Determination of Volcanic Aerosols from Aurora Basin North, an Ice Core from East Antarctica

by

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Since the assessment of the Literature Review and Thesis, the author has made the following alterations to the assessed document. Throughout both the Literature Review and Thesis, numerous spelling corrections have been made from the assessed version of the Literature Review. The following grammatical corrections have been made to the Literature Review.

Page 1.

Original: The sources and seasonal cycles of sea salts is examined, including possible alternative sources and post-depositional movement of some ionic species.

Change: The sources and seasonal cycles of sea salts are examined, including possible alternative sources and post-depositional movement of some ionic species.

Original: The study concludes with an in-depth look of volcanic influences on climate and how eruptions have been interpreted in ice cores.

Change: The study concludes with an in-depth look at volcanic influences on climate and how eruptions have been interpreted in ice cores.

Original: Between 35°N and 35°S the amount of incoming solar radiation exceeds that leaving the atmosphere, resulting in a net warming [*Hidore et al.*, 2009] that drives the general circulation of the atmosphere.

Change: Between 35°N and 35°S, the amount of incoming solar radiation exceeds that leaving the atmosphere, resulting in net warming [*Hidore et al.*, 2009] that drives the general circulation of the atmosphere.

Page 3.

Original: Strength of the vortex is related to the stratospheric wind speeds. These winds are strongest in winter, peaking at 20 km above sea level [*Aristidi et al.*, 2005]. In the spring, the polar vortex decays, leading to an increase in exchange between the troposphere and stratosphere. At this time storms from the southern Atlantic Ocean and Weddell Sea can reach the interior and may assist in the breakup of the continental inversion layer [*Shaw*, 1988], a region of warm air over the colder surface air.

Change: The strength of the vortex is related to the stratospheric wind speeds. These winds are strongest in winter, peaking at 20 km above sea level [*Aristidi et al.*, 2005]. In the spring, the polar vortex decays, leading to an increase in the exchange between the troposphere and stratosphere. At this time storms from the southern Atlantic Ocean and the Weddell Sea can reach

the interior and may assist in the breakup of the continental inversion layer [*Shaw*, 1988], a region of warm air over the colder surface air.

Original: Katabatic winds are generated from downslope movement of very cold, dense air from the continental interior and have a persistent direction [*King and Turner, 1997*].

Change: Katabatic winds are generated from the downslope movement of very cold, dense air from the continental interior and have a persistent direction [*King and Turner, 1997*].

Page 4.

Original: This sublayer is a thin quiet layer of air, a few mm above the surface [*Davidson et al.*, 1996].

Change: This sublayer is a thin quiet layer of air, a few millimeters above the surface [*Davidson et al.*, 1996].

Page 5.

Original: Though less common, movement of chemical species due to temperature or humidity gradients are included in this step [*Davidson et al.*, 1996].

Change: Though less common, the movement of chemical species due to temperature or humidity gradients are included in this step [*Davidson et al.*, 1996].

Page 6.

Original: The most common are sodium (Na^+), chloride   (Cl^-), sulfate (SO_4^{2-}), calcium (Ca^{2+}), magnesium (Mg^{2+}), and potassium (K^+).

Change: The most common are sodium (Na^+), chloride (Cl^-), sulfate (SO_4^{2-}), calcium (Ca^{2+}), magnesium (Mg^{2+}), and potassium (K^+). *(Extra space removed between chloride (Cl^-).)*

Page 7.

Original: Chloride can be deposited as a particulate sea salt or as gaseous hydrochloric acid [*Wagnon et al.*, 1999].

Change: Chloride can be deposited <u>as particulate</u> sea salt or as gaseous hydrochloric acid [*Wagnon et al.*, 1999].

Page 8.

Original: The majority of sulfur compounds in the Southern Ocean are the result of oxidation of dimethyl sulfide. Dimethyl sulfide (DMS) is produced by phytoplankton, especially those associated with sea ice and is found in very high levels within the sea ice zone around the continent [*Abram et al.*, 2013].

Change: The majority of sulfur compounds in the Southern Ocean are the result of <u>the</u> oxidation of dimethyl sulfide. Dimethyl sulfide (DMS) is produced by phytoplankton, especially those associated with sea ice<u>,</u> and is found in very high levels within the sea ice zone around the continent [*Abram et al.*, 2013].

Page 14.

Original: Ash and larger debris settles out of the atmosphere quickly, gases, such as, H_2O, CO_2, SO_2, N_2, and some halogens are released into the atmosphere where their lifetimes become part of the atmospheric residence times of the oxygen, carbon, and sulfur cycles [*Cole-Dai*, 2010].

Change: Ash and larger debris <u>settle</u> out of the atmosphere quickly, gases, such as, H_2O, CO_2, SO_2, N_2, and some halogens are released into the atmosphere where their lifetimes become part of the atmospheric residence times of the oxygen, carbon, and sulfur cycles [*Cole-Dai*, 2010].

Original: Sulfur dioxide is rapidly oxidized into H_2SO_4 in the troposphere before removal by precipitation and has little long term or global impacts.

Change: Sulfur dioxide is rapidly oxidized into H_2SO_4 in the troposphere before removal by precipitation and has little long term or global <u>impact</u>. *(Extra space removed prior to Sulfur.)*

Original: These gases from the largest eruptions have the capacity to alter global climate for several years following the eruption by decreasing the amount of solar radiation that reaches the surface [*McCormick et al.*, 1995; *Robock*, 2000].

Change: These gases from the largest eruptions have the capacity to alter <u>the</u> global climate for several years following the eruption by decreasing the amount of solar radiation that reaches the surface [*McCormick et al.*, 1995; *Robock*, 2000].

Page 15.

Original: Similar global cooling was experienced after the 1963 eruption of Mt. Agung and the 1992 eruptions of Pinatubo and El Chichón [*McCormick et al.*, 1995; *Robock*, 2000; *Sigl et al.*, 2015].

Change: Similar global cooling was experienced after the 1963 eruption of Mt. Agung and <u>the eruptions</u> of Pinatubo and El Chichón [*McCormick et al.*, 1995; *Robock*, 2000; *Sigl et al.*, 2015].

Original: By studying the debris and trace chemistry found in ice cores, the approximate size and location of eruptions can be approximated [*Cole-Dai*, 2010; *Robock*, 2000].

Change: By studying the debris and trace <u>chemicals</u> found in ice cores, the approximate size and location of eruptions can be approximated [*Cole-Dai*, 2010; *Robock*, 2000].

Original: A complete understanding of the climatic effects of volcanism and future / long term changes requires a long record of eruptions and their impacts. Written records usually only include those eruptions that occurred in well populated areas and had significant social / economic impacts [*Brönnimann and Krämer*, 2016].

Change: A complete understanding of the climatic effects of volcanism and <u>future/long term</u> changes requires a long record of eruptions and their impacts. Written records usually only include those eruptions that occurred in well populated areas and had significant <u>social/economic</u> impacts [*Brönnimann and Krämer*, 2016].

Page 16.

Original: This approach was efficient for the time, yet it still missed many small eruptions and often led to confused signals due to the presence of large concentrations of non-volcanic acids or salts.

Change: This approach was efficient for the time, yet it still missed many small eruptions and often led to <u>confusing</u> signals due to the presence of large concentrations of non-volcanic acids or salts.

Page 17.

Original: The approach was improved by the addition of time as a second volcanic criteria, thus eliminating false positives due to seasonally elevated biological signals [*Cole-Dai et al.*, 1997; *Cole-Dai et al.*, 2000; *Ferris et al.*, 2011].

Change: The approach was improved by the addition of time as a second volcanic criterion, thus eliminating false positives due to seasonally elevated biological signals [*Cole-Dai et al.*, 1997; *Cole-Dai et al.*, 2000; *Ferris et al.*, 2011].

Page 18.

Original: Low accumulation sites often were forced to use shorter time periods [*Castellano et al.*, 2005; Cole Dai *et al.*, 2000].

Change: Low accumulation sites often were forced to use shorter time periods [*Castellano et al.*, 2005; *Cole-Dai et al.*, 2000].

Page 19.

Original: Using SO_4^{2-} concentrations for the SP04 core, *Ferris et al.*, [2011] showed that using the smoothed background approach decreased the number events from 76 using the *Cole-Dai et al.*, [1997] approach to 74 using smoothed data.

Change: Using SO_4^{2-} concentrations for the SP04 core, *Ferris et al.*, [2011] showed that using the smoothed background approach decreased the number of events from 76 using the *Cole-Dai et al.*, [1997] approach to 74 using smoothed data.

Original. Using an approach similar to that of EDC where SO_4^{2-} concentrations are considered best represented by a lognormal pattern[*Castellano et al.*, 2005], the number of events was further reduced to 62.

Change: Using an approach similar to that of EDC where SO_4^{2-} concentrations are considered best represented by a lognormal pattern [*Castellano et al.*, 2005], the number of events was further reduced to 62. *(Extra space added between pattern [Castellano et al., 2005].)*

Original: Volcanic fluxes were then computed for those peaks that were greater than the twice the standard deviation above the weighted means.

Change: Volcanic fluxes were then computed for those peaks that were greater than twice the standard deviation above the weighted means.

Page 20.

Original: While the cores used in the study were all of different lengths, they showed varying number of eruptions in the periods where each overlapped.

Change: While the cores used in the study were all of differing lengths, they showed a varying number of eruptions in the periods where each overlapped.

Original: Events dated as 1880 and 1831 only appear in the PS14 record.

Change: Events dated 1880 and 1831 only appear in the PS14 record.

Original: The unknown 1809 eruption however, was found in all 5 cores and had a much narrower flux range, 10.5-16.6 kg/km^2 [*Gauthier et al.*, 2016].

Change: The unknown 1809 eruption, however, was found in all 5 cores and had a much narrower flux range, 10.5-16.6 kg/km^2 [*Gauthier et al.*, 2016].

Page 22.

Original: While the measurement of SO_4^{2-} and to a certain extent acidic signals, are quantitative, the relationship between SO_4^{2-} concentrations and the volcanic impacts may not translate over many eruptions or across magnitudes.

Change: While the measurement of SO_4^{2-}, and to a certain extent acidic signals, are quantitative, the relationship between SO_4^{2-} concentrations and the volcanic impacts may not translate over many eruptions or across magnitudes.

Original: Variations in accumulation rate, removal by wind, presence of sastrugi, and other surface irregularities change both the acidic and SO_4^{2-} signals seen in the preserved ice core record.

Change: Variations in accumulation rate, removal by wind, the presence of sastrugi, and other surface irregularities change both the acidic and SO_4^{2-} signals seen in the preserved ice core record.

Throughout the Thesis, spelling corrections have been made from the assessed version.

The following corrections have been made to the assessed Thesis.

Page 1.

Original: At ABN, the most dominant mode in the ternary plots was sulfate rich, sea salt deficient, indicating the site is heavily influenced on additional sources of sulfate with minimal influence of sea salts.

Change: At ABN, the most dominant mode in the ternary plots was sulfate-rich, sea salt deficient, indicating the site is heavily influenced by additional sources of sulfate with minimal influence of sea salts.

Original: Despite this, the dominance of sulfate lead to difficulty in separating small eruptions from the background sulfate and a weak seasonal cycle. The sulfate record at ABN provides for a useful volcanic ice core record, particularly for estimating the magnitude of the moderate and large eruptions.

Change: Despite this, the dominance of sulfate leads to difficulty in separating small eruptions from the background sulfate and a weak seasonal cycle. The sulfate record at ABN provides for a useful volcanic ice core record, particularly for estimating the magnitude of moderate and large eruptions.

Page 2.

Original: Precise dating and apparent magnitude of eruptions was improved upon by measuring sulfur and later sulfate content.

Change: Precise dating and apparent magnitude of eruptions were improved upon by measuring sulfur and later sulfate content.

Original: High resolution cores from coastal and high accumulation sites have improved dating for the most recent thousand years, but is limited over much longer time scales by thinning and spreading of layers due to compaction of the snow over time.

Change: High-resolution cores from coastal and high accumulation sites have improved dating for the most recent thousand years, but are limited over much longer time scales by thinning and spreading of layers due to compaction of the snow over time.

Original: Recent evidence from the comparisons of the signals of large eruptions across ice cores from the entire continent suggest that not all eruptions have the same deposition pattern over Antarctica [*Sigl et al.*, 2014].

Change: Recent evidence from the comparisons of the signals of large eruptions across ice cores from the entire continent suggests that not all eruptions have the same deposition pattern over Antarctica [*Sigl et al.*, 2014].

Page 3.

Original: Aurora Basin North (71°9′S, 111°22′E) is an inland plateau site in Wilkes Land, East Antarctica (Figure 1), approximately 550 km form Casey station and 584 km northwest of EPICA Dome C (EDC).

Change: Aurora Basin North (71°9′S, 111°22′E) is an inland plateau site in Wilkes Land, East Antarctica (Figure 1), approximately 550 km from Casey station and 584 km northwest of EPICA Dome C (EDC).

Page 4.

Original: Each 1 meter ice core was sectioned and from the center, a 35x35 mm stick was processed using methods established by *Curran and Palmer* [2001].

Change: Each one-meter ice core was sectioned and from the center, a 35x35 mm stick was processed using methods established by *Curran and Palmer* [2001].

Page 5.

Original: The snow accumulation and sampling resolution prohibited monthly comparisons for Na^+, Cl^-, MSA, and SO_4^{2-}, however did allow for seasonal groupings.

Change: The snow accumulation and sampling resolution prohibited monthly comparisons for Na^+, Cl^-, MSA, and SO_4^{2-}, however, did allow for seasonal groupings.

Original: Preliminary estimates using volcanic eruptions and isotope seasonality indicate the entire 299 meters core covers 2675 years, from 2002CE – 673BCE.

Change: Preliminary estimates using volcanic eruptions and isotope seasonality indicate the entire 299m core covers 2675 years, from 2002CE – 673BCE.

Page 7.

Original: By comparing a large number of ice cores and snow pits, *Bertler et al.*, [2005] was able to show a relationship between the Cl⁻/Na⁺ ratio and elevation, concluding that sites below 2000 meters show the least variation.

Change: By comparing a large number of ice cores and snow pits, *Bertler et al.*, [2005] <u>were</u> able to show a relationship between the Cl⁻/Na⁺ ratio and elevation, concluding that sites below 2000 meters show the least variation.

Original: In East Antarctica, the dome shaped plateau makes separating changes in elevation from changes resulting from moving inland. Aerosol and traverse studies have revealed some sea salt size separation at higher elevations [*Benassai et al.*, 2005; *Udisti et al.*, 2012; *Weller and Wagenbach*, 2007].

Change: In East Antarctica, aerosol and traverse studies have revealed some sea salt size separation at higher elevations [*Benassai et al.*, 2005; *Udisti et al.*, 2012; *Weller and Wagenbach*, 2007]. *(Phrase removed and sentences combined for clarity.)*

Page 8.

Original: Prior to 1900, there is a noticeable decrease from spring to summer followed by a sharp rise to peak in autumn.

Change: Prior to 1900, there is a noticeable decrease from spring to summer followed by a sharp rise to <u>a</u> peak in autumn.

Original: Movement does not generally change the shape of the curve, but rather shifts the highest concentrations towards autumn and winter and usually in one direction [*Curran et al.*, 2002; *Mulvaney et al.*, 1992; *Pasteur and Mulvaney*, 2000;].

Change: <u>The movement</u> does not generally change the shape of the curve, but rather shifts the highest concentrations towards autumn and winter and usually in one direction [*Curran et al.*, 2002; *Mulvaney et al.*, 1992; *Pasteur and Mulvaney*, 2000;].

Page 9.

Original: Increased acidic conditions associated with volcanic eruptions has similarly occurred within the ABN ice core.

Change: Increased acidic conditions associated with volcanic eruptions have similarly occurred within the ABN ice core.

Original: In Cosigüina (Figure 5) and UE1809, movement was away from the volcanic peaks in the up core direction.

Change: In Cosigüina (Figure 5) and UE1809, the movement was away from the volcanic peaks in the up core direction.

Page 10.

Original: The SO_4^{2-} signal shown in Figure 2c is similar to other cores from across Antarctica, having highest concentrations in summer and low values in winter.

Change: The SO_4^{2-} signal shown in Figure 2c is similar to other cores from across Antarctica, having the highest concentrations in summer and low values in winter.

Page 11.

Original: Additional comparisons with ice cores with similar site characteristics is required to further define the exact nature of the enhancements.

Change: Additional comparisons with ice cores with similar site characteristics are required to further define the exact nature of the enhancements.

Page 13. Minor correction to formula: Corrected lack of superscript on Na^+

Corrected sentence.
Original: Negative $nssSO_4^{2-}$ values are rarely seen at interior and plateau sites, instead, the nss component often makes up a very low percentage of total SO_4^{2-} values [Becagli et al., 2005; Castellano et al., 2005; Cole-Dai and Mosley Thompson, 1999; Cole-Dai et al., 2000].

Change: Negative $nssSO_4^{2-}$ values are rarely seen at interior and plateau sites, instead, the nss component often makes up a very high percentage of total SO_4^{2-} values [Becagli et al., 2005; Castellano et al., 2005; Cole-Dai and Mosley Thompson, 1999; Cole-Dai et al., 2000].

Page 14.

Original: Both *Cole Dai et al.*, [2000] and *Ferris et al.*, [2011] found that without adding additional temporal criteria, identification will often result in several false positives.

Change: Both *Cole-Dai et al.*, [2000] and *Ferris et al.*, [2011] found that without adding additional temporal criteria, identification will often result in several false positives.

Original: *Cole-Dai et al.*, [2000] was forced by very low snow accumulation to use two consecutive samples.

Change: *Cole-Dai et al.*, [2000] were forced by very low snow accumulation to use two consecutive samples.

Page 15.

Original: With this added criteria, two small eruptions were identified, Galunggung (38.5 meters, Figure 7) and an unknown event in 1942 (18 meters).

Change: With this added criterion, two small eruptions were identified, Galunggung (38.5 meters, Figure 7) and an unknown event in 1942 (18 meters).

Corrected Sentence.
Original: The additional criteria extended the shared Pinatubo / El Chichón eruption period from 1994 to 1996, much longer than the volcanic period in DSS [Plummer et al., 2012], EPICA Dome C (EDC) [Castellano et al., 2005; Gauthier et al., 2016], and WAIS Divide [Sigl et al., 2013].

Change: The additional criteria extended the shared Pinatubo/Cerro Hudson eruption period from 1994 to 1996, much longer than the volcanic period in DSS [Plummer et al., 2012], EPICA Dome C (EDC) [Castellano et al., 2005; Gauthier et al., 2016], and WAIS Divide [Sigl et al., 2013].

Original: Using the above criteria, eight volcanic eruptions were identified with in the study period (table 2).

Change: Using the above criteria, eight volcanic eruptions were identified within the study period (Table 2).

Original: This similar to the SO_4^{2-} signal seen in the Dome A volcanic record [*Jiang et al.*, 2012] and is the result of a shared peak with Tarawera (1886, *Global Volcanism Program*, 2013*)*.

Change: This is similar to the SO_4^{2-} signal seen in the Dome A volcanic record [*Jiang et al.*, 2012] and is the result of a shared peak with Tarawera (1886, *Global Volcanism Program*, 2013*)*.

Page 18.

Original: Sites nearest to each other are likely to have similar volcanic presence, subject to post depositional redistribution.

Change: Sites nearest to each other are likely to have a similar volcanic presence, subject to post depositional redistribution.

Original: There are however, multiple ice cores from different elevations and distances inland across Wilkes and Kaiser Wilhelm II Lands that could be used in place of a transect.

Change: There are, however, multiple ice cores from different elevations and distances inland across Wilkes and Kaiser Wilhelm II Lands that could be used in place of a transect.

Page 19.

Original: The slow and steady decrease towards Mount Brown followed by an increase at ABN is likely due to a shared transport mechanism with biological sulfate as both SO_4^{2-} and MSA could be in the smallest particle sized fractions at this distance [*Pszenny et al.*, 1992].

Change: The slow and steady decrease towards Mount Brown followed by an increase at ABN is likely due to a shared transport mechanism with biological sulfate as both SO_4^{2-} and MSA could be in the smallest particle size fractions at this distance [*Pszenny et al.*, 1992].

Page 20.

Original: Frost flowers are delicate dendritic or faceted ice crystals that grow on the surface of new ice, from a supersaturation of water vapor in the air nearest to the ice surface [*Obbard et al.*, 2009].

Change: Frost flowers are delicate dendritic or faceted ice crystals that grow on the surface of new ice, from the supersaturation of water vapor in the air nearest to the ice surface [*Obbard et al.*, 2009].

Page 21.

Original: A total of eight shallow cores were drilled on Mill Island, however, due to data restrictions, only part the main core and a shallow snow pit were used in this study, a combined total depth of 20 meters or approximately 10 years.

Change: A total of eight shallow cores were drilled on Mill Island, however, due to data restrictions, only part <u>of</u> the main core and a shallow snow pit were used in this study, a combined total depth of 20 meters or approximately 10 years.

Page 24.

Original: For example, loss of SO_4^{2-} due to mirabilite ($Na_2SO_4 \cdot 10H_2O$) precipitation occurs gradually from -8°C to -22°C [*AlvarezAviles et al.*, 2008; *Obbard et al.*, 2009; *Rankin et al.*, 2002].

Change: For example, loss of SO_4^{2-} due to mirabilite ($Na_2SO_4 \cdot 10H_2O$) precipitation occurs gradually from -8°C to -22°C [<u>*Alvarez-Aviles*</u> *et al.*, 2008; *Obbard et al.*, 2009; *Rankin et al.*, 2002].

Original: Samples that have had all SO_4^{2-} lost to mirabilite will have a ratio approximately 46.6% Na^+ and 53.4% Cl^- [*Rankin et al.*, 2002] and will appear near the open diamond in the graph.

Change: Samples that have had all SO_4^{2-} lost to mirabilite will have a ratio <u>of</u> approximately 46.6% Na^+ and 53.4% Cl^- [*Rankin et al.*, 2002] and will appear near the open diamond in the graph.

Page 26.

Original: Instead the correction should be applied to only those samples that show true SO_4^{2-} depletion, those samples in the shaded area of the tern plot.

Change: Instead<u>,</u> the correction should be applied to only those samples that show true SO_4^{2-} depletion, those samples in the shaded area of the <u>ternary</u> plot.

Page 27.

Original: Despite the added biological sulfate, the site is still shows some degree of sulfate depletion.

Change: Despite the added biological sulfate, the <u>site still</u> shows some degree of sulfate depletion.

Original: Nearly all of the samples appear closer to the SO_4^{2-} corner and only one sample is immediately recognized at fractionated.

Change: Nearly all of the samples appear closer to the SO_4^{2-} corner and only one sample is immediately recognized <u>as</u> fractionated.

Original: Unlike GD17 and DSS, the samples trend above the fractionation line, indicating that they may have a fractionated source and / or are more heavily influenced by chloride.

Change: Unlike GD17 and DSS, the samples trend above the fractionation line, indicating that they may have a fractionated source <u>and/or</u> are more heavily influenced by chloride.

Page 28.

Original: It has been proposed that additional SO_4^{2-} may be due to settling of oxidized SO_2 from the stratosphere that only occurs at high elevation sites on the East Antarctic plateau [*Delmas*, 1992; *Preunkert et al.*, 2008].

Change: It has been proposed that additional SO_4^{2-} may be due to <u>the</u> settling of oxidized SO_2 from the stratosphere that only occurs at high elevation sites on the East Antarctic plateau [*Delmas*, 1992; *Preunkert et al.*, 2008].

Page 29.

Original: Krakatau was excluded as it a merged peak in ABN.

Change: Krakatau was excluded as it <u>appears as</u> a merged peak in ABN.

Original: Spring and autumn samples are spread evenly across the entire length of the sea water line and show little preference for side.

Change: Spring and autumn samples are spread evenly across the entire length of the <u>seawater</u> line and show little preference for <u>a</u> side. *(Also shows spelling correction used throughout both Literature Review and Thesis.)*

Original: Using this information, it is unlikely that volcanoes will have much role in the placement of samples on the GD17 or EDC ternary plots. Volcanic eruptions would therefore have limited, if any, influence on the seasonal cycle at GD17, where no reliable volcanic record exists or at EDC where volcanoes are often represented by only one or two samples.

Change: Using this information, it is unlikely that volcanoes will have a large role in the placement of samples on the GD17 or EDC ternary plots. Volcanic eruptions would, therefore, have limited, if any, influence on the seasonal cycle at GD17, where no reliable volcanic record exists or at EDC where volcanoes are often represented by only one or two samples.

Page 30.

Corrected statement.
Original: Instead of showing clear duality similar to DSS, all but three samples are less than 80% SO_4^{2-} and only one appears less than 85% SO_4^{2-}.

Change: Instead of showing clear duality similar to DSS, all but three samples are greater than 80% SO_4^{2-} and only one appears greater than 85% SO_4^{2-}.

Original: Only accurately dating the remainder of the core and accurately assessing the biological SO_4^{2-} will the location's total volcanic influence be known.

