

11-30-1997

# Methanesulfonate in the Greenland Ice Sheet Project 2 Ice Core

E. S. Saltzman

P-Y. Whung

Paul Andrew Mayewski

University of Maine, paul.mayewski@maine.edu

Follow this and additional works at: [https://digitalcommons.library.umaine.edu/ers\\_facpub](https://digitalcommons.library.umaine.edu/ers_facpub)



Part of the [Glaciology Commons](#), and the [Hydrology Commons](#)

---

## Repository Citation

Saltzman, E. S.; Whung, P-Y.; and Mayewski, Paul Andrew, "Methanesulfonate in the Greenland Ice Sheet Project 2 Ice Core" (1997).  
*Earth Science Faculty Scholarship*. 262.

[https://digitalcommons.library.umaine.edu/ers\\_facpub/262](https://digitalcommons.library.umaine.edu/ers_facpub/262)

This Article is brought to you for free and open access by DigitalCommons@UMaine. It has been accepted for inclusion in Earth Science Faculty Scholarship by an authorized administrator of DigitalCommons@UMaine. For more information, please contact [um.library.technical.services@maine.edu](mailto:um.library.technical.services@maine.edu).

## Methanesulfonate in the Greenland Ice Sheet Project 2 Ice Core

E. S. Saltzman

Division of Marine and Atmospheric Chemistry, Rosenstiel School of Marine and Atmospheric Science University of Miami, Miami, Florida

P.-Y. Whung

Cooperative Institute of Marine and Atmospheric Science, Rosenstiel School of Marine and Atmospheric Science University of Miami, Miami, Florida

P. A. Mayewski

Glacial Research Group, Climate Change Research Center, Institute for the Study of Earth, Ocean, and Spaces University of New Hampshire, Durham

**Abstract.** In this paper we present measurements of methanesulfonate in the Greenland Ice Sheet Project 2 (GISP2) ice core. Methanesulfonate is an atmospheric oxidation product of dimethylsulfide. The GISP2 methanesulfonate record contains information about the atmospheric loading of biogenic sulfur over the past 110 kyr and its relationship to climate change. The GISP2 data set supports the inferences made from the Renland ice core from Greenland that the glacial atmosphere over Greenland had reduced concentrations of biogenic sulfur compared with the present day [Hansson and Saltzman, 1993]. We conclude that the flux of biogenic sulfur from the North Atlantic Ocean must have been lower during glacial times and speculate that this decrease may have been related to differences in phytoplankton speciation. The data suggest that changes in direct radiative forcing from biogenic sulfur aerosols would act as negative feedback to the glacial/interglacial climate cycles in this region.

### Introduction

The sulfur cycle is of particular important to atmospheric chemistry because of the role of sulfuric acid as a major aerosol-forming constituent. These aerosols can provide sites for heterogeneous chemical transformations that may not otherwise occur in the atmosphere and are the major source for cloud condensation nuclei over much of the Earth. Sulfuric acid aerosols can interact strongly with incoming solar radiation because of their submicron size and high number density. They also interact with outgoing planetary radiation indirectly via their effects on cloud droplet number and size distribution and, potentially, on cloud duration and areal extent. The precursors for sulfuric acid in air are reduced sulfur gases, primarily sulfur dioxide (SO<sub>2</sub>) from anthropogenic and volcanic sources, and dimethylsulfide (DMS) from biogenic sources. It is well established that the atmospheric sulfur budget has been severely impacted by combustion of fossil fuels, and various estimates place the anthropogenic emissions at roughly 50–75% of the total emissions on a global basis [Langner and Rodhe, 1992; Bates *et al.*, 1992b; Spiro *et al.*, 1992].

Considerable research on the emissions of DMS from the oceans has been done during the past two decades [Andreae, 1990; Bates *et al.*, 1992b; Berresheim *et al.*, 1995; Saltzman,

1995]. However, we have little knowledge of the long-term temporal variability of DMS emissions from the ocean or of the factors which control it. It has been suggested that there are potential feedbacks between the biogenic sulfur cycle and the radiation budget which may affect the climate of the Earth on long timescales [Shaw, 1983; Charlson *et al.*, 1987]. One way to study this question is to examine the record of atmospheric sulfur as deposited in polar ice cores. This record contains evidence of natural variability which can be used to (1) assess the magnitude of potential changes in aerosol radiative forcing and (2) examine the timing of changes in atmospheric sulfur in order to understand the factors controlling them.

In this paper we present measurements of methanesulfonate (MSA) from the Greenland Ice Sheet Project 2 (GISP2) ice core in central Greenland. MSA is an atmospheric oxidation product of DMS which can be useful as a tracer for the origin of sulfur in air or precipitation. Numerous studies have been carried out to examine the distribution of MSA in the modern atmosphere [Saltzman *et al.*, 1983; 1985; Berresheim, 1987; Pszenny *et al.*, 1989; Savoie and Prospero, 1989; Berresheim *et al.*, 1990; Ayers *et al.*, 1991; Bates *et al.*, 1992a; Nguyen *et al.*, 1992; Savoie *et al.*, 1992; Li *et al.*, 1993; Gao *et al.*, 1996; Huebert *et al.*, 1996a; Heuber *et al.*, 1996b; Li *et al.*, 1996]. Whung *et al.* [1994] carried out a detailed study of MSA over the last 200 years at a south central Greenland site. Low-resolution, long-term records have also been obtained from the Vostok and Dome C ice cores in east Antarctica [Saigne and Legrand,

Copyright 1997 by the American Geophysical Union.

Paper number 97JC01377.  
0148-0227/97/97JC-01377\$09 00

1987; Legrand *et al.*, 1991] and the Renland ice core in east Greenland [Hansson and Saltzman, 1993]. Results from these cores revealed significant glacial/interglacial variability. The GISP2 core is unique in that it represents a very high resolution record from the main Greenland Ice Sheet covering more than 110 kyr. In this paper we focus on the long-term trends (0-110 kyr) in the GISP2 record.

### Ice Core Sampling and Analysis

The ice core samples used in this project were obtained from the GISP2 ice core which was drilled during 1990-1993 at Summit, Greenland. The main GISP2 ice core is 3040 m in length. The core was subsampled in the field using band saws to obtain a longitudinal rectangular section for ion analysis. Subsampling of the uppermost 335 m of the core was done by rinsing the subsections with Milli-Q water to remove contamination. In the depth intervals 335-710 and 1370-1510 m, subsamples were mechanically scraped using a rotating carbide bit. For the remainder of the core the subsections were sampled using a continuous concentric melter that yields a radial melt  $\sim 2$  cm in diameter from the center of the subsection.

The strategy for sampling the core was designed to provide biannual resolution for as much of the core as possible. The thickness of individual samples decreased downcore, from  $\sim 50$  cm at 94 m to  $\sim 20$  cm at the base of the core. At the base of the core each sample represented  $\sim 50$  years of accumulation. A subsample of the melt was stored frozen in plastic vials and analyzed at the University of Miami for MSA. The remainder of the melt was used for the analysis of major anions and cations at the University of New Hampshire. In total,  $\sim 11,700$  samples were analyzed for MSA during the course of this project.

