

# Snow chemistry of high altitude glaciers in the French Alps

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## ABSTRACT

Snow samples were collected as snowcores in the accumulation zone of four high altitude glaciers (2980–3540 m.a.s.l.) from each of the 4 highest mountain areas of the French Alps, during 3 consecutive years: 1989, 1990 and 1991. Sampling was performed in spring (~May), before the onset of late spring–summer percolation. The accumulated snow therefore reflects winter and spring conditions. A complementary sampling of fresh-snow was performed on an event basis, on one of the studied glaciers, in 1990 and 1991. All samples were analysed for major ions (but also for total formate and acetate in fresh-snow samples) using ion chromatography. The acidity-alkalinity was accurately determined with a titration technique. The ion balance of alpine snow has been achieved from those analyses. High alpine snow is slightly acid ( $H^+ \sim 3\text{--}20 \mu\text{eq l}^{-1}$ ), but is episodically affected by alkaline saharan dust events. The different sources (pollution, sea-salt and soil dust) affecting the impurity content of snow were identified using principal component analysis. The measured free acidity, mainly from anthropogenic origin, originates from nitric acid scavenging while sulfuric acidity is partially neutralized by atmospheric ammonia and by alkaline soil dust derived species, the contribution of hydrochloric acid being negligible. All ions exhibit higher concentrations in spring than in winter snow, indicating most likely the influence of increased vertical transport from the lower troposphere at this time. The transport of saharan dust is described through three major events reaching the Alps during March 1990 and 1991. Very high concentrations of  $Ca^{2+}$  and  $HCO_3^-$  were measured in corresponding samples, indicating that the solubilisation of  $CaCO_3$  represents the major influence of saharan dust on the impurity content of alpine snow, shifting the pH from acid towards alkaline values. Chemical analysis suggests that during their transport, mineral alkaline particles can react through acid-base neutralization processes, mainly with sulfur, but also with nitrogen compounds, leading to increased deposition rates of  $SO_4^{2-}$ . The potential of deposited alkaline snow layers to neutralize the acidity stored in the snowpack, at the onset of late spring–summer percolation is also assessed.

## 1. Introduction

Global environment changes are recorded in polar ice sheets over time scales ranging from one to thousands of years. The exceptional length of the polar environmental records is explained by the low accumulation rates in these areas and by the large size of the Antarctic and Greenland ice sheets. The information obtained from the analyses of deep ice cores are of prime importance to reconstruct past climates, to investigate the link

between climate and atmospheric chemistry and to document major environmental changes of the past. The global impact of anthropogenic activities is also clearly visible in recent Greenland ice layers.

In non-polar regions, "cold" mountain glaciers also record environmental information, but on much shorter time scales (Wagenbach, 1989). In the Alps, the suitable glaciers for paleo-environmental studies are located at altitudes generally higher than 4000 m.a.s.l. At lower altitudes (3000–4000 m.a.s.l.), alpine temperate glacier fields can also be used for atmospheric studies, but only on the seasonal scale, since summer melting and percolation phenomena strongly disturb the

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chemical stratigraphy of deposited atmospheric impurities. These regions offer the possibility to study the occurrence and deposition of atmospheric trace constituents under hemispheric background conditions, and to assess the relative contributions of the various aerosol sources, in particular their natural versus anthropogenic components. The Alps, which are located in a densely industrialized and populated continent, and at the frontier between two contrasted major climatic zones (the Mediterranean and the Central European), constitute an ideal observatory to scrutinize the impact of acid pollution on the European background atmospheric chemistry.

The ALPTRAC (High Alpine Aerosol and Snow Chemistry Study) sub-project within the EUROTRAC framework, includes a wide snow sampling program performed at the end of the wintery accumulation period, on 14 high altitude ( $\sim 3000\text{--}3500$  m.a.s.l.) glacier fields located along the whole Alpine range from France to Austria, via Italy and Switzerland. The aim of the project is to derive from the chemical analyses of these snow samples a better understanding of the physical and chemical processes responsible for the accumulation of acid and related trace compounds in the Alpine regions. We report in this paper on the data obtained from the 4 French snow sampling sites.

Previous studies are sparse and focused mainly on a single site. They already established the slightly acid ( $4.5 < \text{pH} < 6$ ) nature of alpine snow (Delmas and Aristarain, 1978; Fuhrer, 1984; Psenner and Nickus, 1986; Nefel et al., 1987; Wagenbach et al., 1988; Delmas, 1989; Puxbaum et al., 1988; 1991). Nevertheless, none of these studies reported a balanced ion budget. This hampered the exact reconstruction of the initial association between ions, and the discussion of the chemical composition of snow in terms of sources and origins. As most South European regions (Loye-Pilot et al., 1986; Levin et al., 1990; Losno et al., 1991; Rodà et al., 1993), the Alps are episodically affected by the long-range transport of mineral dust from North–West Africa. The occurrence of saharan dust and the transport patterns towards the Alps (Prodi and Fea, 1978; Delmas, 1989; Schwikowski et al., 1993), the dust fluxes (Wagenbach and Geis, 1989; De Angelis and Gaudichet, 1991) and the aerosol size distribution (Wagenbach and Geis, 1989; Tschiersch et al., 1990; Schwikowski et al., 1990; 1993) have

already been investigated. On the contrary, the impact of saharan dust on the chemical composition of snow is still poorly documented, even if higher concentrations of soil dust derived ions (mainly  $\text{Ca}^{2+}$ ) and eventually  $\text{SO}_4^{2-}$  were observed (Schotterer et al., 1985; Ronseaux and Delmas, 1988; Delmas, 1989; Puxbaum et al., 1991) in coloured snow layers, where  $\text{HCO}_3^-$  was measured instead of  $\text{H}^+$  (Ronseaux and Delmas, 1988; Delmas, 1989), the incorporation of mineral alkaline (calcite-rich) dust into precipitation shifting its pH towards alkaline values.

More precise knowledge of alpine snow chemistry requires a detailed study of the origin, transport and transformation of acid and alkaline species in the high alpine troposphere. For this purpose, we collected in late spring of 1989, 1990 and 1991, the snow accumulated during winter and early spring on four glaciers of the French Alps. This sampling represents a comprehensive spatio-temporal survey of the chemical composition of snow in the Western part of the Alps. In this paper, we report on the soluble impurity content of alpine snow, including  $\text{Na}^+$ ,  $\text{NH}_4^+$ ,  $\text{K}^+$ ,  $\text{Mg}^{2+}$ ,  $\text{Ca}^{2+}$ ,  $\text{H}^+/\text{HCO}_3^-$ ,  $\text{Cl}^-$ ,  $\text{NO}_3^-$ ,  $\text{SO}_4^{2-}$  ions, and also briefly total formate ( $\text{HCOO}_T$ ) and acetate ( $\text{CH}_3\text{COO}_T$ ) obtained from additional fresh-snow samples.

## 2. Experimental

### 2.1. Sampling sites

In order to obtain a satisfactory geographical distribution, we chose our sampling sites in each of the four highest mountain areas of the French Alps. Snowcores were taken in the Mont Blanc massif at Col du Midi (3540 m.a.s.l., referred to and marked as Chamonix in Fig. 1), in the Vanoise massif on Glacier de la Grande Motte (2980 m.a.s.l., referred to and marked as Tignes in Fig. 1), in the Grandes Rousses massif on Glacier du Grand Sablat (3310 m.a.s.l., referred to and marked as Alpe d'Huez in Fig. 1) and in the Ecrins massif on Glacier de la Girose (3360 m.a.s.l., referred to and marked as La Grave in Fig. 1). These glaciers are located close to ski-resorts, allowing easy access, but sampling was performed in their upper part (accumulation zone), in areas not affected by ski activities. A detailed description

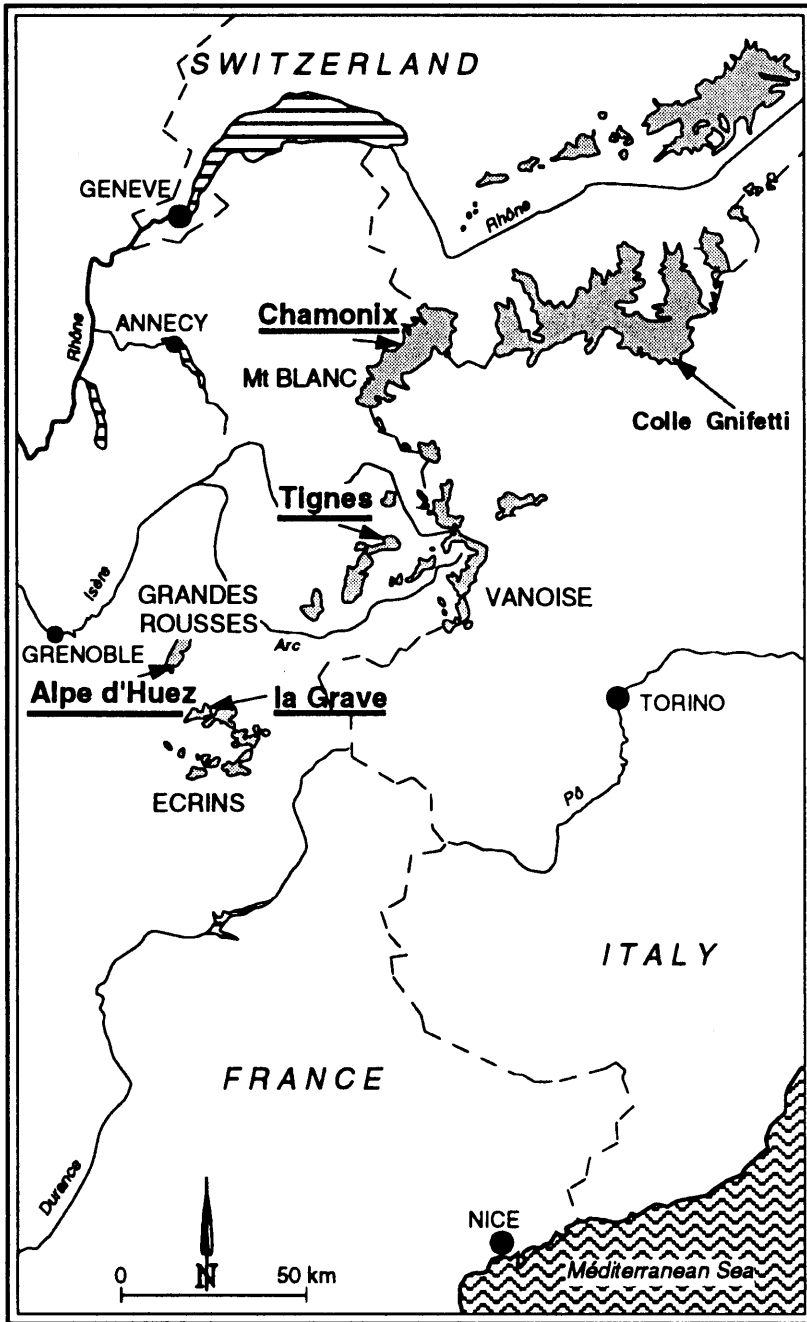


Fig. 1. Map of the Western part of the Alps showing sampling sites referred to in this paper.

of the sites is given by Maupetit (1992). The net snow accumulation (Table 1) was evaluated using both stratigraphic horizons and snow chemistry data (Maupetit, 1992).

