^{34}\text{S}_{\text{SO}_4\text{bio}}$ signature. Concurrent $\delta^{34}\text{S}_{\text{SO}_4}$ and $\delta^{33}\text{S}_{\text{SO}_4}$ measurements could also be used to identify volcanic/stratospheric sulfate and confirm the presence of a large volcanic or stratospheric source in West Antarctica. These measurements can be made by further refining the MC-ICP-MS method, as has been done at the University of St Andrews.

The characterization of sulfate sources in Antarctica is impeded by the limited number of sulfur isotope studies. Additional research is needed to evaluate potential spatial variability in sulfate sources, as demonstrated by the anomalously high volcanic contribution at WAIS compared to East Antarctica and Dyer Plateau (Kunasek et al., 2010). Further research sites in West Antarctica would be particularly valuable because of the lack of data from that region. This issue is addressed in Chapter 4, which focuses on sulfate sources at two more sites in West Antarctica.

3.9 Conclusion

Seasonal $\delta^{34}\text{S}_{\text{SO}_4}$ measurements were made for the Dyer Plateau ice core using the MC-ICP-MS method described in Chapter 2. This is the first seasonal record of $\delta^{34}\text{S}_{\text{SO}_4}$ in ice cores because of previous sample size limitations. Direct $\delta^{34}\text{S}_{\text{SO}_4}$ measurements of the sea ice surface and frost flowers in Antarctica were also completed for the first time. The measured $\delta^{34}\text{S}_{\text{SO}_4}$ of sea salt from the sea ice surface was $21.17 \pm 0.17\text{‰}$, agreeing with the 21.1‰ sulfur isotope signature reported by Rees (1978), which has been the accepted value in previous research. The $\delta^{34}\text{S}_{\text{SO}_4}$ of frost flowers was $21.10 \pm 0.05\text{‰}$, confirming that sea ice formation does not cause sulfur isotope fractionation in Antarctica.

Multiple isotope mixing models suggested a third sulfate source other than sea salt and biogenic activity with a low sulfur isotopic composition at Dyer Plateau. This source is likely volcanic/stratospheric, although another origin cannot be ruled out. Winter and summer deposition of the third sulfate source ranged between 20.7–28.3% and 14.0–19.2%,

respectively, and this seasonality could be due to greater stratospheric input in the winter. The third source sulfate fraction was similar to reported values for volcanic/stratospheric sulfate in East Antarctica (Jonsell et al., 2005; Uemura et al., 2016) but significantly lower than the 72–90% reported at WAIS by Kunasek et al. (2010), suggesting strong spatial variability in sulfate sources. Previous studies have proposed that a lower $\delta^{34}\text{S}_{\text{SO}_4\text{bio}}$ signature could explain the overall low $\delta^{34}\text{S}_{\text{SO}_4}$ values measured in ice cores instead of a third sulfate source. However, the results for Dyer Plateau agreed with the $\delta^{34}\text{S}_{\text{SO}_4\text{bio}}$ signature of $18.6 \pm 0.9\text{‰}$ reported by Patris et al. (2000).

Until sulfate sources in Antarctica are better constrained, it is not possible to use $\delta^{34}\text{S}_{\text{SO}_4}$ as a proxy in sea ice extent reconstructions. Therefore, further research is necessary to look at spatial variability in sulfate sources and further constrain the sulfur isotopic composition of sulfate source end members.

Chapter 4

Spatial variability in sulfate sources in West Antarctica and implications for the past retreat of the Ronne Ice Shelf

4.1 Introduction

4.1.1 Chapter outline

Chapter 3 showed that there is a significant sulfate source in West Antarctica other than sea salt and marine biogenic activity. Numerous ice core studies have attributed this sulfate source to volcanic and/or stratospheric input because it has a low sulfur isotopic composition ($\delta^{34}\text{S}_{\text{SO}_4}$), but the source strength appears to vary by region (Alexander et al., 2003; Baroni et al., 2008; Jonsell et al., 2005; Kunasek et al., 2010; Pruett et al., 2004; Uemura et al., 2016). In East Antarctica, a $\sim 10\text{--}30\%$ volcanic sulfate source has been proposed (e.g., Jonsell et al., 2005; Uemura et al., 2016), which agrees with the Dyer Plateau results discussed in the previous chapter. However, in a West Antarctica study, Kunasek et al. (2010) reported a 72–90% combined input of volcanic and stratospheric sulfate on the West Antarctic Ice Sheet (WAIS). This contradiction necessitates the continued examination of sulfate sources in Antarctica on a spatial scale.

In this chapter, I present $\delta^{34}\text{S}_{\text{SO}_4}$ data for two additional West Antarctic ice cores: Sherman Island and Skytrain Ice Rise. High-resolution $\delta^{34}\text{S}_{\text{SO}_4}$ measurements from Sherman Island allow for another assessment of seasonality in sea salt sulfate ($\text{SO}_{4\text{ss}}^{2-}$), biogenic sulfate ($\text{SO}_{4\text{bio}}^{2-}$) and the third sulfate source ($\text{SO}_{4\text{other}}^{2-}$). However, deeper Sherman Island samples and all Skytrain measurements did not resolve a seasonal signal and instead revealed possible long-term source changes. I also revisit potential variations in the sulfur isotope composition

of biogenic sulfate to further constrain the $\delta^{34}\text{S}_{\text{SO}_4\text{bio}}$ signature. Isotope mixing models are used, as in Chapter 3, to determine the potential origin and magnitude of sulfate sources at each site. Finally, I evaluate changes in sulfate sources at Skytrain Ice Rise to assess the proposed retreat of the Ronne Ice Shelf ~ 8 thousand years ago (ka).

This chapter also includes my analysis of several potentially-volcanic sulfate peaks from each site. Known volcanic eruptions are used to pin down the depth/age scale of ice core records. By confirming the volcanic origin of several sulfate peaks, I could further refine the age scale at each site.

4.2 Methods

4.2.1 Descriptions of ice core sites and core acquisition

4.2.1.1 Sherman Island ice core

Sherman Island ($72^{\circ}40.2'\text{S}$, $099^{\circ}42.8'\text{W}$) is located on the southern end of the Antarctic Peninsula by Thurston Island (Figure 4.1). It is situated within the Abbott Ice Shelf and faces the Bellingshausen and Amundsen Seas. It has an elevation of 415 m and an accumulation rate of 0.47 ± 0.06 m weq/yr (meters water equivalent per year) (Mulvaney et al., 2021). A traditional ice core was not recovered at this site because a Rapid Access Isotope Drill (RAID) from the British Antarctic Survey (BAS) was used. The RAID drill uses an auger instead of a hollow core barrel to collect a record of ice chips and not a solid core. This drilling method is significantly faster than recovering the entire core but has a limited depth resolution. The final ice column was 323 m and spanned the years 780–2020 CE. Throughout this chapter, the Sherman Island samples will be referred to as a ‘core’ for simplicity.

4.2.1.2 Skytrain Ice Rise ice core

Skytrain Ice Rise ($79^{\circ}44.53'\text{S}$, $078^{\circ}33.82'\text{W}$) is located next to the Ronne Ice Shelf east of the Antarctic Peninsula and is over 600 km from the ice edge (Figure 4.1). The drill site has an elevation of 784 m, and the accumulation rate is ~ 0.14 m weq/yr (Mulvaney et al., 2021). Unlike Sherman Island, a solid 651 m ice core was recovered that extended back to the last interglacial period.

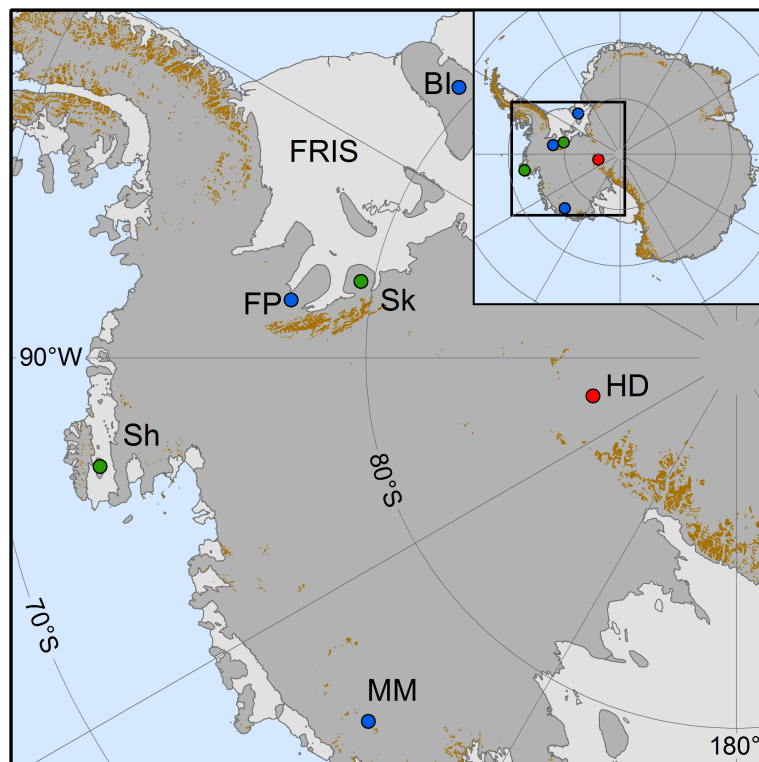


Fig. 4.1 A map of West Antarctica showing the Sherman Island (Sh) and Skytrain Ice Rise (Sk) drill sites. Multiple other drill sites are also shown but were not used in this research. Map from Mulvaney et al. (2021).

4.2.2 Sample preparation

4.2.2.1 Sherman Island ice core

Three sample depths were chosen for analysis from the modern and pre-industrial era and spanned ~1523–2001 (Table 4.1, Figure 4.2). The samples were stored in whirl-pak bags and had been previously melted for ion chromatography (IC) before being refrozen. Sample resolution ranged between 18–24 cm. Once melted, the samples were weighed into Teflon vials to obtain 30 nmol of sulfur for isotope measurements and then dried down at 80°C for column separation. Vials had to be refilled multiple times to dry the complete volume, and all samples were kept refrigerated until the complete volume had been dried.

Potentially-volcanic samples

Five potentially-volcanic peaks were chosen based on previous IC measurements of non-sea salt sulfate ($\text{SO}_{4\text{ns}}^{2-}$) and methanesulfonic acid (MSA), as well as their approximate age as determined by a preliminary age scale (Table 4.1). For example, Figure 4.2 shows two $\text{SO}_{4\text{ns}}^{2-}$ peaks that occurred between 125–129 m and spanned the years 1805–1815. Neither peak aligned with high MSA concentrations, so they were not of biogenic origin. Two known volcanic events occurred in this time period: Tambora in 1815, and an unknown eruption around 1808. By analyzing the $\delta^{34}\text{S}_{\text{SO}_4}$ of each peak, I could confirm their potentially-volcanic origin and add a fixed point to the age scale. The five chosen samples were prepared following the same technique outlined in the preceding paragraph.

Table 4.1 *Sherman Island ice core sample information*

Sample	Depth (m)	Year (CE) ¹	Sample resolution (m)
108–112	17.97–18.90	1999.9–2000.9	0.23–0.24
477–481	89.87–90.80	1884.5–1886.0	0.18–0.19
1142–1146	214.16–215.10	1522.9–1525.4	0.18–0.19
<i>Potentially-volcanic:</i>			
668	125.49	1815.0	0.20
683	128.37	1805.6	0.20
1015	190.50	1603.1	0.13
1087	203.17	1559.3	0.20
1302	244.17	1416.5	0.18

¹According to preliminary age scale

4.2.2.2 Skytrain Ice Rise ice core

Three sample depths were chosen for analysis from the early Holocene, late Holocene, and Last Glacial Maximum (LGM) (Table 4.2). The LGM samples are the focus of Chapter 5 and will not be included in the following discussion. The early Holocene samples from ~10,400 ybp (years before 1950) and the late Holocene samples from ~720 ybp were selected to compare younger ice with relatively high sulfate and sodium (Na^+) concentrations to ice before ~8 ka, which has relatively low sodium and sulfate concentrations (E. Wolff, personal communication, 2021).

Samples were cut at 8 cm resolution; higher resolution was not necessary because seasonal signals did not need to be resolved. Samples were placed in pots made of polyphenylene ether (PPE) plastic that had been cleaned in 10% HCl for 24 hours. The samples were melted

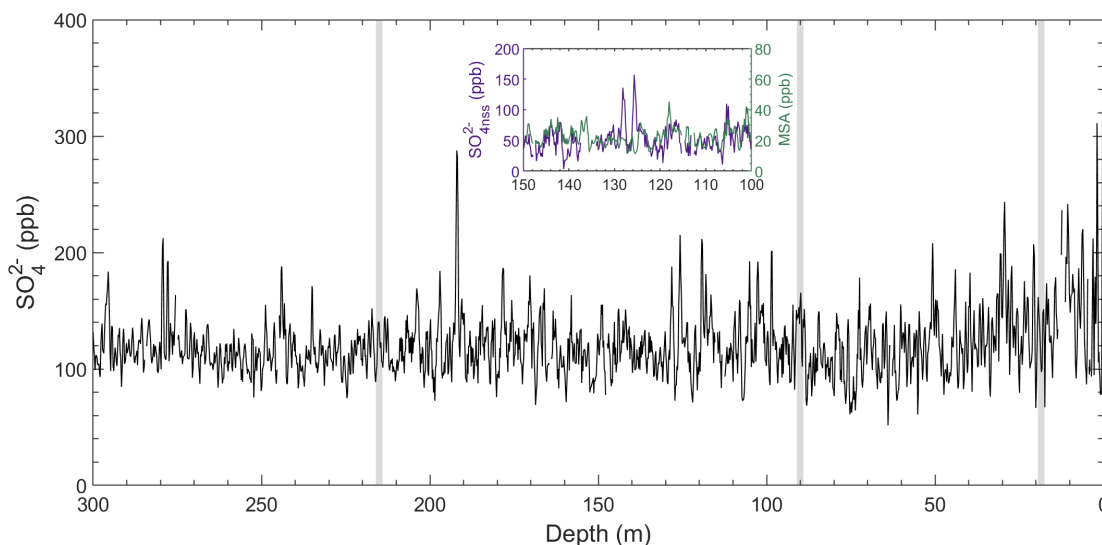


Fig. 4.2 Sulfate concentrations in the first 300 m of the Sherman Island ice core. Grey bars mark the three background sulfate sections chosen for analysis. The inset plot shows the selection of two potentially-volcanic sulfate peaks. The non-sea salt sulfate concentration (purple) was calculated with the sodium concentration and an assumed k -value of 0.25 as discussed in Chapter 3. This record was then compared to MSA concentrations (green) to identify sulfate peaks of potentially-volcanic origin. Unpublished data from Isobel Rowell (personal communication, 2021).

to take a 2 mL aliquot for IC analysis and then refrozen until further processing. Once melted, samples were weighed into Teflon vials to obtain 30 nmol of sulfur and then dried down at 80°C for column separation. Remaining samples were kept in the refrigerator during the dry down process.

Potentially-volcanic samples

Potentially-volcanic samples were chosen based on previously-run IC data for four known eruptions: Tambora in 1815, unknown eruptions in 1809 and 1458, and the Samalas eruption in 1257 (Table 4.2). There were two candidate peaks for each eruption for a total of 8 samples. Samples were cut 5 cm long across the center of the sulfate peak. An adjacent 8 cm background sample was also cut to better identify any anomaly in the $\delta^{34}\text{S}_{\text{SO}_4}$ signal. These samples are not listed in Table 4.2, but they were cut within 0.30 m of the potentially-volcanic sulfate peak. All samples were cut and prepared as described in the preceding paragraph. Final samples were reanalyzed on the IC to confirm ion concentrations.

Table 4.2 *Skytrain Ice Rise ice core sample information*

Sample	Depth (m)	Age ¹ (ybp)	Sample resolution (m)
1391–1395	110.88–111.20	~722–725	0.08
5281–5285	421.95–422.27	~10,366–10,382	0.08
<i>Potentially-volcanic²:</i>		<i>Year¹ (CE)</i>	
46/55	36.24/43.97	1815/Tambora	0.05
47/57	37.49/45.13	1809/Unknown	0.05
111/114	88.21/90.58	1458/Unknown	0.05
126/139	100.20/110.58	1257/Samalas	0.05

¹According to a preliminary age scale

² Each line lists two sample candidates for each eruption. A 0.08 m background sample was also cut within 0.30 m of each potentially-volcanic sulfate peak.

4.2.3 Analytical methods

4.2.3.1 Ion chromatography

All IC analyses were completed at the British Antarctic Survey in Cambridge, England. Measurements were made with a Dionex ICS-4000 Integrion and were performed by lab technicians Jack Humby and Shaun Miller or by Isobel Rowell, a PhD student at the University of Cambridge.

4.2.3.2 Isotope analysis

I performed all isotope measurements via multicollector inductively coupled mass spectrometry (MC-ICP-MS) at the University of Cambridge as outlined in Chapter 2. All measurement uncertainties are reported as 2 standard deviations (2 σ).

4.3 Results

4.3.1 Sherman Island ice core

4.3.1.1 Ion chromatography

There was no significant difference in the concentration of SO_4^{2-} , Na^+ , and MSA across all three Sherman Island core sections (Figure 4.3). The average SO_4^{2-} , Na^+ , and MSA concentrations ranged between 112.0–132.9 ppb, 231.2–204.4 ppb, and 18.9–34.5 ppb, respectively, and a seasonal signal was resolved in the shallow and mid-depth cores. The potentially-volcanic samples had higher SO_4^{2-} concentrations ranging between 163.61–226.80 ppb but

no concurrent increase in Na^+ or MSA concentrations, as expected. The IC data for all samples are shown in Table 4.3.

