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#### <u>a0005</u>

# Glaciochemistry

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# **<u>s0005</u>** Introduction

p0005 Ice cores recovered from polar and high-elevation regions provide a unique and valuable archive of past atmospheric conditions, in large part because of the numerous physical and chemical measurements that can be performed at any given depth, and because the transformation of snow to firn to ice on a glacier or ice sheet provides two basic sets of atmospheric information. First, when firn turns into ice, bubbles are formed that trap ambient air whose composition provides information on atmospheric trace gases (e.g., CO<sub>2</sub>, CH<sub>4</sub>) at the time of ice formation. Second, aerosols and water-soluble gas species can be trapped during precipitation, as well as deposited directly on the snow surface. While the term 'glaciochemistry' is broad and could conceivably encompass all chemical measurements made on icecore samples, in practice it generally represents the soluble mineral and organic components originally deposited on the snow surface (Legrand and Mayewski, 1997). Measurement of the suite of major ions (Na+, Mg2+, Ca2+, K+, NH4+, Cl-,  $NO_3^{-}$ ,  $SO_4^{2-}$ ) represents approximately 95% of the soluble composition of the atmosphere, and therefore provides a powerful tool for investigating modern and past changes in atmospheric chemistry. Ions from soluble organic acids, such as formate  $(HCOO^{-})$ , acetate  $(CH_{3}COO^{-})$ , oxylate  $(C_{2}O_{4}^{-})$ , MS (CH<sub>3</sub>SO<sup>-</sup>), and other volatile species such as hydrogen peroxide  $(H_2O_2)$  and formaldehyde (HCHO) have been measured at various ice-core sites and used to study atmospheric and biogeochemical processes. However, the major ion suite is most commonly measured in ice cores, and there is an extensive dataset available from a globally distributed set of ice-core sites. Because of the varied geographic positions (e.g., elevation, distance from ocean or arid regions, etc.) of these sites, major ion (plus MS) concentrations in ice cores show a wide range of values based on temporal changes in chemical source strength, climate dynamics, and biogeochemical processes. This chapter therefore contains a review of current issues in the field of ice-core glaciochemistry (restricted here to major ions plus MS), and summarizes information related to chemical

sources, transport, deposition, and interpretation in terms of paleoclimate and paleoenvironmental change.

# Glaciochemical Background and Measurement

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Based on atmospheric chemistry principles, the com- p0010 position of precipitation in polar and alpine regions should contain various soluble impurities. These impurities are introduced to the atmosphere either directly as primary aerosols (e.g., dust entrained from terrestrial surfaces), or produced within the atmosphere (secondary aerosols) during the oxidation of trace gases involved in the sulfur, nitrogen, halogen, or carbon cycles. Some soluble ion species have multiple sources (Legrand and Mayewski, 1997); for example,  $SO_4^{2-}$ , can be linked to both primary aerosols (sea salt and dust) as well as secondary aerosols (from the oxidation of sulfur gases produced by volcanic activity, anthropogenic (human) activities, and the biosphere). It is therefore necessary to study all soluble species present in icecore samples in order to understand and reconstruct the original association of the ions. The ionic budget  $(\Sigma; \text{ sum of all ion species present})$  in polar and alpine snow can generally be written as follows (concentrations in microequivalents per liter,  $meqL^{-1}$ ):

$$\sum = [Na^{+}] + [NH_{4}^{+}] + [K^{+}] + [H^{+}] + [Ca^{2+}] + [Mg^{2+}] + [F^{-}] + [Cl^{-}] + [NO_{3}^{-}] + [SO_{4}^{2-}] + [CH_{3}SO_{3}^{-}] + [HCOO^{-}] + [CH_{3}COO^{-}]$$

In most situations, the concentrations of  $F^-$  and <u>p0015</u> the light carboxylates are insignificant. While concentrations of MS are also usually low, the compound is important in the study of the atmospheric sulfur cycle. Therefore,  $\Delta C$ , the imbalance between cations and anions, can usually be simplified to:

$$\Delta C = [Na^+] + [NH_4^+] + [K^+] + [H^+] + [Ca^{2+}] + [Mg^{2+}] - [CL^-] - [NO_3^-] - [SO_4^{2-}]$$