The analysis of the ice core samples for MSA was done using chemically suppressed ion chromatography [Whung *et al.*, 1994]. The instrument used was a modular ion chromatograph with Dionex AG4/AS4 columns and a membrane suppresser. These columns were chosen so as to provide baseline resolution between MSA and pyruvate, which is an occasional contaminant in laboratory air and plastic vials. Samples (5 mL) were loaded onto a Dionex Trace Anion Concentrator (TAC) precolumn, either manually or by an autosampler. Standard addition experiments demonstrated quantitative recovery of analyte from the precolumn. The analysis was carried out isocratically using NaOH eluants (5.55 mM), and the columns were rinsed with 100 mM NaOH between samples to remove strongly bound anions. Standards were prepared by serial dilution of pure methanesulfonic acid (Malinckrodt) and were run daily. The detection limit of the analysis is 0.02 ppb with a precision of better than  $\pm 5\%$  at 1 ppb.

Other sources of data from the GISP2 ice core discussed in this paper include measurements of major ion chemistry (sulfate ( $\text{SO}_4^{2-}$ ), sodium ( $\text{Na}^+$ ), and calcium ( $\text{Ca}^{2+}$ )) made at the University of New Hampshire and oxygen isotope ratios in ice measured by mass spectrometry at the University of Washington [Grootes *et al.*, 1993]. The age-depth relationship used here was developed with a combination of annual layer counting of visible stratigraphy, electrical conductivity measurements, ion chemistry and particulates, and correlation of oxygen isotopic composition of ice and oxygen isotopic composition of  $\text{O}_2$  [Alley *et al.*, 1993; Bender

*et al.*, 1994]. The dating is given in terms of calendar years before present, where "present" is 1950.

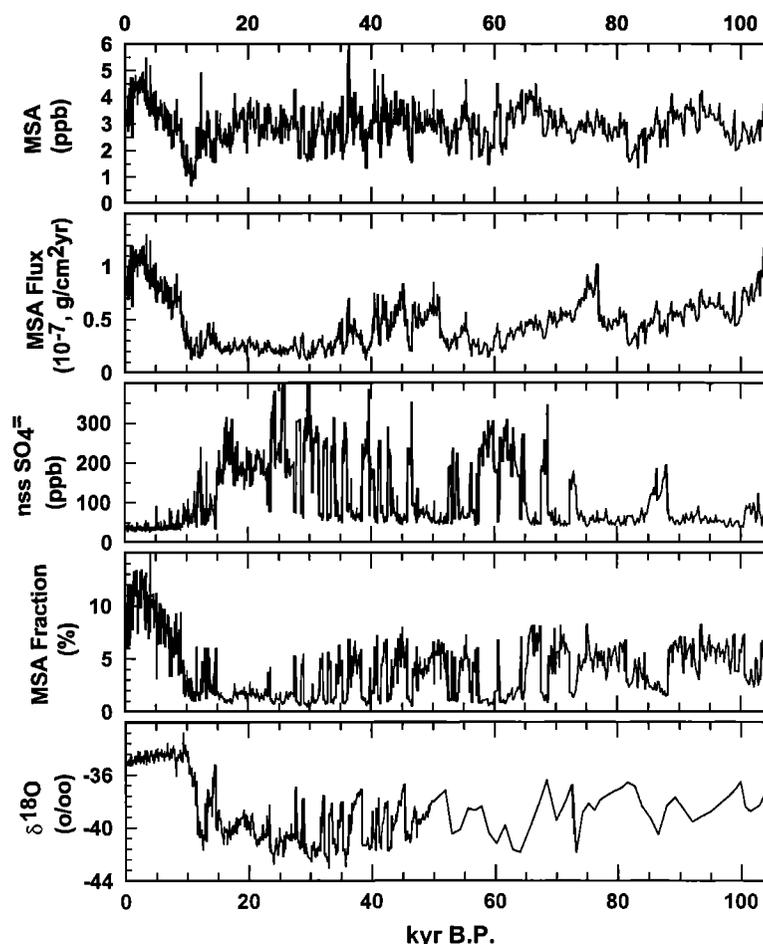
## Results and Discussion

### Long Term Trends

Over the entire length of the GISP2 core, the MSA concentration ranged from 0.04 to 11.82 ppb (ng/kg), with a mean of  $2.9 \pm 1.2$  ( $1\sigma$ , number of samples ( $n$ ) = 11,616). Figure 1 is a plot of the GISP2 data from the surface to a depth of 3040 m, representing  $\sim 110$  kyr. The data shown were averaged at 50-year intervals. Because of thinning of the ice core layers with depth, each 50-year average point consists of up to 25 individual analyses near the surface and as few as one to two near the bottom. Also shown is the oxygen isotopic composition of the ice from Grootes *et al.* [1993], averaged in the same manner.

MSA concentrations do not decrease monotonically with depth in the GISP2 ice core, supporting the inference made from other deep ice cores [Saigne and Legrand, 1987; Legrand *et al.*, 1991; Hansson and Saltzman, 1993] that MSA is chemically stable after burial and below the firm/ice transition. This observation does not preclude modification of the atmospheric MSA signal during deposition and/or firnification. There is evidently a relationship between climate change and ice core MSA concentrations in the core, as evidenced by the marked fluctuations at the glacial/interglacial transition. The Holocene excursion from the mean is positive; that is Holocene MSA concentrations are significantly greater than the mean. This trend is similar to that observed in the Renland ice core drilled in a small ice sheet in east Greenland, isolated from the main Greenland Ice Sheet [Johnsen and Dansgaard, 1992; Hansson and Saltzman, 1993]. It is opposite in sign to the trend observed in Antarctic ice cores [Saigne and Legrand, 1987; Legrand *et al.*, 1991], where the interglacial periods are MSA minima.

Deducing possible trends in paleoatmospheric conditions based on variations in ice core chemical concentrations is complicated by the fact that variations in snow accumulation rate may also influence the ice core record. If a chemical accumulates in ice solely owing to wet deposition, then variations in precipitation or accumulation rate should have a relatively minor effect on the concentration of the chemical in the ice core. If the chemical is deposited predominantly by dry deposition, variations in snow accumulation rate act as a variable diluent. In this case the concentration would vary inversely with the accumulation rate. Such variations may arise either from variations in precipitation rate or variations in the losses of water vapor from the ice sheet due to sublimation. There have been significant changes in accumulation at Summit during the past 110 kyr, as evidenced by both annual layer counting studies [Alley *et al.*, 1993] and glaciological flow modeling [Cutler *et al.*, 1995]. Warm periods are characterized by generally high accumulation rates, while cold periods have low accumulation rates. These changes reflect the thermodynamic effects of changing ice sheet temperatures as well as changes in air mass origin [Bromwich *et al.*, 1993; Kapsner *et al.*, 1995]. One way to illustrate the effect of variable accumulation rate is to calculate the depositional flux in units of mass per unit area per year. The calculation of depositional flux  $F_{\text{MSA}}$  in units of grams per square centimeter per year is:



