

## Chemical composition and shape of snow crystals in Antarctica

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**Summary.** — Fresh snow samples collected in a coastal Antarctic site (Terra Nova Bay) were examined by considering both the chemical composition and ice crystal shape. Measured concentrations in snow samples show that nucleation is the dominant aerosol scavenging process. An additional contribution from phoretic forces to aerosol scavenging during growth of ice crystals can be deduced from the correlation between non sea-salt sulphate ( $\text{nss-SO}_4^{2-}$ ) and methanesulfonic acid (MSA) measured in snow samples. The sea-salt contribution is dominant, as usually observed in the coastal Antarctic stations. By determining sea-salt from  $\text{Na}^+$  concentration, the values of  $4400 \mu\text{g l}^{-1}$ ;  $2400 \mu\text{g l}^{-1}$ ;  $2900 \mu\text{g l}^{-1}$ ;  $650 \mu\text{g l}^{-1}$  were obtained for the examined samples. The  $\text{NO}_3^-/\text{Na}^+$  ratio in fresh snow (range 0.1–0.6), much higher than the value in sea-water (about  $10^{-4}$ ), excludes a marine origin for  $\text{NO}_3^-$  ion, suggesting a continental and/or stratospheric source. Organic compounds (propionate, acetate, formate, MSA and glycolate) were in addition measured in snow samples. Ice crystal replicas were made by collecting crystals on microscope slides, previously covered with a thin layer of 2% formvar in chloroform. Samples were analyzed by a scanning electron microscope (SEM). A large variety of ice crystal habits (needles, hexagonal plates, crystals with branches, dendritic crystals, etc.) were observed. In the examined replicas of different events, cases are noted in which simple plates are prevalent, others in which prevalently complex crystal shapes are observed, and others again in which simple and complex crystal shapes are present simultaneously.

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### 1. – Introduction

The chemical composition of precipitation is determined by the interaction of numerous processes, including spatial distribution of sources, transport, chemical transformation, scavenging of aerosol particles and gases within and below clouds, and the mechanisms of hydrometeor formation (*e.g.*, riming, water vapour deposition).

Scavenging processes involve aerosol particles through different mechanisms (nucleation, inertial impaction, interception, diffusiophoresis, thermophoresis, convective Brownian diffusion, electric effects) and compounds in the gas phase. As a result, the concentration of chemical species in precipitations are found to vary widely and the relationship between the concentrations of pollutants in the atmosphere and in bulk snow or rain is rather complex.

The most complicated scavenging scenario occurs in mixed-phase clouds, *i.e.* clouds containing both supercooled cloud droplets and ice crystals. Because growing ice crystals are always warmer than their environment as a result of the latent heat of sublimation, phoretic forces play an important role in the scavenging of sub-micron aerosol particles.

Ice crystals in stratiform clouds can grow due to the diffusion of water vapour at the expense of existing supercooled cloud droplets (also known as the Bergeron-Findeisen process) or the riming process, *i.e.* collection and freezing of supercooled droplets by falling snow crystals. The latter process depends on the size and shape of ice crystals and droplets diameter. Theoretical and experimental research has shown that the riming process determines a greater concentration of pollutant in hydrometeors than diffusional growth [1-3]. In fact the pollutants present in the supercooled droplets are transferred completely or partially (in the case of dissolved gases) to solid hydrometeors during freezing.

Harimaya [4] and Kikuchi and Uyeda [5] showed that the onset of riming is unlikely for droplets of less than  $10\ \mu\text{m}$  from planar snow crystals. In the case of columnar crystals, a minimum radius of  $25\ \mu\text{m}$  is necessary before riming will occur while hexagonal plates must be a minimum of  $150\ \mu\text{m}$  in radius [6]. Harimaya [4] examined hexagonal plates ( $d = 1580\ \mu\text{m}$ ), finding that the size distribution of accreted droplets has a mode at about  $28\ \mu\text{m}$ , and dendritic crystal ( $d = 2880\ \mu\text{m}$ ) at about  $23\ \mu\text{m}$ .

Stratiform clouds are common over Antarctica, and normally consist of supercooled water droplets, sometimes mixed with ice crystals, presenting a liquid water content of the order of  $0.1\ \text{gm}^{-3}$  [7, 8]. Saxena and Ruggiero [9] observed a bimodal cloud droplet size distribution ( $d_1 = 5\ \mu\text{m}$ ;  $d_2 = 10\ \mu\text{m}$ ) in Antarctic clouds.

The goal of this research is to characterize chemically a few events of fresh snow precipitation during December 2006 at an Antarctic coastal site, considering the different factors which influence the ion concentrations, and taking into account also the influence of crystal shape and size.

## 2. – Theoretical approach

### a) Crystal growth phase

A large variety of ice crystal habits (needles, hexagonal plates, crystals with branches, dendritic crystals, etc.) can be obtained during growth in mixed clouds, depending primarily on air temperature and mixing ratio. From a crystallographic point of view, snow crystals have one common basic shape, namely that of a six-fold hexagonal prism with two basal planes.

Formation of ice crystals in clouds can take place when nucleation particles (*e.g.*, sea-salts, dust and mineral particles) and supercooled water droplets are present. In such conditions ice crystals grow at water saturation and experimental results show that the rate of growth of *a*-axes (basal planes) shows a maximum at  $-15\ ^\circ\text{C}$ , and is much higher than that of the *c*-axis (normal to the basal plane). The growth rate of the *c*-axis shows a maximum at about  $-5\ ^\circ\text{C}$ , a minimum at  $-15\ ^\circ\text{C}$ , and increases at  $T < -20\ ^\circ\text{C}$  [10, 11].

Ice crystals growing in these conditions attain the maximum diameter at about  $-15^{\circ}\text{C}$ , and it is much higher than the thickness (planar crystal). Columnar ice crystal formation is favoured at  $T > -10^{\circ}\text{C}$ , and at  $T > -20^{\circ}\text{C}$ .

As examples of growth time, after growth time of 10 minutes by vapour diffusion at water saturation and in free fall at ambient pressure, a dendrite reaches a dimension of 1.1 mm along the  $a$ -axis ( $T = -15^{\circ}\text{C}$ ), a hexagonal plate 0.27 mm, 0.32 mm, 0.50 mm (at  $T = -12^{\circ}\text{C}$ ,  $-15^{\circ}\text{C}$  and  $-20^{\circ}\text{C}$ , respectively), and crystals with sector-like branches 0.6 mm ( $T = -18^{\circ}\text{C}$ ) [12, 13].

More complex crystals, such as ordinary dendritic crystals, fernlike crystal or stellar crystals with plates at the end, will form at a temperature in the range between  $-13$  and  $-17^{\circ}\text{C}$ , and at high humidity conditions (water saturation or higher) [13]. Conversely, decreased atmospheric pressure increases the growth rate [14].