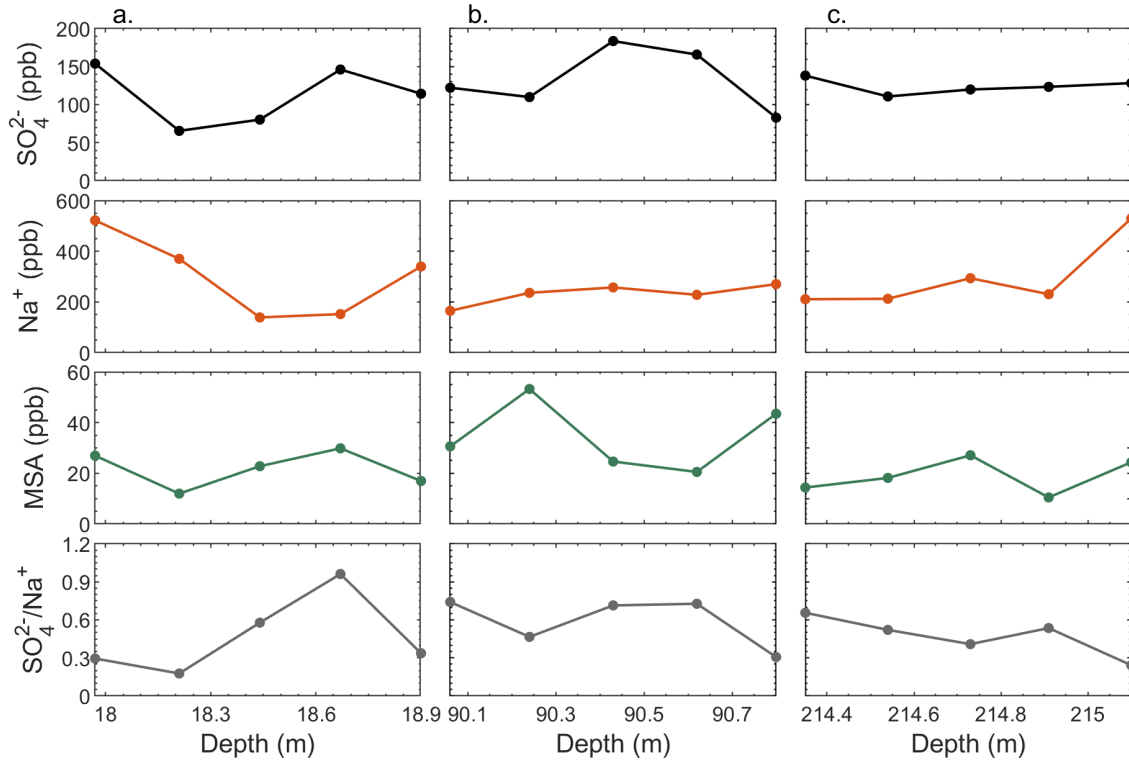


Fig. 4.3 Sulfate, sodium, and MSA concentrations alongside $\text{SO}_4^{2-}/\text{Na}^+$ ratios in the Sherman Island shallow (a), mid-depth (b), and deep (c) ice core sections. A seasonal signal was visible in the shallow and mid-depth cores but was not resolved in the deep core record.

4.3.1.2 Isotope analysis

All Sherman Island $\delta^{34}\text{S}_{\text{SO}_4}$ measurements were completed in a single MC-ICP-MS run. An IAPSO internal seawater standard was analyzed at the start, middle, and end of the sample sequence to assess measurement accuracy. The known $\delta^{34}\text{S}_{\text{SO}_4}$ of the standard was $21.16 \pm 0.11\text{‰}$ ($n = 10$), measured with a Thermo Delta V gas source mass spectrometer (GS-MS) at the University of Cambridge with the assistance of Dr Alexandra Turchyn. The measured $\delta^{34}\text{S}_{\text{SO}_4}$ of the seawater standard throughout the run was 21.17‰ with an external error of $\pm 0.11\text{‰}$ ($n = 9$). Most samples were run in triplicate; however, the nebulizer clogged for sample 108, so only two measurements were made. Reproducibility of sample measurements averaged $\pm 0.11\text{‰}$. All sulfur isotope data are shown in Table 4.3.

Potentially-volcanic samples

All potentially-volcanic samples were analyzed in a single MC-ICP-MS run. The IAPSO internal seawater standard was measured at the beginning and end of the sequence alongside an internal ICP sulfate standard. The known $\delta^{34}\text{S}_{\text{SO}_4}$ of the ICP standard was $3.24 \pm 0.22\text{‰}$ ($n = 10$), measured with a Thermo Delta V GS-MS at the University of Cambridge with the assistance of Dr Alexandra Turchyn. This low $\delta^{34}\text{S}_{\text{SO}_4}$ value was similar to the sulfur isotopic composition of volcanic sulfate, ensuring an analytical check across a wider range of potential $\delta^{34}\text{S}_{\text{SO}_4}$ measurements. The measured $\delta^{34}\text{S}_{\text{SO}_4}$ of the seawater and ICP standard throughout the run was $21.16 \pm 0.08\text{‰}$ ($n = 6$) and $3.11 \pm 0.12\text{‰}$ ($n = 6$), respectively, and the larger $\pm 0.12\text{‰}$ uncertainty was considered the external error. The ICP standard measurement was slightly low but within error of the GS-MS value. Because the primary goal of this analysis was simply to identify volcanic input, I did not consider this small offset to be problematic. Most samples were run in triplicate. However, the nebulizer clogged for a bracketing standard mid-run, and only two measurements were made for sample 683. The reproducibility of sample measurements averaged $\pm 0.11\text{‰}$. All sulfur isotope data are shown in Table 4.3.

4.3.2 Skytrain Ice Rise ice core

4.3.2.1 Ion chromatography

There were notable differences in the SO_4^{2-} , Na^+ , and MSA concentrations in the two Skytrain core sections (Figure 4.4). The ~ 720 ybp samples had an average SO_4^{2-} , Na^+ , and MSA concentration of 74.7 ± 65.2 ppb, 99.1 ± 134.6 ppb, and 4.0 ± 1.3 ppb, respectively. However, the average MSA concentration was only based on two data points. The $\sim 10,400$ ybp samples had an average SO_4^{2-} , Na^+ , and MSA concentration of 50.4 ± 13.6 ppb, 41.8 ± 24.0 ppb, and 11.9 ± 6.4 ppb, respectively. There was significantly more variability in SO_4^{2-} and Na^+ concentrations in the ~ 720 ybp core relative to the $\sim 10,400$ ybp core. The expected low Na^+ concentrations were observed for the $\sim 10,400$ ybp core as noted in earlier IC data. However, the higher Na^+ concentrations in the ~ 720 ybp core were not consistent across the record. Because the $\text{SO}_4^{2-}/\text{Na}^+$ ratio is primarily used to identify seasonal signals, it was not considered in the Skytrain analysis. Four of the background volcanic samples had insufficient amounts of sulfate for isotope analysis. The IC data for all samples are shown in Table 4.4.

Table 4.3 Major ion concentrations and sulfur isotope data for the Sherman Island ice core¹

Sample	n	[SO ₄ ²⁻]	[Na ⁺]	[MSA]	[SO ₄ ²⁻]/[Na ⁺]	$\delta^{34}\text{S}_{\text{SO}_4}$ (‰)	2 σ^2
108	2	153.9	521.7	27.0	0.29	19.10	0.07
109	3	65.5	370.0	12.0	0.18	16.38	0.08
110	3	80.3	138.9	22.8	0.58	16.55	0.05
111	3	146.1	152.0	29.8	0.96	18.36	0.18
112	3	114.3	339.7	17.0	0.34	17.84	0.13
477	3	122.2	165.0	30.6	0.74	18.07	0.09
478	3	109.9	235.9	53.2	0.47	17.89	0.02
479	3	183.6	257.0	24.6	0.71	18.52	0.15
480	3	165.8	228.0	20.5	0.73	18.00	0.16
481	3	82.9	270.1	43.5	0.31	17.66	0.08
1142	3	138.1	210.5	14.4	0.66	18.24	0.13
1143	3	110.7	212.4	18.2	0.52	18.58	0.19
1144	3	119.9	293.5	27.1	0.41	19.29	0.03
1145	3	123.4	230.4	10.5	0.54	18.84	0.15
1146	3	128.3	529.2	24.3	0.24	19.66	0.10
<i>Potentially-volcanic:</i>							
668	3	256.1	154.1	11.9	1.66	2.77	0.12
683	2	226.8	288.7	22.9	0.79	15.20	0.01
1015	3	163.6	162.5	11.6	1.01	10.06	0.15
1087	3	192.5	267.0	26.7	0.72	15.16	0.08
1302	3	182.6	204.6	39.4	0.89	16.41	0.17

¹All concentrations reported in ppb²Sample reproducibility, independent of $\pm 0.11\text{‰}$ and $\pm 0.12\text{‰}$ external error for non-volcanic and potentially-volcanic samples, respectively

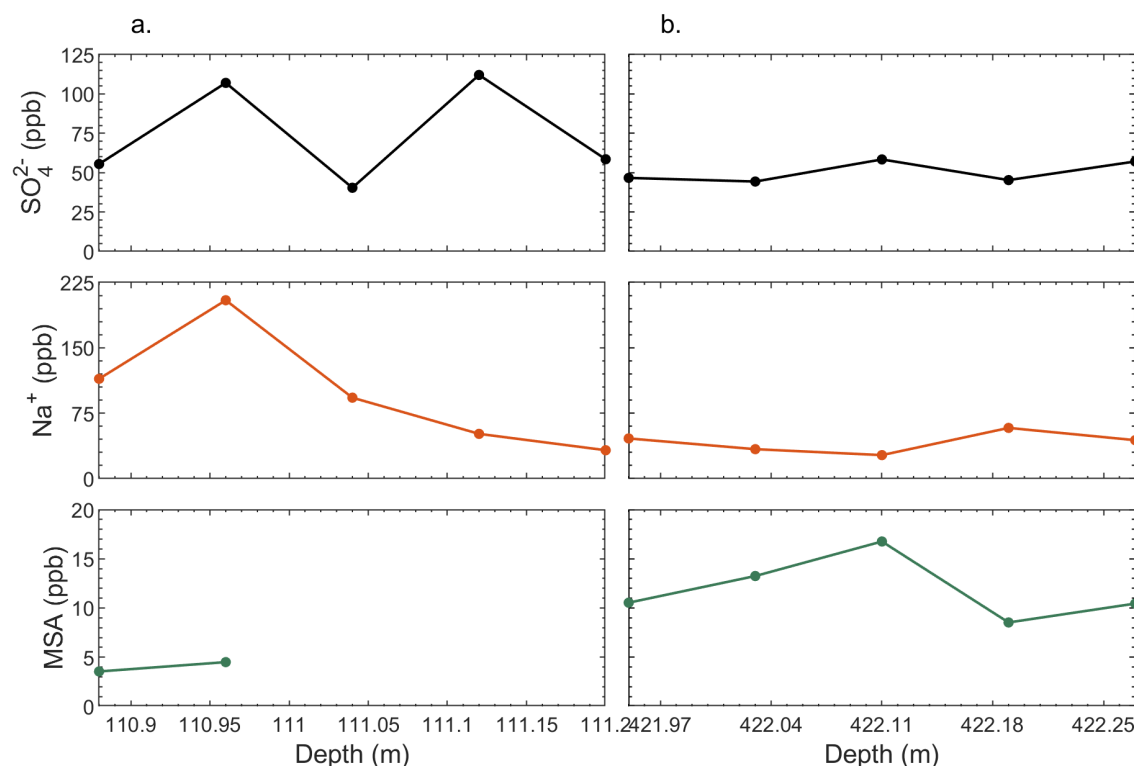


Fig. 4.4 Sulfate, sodium, and MSA concentrations in the ~720 ybp (a) and ~10,400 ybp (b) Skytrain Ice Rise ice core sections.

4.3.2.2 Isotope analysis

All $\delta^{34}\text{S}_{\text{SO}_4}$ measurements were completed in a single MC-ICP-MS run, and all samples were measured in triplicate. The IAPSO seawater internal standard was analyzed at the start and end of the run as well as after the first five samples to assess measurement accuracy and external error. The measured $\delta^{34}\text{S}_{\text{SO}_4}$ of the seawater standard throughout the run was 21.16‰ with an external error of $\pm 0.15\text{‰}$ ($n = 9$). The reproducibility of sample measurements averaged $\pm 0.07\text{‰}$. All isotope data are shown in Table 4.4.

Potentially-volcanic samples

All $\delta^{34}\text{S}_{\text{SO}_4}$ measurements were completed in a single MC-ICP-MS run, and all samples were measured in triplicate. The IAPSO internal seawater standard and the ICP internal standard were analyzed at the start and end of the run as well as after the first five samples. The measured $\delta^{34}\text{S}_{\text{SO}_4}$ of the seawater standard throughout the run was $21.18 \pm 0.10\text{‰}$ ($n = 9$), and the measured $\delta^{34}\text{S}_{\text{SO}_4}$ of the ICP standard was $3.07 \pm 0.14\text{‰}$ ($n = 9$). The larger $\pm 0.14\text{‰}$ uncertainty was considered the external error. As previously discussed, the slightly

low ICP standard $\delta^{34}\text{S}_{\text{SO}_4}$ values were not considered problematic. The reproducibility of sample measurements averaged $\pm 0.10\text{‰}$. All isotope data are shown in Table 4.4.

Table 4.4 Major ion concentrations and sulfur isotope data for the Skytrain Ice Rise ice core¹

Sample	n	[SO ₄ ²⁻]	[Na ⁺]	[MSA]	$\delta^{34}\text{S}_{\text{SO}_4}$ (‰)	2 σ^2
1391	3	58.5	32.5	- ³	16.01	0.03
1392	3	112.0	51.3	- ³	16.21	0.10
1393	3	40.4	92.8	- ³	14.58	0.11
1394	3	107.0	204.5	4.5	15.76	0.13
1395	3	55.5	114.4	3.55	15.13	0.04
5281	3	46.7	46.0	10.54	14.80	0.04
5282	3	44.4	33.7	13.25	15.08	0.05
5283	3	58.4	26.9	16.76	15.33	0.05
5284	3	45.3	59.1	8.53	14.62	0.08
5285	3	57.1	44.0	10.45	14.55	0.10
<i>Potentially-volcanic⁴:</i>						
46a	3	136.4	49.5	8.8	15.04	0.10
46b ⁵	3	23.8	188.0	4.9	-	-
55a	3	216.9	68.9	9.5	16.19	0.09
55b ⁵	3	15.6	39.4	5.4	-	-
47a	3	194.0	56.0	5.6	16.79	0.12
47b ⁵	3	30.4	75.0	3.5	-	-
57a	3	60.3	61.0	- ³	16.97	0.06
57b	3	42.6	155.5	6.6	16.24	0.14
111a	3	243.5	18.7	9.1	17.19	0.16
111b ⁵	3	17.3	36.2	14.1	-	-
114a	3	195.4	55.3	6.4	15.89	0.11
114b	3	53.0	56.1	- ³	14.37	0.12
126a	3	144.0	56.1	4.0	16.61	0.09
126b	3	32.7	130.3	7.1	14.92	0.11
139a	3	242.3	774.6	12.7	18.76	0.06
139b	3	51.7	46.9	- ³	15.41	0.02

¹ All concentrations reported in ppb

² Sample reproducibility, independent of $\pm 0.15\text{‰}$ and $\pm 0.14\text{‰}$ external error for non-volcanic and potentially-volcanic samples, respectively

³ No MSA peak detected

⁴ a and b labels refer to the potentially-volcanic peak and its adjacent background sample, respectively. Not all background samples had a sufficient amount of sulfate for isotope analysis.

⁵ Insufficient sulfur for isotope analysis

4.4 Discussion

4.4.1 Sherman Island ice core

4.4.1.1 Volcanic samples and age scale application

All potentially-volcanic samples appeared to show some degree of volcanic sulfate input. Sample 668 had the greatest volcanic contribution, as its $\delta^{34}\text{S}_{\text{SO}_4}$ value of $2.77 \pm 0.12\text{‰}$ aligned with known volcanic signatures (Nielsen et al., 1991). This result confirmed that sample 668 represented the Tambora eruption and, therefore, it provided a fixed point for the age scale. Though the other samples had higher $\delta^{34}\text{S}_{\text{SO}_4}$ values, they were still well below those of Sherman Island samples 1142–1146, which were at a similar depth and had an average $\delta^{34}\text{S}_{\text{SO}_4}$ of $18.92 \pm 1.13\text{‰}$. Sample 1015 also showed significant volcanic sulfate input, with a $\delta^{34}\text{S}_{\text{SO}_4}$ value of $10.06 \pm 0.15\text{‰}$. The initial age scale placed this peak at the year 1603. The only large eruption recorded in other West Antarctic ice cores around that time period is the Huaynaputia eruption in 1600 (Sigl et al., 2013). Therefore, I would recommend that this peak be fixed at the year 1600 to further refine the age scale.

4.4.1.2 Changes in major ion concentrations: Seasonality in modern samples and a potential shift in sulfate sources over the past 500 years

The Sherman Island IC data showed a seasonal signal in the shallow and mid-depth core sections (Figure 4.3). In the shallow core, SO_4^{2-} , MSA, and $\text{SO}_4^{2-}/\text{Na}^+$ peaks were aligned and roughly out of phase with Na^+ peaks. This pattern is consistent with high biogenic sulfate and low sea salt sulfate emissions in the summer. In the mid-depth core, SO_4^{2-} and $\text{SO}_4^{2-}/\text{Na}^+$ peaks aligned in the summer; however, the MSA peak appeared in the winter, possibly due to MSA migration (Osman et al., 2017). The Na^+ concentration was relatively flat, suggesting low storm activity that winter or perhaps a change in meteorological conditions that affected salt transport. The shallow and mid-depth cores spanned ~ 1 and ~ 1.5 years, respectively, so the five samples in each section resolved a seasonal signal. In the deep core, however, five samples spanned ~ 2.5 years, so no seasonal signal was resolved.

