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where 0.29 is the Na/Al weight ratio in the mean crust (Taylor 1964).

The satisfactory balance of the measured ion concentrations was checked for each sample according to relationship (1). Moreover, the contribution of  $\text{NH}_4^+$ , found to be negligible, was omitted from the calculations. The term excess X (written  $\text{X}^*$  throughout) is commonly employed in the literature on aerosol and precipitation chemistry to designate the non-sea-salt fraction of a compound or ion X. Therefore  $\text{X}^*$  originates from continental dust and/or gas-derived species. A more detailed discussion of this ice chemistry can be found elsewhere (Legrand 1987, Legrand and others, in press).

The Holocene and LGM cases have to be treated separately.

For the Holocene period, Al concentrations are always low (mean value  $2.7 \text{ ng g}^{-1}$ , Table I), showing that terrestrial dust inputs represent 20% of a bulk deposition and a negligible (<3%) fraction of the bulk-soluble deposition (by weight).

An ion balance may be written for the excess fraction of Cl and  $\text{SO}_4$  for the Holocene period:

$$[\text{H}^+] = [\text{SO}_4^{2-}]^* + [\text{NO}_3^-] + [\text{Cl}^-]^* \quad (3)$$

(Nitrate has no significant marine contribution.)

For the Holocene and for Dome C only, two stages may be distinguished according to the values of the Cl/ $\text{Na}_m$  weight ratio (R), which can be either lower or higher than its reference value 1.8 in bulk sea-water.

For the period P1 (corresponding to 0–215 m depth) R is lower than 1.8. For P2 (215–360 m depth) R is higher than 1.8. The chemical process leading to this effect (the reaction of  $\text{H}_2\text{SO}_4$  on sea-salt particles) has been discussed in detail in another paper (Legrand and Delmas, in press).

In brief, for P1,  $[\text{Cl}^-]^*$  is negative, which suggests that some HCl must have escaped from the sea-salt particles. In this way, the precipitation contains only two mineral acids,  $\text{H}_2\text{SO}_4$  and  $\text{HNO}_3$ . It can be demonstrated that excess sulfate may be divided into two fractions. The first is sulfuric acid:

$$[\text{H}_2\text{SO}_4] = [\text{SO}_4^{2-}]^* + [\text{Cl}^-]^* = [\text{SO}_4^{2-}] + [\text{Cl}^-] - 1.29 [\text{Na}^+_m] \quad (4)$$

The second is combined with sodium as an excess of  $\text{Na}_2\text{SO}_4$ :

$$[\text{Na}_2\text{SO}_4] = -[\text{Cl}^-]^* = 1.17 [\text{Na}^+_m] - [\text{Cl}^-] \quad (5)$$

1.17 is the Cl/Na equivalent ratio in bulk sea-water. 1.29 is the sum (1.17 + 0.12), where 0.12 is the  $\text{SO}_4/\text{Na}$  equivalent ratio in bulk sea-water.

For P2 ( $R > 1.8$ ), three mineral acids ( $\text{H}_2\text{SO}_4$ ,  $\text{HNO}_3$  and HCl) are present in the precipitation. In this case  $[\text{H}_2\text{SO}_4]$  is equal to  $[\text{SO}_4^{2-}]^*$ :

$$[\text{H}_2\text{SO}_4] = [\text{SO}_4^{2-}] - 0.12 [\text{Na}^+_m] \quad (6)$$

and [HCl] may be calculated according to (7):

$$[\text{HCl}] = [\text{Cl}^-] - 1.17 [\text{Na}^+_m] \quad (7)$$

For the LGM, the mean value of Al concentrations ( $74 \text{ ng g}^{-1}$ ) indicates that the fraction of soluble elements linked to the terrestrial dust input cannot in this case be neglected in the calculations, i.e. excess  $\text{Mg}^{2+}$  and  $\text{Ca}^{2+}$ . Moreover, the Cl/Na weight ratio R remains close to its reference value (1.8), showing that no fractionation of sea salt occurred at this time ( $[\text{Cl}^-]^*$  equals zero).