**Figure 1.** Fifty-year averaged data from the Greenland Ice Sheet Project 2 (GISP2) ice core for the last 110 kyr. From top - 1) MSA concentration (ppb), 2) MSA flux ( $10^{-7}$  g/cm<sup>2</sup>/yr) see text for explanation, 3) non-seasalt SO<sub>4</sub><sup>2-</sup> concentration (ppb), 4) MSA fraction (%) is defined as  $100 \times \text{MSA} / (\text{nss SO}_4^{2-} + \text{MSA})$ , 5) oxygen isotopic composition of ice (per mil, SMOW; *Grootes. et al.*, 1993).

$$F_{\text{MSA}} = C_{\text{MSA,ice}} \times A_{\text{H}_2\text{O}} \times \rho_{\text{ice}} \quad (1)$$

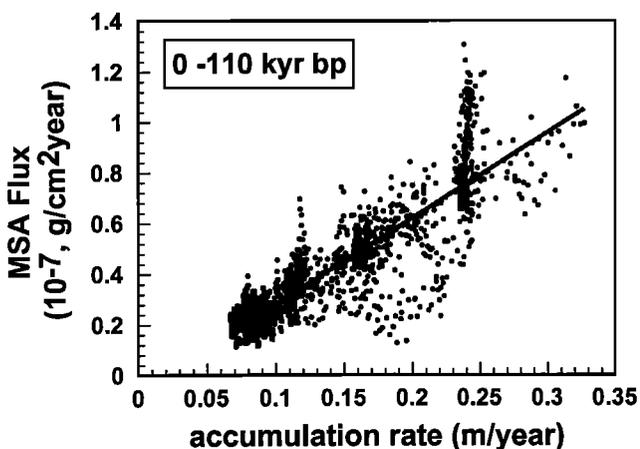
where  $C_{\text{MSA,ice}}$  is the ice core MSA concentration in parts per billion,  $A$  is the accumulation rate in centimeters per year, and  $\rho$  is the ice density in grams per cubic centimeter. A depth profile of the MSA flux is shown in Figure 1. The MSA flux profile exhibits more distinct climatic variability than MSA concentration. There is a major increase in flux associated with the warm periods around 75, 40-55, and 0-10 kyr B.P. The largest change in accumulation rate occurred between the last glacial maximum and the Holocene and was approximately a factor of 5.

Clearly, the interpretation of ice core chemical trends is sensitive to assumptions regarding the relative importance of wet versus dry deposition. *Legrand and Kirchner* [1990] examined the relationship between depositional flux and accumulation rates of nitrate between several East Antarctic sites in order to infer the importance of dry versus wet deposition, making the assumption that the atmosphere over all the sites had essentially uniform chemical composition. *Whung et al.* [1994] examined this relationship for MSA using data from a single shallow ice core from south central Greenland (ice core 20D). *Alley et al.* [1995] used a similar model to examine major ion fluxes from the late glacial portion of the GISP2 ice core. *Whung et al.* [1994] concluded

that dry deposition has been a minor component of the total deposition of MSA during the past 200 years. Those calculations assume that deposition of chemicals to ice obey the following simple model:

$$F_{\text{MSA}} = (C_{\text{MSA,air}} \times V_d) + (C_{\text{MSA,air}} \times S_{\text{MSA}} \times P_{\text{H}_2\text{O}}) \quad (2)$$

where,  $F_{\text{MSA}}$  (grams per square centimeter per year) is as defined above,  $C_{\text{MSA,air}}$  (parts per billion) is the atmospheric concentration of MSA,  $V_d$  (grams per square centimeter per year) is the dry-deposition velocity for MSA-containing aerosols,  $S_{\text{MSA}}$  is the dimensionless scavenging ratio for MSA ( $S_{\text{MSA}} = C_{\text{MSA,precip}} / C_{\text{MSA,air}}$ ), and  $P_{\text{H}_2\text{O}}$  is the precipitation rate in grams per square centimeter per year. If the scavenging ratio, deposition velocity, and atmospheric concentration of MSA remained constant over time, one would expect to find a linear relationship between the depositional flux of MSA and the accumulation rate. The slope of a regression line should reflect the concentration of MSA in precipitation, and the intercept (i.e., the value of the MSA flux when  $P_{\text{H}_2\text{O}} = 0$ ) should reflect the importance of dry deposition. Figure 2 illustrates the relationship between the MSA flux and the accumulation rate for the GISP2 record over the past 110 kyr using the 50-year averaged data shown in Figure 1. Note that accumulation (i.e., precipitation minus sublimation) is used as a proxy for paleoprecipitation, which is not known. The



**Figure 2.** Depositional flux of MSA ( $F_{\text{MSA}}$ ) vs accumulation rate ( $A_{\text{H}_2\text{O}}$ ) [from Cutler *et al.*, 1995]. Each point represents a 50-year average of MSA concentration and accumulation rate. The line shown is a linear least-squares regression and is given in the following equation:  $F_{\text{MSA}} = 3.38 \times A_{\text{H}_2\text{O}} - 0.057$ ,  $r^2 = 0.738$ .

intercept of the linear regression line is slightly negative, but not significantly different from zero at the 95% confidence interval, suggesting that dry deposition is not an important component of the overall flux. This conclusion is in general agreement with field studies of aerosol depositional processes carried out in Greenland [Bergin *et al.*, 1994]. The equation of the regression line from the GISP2 core is similar to that obtained in south central Greenland [Whung *et al.*, 1994].

The inference that dry deposition is not a major component of the overall flux suggests that the ice core MSA concentration should contain the best representation of paleoatmospheric concentrations, while the MSA flux reflects largely the frequency and duration of precipitation events. Given the large number of samples and long duration of the record, there is a surprisingly small amount of scatter in the relationship between MSA flux and accumulation rate (Figure 2). This implies that there is relatively little variability in the atmospheric concentrations of MSA on long timescales. This is particularly true of the period between 20 and 110 kyr B.P. but is less so between 0 and 20 kyr B.P. This period is discussed in more detail below.