### 2.2. Sampling procedure and sample handling

Due to the relatively low chemical concentrations expected, we adopted the sampling protocol developed for polar regions (Legrand and Delmas, 1987). Snowcores (7.5 cm in diameter), obtained using a manual Siple-type auger, were handled by operators wearing clean gloves, packed into plastic bags, and brought back frozen to our laboratory. The cores were then processed using precleaned instruments, in a clean air bench installed in a cold room ( $-10^{\circ}\text{C}$ ). In order to minimize contamination hazards, the snow samples were re-cored with the aid of a small drill according to the procedure described by Legrand and Delmas (1987), and the outer part of the initial cores discarded. 418 samples, hereafter referred to as *snowcores* samples, were obtained from the 12 snowcores collected at the four sites in 1989, 1990 and 1991.

We also performed a fresh-snow sampling on an event basis on Glacier de la Girose (referred to as La Grave), in the immediate vicinity of the snowcore sampling site, using a snowpit sampling technique, and as soon as possible (i.e., 1 to 3 days) after a snowfall event. This additional sampling, specially devoted to the measurement of total formate and acetate, has been performed in 1990 and 1991, between the beginning of January and the end of April. Operators wore clean gloves

and clothes, and a non-emissive particle mask. Samples were directly collected from a pit wall using precleaned air-tight glass flasks, and shipped in a frozen state to our laboratory. Only glass flasks were used throughout, since it has been demonstrated (Saigne et al., 1987), that plastic ware is not suitable for the handling and storage of snow samples intended to be used for the measurement of carboxylic anions at low concentrations. The 154 samples obtained from these two fresh-snow sampling campaigns will be hereafter referred to as *fresh-snow* samples.

### 2.3. Chemical analysis

*Snowcores* samples, first melted and filtered through  $0.4\ \mu\text{m}$  Nuclepore filters, were analysed using a Dionex 2010i ion chromatograph for  $\text{Na}^+$ ,  $\text{NH}_4^+$ ,  $\text{K}^+$ ,  $\text{Cl}^-$ ,  $\text{NO}_3^-$  and  $\text{SO}_4^{2-}$ , and for  $\text{Mg}^{2+}$  and  $\text{Ca}^{2+}$  using a new eluant (25 mMolar HCl, 3 mMolar diaminopropionic acid). In order to minimize the contamination of meltwater samples by atmospheric trace gases, in particular by ammonia (Legrand et al., 1984; Legrand and Delmas, 1987), samples were analysed for monovalent cations and anions shortly after melting and filtering. The precision of these measurements is estimated to 10% (Legrand et al., 1984).

*Fresh-snow* samples were analysed for total formate ( $\text{HCOO}_T$ ) and acetate ( $\text{CH}_3\text{COO}_T$ ),  $\text{Cl}^-$ ,  $\text{NO}_3^-$  and  $\text{SO}_4^{2-}$  using a Dionex 4000i ion chromatograph, and for  $\text{Na}^+$ ,  $\text{NH}_4^+$ ,  $\text{K}^+$ ,  $\text{Mg}^{2+}$  and  $\text{Ca}^{2+}$  using a Dionex 4500i ion chromatograph, with a 5% precision (Legrand

Table 1. Sampling date, core length and water equivalent (mm), and number of samples at all studied sites

Site	Sampling date	Core length	Water eq.	Nb. samples
La Grave	19 April 1989	3470	1540	26
Glacier de la Girose 3360 m.a.s.l.	30 May 1990	3690	1890	35
	7 May 1991	4830	1945	48
Alpe d'Huez	23 May 1989	2980	1710	27
Glacier du Grand Sablat 3310 m.a.s.l.	25 May 1990	3300	1660	33
	30 May 1991	3270	1500	31
Tignes	18 May 1989	2840	1375	27
Glacier de la Grande Motte 2980 m.a.s.l.	18 May 1990	3960	1955	39
	22 May 1991	3235	1510	29
Chamonix	9 June 1989	4510	2430	32
Col du Midi 3540 m.a.s.l.	15 June 1990	4810	2385	48
	28 May 1991	4535	2060	43

et al., 1993). The problem of contamination by gaseous ammonia, formic and acetic acids (Saigne et al., 1987; Legrand et al., 1993) was limited by melting the samples in their air-tight glass flasks just a few minutes prior to the ion chromatographic analyses of both cations and anions.

Thereafter, the samples were stored frozen. They were melted again later and titrated for  $H^+$  (or  $HCO_3^-$ ) according to the method defined by Legrand et al. (1982). The titrator has been recently equipped with a new "Hach One" pH electrode (Maupetit, 1992). This titration based on the Gran's plot method, prevents the influence on the measurements of the carbonic acid produced by atmospheric  $CO_2$  dissolving in the meltwater (Legrand et al., 1982). Note that the acidity data obtained by this method may be different of that deduced from pH measurements. The analytical range for  $H^+$  (or  $HCO_3^-$ ) is 0–20  $\mu eq l^{-1}$ , with a precision of 30% to 10% for  $H^+$  (or  $HCO_3^-$ ) < 2  $\mu eq l^{-1}$  and 20  $\mu eq l^{-1}$ , respectively (Maupetit, 1992).

#### 2.4. Mineralogical analyses

Mineralogical studies were performed using a Transmission Electron Microscope (Jeol 100 CX II) fitted with an X-ray Energy Dispersive System (Tracor 421). Under clean conditions (laminar flow hood within a clean room), snow samples were melted and filtered on previously carbon coated 0.2  $\mu m$  Nuclepore membranes. The filters were then transferred onto electron microscope gold grids according to the procedure detailed by Gaudichet et al. (1986).

Our main purpose was to identify local particles ( $r > 10 \mu m$ ), typical saharan (palygorskite), pollution (microsoot, fly-ash) and volcanic (glass) indicators. Clay minerals were identified using one grid selected by chance. Therefore, the presence of identified minerals and their relative proportions are more qualitative than quantitative, due to the low number of performed analyses. This remark is less valid for soot, fly-ash, volcanic glass and palygorskite fibers which were investigated more systematically by scanning of the grid deposit.

### 3. Results and discussion

#### 3.1. Ion balance

For each sample, we calculated the sum of measured cations ( $\Sigma Cat$ ) and anions ( $\Sigma An$ ) (concentrations expressed in  $\mu eq l^{-1}$ ):

$$\begin{aligned} \Sigma Cat = & [Na^+] + [NH_4^+] + [K^+] + [Mg^{2+}] \\ & + [Ca^{2+}] + [H^+] \end{aligned} \quad (1)$$

$$\begin{aligned} \Sigma An = & [Cl^-] + [NO_3^-] + [SO_4^{2-}] + [HCO_3^-] \\ & + [HCOO^-] + [CH_3COO^-] \end{aligned} \quad (2)$$

For *fresh*-snow samples, the dissociated fractions of carboxylic anions ( $RCOO^-$ ) were included in  $\Sigma An$  (Maupetit and Delmas, 1994, in press), because the weak acidity of  $HCOOH$  is completely measured by this titration, and that of  $CH_3COOH$  only partially (Legrand et al., 1982).

Table 2. Arithmetic mean, standard deviation (SD), minimum and maximum values of analysed ions for the acid and alkaline snowcores samples ( $\mu eq l^{-1}$ )

	Acid snowcores				Alkaline snowcores			
	A. mean	SD	minimum	maximum	A. mean	SD	minimum	maximum
$Na^+$	1.46	2.66	0.02	30.25	3.46	4.55	0.10	24.30
$NH_4^+$	3.94	5.74	0.05	36.00	5.92	6.22	0.70	42.90
$K^+$	0.39	0.90	0	12.10	0.90	1.36	0.02	9.95
$Mg^{2+}$	0.53	0.64	0	6.62	1.92	2.09	0.10	13.50
$Ca^{2+}$	2.98	3.64	0.05	25.25	23.80	25.65	0.60	131.15
$H^+$	5.87	5.84	0.10	41.75	0	0	0	0
$HCO_3^-$	0	0	0	0	12.72	18.16	0.15	85.20
$Cl^-$	1.80	2.72	0	28.40	3.44	4.08	0.20	22.70
$NO_3^-$	4.58	5.13	0	28.90	4.72	4.91	0.55	38.50
$SO_4^{2-}$	8.08	9.74	0.20	62.90	13.88	18.68	0.69	111.10

The parameters ( $a$ ,  $b$  and the correlation coefficient  $r^2$ ) of the linear regression:

$$\sum \text{Cat} = a \sum \text{An} + b \quad (3)$$

were calculated for the *snowcores* (0.95, 1.65 and 0.9927, respectively) and *fresh-snow* samples (0.99, 0.94 and 0.9972, respectively). The slope ( $a$ ) of the regression is close to unity for both data sets. This suggests that most soluble species have been measured. We have no particular explanation however for the small deviation from unity of the *snowcores* regression slope (0.95). The intercept ( $b$ ) of the regression is different from zero, suggesting a small cation excess. In the case of the *snowcores*,

the value of  $b$  ( $1.65 \mu\text{eq l}^{-1}$ ) is likely partly due to a small amount of non-measured carboxylic acids. ( $b$ ) is indeed smaller for the *fresh-snow* samples (0.94). It was observed by Legrand (1987) that the acid eluant (HCl, 14 or 25 mMolar) used for the ion chromatographic measurements of cations is able to solubilize mineral dust. This phenomenon, which could explain this calculated excess-cation amount has already been invoked by Delmas (1989). From dust concentrations measured in alpine snow meltwater after filtration through  $0.4 \mu\text{m}$  Nuclepore filters, this author calculated a maximum cation solubilization of  $1.05 \mu\text{eq l}^{-1}$ , a figure consistent with our intercept values. Finally it is worth noting that, contrary to previous studies which reported an anion deficit of the order of

