

Polar ices chemistry : a past atmosphere reflection

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I ■ INTRODUCTION ■

Because of their geographical position and meteorological conditions, polar regions are of interest for many environmental studies. Being located far from continents, arctic and antarctic regions are recognized as having the cleanest atmospheric environment of the Northern and Southern hemisphere respectively. The relative remoteness of continental polar regions suggests that their atmospheres represent the best modern example of the « background atmosphere » for their respective hemispheres and are therefore very sensitive to any natural and/or anthropogenic change. A second and unique specificity of polar regions comes from the solid precipitation which accumulates on polar ice sheets. Assuming a good knowledge of the relation linking the composition of the atmosphere and that of the snow, studies of polar ice make it possible to reconstruct the paleoenvironment of the Earth as far as several hundred thousands of years back. Over the last decades, national and international programs have ex-

tracted ice cores from Greenland and Antarctica which contain detailed records concerning past climate, and trace gas content of the atmosphere in addition to precipitation chemistry. Firstly, as a consequence of differences in saturation vapour pressure and molecular diffusivity, isotopic fractionation takes place at each phase change of atmospheric water (for detail, see Jouzel, this volume). Because of these processes, stable isotopes of hydrogen and oxygen in Antarctic and Greenland ice cores provide long and detailed proxy records of temperature. Secondly, when firn turns into ice, bubbles are formed trapping atmospheric air. The composition of the gas enclosed in ice bubbles provides a direct measurement of gases such as CO₂ and CH₄ (see Raynaud, this volume). Finally, studies of the ice chemistry and the interpretation of these records in terms of composition of the atmosphere has opened a powerful new scientific field called « glaciochemistry ». Glaciochemical studies have started rather slowly due to technical difficulties linked with the low level samples characterizing polar precipitation and a lack of physical understanding of

Chimie des glaces polaires : un reflet de notre atmosphère passée

Dans ce papier, les auteurs présentent une étude de la composition chimique des impuretés contenues dans les glaces polaires et l'interprétation de ces données en termes de composition chimique de notre atmosphère passée. Cette étude glaciologique portera essentiellement sur les espèces solubles minérales (Na⁺, NH₄⁺, K⁺, Ca⁺⁺, Mg⁺⁺, H⁺, F⁻, Cl⁻, NO₃⁻ et SO₄⁻) et organiques (méthanesulfonate : CH₃ SO₃⁻, carboxylates légers et formaldéhyde : HCHO). Ils décrivent aussi les méthodes de datation des carottes de glace et les difficultés rencontrées pour ces analyses de traces. L'établissement et la signification du budget ionique des précipitations polaires sont ici discutés. Ils présentent les variations spatiales et temporelles de ce budget ionique des précipitations polaires entre les régions et côtes de l'Antarctique et du Groenland pour des périodes de temps couvrant les dernières décades jusqu'à un cycle climatique complet. Ils présentent ce qu'ils ont pu extraire comme informations de tels enregistrements en terme de composition chimique de notre atmosphère passée. En particulier, ils discutent les changements de la charge atmosphérique en aérosols d'origines marine et continentale intervenus en réponse aux grandes variations climatiques du passé. Ils montrent également que tant les phénomènes naturels (éruptions volcaniques et émissions biogéniques en provenance de l'océan) que les émissions anthropiques ont fortement perturbé le cycle atmosphérique du soufre. L'enregistrement des concentrations en acides organiques suggèrent que les émissions en provenance de la biosphère continentale (fréquence des feux de forêts, émissions par la couverture végétale) ont également été fortement influencées par les conditions climatiques passées.

impurity incorporation in snow which sometimes limits the interpretation of snow data in terms of atmospheric chemistry. In spite of these difficulties, these studies have already provided information on paleovolcanism, the response of one atmosphere to other natural phenomena such as major and/or rapid changes in climate and on the response of the high latitude atmosphere to human activities (e.g. acidification of the precipitation, ozone depletion, oxidative capacity of the atmosphere, etc.).

II ■ GLACIOLOGY ■

● 2.1 Dating of snow and ice

Various methods, depending on the required accuracy, the considered time scale and the location (high or low mean annual accumulation rate of snow), can be used to date depth profiles, namely stratigraphical studies, reference horizons, radioactive decay of some radionuclides and ice modelling.