The similar SO_4^{2-} , Na^+ , and MSA concentrations in all three Sherman Island cores suggested either 1) there was no significant change in sulfate sources over the past ~ 500 years, or 2) the partitioning between sulfate sources changed, with some becoming stronger and others becoming weaker. Assuming no significant anthropogenic emissions, any shifts in sources likely involved sea salt or biogenic sulfate and, perhaps, the third sulfate source described in Chapter 3, which may be of volcanic/stratospheric origin. However, because of the longer, ~ 500 -year timespan between cores, I also considered the possibility of changes

in terrestrial sulfate (SO_4^{2-}), which comes primarily from continental dust. To rule out significant terrestrial input, I used the non-sea salt calcium (Ca_{nss}^{2+}) concentration to quantify any SO_4^{2-} that reached Sherman Island. Because Ca^{2+} derives primarily from continental sources, it can be used to trace terrigenous input. The following equation was used, as described in R  thlisberger et al. (2002):

$$[\text{Ca}^{2+}]_{nss} = \frac{[\text{Ca}^{2+}] - [\text{Na}^+] \cdot (\text{Ca}^{2+}/\text{Na}^+)_{ss}}{1 - (\text{Na}^+/\text{Ca}^{2+})_{nss} \cdot (\text{Ca}^{2+}/\text{Na}^+)_{ss}} \quad (4.1)$$

where $(\text{Ca}^{2+}/\text{Na}^+)_{ss}$ is the ratio of calcium to sodium in sea salt, and $(\text{Na}^+/\text{Ca}^{2+})_{nss}$ is the ratio of sodium to calcium in a terrestrial dust source. Respective ratios of 0.038 and 0.56 were used (Bowen, 1979). Terrestrial sulfate was then calculated using the ratio of sulfate to calcium in terrestrial dust ($(\text{SO}_4^{2-}/\text{Ca}^{2+})_{terr}$) as shown below:

$$[\text{SO}_4^{2-}]_{terr} = [\text{Ca}^{2+}]_{nss} \cdot (\text{SO}_4^{2-}/\text{Ca}^{2+})_{terr} \quad (4.2)$$

with $(\text{SO}_4^{2-}/\text{Ca}^{2+})_{terr}$ values of both 0.10 (Bowen, 1979) and 0.18 (Kunasek et al., 2010) evaluated to cover a range of possible terrestrial input. For a ratio of 0.10 and 0.18, terrestrial sulfate was < 1% and < 2% of total sulfate, respectively, in all samples. Although this result ruled out a significant terrestrial sulfate source, sulfur isotope analysis was necessary to further untangle any changes in sulfate sources recorded in the Sherman Island samples.

4.4.1.3 Initial interpretation of sulfur isotope data: A smaller third sulfate source at Sherman Island

The average $\delta^{34}\text{S}_{\text{SO}_4}$ of the shallow, mid-depth, and deep core were $17.65 \pm 2.34\text{‰}$, $18.03 \pm 0.63\text{‰}$, and $18.92 \pm 1.13\text{‰}$, respectively. These values were $\sim 2\text{--}3\text{‰}$ higher than those in the Dyer Plateau ice core, which suggested a greater relative input of SO_4^{2-} ($\delta^{34}\text{S} = 21.1\text{‰}$) compared to sulfate with a lower sulfur isotopic composition, such as SO_4^{2-} . Also, given a $\delta^{34}\text{S}_{\text{SO}_4\text{bio}}$ signature of $\sim 18\text{‰}$, the Sherman Island results could reflect solely biogenic and sea salt sulfate input.

The shallow and mid-depth cores showed a positive correlation between $\delta^{34}\text{S}_{\text{SO}_4}$ and the sulfate concentration (Figure 4.5). This result could be interpreted as seasonal inputs of sulfate with a higher $\delta^{34}\text{S}_{\text{SO}_4}$ signature, such as sea salt. However, high sulfate concentrations are due to increased biogenic input in the summer, which would lead to lower $\delta^{34}\text{S}_{\text{SO}_4}$ values. Therefore, this correlation could reflect the input of SO_4^{2-} , which has a low sulfur isotopic composition and increased winter deposition. The gradually increasing $\delta^{34}\text{S}_{\text{SO}_4}$ with depth

could represent the introduction and/or strengthening of this third sulfate source over time. However, the larger variation in the shallow core also introduced the possibility of small, modern inputs of anthropogenic sulfate. Though previous research has not found evidence of significant anthropogenic emissions, I could not exclude this possibility entirely, and it is discussed in future sections.

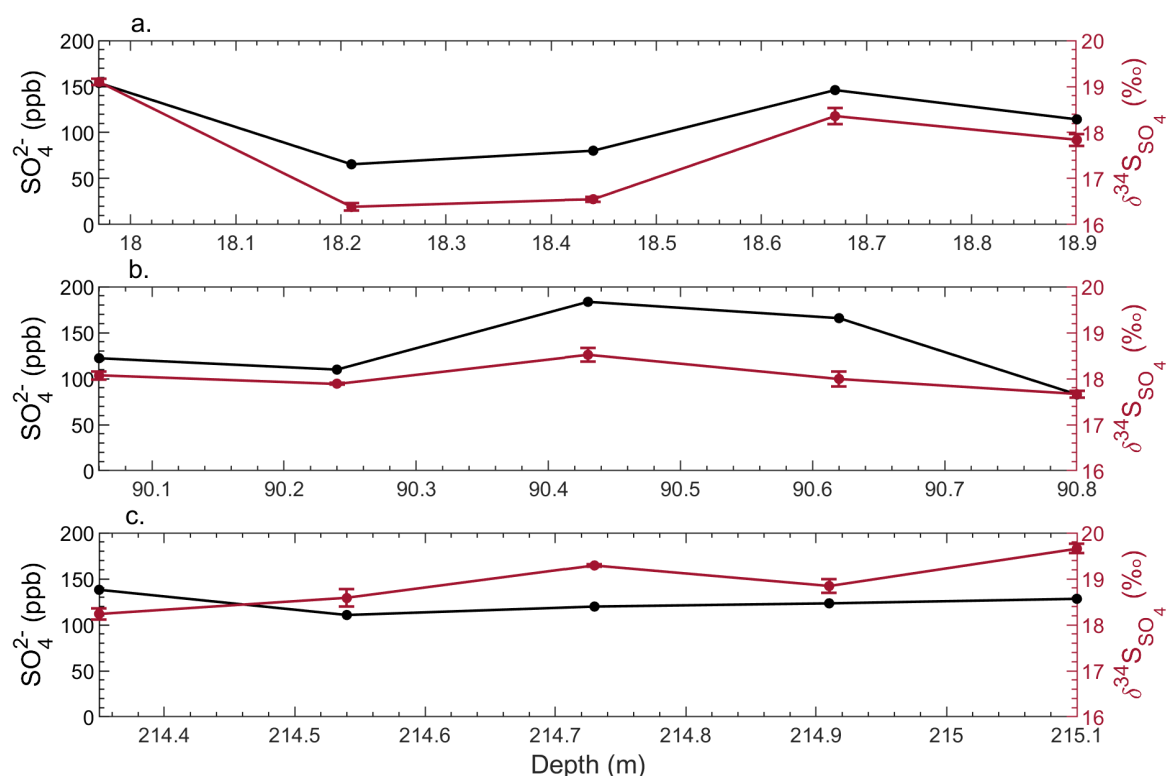


Fig. 4.5 Sulfate concentrations and total $\delta^{34}\text{S}_{\text{SO}_4}$ values in the shallow (a), mid-depth (b), and deep (c) Sherman Island ice core sections.

The magnitude of each sulfate source could be evaluated as a fraction of total sulfate (f) or as a concentration. Wet deposition dominates in West Antarctica because of the high precipitation rate. Because precipitation occurs in relatively short-term events and not as a constant process, snowfall can be thought of as “flushing” sulfate from the atmosphere. Therefore, the snow concentration reflects the atmospheric composition, and a flux calculation is not necessary. As such, the source fraction indicates the amount of sulfate from one source relative to other sources, and the concentration reflects the strength of the source itself.

The initial isotope data suggested that the third sulfate source fraction and/or source strength at Sherman Island was less than at Dyer Plateau. If so, it was possible that Sherman Island would be a better site to constrain the sulfur isotopic composition of biogenic sulfate

because it would reduce the unknown variable. Because of this possibility, I revisited the potential of a two-source isotope mixing model before considering the third sulfate source.

4.4.1.4 A potential two-source sulfate system at Sherman Island

A two-source isotope mixing model was used to quantify SO_4^{2-} and SO_4^{2-} as described in Chapter 3. To review, this approach assumed that sea salt and marine biogenic activity are the sole sources of sulfate and used the following equations to quantify each source fraction:

$$\delta^{34}\text{S}_{\text{SO}_4\text{tot}} = \delta^{34}\text{S}_{\text{SO}_4\text{ss}} \cdot f_{\text{ss}} + \delta^{34}\text{S}_{\text{SO}_4\text{bio}} \cdot f_{\text{bio}} \quad (4.3)$$

$$f_{\text{bio}} = 1 - f_{\text{ss}} \quad (4.4)$$

$$[\text{SO}_4^{2-}]_{\text{ss}} = f_{\text{ss}} \cdot [\text{SO}_4^{2-}]_{\text{tot}} \quad (4.5)$$

$$[\text{SO}_4^{2-}]_{\text{bio}} = f_{\text{bio}} \cdot [\text{SO}_4^{2-}]_{\text{tot}} \quad (4.6)$$

where the *tot* subscript indicates the total sample. The model was run for $\delta^{34}\text{S}_{\text{SO}_4\text{bio}}$ values between 10–20‰ to explore the potential of a different biogenic signature (Figure 4.6).

Only $\delta^{34}\text{S}_{\text{SO}_4\text{bio}}$ values < 16.3‰ produced realistic results; higher values led to a negative source input or a source fraction > 1. At first, this result appeared to conflict with the ~18‰ $\delta^{34}\text{S}_{\text{SO}_4\text{bio}}$ signature found in Chapter 3. However, the calculated sea salt sulfate fraction was positively correlated with the total sulfate concentration, suggesting that sea salt emissions peaked in the summer and biogenic emissions peaked in the winter. This false output showed that sea salt and marine biogenic activity were not the only sulfate sources at Sherman Island. Therefore, I explored the addition of the third sulfate source with a low sulfur isotopic composition, which first required the assignment of a k-value.

4.4.1.5 Using a three-source model to quantify and compare sulfate sources at Sherman Island and Dyer Plateau

The three-source model used in this section is detailed in Chapter 3. To review, the SO_4^{2-} concentration was calculated using an assigned k-value, and the remaining non-sea salt sulfate (SO_4^{2-}) was separated into SO_4^{2-} and SO_4^{2-} using a two-source isotope mixing model over a range of $\delta^{34}\text{S}_{\text{SO}_4\text{other}}$ values. Because the third sulfate source was likely volcanic/stratospheric in origin, $\delta^{34}\text{S}_{\text{SO}_4\text{other}}$ ranged between 0–5‰ based on reported stratospheric and volcanic $\delta^{34}\text{S}_{\text{SO}_4}$ values (Alexander et al., 2003; Burke et al., 2019; Castleman

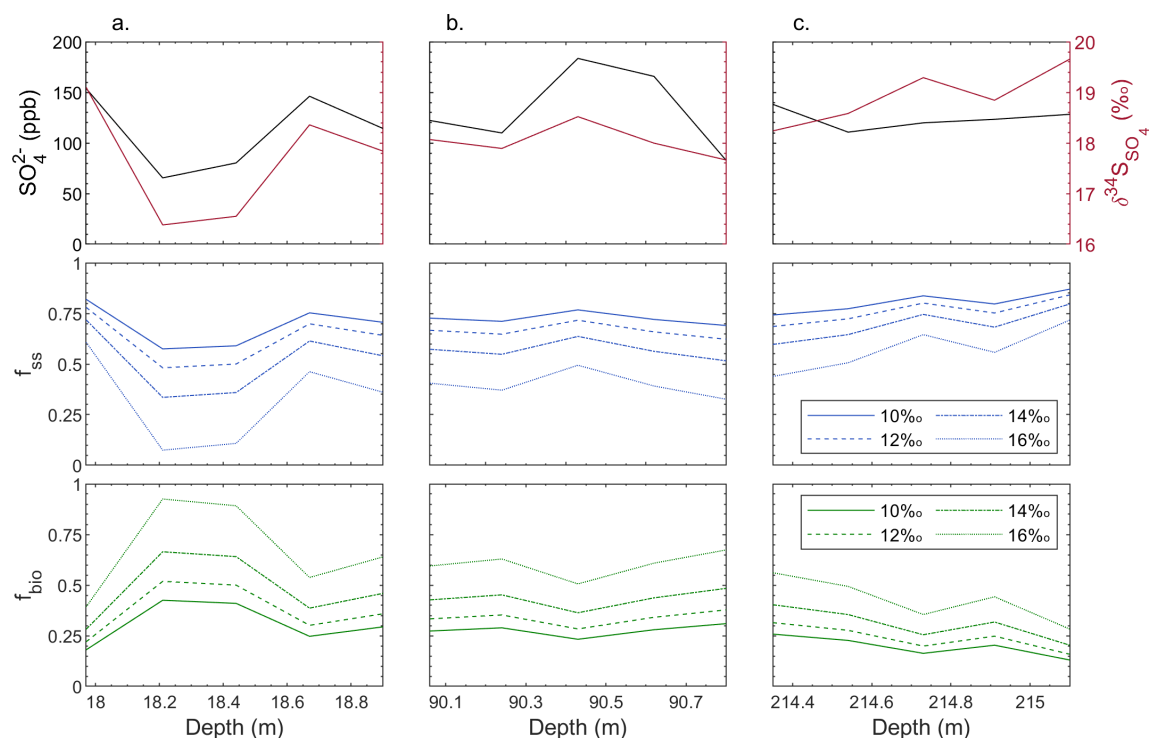


Fig. 4.6 Possible sulfate source fractions of sea salt sulfate (blue) and biogenic sulfate (green) using a two-source isotope mixing model. Source fractions were calculated for $\delta^{34}\text{S}_{\text{SO}_4\text{bio}}$ values between 10–20‰. However, only results for 10–16‰ are shown because higher $\delta^{34}\text{S}_{\text{SO}_4\text{bio}}$ values led to a negative input of sea salt or biogenic sulfate.

et al., 1974; Patris et al., 2000). Before running the mixing model, a k-value needed to be calculated for each core. Though the shallow and mid-depth cores required a seasonal k-value, an annual average was sufficient for the deep core section because it did not resolve seasonal signals.

To determine the k-value, I used the p-TOMCAT chemical transport model to reconstruct the origin of the sea salt reaching Sherman Island, as described in Chapter 3. The model was run with the assistance of Dr Mackenzie Grieman, a postdoctoral researcher at the University of Cambridge. The model was run over the years 1998–2000 with monthly resolution and produced a final k-value of 0.18 for winter/spring and 0.22 for summer/fall. The relatively higher and less-seasonal k-values at Sherman Island relative to Dyer Plateau were likely due to its proximity to open water and the presence of multiple polynyas, which are perennial areas of open water in sea ice (Arrigo et al., 2012). In the winter, the neighbouring Amundsen Sea and Pine Island polynyas have a combined surface area of 4,760 km². These polynyas could serve as a significant source of SO_4^{2-} from the open ocean that would balance out the increased input of SO_4^{2-} from the sea ice surface in winter (Arrigo and Dijken, 2003).

Because the deep section of the Sherman Island core did not resolve a seasonal signal, an average k -value of 0.20 was used.

The three-source model was run for $\delta^{34}\text{S}_{\text{SO}_4\text{bio}}$ values between 15–20‰ to evaluate the potential of a different sulfur isotopic composition for biogenic sulfate. Model results for the shallow and mid-depth Sherman Island cores are shown in Figure 4.7. For all core sections, only $\delta^{34}\text{S}_{\text{SO}_4\text{bio}}$ values ≥ 17.6 ‰ produced realistic results with source fractions between 0–1, which agreed with the $\delta^{34}\text{S}_{\text{SO}_4\text{bio}}$ value of 18.6 ± 0.9 ‰ from Patris et al. (2000) and the Dyer Plateau results in Chapter 3. Therefore, all future plots and discussion will refer to an 18.6‰ biogenic signature. However, to assess the effect of a wider range of possible $\delta^{34}\text{S}_{\text{SO}_4\text{bio}}$ values, I compared model results based on biogenic isotopic compositions of 17.6‰ and 18.6‰. When a $\delta^{34}\text{S}_{\text{SO}_4\text{bio}}$ of 17.6‰ was used, f_{bio} increased 2.2–5.2% with the corresponding decrease in f_{other} , which did not affect my final interpretation.

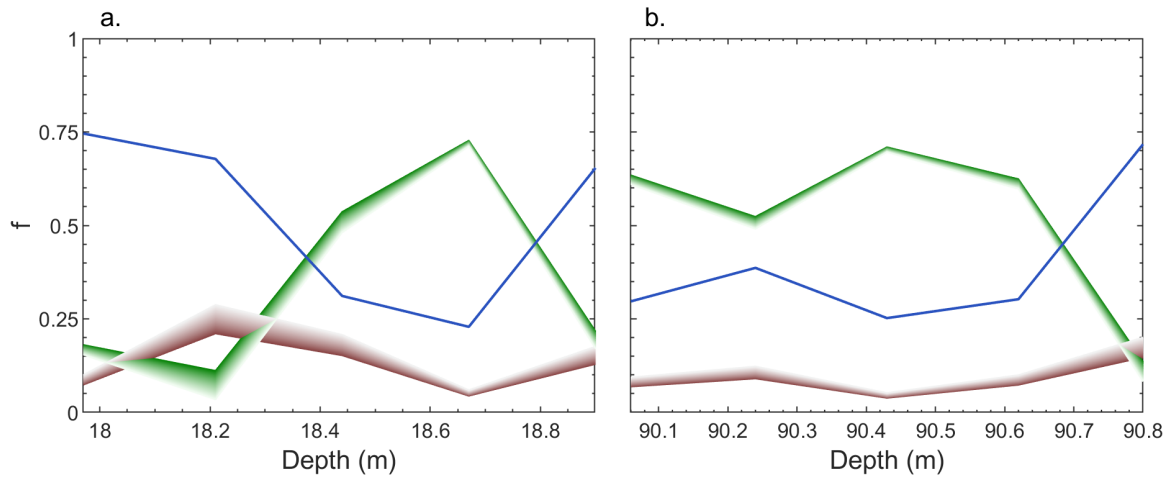


Fig. 4.7 Possible source fractions of sea salt sulfate (blue), biogenic sulfate (green), and the third sulfate source (brown) in the shallow (a) and mid-depth (b) Sherman Island ice core sections. The deep core section is not shown because it did not resolve a seasonal signal. The sea salt fraction was calculated with seasonal k -values determined from the *p*-TOMCAT chemical transport model, and f_{bio} and f_{other} were then quantified with a two-source isotope mixing model. The model was run for $\delta^{34}\text{S}_{\text{SO}_4\text{other}}$ values between 0–5‰, and $\delta^{34}\text{S}_{\text{SO}_4\text{bio}}$ was set at 18.6‰. Model output colors go from dark to light for low to high $\delta^{34}\text{S}_{\text{SO}_4\text{other}}$ values.