Change: Only by accurately dating the remainder of the core and accurately assessing the biological SO_4^{2-} will the location's total volcanic influence be known.

Page 32.

Original: This make large and moderate eruptions easily stand out, but still prohibits easy separation of small eruptions from the background.

Change: This makes large and moderate eruptions easily stand out, but still prohibits easy separation of small eruptions from the background.

Page 33.

Original: The extended record will provide more details into the movement of MSA and provide additional details into the relationship between MSA and biological sulfate and improve the understanding of movement over extended time period.

Change: The extended record will provide more details into the movement of MSA and provide additional details into the relationship between MSA and biological sulfate and improve the understanding of movement over an extended time period.

Abstract

Volcanic eruptions are important natural drivers of short term climate changes and knowledge of their effects will lead to a greater understanding of how the climate system works under future human induced changes. Defining small and moderate eruptions can be challenging and appears to be dependent on individual ice core site characteristics, leading to some confusion regarding their climatic impacts. In this study, ice core aerosol records from a new inland East Antarctica site, Aurora Basin North (ABN), were compared to other Antarctic sites using ternary plots to investigate the characteristics of sea salts. At ABN, the most dominant mode in the ternary plots was sulfate rich, sea salt deficient, indicating the site is heavily influenced on additional sources of sulfate with minimal influence of sea salts. In the period 1800-2000CE, a total of eight volcanic eruptions were identified, in agreement with other ice cores. Despite this, the dominance of sulfate lead to difficulty in separating small eruptions from the background sulfate and a weak seasonal cycle. The sulfate record at ABN provides for a useful volcanic ice core record, particularly for estimating the magnitude of the moderate and large eruptions. By using ternary plots and the ABN sulfate record, characteristics for a useful volcanic ice core record were identified. The ice core site should be where the seasonal sea salt record is maintained and the overall influence of sources other than volcanic sulfate is minimal.

1. Introduction

Earth's stable climate is the result of a balance between incoming and outgoing solar radiation among the atmosphere, ocean, and land surfaces [*Cole-Dai*, 2010]. Climate change is the result of perturbations to this energy balance. Large volcanic eruptions are one of the most important natural drivers of short term climatic changes. By studying their effects, the current understanding of human induced climatic change can be enhanced.

Volcanic impacts on climate are the direct result of interactions between solar radiation, dust, aerosols, and gases released into the atmosphere. Sulfur rich gases are very efficient at scattering visible light, thus changing the planet's albedo and reducing

the amount of energy reaching the surface [*Cole-Dai*, 2010; *McCormick et al.*, 1995; *Robock*, 2000]. Small eruptions usually limit these effects to the local areas. Large, tropical eruptions have the capacity of reaching the stratosphere where the effects can impact the entire planet. Disentangling these effects from other climate drivers requires long term climatic and historical records. Until satellite coverage, these records were limited to populated regions and often only if the eruption caused great socio-economic impacts [*Cole-Dai*, 2010; *Robock*, 2000]. Longer and more complete information often comes from climatic proxy records. Of the many different types, polar ice cores are unique and contain samples of the past atmosphere and volcanic sulfur aerosols within the ice.

Detection of volcanic signals was first achieved by measuring the electrical properties of an ice core [*Cole-Dai*, 2010; *Hammer*, 1977]. Precise dating and apparent magnitude of eruptions was improved upon by measuring sulfur and later sulfate content. Over longer time periods, discrepancies between cores have been noted, often associated with inaccurate dating from low temporal resolution of chemical analysis or post depositional movement of snow layers [*Cole-Dai*, 2010; *Sigl et al.*, 2014]. High resolution cores from coastal and high accumulation sites have improved dating for the most recent thousand years, but is limited over much longer time scales by thinning and spreading of layers due to compaction of the snow over time. Ice cores from the Antarctic plateau receive much less snow accumulation and therefore are not as limited by layer thinning. Some ice core sites receive so little accumulation, sub annual chemical analysis is impossible and dating becomes problematic. These negative effects from both ice core locations can be improved by combining multiple records. Dating of low accumulation sites improves through volcanic synchronization with highly resolved ice cores. By comparing synchronized records of low accumulation sites in East Antarctica, sulfate deposition was found to be uniformly distributed across large regions, even for small eruptions [*Sigl et al.*, 2014]. Volcanic deposition at coastal sites was found to be greater than over the plateau, most likely the result of greater snow deposition. Recent evidence from the comparisons of the signals of large eruptions across ice cores from the entire continent suggest that not all eruptions have the same deposition pattern over Antarctica [*Sigl et al.*, 2014]. While volcanic deposition occurs over large regions, individual ice

cores record the volcanic record slightly differently depending on the location and snow accumulation at the site.

Volcanic deposition is not the only source of aerosols to the ice sheet, to properly interpret the volcanic sulfate signal, other trace ions need to be assessed. This study uses an ice core from a new inland site in Wilkes Land, East Antarctica, as a link between the trace chemical records of coastal and plateau ice cores. Traverses across East Antarctica have shown depositional changes in both sea salts and sulfate are associated with elevation and distance from the coast. To determine if these fluctuations exist within Wilkes Land, where no traverses have crossed, and their possible influences on the volcanic record, the mean concentrations of sodium (Na^+), chloride (Cl^-), sulfate (SO_4^{2-}), and methanesulfonic acid (MSA) were compared across multiple ice cores from various elevations and distances inland. Ternary plots were used to assess the degree of sulfate depletion (fractionation) as well as the possible influences sea salt and any additional sources of sulfate may have on the volcanic sulfate signal. And finally, the volcanic record from this never before sampled region was compared and contrasted with low and high resolved ice cores to gain a better understanding of the differences across depositional regimes.

2. Sample Site and Methods
2.1 Sample Site

The Aurora Basin North (ABN) ice core project was an international drilling effort conducted from December 2013 through January 2014. Eight ice cores of various lengths, snow pits, and radar studies were completed, and an automatic weather station was placed on site for future metrological studies. ABN Main is the longest ice core, 299 meters in total, and was used for the bulk of this study.

Aurora Basin North (71°9′S, 111°22′E) is an inland plateau site in Wilkes Land, East Antarctica (Figure 1), approximately 550 km form Casey station and 584 km northwest of EPICA Dome C (EDC). Mean summer temperature of -25°C and a mean annual temperature of -43°C with wind speeds of 6.4 m/s mainly out of the south-east. It

has a highly variable moderate annual accumulation rate. For the limited time period of this study, the mean accumulation rate is 119.6 kg/m^2/yr (2002-1800). Trace chemistry was analyzed at 2.5 cm resolution, allowing for 3 to 15 samples per year.
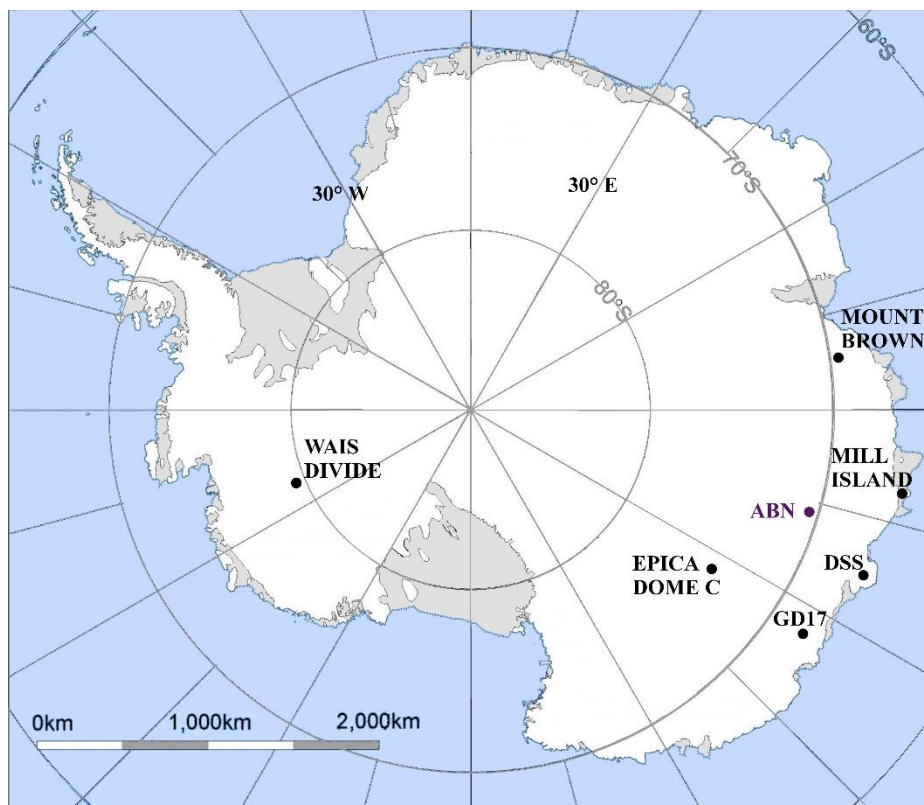

Figure 1. Map of locations used in this study. ABN - Aurora Basin North; DSS - Dome Summit South, Law Dome; WAIS - West Antarctic Ice Sheet.

2.2 Ice Core Sampling Methods

Each 1 meter ice core was sectioned and from the center, a 35x35 mm stick was processed using methods established by *Curran and Palmer* [2001]. The first 76 meters were processed on site and the remaining 223 meters were processed at the ACE CRC/AAD laboratories in Hobart, Australia. The outer 3 mm of each 2.5 cm sample was removed using a microtome blade. Each sample was then collected into a 25 mL Coulter® cup, melted, and refrozen to preserve methanesulfonic acid (MSA). To prevent accidental contamination, all sample preparation was completed while wearing 2 pairs of shoulder length polyethylene gloves and face mask inside a laminar flow hood.

Samples were fully thawed prior to analysis. All vials, caps, and pipette tips were soaked repeatedly and rinsed thoroughly with Milli-Q water at 18.2 MΩ, less than 0.1 μS/cm. From each sample, 6.2 mL was analyzed on a 2 mm microbore Dionex ICS3000 ion chromatograph. Anions were analyzed using an AG18 anion guard column followed by the AS18 cation separation column. Cation analysis was performed using CG12A guard and CS12A separation columns. The species analyzed were sodium (Na^+), potassium (K^+), magnesium (Mg^{2+}), calcium (Ca^{2+}), chloride (Cl^-), sulfate (SO_4^{2-}), nitrate (NO_3^-), and MSA. For this study, only Na^+, Cl^-, SO_4^{2-} and MSA were used.

2.3 Dating Methods

Due to its moderate accumulation and inland location, multiple trace chemical species were used to accurately date ABN. The onset of the eruptions of Pinatubo, Mt. Agung, Krakatau, Tambora, and the unknown eruption (UE) of 1809 were initially set as volcanic reference horizons and matched to the appearance in the highly resolved West Antarctic Ice Sheet (WAIS) Divide core. Annual dating in between these eruptions was established by using the seasonal layers of hydrogen peroxide (H_2O_2), Na^+, and SO_4^{2-}. The start of each year was defined as 1 January and was matched to the highest concentration in the H_2O_2 seasonal cycle [*van Ommen and Morgan*, 1997]. The minimum in Na^+ and Cl^- or the maximum concentrations of SO_4^{2-} were used to clarify ambiguous years. Using this multi species approach, the ABN main core between 4-43 meters was dated seasonally for 202 years (2002-1800). Analysis of the remaining portions of the core is still ongoing. Preliminary estimates using volcanic eruptions and isotope seasonality indicate the entire 299 meters core covers 2675 years, from 2002CE – 673BCE.

3. Results and Discussion
3.1 Seasonal Signals – Sodium and Chloride

The snow accumulation and sampling resolution prohibited monthly comparisons for Na^+, Cl^-, MSA, and SO_4^{2-}, however did allow for seasonal groupings. The record was grouped into four seasonal bins based upon their decimal date and designated as follows:

Spring – September, October, November; Summer – December, January, February; Autumn – March, April, May; Winter – June, July, August. The mean seasonal cycles for each chemical species are shown in Figure 2, plotted over two years to emphasize the differences between each season. Mean concentrations and standard errors for each ion are shown in Table 1. Error bars represent one standard error for that species and season.

Table 1. Mean seasonal concentrations (2002-1800). Error represents one standard error.

Season	Na$^+$ [µEq/L]	Cl$^-$ [µEq/L]	SO$_4^{2-}$ [µEq/L]	MSA [µEq/L]
Spring	0.46 ± 0.014	0.73 ± 0.016	1.04 ± 0.025	0.055 ± 0.0019
Summer	0.39 ± 0.0087	0.64 ± 0.0095	1.05 ± 0.015	0.058 ± 0.0011
Autumn	0.51 ± 0.017	0.75 ± 0.017	1.00 ± 0.020	0.061 ± 0.0017
Winter	0.53 ± 0.013	0.80 ± 0.015	0.99 ± 0.019	0.058 ± 0.0016
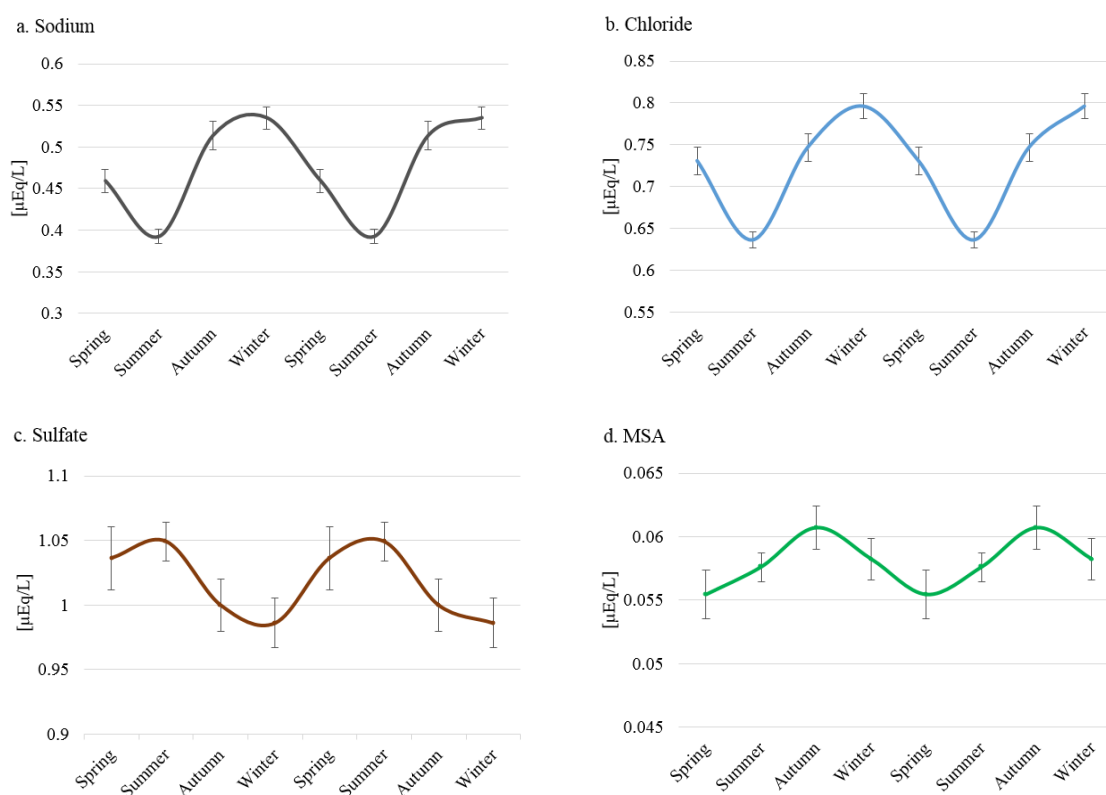
Figure 2. Mean seasonal cycle over 2 years. Each plot individually scaled to show differences between seasons. Error bars represent one standard error.

Sodium and chloride share the well-established Antarctic signal, peaking in winter and decreasing into summer. The winter peak is not as broad as in other ice cores due to the smoothing associated with creating seasonal bins. Similar to other ice cores, the chloride concentration is greater than sodium. As shown in Figure 3, the Cl^- concentration shows a relative enhancement over the expected values using the sea water ratio of 1.16 [*Curran et al.*, 1998]. Additional Cl^- over that of the sea water ratio is not uncommon. Similar findings were noted across the interior of East Antarctica [*Bertler et al.*, 2005], the Fimbul Ice Shelf in Dronning Maud Land [*Mulvaney et al.*, 1993], and the South Pole [*Legrand and* Delmas, 1984; Legrand *and Delmas*, 1988]. By comparing a large number of ice cores and snow pits, *Bertler et al.*, [2005] was able to show a relationship between the Cl^-/Na^+ ratio and elevation, concluding that sites below 2000 meters show the least variation. Above 2000m the ratios become more scattered, reaching values near 20. The degree of enhancement at ABN is over twice that of other nearby sites [*Foster*, 2003; *Wong*, 2007], but is still within the continental variation [*Bertler et al.*, 2005] and could be the result of HCl formation in the presence of H_2SO_4 [*Benassai et al.*, 2005; *Legrand and Delmas*, 1988].
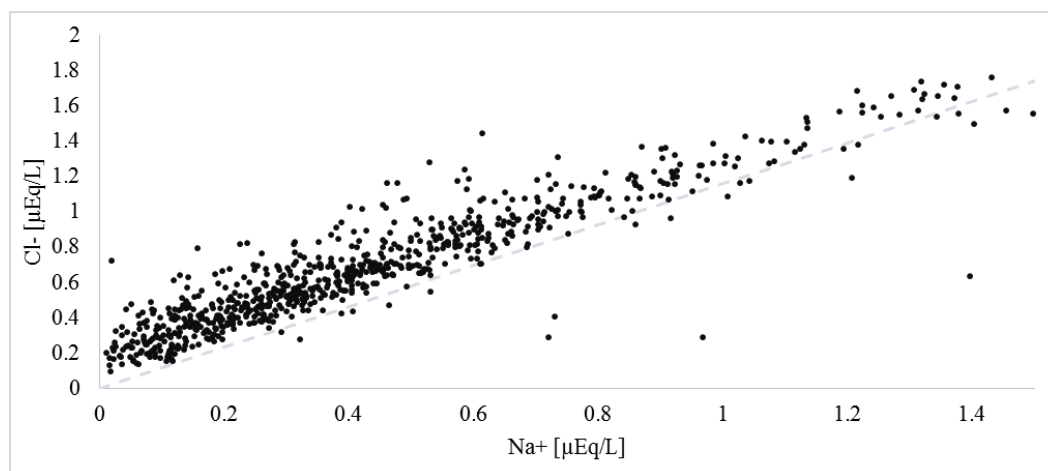

Figure 3. Sodium vs Chloride for individual samples. Gray dotted line represents sea water ratio, 1.16.

In East Antarctica, the dome shaped plateau makes separating changes in elevation from changes resulting from moving inland. Aerosol and traverse studies have revealed some sea salt size separation at higher elevations [*Benassai et al.*, 2005; *Udisti et al.*, 2012; *Weller and Wagenbach*, 2007]. The size separation would naturally decrease

the coarse sea salt fraction leaving behind the fine aerosols produced from gas to particle conversion. At ABN, low Na^+ and Cl^- concentrations are likely the result of differential settling increased Cl^- concentration from additional atmospheric HCl formation, giving the appearance of Cl^- enrichment. Other inland sites have shown that post depositional movement of Cl^- is possible, especially those at very low accumulation sites [*Benassai et al.*, 2005; *Bertler et al.*, 2005; *Wagnon et al.*, 1999]. No post depositional movement was found in the upper meters of the ABN main core, therefore any additional Cl^- from HCl formation may have been retained, increasing the overall Cl^- concentrations.

3.2 Seasonal Signals – MSA

Methanesulfonic acid in Antarctic ice cores is the product of the atmospheric oxidation of dimethylsulfide (DMS) from planktonic productivity in the Southern Ocean [*Abram et al.*, 2013; *Curran et al.*, 2000; *Smith et al.*, 2004]. Where SO_4^{2-} in ice cores has multiple sources, biological production of DMS, and therefore its oxidation products, are the only source of MSA in Antarctica. In some cores, interpretation of the MSA record can be difficult due to significant post-depositional movement.

As seen in Figure 2d, the traditional MSA summer peak appears in autumn. This seasonal shift is not uncommon and has been seen in both high and low accumulation sites [*Curran et al.*, 2002; *Pasteur and Mulvaney*, 2000; *Smith et al.*, 2004; *Wagnon et al.*, 1999]. This shift was investigated further by defining the cycle in 50 year intervals (Figure 4). From 2002-1900, the seasonality is similar to that of the entire record, a gradual increase from spring through summer and peaking in autumn. Prior to 1900, there is a noticeable decrease from spring to summer followed by a sharp rise to peak in autumn. All graphs reveal that the minimum in MSA occurs not in winter as would be expected, but instead, occurs in spring. This shift is likely a combination of the acidic conditions of the core and location induced effects, such as size separation during long range transport and stratospheric inputs. The exact mechanisms for MSA migration are not completely understood, but some patterns have emerged. Movement does not generally change the shape of the curve, but rather shifts the highest concentrations towards autumn and winter and usually in one direction [*Curran et al.*, 2002; *Mulvaney et*

al., 1992; *Pasteur and Mulvaney*, 2000;]. Examination of the entire MSA record at ABN reveals some drift beginning at 14 meters with a consistent shifting within the year. Deeper than 20 m, autumn peaks become the norm and become less predictable. Shifts occur in both up and down core directions and to varying degrees.
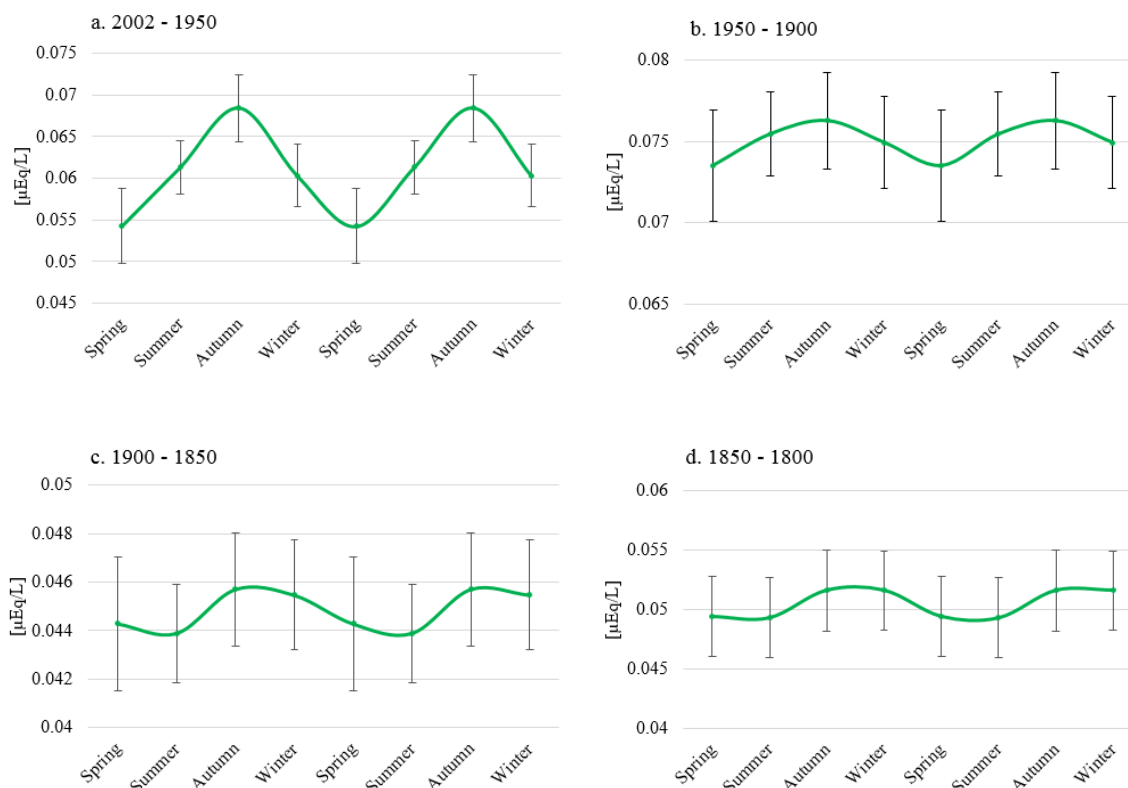

Figure 4. Seasonal plots of MSA in 50 year intervals. Error bars represent 1 standard error for that season.

