Spatial and temporal variability of snow chemical composition and accumulation rate at Talos Dome site (East Antarctica)

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HIGHLIGHTS
• Firn core decontamination is proved to be efficient for all the ions except ammonium.
• Post-depositional storage effects are found for MSA, NO3−, NH4+
• Relatively high accumulation rate allows preservation of nitrate and MSA.
• Undisturbed deposition allows annual snow layer counting by NO3−, nssSO42− and MSA.
• Spatial variability is lower than temporal variability at 5% significance level.

GRAPHICAL ABSTRACT

ABSTRACT

Five snow pits and five firn cores were sampled during the 2003–2004 Italian Antarctic Campaign at Talos Dome (East Antarctica), where a deep ice core (TALDICE, Talos Dome Ice Core, 1650 m depth) was drilled in 2005–2008 and analyzed for ionic content.

Particular attention is spent in applying decontamination procedures to the firn cores, as core sections were stored for approximately 10 years before analysis. By considering the snow pit samples to be unperturbed, the comparison with firn core samples from the same location shows that ammonium, nitrate and MSA are affected by storage post-depositional losses. All the other measured ions are confirmed to be irreversibly deposited in the snow layer. The removal of the most external layers (few centimeters) from the firn core sections is proved to be an effective decontamination procedure.

High-resolution profiles of seasonal markers (nitrate, sulfate and MSA) allow a reliable stratigraphic dating and a seasonal characterization of the samples. The calculated mean accumulation-rate values range from 70 to 85 mm w.e. year−1 in the period 2003–1973 with small differences between two sectors: 70–74 mm w.e. year−1 in the NNE sector (spanning 2003–1996 years) and 81–92 mm w.e. year−1 in the SSW sector (spanning 2003–1980 years). This evidence is interpreted as a coupled effect of wind-driven redistribution processes in accumulation/ablation areas.

Statistical treatment applied to the concentration values of the snow pits and firn cores samples collected in different points reveals a larger temporal variability than spatial one both in terms of concentration of chemical markers and annual accumulation.

Keywords: Ion species Snow layer Talos Dome Spatial variability Accumulation rate
The low spatial variability of the accumulation rate and chemical composition measured in the five sites demonstrates that the TALDICE ice core paleo-environmental and paleo-climatic stratigraphies can be considered as reliably representative for the Talos Dome area.

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1. Introduction

Ice cores drilled in unperturbed deposition areas represent a unique archive of the composition of past atmospheres. Obtaining chemical, isotopic and physical ice core stratigraphies allows reconstructing past environmental and climatic changes on time scales ranging from a few decades to hundreds of thousands of years (e.g., EPICA Community Members, 2004, 2006).

In the framework of the IPICS (International Partnerships in Ice Core Sciences) program, the Talos Dome site (East Antarctica) was chosen for a deep ice core drilling (TALDICE Project). The main goal of the TALDICE project was to obtain high-resolution chemical, isotopic and physical stratigraphies in an East Antarctic site located not far from the coast and characterized by a relatively high accumulation rate of about 80 mm water equivalent per year (here-hence w.e. year\(^{-1}\)) as average 2004–1259 AD (Stenni et al., 2002). These features, together with its position on a geographical dome, are believed to allow reconstruction of the environmental and climatic changes occurring in the Ross Sea–Wilkes Land coast marine sector for the last 200 kyear and to allow a comparison of such stratigraphies with those obtained from the EPICA-Dome C and Taylor Dome ice cores (Bianchi et al., 2003; Frezzotti et al., 2004; Urbini et al., 2006). TALDICE drilling (2005–2008) reached the depth of 1650 m, covering the last 250 kyear (Bazin et al., 2013; Veres et al., 2013). The TALDICE ice core revealed that the Talos Dome site is very sensitive to the climatic variations occurring at regional-to-global scale over the last climate cycle (Stenni et al., 2011). Particular attention was paid to changes in marine and atmospheric circulation and marine productivity in the Ross Sea and Adelie Land sectors (Scarchilli et al., 2011). Its relatively large accumulation rate (with respect to other ice core sites located on the Antarctic Plateau) enables an accurate dating of the core, particularly during the Holocene (the last 11.5 kyear) and the last climatic transition (Buiron et al., 2011).

In order to assess the reliability of the achieved stratigraphic records from a certain site, the site variability needs to be studied by comparing chemical and accumulation data series from snow pits and firn cores sampled in different points.

In particular, the spatial variability should be compared with the temporal variability in order to verify whether the observed temporal changes can be reliably associated to actual environmental or climatic changes or to site variability.

Previous samplings (by snow pits and shallow firn cores) were carried out around Talos Dome area (Becagli et al., 2004, 2005; Benassai et al., 2005; Frezzotti et al., 2005; Sala et al., 2008; Severi et al., 2009) but the sampling sites were distributed in a large area and the sampling strategy was not specifically addressed to evaluate the spatial variability of the TALDICE drilling site.

Aiming to contribute to a better interpretation of the TALDICE stratigraphies and to assess the spatial variability of the Talos Dome area, the samples collected in five snow pits and five firn cores are analyzed evenly distributed at a short distance from the TALDICE site. One site was chosen in the same TALDICE site, and the others at a distance of approximately 500 m along the North, South, West, East cardinal directions.