When a growing snow crystal falls through the atmosphere, its habit and growth rate change as it encounters different temperatures and supersaturations at different levels. With increasing size and fall velocity, diffusion and thermal fields around the crystal are enhanced, leading to more rapid growth. The changing flow patterns, characterized by increasing Reynolds number, also influence the crystal orientation as it falls. Small crystals are oriented at random, but as they grow larger they become stable oriented with the largest dimension being horizontally. Eventually, they begin oscillating and finally tumble as they approach a centimetre dimension.

Let us assume that a snow crystal of one particular habit, formed by growth at a particular temperature and humidity, is suddenly moved into a new environment of different temperature and humidity, where it continues to grow by vapour diffusion. Under such conditions the habit characteristic of the second temperature and humidity conditions become superimposed on the original habit. Thus, a columnar ice crystal suddenly surrounded by conditions characteristic of plate-like growth will develop end-plates.

Generally speaking, the terminal velocity of ice crystals falling steadily in the preferred orientation, which offers the maximum resistance to motion, depends on the drag coefficient, aspect ratio  $w/L$  ( $w$ , width;  $L$ , diameter for plate like form or length for column), and the ice crystal density. The density of natural ice crystals shows considerable variation, depending markedly on the amount of available moisture during growth. Heymsfield [15] found that the ice crystal density decreases with increasing moisture available for growth. Terminal velocity is necessary in order to study ice crystal growth in clouds, evaporation in sub-cloud regions, and in calculations of precipitation rates.

#### b) Ice crystal scavenging

Ice crystals can scavenge aerosol particles or gases during diffusional growth in clouds, or by riming, and during the fall below clouds.

Several field measurements, laboratory studies and theoretical models have been realised to determine the efficiency with which aerosol particles (AP) are scavenged by snow crystals in- and below-clouds [16-22].

Prodi [23] studied the scavenging process of NaCl particles in laboratory experiments by growing ice crystals. Santachiara *et al.* [24] obtained high efficiency aerosol scavenging during planar crystal diffusional growth. In the range of aerosol ( $0.1$ – $0.5\ \mu\text{m}$ ) and crystal diameter ( $30$ – $90\ \mu\text{m}$ ) considered, diffusion and thermophoretic forces play an important role in the scavenging efficiency.

Concerning scavenging of gases during crystal growth, it is important to note the influence of the liquid-like layer (LLL) present at the gas-ice interface, not only very near the melting point, but also considerably below it.

Its existence was first proposed by Faraday [25] to explain the results of experiments on the adhesive properties of ice. Since Faraday's work, there have been a number of experimental and theoretical works [26-28] in favour of the existence of such a layer.

The incorporation of gases into the ice during water vapour diffusion is a multi-step process, involving gas diffusion to the ice surface, accommodation of gas molecules on the surface, diffusion into the LLL of the dissolved molecules (or the products of their chemical conversion) and, finally, their incorporation into bulk ice.

According to Petrenko [29], the surface layer consists of several molecular layers, each possessing specific physical properties, gradually approaching those of the bulk ice.

Certain physical properties of the LLL are intermediate between water and ice. This holds for viscosity and diffusion coefficient, for instance. However, there are two remarkable exceptions to this rule: the optical properties of the LLL film are very similar to those of ordinary water at 0 °C, and the electric conductivity of the ice surface exceeds the electric conductivity of both ice and water by many orders of magnitude.

Temperature plays an important role in the sorption process, since it influences the sticking coefficient, the thickness of LLL, the diffusion coefficient and the gas solubility.

Scavenging of SO<sub>2</sub>, NH<sub>3</sub>, HCl during ice growth by deposition of water vapour in a range temperature 0– – 20 °C was studied by Santachiara *et al.* [30, 31], Mitra *et al.* [32], and Hoog *et al.* [33]. Concerning NH<sub>3</sub>, significant amounts of ammonia (around 200 µg l<sup>-1</sup>) were taken up during ice growth, even at low NH<sub>3</sub> concentrations (1–10 ppbv).

HCl and HNO<sub>3</sub> vapours are rapidly scavenged from the atmosphere during growth and from falling snow [34, 30].

The above laboratory experiments evidence that the gas uptake is a strong function of temperature, and that higher temperature (below the freezing temperature) favours the adsorption of high soluble gases (SO<sub>2</sub> and NH<sub>3</sub>).

The increasing gas uptake with increasing temperature is a result of the LLL, which increases in thickness as the temperature approaches 0 °C.

In addition, as LLL properties are intermediate between water and ice, lowering the temperature, the solubility decreases as it approaches gradually that of ice, which is lower than that of liquid water.

This behaviour is different from results obtained during the freezing of bulk dilute solutions of salts, acids and bases, which show that inorganic ions are partially rejected by ice [35-37]. In this case the preferential incorporation of foreign atoms or radicals into the ice lattice appears to depend mainly on their size and structure, which must be similar to that of the water molecules.

### 3. – Experimental

Fresh surface snow samples were collected (fig. 1) at Campo Icaro (74° 43'; 164° 02') at about two kilometers south of the Italian base of Terra Nova Bay (74° 42' 42" Sud; 164° 07' 14" E), at Faraglioni (74° 42' 55"; 164° 07' 25"), and at Nansen Ice sheet (74° 30' 02" S; 163° 27' 30" E), during the austral summer (December 2006).

Since post-depositional processes may alter the composition of snow chemistry, only fresh surface snow samples were collected, within 12 h of deposition.

Samples were collected using pre-cleaned plastic scrapers and were placed in pre-cleaned high-density polyethylene bottles. Each sample was collected together with a field blank, which was handled, transported and analysed as samples. Samples were kept deep-frozen until laboratory analysis.