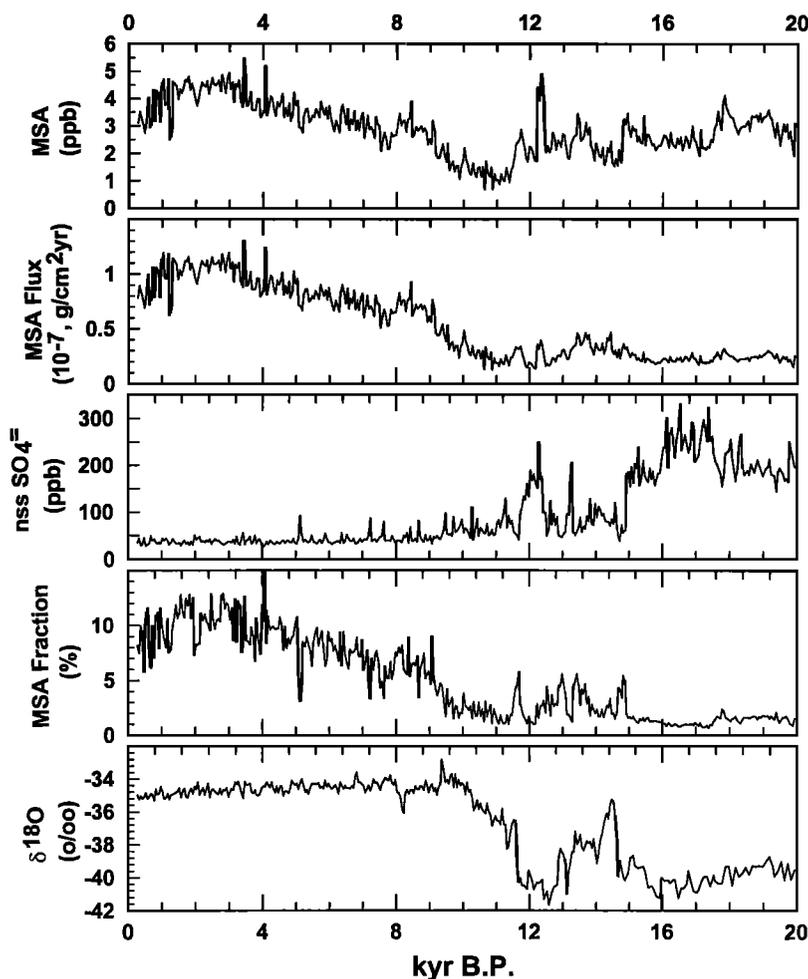
### The Last 20 kyr

Figure 3 is an expanded view of the MSA concentration, depositional flux, and oxygen isotope data covering the last 20 kyr. Prior to the onset of deglaciation (16 kyr B.P.), MSA concentrations were near their historical mean for the previous 80 kyr. During the Bolling-Allerod, ~ 12-16 kyr B.P. as evidenced by the oxygen isotope record, the MSA concentration and flux behaved differently. The concentration profile exhibits more variability, first increasing, then dropping rapidly at ~ 15 kyr B.P. The flux profile does not exhibit such a decrease. The concentration also exhibits a large peak at the Younger Dryas event (12.5 kyr B.P.), which is somewhat suppressed in the flux profile. This is interesting, in that the MSA signal increased at the beginning of the Younger Dryas cooling event, whereas over the record as a whole, colder periods are associated with low MSA levels. Within the Younger Dryas the MSA

concentration and flux decrease, reaching their minima at 11 and 12 kyr B.P., respectively. The Younger Dryas minimum in MSA concentration is actually considerably lower than the level during the last glacial maximum. The flux during the Younger Dryas, on the other hand, is essentially the same as the level during the last glacial maximum. The MSA signals do not reflect the sharp warming at the end of the Younger Dryas (11.5 kyr B.P.) shown in the isotope record. Instead, the MSA concentration and flux both begin to increase gradually at this time. The rate of increase of the MSA signals increases around 10 kyr B.P., when the oxygen isotopic composition suggests that the glacial/interglacial warming transition is complete and the Holocene has begun. The MSA concentration and flux continue to increase until ~ 8 kyr bp where there is a minor but sharp decrease. This feature lags a similar decrease in oxygen isotope ratio at ~ 8.2 kyr bp. At ~ 7.5 kyr B.P., the MSA concentration and flux resume increasing until around 2 kyr B.P. where they reach their maximum for the entire GISP2 record.

The very slow increase in MSA at the beginning of the Holocene clearly suggests that the MSA record reflects responses to changes in climate and atmospheric/ocean circulation, rather than the forces driving climate change. It is surprising that MSA continued to increase for several thousand years after the end of the glacial/interglacial transition, when the isotope record suggests that climate stabilized rapidly. The MSA increase during the Holocene suggests that perhaps there were changes in either surface ocean biology or atmospheric transport that occurred over much longer timescales than the mixing time of the atmosphere or surface ocean.

Overall, during the past 20 kyr the MSA flux clearly behaves more as one would expect for a signal that reflects climatic change, while the concentration profile appears somewhat decoupled from the climate record. This is surprising given our conclusion in the previous section that dry deposition is not significant. Figure 4 is a plot of MSA flux versus accumulation rate for the last 20 kyr B.P. only. The nature of this data is clearly very different from the record as a whole and is not well described by the simple model discussed above (equation (2)). The data set appears to consist of two distinct populations: (1) glacial ice in which the MSA flux is nearly constant over a wide range of accumulation rates and (2) Holocene ice in which there are wide variations in the MSA flux with little variation in accumulation rate. We can speculate on the causes for these trends. The glacial segment of the data is what one might expect from the case in which dry deposition was dominant. There is evidence from several Greenland ice core chemistry records [Herron and Langway, 1985; Hansson, 1994; Alley *et al.*, 1995] that aerosol loading of the atmosphere during the glacial maximum was extremely high owing to the input of both continental dust and sea salt. It is possible that such particles scavenged other chemicals such as MSA, increasing their dry-deposition velocity. Increased wind speed during the glacial compared with interglacial climates should also increase dry-deposition velocities [Petit *et al.*, 1981; Lautenschlager and Hererich, 1990]. However, it seems unlikely that dry deposition would so dominate deposition at the site that the MSA flux would become invariant with water accumulation. The Holocene portion of the record is easier to explain. It appears likely that while Holocene accumulation rates varied little, there must have been significant changes in



**Figure 3.** Fifty year averaged data from the GISP2 ice core for the last 20 kyr bp. From top - 1) MSA concentration (ppb), 2) MSA flux ( $10^{-7}$ g/cm<sup>2</sup>yr) see text for explanation, 3) SO<sub>4</sub><sup>2-</sup> concentration (ppb), 4) MSA fraction defined as  $100 \times \text{MSA}/(\text{nss SO}_4^{2-} + \text{MSA})$ , 5) oxygen isotopic composition of ice (per mil, SMOW; [Grootes. *et al.*, 1993]).

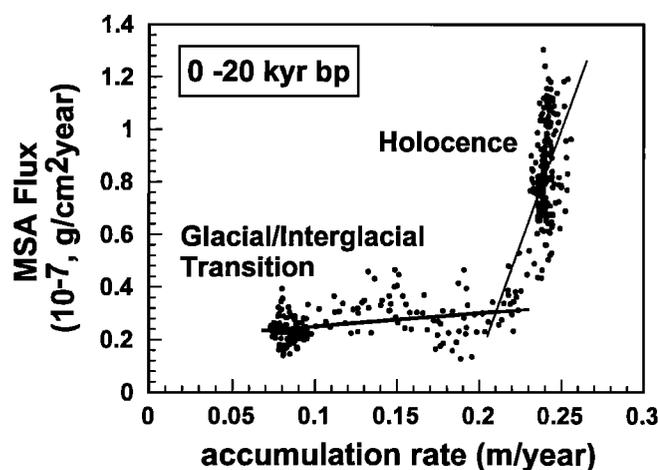
the concentration of MSA in the atmosphere. We believe that this is a case in which the ice core record clearly and unambiguously reflects changes in the atmospheric concentration of MSA.

