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Glaciochemistry of polar ice cores: A review

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GLACIOCHEMISTRY OF POLAR ICE CORES: A REVIEW

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Abstract. Human activities have already modified the chemical composition of the natural atmosphere even in very remote regions of the world. The study of chemical parameters stored in solid precipitation and accumulated on polar ice sheets over the last several hundred thousand years provides a unique tool for obtaining information on the composition of the preindustrial atmosphere and its natural variability over the past. This paper deals with the chemistry of polar ice focused on the soluble mineral (Na^+, NH_4^+, K^+, Ca^{++}, Mg^{++}, H^+, F^-, Cl^-, NO_3^-, SO_4^{--}, and H_2O_2) and organic (methanesulfonate ($CH_3SO_3^-$), formate ($HCOO^-$), acetate (CH_3COO^-), and formaldehyde ($HCHO$)) species and their interpretation in terms of past atmospheric composition (aerosols and water soluble gaseous species).

We discuss ice core dating, the difficulties connected with trace measurements, and the significance of the ionic composition of snow. We examine temporal (from the last decades back to the last climatic cycle) and spatial (including examples from coastal as well as central areas of Greenland and Antarctica) variations in the ionic budget of the precipitation and evaluate ice core studies in terms of the chemical composition of our past atmosphere. We review (1) how Greenland and Antarctic ice cores that span the last few centuries have provided information on the impact of human activities and (2) how the chemistry of deep ice cores provides information on various past natural phenomena such as climatic variations (glacial-interglacial changes, El Niño), volcanic eruptions, and large boreal forest fires.

1. INTRODUCTION

By virtue of their geographical position and meteorological conditions, polar regions are of interest in a variety of environmental studies. First, because they are located far away from continents (where local sources such as wind-blown dust, biogenic emissions from soils and vegetation, or anthropogenic emissions dominate), the Antarctic and, to a lesser extent, Arctic regions provide the cleanest atmospheric environments in their respective hemispheres. The atmosphere in the coastal regions of the Greenland and Antarctic ice sheets is strongly influenced by trace gases and aerosols emitted by surrounding high-latitude oceans, while inland, at more than 3000 m above sea level, this marine input is strongly decreased [*Herron and Langway*, 1979; *Legrand and Delmas*, 1985]. Despite this relative remoteness, the atmosphere of the polar regions is already affected by human activities. The recent development of the so-called ozone hole over Antarctica in spring and the Arctic haze phenomenon over Arctic regions in winter are good examples of the fragility of the atmosphere in these high-latitude regions. A second specific feature of polar regions lies in their meteorological conditions: their well-marked seasonal cycle with a long polar night, their very cold temperatures, and the consequent dryness of the air. The chemical reactivity of the polar atmosphere is considerably reduced (e.g., the quasi-absence of photochemistry during the winter months and the decreased speed of some chemical reactions with lowered temperatures) compared with the situation at midlatitudes. From this point of view, polar regions can be considered as a kind of giant natural laboratory in which it may be simpler than elsewhere to check the complex chemistry governing biogenic (sulfur, nitrogen, and carbon) cycles. A third and unique characteristic of these regions comes from solid precipitation that accumulates on polar ice caps. Assuming a good knowledge of the relation linking the composition of the snow and that of the atmosphere, polar ice cores offer the possibility to reconstruct past atmospheric chemistry and climate of the Earth over time periods as long as several thousands years.

Recognizing the importance of polar regions, in addition to atmospheric monitoring programs, national and international programs have drilled and extracted numerous deep ice cores from Greenland and Antarctica (Figure 1). As a consequence of differences in saturation vapor pressure and molecular diffusivity, isotopic fractionation ($HD^{16}O$ and $H_2^{18}O$ relative to $H_2^{16}O$, the main component of water) takes place at each phase change of atmospheric water [*Dansgaard*, 1954]. Since the heavy isotope content in precipitation decreases with the condensation temperature, stable isotope contents in ice cores provide long and detailed proxy records of past temperature. During the early
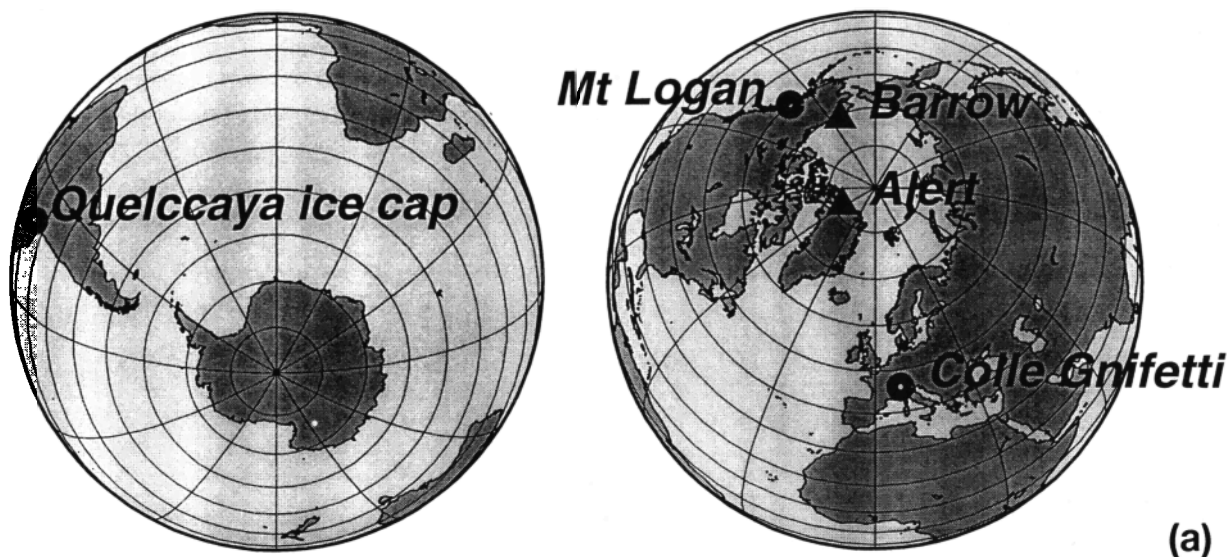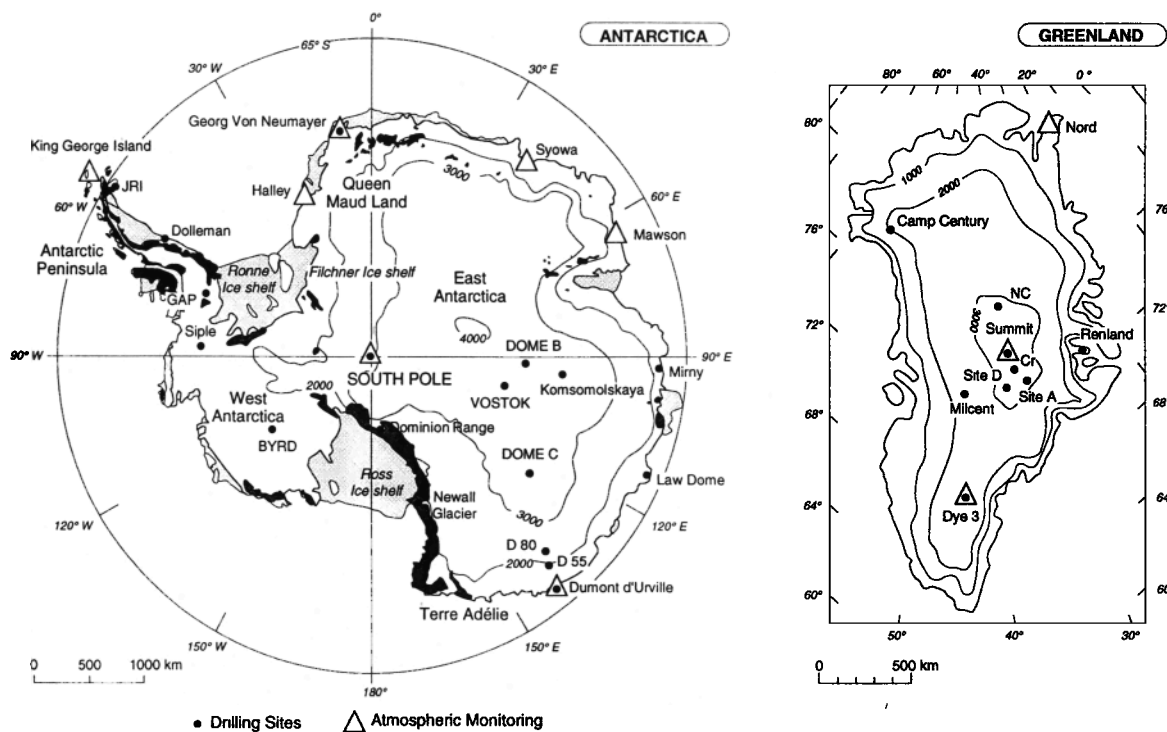
Figure 1. (a) Locations of cold glaciers and great ice sheets. (b) Maps of Antarctica and Greenland, showing locations where deep ice cores have been extracted (dots) and where atmospheric sampling is currently under way (open triangles). In Antarctica, JRI is James Ross Island and GAP is Gomez, Antarctic Peninsula; in Greenland, Cr is Crete and NC is North Central.

lifetime of a freshly fallen snowflake, the sharp edges of the snow crystal are rounded off because the water vapor pressure is inversely proportional to the radius of curvature (the Kelvin effect), leading to a rapid decrease of the specific surface. Furthermore, near the surface, temperature gradients induced by diurnal and seasonal variations lead to evaporation and recondensation of water molecules and to the formation of firn. Deeper down, this firn is compressed by rearrangement of the snow

grains and by plastic deformation. Snow and firn are porous material with density of <200 kg m^{-3} and $200-800$ kg m^{-3}, respectively. At a density of 800 kg m^{-3} the pores start to encapsulate air volumes [*Schwander and Stauffer*, 1984]. In addition to the paleothermometric property of ice, polar ice cores therefore contain two sets of atmospheric information. First, when firn turns into ice, bubbles are formed, trapping atmospheric air whose composition provides information on the trace gas (e.g.,

CO_2 and CH_4) content of the atmosphere at the time of ice formation. Second, aerosols and water soluble gaseous species can be trapped during the formation and the life of cloud droplets and ice crystals in the atmosphere or directly deposited on the snow surface. The chemical composition of impurities trapped in snow and the interpretation of these records in terms of composition of the past atmosphere has opened up a powerful new avenue of ice core research called glaciochemistry. Thus ice cores are unique in that they provide records of aerosols as well as gas constituents in great temporal detail. Along with the temperature records ($\delta^{18}O$ or δD), these chemical records are useful in examining the atmospheric forcing of climate in the past.

Glaciochemical studies are of importance for obtaining proxy atmospheric data at high latitudes, since direct atmospheric measurements are rare and limited in time. They can also provide valuable data concerning paleovolcanism, the response of our atmosphere to other natural phenomena such as major and/or rapid changes in climate, and the response of the high-latitude atmosphere to human activities (e.g., acidification of precipitation, ozone depletion, and oxidative capacity of the atmosphere). Such information can also increase our knowledge of the natural variability of major biogenic cycles.

2. BRIEF HISTORY OF GLACIOCHEMICAL STUDIES

One of the first ice core studies was that conducted in Greenland ice by *Murozumi et al.* [1969] which revealed a 200-fold increase in Pb concentration from several thousand years ago to the mid 1960s due to anthropogenic emissions. Some years after, another pioneering study [*Hammer*, 1977] revealed that numerous volcanic eruptions are recorded as "acid layers" in polar ice. This study stimulated numerous others dealing with the detailed reconstruction of volcanism in the past. These studies permitted estimates of the magnitude of volcanic SO_2 emissions [*Hammer*, 1980; *Legrand and Delmas*, 1987; *Lyons et al.*, 1990; *Delmas et al.*, 1992; *Zielinski et al.*, 1994] providing additional information to that already available from other volcanic magnitude scales such as those based either on atmospheric impact observations (dust veil index [*Lamb*, 1970]) or on dissipated energy (volcanic explosivity index [*Newhall and Self*, 1982]). The studies of deep ice cores first extracted from Greenland (Camp Century) and Antarctica (Byrd and Dome C) revealed that the last glacial age was characterized by higher inputs of marine and continental aerosols compared with present time [*Cragin et al.*, 1977; *Petit et al.*, 1981]. These results were interpreted as an indication of higher wind speed and the presence of enlarged arid areas over the world during the glacial periods. Greenland ice cores have recorded the change in acidification of precipitation (HNO_3 and H_2SO_4) in

the northern hemisphere [*Neftel et al.*, 1985; *Mayewski et al.*, 1986] over time relative to increased emissions of NO_x and SO_2 from fuel combustion. The first studies of methanesulfonate, or MSA ($CH_3SO_3^-$), the only atmospheric source of which is dimethylsulfide (DMS) emitted by marine biota, gave new insight on the past variability of oceanic DMS emissions and their contribution to the natural sulfur cycle [*Saigne and Legrand*, 1987]. Although extensively studied, nitrate remains the species for which it is still most difficult to assess main sources [*Legrand and Kirchner*, 1990] and paleoenvironmental significance [*Wolff*, 1995]. Several workers have investigated the possibility of reconstructing the past oxidative capacity of the atmosphere by studying hydrogen peroxide (H_2O_2) and formaldehyde (HCHO) [*Neftel and Fuhrer*, 1993] in polar ice. Glaciochemical investigations have also been directed toward the measurement of organic species such as black carbon [*Chýlek et al.*, 1992], total organic carbon [*Cachier*, 1995], and carboxylic acids [*Legrand et al.*, 1992a]. These organic species appear to be useful in investigating the history of biomass burning and vegetation emissions from high northern latitudes in the past [*Legrand and De Angelis*, 1995]. In addition to these current ice core studies, intensive investigations of the relationship linking the composition of the air and that of the snow at the time of deposition, the air-snow transfer function, have started in south [*Jaffrezo and Davidson*, 1993] and central [*Dibb et al.*, 1992] Greenland.

