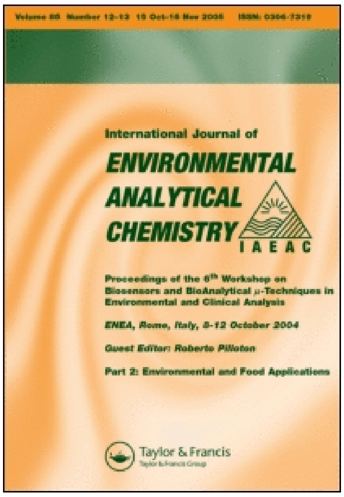

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# CHEMICAL CHARACTERIZATION OF THE LAST 250 YEARS OF SNOW DEPOSITION AT TALOS DOME (EAST ANTARCTICA)

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High-resolution chemical records of main and trace ionic components of snow precipitation over the last 250 years were obtained by analysing the first 36 m of a firn core drilled at Talos Dome, a dome located in the ice divide between northern Victoria Land and Oates Land (East Antarctica Pacific Ocean/Ross Sea sector). The concentration/depth profiles of some relevant chemical parameters are discussed on the basis of a previous stratigraphic dating, set up following the seasonal signatures of non-sea-salt (nss) sulphate deposition and synchronised by using tritium and volcanic temporally known horizons. Particular attention is paid to the study of the temporal trends of the sea spray components ($Na^+$, $Cl^-$, $Mg^{2+}$) and S and N cycle compounds ($nssSO_4^{2-}$, MSA, $NO_3^-$, $NH_4^+$) to understand the main sources, transport mechanisms and depositional processes of these compounds at the deposition site. Good correlations between the sea spray markers show that the primary marine contribution is relevant, though Talos Dome is located at a relatively high altitude (2316 m a.s.l.) and far from the coast line (about 250 km). The study of the snow chemical composition and of the recent (for the last few centuries) atmosphere/snow relationship at Talos Dome is important as a preliminary survey at this station, which will probably be chosen for a deep ice coring project.

*Keywords:* Ion chromatography; Chemical analysis; Firn core; Talos Dome; Antarctica

## INTRODUCTION

Studies of deep ice cores have shown that ice caps constitute a unique environment of natural deposition and, like oceanic sedimentary records, by regular stratification of successive deposition events they preserve a variety of paleoenvironmental and paleoclimatic data over 100 000-year periods [1–4]. Paleoenvironmental data can provide high-resolution information on spatial and temporal variations of soil/atmosphere/sea/snow exchange processes [5,6]. Variations in load and composition of the atmospheric aerosol, recorded in the snow layers, can be related to changes in intensity of main and secondary sources, in transport and atmospheric removal processes and in

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extent, frequency and seasonality of snow accumulation rate, caused by gradual or sudden climatic variations on regional or global scales [5,7]. A reliable interpretation of such paleoenvironmental and paleoclimatic changes can be achieved by the choice of specific chemical markers for sources and transport processes and by studying their temporal profiles over recent times, when matter and energy interchanges at the atmosphere/snow interface can be better studied [5].

In this article we report the results of high-resolution chemical analysis for the first 36 m (corresponding to the last 250 years) of a shallow (about 89-m depth) firn core drilled at Talos Dome (East Antarctica). This station is located on the edge of the Antarctic Ice Sheet, at 2316 m a.s.l., and is characterized by an annual snow accumulation rate of about 80 mm of water equivalent (w.eq.) per year [8]. Concentration/depth profiles are used to reconstruct the environmental variations on regional and global scales that have occurred since the pre-industrial period.

The aim of this study is to evaluate whether Talos Dome is able to give reliable information about changes in the oceanic contribution to snow precipitation in coastal Antarctica, which can be correlated to variations in marine biogenic activity, sea level and atmospheric (Southern Oscillation) and marine circulation. Indeed, unlike deep ice cores drilled in central Antarctica, the coastal domes are more influenced by marine air masses and have higher accumulation rates, so that it possible to obtain information for the last 70 000 years, with a large temporal resolution.

## EXPERIMENTAL

### Sampling

Talos Dome (72°48′S, 159°06′E) is a dome located in the west side of northern Victoria Land (Antarctica) and south-west of United States Antarctic Research Programme mountains (Fig. 1). Talos Dome is located 2316 m a.s.l. on the ice divide between the Southern Ocean (Pacific sector) and the Ross Sea, with a distance from the coast of about 290 and 250 km, respectively [8,9].

During the 1996/97 Antarctic Campaign, an 89.1-m firn core was drilled at Talos Dome, starting from 1.5-m below the surface (in the uppermost layers the poor mechanical characteristics of the snow did not allow recovery of integral firn core sections). In order to obtain a continuous stratigraphy, the most superficial layers were sampled by a 2-m snow pit. Firn core sections were sealed in polyethylene bags. All sampling operations were performed by personnel wearing clean-room clothes. A more detailed description of sampling procedures is reported elsewhere [10–13].