MSA movement at Vostok has been associated with acidic conditions, often during great volcanic SO_4^{2-} deposition [*Wagnon et al.*, 1999]. Increased acidic conditions associated with volcanic eruptions has similarly occurred within the ABN ice core. Movement during Mt. Agung was in the down core direction and not completely free of the SO_4^{2-} peak. During the merged Tarawera / Krakatau eruption, MSA formed two separate peaks on either side of the highest concentration in sulfate. In Cosigüina (Figure 5) and UE1809, movement was away from the volcanic peaks in the up core direction. MSA concentrations near Tambora appear depressed, with a slight shift away from the volcanic peak, in the up core direction. Given the close temporal proximity of the UE1809 and Tambora eruptions and the very large increase in MSA following the

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UE1809 eruption, it is possible that any movement associated with Tambora may be included in the large MSA peak near UE1809.
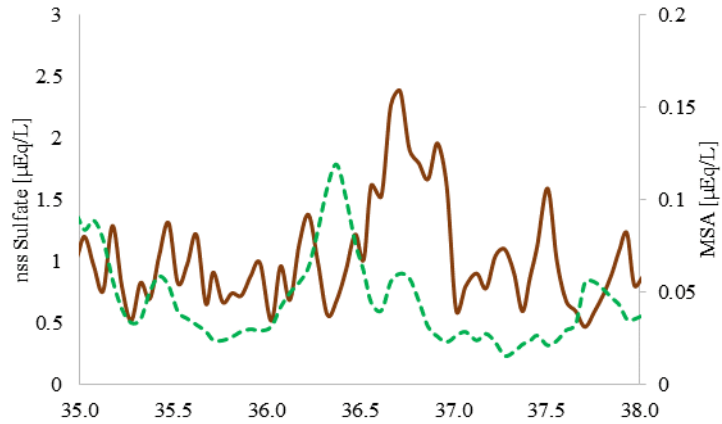

Figure 5. MSA (green dashed) movement during eruption of Cosigüina (solid brown, 36.5-37m).

In the upper meters of the core, where migration of MSA is not immediately noticeable, the $nssSO_4^{2-}$and MSA records trend well, sharing similar seasonal patterns. Aerosol studies at inland locations have revealed similar transport mechanisms for both SO_4^{2-} and MSA, to include long range transport [*Piel et al.*, 2006; *Udisti et al.*, 2012] and gas to particle conversion [*Piel et al.*, 2006; *Wagnon et al.*, 1999]. Given the shared seasonal and transport patterns and the general lack of sea salt influence over SO_4^{2-} at ABN, the SO_4^{2-}/MSA ratio was considered for the removal of the biological $nssSO_4^{2-}$ signal following the method of *Udisti et al.*, [2012]. However, the extended drifts of MSA and subsequent concentration changes during volcanic periods completely disrupted the normal seasonal patterns, making it difficult to reconstruct SO_4^{2-}/MSA ratios.

3.3 Seasonal Signals – Sulfate

The SO_4^{2-} signal shown in Figure 2c is similar to other cores from across Antarctica, having highest concentrations in summer and low values in winter. Known volcanic peaks were removed to determine if their presence had any influence on the seasonal cycle. These signals were visually compared in Figure 6. The very slight change in the slope of the two records between autumn and winter is the result of a greater

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number of autumn samples versus winter samples removed from the record. The obvious difference in the mean seasonal concentrations and standard errors are expected with volcanic additions to the SO_4^{2-} record. The increased error associated with spring in the non-volcanic curve is the result of several instances of shared sodium and sulfate peaks attributed to the intrusion of storms onto the plateau.
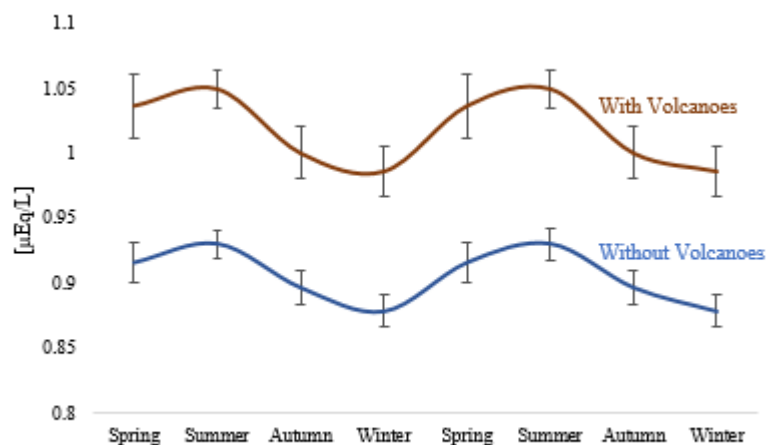

Figure 6. Mean seasonal cycle for SO_4^{2-} with (top) and without volcanic activity (bottom). Plotted over two cycles. Error bars represent 1 standard error.

The entire SO_4^{2-} record for the study time period is shown in Figure 7. Immediately, several large SO_4^{2-} spikes are recognized at 7 m, 29 m, 40 m, and 41 m. These elevated SO_4^{2-} concentrations are the eruptions of Pinatubo, Krakatau, Tambora, and UE1809, the reference horizons used to assist in dating. In general, the SO_4^{2-} concentrations follow established seasonal patterns and have low overall concentrations. The annual variability is high at this site, leading to unusually long elevated SO_4^{2-} concentrations. These elevated periods can last from 6 months to 2 years. Several such periods may be the result of volcanic activity, but not all. Elevated concentrations at 10.5 meters and 24 m, dated to 1976 and 1910, respectively, do not coincide with previously dated eruptions in the Dome Summit South (DSS), Law Dome or WAIS Divide records. While it is possible that these periods may be the result of very small eruptions, lost in the noisy records of the highly resolved ice cores, it is more likely that these increased SO_4^{2-} periods are the result of enhanced biological activity or stratospheric deposition. Additional comparisons with ice cores with similar site characteristics is required to further define the exact nature of the enhancements.
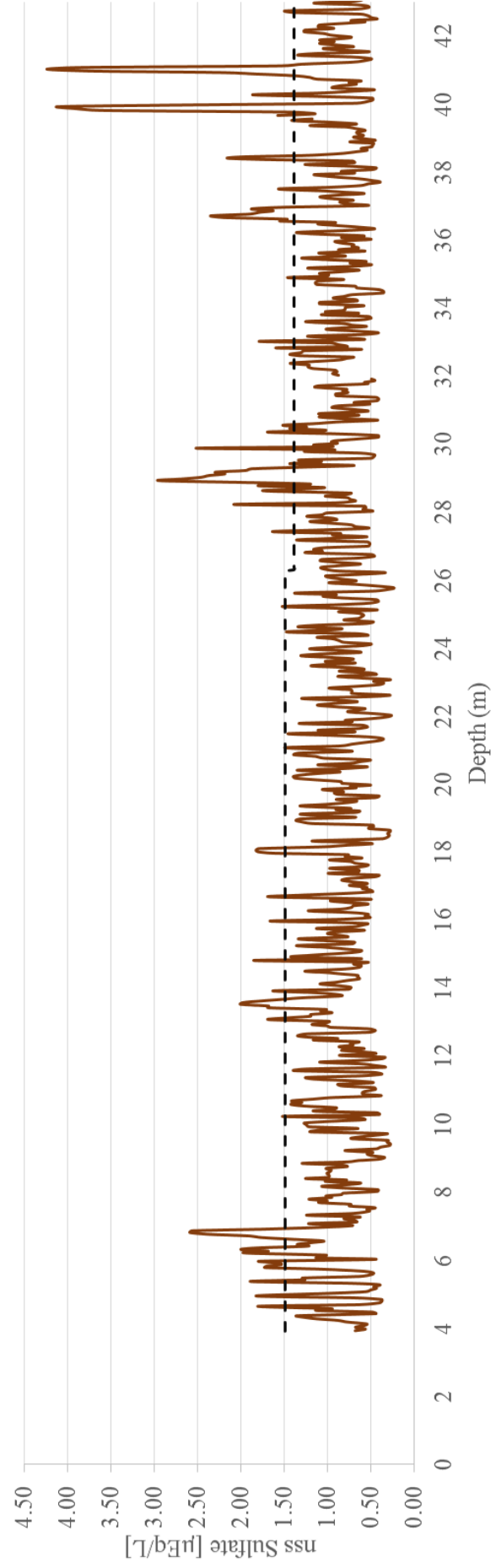
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Figure 7. Sulfate record by depth over study period. Dotted line is mean background plus two standard deviations. See section ## for explanation. Elevated peaks at 40m and 41m are Tambora and UE1809, respectively.

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The SO_4^{2-} measured in polar ice cores arrives from multiple sources. Unlike Greenland, Antarctica is well separated from the continents in the Southern Hemisphere by the vast Southern Ocean, therefore, except for a few ice free areas, continental and human sources have minimal effects in Antarctica. It has been generally accepted that the bulk of most sea salt ions are derived from the surrounding ocean. Indeed, at coastal sites, sea salt ions, Na^+ and Cl^-, have been shown to dominate the sea salt budget [*Bertler et al.*, 2005; *Hara et al.*, 2004; *Kerminen et al.*, 2000; *Wagenbach et al.*, 1998]. At inland sites however, SO_4^{2-} dominates and Na^+ and Cl^- are at minimal levels [*Bertler et al.*, 2005; *Hara et al.*, 2004]. Often this results in a small difference between the sea salt (ss) and non-sea salt (nss) components of sulfate. Separation of the ss component from the nss component often uses the ratio of SO_4^{2-} to another sea salt ion. In this study, Na^+ was used to calculate the nss component of SO_4^{2-} as in the equation below,

$$[SO_4^{2-}]_{nss} = [SO_4^{2-}]_{total} - ((k - fc) \times [Na^+]_{total})$$

where k is the ratio of SO_4^{2-}/Na^+ in sea water, 0.1201 µEq/L, [*Plummer et al.*, 2012] and fc is the fractionation correction, if used. Sodium was chosen as the conservative sea salt tracer because of the higher than expected Cl^- concentrations at ABN.

Use of this equation often leads to negative $nssSO_4^{2-}$ values, indicating a depletion in sulfate. Negative $nssSO_4^{2-}$ values are rarely seen at interior and plateau sites, instead, the nss component often makes up a very low percentage of total SO_4^{2-} values [*Becagli et al.*, 2005; *Castellano et al.*, 2005; *Cole-Dai and Mosley Thompson*, 1999; *Cole-Dai et al.*, 2000]. This was the case at ABN, where no negative values were determined. The mean difference between total and $nssSO_4^{2-}$ over the entire 202 year period is 6.9% ± 6.5%. While it is common for such a small difference to be ignored, the small seasonal variability between individual samples and the large annual variability necessitate the use of $nssSO_4^{2-}$ when determining volcanic influences.

3.4.1 Background and Volcanic Sulfate

Identification of volcanic eruptions in the SO_4^{2-} record requires the accurate discrimination between the seasonal background SO_4^{2-} signal and any volcanic influences. The method used by *Palmer et al.*, [2001], *Palmer*, [2002], *Palmer et al.*, [2002] and *Plummer et al.*, [2012] for the DSS core require a sampling resolution and an extended background period that is impossible within the time period selected for ABN. The shortened background period used by *Castellano et al.*, [2005] allows for identification within the short ABN study period, however, the mathematical smoothing used would cause the loss of several small eruptions. Therefore, a new approach to both defining and removing the seasonal background was attempted. This method combines approaches inspired by those in *Cole-Dai et al.*, [2000], *Castellano et al.*, [2005], and *Plummer et al.*, [2012].

The removal of obvious and well known eruptions is required prior to any seasonal background SO_4^{2-} calculations. In ABN, the obvious peaks include Pinatubo (6.8 meters, Figure 7), Mt. Agung (13.5 meters), Krakatau (29 meters), Tambora (39 meters), and UE1809 (41 meters). The natural annual SO_4^{2-} variability can be quite large, often appearing as extended periods of elevated SO_4^{2-} concentrations. Several smaller and moderate eruptions often appeared within these elevated periods. In these instances, the entire elevated period within the known volcanic period was removed.

Both *Cole Dai et al.*, [2000] and *Ferris et al.*, [2011] found that without adding additional temporal criteria, identification will often result in several false positives. *Plummer et al.*, [2012] used 6 months as the minimum elevated period required for volcanic influence. *Cole-Dai et al.*, [2000] was forced by very low snow accumulation to use two consecutive samples. Neither approach would prove useful at ABN as a result of the moderate snow accumulation and the high natural variability. Instead, both time and a number of consecutive samples were used. To reduce the influence of the increased seasonal variations found in the upper meters of the core, the entire study period was divided into two centuries. The mean number of samples within each year was calculated per century and then rounded to the nearest whole number. This number became the

minimum number of samples within each century for an elevated SO_4^{2-} period to be considered volcanic. The 19th century minimum duration was thus defined as three samples and four samples were required in the 20th century.

The elevated periods were further constricted by defining a minimum elevated concentration. Following the approach of *Cole-Dai et al.*, [1997] and *Cole Dai et al.*, [2000], any elevated SO_4^{2-} above the background and two standard deviations can be considered as a possible volcanic eruption. Again, the minimum seasonal concentration was considered separately for each century, 1.39 µEq/L, and 1.49 µEq/L, for the 19th and 20th centuries, respectively. With this added criteria, two small eruptions were identified, Galunggung (38.5 meters, Figure 7) and an unknown event in 1942 (18 meters). The additional criteria extended the shared Pinatubo / El Chichón eruption period from 1994 to 1996, much longer than the volcanic period in DSS [*Plummer et al.*, 2012], EPICA Dome C (EDC) [*Castellano et al.*, 2005; *Gauthier et al.*, 2016], and WAIS Divide [*Sigl et al.*, 2013]. Volcanic inputs disrupt the general background SO_4^{2-} signal for several years following the onset of the eruption however, the seasonal variation and the high annual variability in this region of the core prevent accurate separation of the volcanic and seasonal influences during this time period. It was therefore concluded that the extended period must be considered volcanic as it meets the above criteria.

3.4.2 Comparing Volcanic Records

Using the above criteria, eight volcanic eruptions were identified with in the study period (table 2). The SO_4^{2-} signal of Krakatau (1883, *Global Volcanism Program*, 2013) is elevated for over five years and with no noticeable decrease in concentrations. This similar to the SO_4^{2-} signal seen in the Dome A volcanic record [*Jiang et al.*, 2012] and is the result of a shared peak with Tarawera (1886, *Global Volcanism Program*, 2013). The number of eruptions at ABN is comparable to the number identified in DSS [*Palmer et al.*, 2002; *Plummer et al.*, 2012], EDC [*Castellano et al.*, 2005 and *Gauthier et al.*, 2016] and WAIS Divide [*Sigl et al.*, 2013], including the shared peaks of Tarawera and Krakatau (Table 2).

Of the nine events identified in the DSS record, eight were shared by ABN, Krakatau and Tarawera counted separately. The higher sampling resolution due to the very high accumulation rates at Law Dome allowed for the separation of Tarawera and Krakatau as well as the identification of El Chichón in 1982. A slight elevated SO_4^{2-} signal was investigated in the early 1980's at ABN, but was excluded as volcanic because it was not greater than the minimum elevated SO_4^{2-} concentration.

Table 2. List of volcanic eruptions by record. Dates from individual sources. *Krakatau and Tarawera peak for ABN only. Shared eruptions are italicized. DSS – *Plummer et al.*, 2012; EDC – *Castellano et al.*, 2005, *Gauthier et al.*, 2016; WAIS Divide – *Sigl et al.*, 2013.

Eruption	**ABN**	**DSS**	**EDC (2005)**	**EDC (2016)**	**WAIS Divide**
Pinatubo/Cerro Hudson	*1992-1996*	*1991.7-1993.9*	*1992*	*1992*	*1991.5-1993.5*
El Chichón		1984.5-1984.8			
Mt. Agung	*1964-1965*	*1964.1-1965.2*	*1964*	*1964*	*1963.6-1965.6*
Unknown				1929	
Unknown	1942.5-1943				
St. Maria					1902.9-1904.3
Tarawera		1887.5-1888.2		1891	1886.5-1887.6
*Krakatau **	*1884-1888*	*1884.5-1885.9*	*1887*	*1885*	*1884-1886.4*
Cotopaxi			1881		
Makjan-Cotopaxi-Fuego			1861		1862.6-1864.6
Unknown				1839	
Cosigüina	1834-1836	1836.7-1837.8		1834	1834.7-1838.2
Babuyan,					1831.7-1833.2
Galunggung	1825.6-1826	1823.4-1823.9			
Tambora	*1816-1819*	*1815.8-1819.3*	*1816*	*1816*	*1815.4-1818.4*
UE1809	*1810-1812*	*1809.7-1811.1*	*1810.5*	*1809*	*1809.4-1812.1*

Of the seven eruptions were identified at EDC by *Castellano et al.*, [2005] and the nine by *Gauthier et al.*, [2016], only five were shared. The ABN volcanic record has all five of these shared eruptions. Additionally, the eruption of Cosigüina is shared by both ABN and the record from *Gauthier et al.*, [2016]. The WAIS Divide ice core contains the greatest number of identified eruptions (10 events) with ABN sharing seven. The eruptions of Santa Maria (1902) and Babuyan, Indonesia (1831) seen in the WAIS Divide ice core do not coincide with any elevated SO_4^{2-} periods at ABN. The final unshared event, the 1861-2 Makjan-Cotopaxi-Fuego eruption exists in an elevated SO_4^{2-} period,

but does not meet the time requirements and was thus excluded. The only ABN peak not shared among the cores is the 1942 event. This event meets the minimum requirements to be considered volcanic, but only just. The peak shape is similar to that seen in Pinatubo, Galunggung, and UE1809. So while the event is not shared by other cores, the shape of the signal and the elevated SO_4^{2-} indicate that it should be included in the ABN volcanic record.

Variation in the number of volcanic peaks is not unusual and is most often found to be the result of individual ice core site characteristics, specifically, accumulation rate and snow redistribution. In the recent study from EDC by *Gauthier et al.*, [2016], the number and apparent size of eruptions varied considerably within the very small study area of approximately 10 m. For example, the eruption of Tambora was only seen in 3 out of the five cores, while UE1809 was seen in all. A study of five snow pits and shallow firn cores in Dronning Maud Land [*Karlöf et al.*, 2005] looked that the variation in accumulation rates over a moderately spaced area and compared these changes across several volcanic eruption time periods. The authors did not find a significant difference in the accumulation rates among the snow pits, but did conclude the variation in the chemistry record was the result of snow redistribution and other post depositional effects. Using one ice core from the South Pole, variation in the number of eruptions was shown to be the result of the choice of background detection method [*Ferris et al.*, 2011]. The number of events detected along the core was reduced from 76 using an identification approach from *Cole-Dai et al.*, [1997] to 74 by simply smoothing the record. The number was further reduced to 62 by using the approach from *Castellano et al.*, [2005], then reduced again to 60 by using a new weighted average approach. In the South Pole study, all of the excluded eruptions were considered small by the standards set by *Ferris et al.*, [2011]. This was not the case in the EDC, where Tambora, often the largest peak in the 19th century, was lost from several cores.

Site location and accumulation rate do have some influence over which volcanoes are seen in an ice core. Additional factors, including how volcanic peaks are identified must be considered in any volcanic comparison study. At ABN, only eight eruptions were within the established criteria. If the minimum concentrations were reduced, four

additional eruptions would be added, all of which are small events found in other ice cores. As each record compared with ABN used a different mathematical approach, the variation found among the cores could be the result of the different detection methods in conjunction with the site accumulation rates. Furthermore, as Antarctica is a very large continent, it is unlikely that volcanic deposition would be similar continent wide. Sites nearest to each other are likely to have similar volcanic presence, subject to post depositional redistribution. It is understandable that in this study, ABN shares more of the same eruptions with DSS. Therefore, to establish a universal Antarctic volcanic record, multiple ice cores from different regions must be compared.

3.5 Intersite Sea Salt Comparison

The study of one ice core in isolation is not sufficient to establish a reliable local or regional understanding of trace ion chemistry in ice cores. To determine a reliable record, multiple ice cores across different regions are required. Sampling along traverses has revealed that trace ionic chemistry varies greatly by Antarctic region and that there is often a large difference between the chemistries of coastal and inland sites [*Benassai et al.*, 2005; *Bertler et al.*, 2005; *Proposito et al.*, 2002]. *Bertler et al.*, [2005] compiled the data of 520 sites and showed that sites under 2000m are heavily influenced by sea salts and have little to no post depositional changes. Multiple traverses across East Antarctica have found similar patterns relating elevation, distance inland, and trace ionic chemistry [*Benassai et al.*, 2005; *Bertler et al.*, 2005; *Proposito et al.*, 2002]. To date, there have been no established transects connecting sites on Law Dome to EDC. There are however, multiple ice cores from different elevations and distances inland across Wilkes and Kaiser Wilhelm II Lands that could be used in place of a transect. *Wong* [2007] and *Inoue* [2015] showed that sea salt concentrations in the near coastal regions follow that of traverses across Terre Adélie and Dronning Maud Land, a rapid decrease in Na^+ concentrations and a slow but steady decrease in SO_4^{2-} concentrations. The addition of ABN extends the transect further inland into the SO_4^{2-} transition zones established by *Proposito et al.*, [2002] and *Benassai et al.*, [2005], increasing the understanding of the variations between Law Dome to EDC. The trace ionic chemistry for ABN and five additional sites from Wilkes and Kaiser Wilhelm II Lands is shown in Table 3.

Table 3. Comparisons of mean ionic concentrations. *Mean values from combined Mount Brown South and U5 cores. All concentrations are in [**µEq/L**]

Core	Altitude	Distance Inland	Na$^+$	Cl$^-$	SO$_4^{2-}$	NssSO$_4^{2-}$	MSA	Reference
ABN 71°9′S, 111°22′E	2690m	500 km	0.47	0.717	0.89	0.84	0.059	This study
Mount Brown* 69°5′S, 85°54′E	2078m	250 km	1.07	1.53	0.66	0.53	0.04	*Foster* 2003
GD17 67°50′S, 127°57′E	1485m	200 km	1.09	1.23	0.50	0.37	0.06	*Wong* 2007
DSS, Law Dome 66°46′S, 112°48′E	1370m	120 km	3.62	4.25	0.78	0.35	0.08	*Wong* 2007
Mill Island 65°33′S, 100°47′E	500m	Offshore	254.13	289.73	20.39	-10.16	0.21	*Inoue* 2015

In a traverse across the EDC drainage area, *Proposito et al.*, [2002] showed primary aerosols decline quickly away from the coast, then slowly decreasing before reaching stable values near 270 km. By using the sites in Table 3, concentrations of primary aerosols follow the same pattern. They are extremely high along the coast, decreasing dramatically within the first 100 km, then decreasing much more slowly, reaching stable values between 200-250 km inland at Mount Brown.

The greatest MSA concentration in Table 3 is seen at Mill Island, reflecting its offshore location and its year-long proximity to the highly productive sea ice edge. Once onto Antarctica, the concentrations generally decrease with increasing distance inland and increasing elevation. The rate of decrease appears to be greatest within the first 120 km followed by a very slow decrease to 250 km before increasing in concentration at ABN. The large decrease in concentrations along the coast is similar to the decreasing rates of the primary aerosols and may likely be due to MSA condensing onto these larger particles [*Hoppel*, 1987; *Kerminen et al.*, 2000; *Legrand and Pasteur*, 1998] and settling out of the atmosphere sooner. The slow and steady decrease towards Mount Brown followed by an increase at ABN is likely due to a shared transport mechanism with biological sulfate as both SO$_4^{2-}$ and MSA could be in the smallest particle sized fractions at this distance [*Pszenny et al.*, 1992].

The mean SO_4^{2-} values seem to decrease from the coast before increasing between GD17 and Mount Brown. A similar increase was noted in the traverse studies of *Proposito et al.*, [2002] and *Benassai et al.*, [2005], both finding a rapid decrease in concentrations to approximately 40 km inland, then a very slow decrease until 250 km from the coast. Past there, concentrations increased to reach stable values between 550 km – 750 km from the coast. The SO_4^{2-} concentrations within Wilkes and Kaiser Wilhelm II Lands follow the same general pattern, however, increasing earlier than in other studies, between 200-250 km inland. *Proposito et al.*, [2002] and *Benassai et al.*, [2005] concluded that primary aerosols (sea salts) dominated the ionic chemistry within the initial 250 km followed by an increasing importance of DMS oxidation and shifts towards smaller, more efficiently transported particles. Additionally, ABN and Mount Brown may also be influenced by long range transport of SO_4^{2-} from mid latitudes or increased stratospheric input given their position under the continental high pressure zone [*Foster*, 2003].

3.6 Intersite Sulfate Comparison

Negative $nssSO_4^{2-}$ values are mostly seen at coastal sites in winter and have been attributed to frost flowers and snow from the sea ice zone. Frost flowers are delicate dendritic or faceted ice crystals that grow on the surface of new ice, from a supersaturation of water vapor in the air nearest to the ice surface [*Obbard et al.*, 2009]. Although field and laboratory studies have shown low levels of SO_4^{2-} within the crystals, [*Alvarez-Aviles et al.*, 2008; *Domine et al.*, 2005; *Hara et al.*, 2012; *Obbard et al.*, 2009; *Roscoe et al.*, 2011], the release and transport of aerosols from these crystals has yet to be confirmed [*Roscoe et al.*, 2011]. Destruction during strong winds has been considered the most likely, as broken flowers have been observed following blizzards in the Arctic [*Obbard et al.*, 2009]. Laboratory studies confirmed destruction in sustained winds and gusts up to 12 m/s, but aerosols were not able to be produced [*Roscoe et al.*, 2011]. *Obbard et al.*, [2009] found that slower wind speeds were capable of moving snow and burying flowers, making blowing snow and not frost flowers a more likely source for SO_4^{2-} depleted aerosols seen in ice cores.