The sampling was carried out during the 2003–2004 Italian Antarctic Campaign, but chemical analysis was not immediately performed. Snow pit and firn core samples have been analyzed for the ion content (inorganic anions and cations and selected organic anions) in 2013–2014.

The main goal of this paper is evaluating the spatial variability of the snow chemical composition and accumulation rate close to the main drilling site and assessing if the TALDICE deep ice core stratigraphies can be considered as reliably representative of the Talos Dome deposition area.

A secondary goal is to evaluate the effects of a long-time storing of firn core sections (about 10 years) on the preservation of the original chemical signatures. For this purpose, a decontamination procedure is applied in order to eliminate a possible contamination of the external snow layers of the firn core sections and the effects of possible post-depositional processes are tested by comparing homologous (same site, similar depth) firn core and snow pit samples.

2. Methodology

2.1. Sampling site

Talos Dome (72°48′S, 159°06′E; 2316 m a.s.l.) is an about 900 km\(^2\) elliptical ice dome, elongated in a NW–SE direction (perpendicular to the prevalent wind direction — Urbini et al., 2008), in Northern Victoria Land, at the edge of the East Antarctic plateau. It is located at about 290 km from the Southern Ocean (Oates Land–George V Land), 250 km from the Ross Sea, and 275 km from the Italian Mario Zucchelli Station (Terra Nova Bay) (Fig. 1). The site is characterized by an annual mean temperature (as recorded at 15 m depth) of —41 °C, and by an annual snow accumulation of about 80 mm w.e. year\(^{-1}\), evaluated over the 1217–1996 AD period (Stenni et al., 2002). Because of the relatively high accumulation rate, ice cores drilled at this site are considered to be suitable for high-resolution records of past environmental and climatic variations.

Five snow pits were dug and five shallow firn cores were drilled during the 2003–2004 Italian Antarctic Campaign. Table 1 reports the basic geographical and glaciological information on the sampling sites.

The snow pits were dug by hand and the samples were collected by inserting pre-cleaned polyethylene vials along a vertical line in the snow wall. During the sampling, particular care was paid in minimizing contamination risk: the pit wall was cleaned by a pre-cleaned stainless steel scraper and personnel wore sterile clothing and polyethylene gloves. The sample depth resolution is 3 cm (external diameter of the vials).

The snow density was measured by inserting a double-side open stainless steel cylinder (whose internal volume is known) every 10 cm into the snow wall. The recovered snow volume was stored in a plastic bag and weighed the same sampling day in a cold laboratory. The mean density is 0.37 g/cm\(^3\) (Severi et al., 2009).

The vials containing the samples were stored in sealed polyethylene bags and kept frozen in insulated boxes for transport to Italy (Severi et al., 2009).

At every site, a shallow firn core was also drilled, in order to increase the sampling depth. The firn core sections were stored in sealed polyethylene bags and kept frozen in insulated boxes for transport to Italy.

2.2. Sampling procedures and analysis

Unlike snow pit samples, for which the contamination risk is quite low once the wall of the pit has been carefully cleaned and clean vials were used to collect and store the samples, firn core sections can undergo serious contamination risks. Contamination can originate from the firn core sampler and from the handling of the firn core sections during
the extraction, cutting and packing procedures. Besides, plastic bags used for firm core sections storing are difficult to be properly cleaned and cannot be an impenetrable barrier for gaseous pollutants during long storing periods. For this reason, firm core sections must be accurately decontaminated during the sub-sampling just before the chemical analysis. Decontamination is performed by eliminating the most external layers (about 2 cm) with a pre-cleaned stainless steel scraper, under a class-100 laminar flow hood inside a cold room (−20 °C). Once a sufficient part of a firm core section is decontaminated, the final 2.5 cm are introduced in a pre-cleaned vial and cut without any other handling. Vials are sealed in a plastic bag and stored at −20 °C. Sub-samples are analyzed within two days after decontamination.

Just before analysis, all the snow pit and firm core samples are melted in a clean room under a class-100 laminar flow hood, still closed in their containers. The vials are placed still closed into a liquid handler autosampler. The samples are sucked by the auto-sampler needle, able to pierce the vial plastic cap, and distributed to a two-ion chromatography system by a FIA device, which is based on a peristaltic pump and two

Table 1
Geographical and glaciological features and sampling details of the five sampling points.