3. STATE OF THE ART IN GLACIOCHEMISTRY

3.1. Dating of Snow and Ice
The establishment of reliable chronologies for ice cores is the first necessary step in glaciochemical studies. Depending on the required accuracy and the time period and the location (high or low annual accumulation rate) under consideration, various methods can be used to provide dating of depth profiles. These include stratigraphic studies, reference horizons, radioactive decay of some radionuclides, and comparison with other records.

In principle, numerous stratigraphical methods based on seasonal changes in the isotopic composition of the ice or in the concentration of impurities, as well as in physical properties of snow, may be used to establish year-by-year dating of ice cores. Summer deposits are often composed of coarser-grained crystals (hoar layers) and packed more loosely than are the fine-grained, more homogeneous, and hard-packed winter deposits [*Gow*, 1965].

The dating of ice layers based on the seasonality of the stable isotope content [*Dansgaard*, 1964] has been applied to numerous ice cores. One advantage of this method is that no special precautions are necessary to prevent sample contamination. However, a damping effect related to diffusion processes occurring during firn formation limits the stable isotope method to the dating

of the upper part of firn in location where the snow accumulation rate is lower than 200 kg m^{-2} yr^{-1} [Johnsen, 1977].

Hydrogen peroxide was found to be one of the clearest seasonal tracers in ice cores [Sigg and Neftel, 1988], at least in sites characterized by high accumulation rates of snow, with a typical summer-to-winter ratio higher than 5 (Figure 2). This is thought to be due to enhanced photochemistry in summer. Such a method does not require extensive contamination control procedures and is rapid (even in the field) by using continuous flow analysis (section 3.3). However, as with the seasonal variation of the stable isotopic content, the H_2O_2 method is also limited to high-accumulation sites because of diffusion and smoothing with depth of the seasonal cycle. Furthermore, such a method cannot be applied to ice with high dust content because of the destruction of H_2O_2 in ice by oxidants [Neftel et al., 1986].

Among the other chemical species currently measured in polar precipitation, calcium and ammonium exhibit very strong seasonal cycles in Greenland, as does sodium in both Antarctic and Greenland snow layers. Concentrations of Na$^+$, a tracer of sea salt, exhibit well-marked winter maxima in both central Greenland (Figure 2) and Antarctic (Figure 3) snow as a consequence of more frequent advection of marine air masses in winter over ice sheets [Herron, 1982; Legrand and Delmas, 1984]. Seasonal variations are weaker for Cl$^-$ than for Na$^+$ (Figures 2 and 3b). Na$^+$ and Cl$^-$ are present in winter layers as sea salt, as suggested by Cl$^-$ to Na$^+$ molar ratios close to the bulk seawater reference value (1.17) (Figures 2 and 3b). In summer, an additional input of HCl (section 4) can take place, leading to a maximum of the ratio and hence a weaker seasonal variation for Cl$^-$ compared with Na$^+$. Calcium, which has two sources (a marine source as well as continental dust (section 4)), exhibits little variation (Figure 3b) in Antarctica, while well-marked spring maxima are seen in Greenland snow (Figure 2). At the south pole the marine and dust contributions to total Ca^{++} remain in the same order of magnitude; the marine input, which is maximum in winter, tends to overshadow the dust contribution, which peaks in summer. In Greenland, because of the proximity of continents (Figure 1), the dust input predominates and peaks in spring [Steffensen, 1988; Whitlow et al., 1992]. While no NH$_4^+$ seasonal cycle is detected in Antarctica (Figure 3a), higher mean concentrations with strong summer maxima are seen in Greenland snow layers (Figure 2) related to NH$_3$ biospheric emissions from continents (section 5.3). Acidic species like NO$_3^-$, SO$_4^{--}$, and MSA exhibit moderate maxima in spring and summer in both Greenland and Antarctic snow (Figures 2 and 3). MSA is a special case, for which the seasonality exhibits a complex picture. Indeed, while no clear seasonal feature is found in central Antarctica (Figure 3a), a strong summer maximum has been detected in surface snow layers in coastal

Antarctic regions [Mulvaney et al., 1992] and is thought to be due to the proximity of biological DMS production from the polar ocean. However, Mulvaney et al. [1992] noticed winter maxima in deeper layers, likely because of a relocalization of the MSA from summer to winter layers during firn diagenesis. Electric conductivity measurement (ECM), a quantitative estimate of acidity, provides continuous high-resolution profiles and presents the advantages of being a nondestructive technique (as opposed to chemical methods) and of being easy to utilize in the field. The acidity exhibits moderate seasonal variations (by a factor of 2–3) at several Greenland and Antarctic locations [Hammer, 1980; Legrand et al., 1982; Hammer et al., 1994]. However, ECM profiles are markedly subdued in the alkaline ice characteristic of ice ages in Greenland (section 4.2). In conclusion, various parameters, depending on location, are useful in establishing the snow layer stratigraphy, and the dating accuracy is greatly improved when several parameters are considered together (see Figures 2 and 3). Such a multispecies approach has been successfully applied in dating deep Greenland ice cores [Dansgaard et al., 1993; Alley et al., 1993].

Some large and well-documented past atmospheric perturbations can be used as "reference horizons." They represent an independent way to scale the counting of years provided by stratigraphic methods. Furthermore, such horizons are of special interest for dating ice cores from low-accumulation areas when the aforementioned stratigraphic methods are not as useful. The spread of radioactive debris over the planet (via the stratosphere) has served to date snow layers deposited in 1955 and 1963–1965 [Picciotto and Wilgain, 1963]. Similarly, by their SO$_2$ emissions, large-magnitude volcanic eruptions have provided numerous reference horizons in polar ice cores. For instance, the 1815 eruption of Tambora on the island of Sumbawa in Indonesia which injected 34 to 114 Tg (1 Tg = 10^{12} g) of SO$_2$ into the stratosphere [Devine et al., 1984; Sigurdsson and Carey, 1992] is recorded in both Greenland [Hammer, 1977] and Antarctica [Legrand and Delmas, 1987]. The Tambora reference layer assures a good estimate of the mean snow accumulation rate over the last 200 years, even in locations where seasonal parameters are not recorded in snow layers because of low snow accumulation (the high East Antarctic plateau, for instance [Legrand and Delmas, 1987]). The Laki (Iceland) eruption in 1783 also represents a good absolute horizon for dating Greenland ice cores [Clausen and Hammer, 1988] covering the last 2 centuries. However, the 59 Tg of SO$_2$ emitted by this eruption did not penetrate the tropopause [Devine et al., 1984] and are therefore not detected in Antarctic snow [Legrand and Delmas, 1987]. Farther back in the past, because information on volcanic eruptions is limited and not very precise, volcanic debris found in ice layers is useful in reconstructing the history of past volcanism. A particularly good example is the huge perturbation detected in both Greenland and Antarctica around the
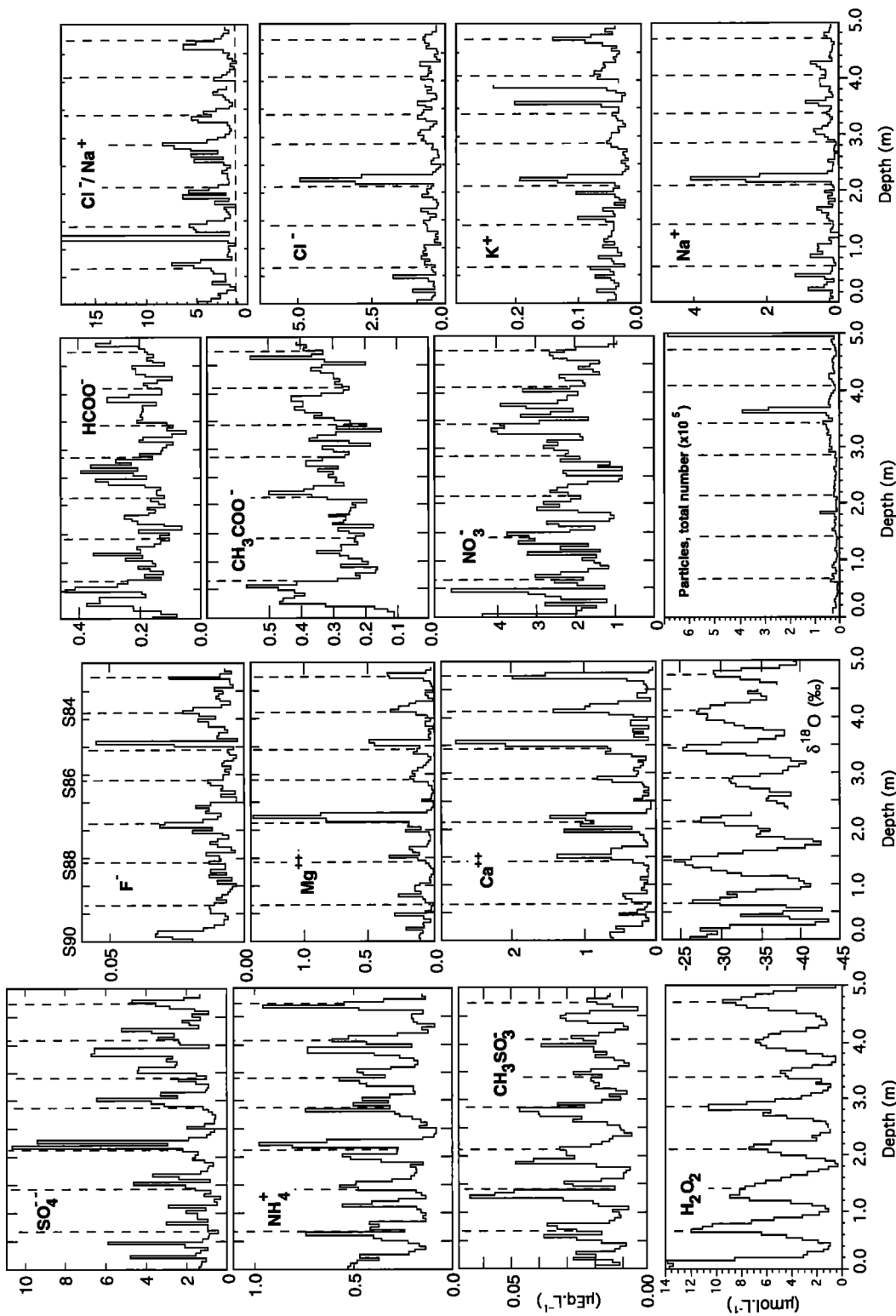
Figure 2. Concentrations of anions, cations (in microequivalents per liter), and Cl⁻ to Na⁺ molar ratios (the reference value of the molar ratio in seawater, 1.17, is reported) in snow layers deposited between 1983 and 1990 at Summit (central Greenland) along with profiles of $\delta^{18}O$ (per mil) (P. Grootes, personal communication, 1993), H_2O_2 (in micromoles per liter) (S. Drummond, personal communication, 1993) and the total number of particles per milliliter (G. Zielinski, personal communication, 1993). Vertical dashed lines refer to summer seasons (e.g., S90).
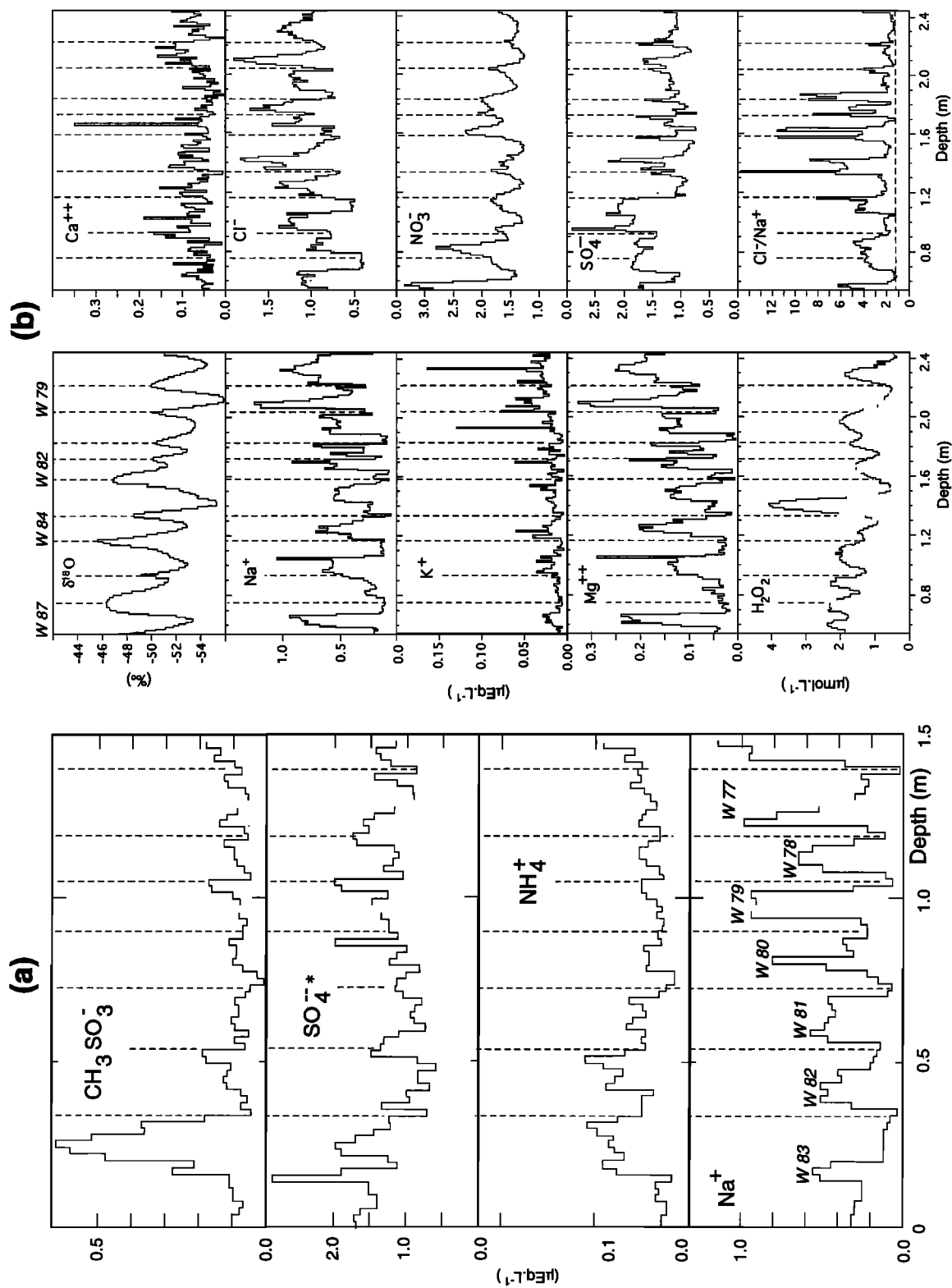
Figure 3. (a) Concentrations of $CH_3SO_3^-$, excess sulfate (SO_4^{--}*), NH_4^+, and Na^+ in a snow pit from the south pole covering the years 1976–1983 (adapted from *Legrand et al.* [1992b, Figure 7] with kind permission from Kluwer Academic Publishers). (b) Concentrations of major ions and Cl^-/Na^+ molar ratios in another pit from the south pole covering the years 1978–1987 along with the $\delta^{18}O$ and H_2O_2 profiles (adapted from *Whitlow et al.* [1992, Figure 1] with kind permission from Elsevier Science Ltd., Oxford, England). Vertical dashed lines refer to summer seasons; W denotes winter seasons (e.g., W87).