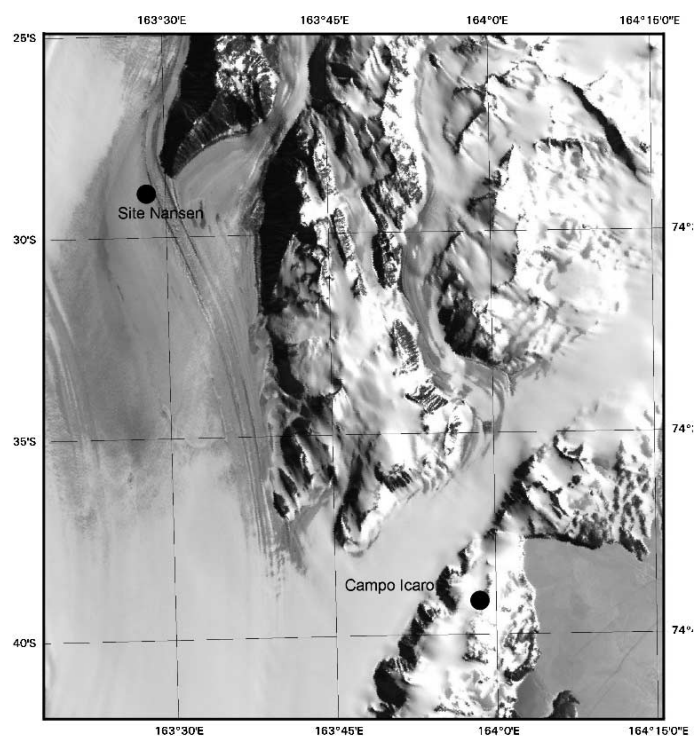


Fig. 1. – Location map.

Care was taken to minimize contamination both in the laboratory and in the field. Just before the analysis, snow samples were left to melt still closed in their containers (Coulter-Counter-type accuvettes), locked in a specifically designed autosampler tray, under a class-100 laminar-flow hood. Ion chromatographic injection was carried out by drawing up the melted sample with a stainless steel needle connected to a remote controlled peristaltic pump. The sample flow was split in three ways, filtered on a  $0.45\ \mu\text{m}$  Teflon membrane and injected into a pre-concentrator (for fluoride and organic anion determination) or  $250\ \mu\text{m}$  loop (for inorganic anions and inorganic cations separations) connected to three ion-chromatographic devices (one Dionex DX500 gradient and two Dionex ICS-1000 systems) equipped with electrochemical suppression of background conductivity. A personal computer controlled autosampler movements, operation times and valve shifts (including load/injection procedure inside the ion chromatography system). All operations and ion chromatographic measurements were carried out inside a class-10000 clean room.

Inorganic cations ( $\text{Na}^+$ ,  $\text{NH}_4^+$ ,  $\text{K}^+$ ,  $\text{Mg}^{2+}$  and  $\text{Ca}^{2+}$ ) were determined using a Dionex CG12A 4 mm guard column and a CS12A 4 mm analytical column with  $\text{H}_2\text{SO}_4$  22.5 mM (1.5 ml/min) as eluent. The sample was injected through a  $250\ \mu\text{L}$  loop washed with at least a four times higher sample volume in order to avoid memory effects.

Inorganic anions ( $\text{Cl}^-$ ,  $\text{NO}_3^-$ ,  $\text{SO}_4^{2-}$ ) and  $\text{C}_2\text{O}_4^{2-}$  (oxalate) were analysed using a Dionex AG4A-SC 4 mm guard column and an AS4A-SC 4 mm analytical column with a 2.5 mM  $\text{Na}_2\text{CO}_3$  + 2.5 mM  $\text{NaHCO}_3$  buffer solution as eluent at 2.0 ml/min. Also for this determination, the injected sample volume was  $250\ \mu\text{L}$ , loaded as previously described for cation analysis.

TABLE I. – *Meteorological data.*

Sampling site	Date	$T(^{\circ}\text{C})$	$V(\text{m s}^{-1})$	Direction	r.h.(%)	$p(\text{hPa})$
		Mean $\pm$ SD	Mean $\pm$ SD	Mean $\pm$ SD	Mean $\pm$ SD	
1-Faraglioni	10/12/2006	$-5.8 \pm 0.8$	$7.4 \pm 5.9$	$220 \pm 98$	$76 \pm 6$	959
2-Nansen	13/12/2006	$-5.7 \pm 2.2$	$2.3 \pm 1.3$	$227 \pm 85$	$68 \pm 9$	980
3-Icaro	24/12/2006	$-6.3 \pm 0.7$	$6.8 \pm 3.2$	$307 \pm 36$	$54 \pm 5$	956
4-Nansen	26/12/2006	$-7.8 \pm 0.6$	$2.8 \pm 1.4$	$162 \pm 54$	$85 \pm 5$	957

Fluoride and organic anions (acetate, formate, pyruvate, glycolate and methane-sulphonate) were determined using a Dionex AG11 4 mm guard column and a Dionex AS11 4 mm separation column, with a sodium tetraborate eluent gradient from 0.075 to 1.5 mM (at 2.0 ml/min). Due to the low concentration of organic compounds in the snow, we used a larger sample volume: 1.0 ml injected in a low-pressure Ion Pac TAC-2,  $3 \times 35$  mm pre-concentration column.

Conductivity suppression was performed by Dionex ASRS-Ultra II 4 mm (anions) or Dionex CSRS-Ultra II 4 mm (cations) self-regenerating suppressor.

Blank values were at least two orders of magnitude lower than inorganic components and at least one order of magnitude lower than organic compounds determined in the snow samples. When necessary, blank values were subtracted from the sample concentrations. Detection limits (calculated as three times the standard deviation of ten repetition of a blank) ranged from 0.08 ppb for  $\text{Mg}^{2+}$  or  $\text{NH}_4^+$  to around 0.5 ppb for organic acids and nitrate. Reproducibility was evaluated as the relative standard deviation of ten repetitions of standard solutions with concentrations in the range 2–5 ppb and was always better than 5% for inorganic anions and cations and better than 2% for organic anions.

The quantification of chemical components in the snow samples was carried out with 5-points calibration curves using standard solutions, in the concentration range of the analysed samples, freshly prepared by dilution in Milli-Q (by Millipore, Billerica, MA, USA) water (resistivity  $> 18 \text{ M}\Omega$ ) of 1 g/L Merck (Darmstadt, Germany) certified IC standards.

In addition ice crystal replicas were made by collecting crystals on microscope slides, previously covered with a thin layer of 2% formvar in chloroform.

The slides were then placed inside a dessicator, where crystals and chloroform evaporate. Slides with crystal replicas are first of all examined at optical microscope, to choose slides area where crystal imprints are clear. Then selected areas were prepared for the SEM observation.

#### 4. – Meteorological data

Table I shows the meteorological data (mean value of air temperature, wind speed and direction, relative humidity, pressure) recorded at Rita (automatic weather station valid for Faraglioni and Icaro) and at Nansen where the measuring station consists of a meteorological mast (12 m height) equipped with a three-dimensional ultrasonic anemometer, Omnidirectional R3 (Gill Instruments), operating at 100 Hz in calibrated mode. A low-response thermo-hygrometer Rotronic MP100A (Campbell Scientific) is used to detect relative humidity and air temperature.