<table>
<thead>
<tr>
<th>Sampling site</th>
<th>Sample type</th>
<th>Latitude (S)</th>
<th>Longitude (E)</th>
<th>Start depth (cm)</th>
<th>Total depth (cm)</th>
<th>Number of samples</th>
<th>Geographical position</th>
</tr>
</thead>
<tbody>
<tr>
<td>TD03-04 DP B</td>
<td>Snow pit</td>
<td>72°49’04.6″</td>
<td>159°10’30.9″</td>
<td>0</td>
<td>577</td>
<td>177</td>
<td>Central</td>
</tr>
<tr>
<td>TD03-04 C</td>
<td>Firm core</td>
<td>72°49’04.6″</td>
<td>159°10’30.9″</td>
<td>60.9</td>
<td>695.6</td>
<td>178</td>
<td>Central</td>
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<tr>
<td>TD03-04 SP1 B</td>
<td>Snow pit</td>
<td>72°48’50.7″</td>
<td>159°10’59.0″</td>
<td>0</td>
<td>204</td>
<td>67</td>
<td>North</td>
</tr>
<tr>
<td>TD03-04 SP1</td>
<td>Firm core</td>
<td>72°48’50.7″</td>
<td>159°10’59.0″</td>
<td>22.3</td>
<td>503.8</td>
<td>157</td>
<td>North</td>
</tr>
<tr>
<td>TD03-04 SP2 B</td>
<td>Snow pit</td>
<td>72°48’56.2″</td>
<td>159°09’44.5″</td>
<td>0</td>
<td>202</td>
<td>64</td>
<td>West</td>
</tr>
<tr>
<td>TD03-04 SP2</td>
<td>Firm core</td>
<td>72°48’56.2″</td>
<td>159°09’44.5″</td>
<td>31.0</td>
<td>453.4</td>
<td>104</td>
<td>West</td>
</tr>
<tr>
<td>TD03-04 SP3 B</td>
<td>Snow pit</td>
<td>72°49’18.3″</td>
<td>159°10’02.1″</td>
<td>0</td>
<td>227</td>
<td>71</td>
<td>South</td>
</tr>
<tr>
<td>TD03-04 SP3</td>
<td>Firm core</td>
<td>72°49’18.3″</td>
<td>159°10’02.1″</td>
<td>13.3</td>
<td>542.8</td>
<td>137</td>
<td>South</td>
</tr>
<tr>
<td>TD03-04 SP4 B</td>
<td>Snow pit</td>
<td>72°49’13.0″</td>
<td>159°11’16.9″</td>
<td>0</td>
<td>209</td>
<td>66</td>
<td>East</td>
</tr>
<tr>
<td>TD03-04 SP4</td>
<td>Firm core</td>
<td>72°49’13.0″</td>
<td>159°11’16.9″</td>
<td>0</td>
<td>697.9</td>
<td>303</td>
<td>East</td>
</tr>
</tbody>
</table>
distribution valves (Morganti et al., 2007). This procedure eliminates any further handling and avoids any contact between the samples and the laboratory atmosphere, reducing the contamination risk. Parallel IC measurements are performed for the anion (F\(^-\), Acetate, Formate, MSA, Cl\(^-\), NO\(_3^−\), SO\(_4^{2-}\), C\(_3\)O\(_2\)\(^2-\) and cation (Na\(^+\), NH\(_4^+\), K\(^+\), Mg\(^{2+}\), Ca\(^{2+}\)) determination, by using the method described in Morganti et al. (2007).

3. Results and discussions

3.1. Results of decontamination procedures

Beside the contamination evaluation, the long-time storage of the firn core section gives the opportunity to study the possible migration/diffusion/volatilization effects on the preservation of the chemical signal. To this end, one section for every firn core is scraped and two concentric layers (external and intermediate layer), about 1 cm thick each, are collected. The rest of the firn core section, hereafter named “core layer”, is assumed to be sufficiently decontaminated for ion analysis. The three layers are analyzed and the results are compared in order to confirm the initial hypothesis.

For measurements of Na\(^+\), Cl\(^-\), Mg\(^{2+}\), Ca\(^{2+}\) and K\(^+\), the external layer usually shows higher concentrations, while the intermediate and the core layers show similar values. Fig. 2a and b show the results for Na\(^+\) (Cl\(^-\), Mg\(^{2+}\), and K\(^+\) show similar behavior) and Ca\(^{2+}\), respectively. This pattern clearly demonstrates that contamination affects just the most external firn core layer, probably by deposition and/or uptake of dust and salts particles, as already found in previous works (Chisholm et al., 1995; Gabrielli et al., 2006; Tao et al., 2001). These particles are incorporated in the firn lattice as micro-inclusions (e.g. Ohno et al., 2014) and are not able to move inside the firn layers. Since the intermediate layer shows very similar concentration values (equal for Na\(^+\), Cl\(^-\), Mg\(^{2+}\) and K\(^+\)) to those measured in the core layer (then reaching a kind of concentration plateau — Candelone et al., 1994), we are confident that removing such two layers (i.e., the most external 2 cm) is a suitable decontamination procedure. Also, in some firn core sections (TD03-04 SP1 — blue squares, TD03-04 SP3 — pink equilateral triangles and TD03-04 SP4 — green rectangular triangles for Na\(^+\); TD03-04 SP1 — blue squares and TD03-04 SP3 — pink equilateral triangles for Ca\(^{2+}\)), no significant contamination is measured even in the external layer.

However, in order to reliably check the efficiency of the decontamination procedure, the “core” samples, assumed to represent the pristine, non-contaminated sample are compared with the snow pits samples collected at the same site, taken as “cleanliness” reference in this case, given the minimal contamination risk provided by the snow pit sampling (as explained above).

At this purpose we choose to apply an analysis of variance (ANOVA) statistical tool. Indeed ANOVA test is proved to be useful to determine whether there are any significant differences between the means of some independent groups. A one-way ANOVA test is run for each one of the most relevant markers (sodium, sulfate, nitrate, MSA, chloride, magnesium and calcium) between the “core” concentration values of the selected firn core sections and the corresponding (in depth) values from the snow pit samples collected at the same site. Out of the five sites, only three of them show corresponding depths of both firn core sections and show pit samples, thus we run this test only for TD03-04 SP3, TD03-04 SP4 and TD03-04 C sites. F values lower than critical F values indicate a statistically significant similarity with a statistical significance level higher than 5% and specified by the p values (up to 1). In Table 2, such F values lower than critical F are reported in bold, as well as corresponding p values.