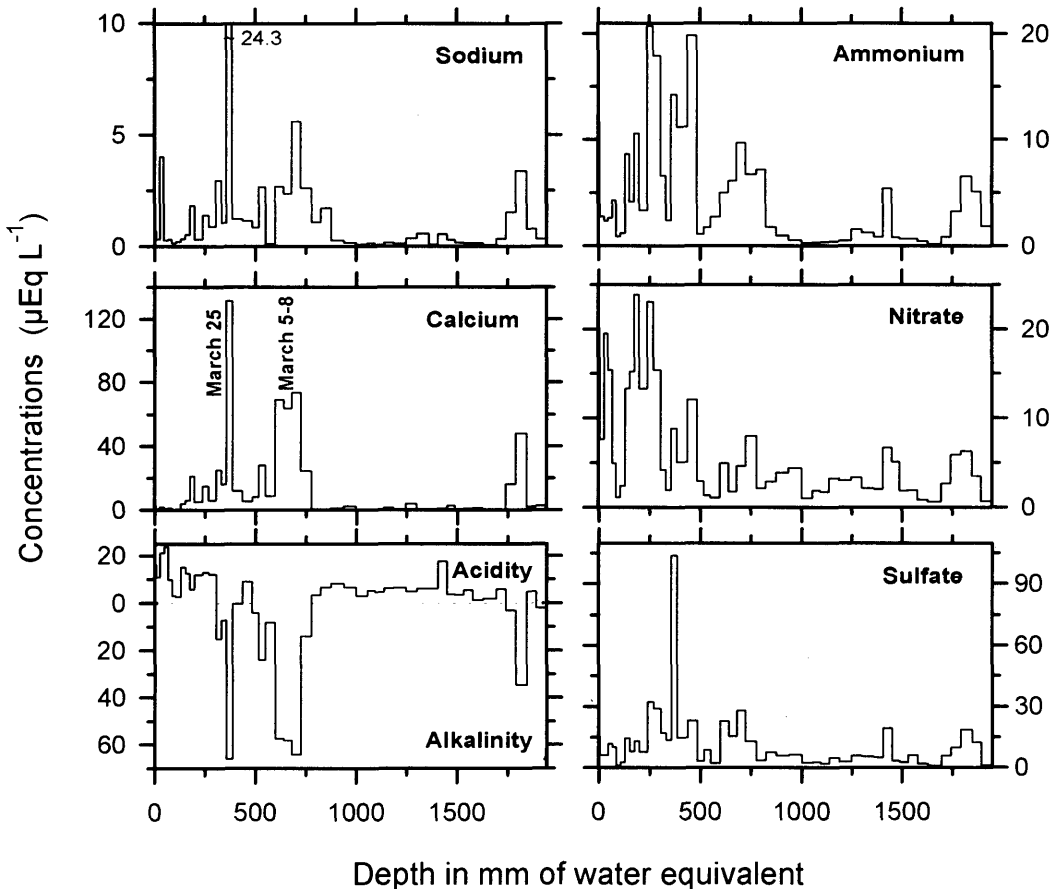


Fig. 2. Concentration profiles ( $\mu\text{eq l}^{-1}$ ) of  $\text{Na}^+$ ,  $\text{Ca}^{2+}$ ,  $\text{NH}_4^+$ ,  $\text{H}^+$  (or  $\text{HCO}_3^-$ ),  $\text{NO}_3^-$  and  $\text{SO}_4^{2-}$  in the La Grave 1991 snowcore, from late summer-fall 1990 (right) to May 1991 (left).

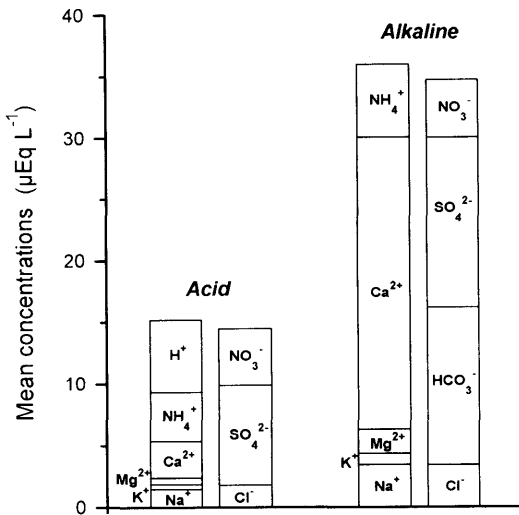


Fig. 3. Mean concentrations ( $\mu\text{eq l}^{-1}$ ) of acid and alkaline snowcores samples (arithmetic values from Table 2).

15–20% (Ronseaux and Delmas, 1988; Delmas, 1989; Puxbaum et al., 1991), an almost perfect ion balance of the alpine snow has been achieved during this study.

### 3.2. General data presentation

The concentration profiles of some of the measured ions ( $\text{Na}^+$ ,  $\text{Ca}^{2+}$ ,  $\text{NH}_4^+$ ,  $\text{H}^+$  (or

$\text{HCO}_3^-$ ),  $\text{NO}_3^-$  and  $\text{SO}_4^{2-}$ ) in the *La Grave 1991 snowcore*, are shown in Fig. 2. In “normal” conditions (absence of saharan dust transport), the high alpine snow is slightly acid, with winter  $\text{H}^+$  concentrations of 2–5  $\mu\text{eq l}^{-1}$ , increasing in spring to 10–20  $\mu\text{eq l}^{-1}$ . The pH of snow is occasionally sharply shifted towards alkalinity,  $\text{HCO}_3^-$  being measured instead of  $\text{H}^+$ . The three major peaks observed on the *La Grave 1991 snowcore*  $\text{H}^+$ / $\text{HCO}_3^-$  profile at respective depths of 300–400, 600–700 and 1800 (mm of water equivalent), present two saharan dust events identified and dated to 24–25 March 1991 and 5–8 March 1991, and a third one occurring presumably in late summer or fall 1990. Then,  $\text{HCO}_3^-$  is remarkably linked to  $\text{Ca}^{2+}$ , suggesting that the main soluble part of mineral dust is associated with  $\text{CaCO}_3$ . In fact, the chemical composition of coloured snow layers characteristic of mineral dust transport, completely differs from “normal” acid snow (Fig. 3). Therefore, we divided the snowcores data set in two categories, corresponding to the acid and alkaline samples. Subsection 3.3 of this paper is dedicated to the “normal” acid alpine precipitation, while the impact of saharan dust on the snow chemistry is discussed in Subsections 3.4 and 3.5.

Arithmetic mean, standard deviations, minimum and maximum concentrations of the acid and alkaline snowcores samples are summarized in

Table 3. Volume weighted means ( $\mu\text{eq l}^{-1}$ ) of measured ions at the different sampling sites: LG: La Grave, AH: Alpe d'Huez, T: Tignes, C: Chamonix

	$\text{Na}^+$	$\text{NH}_4^+$	$\text{K}^+$	$\text{Mg}^{2+}$	$\text{Ca}^{2+}$	$\text{H}^+$	$\text{Cl}^-$	$\text{NO}_3^-$	$\text{SO}_4^{2-}$	$\text{HCO}_3^-$	$\text{CH}_3\text{COO}^-$
LG 1989	0.61	2.65	0.15	0.38	1.82	4.00	0.88	2.62	6.13	—	—
LG 1990	4.37	5.38	1.44	0.77	3.64	5.05	5.03	4.08	8.98	—	—
LG 1991	0.49	3.43	0.17	0.21	2.11	6.67	0.78	5.44	7.57	—	—
AH 1989	2.25	5.73	0.55	0.85	4.13	3.29	2.75	3.34	10.57	—	—
AH 1990	2.95	2.26	0.46	0.71	2.89	4.52	3.27	2.15	5.80	—	—
AH 1991	1.58	2.10	0.42	0.23	1.82	5.13	1.58	2.98	5.95	—	—
T 1989	2.01	3.95	0.47	0.61	3.02	4.38	2.19	3.90	7.61	—	—
T 1990	0.98	1.79	0.26	0.44	3.13	3.85	1.10	2.21	4.39	—	—
T 1991	0.60	3.71	0.20	0.65	4.30	6.65	1.01	6.93	8.39	—	—
C 1989	1.00	3.54	0.29	0.61	3.24	3.75	1.40	4.20	6.81	—	—
C 1990	1.32	4.95	0.34	0.64	2.75	6.74	1.64	4.93	9.42	—	—
C 1991	0.50	4.09	0.25	0.33	2.62	7.35	0.96	6.28	8.39	—	—
FS 1990*	0.88	2.24	0.07	0.26	1.21	5.34	1.04	3.40	4.16	0.58	0.61
FS 1991	0.37	3.80	0.16	0.25	2.09	5.71	0.51	4.26	6.07	0.65	0.51

FS: Fresh-snow (La Grave). \* arithmetic means.

Table 4. Ion correlation matrix for the 345 acid snowcores samples

	Na <sup>+</sup>	NH <sub>4</sub> <sup>+</sup>	K <sup>+</sup>	Mg <sup>2+</sup>	Ca <sup>2+</sup>	H <sup>+</sup>	Cl <sup>-</sup>	NO <sub>3</sub> <sup>-</sup>	SO <sub>4</sub> <sup>2-</sup>
Na <sup>+</sup>	1	0.179	0.816	0.536	0.360	-0.062	0.977	0.089	0.202
NH <sub>4</sub> <sup>+</sup>		1	0.378	0.487	0.527	0.636	0.262	0.768	0.901
K <sup>+</sup>			1	0.411	0.424	0.081	0.777	0.267	0.370
Mg <sup>2+</sup>				1	0.723	0.158	0.581	0.388	0.583
Ca <sup>2+</sup>					1	0.144	0.387	0.501	0.622
H <sup>+</sup>						1	0.018	0.782	0.736
Cl <sup>-</sup>							1	0.179	0.269
NO <sub>3</sub> <sup>-</sup>								1	0.746
SO <sub>4</sub> <sup>2-</sup>									1

Table 2, and the winter-spring volume weighted means for each of the different sampling sites are reported in Table 3. All our measurements are in good agreement with previously reported data (Psenner and Nickus, 1986; Neftel et al., 1987; Puxbaum et al., 1988; 1991; Maupetit et al., 1993). The volume weighted mean concentrations of NH<sub>4</sub><sup>+</sup>, H<sup>+</sup>, NO<sub>3</sub><sup>-</sup> and SO<sub>4</sub><sup>2-</sup> (Table 3) are rather constant at each sampling site from year to year, or for one particular year, from site to site, suggesting that, both on-site interannual variations and yearly spatial distribution of mean concentrations in winter-spring acid snow are homogeneous for those ions at the scale of the French Alps. On the contrary, the volume weighted means of Na<sup>+</sup>, K<sup>+</sup>, Mg<sup>2+</sup>, Ca<sup>2+</sup> and Cl<sup>-</sup> are present in wider concentration ranges, indicating more episodic and scattered inputs, and therefore, more important spatial and temporal variations. *Fresh-snow* chemical concentrations are slightly lower than the corresponding *La Grave snowcores* concentrations, eventually due to post-depositional effects such as snow erosion by wind or dry deposition, but more likely due to the different time periods (January to April, and end of summer to May, respectively) covered by the two samplings.

