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Scientific paper

## Linking Antarctic glaciochemical records to past climate conditions

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**Abstract:** Deep Antarctic ice cores document the former states of the climatic system, the atmosphere, and the marine and terrestrial biospheres. However, questions do remain in the interpretation and the reliability of ice core chemical profiles in terms of atmospheric information. Data from the Dome C, Vostok, Dome F, and EPICA deep ice cores are used and compared in the discussions. First of all, the transfer functions of various gaseous and particulate compounds are not entirely understood and in the case of acid gases, strong post-deposition effects are observed at central Antarctic sites. It is emphasised that marine primary and secondary aerosol species may strongly interact during their long-range transport. Continental aerosol is important for the Antarctic impurity budget only in glacial environmental conditions. Its composition, as derived from Antarctic ice core glaciochemistry is discussed. As for the case of marine aerosol, the reaction of primary and gas-derived aerosol has to be considered. Finally, the possible impact of continental dust on marine biogenic activity shortly is discussed in the light of glaciochemical results.

**key words:** central Antarctica, ice cores, chemistry, aerosol, interactions

### 1. Introduction

Antarctic snow encapsulates information about past climate and atmospheric chemistry (Delmas, 1992). Over the last decades, deep Antarctic ice cores have provided unique information about the former states of the climatic system, atmosphere, marine and terrestrial biospheres of a significant part of the world. They made possible the development and test of predictive, multicomponent earth system models within the framework of the known natural variability of several atmospheric key parameters. Observed changes are frequently relevant to the global scale (*e.g.* in the case of greenhouse gases) or only to southern latitudes (*e.g.* for aerosol components). Isotope ratios of the water molecule (H & O isotopes) are excellent proxies for atmospheric temperature. The determination of these ratios by mass spectrometry is relatively fast and easy. Analytical techniques do exist to obtain also reliable data on a wide spectrum of atmospheric chemical species recorded in ice cores. The depth profiles of the trace gases present in the air bubbles entrapped in ice have documented successfully and in detail the greenhouse effect changes over the last ice ages (Raynaud *et al.*, 1993; Petit *et al.*, 1999). On the other hand, the interpretation of the glaciochemical records

(*i.e.* of ice chemistry) in terms of past environmental changes is dragging. Why? First of all because we have to imagine how worked the environmental system (a combination of continental, marine and atmospheric processes) in past climatic conditions. Second, because past atmospheric information reconstructed from glaciochemical records may be biased due to the imperfect knowledge we have of the transfer functions, *i.e.* of the way atmospheric impurities are deposited in the snow and incorporated in the ice. Moreover, the conservation of the chemical records may, in certain cases, be questionable. Once these difficulties are overcome, it may be expected that the information obtained from the water isotope records would be considerably reinforced and enlarged by using adequately glaciochemical archives.

The aim of the following discussion is to contribute to the scope and relevance of the paleodata recovered from deep Antarctic ice cores, in particular in terms of past aerosol composition and atmospheric chemistry.

The following issues will be addressed:

- The understanding of air/snow transfer functions, probably different for the gaseous and particulate compounds, is a pre-requisite for the use of chemical records. Recent studies concerning central Antarctic firn layers have demonstrated that marked post-deposition processes may affect several species like nitrate, methanesulfonate and chloride.
- The nature and origin of the Antarctic aerosol in present and past climatic conditions has to be revisited in the light of recent findings in the field of atmospheric chemistry. The possible modifications of the continental and marine aerosols during their transport to Antarctica will be examined and discussed using the chemical data obtained from the Dome C and EPICA, Vostok, Dome F ice cores which were recovered in different geographical regions of the Antarctic continent.
- Finally, data presently available from these deep ice cores can be of great interest to document the possible link between high dust production and low atmospheric CO<sub>2</sub> concentrations. Do we have any evidence from ice core data that glacial continental aridity gave a boost to marine paleoproductivity?

## 2. About the deposition of atmospheric impurities in Antarctic snow

On the global scale, atmospheric particulate species are deposited according to two major mechanisms: wet and dry deposition. Wet deposition is the fraction scavenged at cloud level or below clouds by falling raindrops or snowflakes. This fraction is generally dominant everywhere. Dry deposition is linked to the deposition of the particles to the ground, independently from water precipitation. A review of these processes in the Antarctic can be found in Davidson (1989). On the central Antarctic plateau, in particular in regions of extremely low snow accumulation rate (thereafter “SAR”), it has been observed that, even though the true deposition processes are far from being fully elucidated, the role of dry deposition is dominant for particulate species. During the ice age, as SAR was about 2–3 times lower than its interglacial value (Petit *et al.*, 1999; Watanabe *et al.*, 1999a), dry deposition was markedly enhanced. The empirically linear relationship linking the concentration ( $C_i$  in ng/g) of a specific compound “*i*” to SAR is generally established in present climatic conditions by measuring  $C_i$  in Antarctic regions of various SAR values and plotting  $C_i$  as a function of SAR. The relationship is also valid for sea salt species and nssSO<sub>4</sub> (De Angelis *et al.*, 1997). The relationship, empirically obtained, has been applied to long-term records in order