A statistically significant similarity is found for all the three sites for sulfate and chloride, for two sites out of five for sodium, magnesium and calcium while a significant difference is finally found for MSA and nitrate. Such a result shows that the decontamination is efficient in removing the external contamination for sulfate and chloride and mostly also for sodium, magnesium and calcium while nitrate and MSA are expected to be different due to post-depositional processes involving the migration of methanesulphonate from summer to winter layers, as observed by Pasteur and Mulvaney (2000), possibly also leading to a loss of MSA into the atmosphere (Delmas et al., 2003). In fact, both for MSA and nitrate, concentrations are definitely higher in the snow pit than in the firn core due to post-depositional migration of MSA and nitrate acidic forms towards the external atmosphere occurring in the latter, enriching the outer layers, then removed by decontamination and leaving a lower concentration than original in the “core” layer.

The ions mainly related to secondary aerosol (nitrate, MSA, ammonium) have gas-phase precursors and could be contaminated by uptaking gas-phase compounds from the storehouse or laboratory atmosphere (ammonium) or could be affected by post-depositional processes, such as movement in the firn lattice and re-emission into the atmosphere by acid–base exchanges for MSA and nitrate (Grannas et al., 2007 and references therein, Wagnon et al., 1999; Traversi et al., 2009).

Fig. 2 also shows the pattern of nitrate (2c), sulfate (2d), MSA (2e) and ammonium (2f). Nitrate shows similar concentrations in the three layers for four of the five firn cores. This evidence could suggest that no significant contamination or post-depositional processes affect the nitrate record. However, the TD03-04 SP3 core (pink equilateral triangles) shows a different feature, with a progressive concentration increase from the external to the core layer. As mentioned above, this pattern can be explained by the loss of gaseous HNO\(_3\) towards the atmosphere by diffusion processes. This loss is more evident as the firn layer is closer to the firn–atmosphere interface. Indeed, as discussed below, the majority of the samples are acidic (see Ion Balances in Section 3.3) and nitrate can be present as HNO\(_3\) in the original deposition or after acidic exchange with H\(_2\)SO\(_4\). The HNO\(_3\) volatile species can move through the porous firn, driven by a concentration gradient. This possibility is enhanced by the fact that firn cores are shallow (maximum depth: 6.95 m) and the f irmification processes were just started and not yet able to significantly change the initial low density and high porosity of snow deposition layers. Nitrate loss from snow superfi cial layers in Antarctica is well documented, especially in low accumulation sites, such as Vostok (Wagnon et al., 1999) and Dome C (Traversi et al., 2009; Savarino et al., 2007).

Sulfate shows a high variability among the firn cores and it is difficult to evaluate possible contamination effects. However, TD03-04 C (red dots), TD03-04 SP2 (purple diamonds) and, partially, TD03-04 SP4 (green rectangular triangles) firn cores show higher concentrations in the external layer. Intermediate and core layers generally show similar concentration values, again supporting that the decontamination procedure gives reliable results.

MSA shows a progressive concentration decrease from the external to the core layer, with the exception of the TD03-04 SP3 (pink equilateral triangles) firn core, where all the layers have similar concentrations. Since its only source is marine phytoplanktonic activity (via dimethylsulﬁ de — DMS-emission at the sea–air interface and consequent oxidation to MSA and HSO\(_4^−\) into the atmosphere; Legrand and Feniet-Saigne, 1991; Legrand et al., 1991), contamination during the sampling or the storage cannot be occurred. On the other hand, the acidic form of MSA is affected by post-depositional effects, especially in low-accumulation sites (Wagnon et al., 1999; Traversi et al., 2009). Such effects can involve a re-emission into the atmosphere as well as simple movements in the firn layers. By assuming that the post-depositional MSA movement inside the firn layers at Talos Dome is effective, we can consider that MSA moves as long as its acidic form is not neutralized (Pasteur and Mulvaney, 2000). Such diffusion processes can move the MSA from the inner part of the firn core to the external side. However, its possible re-emission into the atmosphere is blocked by the higher concentrations of dust and sea salt (by contamination), which are able to neutralize the MSA acidic form, giving MSA stable salts (Pasteur and Mulvaney, 2000).
The pattern of ammonium is complex and difficult to interpret. Indeed, especially in porous firn, ammonium can be affected by two opposite processes: contamination by ammonia uptake and post-depositional re-emission of ammonia (Littot et al., 2002; Saigné et al., 1987; Udisti et al., 1994). Fig. 2f shows three different patterns: TD03-04 C (red dots) and TD03-04 SP1 (blue squares) firn cores.

Fig. 2. Average concentration of selected ions in the selected section of every core. Red dots represent the TD03-04 C (Central) core; blue squares the TD03-04 SP1 (North) core; purple diamonds the TD03-04 SP2 (West) core; pink equilateral triangles the TD03-04 SP3 (South) core and green rectangular triangles the TD03-04 SP4 (East) core. Error bars represent measurement standard deviation. (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article.)
show constant very low values in all the three layers; TD03-04 SP2 (purple diamonds) and, especially, TD03-04 SP4 (green rectangular triangles) exhibit a decreasing trend from the external to the core layer; finally, TD03-04 SP3 (pink equilateral triangles) shows an opposite trend, with a progressive concentration decrease from the core to external layer. A tentative explanation can involve contamination and re-emission post-depositional processes. Since contamination from the laboratory or storehouse atmosphere is very probable, the TD03-04 SP2 (purple diamonds) and TD03-04 SP4 (green rectangular triangles) profiles can enlighten this kind of contamination, very high in the external layer and yet effective in the core layer.

