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Correlations between concentrations of acids and oxygen isotope ratios in polar surface snow

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ABSTRACT

Investigation of centimeter-scale snow surface chemistry has been carried out at two polar sites with different site characteristics–in Dronning Maud Land, Antarctica and on the Greenland ice sheet, respectively. Large variations in both impurity content and stable oxygen isotope ratios (δ^{18}O) were found on the submeter scale. δ^{18}O and the concentration of nitrate correlated at both sites (r = 0.81 and 0.82, respectively). At the Antarctic site, δ^{18}O is also correlated to concentrations of methanesulphonate (r = 0.84) and sulphate (r = 0.83) while no such correlation exists at the Greenland site. Instead, a strong anticorrelation (r = –0.85) between sulphate and methanesulphonate is found among the samples from the Greenland site. The ions correlating with δ^{18}O at the two sites were probably deposited as acids. Our tentative explanation is that local redeposition of water vapour enriching the snow surface with the lighter isotopes is associated with simultaneous enhanced scavenging of the acids. The responsible process thereby significantly alters the chemical signals of the snow surface.

1. Introduction

Investigations on the impurity content in deposited precipitation in Polar Regions have the primary aim to get a picture of present or past atmospheric conditions, which demands an understanding of a complex series of air–snow transfer functions. Results from simultaneous air and snow measurements (e.g. Jaffrezo et al., 1994; Dibb et al., 1998; Wolff et al., 1998), snow pit and surface snow analysis (e.g. Goto-Azuma et al., 1997; Stenberg et al., 1998; Kreutz et al., 1999; Udisti et al., 1999; Wagnon et al., 1999; Udisti et al., 2004; Weller et al., 2004; Kärkäs et al., 2005) have enhanced the understanding of the air-snow transfer functions both qualitatively and quantitatively. Governing air-snow transfer processes will change with the climatic and environmental conditions, which must be considered in interpretations of the deep ice core records (e.g. Röthlisberger et al., 2000; 2003).

The concentration of a chemical species in the precipitation is a function of the atmospheric concentration and the scavenging ratio. Snow can be formed by either the Bergeron process (growth of ice crystals by condensation of water vapour sublimated from super-cooled droplets) or riming (collection of super-cooled droplets on ice particles), where the latter process seems to be more effective in scavenging trace species (Dixon et al., 1995). Riming occurs also at ground level in cold super-saturated air masses and can thereby act as an effective additional scavenging process. Once deposited on the ground dry depositional processes will be able to alter the concentration in the snow, which in addition to gravitational settling also includes the filtering effect the upper snow layer have on air flows (Cunningham and Waddington, 1993) and adsorption of gases on snow crystals (Davidson et al., 1996). Reemission to the atmosphere of volatile acids (HNO_3, CH_3SO_3H, HCL) has been proposed to be an important postdepositional loss process on low accumulation sites in Antarctica decreasing the concentrations in firn (Wagnon et al., 1999; Delmas et al., 2003; Weller et al., 2004). Sublimation of settled snow and wind blown snow will enrich conservatively deposited species, but the concentration will remain stable for species that are volatilized from the sublimated snow (Pomeroy and Jones, 1996; Ginot et al., 2001). Spatial gradients in concentrations of trace species in snow arise from differences in influence in one or several of the above-mentioned concentration controlling processes. By analysing the spatial gradients in snow chemistry in relation to other environmental conditions, information on governing air-snow transfer processes can be obtained. This can be applied from the largest (i.e. comparison between Greenland and Antarctica) to the smallest scale feasible for snow sampling.

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The $\delta^{18}O$ signal of water isotopes in the deposited precipitation is correlated with the condensation temperature (Dansgaard, 1964) and is commonly used to infer the paleo-temperature at the deposition site (e.g. Johnsen et al., 1995). The amplitude of the annual cycles observed in vertical section from snow pits reflects the seasonal variation in $\delta^{18}O$ of the precipitation diminished by diffusion in the snow pack after deposition (Johnsen, 1977). However, both surface snow and buried snow layers are subjected to redeposition processes altering the original $\delta^{18}O$ signal (e.g. Moser and Stichler, 1980; Friedman et al., 1991; Satake and Kawada, 1997; Neumann et al., 2005)

We present results from centimeter-scale snow surface sampling at two sites with different characteristics; in near-coastal Dronning Maud Land, Antarctica and on the Greenland ice sheet, respectively. We have analysed ion concentrations and $\delta^{18}O$ in order to characterize the snow chemistry at the two sites. By using correlations found between $\delta^{18}O$ and ion concentrations and by comparing the characteristics of the two sites, we suggest a possible concentration controlling mechanism occurring at the snow surface coupling the $\delta^{18}O$ signal and concentrations of anions deposited as acids.