beginning of the twelfth century, dated by *Langway et al.* [1988] at A.D. 1259 using isotopic seasonal signals that had survived in a deep Greenland core (Milcent; mean accumulation of 350 kg m^{-2} yr^{-1}). This previously unknown reference layer has been used to compare numerous ice cores. The late Pleistocene eruption of Toba, the largest explosive eruption documented from the Quaternary [*Ninkovich et al.*, 1978], provides an excellent absolute reference horizon at ~72,000 years B.P. in deep ice cores. Very recent studies have revealed a huge sulfate perturbation at this time in Greenland that has been attributed to this megaeruption [*Zielinski et al.*, 1996]. The Vostok record from Antarctica also reveals a huge sulfate perturbation at this time [*Petit et al.*, 1995].

Radioactive isotopes present either in ice bubbles like ^{85}Kr (half life T of 11 years) and ^{14}C (T = 5730 years) or in water like tritium (T = 12 years) or in aerosols like ^{210}Pb (T = 22 years), ^{32}Si (T = 172 years), ^{10}Be (T = 1.5 × 10^6 years), and ^{36}Cl (T = 301,000 years) can be useful for dating ice cores. Although radioactive measurements provide a powerful way to obtain absolute age determination specially for very old ice (see *Stauffer* [1989] for a review), several problems have not yet been solved, in particular the uncertainty in changes of the initial concentration in the past atmosphere. Recent studies of ^{210}Pb suggest that in both the north [*Dibb*, 1992] and south [*Lambert et al.*, 1989] polar regimes the atmospheric burden is not constant over time and may depend on the intensity of the long-range transport of air masses between continental sources and high latitudes, prompting careful reassessment of ^{210}Pb-based radiochronologies. Finally, the study of ^{10}Be, a long-lived cosmogenic radioisotope produced by cosmic-ray-induced spallation reactions with nitrogen and oxygen, is helpful for dating deep ice cores [*Raisbeck and Yiou*, 1985]. Assuming constant production and deposition over the time, the ^{10}Be ice level reflects the amount of snow precipitation (see *McHargue and Damon* [1991] for a review).

For deep ice cores, chronological information is obtained mainly by comparing isotopic profile features documenting large climatic change events with those found in other proxy records. For instance, during glacial periods, because of the storage of isotopically depleted solid precipitation over the continents, a significant isotope enrichment of the ocean occurred and was recorded in ^{18}O of CaCO$_3$ from benthic foraminifera.

In summary, the dating of an ice core, its accuracy, and the applied methods depend largely on the amount of precipitation at the site. In sites characterized by an accumulation rate lower than 50 kg m^{-2} yr^{-1}, the East Antarctic plateau for instance, no accurate dating can be established, the seasonal signals having been strongly erased by the action of wind at the surface. In such cases, only a mean accumulation rate between two reference horizons can be calculated. As long as the annual accumulation rate is higher than 100 kg m^{-2} yr^{-1}, it is possible to count years by checking seasonal variations

of several chemical species (Ca^{++}, Na$^+$, NH$_4^+$, etc.). We here emphasize the usefulness of Na$^+$, for which no smoothing of seasonal variations occurs with depth and which exhibits well-marked winter maxima in both Greenland and Antarctic snow. In addition to the stable isotopes, other chemical species (H$_2$O$_2$, NO$_3^-$, etc.) can be used to count the years at sites having accumulation rates higher than 200 kg m^{-2} yr^{-1}, where diffusion processes did not completely smooth the initial seasonal cycle.

3.2. Site Suitability

Since the International Geophysical Year in 1957, a large number of ice cores have been extracted from numerous ice caps and cold glaciers over the world. The multiplicity of ice core drillings was motivated by two major reasons. First, many of the chemical parameters of interest are related to short-lived species in the atmosphere, and the examination of several records is therefore needed in drawing overall conclusions. Second, an ideal site does not exist, and depending on the scientific purpose, some sites are more adequate than others. For instance, long-term records spanning several thousands of years, which are dedicated to the study of the coupling between climate and atmospheric chemistry, are established along ice cores extracted in sites where the accumulation rate is rather low, rendering difficult the examination of seasonal variations. Conversely, detailed investigation of recent trends is highlighted when the seasonality of species can be checked over time. This can be achieved only in sites with a sufficient accumulation rate.

The physical and chemical environments of Antarctica and Greenland share some similarities but are different. The south polar region is a continent (Antarctica) surrounded by oceans, while the north polar region contains a more limited ice sheet (Greenland) and an ice-covered ocean surrounded by continents where human activities are very important (Figure 1). Such geographical differences lead to different atmospheric circulation regimes, in particular a more intense transport between middle and high latitudes in the northern than in the southern hemisphere, particularly in summer [*Nakamura and Oort*, 1988]. Therefore studies of both Greenland and Antarctic records are needed to investigate global change.

From both Antarctica and Greenland, several ice cores spanning the last great climatic transition from Pleistocene to Holocene have been obtained over the last few decades (Table 1). The longest Antarctic record has been obtained at Vostok, East Antarctica, covering more than 220,000 years [*Jouzel et al.*, 1993]. Byrd station is located at a lower altitude, in West Antarctica, and its record spans the last 70,000 years [*Jouzel et al.*, 1989]. These records are useful in comparing changes in West and East Antarctica that occurred over the last 70,000 years. Some other cores have been obtained from coastal Antarctic regions (D10 in Adélie Land; Dominion

TABLE 1. Conversion of Molar Units into Mass Units

Species	Formula	Mass by Mass Equivalent of 1 Molar Unit, $ng\ g^{-1}$
Proton	H^+	1
Ammonium	NH_4^+	18
Potassium	K^+	39
Magnesium	Mg^{++}	12
Calcium	Ca^{++}	20
Sodium	Na^+	23
Fluoride	F^-	19
Formate	$HCOO^-$	45
Acetate	CH_3COO^-	59
Oxalate	$C_2O_4^{--}$	88
Methanesulfonate (MSA)	$CH_3SO_3^-$	95
Chloride	Cl^-	35.5
Nitrate	NO_3^-	62
Sulfate	SO_4^{--}	48
Formaldehyde	$HCHO$	30
Hydrogen peroxide	H_2O_2	34

Through the entire paper, two kinds of units are used to express the concentration of species present in polar precipitation. As is common in the literature, we indicate a mass by mass concentration in nanograms per gram. However, when checking the ionic budget, it is preferable to use a molar unit; the microequivalent per liter (1 μEq L^{-1} = 1 μmol L^{-1} times the valence of the species) is used for ionic species, and $HCHO$ and H_2O_2 are given in micromoles per liter.

Range and Law Dome). Although the interpretation of the corresponding profiles is less straightforward because the impurity content is influenced by changes in elevation and ice flow, such studies provide useful information on spatial variations of the ice chemistry [*Legrand and Delmas*, 1985; *Mayewski et al.*, 1990a].

Camp Century (NW Greenland) and Dye 3 (SE Greenland) cores have documented the last 100,000 years in Greenland [*Dansgaard et al.*, 1982]. A third Greenland ice core was also drilled on the small separate Renland ice cap (East Greenland) and completely covers the last glacial-interglacial cycle (120,000 years). Recently, two deep drilling projects (the U.S. Greenland Ice Sheet Project (GISP) 2 and the European Greenland Ice Core Project (GRIP)) reached to and nearly to bedrock, respectively, at Summit (central Greenland). Like Vostok, the cores cover the entire last glacial-interglacial cycle and extend to the penultimate glacial age [*Grootes et al.*, 1993; *Dansgaard et al.*, 1993]. They provide the most detailed glaciochemical data ever collected.

Over shorter time periods (the last few decades up to the last millennia), numerous Antarctic and Greenland depth profiles have been investigated for various purposes including the response of the atmosphere to anthropogenic emissions. Such data obtained in various locations where the snow accumulation rate is highly variable are also useful for comparing the snow impurity content as a function of elevation, latitude, and snow accumulation rates. Others cores have also been extracted from cold glaciers located at temperate latitudes:

Mount Logan in Alaska, Colle Gnifetti in the Alps, and Quelccaya in the Peruvian Andes (see Figure 1).

3.3. Analytical Procedures

Another important problem that needs to be addressed and solved to obtain valuable chemical records from firn and ice is the reliability of data. Because of the remoteness of these regions, special sampling and measurement techniques are required to determine extremely low content of impurities characterizing polar precipitation. Progress has been hampered in the past because the reported data have suffered from contamination problems.

During the drilling procedure, firn and ice cores have generally been appreciably contaminated over their outside portions. Several procedures have been applied to discard contamination from the outside of cores as detailed by *Legrand et al.* [1984, 1993] and *Boutron and Patterson* [1986]. Over the last 20 years, successive improvements of the analytical techniques have been performed, permitting more sensitive and rapid analyses of an extended number of species. As an example, it is now possible to measure all the anions and cations of interest (except H^+) within 15 min at the nanogram per gram level by using ion chromatography and a 5-mL total sample volume [*Buck et al.*, 1992; *Legrand et al.*, 1993].

Finally, more recent efforts have been dedicated to the development of continuous measurements permitting rapid and high-resolution measurements. A melting technique combined with continuous flow analysis has been recently developed [*Sigg et al.*, 1994] and successfully used on Greenland ice cores [*Fuhrer et al.*, 1993] with spatial resolution of the order of 1 cm for $HCHO$, Ca^{++}, H_2O_2, and NH_4^+.

3.4. The "Air-Snow" Transfer Function

Polar ice cores are one of the better archives containing chemical information on the composition of the atmosphere in the past. However, the translation of ice core data in terms of changing atmosphere is sometimes difficult because of our presently limited knowledge of parameters controlling the relationship between the composition of solid precipitation and that of the atmosphere at the time of deposition. This problem is, to a large extent, linked to the absence of atmospheric data in these regions. Glaciochemists have worked empirically in the 1970s, assuming that these unknown processes can be neglected in interpreting ice records in terms of atmospheric changes. Recent studies have started to investigate to what extent and for which species such an assumption is valid.

Because some species are nonreactive and nonvolatile, they are irreversibly trapped in snow layers. This is the case for species derived from sea salt, soil dust, and black and total organic carbon, as well as for sulfur-derived aerosols. Several recent programs, initiated at Dye 3 (south Greenland) in 1989 and now running (1989–1996) at Summit (central Greenland), have dealt