Sulfate depletion at inland sites is difficult to determine as these sites are heavily influenced by SO_4^{2-} and generally lack sea salts through differential settling during transport. Negative $nssSO_4^{2-}$ values were not seen at ABN by using the usual calculations, therefore other methods to test for frost flower influences were used. Ternary plots were created for each location in Table 3 and EDC (Figure 8) following the methods in *Rankin et al.*, [2002] and *Weller and Wagenbach* [2007]. The lengthy DSS record has been restricted to the ABN time period, approximately 130 meters of the entire DSS core. If restricted to the ABN time period, data availability and the low sampling resolution of the EDC core would have only provided a few dozen samples, therefore the record used in this study has been extended to 50 meters. The GD17 and Mount Brown records were considerably shorter than the ABN study period, therefore each record was considered in its entirety. Two very short firn cores (Mount Brown South and U5) from the Mount Brown area were combined to provide a better representation of the area. A total of eight shallow cores were drilled on Mill Island, however, due to data restrictions, only part the main core and a shallow snow pit were used in this study, a combined total depth of 20 meters or approximately 10 years. Due to data limitations, seasonal plots were only created for DSS, ABN, and GD17.
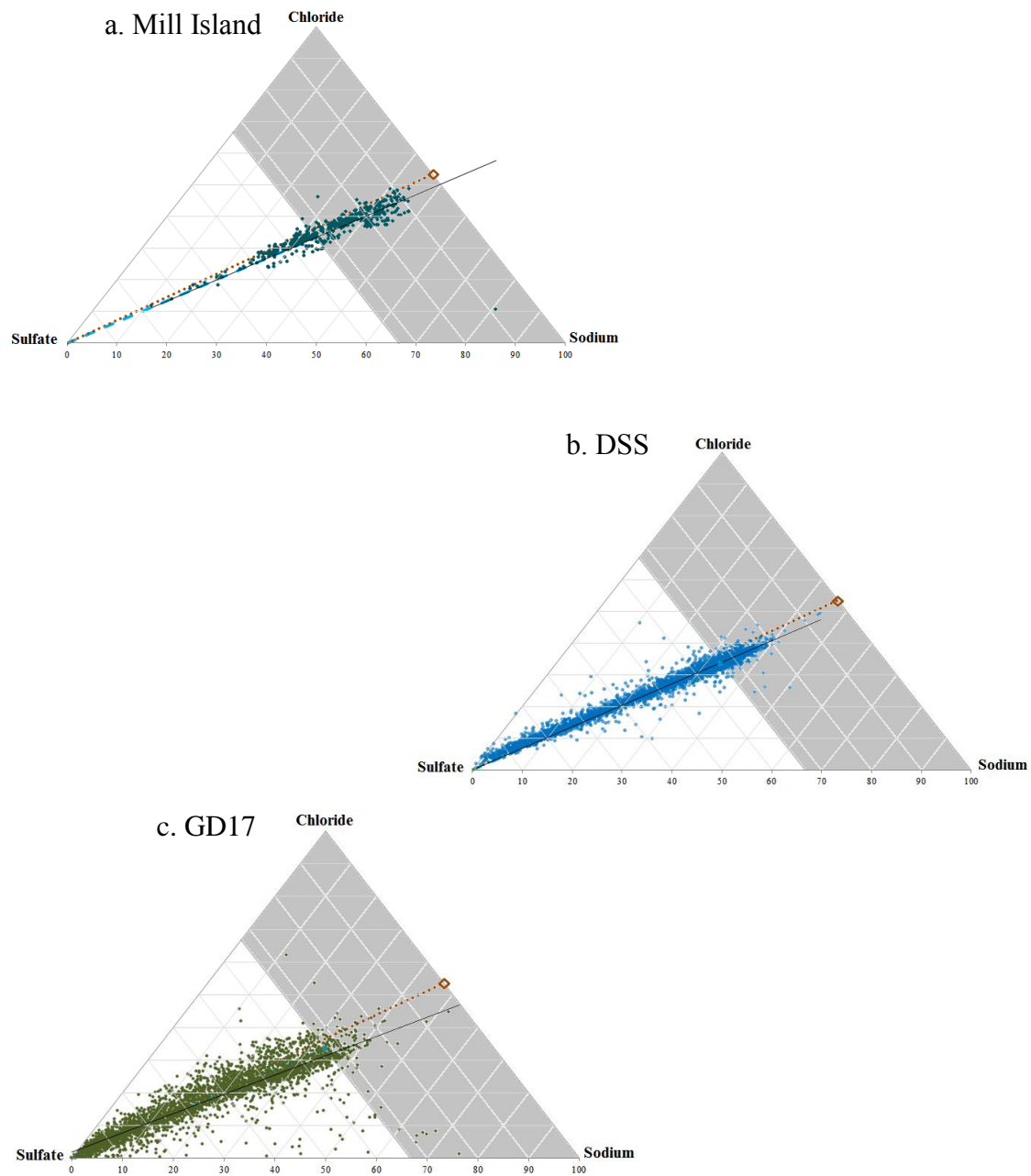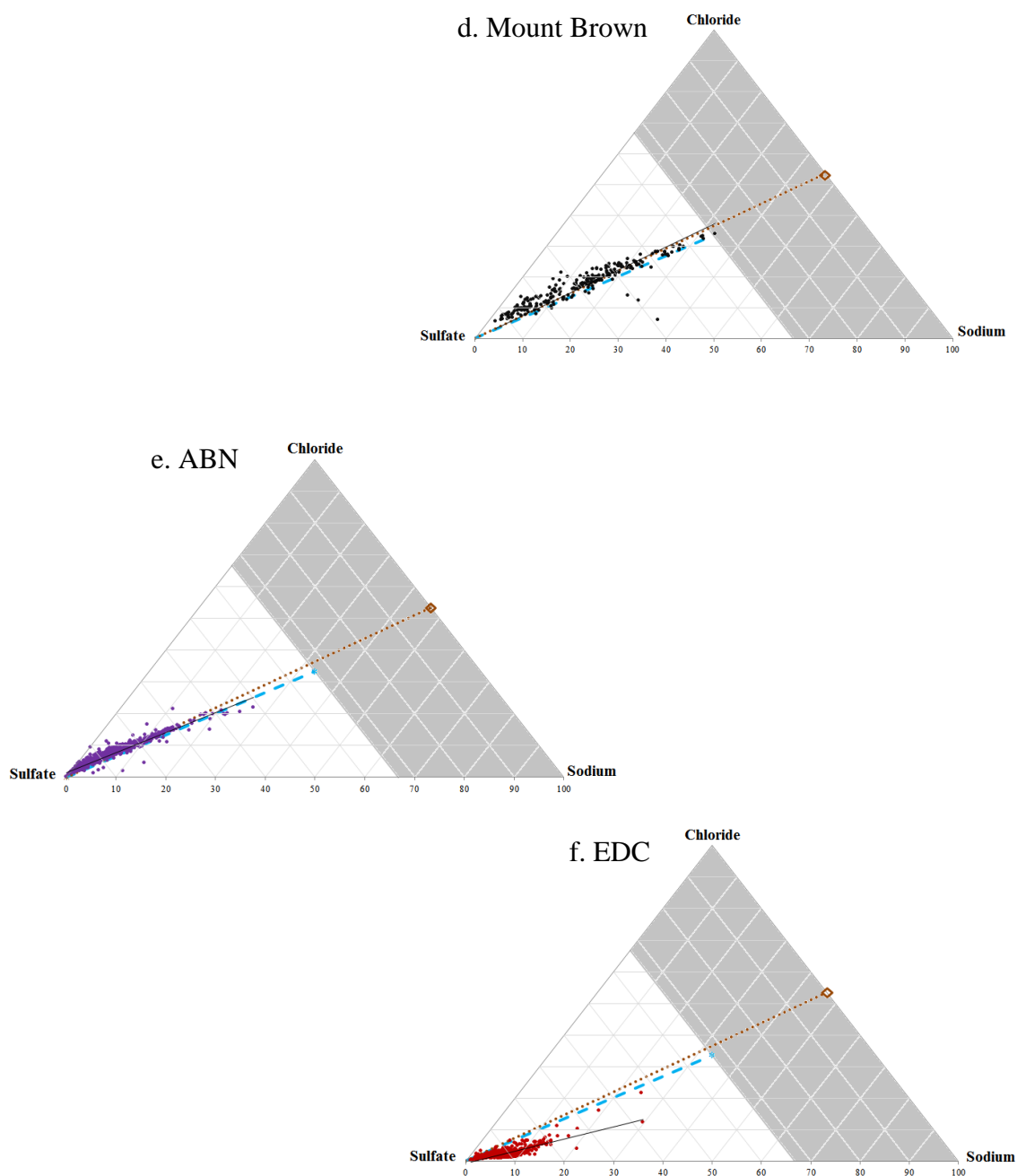
Figure 8. Ternary plots of SO_4^{2-}, Na^+, and Cl^- for ice cores listed in table 3 and EDC, normalized to ensure a sample with a similar sea salt ratio to seawater is near the center of the triangle (asterisk). The open diamond shows where a sample would be if completely depleted in SO_4^{2-} and only partially in sodium. Lines connecting asterisk and diamond to SO_4^{2-} corner indicate either sea water sourced or fractionated sourced aerosol with additional biogenic SO_4^{2-}. Each corner represents 100% of each ion respectively.

Figure 8 continued. Ternary plots of SO_4^{2-}, Na^+, and Cl^- for ice cores listed in table 3 and EDC, normalized to ensure a sample with a similar sea salt ratio to seawater is near the center of the triangle (asterisk). The open diamond shows where a sample would be if completely depleted in SO_4^{2-} and only partially in sodium. Lines connecting asterisk and diamond to SO_4^{2-} corner indicate either sea water sourced or fractionated sourced aerosol with additional biogenic SO_4^{2-}. Each corner represents 100% of each ion respectively.

Most often used in studying minerology, a ternary, or triangle, plot is used to understand the relationships between three variables. When comparing sea salts in ice samples, the three most compared ions are SO_4^{2-}, Na^+, and Cl^-. All samples in Figure 8 have been normalized using the equations from *Rankin et al.*, [2002] or *Weller and Wagenbach* [2007], according to the original concentration units in the data set. Normalization will place any samples with similar ratios to that of bulk seawater in the exact center of the triangle (marked by an asterisk). Samples that fall along the line connecting the sea water ratio to the SO_4^{2-} corner indicate sea water sourced samples that have additional SO_4^{2-} sources other than sea water.

Fractionation within frost flowers occurs over a variety of temperatures and results in various proportions of each ion lost. For example, loss of SO_4^{2-} due to mirabilite ($Na_2SO_4 \cdot 10H_2O$) precipitation occurs gradually from -8°C to -22°C [*Alvarez-Aviles et al.*, 2008; *Obbard et al.*, 2009; *Rankin et al.*, 2002]. Relative to the loss of SO_4^{2-}, Na^+ concentrations tend to decrease at a much slower rate and Cl^- remains unchanged [*Alvarez-Aviles et al.*, 2008; *Obbard et al.*, 2009]. Samples that have had all SO_4^{2-} lost to mirabilite will have a ratio approximately 46.6% Na^+ and 53.4% Cl^- [*Rankin et al.*, 2002] and will appear near the open diamond in the graph. Points along a line connecting the diamond to the SO_4^{2-} corner are consistent with fractionated aerosol containing additional inputs of sulfate. Below -22°C, fractionation continues to occur with the loss of chloride and the continued loss of sodium. The ternary plots used in this study do not easily represent this loss. It is therefore assumed that any sample falling towards the right side of the triangle will be considered fractionated to some degree. This has been represented by the shaded area following the parallel SO_4^{2-} line crossing the perfect sea water ratio point.

Mill Island is the most unusual of the triangle plots (Figure 8a) revealing significant SO_4^{2-} depletion as most samples are within the shaded area. While similar to the other plots in that it follows the sea water line, there seems to be a slight shift towards increased Cl^- concentrations. These findings confirm those found by *Inoue* [2015], concluding the sea salts at Mill Island are highly fractionated. *Inoue* [2015] found the concentrations of all sea salts were often over 1000 times higher than those found on the

continent and attributed these findings to the island's proximity to the ice shelf. Upon further examination with wind speed and direction, it was determined that that the dominant source of sea salts was frost flowers forming on new sea ice along the eastern boundary of the sea ice zone between Mill and Barrier Islands. In the triangle plot shown here, most samples fall between the sea water and frost flower fractionation lines. However, samples influenced by added sulfate, trend along the sea water line. This suggests that the samples are indeed from both frost flower and a sea water sources, agreeing in part with the conclusions of *Inoue* [2015]. The extremely high sea salt values seen at Mill Island necessitated the use of a very unusual fractionation correction when determining the nss SO_4^{2-} concentrations. However, once corrected, three eruptions, Pinatubo, El Chichón, and Mt. Agung were identified from the entire record [*Inoue*, 2015]. Similar to ABN, there were several periods of elevated $nssSO_4^{2-}$ that could have easily been mistaken for a volcanic period. Given the high concentrations of sea salts, the influence of $ssSO_4^{2-}$ over the volcanic SO_4^{2-} is quite large, and thus this site would not be a good site for volcanic identification.

Law Dome extends away from the coast and despite being elevated to over 1370 meters [*Curran et al.*, 1998], it is still heavily influenced by winter storms [*McMorrow et al.*, 2002]. The ternary plot for DSS (Figure 8b) reflects the strong influence of sea salts by having the greatest density of samples clustered around the perfect sea water ratio. The remaining samples trend continuously along the sea water line towards the SO_4^{2-} corner indicating that these samples are likely sourced from sea water as well as additional biological and volcanic sulfate.

Seasonal differences in sea salts are most clearly seen with the DSS seasonal ternary plot (Figure 9a). As expected summer (December-February) values are more heavily concentrated near the SO_4^{2-} corner, indicating the strong presence of added biological sulfate. Several points do fall near the sea water ratio and also into the fractionated area. It is possible that these points may have been incorrectly dated by a few weeks or represent sea salts from sea ice that was not yet melted. Winter (April –July) samples are heavily concentrated near the sea water center point reflecting the dominance of coastal winter storms, however, not all points appear in the fractionated zone. Only

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approximately 42% of all winter points appear in the shaded area and most are near the dividing line. This indicates that universally applying a fractionation correction to all samples or seasonally is incorrect. Doing so will remove the incorrect fraction of $ssSO_4^{2-}$ from the measured SO_4^{2-} values. Instead the correction should be applied to only those samples that show true SO_4^{2-} depletion, those samples in the shaded area of the tern plot.
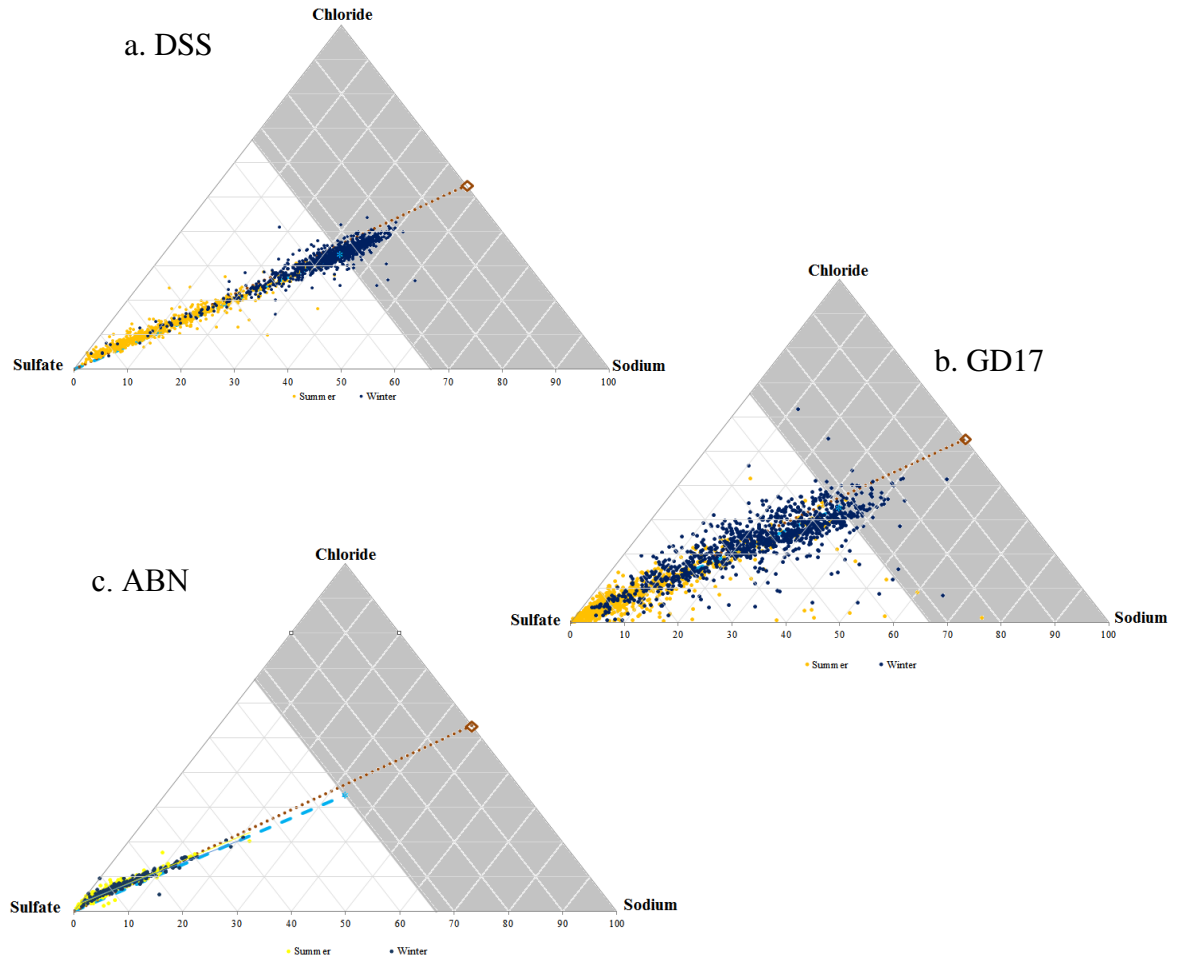

Figure 9. Ternary plots separating normalized samples into summer (yellow) and winter (blue) for Dome Summit South (a), GD17 (b), and Aurora Basin North (c). See text for seasonal separation criteria. Sea water and sulfate depletion represented as in Figure 8.

Unlike the other plots in this study, the samples in GD17 do not trend along either the sea water or fractionation lines. Instead, a linear trend line through the samples crosses both lines near the SO_4^{2-} corner before falling below the sea water line. This could be the result of a decrease in Na^+ and Cl^- influences, yet an indication the site is not completely free from coastal storms. It may also reflect the size separation of sea salt ions noted during traverse studies across other areas of East Antarctica or an additional stratospheric transport pathway. The heavy SO_4^{2-} concentration is similar to DSS and reflects the strong influence on summer biological sulfate. Despite the added biological sulfate, the site is still shows some degree of sulfate depletion. When all samples are considered, approximately 26% have possible fractionated aerosols. Of those, only approximately 6.4% may have frost flower origins. These values are strikingly similar to those determined by *Wong* [2007], with 22.8% of total samples being fractionated and only 4.9% having frost flower influences. The differences are likely the result of the different fractionation criteria, the large degree of spreading in the ternary plot, and different analytical techniques used

Mount Brown is located slightly further inland, at approximately 250 km from the nearest coast, but is at a much higher elevation [*Foster*, 2003]. The ternary plot (Figure 8d) reflects these changes when compared to both GD17 and DSS. Nearly all of the samples appear closer to the SO_4^{2-} corner and only one sample is immediately recognized at fractionated. This sample is from the U5 core and not Mount Brown South, confirming the findings of *Wong* [2007] and *Inoue* [2015] that show Mount Brown South is a non-fractionated site. Unlike GD17 and DSS, the samples trend above the fractionation line, indicating that they may have a fractionated source and / or are more heavily influenced by chloride. By trending this line, the ternary plot adds new information regarding the site. *Wong* [2007] and *Inoue* [2015] were able to show one site did not contain any fractionated samples. However, the plot indicates that the region may have some fractionated aerosols. Unfortunately, only seasonal information will be able to conclusively determine the reason for the trend. Seasonality was not determined at this site due to the plot being a combination of two very short (combined length of 16 meters) firn cores.

ABN is an even larger step inland and this is clearly noted in the ternary plot. The majority of points are clumped near the SO_4^{2-} corner and like Mount Brown trend the fractionation line, and reveal enriched Cl^- levels. Unlike the other sites, the density of points is pushed further towards the SO_4^{2-} corner and has a very abrupt end, at 70% SO_4^{2-}. There are no samples in the shaded sulfate depleted region and therefore no evidence for fractionated aerosols at the site. This does not immediately discount the possibility of fractionated sea salts reaching this location. A SO_4^{2-} depleted sea salt sample may have been deposited, but would have been overwhelmed with SO_4^{2-} from additional sources. This confirms the initial $nssSO_4^{2-}$ calculations and the small differences between the total and $nssSO_4^{2-}$ components. All seasons from ABN remain very close to the SO_4^{2-} corner (Figure 9c). Summer samples appear to be slightly shifted towards higher percentages of chloride and winter samples appear to be more spread along the fractionation line.

Sampling along multiple inland traverses have shown that sea salts are much heavier and settle out quickly as they are transported inland [*Bertler et al.*, 2005; *Mulvaney* et al 1993; *Proposito et al.*, 2002]. They are larger and therefore more prone to scavenging by wet deposition. Sulfate has been shown to travel greater distances inland due to its small size [*de Mora et al.*, 1997; *Udisti et al.*, 2012] and may likely be one reason ABN appears dominated by sulfate. It has been proposed that additional SO_4^{2-} may be due to settling of oxidized SO_2 from the stratosphere that only occurs at high elevation sites on the East Antarctic plateau [*Delmas*, 1992; *Preunkert et al.*, 2008]. The dating at ABN does not discount a delayed arrival of biological influences, as several years have SO_4^{2-} peaks appearing after the peak in oxygen isotopes. As the ternary plot does not distinguish between sources, it is impossible to determine the exact reason for the apparent increase in SO_4^{2-} nor the increase in chloride. The ABN plot does emphasize the trend of increasing SO_4^{2-} influence with increasing distance from the coastline.

The sampling resolution is very low at EDC, often limited to one sample or less per year. If limited to only the time period shared with ABN, this low sample resolution would not provide enough details to draw any reliable conclusions. To account for this, the number of samples was increased to cover 50 m. It is the only plot in the group that does not trend along either the sea water line or the fractionation line. Instead the graph

appears to fall below the sea water line and lies more spread along the bottom of the triangle near the SO_4^{2-} corner. Post depositional loss of Cl^- usually occurs at sites with less than 40 kg/m^2/yr [*Mahalinganathan et al.*, 2012]. DMC is the only site within this study that falls below this threshold with a mean accumulation rate of 25 kg/m^2/yr [*Gauthier et al.*, 2016], therefore it should be the only one showing a serious depletion in chloride. By following the trend of less fractionation with increased distance inland, there should be no fractionation at this site. Only by extending the sampling period to beyond 100 meters do three samples appear to have some moderate fractionation (not shown). If these samples are truly fractionated, DMC can still be considered free of fractionation as these three samples represent 0.25% of all samples considered at 100 meters.

To determine if volcanic SO_4^{2-} has any influence on the placement of samples in the ternary plot, four of the largest volcanic eruptions were chosen from the shared DSS and ABN records, Pinatubo, Mt. Agung, Tambora, and UE1809. Krakatau was excluded as it a merged peak in ABN. Each volcano in DSS was separated into their respective season according to the dating used in the seasonal plot above (Figure 10a). The volcanoes do not appear to have any influence on the placement of samples in the graph having the same density groupings as the entire record. Spring and autumn samples are spread evenly across the entire length of the sea water line and show little preference for side. Across these four eruptions, indications of fractionated samples are not present. It would appear that the additional volcanic SO_4^{2-} is sufficient to hide any SO_4^{2-} depletion that otherwise would normally occur. These four volcanoes, including the two largest in the study period, represent 32 samples. There are nine volcanoes in the sampling period. Due to layer thinning, the number of samples per volcano will decrease deeper into the record. Given that the entire sampling period contains over 3000 samples, including volcanoes, it is unlikely that the absence of the volcanoes will have any impact on the density groupings. Using this information, it is unlikely that volcanoes will have much role in the placement of samples on the GD17 or EDC ternary plots. Volcanic eruptions would therefore have limited, if any, influence on the seasonal cycle at GD17, where no reliable volcanic record exists or at EDC where volcanoes are often represented by only one or two samples.