TABLE II. – *Chemical analysis of fresh snow samples ( $\mu\text{g l}^{-1}$ ).*

Sampling site	Date	Na <sup>+</sup>	NH <sub>4</sub> <sup>+</sup>	K <sup>+</sup>	Mg <sup>2+</sup>	Ca <sup>2+</sup>	Cl <sup>-</sup>	NO <sub>3</sub> <sup>-</sup>	SO <sub>4</sub> <sup>2-</sup>	F <sup>-</sup>
1-Faraglioni	10/12/2006	1358.9	23.7	73.2	215.10	104.4	2610.7	144.5	854.4	0.98
2-Nansen	13/12/2006	743.0	14.2	91.9	118.41	126.6	1429.0	238.9	620.3	3.47
3-Icaro	24/12/2006	887.8	54.6	45.1	101.18	56.4	1307.0	321.4	831.3	1.67
4-Nansen	26/12/2006	198.9	13.0	8.9	21.40	15.8	388.3	127.4	173.8	0.97

## 5. – Chemical composition of fresh-snow samples: results and discussion

### a) Inorganic compounds

Table II shows the concentration of water soluble inorganic ions in the fresh snow samples.

In order to evaluate the contribution of the various sources (marine, anthropogenic and natural), it is assumed that all Na<sup>+</sup> is of marine origin, and the mass ratios Cl<sup>-</sup>/Na<sup>+</sup>, SO<sub>4</sub><sup>2-</sup>/Na<sup>+</sup> and K<sup>+</sup>/Na<sup>+</sup> in the samples and in sea-water are compared (table III).

As sea-water ratio the commonly reported value is considered (Handbook of Chemistry and Physics), even if in the Ross Sea the values could be somewhat different. For example Saxena and Ruggiero [9] report for Cl<sup>-</sup>/Na<sup>+</sup>, SO<sub>4</sub><sup>2-</sup>/Na<sup>+</sup>, 1.63 and 0.20, respectively, in the Ross Sea.

The Cl<sup>-</sup>/Na<sup>+</sup> ratio in samples 1, 2 and 4 is comparable with the reference value, suggesting a small scavenging of HCl in the air. The measured ratio suggests that cloud condensation nuclei (CCN), consisting primarily of sea-salt, produce cloud droplets, which subsequently rise in cloud and freeze, maintaining the Cl<sup>-</sup>/Na<sup>+</sup> ratio fairly constant.

Sample 3 shows a chlorine loss, and presents high concentrations of NO<sub>3</sub><sup>-</sup>, SO<sub>4</sub><sup>2-</sup> and MSA (reported in table VIII). This is in accordance with the published reports that chlorine loss in the aerosol is primarily due to H<sub>2</sub>SO<sub>4</sub>, HNO<sub>3</sub>, MSA and dicarboxylic acids [38-40].

Kerminen *et al.* [40] at the Finnish station Aboa (150 km from the open Ocean) in Antarctica, measured an average chloride loss in aerosol of more than 90% for sub-micron particles and about 50% for particles larger than 3  $\mu\text{m}$ .

Concerning K<sup>+</sup>/Na<sup>+</sup>, Mg<sup>2+</sup>/Na<sup>+</sup> and Ca<sup>2+</sup>/Na<sup>+</sup> ratios, they are comparable to the sea-water ones, except for sample 2 (Nansen), which shows K<sup>+</sup>/Na<sup>+</sup> and Ca<sup>2+</sup>/Na<sup>+</sup> about 3 times higher. K<sup>+</sup> is generally present in wind-blown soil, and also Ca<sup>2+</sup>. Ghermandi *et al.* [41] measured the total concentration of several elements in recent snow from a coastal Antarctic site (Terra Nova Bay) and found that most of the elements

TABLE III. – *Inorganic ion ratios in snow samples and sea-water.*

Sample	SO <sub>4</sub> <sup>2-</sup> /Na <sup>+</sup>	Cl <sup>-</sup> /Na <sup>+</sup>	K <sup>+</sup> /Na <sup>+</sup>	Mg <sup>2+</sup> /Na <sup>+</sup>	Ca <sup>2+</sup> /Na <sup>+</sup>	NO <sub>3</sub> <sup>-</sup> /Na <sup>+</sup>
1	0.63	1.92	0.054	0.158	0.077	0.106
2	0.83	1.92	0.124	0.159	0.170	0.321
3	0.94	1.47	0.051	0.114	0.063	0.362
4	0.87	1.95	0.045	0.108	0.080	0.640
S.W.	0.25	1.81	0.036	0.129	0.038	$\approx 10^{-4}$

TABLE IV. –  $Nss-SO_4^{2-}$  concentration and  $MSA/nss-SO_4^{2-}$ ,  $nss-SO_4^{2-}/SO_4^{2-}$  ratios.

Sample	$nss-SO_4^{2-}$ $\mu g l^{-1}$	$MSA/nss-SO_4^{2-}$	$nss-SO_4^{2-}/SO_4^{2-}$ %
1	514.6	0.35	60.2
2	434.6	0.27	70.1
3	609.4	0.59	73.3
4	124.1	0.43	71.4

studied (especially Mg, K, Ca, Si and Al) are present in excess of the typical sea-salt ratio, implying the existence of a crustal component, in addition to a sea source for these chemical species at Terra Nova Bay.

As regards the  $SO_4^{2-}/Na^+$  ratio, the concentration of  $nss-SO_4^{2-}$  is calculated using  $Na^+$  as the reference elements for the sea-salt contribution, using eq. (1):

$$(1) \quad nss-SO_4^{2-} = SO_4^{2-} - 0.25 Na^+,$$

where 0.25 is the  $SO_4^{2-}/Na^+$  mass ratio in sea-water.

Table IV shows the calculated concentrations of  $nss-SO_4^{2-}$ , and the ratios  $MSA/nss-SO_4^{2-}$ ,  $nss-SO_4^{2-}/SO_4^{2-}$ .

The  $SO_4^{2-}/Na^+$  ratio, even if higher than in sea-water ratio (by 2.5 to 3.8 times), is much lower than the values measured at marine sites influenced by anthropogenic activity.