The concentrations of total formate and acetate were measured in the *fresh-snow* samples (Table 3). Since the alpine snow organic acidity has been discussed in details elsewhere (Maupetit and Delmas, 1994, in press), we give here only some major features about formate and acetate snow concentrations. HCOO<sub>T</sub> and CH<sub>3</sub>COO<sub>T</sub> are generally present in very low concentrations: 0.3–0.6 μeq l<sup>-1</sup> in winter snow (January–February), increasing to 0.6–1.2 μeq l<sup>-1</sup> in early spring snow (March–April). Those results are

confirming the only available data of formate (0.3–1 μeq l<sup>-1</sup>) previously reported by Neftel et al. (1987). The maximum contribution of HCOOH and CH<sub>3</sub>COOH to the measured free acidity is generally less than 10% for each acid. Therefore, they do not contribute significantly to the acidity budget of alpine snow, and their contribution to the total ionic load is also low (~5%). Those findings do not confirm the assumption made by Delmas (1989) and Puxbaum et al. (1991), to explain their observed anion deficit, that HCOO<sub>T</sub> and CH<sub>3</sub>COO<sub>T</sub> should be present in alpine snow at rather high concentration levels.

### 3.3. "Normal" alpine acid snow

3.3.1. Sources of impurities contributing to high alpine snow chemistry. In order to identify the

Table 5. Results of the PCA: factor loadings, % of explained variance and eigenvalue for each of the factors, communalities (h<sup>2</sup>) and standard error (σ<sub>s</sub>) for each of the variables, for the acid snowcores samples

	F1	F2	F3	h <sup>2</sup>	σ <sub>s</sub>
Na <sup>+</sup>	0.050	0.967	0.195	0.975	0.009
NH <sub>4</sub> <sup>+</sup>	0.859	0.098	0.302	0.838	0.022
K <sup>+</sup>	0.270	0.861	0.126	0.830	0.022
Mg <sup>2+</sup>	0.289	0.364	0.790	0.839	0.022
Ca <sup>2+</sup>	0.340	0.190	0.853	0.879	0.019
H <sup>+</sup>	0.927	-0.103	-0.172	0.901	0.017
Cl <sup>-</sup>	0.135	0.936	0.217	0.941	0.013
NO <sub>3</sub> <sup>-</sup>	0.897	0.007	0.180	0.837	0.022
SO <sub>4</sub> <sup>2-</sup>	0.871	0.087	0.385	0.915	0.016
% var.	51.9	26.6	9.9		
eigenvalue	4.67	2.40	0.89		



different contributions to the impurity content of high alpine snow, we performed a varimax rotated Principal Component Analysis (PCA). The PCA involved 9 initial variables ( $\text{Na}^+$ ,  $\text{NH}_4^+$ ,  $\text{K}^+$ ,  $\text{Mg}^{2+}$ ,  $\text{Ca}^{2+}$ ,  $\text{H}^+$ ,  $\text{Cl}^-$ ,  $\text{NO}_3^-$ ,  $\text{SO}_4^{2-}$  concentrations) and 345 observations (acid snowcores samples). The principal components are derived from the correlation matrix of the ions given in Table 4. We used three factors which explained 88% of the total variance (the third factor accounting for only 10% of total variance). Factor loadings, their uncertainties and the communalities (which are all close to unity) of each variable are presented in Table 5.

The first factor (F1) is loaded with  $\text{H}^+$ ,  $\text{NH}_4^+$ ,  $\text{NO}_3^-$  and  $\text{SO}_4^{2-}$  and will be labelled acid, because it contains the measured free acidity of alpine snow, together with its two associated anions ( $\text{NO}_3^-$  and  $\text{SO}_4^{2-}$ ).  $\text{NH}_4^+$  is present in F1 as a combination of the secondary ammonium-sulfate aerosol, as discussed later.

Non-sea-salt sulfate ( $\text{nssSO}_4^{2-}$ ) was calculated from:

$$\text{nssSO}_4^{2-} = \text{SO}_4^{2-} - 0.121\text{Na}^+, \quad (4)$$

using  $\text{Na}^+$  as the seawater reference species, 0.121 as the  $\text{SO}_4^{2-}/\text{Na}^+$  ratio in bulk seawater (Wilson, 1975), and concentrations expressed in  $\mu\text{eq l}^{-1}$ .

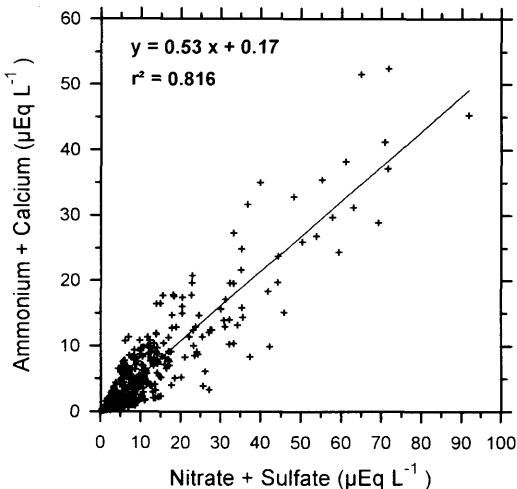


Fig. 4. Relationship between the sums of  $\text{NH}_4^+$  and  $\text{Ca}^{2+}$ , and of  $\text{NO}_3^-$  and  $\text{SO}_4^{2-}$  ( $\mu\text{eq l}^{-1}$ ) for the acid snowcores samples. The solid line represents the linear regression fit.

Due to the relatively low measured  $\text{Na}^+$  concentrations,  $\text{nssSO}_4^{2-}$  is representing generally more than 95% of the total  $\text{SO}_4^{2-}$ , and we assumed our measured  $\text{SO}_4^{2-}$  to  $\text{nssSO}_4^{2-}$ .

It is not easy to estimate the respective contributions of natural and anthropogenic sources to  $\text{NO}_3^-$  and  $\text{SO}_4^{2-}$ , and to the resulting strong acidity. Nevertheless, the chemical composition of snow at Colle Gnifetti (4450 m.a.s.l., Monte Rosa, Swiss Alps, Fig. 1) changed from being alkaline ( $\text{HCO}_3^- \sim 5 \mu\text{eq l}^{-1}$ ) at the beginning of our century, to acid conditions ( $\text{H}^+ \sim 6 \mu\text{eq l}^{-1}$ ) nowadays (D. Wagenbach, personal communication), due to a 4- to 5-fold increase of both  $\text{NO}_3^-$  and  $\text{SO}_4^{2-}$ , reflecting the increasing influence of anthropogenic emissions of  $\text{NO}_x$  and  $\text{SO}_2$  (Wagenbach et al., 1988). The same tendency was also observed at the Col du Dôme (4250 m.a.s.l., Mont Blanc, French Alps, Fig. 1) where the snow was alkaline before 1960 (Delmas and Aristarain, 1978), while it is actually acid ( $\text{H}^+ \sim 6 \mu\text{eq l}^{-1}$ ; Maupetit, 1992). This picture is consistent with the fact that actually in Europe, the anthropogenic emissions of  $\text{SO}_2$  and  $\text{NO}_x$ , which are subsequently oxidized in the troposphere into sulfuric and nitric acids, are largely dominant over their natural contributions. Therefore, the actual alpine snow acidity appears to be mainly from anthropogenic origin, and F1 represents the European pollution sources.

$\text{NH}_4^+$  originates from atmospheric ammonia ( $\text{NH}_3$ ), naturally emitted by soils, but also by anthropogenic activities (livestock wastes, fertilizers and some industrial activities), actually dominant in Europe (Buijsman et al., 1987). The better correlation of  $\text{NH}_4^+$  with  $\text{SO}_4^{2-}$  than with  $\text{NO}_3^-$  (0.901 and 0.768, respectively) suggest that ammonia reacts more readily with sulfuric than with nitric acid, as expected from aerosol equilibrium model, ammonium-sulfate being a more stable aerosol form than ammonium-nitrate (Bassett and Seinfeld, 1983). The slope of the regression line between  $\text{NH}_4^+$  and  $\text{SO}_4^{2-}$  (slope: 0.53, intercept: 0.35,  $r^2 = 0.811$ ) is close to 0.5, suggesting the stoichiometry of  $\text{NH}_4\text{HSO}_4$ , as reported for winter and spring snow (Puxbaum et al., 1991) and for anthropogenic sulfate aerosol in the Arctic (Barrie and Barrie, 1990). As sulfate is present in alpine precipitation in a combination of ammonium-sulfate but also of calcium-sulfate aerosol (Ronseaux and Delmas, 1988; Delmas,

1989), the potential sulfuric acidity is partially buffered, and the measured free acidity of snow is mainly associated to nitrate as suggested by the strong correlation between  $H^+$  and  $NO_3^-$  (0.782). This association has been already observed (Nefel et al., 1987; Delmas, 1989; Puxbaum et al., 1991), may reflect the importance of  $HNO_3$  gas-phase scavenging by alpine snow (Baltensperger et al., 1992).

The second factor (F2) loaded with  $Na^+$  and  $Cl^-$ , but also with  $K^+$ , will be labelled *sea-salt*. The very close correlation between  $Na^+$  and  $Cl^-$  (slope: 1.00, intercept: 0.34,  $r^2 = 0.955$ ), suggests that they are both coming from the sea-salt aerosol produced by the bubble bursting phenomenon at the sea surface. The  $Cl^-/Na^+$  ratio in the acid *snowcores* samples (1.00) is slightly lower than the seawater ratio (1.16; Wilson, 1975). This can be explained by a chlorine loss due to the reaction of sea-salt aerosols with atmospheric acids ( $H_2SO_4$ ,  $HNO_3$ ) according to:



or by a fraction of soil-dust derived sodium, possibly resulting from cation exchange reactions between mineral dust and protons in the atmosphere (Sequeira, 1991), or during ion chromatographic analysis (Legrand, 1987). We privileged the hypothesis of the presence of a fraction of soil-dust derived sodium, since the  $Cl^-/Na^+$  ratio of alkaline *snowcores* samples (0.88, Table 6) is still more depleted compared to the seawater ratio. In fact, when we re-calculated the  $Cl^-/Na^+$  ratio (Table 6) using  $Ca^{2+}$  as dust tracer, and discarding from the acid *snowcores* the samples with  $Ca^{2+} > 6 \mu eq l^{-1}$  (two times  $Ca^{2+}$  mean value for the data set, Table 2), and then samples with  $Ca^{2+} > 3 \mu eq l^{-1}$ , we found for latter

Table 6. Number of samples ( $N$ ), slope ( $a$ ), intercept ( $b$ ) and correlation coefficient ( $r^2$ ) of the regression line  $Cl^- = a.Na^+ + b$ , for different *snowcores* samples categories

	$N$	$a$	$b$	$r^2$
alkaline	71	0.88	0.38	0.970
acid	345	1.00	0.34	0.955
acid with $Ca^{2+} < 6 \mu eq l^{-1}$	307	1.13	0.19	0.947
acid with $Ca^{2+} < 3 \mu eq l^{-1}$	231	1.19	0.11	0.955

samples a  $Cl^-/Na^+$  ratio (1.19) then very close to the seawater ratio (1.16), indicating that the sea-salt aerosol is likely the most important source of  $Cl^-$  and  $Na^+$  in high alpine snow. We therefore conclude that reaction (5) had little influence in our case, and that the observed deviation from the bulk seawater  $Cl^-/Na^+$  ratio is due to a small fraction of crustal sodium.