Likewise, the balance achieved between cations  $\underline{p0020}$ and anions ( $\Delta C = 0$ ), a useful measure for evaluating original chemical deposition forms, can be calculated as:

$$[Na^{+}] + [NH_{4}^{+}] + [K^{+}] + [H^{+}] + [Ca^{2+}] + [Mg^{2+}]$$
  
= [Cl<sup>-</sup>]-[NO\_{3}^{-}]-[SO\_{4}^{2-}]

Deposition of primary and secondary aerosols to p0025 the snow surface occurs via several mechanisms, and

therefore using soluble ion data to reconstruct past atmospheric chemical concentrations requires some knowledge of these processes. In the case of wet deposition, the aerosol falls within or is attached to a snowflake after either serving as a condensation nucleus or by being scavenged by the falling snowflake. During dry deposition, the air-to-snow transfer occurs without any associated water transfer. To account for these processes when using ice-core glaciochemical data, two procedures are common: i) icecore time series of ion concentrations (e.g., parts per billion (ppb) or  $meqL^{-1}$ ) are interpreted directly, and ii) the estimated chemical flux (e.g., in nanograms per square centimeter per year,  $ngcm^{-2}yr^{-1}$ ) is calculated and interpreted. Chemical fluxes are calculated by multiplying the sample concentration by the estimated H<sub>2</sub>O flux (accumulation). In some cases, a qualitative examination of either concentration or flux time series yields similar results. For example, the deposition of Ca<sup>2+</sup> on the Antarctic polar plateau was clearly higher during the Last Glacial Maximum (LGM) when either ice-core concentration and flux estimates are viewed (Figure 1). However, detailed quantitative analyses often require a more rigorous knowledge of site-specific air-now transfer functions, and justification for using either concentration or flux time series is necessary (Meeker et al., 1997). In addition, any postdepositional modification of the original chemical signal needs to be taken into account when reconstructing past atmospheric concentrations (Barnes et al., 2003).

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Glaciochemical measurement techniques have evolved over the past 30 years, however the majority of soluble ion data have been, and continue to be, produced by ion chromatography (IC). Advances in IC technology have allowed much lower concentration measurements to be made with high precision,

such that data produced from the most remote and pristine polar and alpine locations are now reasonably routine. Analytical challenges still occur in certain situations, such as with samples collected from arid regions that have very high ion concentrations and particulate material that impede IC column performance. Decontamination of recovered ice cores is crucial to producing reliable glaciochemical data, and is as important as the chemical measurement itself. Most methods involve removing the outer portion of the core by rinsing with ultra-pure water, or by the physical removal of the outer core by scraping. More recently, several international groups have developed continuous melting systems that utilize a heated melting head that produces samples from the inner and outer portions of the core, thereby avoiding contamination from the outer core and providing the opportunity for high-resolution (small depth interval) measurements. Samples are either collected discretely (e.g., the melt water stream is collected into individual sample vials at a specified interval), or injected directly into an instrument during continuous flow analysis (CFA). When samples are collected discretely, standard IC techniques are used to analyze a full suite of ion species. In CFA, reagents are added to the sample stream, and measurement is typically via fluorometric (Na<sup>+</sup>, NH<sub>4</sub><sup>+</sup>, Ca<sup>2+</sup>) or absorption  $(Na^+, NO_3^-)$  techniques. A third analytical method has recently been developed, known as fast ion chromatography (FIC), and is designed specifically for high-resolution ice-core measurements, where a portion of the steady sample stream is injected into an IC at a specified time interval. FIC and CFA techniques currently have limitations in terms of the number of ion species that can be analyzed; however, as techniques evolve other species will likely be added. Good agreement is found when ion concentrations



 $\underline{f0005}$  **Figure 1** Nonsea-salt (nss) Ca<sup>2+</sup> concentrations (black) from the Taylor Dome, Antarctica ice core (Mayewski *et al.*, 1996), and 50-year average nssCa<sup>2+</sup> flux values (red) from the EPICA Dome C, Antarctica ice core (Rothlisberger *et al.*, 2002).

measured on the same samples with the three different methods are compared (Littot *et al.*, 2002). Soluble ion concentrations are typically reported in either mass-by-mass units (e.g., ppb), or molar units (micromoles per liter (mmolL<sup>-1</sup>) or meqL<sup>-1</sup>).

# <u>s0015</u> Glaciochemical Sources and Spatial/ Temporal Variability

p0035 The sources of soluble ion species in polar and alpine ice cores can be grouped into several general categories based on the original aerosol formation process. Because several ion species have multiple sources, basic statistical techniques are often applied to differentiate compounds responsible for ion deposition. More recently, multivariate techniques have been developed to deal with multiple chemical sources in a more quantitative fashion, in addition to accounting for factors inherent in icecore glaciochemical studies such as nonuniform sampling, nonstationary process, and sporadic events (Meeker *et al.*, 1995).