#### Relationship Between MSA and Sulfate

The relationship between MSA and SO<sub>4</sub><sup>2-</sup> in the GISP2 ice core can provide some insight into the origin of atmospheric sulfur over Greenland and its relationship to climate. The MSA to non-sea salt sulfate (nss SO<sub>4</sub><sup>2-</sup>) ratio (expressed as the MSA fraction) can be used as a tracer for the input of biogenic sulfur into a given air mass or ice core. The MSA fraction is defined as  $100 \times \text{MSA}/(\text{SO}_4^{2-} + \text{MSA})$  [Whung *et al.*, 1994]. MSA fraction for the GISP2 ice core is shown in Figures 1 and 3. For those calculations we used the GISP2 Na<sup>+</sup> record to obtain the sea-salt component of the total sulfate. Sea-salt SO<sub>4</sub><sup>2-</sup> is a small fraction of the total sulfate (<6%) in the core.

The variability of SO<sub>4</sub><sup>2-</sup> in the GISP2 ice core is strikingly different from that of MSA (Figure 1). During glacial conditions, MSA fraction was highly variable, ranging from 8% during the warmer periods to 0.2% during the cold periods. This variability in MSA fractions was driven largely

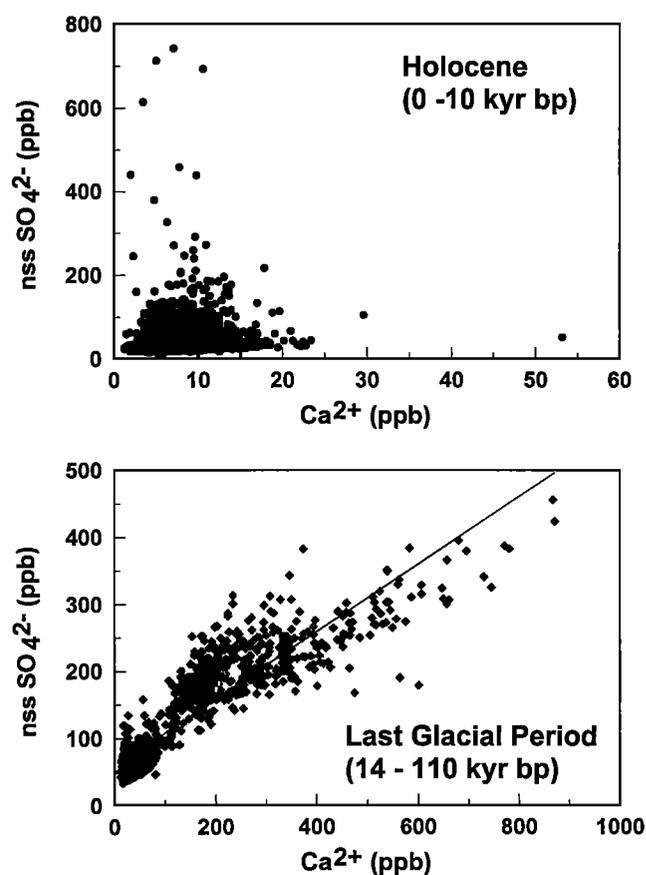
by variability in the SO<sub>4</sub><sup>2-</sup> levels. SO<sub>4</sub><sup>2-</sup> concentrations ranged from a baseline concentration of 50–60 ppb during the warmer periods to 200–300 ppb during cold periods, while MSA concentrations varied by only a factor of 2. The general pattern of SO<sub>4</sub><sup>2-</sup> variability in glacial conditions mirrors that of a number of major ions in the core, including Na<sup>+</sup> and Ca<sup>2+</sup>, reflecting higher wind speeds, aridity, and exposure of continental shelves associated with cold climates. A similar pattern was observed for SO<sub>4</sub><sup>2-</sup> in the Dye 3, Camp Century, and Renland ice cores [Herron and Langway, 1985; Hansson, 1994]. Holocene SO<sub>4</sub><sup>2-</sup> concentrations were generally low and uniform, with baseline concentration of 40–50 ppb. As the Holocene progressed, the MSA fractions increased from 2 to >10%, driven largely by the trend of increasing MSA concentrations. The MSA fraction peaked at approximately 350 year B.P., corresponding to the maximum in MSA concentration. The relationship among MSA fraction, MSA concentration, and SO<sub>4</sub><sup>2-</sup> concentration suggests that there is a major SO<sub>4</sub><sup>2-</sup> source that is not associated with the oceanic emissions of DMS. The two potential sources are terrestrial and volcanic emissions. The terrestrial contribution can be estimated by examining the relationship between nss SO<sub>4</sub><sup>2-</sup> and Ca<sup>2+</sup> (Figure 5). Although there is a strong correlation



**Figure 4.** MSA flux ( $F_{\text{MSA}}$ ) vs. water accumulation rate ( $A_{\text{H}_2\text{O}}$ ) for the period 0-20 kyr bp in the GISP2 ice core. The linear regression is expressed as  $F_{\text{MSA}} = 17.604 \times A_{\text{H}_2\text{O}} - 3.4$  ( $r^2 = 0.29$ ) for the Holocene and,  $F_{\text{MSA}} = 0.586 \times A_{\text{H}_2\text{O}} + 0.19$  ( $r^2 = 0.14$ ) for the glacial/interglacial transition.

between  $\text{nss SO}_4^{2-}$  and  $\text{Ca}^{2+}$  during glacial times, the slope of a linear regression line yields a value of  $\sim 0.5$ . The mean sedimentary  $\text{SO}_4^{2-}/\text{Ca}^{2+}$  weight ratio is  $\sim 0.1$  [Holland, 1978; Mason and Moore, 1982], suggesting that weathering products contribute  $< 20\%$  of the total sulfate in the GISP2 ice core. In order for the calcium-related sulfate to be a major  $\text{SO}_4^{2-}$  source, it would have to have a significant component of pure gypsum. The observed  $\text{SO}_4^{2-}/\text{Ca}^{2+}$  ratio of 0.5 could be obtained for a mixture of  $\sim 80\%$  average crustal material and 20% gypsum.

An alternative hypothesis is that the elevated  $\text{nss SO}_4^{2-}$  concentrations associated with cold climates are derived from volcanic sources. Recent model simulations of the atmospheric sulfur budget suggest that noneruptive emissions of volcanic  $\text{SO}_2$  are a significant component of the Arctic atmospheric sulfur budget, particularly for the mid troposphere and upper troposphere [Langner and Rodhe, 1992; Chin and Jacob, 1996]. It should be noted that the direct, measurement-based source estimates for noneruptive emissions are highly uncertain [Bates et al., 1992b]. If, in fact, volcanic emissions are the principle source for elevated  $\text{SO}_4^{2-}$  during cold climates, one must find a mechanism for modulating such emissions in synchronicity with climatic changes. It has been proposed that changes in the rate of volcanic emissions control climate change [Pollack et al., 1976; Rampino and Self, 1982], and some evidence has been presented that the frequency of volcanic eruptions has varied over time [Zielinski et al., 1994]. Volcanoes may influence climate through both the explosive injection of aerosols and gases into the stratosphere and, possibly, through the emissions of  $\text{SO}_2$  into the troposphere. However, it does not seem likely that variations in volcanic emissions dominate climate variability on all the timescales exhibited in the GISP2 and other ice core records. Alternatively, the modulation of the ice core  $\text{SO}_4^{2-}$  signal may reflect changes in atmospheric transport patterns resulting from climate change due to other, unrelated causes. The increased dust loading in GISP2 glacial ice suggests that meridional transport was enhanced during cold climates and perhaps indicates that the source of elevated glacial  $\text{SO}_4^{2-}$  levels was at low or midlatitudes.