with the study of the air-snow transfer function for species derived from sea salt, dust, and sulfur (MSA and SO_4^{--}) aerosols [*Dibb et al.*, 1992; *Jaffrezo and Davidson*, 1993]. On the basis of simultaneous measurements in solid precipitation and in the atmospheric boundary layer at the time of deposition, *Jaffrezo et al.* [1994] and *Mosher et al.* [1993] have shown that seasonal signals recorded in ice qualitatively reflect changes observed in the atmosphere over the year. However, quantitative estimates of past atmospheric concentrations of these chemical species are unavailable owing to a lack of understanding of the processes that transfer atmospheric chemical species to the surface snow and their changes over the past. In polar regions, wet deposition processes affecting chemical species include snowfall, clear-sky precipitation (diamond dust), deposition of cloud water onto the ground (fog), and snow drifting. Dry deposition processes include direct impaction of gas or aerosols and filtration of aerosol through the upper part of the firn (the "wind pumping effect" [*Cunningham and Waddington*, 1993]). An apportionment of the different deposition processes was performed for the summer season in central Greenland [*Bergin et al.*, 1995]. Although snow deposition is the dominant process during the summer at this site, it is shown that deposition of species with fog may contribute as much as one third and that dry deposition is also significant. However, the respective contributions of wet and dry deposition modes to the total deposition are not well quantified for many sites. It is likely that in most high-altitude polar regions characterized by very cold temperatures, dry air, and very low annual accumulation rate of snow, a large fraction of impurities are deposited directly onto the snow surface. Thus changes in past snow accumulation rates in conjunction with changes in meteorological conditions could lead to a variable dilution of the dry flux, hence modulating concentrations in ice, even if atmospheric concentrations remained unchanged. An accurate interpretation of ice core data therefore requires knowledge of the mean snow accumulation rate over the past as well as of the relative contribution of dry processes to the total deposition of impurities. Comparison of total deposition fluxes observed at various locations characterized by different snow accumulation rates can be used to estimate the contribution of the dry flux to the total (dry plus wet) flux at a specific polar site. As seen in Figure 4, for instance, the sulfate concentrations observed at various Greenland or Antarctic sites are inversely proportioned to the snow accumulation rate: the lower the snow accumulation, the higher the concentrations. Similar effects have been previously identified by *Legrand and Delmas* [1988] for sea salt components. Thus at a site characterized by very low snow accumulation rate (e.g., central Antarctica), a 10°C decrease in local temperature that occurred some 15,000 years ago (see section 5.3) might lead to a drier atmosphere and to a reduction of the annual snow accumulation rate by a factor of 2 [*Lorius et al.*, 1985]. Such a reduction of the
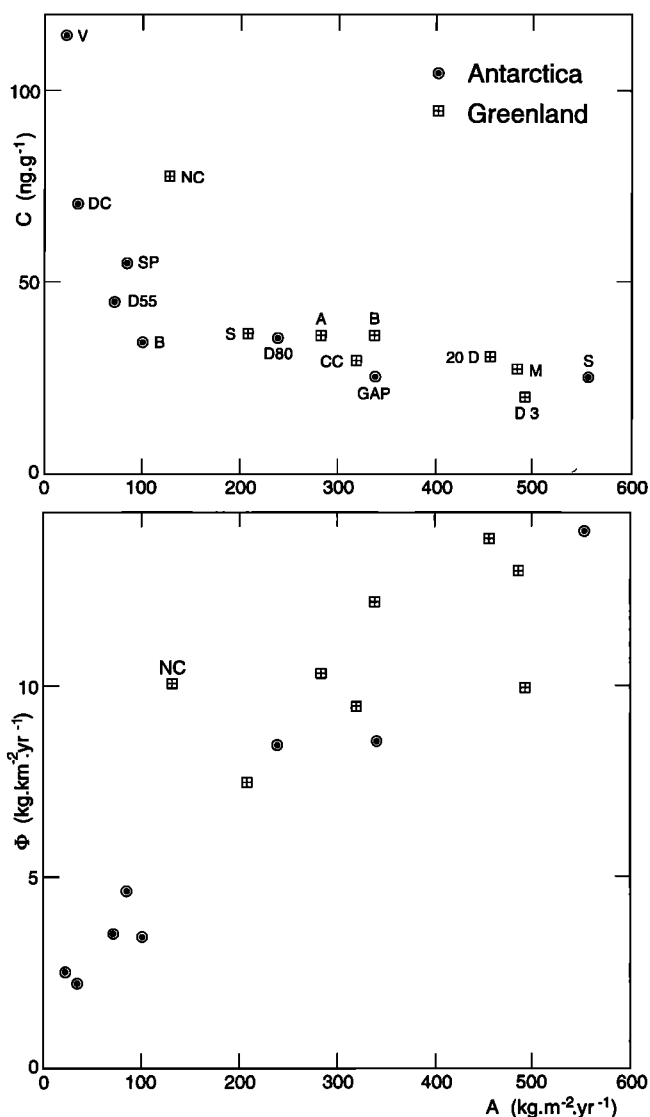
Figure 4. Excess sulfate concentrations C and deposition fluxes Φ in ice deposited at Greenland and Antarctic sites (preindustrial era), as a function of mean annual accumulation rate of snow (A). Antarctic sites are labeled V (Vostok), DC (Dome C), SP (South Pole), B (Byrd), D55 and D80 (Adélie Land), S (Siple), and GAP (Gomez, Antarctic Peninsula); Greenland sites are NC (North Central), S (Summit), CC (Camp Century), A, B, 20D, and D3 (Dye 3). Adapted from *Legrand* [1995] (copyright Springer-Verlag).

snow accumulation rate during ice ages with respect to the present leads to an enhancement by as much as a factor of 2 for the content of impurities in ice, even if atmospheric concentrations remained unchanged.

Species present in the atmosphere in the gas phase exhibit additional complexities compared with aerosols because they sometimes interact strongly with ice. The processes involved in the transfer function of such water soluble trace gases include their incorporation in water droplets, their fate during the freezing of liquid or supercooled droplets, and their incorporation during the growth of ice crystals in the atmosphere. Postdeposition
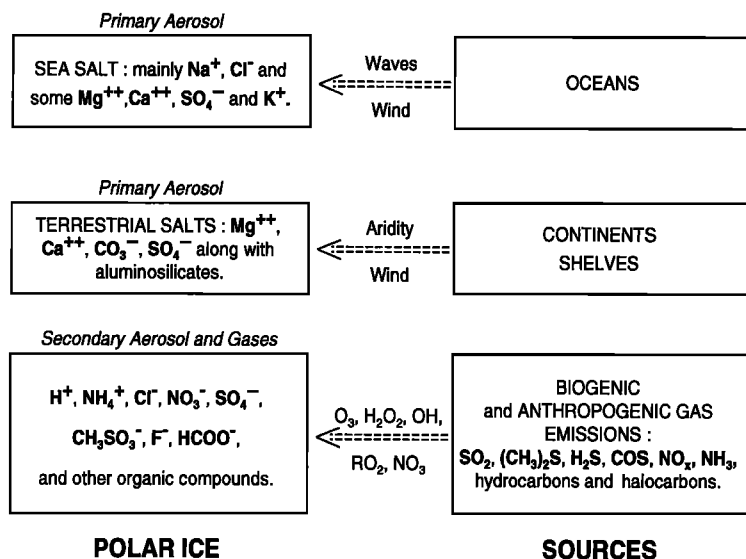
Figure 5. Scheme showing various soluble impurities expected to be trapped in polar snow layers and their corresponding origins and sources.

processes, such as diffusion from the gas phase to the ice crystalline lattice and redistribution in firn after snow deposition can also be important. This last process is enhanced for those gases that have a significant vapor pressure over the ice. It has been observed for HCHO [Staffelbach et al., 1991], H_2O_2 [Sigg et al., 1992], HNO₃ [Mayewski and Legrand, 1990; Neubauer and Heumann, 1988], the light carboxylic acids [Legrand et al., 1992a], and HCl [De Angelis and Legrand, 1995]. Thus it must be stressed that the records of these species in firn do not reflect atmospheric signals, as was recently reviewed by Legrand et al. [1996].

4. ICE AND SNOW CHEMISTRY

From our knowledge of the atmospheric chemistry, we expect to find in polar precipitation various soluble and insoluble impurities (Figure 5). These impurities are either introduced directly into the atmosphere ("primary aerosols") like sea salt and dust emitted by the wind from marine and continental surfaces, or produced within the atmosphere during oxidation of trace gases involved in the sulfur, nitrogen, halogen and carbon cycles. As can be seen from Figure 5, while Al is an excellent tracer of continental dust, the situation becomes more complex for many other chemical species that are produced by more than one source. For instance, the presence of SO_4^{--} in ice can be linked to primary marine (sea salt) or continental ($CaSO_4$) inputs. It can also be due to the presence of H_2SO_4 produced during the atmospheric oxidation of SO_2, which is introduced into the atmosphere during volcanic eruptions, by human activities since the middle of the last century, or by the oxidation of various S compounds emitted from the biosphere (Figure 6). This example illustrates the need to perform a study of all soluble species present in ice in order to be able to reconstruct the initial associ-

ation between the ions. Once these associations are known, it becomes easier to discuss the possible sources from which the ions are derived.

4.1. Mean Antarctic Ionic Balance

Comprehensive studies of soluble species present in ice have been conducted for central as well as coastal Antarctic regions. The imbalance between cations and anions (denoted ΔC) represents less than 5% of the
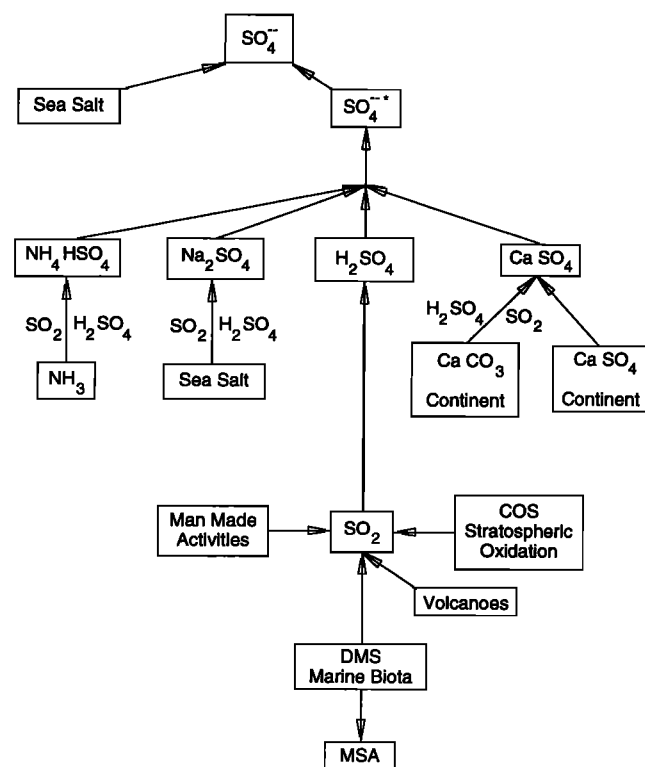

Figure 6. Possible sources of sulfate and MSA present in polar ice. Adapted from Legrand [1995] (copyright Springer-Verlag).

TABLE 2. Present Available Deep Polar Ice Core Records Spanning the Last Great Climatic Change (15,000 Years B.P.) Extracted in Greenland

Location	Depth, m	Drilling Year	Ice Thickness, m	Elevation, m	T, °C	A, kg $m^{-2}\,yr^{-1}$	Age, kyr
			Greenland				
Camp Century	1387	1966	1387	1885	−24	320	120
Dye 3	2037	1981	2037	2486	−20	496	100
Renland	324	1988	324	2340	−18	450	140
Summit	3030	1992–93	3050	3230	−32	200	250
			Antarctica				
Byrd	2163	1968	2163	1530	−28	160	70
Dome C	905	1978	3400	3240	−53	34	40
Dome B	780	1988	3460	3600	−58	31	~30
Vostok	2546	1989	3700	3490	−56	23	220
Law Dome	1200	1993	1200	1370	−22	63	~50
D 10	300	1974	300	270	−14	150	~20
Dominion Range	201	1984	201	2780	−37	350	~20
Komsomolskaya	850	1983	3550	3498	−53	50	14

T and A refer to mean annual temperature and accumulation rate of water, respectively.

ionic budget Σ (concentrations are expressed in microequivalents per liter; conversions from molar to mass units are given in Table 2), which is very satisfactory when considering experimental errors:

$$\Delta C = [Na^+] + [NH_4^+] + [K^+] + [H^+] + [Ca^{++}]$$
$$+ [Mg^{++}] - [F^-] - [Cl^-] - [NO_3^-] - [SO_4^{--}]$$
$$- [CH_3SO_3^-] - [HCOO^-] - [CH_3COO^-] \quad (1)$$

$$\Sigma = [Na^+] + [NH_4^+] + [K^+] + [H^+] + [Ca^{++}]$$
$$+ [Mg^{++}] + [F^-] + [Cl^-] + [NO_3^-] + [SO_4^{--}]$$
$$+ [CH_3SO_3^-] + [HCOO^-] + [CH_3COO^-] \quad (2)$$

Na^+, H^+, Ca^{++}, Mg^{++}, Cl^-, NO_3^-, and SO_4^{--} are major ions present in Antarctic ice deposited under present-day as well as past colder climates [Legrand, 1987; Mulvaney and Peel, 1988]. NH_4^+ and K^+ represent a minor contribution (<0.2 µeq L^{-1}) compared with the total ionic budget ($5 < \Sigma < 30$ µeq L^{-1}). $CH_3SO_3^-$ accounts for 0.2 µeq L^{-1} [Legrand et al., 1992b; Mulvaney et al.,

1992], while F^- and the light carboxylates represent an insignificant part of the ionic budget [Legrand and Saigne, 1988]. The balance achieved between cations and anions ($\Delta C = 0$) in Antarctic ice can be therefore expressed as

$$[Na^+] + [Mg^{++}] + [Ca^{++}] + [H^+] = [Cl^-] + [NO_3^-]$$
$$+ [SO_4^{--}] \quad (3)$$

In coastal areas, owing to the large contribution of sea salt, Na^+, Cl^-, Mg^{++}, Ca^{++}, and a portion of the SO_4^{--} represent a dominant part (~80%) of the ionic budget (Table 3). Farther inland, the sea salt input is strongly decreased, and other contributions to the ionic budget become dominant (65–80% (Table 3)). Subtracting the sea salt contribution from (3) using the Na content and the seawater ratio of major ions from Holland [1978], we obtain the basic equation describing these other contributions:

$$[H^+] + [Ca^{++}]^* + [Mg^{++}]^* = [Cl^-]^* + [NO_3^-]$$
$$+ [SO_4^{--}]^* \quad (4)$$

TABLE 3. Reduced Expression of Equation (4) Depending on the Time Period and Site Considered, Partitioning of Soluble Species, and Contribution of Insoluble Species to the Total Mass of Impurities Found in Antarctic Ice

	Coastal Areas (Present Climate)	Central Area (Present Climate)	Central Area (Glacial Age)
Equation (4)	$[H^+] =$ $[NO_3^-] + [SO_4^{--}]^*$	$[H^+] = [Cl^-]^* +$ $[NO_3^-] + [SO_4^{--}]^*$	$[Ca^{++}]^* + [Mg^{++}]^* +$ $[H^+] = [NO_3^-] + [SO_4^{--}]^*$
Sea salt, %	85	36	54
HCl, %	···	22	···
HNO₃, %	5	6	2
H₂SO₄, %	10	36	16
Terrestrial salts, %	···	···	26
Insoluble species, %	2	6	62