For the shallow section of the Sherman Island core, the k -value for the sample at 18.2 m had to be set to 0.12 instead of the 0.18 determined from the *p*-TOMCAT model. A k -value > 0.12 led to a negative input of SO_4^{2-} , implying that sea ice was the main source of sea salt at that time. This finding could reflect different meteorological conditions or perhaps a smaller polynya area, which can vary greatly in size from year to year (Maqueda et al., 2004).

Overall, this low k -value showed that air mass trajectories did not pass over the open ocean or polynyas at that time.

The mid-depth core showed the expected seasonal signals, with high f_{bio} and low f_{ss} in the summer and an increased f_{other} in the winter. No seasonal signal was visible in the deep core section. Annual and seasonal source averages for all cores are shown in Table 4.5. Unless a season is stipulated, the average value is defined as the annual average across the total range of $\delta^{34}S_{SO_4 other}$ values used in the source model.

Overall, Sherman Island showed a larger sea salt source fraction than Dyer Plateau, where the average winter f_{ss} was $< 27\%$ with only one sample exceeding 50% , and the average summer f_{ss} was $< 10\%$. This result was likely due to Sherman Island's lower elevation and its proximity to the Amundsen Sea. The comparatively flat topography of Sherman Island could also play a role because it decreases the chance of sea salt loss due to increased precipitation prior to the deposition site. This could also contribute to the lower biogenic/sea salt sulfate ratio at Sherman relative to Dyer Plateau, because sea salt is depleted more quickly than biogenic sulfate during transport (Minikin et al., 1994). This effect was greatest in the shallow Sherman core, which had an average f_{bio} of 13.4% in the winter compared to 38.4% in the mid-depth core and 49.1% in the Dyer Plateau core. This significant decrease could be explained by a smaller polynya area and, therefore, decreased biogenic emissions. A smaller polynya was also invoked as a potential explanation for a low k -value, as described above. However, this conclusion is limited by the short ice core records and cannot be stated with certainty.

The third sulfate source fraction in all Sherman Island cores was lower than at Dyer Plateau, averaging 14.4% , 9.5% , and 5.6% in the shallow, mid-depth, and deep core, respectively, compared to 19.4% in the Dyer Plateau core. The same seasonality in the third sulfate source was observed at Sherman Island, with both a higher f_{other} and SO_4^{2-} concentration in the winter. These source values also appeared to increase over time. This change could reflect interannual variability, but a small anthropogenic input in the shallow core was also considered. Assuming the shallow core has the same SO_4^{2-} concentration as the mid-depth core, a 1.0 – 4.5% anthropogenic fraction of total sulfate would create the observed $\delta^{34}S_{SO_4}$ signal in the shallow core, given an anthropogenic $\delta^{34}S_{SO_4}$ of 4.4‰ (Seguin et al., 2014). However, no anthropogenic sulfate has been reported previously, and this theory does not explain the seasonality of the third source sulfate input. If the observed increase is a true climate signal, it could suggest changes in stratospheric circulation or the amount of sulfate aerosols in the stratosphere. However, longer ice core records are necessary to test this theory.

Although the third sulfate source fraction was smaller at Sherman Island than at Dyer Plateau, the SO_4^{2-} concentration was not significantly different. When averaged across all

Table 4.5 Sulfate sources at Sherman Island: Seasonal source fractions and concentrations¹

	Annual fraction of total SO_4^{2-}	Winter fraction of total SO_4^{2-}	Summer fraction of total SO_4^{2-}	Annual [SO_4^{2-}]	Winter [SO_4^{2-}]	Summer [SO_4^{2-}]
<i>Shallow core</i>						
Sea salt ²	52.41	66.61	27.01	58.61	59.61	29.21
Biogenic	31.0–35.5	10.2–16.5	59.6–63.2	37.6–41.9	10.9–16.1	71.3–74.7
Third source	12.2–16.6	17.0–23.3	9.8–13.4	11.7–16.0	14.3–19.5	9.3–12.7
<i>Mid-Depth Core</i>						
Sea salt	36.5	48.7	30.5	45.5	45.5	53.4
Biogenic	52.6–55.5	36.4–40.4	61.3–63.5	74.1–77.6	36.8–40.5	107.3–111.1
Third source	8.0–10.9	11.0–15.0	5.9–8.1	9.7–13.3	10.3–14.1	10.3–14.0
<i>Deep-Core</i>						
Sea salt	47.5			59.0		
Biogenic	46.1–47.4			57.1–59.2		
Third source	4.7–6.4			5.8–8.0		

¹Fractions reported as a % and concentrations reported in ppb

²No range for sea salt fraction, which is calculated with seasonal k-values and does not depend on $\delta^{34}\text{S}_{\text{SO}_4\text{other}}$

cores, the $\text{SO}_{4\text{other}}^{2-}$ concentration at Sherman Island was 10.8 ± 3.5 ppb compared to 9.3 ± 5.6 ppb at Dyer Plateau. This similarity showed that the overall strength of the third sulfate source was roughly the same at both sites. If the third sulfate source is volcanic/stratospheric, these results imply minimal spatial variance in volcanic/stratospheric sulfate and/or similar stratospheric intrusion at both sites.

The different f_{other} values at each site likely result from different strengths in the sea salt and biogenic sulfate sources. This was apparent in the concentration of $\text{SO}_{4\text{ss}}^{2-}$ and $\text{SO}_{4\text{bio}}^{2-}$ at Sherman Island and Dyer Plateau, which averaged 54.4 ppb and 57.9 ppb, and 5.9 ppb and 30.6 ppb, respectively. The larger input of sea salt and biogenic sulfate at Sherman Island led to a smaller f_{other} value. This result further highlighted the likely impact of site elevation, proximity to the sea, and the surrounding topography. Additional site studies are needed to explore this theory, which I also address in the following Skytrain Ice Rise discussion.

4.4.2 Skytrain Ice Rise

4.4.2.1 Volcanic samples and age scale application

Unfortunately, none of the Skytrain samples had a clear input of volcanic sulfate. In fact, all potentially-volcanic sulfate peaks had a higher $\delta^{34}\text{S}_{\text{SO}_4}$ value than the adjacent background sample, which is the opposite of what would be expected for a volcanic signal (Table 4.4). Furthermore, no measured $\delta^{34}\text{S}_{\text{SO}_4}$ value was significantly lower than the typical values seen in the other Skytrain samples, which had an average $\delta^{34}\text{S}_{\text{SO}_4}$ of $15.54 \pm 1.35\text{‰}$. The greatest outlier was sample 139a, which had a $\delta^{34}\text{S}_{\text{SO}_4}$ value of $18.76 \pm 0.06\text{‰}$. However, this sulfate peak aligned with a large sodium peak, which explained the high $\delta^{34}\text{S}_{\text{SO}_4}$ value due to increased sea salt input. This result highlighted the difficulty of identifying volcanic sulfate peaks in the Skytrain ice core. Additional potentially-volcanic peaks will likely be analyzed by the team dating the ice core to further refine their age scale.

4.4.2.2 Changes in major ion concentrations between ~10,400–720 ypb: A potential retreat of the Ronne Ice Shelf

Both Skytrain ice core sections spanned multiple years, so no seasonal signal could be resolved. The average sulfate concentration in the ~10,400 ybp core section was ~25 ppb lower than in the ~720 ybp core section with less variability because of the lower-resolution in deeper ice cores. The higher sulfate concentrations in the younger core suggested either 1) at least one sulfate source became stronger between ~10,400–720 ybp, or 2) a new sulfate source was established. Because of the limited number of Skytrain samples, I examined a longer sulfate concentration record for Skytrain Ice Rise to assess the validity of this

conclusion. This record had previously been measured via continuous flow analysis (CFA) at the British Antarctic Survey and was obtained from Dr Mackenzie Grieman (personal communication, 2021). The record showed an increase in sulfate concentrations at ~ 8 ka from ~ 40 ppb to ~ 100 ppb, which confirmed my observation for the Skytrain samples (Figure 4.8).

The increase in sulfate concentrations at ~ 8 ka may be related to the retreat of the Ronne Ice Shelf, which would have increased both sea salt and biogenic sulfate emissions. However, before further exploring this theory, the possibility of a terrestrial dust source needed to be considered. Terrestrial sulfate was quantified with Ca_{nss}^{2+} by the same method used for the Sherman Island ice core. The Ca_{nss}^{2+} concentration was first calculated with IC data, but this resulted in a terrestrial sulfate fraction $> 16\%$. Furthermore, when Ca_{nss}^{2+} was used to quantify non-sea salt sodium (Na_{nss}^+) as in Röthlisberger et al. (2002), it led to a Na_{nss}^+ fraction $> 44\%$, which was not realistic. After re-examining the IC data, I noticed that the Ca^{2+} concentrations were too high, perhaps due to contamination during cutting the samples. Instead, I used CFA data from similar depths as the samples. For CFA analysis, the ice core is analyzed as a stick of ice and does not need to be cut for individual samples, which would reduce the potential for contamination. The CFA data showed a SO_{4terr}^{2-} and Na_{nss}^+ source fraction $< 2.1\%$ and $< 6.1\%$, respectively, confirming minimal terrestrial input. The CFA and IC-determined sulfate concentrations agreed with each other, so any contamination that occurred did not affect sulfate.

To address the Ronne Ice shelf theory, I considered both the sea salt and biogenic sulfate contribution. If the ice shelf retreated, a new area of ocean would be uncovered and become a source of sea salt and biogenic sulfate production. Furthermore, Skytrain Ice Rise would be closer to the coast, so the strength of these new sources would increase. A ~ 180 ppb rise in Na^+ concentrations between the core sections suggested a potential increase in sea salt input, which was supported by a concurrent rise in Cl^- concentrations. The high Na^+ and Cl^- concentrations only spanned half the core, but the peak extended > 2.5 years, so the observed increase was not a short-term event.

As with sulfate, sodium concentrations in the Skytrain samples were compared to the complete Skytrain record, which confirmed the observed increase. The lack of MSA IC data for the ~ 720 ybp core did not enable a direct comparison between the two Skytrain core sections. However, the complete CFA Skytrain record showed a concurrent rise in MSA concentrations at ~ 8 ka that suggested increased biogenic emissions (Figure 4.8). The trends in Na^+ and MSA were both consistent with an ice shelf retreat. However, to better characterize these changes and their relationship to the Ronne Ice Shelf, $\delta^{34}\text{S}_{\text{SO}_4}$ data needed to be evaluated.

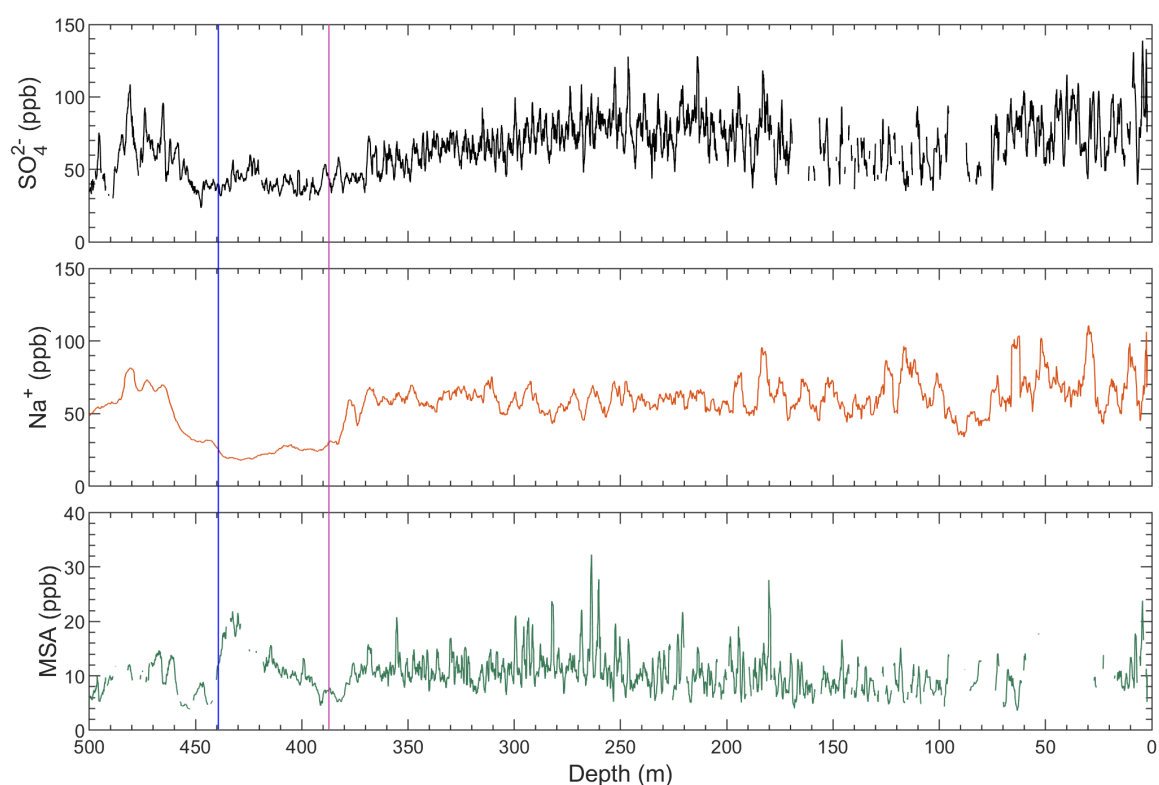


Fig. 4.8 Sulfate, sodium, and MSA concentrations for a 500 m ($\sim 36,000$ year) section of the Skytrain Ice Rise ice core, smoothed with a 20-point moving average. The blue line marks the end of the Last Glacial Maximum. The purple line at ~ 8 ka marks the increase in major ion concentrations that has been proposed as the retreat of the Ronne Ice Shelf. Unpublished data are based on a preliminary age scale and obtained from Dr Mackenzie Grieman (personal communication, 2021).

4.4.2.3 Initial interpretation of sulfur isotope data

The average $\delta^{34}\text{S}_{\text{SO}_4}$ of the ~ 720 ybp and $\sim 10,400$ ybp Skytrain cores was $15.54 \pm 1.35\text{‰}$ and $14.87 \pm 0.65\text{‰}$, respectively. The greater variation in the ~ 720 ybp core could be due to less smoothing in the shallower core; at $\sim 10,400$ ybp, annual layers are already thinned to below 2 cm. Though these values were based on short ice core records, the higher $\delta^{34}\text{S}_{\text{SO}_4}$ values in the ~ 720 ybp could suggest a greater relative sea salt and/or biogenic sulfate source, which would align with the Ronne Ice Shelf theory.

The relatively low $\delta^{34}\text{S}_{\text{SO}_4}$ values in both cores also suggested input from the third sulfate source that was seen at the other sites. Skytrain $\delta^{34}\text{S}_{\text{SO}_4}$ values were $\sim 3\text{‰}$ lower than at Sherman Island and similar to the $15.96 \pm 3.26\text{‰}$ value from the Dyer Plateau ice core. The Skytrain data also showed the same positive correlation between $\delta^{34}\text{S}_{\text{SO}_4}$ and sulfate concentrations that was seen at Sherman Island (Figure 4.9), though these fluctuations did not represent a seasonal signal. These results suggested that the third sulfate source was present at all sites but with a different relative input or source strength. Based on initial data, Skytrain appeared more similar to Dyer Plateau than Sherman Island; however, an isotope mixing model was necessary to identify and quantify each sulfate source.