**Figure 5.** The relationship between  $\text{nss SO}_4^{2-}$  and  $\text{Ca}^{2+}$  in the GISP2 ice core for the Holocene (0-10 kyr bp) and last glacial period (14 - 110 kyr bp). The regression line is expressed as  $[\text{nss SO}_4^{2-}] = 0.5 \times [\text{Ca}^{2+}] + 57.65$  and  $r^2 = 0.83$ .

Although the Holocene MSA fractions are larger than those in glacial ice, they are still lower than expected for high-latitude sites dominated by marine biogenic sources. For example, the mean summertime MSA fractions in aerosols at Mace Head, Ireland ( $53.32^\circ\text{N}$ ,  $9.85^\circ\text{W}$ ), and Mawson, Antarctica ( $67.60^\circ\text{S}$ ,  $62.50^\circ\text{E}$ ), are 18.4% and 26.3%, respectively [Galloway et al., 1993; Savoie et al., 1993]. Whung et al. [1994] argued that low-MSA fractions in Greenland ice reflect transport of marine aerosols from lower latitudes to the Greenland ice sheet. Marine boundary layer aerosols in tropical and subtropical regions exhibit MSA fractions in the 5-10% range [Savoie et al., 1989]. Therefore biogenic input with a mean MSA fraction of 10% could explain the observed Holocene values, with no input of volcanic sulfur. If the biogenic component of the sulfur in Holocene ice was high latitude in origin with an MSA fraction of 25%, an additional  $\text{SO}_4^{2-}$  source is needed. This source, presumably volcanic, would need to be 1.5 times as large as the biogenic input in order to obtain the observed Holocene MSA fractions.

There is no evidence in the GISP2 core for an increase in the MSA fraction of biogenic-derived aerosols in the glacial atmosphere. This is surprising, as one might expect that during colder conditions the aerosol might look chemically more like that in cold regions today. This was observed at Vostok, Antarctica [Legrand et al., 1991]. The decrease in MSA fraction in the GISP2 core during cold periods must indicate that either (1) the biogenic sources were shifted to

lower latitudes and warmer waters compared with the source regions affecting Greenland today or (2) additional sulfur from nonmarine sources impacted the site.

During deglaciation and into the Holocene the MSA fraction increased from its minimum of ~ 1% at 11 kyr to its maximum of 12% around 3 kyr B.P. These variations are driven largely by the changes in MSA concentration and most likely reflect changes in the North Atlantic biogenic sulfur source strength. An interesting aspect of the record is that the MSA concentration and MSA fraction continue to increase long after the oxygen isotopic signal suggests that Holocene climate stabilized (7-8 kyr B.P.). As mentioned earlier, such a long time constant is not expected for changes in surface ocean or atmospheric circulation, and we would not have expected to see such a gradual change for a biogenic emission like DMS. The data imply that it took several thousand years for the biogenic sulfur cycle over the North Atlantic Ocean to establish its current pattern. The fact that MSA fractions were increasing during this period suggests that the phenomenon may be related to the establishment of the high-latitude fauna that generate high-MSA fraction aerosols compared with low latitude sources.

#### Relationship Between MSA and Sodium

As mentioned above, the Na<sup>+</sup> record exhibits a marked increase in both mean concentration and variability during glacial periods [Mayewski *et al.*, this issue]. Typical glacial Na<sup>+</sup> concentrations were of the order of 30 parts per billion, while Holocene values were only 5 ppb. This increase suggests that glacial wind speeds were significantly greater than those of interglacials and that the trajectories of air masses influencing precipitation at Summit were in contact with the sea surface. This is a key point that places an important constraint on the interpretation of the MSA data. The increase in glacial Na<sup>+</sup> concentrations means that if glacial sea surface DMS concentrations were similar to today, the air/sea exchange of DMS and the eventual MSA concentration in glacial ice should have increased many fold over Holocene levels. The increase in Na<sup>+</sup> effectively counters the argument that sea ice expansion in the glacial North Atlantic restricted the area available as a source region for DMS emissions. Even to maintain a constant supply of MSA to Summit, given the increased wind speeds, one must conclude that the concentration of DMS decreased significantly in the source regions. This interpretation requires that the Na<sup>+</sup> in the GISP2 ice core be derived from seawater, rather than terrestrial sources. This appears likely, given that the Na<sup>+</sup> to Cl<sup>-</sup> ratio during the periods of elevated Na<sup>+</sup> is similar to that of modern seawater.

The cause of the apparent decrease in surface ocean DMS in the glacial North Atlantic Ocean is not known. We hypothesize that this phenomenon reflects differences in the phytoplankton ecology of the glacial North Atlantic Ocean compared with today. It is well known that glacial sediments in the North Atlantic are coccolith-depleted, and it has been suggested that this reflects a major southward shift of the oceanographic polar front compared with its present-day position [CLIMAP Project Members, 1981]. Coccolithophora are among the major groups of phytoplankton known to produce DMS, and their decreasing abundance in the glacial polar ocean may have influenced atmospheric MSA levels. It is likely that other polar and subpolar DMS-producing fauna that do not leave a sedimentary record such as Phaeocystis

[Keller *et al.*, 1989] were also displaced southward in the glacial ocean.

#### Conclusions

The MSA record from the GISP2 ice core gives a qualitative picture of how climate changes affected the atmospheric burden of biogenic sulfur over Greenland during the past 110 kyr. The record indicates that warmer climates were characterized by higher levels of biogenic sulfur than cold periods. These changes are opposite in trend from those observed in ice core records from Antarctica [Legrand *et al.*, 1991] and suggest that the biological state of the Southern and North Atlantic Oceans responded quite differently to climatic changes. It is important to understand the causes of such differences.

If we assume that the variations in MSA reflect variations in the abundance of DMS-derived submicron SO<sub>4</sub><sup>2-</sup> aerosol, then the GISP2 record implies a radiative forcing that provides a negative climatic feedback. For example, the transition from the last glacial maximum to the Holocene was accompanied by an increase in biogenic sulfur emissions. This increase would act to cool the Earth's surface and tend to limit the warmth of the interglacial. This was the sense of the feedback originally proposed by Shaw [1983] and Charlson *et al.* [1987]. This feedback is opposite from that inferred from the Antarctic Vostok ice core record [Legrand *et al.*, 1988], where colder conditions were associated with higher levels of biogenic sulfur. It is also important to note that the aerosol radiative forcing in Greenland has several additional components: seasalt, terrestrial, and volcanic aerosols. All were probably large during glacial times compared with today. Sea-salt and terrestrial aerosols have very different size distributions and chemical composition from that of the marine, DMS-derived aerosols and hence have different radiative properties. All three components must be taken into account in order to understand the overall climatic feedback associated with long-term changes in atmospheric aerosol loading.