Firn core and snow-pit samples were stored at −20°C until analysis. After decontamination by removing the most superficial layer, the firn core was sub-sampled at 2.5–3.5-cm resolution in the Laboratory of Glaciology of the University of Milan Bicocca.

### Experimental

### *Apparatus*

Chemical analysis was performed by conductivity-suppressed ion chromatography (IC) for inorganic anions ($F^-$, $Cl^-$, $NO_3^-$, $SO_4^{2-}$), organic anions (acetate, propionate formate, methanesulphonate and pyruvate) and cations ($Na^+$, $NH_4^+$, $K^+$, $Mg^{2+}$, $Ca^{2+}$).

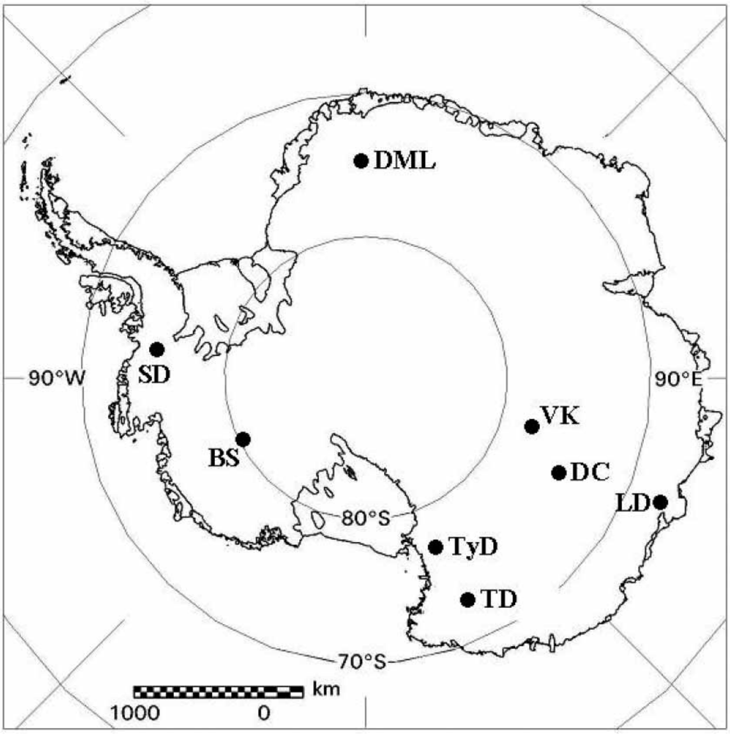

FIGURE 1 Map of Antarctica showing the Talos Dome core site (TD) and other deep ice core sites: Byrd (BS), Dome C (DC), Vostok (VK), Dronning Maud Land (DML), Siple Dome (SD), Taylor Dome (TyD) and Law Dome (LD).

TABLE I Operational conditions for IC measurements

| | *Inorganic anions* | *Organic anions + $F^-$* | *Cations* |
|---|---|---|---|
| IC apparatus | Dionex DX 500 | Dionex DX 500 | Dionex DX 120 |
| Injection system | Dionex TAC-2 preconcentrator | Dionex TAC-2 preconcentrator | Loop |
| Volume injected | 1.0 mL | 1.0 mL | 1.0 mL |
| Guard column | Dionex AG4A 4 mm | Dionex AG11 4 mm | Dionex CG12 4 mm |
| Separation column | Dionex AS4A 4 mm | Dionex AS11 4 mm | Dionex CS12 4 mm |
| Eluent | $NaHCO_3$ 1.3 Mn<br>$Na_2CO_3$ 1.4 Mn | $Na_2B_4O_7$ 3-30 mM | $H_2SO_4$ 25 mM |
| Eluent flux | 2.5 mL/min | 2.0 mL/min | 1.5 mL/min |
| Elution | Isocratic | Gradient with cleaning step | Isocratic |

The samples were melted, still closed in their containers, under a class-100 laminar-flow hood, filtered on a 0.45-μm Teflon membrane and directly injected into three Dionex IC systems, for the simultaneous determination of inorganic anions, organic anions + fluoride and cations. The three IC devices were equipped with eluent degassing modules, electrochemical conductivity suppressors and conductivity cells as detectors. The IC apparatus and the operative conditions are summarized in Table I.

Particular care was taken to open the containers as little as possible, in order to minimise any uptake of ammonia and carboxylic acids from the laboratory atmosphere [10–13].

### *Reagents*

Stock standard solution ($1.000\,\mathrm{g\,L^{-1}}$) were directly purchased from Merck, when available, or obtained from "reagent grade" Merck or Fluka reagents dissolved in ultra-pure water (resistivity $>18\,\mathrm{M\Omega}$). Standard solutions at microgram per litre levels were prepared daily in pre-cleaned polyethylene bottles, using water from a UHQ Elgastat apparatus fed by Milli-Q water.