In principle, numerous stratigraphical methods based on the seasonal changes in the isotopic composition of the ice or in the content of various atmospheric trace species (sea salt, dust, H_2O_2 for instance), as well as in the physical properties of snow (layer of depth hoar alternating with relatively fine-grained strata, the former corresponding to metamorphism of the surface snow layers [1]) may be used to establish accurate (year-by-year) dating of ice cores. As long as the yearly snow accumulation is sufficient and the annual layering not excessively disturbed by surface wind, such seasonal changes provide fairly accurate year-by-year dating of snow layers both in Greenland and in Antarctica, at least down to a certain depth. The dating of snow layers using the seasonal isotopic composition of water [2] was first successfully applied along numerous ice cores. One great advantage of such isotopic measurements is that, as opposed to the case of other chemical measurements, they do not require special cautions to prevent the contamination of samples. However a damping effect related to diffusion processes occurring during firnification limits such a dating method to the upper part of firn at locations where the annual accumulation rate is less than 20 cm of ice [3]. Hydrogen peroxide was found to be one of the clearest seasonal tracers in ice cores [4] with a typical summer to winter ratio of 5. Such a method has the advantage of being easy and fast to set up even in the field but is also limited because of the smoothing with depth of the seasonal cycle [5]. Other chemical species representing potential means of obtaining accurate dating include sodium [6] [7], calcium [8] and dust [9], the contents of which all exhibits very strong seasonal cycles in Antarctica and in Greenland snow layers and for which no smoothing effect with depth occurs.

Some large and well documented atmospheric perturbations of the past can be used as « reference horizons ». Such reference horizons represent an independent way to check the age of certain layers when the preceding methods are applied and are of special interest for dating ice cores from low accumulation areas when the preceding stratigraphical methods fail. The spread of radioactive debris over the entire world (via the stratosphere) has served to date snow layers deposited in 1955 and 1965 [10]. Similarly by their SO_2 emissions, volcanic eruptions of large

magnitude have provided numerous reference horizons in polar ice cores. For instance, the eruption of Tambora (1815), which injected a large amount of SO_2 into the stratosphere, is recorded in both Greenland [11] and Antarctica [12] and guarantees a good estimation of the mean snow accumulation rate over the last 200 years. Over longer time periods, other stratigraphical markers can also be used. Although such stratigraphical markers cannot provide absolute dating because they are generally not historically documented, they are of great interest in comparing depth profiles obtained at different sites. For instance, the discovery of Yiou *et al.* [13] of two well-defined ^{10}Be peaks along the Vostok core corresponding approximately to 60,000 and 35,000 years BP, probably in relation with large solar activity modulation, is of great interest in such topics. Measurements of radioactive isotopes present either in bubbles of the ice like ^{85}Kr (half-time of 11 yrs), ^{14}C (5 730 yrs), in water like tritium (12 yrs) or in aerosols like ^{210}Pb (22 yrs) and ^{32}Si (172 yrs) are a powerful way to obtain absolute age determination. However, several problems have not been solved in particular the uncertainty in the changes of the initial concentration in the past atmosphere.

Along deep ice cores, chronological information is mainly obtained by comparing isotopic profile features reflecting great climatic changes both in ice and in other climatic records (sea level recorded in sea sediment for instance) which have been dated independently. A special case exists for deep ice cores extracted in margin areas of ice sheets, which can provide valuable information for glaciochemical studies, in particular concerning the impact of the local marine source of impurities. Here because of an important ice flow phenomenon, the age of ice layers becomes a more complex function of the depth and the origin of the ice and the dating of such deep ice cores requires ice flow modelling.

● 2.2 Which site is adequate for which purpose

The physical and chemical environment of Antarctica and Greenland share some similarities but on closer inspection are very different. South polar region is a continent (Antarctica) surrounded by oceans while north polar region is an ice-covered ocean surrounded by continents where man-made activities are very important and by an ice sheet (Greenland). Such geographical differences lead to different atmospheric circulation regimes, in particular a more intense transport between mid and high latitudes in the Northern than in the Southern hemisphere.