Post-depositional re-emission of ammonia into the atmosphere is likely to be negligible due to the marked acidic character of all the snow layers, stabilizing ammonia as ammonium salts, thus not favoring the release of gaseous ammonia.

The TD03-04 SP3 (pink equilateral triangles) pattern can be tentatively explained by considering the higher variability of the ammonium values in this firn core section (see Fig. 2f).

The relevance of the contamination process by uptake for ammonium is shown also comparing snow pitvalues with the corresponding firn core ones. The latter are lower than the snow pit samples, suggesting a contamination by ammonium of the snow pit.

### 3.2. Dating

A reliable snow pit or ice/firn core dating is basic for a correct interpretation of the stratigraphic record and for an effective comparison with analogous data from other sites. When the accumulation rate is sufficiently high to preserve seasonal depositions, the stratigraphic method offers the most reliable and time resolved dating. The method is based on the identification and counting of the annual snow layer, by using chemical seasonal markers. Based on previous studies on snow pits and shallow firn cores sampled in Northern Victoria Land, a multiparametric method is used (Udisti, 1996), which is based on a set of seasonal chemical markers. In this case, NO$_3^-$, nssSO$_4^{2-}$ and MSA have been selected, because these compounds show sharp summer maxima.

The main source of nitrate in polar snow is still not fully understood, due to the large variety of nitrate-precursor (nitrogen oxides) sources; they include lighting, cosmic rays, biomass burning, stratospheric N$_2$O oxidation and sedimentation of polar stratospheric clouds, and re-emission from snow layers (e.g. Savarino et al., 2007). However, the nitrate profile exhibits a clear seasonal pattern (with maxima in late-summer), which can be used for stratigraphic dating (Traversi et al., 2008; Becagli et al., 2004). non-sea-salt SO$_4^{2-}$ and MSA show a similar pattern, because their major source in Antarctica is the atmospheric oxidation of DMS, emitted by phytoplanktonic activity, whose bloom occurs in January–February (austral summer) in the marine areas near Northern Victoria Land (Udisti, 1996; Becagli et al., 2004).

To be able to compare summer maxima on a mathematical basis, in order to try to highlight even less pronounced peaks, all annual peaks for each series relative to the various components are standardized. In this way, it is possible to recognize the annual trends more clearly, as reported in Fig. 3 on the left.

By summing the corresponding standardized values of all three components first and then the ones of NO$_3^-$ and nssSO$_4^{2-}$ only, point by point, it is possible to obtain two new temporal profiles as function of depth. In this way, it is possible to better highlight peaks occurring close to other higher peaks, which appear to have a fairly clear connotation of summer maximum (Udisti, 1996).

In most cases, in order to detect summer maxima, it is enough to examine directly the standardized sum profile of NO$_3^-$ and nssSO$_4^{2-}$ but in certain cases the sum with MSA is crucial to select definitively some summer peaks which would otherwise have been very doubtful.

Fig. 3 (plot on the right) shows the dating achieved for the TD03-04 DP B (central) snow pit. It is possible to identify 24 annual peaks with a high accuracy. The peaks later ascribed to the year 1995 and 1988 are confirmed by the sum with MSA; the year 1985 appears as a shoulder to a higher peak but it selects as a summertime maximum once having considered the sum with MSA; the peaks 2001, 1998 and 1975 can objectively be attributed both to distinct years and to the same year. As a conclusion, it is possible to identify 27 “certain” peaks and 3 “uncertain” peaks, yielding a relative uncertainty of 10%. This value is acceptable for the purpose of estimating single annual accumulation rate and to distinguish summer from winter samples for the ion balance.

### 3.3. Ion balance

In order to achieve an overview of the average chemical composition and load of the measured ion species in Talos Dome snow layers, ion balances (as μeq/L) are calculated from the average value of each component in every snow pit. The result is shown as stack columns in Fig. 4.

Since the evaluation of the H$^+$ is very difficult in polar snow and CO$_2^-$ and HCO$_3^-$ ions are not measured by ion chromatography (a carbonate/bicarbonate buffer is used as eluent), such ions are estimated from the ion-balance disequilibrium. In this way, the anion excess is interpreted as missing H$^+$ concentration and the cation excess as the loss of the carbonate/bicarbonate contribution (Legrand and Delmas, 1984).

In Fig. 4, one can observe that primary (marked by Na$^+$, Cl$^-$, partially SO$_4^{2-}$) and secondary (SO$_4^{2-}$, MSA) marine sources are the major contributors to the chemical composition of the aerosol deposited at this site. Nitrate is also a major ion, but, as previously noted, its sources to polar snow are yet under debate (Wolff et al., 2008; Traversi et al., 2012).

