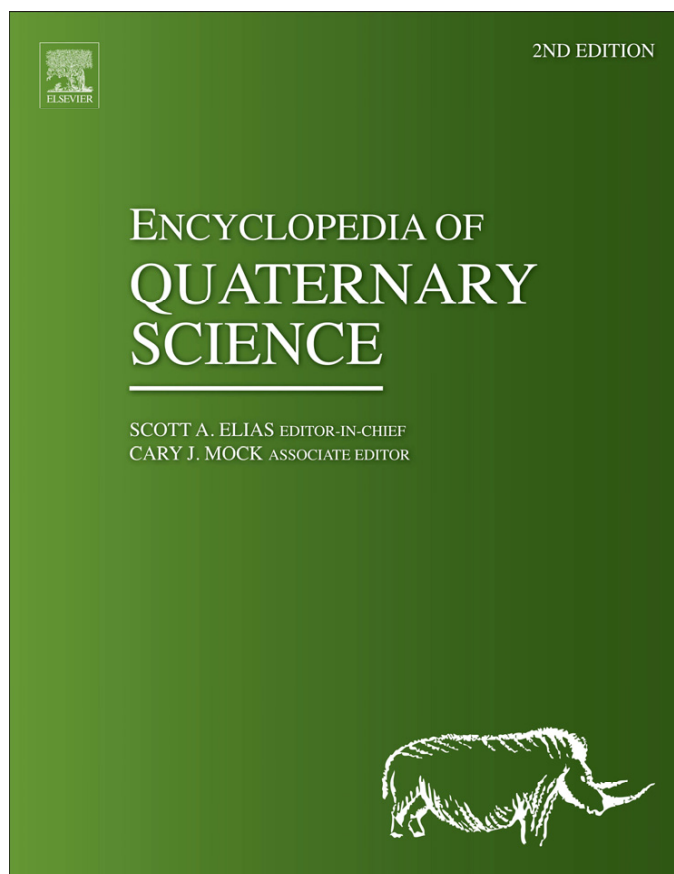


Provided for non-commercial research and educational use.
Not for reproduction, distribution or commercial use.

This article was originally published in the *Encyclopedia of Quaternary Science* published by Elsevier, and the attached copy is provided by Elsevier for the author's benefit and for the benefit of the author's institution, for non-commercial research and educational use including without limitation use in instruction at your institution, sending it to specific colleagues who you know, and providing a copy to your institution's administrator.



All other uses, reproduction and distribution, including without limitation commercial reprints, selling or licensing copies or access, or posting on open internet sites, your personal or institution's website or repository, are prohibited. For exceptions, permission may be sought for such use through Elsevier's permissions site at:

<http://www.elsevier.com/locate/permissionusematerial>

Kreutz K.J., and Koffman B.G. (2013) Glaciochemistry. In: Elias S.A. (ed.) *The Encyclopedia of Quaternary Science*, vol. 2, pp. 326-333. Amsterdam: Elsevier.

© 2013 Elsevier Inc. All rights reserved.

Glaciochemistry

K J Kreutz and B G Koffman, University of Maine, Orono, ME, USA

© 2013 Elsevier B.V. All rights reserved.

This article is a revision of the previous edition article by K. Kreutz, volume 2, pp. 1192–1199, © 2007, Elsevier B.V.

Introduction

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., CO₂, CH₄) 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 ice core 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⁻, NO₃⁻, and SO₄²⁻) 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 (CH₃COO⁻), and oxylate (C₂O₄⁻), methylsulfonate (CH₃SO₃⁻; MS⁻), and other volatile species such as hydrogen peroxide (H₂O₂) 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 article 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. For a more thorough understanding of the range of chemical species studied in ice cores, see elsewhere in this encyclopedia.

Glaciochemical Background and Measurement

The composition of precipitation in polar and alpine regions contains various soluble impurities, 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, SO₄²⁻ 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 ice core samples in order to understand and reconstruct the original association of the ions. The ionic budget (\sum ; sum of all ion species present) in polar and alpine snow can generally be written as follows (concentrations in microequivalents per liter, $\mu\text{eq L}^{-1}$):

$$\begin{aligned} \sum = & [\text{Na}^+] + [\text{NH}_4^+] + [\text{K}^+] + [\text{H}^+] + [\text{Ca}^{2+}] + [\text{Mg}^{2+}] \\ & + [\text{F}^-] + [\text{Cl}^-] + [\text{NO}_3^-] + [\text{SO}_4^{2-}] + [\text{CH}_3\text{SO}_3^-] \\ & + [\text{HCOO}^-] + [\text{CH}_3\text{COO}^-] \end{aligned}$$

In most situations, the concentrations of F⁻ and the light carboxylates are insignificant. While measurements of MS⁻ are important in the study of the atmospheric sulfur cycle, concentrations of the compound are usually low. Therefore, ΔC , the imbalance between cations and anions, can usually be simplified to:

$$\begin{aligned} \Delta C = & [\text{Na}^+] + [\text{NH}_4^+] + [\text{K}^+] + [\text{H}^+] + [\text{Ca}^{2+}] + [\text{Mg}^{2+}] \\ & - [\text{Cl}^-] + [\text{NO}_3^-] + [\text{SO}_4^{2-}] \end{aligned}$$