## RESULTS AND DISCUSSION

Among the chemical species determined in the Talos Dome firn core, some preliminary results about the high-resolution temporal distribution of sea spray markers ($Na^+$, $Cl^-$, $Mg^{2+}$), sulphur cycle compounds (non-sea-salt sulphate ($nssSO_4^{2-}$) and methanesulphonate (MSA)) and nitrogen cycle compounds ($NH_4^+$, $NO_3^-$) are reported. The fundamental statistical parameters for each component are shown in Table II.

### Sea Spray

$Cl^-$, $Na^+$, $Mg^{2+}$ and a part of total sulphate ($totSO_4^{2-}$) are the typical components of primary marine aerosol (sea spray) which constitutes the main aerosol source in the low-altitude Antarctic coastal areas [14].

In Antarctica sea spray components show wider spatial and temporal variations than the other components present in the snow. Atmospheric aerosol measurements revealed high concentrations in coastal areas ($3.2\,\mathrm{\mu g\,m^{-3}}$ measured at Palmer Station in the Antarctic Peninsula [15]) and very low concentrations in the colder and higher inner plateau areas ($0.062\,\mathrm{\mu g\,m^{-3}}$ at the South Pole [16]). In coastal zones influenced by the katabatic winds, able to deflect the marine air masses, the values for typical sea spray components are lower than at similar coastal stations not affected by katabatic wind (for example, $0.27\,\mathrm{\mu g\,m^{-3}}$ were measured at the Australian Mawson station [15]).

TABLE II Fundamental statistical parameters for some ions determined by IC

| | $Na^+$ | $Cl^-$ | $Mg^{2+}$ | $SO_4^{2-}$ | $nssSO_4^{2-}$ | *MSA* | $NO_3^-$ | $NH_4^+$ |
|---|---|---|---|---|---|---|---|---|
| *n*° values | 1109 | 1111 | 1108 | 1111 | 1107 | 1106 | 1111 | 1109 |
| Min | 2.9 | 8.7 | 0.2 | 12.5 | 3.3 | 0.7 | 11.2 | 0.3 |
| Max | 240.3 | 918.1 | 30.6 | 398.0 | 390.7 | 64.2 | 174.2 | 62.2 |
| Mean | 30.7 | 65.3 | 5.2 | 64.2 | 56.3 | 5.8 | 60.1 | 9.5 |
| Std dev. | 25.7 | 54.7 | 3.7 | 33.1 | 32.0 | 4.8 | 17.8 | 6.4 |
| Median | 24.2 | 52.9 | 4.2 | 58.9 | 51.4 | 4.6 | 57.9 | 7.9 |
| 25° perc | 16.0 | 38.9 | 2.7 | 43.5 | 35.9 | 3.1 | 47.0 | 5.4 |
| 75° perc | 36.5 | 73.3 | 6.5 | 77.1 | 68.5 | 6.8 | 69.4 | 11.7 |

Concentrations are given in $\mathrm{\mu g\,L^{-1}}$.

Measurements of superficial snow, firn and ice core samples from several stations in Terra Nova Bay, which is a coastal area located between the Ross Sea and the Talos Dome area, show a high frequency of sea spray spikes in snow layers deposited in the winter period [12,13,17,18]. This seasonal pattern is lower in stations located at altitudes above 1500 m a.s.l., where an atmospheric aerosol fractionation already occurs by selective deposition of the coarsest aerosol particles, which are mainly linked to the primary marine aerosol [14].

Sodium is considered as a more reliable marker for sea spray [17,18] than chloride and magnesium. In coastal northern Victoria Land region, alternative sources for $Na^+$ (mainly coming from crustal input) are extremely low with respect to the sea contribution [14,18]. In contrast, Mg and chloride have other important sources, such as crustal inputs (Mg) and volcanic emissions ($Cl^-$), which become more evident where the sea spray contribution is lower (i.e., when altitude or distance from the sea increases). In any case, $Na^+$ transport processes do not seem to undergo the fractionating phenomena affecting other sea spray components. Such processes are demonstrated by selective depositions of $Mg^{2+}$ salts or chloride losses by HCl formation, through the exchange reaction between NaCl and $H_2SO_4$. As a consequence, measurements of samples collected in snow pits dug at stations located at different geographic positions showed variations of the $Mg^{2+}/Na^+$ and $Cl^-/Na^+$ ratios, as altitude and/or distance from the sea change, even if a good correlation among the three sea spray components was generally preserved [18].