to “correct” concentrations obtained in ice and calculate past atmospheric concentration changes of the studied element. A few species, such as  $^{10}\text{Be}$ , are considered as entirely “dry” deposited: measurements indicate that the concentration of this radionuclide in central polar snow is inversely proportional to SAR (Mazaud *et al.*, 1994). In other words, deposition fluxes ( $C_i \times \text{SAR}$ ) of such species are, in principle, approximately constant over the ice sheet, provided its atmospheric source is stable in space and time. Up to now, no theory has been found in support of this observation, but  $^{10}\text{Be}$  concentration is commonly used for estimating past SAR, assuming that  $^{10}\text{Be}$  production rates have been constant over the various climatic conditions (with the exception of particular specific periods of higher productivity (Raisbeck *et al.*, 1987)). In conclusion, in the absence of solid theoretical studies about aerosol deposition mechanisms in these regions, the relationships which are used are only empirical.

The case of gaseous acids (thereafter called “GAS” for gaseous acid species) is still worse. Most atmospheric gases (permanent air constituents), routinely determined in ice cores, are incorporated in the ice at close off level, when firn transforms into ice (Schwander, 1989). Their ice records are generally reliable in terms of past atmospheric composition, except the case of a few compounds which may be generated or may react in situ (*e.g.* CO and CO<sub>2</sub>), a phenomenon which has been observed in Greenland, but never in the Antarctic. On the other hand, the case of gases having an interaction with ice (*e.g.* HNO<sub>3</sub>, HCl, MSA, carboxylic acids... all trace gases of great geochemical interest) deserves special attention.

The deposition mechanism of GAS has been documented recently. On the basis of Antarctic observations, it was concluded that, contrary to aerosol particles, HNO<sub>3</sub> is only wet-deposited (Legrand and Kirchner, 1990). However, this view has to be changed in the light of the discovery of the post deposition phenomena affecting GAS, and in particular HNO<sub>3</sub> (Wolff, 1995). Measurements in snow pits (De Angelis and Legrand, 1995; Röthlisberger *et al.*, 2000) and shallow cores (Wagnon *et al.*, 1999) have demonstrated that deposited GAS may be partly reemitted to the atmosphere (see below), indicating that nitrate records in shallow snow layers are uncertain and unreliable, in particular in central regions where SAR is very low. In addition to these physical-chemical processes, the recent discovery of alkyl nitrates in Antarctic snow (Jones *et al.*, 1999) is adding to the confusion, since these compounds probably decompose into nitrate later. Additional phenomena have been detected in the Arctic regarding the role of the upper snow layers in polar atmospheric chemistry and in the air/snow exchanges (Honrath *et al.*, 1999).

Initial GAS concentrations in the snow are strongly reworked during snow metamorphism processes, which affect snow crystals soon after their deposition (Davis *et al.*, 1996). Due to multiple evaporation/condensation cycles, crystal size grows rapidly in the first upper meters, slower below. Lower than about ten meters, ice grain sintering takes over. During snow metamorphism, gases present in the crystals either as dissolved, entrapped or adsorbed species, are released to the gaseous phase. As long as communication of interstitial air with the free atmosphere is relatively easy (until about 10 m depth), excess GAS amounts may leave the firn and return to the free atmosphere. Then some gases, *e.g.* HNO<sub>3</sub> or HCl, may be lost for the ice (see Delmas *et al.*, 2003, for the case of MSA). When metamorphism occurs below 10 m depth, released GAS could accumulate in the interstitial air and be entrapped again in the air bubbles at pore close off, *i.e.* together with the other common, non-interactive, gases. All these processes are still unclear, but may be suspected to occur. Preliminary observations have to be confirmed.

Such effects depend strongly on snow accumulation rate (SAR). They are particularly well marked when  $SAR < 5 \text{ g/cm}^2/\text{a}$ , *i.e.* at sites like Dome F, Dome C or Vostok. As SAR decreases by at least a factor 2 during LGM, it can be speculated that  $\text{HNO}_3$ , HCl and MSA concentrations are strongly reduced in the firn during that periods. Finally, another process has to be considered for that species: ice acidity. From the impact of volcanic eruptions on GAS profiles (Legrand and Kirchner, 1990; Wagon *et al.*, 1999), it can be deduced that ice acidity could modulate the amount of GAS adsorbed/co-condensated on ice crystals in the firn layers. It has been demonstrated that HF is also strongly displaced in ice by volcanic acidity (De Angelis and Legrand, 1994). Little is known about this effect, but it should be evaluated in the future. Similarly, the possible reaction, in the solid phase, of acid gases with alkaline dust particles has to be investigated.