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

$$\begin{aligned} & [\text{Na}^+] + [\text{NH}_4^+] + [\text{K}^+] + [\text{H}^+] + [\text{Ca}^{2+}] + [\text{Mg}^{2+}] \\ & = [\text{Cl}^-] + [\text{NO}_3^-] + [\text{SO}_4^{2-}] \end{aligned}$$

Deposition of primary and secondary aerosols to the glacier or ice sheet 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 being scavenged by the falling snowflake. During dry deposition, the air-to-surface transfer occurs without any associated water transfer. To account for these processes when using ice core glaciochemical data, two procedures are common: (1) ice core time series of ion concentrations (e.g., parts per billion [ppb] or $\mu\text{eq L}^{-1}$) are interpreted directly, and (2) the estimated chemical flux (e.g., $\text{ng cm}^{-2} \text{year}^{-1}$) is calculated and interpreted. Chemical fluxes are calculated by multiplying the sample concentration by the estimated H₂O flux (accumulation). In some cases, a qualitative examination of either concentration or flux time series yields similar results. For example, the deposition of Ca²⁺ on the Antarctic polar plateau and coastal sites was clearly higher during the Last Glacial Maximum (LGM) when either ice core

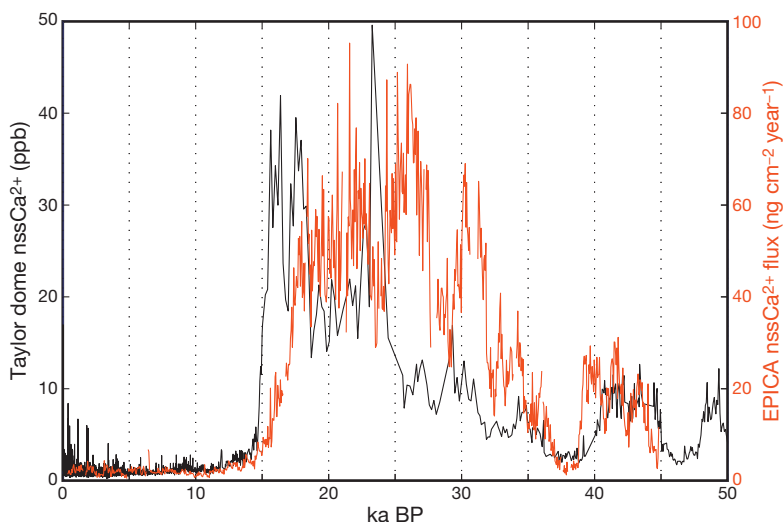


Figure 1 Nonsea salt (nss) Ca^{2+} concentrations (black) from the Taylor Dome, Antarctica ice core (Mayewski et al., 1996), and 50-year average nssCa^{2+} flux values (red) from the EPICA Dome C (EDC), Antarctica ice core (Rothlisberger et al., 2002).

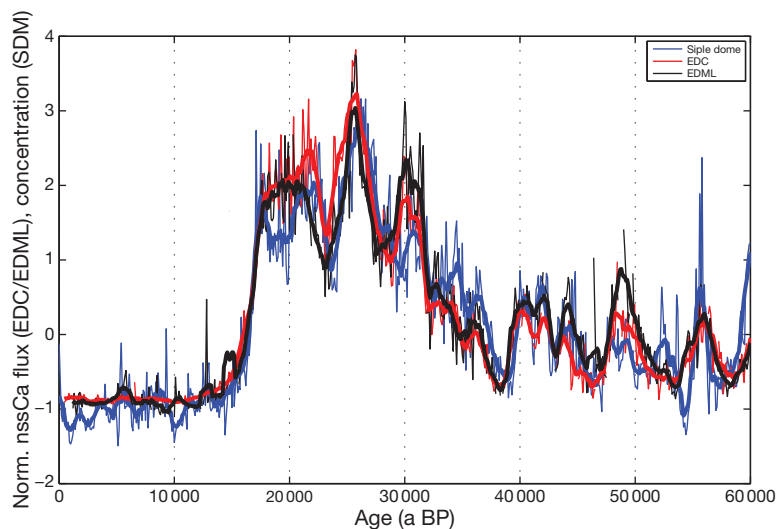


Figure 2 nssCa^{2+} fluxes from the EPICA Dome C (Fischer et al., 2007) and EPICA Dronning Maud Land (EDML; Fischer et al., 2007) ice cores, and nssCa^{2+} concentrations from the Siple Dome ice core, West Antarctica (Mayewski et al., 2009).

concentration or flux estimates are viewed (Figures 1 and 2). However, detailed quantitative analyses often require a more rigorous knowledge of site-specific air-snow-surface transfer functions, and justification for using either concentration or flux time series is necessary (e.g., 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 (e.g., Barnes et al., 2003).