From both Antarctica and Greenland, several ice cores spanning the last great climatic change (10-18 kyrs B.P.) have been obtained over the last decades. The longest antarctic record has been obtained at Vostok (East Antarctica), covering completely the last climatic cycle (220,000 years ; [14]). Camp Century (N.W. Greenland) and Dye 3 (S.E. Greenland) cores have documented the last 100,000 years in Greenland [15]. Very recently, two deep drilling projects (American GISP and European GRIP) have reached the bedrock at Dome Summit (Central Greenland) and, similarly to Vostok, the cores cover more than an entire climatic cycle [16, 17]. These two ice cores, along with the Vostok core, provide the richest glaciochemical data ever collected. Over shorter time periods (from last decades up to a few thousands years ago), numerous

Antarctic and Greenland depth profiles have been investigated for various purposes including the response of our atmosphere to anthropogenic emissions. Such data obtained in various locations where the snow accumulation rate is highly variable are also useful to compare the snow impurity content as a function of elevation, latitude and snow accumulation rates.

III ■ ANALYTICAL PROCEDURES ■

Because of the remoteness of these regions, the use of special sampling and measurement techniques is required to determine the extremely low impurity contents. Progress was hampered in the past because reported data had suffered from contamination problems.

● 3.1 Sampling and sub-sampling

In the first upper meters of snow, it is always possible to collect snow samples free of contamination from pits as long as certain conditions are respected during the sampling (sterile clothing and gloves for operators, appropriate materials for utensils and storage flasks). Further down, it becomes rapidly difficult to dig a pit and samples are extracted by drilling the firm and the ice. The outside surfaces of these cores are generally significantly contaminated during the drilling procedure. Two kinds of procedures can be used to remove contamination from the outside part of the cores either by using an ice core lathe equipped with a stainless steel knife or by melting and washing the ice with ultrapure water.

Another problem comes from the choice of the material used for storing the samples. As far as mineral species are concerned, teflon and various plastic and glass materials can be used after tedious washing with ultrapure water in a microwave oven and/or in an ultrasonic bath. On the other hand, organic acid measurements strictly require the use of glass instead of plastic and teflon to store the samples [18]. After the decontamination procedure, samples have to be frozen until the time of the analyses in order to minimize loss on the walls of vials. It is also important to minimize the time during which the sample remains in the liquid phase in order to limit losses by biological activity for organic acids [19] and by oxidation for H_2O_2 [20].

Finally, since some species of interest are present in the gas phase in the ambient air of our laboratories, special precautions have to be taken when melting the samples. Indeed, a clean air bench prevents sample contamination from solid impurities but not at all from several trace gases such as HNO_3 , NH_3 and volatile organic acids. For instance, Legrand *et al.* [19] observed rapid contamination in an ultrapure water sample exposed to the atmosphere within a clean air bench for NH_4^+ , $HCOO^-$, CH_3COO^- and NO_2^- (at a mean rate of 10, 5, 18 and 2.5 ng.g^{-1} per hour respectively). With respect to the Antarctic level of these species in ice (one ng.g^{-1} or less), such an effect is dramatic. To prevent the samples from such rapid contamination, it is highly recommended to put them in air-tight glass bottles kept closed during the melting step.

● 3.2 Analytical techniques

By the end of the 70's, a method, rapid, sensitive and well adapted to our purpose in studying the soluble part of impurities present in ice appeared: the ionic chromatography. It is now possible to measure all the cations and anions of interest, including organic ions, within about 15 min, at trace levels (one ng.g^{-1} or less), with only a 5 ml total sample volume [19]. Considering the need for establishing an ionic balance of the melted ice and snow sample, measurement of proton concentrations, which cannot be achieved using ion chromatography, is needed. Basically two methods have been used to determine proton concentrations in polar precipitation. The first is a non-destructive method developed by Hammer [21] which uses the solid conductivity of the ice. The second method is an acid titration of the melted sample with an initial addition of acid to prevent samples from the dissolution of the CO_2 of the atmosphere [22].