**Acknowledgments.** The authors wish to acknowledge many people who participated in the field and laboratory operations that contributed to this work. These include Matthew Davis, Gary Dearman, Claire Germain, and Michele Zetwo. We also wish to thank the GISP2 Science Management Organization (especially Mark Twickler and Michael Morrison), the PICO drilling and logistical support team, and all the individuals who worked on the GISP2 core processing line and ice core dating. Michele Rowand provided invaluable assistance in the preparation of this manuscript. This research was supported by National Science Foundation grants DPP8822600 and DPP9322518.

#### References

- Alley, R.B., *et al.*, Abrupt increase in Greenland snow accumulation at the end of the Younger Dryas event, *Nature*, *361*, 527-529, 1993.
- Alley, R.B., R.C., Finkel, K. Nishiizumi, S. Anandakrishnan, C.A. Shuman, G.R. Mershon, G.A. Zielinski, and P.A. Mayewski, Changes in continental and sea-salt atmospheric loadings in central Greenland during the most recent deglaciation: model-based estimates, *J. Glaciol.*, *41*(139), 503-514, 1995.
- Andreae, M.O., Ocean-atmosphere interactions in the global biogeochemical sulfur cycle, *Mar. Chem.*, *30*, 1-29, 1990.
- Ayers, G.P., J.P. Ivey, and R.W. Gillett, Coherence between seasonal cycles of dimethyl sulphide, methanesulphonate and sulphate in marine air, *Nature*, *349*, 404-406, 1991.

- Bates, T.S., J.A. Calhoun, and P.K. Quinn, Variations in the methanesulfonate to sulfate molar ratio in submicrometer marine aerosols particles over the South Pacific Ocean, *J. Geophys. Res.*, **97**, 9859-9865, 1992a.
- Bates, T.S., B.K. Lamb, A. Guenther, J. Dignon, and R.E. Stoiber, Sulfur emissions to the atmosphere from natural sources, *J. Atmos. Chem.*, **14**, 315-337, 1992b.
- Bender, M., T. Sowers, M.L. Dickson, J. Orcharo, P. Grootes, P.A. Mayewski, and D.A. Meese, Climate connections between Greenland and Antarctica during the last 100,000 years, *Nature*, **372**, 663-666, 1994.
- Bergin, M.H., J.L. Jaffrezo, C.I. Davidson, R. Caldow, and J. Dibb, Fluxes of chemical species to the Greenland ice sheet at Summit by fog and dry deposition, *Geochim. Cosmochim. Acta*, **58**, 3207-3215, 1994.
- Berresheim, H., Biogenic sulfur emissions from Antarctic waters, *J. Geophys. Res.*, **92**, 13,245-13,262, 1987.
- Berresheim, H., M.O. Andreae, G.P. Ayers, R.W. Gillett, J.T. Merrill, V.J. Harris, and W.L. Chameides, Airborne measurements of dimethylsulfide, sulfur dioxide, and aerosol ions over the Southern Ocean south of Australia, *J. Atmos. Chem.*, **10**, 341-370, 1990.
- Berresheim, H., P.H. Wine, and D.D. Davis, Sulfur in the atmosphere, in: *Composition, Chemistry, and Climate of the Atmosphere*, edited by H.B. Singh, p. 251-307, Van Nostrand Reinhold, New York, 1995.
- Bromwich, D.H., F.M. Robasky, R.A. Keen, and J.F. Bolzan, Modeled variations of precipitation over the Greenland ice sheet, *J. Clim.*, **6**(1), 1253-1268, 1993.
- Charlson, R.J., J.E. Lovelock, M.O. Andreae, and S.G. Warren, Oceanic phytoplankton, atmospheric sulphur, cloud albedo and climate, *Nature*, **326**, 655-661, 1987.
- Chin, M., and D.J. Jacob, Anthropogenic and natural contributions to tropospheric sulfate: A global model analysis. *J. Geophys. Res.*, **101**, 18,691-18,699, 1996.
- CLIMAP Project Members, Seasonal reconstructions of the Earth's surface at the last glacial maximum, *Map Ser. MC-36, Geol. Soc. of Am. Boulder, Colo.*, 1981.
- Cutler, N.N., C.F. Raymond, E.D. Waddington, D.A. Meese, and R.B. Alley, The effect of ice sheet thickness change on the accumulation history inferred from GISP2 layer thicknesses, *Ann. Glaciol.*, **21**, 26-32, 1995.
- Gao, Y. A. Arimoto, R.A. Duce, L.Q. Chen, M.Y. Zhou, and D.Y. Gu, Atmospheric non-sea-salt sulfate, nitrate and methanesulfonate over the China Sea., *J. Geophys. Res.*, **101**, 12,601-12,611, 1996.
- Galloway, J.N., D.L. Savoie, W.C. Keene, and J.M. Prospero, The temporal and spatial variability of scavenging ratios for nss sulfate, nitrate, methanesulfonate and sodium in the atmosphere over the North Atlantic Ocean. *Atmos. Environ.*, **27 Part A**, 235-250, 1993.
- Grootes, P.M., J.W.C., Stuiver, S. Johnson, and J. Jouzel, Comparison of oxygen isotope records from the GISP2 and GRIP Greenland ice cores, *Nature*, **366**, 552-554, 1993.
- Hansson, M.E., The Renland ice core. A Northern Hemisphere record of aerosol composition over 120,000 years, *Tellus, Ser. B*, **46**, 390-418, 1994.
- Hansson, M.E., and E.S. Saltzman, The first Greenland ice core record of methanesulfonate and sulfate over a full glacial cycle, *J. Geophys. Res. Lett.*, **20**, 1163-1166, 1993.
- Herron, M.M. and C.C. Langway Jr., Chloride, nitrate, and sulfate in the Dye 3 and Camp Century Greenland ice cores in *Greenland Ice Core: Geophysics, Geochemistry, and the Environment, Geophys. Monogr. Ser.*, vol. 33, edited by C.C. Langway, Jr., J. Oeschger, and W. Dansgaard, pp. 77-84, AGU, Washington D.C., 1985.
- Holland, H.D., in *The Chemistry of the Atmosphere and Oceans*, John Wiley, New York, 1978.
- Huebert, B.J., L.Z. Zhuang, and S. Howell, Sulfate, nitrate, methanesulfonate, chloride, ammonium, and sodium measurements from ship, island, and aircraft during the Atlantic Stratocumulus Transition Experiment marine aerosol gas-exchange, *J. Geophys. Res.*, **101**, 4413-4423, 1996a.
- Huebert, B.J., D.J. Wylie, L. Zhuang, and J.A. Heath, Production and loss of methanesulfonate and non-sea salt sulfate in the equatorial Pacific marine boundary layer, *Geophys. Res. Lett.*, **23**, 7737-7740, 1996b.
- Johnsen, S.J., and W. Dansgaard, On flow model dating of stable isotope records from Greenland ice cores, in *The Last Deglaciation, Absolute and Radiocarbon Chronologies*, edited by E. Bard, *NATO ASI Ser., Ser. I*, **2**, 13-24, 1992.
- Kapsner, W.R., R.B. Alley, C.A. Shuman, S. Anandkrishnan, and P.M. Grootes, Dominant influence of atmospheric circulation on snow accumulation in Greenland over the past 18,000 years, *Nature*, **373**, 52-54, 1995.
- Keller, M.D., W.K. Bellows, and R.R.L. Guillard, Dimethyl sulfide production in marine phytoplankton, in *Biogenic Sulfur in the Environment, Am. Chem. Soc. Sym. Ser.*, vol. 393, 167-182, Washington, DC, 1989, edited by E. Saltzman and W.J. Cooper.
- Langner, J. and H. Rodhe, A global three-dimensional model of the tropospheric sulfur cycle, *J. Atmos. Chem.*, **13**, 225-263, 1992.
- Lautenschlager, M., and K. Herterich, Atmospheric response to ice age conditions: Climatology near the Earth's surface, *J. Geophys. Res.*, **95**, 22,547-22,557, 1990.
- Legrand, M., R.J. Delmas, and R.J. Charlson, Climate forcing implications from Vostok ice-core sulphate data, *Nature*, **334**, 418-420, 1988.
- Legrand, M., C. Feniet-Saigne, E.S. Saltzman, C. Germain, N.I. Barkov, and V.N. Petrov, Ice-core record of oceanic emissions of dimethyl sulphide during the last climate cycle, *Nature*, **350**, 144-146, 1991.
- Legrand, M., and S. Kirchner, Origins and variations of nitrate in South Polar precipitation. *J. Geophys. Res.*, **95**, 3493-3508, 1990.
- Li, S.-M., L.A. Barrie, R.W. Talbot, R.C. Harriss, C.I. Davidson, and J.-L. Jaffrezo, Seasonal and geographic variations of methane sulfonic acid in the Arctic troposphere, *Atmos. Environ., Part A*, **27**, 3011-3024, 1993.
- Li, S.-M., L.A. Barrie, and D. Toom, Seasonal variations of methanesulfonate, non-sea-salt sulfate, and sulfur dioxide at three sites in Canada, *J. Geophys. Res.*, **101**, 4165-4173, 1996.
- Mason, B., and C.B. Moore, *Principles of Geochemistry*, pp. 176-177, John Wiley, New York, 1982.
- Mayewski, P.A., L.D. Meeker, M.S. Twickler, S. Whitlow, Q. Yang, and M. Prentice, Major features and forcing of high-latitude northern hemisphere atmospheric circulation using a 110,000-year-long glaciochemical series, *J. Geophys. Res.*, this issue.
- Nguyen, B.C., N. Mihalopoulos, J.P. Putaud, A. Gaudry, L. Gallet, W. Keene, and J.N. Galloway, Covariations in oceanic dimethyl sulfide, its oxidation products and rain acidity at Amsterdam Island in the Southern Indian Ocean, *J. Atmos. Chem.*, **15**, 39-53, 1992.
- Petit, J.-R., M. Briat, and A. Royer, Ice age aerosol content from East Antarctic ice core samples and past wind strength, *Nature*, **293**, 391-394, 1981.
- Pollack, J.B., O.B. Toon, C. Sagan, A. Summers, B. Baldwin, and W. Van Camp, Volcanic explosions and climatic change: A theoretical assessment, *J. Geophys. Res.*, **81**, 1071-1083, 1976.
- Pszenny, A.A., A.J. Castelle, J.N. Galloway, and R.A. Duce, A study of the sulfur cycle in the Antarctic marine boundary layer, *J. Geophys. Res.*, **94**, 9818-9830, 1989.
- Rampino, M.R., and S. Self, Historic eruptions of Tambora (1815), Krakatau (1883), and Agung (1963), their stratospheric aerosols, and climatic impact, *Quat. Res.*, **18**, 127-143, 1982.
- Saigne, C., and M. Legrand, Measurements of methanesulphonic acid in Antarctic ice, *Nature*, **330**, 240-242, 1987.
- Saltzman, E.S., D.L. Savoie, R.G. Zika, and J.M. Prospero, Methane sulfonic acid in the marine atmosphere, *J. Geophys. Res.*, **88**, 10,897-10,902, 1983.
- Saltzman, E.S., D.L. Savoie, J.M. Prospero, and R.G. Zika, Methanesulfonic acid and non-sea-salt sulfate in Pacific air: Regional and seasonal variations, *J. Atmos. Chem.*, **4**, 227-240, 1985.
- Saltzman, E.S., Ocean/Atmosphere Cycling of Dimethylsulfide, in *Global Environmental Change, in Ice Core Studies of Global Biogeochemical Cycles, NATO ASI Ser., Ser. I*, vol. 30., 65-90, edited by R.J. Delmas, 1995.
- Savoie, D.L., and J.M. Prospero, Comparison of oceanic and continental sources of non-sea-salt sulphate over the Pacific Ocean, *Nature*, **339**, 685-687, 1989.
- Savoie, D.L., J.M. Prospero, and R.T. Nees, Non-sea-salt sulfate and nitrate in trade wind aerosols at Barbados: Evidence for long-range transport, *J. Geophys. Res.*, **94**, 5069-5080, 1989.