Soluble species (sea salt, HCl, HNO₃, H₂SO₄, and terrestrial salts) are expressed as percentages of the total ionic budget, and insoluble species are given as percentages of the total mass of impurities. Dots indicate fractions lower than 1%. Adapted from Legrand [1987].
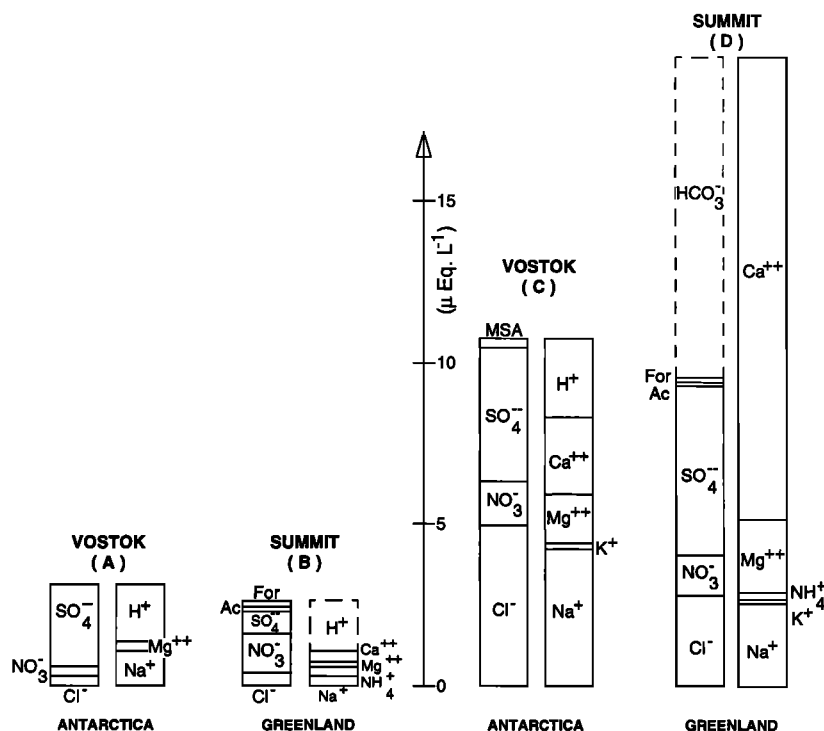
Figure 7. Mean ionic ice composition corresponding to present climate in (A) Antarctica and (B) Greenland and to the last glacial maximum in (C) Antarctica and in (D) Greenland. Dashed lines in Figures 7b and 7d indicate that acidity measurements are not yet available. Abbreviations For and Ac stand for formate and acetate, respectively. Adapted from *Legrand* [1995] (copyright Springer-Verlag).

where $[X]^* =$ "excess X" represents the non–sea salt contribution of X.

In snow deposited under present climatic conditions, Ca^{++*} and Mg^{++*} are present at low levels in relation to weak terrestrial inputs [*Legrand et al.*, 1988]. $[Cl^-]^*$ can have positive, negative, or zero values, and (4) can be reduced to

$$[H^+] = [Cl^-]^* + [NO_3^-] + [SO_4^{--}]^* \qquad (5)$$

In coastal regions, $[Cl^-]^*$ is close to zero, suggesting that aside from the large sea salt content, the snow contains acidic NO_3^- and SO_4^{--}. In central areas, where $[Cl^-]^*$ is not zero, (5) indicates that in addition to sea salt, the Antarctic ice deposited under present climate contains HNO_3 and H_2SO_4 plus either Na_2SO_4 or HCl corresponding to negative or positive $[Cl^-]^*$ values, respectively, as detailed by *Legrand and Delmas* [1988].

During the last glacial maximum (15,000 to 20,000 years B.P.), $[Ca^{++}]^*$ and $[Mg^{++}]^*$ are significant, and $[Cl^-]^*$ is close to zero. As was detailed by *Legrand et al.* [1988], Antarctic ice corresponding to such glacial conditions contains HNO_3, H_2SO_4, sea salt, and terrestrial salts (Ca^{++*} and Mg^{++*} associated with SO_4^{--*} and NO_3^-). On the basis of CO_2 measurements, *Legrand* [1987] noticed an absence of carbonates associated with Ca^{++} in this glacial Antarctic ice.

The contribution of insoluble species can be estimated from Al determinations and by using the ratio of elements to aluminium of the mean crust [*Taylor*, 1964]. As is summarized in Table 3, under present climatic conditions, soluble species dominate the mass of impurities present in Antarctic snow with a main contribution from sea salt and an increasing contribution of mineral

acids (H_2SO_4, HCl, and HNO_3) farther inland. In Antarctic ice corresponding to the last glacial maximum, insoluble species become predominant, representing at least 50% of the total mass of impurities present. Similarly, terrestrial salts, which are present at insignificant levels under present climatic conditions, represented some 25% of the total ionic budget of Antarctic ice deposited during the last glacial maximum.

4.2. Mean Greenland Ionic Balance

The ionic budget of Greenland ice has not yet been fully characterized because only a few direct acidity measurements have been made. We report here a preliminary view recently obtained from Summit ice, deposited both under present climatic conditions (Figure 7b) and during the last glacial maximum (Figure 7d). These balances are based only on ion chromatograph data without simultaneous H^+ measurements. One notable feature of the ionic budget of Greenland ice, in contrast to Antarctic ice, is the presence of a significant amount of NH_4^+ and carboxylic acid. This has been interpreted as due to a larger impact of continental biospheric emissions (see section 5.4). Note also that in contrast to Antarctic snow deposited under present-day climate, Greenland snow contains significant amounts of non–sea salt calcium. As suggested by change in Ca^{++}, both Greenland and Antarctic ice reveal enhanced input of soil dust during the last glacial maximum as compared with the present warm climate. However, it appears that during such cold climate the ice was alkaline in Greenland, as was previously suggested by ECM measurements [*Hammer et al.*, 1985; *Taylor et al.*, 1993], and remained acidic in Antarctica.
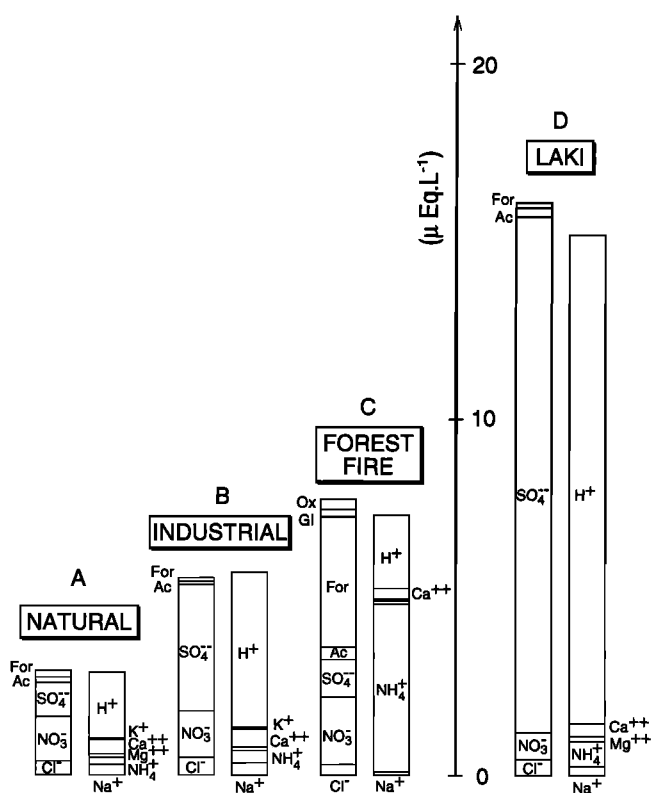
4.3. Short-Term Variations of the Mean Ionic Balance

Aside from long-term changes of the ionic budget of polar ice in response to great climatic variations depicted in Figure 7, the chemistry of Greenland and Antarctic ice has also been sporadically disturbed by volcanic inputs (Figure 8d), which led to large inputs of H_2SO_4 and sometimes of HCl and HF. Furthermore, the Greenland ice ionic budget, in contrast to the Antarctic one, reveals large and sudden enhancements of $HCOO^-$ and NH_4^+ levels (Figure 8c), which are related to biomass burning events at high northern latitudes (see section 5.2). Finally, as can be seen in Figure 8b, human activities, notably fossil fuel burning (see section 5.1) have significantly enhanced the level of several acidic species (NO_3^-, SO_4^{--}, and to a lesser extent F^-, Cl^-, and the light carboxylates) in Greenland snow deposited since 1940.
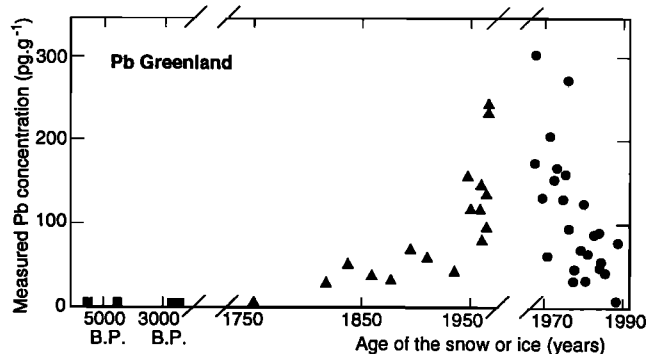
5. WHAT WE HAVE LEARNED FROM POLAR ICE CORE STUDIES

5.1. Atmospheric Impact of Human Activities Inferred From Secular Ice Core Profiles

Greenland and Antarctic chemical profiles covering the last 200 years have provided a wealth of information

Figure 9. Trend in Pb concentrations of Greenland snow layers for the time period 1750–1989. Circles represent data from *Boutron et al.* [1991] in Summit (central Greenland), triangles represent data from *Murozumi et al.* [1969] in northwest Greenland snow, and squares are data from *Murozumi et al.* [1969] and *Ng and Patterson* [1981] in Greenland Holocene ice. Adapted from *Boutron et al.* [1994, Figure 5b] with kind permission from Elsevier Science Ltd., Oxford, England.

Figure 8. Comparison of mean ionic composition of Greenland snow deposited during (a) the preindustrial era, (b) a more recent period (1980), (c) a forest fire, and a (d) volcanic year (Laki, 1783). Abbreviations For, Ac, Gl, and Ox stand for formate, acetate, glycolate, and oxalate, respectively.

on the impact of human activities on the chemistry of the atmosphere in both hemispheres. As far as the species of concern are present in the atmosphere as aerosols (sulfate and metals, for instance), we can speculate that ice core records covering the last decades reflect changes in the atmospheric concentrations, since no change of the transfer function is expected over this time period (section 3.4).

A particularly important finding is the changing concentration of lead in Greenland snow. At the time of the Industrial Revolution (1770–1780), Pb concentrations of Greenland ice were close to 10 pg g^{-1} (1 pg = 10^{-12} g) and then steadily increased, reaching 50 pg g^{-1} in the 1900s (Figure 9), as a consequence of anthropogenic emissions in the northern hemisphere mainly due to nonferrous metal industry. Concentrations then increased by a factor of 4 from 1930 to the 1960s, with a particularly rapid increase after 1940. These results were interpreted as a consequence of the massive increase in the use of Pb alkyl antiknock additives in automobile and aviation gasoline, which reached 0.5 Mt per year in 1970, the United States alone accounting for 65% of the total [*Nriagu*, 1990]. A decrease by a factor of 7.5 from the 1960s to the end of the 1980s is observed (Figure 9) which is undoubtedly due the massive fall in the use of alkyl Pb additives in gasoline, in particular in the United States. Recent investigations of lead isotopes in Greenland snow provided a powerful tool for identifying the source regions contributing pollutants to Greenland. As an example, the $^{206}Pb/^{207}Pb$ ratios measured by *Rosman et al.* [1993] in Greenland snow, together with the isotopic fingerprints of emissions from United States and Eurasia, suggest that the United States alone accounted for two thirds of the Pb present in Greenland snow in the early 1970s. Since 1980, the U.S. contribution has dropped sharply, with Eurasia accounting for 75% of the

TABLE 4. Recent Concentration Changes of Several Species Over the Last Century Recorded in a Summit (Central Greenland) Ice Core

| Species	Preindustrial Level	Recent Level (Time Period)	References
SO_4^{--}*	26 ng g^{-1}	85 ng g^{-1} (1950–1989)	Mayewski et al. [1993]
NO_3^-	68 ng g^{-1}	120 ng g^{-1} (1950–1989)	Mayewski et al. [1993]
Cl^-*	4 ng g^{-1}	9 ng g^{-1} (1950–1989)	Mayewski et al. [1993]
F^-	0.06 ng g^{-1}	0.19 ng g^{-1} (1971–1989)	De Angelis and Legrand [1994]
Zn	30 pg g^{-1}	70 pg g^{-1}(1971–1989)	Candelone et al. [1995]
Cu	3 pg g^{-1}	8 pg g^{-1}	Candelone et al. [1995]
Cd	0.2 pg g^{-1}	1.8 pg g^{-1}	Candelone et al. [1995]
Pb	1 pg g^{-1}	250 pg g^{-1} (1960s)	Murozumi et al. [1969], Boutron et al. [1991]
HCHO	2–3 ng g^{-1} (1700–1900)	5 ng g^{-1} (1980s)	Staffelbach et al. [1991]
H_2O_2	4 μmol L^{-1} (1750–1960)	5 μmol L^{-1} (1960–1989)	Sigg and Neftel [1991]
$HCOO^-$	7.7 ± 2.3 ng g^{-1} (1767–1945)	6.3 ± 2.4 ng g^{-1} (1845–1980)	Legrand and De Angelis [1996]
CH_3COO^-	6.5 ± 1.9 ng g^{-1} (1767–1945)	9.8 ± 3.2 ng g^{-1} (1845–1980)	Legrand and De Angelis [1996]

Pb deposited at present in Greenland. An increase of Pb levels from 2 pg g^{-1} in 1920 to 8 pg g^{-1} in 1980 was also detected in Antarctic snow [Wolff and Suttie, 1994], reflecting the increase of leaded gasoline use in the southern hemisphere. Finally, changes of Zn, Cd, and Cu levels are also detected in recent Greenland snow (Table 4) as a result of growing emissions to the atmosphere by nonferrous metal production [Nriagu and Pacyna, 1988].