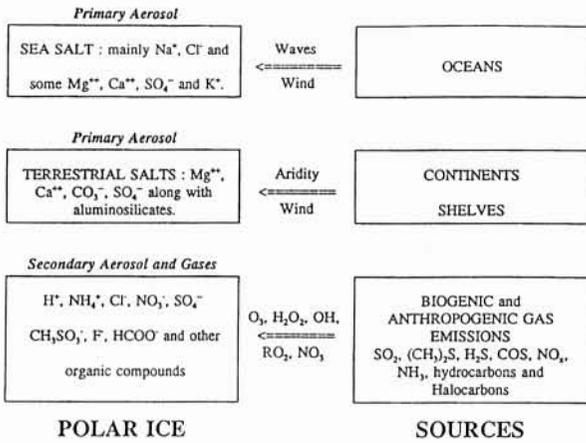
IV ■ ICE AND SNOW CHEMISTRY ■

With respect to our knowledge of the chemistry of the atmosphere, we expect to find in polar precipitation various soluble and insoluble impurities (*fig. 1*). These impurities are either introduced directly into the atmosphere (so called primary aerosols such as sea salt and dust emitted by the wind from marine and continental surfaces) or produced within the atmosphere along various oxidation processes involving numerous trace gases mainly derived from Sulphur, Nitrogen, Halogen and Carbon cycles. As is clearly shown in *figure 1*, while aluminium present in polar precipitation can be used to trace back to continental primary emissions, the problem concerning many other ions is more complex. For instance, the presence of sulphate 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 itself being directly introduced in the atmosphere during volcanic eruptions or by human activities or produced by the oxidation of various S-compounds emitted from the biosphere. Sulphuric acid can thereafter react on particles (sea salt and soil dust) and with gas (NH_3) to produce Na_2SO_4 , $CaSO_4$ and NH_4HSO_4 or $(NH_4)_2SO_4$. This example illustrates the need to perform a comprehensive study of soluble species in order to be able to reconstruct the initial association between the ions. Once these associations are known, it becomes easier to discuss the possible sources from which the ions are derived.

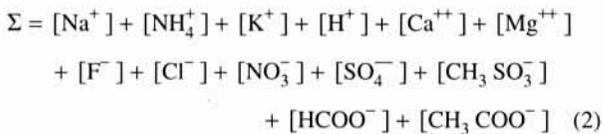
● 4.1 Mean Antarctic ionic balance

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 (noted ΔC) represents less than 5 % of the ionic budget (noted Σ) (concentrations expressed in $\mu\text{Eq/l}$, i.e. in μmole times the valence):

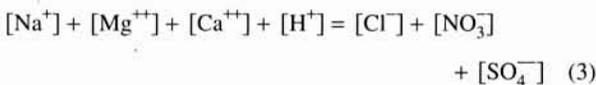
$$\begin{aligned} \Delta C = & [Na^+] + [NH_4^+] + [K^+] + [H^+] + [Ca^{++}] + [Mg^{++}] \\ & - [F^-] - [Cl^-] - [NO_3^-] - [SO_4^{--}] - [CH_3SO_3^-] \\ & - [HCOO^-] - [CH_3COO^-] \quad (1) \end{aligned}$$



1. Scheme showing various soluble impurities expected to be trapped in polar snow layers and their corresponding origins and sources [23].

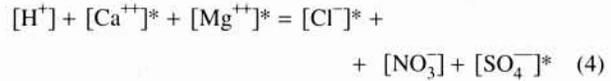


Na^+ , H^+ , Ca^{++} , Mg^{++} , Cl^- , NO_3^- and SO_4^- represent major ions present in ice deposited in antarctic (coastal and central) regions under present climatic conditions as well as during past colder climate [24, 25]. NH_4^+ and K^+ represent a weak contribution ($< 0.2 \mu\text{Eq/l}$) compared with the total ionic budget ($5 < \Sigma < 30 \mu\text{Eq/l}$). Recent studies point to a CH_3SO_3^- content close to $0.2 \mu\text{Eq.l}^{-1}$ [26, 27]. F^- and carboxylates account for an insignificant part of the ionic budget [28, 18, 29]. The balance achieved between cations and anions ($\Delta C = 0$) of the antarctic ice can be therefore expressed as:



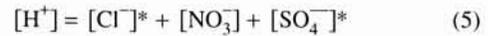
In coastal areas, due to the large contribution of sea salt input, Na^+ , Cl^- , Mg^{++} , Ca^{++} , K^+ and a part of SO_4^- represent a dominant part of the ionic budget (more than 80%) [24] of the ice. Further inland and for present climate, this sea salt input is strongly decreased and other contributions to the ionic composition of snow become dominant (65 to 80%, depending on sites) [24].