With reference to Table I,  $\text{K}^*$  can be neglected and if we subtract the sea-salt contribution on both sides of Equation 1, we obtain:

$$[\text{H}^+] + [\text{Ca}^{2+}]^* + [\text{Mg}^{2+}]^* = [\text{NO}_3^-] + [\text{SO}_4^{2-}]^* \quad (8)$$

The overall chemistry of the ice impurities is highly intricate, mainly due to this important terrestrial contribution (see section 3.1).

However, relationships (1), (2) and (6) are still valid and have been used to calculate the various fractions reported in Tables I and II.

### 3. RESULTS AND DISCUSSION

We shall examine the impact of the climatic change successively on the three major contributions to impurity deposits in Antarctic snow. The depth profiles discussed are shown in Figure 1 (Dome C ice core).

#### 3.1. Terrestrial material

At Dome C, the Al concentrations found in our samples (Table I) clearly confirm the findings of others of a great contrast between LGM and Holocene aerosol

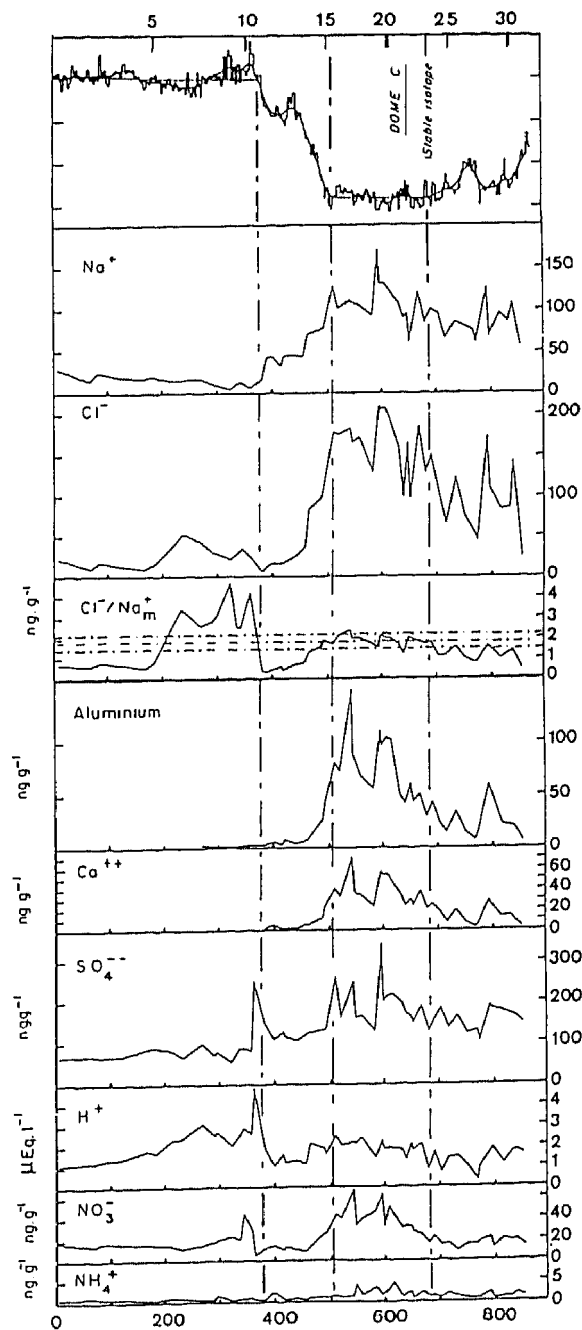


Fig.1. Depth (in m of ice) variations of  $\delta^{18}\text{O}$  (‰),  $\text{Na}^+$ ,  $\text{Cl}^-$ ,  $\text{Cl}^-/\text{Na}_m^+$ , Al,  $\text{Ca}^{2+}$ ,  $\text{SO}_4^{2-}$ ,  $\text{H}^+$ ,  $\text{NO}_3^-$  and  $\text{NH}_4^+$  in the Dome C ice core. Dashed lines on the  $\text{Cl}^-/\text{Na}_m^+$  profile refer to the bulk sea-water reference ratio (in weight). Vertical dashed lines define the Holocene and LGM stages. The scale at the top of the isotopic profile refers to years B.P. chronology and is taken from Lorius and others (1979).