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; e.g., Buck et al., 1992; Curran and Palmer, 2001; Legrand et al., 1984). 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. Early methods (still frequently used at high-accumulation sites) involved 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; Osterberg et al., 2006), or injected directly into an instrument during continuous flow analysis (CFA; e.g., Fuhrer et al., 1993; Kaufmann et al., 2008; Rothlisberger et al., 2000; Sigg et al., 1994). 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^+ , NH_4^+ , Ca^{2+}) 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 (Cole-Dai et al., 2006; Traversi et al., 2009; Wolff et al., 2006). 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 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 ($\mu\text{mol L}^{-1}$ or $\mu\text{eq L}^{-1}$).

Glaciochemical Sources and Spatial/Temporal Variability

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, statistical techniques are often applied to differentiate compounds responsible for ion deposition. In particular, multivariate techniques have been developed to deal with multiple chemical sources in a more quantitative fashion, in addition to accounting for factors inherent in ice core glaciochemical studies such as nonuniform sampling, nonstationary processes, and sporadic events (Meeker et al., 1995; Peixoto and Oort, 1992).

Sea Salt Aerosol

Sea salt aerosols are one of the major sources of impurities in polar ice cores, and contribute a significant portion of several species (notably Na^+ , Cl^- , SO_4^{2-} , and Mg^{2+}) to the ion balance. Originally, the source of the sea salt aerosol reaching coastal and inland plateau sites was thought to be primarily 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 (particularly ssNa) 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). A sea ice source is supported by the chemical signature of sea salt aerosols (e.g., depletion of SO_4^{2-}) during winter (e.g., Rothlisberger et al., 2010). Both of these factors (atmospheric dynamics and sea ice) likely contribute to sea salt deposition at a particular polar site, with each process being relatively more important on different timescales. 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 (Grumet et al., 2001). On glacial–interglacial timescales, sea salt records from Greenland (Figure 3; Mayewski et al., 1997) and Antarctica (Rothlisberger et al., 2002; Wolff et al., 2010) display significant concentration increases during glacial periods, suggesting the influence of both enhanced atmospheric transport

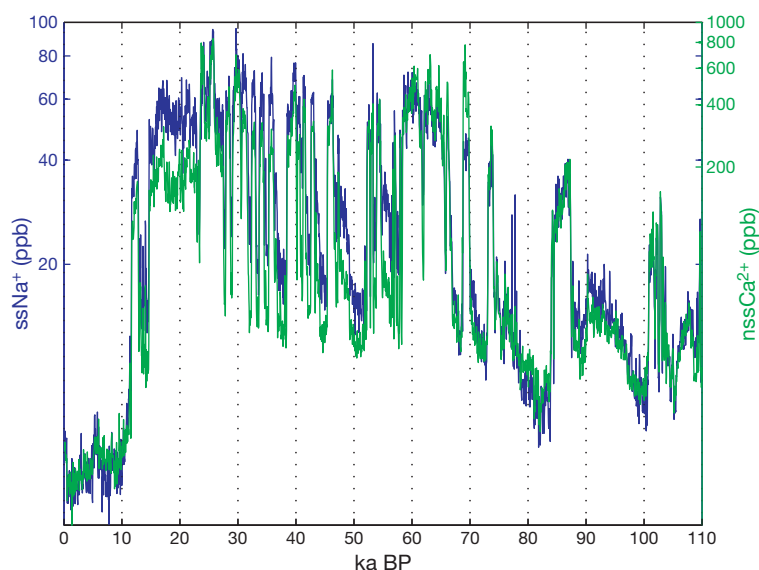


Figure 3 Sea salt (ss) Na^+ concentrations and nssCa^{2+} concentrations from the GISP2 ice core (Mayewski et al., 1997). Both datasets are 50-year averages.

and sea ice extent. At peak glacial conditions, however, ice core sea salt records may not be sensitive to sea ice variability; thus, incorporation of marine sediment core data can be useful (Rothlisberger et al., 2010). 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 (Kang et al., 2004). 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 elevation and accumulation rate (Thompson et al., 1998; Yalcin et al., 2006).

The calculation of the percentage of sea salt in any particular sample is an important step in determining 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^+ is generally thought to have no other significant source, and after deposition behaves conservatively. In this case, calculation of nssCa^{2+} , for example, would be:

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

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

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

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

where R_c is the $\text{Ca}^{2+}/\text{Na}^+$ 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 where the relative important of sea salt 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).