The observation of the absence of excess-chloride indicates that HCl does not contribute to the acidity budget of snow in the Western part of the Alps. This conclusion is not surprising since in Western Europe, HCl is supposed to represent only a minor source (less than 2%) of atmospheric acidity (Lightowlers and Cape, 1988). HCl can be produced according to reaction (5), but man-made emissions, mostly from coal burning and waste incineration, represent the major sources of HCl in Europe (Lightowlers and Cape, 1988). Since HCl is highly soluble and dissolves readily at low elevations in cloud or rain water, it is preferentially deposited close to its sources, even if long-range transport is possible within non precipitating clouds. This remark is consistent with the assumption that, in winter, the highest alpine regions are almost not influenced by polluted air masses from lower regions, where HCl is emitted, and are representative of the free troposphere over Western Europe.

The PCA indicates that  $K^+$  is associated to  $Na^+$  and  $Cl^-$  in the *sea-salt* component. In fact, on average, more than 86% of  $K^+$  is of non-sea-salt origin, and is indeed mainly crustal. This statistical association should more reflect a simultaneous deposition effect than a common source effect.

Finally, the third factor (F3) is loaded with  $Ca^{2+}$  and  $Mg^{2+}$  and will be labelled soil dust, because  $Ca^{2+}$  is the main measured ions in dust containing samples (Tables 2, 10). The background level of soil dust derived species is of natural origin: wind erosion of minerals such as calcium carbonate ( $CaCO_3$ ), dolomite ( $CaMg(CO_3)_2$ ) or gypsum ( $CaSO_4$ ), but also from anthropogenic origin: cement or power plants emissions (Kumai, 1985; Marquardt and Ihle, 1988). In particular, the solubilisation of lime ( $CaO$ ) or  $MgO$  may contribute to neutralize the acidity and increase the pH of precipitation (Marquardt and Ihle, 1988), as well as calcium-rich fly-ash (Kumai, 1985).

Table 7. Volume-weighted mean concentrations ( $\mu\text{eq l}^{-1}$ ) for the La Grave 1991 snowcore over different time periods

	Before March 1991	March to May 1991	All period
Na <sup>+</sup>	0.33	0.88	0.50
NH <sub>4</sub> <sup>+</sup>	1.03	9.24	3.56
K <sup>+</sup>	0.11	0.35	0.18
Mg <sup>2+</sup>	0.13	0.47	0.24
Ca <sup>2+</sup>	1.34	5.43	2.60
H <sup>+</sup>	5.13	11.37	7.05
Cl <sup>-</sup>	0.58	1.60	0.90
NO <sub>3</sub> <sup>-</sup>	2.99	13.37	6.19
SO <sub>4</sub> <sup>2-</sup>	3.67	14.48	7.00

The acid-base balance of alpine snow can be roughly summarized as follow: the acidity of high alpine snow is due to the strong acids H<sub>2</sub>SO<sub>4</sub> and HNO<sub>3</sub>, end products of the atmospheric oxidation of SO<sub>2</sub> and NO<sub>x</sub>, mainly from anthropogenic origin nowadays in Europe. The contribution of HCl can be neglected. Atmospheric NH<sub>3</sub> and soil-dust derived aerosols (assimilated to CaCO<sub>3</sub>) are able to buffer ~50% of strong atmospheric acidity (Fig. 4). Without the neutralizing action of those alkaline species, the level of free acidity in the French Alps recent snow should be doubled.

3.3.2. Winter-spring seasonal transition. The seasonal pattern of alpine precipitation chemistry, with very low concentrations in winter increasing during spring and summer (Puxbaum et al., 1991; Maupetit, 1992; Maupetit et al., 1993), can be partially observed from the La Grave 1991 snowcore NH<sub>4</sub><sup>+</sup>, NO<sub>3</sub><sup>-</sup> and SO<sub>4</sub><sup>2-</sup> profiles (Fig. 2). For this sampling, the volume weighted means of major ions are reported in Table 7, for the separated winter (prior to March) and spring (March to May) periods. The volume weighted means of the overall period calculated in Table 7 as a composition of the March and May snowcores, are therefore slightly different from the La Grave 1991 mean concentrations, calculated in Table 3, from the entire May snowcore. Compared to winter snow, all ions show a 2- to 4-fold increase (8-fold for NH<sub>4</sub><sup>+</sup>) in early spring snow. This seasonal variation is consistent with data from continuous aerosol monitoring in the Alps, where higher aerosol concentrations were found in spring and summer than in winter (Baltensperger et al., 1991). These observations indicate that in winter, the high alpine sites are generally not affected by polluted air masses from lower regions, while during other seasons, thermal convection induced vertical transport significantly affects even the highest sites located well above 4000 m.a.s.l. (Baltensperger et al., 1991; Maupetit, 1992). Thus,

Table 8. Volume weighted means ( $\mu\text{eq l}^{-1}$ ) of H<sup>+</sup>, NH<sub>4</sub><sup>+</sup>, Ca<sup>2+</sup>, NO<sub>3</sub><sup>-</sup> and SO<sub>4</sub><sup>2-</sup> in snow (or rain at the lowest altitude sites) from european mountain sites at different altitudes (m.a.s.l.); glaciers represents a compilation of 10 alpine glaciers from the Swiss, Italian and Austrian Alps

Site (Country)	Alt.	Sampling time	H <sup>+</sup>	NH <sub>4</sub> <sup>+</sup>	Ca <sup>2+</sup>	NO <sub>3</sub> <sup>-</sup>	SO <sub>4</sub> <sup>2-</sup>	Ref.
Col du Dôme (F)	4250	winters 1988-1991	3.58	1.02	1.07	1.7	3.02	Maupetit (1992)
Col du Dôme (F)	4250	spring 1988-1991	8.49	9.75	5.48	6.64	13.78	Maupetit (1992)
La Grave (F)	3360	winter 1990/91	5.13	1.03	1.34	3	3.67	This work
La Grave (F)	3360	spring 1991	11.37	9.24	5.43	13.37	14.48	This work
La Grave (F)	3360	winter-spring 1991	7.05	3.56	2.6	6.2	7	This work
Glaciers (CH-I-A)	~3000	winter 1990/91	—	1.2-5.4	1.45-21.2	3.6-10.95	4.1-6.9	Maupetit et al. (1993)
Glaciers (CH-I-A)	~3000	spring 1991	—	6.2-12.8	8.4-16.5	8.4-25.9	10.6-18.9	Maupetit et al. (1993)
Glaciers (CH-I-A)	~3000	winter-spring 1991	—	4.6-7.7	5.9-13.2	6.6-17	8-13.1	Maupetit et al. (1993)
Innervillgraten (A)	1730	winter 1984/85	12.9	13.6	—	8.6	13.1	Puxbaum et al. (1988)
Le Casset (F)	1650	winter 1986/87	2.2	2.3	9.3	4.1	5.2	Delmas (1989)
Le Casset (F)	1650	winter 1987/88	4.7	2.8	3.6	4.4	5.6	Delmas (1989)
Ciste Mhearad (GB)	1100	winter-spring 1987	38	9.8	2.5	20.4	32.5	Davies et al. (1992)
Kufstein (A)	700	winter 1984/85	19.8	30.7	—	33.6	33.7	Puxbaum et al. (1988)
Col du Donon (F)	700	spring 1985	28.7	71.1	6.4	54.8	33.9	Colin et al. (1989)
Bern (CH)	540	winter 1982/83	22.6	20.4	10.9	15	23.8	Fuhrer (1984)
Bern (CH)	540	spring 1983	32.2	41.6	17.4	32.9	43.7	Fuhrer (1984)

the high alpine troposphere appears to be characteristic of free tropospheric conditions during wintertime. In Table 8, we compiled the volume weighted mean concentrations of the ions contributing to the acid-base balance of precipitation in mountain sites at different altitudes. Most of this data were obtained from snowpack samplings in winter and spring, and can be directly compared, except for the low altitude sites (Innervillgraten, Kufstein and Bern) where samples were collected with automatic samplers, and where precipitation occurs as rain in springtime. During wintertime, snow concentrations are extremely low at alpine site whose elevation is higher than 3000 m.a.s.l., especially in the French Alps which are in the low side of the values reported for the other alpine glaciers. The concentrations are increasing with decreasing altitude, and with the increasing influence of anthropogenic activities (Kufstein, Col du Donon, city of Bern). This observation suggests that winter precipitation samples collected at high alpine sites (> 3000 m.a.s.l.) are representative of the continental free troposphere over Europe.

*3.3.3. Spatial and temporal variations of snow chemistry in the French Alps.* As the snow accumulation rates (Table 1) and the volume weighted mean concentrations (Table 3), the ionic loads at the end of the accumulation period reported in Table 9 for each of the sampling sites, fall also within a comparable range. The most important on-site yearly variations of the ionic loads (up to a

factor of three) are observed for sea-salt ( $\text{Na}^+$ ,  $\text{Cl}^-$ ) and soil dust ( $\text{K}^+$ ,  $\text{Mg}^{2+}$ ,  $\text{Ca}^{2+}$ ,  $\text{HCO}_3^-$ ) derived ions. These variations can be explained by the episodic character of saharan dust transport towards the Alps during winter and spring, with very high concentrations of soil dust derived ions, but also of sea-salt ions (see Subsection 3.4). On the contrary, the deposition rates of the ions ( $\text{H}^+$ ,  $\text{NH}_4^+$ ,  $\text{NO}_3^-$ ,  $\text{SO}_4^{2-}$ ) contributing to the acid-base equilibrium of alpine snow, are very comparable on the geographical scale of the French Alps, and from year to year. Despite this relative homogeneous distribution, during this three year study, the mean ionic loads of  $\text{H}^+$ ,  $\text{NH}_4^+$ ,  $\text{NO}_3^-$  and  $\text{SO}_4^{2-}$  were respectively 12.35, 9.95, 11.57 and 19.71  $\text{m eq m}^{-2}$  at Chamonix, and 6.25, 6.53, 6.38 and 13.84  $\text{m eq m}^{-2}$  at La Grave, Alpe d'Huez and Tignes taken all together. Thus,  $\text{H}^+$  and  $\text{NO}_3^-$  ionic loads were two times higher, and  $\text{NH}_4^+$  and  $\text{SO}_4^{2-}$  ionic loads were one and a half time higher at Chamonix than on the other studied glaciers. The importance of the vertical transport of polluted air from lower regions has already been invoked to explain the seasonal pattern of alpine snow chemistry, but it is unlikely that this effect should be responsible for this difference. Another explanation could be linked to a local or regional pollution source, and we can make the assumption that the increasing international transport between France and Italy across the Mont Blanc tunnel (1.9 million vehicles in 1990) may represent a