## SOLUBLE IMPURITIES IN FOUR ANTARCTIC ICE CORES OVER THE LAST 30 000 YEARS

by

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### ABSTRACT

The chemical composition of soluble impurities along the Dome C ice core covering approximately the last 30 000 years is reported and interpreted in terms of atmospheric contributions. Terrestrial and sea-salt inputs are known to have been much higher during the Last Glacial Maximum (LGM) than during the Holocene period. For this reason, the gas-derived compounds (mainly  $H_2SO_4$  and  $HNO_3$ ) which dominate the chemistry of present-day snow are minor components in LGM snow. The exact calculation of each of the various contributions has been made possible by the determination of all major ions ( $H^+$ ,  $Na^+$ ,  $K^+$ ,  $NH_4^+$ ,  $Mg^{2+}$ ,  $Ca^{2+}$ ,  $NO_3^-$ ,  $SO_4^{2-}$  and  $Cl^-$ ) in the samples. Three additional deep ice cores from other Antarctic areas have also been analyzed, but in a less comprehensive manner than the Dome C core. The differences observed at the four study sites increase the general understanding of the past atmospheric chemistry of the Southern Hemisphere.

### 1. INTRODUCTION

The chemical analysis of deep ice cores is invaluable in reconstructing paleo-environments. The interpretation of the data obtained is, however, complex, because several factors (source intensity, transport or deposition phenomena, atmospheric transformations) can influence the chemical composition of snow. We shall examine the chemical changes in Antarctic precipitation on a 30 000 year time-scale.

The background Antarctic aerosol has three main sources: continental dust, sea salt (both forming the primary aerosol fraction) and gas-derived particles (secondary aerosol). The relative importance of each of these sources depends strongly on climatic conditions.

Recent studies of present-day central Antarctic aerosol have demonstrated that gas-derived sulfuric aerosol is largely dominant, continental and marine inputs being relatively modest (Shaw 1980 and 1982, Cunningham and Zoller 1981). The chemical composition of snow reflects this trend, but another mineral acid,  $HNO_3$ , which is mainly present in the Antarctic atmosphere as a trace gas, is also found in significant amounts in the precipitation (Legrand and Delmas 1986).  $HCl$ , another gaseous trace compound, has also been detected in central Antarctic snow (Legrand and Delmas 1984, Legrand and Delmas, in press).

This schematic description is valid for the entire Holocene period (approximately the last 10 000 years) (Legrand 1985). On the other hand, the ratio between primary and secondary aerosol contributions was significantly different during the last ice age, in particular at its end — the Last Glacial Maximum (LGM). Cragin and others (1977), Petit and others (1981) and De Angelis and others (1987) have shown that the deposition of marine aerosol and, above all, of continental dust strongly increased during the LGM, in response to enhanced poleward transport, the expansion of desert areas and greater continental shelf exposure (due to lowering of the sea-level) on the continents of the Southern Hemisphere.

Marine and terrestrial contributions to Antarctic impurity deposition were so high at this time that the gas-derived compounds, apparently little influenced by climate changes, are difficult to identify among ice

impurities dominated by this primary aerosol fraction (Legrand 1985, Palais and Legrand 1985).

However, gas-derived compounds (essentially the three mineral acids  $H_2SO_4$ ,  $HNO_3$  and  $HCl$ ) are of prime interest in investigating past biogeochemical cycles. The major aim of this paper is to explain how to "extract" this contribution from deep Antarctic ice-core profiles of major ions ( $Na^+$ ,  $NH_4^+$ ,  $K^+$ ,  $Ca^{2+}$ ,  $Mg^{2+}$ ,  $H^+$ ,  $Cl^-$ ,  $NO_3^-$  and  $SO_4^{2-}$ ). We principally use the Dome C ice-core data set, but the results obtained on three other deep ice cores located in other Antarctic areas (Vostok station (VS), D10 in Terre Adélie, and Byrd Station (BS)) provide additional information of great interest in increasing general understanding of the past environment of the Southern Hemisphere. Advantages of this study over earlier work include:

- (a) the comparison of several deep ice cores from various Antarctic areas (where the accumulation rate of snow, the temperature and the elevation are very different),
- (b) concentration values are available for all major ions present in the ice.