The antarctic Na content measured using ion chromatography corresponds to the sum of two fractions: the first, mainly marine in origin, is soluble in water, the second coming along with dust is not solubilized during the melting step but is later during the elution in the ion chromatograph [24]. It is therefore necessary to correct Na data from this dust contribution using the Al content of the sample, in particular for ice corresponding to the glacial age (see further discussion). Subtracting the sea salt contribution from equation (3) using the Na content (after the above mentioned correction) and the sea salt composition from Holland [30], we obtain the basic equation which describes these other contributions:



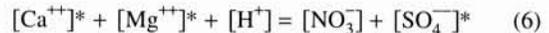
where $[\text{X}]^*$ = « excess-X » representing the non sea salt contribution of X.

In snow deposited under present climatic conditions, Ca^{++} and Mg^{++} are present at low levels in relation to weak terrestrial inputs [31]. $[\text{Cl}^-]^*$ can have positive, negative or zero values and the equation (4) is here reduced to:



In coastal regions, this quantity is close to zero, suggesting that aside from the large sea salt content, the snow contains HNO_3 and H_2SO_4 . In central areas, where $[\text{Cl}^-]^*$ is not zero, equation 5 indicates that besides sea salt, the ice deposited under present climatic conditions contains HNO_3 and H_2SO_4 plus either Na_2SO_4 or HCl corresponding to negative or positive $[\text{Cl}^-]^*$ values.

During colder climate, $[\text{Ca}^{++}]^*$ and $[\text{Mg}^{++}]^*$ are significant, $[\text{Cl}^-]^*$ is close to zero and equation 4 becomes:

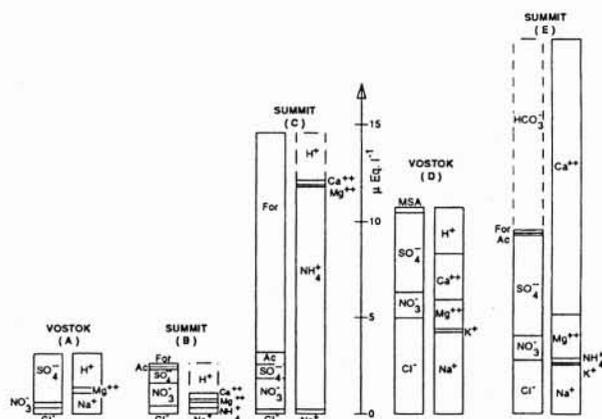


As discussed by Legrand *et al.* [31], ice corresponding to such glacial conditions contains HNO_3 , H_2SO_4 , sea salt and terrestrial salts (Ca^{++} and Mg^{++} associated with SO_4^- and NO_3^-) and an absence of carbonates.

The contribution of insoluble species can be estimated from aluminium determinations and using the composition of the mean crust [32]. Under present climatic conditions, soluble species dominate the mass of impurities present in Antarctic snow deposits with a main contribution from sea salt and an increasing contribution of mineral acids (H_2SO_4 , HCl and HNO_3) further inland. In Antarctic ice corresponding to glacial conditions, insoluble species become predominant, representing a good half of the total mass. Similarly, terrestrial salts which are present at insignificant levels under present climatic conditions represented some 25% of the total ionic budget of glacial Antarctic ice.

4.2 Mean Greenland ionic balance

The ionic budget of Greenland ice has not yet been fully characterized and we report here a preliminary view (fig. 2B, 2C and 2E) recently obtained from Summit ice, deposited under present climatic conditions and during a cold climate, based only on ion chromatographic data (Legrand *et al.*, unpublished data) without simultaneous H^+ measurements. One notable feature of the ionic budget of Greenland ice is, in contrast to Antarctic ice, the presence of a significant amount of NH_4^+ and organic acid (fig. 2B) in relation to a larger impact of continental biospheric emissions. Moreover, as suggested by changes in Na^+ and Ca^{++} (fig. 2D and 2E), both Greenland and Antarctic ice cores reveal enhanced input of sea salt and soil dust during the Glacial Age as compared with the present warm climate stage. However it appears that during such cold climate the ice was alkaline in Greenland and remained acidic in Antarctica.



2. Mean ionic ice composition corresponding to present climate in Antarctica (2A), Greenland (2B) and to glacial age in Antarctica (2D) and in Greenland (2E). Dashed lines are used when acidity measurements are not yet available. Figure 2C corresponds to sporadic changes in the mean Greenland ice composition (adapted from [23]).