# s0020 Sea Salt Aerosol

<u>p0040</u> Sea-salt aerosols are some of the major impurities in polar ice cores, and contribute a significant portion of several species (notably Na<sup>+</sup>, Cl<sup>-</sup>, and Mg<sup>2+</sup>) to the ion balance. Originally, the source of the sea-salt aerosol reaching coastal and inland plateau sites was thought primarily to be bubbles bursting over open ocean water. Because ion species associated with sea salt typically peak during winter, and also show elevated concentrations during glacial periods, the role of sea ice was not clear. Increased sea ice extent during winter and glacial periods should presumably lead to a decrease in the amount of sea-salt aerosol

reaching a particular site. One possibility for explaining this discrepancy is that increased storminess over the ocean and enhanced transport of sea-salt aerosols inland during winter and glacial periods more than offsets the greater distance (Petit et al., 1999). Another possibility is that sea-salt aerosol is produced from newly formed sea ice, where highly saline brine and fragile frost flowers form a very effective source of aerosol in the winter (Wolff et al., 2003). Both of these factors (atmospheric dynamics and sea ice) likely contribute to sea-salt deposition at a particular polar site, with the relative importance of each process varying with timescale. Correlation of annually dated sea-salt time series in Antarctica (Kreutz et al., 2000) and Greenland (Meeker and Mayewski, 2002) with sea-level pressure records suggests a strong transport influence at these sites and timescales, while an ice-core sea-salt record from the Penny Ice Cap, Baffin Island is significantly correlated with local sea ice extent. On glacial-interglacial sea-salt records from Greenland timescales, (Figure 2; Mayewski et al., 1997) and Antarctica (Rothlisberber et al., 2002) display significant concentration increases, suggesting the influence of both enhanced atmospheric transport and sea ice extent during the LGM. For high-elevation sites in mid- and low-latitude regions, the contribution of sea-salt aerosol varies greatly depending on location relative to an ocean source. In Asia, most ice-coring sites are located far from a marine source, and therefore sea salt contributes little to the overall ion budget. In coastal ranges (e.g., St. Elias Mountains in Alaska/ Yukon) or sites relatively close to the ocean (e.g., the Andes), the relative contribution of sea-salt aerosol depends on local conditions.

The calculation of the percentage of sea salt in any p0045 particular sample is an important step in determining



 $\frac{f0010}{Both}$  Figure 2 Sea salt (ss) Na<sup>+</sup> concentrations and nonsea-salt (nss) Ca<sup>2+</sup> concentrations from the GISP2 ice core (Mayewski *et al.*, 1997). Both datasets are 50-year averages.

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the relative contribution to various species. The simplest calculation is based on the assumption that one ion species is derived solely from sea salt, and therefore standard seawater ion ratios can be used to calculate the sea salt (ss) and nonsea salt (nss) contribution for other species. In Antarctica, Na<sup>+</sup> is generally thought to have no other significant source, and after deposition behaves conservatively. In this case, calculation of nssCa<sup>2+</sup>, for example, would be:

$$\left[nssCa^{2+}\right] = \left[Ca^{2+}\right] - \left[Na^{+}\right] \times (R_m)$$

where  $R_{\rm m}$  is the Ca<sup>2+</sup>/Na<sup>+</sup> ratio (0.038) found in marine aerosols. A slightly more sophisticated approach is to recognize that some Na<sup>+</sup> derives from other sources, and therefore to solve two equations simultaneously:

$$[ssNa^+] = [Na^+] - \frac{[nssCa^{2+}]}{R_c}$$
$$[nssCa^{2+}] = [Ca^{2+}] - [ssNa^+] \times R_m$$

where  $R_c$  is the Ca<sup>2+</sup>/Na<sup>+</sup> ratio (1.78) found in average crust. Finally, models that estimate ss and nss components by an iterative process in which each sample is tested to determine which species is the most conservative (limiting) are useful for time-series calculations in which the relative important of seasalt aerosols may change (O'Brien *et al.*, 1995). All of these methods assume that fractionation of sea-salt aerosols during transport via reaction with acids, and possible loss after deposition, does not occur (Rothlisberger *et al.*, 2003).