Our discussion will be focused on the contrast between the two major climatic conditions: the LGM and the Holocene. A detailed study of the transition has been reported elsewhere (Legrand and Delmas 1987).

### 2. EXPERIMENTAL METHODS AND BASIC EQUATIONS

As the Dome C ice core is the backbone of this paper, we shall describe in detail only this sample set. However, the other ice cores have been analyzed in a very similar manner. Along the Dome C ice core, 55 sections were selected, each of them covering approximately 5 years. Surface contaminants were removed by thoroughly washing the ice pieces with ultra-pure water in a clean-air cabinet.

The efficiency of this procedure has already been tested and reported (Legrand and others 1984). Major ions and cations were measured by ion chromatography (IC), except  $H^+$ , which was titrated (Legrand and others 1982). Aluminium values, obtained on aliquots of the melt-water samples by neutron activation, served to assess the amounts of continental dust. Note that the acidic eluent used in the Dionex ion chromatograph for cationic determinations takes into solution Na-bearing dust particles, so that IC gives total sodium (as does atomic absorption) and not only the water-soluble part of sodium; such a phenomenon is not found with other species (Legrand 1987).

The ion balance of the measured soluble impurities may be written (concentrations in  $\mu Eq l^{-1}$ ):

$$[Na^+_m] + [NH^+_4] + [K^+] + [Ca^{2+}] + [Mg^{2+}] + [H^+] = [Cl^-] + [NO^-_3] + [SO^{2-}_4] \quad (1)$$

$Na^+_m$  is sea-salt sodium. It is obtained from total  $Na^+$  using relationship (2) (concentrations in  $ng g^{-1}$ ):

$$Na^+_m = Na - 0.29A1 \quad (2)$$

TABLE II. CONCENTRATIONS OF  $\text{Na}_m^+$ , Al,  $\text{H}_2\text{SO}_4$  AND  $\text{HNO}_3$  (IN  $\text{ng g}^{-1}$ ) AND  $\text{Cl}^-/\text{Na}_m^+$  (IN WEIGHT) FROM VARIOUS ANTARCTIC DEEP ICE CORES FROM THE TWO CLIMATIC STAGES.

H: Holocene; LGM: Late Glacial Maximum; r is the ratio LGM/H.

Location (elevation)		$\text{Na}_m^+$	$\text{Cl}^-/\text{Na}_m^+$ (*)	Al	$\text{H}_2\text{SO}_4$	$\text{HNO}_3$
Dome C (3240 m)	HOL	15		2.7	118	18
	LGM	87	$1.9 \pm 0.3$	74.0	138	11
	r	5.6		27.4	1.2	0.6
Vostok Station (3400 m)	HOL	22	$0.7 \pm 0.8$	3.0	174	14
	LGM	104	$1.8 \pm 0.2$	97.0	272	14
	r	4.7		32	1.6	1.0
Byrd Station (1500 m)	HOL	25	$1.8 \pm 0.4$	1.5	56	38
	LGM	52	$1.9 \pm 0.1$	11.5	74	45
	r	2.1		8	1.3	1.2
D10 (2000 m)	HOL	12	$1.5 \pm 0.2$	0.9	56	38
	LGM	37	$2.1 \pm 0.2$	16	108	47
	r	3.1		18	2.0	1.2

(\*) As reported in Table I, the Holocene value of  $\text{Cl}/\text{Na}_m$  at Dome C is either  $0.68 \pm 0.1$  or  $3.12 \pm 0.78$ , depending on the period under consideration.

mainly for central Antarctic snow during the Holocene. The assumption about a more turbulent atmosphere during the LGM is therefore indirectly confirmed by these results.