4.3 Short term variations of the mean ionic balance

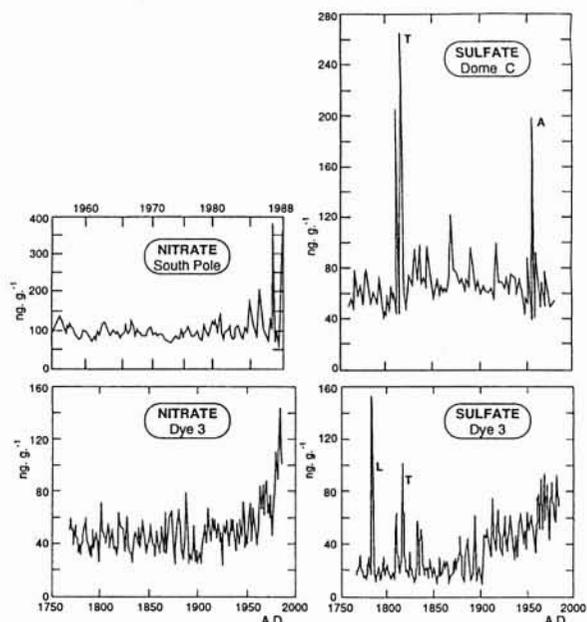
Aside from long term changes of the ionic budget of both Greenland and Antarctic ice in response to great climatic variations, the chemistry of Greenland and Antarctic ice has also been sporadically disturbed by volcanic inputs which led to strong enhancements of the H_2SO_4 (see further discussion) and sometimes of the HCl and HF contribution [33]. Furthermore, the Greenland ice ionic budget, in contrast to the Antarctic one, reveals large and sudden enhancements of formate and ammonium levels as well (fig. 2C) which are related to high northern latitude biomass burning debris [34]. Finally, as discussed in section 5.1, human activities (specially fossil fuel burning) have disturbed to a large extent the ionic composition of recent Greenland snow deposits with enhanced nitrate and sulphate inputs.

V ■ 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 profiles covering the last 200 years have provided useful informations on the impact of human activities on the chemical composition of the northern and southern hemispheres respectively. For instance, in contrast to the Antarctic sulphate level, the Greenland one (fig. 3) reveals the increasing SO_2 fossil fuel burning emissions of the Northern hemisphere.

The 200-year NO_3^- profile obtained in Greenland ice (fig. 3) demonstrates the recent increase due to long range transport of pollution from middle northern latitudes [35]. Over the two last centuries, the NO_3^- ice content at the South Pole remains fairly constant but an increase of the spring-summer maximum in NO_3^- appears in very recent



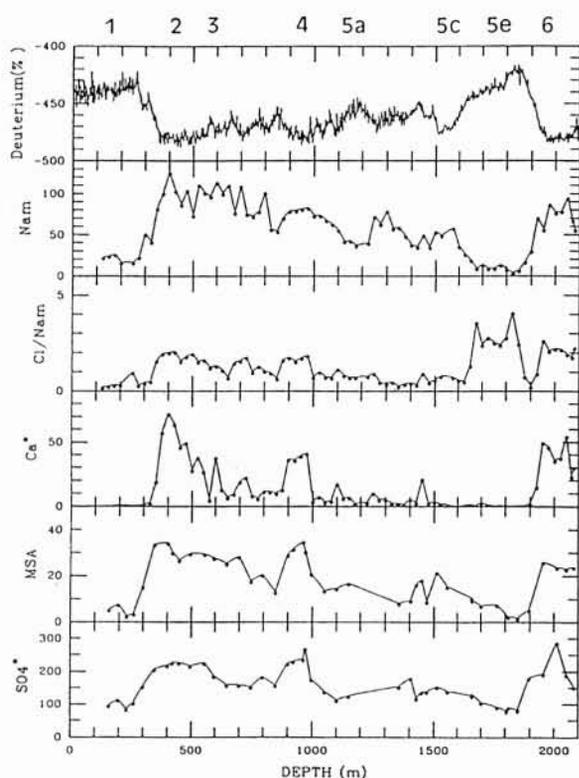
3. Recent evolution of the SO_4 and NO_3^- content of Greenland (Dye 3, [36]) and of Antarctic snow layers (Dome C, [7]). Note the sporadic large increases of the sulphate level which correspond to volcanic eruptions (L : Laki in 1783 ; T : Tambora in 1815 ; A : Mt Agung in 1963).