Figure 2 shows the depth/concentration profiles of the sea spray components in the first 36 m of the Talos Dome firn core. The three components show very similar profiles. The sodium profile shows many spikes, caused by sea storm events, distributed

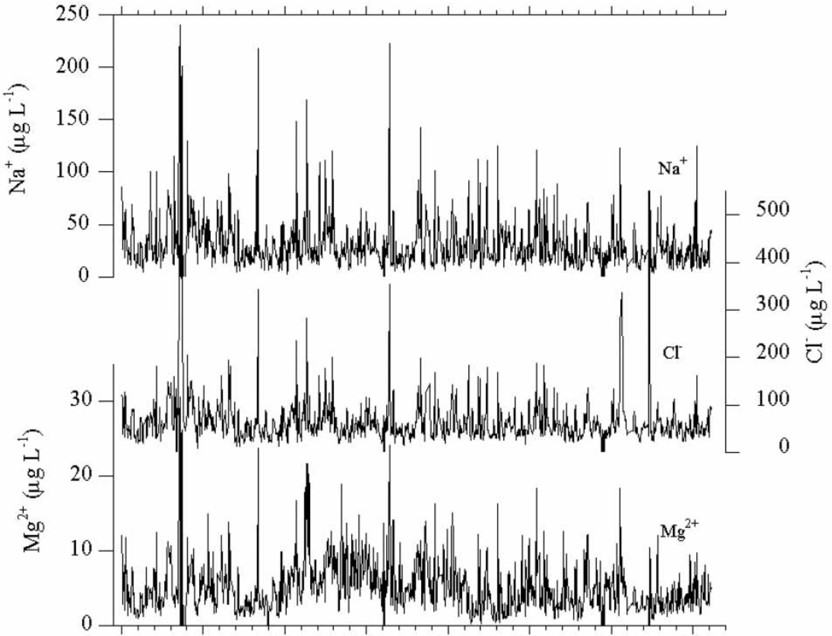

FIGURE 2 $Na^+$, $Cl^-$ and $Mg^{2+}$ concentration/depth profiles for the first 36 m of Talos Dome firn core.

along the whole profile, with concentrations up to 240 ppb, about ten times higher than median value (24.2 ppb). The highest peak, recorded at around 3.40 m, covers a large depth range suggesting a large snow deposition. On the other hand, the event recorded at 16.50 m shows a similar $Na^+$ concentration (maximum concentration 225 ppb), but a lower depth extension, leading to a lower $Na^+$ flux. The $Na^+$ mean values at Talos Dome (30.7 $\mu g\,L^{-1}$) are slightly higher than those determined in snow-pit samples collected at Dome C (25.3 $\mu g\,L^{-1}$) [19], a plateau station located about 1100 km inland, at 3230 m a.s.l. On the contrary, the $Na^+$ content at Talos Dome is significantly lower than at Hercules Névé (62.7 $\mu g\,L^{-1}$) [14], a coastal station in northern Victoria Land (about 80 km inland) located at about 3000 m a.s.l. These results point out the fractionating effects of atmospheric aerosol due to altitude and, more significantly, to distance from the sea, as reported elsewhere [14,18,20].

The chloride concentration/depth profile (Fig. 2) is similar to that of $Na^+$, showing in-phase concentration spikes. A very good agreement is observed for the two above-mentioned events recorded at 3.40 m (480 ppb) and at 16.50 m (350 ppb). On the contrary, the high $Cl^-$ peak at about 32.50 m is not shown by the other sea spray components, so this peak could be ascribed to HCl deposition. In this depth range, the sulphate profile does not show any spike, supporting the hypothesis that this extra sea spray peak originates from HCl formation following a submarine volcanic eruption. This event, dated AD 1795 [8] has previously been observed in an ice core drilled at the South Pole [21].

The magnesium profile shows the same spikes as sodium, but some differences are visible in the background trend. The most evident difference among $Mg^{2+}$ and $Na^+$ or $Cl^-$ profiles is a sharp increase in the background values in the 10–21-m depth range, corresponding to AD 1870–1944 [8]. Although the reason for such a pattern should be further investigated, we suppose that it could be related to a dry period occurring in the Southern hemisphere [22] enhancing the crustal source of $Mg^{2+}$ in Antarctic deposition. Indeed, a similar pattern is also shown in the fluoride, formate and formaldehyde profiles [22], which are typical markers of biomass burning events occurring more frequently in dry periods. Figure 3 shows the correlation between $Cl^-$ and $Na^+$

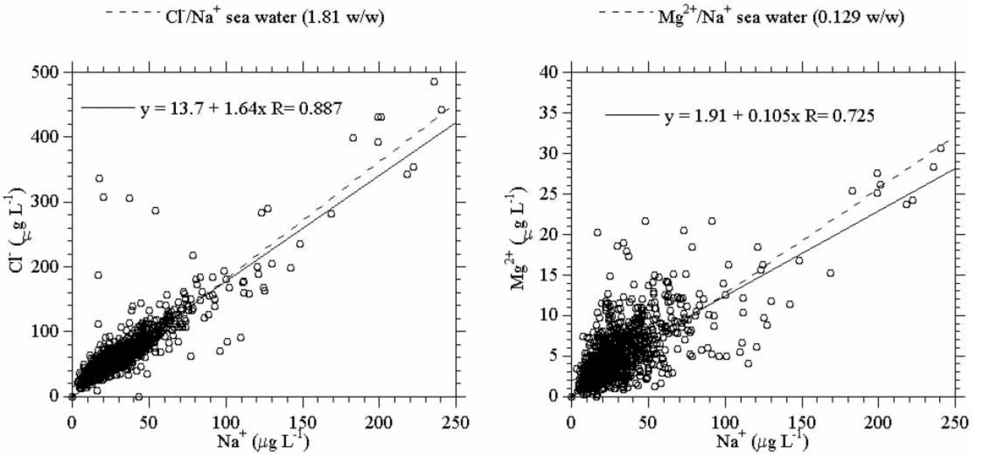

FIGURE 3 Correlation plots of $Cl^-$ and $Mg^{2+}$ as functions of $Na^+$. The dashed lines represent the $Cl^-/Na^+$ (left) and $Mg^{2+}/Na^+$ (right) ratios in sea water.