In contrast to the Antarctic SO_4^{--} levels, those in Greenland (Figure 10) reveal an increase at the turn of the last century. Except for volcanic eruptions (e.g., Laki in 1783 and Tambora in 1815), sulfate levels remained close to 20–30 ng g^{-1} in south and central Greenland snow from 1760 to 1903. Discarding the 1912 Katmai layer, the sulfate level was 2 times lower over the time period 1760–1903 than between 1903 and 1950 in both south and central Greenland snow. From 1950 to 1970 a further increase up to 70 and 110 ng g^{-1} is observed in snow from south and central Greenland, respectively. The course of these increases is in broad agreement with the expected effect of growing SO_2 emissions, which have increased from 2.5 to 90 Tg of S per year from 1860 to 1980, most of it being in the northern hemisphere [Moller, 1984]. The south Greenland sulfate trend is similar to that of the U.S. SO_2 emissions [Mayewski et al., 1990b], suggesting a primarily U.S. source for this region. The more pronounced sulfate increase after 1940 in central than in south Greenland might be due to a stronger influence of Eurasian sources via more frequent advections of polluted air masses originating from Arctic regions in winter [Barrie, 1986] in this region. Finally, a decreasing trend of sulfate is seen in Greenland snow deposited since 1980 and likely reflects abatement measures that have taken place in industrialized countries to reduce the SO_2 emissions to the atmosphere.

The south Greenland NO_3^- profile exhibits an increasing trend since around 1950 (Figure 10). To discuss whether the record of this water soluble species reflects an atmospheric signal or an artifact linked with post-depositional effect in the firn (section 3.4), we must examine trends recorded at other Greenland sites. Although Summit has an accumulation rate nearly 2.5 times lower than that of Dye 3, leading to a different depth-age relationship, similar temporal changes of nitrate are observed at Dye 3 and Summit (Figure 10). This indicates that the recent NO_3^- trend in Greenland ice is an atmospheric signal resulting from growing NO_x emissions in the northern hemisphere, which mainly originate from fossil fuel burning in the automobile traffic [Hameed and Dignon, 1988]. Over the last 2 centuries the NO_3^- ice content at the south pole remained fairly constant, except for an increase of the spring-summer maxima in very recent years (Figure 10). This was interpreted as a possible indication of a recent enhanced denitrification from the lower stratosphere due to the stratospheric cooling that accompanied the recent development of the Antarctic ozone depletion [Mayewski and Legrand, 1990]. However, in a recent study of a new snow pit dug at South Pole in 1994, Dibb and Whitlow [1996] were unable to find the 1987 and 1988 maxima and found a strong peak in spring 1994, near the surface. They therefore concluded that these spring nitrate peaks are not related to an atmospheric signal and must account for postdepositional effects.

As summarized in Table 4, recent changes are also detected for other species in recent Greenland snow layers. However, as is the case for nitrate, the interpretation of these trends must be considered with some caution because these chemical species are present in the atmosphere in the gas phase. The excess chloride trend could be related to growing direct anthropogenic HCl emissions and/or a consequence of the acidification of the atmosphere leading to a more efficient degassing of HCl from sea salt aerosols [Mayewski et al., 1993]. The recent increase of fluoride levels may be due to growing coal-burning emissions [De Angelis and Legrand, 1994]. However, for these two halogenated species, available
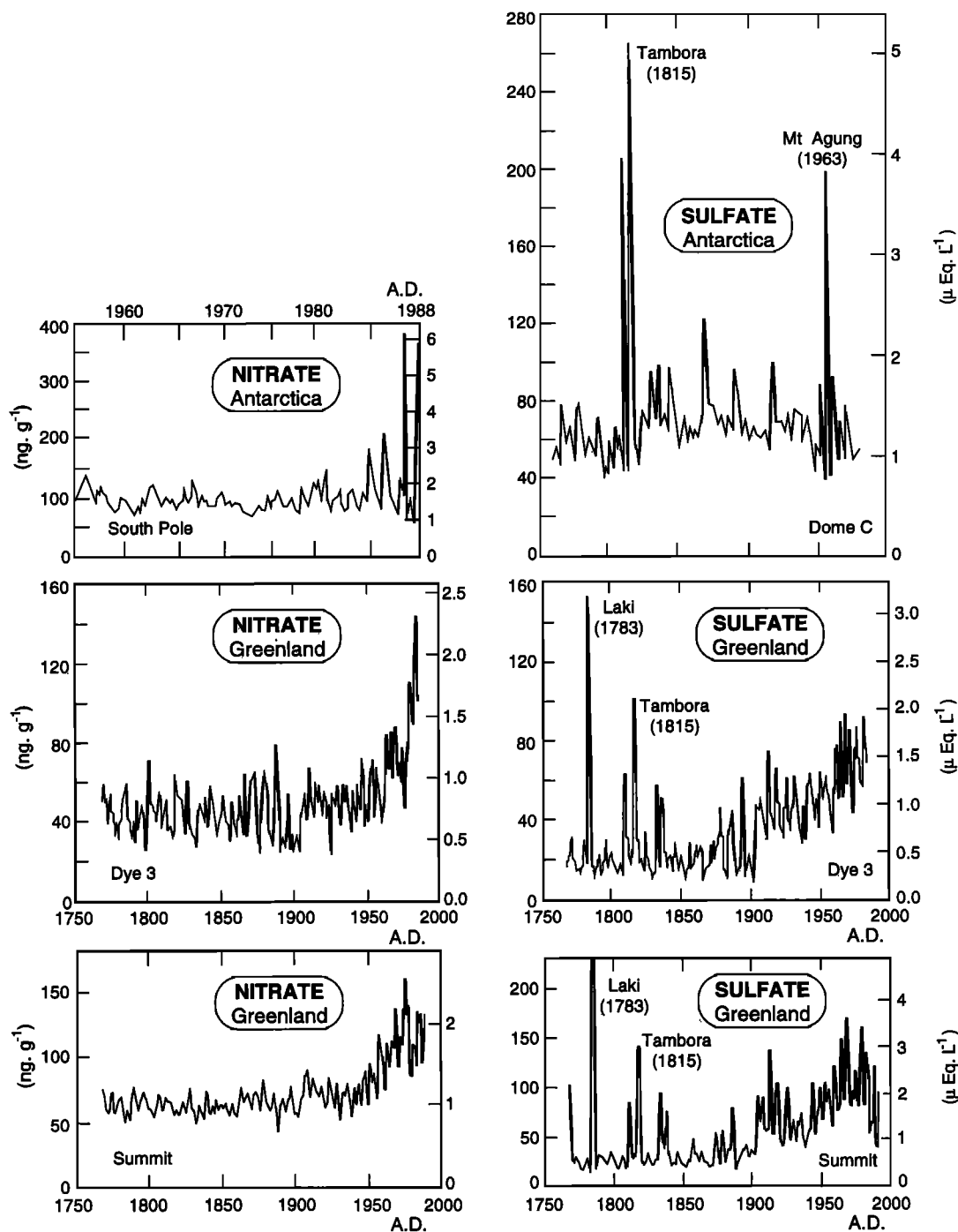
Figure 10. Recent evolution of the SO_4^{--} and NO_3^- content of south Greenland (Dye 3, adapted with permission from *Nature* [*Mayewski et al.*, 1990b]; copyright Macmillan Magazines Ltd.), central Greenland (Summit, adapted from *Legrand and De Angelis* [1996]), and Antarctic snow layers (Dome C [*Legrand and Delmas*, 1988] and South Pole (adopted with permission from *Nature* [*Mayewski and Legrand*, 1990]; copyright Macmillan Magazines Ltd.)). Volcanic events recorded by sulfate spikes are indicated.

ice data remain limited, and the interpretation in terms of atmospheric signals needs further work.

H_2O_2 is the only oxidant from the atmosphere that can be studied in polar ice to help reconstruct the oxidative capacity of the atmosphere. The most promising record for reconstruction of atmospheric trends was obtained at several Greenland sites by *Sigg and Neftel*

[1991] and gives evidence of a 50% increase in the mean concentration over the last decades (Figure 11) in agreement with the expected effect of growing emissions of NO_x, CH_4, and CO [*Thompson*, 1992]. Although HCHO is not an oxidant, it is an oxidation product of hydrocarbons, and its ice record may be useful to establish past oxidative capacity of the atmosphere. *Staffelbach et al.*
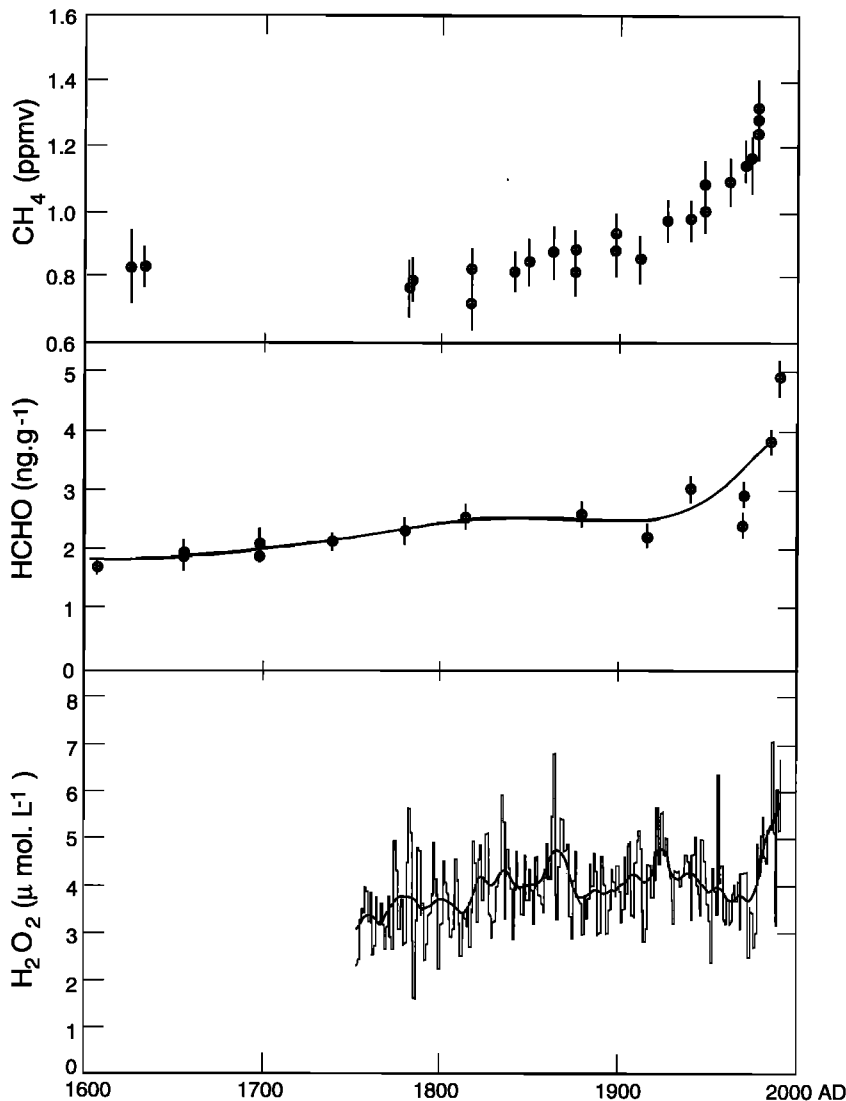
Figure 11. Trend of methane, HCHO (adapted with permission from *Nature* [*Staffelbach et al.*, 1991]; copyright Macmillan Magazines Ltd.), and H_2O_2 (adapted with permission from *Nature* [*Sigg and Neftel*, 1991]; copyright Macmillan Magazines Ltd.) concentrations in Summit (Greenland) ice cores spanning the last centuries.

[1991] investigated HCHO in polar ice and showed a recent increase of HCHO concentrations in recent Greenland snow layers (Figure 11). This increase corresponds with increasing methane concentrations over the time period [*Etheridge et al.*, 1992]. However, H_2O_2 and HCHO are not irreversibly trapped in snow, and in the future a better quantitative understanding of the transfer function has to be developed.