- Savoie, D.L., J.M. Prospero, R.J. Larsen, and E.S. Saltzman, Nitrogen and sulfur species in aerosols at Mawson, Antarctica, and their relationship to natural radionuclides, *J. Atmos. Chem.*, *14*, 181-204, 1992.
- Savoie, D.L., J.M. Prospero, R.J. Larsen, F. Huang, M.A. Izaguirre, T. Huang, T.H. Snowdon, L. Custals, and C.G. Sanderson, Nitrogen and sulfur species in Antarctic aerosols at Mawson, Palmer station, and Marsh (King George Island), *J. Atmos. Chem.*, *17*, 95-122, 1993.
- Shaw, G.E., Bio-controlled thermostasis involving the sulfur cycle, *Clim. Change*, *5*, 297-303, 1983.
- Spiro, P.A., D.J. Jacob, and J.A. Logan, Global inventory of sulfur emissions with 1° x 1° resolution, *J. Geophys. Res.*, *97*, 6023-6036, 1992.
- Whung, P.-Y., E.S. Saltzman, M.J. Spencer, P.M. Mayewski, and N. Gundestrup, A two hundred year record of biogenic sulfur in a south Greenland ice core (20D), *J. Geophys. Res.*, *99*, 1147-1156, 1994.
- Zielinski, G.A., P.A. Mayewski, L.C. Meeker, S. Whitlow, M.S. Twickler, M. Morrison, D.A. Meese, A.J. Gow, and R.B. Alley, Record of volcanism since 7000 B.C. from the GISP2 Greenland ice core and implications for the volcano-climate system, *Science*, *264*, 948-952, 1994.
- P.A. Mayewski, Glacial Research Group, Climate Change Research Center, Institute for Study of Earth, Ocean and Space, University of New Hampshire, Durham, NJ 03824.
- E.S. Saltzman, Division of Marine and Atmospheric Chemistry, Rosenstiel School of Marine and Atmospheric Science, University of Miami, Miami, FL 33149.
- P.-Y. Whung, Cooperative Institute of Marine and Atmospheric Science, Rosenstiel School of Marine and Atmospheric Science, 4600 Rickenbacker Causeway, Miami, FL 33149 (e-mail: pwhung@rsmas.miami.edu)

(Received January 28, 1996; revised December 2, 1996; accepted December 4, 1996.)