concentrations (expressed as $\mu g\,L^{-1}$). The good fit ($R = 0.863$, $n = 1100$) and the slope of the linear regression (1.62, very close to the $Cl^-/Na^+$ ratio in sea water: 1.81 w/w), suggest that sea spray is the dominant source for both $Na^+$ and $Cl^-$ at Talos Dome. The positive intercept shows additional chloride sources, possibly HCl deposition from volcanic emission and $NaCl/H_2SO_4$ atmospheric exchange. This pattern, already observed at coastal stations [18], demonstrates that other sources for $Cl^-$ become quantitatively more important when sea spray contribution is low. At Talos Dome, such alternative $Cl^-$ sources are not significant in samples with $Na^+$ concentrations higher than 50 ppb, as shown by the $Cl^-/Na^+$ ratio, which tends to the sea water ratio (1.81 w/w).

Magnesium correlation with sodium ($R = 0.725$, $n = 1108$, see Fig. 3) is poorer than the $Cl^-$ correlation ($R = 0.887$, $n = 1109$) and really driven by a few samples characterised by high sea spray content. The linear regression slope (0.106) is lower than the sea water composition ($Mg^{2+}/Na^+ = 0.129$ w/w, dashed line), but the layers recording sea storm events have $Mg^{2+}/Na^+$ ratios very close to the sea water ratio. As with chloride, the positive intercept points to extra sources for magnesium, mainly crustal inputs.

## Oxidized Sulphur Compounds

The variations of marine productivity can be investigated through the seasonal behaviour and the spatial and temporal distribution of two sulphur cycle components, MSA and $nssSO_4^{2-}$ arising from atmospheric oxidation of dimethylsulphide (DMS), produced by phytoplankton metabolic activity [23]. The study of temporal changes of such sulphur compounds in the snow deposition by ice core analysis can constitute an effective and selective tool to reconstruct the phytoplanktonic activity and its effects on the global climate changes, even for the remote past [6,23,24]. $nssSO_4^{2-}$ was calculated in every sample by subtracting from the total sulphate concentration the contribution given by sea spray, calculated using $Na^+$ concentration as a univocal marker of the sea spray source [25]

$$[nssSO_2^{2-}] = [SO_4^{2-}]_{tot} - 0.253[Na^+]$$

where 0.253 is the sea water sulphate/sodium ratio (w/w).

MSA is only produced by biological marine life [24,26], while the $nssSO_4^{2-}$ arises from other sources such as volcanic and anthropogenic emissions or crustal erosion [27,28]. Nevertheless, in Antarctica the biogenic source of $nssSO_4^{2-}$ is dominant, especially in summer [23,29]. Indeed, at Talos Dome, the main contribution to the sulphate budget is given by $nssSO_4^{2-}$, which constitutes about 88% of total sulphate (Table II); such a percentage is intermediate between the relative $nssSO_4^{2-}$ contributions measured at Hercules Névé (75%) [20] and at Dome C (95%) [19].

The strong seasonality of DMS production leads to an analogous seasonal behaviour of MSA and $nssSO_4^{2-}$, which show maximum concentrations in aerosol and then in snow precipitation during the phytoplanktonic bloom and in the following period [15,23,30]. Many authors have used seasonal variations of $nssSO_4^{2-}$, and sometimes of MSA, as a reliable seasonal marker in stratigraphic snow-layer dating [29,31–34]. Figure 4 shows the $nssSO_4^{2-}$ concentration/depth profile in the 14–18.6-m depth interval

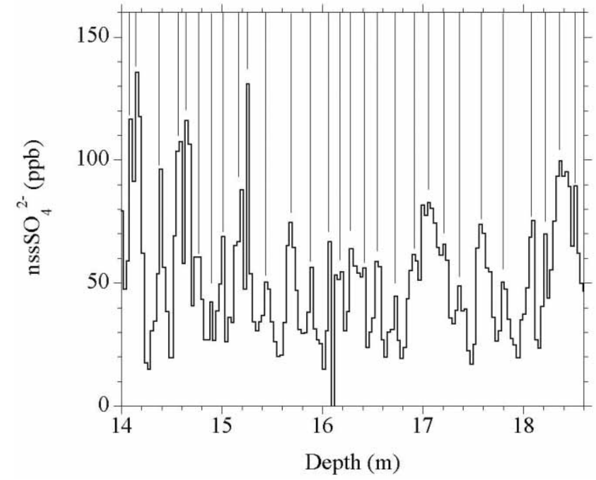

FIGURE 4 nssSO$_4^{2-}$ profile in the 14–18.6-m depth interval showing a seasonal pattern. Summer maxima are marked by vertical lines.