All the snow pit samples clearly show a large contribution of free acidity (H$^+$ concentration accounts for about 1 μeq/L). It is interesting to note that ammonium accounts for a significant fraction of the cationic budget (23%). Hence, ammonia is supposed to be the major neutralizer agent for acidic species, especially sulfuric and nitric acids, and it plays a relevant role as pH-regulator in the marine boundary layer (MBL), as first proposed by Bouwman et al. (1997). Indeed, NH$_4^+$ and sulfate are often associated in the atmospheric aerosol because they arise from marine activity (Kaufmann et al., 2010). In off-shore oceanic areas, NH$_4^+$ mainly originates from the biological decomposition of organic matter, with a highly variable contribution of zooplankton, as well (Johnson
et al., 2007). Johnson and Bell (2008) recently developed the concept of "co-emission", suggesting interaction processes between nssSO$_4^{2-}$ and NH$_4^+$ in the MBL. According to this hypothesis, the interaction is mainly driven by the acidity of the DMSP (dimethylsulfoniopropionate) oxidation products (mainly sulfuric acid) that controls the bidirectional NH$_4^+$ flux from the ocean surface towards neutralization. The equilibrium of this process depends on the sea surface temperature and, hence, at the first order, on latitude. Sulfuric acidity is partially or totally neutralized by NH$_3$, giving (NH$_4$)$_2$SO$_4$ and (NH$_4$)$_2$SO$_4$, respectively (e.g. Johnson and Bell, 2008). The limiting factor of this neutralization usually is the atmospheric concentration of ammonia. In the analyzed snow-pit samples, a significant correlation between NH$_4^+$ and SO$_4^{2-}$ ratio is not found, and the NH$_4^+/SO_4^{2-}$ mean ratio is 2.2 ± 1.8 (mol/mol), demonstrating the presence of (NH$_4$)$_2$SO$_4$, as an average, although a large variability has to be noted.

This result appears to be generally higher than previous aerosol and snow data from Antarctic sites. In particular, Legrand et al. (1998) provides ratios of around 0.3 mol/mol for coastal snow samples.

As concerning aerosol samples, Ooki et al. (2007) find values around 0.4 mol/mol in the South Pacific, Norman and Leck (2005) and Virkkula et al. (2006) find values around 0.3 mol/mol in the Southern Indian Ocean and at Finnish Antarctic research station Aboa (73°03’S, 13°25’W) respectively.

On the other hand, Johnson and Bell (2008) report molar NH$_4^+$/SO$_4^{2-}$ ratio of 0.7–2 mol/mol in aerosol samples collected along the whole year at Mawson (Antarctica) where a significant variability is also present.

The largely higher NH$_4^+$/SO$_4^{2-}$ ratio found in our snow pit samples is likely due to the above mentioned uptake of ammonia during storage but this unexpected result decidedly needs further investigation.

According to the snow pit dating, the samples have been sorted by seasonality. It is possible to identify 5 to 8 samples per year allowing the discrimination of summer and winter layers in order to study possible variations of chemical composition from summer to winter period.

Fig. 5 reports the ion balances evaluated on the summer and winter mean values, calculated on the entire data set.

The total ionic load is larger in the summer layers (3.5–5 μeq/L), with respect to the winter snow depositions (2.5–3.5 μeq/L). The stoichiometric anion excess marks a significant contribution of free acidity in both seasons. It has to be taken into account that such an acidic contribution is probably underestimated due to a possible contamination of ammonia during sample storage.

As expected, the free acidity is larger in the summer samples (35–65% of the total ion budget), due to the deposition of biogenic sulfuric acid. The percentage contribution of nitric acid is relevant, too. This evidence can mean that nitrate sources (especially stratosphere–troposphere transport and re-emission of NO$_3^-$ from the snow surface) are more intense in this season. In addition, we have to note that meridional transport of nitrate and sulfate from lower latitudes is more efficient in summer, due to the weakening of the polar vortex (Hara et al., 2008). Finally, higher temperature and intense solar irradiation make more efficient the photochemical oxidation of NO$_3^-$ and SO$_2$ to nitric and sulfuric acid. On the contrary, chloride is almost counterbalanced by the Na$^+$ concentration, then demonstrating its sea spray origin. During winter, free acidity is lower, accounting for 16–45% of the total ion budget.

3.4. Spatial and temporal variability of chemical markers and accumulation rate

The snow pit and firm core data set is evaluated in order to study the spatial variability of the Talos Dome site. The inter-site variability is calculated by comparing average and standard deviation values measured on the snow pits and firm core sampled in each site (Table 15 supplementary material) and through distribution plots (Fig. 6), where median values, 5th, 25th, 75th and 95th percentiles are shown for every chemical component measured in every snow pit and firm core.

Table 15 shows that for all the studied components, spatial variability, indicated by the standard deviation of the site means, is always lower than the temporal variability, indicated by standard deviation for each sampling point.

In particular, calculating the ratios between temporal and spatial variability, they are always larger than 3 for all the components, reaching values of 6, except for Ca$^{2+}$ that exhibits a comparable spatial and temporal variability for one site (TD03-04 SP2).

Such a good similarity, among the sampling points, is also shown by percentile plots. The median values are highlighted in each plot, to
provide an indication of the background levels and the concentration ranges spanned by the different percentiles.

For each preserved ion, 10 boxes are reported, one for every single snow pit and firn core retrieved from the five different points of the site, displayed with the same scale of concentration. For ions affected by post depositional processes during the storage only the data from snow pits are reported.