In addition to  $\text{HNO}_3$ , HCl and MSA, it can be expected that other minor trace gases such as carboxylic acids, formaldehyde, hydrogen peroxide, etc. behave similarly in Antarctic firn layers. However, recent studies including field and laboratory measurements as well as model calculation have considerably improved our understanding of the cases of formaldehyde, and hydrogen peroxide in upper firn layers (Anklin and Bales, 1997; Hutterli *et al.*, 1999; Burkhart *et al.*, 2002).

In conclusion, the deposition processes of aerosol and GAS in Antarctica are now relatively well documented, but the cases of the important species HCl,  $\text{HNO}_3$  and MSA would still deserve further investigation and modelling.

### **3. Major components of the aerosol deposited in Antarctic snow and their interactions**

#### *3.1. Introduction*

The relative amounts of primary and secondary aerosol have been very variable in the past. The amount of continental dust (in particular insoluble microparticles), which is very low in present climatic conditions, was considerably high during ice ages. On the other hand, its composition has been relatively stable over times (Delmas and Petit, 1994). Secondary aerosol (mostly sulfur compounds) is presently the dominating fraction of the deposited impurities. For glacial conditions, ice core data from most deep ice cores reveal that the composition of the Antarctic aerosol changed dramatically, in relation with environmental changes (Petit *et al.*, 1981; Thompson and Mosley-Thompson, 1981; De Angelis *et al.*, 1987). The input of primary aerosol was overwhelming at that time, whereas secondary aerosol increased also, but to a lesser extent (Legrand *et al.*, 1988a).

#### *3.2. Production and transport of marine compounds*

Antarctica is a continent surrounded by vast oceans where winds are blowing violently all over the year. It is understandable that the amount of marine aerosol produced in these regions is considerable. However, due to the prevalent circumpolar atmospheric circulation and the occurrence of frequent katabatic winds over coastal regions, the transport of marine aerosol to central Antarctic regions is limited, only sporadic and strongly seasonal. The penetration of marine air masses inland is much more frequent in winter than in summer, due to the anticyclonic conditions prevailing during summer months over the Antarctic continent. Moreover, it has been shown that storms are infrequent on the central plateau and sea-salt

(and related species) deposition occurs by a small number of short duration events. Several sea-salt related species are commonly determined in the ice: sodium, magnesium, chloride, etc. These elements may be used as tracers of the marine contribution.

Finally, the ocean is a source of various gaseous species which transform in the atmosphere into secondary aerosol particles. The most important one is DMS (dimethylsulfide), which is produced in the ocean by biogenic activity. Being poorly soluble in sea water, DMS evolves to the atmosphere, where it oxidizes mainly into sulfuric and methanesulfonic acids. These two last compounds are both commonly determined in Antarctic precipitation.

### 3.3. *Sea salt deposits in the Antarctic*

Over the ocean and the continents, the concentration of marine aerosol strongly decreases with altitude. In the Antarctic, this effect is probably also occurring, but blurred by the fact that the elevation and the distance to the sea are closely related, at least for the first hundred km. On the upper Antarctic plateau where elevation is generally higher than 2500 m, sea-salt concentration in the air masses is therefore generally very low, except during limited time periods (see below). Sodium concentrations at Dome C and Dome F, both locations located about 800 km from the coast, are  $0.9 \pm 0.3$  and  $1.34 \pm 0.71$   $\mu\text{m/l}$ , respectively (mean values for the upper 200 m firn layers). Despite the difference of SAR at the sites (3.4 and 2.7, respectively), these figures suggest a relatively higher marine influence at Dome F than Dome C, at least during the second half of the Holocene.

Sea-salt concentration in central Antarctic snow is rather paradoxical: they are highest in winter, just when the distance to the open water is maximum (Wagenbach *et al.*, 1998a). However, the meteorological events that transport sea salt inland are more frequent in winter than in summer, as already mentioned. This can explain why the distance to the open water has, after all, little influence on the concentration of sea salt in central Antarctic precipitation.

During the ice age, sodium measurements in ice cores reveal that sea salt concentration was markedly higher than in interglacial conditions (De Angelis *et al.*, 1987). A LGM/Holocene ratio of about 4–5 for central Antarctic sites (LGM=Last Glacial Maximum) is found. About half of this effect is due to the change of snow accumulation rate. The explanation put forward to this observation is that sea salt aerosol production was higher than now due to stronger winds and that meridian transport was enhanced. However, model calculation fail to describe correctly the observed concentration changes (Genthon, 1992).

### 3.4. *Sulfur species*

Two major sources of S-compounds are responsible for the sulfate aerosol encountered in remote oceanic areas: particulate sea salt production by bubble bursting and marine gaseous emissions of biological dimethylsulfide (DMS).