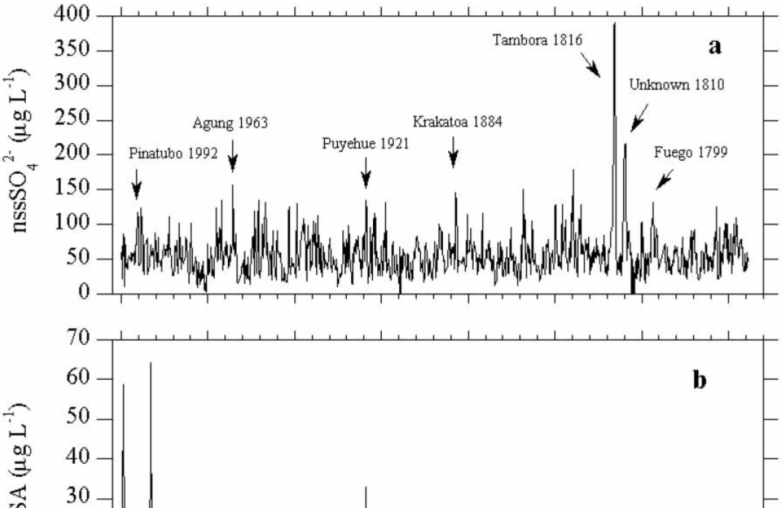

FIGURE 5 nssSO$_4^{2-}$ and MSA concentration/depth profiles for the first 36 m of Talos Dome firn core.

along the Talos Dome firn core. As found for more coastal stations in northern Victoria Land [29,30,34]), a seasonal pattern is detectable, and it was used by Stenni *et al.* [8] for firn core dating. Figure 5 shows the nssSO$_4^{2-}$ profile along the 36-m core, the observed concentration peaks superimposed on the seasonal trend can be ascribed to volcanic eruptions. The signatures of Pinatubo (1991), recorded at 0.92 m, and the characteristic double peak corresponding to Tambora (1816) and to a unknown volcanic eruption (1810), recorded around 29-m depth, have been used as temporal horizons to set the stratigraphic dating [8]. On the basis of this preliminary setting, the Agung (1963), Puyehue (1921), Krakatoa (1884) and Fuego (1799) eruptions were also recognised, and the related signatures were used to improve the dating by using a larger number of temporal horizons [8].

Figure 5b shows the Talos Dome MSA profile. In the uppermost layers, two spikes, with the highest concentrations (58 and 64 ppb, respectively) found in the whole firn core, are clearly evident. These peaks could be caused by particular intense climatic events or could appear particularly prominent as a consequence of smoothing effects, caused by diffusive processes, affecting the deeper snow layers and able to decrease the MSA concentration [35]. MSA movements in firn layers, if they occur, smooth the spikes but do not delete the general oscillation pattern. On the basis of the stratigraphic dating [8], the period of such oscillating trends was calculated to cover a few years. MSA peaks could be related to changes in atmospheric circulation (Southern Oscillation events) [6]. Increases in MSA snow concentration could also be correlated to changes in sea-ice extent: a large sea-ice cover around the Antarctic coast is considered to be a positive factor for enhanced phytoplanktonic growth and thus for a higher DMS production [36]. In addition, the production of MSA by oxidation of DMS is favoured (with respect to $H_2SO_4$ formation) at low temperature [6], which could be linked to a large sea-ice extent.

As expected for this station, located at high altitude and far from the sea, the correlation between MSA and nss$SO_4^{2-}$ is missing, because extra-DMS nss$SO_4^{2-}$ sources are relevant here. As already found for coastal stations [30], an enrichment in nss$SO_4^{2-}$ content is observed when the biogenic contribution (expressed by MSA concentration) is low. Indeed, Fig. 6 shows that, for high MSA concentrations, the nss$SO_4^{2-}$/MSA ratio settles to value around 3 (w/w) confirming the values of 2.7 w/w obtained in coastal stations located in northern Victoria Land [30].

The MSA fraction is defined as the ratio between the MSA content and the total biogenic oxidised sulphur: MSA/(MSA+nss$SO_4^{2-}$). Such a ratio is dependent on latitude, altitude and distance from the sea of the sampling stations. In northern Victoria Land, the MSA fraction is around 0.22 (w/w) [30]. This value is consistent with those reported for aerosol samples over the circum-Antarctic oceans, where a mean MSA fraction of about 0.3 (w/w) was calculated, with values up to 0.5 (w/w) [37,38]. At Talos Dome, a lower MSA fraction was measured (0.08 w/w), in accord with the station's geographical position (far from the sea and at high altitude). This value is very close to that found at Dome C (0.05 w/w, unpublished data). This coastal–inland pattern could be explained by considering a roughly constant regional biogenic nss$SO_4^{2-}$ content (with a seasonal pattern), which, in plateau and semi-plateau stations, is strongly affected by long-range transport contributions, such as volcanic $H_2SO_4$ inputs or arrivals of marine air masses coming from lower latitudes and characterised by lower MSA/nss$SO_4^{2-}$ ratios (because of the higher temperatures in the source areas) [39].