## <u>s0025</u> Terrestrial Dust

p0050 Dust records from polar and alpine ice cores have been widely used to infer past changes in atmospheric circulation and climatic conditions in the dust source region. The nss fraction of several species in the atmosphere is either wholly (in the case of  $Ca^{2+}$ ,  $Mg^{2+}$ ,  $Na^+$ ) or partially (in the case of K<sup>+</sup>,  $SO_4^{2-}$ ,  $NO_3^-$ ,  $Cl^-$ ) the result of soluble evaporite (e.g., carbonates, gypsum, halite) minerals derived from terrestrial deposits. Snow samples and ice cores collected from sites located close to arid regions therefore have a correspondingly high dust load. High-elevation sites in Asia, either on or near the Tibetan Plateau, show elevated concentrations of all measured ions related to dust input (Thompson et al., 1997), as do European alpine sites influenced by Saharan dust (Schwikowski et al., 1999). Likewise, South American sites near the dry Altiplano region have enhanced ion concentrations during periods of lake desiccation (Thompson et al., 1998). In modern polar snow, the terrestrial dust contribution is

usually small due to the large distance from available sources (Legrand and Mayewski, 1997), and in general dust only contributes a measurable nss fraction to  $Ca^{2+}$  and potentially  $Mg^{2+}$  and  $K^+$ . Exceptions exist in ice-free regions such as the Dry Valleys of Antarctica, where exposed soils provide a source of soluble particulate material. During the Holocene, changes in dust transport to Greenland are reflected in ice-core nssCa<sup>2+</sup>, nssMg<sup>2+</sup>, and nssK<sup>+</sup> concentrations (O'Brien et al., 1995), and correlation with instrumental data indicates that an Asian source is most probable (Meeker and Mayewski, 2002). During the LGM, nss concentrations showed dramatic increases on the Antarctic (Figure 1) and Greenland (Figure 2) polar plateaus, as well as significant millennial-scale variability (Mayewski et al., 1996; 1997; Petit et al., 1999; Rothlisberger et al., 2002). Modeling studies suggest that changes in LGM climate (increased surface wind speed, reduced atmospheric and soil moisture, higher aerosol transport efficiency) and vegetation were largely responsible for the observed increases in dust deposition.

## **Volcanic Aerosols**

Volcanic eruptions emit large amounts of particulate p0055 matter and gases (mainly SO<sub>2</sub>) into various levels of the atmosphere, depending on eruption intensity and magma composition. Sulfate aerosols formed from the atmospheric oxidation of SO<sub>2</sub> and gas-to-particle conversions can be transported on regional-to-global scales, particularly when injected into the stratosphere, and are irreversibly deposited on alpine glaciers and polar ice sheets. Sulfate ice-core stratigraphy can be used to interpret the impact of individual eruptions on the atmospheric aerosol load, and any associated climate impacts. In addition to  $SO_4^{2-}$ , volcanic aerosols can also contribute other species to the overall ionic budget, including Cl<sup>-</sup> and F<sup>-</sup> (Herron, 1982). In the Northern Hemisphere, several ice-core locations record both global and local/regional scale eruptions, particularly from the Icelandic and North Pacific regions (Zielinski et al., 1994). Antarctic ice-core records, especially those from the polar plateau, are generally removed from any local-scale volcanic signals and therefore provide complementary estimates of explosive global-scale eruptions (Cole-Dai et al., 2000) for use in bipolar comparisons (Langway et al., 1995). Several methods are used to estimate the contribution of volcanic  $nssSO_4^{2-}$  to the total  $SO_4^{2-}$  deposition, including smoothing and residual analysis, multivariate statistics, and definitions based on signals above a standard deviation cutoff. Ice-core-based reconstructions of past volcanic eruption frequency and

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**Figure 3** Volcanic  $SO_4^{2-}$  concentrations from the GISP2 ice core (Zielinski *et al.*, 1994). The volcanic fraction of total  $SO_4^{2-}$ f0015 concentration are residuals calculated using a low-tension robust spline method. Year BP, years before present.

intensity have, for example, identified an increase in volcanic activity in the early Holocene (Zielinski et al., 1994; Figure 3), possibly related to climatic cooling, and in the late Holocene (Castellano et al., 2005). In addition, ice-core volcanic eruption histories are often used in climate forcing estimates input to climate models.