Sulfate and sodium in bulk sea water are in the weight ratio 1:4. This ratio, which is stable all over the world, is commonly used to estimate in aerosol the fraction of sulfate originating from sea salt. Chloride has also been used as the marine reference element, but sodium is recommended due to the loss of HCl that frequently affects sea salt aerosol during its atmospheric transport, in particular to central Antarctic regions (see below). In any case, in central Antarctic regions, the concentration of sea salt sulfate is very low in comparison to gas-derived sulfate (also called non-sea-salt- or nss-sulfate).

Nss-sulfate is an important component of atmospheric aerosol—and consequently also

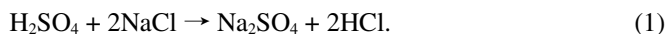
of ice core impurities—, since, in the form of H<sub>2</sub>SO<sub>4</sub> aerosol, it can affect global climate in various ways (see *e.g.* Watson and Liss, 1998). On the global scale and in pre-industrial conditions, DMS is the major source of fine sulfate aerosol. However, H<sub>2</sub>SO<sub>4</sub> may also have sporadically a volcanic origin (see below), so that sulfate concentration changes in Antarctic snow are not only linked to DMS emissions, *i.e.* to marine biogenic activity changes.

Methanesulfonate ion, either in the form of methanesulfonic acid (HCH<sub>3</sub>SO<sub>3</sub> or MSA) or as a salt, is the other major S-containing species originating from DMS oxidation (Yin *et al.*, 1990). It is present in the marine aerosol in relatively small amounts along with nss-SO<sub>4</sub>. MSA, exclusively derived from DMS and therefore considered as a unique tracer of marine biogenic activity, is of particular importance in glaciochemical studies. At low and mid-latitudes, the ratio MSA/nssSO<sub>4</sub> is less than 0.1, but it has been found that at sub-Antarctic latitudes it can reach values >1 (Koga *et al.*, 1991; Bates *et al.*, 1992). However, in central Antarctic snow, measurements show that SO<sub>4</sub> concentrations are generally 10 times higher than the ones of MSA (Legrand *et al.*, 1992). This observation, specific for areas of extremely low snow accumulation rates, can have an atmospheric origin, but it is more likely explained by the loss of MSA observed in firn due to post-deposition phenomena, as earlier mentioned.

It has been proposed above that during the ice age the transport of sea-salt aerosol was strongly enhanced due to a greater number of storms penetrating the central Antarctic troposphere in summer. It can be deduced that these inputs of marine air masses in summer brought along with them DMS-derived sulfur species (excess-sulfate and MSA) which are commonly present in the summer troposphere. Moreover, the depth profiles of Na, nssSO<sub>4</sub> and MSA look similar, except for some limited periods where MSA diverges from the other two species.

### 3.5. Interaction between sea salt aerosol and the sulfur cycle

Acid and alkaline gaseous and particulate substances present in the marine atmosphere interact strongly. Sea salt aerosol undergoes rapid chemical transformations involving the scavenging and loss of gases, and aqueous phase reactions, as described by various authors (*e.g.* Sievering *et al.*, 1992; Chameides and Stelson 1992; O'Dowd *et al.*, 1997). Consequently, it can be assumed that maritime air masses transported over long distances do not contain sea salt and acid nssSO<sub>4</sub> aerosol when reaching central Antarctica, but an intimate mixture of chemical compounds resulting from the acid/base reactions earlier mentioned, in particular in summer when biogenic sulfate concentration is high. Schematically, the most important reaction is the following:



The interaction has been demonstrated for the Antarctic by a number of aerosol studies (Wouters *et al.*, 1990; McInnes *et al.*, 1994; Mouri *et al.*, 1996; Kerminen *et al.*, 2000). Instead of H<sub>2</sub>SO<sub>4</sub>, other acid species (HNO<sub>3</sub>, HCl, MSA, organic acids...) can also interact with sea salt. In present climatic conditions, the interaction should be weak in winter, just when sea-salt aerosol transport to central Antarctic regions is peaking, due to the low H<sub>2</sub>SO<sub>4</sub> content of the sub-polar troposphere in that season (Legrand and Pasteur, 1998).

On the high central Antarctic Plateau, the observation of fractionated sea salt aerosol is common in summer. The phenomenon has been demonstrated by glaciochemical measure-

ments at the South Pole (Delmas *et al.*, 1982; Legrand and Delmas, 1984) as at several other sites (Legrand and Delmas, 1988). The ratio  $R=Cl/Na$  is commonly used to estimate the fractionation of sea salt aerosol caused by reaction (1). The reference value  $R_0$  of  $R$  in bulk seawater is 1.8 (weight ratio) and 1.17 (molar ratio).  $R$  exhibits a complex pattern for the Holocene at Dome C, with periods where  $R>R_0$ , others where  $R<R_0$  (Legrand and Delmas, 1988; De Angelis *et al.*, 1997). During the LGM, the observed fractionation is very small (De Angelis *et al.*, 1987; Legrand *et al.*, 1988a), as nowadays in winter conditions. At Dome F, the fractionation effect is less marked for the Holocene, may be due to the shorter trajectories of the air masses to Dome F in comparison to Dome C or Vostok, but nevertheless present (Fig. 1) (Watanabe *et al.*, 1999a). This diagram shows also that the lowest sea salt concentration is, the highest is the fractionation. The absence of sea salt fractionation in glacial conditions could be explained by the re-scavenging of gaseous HCl by alkaline marine aerosol, which was present in large excess in the sub-Antarctic atmosphere at that time. It can be assumed also that not enough  $H_2SO_4$  was available in glacial conditions to neutralize the large amounts of alkaline primary aerosol species (sea salt and continental dust) transported by the atmosphere of that time.