The same four volcanoes were plotted for ABN (Figure 10b), totaling 47 samples out of the approximate 790 total samples. Instead of showing clear duality similar to DSS, all but three samples are less than 80% SO_4^{2-} and only one appears less than 85% SO_4^{2-}. As with DSS, it is not likely that volcanoes have an impact on the density of the overall plot. These four events make up approximately 6% of the total number of samples. Removing the volcanic eruptions does not visually change the overall plot indicating that volcanic sulfate is only a minor contributor to the total SO_4^{2-} seen at the site. If ABN is less affected by biological SO_4^{2-} due to its inland location most SO_4^{2-} must then be sourced from long range transport and stratospheric sources, leading to the identification of more small and moderate eruptions. At this time, only eight volcanoes have been properly identified and dated within the study period. Preliminary analysis shows that of the 25 largest volcanic eruptions for the past 2500 years [*Sigl et al.,* 2015], the entire ABN main core may possess 14. Only accurately dating the remainder of the core and accurately assessing the biological SO_4^{2-} will the location's total volcanic influence be known.
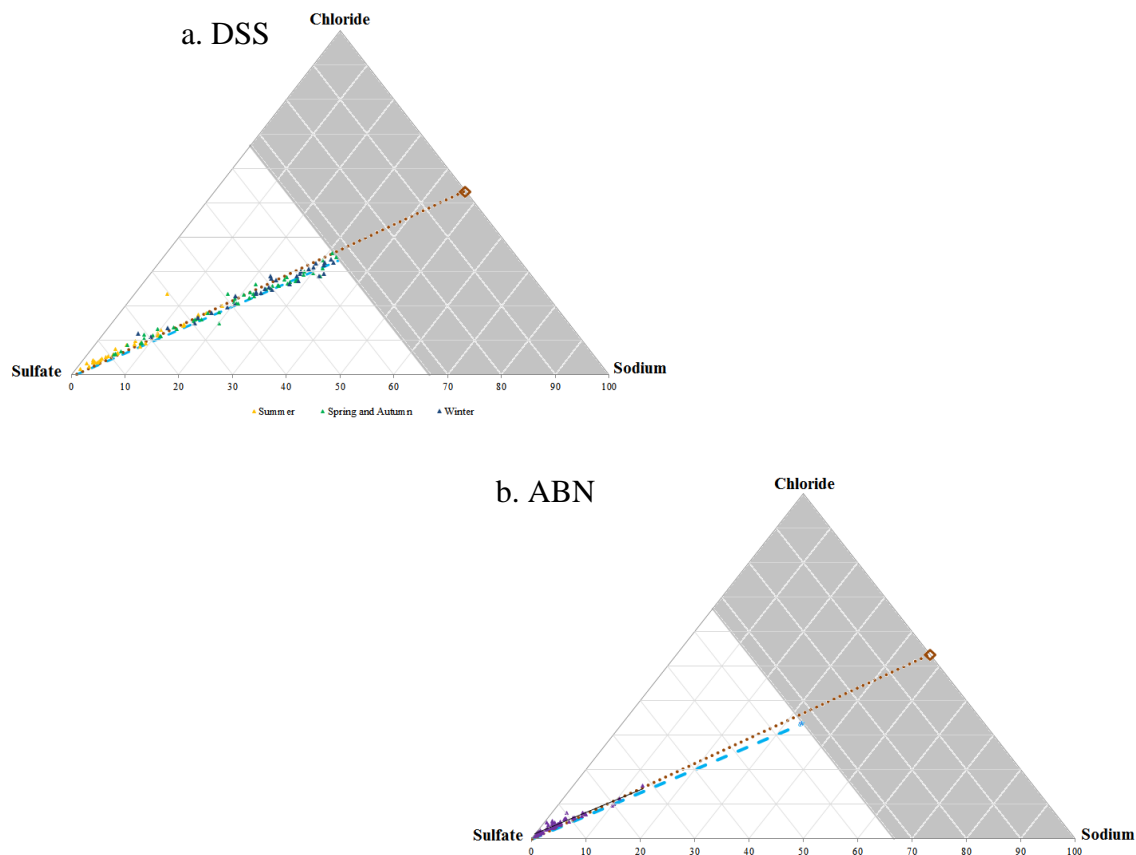
Figure 10. Ternary plots showing the placement of normalized samples from eruptions of Pinatubo, Mt. Agung, Tambora, and UE1809. Dome Summit South (DSS) samples are separated into seasons, summer (yellow), winter (blue), spring and autumn (green). See text for separation of seasons. The plot for Aurora Basin North (ABN) is for the same four volcanic eruptions, not separated by seasons due to the tight grouping. Sea water and sulfate depletion represented as in Figure 8.

It would seem that the location of an ice core site would play a very important role in the determination of which volcanic peaks could be identified in the records. Higher accumulation sites, such as DSS, are located mainly near the coast, where snow accumulation is due to wet deposition from coastal storms, warmer temperatures, and lower elevations. These sites are subjected to large seasonal cycles of SO_4^{2-} concentrations from both sea salt and biological influences, prohibiting easy identification of small and some moderate eruptions. Large eruptions often deposit enough SO_4^{2-} to overcome the seasonal changes, but are still subject to some interference. Sites located further inland have less sea salt and biological SO_4^{2-} inputs and therefore the

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added SO_4^{2-} from volcanoes easily stands out from the seasonal changes. However, low accumulation can lead to difficulty in establishing accurate dating and separation of the volcanic influence from the background. Finding the best volcanic record requires a balance between the two extremes. Aurora Basin North is located well away from the coast and has sufficient accumulation to facilitate accurate dating, giving the site a low and fairly stable seasonal sulfate cycle. This make large and moderate eruptions easily stand out, but still prohibits easy separation of small eruptions from the background.

By using the ternary plots, ABN can be considered a suitable site for volcanic studies over DSS because nearly all of the ABN sample points are near the SO_4^{2-} corner. The spread, seasonality, and concentration of samples indicate that DSS has a very strong dependence on winter storms and therefore will see a well-defined seasonal cycle, however volcanoes will be mixed within this seasonal signal. By using the plots, the best site for volcanic studies would be one where the samples are uniformly spread across the sea water line and shifted slightly towards the SO_4^{2-} corner. From those used in this study, the Mount Brown area would be an ideal site as it is only moderately influenced by sea salts, sees little fractionation, and contains additional, but is not overly dominated by sulfate.

4. Conclusions

The accumulation rate at ABN adequately preserves the seasonal signals allowing for some sub annual dating, however, the inland location does not minimize the biological SO_4^{2-} signal well enough to fully separate $nssSO_4^{2-}$ from $ssSO_4^{2-}$. Use of the SO_4^{2-}/MSA ratio was considered a possible method for removing some of the biological $nssSO_4^{2-}$ signals, but proved unreliable due to the degree and unpredictable nature of MSA migration surrounding the volcanic peaks.

A number of large and moderate eruptions were separated from the general background SO_4^{2-} record using a new identification technique. The technique improved upon other methods in that the requirements changed with time. This allowed for easy identification of two small periods in 1942CE and 1825CE that would have been

otherwise overlooked. Several small eruptions were often able to be distinguished by an elevated signal, but not so high as to be above the minimum SO_4^{2-} concentration. Further division of the volcanic criteria will improve the accuracy of peak identification and likely result in additional eruptions.

The ternary plot is a useful visualization to quickly determine the fractionation of a site, its general location in East Antarctica, and the clarity of its volcanic record. It easily shows that coastal and near coastal sites have some sea salt fractionation while inland sites do not. The plot also confirms the findings of previous traverse studies indicating sea salts do not travel far inland, reaching stable values between 200-250 km inland. Past this point, sulfate clearly dominates, as seen at plateau sites such as ABN, Mount Brown, and EDC. The ternary plot also reflects the post-depositional loss of Cl^- at very low accumulation sites, with samples falling near the bottom of the plot while Na^+ levels show little to no change. Most importantly, the plot reveals that applying one correction for $nssSO_4^{2-}$ across all samples is incorrect. If the correction is too large, it will likely cause some samples to be incorrectly presumed fractionated. Unexpectedly, the plot shows that it isn't always winter samples that become fractionated. Depending on the site, summer may appear fractionated as the plot cannot readily distinguish between sources of the ions. While it is unable to distinguish volcanic SO_4^{2-} from biological or $ssSO_4^{2-}$, the plots are able to show the influence of volcanic eruptions on the overall site characteristics.

Analysis of the ABN ice core is still ongoing, and with its completion, the identification of additional large eruptions will extend the volcanic record. The additional eruptions will allow for better comparisons with other ice cores and improve the understanding of the differences between coastal and plateau ice core records. The extended record will provide more details into the movement of MSA and provide additional details into the relationship between MSA and biological sulfate and improve the understanding of movement over extended time period. As ABN is located under the continental high pressure zone, a complete understanding of the tropospheric and stratospheric inputs to the deposition at Aurora Basin North are needed before the entire volcanic record can be uncovered and volcanic deposition can be calculated.

References

Abram, Nerilie J., Eric W. Wolff, and Mark AJ Curran. "A review of sea ice proxy information from polar ice cores." *Quaternary Science Reviews* 79 (2013): 168-183.

Alvarez-Aviles, Laura, William R. Simpson, Thomas A. Douglas, Matthew Sturm, Donald Perovich, and Florent Domine. "Frost flower chemical composition during growth and its implications for aerosol production and bromine activation." *Journal of Geophysical Research: Atmospheres* 113, no. D21 (2008).

Becagli, Silvia, Marco Proposito, Silvia Benassai, Roberto Gragnani, Olivier Magand, Rita Traversi, and Roberto Udisti. "Spatial distribution of biogenic sulphur compounds (MSA, nssSO$_4^{2-}$) in the northern Victoria Land–Dome C–Wilkes Land area, East Antarctica." *Annals of Glaciology* 41, no. 1 (2005): 23-31.

Benassai, Silvia, Silvia Becagli, Roberto Gragnani, Olivier Magand, Marco Proposito, Ilaria Fattori, Rita Traversi, and Roberto Udisti. "Sea-spray deposition in Antarctic coastal and plateau areas from ITASE traverses." *Annals of Glaciology* 41, no. 1 (2005): 32-40.

Bertler, Nancy, Paul Andrew Mayewski, Alberto Aristarain, P. Barrett, S. Becagli, R. Bernardo, S. Bo *et al.* "Snow chemistry across Antarctica." *Annals of Glaciology* 41, no. 1 (2005): 167-179.

Castellano, E., Silvia Becagli, M. Hansson, M. Hutterli, J. R. Petit, M. R. Rampino, M. Severi, Jørgen Peder Steffensen, Rita Traversi, and Roberto Udisti. "Holocene volcanic history as recorded in the sulfate stratigraphy of the European Project for Ice Coring in Antarctica Dome C (EDC96) ice core." *Journal of Geophysical Research: Atmospheres* 110, no. D6 (2005).

Cole-Dai, Jihong, Ellen Mosley-Thompson, and Lonnie G. Thomn. "Annually resolved southern hemisphere volcanic history." *Journal of Geophysical Research* 102, no. D14 (1997): 16-761.

Cole-Dai, Jihong, and Ellen Mosley-Thompson. "The Pinatubo eruption in South Pole snow and its potential value to ice-core paleovolcanic records." *Annals of Glaciology* 29, no. 1 (1999): 99-105.

Cole-Dai, Jihong, Ellen Mosley-Thompson, Shawn P. Wight, and Lonnie G. Thompson. "A 4100-year record of explosive volcanism from an East Antarctica ice core." *Journal of Geophysical Research: Atmospheres* 105, no. D19 (2000): 24431-24441.

Cole-Dai, Jihong. "Volcanoes and climate." *Wiley Interdisciplinary Reviews: Climate Change* 1, no. 6 (2010): 824-839.

Curran, Mark AJ, Tas D. Van Ommen, and Vin Morgan. "Seasonal characteristics of the major ions in the high-accumulation Dome Summit South ice core, Law Dome, Antarctica." *Annals of Glaciology* 27, no. 1 (1998): 385-390.

Curran, Mark AJ, and Graham B. Jones. "Dimethyl sulfide in the Southern Ocean: Seasonality and flux." *Journal of Geophysical Research: Atmospheres (1984–2012)* 105, no. D16 (2000): 20451-20459.

Curran, Mark AJ, and Anne S. Palmer. "Suppressed ion chromatography methods for the routine determination of ultra low level anions and cations in ice cores." *Journal of Chromatography* A 919, no. 1 (2001): 107-113.

Curran, Mark AJ, Anne S. Palmer, Tas D. Van Ommen, Vin I. Morgan, Katrina L. Phillips, Alison J. McMorrow, and Paul A. Mayewski. "Post-depositional movement of methanesulphonic acid at Law Dome, Antarctica, and the influence of accumulation rate." *Annals of Glaciology* 35, no. 1 (2002): 333-339.

Delmas, Robert J. "Free tropospheric reservoir of natural sulfate." *Journal of atmospheric chemistry* 14.1-4 (1992): 261-271.

de Mora, S. J., D. J. Wylie, and A. L. Dick. "Methanesulphonate and non-sea salt sulphate in aerosol, snow, and ice on the East Antarctic plateau." *Antarctic Science* 9.01 (1997): 46-55.

Domine, Florent, Anne Sophie Taillandier, William R. Simpson, and Ken Severin. "Specific surface area, density and microstructure of frost flowers." *Geophysical research letters* 32, no. 13 (2005).

Ferris, Dave G., Jihong Cole-Dai, Angelica R. Reyes, and Drew M. Budner. "South Pole ice core record of explosive volcanic eruptions in the first and second millennia AD and evidence of a large eruption in the tropics around 535 AD." *Journal of Geophysical Research: Atmospheres* 116, no. D17 (2011).

Foster, Annette F. M. "Wilhelm II Land as a Future Ice Core Paleoclimate Research Site." Honors Thesis, University of Tasmania, 2003.

Gautier, E., J. Savarino, J. Erbland, A. Lanciki, and P. Possenti. "Variability of sulfate signal in ice core records based on five replicate cores." *Climate of the Past* 12, no. 1 (2016): 103-113.

Global Volcanism Program, 2013. Volcanoes of the World, v. 4.4.3. Venzke, E (ed.). Smithsonian Institution. http://dx.doi.org/10.5479/si.GVP.VOTW4-2013 (http://volcano.si.edu/gvp_about.cfm)

Hammer, C. U. "Past volcanism revealed by Greenland ice sheet impurities." *Nature* 270 (1977): 482-486.

Hara, Keiichiro, Kazuo Osada, Mizuka Kido, Masahiko Hayashi, Katsuji Matsunaga, Yasunobu Iwasaka, Takashi Yamanouchi, Gen Hashida, and Toru Fukatsu. "Chemistry of sea-salt particles and inorganic halogen species in Antarctic regions: Compositional

differences between coastal and inland stations." *Journal of Geophysical Research: Atmospheres* 109, no. D20 (2004).

Hara, Keiichiro, Kazuo Osada, Mizuka Kido, M. Yabuki, and Takashi Yamanouchi. "Seasonal variation of fractionated sea-salt particles on the Antarctic coast." *Geophysical Research Letters* 39, no. 18 (2012).

Hoppel, W. A. "Nucleation in the MSA-water vapor system." *Atmospheric Environment (1967)* 21, no. 12 (1987): 2703-2709.

Inoue, Mana. "A Glaciochemical Study of the Mill Island Ice Core." PhD diss., University of Tasmania, 2015.

Jiang, Su, Jihong Cole-Dai, Yuansheng Li, Dave G. Ferris, Hongmei Ma, Chunlei An, Guitao Shi, and Bo Sun. "A detailed 2840 year record of explosive volcanism in a shallow ice core from Dome A, East Antarctica."*Journal of Glaciology* 58, no. 207 (2012): 65-75.

Karlöf, Lars, Elisabeth Isaksson, Jan-Gunnar Winther, Niels Gundestrup, Harro AJ Meijer, Robert Mulvaney, Michel Pourchet *et al.* "Accumulation variability over a small area in east Dronning Maud Land, Antarctica, as determined from shallow firn cores and snow pits: some implications for ice-core records." *Journal of Glaciology* 51, no. 174 (2005): 343-352.

Kerminen, Veli-Matti, Kimmo Teinilä, and Risto Hillamo. "Chemistry of sea-salt particles in the summer Antarctic atmosphere." *Atmospheric Environment* 34, no. 17 (2000): 2817-2825.

Legrand, Michael R., and Robert. J. Delmas. "The ionic balance of Antarctic snow: a 10-year detailed record." *Atmospheric Environment* 18.9 (1984): 1867-1874.

Legrand, Michel R., and Robert J. Delmas. "Formation of HCl in the Antarctic atmosphere." *Journal of Geophysical Research: Atmospheres* 93, no. D6 (1988): 7153-7168.

Legrand, Michel, and Elizabeth Claire Pasteur. "Methane sulfonic acid to non-sea-salt sulfate ratio in coastal Antarctic aerosol and surface snow." *Journal of Geophysical Research: Atmospheres* 103, no. D9 (1998): 10991-11006.

Mahalinganathan, K., M. Thamban, C. M. Laluraj, and B. L. Redkar. "Relation between surface topography and sea-salt snow chemistry from Princess Elizabeth Land, East Antarctica." *The Cryosphere* 6, no. 2 (2012): 505-515.

McCormick, M. Patrick, Larry W. Thomason, and Charles R. Trepte. "Atmospheric effects of the Mt Pinatubo eruption." *Nature* 373, no. 6513 (1995): 399-404.

McMorrow, Alison J., Mark AJ Curran, Tas D. Van Ommen, Vin I. Morgan, and Ian Allison. "Features of meteorological events preserved in a high-resolution Law Dome (East Antarctica) snow pit." *Annals of Glaciology* 35, no. 1 (2002): 463-470.

Mulvaney, Robert, Elizabeth C. Pasteur, David A. Peel, Eric S. Saltzman, and Pai-Yei Whung. "The ratio of MSA to non-sea-salt sulphate in Antarctic Peninsula ice cores." *Tellus B* 44, no. 4 (1992): 295-303.

Mulvaney, Robert, and Eric W. Wolff. "Evidence for winter/spring denitrification of the stratosphere in the nitrate record of Antarctic firn cores." *Journal of Geophysical Research: Atmospheres (1984–2012)* 98.D3 (1993): 5213-5220.

Obbard, Rachel W., Howard K. Roscoe, Eric W. Wolff, and Helen M. Atkinson. "Frost flower surface area and chemistry as a function of salinity and temperature." *Journal of Geophysical Research: Atmospheres* 114, no. D20 (2009).

Palmer, Anne S., Tas D. Ommen, Mark AJ Curran, Vin Morgan, Joe M. Souney, and Paul A. Mayewski. "High-precision dating of volcanic events (AD 1301–1995) using ice cores from Law Dome, Antarctica." *Journal of Geophysical Research: Atmospheres (1984–2012)* 106, no. D22 (2001): 28089-28095.

Palmer, Anne S. "Trace Ion Chemistry of Law Dome Ice Cores." PhD diss., University of Tasmania, 2002.

Palmer, Anne S., Vin I. Morgan, Mark AJ Curran, Tas D. Van Ommen, and Paul A. Mayewski. "Antarctic volcanic flux ratios from Law Dome ice cores." *Annals of Glaciology* 35, no. 1 (2002): 329-332.

Pasteur, Elizabeth C., and Robert Mulvaney. "Migration of methane sulphonate in Antarctic firn and ice." *Journal of geophysical research* 105, no. D9 (2000): 11525-11534.

Piel, Claudia, Rolf Weller, M. Huke, and D. Wagenbach. "Atmospheric methane sulfonate and non-sea salt sulfate records at the EPICA deep-drilling site in Dronning Maud Land, Antarctica." *Journal of Geophysical Research-Atmospheres, 111, D03304,* (2006).

Plummer, Christopher T., Mark A. J. Curran, Tas. D. van Ommen, Sune Olander Rasmussen, Andrew D. Moy, Tessa R. Vance, Henrik Brink Clausen, Bo Møllesøe Vinther, and Paul A. Mayewski. "An independently dated 2000-yr volcanic record from Law Dome, East Antarctica, including a new perspective on the dating of the 1450s CE eruption of Kuwae, Vanuatu." *Climate of the Past* 8, no. 6 (2012): 1929-1940.

Preunkert, Susanne, Bruno Jourdain, Michel Legrand, Roberto Udisti, Silvia Becagli, and Omar Cerri. "Seasonality of sulfur species (dimethyl sulfide, sulfate, and methanesulfonate) in Antarctica: Inland versus coastal regions." *Journal of Geophysical Research: Atmospheres* 113, no. D15 (2008).

Proposito, Marco, Silvia Becagli, Emiliano Castellano, Onelio Flora, Laura Genoni, Roberto Gragnani, Barbara Stenni, Rita Traversi, Roberto Udisti, and Massimo Frezzotti. "Chemical and isotopic snow variability along the 1998 ITASE traverse from Terra Nova Bay to Dome C, East Antarctica." *Annals of Glaciology* 35, no. 1 (2002): 187-194.

Pszenny, Alexander AP. "Particle size distributions of methanesulfonate in the tropical Pacific marine boundary layer." *Journal of atmospheric chemistry* 14, no. 1-4 (1992): 273-284.

Rankin, Andrew M., Eric W. Wolff, and Seelye Martin. "Frost flowers: Implications for tropospheric chemistry and ice core interpretation." *Journal of Geophysical Research: Atmospheres* 107, no. D23 (2002).

Robock, Alan. "Volcanic eruptions and climate." *Reviews of Geophysics* 38, no. 2 (2000): 191-219.

Roscoe, Howard K., B. Brooks, A. V. Jackson, M. H. Smith, S. J. Walker, Rachel W. Obbard, and Eric W. Wolff. "Frost flowers in the laboratory: Growth, characteristics, aerosol, and the underlying sea ice." *Journal of Geophysical Research: Atmospheres* 116, no. D12 (2011).

Sigl, Michael, Joseph R. McConnell, Lawrence Layman, Olivia Maselli, Ken McGwire, Daniel Pasteris, Dorthe Dahl-Jensen *et al.* "A new bipolar ice core record of volcanism from WAIS Divide and NEEM and implications for climate forcing of the last 2000 years." *Journal of Geophysical Research: Atmospheres* 118, no. 3 (2013): 1151-1169.

Sigl, Michael, Joseph R. McConnell, Matthew Toohey, Mark Curran, Sarah B. Das, Ross Edwards, Elisabeth Isaksson *et al.* "Insights from Antarctica on volcanic forcing during the Common Era." *Nature Climate Change* 4, no. 8 (2014): 693-697.

Sigl, Michael, M. Winstrup, Joseph R. McConnell, K. C. Welten, Guy Plunkett, F. Ludlow, U. Büntgen *et al*. "Timing and climate forcing of volcanic eruptions for the past 2,500 years." *Nature* (2015).

Smith, Barbara T., Tas D. van Ommen, and Mark AJ Curran. "Methanesulphonic acid movement in solid ice cores." *Annals of Glaciology* 39, no. 1 (2004): 540-544.

Udisti, R., U. Dayan, S. Becagli, M. Busetto, D. Frosini, M. Legrand, F. Lucarelli *et al.* "Sea spray aerosol in central Antarctica. Present atmospheric behaviour and implications for paleoclimatic reconstructions." *Atmospheric Environment* 52 (2012): 109-120.

van Ommen, Tas D., and Vin Morgan. "Calibrating the ice core paleothermometer using seasonality." *Journal of Geophysical Research: Atmospheres* 102, no. D8 (1997): 9351-9357.

Wagenbach, Dietmar, Francois Ducroz, Robert Mulvaney, L. Keck, Andrew Minikin, Michel Legrand, J. S. Hall, and Eric W. Wolff. "Sea-salt aerosol in coastal Antarctic

regions." *Journal of Geophysical Research: Atmospheres* 103, no. D9 (1998): 10961-10974.

Wagnon, Paul, Robert J. Delmas, and Michel Legrand. "Loss of volatile acid species from upper firn layers at Vostok, Antarctica." *Journal of Geophysical Research: Atmospheres (1984–2012)* 104.D3 (1999): 3423-3431.

Weller, Rolf, and Dietmar Wagenbach. "Year-round chemical aerosol records in continental Antarctica obtained by automatic samplings." *Tellus B* 59, no. 4 (2007): 755-765.

Wong, Gifford. "The Sea Salt Signal in Ice Core GD17." Honors Thesis, University of Tasmania, 2007.

Determination of Volcanic Aerosols from Aurora Basin North, an Ice Core from East Antarctica

A Literature Review

by

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Abstract

This work reviews current research in Antarctic firn and ice core studies, atmospheric transport, and the different types of deposition of trace ions to ice sheets. The sources and seasonal cycles of sea salts is examined, including possible alternative sources and post-depositional movement of some ionic species. A brief review of sea salt fractionation and sulfate depletion is reviewed in the context of frost flowers, crystals formed on ice and the most likely source of these specific fractionated aerosols. The study concludes with an in-depth look of volcanic influences on climate and how eruptions have been interpreted in ice cores.