Table 9. Total water equivalent (mm) and ionic loads ( $\text{meq m}^{-2}$ ) at the end of the accumulation period at the different sampling sites: LG: La Grave, AH: Alpe d'Huez, T: Tignes, C: Chamonix (and % due to alkaline samples)

	Wat. eq.	$\text{Na}^+$	$\text{NH}_4^+$	$\text{K}^+$	$\text{Mg}^{2+}$	$\text{Ca}^{2+}$	$\text{H}^+$	$\text{Cl}^-$	$\text{NO}_3^-$	$\text{SO}_4^{2-}$	$\text{HCO}_3^-$
LG 1989	1540 (34)	2.61 (77)	5.97 (55)	0.47 (68)	1.44 (74)	14.02 (87)	4.01 (0)	3.01 (71)	5.30 (50)	14.29 (57)	5.66 (100)
LG 1990	1890 (21)	7.61 (14)	9.74 (17)	2.44 (12)	1.57 (27)	11.43 (52)	7.57 (0)	8.63 (13)	7.40 (17)	16.78 (20)	2.61 (100)
LG 1991	1945 (30)	2.55 (74)	8.00 (41)	0.65 (63)	1.53 (81)	23.56 (88)	9.54 (0)	2.72 (61)	9.88 (25)	20.46 (49)	14.4 (100)
AH 1989	1710 (33)	4.84 (47)	11.77 (44)	1.40 (55)	1.80 (46)	14.05 (66)	3.76 (0)	5.35 (41)	6.69 (43)	19.15 (37)	4.54 (100)
AH 1990	1660 (15)	5.15 (22)	4.54 (32)	0.77 (18)	1.55 (38)	9.60 (59)	6.15 (0)	5.69 (22)	4.11 (29)	10.36 (24)	2.72 (100)
AH 1991	1500 (12)	2.60 (20)	3.66 (25)	0.66 (17)	0.72 (58)	7.72 (69)	6.73 (0)	2.55 (19)	4.63 (18)	10.85 (28)	3.20 (100)
T 1989	1375 (15)	2.92 (19)	5.41 (14)	0.75 (17)	1.04 (14)	5.83 (18)	5.14 (0)	3.17 (19)	5.60 (18)	10.82 (18)	0.46 (100)
T 1990	1955 (20)	2.82 (47)	3.73 (28)	1.08 (64)	1.10 (40)	15.00 (69)	5.80 (0)	3.01 (45)	4.82 (31)	10.05 (34)	6.31 (100)
T 1991	1510 (25)	1.15 (42)	5.96 (30)	0.39 (41)	1.37 (46)	8.40 (42)	7.52 (0)	1.83 (37)	9.03 (13)	11.82 (20)	1.96 (100)
C 1989	2430 (7)	2.66 (12)	8.33 (3)	0.79 (14)	1.51 (7)	7.79 (5)	8.44 (0)	3.59 (9)	9.75 (2)	15.90 (3)	0.03 (100)
C 1990	2385 (2)	4.20 (26)	13.58 (15)	1.00 (20)	2.13 (30)	11.01 (42)	15.76 (0)	4.68 (18)	13.33 (14)	27.23 (19)	0.28 (100)
C 1991	2060 (10)	1.07 (18)	7.94 (10)	0.49 (12)	0.74 (23)	6.68 (32)	12.85 (0)	1.99 (16)	11.62 (6)	15.99 (8)	0.49 (100)

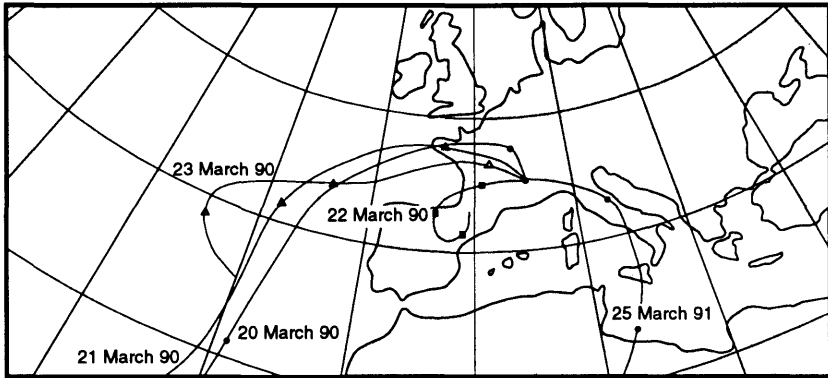


Fig. 5. 700 hPa air mass back-trajectories arriving at La Grave on 20–23 March 1990.

possible pollution source. Typical vehicle exhaust tracers should be investigated in future snow chemistry studies in the Mont Blanc area in order to check this hypothesis.

### 3.4. Three case studies of Saharan dust transport towards the Alps

Three days isobaric back-trajectories arriving at Glacier de la Girose, La Grave were computed every 6 h on the basis of ECMWF wind fields, at 850, 700 and 500 hPa by the Institute of Meteorology and Geodynamics of Vienna University (Austria), in the framework of the ALPTRAC project. We mainly used the 700 hPa level trajectory ( $\sim 3000$  m.a.s.l.) which fits better to the altitude of our sampling site.

For all examined samples, at first sight, no local particles ( $r > 10 \mu\text{m}$ ) were found, and all observed material is characteristic of long-range transport. Their typical mineralogical composition consists in a mixture of quartz, feldspars and clays (mainly illite), and for some of the samples submicronic kaolinites and palygorskite fibers (Table 10). The association of those insoluble particles with high amounts of soluble calcium carbonate is typical of aeolian dust originating from North–West Africa (Schütz and Sebert, 1987; Coudé-Gaussen, 1991).

**3.4.1. 20–23 March 1990.** This first case of saharan dust transport occurred during an intensive ALPTRAC fieldwork campaign (Tschiersch et al., 1990; Schwikowski et al., 1990; 1993). Dust was first transported westward to the African coast, then picked up by an extended trough over

the Atlantic Ocean and transported northward, and finally was brought to the Alps in a westerly flow. A cold front embedded in this flow caused precipitation (dated to March 25 at La Grave) and ended this episode which affected all the Alps (Schwikowski et al., 1993). 72 hours back-trajectories arriving at La Grave and plotted for this period (Fig. 5) show only the end of this indirect transport from Africa which last more than a week (Schwikowski et al., 1993). This event appears clearly in the *Tignes 1990 snowcore* (Fig. 6),

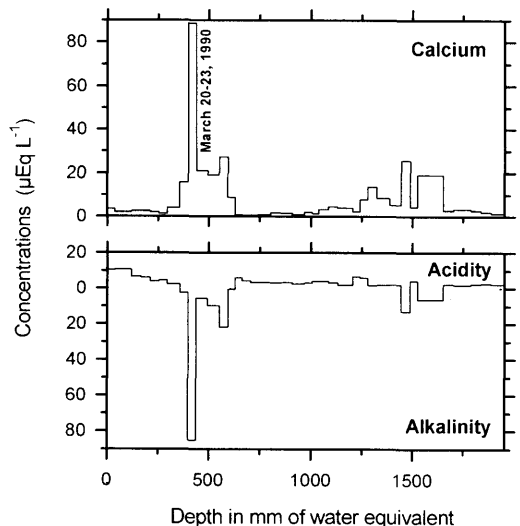


Fig. 6. Concentration profiles ( $\mu\text{eq l}^{-1}$ ) of  $\text{Ca}^{2+}$  and  $\text{H}^+$  (or  $\text{HCO}_3^-$ ) in the *Tignes 1990 snowcore*, from late summer-fall 1989 (right) to May 1990 (left).

and was also observed on the other studied glaciers of the French Alps (Maupetit, 1992). We measured very high concentrations of  $\text{Na}^+$  and  $\text{SO}_4^{2-}$  ( $75 \mu\text{eq l}^{-1}$  and  $88 \mu\text{eq l}^{-1}$ , respectively, Table 10).

**3.4.2. 5–8 March 1991.** This second case is due to a very active trough of low pressure centered westward of the Portuguese coast, which caused important precipitations over the Alps. Back-trajectories suggest that air masses swept the extreme North–West of Africa (Morocco and Western Algeria) and crossed very quickly the Mediterranean before reaching alpine reliefs (Fig. 7). This case represents the most rapid and direct dust transport pathway from the Sahara, and its chemical fingerprint can be observed in the *La Grave 1991 snowcore* (Fig. 2). During this event, the  $\text{Ca}^{2+}$  and  $\text{HCO}_3^-$  concentrations were almost equivalent ( $120.7$  and  $109.3 \mu\text{eq l}^{-1}$ , respectively), while the  $\text{SO}_4^{2-}$  and  $\text{Na}^+$  concentrations were low ( $6.5$  and  $1 \mu\text{eq l}^{-1}$ , respectively). The same pattern was also observed (Fig. 2) for the *La Grave 1991 snowcore*  $\text{Ca}^{2+}$ ,  $\text{HCO}_3^-$  and  $\text{SO}_4^{2-}$  concentrations ( $\sim 70$ ,  $60$  and  $20 \mu\text{eq l}^{-1}$ , respectively). We therefore labelled this case as “*pure CaCO<sub>3</sub>*”.

We associated to the 5–8 March 1991 event, the 9 March 1990 event which is similar for both probable source regions and transport pathway. The only difference between these two cases is due to a weak high pressure system in the Eastern Mediterranean which pushed away the air mass above eastern Spanish coasts (Fig. 7). Then microsoot particles, and higher  $\text{SO}_4^{2-}$  concentra-

tions were found (Table 10), suggesting interactions of the saharan air mass with polluted air from industrial regions, like Catalonia in North-Eastern Spain.

**3.4.3. 25 March 1991.** The perturbation which caused precipitation at La Grave on the 25 March 1991 was due to an active trough, centered in the Mediterranean westward of Sardinia. The air mass crossed the Mediterranean anticlockwise and reached the Alps after a passage above Italia (Fig. 7). The transport last more than 2 days and the probable sources may be located in Libya, as suggested by back-trajectory and by mineralogical analysis of palygorskite fibers (Table 10). The observation of those fibers, which should be formed preferentially in carbonated crusts (Coudé-Gaussen, 1991), together with calcium carbonate, is typical from North Algerian and North–West Libyan regions (Schütz and Sebert, 1987; Coudé-Gaussen, 1991). High concentrations of  $\text{SO}_4^{2-}$  and microsoot particles were also found (Table 10), indicating a possible influence of pollution sources, presumably from Northern Italy.