Terrestrial Dust

Dust records from polar and alpine ice cores have been widely used to infer past changes in atmospheric circulation and climatic/environmental conditions in dust source regions. Dust is important in the climate system because of its scattering effect on incoming solar radiation, and dust particles also serve as cloud condensation nuclei. Dust is also an important source of the trace nutrient iron (Fe) to the world's oceans, where it can have a fertilizing effect on primary production and nitrogen fixation (e.g., Martin et al., 1990; Moore et al., 2009). Thus, ice core measurements of dust allow us to estimate the magnitude of these effects through time. Measurement of dust (mineral aerosols) in polar ice cores can be accomplished in several ways, including both direct and proxy measurements. The most commonly used dust proxy is nssCa^{2+} , as the major portion of

nssCa^{2+} detected in ice cores comes from continental dust (Legrand and Mayewski, 1997) and it can be measured in a straightforward manner using IC. While it has been shown to record major changes in dust deposition on glacial–interglacial timescales (Figures 1–3) nssCa^{2+} varies in its reproducibility of insoluble particle measurements by up to a factor of 2 between low (interglacial) and high (glacial) dust concentrations (Ruth et al., 2008). This may indicate variable dust composition, and in fact, work in East Antarctica has found evidence of calcium carbonates at coastal sites (Sala et al., 2008). Ruth et al. (2008) suggest that quantitative reconstruction of dust deposition depends on the analysis method used.

In addition to nssCa^{2+} , the nss fractions of several other species (including Mg^{2+} , Na^+ , K^+ , SO_4^{2-} , NO_3^- , Cl^-) can be linked to insoluble silicate or soluble carbonate or evaporite (e.g., gypsum, halite) minerals derived from terrestrial sites. 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, Antarctica, where exposed soils provide a source of soluble particulate material (Williamson et al., 2007). During the Holocene, changes in dust transport to Greenland are reflected in ice core nssCa^{2+} , nssMg^{2+} , and nssK^+ concentrations (O'Brien et al., 1995), and correlation with instrumental data as well as trace element isotopic work indicates that an Asian source is most probable (Bory et al., 2003; Meeker and Mayewski, 2002).

During the LGM, nssCa^{2+} concentrations show dramatic increases on the Antarctic (Figures 1 and 2) and Greenland (Figure 3) polar plateaus, as well as significant millennial-scale variability (Mayewski et al., 1996, 1997; Petit et al., 1999; Rothlisberger et al., 2002). In general, atmospheric dust loadings globally were a factor of 2–4 higher during glacial periods than during interglacials, with the northern hemisphere producing the majority of dust on a global scale (Fischer et al., 2007; Kohfeld and Harrison, 2002; Lambert et al., 2008; Maher et al., 2010). Modeling studies have suggested 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 (e.g., Mahowald et al., 2006), while glacial activity may have been an important local factor (Sugden et al., 2009). However, a synthesis of empirical and modeling results that tests these various factors points to wind gustiness as a primary first-order driver of dust emissions during the LGM (McGee et al., 2010).

Volcanic Aerosols

Volcanic eruptions emit large amounts of particulate matter and gases (mainly SO_2) to different heights in the atmosphere

depending on eruption intensity and magma composition. Sulfate aerosols formed from the atmospheric oxidation of SO_2 and gas-to-particle conversions can be transported on regional to global scales, particularly when injected into the stratosphere (upper atmosphere), and are 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^- and F^- (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). In the Southern Hemisphere, ice core records from coastal (Talos Dome) and West Antarctic sites (Kurbatov et al., 2006; Langway et al., 1995) also show a mixture of global and local/regional eruptions. In contrast, East Antarctic plateau ice cores generally are removed from any local-scale volcanic signals and therefore provide complementary estimates of explosive global-scale eruptions for use in bipolar comparisons (Cole-Dai et al., 2000). 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. Isotopic analysis of sulfate can be used to differentiate among sources; for example, in West Antarctica, volcanic and stratospheric sources of sulfate dominate, while marine sources are more important in East Antarctica (e.g., Kunasek et al., 2010; Pruet et al., 2004). Ice core-based reconstructions of past volcanic eruption frequency and intensity have, for example, identified an increase in volcanic activity in the early Holocene (Zielinski et al., 1994; Figure 4), 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.

Biogenic Emissions

Biogenic emissions play a large role in the atmospheric sulfur cycle. In the remote unpolluted marine atmosphere, oxidation of dimethylsulfide (DMS) released from marine organisms represents a major source of nssSO_4^{2-} , both on local and global scales. In addition, the oxidation of DMS also produces methanesulfonic acid (measured as methylsulfonate; 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 potential tool for deconvolving marine biogenic from nonbiogenic sulfur sources, and potentially for 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 $\text{MS}^-/\text{nssSO}_4^{2-}$ (R) in ice cores may provide a tool for estimating marine emissions. Such measurements are particularly relevant in Antarctica, given the surrounding open and ice-covered 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 inland Antarctic ice cores sites 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 ice core 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.,