### 3.3 Secondary aerosol

The amount of a component in excess of its marine or crustal components can be evaluated using the relationships given in section 2. This amount is linked to environmental chemical processes as well as to source and transport phenomena.

### Sulfate

Sulfate is the key component in Antarctic atmospheric chemistry, particularly its non-sea-salt fraction, which is mostly linked to marine biogenic emissions. From the amount of excess sulfate measured in the ice cores, it should be possible (in principle) to find how marine biogenic activity of the sub-Antarctic ocean has varied in the past. In the Dome C ice core, it is clear that the excess sulfate level ( $\text{SO}_4^*$ ) was much higher during the LGM than during the Holocene (by a factor of 2.3, see Table I). Is that to say that marine biogenic activity was twice as high during the LGM? In fact, for several reasons this important conclusion has to be formulated with caution.

First of all, snow-accumulation rates at Dome C during the LGM were lower than they are now by a factor of 2. This phenomenon may therefore have enhanced the observed  $\text{SO}_4^*$  concentrations in ice. Although the dependence of sulfate concentration on the snow-accumulation rate is not well established (Herron 1982, Legrand 1985),  $\text{SO}_4^*$  is probably not deposited only by the dry process (Legrand 1987) and in this way the reduced accumulation rate of snow can enhance  $\text{SO}_4^*$  by a factor lower than 2.

Moreover, as already pointed out in this paper, an important fraction of ice-age  $\text{SO}_4^*$ , directly linked to the inputs of terrestrial dust, is not - strictly speaking - excess sulfate (which is generally in the form of  $\text{H}_2\text{SO}_4$ ) but, rather, "terrestrial salts", probably formed (at least partly) by the reaction of  $\text{H}_2\text{SO}_4$  with terrestrial carbonates. Using all the ionic concentrations determined in our samples, it has been possible to calculate the acid fraction of excess sulfate (designated  $\text{SO}_4^{2-a}$  in Table I). If we compare the values of  $\text{SO}_4^{2-a}$  before and after the climatic change, we find an LGM/Holocene ratio of only 1.2, compared to 2.3 for  $\text{SO}_4^*$

(Table I). This ratio is 1.6, 1.3 and 2.0 at VS, BS and D10 respectively. In this sense, it is difficult to draw definite conclusions. If the amount of sulfate bound to Ca and Mg as "terrestrial salts" could also be considered as gas-derived, then this increase would be much more significant: it could reflect a higher marine biogenic activity during the LGM. However, a better understanding of the exact origin of these terrestrial salts, and more complete glaciochemical measurements of the BS, VS and D10 ice cores will be required before such a conclusion can be drawn.

### Nitrate

We have discussed the origin of  $\text{HNO}_3$  in Antarctic snow elsewhere (Legrand and Delmas 1986) and suggested that this acid is most probably formed by tropical or mid-latitude lightning. As proposed earlier, the total nitrate measured in LGM is contributed not only by  $\text{HNO}_3$ , but also by neutral nitrate salt (in the form of "terrestrial salts"). This fraction, strongly correlated with the aluminium input, is even dominant (three-quarters of the total) at this time at Dome C (Table I). If we consider here only the acid fraction ( $\text{HNO}_3$ ), it may be observed that the LGM/Holocene ratio is 0.6 at Dome C, 1.0 at VS and 1.2 at BS and D10. The overall change for the four sites of this study is therefore weak.  $\text{HNO}_3$  is the compound exhibiting the smallest temporal concentration variations, whereas its spatial variability is high in the Antarctic (Legrand and Delmas 1986).

### 4. CONCLUSION

The interpretation of the chemical profiles obtained from ice cores is complicated by the fact that the ice-age atmosphere was heavily loaded with continental dust and sea-salt particles. Provided that all major ions are determined, it is possible to unravel the various snow-chemistry contributions both for glacial and for non-glacial climatic conditions. This has been done in a comprehensive study of soluble species in the Dome C ice core covering the last 30 000 years. It has been possible to demonstrate that the large sulfate and nitrate concentrations observed in LGM ice are mostly linked to the high continental aerosol inputs. The marine excess sulfate was slightly higher during the LGM than during the Holocene. This could indicate enhanced marine biogenic activity in ice-age climatic conditions in comparison with its present-day level.