Reaction (1) has also consequences on the sulfur aerosol constituents. It may be assumed that the interaction of sea salt with atmospheric acids was probably very important for glacial periods, when high amounts of sea salt were transported to the polar high latitudes, in summer as in winter. Moreover, the distance from the open ocean to the ice sheet was considerably enhanced, which increased the contact time between the sulfur species ( $H_2SO_4$  and MSA) and sea salt aerosol. The excellent correlation ( $r^2=0.72$ ) found when plotting MSA as a function of Na suggests that MSA was transported along with sea salt particles (Fig. 2, based on Vostok data from Legrand *et al.*, 1991). Such a correlation is not observed for the Holocene. Moreover, MSA and  $nssSO_4$  concentrations themselves are also correlated (Fig. 3), suggesting that, at this time, both species were associated in the air and deposited together in the Antarctic. This observation could be due to the scavenging of MSA and  $nssSO_4$  fine

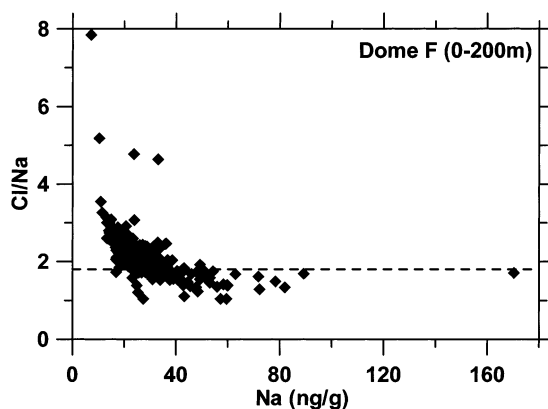


Fig. 1. Dome F sodium and chloride data for the late Holocene showing the fractionation of sea salt aerosol. The  $Cl/Na$  weight ratio plotted as a function of the amount of sea salt (Na is used as the reference element for sea salt) indicates that the fractionation of sea salt is higher for low sea salt concentrations. The stippled line indicates the  $Cl/Na$  weight ratio in bulk seawater (1.8).

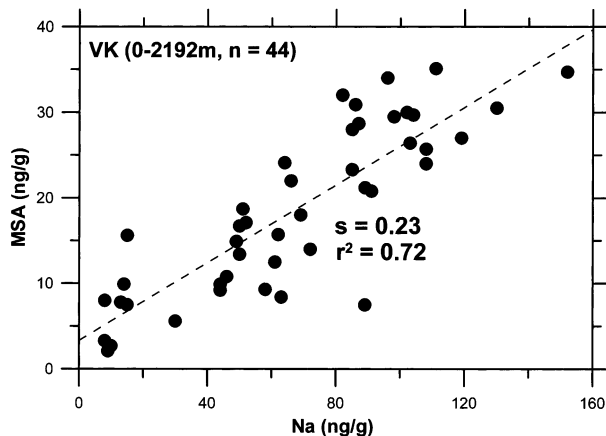


Fig. 2. Correlation linking Na and MSA concentrations (in ng/g) in the Vostok ice core (data from Legrand *et al.*, 1988a, 1991).

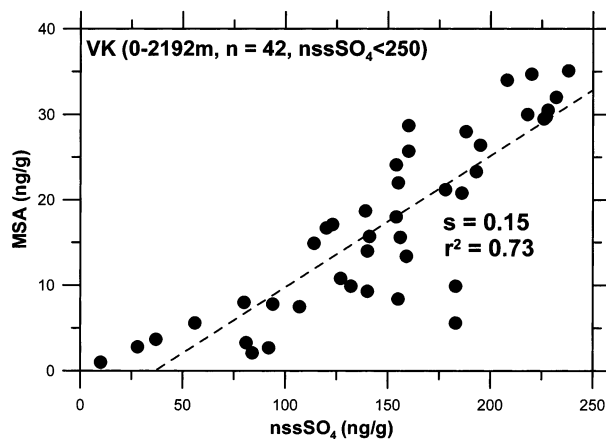


Fig. 3. Correlation linking nssSO<sub>4</sub> and MSA concentrations in the Vostok ice core (data from Legrand *et al.*, 1991). High nssSO<sub>4</sub> levels (nssSO<sub>4</sub> > 250 ng/g) of volcanic origin are not included.

aerosol (or gas) by sea salt particles. The slope (0.15) of the straight line shown in Fig. 3 could represent the atmospheric ratio MSA/nssSO<sub>4</sub> in the mid-latitude source regions where the two species were produced in ice age conditions. The value is in agreement with the present ratio at these latitudes (Bates *et al.*, 1992). Note that the correlations obtained in Figs. 2 and 3 for ion concentrations are free from any influence of accumulation rate changes.