#### s0035 Biogenic Emissions

Biogenic emissions play a large role in the atmop0060 spheric sulfur cycle, primarily through the oxidation of reduced sulfur species released by various natural sources. In the remote, unpolluted marine atmosphere, oxidation of dimethylsulfide (DMS) released from marine organisms represents a major source of nssSO4<sup>2-</sup>, both on local and global scales. In addition, the oxidation of DMS also produces methanesulfonic acid (measured as MS), and this formation pathway is the only known source of MS. Therefore, the measurement of both  $nssSO_4^{2-}$  and MS in ice cores represents a useful tool for deconvolving marine biogenic from nonbiogenic sulfur sources, and potentially for the reconstruction of past changes in DMS emissions and hence ocean productivity (Legrand, 1995). Given that MS and  $nssSO_4^{2-}$  both exist as submicron aerosols, and therefore should have similar atmospheric transport and deposition processes, the ratio of MS/nss  $SO_4^{2-}(R)$  in ice cores may provide a tool for estimating marine emissions. Such measurements are particularly relevant in Antarctica, given the surrounding open and icecovered ocean regions, and to a somewhat lesser extent in Northern Hemisphere sites that are located near coastal regions. Recent sulfur aerosol and surface snow studies and modeling results have shown

that R values vary spatially in Antarctica, seasonal values vary based on transport and chemical source region, and that inland Antarctic ice cores site and R values may provide large-scale estimates of bioproductivity. Therefore, with careful study of Antarctic snow and ice cores, R values may lead to an improved understanding of the oxidative capacity of the atmosphere, the temperature of the atmospheric oxidation of DMS, and the aging of marine air masses during their transport from source regions to Antarctica. Because the oxidation of DMS is the only known source of MS, several authors have used icecore MS concentrations to investigate past variability in the sulfur cycle, particularly the relationships among productivity, climate, and sea ice. MS concentrations from the Vostok ice core (Legrand et al., 1991) display an increase during the LGM, suggesting enhanced ocean productivity during periods of colder temperatures and decreased greenhouse gas concentrations. On shorter (interannual) timescales, correlations between South Pole ice core MS concentrations and the El Niño-Southern Oscillation have been found (Meyerson et al., 2002), indicating a link between low- and high-latitude ocean/atmosphere circulation and marine productivity. Finally, several authors have found correlations between snow and ice-core MS concentrations and sea-ice extent (Curran et al., 2003), suggesting that algal productivity within and on top of sea ice may contribute to atmospheric DMS, and hence influence ice-core MS values.

Ice-core NH<sub>4</sub><sup>+</sup> concentrations primarily arise from p0065 biological emissions of ammonia from plants, soils, animals, bacterial decomposition, burning of biological materials (forest and grass fires), and potentially

from marine biological emissions. In the high-latitude Northern Hemisphere, NH4+ is present in significant amounts in precipitation, and ice-core time-series have been useful for reconstructing the history of forest fires from the boreal zone (Savarino and Legrand, 1998). On longer (multidecadal to glacial-interglacial) timescales, NH4<sup>+</sup> concentrations in Greenland are mainly related to continental biogenic emissions from soils, and no evidence has been found for a significant marine contribution. A study of NH4<sup>+</sup> concentrations in the GISP2 core (Meeker et al., 1997) found that orbital parameters (summer forcing associated with the precessional cycle) and ice volume exerted a strong control on continental biogenic emissions over the past 110,000 years (Figure 4). In Antarctica, NH<sub>4</sub><sup>+</sup> concentrations in coastal aerosol and snow are highly variable and likely related to ornithogenic (penguin) soils, while oceanic emissions appear to play a minor role. Therefore, the low concentrations of NH4<sup>+</sup> from inland sites remain difficult to both measure and interpret. In alpine regions, industrial and agricultural emissions likely impact snow and ice-core NH<sub>4</sub><sup>+</sup> concentrations.

## **<u>s0040</u>** Nitrogen Cycling

<u>p0070</u> To study past changes in atmospheric  $NO_x$  (NO and  $NO_2$ ) concentration, nitrate ( $NO_3^-$ ), an oxidation product of  $NO_x$ , has often been measured in polar ice cores (Wolff, 1995). Some features in  $NO_3^-$  records can be readily explained, such as the clear increase since 1940 in Greenland ice cores attributed to  $NO_x$  emissions from industrialized countries. However, the interpretation of  $NO_3^-$  records beyond



<u>f0020</u> **Figure 4** Ammonium ( $NH_4^+$ ) concentration from the GISP2 ice core (Meeker *et al.*, 1997). The green line is 50-year averaged data, and the black line is a low-tension robust spline chosen to highlight millennial-scale variability.