1.1 Overview of Antarctic Circulation

Between 35°N and 35°S the amount of incoming solar radiation exceeds that leaving the atmosphere, resulting in a net warming [*Hidore et al.*, 2009] that drives the general circulation of the atmosphere. This warming forces air to rise creating a low pressure zone near the equator (Figure 1). As the air rises, it cools, condenses, and sinks between 20°-35°, forming a band of high pressure (the trade winds) on either side of the equator. Not all of the air from the equator sinks in this area, some continues towards the poles. Winds poleward of 30° latitude form the westerly winds [*Hidore et al.*, 2009]. In the Southern Hemisphere, where these two air masses meet is the polar front, an area of low pressure usually located between 60°S-65°S [*Turner and Pendlebury*, 2004]. As the cold air from the south moves over warmer, oceanic surface waters to the north, strong baroclinic instabilities and convection occur, which together with high cyclonic vorticity result in the formation of numerous mesoscale and synoptic scale cyclonic systems around the edge of the Antarctic continent [*Turner and Pendlebury*, 2004]. These low pressure centers tend to move with the westerlies around the Antarctic region and drift southwards into the edge of the polar cell region (Figure 2), becoming part of a circumpolar trough surrounding the continent [*King and Turner*, 1997; *Turner*, 2003]. The low pressure systems inside the trough are responsible for the high snowfall and warmer weather along the coast of Antarctica. Over the continent, the polar cell is a region of high pressure centered on the continent's highest mass (Dome A region, see Figure 2) and the source for easterly and katabatic winds. These winds are balanced by the spiraling southwards of the upper air westerlies to give subsidence over the central south polar region.
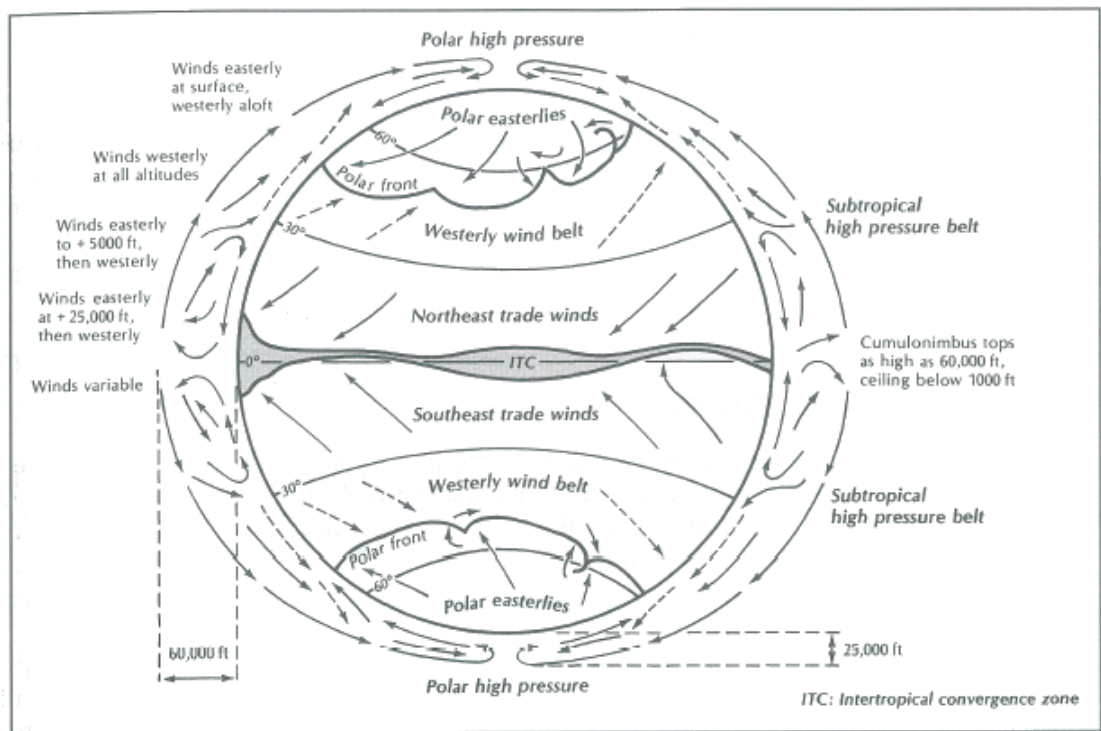
Figure 1. Diagram of general atmospheric circulation, from *Hidore et al.*, 2009, Chapter 5.
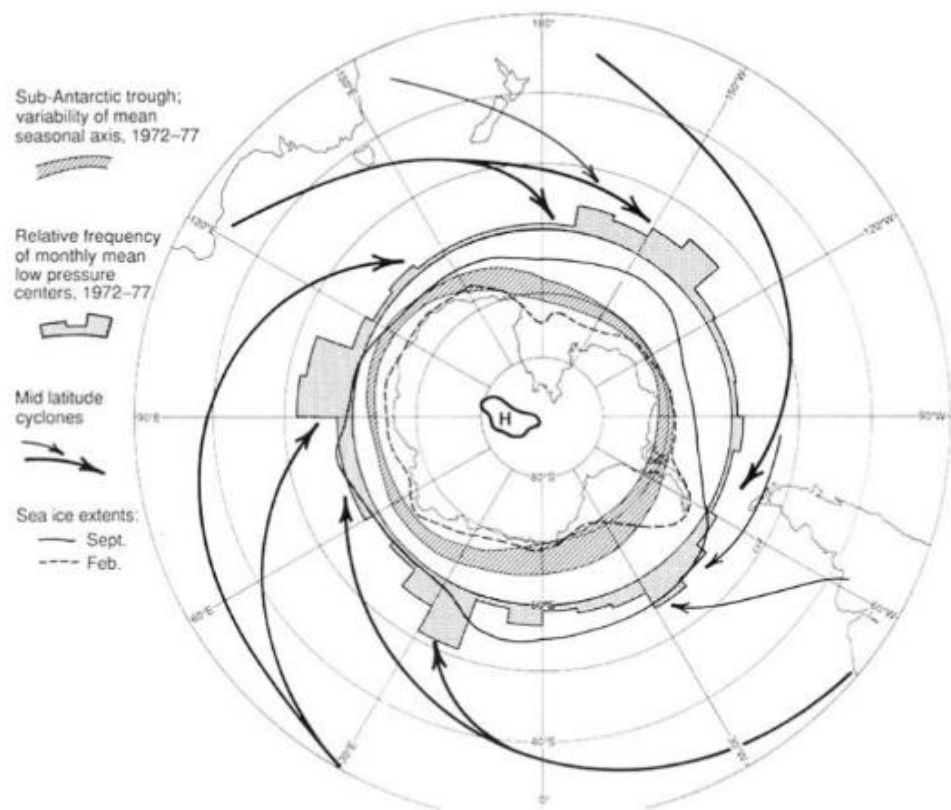

Figure 2. Schematic summarizing dominant features of Antarctic winds, from *Oliver*, 2008.

The circumpolar vortex is a large temperature gradient between the coast and the open ocean [*Aristidi et al.*, 2005]. It circles clockwise approximately 14 km above the Antarctic surface and about the highest mass of the continent and not the pole. Strength of the vortex is related to the stratospheric wind speeds. These winds are strongest in winter, peaking at 20 km above sea level [*Aristidi et al.*, 2005]. In the spring, the polar vortex decays, leading to an increase in exchange between the troposphere and stratosphere. At this time storms from the southern Atlantic Ocean and Weddell Sea can reach the interior and may assist in the breakup of the continental inversion layer [*Shaw*, 1988], a region of warm air over the colder surface air. Its weakening allows mid tropospheric marine air masses to reach the continental surface [*Shaw*, 1988].

The troposphere is the lowest layer of Earth's atmosphere and is where most weather occurs. The stratosphere lies above the troposphere, separated by a layer of temperature stability, labeled the tropopause. The tropopause is highest near the equator, and slopes down towards the poles where it can be as low as 6-8 km above sea level [*Stohl et al.*, 2003]. Long range transport from the equator occurs in the stratosphere, where residence times are lengthened [*Cole-Dai*, 2000] and temperatures are colder [*Holton et al.*, 1995]. The atmospheric residence time of aerosols in the troposphere is driven by local weather patterns and precipitation. Exchange between the two layers occurs regularly in the mid and high latitudes along isentropic surfaces (areas of constant potential surfaces, [*Holton et al.*, 1995]) and through breaks or folds in the tropopause associated with low pressure systems and cyclonic activity [*Stohl et al.*, 2003].

1.2.2 Katabatic Winds

Katabatic winds are generated from downslope movement of very cold, dense air from the continental interior and have a persistent direction [*King and Turner, 1997]*. They occur in the lowest 10 - 100 m of the surface. They are the strongest surface winds found on the continent, however, are not experienced everywhere along the Antarctica coast. They are usually associated with glacial topography or steep valleys. The winds are strongest during winter, when the temperature difference between the interior and the coast is greatest. Katabatic winds can prevent poleward transportation of sea salt particles near the surface by preventing vertical mixing

between the upper and lower sections of the inversion layer [*Hara et al.*, 2004; *Shaw*, 1988]. These winds can have dramatic impacts on a location's snow redistribution processes and are the main cause of surface movement, sastrugi, snow dunes, and pitted patterns [*Proposito et al.*, 2002]. These features are spread across the ice sheet randomly from the interactions between air and the ice sheet surface, affecting both snow accumulation and chemistry during firnification [*Harder et al.*, 2000].

1.2.2 Antarctic Precipitation

Precipitation is greatest along the coastal and peninsula areas [*Frezzotti et al.*, 2013; *Turner*, 2003; *Turner and Pendlebury*, 2004]. These regions are heavily influenced by moisture rich marine air brought by low pressure systems. The amount of snow varies, but is influenced by latitude, topography, and katabatic winds. The peninsula is the warmest and wettest region in Antarctica [*Turner*, 2003] and may experience some rain on its most northern reaches. The rest of the coast, though warmer than the interior, usually only receives solid precipitation. Most precipitation in the interior is in the form of diamond dust [*Turner*, 2003], ice crystals falling from apparently clear skies or very thin cirrus clouds [*King and Turner*, 1997; *Turner*, 2003], and is usually less than 5-7 $kg/m^2/yr$ [*Turner*, 2003], making Antarctica the driest continent on Earth. Because of the continent's location under a uniquely semi-permanent high pressure zone and its dome shape with steep coastal topography, storms are rare in the interior [*Shaw*, 1988; *Turner*, 2003].

1.3 Aerosol Deposition Mechanisms – Dry

Dry deposition occurs continuously and is assumed to occur in 3 major steps [*Davidson et al.*, 1996]. If particles are large enough to settle by gravity, sedimentation is included in this process. The first major step is aerodynamic transport, where chemicals are moved from the free atmosphere to the viscous sublayer. This sublayer is a thin quiet layer of air, a few mm above the surface [*Davidson et al.*, 1996]. Movement can occur through eddy diffusion in the atmosphere moving particles from high to low concentrations. Gases that have desorbed from the surface also exist within this layer. If the particles and gases are permanently removed from the atmosphere, a gradient of particle movement to the snow will also form.

Boundary layer transport is the second step and involves mechanisms that move particles and gases from the viscous sublayer to the surface [*Davidson et al.*, 1996]. This can occur by diffusion of particles through a concentration gradient due to thermal motion or wind eddies. Interception, impaction, sedimentation, and gas sorption directly onto the surface can also occur. Though less common, movement of chemical species due to temperature or humidity gradients are included in this step [*Davidson et al.*, 1996].

The third step determines if the particles sink into the sublayer or rebound off the surface and return to the atmosphere [*Davidson et al.*, 1996]. Liquid water on the surface may allow particles to dissolve, while dry surfaces may cause particles to rebound. Soluble gases may sorb onto the snow, while insoluble and unreactive gases may not [*Davidson et al.*, 1996].

Wind pumping moves chemical species through the spaces of porous snow [*Davidson et al.*, 1996], trapping submicron aerosols and enhancing their deposition [*Harder et al.*, 2000]. These effects often occur in areas of low snow accumulation and high surface irregularities. Longitudinal erosional features, sastrugi, create pressure gradients in the snow affecting surface permeability and the concentrations of chemical species within the upper snow and firn layers [*Davidson et al.*, 1996; *Harder et al.*, 2000].

1.4 Aerosol Deposition Mechanisms – Wet

In regions along the coast, particles and gases are removed through several processes beginning with moisture growth around ice crystals. Nucleation scavenging occurs when particles and gases in the nucleation mode (0.02-0.03 µm, [*O'Dowd et al.*, 1997]) are removed as cloud condensation nuclei (ccn) in the form of snowflakes or ice crystals [*Davidson et al.*, 1996]. As temperatures decrease within the cloud, ice begins to form around these particles. As more ice particles form, some liquid water droplets evaporate, leaving behind the ccn to become ice nuclei or become part of another existing ice crystal. Over time, the ice and water crystals grow, collide, and become larger. Liquid water on the surface of the ice crystal can scavenge soluble gases [*Davidson et al.*, 1996]. During precipitation, falling raindrops and snowflakes

may scavenge particles and gases through collisions and sedimentation on their way to the surface.

1.5. Aerosol Deposition Mechanisms – Fog

Liquid or ice fog on the ice sheet is common and may have higher chemical concentrations than snow [*Davidson et al.*, 1996]. The concentration of chemicals within the fog is not constant with time and nucleation is assumed to be the only scavenging mechanism occurring within. Evaporation of droplets and crystals in the fog release particles and gases back into the atmosphere where they can then react to form new gases inside the fog or escape to the surface or free atmosphere.

1.6 Sea Salts

Marine aerosols are comprised of primary and secondary aerosols. Sea spray (salt) ions are the main component of primary aerosols to Antarctica. The term sea salt refers to those chemical species that are derived from the chemical constituents of seawater. The most common are sodium (Na^+), chloride (Cl^-), sulfate (SO_4^{2-}), calcium (Ca^{2+}), magnesium (Mg^{2+}), and potassium (K^+). They originate from bubble bursting during white cap formation and are carried by surface winds over the open water [*Abram et al.*, 2013; *Udisti et al.*, 2012]. These bubbles produce film and jet drops (sizes up to 2 μm) and are most concentrated in breaking waves and wind speeds greater than 3-4 m/sec [O'Dowd *et al.* 1997]. At greater wind speeds, those faster than 7-11 m/sec, wave crests are essentially torn and sea salts are injected directly into the marine boundary layer [*O'Dowd et al.*, 1997]. Once in the air, they evaporate and form concentrated saline drops or crystals in sizes ranging from 0.8-4 μm. They are hygroscopic and are a source of ccn in the marine boundary layer. In Antarctica, they contribute to the optical properties of aerosols in summer, affecting cloud coverage and albedo [*Becagli et al.*, 2005; *Curran and Jones*, 2000; *Robock*, 2000], and therefore the hydrological cycle. In winter, sea salts make up the most important alkaline aerosol counterpart for acidic chemical species to the continent [*Udisti et al.*, 2012]. Secondary aerosols are those from sources other than sea water and are primarily non-sea salt SO_4^{2-} and other organic species. These aerosols are formed from gas to particle conversions as well as nucleation and condensation onto atmospheric snow and ice [*O'Dowd et al.*, 1997].

Marine aerosols are divided into four size groups. New particles from gas to particle conversions have the smallest radius at approximately 0.005 μm [*O'Dowd et al.*, 1997]. Particles that have sizes between 0.02-0.03 μm are considered in nucleation mode. Those from 0.1-0.2 μm are in accumulation mode and are typical of primary aerosols. The largest sea salts and aerosols, those in the super micron sizes, greater than 2 μm, are considered coarse mode [*Hara et al.*, 2012]. Secondary aerosols are mainly thought to comprise the new particle and nucleation modes. Condensation nuclei are the smallest sized particles in the atmosphere and are optically inactive [*Shaw*, 1988]. Those particles that are larger than 1 μm are almost exclusively primary aerosols and continental dust particles [*O'Dowd et al.*, 1997].

1.7 Additional Sources – Chloride

Chloride can be deposited as a particulate sea salt or as gaseous hydrochloric acid [*Wagnon et al.*, 1999]. Hydrochloric acid (HCl) is known to form from the reaction of sea salts with sulfuric (H_2SO_4) or nitric (HNO_3) acids [*Wagnon et al.*, 1999; *Mahalinganathan et al.*, 2012].

$$NaCl + HNO_3 \rightarrow HCl_{(g)} + NaNO_3$$
$$2NaCl + H_2SO_4 \rightarrow 2HCl_{(g)} + Na_2SO_4$$
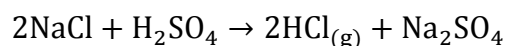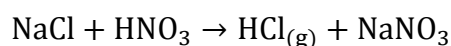
The reaction is more effective inland due to enhanced transport of SO_4^{2-} and of HCl aerosols inland [*Mulvaney et al.*, 1993]. The formation of HCl is highly dependent on the accumulation rate, with Cl^- loss becoming significant below a rate of 40 $kg/m^2/yr$ [*Mahalinganathan et al.*, 2012]. An approximate accumulation rate of 80 $kg/m^2/yr$ was found to be enough to prevent significant Cl^- loss [*Benassai et al.*, 2005]. High concentrations of Cl^- were found in the interior of East Antarctica by *Bertler et al.* [2005] and at Dome C and the South Pole by *Legrand and Delmas*, [1988]. The elevated values were attributed to Cl^- precipitation through atmospheric HCl formation and some reemission from the surface. Signs of reemission and enhanced deposition through wind pumping are seen in ice cores as elevated concentrations towards the surface and decrease with depth within the firn [*Wagnon et al.*, 1999]. Chloride has also been shown to be displaced by very acidic conditions, such as those associated with strong volcanic peaks [*Wagnon et al.*, 1999].

1.8 Alternate Sources - Sulfur Aerosols

The majority of sulfur compounds in the Southern Ocean are the result of oxidation of dimethyl sulfide. Dimethyl sulfide (DMS) is produced by phytoplankton, especially those associated with sea ice and is found in very high levels within the sea ice zone around the continent [*Abram et al.*, 2013]. These particles affect the radiation balance of the atmosphere by absorbing heat in the stratosphere and scattering some solar radiation into space [*Curran and Jones*, 2000; *Robock*, 2000]. They can indirectly affect the climate by increasing the Earth's albedo by forming ccn and feeding cloud formation [*Becagli et al.*, 2005; *Curran and Jones*, 2000; *Robock*, 2000]. Oxidation is initiated through reactions with hydroxyl radicals (Figure 3) and can proceed either through the addition or removal of a hydrogen ion [*Mulvaney et al.*, 1992]. Each can lead to an end product of sulfur dioxide (SO_2), but while this end product is favored by the abstraction method, the addition of H^+ favors an end product of studies have shown that each pathway favors a single end product [*Legrand and Pasteur*, 1998; *Mulvaney et al.*, 1992; *Preunkert et al.*, 2008]. Laboratory and field studies have shown that these reactions are sensitive to temperature, with colder temperatures more likely to result in the addition method with increased methanesulfonic acid (MSA) products [*Legrand and Pasteur*, 1998; *Mulvaney et al.*, 1992].
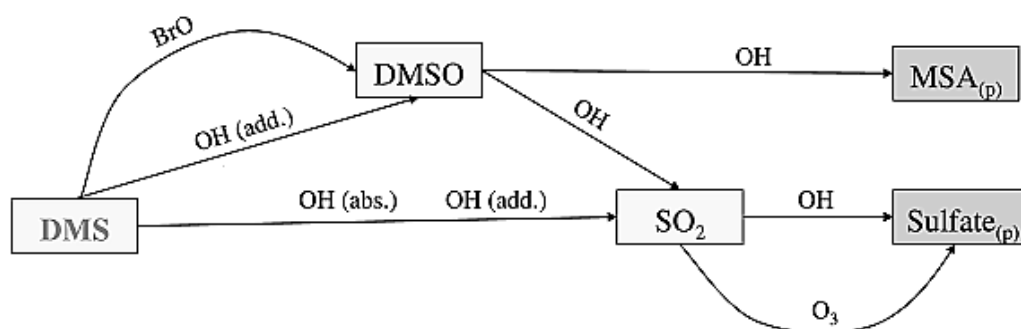

Figure 3. Simplified DMS oxidation pathways. add. - addition pathway, abs. – abstraction pathway. Adapted from *Preunkert et al.*, 2008.

Atmospheric aerosol studies at Dome C, Vostok, and Kohnen have shown that MSA can exist as either a fine particulate or gas [*Piel et al.*, 2006; *Udisti et al.*, 2012; *Wagnon et al.*, 1999]. Wind pumping can move these small particles and gases through the porous firn layers, trapping the particles and enhancing dry deposition

rates [*Harder et al.*, 2000] effectively concentrating the ions in the upper meters of the ice sheet. This was found in shallow cores from Vostok, which also showed a decrease in concentrations with depth [*Wagnon et al.*, 1999]. The decrease in concentrations suggests that post depositional loss may also occur as a result of reemission to the atmosphere [*Becagli et al.*, 2005; *Piel et al.*, 2006].

1.8.1 MSA Migration

Methanesulfonic acid is an important trace ion constituent, having connections to biological activity and sea ice extent [*Abram et al.*, 2013; *Curran et al.*, 2003; *Smith et al.*, 2004]. Higher concentrations occur during summer due to the increased presence of biological activity and local production of DMS. In some cores, the MSA signal is difficult to interpret. As the species undergoes multiple post depositional movements at both low accumulation sites, [*Abram et al.*, 2013; *Preunkert et al.*, 2008] and high accumulation sites such as Law Dome [*Curran et al.*, 2002; *Smith et al.*, 2004], Siple Dome [*Kreutz et al.*, 1998], Byrd station [*Langway et al.*, 1994], and Dyer Plateau [*Pasteur and Mulvaney*, 2000]. The movement most often noted is migration from its usual summer peak towards autumn and winter. The exact mechanism is not clearly understood and simple diffusion, smoothing, and percolation have been proposed and subsequently eliminated because little to no peak degradation has been associated with this type of movement [*Pasteur and Mulvaney*, 2000; *Wagnon et al.*, 1999]. Mixtures of MSA and water can remain liquid at temperatures down to -70°C making movement driven by gravity or capillary action along grain boundaries possible [*Smith et al.*, 2004]. A mechanism involving liquid or vapor phase diffusion and subsequent trapping by the formation of a cation salt in the winter layer has also been suggested [*Curran et al.*, 2002]. Migration out of highly acidic volcanic layers was seen in some ice cores from Vostok [*Wagnon et al.*, 1999].

1.8.2 Sulfate

In coastal regions, local DMS production is considered the only source of MSA [*de Mora et al.*, 1997]. The same cannot be stated for SO_4^{2-}, which has multiple sources, especially over the plateau (Figure 4). Sulfate exists as both a primary aerosol, having a sea salt (ss) component, and as a secondary aerosol with multiple non-sea salt (nss) components. Non-sea salt SO_4^{2-} can be sourced from continental

sources, volcanic eruptions [*Hammer*, 1977], subsidence from polar stratospheric clouds [*Delmas*, 1992; *Minikin et al.,* 1998; *Piel et al.*, 2006], as well as long range transport of SO_2 [*Proposito et al.*, 2002] and enhanced SO_2 conversion to H_2SO_4 [*Delmas, 1992; Preunkert et al.*, 2008].
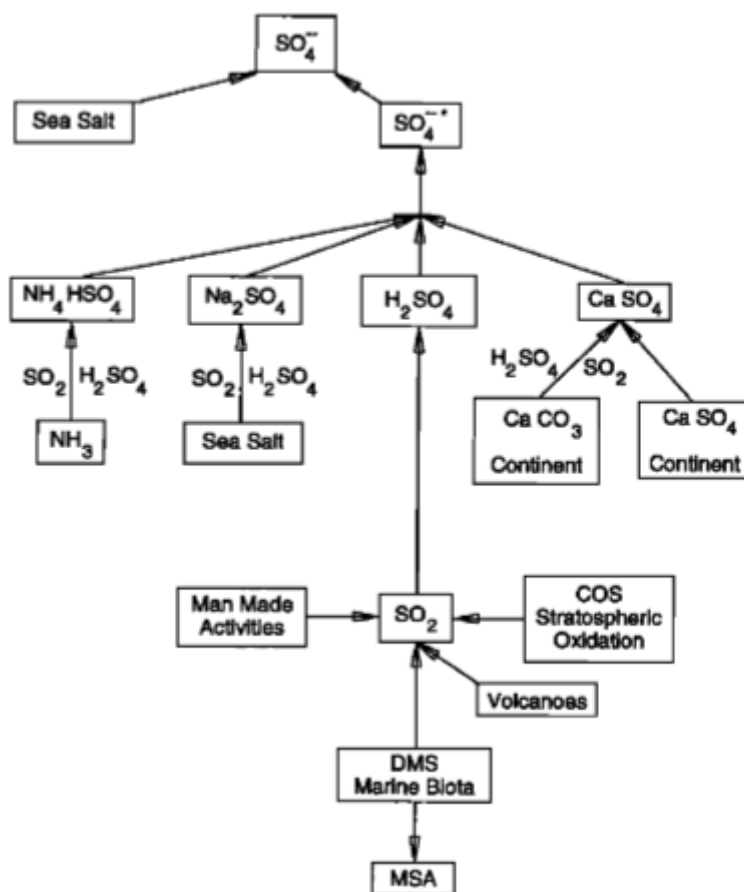

Figure 4. Sources of sulfate found in polar ice. Figure taken from *Legrand and Mayewski*, 1997, as adapted from *Legrand*, 1995.