### 3.6. Crustal material

In present climatic conditions, the amount of continental material (in particular insoluble microparticles) reaching Antarctica is much lower than the marine aerosol contribution. It is composed of soil dust particles (crustal dust) lifted by winds from arid regions located for a few cases in Antarctica but mostly in surrounding continents (mainly South America,



less frequently Australia and South Africa). The insoluble part of the dust deposited in the snow is commonly estimated by microparticle counting. Aluminum, generally measured by atomic absorption, was used in the past as the reference element for calculating this fraction. It has been shown that soluble calcium (as determined by ion chromatography) may be used instead, once corrected for its sea-salt fraction (De Angelis *et al.*, 1987; Legrand *et al.*, 1988a).

At Dome C, the following empirical relationship has been found for glacial extrema:

$$\text{Ca} = 0.469 \text{ Al} + 1.08. \quad (2)$$

As, in most recent glaciochemical studies, calcium is, for practical reasons, more frequently determined than aluminium, it is common to calculate and discuss continental dust using Ca as a tracer. However, it is important to stress that the Al/Ca ratio varies from one Antarctic region to another and may have different values in glacial and interglacial conditions (De Angelis *et al.*, 1992).

The geographical origin of dust may be determined by various methods, *e.g.* particle identification by scanning electron microscopy (Gaudichet *et al.*, 1986), isotope ratio measurements (Basile *et al.*, 1997), etc.

Ice core studies have revealed the dustiness of the ice age atmosphere. Dome C and Vostok microparticle, aluminum and calcium measurements have shown that the LGM flux of dust was 10 to 20 times greater than that of the Holocene (Petit *et al.*, 1981, 1990; De Angelis *et al.*, 1984). Most recent measurements lead to still higher figures, due to a more accurate determination of Holocene concentrations (Table 1, from Delmonte *et al.*, 2002b). Dome F measurements confirm this observation (Watanabe *et al.*, 1999a). Calcium concentrations are rather similar for the LGM in Dome F (mean value in the range 1–2  $\mu\text{m/l}$ ) and Vostok ice (1.25  $\mu\text{m/l}$ ). These Antarctic findings can be explained by the environmental conditions prevailing during the LGM in the southern part of South America: the important extension of the Patagonian desert towards Falkland Islands caused by sea-level lowering, an intensification of the westerlies, an increased aridity, a less efficient scavenging of dust from a drier atmosphere and, to a lesser extent probably (Lunt and Valdes, 2001), by an increase of the meridional transport (Delmonte *et al.*, 2002b).

Continental aerosol does not contain only soil dust, but also various compounds produced in continental regions, in particular by or from plants (ammonium, nitrate, soot, organic compounds...), and transported to Antarctica along with dust. Of course, in interglacial climatic conditions, this component of the Antarctic aerosol system is very low. For instance, biomass burning products are hard to detect in present Antarctic aerosol (Wolff and

Table 1. Comparison of dust concentrations ( $\text{ng g}^{-1}$ ) in central Antarctic ice in glacial and interglacial climatic conditions (from Delmonte *et al.*, 2002a). Mean Holocene values of accumulation rate ( $\text{g cm}^{-2} \text{ a}^{-1}$ ) at study sites are given in brackets. Note that Dome C and EPICA drilling sites, both located on the same dome, but 75 km apart, have different accumulation rates (3.4 and 2.7  $\text{g cm}^{-2} \text{ a}^{-1}$ , respectively).

	Average dust Holocene	Average dust LGM	LGM/Holocene ratio
Dome C (3.4)	23	640	28
EPICA (2.7)	15	790	53
Vostok (2.2)	35	849	24
Dome B (3.8)	25	875	35

Cachier, 1998) and Holocene ice (Chylek *et al.*, 1992). No information is presently available for ice age conditions.

### 3.7. Nitrogen compounds (nitric acid, particulate nitrate and ammonium)

Nitrate (either in the form of nitric acid or of a salt) is the most important nitrogen species (except molecular nitrogen  $N_2$ ) determined in Antarctic snow. In present climatic conditions, nitrate is mostly deposited as gaseous nitric acid ( $HNO_3$ ) (Legrand and Delmas, 1986), but recent measurements show that organic nitrate may also be present (Jones *et al.*, 1999). In glacial periods, glaciochemical data demonstrate that particulate nitrate salt was dominant (Legrand *et al.*, 1988a; Röthlisberger *et al.*, 2000, 2002).