The excess sulphate of aerosol in Antarctica is higher in summer [42] and is due to oxidation of dimethylsulfide (DMS) produced in sea-water due to the activity of various phyto- and zoo-planktonic species. Once released into the atmosphere, DMS will follow an oxidation scheme controlled principally by hydroxyl radical (OH) during the day,

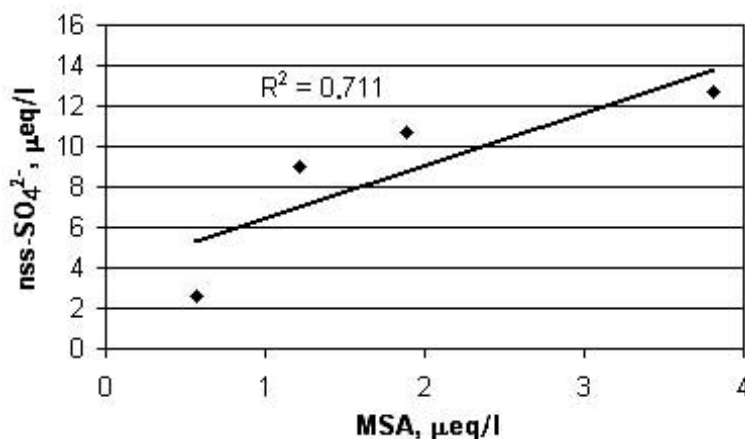


Fig. 2. –  $MSA$  as a function of  $nss-SO_4^{2-}$ .



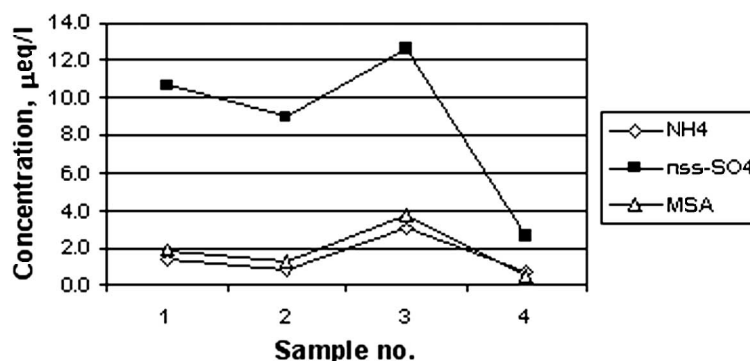


Fig. 3. – MSA,  $\text{NH}_4^+$  and  $\text{nssSO}_4^{2-}$  concentrations ( $\mu\text{eq l}^{-1}$ ).

and nitrate radical ( $\text{NO}_3$ ) at night, thus producing either MSA or  $\text{SO}_2$ , which is further oxidized to sulphate. In fact, MSA can be considered an indicator for DMS particulate oxidation products, as is confirmed by the high correlation between MSA and  $\text{nssSO}_4^{2-}$  ( $R^2 = 0.71$ ) measured in snow samples (fig. 2).

In addition  $\text{nssSO}_4^{2-}$ , MSA and  $\text{NH}_4^+$  show the same trend (fig. 3). A similar behaviour is reported by Legrand *et al.* [43] in the aerosol samples collected in the boundary layer at a coastal Antarctic site (Neumayer station).

For  $\text{nssSO}_4^{2-}$ , MSA and  $\text{NH}_4^+$ , Savoie *et al.* [44] measured very strong and sharply defined seasonal cycles, with maxima during the austral summer, being more than an order of magnitude higher than the winter minima, in aerosols at Mawson station, Antarctica.

The correlation between  $\text{nssSO}_4^{2-}$  and MSA measured in snow samples may confirm a common marine biological source for these compounds, which can be scavenged from ice crystals with a similar efficiency, first of all due to thermo- and diffusiophoretic forces, as both are concentrated in the fine particles [45]. Accordingly Legrand and Pasteur [46] found a similar seasonal trend in the aerosol and in surface snow for the ratio  $\text{MSA}/\text{nssSO}_4^{2-}$  at Halley, a coastal Antarctic station. In summer the mean ratio  $\text{MSA}/\text{nssSO}_4^{2-}$  in snow is about 0.3, a value comparable with our experimental data.

The  $\text{NH}_4^+$  concentration in snow samples is much lower than that of  $\text{SO}_4^{2-}$  and  $\text{NO}_3^-$  one; thus it is assumed that  $\text{SO}_4^{2-}$  and  $\text{NO}_3^-$  in the ice crystal did not originate from  $\text{NH}_4\text{NO}_3$  and  $(\text{NH}_4)_2\text{SO}_4$  aerosol scavenging.

The very low degree of ammonia neutralization of sulphur derived aerosol species in the summer atmosphere in coastal Antarctic regions, suggests that emission fluxes from sea-water of DMS, which is oxidized to  $\text{SO}_2$ ,  $\text{H}_2\text{SO}_4$  and MSA, is prevalent with respect to that of  $\text{NH}_3$  [43].

This could depend on a different degree of biological productivity of DMS and  $\text{NH}_3$ , or on the sea-air exchange process. It should be borne in mind that a highly soluble gas such as ammonia is controlled by the diffusive resistance in the gas phase, while for moderately soluble gas such as DMS, the air/sea exchange is controlled by the flux resistance of the liquid side of the interface and is strongly dependent on wind speed.

The  $\text{NO}_3^-/\text{Na}^+$  ratio in fresh snow (0.1–0.6) is much higher than that of sea-water (about  $10^{-4}$  [9]), and therefore a marine origin can be excluded for nitrate.

Continental and stratospheric (sedimentation of nitrite acid trihydrate particles formed in polar stratospheric clouds) sources are suggested to explain the background nitrate level [47].

TABLE V. – Concentrations of sea-salt in air and in fresh snow.

Site	Elevation, m asl	Distance to coast, km	Air, ng m <sup>-3</sup>	Snow, μg l <sup>-1</sup>
1) Halley	10	15	200	1400
2) Neumayer	< 42	10	850	1700
3) Dumont d'Urville	40	< 1	1400	90 × 10 <sup>3</sup>
4) Mawson		< 1	470	
5) Palmer	Coastal site		3900	
6) Marsh	Coastal site		10.200	
7) South Pole	2800	> 1500	62	
8) Terra Nova Bay	Coastal site		2100	
9) South Pole	2800	> 1500	61	

1) [53]; 2) [54]; 3) [55] (sampled during winter season only); 4-5-6) [56]; 7) [43]; 8) [57]; 9) [58].

The experimental results of Ullerstam and Abbatt [48], Diehl *et al.* [49], and field observations reported by Schwikowski *et al.* [50] suggest that gas phase scavenging may be significant for HNO<sub>3</sub>. It was consequently assumed that nitric acid vapour is adsorbed during the growth of ice crystals.

Higher NO<sub>3</sub><sup>-</sup> values in late spring and mid-summer in air and fresh snow have been reported [51, 47].

Determining sea-salt concentrations from Na concentration (3.248 Na) for examined samples, the values of 4400 μg l<sup>-1</sup>; 2400 μg l<sup>-1</sup>; 2900 μg l<sup>-1</sup>; 650 μg l<sup>-1</sup> were obtained. The sea-salt contribution is dominant due to the coastal position of the sampling site.

Table V shows a few published data of sea-salt concentrations in the Antarctic atmosphere and in fresh snow samples. The values reported for Halley and Neumayer sites are comparable with the data obtained here.