## Nitrate and Ammonium

At present, the origin of nitrate found in polar regions is not fully understood and is a matter of discussion. The controversy is mainly focused on the extent of stratospheric contribution to nitrate deposition [40] in the polar areas and whether the nitrate record can be used as a proxy marker for several climatic and environmental events, such as changes in solar activity, atmospheric oxidizing capacity, atmospheric $NO_x$ content, stratosphere–troposphere interchanges and the effects of nuclear explosions, meteorite fall and supernovas [41].

Risbo *et al.* [41] suggest a predominantly stratospheric origin for nitrate in Antarctica, compared to supernovas, auroras and cosmic ray contributions, on the basis that $HNO_3$ summer maxima observed in Greenland snow are in phase with maximum stratosphere/troposphere exchange periods. Legrand and Delmas [42] favour the hypothesis that lightning in the circum-tropical areas, followed by long-range transport processes toward the poles, is a significant nitrate source. The same authors have also postulated that nitrate in Antarctica is deposited mainly as $HNO_3$, since this acid is present in the gas phase in the atmosphere.

Figure 7 shows the concentration/depth profiles of $NO_3^-$ and $NH_4^+$ measured at Talos Dome. The nitrate profile exhibits a seasonal pattern which was used together with nss$SO_4^{2-}$ profiles for stratigraphic dating [8]. The mean nitrate concentration in the first 36-m firn core is $60.1 \pm 17.8\,\mu g\,L^{-1}$, a value similar to those measured in coastal areas of northern Victoria Land [20]. Therefore, nitrate background levels seem to be quite constant in coastal and semi-plateau areas and its spatial distribution is not significantly influenced by changes in altitude or distance from the sea. On the contrary, at more inland stations, nitrate levels are much lower, as measured at Vostok [43] and at Dome C [19]. However, the nitrate decrease toward plateau areas is not correlated to a real difference in depositional fluxes, caused by fractionating processes in the atmospheric aerosol during inland transport, but is due to post-depositional re-emission of $HNO_3$ into the atmosphere [19,43,44]. Such post-depositional processes are mainly driven by snow accumulation rate, snow acidity and contemporaneous presence of alkaline dust, able to fix $HNO_3$ as a non-volatile salt [45]. Therefore, in stations characterised by low snow accumulation rates, which are the chosen sites for deep ice coring, nitrate is not conservative and does not allow a reliable reconstruction of paleo-atmospheric composition.

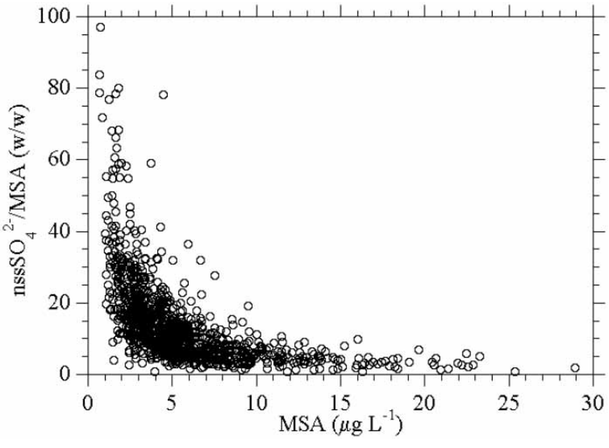

FIGURE 6 nss$SO_4^{2-}$/MSA ratio (w/w) reported as a function of MSA concentration for the first 36 m of Talos Dome firn core.

Fortunately, at Talos Dome, nitrate does not show any decreasing trend in the uppermost snow layers, so post-depositional processes do not seem to affect the preservation of nitrate in snow layers. Therefore, a mean accumulation rate of about 80 $kg\,m^{-2}\,yr^{-1}$ seems to be sufficient to prevent nitrate re-emission into the atmosphere, making this compound a conservative marker at this station. A nitrate concentration/depth profile measured in a deep ice core drilled at Talos Dome could allow the reconstruction of the changes of nitrogen compounds (with particular attention to $NO_x$) in the paleo-atmospheres and a study of their relationships with the climatic system.

Ammonium is the second most abundant nitrogen species in polar ice. Its concentrations in Antarctic ice are about one order of magnitude lower than in Greenland ice [6]. Anthropic and natural biogenic contributions are higher in Greenland, supporting the hypothesis that continental inputs (such as exhalations from soil, cattle-breeding and biomass burning from natural fires and anthropic agricultural activity) are dominant in the ammonium budget [6]. For coastal areas of Antarctica, some authors postulate a significant oceanic source of ammonium, coming from the metabolic process of marine organisms [46] and penguin colonies [47].