Starting with the sea salt components ($\text{Na}^+$ and $\text{Cl}^-$), shown in Fig. 6a and b, the different snow pits and cores show a small variability of the median value, falling within the 13–20 and 30–40 $\mu$g/L range,
respective. Also the 25th and 75th percentile levels do not show a considerable variability whereas a significant difference in concentration levels can be observed for the 95th percentile. Looking into detail at every sampling point, snow pits and firn cores show very similar median levels although firn cores generally show a larger value distribution than the corresponding snow pit. This feature can be explained both by a moderate difference in analysis resolution (2.5 cm versus 3 cm) and by the different length between snow pits and firn cores, which cover different deposition years. As visible in Table 1S, also average and standard deviation values in the all the stratigraphic series appear to be similar. The statistical significance of such a similarity is shown by the results of ANOVA treatment (see later). As concerning the percentile plots for Ca²⁺ and F⁻ (Fig. 6c and e), one can observe again an evident similarity for the absolute median levels, for all the three components falling in the 2−5, and 0.1−0.4 μg/L range, respectively. Nevertheless, despite the similarity of the absolute concentrations, especially for F⁻, percentage difference in the median values (and even more for the 75th and 95th percentiles) are large. Relative concentration differences even reach 200%, such as for the central snow pit and corresponding central core. As concerning fluoride, such a gap is very likely due to the higher measurement uncertainty linked to low values of this component. In fact the relative standard deviation, calculated at a concentration close to the mean sample values, is around 1.1%, against 0.1% of sulfate or 0.7% of chloride.

Regarding NO₃⁻ (Fig. 6f), median values fall within the 30−55 μg/L range and also the width of the 25th−75th percentile box is quite similar for all the sampling points. Similarly to the sea salt components, significant differences can be observed only for the outliers, i.e. the values belonging to the 75th−90th percentile range. Also in this case, the average values (Table 1S) confirm the results of the value distribution with a homogeneity of values, ranging from 34.4 ± 13.2 to 61.5 ± 32.3 μg/L and presenting standard deviations perfectly covering such a difference in mean values.

An analogous consideration can be drawn for SO₄²⁻ (Fig. 6d) showing even a larger homogeneity. In fact, background values are comprised within the 33−48 μg/L range and also close 25th and 75th percentiles for the different points.

Also mean values appear to be comparable, spanning the 39.6−60.1 μg/L concentration range, with an internal variability perfectly covering the external one (standard deviations of 22.4 and 70.7 μg/L, respectively, for the mentioned mean values).

As concerning MSA, it shows higher values in snow pits than in firn cores, very likely due to diffusion processes leading MSA to move from the inner to the external part of ice cores, as previously discussed. Such an evidence can be easily observed by looking at median values but especially considering the 75th percentiles (Fig. 6g). An analogous observation can be made for NH₄⁺ (Fig. 6f), easily measured in pits and hardly detectable in firn cores, again due to post-depositional losses of gas-phase ammonia.

As concerning the study of the accumulation rate variability at Talos Dome, the annual mean accumulation rate for every year and the mean annual accumulation rate for every firn core and snow pit for the time period covered by the whole record length are calculated. Analyzing firn cores and snow pits, average values are found to range between 70.3 and 85.4 mm w.e. (water equivalent) year⁻¹, although annual accumulation presents a large variability (as it usually occurs in many Antarctic sites), with values ranging from 21.5 to 193.9 mm w.e. year⁻¹. The calculated values of accumulation rate are in excellent agreement with the annual accumulation pattern measured during the 1996−1998 time period from stake measurements (Urbini et al., 2008). They show a large variability, from 50 to 112 mm w.e. year⁻¹ each year, with an average value of 86 mm w.e. year⁻¹.

The accumulation rate measured for recent time period (2003−1973) agree with the mean accumulation rate of 80.5 mm w.e. year⁻¹ for the last 779 year of deposition by Stenni et al. (2002).

The variability observed among different years and between different measurements (direct measurements through stakes and indirect measurement by reconstruction from firn stratigraphies) can be explained by two effects. The first is an actual variability of precipitation extent (as concerning the interannual variability for a single measurement series) and the second is related to processes disturbing the regular layering of snow depositions such as post-depositional redistribution processes, mainly due to the action of wind scouring. The stakes variability associated to the height of sastrugi (up to 20 cm) is probably
suggesting that the time series based on TD core contains a random element caused by the surface irregularities that Fisher et al. (1985) defines as “local noise”. Stake measurements and sastrugi heights suggest that the annual local noise in snow accumulation can be ±30 mm w.e., which constitutes about 35% of the average annual accumulation (Stenni et al., 2002). Previous work by Frezzotti et al. (2007) shows that the largest irregularity in snow morphology occurs in early summer whereas the minimum is recorded in late summer thus limiting the layering disturbance only to the summer season. In this way, annual signal can still be identified. Our results show indeed that such redistribution processes are not able to mix summer and winter layers because of a clear seasonal signal is observed and used for stratigraphic dating.

Previous studies on the same site, Frezzotti et al. (2004, 2007) reported that accumulation decreases downwind of TD (N-NE) and is higher in the SSW sector. TD surface contour lines are elliptical and elongated in a NW–SE direction; the NW and NE slopes are steeper. The elongation direction of the dome is perpendicular to the prevalent wind direction and parallel to both the outcropping Outback Nunataks (50 km North to TD) and the sharp NW–SE ridge in the bedrock. At TD, wind blows uphill from the SW with a gradient of 1–2 m km⁻¹ for a distance of 100 km. As pointed out by Frezzotti et al. (2007), the higher accumulation in the SSW sector can be correlated with reduced wind-driven sublimation in this area, which is due to the positive slope gradient that reduces wind velocities. In this work, we find a statistically significant agreement among the calculated accumulation rates (see later). The slight differences actually appear to follow the pattern observed by Frezzotti et al. (2007), with accumulation rate in SSW sector (SP2 and SP3 points or West and South point: 92 and 81 mm w.e. year⁻¹ respectively) higher than those in NNE sector (SP1 and SP4 or North and East points: 70 and 74 mm w.e. year⁻¹ respectively).