### 5. ACKNOWLEDGEMENTS

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TABLE I. CHEMISTRY OF DOME C ICE. MEAN CONCENTRATIONS OF ALL MEASURED (OR CALCULATED) PARAMETERS IN THE TWO ISOTOPIC STAGES: HOLOCENE (0-361 m, 0-11500 B.P.) AND LGM (510-689 m, 15500-23000 B.P.).

$\Sigma$  is the sum of ionic concentrations. Subscripts a and t used with  $\text{NO}_3^-$  and  $\text{SO}_4^{2-}$  refer to acidic and terrestrial contributions respectively ( $\text{NO}_3^-_t$  is calculated from Al content,  $\text{NO}_3^-_a$  is then deduced from  $\text{NO}_3^-$ ,  $\text{SO}_4^{2-}_t$  is calculated by subtracting  $\text{NO}_3^-_t$  to the sum of  $\text{Ca}^{2+}$  and  $\text{Mg}^{2+}$ ; see detailed calculation in Legrand 1985 and Legrand and others, in press). All concentrations are in  $\mu\text{Eq l}^{-1}$ , except Al, which is expressed in  $\text{ng g}^{-1}$ . The  $\text{Cl}^-/\text{Na}^+_m$  ratio is calculated in weight concentrations.

Species	HOLOCENE		LGM	LGM/HOL.
	(0-215 m) P1	(215-360 m) P2		
Na	0.93	0.51	4.70	6.7
$\text{Na}^+_m$	0.90	0.49	3.78	5.6
$\text{Cl}^-$	0.42	0.94	4.62	6.3
$\text{Cl}^-/\text{Na}^+_m$	$0.68 \pm 0.10$	$3.12 \pm 0.78$	$1.88 \pm 0.3$	
$\text{Mg}^{2+}$	0.18		1.47	8
$\text{Mg}^{2+*}$	0.03		0.65	22
$\text{Ca}^{2+}$	0.09		1.83	20
$\text{Ca}^{2+*}$	0.03		1.66	27
$\text{K}^+$	0.02		0.15	10
$\text{K}^{++}$	< 0.01		0.07	
$\text{NH}_4^+$	0.04		0.12	2.7
$\text{H}^+$	2.1		1.9	0.9
$\text{NO}_3^-$	0.31		0.63	2.0
$\text{NO}_3^-_a$	0.29		0.18	0.6
$\text{NO}_3^-_t$	0.02		0.45	22.5
$\text{SO}_4^{2-}$	1.58		3.89	2.5
$\text{SO}_4^{2+*}$	1.49		3.43	2.3
$\text{SO}_4^{2-}_t$	0.09		1.78	20.0
$\text{SO}_4^{2-}_a$	1.23		1.44	1.2
$\Sigma$	5.6		18.3	3.3
Al	2.7		74.0	27

compositions (mean Al concentrations of 74.0 and 2.7  $\text{ng g}^{-1}$  respectively). This effect is less marked at low-elevation sites, such as D10 (2000 m) and BS (1500 m) (factors of 18 and 8 respectively), than on the high Antarctic plateau (27 at Dome C and 32 at VS) (see Table II). Although this difference can partly be explained by a dry-deposition process of these impurities, it is probably also due to the fact that continental aerosols are preferentially transported long distances above 3000 m (Delany and others 1973).

It has been proposed that the snow-accumulation rates at Vostok and Dome C decreased by a factor of 2 between the LGM and Holocene periods (Raisbeck and others 1981, Lorius and others 1985, Yiou and others 1985). This change may partly (but not entirely) explain the effects observed

on the Al concentrations in central Antarctic areas. Most of the decrease is attributable to the lowering of the Equator-Pole temperature gradient (CLIMAP Project Members 1981), which modulates the meridional and zonal circulation in the Southern Hemisphere. Petit and others (1981) and De Angelis and others (1984) have found, both in the Dome C and in the Vostok ice cores, a shift in the microparticle volume distribution between the LGM and the Holocene, due to faster atmospheric transport towards the Pole in glacial climatic conditions.