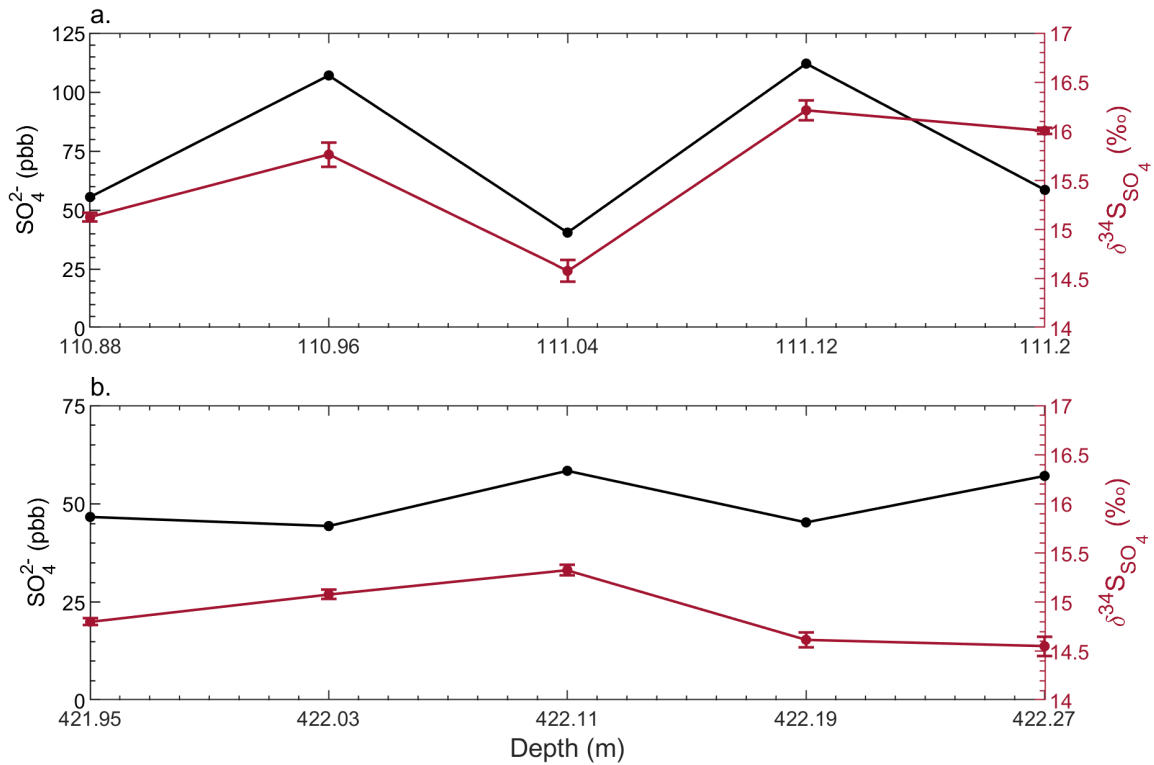


Fig. 4.9 Sulfate concentrations and total $\delta^{34}\text{S}_{\text{SO}_4}$ values in the ~ 720 ybp (a) and $\sim 10,400$ ybp (b) Skytrain ice core sections.

4.4.2.4 Using a three-source model to quantify and compare sulfate sources at Skytrain Ice Rise, Sherman Island, and Dyer Plateau

I used the p-TOMCAT chemical transport model to determine an average k-value for both Skytrain core sections as described for the deep Sherman Island core. The p-TOMCAT model produced a k-value of 0.2, which was used for both cores. The three-source model was run for $\delta^{34}\text{S}_{\text{SO}_4\text{other}}$ values between 0–5‰, and $\delta^{34}\text{S}_{\text{SO}_4\text{bio}}$ was set as 18.6‰. Model results are shown in Table 4.6.

Table 4.6 Sulfate source fractions and concentrations at Skytrain Ice Rise¹

	Fraction of total SO_4^{2-}	$[\text{SO}_4^{2-}]$
<i>~720 ypb</i>		
Sea salt ²	29.11	19.91
Biogenic	43.0–50.5	35.4–40.6
Third source	20.4–27.9	14.3–19.5
<i>~10,400 ypb</i>		
Sea salt	17.11	8.41
Biogenic	52.4–60.6	26.7–30.8
Third source	22.3–30.5	11.2–15.3

¹Fractions reported as a % and concentrations reported in ppb

²No range for sea salt fraction, which is calculated with a k-value and does not depend on $\delta^{34}\text{S}_{\text{SO}_4\text{other}}$

The average sea salt source fraction increased 12.0% between ~10,400–720 ybp, and the biogenic fraction decreased 9.8%. The strength of the sea salt and biogenic sources increased, but the larger relative increase in the SO_4^{2-} concentration showed a shift toward a more sea salt-driven system. Despite this change, biogenic activity remained the dominant sulfate source at Skytrain Ice Rise, accounting for almost half of total sulfate. This result was similar to Sherman Island, with average biogenic sulfate fractions of 46.8% and 44.7%, respectively, but it was lower than the 64.4% biogenic fraction seen at Dyer Plateau. As previously discussed, this could reflect the lower elevation and flatter topography of Skytrain Ice Rise compared to Dyer Plateau. However, the sea salt sulfate fraction in the ~720 ypb Skytrain core was lower than average Sherman Island value. This could result from the further transport distance from the marine source to Skytrain Ice Rise, which would cause increased sea salt loss relative to biogenic sulfate (Minikin et al., 1994).

The third sulfate source fraction increased 2.2% between ~10,400–720 ybp, with a final SO_4^{2-} concentration of 16.9 ppb. This concentration was twice that seen at Sherman Island and Dyer Plateau, which could contradict my previous theory of spatial uniformity in stratospheric sulfate. However, this conclusion is based on very limited data, and the

varying results may just reflect short-term variability in sources. Because no seasonal data was available at Skytrain Ice Rise, it was not possible to confirm a primarily winter input of the third sulfate source, which would have supported a stratospheric origin.

4.4.2.5 Implications for a past retreat of the Ronne Ice Shelf

The observed increase in sea salt and biogenic sulfate concentrations was consistent with the theory of a retreat of the Ronne Ice Shelf. A smaller ice shelf would expose more open ocean for the formation of sea ice or marine biogenic activity, which would increase the overall sulfate flux. The greater increase in sea salt relative to biogenic sulfate could also point to ice shelf retreat. Minikin et al. (1994) showed that sea salt is lost 3x more quickly than biogenic sulfate during transport; therefore, a shorter distance from source emission to the deposition site would affect sea salt sulfate more than biogenic sulfate. If decreased transport distance was not the cause for this difference, it would suggest that sea ice formed in the newly-uncovered ocean produced more sulfate than increased marine biogenic activity, which seems unlikely.

4.5 Spatial comparison of sulfate sources in Antarctica

The third source sulfate fraction at Dyer Plateau, Sherman Island, and Skytrain Ice Rise fell within the range of reported values for volcanic/stratospheric sulfate in East Antarctica (Figure 4.10, Table 4.7). The greatest difference was found at Sherman Island, which had an average third source fraction of $9.80 \pm 2.12\%$ across all cores. This fraction was at least $\sim 10\%$ lower than reported for all other sites except for at the South Pole (Patris et al., 2000) and Dronning Maud Land (DML) (Uemura et al., 2016), which presented a volcanic/stratospheric sulfate fraction of 0–8.0% and $6.0 \pm 16\%$, respectively. However, additional studies at South Pole and DML found volcanic/stratospheric fractions of $27.7 \pm 6.9\%$ (Baroni et al., 2008) and 10–20% (Jonsell et al., 2005), respectively, showing great spatial and, perhaps, temporal variability. None of the three Sherman Island cores agreed with the high fraction of volcanic/stratospheric sulfate reported in West Antarctica (Kunasek et al., 2010; Pruett et al., 2004), further suggesting that WAIS is an anomalous site.

The same spatial variability was found in the $\text{SO}_{4\text{other}}^{2-}$ concentration at all Antarctica sites (Table 4.7). As discussed above, two studies at both the DML and South Pole reported both low and high $\text{SO}_{4\text{other}}^{2-}$ concentrations, further suggesting temporal variability in third source strength. The Vostok ice core was a major outlier, with a $\text{SO}_{4\text{other}}^{2-}$ concentration of 58.9 ± 12.6 ppb compared to the average 14.5 ± 6.5 ppb at other sites. Excluding the Vostok study, the $\text{SO}_{4\text{other}}^{2-}$ concentrations at Dyer Plateau, Sherman Island, and Skytrain Ice Rise were not

significantly different than at the other Antarctica sites, including those in West Antarctica. This finding suggests that the large third source fractions reported at WAIS may be related to lesser SO_{4ss}^{2-} and SO_{4bio}^{2-} input and not the strength of the third sulfate source.

Overall, the spatial variability of sulfate sources shows no clear difference between East and West Antarctica as previously proposed. However, sulfur isotope ratios need to be measured in more ice cores to fill out a map of sources around Antarctica and better evaluate potential causes of source variability.

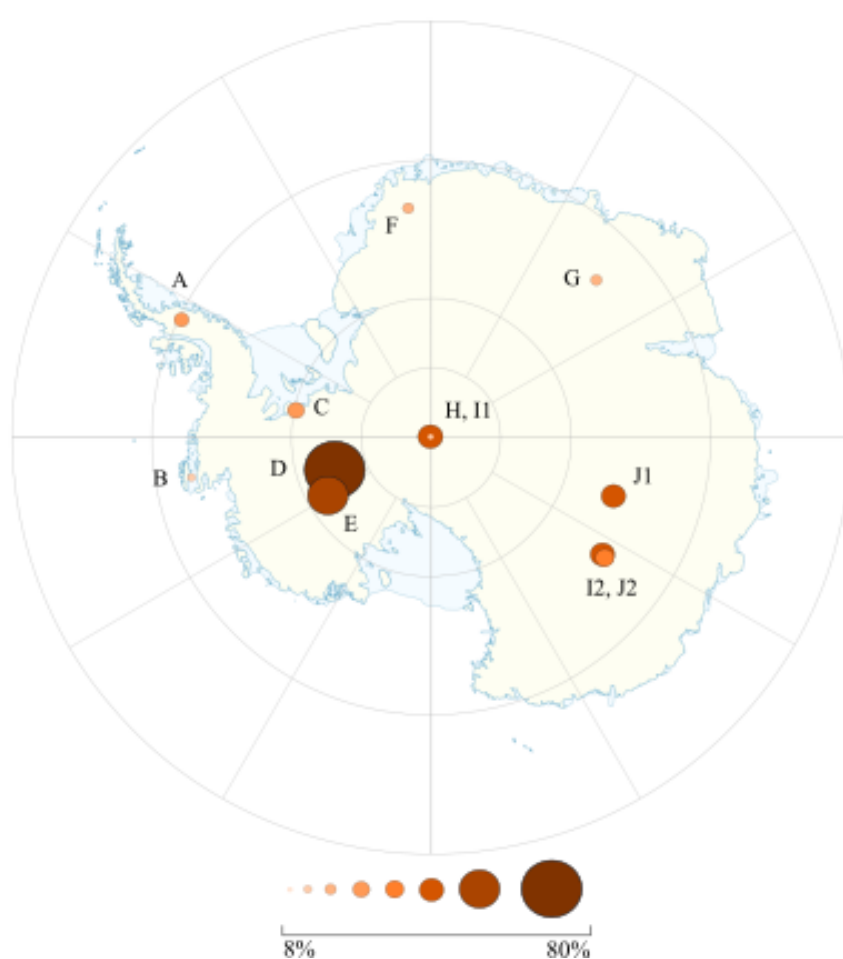


Fig. 4.10 Map showing spatial variance in a third sulfate source with a low sulfur isotopic composition. The relative size of the marker represents the third source fraction of total sulfate. See Table 4.7 for details.

Table 4.7 Reported third sulfate source fractions and concentrations in East and West Antarctica

Map marker	Site	$\delta^{34}\text{S}_{\text{SO}_4}$ (‰)	Fraction of total SO_4^{2-} (%)	$[\text{SO}_4^{2-}]_{\text{other}}$ (ppb)	Reference
A	Dyer Plateau	15.96 ± 3.26	20.6 ± 4.5	9.3 ± 5.6	This work ¹
B	Sherman Island	18.20 ± 1.81	9.8 ± 2.1	10.8 ± 3.5	This work ¹
C	Skytrain Ice Rise	15.54 ± 1.35	25.3 ± 4.7	15.8 ± 6.5	This work ¹
D	WAIS	4.0–9.3	72–90	20.1–25.2	Kunasek et al., 2010 ²
E	RIDSA	3.1–9.9	~ 42	14.3 $\pm$ 3.1	Pruett et al., 2004 ³
F	Dronning Maud Land	14.6	10–20	8.4–16.8	Jonsell et al., 2005 ⁴
G	Dronning Maud Land	14.8–16.9	6 $\pm$ 16	2.1–5.0	Uemura et al., 2016
H	South Pole	17.7–18.1	0.0–8.0	0.0–4.0	Patris et al., 2000
I1	South Pole	10.98–14.43	27.7 $\pm$ 6.9	14.1 $\pm$ 3.5	Baroni et al., 2008 ⁵
I2	Dome C	11.45–15.30	24.3 $\pm$ 7.8	18.9 $\pm$ 6.7	Baroni et al., 2008 ⁶
J1	Vostok	9.5–14.3	36.1 $\pm$ 1.8	58.9 $\pm$ 21.6	Alexander et al., 2003 ⁷
J2	Dome C	10.5–12.1	33.7 $\pm$ 2.6	24.1 $\pm$ 2.1	Alexander et al., 2003

¹ Averaged values for $\delta^{34}\text{S}_{\text{SO}_4\text{other}}$ between 0–5‰ and a $\delta^{34}\text{S}_{\text{SO}_4\text{bio}}$ of 18.6‰² Calculated with average $[\text{SO}_4^{2-}]$ of 28 ppb, approximated from reference data³ Calculated with a stratospheric third source $\delta^{34}\text{S}_{\text{SO}_4}$ of -12‰ as suggested in paper⁴ Calculated with average $[\text{SO}_4^{2-}]$ of shallow cores⁵ Calculated assuming $f_{\text{ss}} = 6\%$ as per Patris et al. (2000) and a volcanic/stratospheric third source $\delta^{34}\text{S}_{\text{SO}_4}$ of 0‰⁶ Calculated assuming average $f_{\text{ss}} = 6.8\%$ as per Alexander et al. (2003) and a volcanic/stratospheric third source $\delta^{34}\text{S}_{\text{SO}_4}$ of 0‰⁷ Assuming $k = 0.25$ to calculate $[\text{SO}_4^{2-}]$ and a volcanic/stratospheric third source $\delta^{34}\text{S}_{\text{SO}_4}$ of 0‰

4.6 Future work

The primary limitation in this study was the short timespan of each core, which made it difficult to separate short-term fluctuations from true climate signals. Therefore, $\delta^{34}\text{S}_{\text{SO}_4}$ needs to be measured for additional ice core records. Ideally, measurements would be made for a long, complete ice core record, such as the Skytrain Ice Rise ice core. However, the time required for such measurements would be extensive. Instead, measuring small core sections within a long, continuous record could also help place findings in context to identify long-term climate signals.

In addition to longer records, a greater spatial range of ice cores should be studied. The Dyer Plateau, Sherman Island, and Skytrain Ice Rise ice cores all had a third source sulfate fraction $< 25\%$, which is significantly smaller than the volcanic/stratospheric source estimates from other ice core studies in West Antarctica. Similarly, numerous sites in East Antarctica showed variable fractions of volcanic/stratospheric sulfate ranging between 6.0–38.4%. This suggests a possible spatial variability in sulfate sources on a smaller scale than East versus West Antarctica; however, further studies are necessary to explore this theory.

It would also be interesting to analyze an ice core on the coast of the Antarctic Peninsula to determine how topography affects the final sulfate deposition. This was attempted with the Bryan Coast ice core described in Chapter 3, which had issues with large particulate matter in the samples. However, if an appropriate filter technique was developed, this analysis would be feasible.

4.7 Conclusion

Sulfur isotope ratios were measured in two ice cores from West Antarctica: Sherman Island and Skytrain Ice Rise. This $\delta^{34}\text{S}_{\text{SO}_4}$ data was combined with that for Dyer Plateau in Chapter 3, and a three-source model was used to create a spatial map of sulfate sources in Antarctica. Several potentially-volcanic samples were also analyzed at each site. Two sulfate peaks in the Sherman Island ice core were confirmed to be of volcanic origin and have been recommended as fixed points to refine the preliminary age scale.

Model results for the Sherman Island shallow and mid-depth core sections showed the same seasonal signals in $\text{SO}_{4\text{ss}}^{2-}$, $\text{SO}_{4\text{bio}}^{2-}$, $\text{SO}_{4\text{other}}^{2-}$, and $\delta^{34}\text{S}_{\text{SO}_4}$ as seen in the Dyer Plateau core, further supporting the theory of a stratospheric source with increased winter input. The three-source model was also used to reconstruct changes in sulfate sources at Skytrain Ice Rise between $\sim 10,400$ –720 ypb and showed an increase in sea salt and biogenic sulfate concentrations. This finding supported the proposed retreat of the Ronne Ice Shelf at ~ 8

ka, which would have increased the ocean area available for sea ice formation and marine biogenic activity.

The third source sulfate fraction at Sherman Island and Skytrain Ice Rise was $9.8 \pm 2.1\%$ and $25.3 \pm 4.7\%$, respectively, with the Sherman Island fraction averaged across three cores. These values were significantly below the 72-90% fraction of volcanic/stratospheric sulfate proposed by Kunasek et al. (2010) for the West Antarctic Ice Sheet, and they fell within the range of multiple studies in East Antarctica. Combined with the results for Dyer Plateau, these findings do not suggest a major difference in sulfate sources between East and West Antarctica but instead significant spatial variability on a smaller scale. Additional ice core $\delta^{34}\text{S}_{\text{SO}_4}$ measurements are needed to explore both spatial and long-term changes in sulfate sources around Antarctica.

Chapter 5

Changes in sulfate sources in West Antarctica from the Last Glacial Maximum to the Holocene

5.1 Introduction

5.1.1 Chapter outline

In this chapter, I report measurements of the sulfur isotopic composition of sulfate ($\delta^{34}\text{S}_{\text{SO}_4}$) for Skytrain Ice Rise ice core samples from the Last Glacial Maximum (LGM). I compare these results to the early and late Holocene samples discussed in Chapter 4 and identify glacial/interglacial changes in the sulfur isotopic composition. Assuming no sulfur isotope fractionation during formation and/or transport, I use a three-source mixing model to quantify sea salt sulfate ($\text{SO}_{4\text{ss}}^{2-}$), biogenic sulfate ($\text{SO}_{4\text{bio}}^{2-}$), and a third sulfate source with a low sulfur isotopic composition ($\text{SO}_{4\text{other}}^{2-}$), attributed to volcanic/stratospheric input in Chapters 3 and 4. I evaluate how this third source has changed over time and the potential causes of this shift. I then consider possible variations in the sulfate-to-calcium ratio of terrestrial dust sources, how this would affect our interpretation of terrestrial input in Antarctica, and what this could reveal about changes in marine biogenic activity during the LGM. Finally, I use these findings to re-evaluate my previous interpretation of terrestrial dust input in non-glacial ice cores.