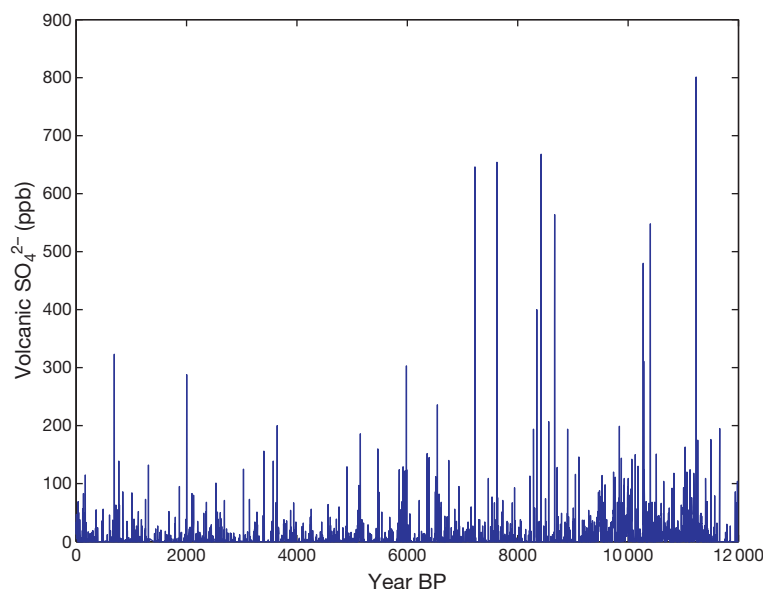


Figure 4 Volcanic SO_4^{2-} concentrations from the GISP2 ice core (Zielinski et al., 1994). The volcanic fraction of total SO_4^{2-} concentration are residuals calculated using a low-tension robust spline method.

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 (Abram et al., 2007; Curran et al., 2003; Rhodes et al., 2009), 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_4^+ concentrations primarily arise from biological emissions of ammonia from plants, soils, and animals, bacterial decomposition, burning of biological materials (forest and grass fires), and potentially marine biological emissions. In the high-latitude Northern Hemisphere, NH_4^+ 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, NH_4^+ 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 NH_4^+ concentrations in the Greenland Ice Sheet Project 2 (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 5). In Antarctica, NH_4^+ 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 NH_4^+ from inland sites remain

difficult both to measure and to interpret. In alpine regions, industrial and agricultural emissions likely impact snow and ice core NH_4^+ concentrations.

Nitrogen Cycling

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 (e.g., Wolff, 1995). Some features in the 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 (Mayewski et al., 1986). However, the interpretation of NO_3^- records beyond the anthropogenic era in Greenland, and in Antarctica in general, remains difficult. Several minor sources of NO_x have been suggested, including meteorite impact, supernovae, and solar modulation (sunspot cycle, solar proton events). The main sources are considered to be NO_x production in the stratosphere and troposphere by lightning. Recent studies of atmospheric NO_y (NO_x , HNO_3 , N_2O_5 , particulate and organic nitrates) have shown considerable amounts of organic nitrate, further complicating the interpretation of ice core NO_3^- time-series records. Studies have demonstrated that depositional and postdepositional processes have a strong influence on NO_3^- concentrations preserved in snow and ice cores (Wolff, 1995; Wolff et al., 2010 and references therein). In particular, it appears that changes in climate (temperature and accumulation rate) and atmospheric chemistry (Ca^{2+} concentrations) had a strong impact on the preservation of NO_3^- during the Holocene and LGM in the polar regions. At sites where potential NO_3^- sources may be close, changes in forest cover and local terrestrial biogeochemistry may explain glacial-interglacial NO_3^- concentration changes (Thompson et al., 1998).

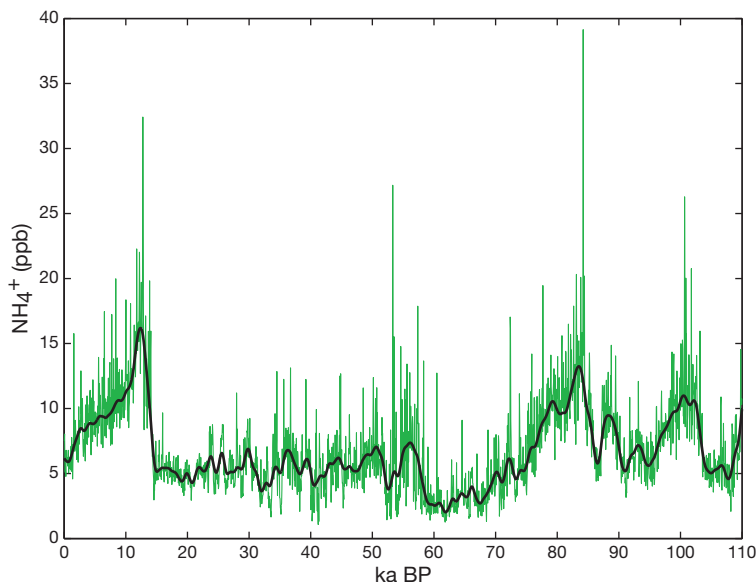


Figure 5 Ammonium (NH_4^+) concentration from the GISP2 ice core (Meeker et al., 1997). The green line is 50-year averaged data, and the black line is a low-tension robust spline chosen to highlight millennial-scale variability.