The ammonium profile (Fig. 7) shows background values around 10 ppb, modulated by a series of peaks with concentrations up to six times higher.

The mean percentage of $NH_4^+$, with respect to total N species ($NO_3^-$ and $NH_4^+$) at Talos Dome is around 13%; this value is similar to that measured in northern Victoria Land coastal sites (e.g., 11% at Hercules Névé, 13% at McCarthy Ridge). In fact, these components are mainly distributed in the gas phase in the atmosphere (as ammonia and nitric acid) and their distribution is poorly influenced by altitude

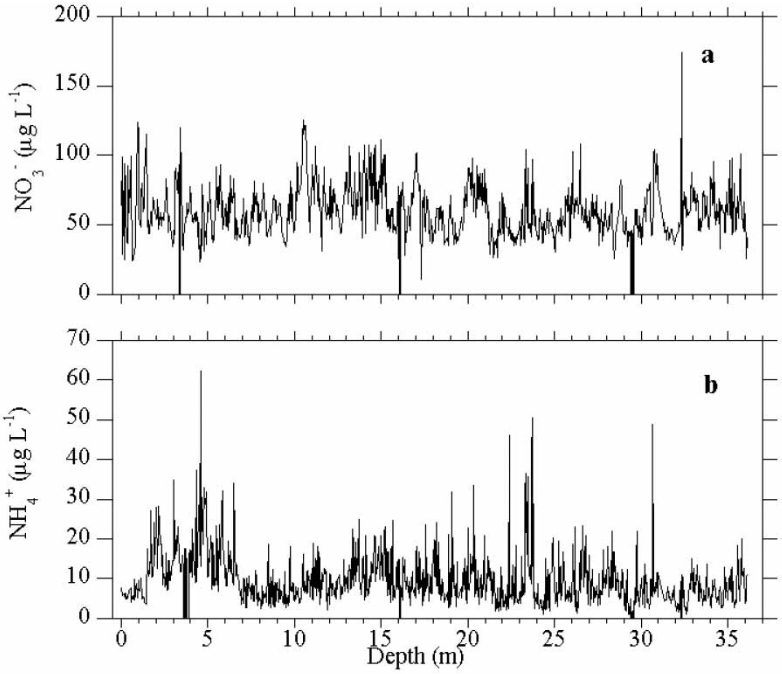

FIGURE 7 $NO_3^-$ and $NH_4^+$ concentration/depth profiles for the first 36 m of Talos Dome firn core.

and distance from the sea. Conclusions of the value of the relative percentages of nitrogen species cannot be drawn on the basis of results from Antarctic plateau stations, because $NO_3^-$ measured at stations with low snow accumulation rates is affected by post-depositional processes (see above) [11,12].

Given the complexity of the processes affecting the spatial and temporal distribution of nitrogen cycle compounds (sources, transport processes, depositional and post-depositional effects), more comparative studies on the aerosol–snow exchange at several stations, differing in geographical position and in snow accumulation rate, are needed to understand the variation of the nitrogen cycle in the past glacial–interglacial climatic cycles, when large changes in accumulation rate and snow acidity occurred.

## CONCLUSIONS

Owing to its geographical position and snow accumulation rate, Talos Dome presents some peculiar features and it is able to provide information about past atmospheric composition which is complementary to that from plateau stations.

As regards primary sea spray components ($Na^+$, $Cl^-$, $Mg^{2+}$), Talos Dome is more similar to coastal than to plateau stations, showing good linear correlations among the three components, with slopes close to sea water composition. For samples having low sea spray content, indicated by $Na^+$ low concentration, contributions from sources other than sea spray are evident for $Cl^-$ and $Mg^{2+}$.

The $nssSO_4^{2-}$ profile was shown to be just as useful for stratigraphic dating as the profile from coastal stations, since the seasonal pattern is still detectable; nevertheless, the most intense volcanic signatures, superimposed on the seasonal cycle, are evident just as they are at plateau stations.

At Talos Dome MSA profiles show typical seasonal behaviour only in the most superficial layers; instead, the multi-year oscillation shown in MSA profiles could be related to changes in sea-ice extent in the surrounding oceanic areas or to more efficient marine aerosol production and meridional transport processes caused by variation in climatic conditions and atmospheric circulation, such as Southern Oscillation effects.

The nitrate profile at this station shows a seasonal pattern similar to that observed in more coastal stations. This seasonal pattern could be useful for stratigraphic snow layer dating. The relatively low snow accumulation rate allows longer temporal records than at coastal stations but, on the other hand, it is sufficiently high to preserve nitrate from post-depositional losses, which are observed in plateau stations characterized by lower accumulation rates.

The preliminary study of the first 36 m of Talos Dome firn core suggests that chemical analysis of a deep ice core drilled at this station will be able to provide a reliable and detailed paleo-record of changes in marine (primary and secondary aerosol) and sulphur and nitrogen cycle contributions, which can be correlated to past variations of climatic and environmental conditions.

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