5.1.2 Sulfate sources in glacial vs interglacial periods

The comparison of glacial and interglacial periods reveals the global response to a large climate transition. By studying these large-scale changes, we can better evaluate the behaviour of the current climate system and how it will be affected by a changing climate. The Last Glacial Period (LGP) extended from ~ 115 – 12 thousand years ago (ka), with the LGM spanning 26.5 – 19 ka (Clark et al., 2009). Ice core records span the past 800 thousand years and are, therefore, a valuable tool to study glacial/interglacial transitions (EPICA community members, 2004). For example, a primary objective of the Skytrain Ice Rise ice core is to explore the potential collapse of the West Antarctic Ice Sheet during the last interglacial (Bamber et al., 2009).

The Skytrain Ice Rise ice core is also an excellent opportunity to assess differences in the sulfur isotopic composition of sulfate deposited on the ice on a glacial/interglacial scale. This shift in $\delta^{34}\text{S}_{\text{SO}_4}$ could reveal changes in sulfate sources over time and how they relate to the climate system, e.g., how changes in biogenic emissions may have affected radiative cooling (Charlson et al., 1987). An ice core study in East Antarctica reported $\delta^{34}\text{S}_{\text{SO}_4}$ values in the LGM that are $\sim 4\%$ lower than in the Holocene (Alexander et al., 2003). They ruled out stratospheric sulfate as a source of these low $\delta^{34}\text{S}_{\text{SO}_4}$ values because of the lack of mass-independent fractionation (MIF) of the oxygen isotopic composition of sulfate ($\Delta^{17}\text{O}$) caused by exposure to ultraviolet light in the stratosphere. They also eliminated a terrestrial dust source based on low concentrations of calcium (Ca^{2+}) in the ice, which derives primarily from terrigenous material (Wolff et al., 2010). Instead, Alexander et al. (2003) attributed this sulfur isotope depletion to sulfur isotope fractionation during transport, which would increase in glacial periods because of the greater distance from marine sources to the deposition site. Based on this conclusion, sulfur isotope ratios in ice could not be used to partition sulfate sources because conservation of the source $\delta^{34}\text{S}_{\text{SO}_4}$ value could not be assumed.

However, subsequent studies have rebutted the hypothesis of sulfur isotope fractionation during transport. Uemura et al. (2016) measured sulfur isotope ratios in a transect of shallow cores in East Antarctica and found remarkably consistent $\delta^{34}\text{S}$ of non-sea salt sulfate ($\text{SO}_{4\text{ns}}^{2-}$) ranging between 14.8 – 16.9% . Ishino et al. (2019) advanced this finding by conducting $\delta^{34}\text{S}_{\text{SO}_4}$ aerosol measurements at Dome C and Durmont d’Urville Station in East Antarctica and found minimal sulfur isotope fractionation with inland transport. Instead, recent studies have revisited the idea of a large terrestrial sulfate source ($\text{SO}_{4\text{terr}}^{2-}$) during glacial periods concurrent with a decrease in biogenic emissions as a cause of the observed low $\delta^{34}\text{S}_{\text{SO}_4}$ values (Goto-Azuma et al., 2019; Ishino et al., 2019).

5.1.3 The nature of the terrestrial sulfate source and biogenic emissions during glacial periods

Terrestrial sulfate that reaches Antarctica is primarily from dust including crustal minerals such as CaSO_4 (gypsum) (Goto-Azuma et al., 2019; Wolff et al., 2006). Henceforth, the terrestrial source and $\text{SO}_4^{2-}_{terr}$ will refer to continental dust input unless stipulated otherwise. The sulfur isotopic composition of $\text{SO}_4^{2-}_{terr}$ varies significantly depending on the dust source, with reported values between 0–20‰ (Nielsen et al., 1991). A large terrestrial sulfate source with a low sulfur isotopic composition could act as a strong lever to pull down $\delta^{34}\text{S}_{\text{SO}_4}$ values in glacial periods.

The theory of a large terrestrial sulfate source and a smaller biogenic sulfate source during glacial periods challenges some previous ice core studies. Legrand et al. (1991, 1988b) reported higher concentrations of $\text{SO}_4^{2-}_{nss}$ and methanesulfonic acid (MSA) in the Vostok ice core during glacial periods. They attributed these high concentrations to increased biogenic emissions of dimethylsulfide (DMS), which oxidizes to MSA and SO_4^{2-} . However, the higher concentration of $\text{SO}_4^{2-}_{nss}$ and MSA in ice cores may be due to the lower accumulation rate during glacial periods and not reflect a change in marine biogenic emissions (Wolff et al., 2006). Furthermore, $\text{SO}_4^{2-}_{nss}$ concentrations in both EPICA ice cores were stable across glacial/interglacial cycles (Kaufmann et al., 2010). Marine sediment cores actually show a decrease in biogenic activity in the region south of the Antarctic Polar Front in glacial periods based on decreased biogenic carbon export (Kohfeld et al., 2005). Therefore, the necessary decrease in biogenic emissions to account for a large terrestrial source in glacial periods would reconcile the difference between ice core and marine sediment core studies.

The origin of terrestrial sulfate that reaches Antarctica can vary. Terrestrial dust can be directly transported to and deposited on the ice surface, which is called a primary source. Secondary gypsum can also be formed by the reaction of calcium carbonate (CaCO_3), a major component of terrestrial dust, with $\text{SO}_4^{2-}_{bio}$ during transport. Primary terrestrial sources have a range of sulfur isotopic compositions and could contribute to the lower glacial $\delta^{34}\text{S}_{\text{SO}_4}$ values (Nielsen et al., 1991). However, secondary gypsum is expected to have the same sulfur isotopic composition as biogenic sulfate (18‰), so it would not cause lower $\delta^{34}\text{S}_{\text{SO}_4}$ values in the ice. Therefore, the theory of a large glacial terrestrial source depends largely on the origin and formation mechanism of $\text{SO}_4^{2-}_{terr}$ deposited on the ice.

5.1.4 Quantifying the terrestrial sulfate source

The amount of $\text{SO}_4^{2-}_{terr}$ in an ice core can be quantified using the Ca^{2+}_{nss} concentration in the ice and the ratio of sulfate-to-calcium in the terrestrial source ($(\text{SO}_4^{2-}/\text{Ca}^{2+})_{terr}$), as described

in Röthlisberger et al. (2002) and calculated in previous chapters. Many studies have used a $(\text{SO}_4^{2-}/\text{Ca}^{2+})_{terr}$ ratio of 0.1 or 0.18 based on average soil values (e.g., Bowen, 1979; Kunasek et al., 2010; Patris et al., 2002). Kaufmann et al. (2010) used a $(\text{SO}_4^{2-}/\text{Ca}^{2+})_{terr}$ ratio of 0.5 as an uppermost limit based on values from preindustrial Saharan dust plumes (Wagenbach et al., 1996). Even with this higher ratio, Kaufmann et al. (2010) calculated a maximum terrestrial source fraction of 16% of total sulfate, which is too small to account for the low glacial $\delta^{34}\text{S}_{\text{SO}_4}$ values. However, $(\text{SO}_4^{2-}/\text{Ca}^{2+})_{terr}$ ratios are source dependent and highly variable (Wolff et al., 2010). Furthermore, the $(\text{SO}_4^{2-}/\text{Ca}^{2+})_{terr}$ ratio has to represent not only primary sulfate input, e.g., from soils, but also if/how that ratio could be affected by secondary gypsum formation. If the true $(\text{SO}_4^{2-}/\text{Ca}^{2+})_{terr}$ ratio in an ice core is sufficiently high, it could allow for a large terrestrial source.

This argument has been invoked by Goto-Azuma et al. (2019) as a possible mechanism to explain a large terrestrial dust source in glacial periods. In a study of several ice cores from East Antarctica, Goto-Azuma et al. (2019) suggested that primary gypsum, which has a $\text{SO}_4^{2-}/\text{Ca}^{2+}$ ratio of 2.4, is a major source of SO_4^{2-} to Antarctica in the LGP. Studies have reported soils in Patagonia with ~ 2.4 ratios (Bouza et al., 2007), and gypsum-rich evaporites are well-documented around South America, a significant source region of dust to Antarctica (Drewry et al., 1974). Using this 2.4 ratio, Goto-Azuma et al. (2019) found that SO_4^{2-} accounted for up to 76% of SO_4^{2-} in the Dome F and EDML ice cores and up to 64% of SO_4^{2-} in the EDC ice core during the LGP. To account for secondary gypsum input, they also evaluated $(\text{SO}_4^{2-}/\text{Ca}^{2+})_{terr}$ ratios between 1.3–2.4 and found that SO_4^{2-} still contributed almost 40% of SO_4^{2-} at the lowest ratio. Overall, this argument may support the possibility of a large terrestrial source in Antarctica during glacial periods.

The terrestrial source theory was also considered by Ishino et al. (2019), who re-evaluated glacial/interglacial $\delta^{34}\text{S}_{\text{SO}_4}$ data from the Dome C and Vostok ice cores measured by Alexander et al. (2003). Ishino et al. (2019) did not specify a gypsum source but instead defined a non-sea salt, non-marine biogenic sulfate source that included volcanic, stratospheric, and long-range transport from other continents, including potential dust input. They assigned this source a $\delta^{34}\text{S}_{\text{SO}_4}$ signature of 0–5‰ and determined that it accounted for $\sim 50\%$ of SO_4^{2-} in glacial periods. This finding also supports the possibility of a large terrestrial sulfate source provided it has a sufficiently low sulfur isotopic composition. However, glacial $\delta^{34}\text{S}_{\text{SO}_4}$ data are confined to a single study consisting of only a handful of data points from East Antarctica, and further studies are needed to evaluate how continental and biogenic sources change on glacial/interglacial timescales. My comparison of LGM and Holocene $\delta^{34}\text{S}_{\text{SO}_4}$ values in the Skytrain Ice Rise ice core builds on the glacial $\delta^{34}\text{S}_{\text{SO}_4}$ data from Alexander et al. (2003) and is a valuable contribution to these research questions.

5.2 Methods

5.2.1 Description of Skytrain Ice Rise and sample preparation

The location of Skytrain Ice Rise and the sample preparation process were described in Chapter 4. Four 8 cm samples from the LGM were analyzed between the depths 477.85–478.09 m. Samples were labelled 5981–5984 and spanned the years $\sim 24,660$ – $24,740$ ybp (years before 1950) based on a preliminary age scale.

5.2.2 Analytical methods

5.2.2.1 Ion chromatography

All ion chromatography (IC) analyses were completed at the British Antarctic Survey (BAS) in Cambridge, England. Measurements were made with a Dionex ICS-4000 Integrion and were performed by lab technicians Jack Humby and Shaun Miller or by Isobel Rowell, a PhD student at the University of Cambridge.

5.2.2.2 Isotope analysis

I performed all isotope measurements via multicollector inductively coupled mass spectrometry (MC-ICP-MS) at the University of Cambridge as outlined in Chapter 2. All measurement uncertainties are reported as 2 standard deviations (2σ).

5.3 Results

5.3.1 Ion chromatography

The SO_4^{2-} , sodium (Na^+), and MSA concentrations of the glacial samples averaged 91.1 ± 64.7 ppb, 70.0 ± 8.1 ppb, and 7.4 ± 4.6 ppb, respectively. The SO_{4ns}^{2-} concentration was calculated using a k-value of 0.15, which was lowered from the 0.2 value determined by the p-TOMCAT model in Chapter 4 to account for increased sea ice extent during the LGM. All concentrations are shown in Table 5.1 along with the early and late Holocene data from Chapter 4 for comparison. The average LGM SO_4^{2-} and Na^+ concentrations were significantly higher than the respective 50.4 ± 13.6 ppb and 41.8 ± 24.0 ppb concentrations in the early Holocene core. They were also on average higher than, but overlapping with, the concentrations measured in the late Holocene. In the LGM, the SO_{4ns}^{2-} concentration was ~ 20 – 30% higher than in either Holocene core section. The average MSA concentration

was slightly lower than in the early Holocene samples and slightly higher than the late Holocene samples, but this small difference may not be significant because of the wide range in data. However, all concentrations were within the range seen in ICP-MS and fast ion chromatography (FIC) analysis for the ice surrounding these samples. These measurements had been completed in 2020 at BAS for the complete Skytrain Ice Rise ice core and were obtained from Dr Mackenzie Grieman (personal communication, 2021).

Table 5.1 Major ion concentrations for all Skytrain Ice Rise ice core samples¹

	LGM (~24,700 ypb)	Early Holocene (~10,400 ypb)	Late Holocene (~720 ybp)
[SO ₄ ²⁻]	91.1 ± 64.7	50.4 ± 13.6	74.7 ± 65.2
[SO ₄ ²⁻] _{nss}	82.3 ± 64.5	48.0 ± 13.8	62.9 ± 66.4
[Na ⁺]	70.0 ± 8.1	41.8 ± 24.0	99.1 ± 134.6
[MSA]	7.4 ± 4.6	11.9 ± 6.4	5.1 ± 3.1 ²

¹All concentrations reported in ppb

²Because of IC error, calculated from ICP-MS data at a corresponding depth.

5.3.2 Isotope analysis

The four glacial Skytrain samples were analyzed in the same MC-ICP-MS run as the Holocene samples described in Chapter 4. An IAPSO seawater internal standard was analyzed at the start and end of the run as well as after the first five samples to assess measurement accuracy. The known $\delta^{34}\text{S}_{\text{SO}_4}$ of the standard was $21.16 \pm 0.11\text{‰}$ ($n = 10$), measured with a Thermo Delta V gas source mass spectrometer (GS-MS) at the University of Cambridge with the assistance of Dr Alexandra Turchyn. The measured $\delta^{34}\text{S}_{\text{SO}_4}$ of the seawater standard throughout the run was 21.16‰ with an external error of $\pm 0.16\text{‰}$ ($n = 6$). The average $\delta^{34}\text{S}_{\text{SO}_4}$ value of the glacial samples was $11.01 \pm 0.70\text{‰}$, and the reproducibility of sample measurements averaged $\pm 0.08\text{‰}$. All isotope data are shown in Table 5.2.

Table 5.2 Sulfur isotope data for Skytrain Ice Rise glacial samples

Sample	n	$\delta^{34}\text{S}_{\text{SO}_4}$ (‰)	2 σ^1
5981	3	11.20	0.08
5982	3	10.69	0.05
5983	3	11.40	0.15
5984	3	10.73	0.05

¹Sample reproducibility, independent of $\pm 0.16\text{‰}$ external error

5.4 Discussion

5.4.1 Initial interpretation of glacial/interglacial sulfur isotope data

The $\delta^{34}\text{S}_{\text{SO}_4}$ values for LGM samples in the Skytrain Ice Rise ice core were 3–5‰ lower than for all Holocene samples. This result agreed with Alexander et al. (2003), who reported up to $\sim 4\text{‰}$ lower $\delta^{34}\text{S}_{\text{SO}_4}$ values in the LGM relative to the surrounding interglacial periods for the Dome C and Vostok ice cores, albeit with very high scatter. The Dome C Holocene values from Baroni et al. (2008) also supported this result (Table 5.3). Therefore, my findings extended the observation of a glacial/interglacial shift in $\delta^{34}\text{S}_{\text{SO}_4}$ values from East to West Antarctica.

Table 5.3 *Reported glacial and interglacial $\delta^{34}\text{S}_{\text{SO}_4}$ values in East and West Antarctica*

Location	Time period	$\delta^{34}\text{S}_{\text{SO}_4}$ (‰)	Reference
Skytrain Ice Rise	Late Holocene	14.58–16.21	This work
	Early Holocene	14.55–15.33	This work
	Glacial	10.69–11.40	This work
Dome C	Holocene	12.0–13.4	Alexander et al., 2003
	Glacial	10.1–12.7	Alexander et al., 2003
	Holocene	11.45–15.30	Baroni et al., 2008
Vostok	Holocene	9.5–14.3	Alexander et al., 2003
	Eemian	13.6–15.4	Alexander et al., 2003
	Glacial	12.0–12.6	Alexander et al., 2003

5.4.2 Quantifying sulfate sources with a three-source mixing model

A three-source mixing model was used to quantify $\text{SO}_{4\text{ss}}^{2-}$, $\text{SO}_{4\text{bio}}^{2-}$, and $\text{SO}_{4\text{other}}^{2-}$ as described in Chapters 3 and 4. For this model, $\text{SO}_{4\text{other}}^{2-}$ included volcanic/stratospheric sulfate as well as any potential terrestrial input. To review, $\text{SO}_{4\text{ss}}^{2-}$ was quantified using the Na^+ concentration and a designated k-value. A two-source isotope mixing model was then used to calculate $\text{SO}_{4\text{bio}}^{2-}$ and $\text{SO}_{4\text{other}}^{2-}$. The $\delta^{34}\text{S}_{\text{SO}_4}$ of sea salt was set to 21.1‰ (Rees, 1978, supported by this research) and $\delta^{34}\text{S}_{\text{SO}_4\text{bio}}$ was set to 18.6‰ (Patris et al., 2000, supported by this research). To account for the complete range of possible terrestrial sulfur isotopic compositions, $\delta^{34}\text{S}_{\text{SO}_4\text{other}}$ initially ranged between 0–20‰ (Nielsen et al., 1991). However, it was quickly apparent that the larger $\delta^{34}\text{S}_{\text{SO}_4\text{other}}$ values were not possible because they led to a very low or negative $\text{SO}_{4\text{bio}}^{2-}$ input. Therefore, I constrained the possible decrease in the biogenic fraction of total sulfate to 50% based on the findings of Goto-Azuma et al. (2019)

and Ishino et al. (2019), who reported a maximum decrease of 46% and 33%, respectively. Given these parameters, the possible range of $\delta^{34}\text{S}_{\text{SO}_4\text{other}}$ values narrowed to 0–5.5‰, which was used in all future models. Model results are shown in Table 5.4. Previous results for the early and late Holocene Skytrain samples are included for comparison.