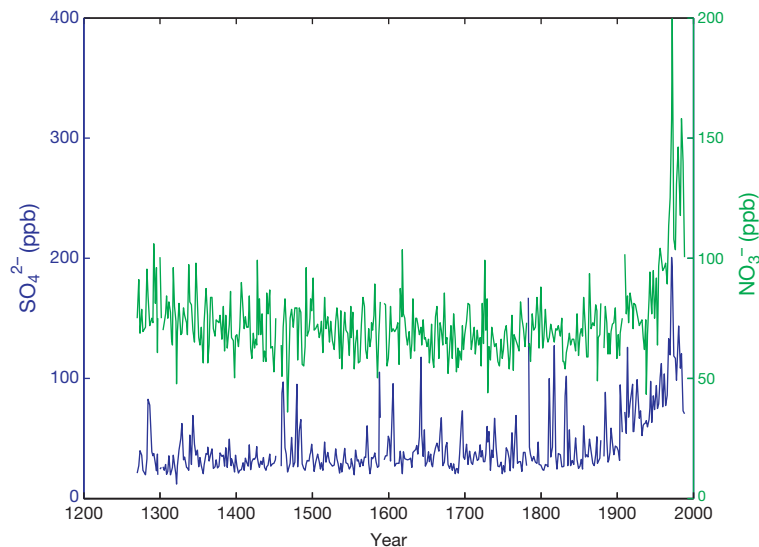


Figure 6 Sulfate (SO_4^{2-} ; blue) and nitrate (NO_3^- ; green) concentrations from the GISP2 ice core (Mayewski et al., 1986, 1990), showing a clear increase in the twentieth century due to anthropogenic emissions.

Anthropogenic Emissions

Emissions of SO_2 and NO_x from industrial processes and 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 (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 6; Mayewski et al., 1986, 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 in a single ice core record through the use of stable isotopic analysis. 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 (Pruett et al., 2004). At the present time, there is no convincing evidence for an anthropogenic impact on SO_4^{2-} or NO_3^- concentrations in Antarctica.

See also: **Ice Cores:** History of Research, Greenland and Antarctica. **Ice Core Methods:** Biological Material; Chronologies; CO_2 Studies; Conductivity Studies; Methane Studies; Microparticle and Trace Element Studies; Overview; Stable Isotopes.

References

- Abram N, Mulvaney R, Wolff E, and Mudelsee M (2007) Ice core records as sea ice proxies: An evaluation from the Weddell Sea region of Antarctica. *Journal of Geophysical Research* 112: D15101.
- Barnes PRF, Wolff EW, Mader HM, 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–ACH 17-14.
- Bory A, Biscaye P, Piotrowski A, and Steffensen J (2003) Regional variability of ice core dust composition and provenance in Greenland. *Geochemistry, Geophysics, Geosystems* 4: 1107. <http://dx.doi.org/10.1029/2003GC000627>.
- Buck CF, Mayewski PA, and Whitlow SI (1992) Determination of major ions in snow and ice by ion chromatography. *Journal of Chromatography. A* 594: 225–228.
- 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: D06114. <http://dx.doi.org/10.1029/2004JD005259>.
- Cole-Dai J, Budner D, and Ferris D (2006) High speed, high resolution, and continuous chemical analysis of ice cores using a melter and ion chromatograph. *Environmental Science & Technology* 40: 6764–6769.
- Cole-Dai J, Mosley-Thompson E, Wight S, and Thompson LG (2000) A 4100-year record of explosive volcanism from an East Antarctica ice core. *Journal of Geophysical Research* 105: 24431–24441.
- Curran MAJ and Palmer A (2001) Suppressed ion chromatography methods for the routine determination of ultra low level anions and cations in ice cores. *Journal of Chromatography A* 919: 107–113.
- Curran MAJ, Van Ommen T, Morgan V, Phillips KL, and Palmer AS (2003) Ice core evidence for Antarctic sea ice decline since the 1950's. *Science* 302: 1203–1206.
- Fischer H, et al. (2007) Reconstruction of millennial changes in dust emissions, transport, and regional sea ice coverage using the deep EPICA ice cores from the Atlantic and Indian Ocean sector of Antarctica. *Earth and Planetary Science Letters* 260: 340–354.
- Fuhrer K, Nefftel A, Anklin M, and Maggi V (1993) Continuous measurements of hydrogen peroxide, formaldehyde, calcium, and ammonium concentrations along the new GRIP ice core from Summit, Central Greenland. *Atmospheric Environment* 27A: 1873–1880.
- Grumet N, Wake C, Mayewski P, Zielinski G, Koerner R, and Fisher D (2001) Variability of sea-ice extent in the Baffin Bay over the last millennium. *Climatic Change* 49: 129–145.
- Herron MM (1982) Impurity sources of F^- , Cl^- , NO_3^- and SO_4^{2-} in Greenland and Antarctic precipitation. *Journal of Geophysical Research* 87: 3052–3060.
- Kang S, Mayewski P, Qin D, Sneed S, Ren J, and Zhang D (2004) Seasonal differences in snow chemistry from the vicinity of Mt. Everest, central Himalayas. *Atmospheric Environment* 38: 2819–2829.