### 3.5. The impact of Saharan dust on high alpine glacier snow chemistry

Mean, standard deviation and extreme values of the distribution of the alkaline snowcores concentrations are summarized in Table 2. All ions are present in a wide concentration range. Compared to the acid samples, *alkaline snowcores* samples present much higher concentrations of soil-dust derived ions ( $\text{K}^+$ ,  $\text{Mg}^{2+}$ ,  $\text{Ca}^{2+}$ ,  $\text{HCO}_3^-$ ), but also of sea-salt ions ( $\text{Na}^+$ ,  $\text{Cl}^-$ ) and of  $\text{SO}_4^{2-}$  (>97%

Table 10. Date of snowfall, ionic concentrations ( $\mu\text{eq l}^{-1}$ ), number of mineralogical analysis performed, and mineralogical observations for the main dust events in *La Grave fresh-snow* during 1989/1990 and 1990/1991 winters

Date	Concentrations ( $\mu\text{eq l}^{-1}$ )				No. analyses	quartz	feld.	Phyllosilicates					Micro-soot	Fly ash	Volcanic glass	
	$\text{Na}^+$	$\text{Ca}^{2+}$	$\text{HCO}_3^-$	$\text{SO}_4^{2-}$				Ill.	smect.	kaol.	palyg.	chlor.				
3/25/90	75.5	219.5	164.3	88	8	+		++								(+)
3/9/90	10.65	59	35.5	26.3	15	+	+	++								(+)
3/7/91	1	120.7	109.3	6.5	12			+								
3/25/91	0.87	18.4	10.4	7.45	11			+	++	(+)	(+)					
3/25/91	2.42	29.3	14.7	15.4	8			++	(+)	+						
3/25/91	175	337	267	215	11	+	+	++				+				

Relative abundance: (+), +, ++ : scarce, abundant, very abundant, respectively.

feld. = feldspar, Ill. = illite, smect. = smectite, kaol. = kaolinite, palyg. = palygorskite, chlor. = chlorite.

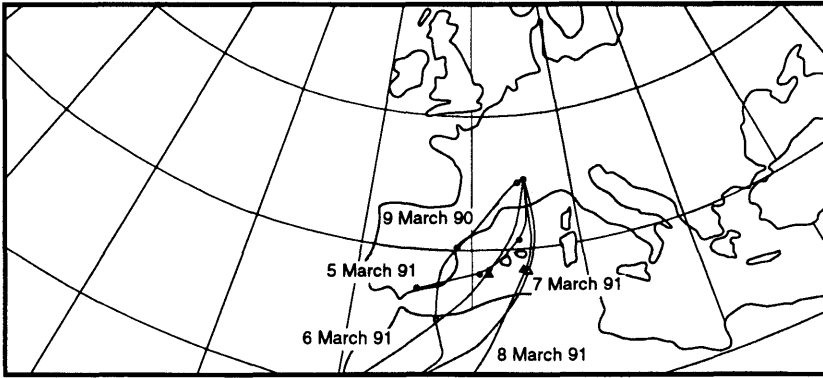
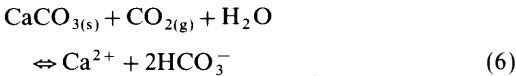


Fig. 7. 700 hPa air mass back-trajectories arriving at La Grave, on 9 March 1990, 5–8 March 1991 and 25 March 1991.

of non-sea-salt origin). The main soluble fraction of dust containing samples appears to be derived from calcium carbonate dissolution. Indeed, the representative dissolution reaction of  $\text{CaCO}_3$  in an open system leads to the presence of calcium and bicarbonate ions (Stumm and Morgan, 1981), according to:



The % of alkaline samples contribution to the total deposition rate is presented in Table 9. While alkaline samples account for only 10 to 35% of the net water accumulation, they can represent from 20 to 85% of soil-dust derived ions ( $\text{K}^+$ ,  $\text{Mg}^{2+}$  and mainly  $\text{Ca}^{2+}$ ) deposition, from 15 to 75% of sea-salt ions ( $\text{Na}^+$ ,  $\text{Cl}^-$ ) deposition, and from 20 up to 55% of  $\text{SO}_4^{2-}$  deposition. They can also represent in some cases (La Grave 1989 and 1991; Alpe d'Huez 1989; Tignes 1990), a significant contribution to  $\text{NO}_3^-$  and  $\text{NH}_4^+$  total ionic loads. These observations are not particularly surprising for terrigenous ions due to their obvious saharan origin. More surprising is the link between mineral dust, sea-salt ions and acid compounds (in particular  $\text{SO}_4^{2-}$ ). This association suggests that, during their transport towards the Alps, the saharan air masses are influenced by air from lower altitudes. In fact, the meteorological situations (frontal systems) causing dust transport, allow vertical exchanges (Whelpdale and Moody, 1990)

between the upper tropospheric layers and the marine boundary layer above the Mediterranean or the Atlantic, and the continental boundary layer above continents or when reaching alpine reliefs. Considering that, during this transport, cloud droplets undergo several cycles of evaporation-condensation before being deposited as precipitation, this processing by clouds leads to an internal mixture of mineral dust, sea-salt aerosols

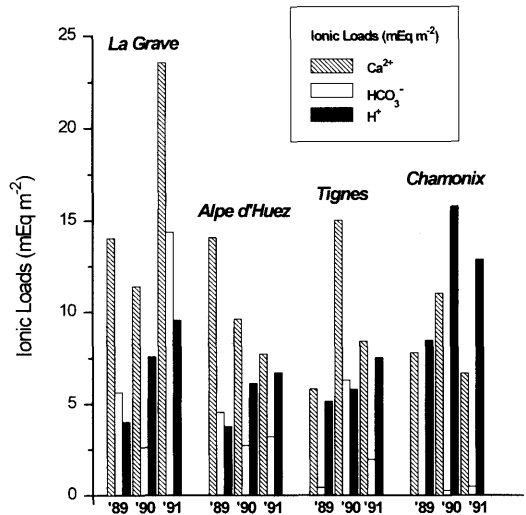


Fig. 8. Ionic loads ( $\text{meq m}^{-2}$ ) of  $\text{Ca}^{2+}$ ,  $\text{HCO}_3^-$  and  $\text{H}^+$  at the end of the accumulation periods 1989, 1990 and 1991 on each sampling sites (arithmetic values from Table 9).

and anthropogenic compounds, as already pointed out by Andreae et al. (1986).

We illustrated in Fig. 8 the spatio-temporal variations of saharan dust deposition onto French Alps glaciers. Due to the highly episodic character of dust transport towards Europe, the on-site interannual variations of  $\text{Ca}^{2+}$  and  $\text{HCO}_3^-$  deposition to the snowcover is relatively important. Spatial variations at the scale of the French Alps can also be important and seems to be influenced by transport pathways. For instance, in 1990, the main dust event (20–23 March 1990) reached the Alps in a westerly flow (Fig. 5), affecting rather evenly the different glaciers located along a north–south transect, while in 1991, the two main events (5–8 March and 25 March 1991) arrived in southerly flows (Fig. 7), causing important precipitations on the first encountered reliefs, affecting much more the Southern (in particular La Grave) than the Northern French Alps.

*3.5.1. Neutralizing reactions between alkaline dust particles and acid compounds during transport.* As already mentioned, in case of dust transport, the chemical composition of snow consists in a mixture of dust particles, sea-salt ions and pollution compounds, indicating cloud processed interactions between these species, and in particular between alkaline particles and atmospheric acid compounds. Based on our observation of the 5–8 March 1991 event, we made the hypothesis that calcite ( $\text{CaCO}_3$ ) was the main saharan dust soluble species, and the dominant form of calcium against gypsum ( $\text{CaSO}_4$ ). This assumption is consistent with dust observations in North–West African source regions (Paquet et al., 1984; Schütz and Seibert, 1987; Coudé-Gaussen, 1991), and after transport (Loye-Pilot et al., 1986). Therefore, if we make the assumption that the main unaltered mineral dust soluble species is  $\text{CaCO}_3$ , the occurrence of acid-base reactions should be reflected by calcite neutralization, which can be characterized by the  $\text{HCO}_3^-/\text{Ca}^{2+}$  ratio. In order to assess this potential effect, we considered the whole *alkaline snowcores* data set, and divided it into three groups according to the  $\text{HCO}_3^-/\text{Ca}^{2+}$  ratio of each sample:

group (1):  $\text{HCO}_3^-/\text{Ca}^{2+} > 0.75$

group (2):  $0.30 < \text{HCO}_3^-/\text{Ca}^{2+} < 0.75$

group (3):  $\text{HCO}_3^-/\text{Ca}^{2+} < 0.30$

Then, we observed the distributions of  $\text{SO}_4^{2-}$ ,  $\text{NO}_3^-$  and  $\text{NH}_4^+$  within each group (Fig. 9).

Considering that in the first group neutralizing reactions almost did not occur, we made the hypothesis that the calcium which is not in the form of calcite represents natural gypsum, roughly estimated, from the slope of the regression line between  $\text{SO}_4^{2-}$  and  $\text{Ca}^{2+}$ , to be  $\sim 13\%$  of total calcium. Within the first group, no clear trends are observed for  $\text{SO}_4^{2-}$  (small increase representing soil-dust derived  $\text{CaSO}_4$ ),  $\text{NO}_3^-$  and  $\text{NH}_4^+$ . Thus, this first group is likely to be representative of saharan dust aerosols nearly unaltered during transport. In the second group,  $\text{SO}_4^{2-}$  is increasing with  $\text{Ca}^{2+}$  and decreasing  $\text{HCO}_3^-$ , indicating the beginning of neutralization reactions.  $\text{NO}_3^-$  and  $\text{NH}_4^+$  are still not affected. Finally, in the third group, supposed to represent the strong neutralization case,  $\text{SO}_4^{2-}$  present a sharp increase with increasing  $\text{Ca}^{2+}$  ( $\text{SO}_4^{2-}$  is then present as a neutral salt), and  $\text{NO}_3^-$  and  $\text{NH}_4^+$  also present higher concentrations.

The case of Chamonix provides another evidence of the occurrence of such neutralization reactions. The deposition of mineral dust is not significantly different at Chamonix than at Tignes or Alpe d'Huez if we take  $\text{Ca}^{2+}$  as indicator, while the  $\text{HCO}_3^-$  deposition is extremely low (Table 9). As already pointed out in Subsection 3.3, the snow acidity is two times higher at Chamonix, and  $\text{Ca}^{2+}$  is always deposited here under an almost fully neutralized form.

The neutralization reactions of calcite-rich particles appears to occur firstly with sulfur ( $\text{H}_2\text{SO}_4$  or  $\text{SO}_2$ ), and then with nitrogen ( $\text{HNO}_3$  or  $\text{NO}_2$ ) compounds. This is in good agreement with observations of Antarctic (Legrand et al., 1988) and Greenland ice (M. Legrand, personal communication) during the last glacial stage. It remains difficult from our results to detail or to propose reaction mechanisms, and in particular to detail if those reactions occur at the surface of particles or in cloudwater liquid phase. Several reactions were proposed to explain this frequently observed association between sulfur compounds and mineral dust (Schotterer et al., 1985; Andreae et al., 1986; Talbot et al., 1986; 1990; Iwasaka et al., 1988; Legrand et al., 1988; Winchester and Wang, 1989; Savoie et al., 1989; Okada et al., 1990; Li and Winchester, 1990; Levin et al., 1990; Mamane et al., 1992). In particular the mecha-



nisms of  $\text{SO}_2$  adsorption at the surface of dust particles and subsequent oxidation in  $\text{H}_2\text{SO}_4$ , or direct adsorption of  $\text{H}_2\text{SO}_4$  (Winchester and Wang, 1989; Li and Winchester, 1990), the dissolution of  $\text{SO}_2$  in a liquid film around dust particles and liquid phase oxidation, or the direct dissolution of  $\text{H}_2\text{SO}_4$  (Iwasaka et al., 1988; Okada et al., 1990), and the metal oxide catalysed transformation of  $\text{SO}_2$  to  $\text{SO}_4^{2-}$  on  $\text{CaCO}_3$  (Hutchinson et al., 1992) have been investigated in details.