Table 5.4 Sulfate sources at Skytrain Ice Rise in the LGM, early, and late Holocene, not accounting for potential terrestrial sulfate input¹

	LGM (~24,700 ypb)	Early Holocene (~10,400 ypb)	Late Holocene (~720 ybp)
f_{ss}	15.9	17.1	29.1
f_{bio}	23.1–41.2	52.4–60.0	43.0–50.5
f_{other}	43.0–61.0	22.3–30.5	20.4–27.9
$[\text{SO}_4^{2-}]_{ss}$	13.6	8.4	19.8
$[\text{SO}_4^{2-}]_{bio}$	21.9–38.3	26.7–30.8	35.4–40.6
$[\text{SO}_4^{2-}]_{other}$	39.2–55.6	11.2–15.3	14.3–19.5

¹ All fractions reported as percent, all concentrations reported in ppb

The SO_4^{2-} concentration was higher in the LGM relative to the early Holocene, but the sea salt fraction of total sulfate was lower. This result was because of the greater third source emissions, which led to a smaller relative contribution of SO_4^{2-} despite a stronger sea salt source. However, the SO_4^{2-} concentration was calculated with a k-value of 0.15 compared to the 0.20 value used for Holocene samples. If a 0.20 k-value had been used for the LGM samples, the SO_4^{2-} concentration would have increased by an additional 33%, and the sea salt fraction would have actually increased to 21.2%. However, the expanded sea ice in the LGM required a lower k-value, so the low sea salt fraction was likely a better representation of sulfate sources at that time. The ICP-MS data from BAS further supported this conclusion because it showed minimal change in the sea salt concentration over that time period.

The large range in possible SO_4^{2-} concentrations was caused by the large input of SO_4^{2-} , which caused relatively small changes in $\delta^{34}\text{S}_{\text{SO}_4\text{other}}$ to have a large effect on source partitioning in the isotope mixing model. The average concentration of SO_4^{2-} in the LGM was ~32 ppb larger than in the early and late Holocene samples. In previous chapters, I attributed SO_4^{2-} entirely to volcanic/stratospheric sulfate. However, volcanic/stratospheric sulfate seemed unlikely to have increased by this amount. Furthermore, Alexander et al. (2003) argued against a stratospheric source, as discussed in the introduction. Taken together, these results pointed to a terrestrial source as a possible explanation for greater SO_4^{2-} and lower $\delta^{34}\text{S}_{\text{SO}_4}$ values in glacial periods. To evaluate this possibility, the potential range of $(\text{SO}_4^{2-}/\text{Ca}^{2+})_{terr}$ ratios needed to be examined.

5.4.3 Potential terrestrial dust input within the standard range of $(\text{SO}_4^{2-}/\text{Ca}^{2+})_{terr}$ ratios

I first quantified SO_4^{2-} in the Skytrain Ice Rise ice core based on $(\text{SO}_4^{2-}/\text{Ca}^{2+})_{terr}$ ratios between 0.1–0.5 as used in previous research. Even when using the largest ratio of 0.5, the maximum SO_4^{2-} concentration in the glacial Skytrain samples was 3.7–10.4 ppb, or 4.5–12.3% of total sulfate. This SO_4^{2-} fraction was greater than the < 3.4% terrestrial fraction in the Holocene cores; however, it was not large enough to account for the ~32 ppb higher SO_4^{2-} concentration in the LGM. Assuming the largest possible concentration of SO_4^{2-} in the LGM (10.4 ppb), the non-terrestrial component of SO_4^{2-} would still have had to be 171% greater in the LGM than in the early Holocene, which seemed unlikely. Therefore, a wider range of possible $(\text{SO}_4^{2-}/\text{Ca}^{2+})_{terr}$ ratios was considered.

5.4.4 Potential terrestrial dust input with an expanded range of possible $(\text{SO}_4^{2-}/\text{Ca}^{2+})_{terr}$ ratios

To test various $(\text{SO}_4^{2-}/\text{Ca}^{2+})_{terr}$ ratios, SO_4^{2-} was subtracted from total sulfate, and an isotope mixing model was used to quantify SO_4^{2-} , SO_4^{2-} , SO_4^{2-} , and SO_4^{2-} as described in the preceding chapters. For this model, SO_4^{2-} represented the same third sulfate source described in previous chapters that was likely volcanic/stratospheric in origin. The first step was to quantify SO_4^{2-} using the Na^+ concentration and k-value. However, because of the significant dust input, not all Na^+ was from sea salt. Therefore, the concentration of sea salt sodium (Na_{ss}^+) was first calculated using the following equation:

$$[\text{Na}^+]_{ss} = \frac{[\text{Na}^+] - [\text{Ca}^{2+}]_{nss} \cdot (\text{Na}^+/\text{Ca}^{2+})_{terr}}{1 - (\text{Na}^+/\text{Ca}^{2+})_{terr} \cdot (\text{Ca}^{2+}/\text{Na}^+)_{ss}} \quad (5.1)$$

where $(\text{Na}^+/\text{Ca}^{2+})_{terr}$ and $(\text{Ca}^{2+}/\text{Na}^+)_{ss}$ were 0.56 and 0.038, respectively, as per Röthlisberger et al. (2002). Sea salt sodium was then multiplied by the k-value to quantify SO_4^{2-} and SO_4^{2-} .

The SO_4^{2-} concentration was then calculated for $(\text{SO}_4^{2-}/\text{Ca}^{2+})_{terr}$ ratios between 0.10–2.4. The SO_4^{2-} contribution was subtracted from SO_4^{2-} , and the remaining SO_4^{2-} was attributed to volcanic/stratospheric sulfate with a $\delta^{34}\text{S}_{\text{SO}_4^{2-}}$ signature of 2.6‰ (Castleman et al., 1974). The mixing model was then run for each $(\text{SO}_4^{2-}/\text{Ca}^{2+})_{terr}$ ratio over a range of $\delta^{34}\text{S}_{\text{SO}_4^{2-}}$ values between 0–5.5‰ based on the possible range determined in the first model test. Results are shown in Table 5.5.

When a $(\text{SO}_4^{2-}/\text{Ca}^{2+})_{terr}$ ratio of 1.6 was used, terrestrial input accounted for the higher SO_4^{2-} concentration in the LGM while retaining the volcanic/stratospheric sulfate component from the early Holocene. However, if all non-sea salt, non-biogenic sulfate in the LGM was considered terrestrial with no volcanic/stratospheric input, then a $(\text{SO}_4^{2-}/\text{Ca}^{2+})_{terr}$ ratio of 2.2 was necessary. These ratios were within the likely range discussed by Goto-Azuma et al. (2019) and suggested some primary input of a sulfate-rich terrestrial source like gypsum. However, the model required a $\delta^{34}\text{S}_{\text{SO}_4terr}$ value between 0–5.5‰, which is lower than the typical sulfur isotopic composition of potential gypsum sources (e.g., Palmer et al., 2004; Toulkeridis et al., 1998). This disagreement raised the question of a different terrestrial source origin.

Different $(\text{SO}_4^{2-}/\text{Ca}^{2+})_{terr}$ ratios also affected the relative importance of SO_4^{2-} emissions in the LGM compared to the Holocene. In the early Holocene, SO_4^{2-} accounted for 63.6–73.3% of SO_4^{2-} , while in the LGM this fraction was only 34.4–49.0%. This average ~25% change in the SO_4^{2-} fraction was slightly larger than the values found by Ishino et al. (2019), who reported that SO_4^{2-} was $59 \pm 11\%$ of SO_4^{2-} in interglacial periods and only $48 \pm 10\%$ in glacial periods. However, my results overall supported a lesser biogenic sulfate source in glacial periods.

5.4.5 The relationship between Ca_{nss}^{2+} and SO_4^{2-} in LGM and Holocene Skytrain Ice Rise ice core samples

To further explore the relationship between sulfate and calcium in potential terrestrial sources, I placed the limited Skytrain LGM samples in context of the longer ICP-MS dataset. The Ca_{nss}^{2+} and SO_4^{2-} concentrations were calculated for ~5-meter core sections extending ~2.5 m on either side of each Skytrain sample, including the LGM and both Holocene core sections. The Ca_{nss}^{2+} concentration was then plotted against the SO_4^{2-} concentration to see how terrestrial sources may have changed over time (Figure 5.1).

A best fit line for the LGM samples had a slope of 1.55, which agreed with the earlier model output showing that a $(\text{SO}_4^{2-}/\text{Ca}^{2+})_{terr}$ ratio of 1.6 attributed increased SO_4^{2-} in the LGM to terrestrial input. When the model was rerun with a $(\text{SO}_4^{2-}/\text{Ca}^{2+})_{terr}$ ratio of 1.55, terrestrial sulfate accounted for 43% of SO_4^{2-} in the Skytrain samples. This result agreed with Goto-Azuma et al. (2019), who found that for a $(\text{SO}_4^{2-}/\text{Ca}^{2+})_{terr}$ ratio of 1.5, terrestrial sulfate contributed 48%, 40%, and 44% of SO_4^{2-} in the Dome F, EDC, and EDML ice cores, respectively. Despite this agreement, the necessity of a low $\delta^{34}\text{S}_{\text{SO}_4terr}$ value made it difficult to conclude that gypsum was the primary source of terrestrial sulfate in the Skytrain Ice Rise ice core in the LGM. This idea is discussed further in the following section.

Table 5.5 Sulfate sources at Skytrain Ice Rise in the LGM based on an expanded range of $(SO_4^{2-}/Ca^{2+})_{terr}$ ratios to account for potential terrestrial sulfate input¹

	$(SO_4^{2-}/Ca^{2+})_{terr}$					
	0.10	0.18	0.5	1.6	2.2	2.4
f_{ss}	14.9	14.9	14.9	14.9	14.9	14.9
f_{bio}	34.9–35.8	34.6–36.1	33.1–37.4	28.2–41.8	25.5–44.2	24.6–45.0
f_{other}	46.9–47.8	44.6–46.1	35.4–39.6	3.7–17.3	-13.6–5.1	-19.4–1.1
f_{terr}	2.5	4.5	12.4	39.7	54.5	59.5
$[SO_4^{2-}]_{ss}$	12.7	12.7	12.7	12.7	12.7	12.7
$[SO_4^{2-}]_{bio}$	32.6–33.3	32.3–33.6	31.1–34.7	27.0–38.4	24.7–40.5	23.9–41.1
$[SO_4^{2-}]_{other}$	43.0–43.7	41.1–42.3	33.3–36.9	6.6–18.1	-8.0–7.8	-12.9–4.4
$[SO_4^{2-}]_{terr}$	2.1	3.8	10.4	33.4	45.9	50.1

¹ All fractions reported as percent, all concentrations reported in ppb

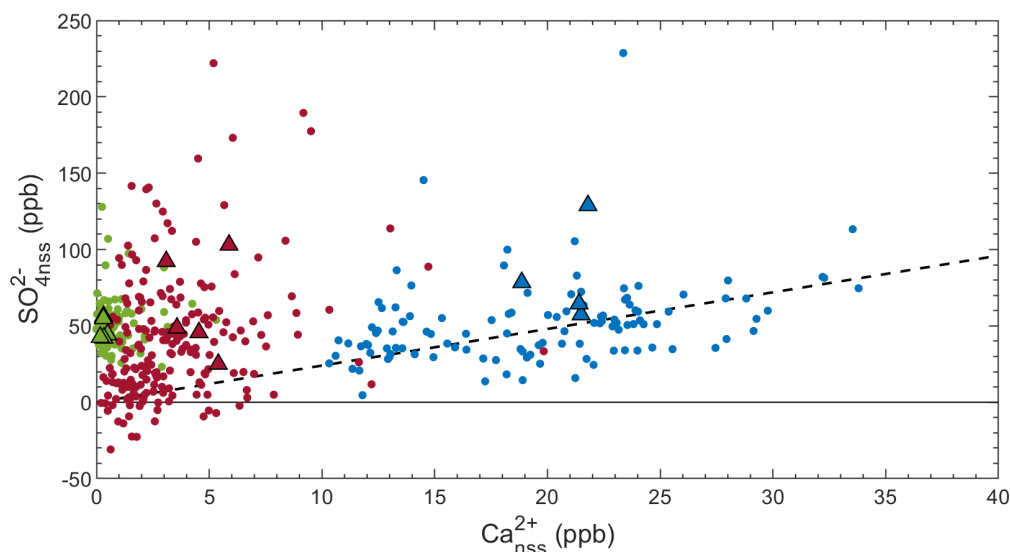


Fig. 5.1 Plot of non-sea salt sulfate and non-sea salt calcium for Skytrain Ice Rise ice core samples from the LGM (blue), early Holocene (green), and late Holocene (red). Dots represent data from ICP-MS analysis performed at BAS. Triangles show the samples measured in this research. The dashed line marks a $(\text{SO}_4^{2-}/\text{Ca}^{2+})_{\text{terr}}$ ratio of 1.55.

In contrast to the LGM samples, the early Holocene samples were tightly clustered by the y-axis, suggesting minimal $\text{Ca}_{\text{nss}}^{2+}$ input and little relationship between $\text{Ca}_{\text{nss}}^{2+}$ and $\text{SO}_{4\text{nss}}^{2-}$. Therefore, a terrestrial dust source was likely insignificant at that time, as reported in Chapter 4. In the late Holocene samples, however, the $\text{Ca}_{\text{nss}}^{2+}$ concentration increased to up to ~ 8 ppb, and samples had a wider distribution in $\text{SO}_{4\text{nss}}^{2-}$ concentrations. This suggested that not only did terrestrial input increase, but it may have been derived from sources with varying $(\text{SO}_4^{2-}/\text{Ca}^{2+})_{\text{terr}}$ ratios. Also, the late Holocene samples did not follow the same 1.55 slope seen for the LGM samples, perhaps pointing to a different source region. The reason for increased dust input in the late Holocene relative to the early Holocene is unclear, but possible explanations include changes in source region, a drier climate, or changes in vegetation that led to a larger source area.

Some late Holocene samples showed a negative $\text{SO}_{4\text{nss}}^{2-}$ concentration regardless of the k-value, the cause of which was also unclear but could be related to a different $(\text{Na}^+/\text{Ca}^{2+})_{\text{terr}}$ ratio at the source region. The ~ 45 ppb spread in $\text{Ca}_{\text{nss}}^{2+}$ concentrations was less than in the LGM, where $\text{Ca}_{\text{nss}}^{2+}$ concentrations ranged between 10.3–74.6 ppb. This difference could have resulted from a more constant emission strength and/or deposition. The $\text{SO}_{4\text{nss}}^{2-}$ concentration was relatively stable across all samples, with slightly higher values in the LGM. This stability may reflect lower biogenic emissions in the LGM balancing out the increased terrestrial source.

5.4.6 Final evaluation of a terrestrial sulfate source at Skytrain Ice Rise during the LGM

The origin of the potential large terrestrial sulfate source in the LGM is unclear. The relationship between $\text{SO}_{4\text{NSS}}^{2-}$ and $\text{Ca}_{\text{NSS}}^{2+}$ in the LGM appears to agree with Goto-Azuma et al.'s (2019) proposed gypsum-rich dust source. However, as noted above, this theory is not consistent with the low glacial $\delta^{34}\text{S}_{\text{SO}_4}$ values reported by Alexander et al. (2003) and also seen in Skytrain Ice Rise ice core. Based on the Skytrain ice core results, the terrestrial sulfate source should have a sulfur isotopic composition of $\sim 0\text{--}5\text{‰}$, which is lower than the literature values for gypsum sources.

The $\delta^{34}\text{S}_{\text{SO}_4}$ of gypsum varies depending on its origin and process of formation. Gypsum from marine deposits has a similar $\delta^{34}\text{S}_{\text{SO}_4}$ as seawater, around $\sim 21\text{‰}$ (Toulkeridis et al., 1998), while average volcanic gypsum $\delta^{34}\text{S}_{\text{SO}_4}$ values between $-5.5\text{--}0\text{‰}$ have been reported (Serafimovski et al., 2015; Toulkeridis et al., 1998). Gypsum in soils is usually a combination of these two sources, and $\delta^{34}\text{S}_{\text{SO}_4}$ values have been found around $11\text{--}20\text{‰}$ (Farpoor and Krouse, 2008; Toulkeridis et al., 1998). Gypsum from cave deposits has a very negative sulfur isotopic composition as low as $< -30\text{‰}$ (Bottrell, 1991), while gypsum in evaporites has a high sulfur isotopic composition typically between $20\text{--}25\text{‰}$, though higher values have been reported (Palmer et al., 2004). Therefore, it is unlikely that any gypsum source reaching Antarctica has a sufficiently low sulfur isotopic composition to produce the $3\text{--}5\text{‰}$ lower glacial $\delta^{34}\text{S}_{\text{SO}_4}$ values measured in the Skytrain Ice Rise ice core. These gypsum $\delta^{34}\text{S}_{\text{SO}_4}$ values particularly contradict Goto-Azuma et al.'s (2019) proposal of evaporites in South America as a potential gypsum source to Antarctica.

Overall, the results from the Skytrain Ice Rise ice core suggest a large sulfate-rich source with a low sulfur isotopic composition during the LGM. Because this source cannot be explained by high gypsum input, other non-sea salt, non-marine biogenic sources must be considered. Volcanic/stratospheric sulfate has a low sulfur isotopic composition, but it seems unlikely that volcanic activity and/or stratospheric input would be $\sim 2\text{x}$ higher in the LGM relative to the Holocene. Continental biogenic activity has a $\delta^{34}\text{S}_{\text{SO}_4}$ value between $0\text{--}5\text{‰}$ (Alexander et al., 2003; Patris et al., 2000), but input is minimal because of the remoteness of Antarctica, and a 50% greater source during the LGM does not seem probable. Furthermore, the clear correlation between $\text{SO}_{4\text{NSS}}^{2-}$ and $\text{Ca}_{\text{NSS}}^{2+}$ in the Skytrain glacial samples indicates that $\text{SO}_{4\text{NSS}}^{2-}$ likely derives from a terrigenous source, assuming this relationship is not solely due to secondary gypsum formation. I am not aware of any reports of a source that fits this description. However, different climate conditions in the LGM, such as a low sea level and newly-exposed continental shelves, open the possibility of such a source during glacial periods.