- Kaufmann PR, Federer U, Hutterli MA, et al. (2008) An improved continuous flow analysis system for high-resolution field measurements on ice cores. *Environmental Science & Technology* 42: 8044–8050.
- Kohfeld KE and Harrison RM (2002) DIRTMAP: The geological record of dust. *Earth-Science Reviews* 54(1–3): 81–114.
- Kreutz KJ, Mayewski PA, Pittalwala II, Meeker LD, Twickler MS, and Whitlow SI (2000) Sea-level pressure variability in the Amundsen Sea region inferred from a West Antarctic glaciochemical record. *Journal of Geophysical Research* 105: 4047–4059.
- Kunasek S, Alexander B, Steig E, et al. (2010) Sulfate sources and oxidation chemistry over the past 250 years from sulfur and oxygen isotopes of sulfate in a West Antarctic ice core. *Journal of Geophysical Research* 115: D18313. <http://dx.doi.org/10.1029/2010JD013846>.
- Kurbatov A, Zielinski G, Dunbar N, et al. (2006) A 12,000 year record of explosive volcanism in the Siple Dome ice core, West Antarctica. *Journal of Geophysical Research* 111: D12307. <http://dx.doi.org/10.1029/2005JD006072>.
- Lambert F, Delmonte B, Petit J, et al. (2008) Dust-climate couplings over the past 800,000 years from the EPICA Dome C ice core. *Nature* 452: 616–619.
- Langway CCJ, Osada K, Clausen HB, Hammer CU, and 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 review. In: Delmas R (ed.) *Ice Core Studies of Global Biogeochemical Cycles*, pp. 91–120. New York: Springer.
- Legrand M, De Angelis M, and Delamas RJ (1984) Ion chromatographic determination of common ions at ultratrace levels in Antarctic snow and ice. *Analytica Chimica Acta* 156: 181–192.
- Legrand M, Feniet-Saigne C, Saltzman ES, Germain C, Barkov NI, and Petrov VN (1991) Ice-core record of oceanic emissions of dimethylsulphide during the last climate cycle. *Nature* 350: 144–146.
- Legrand M and Mayewski PA (1997) Glaciochemistry of polar ice cores: A review. *Reviews of Geophysics* 35: 219–243.
- Littot GC, Mulvaney R, Rothlisberger R, et al. (2002) Comparison of analytical methods used for measuring major ions in the EPICA Dome C (Antarctica) ice core. *Annals of Glaciology* 35: 299–305.
- Maher BA, Prospero J, Mackie D, Gaiero D, Hesse P, and Balkanski Y (2010) Global connections between aeolian dust, climate and ocean biogeochemistry at the present day and at the last glacial maximum. *Earth-Science Reviews* 99: 61–97.
- Mahowald N, Muhs D, Levis S, et al. (2006) Change in atmospheric mineral aerosols in response to climate: Last glacial period, preindustrial, modern, and doubled carbon dioxide climates. *Journal of Geophysical Research* 111: D10202. <http://dx.doi.org/10.1029/2005JD006653>.
- Martin JH, Gordon RM, and Fitzwater SE (1990) Iron in Antarctic waters. *Nature* 345: 156–158.
- Mayewski PA, Lyons WB, Spencer MJ, Twickler MS, Buck CF, and Whitlow S (1990) An ice-core record of atmospheric response to anthropogenic sulfate and nitrate. *Nature* 346: 554–556.
- Mayewski PA, Lyons WB, Spencer MJ, et al. (1986) Sulfate and nitrate concentrations from a South Greenland ice core. *Nature* 232: 975–977.
- Mayewski PA, Meredith MP, Summerhayes CP, et al. (2009) State of the Antarctic and Southern Ocean climate system. *Reviews of Geophysics* 47: RG1003, 38 pp.
- Mayewski PA, Meeker LD, Twickler MS, et al. (1997) Major features and forcing of high latitude northern hemisphere atmospheric circulation over the last 110,000 years. *Journal of Geophysical Research* 102: 26345–26366.
- Mayewski PA, Twickler MS, Whitlow SI, et al. (1996) Climate change during the deglaciation in Antarctica. *Science* 272: 1636–1638.
- McGee D, Broecker W, and Winckler G (2010) Gustiness: The driver of glacial dustiness? *Quaternary Science Reviews* 29: 2340–2350.
- Meeker LD and Mayewski PA (2002) A 1400 year long record of atmospheric circulation over the North Atlantic and Asia. *The Holocene* 12: 257–266.
- Meeker LD, Mayewski PA, and Bloomfield P (1995) A new approach to glaciochemical time series analysis. In: Delmas RJ (ed.) *Ice Core Studies of Global Biogeochemical Cycles*. Berlin: Springer-Verlag.
- Meeker LD, Mayewski PA, Twickler MS, Whitlow SI, 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: 26489–26504.
- Meyerson E, Mayewski PA, Kreutz KJ, Meeker LD, Whitlow SI, and Twickler MS (2002) The polar expression of ENSO and sea-ice variability as recorded in a South Pole ice core. *Annals of Glaciology* 35: 430–436.
- Moore CM, Mills MM, Achterberg EP, et al. (2009) Large-scale distribution of Atlantic nitrogen fixation controlled by iron availability. *Nature Geoscience* 2: 861–871.