Usually higher sea-salt concentrations are measured in winter [52, 53]. Maupetit and Delmas [51] measured (Dumont d'Urville, 1984) the maximum of sea-salt concentration in fresh winter snow and the minimum in summer snow.

Kerminen *et al.* [40], measured sea-salt particle concentration in a summer campaign (81 ng m<sup>-3</sup>, range 26–270 ng m<sup>-3</sup>). The said value is about a factor 5 greater than the average sea-salt concentrations at South Pole, but clearly lower than the concentrations typically observed at coastal Antarctica.

Table VI and table VII show published concentrations of soluble inorganic ions and MSA in Antarctic aerosol (ng m<sup>-3</sup>) and in fresh snow samples (μg l<sup>-1</sup>). A high variation of concentration for different sites and seasons can be noted.

#### b) Organic compounds

Table VIII reports the concentrations of water soluble organic anions (acetate, formate, MSA and glycolate) measured in snow samples. Propionate, pyruvate and oxalate were below the detection limit.

Carboxylic acid are found in the gaseous and particulate phase, as well as in rainwater and snow, due to water solubility. Carboxylic compounds with a low molecular weight (*e.g.*, formic and acetic acids) are more common in the gaseous than in the particulate

TABLE VI. – Concentrations of soluble inorganic ions and MSA in Antarctic aerosol ( $ng\ m^{-3}$ ).

	Na <sup>+</sup>	Cl <sup>-</sup>	Ca <sup>2+</sup>	Mg <sup>2+</sup>	Nss-K <sup>+</sup>	Nss-SO <sub>4</sub>	NH <sub>4</sub> <sup>+</sup>	MSA <sup>-</sup>	NO <sub>3</sub> <sup>-</sup>	SO <sub>4</sub> <sup>2-</sup>
1	25	18				222	41	70	11	
2	172	290	27	27					168	386
3	62									
4						16 <sup>a</sup> ; 50 <sup>b</sup> ; 106 <sup>c</sup>		15 <sup>b</sup> ; 35 <sup>c</sup>		
5						50 <sup>a</sup> ; 147 <sup>b</sup> ; 270 <sup>c</sup>		2.4 <sup>a</sup> ; 20 <sup>b</sup> ; 49 <sup>c</sup>		
6						41 <sup>a</sup> ; 151 <sup>b</sup> ; 314 <sup>c</sup>		3.6 <sup>a</sup> ; 38.3 <sup>b</sup> ; 108 <sup>c</sup>		
7						240 <sup>c</sup>		4.1 <sup>a</sup> ; 49 <sup>b</sup> ; 122 <sup>c</sup>		
8		2008				362				643
9					34 ± 16 <sup>d</sup> ; 44 ± 17 <sup>c</sup>	187 ± 69 <sup>d</sup> ; 345 ± 79 <sup>c</sup>	232 ± 70 <sup>d</sup> ; 256 ± 68 <sup>c</sup>	6.6 ± 2.5 <sup>d</sup> ; 52 ± 19 <sup>c</sup>		
10									35.6 ± 6.7	
11									23 ± 5.8	
12									27	
13	1200					99	25	49	18	
14a	547	971	53	71	36	362	219	62	32.7	496
14b	506	1017	32	62	10	320	144	60	29	447
14c	934	1774	41	115	1	296	102	57	26	550

1) [40] [Aboa, summer,1997-1998]; 2) [65] [Ross sea, summer]; 3) [53] [Halley, 10 m. a.s.l., Febraury 1991, 10 m abs]; 4) [42] [Halley, 1991-1992; a, winter; b, mean; c, summer]; 5) [42] [Dumont d'Urville, 5 m. a.s.l., 1991-1995; a, winter; b, mean; c, summer]; 6) [42] [Neumayer, 1983-1995; a, winter; b, mean; c, summer]; 7) [56] [Palmer, December 1990-January 1991; a, winter; b, mean; c, summer]; 8) [42] [Dumont d'Urville, 28 January 1994]; 9) [43] [Dumont d'Urville, 1994-1995; c, summer; d, spring]; 10) [47] [Neumayer, 1983-1995]; 11) [47] [Dumont d'Urville, 1991-1994]; 12) [44] [Mawson, 1987-1991]; 13) [56] [Palmer, April 1990 to June 1991]; 14) [43] [ Dumont d'Urville, summer 1993/1994: a-Labo3; b-Hall Fusée; c-Ile du Gouverneur].

phase, while dicarboxylic acids (*e.g.*, oxalic acid) are prevalently encountered in the particulate phase, due to a vapour pressure lower by a factor of at least  $10^4$  than that of monocarboxylic acids.

Organic aerosols over the coast of Antarctica can be due to the organic matter emitted by the sea and its subsequent photo-chemical oxidation. The organic compounds should contribute to the formation of cloud condensation nuclei [60,61]. Dibb and Arsenault [62] suggest the production of monocarboxylic acids within the snowpack due to the oxidation of carbonyls and alkenes.

Cincinelli *et al.* [63] found that the same classes of organic compounds (n-alkanes, phthalates and polycyclic aromatic hydrocarbons) found in sea-water were also present in fresh snow, meaning that organic compounds are transferred into the atmosphere by marine aerosol, and afterwards scavenged by ice crystals.

TABLE VII. – Concentrations of inorganic ions in snow samples ( $\mu\text{g l}^{-1}$ ).

	Na <sup>+</sup>	NH <sub>4</sub> <sup>+</sup>	K <sup>+</sup>	Mg <sup>2+</sup>	Ca <sup>2+</sup>	Cl <sup>-</sup>	NO <sub>3</sub> <sup>-</sup>	SO <sub>4</sub> <sup>2-</sup>	nssSO <sub>4</sub> <sup>2-</sup>	MSA	F <sup>-</sup>
1	2800	216	430	681	1042	4538	28	20			247
2	530 ± 830	7.5 ± 9.3							149 ± 160	44 ± 61	
3	4.6 × 10 <sup>4</sup>					7.8 × 10 <sup>4</sup>	198	1309			
4	430										
5							65 <sup>a</sup> ; 84 <sup>b</sup> ; 79 <sup>c</sup>				
6a	414		13.7	48.6	16	742	18.6	197			
6b	32		7.8	3.6	4	53	49.6	24			
6c	83		21.5	9.7	4	216	205	77			

1) [59] [Palmer Station, January-February 1994]; 2) [43] [Neumayer 1989-1992]; 3) [9] [Mc Murdo station, January 1983]; 4) [53], [Halley, 10 m a.s.l.; 1991-1993]; 5) [47] [a: Dumont d'Urville, January 1991 to December 1993; b: Halley, January 1991 to December 1992; c: Halley, January 1984 to December 1992]; 6) [51] [Dumont d'Urville; a:01/11/1984; b: 01/25/1984;c:12/08/1984].