Finally, the levels of light carboxylates are decreasing in recent Greenland snow layers (Table 4). It has been suggested that the expected trend of increasing concentrations of carboxylic acids produced by anthropogenic emissions of hydrocarbons (CH_4 and nonmethane hydrocarbons) is counteracted by a simultaneous increase of the atmospheric acidity related to growing fossil fuel combustion (HNO_3 and H_2SO_4), which in turn has led to a less efficient uptake of these weak acids into precipitation [*Legrand and De Angelis*, 1995].
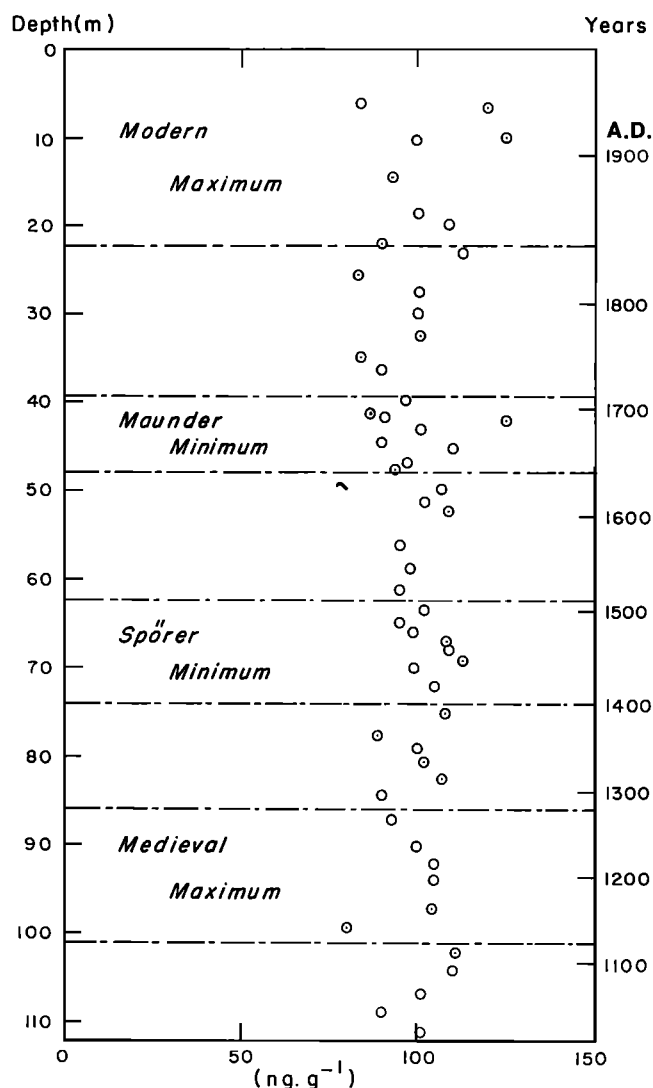
5.2. The Natural Preindustrial Atmosphere

Polar ice cores spanning the last 11,500 years permit the investigation of the natural variability of the chem-
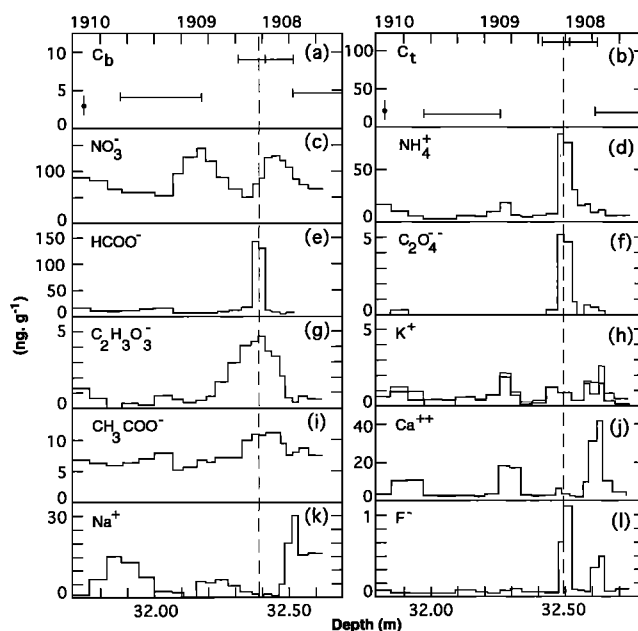
istry of the atmosphere under present climatic conditions. Because of a lack of atmospheric studies in these regions, such ice core data may highlight the main sources of impurities that control the final composition of the atmosphere in these high-latitude regions. Aside from Na^+, Mg^{++}, K^+, and Ca^{++}, which are derived from sea salt and/or soil dust (Figure 5), origins and sources of other important chemical species present in polar ice like nitrogen-derived (NO_3^- and NH_4^+) and sulfur-derived (SO_4^{--} and MSA) species, halogens (Cl^- and F^-), and the light carboxylates exhibit a more complex picture.

Various natural sources of nitrogen oxides (NO_x, the main atmospheric precursors of nitrate) including soil exhalation, biomass burning, lightning, galactic cosmic rays, stratospheric oxidation of N_2O, and ionospheric dissociation of N_2 can contribute to the NO_3^- budget of polar precipitation [*Legrand and Kirchner*, 1990]. Modeling studies have suggested that in addition to lightning, stratospheric N_2O oxidation may represent a major contributor to Antarctic ice [*Legrand et al.*, 1989]. Although large numbers of ice core NO_3^- data exist, we are still

unable to clearly identify the major sources of NO_x influencing the polar regions. A detailed review of NO_3^- records has been recently published by *Wolff* [1995], so we will mention only a few observations here. The absence of convincing variations in the NO_3^- level of south polar ice during the two last minima of solar activity (Maunder and Spörer minima (Figure 12) suggests that the NO_x production from N_2 dissociation above the stratopause, which is strongly modulated by solar activity, does not contribute significantly to the Antarctic NO_3^- budget [*Legrand and Kirchner*, 1990]. The removal of HNO_3 from the polar lower stratosphere in winter is a well-documented phenomenon [*Fahey et al.*, 1990], likely due to the formation of polar stratospheric clouds (PSCs), which subsequently undergo gravitational sedimentation. Because HNO_3 is much more abundant in the stratosphere than in the troposphere, such a process


Figure 13. Chemical signature of a narrow formate-rich event: (a) black and (b) total carbon, (c) nitrate, (d) ammonium, (e) formate, (f) oxalate, (g) glycolate, (h) potassium (light line) and excess potassium (heavy line), (i) acetate, (j) calcium, (k) sodium, and (l) fluoride concentrations. Vertical bars in Figures 13a and 13b refer to concentration levels observed by *Cachier* [1995] along 20 other core sections taken along a 70-m-depth Summit (Greenland) core. Adapted from *Legrand et al.* [1995] (copyright Springer-Verlag).

Figure 12. NO_3^- content of South Pole snow over the last millennium. Periods of high and low solar activities are delimited by dashed lines. Adapted from *Legrand and Kirchner* [1990].

certainly can contribute to the nitrate budget of the lower atmosphere in polar regions. Several authors [e.g., *Mulvaney and Wolff*, 1993] have scrutinized Antarctic ice records. Although it remains to be proven, some NO_3^- peaks seen in ice cores may be PSC signals, suggesting a significant stratospheric contribution to the Antarctic NO_3^- ice budget. Finally, from the observation of enhanced NO_3^- content of the Greenland ice deposited during the Younger Dryas (see section 5.3), *Wolff* [1995] suggested that soil exhalation may also be an important source of NO_3^- to Greenland ice.

While NO_3^- concentrations in most of Antarctica are slightly less than those seen in preindustrial Greenland ice [*Wolff*, 1995], NH_4^+, the second most abundant nitrogen-derived species present in polar ice, exhibits concentrations 1 order of magnitude lower in Antarctic than in Greenland ice (Figure 7). Given the geographical position of the two ice caps, such a difference supports the idea that continental emissions such as soil exhalation, biomass burning, and animals dominate the atmospheric ammonia budget. *Legrand et al.* [1992a] and *Whitlow et al.* [1994] showed that the NH_4^+ level of Greenland precipitation has often been sporadically enhanced in the past, with such large NH_4^+ perturbations accompanied by large increases of organic species (Figure 13). *Legrand et al.* [1995] attributed these NH_4^+ increases to forest fires occurring in summer at high northern lati-
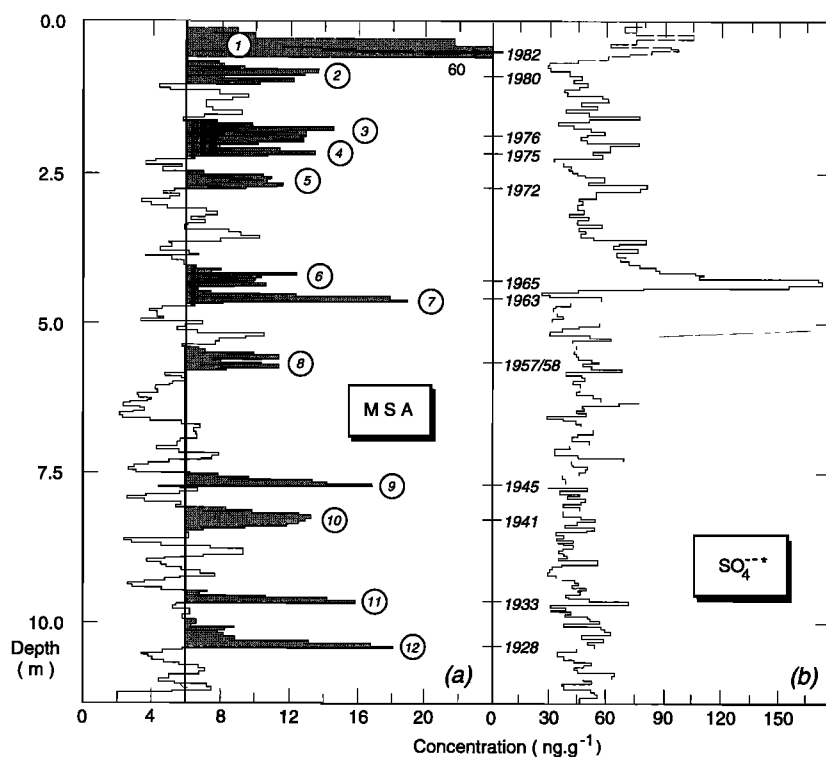
Figure 14. Excess sulfate and MSA concentrations in south polar snow layers deposited from 1922 to 1984. Strong El Niño events occurred in 1925–1926 (peak 12), 1941 (peak 10), 1957–1958 (peak 8), 1972–1973 (peak 5), and 1982–1983 (peak 1). Adapted from *Legrand and Feniet-Saigne* [1991].

tudes. Finally, despite the proximity of ocean around Antarctica, the very low ammonium level of precipitation in these regions is an argument against the existence of a net source of ammonia from the polar ocean, as is sometimes suggested [*Quinn et al.*, 1990].

In addition to sporadic volcanic eruptions of large magnitude, numerous sources can be of importance for the budget of excess sulfate in polar regions. They include sulfate production from emissions of DMS by marine biota, volcanic degassing into the troposphere, and the stratospheric reservoir. Fifteen years ago, it was a well-accepted idea among workers that the background SO_4^{--} level of Antarctic ice is mainly marine and biogenic in origin (see *Legrand* [1995] for a review). Since then, other studies have investigated the role of marine biogenic emissions through simultaneous measurements of MSA and sulfate content of polar ice. Indeed, next to sulfate, MSA is the second most important oxidation product of DMS, but in contrast to SO_4^{--}, DMS oxidation is the only source of MSA. MSA therefore is potentially an important tracer for biogenic sulfate production. Marine phytoplankton are particularly abundant in the ice edge zone, where the sea ice is thin enough to allow light penetration for growth [*Sakshaug and Skjoldal*, 1989]. The precursor for DMS in seawater is dimethylsulfoniopropionate (DMSP), an osmoregulator in plankton cells. High salinity in brine pockets of sea ice may involve an increase in DMSP production [*Gibson et al.*, 1990]. Coastal Antarctic ice studies have shown that the content of sulfur-derived species has fluctuated over the last century [*Welch et al.*, 1993; *Peel and Mulvaney*, 1992; *Pasteur et al.*, 1995]. However, no

overall conclusion concerning the role of sea ice on DMS production in coastal Antarctic areas emerges from these studies, maybe because of the strong influence of very local meteorological conditions at these sites. We here report the study achieved at the south pole (Figure 14) for which incoming air masses are typically very well mixed. The excess sulfate (SO_4^{--}*) content deposited at the south pole over the time period 1922–1983 remained rather stable over time except for short-term increases after the Mount Agung (1963) and the El Chichón (1982) eruptions. In contrast, the MSA profile shows several sporadic increases that, taking into account the dating uncertainty of snow layers, seem to be correlated to major El Niño–Southern Oscillation events of the last 60 years (1925–1926, 1941, 1957–1958, 1972–1973, and 1982–1983, Figure 14). *Legrand and Feniet-Saigne* [1991] suggested that these MSA peaks are related to an enhanced DMS concentration in the Antarctic marine atmosphere during El Niño years possibly resulting from higher sea surface wind speeds, which could lead to more efficient air-sea exchange of DMS. Another plausible explanation is that this increase is due to increased sea ice extent or duration during the El Niño years, which could therefore cause higher DMS emissions at high southern latitudes. Marine biogenic emissions are lower at high northern latitudes compared with the high southern ones (23 × 10^9 and 54 × 10^9 mol Sulfur yr^{-1}, respectively, between 50° and 85° [*Bates et al.*, 1992]). The observation of a very similar relationship between excess SO_4^{--} deposition fluxes and snow accumulation rates in both Greenland and Antarctic snow (Figure 4) therefore suggests that another source of

sulfate has to be considered at high northern latitudes in order to counteract lower marine biogenic emissions. As reported by *Bates et al.* [1992], noneruptive volcanic sulfur emissions (Kamchatka, Iceland, and Aleutians) are higher at high northern latitudes compared with high southern latitudes (45×10^9 and 1×10^9 mol S yr^{-1}, respectively, between 50° and 85°) and are of the same order of magnitude as the biogenic emissions.

5.3. Atmospheric Chemistry Changes Over the Last Climatic Cycle (120,000 Years)

Studies of deep ice cores extracted from Greenland and Antarctica provide a powerful method of investigating the response of our environment to major climatic variations.