For the LGM, more than half of the impurity deposits at Dome C are due to the "insoluble" fraction, but we have discovered that this input of crustal insoluble material is accompanied by other components in a water-soluble form. For instance, the excess  $\text{Mg}^{2+}$  ( $\text{Mg}^*$ ) and excess  $\text{Ca}^{2+}$  ( $\text{Ca}^*$ ) concentrations are closely correlated with aluminium concentrations (correlation factors 0.80 and 0.93 respectively). The overall chemistry of the ice is therefore complex, due to these terrestrial contributions, which comprise insoluble dust (soil particles) and "terrestrial salts" ( $\text{Mg}^*$  and  $\text{Ca}^*$  associated partly with  $\text{NO}_3^-$  and partly with  $\text{SO}_4^{2-}$ ) - the origin of the latter chemical compounds remains unexplained. Consequently, one part of excess sulfate was neutral at this time. Moreover, nitrate was also in particle form (excess nitrate, designated  $\text{NO}_3^-_t$  in Table I) and it has been found to be highly correlated with aluminium concentrations (Legrand 1985). For the Holocene these "terrestrial salts" are present in ice in negligible amounts (as can be calculated from Al concentrations) (see Table I).

However, neither carbonates nor bicarbonates have been detected in the LGM ice (Legrand 1987), contrary to observations in Greenland ice cores (Hammer and others 1985). The aerosol emitted from desert areas generally contains carbonated minerals in addition to neutral salt (for instance,  $\text{CaSO}_4$ ) (Prospero and others 1981).

This could be explained by the neutralization of these alkaline compounds by atmospheric acids during transport from low latitudes (where the production areas are located) to polar latitudes. It is an indication that the buffering capacity of the terrestrial dust towards the natural atmospheric acidity was also important at this time in the Southern Hemisphere.

### 3.2. Sea salt

Whereas terrestrial dust content at Dome C decreased by a factor of 27 when passing from the LGM to the Holocene climate, the ionic budget diminished to a much smaller extent. A factor of 3.3 is calculated from the concentrations expressed in  $\mu\text{Eq l}^{-1}$  (Table I). The major part of this decrease in soluble species is indeed linked to the six-fold decrease in the sea-salt deposition.  $\text{Mg}^{2+}$ ,  $\text{K}^+$  and  $\text{Ca}^{2+}$ , contributed by both sea-salt and terrestrial sources, but in varying proportions, decreased by factors of 8, 10 and 20 respectively.

At Vostok and Dome C, the sea-salt deposition (as reflected by the  $\text{Na}^+_m$  values) between the LGM and the Holocene decreased by a factor of 4.7 and 5.7 respectively, whereas at lower elevations the corresponding factors are 2.1 (BS) and 3.1 (D10). In other words, as in the case of Al, the effect of the climatic change on sea-salt concentrations appears to be much more marked at high than at low elevations. As an explanation, we propose that atmospheric turbulence, significantly lower now than during the LGM, injected relatively large amounts of sea salt into the upper tropospheric layers, an effect which is reflected by the sodium content of the Dome C and Vostok ice layers. However, a very similar spatial variability (established from the four ice cores studied) is found for the two periods: 12-25  $\text{ng g}^{-1}$  for the Holocene and 37-104  $\text{ng g}^{-1}$  for the LGM. The  $\text{Na}^+_m$  values are lowest at D10, the station closest to the coast in this study. This indicates that the distance from the sea is not the most important parameter determining the sea-salt content of snow. In this respect, elevation appears to be a much more important factor.

The  $\text{Cl}^-/\text{Na}^+_m$  ratio (R) has been proposed as an indicator of atmospheric turbulence, the fractionation of sea salt occurring only in stable air conditions (Legrand 1985, Legrand and Delmas, in press [b]). When air circulation is rapid, R values close to 1.8 may be expected. In Table II, note that  $\text{Cl}^-/\text{Na}^+_m$  ratios different from 1.8 are found

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