the anthropogenic era in Greenland, and in Antarctica in general, remains difficult. Several minor sources of NO<sub>x</sub> have been suggested, including meteorite impact, supernovas, and solar modulation (sunspot cycle, solar proton events). The main sources are considered to be NO<sub>x</sub> production in the stratosphere and tropospheric lightning. Recent studies of atmospheric NO<sub>v</sub> (NO<sub>x</sub>, HNO<sub>3</sub>, N<sub>2</sub>O<sub>5</sub>, particulate and organic nitrates) concentrations have shown considerable amounts of organic nitrate, further complicating the interpretation of ice-core NO<sub>3</sub><sup>-</sup> time-series records. Recent studies demonstrate that depositional and postdepositional processes have a strong influence on NO<sub>3</sub><sup>-</sup> concentrations preserved in snow and ice cores (Wolff, 1995). In particular, it appears that changes in climate (temperature and accumulation rate) and atmospheric chemistry (Ca<sup>2+</sup> concentrations) had a strong impact on the preservation of NO<sub>3</sub><sup>-</sup> during the Holocene and LGM in the polar regions. At sites where potential NO<sub>3</sub><sup>-</sup> sources may be close, changes in forest cover and local terrestrial biogeochemistry may explain glacial-interglacial NO<sub>3</sub><sup>-</sup> concentration changes (Thompson et al., 1998).

## **Anthropogenic Emissions**

Emissions of  $SO_2$  and  $NO_x$  from industrial processes p0075and fossil fuel use have been a source for  $SO_4^{2-}$  and  $NO_3^-$  since the end of the nineteenth century in Greenland, the Canadian Arctic, Svalbard, and the European Alps (Goto-Azuma and Koerner, 2001; Schwikowski *et al.*, 1999). For example, trends of increasing  $SO_4^{2-}$  and  $NO_3^-$  over the 50–100 years leading up to the 1970s are evident in data from South Greenland (Figure 5; Mayewski *et al.*, 1986;



**Figure 5** Sulfate  $(SO_4^{2-}; blue)$  and nitrate  $(NO_3^-; green)$  concentrations from the GISP2 ice core (Mayewski *et al.*, 1986; 1990), showing a clear increase in the twentieth century due to anthropogenic emissions.

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1990). In the Alps, population centers are located close to ice-core sites, and therefore determining the sources responsible for  $SO_4^{2-}$  and  $NO_3^{-}$  is relatively straightforward (Schwikowski et al., 1999). In the Arctic, long-range transport of pollutant aerosol makes source identification more difficult due to mixing. Different approaches have been used to distinguish source contributions, including statistical analysis and time-series correlation of spatially distributed records (Goto-Azuma and Koerner, 2001). Results suggest that it may be possible to separate multiple anthropogenic sources from different regions to a single ice-core record, although additional isotope geochemical data is often more diagnostic. Long-term records of possible anthropogenic impact on atmospheric  $SO_4^{2-}$  and  $NO_3^{-}$  in Asia do not exist, in part because of the masking effect from large terrestrial dust inputs. However, stable sulfur isotope ratios in Asian snow suggest that anthropogenic  $SO_4^{2-}$  can be distinguished. At the present time, there is no convincing evidence for an anthropogenic impact on  $SO_4^{2-}$  or  $NO_3^{-}$  concentrations in Antarctica.

# Abbreviations

CFA	continuous flow analysis
DMS	dimethylsulfide
FIC	fast ion chromatography
IC	ion chromatography
LGM	Last Glacial Maximum
MS	methylsulfonate
nss	nonsea salt
ppb	part per billion
SS	sea salt
years BP	years before present

*See also:* Overview of Ice Core Research (00328); History of Ice Coring in Greenland and Antarctica (00329); Ice core chronologies (00330); Conductivity Studies (00333); Microparticle and Trace Element Studies (00336).

# References

- b0005 Barnes, R. F., Wolff, E. W., Mader, H. M., Udisti, R., Castellano, E., and Rothlisberger, H. (2003). Evolution of chemical peak shapes in the Dome C, Antarctic, ice core. *Journal of Geophysical Research* 108 ACH 17-1-17-14.
- b0010 Castellano, E., Becagli, S., Hansson, M., *et al.* (2005). 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* **110**.
- b0015 Cole-Dai, J., Mosley-Thompson, E., Wight, S., and Thompson, L. G. (2000). A 4100-year record of explosive volcanism from an East Antarctica ice core. *Journal of Geophysical Research* 105, 24,431–24,441.