Numerous Greenland and Antarctic ice cores have revealed that the sea salt content of ice has been strongly modulated by past climatic conditions. For instance, the Na$^+$ profile in the Vostok core (Figure 15), which spans the last climatic cycle, shows low values during warm stages and a gradual increase of concentration over the
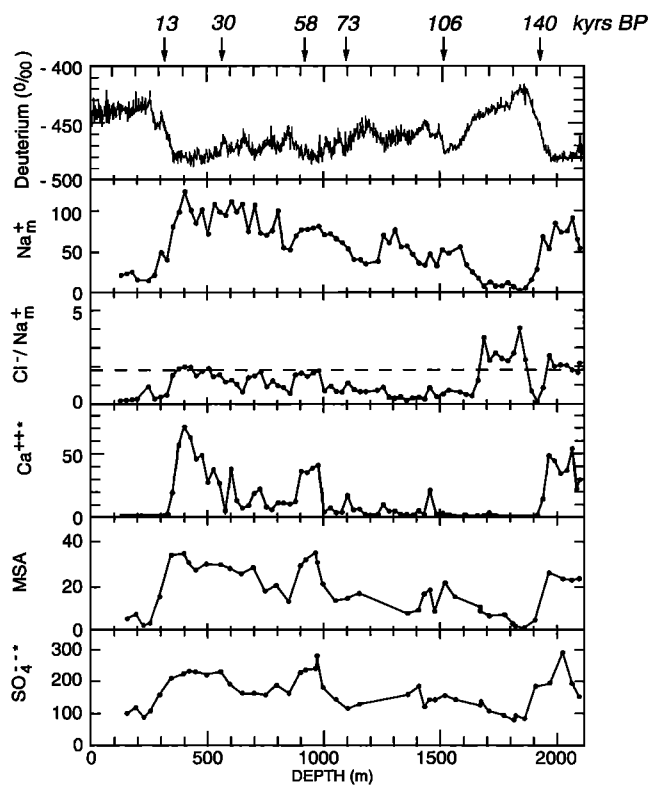

Figure 15. Vostok (Antarctica) ice core profiles (0–160,000 years B.P.): Deuterium isotope data are from *Jouzel et al.* [1987] (reprinted with permission from *Nature*; copyright Macmillan Magazines Ltd.); marine sodium, Cl/Na$_m$ weight ratio (the reference value of the weight ratio in sea water, 1.8, is reported), and excess calcium are from *Legrand et al.* [1988] (reprinted with kind permission from Elsevier Science Ltd., Oxford, England); and MSA, and excess sulfate are from *Legrand et al.* [1991] (reprinted with permission from *Nature*; copyright Macmillan Magazines Ltd.).
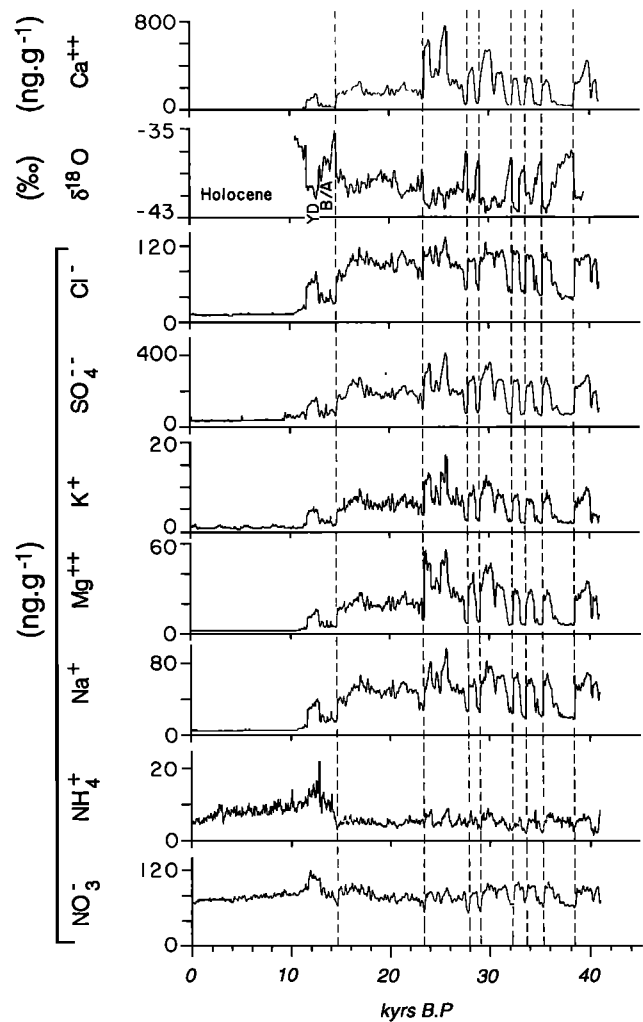
Figure 16. Summit (Greenland) GISP 2 ice core profiles of major ions and δ^{18}O over the last 40,000 years. YD is the Younger Dryas stage (11,500–12,700 years B.P.), B/A are Bolling and Allerod interstades (12,700–14,450 years B.P.). Adapted with permission from *Mayewski et al.* [1994]. Copyright 1994 American Association for the Advancement of Science.

last ice age. As was mentioned in section 3.4, the Na$^+$ content of ice exhibits an accumulation rate effect linked with the dry deposition process. Some of the observed changes along the Vostok core are therefore linked to the reduction of the snow accumulation rate between warm stages and the last glacial age. However, such an effect can only explain 25% of observed changes, and the remaining variations are representative of actual atmospheric sea salt concentration changes. Similar changes in sodium content are also recorded in Greenland deep ice cores [*Hansson*, 1994; *Mayewski et al.*, 1994]. Such data therefore suggest that during cold climates, despite a sea ice expansion by several hundred kilometers around the two ice caps [*COHMAP Members*, 1988] that increased the distance from the open ocean to these regions, the sea salt content of the atmosphere was enhanced. That was interpreted as a greater production
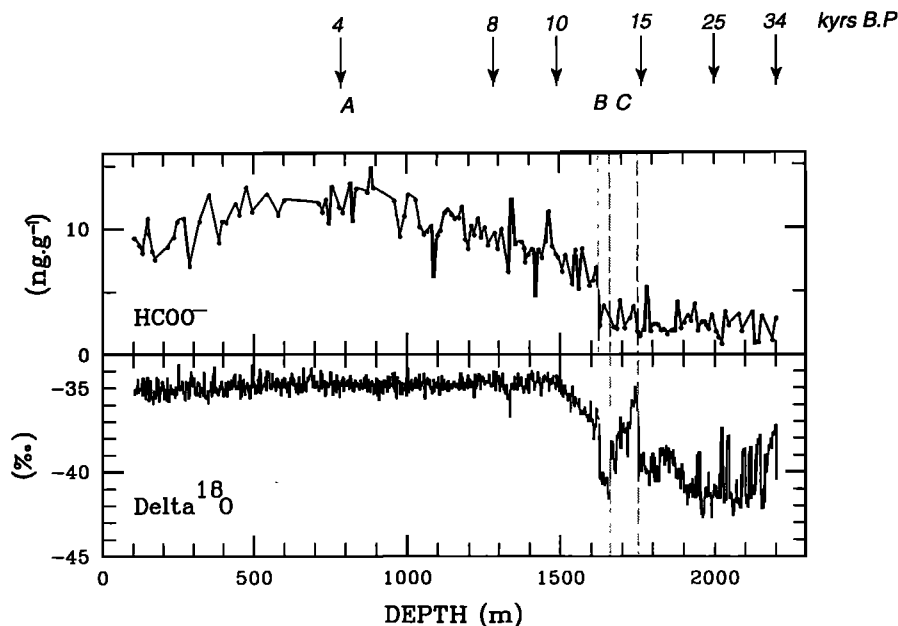
Figure 17. Formate background levels in the Summit (Greenland) GRIP core along with the stable isotope profile over the last 34,000 years. Vertical dashed lines refer to the successive stages A–C, where A is the Holocene (0–11,500 years B.P.), B is the Younger Dryas (11,500–12,700 years B.P.), and C is the Bolling and Allerod interstades (12,700 to 14,450 years B.P.). Adapted from *Legrand and De Angelis* [1995].

rate of sea salt due to higher wind speeds at the sea surface and/or a more efficient meridional transport between middle and high latitudes at this time [*Petit et al.*, 1981; *Legrand et al.*, 1988].

Greenland and Antarctic ice deposited during very cold climate contains much more dust than ice deposited at the present time as depicted by the calcium profiles (Figures 15 and 16). On the basis of Sr and Nd isotopic studies, *Biscaye et al.* [1997] concluded that dust source areas for Greenland were located in east Asia at this time. The very large dust content of Greenland glacial ice suggests that the atmospheric circulation at high northern latitudes expanded to include these source regions [*Mayewski et al.*, 1994]. Such a southward shift of the general circulation in the northern hemisphere might have been driven by the buildup of the great continental ice sheet (the Laurentides) over North America, as suggested by model studies [*COHMAP members*, 1988]. The situation was different in the southern hemisphere, and the enhancement of dust content in Antarctic ice during the Ice Age was interpreted as an indication of expansion of arid areas and emergence of portions of the continental shelves [*Petit et al.*, 1981; *De Angelis et al.*, 1987].

In contrast to sea salt and soil dust, which show similar variations over past climate changes on both ice sheets, the relationship between sulfur-derived species and climate is very different between Greenland and Antarctica. Simultaneous studies of MSA and SO_4^{--} were first performed in the Vostok core and showed similar trends (Figure 15) for both species, with a moderate glacial-interglacial increase. Such a picture sup-

ports the conclusion that excess SO_4^{--} is mainly marine and biogenic in origin in Antarctica and suggests that marine DMS emissions have been modulated by past climatic conditions [*Legrand et al.*, 1991] in the southern hemisphere. The observation of a fourfold increase during the last glacial maximum in the Dome C core for mercury, which is related to marine biogenic emissions, is another supportive evidence for changes in bioproductivity in response to past climate [*Vandal et al.*, 1993]. As seen in Figure 16, a larger increase in SO_4^{--} is seen in Greenland than in Antarctica during glacial times. Such large enhancements of the sulfate level are well correlated to the calcium increases (Figure 16). Enhanced levels of SO_4^{--} in Greenland glacial ice are accompanied by lower concentrations of MSA with respect to present climatic conditions, as reported by *Hansson and Saltzman* [1993] in the Renland deep ice core. This suggests that DMS emissions were lower at high northern latitudes during the ice age and that enhanced sulfate levels are related to nonbiogenic sulfur sources at this time (gypsum emissions from deserts, for instance). Such a contrast between Antarctic and Greenland cores suggests that biogenic marine emissions may not have been modified in a similar way by past climatic conditions in the two hemispheres.

Aside from sporadic perturbations related to biomass burning events (see section 5.2), carboxylic acids and ammonium are present at the 5–10 ng g^{-1} level in Greenland precipitation, where in contrast to Antarctic precipitation, they represent a significant contribution to the ionic budget (Figure 7). Ammonium (Figure 16) and carboxylic acids (Figure 17) reveal lower concentrations

TABLE 5. Sources Influencing the Background Level and Providing Short-Term Variations of Various Chemical Impurities Present in Polar Precipitation Over the Preindustrial Era

Species	Background	Short-Term Inputs
$Na^{+ \cdot}$	sea salt	volcanic ash
NH_4^+	soil exhalation	forest fires
K^+	sea salt, soil dust	volcanic ash
Mg^{++}	sea salt, soil dust	volcanic ash
Ca^{++}	soil dust, sea salt	volcanic ash
F^-	soil dust	volcanic plumes
Carboxylic acids	vegetation emissions	forest fires
MSA	marine biota	
NO_3^-	lightning, biomass burning, N_2O oxidation, soil exhalation	polar stratospheric clouds (?)
Cl^-	sea salt, sea salt alteration	volcanic plumes
SO_4^{--}*	marine biota, noneruptive volcanism	volcanic plumes

during cold stages compared with values observed during warm stages in Greenland. This variation in response to past climatic conditions has been attributed to weakened continental biogenic emissions from soils [*Fuhrer et al.*, 1996] and vegetation [*Legrand and De Angelis*, 1996]). For example, the background level of formate was 5 times lower during the last glacial maximum when compared with present climate (Figure 17). During the last glacial-interglacial transition, its concentration increased as the great ice sheet that covered North America retreated, permitting the establishment and growth of boreal vegetation [*Legrand and De Angelis*, 1995].

5.4. Summary

Ice core chemistry studies have provided some important information on the chemistry of the past atmosphere over various time periods including the industrial and preindustrial eras and the last glacial cycle. Greenland ice cores indicate that human activities have already significantly enhanced the acidity (HNO_3, H_2SO_4, HCl, and HF) and heavy metal content of the northern hemisphere' atmosphere. They also suggest that anthropogenic emissions may have changed the oxidative capacity of the atmosphere. Ice cores covering the preindustrial era reveal that large volcanic eruptions have strongly disturbed the chemistry of polar atmosphere in both hemispheres. The high northern latitude atmosphere has also been sporadically disturbed by boreal forest fires. The aerosol content of our "natural" atmosphere is very sensitive to climatic variations, with enhanced inputs of sea salt and dust, and to a lesser extent, sulfur-derived species, during glacial conditions. In contrast, continental biospheric emissions have likely been strongly limited, at least at high northern latitudes, during colder climates. Such ice core studies have highlighted our knowledge of main sources of impurities driving the chemical composition of these background high-latitude atmospheres as summarized in Table 5.

6. PERSPECTIVES

With respect to our present knowledge of the relationships linking the composition of the precipitation and that of the atmosphere at the time of deposition, ice core data interpretation related to aerosols (sea salt, soil dust, sulfur-derived species) is more straightforward in terms of atmospheric chemistry changes than that for reactive gases (HNO_3, HCl, H_2O_2, HCHO, and the carboxylic acids). In the future, with the aim of increasing the capability of describing the chemistry of our atmosphere and its natural variability in the past, there is an urgent need to give strong impetus to investigating the air-snow relationships for various chemical species. The transfer functions of gaseous species that interact strongly with ice are the most complex and require both field studies and laboratory experiments.

In addition to such fundamental aspects, much more information may be extracted from ice cores. For instance, the use of adequate mathematical procedures for extracting sporadic events, secular trends, and periodicities found in the data sets, as recently developed by *Mayewski et al.* [1993], will increase the quantity and the quality of information extracted from the records. The studies of other chemical species like those derived from methyl halogens (CH_3I, CH_3Br) will certainly provide new information concerning the key role of marine biogenic emissions on the chemistry of our natural atmosphere. Finally, studies dedicated to organic matter and its speciation will likely reveal numerous tracers of biogenic processes and possibly help in reconstructing past oxidative capacity of the atmosphere.

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