The different behaviour of  $\text{SO}_4^{2-}$  and  $\text{NH}_4^+$  in presence of  $\text{CaCO}_3$  seems to indicate that these ions are not involved as ammonium-sulfate aerosols. Thus, the sulfate pattern observed in Fig. 9 is more likely due to the neutralization of calcite by  $\text{H}_2\text{SO}_4$  or  $\text{SO}_2$ .

Concerning nitrate and ammonium, the trends observed in Fig. 9 are less obvious than for sulfate,

and their concentrations are only significantly increasing in the strong neutralization case (group 3).

The association between nitrate and mineral dust has also been already reported (Schotterer et al., 1985; Legrand et al., 1988; Ganor and Pueschel, 1988), and the heterogeneous reactions of  $\text{NO}_2$  and  $\text{HNO}_3$  on  $\text{CaCO}_3$  studied (Ganor and Pueschel, 1988; Mamane and Gottlieb, 1992). As revealed by the different cases presented in Subsection 3.4, the high concentrations of sulfate and nitrate associated to mineral dust are observed when the saharan air mass appears to be, to some extent, influenced by polluted air. Therefore, at first sight, the dust-related sulfate and nitrate are likely to be mainly derived from european anthropogenic sources. Aerosol observations of dust-derived  $\text{NO}_3^-$  and  $\text{SO}_4^{2-}$  at Barbados (Savoie et al., 1989) and in Central Amazonia (Talbot

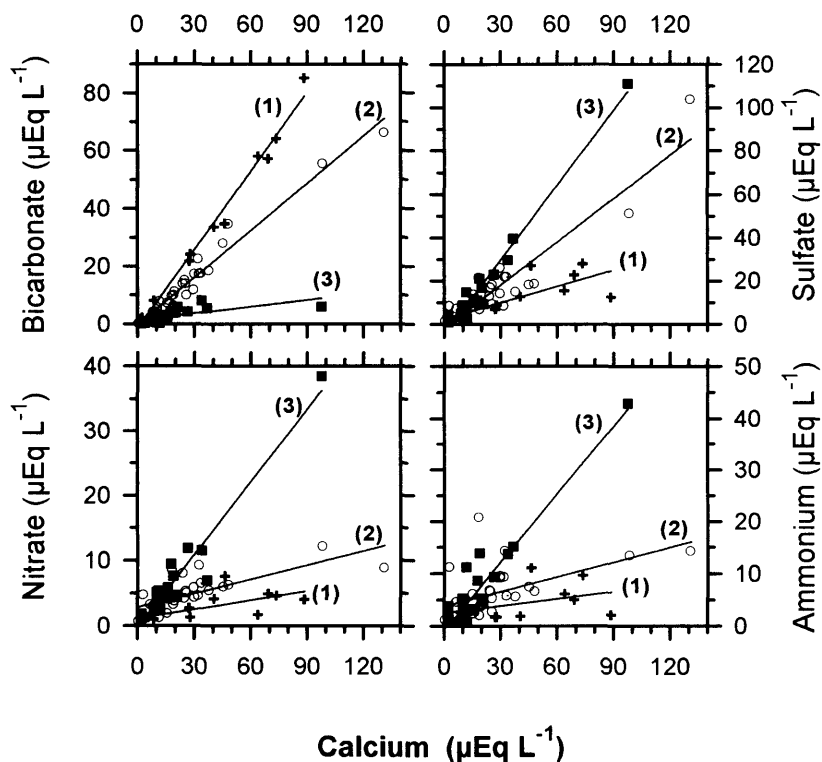


Fig. 9. Relationship between  $\text{HCO}_3^-$ ,  $\text{SO}_4^{2-}$ ,  $\text{NO}_3^-$ ,  $\text{NH}_4^+$  and  $\text{Ca}^{2+}$  ( $\mu\text{eq l}^{-1}$ ) for the alkaline *snowcores* samples, separated in groups 1, 2 and 3 (see text for explanation), the solid line represents the linear regression fits.

et al., 1990) provided indications that the biomass burning products emitted in tropical Africa, south of the Sahara, could be long-range transported in association with mineral dust. Indeed, fires are frequent throughout the sub-saharan belt during the dry season and represent a significant source of sulfur and nitrogen oxides (Andreae et al., 1988; Crutzen and Andreae, 1990). Generally, the northward transport of biomass burning products emitted in tropical Africa is limited by the Inter-tropical Convergence Zone (ITCZ), but vertical convection in the ITCZ allow burning emissions to reach the upper troposphere, and to be long-range transported (Crutzen and Andreae, 1990). Therefore, it remains unclear if tropical fires can have a significant impact on the North–West African regions, and on Southern Europe, when particular meteorological conditions allows long-range transport from Africa. Although, if we cannot entirely rule out that biomass burning south of the Sahara can account for the high sulfate, nitrate and ammonium concentrations in some of our snow samples, we do not think that they represent the main explanation for the patterns observed in Fig. 9.

Concerning  $\text{NH}_4^+$ , its association with  $\text{Ca}^{2+}$  is, as for  $\text{NO}_3^-$ , less obvious than for  $\text{SO}_4^{2-}$ , and is more surprising since ammonium originates from atmospheric ammonia. Thus, other explanations than acid-base neutralizations, have to be invoked in order to explain this dust-related ammonium.  $\text{NH}_4^+$  is generally present in the high alpine atmosphere as a combination of ammonium-sulfate aerosols, which can be removed by different scavenging processes. In particular, in presence of saharan dust, the brownian impaction process of ammonium-sulfate submicronic aerosols on larger mineral aerosols should be enhanced. Another possible explanation is that, as the ammonium-sulfate aerosol is not in its neutral form  $(\text{NH}_4)_2\text{SO}_4$ , but in a stoichiometry closer to  $\text{NH}_4\text{HSO}_4$ , it can react with alkaline dust through neutralization reactions. Finally, we observed a good correlation between  $\text{NH}_4^+$  and  $\text{NO}_3^-$  for the *alkaline snowcores* samples (slope: 1.12, intercept: 0.62,  $r^2 = 0.89$ ), indicating a possible contribution of  $\text{NH}_4\text{NO}_3$  aerosols. As reported from atmospheric equilibrium aerosol model,  $\text{NH}_4\text{NO}_3$  can be formed if the initial liquid phase acidity is fully neutralized (Bassett and Seinfeld, 1983). As during dust events  $\text{CaCO}_3$  does efficiently neutralize sul-

furic acidity (Fig. 9), the formation of  $\text{NH}_4\text{NO}_3$  aerosol becomes possible.

Hence, calcite-rich particles from the Sahara are able to react through acid-base neutralization with atmospheric sulfur species ( $\text{SO}_2$  or  $\text{H}_2\text{SO}_4$ ), presumably mainly of anthropogenic origin, contributing to enhanced deposition rates of  $\text{SO}_4^{2-}$  to high alpine snowfields. Considering that mineral dust is the major component of aerosols in the Sahara surroundings and in some other desert areas of the world, then alkaline precipitation most likely represents a major sink of atmospheric sulfur compounds. It remains unclear from our results what the main reasons for the observed dust-related nitrate and ammonium are.

*3.5.2. Neutralization of the acidity stored in the snowpack.* When alpine regions are not influenced by mineral dust transport, alpine glaciers store acid precipitation in consecutive snow layers. The occurrence of saharan dust leads to a few alkaline layers embedded within the winter–spring snowpack. Since studied glaciers are temperate and hence impurities are washed out during late spring–summer percolation (see, e.g., review by Tranter, 1991), we want here to discuss about the potential of such alkaline layers to neutralize the accumulated acidity. During melting, soluble species undergo fractionation from snow into meltwater (Tranter, 1991). In other words, 80 to 90% of the soluble species will be washed out from the snowcover, during the first 25% of its melting. The neutralization efficiency of dust particles also depends on their relative position in the snowpack (Delmas, 1989). Generally, the snow is more acid in spring than in winter, and we can simply describe the beginning of melting with meltwater percolating from the more acid spring surface layers, through deeper layers including dust bands deposited in early spring, as in March 1990 and 1991, or in late summer–fall as commonly observed at the bottom of the snowcores.

We reported in Fig. 8, the ionic loads of  $\text{H}^+$  at the end of the accumulation period. For La Grave, Alpe d'Huez and Tignes, the amount of  $\text{HCO}_3^-$  is theoretically able to neutralize partially, or even completely (La Grave 1989 and 1991, Alpe d'Huez 1989 and Tignes 1990) the acidity stored in the accumulated snowpack. Thus, mineral dust most likely represents an important acidity buffering agent, at the onset of melting, for temperate glaciers.

#### 4. Summary and conclusions

In absence of alkaline dust transport from the Sahara, the high alpine snow is slightly acid ( $H^+ \sim 3\text{--}20 \mu\text{eq l}^{-1}$ ). This acidity, mainly of anthropogenic origin, is principally due to nitric acid, sulfuric acidity being partially neutralized by atmospheric ammonia and by soil-dust derived aerosols before being deposited. Without the buffering action of alkaline species, the free acidity of high alpine snow should be doubled. Winter precipitation at high altitudes in the Alps appears to be representative for continental free tropospheric conditions over Western Europe. Compared to winter, all measured ions are presenting a sharp increase in spring snow, indicating the importance of upward transport from lower altitude polluted regions on the impurity content of high alpine snow.

Both air-mass trajectories and mineralogical analyses confirmed that all major dust events reaching the Alps originated from the saharan regions. Very high concentrations of  $Ca^{2+}$  and  $HCO_3^-$  in corresponding samples, indicate that solubilisation of calcite ( $CaCO_3$ ) represents the major influence of saharan dust on the soluble fraction of alpine precipitation, changing its pH from slightly acid to alkaline conditions. Based on the observation of calcite neutralization, acid-base reactions were investigated: calcite-rich saharan dust par-

ticles are able to react with atmospheric sulfur species ( $SO_2$  or  $H_2SO_4$ ) and, to a lesser extent, with nitrogen species ( $HNO_3$  or  $NO_2$ ). It is suggested that, on a global scale, the neutralization by alkaline dust could be an important deposition process of sulfur species. Calcium carbonate particles deposited in the snowpack represent an important buffering agent for the acidity accumulated during winter and spring, at the onset of late spring–summer percolation.

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