## Glaciochemistry

- Curran, M. A. J., Van Ommen, T., Morgan, V., Phillips, K. L., and <u>b0020</u> Palmer, A. S. (2003). Ice core evidence for Antarctic sea ice decline since the 1950s. *Science* **302**, 1203–1206.
- Herron, M. M. (1982). Impurity sources of F<sup>-</sup>, Cl<sup>-</sup>, NO<sub>3</sub><sup>-</sup> and <u>b0025</u> SO<sub>4</sub><sup>2-</sup> in Greenland and Antarctic precipitation. *Journal of Geophysical Research* 87, 3052–3060.
- Kreutz, K. J., Mayewski, P. A., Pittalwala II, Meeker, L. D., <u>b0030</u> Twickler, M. S., and Whitlow, S. I. (2000). Sea-level pressure variability in the Amundsen Sea region inferred from a West Antarctic glaciochemical record. *Journal of Geophysical Research* 105, 4047–4059.
- Langway, C. C. J., Osada, K., Clausen, H. B., Hammer, C. U., and <u>b0035</u> Shoji, H. (1995). A 10-century comparison of prominent bipolar volcanic events in ice cores. *Journal of Geophysical Research* 100, 16241–16247.
- Legrand, M. (1995). Sulphur-derived species in polar ice: a <u>b0040</u> review. In *Ice Core Studies of Global Biogeochemical Cycles* (R. Delmas, Ed.), pp. 91–120. , pp. 91–120. Springer, New York.
- Legrand, M., and Mayewski, P. A. (1997). Glaciochemistry <u>b0045</u> of polar ice cores: a review. *Reviews of Geophysics* **35**, 219–243.
- Legrand, M., Feniet-Saigne, C., Saltzman, E. S., Germain, C., <u>b0050</u> Barkov, N. I., and Petrov, V. N. (1991). Ice-core record of oceanic emissions of dimethylsulphide during the last climate cycle. *Nature* **350**, 144–146.
- Littot, G. C., Mulvaney, R., Rothlisberger, R., *et al.* (2002). <u>b0055</u> Comparison of analytical methods used for measuring major ions in the EPICA Dome C (Antarctica) ice core. *Annals of Glaciology* **35**, 299–305.
- Mayewski, P. A., Lyons, W. B., Spencer, M. J., *et al.* (1986). <u>b0060</u> Sulfate and nitrate concentrations from a South Greenland ice core. *Nature* 232, 975–977.
- Mayewski, P. A., Lyons, W. B., Spencer, M. J., Twickler, M. S., <u>b0065</u> Buck, C. F., and Whitlow, S. (1990). An ice-core record of atmospheric response to anthropogenic sulfate and nitrate. *Nature* 346, 554–556.
- Mayewski, P. A., Meeker, L. D., Twickler, M. S., *et al.* (1997). <u>b0070</u> Major features and forcing of high latitude northern hemisphere atmospheric circulation over the last 110,000 years. *Journal of Geophysical Research* **102**, 26,345–26,366.
- Mayewski, P. A., Twickler, M. S., Whitlow, S. I., *et al.* (1996). <u>b0075</u> Climate change during the deglaciation in Antarctica. *Science* **272**, 1636–1638.
- Meeker, L. D., and Mayewski, P. A. (2002). A 1400 year long <u>b0080</u> record of atmospheric circulation over the North Atlantic and Asia. *The Holocene* **12**, 257–266.
- Meeker, L. D., Mayewski, P. A., and Bloomfield, P. (1995). A new <u>b0085</u> approach to glaciochemical time series analysis. In *Ice Core Studies of Global Biogeochemical Cycles* (R. J. Delmas, Ed.). Springer-Verlag, Berlin.
- Meeker, L. D., Mayewski, P. A., Twickler, M. S., Whitlow, S. I., <u>b0090</u> and Meese, D. (1997). A 110,000-year history of change in continental biogenic emissions and related atmospheric circulation inferred from the Greenland Ice Sheet Project ice core. *Journal of Geophysical Research* **102**, 26,489–26,504.
- Meyerson, E., Mayewski, P. A., Kreutz, K. J., Meeker, L. D., <u>b0095</u> Whitlow, S. I., and Twickler, M. S. (2002). The polar expression of ENSO and sea-ice variability as recorded in a South Pole ice core. *Annals of Glaciology* **35**, 430–436.
- O'Brien, S. R., Mayewski, P. A., Meeker, L. D., Meese, D. A., <u>b0100</u> Twickler, M. S., and Whitlow, S. I. (1995). Complexity of Holocene climate as reconstructed from a Greenland ice core. *Science* **270**, 1962–1963.