years (fig. 3). A possible interpretation of such recent variations in terms of atmospheric changes is the denitrification of the lower stratosphere by sedimentation of polar stratospheric clouds [36, 37]. However, such a conclusion must be treated with some cautions. Indeed, it could also be that this species, initially trapped on and/or in snow flakes, is subsequently redistributed in the firn during firnification processes leading to a smoothing of the seasonal signal with depth.

5.2 Atmospheric chemistry changes over the last great climate changes (100,000 years)

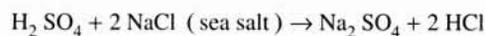
Chemical studies of deep ice cores extracted in Greenland and Antarctic sites are powerful way to investigate the response of our environment to large climatic variations.

The sea salt content of polar ice has been strongly modulated by past, climatic conditions. For instance, the Na_m^+ profile along the Vostok core which spans the last climatic cycle (fig. 4b) shows low values during warm stages and a gradual increase over the Last Glacial Age. The Na_m^+ content of ice corresponding to present day climatic conditions exhibits an accumulation rate effect linked with the dry deposition process [7]. 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 variations, and the remaining variations are representative of anodal atmospheric sea salt concentration changes. Such data therefore suggest that during cold climate, in spite of a large sea ice expansion (up to 1,000 km) which increased



4. Vostok ice core profiles : (a) Deuterium isotope from Jouzel *et al.* (1987), (b) marine sodium, (c) Cl/Na_m weight ratio, (d) excess-calcium from [38], (e) MSA, (f) excess-sulphate from [38]. b, d, e, f are reported in ng - g⁻¹.

the distance from the open ocean to the high antarctic plateau, the sea salt content of the antarctic atmosphere was enhanced reflecting a greater production rate of sea salt due to higher wind speed at the sea surface and/or a more efficient meridional transport between mid and high latitudes. The Cl/Na_m ratio varies widely over the last 160,000 yrs (*fig. 4c*) on both sides of the bulk sea water reference value (1.8) but remains very close to 1.8 under full glacial conditions. It was suggested that the sea salt aerosol can be altered during its transport from oceans towards the high plateau of ice sheets [7]. Indeed, as previously discussed in section 4.1, we identify HCl and Na₂SO₄ in ice deposited under present climatic conditions according to the sea salt reaction :



The absence of sea salt fractionation during very cold stages suggested by Cl/Na_m values close to 1.8 could reflect the high turbulence of the atmosphere which probably limited the efficiency of the preceding reaction.

Greenland and Antarctica ice deposited during cold climate conditions contains much more dust than ice deposited at present time. Such an enhancement of dust content of ice over the last glacial period likely reflects more effective atmospheric transport between source regions and high latitudes as well as the expansion of arid areas and emergence of parts of the continental shelves [39, 40]. As opposed to the marine sodium, dust increases during the last Glacial age are poorly correlated to the climate (cor-

relation coefficient of 0.45 instead of 0.85 for sea salt). Indeed, the Vostok Ca⁺⁺ (a good tracer of dust, [31]) profile (*fig. 4d*) indicates that while calcium contents were strongly enhanced during extremely cold periods (i.e. at 400, 950 and 2000 m depth), they remain relatively low during interstadial conditions. Such a non-linear response of the dust content of ice to the climate suggests that aridity developed in the past when very cold climatic conditions were established.

Simultaneous studies of MSA and sulphate species were first performed along the Vostok core. They show similar trends (*fig. 4e and 4f*) for both sulphate and MSA, with a moderate glacial-interglacial increase suggesting that SO₄^{-*} is mainly derived from DMS marine emissions in Antarctica [38] and that these marine biogenic emissions have been modulated by past climatic conditions.

Such chemical studies of deep polar ice cores indicates that the composition of our atmosphere have been significantly modified in response to past climatic variations. It appears that both primary (sea salt and soil dust) and in a lesser extend secondary (sulphate and MSA) aerosols have increased over glacial periods. Given the potential impact of aerosols in forcing the climate, such data are of importance for climate modelling studies.

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