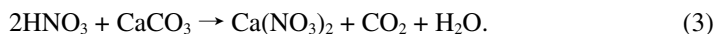
As earlier mentioned in chapter 2, deposition mechanisms of the  $HNO_3$  “GAS” are unknown and serious post-depositional effects have been observed in the upper snow and firn layers. The origin itself of nitrate in the Antarctic atmosphere is far from being understood. We can envisage a tropospheric or a stratospheric origin and nitrate may be formed locally or long-range transported. N-isotope studies, although strong effects have been found, did not allow to unravel these multiple issues due to a strong postdeposition effect (Freyer *et al.*, 1996; Wagenbach *et al.*, 1998b).

Globally, atmospheric nitrate originates essentially from a pool of several reactive gases called  $NO_x$  (see *e.g.* Bradshaw *et al.*, 2000). It is most common in the free troposphere over continents. In pre-industrial conditions, sources of atmospheric nitrate are various (Table 2, derived from Bradshaw *et al.*, 2000).  $NO_x$  gases are emitted at low elevation by soils, biomass burning and lightning or in the free troposphere by lightning, ammonia oxidation and stratospheric inputs. On the global scale, lightning, biomass burning and soil emissions are clearly dominant, but the Antarctic is a region remote from continents.  $HNO_3$  could also be partly in the form of trapped  $HNO_3$  having settled from the polar stratosphere as type II PSC (Polar Stratospheric Clouds) large sized particles (Van Allen *et al.*, 1995). In this case,  $HNO_3$  remaining in the firn below 4 m depth could possibly be linked to this stratospheric contribution. More work has to be done to lend some support to this proposal. What are therefore the most plausible origins of Antarctic snow  $NO_3$ ? Since about 15 years, the question remains open (Legrand and Delmas, 1986; Legrand and Kirchner, 1990; Jones *et al.*, 1999; Watanabe *et al.*, 1999b). Due to the remoteness of Antarctica from most continental areas, biomass burning has been considered for long as a minor contributor to Antarctic nitrate. Organic compounds linked with biomass burning have been detected in the Peninsula area (Wolff and Cachier, 1998), but no data is available for central regions. Recent studies have shown that

Table 2. Natural sources of tropospheric  $NO_x$  in Teragrams of N per year (figures recommended by Bradshaw *et al.*, 2000).

Natural sources	Tg N/yr
Stratosphere	0.12 (0.08–1)
Lightning (free troposphere)	4 (2–16)
$NH_3$ oxidation	0.6 (0.3–3)
Biomass burning (present)	8.5 (4–16)
Soils (biogenic)	5.5 (3–8)
Lightning (ground level)	2.5 (1.2–10)
Oceans	0.5 (<1)
Total (natural)	21.72

continental air masses may easily reach Antarctica and modulate the input of continental trace species to the Antarctic atmosphere and ice sheet (Lunt and Valdes, 2001). The lifetime of nitric acid in the mid-latitude continental troposphere is relatively short. When alkaline dust is also present, nitrate salt is formed according to reaction (3) and the lifetime of nitrate is considerably increased, making possible its transport over the subantarctic ocean from South America, Australia, Africa to the Antarctic.



This phenomenon has been observed in Africa and Asia where desert dust, lifted to high altitudes, is able to react with  $\text{HNO}_3$  (Dentener *et al.*, 1996; Hara *et al.*, 1999; Song and Carmichael, 2001). It could be taken into account to explain the high nitrate concentrations observed in Antarctic ice for glacial periods. Ice core studies show that continental dust transport -as demonstrated by calcium or aluminium measurements- was strongly enhanced (up to 30 times) during ice ages. Nitrate concentration is also very high during these periods, suggesting the transport of  $\text{Ca}(\text{NO}_3)_2$  or  $\text{CaHNO}_3$  along with continental dust (Fig. 4). The slope (2.7) of the linear relationship is close to the stoichiometric ratio of neutral nitrate. Röthlisberger *et al.* (2000) found a similar figure for the new Dome C ice core. Legrand *et al.* (1999) pointed out a similar relationship over the last two climatic cycles at Vostok, but with a lower slope. Therefore, as reaction (1) is the key reaction for the marine atmosphere, reaction (3) is typical of continental regions.

In conclusion, it may be assumed that, in glacial climatic conditions, the air masses leaving the south American continent toward south contained probably calcium nitrate, *i.e.* a buffered aerosol, of low acidity and alkalinity.