Separation of the ss component from the nss component uses the ratio of SO_4^{2-} to another sea salt ion, usually Na^+,

$$[SO_4^{2-}]_{nss} = [SO_4^{2-}]_{total} - \left((k - fc) \times [Na^+]_{total}\right)$$

where k is the ratio of SO_4^{2-}/Na^+ in sea water and fc is a fractionation correction if used. Use of the equation without correcting for fractionation (SO_4^{2-} depletion) often leads to negative $nssSO_4^{2-}$ values, especially in winter, indicating a depletion in SO_4^{2-} relative to sea water. Sulfate has not been shown to migrate over time, thus it was

assumed that negative values must be the result of an additional or alternate $ssSO_4^{2-}$ source to the continent.

Negative $nssSO_4^{2-}$ values are rarely seen at interior and plateau sites. Instead, $nssSO_4^{2-}$appears to make up a very low percentage of total SO_4^{2-} values [*Becagli et al.*, 2005; *Castellano et al.*, 2005; *Cole-Dai and Mosley-Thompson*, 1999; *Cole-Dai et al.*, 2000]. These low $nssSO_4^{2-}$ values have been attributed to long range transport of SO_4^{2-} ions from mid latitudes, increased DMS oxidation, and decreased concentrations due to size sedimentation during transport. Sea salt ions are known to have large particle sizes [*Benassai et al.*, 2005] leading to shortened atmospheric residence times in the troposphere [*Becagli et al.*, 2005]. Aerosol studies at EPICA Dome C (EDC) have shown that larger sea salt particles were only present in storms from the Pacific / Indian Ocean sectors. Storms out of the Atlantic Ocean had travelled a greater distance over the plateau, losing most of the larger sized particles along the way [*Udisti et al.*, 2012].

Both SO_4^{2-} and MSA were shown to be in the smallest sized fractions at EDC [*Udisti et al.*, 2012] and Kohnen [*Weller and Wagenbach*, 2007] as well as in the gas phase at Vostok [*Wagnon et al.*, 1999]. *Pzenny et al.*, [1992] showed that $nssSO_4^{2-}$ is associated with submicron particles, but MSA could also be found on larger particles. This size difference is in agreement with laboratory studies that show MSA is capable of condensing onto larger particles [*Hoppel*, 1987; *Kerminen et al.*, 2000; *Legrand and Pasteur*, 1998]. In a traverse across the EDC drainage area, *Proposito et al.*, [2002] and *Benassai et al.*, [2005] showed sea salts decline quickly away from the coast, reaching stable values at 270 km inland. Sulfate concentrations had similar decreases to 250 km and differed in that they sharply increased to reach stable values between 550-750 km from the coast. The authors concluded that primary aerosols (sea salts) dominated the chemistry to approximately 250 km from the coast. Afterwards, the $nssSO_4^{2-}$ component of DMS oxidation is more important, likely the result of a shift to a smaller particle size.

Given the similar seasonality of $nssSO_4^{2-}$ and MSA the ratio of $nssSO_4^{2-}$/MSA has been used to better constrain the biological component of $nssSO_4^{2-}$[*Udisti et al.*, 2012]. The high degree of post depositional movement of MSA seen in some ice cores and a lack of a complete understanding of DMS oxidation has prevented

accurate use of the ratio in ice cores. Loss of MSA through differential settling during transport further complicates using the ratio to decipher past atmospheric concentrations. The ratio may be further compromised by changes in temperature and humidity conditions that could change not only the amount of MSA produced, but also the phase in which it is transported [*Legrand and Pasteur*, 1998]. MSA is more hygroscopic than SO_4^{2-} and is therefore more likely to form ccn [*O'Dowd et al.*, 1997] and be removed through wet deposition [*Becagli et al.*, 2005]. The increased oxidative capacity of the atmosphere over the plateau favors continued SO_2 oxidation to SO_4^{2-} and photochemical destruction of MSA within the firn layers [*Preunkert et al.*, 2008] would further disrupt any ratio initially set by DMS oxidation.

1.9 Frost Flowers

One of the major findings early in the examination of ice cores was negative $nssSO_4^{2-}$ values, especially in coastal cores during periods of high concentrations of sea salts. Since both SO_4^{2-} and Na^+ ions have sea salt components, any significant depletion in SO_4^{2-} would likely be the result of an additional or alternate source of sea salt to coastal Antarctica. Frost flowers first became of interest as a source of variations discovered in the albedo and remote sensing signature of ice cores. Chemical analysis of the flowers proved they are depleted in SO_4^{2-} from the precipitation of mirabilite ($Na_2SO_4 \cdot 10H_2O$) [*Rankin et al.*, 2000; *Rankin et al.*, 2002] and thus a possible alternate source of SO_4^{2-} depleted sea salts.

Frost flowers are dendritic or faceted ice crystals that grow on the surface of new sea ice [*Rankin et al.*, 2000; *Rankin et al.*, 2002] and fresh water ice in winter from a supersaturation water vapor that forms in the air nearest to the ice surface [*Alvarez-Aviles et al.*, 2008; *Domine et al.*, 2005; *Hara et al.*, 2012; *Obbard et al.*, 2009]. These flowers form on new sea ice in open leads where warmer surface water is exposed to very cold air [*Obbard et al.*, 2009]. When new ice forms, salts are excluded resulting in a thin layer of highly saline fluid that can be several degrees warmer than the air over the ice surface. As the sea ice grows thicker it expels more brine, and becomes an insulating barrier allowing the ice surface underneath to cool. This causes the brine channels to constrict and any additional growth forces brine out onto the surface. This brine layer serves as a source of excess water vapor, quickly making the air just above the ice supersaturated. Tiny crystals begin to form on small

bumps or imperfections above the brine layer, quickly growing and spreading [*Alvarez-Aviles et al.*, 2008; *Domine et al.*, 2005; *Obbard et al.*, 2009; *Roscoe et al.*, 2011]. Flowers that exist within the brine layer are able to wick the brine through surface tension and or concentration gradients. This leads to an increase in bulk salinity, the concentration of ions in solution, and can reach levels above sea water [*Obbard et al.*, 2009].

Sulfate depletion within frost flowers is the result of mirabilite precipitation beginning at -8°C [*Obbard et al.*, 2009]. Since there is more Na^+ than SO_4^{2-} in sea water, the loss of Na^+ is less relative to SO_4^{2-} and thus the SO_4^{2-}/Na^+ ratio decreases in the crystals to below that of sea water. Additional precipitates, such as hydrohalite ($NaCl \cdot 2H_2O$, loss of Cl^- and additional Na^+) form at -22°C and potassium and magnesium precipitate at -34°C [*Obbard et al.*, 2009].

There are two types of frost flowers, dry- those that have yet to wick brine, and wet- those that have incorporated brine into their crystal structure [*Alvarez-Aviles et al.*, 2008]. Crystal growth depends on the air and surface temperatures, humidity, and the initial chemical composition of the ice and brine. Studies of flowers grown under laboratory conditions show that growth and structure changes fluctuate when temperature and saturation levels change. This confirms findings from field collections that show unusual shapes on some flowers but not others within the same field. These changes in shapes confirm that crystal growth occurs in stages leading to a fairly rigid outer structure [*Obbard et al.*, 2009].

The flowers' dendritic crystal structure increases the surface area of the ice, providing additional sites for atmospheric reactions and aerosol production [*Domine et al.*, 2005; *Rankin et al.*, 2002]. Early estimates of the surface area ranged from 50 - 1000 m^2 per m^2 of sea ice. Additional analysis suggests that these values were overestimated and that the true surface area is much lower, ranging from 1.4 m^2 per m^2 of sea ice for dry flowers [*Domine et al.*, 2005; *Obbard et al.*, 2009] to 1.76 - 2.14 m^2 per m^2 of sea ice for mixed flowers [*Obbard et al.*, 2009] calling into question the actual influence the flowers have on aerosol production and transport over Antarctica.

The exact mechanism for aerosol production has not been firmly established. Destruction due to strong winds has been considered the most likely, as when *Obbard*

et al., [2009] observed large flowers being moved slightly downwind following a windy snow storm. Laboratory studies showed that flowers could be destroyed by sustained winds and gusts up to 12m/s, but aerosols were not produced [*Roscoe et al.*, 2011]. *Obbard et al.*, [2009] found that slower wind speeds were capable of moving snow and burying some flowers, making blowing snow and not frost flowers a more likely source for SO_4^{2-} depleted aerosols.

1.10 Volcanic Influences on Climate

Local and regional impacts of volcanic eruptions are the direct result of large volumes of solid ash and gases released into the atmosphere over a short time period. Ash and larger debris settles out of the atmosphere quickly, gases, such as, H_2O, CO_2, SO_2, N_2, and some halogens are released into the atmosphere where their lifetimes become part of the atmospheric residence times of the oxygen, carbon, and sulfur cycles [*Cole-Dai*, 2010]. The amounts of water vapor and CO2 ejected are small relative to their respective atmospheric reservoirs and therefore have limited climatic effects [*Cole-Dai*, 2010]. Sulfur dioxide is rapidly oxidized into H_2SO_4 in the troposphere before removal by precipitation and has little long term or global impacts. In the stratosphere, the same conversion requires several weeks to months. These emissions have longer and more widespread impacts due to increased residence times and the increased volume usually associated with eruptions reaching into the stratosphere [*Cole-Dai*, 2010; *Robock*, 2000].

Volcanic eruptions are considered one of the most important short term natural climatic drivers in that their debris alters the atmospheric reflectivity and changes the energy balance of the planet [*Cole-Dai*, 2010; *Robock*, 2000]. Stratospheric sulfur-rich gases and particles usually exist as hydrated H_2SO_4 aerosols that are efficient at scattering visible light [*Cole-Dai*, 2010; *McCormick et al.*, 1995; *Robock,* 2000]. Their presence increases the optical depth of the atmosphere and thus the atmospheric albedo. Interactions with both incoming and outgoing infrared radiation result in the cooling of the surface and lower troposphere and warming of the stratosphere. These gases from the largest eruptions have the capacity to alter global climate for several years following the eruption by decreasing the amount of solar radiation that reaches the surface [*McCormick et al.*, 1995; *Robock*, 2000]. For example, the extended eruption of Tambora (1815) resulted in a global cooling of the following year and

1816 being known as the "year without a summer" [*Brönnimann and Krämer*, 2016; *Cole-Dai et al.*, 2009]. Similar global cooling was experienced after the 1963 eruption of Mt. Agung and the 1992 eruptions of Pinatubo and El Chichón [*McCormick et al.*, 1995; *Robock*, 2000; *Sigl et al.*, 2015].

To wholly understand the impact of human induced climatic changes, natural changes and impacts need to be assessed. Aerosol and dust particles found in ice cores can assist in the understanding of volcanic impacts. By studying the debris and trace chemistry found in ice cores, the approximate size and location of eruptions can be approximated [*Cole-Dai*, 2010; *Robock*, 2000]. By combining the records of many ice cores with other climate proxies and written historical records, a better understanding of volcanic effects can be achieved. These effects can aid in models of future human induced climate changes and improve both atmospheric and ocean temperature predictions.

1.10.1 Volcanic Flux Calculations – Introduction

A complete understanding of the climatic effects of volcanism and future / long term changes requires a long record of eruptions and their impacts. Written records usually only include those eruptions that occurred in well populated areas and had significant social / economic impacts [*Brönnimann and Krämer*, 2016]. Reliable records of active volcanoes and past eruptions began in the mid 1800's. Geological studies improved the records beginning in the early 20th century. A global network and monitoring program began in the mid 1950's and satellites have increased coverage towards the end of the 20th century. As part of the United States, Department of Mineral Sciences, National Museum of Natural History, the Smithsonian Institution's Global Volcanism Program has combined all published records and maintains a comprehensive record of all active and inactive volcanoes for the last 10,000 years (http://volcano.si.edu/gvp_about.cfm).

Hammer [1977] was the first to measure volcanic presence in Greenland ice cores by detecting the changes in acid content through changes in electrical conductivity. Southern Hemisphere volcanic records began with a continuous 770 year volcanic record from East Antarctica also based on electrical conductivity measurements [*Moore et al.*, 1991]. *Delmas et al.*, [1992] presented a 1000 year

record based on both electrical conductivity and SO_4^{2-} measurements from several South Pole cores. By 1994, when the longest (to date) Greenland record of continuous SO_4^{2-} measurements was published, volcanic presence was mostly determined through electrical conductivity and only supplemented with SO_4^{2-} measurements [*Cole-Dai et al.*, 1997]. This approach was efficient for the time, yet it still missed many small eruptions and often led to confused signals due to the presence of large concentrations of non-volcanic acids or salts. Sizes of the volcanic signal would fluctuate depending on various physical properties of the ice itself or by changes in the temperature of the air surrounding the core [*Cole-Dai et al.*, 1997]. Dating the results was problematic as these methods used mathematical models that required constant accumulation rates. This would lead to large errors in dating as the amount of snow falling in any one area is not constant over time.

1.10.2 Volcanic Flux Calculations – Improvements

Cole-Dai et al., [1997] presented the first volcanic SO_4^{2-} record for the Southern Hemisphere by using two cores from the Antarctic Peninsula. These records improved upon the previous volcanic chronology by using a novel multi parameter approach to annual dating. Instead of solely relying on accumulation rates, dating was completed by using the natural seasonal changes of oxygen isotopes and ions over the course of the year. By using two cores, the deposition dates of several eruptions were confirmed, proving that moderate and large eruptions could be seen across regions. While other studies [*Dai et al.*, 1991; *Langway et al.*, 1988; *Thompson et al.*, 1994] presented SO_4^{2-} concentrations, acid signals, and flux (volcanic deposition seen over the course of the eruption) calculations for individual events, *Cole-Dai et al.*, [1997] was the first to present continuous volcanic SO_4^{2-} fluxes for an entire ice core. The work pioneered a new approach using SO_4^{2-} fluxes to find additional unknown small and moderate volcanoes.

The approach of *Cole-Dai et al.*, [1997] first smoothed the data with a 3-sample running mean to remove noise resulting from the sampling resolution. Since volcanic SO_4^{2-} in Antarctica is superimposed onto a variable background level of SO_4^{2-}, the authors first calculated and removed this variable background from the volcanic period. To remove obvious bias in the background concentrations, known and suspected volcanic peaks were first removed. The average and standard deviation

of the remaining smoothed annual fluxes were computed. Any remaining peak that was higher than twice the standard deviation was considered volcanic. The approach proved successful by identifying 18 events from one core and 15 from the second shorter core, an improvement over the combined 14 eruptions from two cores from the South Pole using electrical measurements [*Cole-Dai et al.*, 1997; *Delmas et al.*, 1992].

The approach was improved by the addition of time as a second volcanic criteria, thus eliminating false positives due to seasonally elevated biological signals [*Cole-Dai et al.*, 1997; *Cole-Dai et al.*, 2000; *Ferris et al.*, 2011]. Accumulation rates were later added for the calculation of annual SO_4^{2-} fluxes and sample lengths of individual samples for total volcanic fluxes [*Cole-Dai et al.*, 1997]. These additions proved useful and showed that total fluxes of eruptions could be achieved at sites with moderate to high sample resolution. By using many snow pits across a wide area in the South Pole, *Cole-Dai and Mosley-Thompson* [1999] showed that volcanic fluxes can vary spatially. The authors attributed this variation to the spatial variability in accumulation rates across the sampling area. They proposed that the fluctuations in accumulation rates were due to surface irregularities and redistribution by winds leading to changes in densities of individual snow layers.

Dating of events continued to improve with the addition of longer, independent, sub-annually dated ice cores, such as Dome Summit South (DSS) from Law Dome [*Palmer et al.*, 2001; *Palmer*, 2002; *Plummer et al.*, 2012]. With these cores, Tarawera was separated from Krakatau and the dating of Kuwae was clarified [*Palmer et al.*, 2001; *Plummer et al.*, 2012]. New eruptions, such as the 1758-1760 eruption of Jorullo-Taal [*Castellano et al.*, 2005; *Cole-Dai et al.*, 2000], and some subantarctic volcanoes were identified in many of the low accumulation sites [*Castellano et al.*, 2005; *Ren et al.*, 2010]. With additional volcanoes identified and accurately dated from highly resolved ice cores, dating of inland sites improved through volcanic synchronization, the matching of volcanic peaks. This provided time markers that could be used as definitive dates and allowed other events in ice cores to be accurately dated. With improvements, this led to a highly detailed dating schedule for all of Antarctica using multiple ice cores across the entire continent. [*Sigl et al.*, 2014; *Sigl et al.*, 2015]

With additional high resolution cores, the flux calculation continued to improve and become more site specific. Some sites used different smoothing or down sampling methods to reduce the noisy background fluctuations [*Castellano et al.*, 2005; *Plummer et al.*, 2012; *Sigl et al.*, 2013] and some improved the thinning models used to calculate accumulation rates [*Jiang et al.*, 2012]. High resolution sites found volcanic fluxes were best represented by using a 31-year centered mean (as used by *Plummer et al.*, [2012]) or running background mean (or median, *Sigl et al.*, [2013]). Low accumulation sites often were forced to use shorter time periods [*Castellano et al.*, 2005; Cole Dai *et al.*, 2000]. Short cores from the South Pole calculated the average background over the entire length of the core [*Cole-Dai* and *Mosley-Thompson*, 1999]. Considerations for elevated volcanic signals also varied. Dome A used a minimum time of one year [*Jiang et al.*, 2012], similar to that used by *Delmas et al.*, [1992] for two cores from the South Pole. *Plummer et al.*, [2012] used a minimum period of six months for DSS as did *Ferris et al.*, [2011] for the 2004 South Pole ice core. An early study from Plateau Remote considered two consecutive samples to be volcanic [*Cole-Dai et al.*, 2000]. Identification of peaks also began to vary from the initial two standard deviations above the background to more complicated methods of using running means and running medians [*Sigl et al.*, 2013; *Traufetter et al.*, 2004]. Low accumulation sites such as DT-263 [*Liya et al.*, 2006] and Plateau Remote [*Cole-Dai et al.*, 2000] continued to use the *Cole-Dai et al.*, [1997] approach. Computer algorithms have been used, especially at low accumulation sites such as EDC [*Gauthier et al.*, 2016], further improving the identification of moderate to large eruptions.

Studies of sea salt sources introduced the possibility of fractionated SO_4^{2-} being recorded in coastal sites [*Inoue*, 2015; *Rankin et al.*, 2000; *Rankin et al.*, 2002; *Wolff et al.*, 2003]. Some sites found that $nssSO_4^{2-}$ was more representative of volcanic signals rather than total SO_4^{2-}. Ice cores drilled on Law Dome and Siple Dome accounted for this fractionation in their $nssSO_4^{2-}$ calculations [*Kreutz et al.*, 1998; *Palmer*, 2002; *Palmer et al.*, 2002; *Plummer et al.*, 2012]. Studies in low accumulation sites have determined the $nssSO_4^{2-}$ concentrations do not make a significant contribution to the total SO_4^{2-} budget and some did not make a distinction when calculating the volcanic flux [*Castellano et al.*, 2005; *Cole-Dai et al.*, 2000]. Most recently, a highly resolved ice core from the West Antarctic Ice Sheet (WAIS) Divide calculated volcanic fluxes using an integrated SO_4^{2-} content from only the

volcanic peaks of nss sulfur after they were removed from the 31-year running mean [*Sigl et al.*, 2013]. A novel approach by *Ferris et al.*, [2011] used a weighted annual average and identified volcanic peaks as six consecutive months greater than two standard deviations above the background weighted annual average.

Despite all of the various methods used to calculate backgrounds and fluxes, the basic formula remained the same. The flux for a volcano was determined by multiplying the residual (total minus background) SO_4^{2-} concentration by an accumulation rate.

$$[SO_4^{2-}]_{total} - [SO_4^{2-}]_{background} \times \text{accumulation rate}$$

Total volcanic fluxes were determined by the sum of all fluxes for an event. These fluxes are often called annual fluxes in low accumulation cores due to the low sample resolution, but the principle is similar. Despite all of the variations in calculations, it was assumed that fluxes would be relatively similar across sites. Instead, fluxes and normalized fluxes were shown to vary among sites likely resulting from the differences in flux calculations [*Budner and Cole-Dai*, 2003; *Palmer et al.*, 2001].

1.10.3 Variability in Published Values

Sulfate concentrations can vary greatly over seasons and over longer time periods. Smoothing the data over long time periods often minimizes this variation and allows for easier detection of peaks. However, when using smoothed data, smaller eruptions are lost and moderate eruptions are not easily identified. Using SO_4^{2-} concentrations for the SP04 core, *Ferris et al.*, [2011] showed that using the smoothed background approach decreased the number events from 76 using the *Cole-Dai et al.*, [1997] approach to 74 using smoothed data. Using an approach similar to that of EDC where SO_4^{2-} concentrations are considered best represented by a lognormal pattern[*Castellano et al.*, 2005], the number of events was further reduced to 62. Ultimately, the weighted annual average approach used for computing the volcanic fluxes in the SP04 core reduced the number of events again to 60. Volcanic fluxes were then computed for those peaks that were greater than the twice the standard deviation above the weighted means. This approach lost all small eruptions, those

with a flux of less than 7.5 kg/km^2, but did not seem to affect the moderate and larger eruptions.

The *Ferris et al.*, [2011] study assumed similar atmospheric and snow deposition conditions for all of the South Pole ice cores. While the cores used in the study were all of different lengths, they showed varying number of eruptions in the periods where each overlapped. Eight volcanic events were found in the PS14 ice core, dating between 1964-1809 (see *Delmas et al.*, [1992] for South Pole core details). The PS1 core is longer and therefore has a greater number of events, but does not contain all of the same events found in PS14. Events dated as 1880 and 1831 only appear in the PS14 record. The Tambora flux is slightly larger in PS14, however, the 1809 eruption is greater in PS1. *Ferris et al.*, [2011] investigated this variability along with the flux values of two additional South Pole cores, SP01 and SP04. The number of eruptions found within each core varied from 22 with the combined PS1 and PS14 cores (listed as SP84 in *Ferris et al.*, [2011]) to 34 in SP01. The longest core in the study. Some of this variation was addressed by and determined to be due to slight variations in accumulation rates, changes in surface topography, and the various detection methods used.

Small scale spatial variability at low accumulation sites was addressed recently at EDC, by comparing five ice cores drilled within approximately 1m of each other. Each core was exactly the same length, 100 m, and had the same average annual accumulation rate of 25 kg/m^2/yr, giving a total core length of approximately 2500 years [*Gauthier et al.*, 2016]. In these five cores, the number of peaks varied from 47 and 54. The 1641 Mt. Parker eruption was found in all five cores, dated to 1646, with fluxes ranging from 10.1-17.5 kg/km^2 [*Gauthier et al.*, 2016]. The eruption of Tambora, often used to date cores due to its very large flux, was only seen in 3 out of the 5 cores, with fluxes ranging from 1.8-13.1 kg/km^2. The unknown 1809 eruption however, was found in all 5 cores and had a much narrower flux range, 10.5-16.6 kg/km^2 [*Gauthier et al.*, 2016]. The loss of Tambora in this study was attributed to snow drift and surface roughness. Both *Ferris et al.*, [2011] and *Gauthier et al.*, [2016] limited these post depositional effects to sites with low accumulation rates. Sites with higher accumulation were believed to have less post depositional effects and therefore would have less variability in their volcanic flux record.

There has been no well-defined boundary between low and high accumulation rates. For most chemical species, the boundary is set based on the lowest limit for post depositional movement usually between $50 - 100$ kg/m^2/yr and is dependent on chemical species [*Benassai et al.*, 2005; *Legrand and Mayewski*, 1997; *Proposito et al.*, 2002]. *Poynter et al.*, [2016] looked at four Law Dome cores drilled within 35 km from each other. The sites had varied accumulation rates ranging from 137.55 kg/m^2/yr to 1247.12 kg/m^2/yr, yet maintained similar site characteristics. They were considered close enough to have similar atmospheric effects and similar aerosol depositional loadings. The study looked at the variation among the fluxes within the cores and found that each core recorded the flux in a different manner. In three of the four cores, the average flux of Tambora and UE1809 were similar, however two of the three cores showed UE1809 had the larger flux. It was concluded that because the sites had similar aerosol loadings, that the differences were due to other factors, including differences in accumulation rates.