The lower accumulation in the downwind sector can be ascribable to an increase in wind-driven redistribution processes, which is determined by the increase in the surface slope towards the Southern Ocean (Urbini et al., 2008). Such redistribution processes seem to affect also the distribution of concentration values of most of markers. In fact, as visible from the Fig. 7 the box containing the 50% of values at East site is larger and shifted towards higher values with respect to the other sites, and especially the West site.

However, in order to assess the statistical significance of the similarity among the different sites, in terms of accumulation rate and chemical composition, a one-way between subjects ANOVA is conducted to compare the values corresponding to the same common period in the five ice cores analyzed (2004–1995), for each of the eight markers: sodium, sulfate, nitrate, MSA, chloride, fluoride, magnesium and calcium. As it can be observed from Table 3, all these species show a statistically significant similarity at the p higher than 0.05 level for the five cores. A particularly high significance is found for the annual accumulation rate among the five ice cores in the same period.

4. Conclusions

A reliable evaluation of the spatial variability in snow accumulation rate and chemical composition of the snow deposition in the Talos Dome area is accomplished by analyzing ten stratigraphic records (five snow pits and five shallow firn cores) in sites evenly distributed around the TALDICE drilling site.

These results complement, verify, and increase the paleo-records collected at other near-coastal sites and in the whole TALDICE ice core serving as a modern calibration of older records. In fact, the higher temporal resolution achieved with the analyzed firn cores and snow pits, with respect to TALDICE ice core allows testing the possible relationships of chemical markers with current and available measurements of climatic and environmental parameters (sea ice extent, solar activities, etc.).

An initial study on the possible post-depositional changes induced by the long term storing of firn core sections, which is based on the comparison between homologous snow pit and firn core samples, reveals that the used decontamination procedure is effective for all the measured ions, with the exception of ammonium. In fact, we observe that with concentric layers, the concentration of both halfway and core layers results to be comparable or lower than the external layer. Moreover, it appears that the radial migration is significant for some ions (nitrate and, in particular, MSA), also due to the particular characteristics of the material analyzed, which is porous firn. These data confirm the importance of analyzing this kind of matrix as soon as possible after collection, in order to prevent in firn post-depositional processes from occurring. Thanks to the marked seasonal pattern of selected parameters, it is possible to accomplish an accurate dating of the firn cores and snow pit. All the snow pits show an evident quite reproducible acidic character, with primary (Na⁺, Cl⁻, partially SO₄²⁻) and secondary (SO₄²⁻, MSA) marine sources, together with nitrate/nitric acid as the major contributors to the chemical composition. Also ammonium contributes with 23% to the cationic budget. The total ionic load is larger during the summer period, with values comprised within the 35% and 65% of the free acidity, against 16–45% observed in winter.

The different snow pits and cores show a small variability of the median values regarding sea salt components (Na⁺, Cl⁻, and Mg²⁺, Ca²⁺, K⁺, F⁻, NO₃⁻ and SO₄²⁻. As concerning MSA, it shows higher values in snow pits than in firn cores, very likely due to diffusion processes leading MSA to move from the inner to the external part of ice cores. A similar observation can be made for NH₄⁺, which in firn cores is almost missing, due to post-depositional losses of gas-phase ammonia.

As concerning the study of the accumulation rate variability at Talos Dome, average values are found to range between 70.3 to 85.4 mm w.e. year⁻¹, and small differences from one point to another (e.g. 70 and 74 mm w.e. year⁻¹ in the NNE part against 92 and 81 mm w.e. year⁻¹ in the SSW part) of the site are found and

Fig. 7. Percentile plot of accumulation rate of firn cores and snow pit with their median value.
interpreted in terms of wind-driven redistribution processes and accumulation areas. This agreement is a representation of the representativeness of the different sampling points at Talos Dome site. The studied ion balance confirms the similarity of the sampled sites in terms of average chemical composition and absolute concentrations of ionic markers, supporting the reliability of Talos Dome site for paleo-climatic studies. The ANOVA test confirms a significant similarity among all the sampling points for chemical components, and, even more significantly, for accumulation rate. Even more importantly, the comparison of the different sampling points studied at Talos Dome shows a larger temporal variability than spatial one both in terms of concentration of chemical markers and annual accumulation rate. Indeed, the calculated relative spatial variability for each chemical marker appears to be at least four times lower than the corresponding temporal variability. In this way the variations in concentration along the records, can be ascribed to real environmental changes rather than site variability. The obtained results support the suitability of this site in providing stratigraphic information representative for all the Talos Dome area. This is also especially important in interpreting the paleo-environmental and paleo-climatic changes observed along the TALDICE deep ice core.

Supplementary data to this article can be found on the website at: http://doi.org/10.1016/j.scitotenv.2016.01.087.

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References


matics 11, 561.


Table 3

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