Finally, ammonium concentrations in central Antarctic ice cores are in the range 1–3 ng/g (Legrand and Delmas, 1988), with higher concentrations for ice-age than for interglacial ice. A figure of 3 is found in the Vostok core (Petit *et al.*, 1999) for this ratio. In principle, except for coastal locations, ammonium is linked to continental biogenic activity (soil emissions and biomass burning, (Fuhrer *et al.*, 1996)), but data presently available for Antarctica are unconvincing, partly because of analytical uncertainties, particularly high for interglacial

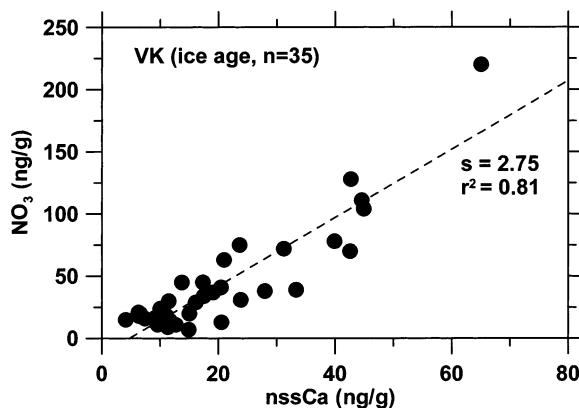


Fig. 4. Correlation linking nitrate concentration (ng/g) to continental dust (reference element nssCa, in ng/g) in the glacial part of the Vostok ice core (data from Legrand *et al.*, 1988a).

concentration levels (Legrand *et al.*, 1999).

#### 4. About the possible link between continental dust and marine paleoproductivity

A link has been proposed between continental dust and the composition of the marine atmosphere. Martin (1990) hypothesized that dust-derived iron supply to the ocean could fertilize the ocean and enhance the marine biological pump of CO<sub>2</sub>. The hypothesis was tested *in situ*, e.g. in the modern South Pacific ocean (Behrenfeld and Kolber, 1999). Encouraging results were also obtained for the last two deglaciations from marine sediment cores (Ikehara *et al.*, 2000). One of the frequently asked questions to glaciologists is: do your Antarctic ice-core data support Martin's hypothesis that the enhanced dust inputs to the subAntarctic ocean during ice ages stimulated regional marine productivity? Deep Antarctic ice cores contain, in principle, relevant information to document the issue. It has been shown that ice core data indicate a very significant increase of the atmospheric content of continental dust (therefore of iron) during glacial periods. Moreover, ice age aerosol contained more nitrate, another nutrient of phytoplanktonic activity. Ice core data indicate also much higher concentrations of sulfate and MSA in ice age conditions. Some authors (Legrand *et al.*, 1988b, 1991) proposed therefore that there is a link between dust inputs to the ocean and marine biogenic activity. However, the high sulfate and MSA concentrations observed for ice age conditions may have other causes (the interaction of sea salt with the sulfur cycle, as earlier explained, see Section 3) leading to the conclusion that this link is not yet demonstrated. Present ice-core data are encouraging, but nevertheless still inconclusive, and more work has to be done about this important question.

#### 5. Conclusions

In LGM climatic conditions, the production and transport of both continental and marine air masses to Antarctica was strongly enhanced in comparison to the present-day situation. Continental deposits in Antarctic ice were higher in relation with the larger area of source regions and stronger winds, and secondarily with the enhancement of the meridian transport. For marine aerosol species (sea salt and sulfur species) the increase could mainly be due to the fact that their transport in summer months was as high as in winter, in relation with permanence of a wide-spread sea-ice cover all over the year during the LGM.

The role of dry deposition in the concentration increase of most aerosol species was probably high for glacial periods, but it can be estimated.

Recent studies carried out at various latitudes have demonstrated that gaseous acid species may interact strongly with airborne alkaline particles. The interaction of sea salt with the sulfur cycle is typical of the marine atmosphere. On the other hand, the interaction of dust (in particular carbonates) with the nitrogen cycle may be considered as typical of the continental atmosphere. An interaction of continental aerosol with sea-salt aerosol is also probable on the way between source regions and the Antarctic ice sheet. All these interactions have to be considered when studying the chemical composition of the impurities determined in Antarctic ice cores, in particular in glacial environmental conditions when primary aerosol species were present in significant amounts in the Antarctic atmosphere and dominated snow chemistry. Experiments have to be carried out to determine the chemical composition of the

individual particles entrapped in the ice lattice and to demonstrate that the atmospheric interactions earlier mentioned did occur in the past between primary and secondary aerosol species. These processes have to be introduced in the models used for simulating S and N biogeochemical cycles in the Antarctic atmosphere, in particular for past climatic conditions. The loss of the gaseous acid species pointed out in central Antarctic firn layers has now to be quantified both by *in situ* measurements and modelling. This could give a boost to the studies of the deep ice cores currently extracted at various Antarctic sites and lead to the understanding of pending issues of great interest for climatologists, such as the possible increase of marine biogenic activity in glacial climatic conditions, a question presently not supported by glaciochemical data obtained from Antarctic ice cores.

Finally, it is strongly recommended to couple ice core analyses with atmospheric chemistry and air-snow studies at deep drilling site, in order to document locally 1) the composition of atmospheric gaseous and particulate species deposited to the snow, 2) the way these species are recorded in the ice at extremely low accumulation sites. Such studies carried out recently in central Greenland and Antarctic regions have already given encouraging results.

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