A study in a high plateau site in Dronning Maud Land looked that the variation in accumulation rates across a small area and also compared these changes across several volcanic eruption time periods [*Karlöf et al.*, 2005]. The study consisted of five snow pits and shallow firn cores distributed between 3.5 - 7 km from each other and all near a medium length core drilled in 1996/1997. Accumulation rates for the firn cores were divided into six time periods. These time periods varied in length, but were separated by major eruptions, so that only one large eruption occurred within each time period (UE1809 and Tambora were in two separate time periods). Accumulation rates between these two time periods differed from 0-1 kg/m^2/yr and showed no correlation to SO$_4^{2-}$ concentrations. *Karlöf et al.*, [2005] did not find a significant difference in the accumulation rates among the five snow pits. The study did attribute differences in the chemistry record to snow redistribution and other post depositional effects. The snow pit with the highest accumulation rate also had the highest mean SO$_4^{2-}$ concentration. This does not necessarily indicate that snow accumulation has an effect on SO$_4^{2-}$ concentration because the same was not true of the lowest accumulation site. Differences were again attributed to post depositional effects.

1.11 Conclusion

Sea salts from bubble bursting and winds blown over wave crests are the dominant source of primary aerosols to coastal Antarctica. The continent is surrounded by sea ice that changes its area both seasonally and yearly, making transport pathways of sea salt aerosols even more complex. As the sea ice grows, it reduces the open sea near the coast and increases the distance sea salt aerosols have to travel to reach the ice sheet. It also facilitates the growth of frost flowers that may or may not influence sea salt concentrations seen in ice cores. By assuming a single source, sea salts can be useful as past environmental and climatic markers and can assist in past climate reconstructions. However, measurements across Antarctica have revealed varying concentrations spatially and temporally, evidence that fractionation of sea salt components is occurring. Fractionation can occur in the atmosphere or in the snow layers between chemical species and gaseous HNO_3 and H_2SO_4. These reactions lead to the formation of HCl. Fractionation can also occur from the precipitation of mirabilite on sea ice. To clarify the transport pathways, sources, and depositional mechanisms, large datasets from both inland and coastal locations are required.

Studies often infer that the most important climatic factor of an eruption is the sulfur content or aerosol mass loading, not how large the explosion is [*Cole-Dai*, 2010]. While the measurement of SO_4^{2-} and to a certain extent acidic signals, are quantitative, the relationship between SO_4^{2-} concentrations and the volcanic impacts may not translate over many eruptions or across magnitudes. The climatic changes depend on the amount and distribution of the aerosol particles as well as the latitude of the eruption and the atmospheric circulation during and after the event. Ice cores can only record the acidic and SO_4^{2-} signals that are deposited onto the snow surface. For this reason, only some large eruptions from the tropics and those in the Southern Hemisphere are recorded in Antarctica. Variations in accumulation rate, removal by wind, presence of sastrugi, and other surface irregularities change both the acidic and SO_4^{2-} signals seen in the preserved ice core record. Concentrations of SO_4^{2-} in ice cores are not able to distinguish between one large eruption or several small events. Nearby eruptions will appear as larger than some global eruptions simply due to their proximity to the drilling site. To minimize these effects, the records of several near-by cores are used to create a spatially representative volcanic record. This will still lead

to problems if volcanic records are compared across regions, such as comparing cores from East Antarctica to those from the peninsula. Locally, accumulation rates can vary and these local changes will have unforeseen impacts on volcanic fluxes.

References

Abram, Nerilie J., Eric W. Wolff, and Mark AJ Curran. "A review of sea ice proxy information from polar ice cores." *Quaternary Science Reviews* 79 (2013): 168-183.

Alvarez-Aviles, Laura, William R. Simpson, Thomas A. Douglas, Matthew Sturm, Donald Perovich, and Florent Domine. "Frost flower chemical composition during growth and its implications for aerosol production and bromine activation." *Journal of Geophysical Research: Atmospheres* 113, no. D21 (2008).

Aristidi, E., K. Agabi, M. Azouit, E. Fossat, J. Vernin, T. Travouillon, J. S. Lawrence et al. "An analysis of temperatures and wind speeds above Dome C, Antarctica." *Astronomy & Astrophysics* 430, no. 2 (2005): 739-746.

Becagli, Silvia, Marco Proposito, Silvia Benassai, Roberto Gragnani, Olivier Magand, Rita Traversi, and Roberto Udisti. "Spatial distribution of biogenic sulphur compounds (MSA, nssSO42−) in the northern Victoria Land–Dome C–Wilkes Land area, East Antarctica." *Annals of Glaciology* 41, no. 1 (2005): 23-31.

Benassai, Silvia, Silvia Becagli, Roberto Gragnani, Olivier Magand, Marco Proposito, Ilaria Fattori, Rita Traversi, and Roberto Udisti. "Sea-spray deposition in Antarctic coastal and plateau areas from ITASE traverses." *Annals of Glaciology* 41, no. 1 (2005): 32-40.

Bertler, Nancy, Paul Andrew Mayewski, Alberto Aristarain, P. Barrett, S. Becagli, R. Bernardo, S. Bo et al. "Snow chemistry across Antarctica." *Annals of Glaciology* 41, no. 1 (2005): 167-179.

Brönnimann S., Krämer D. "Tambora and the "Year Without a Summer" of 1816. A Perspective on Earth and Human Systems Science". *Geographica Bernensia* G 90. (2016).

Budner, Drew, and Jihong Cole-Dai. "The number and magnitude of large explosive volcanic eruptions between 904 and 1865 AD: Quantitative evidence from a new South Pole ice core." *Volcanism and the Earth's Atmosphere* (2003): 165-176.

Castellano, E., Silvia Becagli, M. Hansson, M. Hutterli, J. R. Petit, M. R. Rampino, M. Severi, Jørgen Peder Steffensen, Rita Traversi, and Roberto Udisti. "Holocene volcanic history as recorded in the sulfate stratigraphy of the European Project for Ice Coring in Antarctica Dome C (EDC96) ice core." *Journal of Geophysical Research: Atmospheres* 110, no. D6 (2005).

Cole-Dai, Jihong, Ellen Mosley-Thompson, and Lonnie G. Thomn. "Annually resolved southern hemisphere volcanic history." *Journal of Geophysical Research* 102, no. D14 (1997): 16-761.

Cole-Dai, Jihong, and Ellen Mosley-Thompson. "The Pinatubo eruption in South Pole snow and its potential value to ice-core paleovolcanic records." *Annals of Glaciology* 29, no. 1 (1999): 99-105.

Cole-Dai, Jihong, Ellen Mosley-Thompson, Shawn P. Wight, and Lonnie G. Thompson. "A 4100-year record of explosive volcanism from an East Antarctica ice

core." *Journal of Geophysical Research: Atmospheres* 105, no. D19 (2000): 24431-24441.

Cole-Dai, Jihong, David Ferris, Alyson Lanciki, Joël Savarino, Mélanie Baroni, and Mark H. Thiemens. "Cold decade (AD 1810–1819) caused by Tambora (1815) and another (1809) stratospheric volcanic eruption." *Geophysical Research Letters* 36, no. 22 (2009).

Cole-Dai, Jihong. "Volcanoes and climate." *Wiley Interdisciplinary Reviews: Climate Change* 1, no. 6 (2010): 824-839.

Curran, Mark AJ, and Graham B. Jones. "Dimethyl sulfide in the Southern Ocean: Seasonality and flux." *Journal of Geophysical Research: Atmospheres (1984–2012)* 105, no. D16 (2000): 20451-20459.

Curran, Mark AJ, Anne S. Palmer, Tas D. Van Ommen, Vin I. Morgan, Katrina L. Phillips, Alison J. McMorrow, and Paul A. Mayewski. "Post-depositional movement of methanesulphonic acid at Law Dome, Antarctica, and the influence of accumulation rate." *Annals of Glaciology* 35, no. 1 (2002): 333-339.

Curran, Mark AJ, Tas D. van Ommen, Vin I. Morgan, Katrina L. Phillips, and Anne S. Palmer. "Ice core evidence for Antarctic sea ice decline since the 1950s." *Science* 302, no. 5648 (2003): 1203-1206.

Dai, Jihong, Ellen Mosley-Thompson, and Lonnieg Thonpson. "Ice core evidence for an explosive tropical volcanic eruption 6 years preceding Tambora." *Journal of Geophysical Research* 96, no. 17 (1991): 361-17.

Davidson, Cliff I., Michael H. Bergin, and Hampden D. Kuhns. "The deposition of particles and gases to ice sheets." In Chemical exchange between the atmosphere and polar snow, pp. 275-306. Springer Berlin Heidelberg, 1996.

Delmas, Robert J. "Free tropospheric reservoir of natural sulfate." *Journal of atmospheric chemistry* 14.1-4 (1992): 261-271.

Delmas, Robert J., Severine Kirchner, Julie M. Palais, and Jean-Robert Petit. "1000 years of explosive volcanism recorded at the South Pole." *Tellus* B 44, no. 4 (1992): 335-350.

de Mora, S. J., D. J. Wylie, and A. L. Dick. "Methanesulphonate and non-sea salt sulphate in aerosol, snow, and ice on the East Antarctic plateau." *Antarctic Science* 9.01 (1997): 46-55.

Domine, Florent, Anne Sophie Taillandier, William R. Simpson, and Ken Severin. "Specific surface area, density and microstructure of frost flowers." *Geophysical research letters* 32, no. 13 (2005).

Ferris, Dave G., Jihong Cole-Dai, Angelica R. Reyes, and Drew M. Budner. "South Pole ice core record of explosive volcanic eruptions in the first and second millennia AD and evidence of a large eruption in the tropics around 535 AD." *Journal of Geophysical Research: Atmospheres* 116, no. D17 (2011).

Frezzotti, M., C. Scarchilli, S. Becagli, M. Proposito, and S. Urbini. "A synthesis of the Antarctic surface mass balance during the last 800 yr." *The Cryosphere* (2013).

Gautier, E., J. Savarino, J. Erbland, A. Lanciki, and P. Possenti. "Variability of sulfate signal in ice core records based on five replicate cores." *Climate of the Past* 12, no. 1 (2016): 103-113.

Global Volcanism Program, 2013. Volcanoes of the World, v. 4.4.3. Venzke, E (ed.). Smithsonian Institution. http://dx.doi.org/10.5479/si.GVP.VOTW4-2013 (http://volcano.si.edu/gvp_about.cfm)

Hammer, C. U. "Past volcanism revealed by Greenland ice sheet impurities." *Nature* 270 (1977): 482-486.

Hara, Keiichiro, Kazuo Osada, Mizuka Kido, Masahiko Hayashi, Katsuji Matsunaga, Yasunobu Iwasaka, Takashi Yamanouchi, Gen Hashida, and Toru Fukatsu. "Chemistry of sea-salt particles and inorganic halogen species in Antarctic regions: Compositional differences between coastal and inland stations." *Journal of Geophysical Research: Atmospheres* 109, no. D20 (2004).

Hara, Keiichiro, Kazuo Osada, Mizuka Kido, M. Yabuki, and Takashi Yamanouchi. "Seasonal variation of fractionated sea-salt particles on the Antarctic coast." *Geophysical Research Letters* 39, no. 18 (2012).

Harder, Susan, Stephen G. Warren, and Robert J. Charlson. "Sulfate in air and snow at the South Pole: Implications for transport and deposition at sites with low snow accumulation." *Journal of Geophysical Research: Atmospheres (1984–2012)* 105.D18 (2000): 22825-22832.

Hidore, John J., John E. Oliver, Mary Snow, and Rich Snow. 2010. *Climatology : an atmospheric science*. n.p.: New York : Prentice Hall, 2010.

Holton, James R., Peter H. Haynes, Michael E. McIntyre, Anne R. Douglass, Richard B. Rood, and Leonhard Pfister. "Stratosphere-troposphere exchange." *Reviews of geophysics* 33, no. 4 (1995): 403-439.

Hoppel, W. A. "Nucleation in the MSA-water vapor system." *Atmospheric Environment (1967)* 21, no. 12 (1987): 2703-2709.

Inoue, Mana. "A Glaciochemical Study of the Mill Island Ice Core." PhD diss., University of Tasmania, 2015.

Jiang, Su, Jihong Cole-Dai, Yuansheng Li, Dave G. Ferris, Hongmei Ma, Chunlei An, Guitao Shi, and Bo Sun. "A detailed 2840 year record of explosive volcanism in a shallow ice core from Dome A, East Antarctica."*Journal of Glaciology* 58, no. 207 (2012): 65-75.

Karlöf, Lars, Elisabeth Isaksson, Jan-Gunnar Winther, Niels Gundestrup, Harro AJ Meijer, Robert Mulvaney, Michel Pourchet et al. "Accumulation variability over a small area in east Dronning Maud Land, Antarctica, as determined from shallow firn cores and snow pits: some implications for ice-core records." *Journal of Glaciology* 51, no. 174 (2005): 343-352.

Kerminen, Veli-Matti, Kimmo Teinilä, and Risto Hillamo. "Chemistry of sea-salt particles in the summer Antarctic atmosphere." *Atmospheric Environment* 34, no. 17 (2000): 2817-2825.

King, John Christopher, and John Turner. *Antarctic meteorology and climatology*. Cambridge University Press, 2007.

Kreutz, Karl J., Paul Andrew Mayewski, Sallie I. Whitlow, and Mark S. Twickler. "Limited migration of soluble ionic species in a Siple Dome, Antarctica, ice core." *Annals of Glaciology* 27 (1998): 371.

Langway Jr, C. C., H. B. Clausen, and C. U. Hammer. "An inter-hemispheric volcanic time-marker in ice cores from Greenland and Antarctica." *Ann. Glaciol* 10 (1988): 102-108.

Langway, CC Jr, K. Osada, H. B. Clausen, Claus U. Hammer, and H. Shoji. "A 10-century comparison of prominent bipolar volcanic events in ice cores." *Journal of Geophysical Research: Atmospheres (1984–2012)* 100, no. D8 (1995): 16241-16247.

Legrand, Michel R., and Robert J. Delmas. "Formation of HCl in the Antarctic atmosphere." *Journal of Geophysical Research: Atmospheres* 93, no. D6 (1988): 7153-7168.

Legrand, Michel. "Sulphur-derived species in polar ice: a review." In *Ice core studies of global biogeochemical cycles*, pp. 91-119. Springer Berlin Heidelberg, 1995.

Legrand, Michel, and Paul Andrew Mayewski. "Glaciochemistry of polar ice cores: a review." *Reviews of geophysics* 35.3 (1997): 219.

Legrand, Michel, and Elizabeth Claire Pasteur. "Methane sulfonic acid to non-sea-salt sulfate ratio in coastal Antarctic aerosol and surface snow." *Journal of Geophysical Research: Atmospheres* 103, no. D9 (1998): 10991-11006.

Liya, Zhou, Yuansheng Li, Dejun Tan, Bo Sun, Jiawen Ren, Lijia Wei, and Henian Wang. "A 780-year record of explosive volcanism from DT263 ice core in east Antarctica." *Chinese Science Bulletin* 51, no. 22 (2006): 2771-2780.

Mahalinganathan, K., M. Thamban, C. M. Laluraj, and B. L. Redkar. "Relation between surface topography and sea-salt snow chemistry from Princess Elizabeth Land, East Antarctica." *The Cryosphere* 6, no. 2 (2012): 505-515.

McCormick, M. Patrick, Larry W. Thomason, and Charles R. Trepte. "Atmospheric effects of the Mt Pinatubo eruption." *Nature* 373, no. 6513 (1995): 399-404.

Minikin, Andreas, Michel Legrand, Julie Hall, Dietmar Wagenbach, Christoph Kleefeld, Eric Wolff, Elizabeth Claire Pasteur, and François Ducroz. "Sulfur-containing species (sulfate and methanesulfonate) in coastal Antarctic aerosol and precipitation." *Journal of Geophysical Research: Atmospheres* 103, no. D9 (1998): 10975-10990.

Moore, John C., Hideki Narita, and Norikazu Maeno. "A continuous 770-year record of volcanic activity from East Antarctica." *Journal of Geophysical Research: Atmospheres* 96, no. D9 (1991): 17353-17359.

Mulvaney, Robert, Elizabeth C. Pasteur, David A. Peel, Eric S. Saltzman, and Pai-Yei Whung. "The ratio of MSA to non-sea-salt sulphate in Antarctic Peninsula ice cores." *Tellus B* 44, no. 4 (1992): 295-303.

Mulvaney, Robert, and Eric W. Wolff. "Evidence for winter/spring denitrification of the stratosphere in the nitrate record of Antarctic firn cores." *Journal of Geophysical Research: Atmospheres (1984–2012)* 98.D3 (1993): 5213-5220.

Obbard, Rachel W., Howard K. Roscoe, Eric W. Wolff, and Helen M. Atkinson. "Frost flower surface area and chemistry as a function of salinity and temperature." *Journal of Geophysical Research: Atmospheres* 114, no. D20 (2009).

O'Dowd, Colin D., Michael H. Smith, Ian E. Consterdine, and Jason A. Lowe. "Marine aerosol, sea-salt, and the marine sulphur cycle: A short review." *Atmospheric Environment* 31, no. 1 (1997): 73-80.

Oliver, John E., ed. *Encyclopedia of world climatology*. Springer Science & Business Media, 2008.

Palmer, Anne S., Tas D. Ommen, Mark AJ Curran, Vin Morgan, Joe M. Souney, and Paul A. Mayewski. "High-precision dating of volcanic events (AD 1301–1995) using ice cores from Law Dome, Antarctica." *Journal of Geophysical Research: Atmospheres (1984–2012)* 106, no. D22 (2001): 28089-28095.

Palmer, Anne S. "Trace Ion Chemistry of Law Dome Ice Cores." PhD diss., University of Tasmania, 2002.

Palmer, Anne S., Vin I. Morgan, Mark AJ Curran, Tas D. Van Ommen, and Paul A. Mayewski. "Antarctic volcanic flux ratios from Law Dome ice cores." *Annals of Glaciology* 35, no. 1 (2002): 329-332.

Pasteur, Elizabeth C., and Robert Mulvaney. "Migration of methane sulphonate in Antarctic firn and ice." *Journal of geophysical research* 105, no. D9 (2000): 11525-11534.

Piel, C., Rolf Weller, M. Huke, and D. Wagenbach. "Atmospheric methane sulfonate and non-sea salt sulfate records at the EPICA deep-drilling site in Dronning Maud Land, Antarctica." *Journal of Geophysical Research-Atmospheres, 111, D03304,* (2006).

Plummer, Christopher T., Mark A. J. Curran, Tas. D. van Ommen, Sune Olander Rasmussen, Andrew D. Moy, Tessa R. Vance, Henrik Brink Clausen, Bo Møllesøe Vinther, and Paul A. Mayewski. "An independently dated 2000-yr volcanic record from Law Dome, East Antarctica, including a new perspective on the dating of the 1450s CE eruption of Kuwae, Vanuatu." *Climate of the Past* 8, no. 6 (2012): 1929-1940.

Proposito, Marco, Silvia Becagli, Emiliano Castellano, Onelio Flora, Laura Genoni, Roberto Gragnani, Barbara Stenni, Rita Traversi, Roberto Udisti, and Massimo Frezzotti. "Chemical and isotopic snow variability along the 1998 ITASE traverse from Terra Nova Bay to Dome C, East Antarctica." *Annals of Glaciology* 35, no. 1 (2002): 187-194.

Poynter, Samuel D.H., Mark J. Curran, Christopher T. Plummer, Andrew D. Moy, Tas D. van Ommen, Jason Roberts, Joe McConnell, David Etheridge. "Volcanic Signal in Ice Core Records from Law Dome, East Antarctica." Poster. International Partnerships in Ice Core Sciences. Hobart, Tasmania, Australia. March 2016.

Preunkert, Susanne, Bruno Jourdain, Michel Legrand, Roberto Udisti, Silvia Becagli, and Omar Cerri. "Seasonality of sulfur species (dimethyl sulfide, sulfate, and methanesulfonate) in Antarctica: Inland versus coastal regions." *Journal of Geophysical Research: Atmospheres* 113, no. D15 (2008).

Proposito, Marco, Silvia Becagli, Emiliano Castellano, Onelio Flora, Laura Genoni, Roberto Gragnani, Barbara Stenni, Rita Traversi, Roberto Udisti, and Massimo Frezzotti. "Chemical and isotopic snow variability along the 1998 ITASE traverse from Terra Nova Bay to Dome C, East Antarctica." *Annals of Glaciology* 35, no. 1 (2002): 187-194.

Pszenny, Alexander AP. "Particle size distributions of methanesulfonate in the tropical Pacific marine boundary layer." *Journal of atmospheric chemistry* 14, no. 1-4 (1992): 273-284.

Rankin, Andrew M., Vanessa Auld, and Eric W. Wolff. "Frost flowers as a source of fractionated sea salt aerosol in the polar regions." *Geophysical Research Letters* 27.21 (2000): 3469-3472.

Rankin, Andrew M., Eric W. Wolff, and Seelye Martin. "Frost flowers: Implications for tropospheric chemistry and ice core interpretation." *Journal of Geophysical Research: Atmospheres* 107, no. D23 (2002).

Ren, Jiawen, Chuanjin Li, Shugui Hou, Cunde Xiao, Dahe Qin, Yuansheng Li, and Minghu Ding. "A 2680 year volcanic record from the DT-401 East Antarctic ice core." *Journal of Geophysical Research: Atmospheres* 115, no. D11 (2010).

Robock, Alan. "Volcanic eruptions and climate." *Reviews of Geophysics* 38, no. 2 (2000): 191-219.

Roscoe, Howard K., B. Brooks, A. V. Jackson, M. H. Smith, S. J. Walker, Rachel W. Obbard, and Eric W. Wolff. "Frost flowers in the laboratory: Growth, characteristics, aerosol, and the underlying sea ice." *Journal of Geophysical Research: Atmospheres* 116, no. D12 (2011).

Shaw, Glenn E. "Antarctic aerosols: A review." *Reviews of Geophysics* 26.1 (1988): 89-112.

Sigl, Michael, Joseph R. McConnell, Lawrence Layman, Olivia Maselli, Ken McGwire, Daniel Pasteris, Dorthe Dahl-Jensen *et al.* "A new bipolar ice core record of volcanism from WAIS Divide and NEEM and implications for climate forcing of

the last 2000 years." *Journal of Geophysical Research: Atmospheres* 118, no. 3 (2013): 1151-1169.

Sigl, Michael, Joseph R. McConnell, Matthew Toohey, Mark Curran, Sarah B. Das, Ross Edwards, Elisabeth Isaksson *et al.* "Insights from Antarctica on volcanic forcing during the Common Era." *Nature Climate Change* 4, no. 8 (2014): 693-697.

Sigl, Michael, M. Winstrup, Joseph R. McConnell, K. C. Welten, Guy Plunkett, F. Ludlow, U. Büntgen *et al.* "Timing and climate forcing of volcanic eruptions for the past 2,500 years." *Nature* (2015).

Smith, Barbara T., Tas D. van Ommen, and Mark AJ Curran. "Methanesulphonic acid movement in solid ice cores." *Annals of Glaciology* 39, no. 1 (2004): 540-544.

Stohl, A., P. Bonasoni, P. Cristofanelli, W. Collins, Johann Feichter, A. Frank, C. Forster et al. "Stratosphere-troposphere exchange: A review, and what we have learned from STACCATO." *Journal of Geophysical Research: Atmospheres* 108, no. D12 (2003).

Thompson, Lonnie G., D. A. Peel, E. Mosley-Thompson, R. Mulvaney, J. Dal, P. N. Lin, M. E. Davis, and C. F. Raymond. "Climate since AD 1510 on Dyer Plateau, Antarctic Peninsula: evidence for recent climate change." *Annals of Glaciology* 20, no. 1 (1994): 420-426.

Traufetter, Fidan, Hans Oerter, Hubertus Fischer, Rolf Weller, and Heinz Miller. "Spatio-temporal variability in volcanic sulphate deposition over the past 2 kyr in snow pits and firn cores from Amundsenisen, Antarctica." *Journal of Glaciology* 50, no. 168 (2004): 137-146.

Turner, John. "The meteorology and climatology of the Antarctic plateau." Memorie della Societa Astronomica Italiana Supplementi 2 (2003): 26.

Turner, John, and Stephen Pendlebury. *The international Antarctic weather forecasting handbook.* British Antarctic Survey, 2004.

Udisti, R., U. Dayan, S. Becagli, M. Busetto, D. Frosini, M. Legrand, F. Lucarelli *et al.* "Sea spray aerosol in central Antarctica. Present atmospheric behaviour and implications for paleoclimatic reconstructions." *Atmospheric Environment* 52 (2012): 109-120.

Wagnon, Paul, Robert J. Delmas, and Michel Legrand. "Loss of volatile acid species from upper firn layers at Vostok, Antarctica." *Journal of Geophysical Research: Atmospheres (1984–2012)* 104.D3 (1999): 3423-3431.

Weller, Rolf, and Dietmar Wagenbach. "Year-round chemical aerosol records in continental Antarctica obtained by automatic samplings." *Tellus B* 59, no. 4 (2007): 755-765.

Wolff, Eric W., Andrew M. Rankin, and Regine Röthlisberger. "An ice core indicator of Antarctic sea ice production?." *Geophysical Research Letters* 30.22 (2003).