- O'Brien SR, Mayewski PA, Meeker LD, Meese DA, Twickler MS, and Whitlow SI (1995) Complexity of Holocene climate as reconstructed from a Greenland ice core. *Science* 270: 1962–1963.
- Osterberg EO, Handley M, Sneed S, Mayewski P, and Kreutz K (2006) Continuous ice core melter system with discrete sampling for major ion, trace element, and stable isotope analysis. *Environmental Science & Technology* 40: 3355–3361.
- Peixoto J and Oort A (1992) *Physics of Climate*, 520 pp. New York, USA: American Institute of Physics.
- Petit JR, 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.
- Pruett L, Kreutz K, Mayewski P, and Wadleigh M (2004) Sulfur isotopic measurements from a West Antarctic ice core: Implications for sulfate source and transport. *Annals of Glaciology* 39: 161–165.
- Rhodes RH, Bertler N, Baker J, Sneed S, Oerter H, and Arrigo K (2009) Sea ice variability and primary productivity in the Ross Sea, Antarctica, from methylsulphonate snow record. *Geophysical Research Letters* 36: L10704, 5pp. <http://dx.doi.org/10.1029/2009GL037311>.
- Rothlisberger R, Bigler M, Hutterli M, Sommer S, and Stauffer B (2000) Technique for continuous high-resolution analysis of trace substances in firn and ice cores. *Environmental Science & Technology* 34: 338–342.
- Rothlisberger R, Crosta X, Abram N, Armand L, and Wolff E (2010) Potential and limitations of marine and ice core sea ice proxies: An example from the Indian Ocean sector. *Quaternary Science Reviews* 29: 296–302.
- Rothlisberger R, Mulvaney R, Wolff EW, 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: 1963–1966.
- 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 <http://dx.doi.org/10.1029/2003JD003604>.
- Ruth U, et al. (2008) Proxies and measurement techniques for mineral dust in Antarctic ice cores. *Environmental Science & Technology* 42: 5675–5681.
- Sala M, Delmonte B, Frezzotti M, et al. (2008) Evidence of calcium carbonates in coastal (Talos Dome and Ross Sea area) East Antarctica snow and firn: Environmental and climatic implications. *Earth and Planetary Science Letters* 271: 43–52.
- 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.
- Schwikowski M, Brüttsch S, Gäggeler HW, and Schotterer U (1999) A high-resolution air chemistry record from an Alpine ice core: Fiescherhorn glacier, Swiss Alps. *Journal of Geophysical Research* 104: 13709–13719.
- Sigg A, Fuhrer K, Anklin M, Staffelbach T, and Zurmühle D (1994) A continuous analysis technique for trace substances in ice cores. *Environmental Science & Technology* 28: 204–209.
- Sugden D, McCulloch R, Bory A, and Hein A (2009) Influence of Patagonian glaciers on Antarctic dust deposition during the last glacial period. *Nature Geoscience* 2: 281–285.
- Thompson LG, Davis ME, Mosley-Thompson E, et al. (1998) A 25,000-year tropical climate history from Bolivian ice cores. *Science* 282: 1858–1864.
- Thompson LG, Yao T, Davis ME, et al. (1997) Tropical climate instability: The last glacial cycle from a Qinghai-Tibetan ice core. *Science* 276: 1821–1825.
- Traversi R, et al. (2009) Sulfate spikes in the deep layers of EPICA-Dome C ice core: Evidence of glaciological artifacts. *Environmental Science & Technology* 43: 8737–8743.
- Williamson B, Kreutz K, Mayewski P, et al. (2007) A coastal transect of McMurdo Dry Valleys (Antarctica) snow and firn: Marine and terrestrial influences on glaciochemistry. *Journal of Glaciology* 53: 681–685.
- Wolff EW (1995) Nitrate in polar ice. In: Delmas RJ (ed.) *Ice Core Studies of Global Biogeochemical Cycles*. NATO ASI Series. New York: Springer-Verlag.
- Wolff E, Rankin AM, and Rothlisberger R (2003) An ice core indicator of Antarctic sea ice production? *Geophysical Research Letters* 30: 2158. <http://dx.doi.org/10.1029/2003GL01854>.
- Wolff E, et al. (2006) Southern Ocean sea-ice extent, productivity, and iron flux over the past eight glacial cycles. *Nature* 440: 491–496.
- Wolff E, et al. (2010) Changes in environment over the last 800,000 years from chemical analysis of the EPICA Dome C ice core. *Quaternary Science Reviews* 29: 285–295.
- Yalcin K, Wake C, Kang S, and Kreutz K (2006) Seasonal and spatial variability in snow chemistry at Eclipse Icefield, Yukon, Canada. *Annals of Glaciology* 43: 200–204.
- Zielinski GA, Mayewski PA, Meeker LD, et al. (1994) Record of volcanism since 7000 B.C. from the GISP2 Greenland ice core and implications for the volcano-climate system. *Nature* 264: 948–952.