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- b0105 Petit, J. R., Jouzel, J., Raynaud, D., *et al.* (1999). Climate and atmospheric history of the past 420,000 years from the Vostok ice core, Antarctica. *Nature* **399**, 429–436.
- b0110 Rothlisberger, R., Mulvaney, R., Wolff, E., *et al.* (2003). Limited dechlorination of sea-salt aerosols during the last glacial period: evidence from the European Project for Ice Coring in Antarctica (EPICA) Dome C ice core. *Journal of Geophysical Research* 108, 4256.
- <u>b0115</u> Rothlisberger, R., Mulvaney, R., Wolff, E. W., *et al.* (2002). Dust and sea salt variability in central East Antarctica (Dome C) over the last 45 kyrs and its implications for southern high-latitude climate. *Geophysical Research Letters* **29**, 1963.
- <u>b0120</u> Savarino, J., and Legrand, M. (1998). High northern latitude forest fires and vegetation emissions over the last millennium inferred from the chemistry of a central Greenland ice core. *Journal of Geophysical Research* **103**, 8267–8279.
- <u>b0125</u> Schwikowski, M., Brütsch, S., Gäggeler, H. W., and Schotterer, U. (1999). A high-resolution air chemistry record from an Alpine

ice core: Fiescherhorn glacier, Swiss Alps. Journal of Geophysical Research 104, 13,709–13,719.

- Thompson, L. G., Davis, M. E., Mosley-Thompson, E., et al. <u>b0130</u> (1998). A 25,000-year tropical climate history from Bolivian ice cores. Science 282, 1858–1864.
- Thompson, L. G., Yao, T., Davis, M. E., et al. (1997). Tropical <u>b0135</u> climate instability: the last glacial cycle from a Qinghai-Tibetan ice core. Science 276, 1821–1825.
- Wolff, E., Rankin, A. M., and Rothlisberger, R. (2003). An ice core <u>b0140</u> indicator of Antarctic sea ice production? *Geophysical Research Letters* 30, 2158.
- Wolff, E. W. (1995). Nitrate in polar ice. In *Ice Core Studies of Global Biogeochemical Cycles* (R. J. Delmas, Ed.), NATO ASI Series, Springer-Verlag, New York.
- Zielinski, G. A., Mayewski, P. A., Meeker, L. D., et al. (1994). <u>b0150</u> Record of volcanism since 7000 B.C. from the GISP2 Greenland ice core and implications for the volcano-climate System. Nature 264, 948–952.

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> Abstract: Glaciochemical measurements in polar and alpine ice cores provide a unique opportunity to study natural and anthropogenic impacts on atmospheric chemistry, as well as to interpret past changes in climate dynamics and biogeochemistry. While many different soluble mineral and organic constituents can be measured in snow and ice, most studies focus on the major ions (Na<sup>+</sup>, Mg<sup>2+</sup>, Ca<sup>2+</sup>, K<sup>+</sup>, NH<sub>4</sub><sup>+</sup>, Cl<sup>-</sup>, NO<sub>3</sub><sup>-</sup>, SO<sub>4</sub><sup>2-</sup>) that represent a majority of the soluble chemistry of the atmosphere, as well as organic acids (e.g., methylsulfonate (MS), CH<sub>3</sub>SO<sup>-</sup>). Sources for these ions include sea-salt, terrestrial dust, and biological and anthropogenic emissions, and in many cases these ions are important components of the sulfur and nitrogen biogeochemical cycles. Because several of the major ions have multiple sources, measurement of the full suite of ions in conjunction with statistical analysis can lead to detailed interpretation of past atmospheric conditions. Improvements in analytical measurement techniques have led to a global distribution of ice-core glaciochemical datasets on timescales ranging from seasonal to glacial-interglacial that can be used to study the spatial and temporal variability in chemical source, transport, and depositional processes.

> Keywords: Aerosols, Atmospheric circulation, Biogeochemistry, Climate dynamics, Geochemistry, Glaciochemistry, Ice cores, Pollution, Sea ice, Soluble major ions, Sulfur cycle

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