TABLE VIII. – Concentrations of water soluble organic anions ( $\mu\text{g l}^{-1}$ ).

Sample	Acetate	Glycolate	Formate	MSA
1	12.4	7.7	14.1	179.2
2	13.2	7.2	9.9	115.3
3	4.6	d.l.	4.3	361.9
4	2.6	d.l.	2.1	53.8

In the examined samples the acetate concentration is comparable with that of formate.

To our knowledge there are no published data on the considered organic compounds in fresh snow, to allow a comparison, except for MSA. Legrand *et al.* [43] (Neumayer 1989-1992) measured a concentration of MSA ( $44 \pm 61 \mu\text{g l}^{-1}$ ), lower than the values measured in the present samples. Maupetit and Delmas [51] obtained at Dumont d'Urville concentrations ranging from 0 to  $44 \mu\text{g l}^{-1}$ , with a mean value of  $6.5 \mu\text{g l}^{-1}$ .

## 6. – Ice crystal shape and chemical composition

Event	Observed crystal
10/12/2006	Circular plate: 100–600 $\mu\text{m}$ ; hexagonal plate: 300–450 $\mu\text{m}$
13/12/2006	Hexagonal plate: 150–300 $\mu\text{m}$ ; dendrite crystal with plate: $\approx 1500 \mu\text{m}$ ; assemblage of minute crystals; plate with simple extension: $\approx 900 \mu\text{m}$
24/12/2006	Crystal with branches: $\approx 500 \mu\text{m}$ ; dendrite: $\approx 2400 \mu\text{m}$ ; stellar crystal with plates: $\approx 1200 \mu\text{m}$
26/12/2006	Hollow column; dendrite: $\approx 1800 \mu\text{m}$

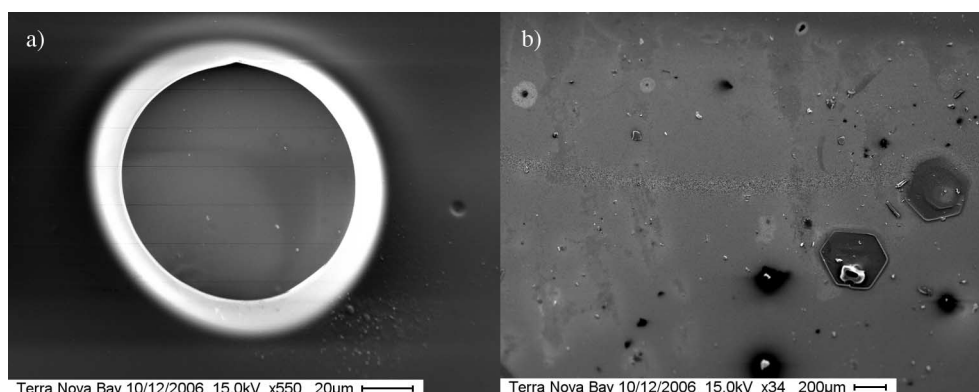


Fig. 4. – SEM images of ice crystal replicas. a) Circular crystal; b) hexagonal plate.

In the examined replica of the different events, there are events where simple plane crystals are prevalent (10/12/2006), events characterized by prevalently complex crystal shapes (24/12/2006), and events where simple and complex crystal shapes are present simultaneously (13/12/2006).

The chemical composition of ice crystals and consequently of snow depends on many parameters: the chemical composition of ice forming nuclei (IFN) or cloud condensation nuclei (CCN) on which cloud droplets form, ice crystal size (as growth due to water vapour diffusion dilutes the initial concentration), ice crystal shape and growth time (parameters that influence the scavenging of aerosol and gases) and the air concentrations of aerosol and gases.

Considering a CCN particle consisting primarily of sea-salts, which produces a cloud droplet and subsequently rises in the cloud and freezes, the  $\text{Cl}^-/\text{Na}^+$  ratio should remain fairly constant after freezing. In the crystal replicas no riming process was observed.

Event 1 (10/12/2006) reveals the presence of hexagonal plates (300–450  $\mu\text{m}$  diameter) and circular plates (100–600  $\mu\text{m}$  in diameter) (fig. 4). The presence of simple hexagonal ice crystals without any internal structure and circular crystals suggest growth occurred at a temperature higher than  $-5^\circ\text{C}$  [10, 64].

As the growth time of ice crystals increases with temperature, the above conditions reduce the growth time.

The higher concentration of  $\text{Na}^+$  and  $\text{Cl}^-$  could depend on a low dilution of IFN or CCN, due to relatively small ice crystal diameter, and/or a higher scavenging efficiency due to fall velocity, higher than for shapes not present in this event (crystal with branches, dendrite, stellar crystal).

Event 2 (13/12/2006) shows hexagonal plates: 150–300  $\mu\text{m}$ ; stellar crystals with plates:  $\approx 1000 \mu\text{m}$ ; dendrite crystals with plates:  $\approx 1500 \mu\text{m}$ ; a combination of side planes (fig. 5). The presence of crystals in which various habits are superimposed indicates that during the fall inside the cloud, variations in the air temperature and mixing ratio took place.

Event 3 (24/12/2006) evidences mostly complex crystal shapes (crystals with branches  $\approx 500 \mu\text{m}$ ; dendrites  $\approx 2400 \mu\text{m}$ ; stellar crystal with plates  $\approx 1200 \mu\text{m}$ ) (fig. 6). The low concentrations of Na and Cl could depend on nucleation scavenging and high dilution due to relatively high ice crystal diameters. The high concentrations of  $\text{NO}_3^-$ ,  $\text{NH}_4^+$ ,  $\text{SO}_4^{2-}$  could arise from vapour scavenging due to high free-fall time below cloud, as a result of low terminal velocity.

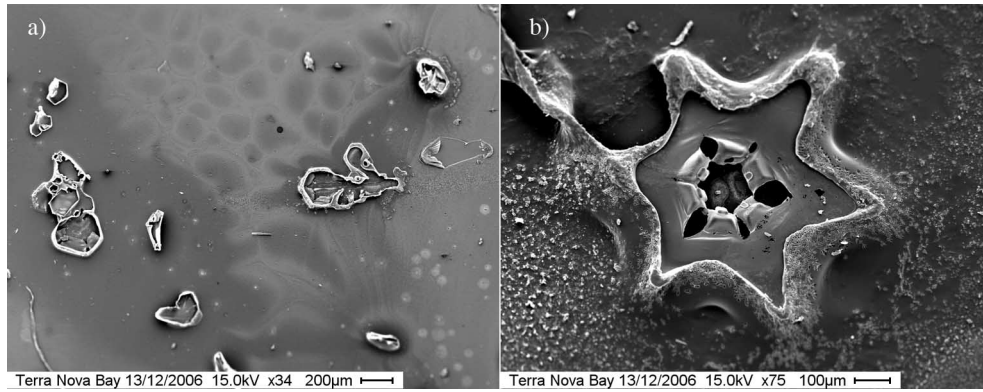


Fig. 5. – a) Hexagonal plate, assemblage of minute plates, and fractured dendritic crystal with plates at ends; b) plate with simple extensions.