5.4.7 Re-evaluating terrestrial dust input in non-glacial ice cores with an expanded range of $(\text{SO}_4^{2-}/\text{Ca}^{2+})_{terr}$ ratios

The Skytrain ice core results highlight the importance of the composition of terrestrial dust sources, which has a large effect on the interpretation of sulfate sources in Antarctica. For example, I previously considered the larger Ca_{nss}^{2+} concentration in the late Holocene Skytrain samples to be insignificant because it resulted in $< 2\%$ terrestrial sulfate. However, this calculation was based on a $(\text{SO}_4^{2-}/\text{Ca}^{2+})_{terr}$ ratio of 0.18. If higher $(\text{SO}_4^{2-}/\text{Ca}^{2+})_{terr}$ ratios are possible, it could alter my initial interpretation of non-glacial cores, including not only the Holocene Skytrain samples, but also the Sherman Island and Dyer Plateau ice cores that were discussed in Chapters 3 and 4. To explore this scenario, I reanalyzed the data from these cores after subtracting the increased possible SO_{4terr}^{2-} input from the total sulfate concentration. Results showed that increased $(\text{SO}_4^{2-}/\text{Ca}^{2+})_{terr}$ ratios did not significantly affect all cores because of their low Ca_{nss}^{2+} concentrations. However, the volcanic/stratospheric sulfate source in the late Holocene Skytrain core decreased by ~ 35 ppb, or $\sim 40\%$ of total sulfate.

Despite these revised source estimates, the argument for a large terrestrial source in the LGM does not necessarily apply to Holocene cores. A primary terrestrial source with a high $(\text{SO}_4^{2-}/\text{Ca}^{2+})_{terr}$ ratio and low $\delta^{34}\text{S}_{\text{SO}_4}$ signature is an appealing explanation for low glacial $\delta^{34}\text{S}_{\text{SO}_4}$ values, but this argument is limited by the unknown origin of such a source. As previously mentioned, during the LGM, newly-exposed continental shelves offer a possible source of sulfate-rich material to be transported to and deposited on the Antarctic Ice Sheet. However, it is difficult to make this argument for modern cores because no suitable terrestrial source is known. Therefore, though the Skytrain LGM data led to my consideration of a terrestrial source with unexpectedly high $(\text{SO}_4^{2-}/\text{Ca}^{2+})_{terr}$ ratios, I did not consider this a likely enough possibility in the Holocene to form a primary scenario in earlier chapters.

5.5 Future work

Additional glacial $\delta^{34}\text{S}_{\text{SO}_4}$ measurements need to be made for deep Antarctic ice cores to expand the currently limited dataset. These studies could reveal if the measured low glacial $\delta^{34}\text{S}_{\text{SO}_4}$ values are uniform across the continent and if/how this could relate to changes in sulfate sources. Furthermore, more information is needed about the composition of terrestrial dust reaching Antarctica. Future studies could examine dust from potential source regions like Patagonia or the Ellsworth Mountains in West Antarctica, and the insoluble dust in the ice core could also be analyzed. This data could better constrain possible $(\text{SO}_4^{2-}/\text{Ca}^{2+})_{terr}$ ratios and the sulfur isotopic composition of terrestrial input. Determining when the terrestrial

source decreased between the LGM and the Holocene could also reveal information about past climate events, such as the timing of ice sheet retreat during the termination of the LGM. Lastly, potential long-term changes in sulfate sinks and transport/deposition processes should also be considered as a mechanism for changes in sulfate source concentrations in ice without changes in source emissions.

5.6 Conclusion

Sulfur isotope ratios were measured in LGM samples from the Skytrain Ice Rise ice core. Results were compared to the Skytrain Holocene $\delta^{34}\text{S}_{\text{SO}_4}$ data described in Chapter 4 to assess the potential of a large terrestrial sulfate source during the LGM. Glacial $\delta^{34}\text{S}_{\text{SO}_4}$ values were 3–5‰ lower than Holocene values, agreeing with the observations of Alexander et al. (2003) in East Antarctic ice cores.

A three-source mixing model showed that $\text{SO}_4^{2-}_{\text{other}}$ was 43.0–58.8% of total sulfate in the LGM, significantly higher than 22.3–30.5% in the early Holocene. The biogenic sulfate fraction also increased from 23.1–41.2% in the LGM to 52.4–60.0% in the early Holocene. It seemed unlikely that the ~50% greater $\text{SO}_4^{2-}_{\text{other}}$ fraction in the LGM could reflect changes in only volcanic/stratospheric sulfate or other minor sources, so a large terrestrial dust source was considered.

To allow for a large terrestrial input, the possible range of $(\text{SO}_4^{2-}/\text{Ca}^{2+})_{\text{terr}}$ ratios was re-evaluated. A $(\text{SO}_4^{2-}/\text{Ca}^{2+})_{\text{terr}}$ ratio of 1.55 allowed for the entire increase of $\text{SO}_4^{2-}_{\text{other}}$ in the LGM to derive from terrestrial sources. The calculated $\text{SO}_4^{2-}_{\text{terr}}$ fraction of $\text{SO}_4^{2-}_{\text{ns}}$ was 43%, which agreed with the 40–48% values reported by Goto-Azuma et al. (2019) for the Dome F, EDC, and EDML ice cores. A $(\text{SO}_4^{2-}/\text{Ca}^{2+})_{\text{terr}}$ ratio of 1.55 could signify a combination of primary and secondary terrestrial gypsum input, but the sulfur isotopic composition of likely gypsum sources is too high to explain the low $\delta^{34}\text{S}_{\text{SO}_4}$ values. Therefore, another sulfate-rich dust source is more likely, but its origin is unclear.

Although a terrestrial source with a large $(\text{SO}_4^{2-}/\text{Ca}^{2+})_{\text{terr}}$ ratio and a low sulfur isotopic composition is an attractive explanation for low glacial $\delta^{34}\text{S}_{\text{SO}_4}$ values, this argument becomes difficult for modern cores because no mobile sulfate-rich dust source is known. Overall, to better characterize sulfate sources in Antarctica and how they have changed on a glacial/interglacial scale, further information is needed about the origin and composition of potential terrestrial sources.

Chapter 6

Conclusion

6.1 Overview

The original aim of this research was to develop a new sea ice proxy based on the sulfur isotopic composition of sulfate ($\delta^{34}\text{S}_{\text{SO}_4}$) in Antarctic ice cores. To accomplish this goal, I established a method at the University of Cambridge to measure $\delta^{34}\text{S}_{\text{SO}_4}$ using multicollector inductively coupled mass spectrometry (MC-ICP-MS). This technique enabled the measurement of < 30 nmol of sulfur compared to the ~ 1 μmol previously required per sample for gas source mass spectrometry (GS-MS). However, my initial results showed that sulfate sources in Antarctica were too poorly constrained to use $\delta^{34}\text{S}_{\text{SO}_4}$ in a sea ice proxy. Therefore, the primary focus of this thesis was to reconstruct sulfate sources in West Antarctica and determine how sources change on a seasonal, spatial, and glacial/interglacial scale.

6.2 Seasonality of sulfate sources in West Antarctica and the identification of a third sulfate source

I reported the first seasonal record of $\delta^{34}\text{S}_{\text{SO}_4}$ in ice cores, which was measured in the Dyer Plateau ice core from the Antarctic Peninsula. This high-resolution record was possible because of the small sample volume needed to measure sulfur isotope ratios via MC-ICP-MS compared to the kilograms of ice required for standard GS-MS analysis. Because of Dyer Plateau's proximity to the coast, it provided an excellent opportunity to reconstruct changes in sea ice extent, which has large seasonal variability in Antarctica. In theory, $\delta^{34}\text{S}_{\text{SO}_4}$ could be used to quantify total sea salt sulfate ($\text{SO}_{4\text{ss}}^{2-}$). The $\text{SO}_{4\text{ss}}^{2-}/\text{Na}^+$ ratio in the ice core could then be used to determine how much sea salt came from the sea ice surface and reconstruct changes in sea ice extent over time.

This proxy is based on the assumption that sea salt and marine biogenic activity are the only significant sulfate sources, excepting periods of volcanic activity. However, $\delta^{34}\text{S}_{\text{SO}_4}$ measurements revealed that the background sulfate signal was more complicated than expected. This result suggested either an additional sulfate source, or a different sulfur isotopic composition of $\text{SO}_{4\text{ss}}^{2-}$ and/or biogenic sulfate ($\text{SO}_{4\text{bio}}^{2-}$) than previously thought. To address these questions, I made the first direct $\delta^{34}\text{S}_{\text{SO}_4}$ measurements of the sea ice surface in Antarctica and confirmed that the $\delta^{34}\text{S}_{\text{SO}_{4\text{ss}}}$ signature of 21‰ reported by Rees (1978) can be used in Antarctic sulfate source studies. I then evaluated the possibility of a third sulfate source ($\text{SO}_{4\text{other}}^{2-}$) with a low sulfur isotopic composition using a three-source mixing model for a range of $\delta^{34}\text{S}_{\text{SO}_{4\text{other}}}$ values. The third sulfate source appeared volcanic/stratospheric in origin, with a $\delta^{34}\text{S}_{\text{SO}_{4\text{other}}}$ value likely between 0–5‰ based on the typical sulfur isotopic composition of volcanic/stratospheric sulfate.

Model results agreed with the $\delta^{34}\text{S}_{\text{SO}_{4\text{bio}}}$ signature of $\sim 18\text{‰}$ reported by Patris et al. (2000) and showed that the third sulfate source contributed 20.7–28.3% of total sulfate in the winter and 14.0–19.2% of total sulfate in the summer. This seasonality further strengthened the theory of a stratospheric source based on the known winter increase in stratospheric deposition due to a strong polar vortex. This finding was also supported by previous ice core studies that have reported a significant volcanic/stratospheric sulfate source in numerous Antarctic ice cores. Overall, the Dyer Plateau results show that $\delta^{34}\text{S}_{\text{SO}_4}$ cannot be used to reconstruct sea ice extent until sulfate sources in Antarctica have been better constrained.

6.3 Spatial variability in sulfate sources in Antarctica

Having identified a third sulfate source in the Dyer Plateau ice core, I then explored if this source is ubiquitous across Antarctica and how it may change on a spatial scale. I analyzed two additional ice cores from West Antarctica: Sherman Island and Skytrain Ice Rise. The same three-source mixing model was used, and results agreed with the $\delta^{34}\text{S}_{\text{SO}_{4\text{bio}}}$ signature of $\sim 18\text{‰}$ that was previously determined. The third sulfate source accounted for $9.8 \pm 4.4\%$ and 24.2% of total sulfate at Sherman Island and Skytrain Ice Rise, respectively, with the Sherman Island fraction averaged across three core sections. Despite these different source fractions, the $\text{SO}_{4\text{other}}^{2-}$ concentration was similar at all sites, suggesting that this difference resulted primarily from changes in biogenic and sea salt sulfate emissions.

The $\text{SO}_{4\text{other}}^{2-}$ fraction of total sulfate at Sherman Island, Skytrain Ice Rise, and Dyer Plateau were similar to the fraction of volcanic/stratospheric sulfate in East Antarctica, which has been reported between 6.0–38.4% (e.g., Baroni et al., 2008; Patris et al., 2000). In contrast, the fraction of $\text{SO}_{4\text{other}}^{2-}$ at Sherman Island, Skytrain Ice Rise, and Dyer Plateau was

significantly lower than on the West Antarctic Ice Sheet (WAIS), where Kunasek et al. (2010) reported a volcanic/stratospheric source fraction between 72–90% of total sulfate. Sulfur isotope ratios had not previously been measured at any other site in West Antarctica, and the results from the Sherman Island, Skytrain Ice Rise, and Dyer Plateau ice cores suggest that the WAIS site may be anomalous. However, additional ice core studies are necessary to strengthen this conclusion. Overall, my results suggest that there is no distinct difference in the third sulfate source between East and West Antarctica, but that $\text{SO}_{4\text{other}}^{2-}$ may vary significantly on a smaller spatial scale.

I also analyzed both early and late Holocene sections of the Skytrain Ice Rise ice core from $\sim 10,400$ ybp (years before 1950) and ~ 720 ybp, respectively. Results showed an increase in sea salt and biogenic sulfate emissions between $\sim 10,400$ – 720 ybp, supporting the theory of a retreat of the Ronne Ice Shelf at $\sim 8,000$ ybp. The larger increase in sea salt relative to biogenic sulfate also supported this theory because sea salt sulfate is lost more quickly during transport than biogenic sulfate (Minikin et al., 1994). Therefore, a shorter transport distance caused by a retreat in the Ronne Ice Shelf would have a greater effect on the strength of the sea salt source. This finding shows that sulfate source reconstructions can be used to constrain large climate events in the past.

6.4 A potential large terrestrial source in West Antarctica during the LGM

I continued exploring temporal variability in sulfate sources by evaluating glacial/interglacial changes in $\delta^{34}\text{S}_{\text{SO}_4}$ in the Skytrain Ice Rise ice core. The measured glacial $\delta^{34}\text{S}_{\text{SO}_4}$ values were 3–5‰ lower in the Last Glacial Maximum (LGM), which agreed with Alexander et al. (2003), who reported ~ 4 ‰ lower glacial $\delta^{34}\text{S}_{\text{SO}_4}$ values in the Dome C and Vostok ice cores in East Antarctica. Earlier research has suggested a large terrestrial dust source ($\text{SO}_{4\text{terr}}^{2-}$) and decreased biogenic emissions in glacial periods as an explanation for this isotope discrepancy (Goto-Azuma et al., 2019; Ishino et al., 2019).

Using a three-source mixing model, I showed that $\text{SO}_{4\text{other}}^{2-}$ (comprising volcanic/stratospheric sulfate and $\text{SO}_{4\text{terr}}^{2-}$) would account for 43.0–61.0% of total sulfate in the LGM. This fraction is based on $\delta^{34}\text{S}_{\text{SO}_{4\text{other}}}$ values between 0–5.5‰, which fall within the range of possible terrestrial isotopic compositions but limit the decrease in the biogenic fraction of sulfate in the LGM to $< 50\%$. Final biogenic emissions in the LGM were 23.1–41.2% of total sulfate compared to 52.4–60.0% in the early Holocene. These results agreed with the proposed theory of a large terrestrial source and a lesser biogenic source in glacial periods.

In order for $\text{SO}_{4\text{other}}^{2-}$ to include a large terrestrial dust component, the sulfate-to-calcium ratio of the terrestrial sulfate source needed to be ~ 1.55 . This ratio allowed the increase in $\text{SO}_{4\text{other}}^{2-}$ in the LGM to derive entirely from terrestrial input. The ~ 1.55 ratio is significantly higher than the mean soil $\text{SO}_4^{2-}/\text{Ca}^{2+}$ ratio of 0.10 or 0.18 that is typically used in ice core research. This high value suggests a sulfate-rich terrestrial source like gypsum (CaSO_4) either deposited directly on the ice or formed by the reaction of calcium carbonate (CaCO_3) in dust with $\text{SO}_{4\text{bio}}^{2-}$ during transport. However, the sulfur isotopic composition of gypsum is too high to cause the observed decrease in glacial $\delta^{34}\text{S}_{\text{SO}_4}$ values. Therefore, a different sulfate-rich terrestrial source is a more probable explanation for the LGM results, but its origin is unclear. This result highlights the importance of the terrestrial dust composition when partitioning sulfate sources.

6.5 Continued work to improve the constraint of sulfate sources in Antarctica

To pursue the possibility of a new sea ice proxy based on sulfur isotope ratios, sulfate sources in Antarctica need to be better understood. Direct $\delta^{34}\text{S}_{\text{SO}_4}$ measurements of marine aerosols would further constrain the $\delta^{34}\text{S}_{\text{SO}_{4\text{bio}}}$ signature, and measurements could be conducted at various locations around Antarctica to determine any spatial variability. It would also be interesting to measure the sulfur isotopic composition of MSA in marine aerosols to quantify any sulfur isotope fractionation during the oxidation of biogenic DMS emissions. Concurrent $\delta^{34}\text{S}_{\text{SO}_4}$ and $\delta^{33}\text{S}_{\text{SO}_4}$ measurements would help identify volcanic/stratospheric sulfate in an ice core, which would also inform the partitioning of sulfate sources. The MC-ICP-MS method detailed in Chapter 2 can be further developed to complete these measurements at the University of Cambridge.

Perhaps most importantly, additional $\delta^{34}\text{S}_{\text{SO}_4}$ measurements need to be conducted around Antarctica to build on the relatively limited current dataset. West Antarctica in particular needs to be further explored. Lastly, longer ice core records could better reveal long-term trends in sulfate sources. By determining how the sulfur isotopic composition of sulfate varies across different climate events, we can gain a better idea of the relationship between the third sulfate source and other climate and chemical changes. For example, if $\delta^{34}\text{S}_{\text{SO}_4}$ changes in concert with calcium concentrations, it would strengthen the argument for an increased terrestrial source during the LGM because calcium derives primarily from terrestrial dust. However, to explore this theory, we need to evaluate $\delta^{34}\text{S}_{\text{SO}_4}$ in ice cores through the glacial termination.

6.6 Concluding remarks

In this thesis, I have highlighted the importance of expanding $\delta^{34}\text{S}_{\text{SO}_4}$ measurements in Antarctic ice cores. The same background sulfate sources cannot be assumed for all ice core studies because sulfate sources vary on a spatial and temporal scale. Therefore, additional shallow and deep ice cores in both West and East Antarctica need to be analyzed. By reconstructing how sulfate sources change over time, we can further constrain past climate events. However, before $\delta^{34}\text{S}_{\text{SO}_4}$ can be used for small scale reconstructions such as sea ice extent, we need to revisit the larger picture of sulfate sources in Antarctica.

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