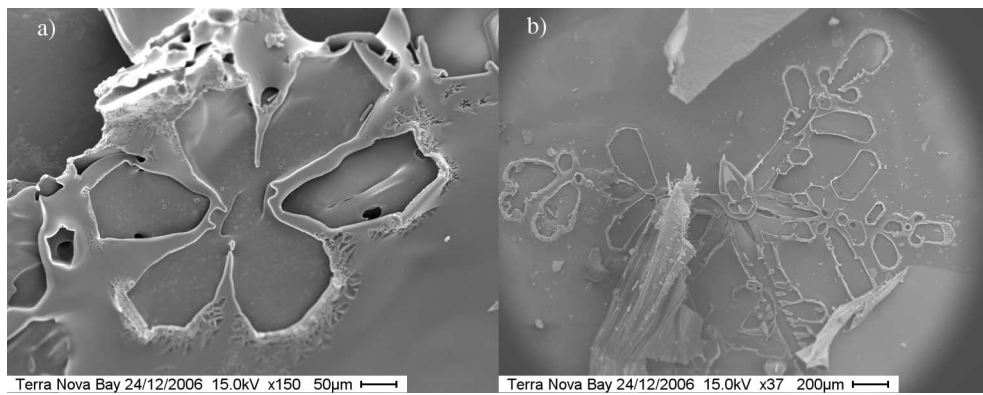


Fig. 6. – a) Crystal with branches; b) dendritic crystal.

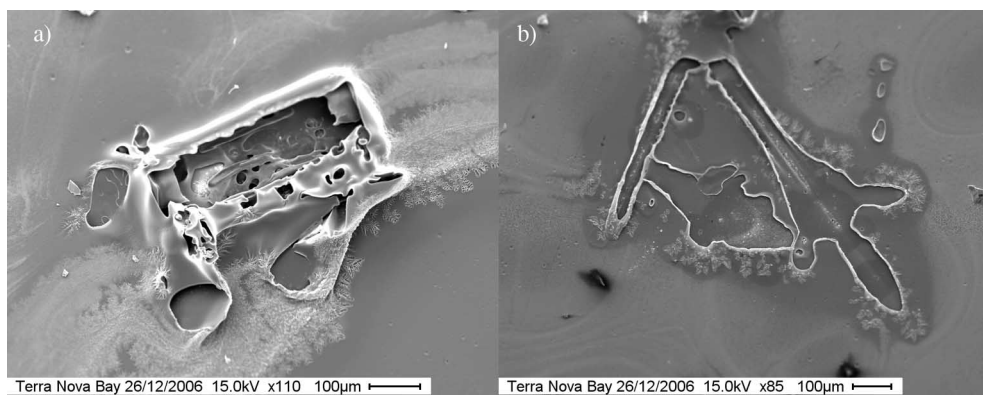


Fig. 7. – a) Hollow column; b) fractured dendritic crystal.

Event 4 (26/12/2006) reveals the presence of hollow columns and large dendrites (about 1800  $\mu\text{m}$  diameter) (fig. 7). Large crystals and the lower concentration of vapours, gases, and aerosol in the atmosphere due to late last snow fall event (24/12/2006), could explain the low concentrations observed in fresh snow.

## 7. – Conclusions

Despite the small number of snowfall events examined (December 2006), it is possible to draw the following conclusions.

Measured concentrations in snow samples show that the sea-salt contribution is dominant, as usually observed in the coastal Antarctic stations. By determining sea-salt from  $\text{Na}^+$  concentration, the values of 4400  $\mu\text{g l}^{-1}$ ; 2400  $\mu\text{g l}^{-1}$ ; 2900  $\mu\text{g l}^{-1}$ ; 650  $\mu\text{g l}^{-1}$  were obtained for the examined samples.

The ratio in snow samples of soluble inorganic ions with respect to  $\text{Na}^+$  (reference element of marine source), comparable or a little higher than values in sea-water, suggests that the prevalent aerosol scavenging is due to the nucleation process. Cloud condensation nuclei (CCN), consisting primarily of sea-salt in Antarctic area, produces cloud droplets, which subsequently freeze.

A contribution from thermo- and diffusiophoretic forces to aerosol scavenging process during growth of ice crystals due to the diffusion of water vapour, can be deduced from the correlation between  $\text{nssSO}_4^{2-}$  and MSA ( $R^2 = 0.71$ ) measured in snow samples.

In fact  $\text{nssSO}_4^{2-}$  and MSA present a common marine biological source, both being derived from oxidation of DMS released into the atmosphere by the sea-water. Since both are concentrated in the fine particles, a similar scavenging efficiency is expected.

The  $\text{NO}_3^-/\text{Na}^+$  ratio in fresh snow (range 0.1–0.6), much higher than the value in sea-water (about  $10^{-4}$ ), excludes a marine origin for  $\text{NO}_3^-$  ion, suggesting a continental and/or stratospheric source.

Concerning organic compounds, propionate, pyruvate and oxalate were below detection limit, while acetate, formate, MSA and glycolate were measured in snow samples.

Organic aerosol, originating from matter emitted by the sea and subsequently oxidized, could contribute to the formation of cloud condensation nuclei or be scavenged during crystal growth.

The chemical composition of ice crystals, and consequently of snow, depends on many parameters, *i.e.* the chemical composition of IFN or CCN, and scavenging process during ice crystal growth, or the fall below clouds. In the crystal replicas no riming process was observed.

Scavenging efficiency is related to the diameter and shape of ice crystal, which depend on air temperature and relative humidity.

High concentrations of  $\text{Na}^+$  and  $\text{Cl}^-$  are noted in events characterized by small ice crystals, and small concentrations in events showing large crystals.

Relatively high concentrations of  $\text{NO}_3^-$ ,  $\text{NH}_4^+$ ,  $\text{SO}_4^{2-}$  in snow events showing crystals with complex shape and low terminal velocity, could depend on vapour scavenging due to high free fall time below cloud.

In the case of snow short-spaced events, the latter shows low concentrations of ions, due to lower atmospheric pollutant concentrations.

\* \* \*

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