2. Characteristics of sampling sites

Surface snow samples were collected on two different locations; at Camp Maudheimsvidda (CM), Dronning Maud Land, Antarctica; and on the Greenland ice sheet (denoted NG) close to the deep drilling site of the North Greenland Ice Core Project (NGRIP). Snow pit sampling was also performed simultaneously with the snow surface sampling to give a handle on the seasonal variation in snow chemistry.

The CM sampling site is located in Dronning Maud Land, 10 km south of the nunatak Basen, where the Swedish and Finnish research stations Wasa and Aboa are situated. The site is located about 150 km from the coast and at 360 m a.s.l. The annual accumulation rate for the years 1998–2001 was obtained by a sonic altimeter and yielded 18 ± 4 cm w.eq./yr (Reijmer and van der Broeke, 2003). This is in good agreement with the mean accumulation rate of 22 cm w.eq./yr, which was obtained for the period 1958–1998 by bomb cesium (Holmlund et al., 2000). The meteorological conditions at CM are influenced by a combination of transient cyclones originating in the Southern Ocean travelling eastwards parallel to the coast and katabatic winds from the Antarctic plateau (Reijmer, 2001). The mean annual temperature 1999–2003 was –17 °C, and mean January temperature for the years 1999–2004 was –6 °C (unpublished data, personal communication, C. Reijmer, 2005). Sublimation is according to energy balance calculations significant in the area (van der Broeke et al., 2004).

The NGRIP drill site on the Greenland ice sheet is located at approximately 2950 m a.s.l. The present accumulation rate is about 17 cm w.eq./yr (North Greenland Ice Core Project members, 2004) and the mean annual temperature is –30 °C (Steffen and Box, 2001). During winter time, a high pressure is located over the ice sheet, which vanishes in the summer period and replaced by a dominantly zonal flow with migratory low pressure systems bringing moisture to the ice cap (Putnins, 1970).

The influence of anthropogenic activity on the snow chemistry on the two sites is contrastive. The Greenland snow chemistry is influenced by emissions from combustion of fossil fuels giving increased acidity and increased concentrations of NO_3^- and SO_4^{2-} compared to the natural levels, while the influence from anthropogenic sources is very limited in Antarctica (Legrand and Mayewski, 1997).

3. Sampling and analyses

Surface samples were collected at one occasion during the summer season at each site and the corresponding snow pit was dug at the same site after collection of the surface samples.

At CM in total 40 surface samples (CMs) were collected in February 2004 along a 10-meter surface profile (73°06.5′ S, 13°08.6′ W). The first meter was sampled with 5 cm resolution, while the remaining part was sampled with 50 cm resolution. The sampled surface was characterized by relatively hard and coarse snow, with a microtopography of about 10 cm. Snow samples were collected by scraping the surface with a 30-ml plastic container, known as Coulter Counter Accuvette, with an opening diameter of 3 cm. The sampling depth was thereby about 2–3 cm. The lid was placed immediately after sampling. Samples were transported and stored in frozen state and melted just prior to analysis. No snowfall occurred between the arrival to the site and sampling and it can therefore not be determined when the last snowfall event prior to sampling took place. An automatic weather station close to the sampling site recorded low pressure and cloudy conditions 5 days prior to the sampling, possibly associated with light snow fall according to the sonic altimeter (unpublished data, personal communication, C. Reijmer, 2005). The snow pit dug at CM (CMp) was sampled down to 2-m depth with a 2.5-cm depth-resolution by pushing an Accuvette vertically in to the wall. According to the $\delta^{18}O$ record the depth profile contained almost three years of accumulation, though the seasonality cycles are not distinct (Fig. 1a). The sampled profile contained a few hard crusts, which could possibly be attributed to a refrozen partial melted surface, distorting the depth profile, though no regular ice-lenses were present.

On the NG site on Greenland the surface samples (hereafter denoted NGs) were collected in July 2003 at a site 7 km south (75°05.4′ N, 42°33.7′ W) of the NGRIP camp and collected in a similar manner as on CM. In total 115 surface samples were collected in two 11-m long surface profiles with the same starting point but heading perpendicular to each other (north and west). The first and last meter of the surface

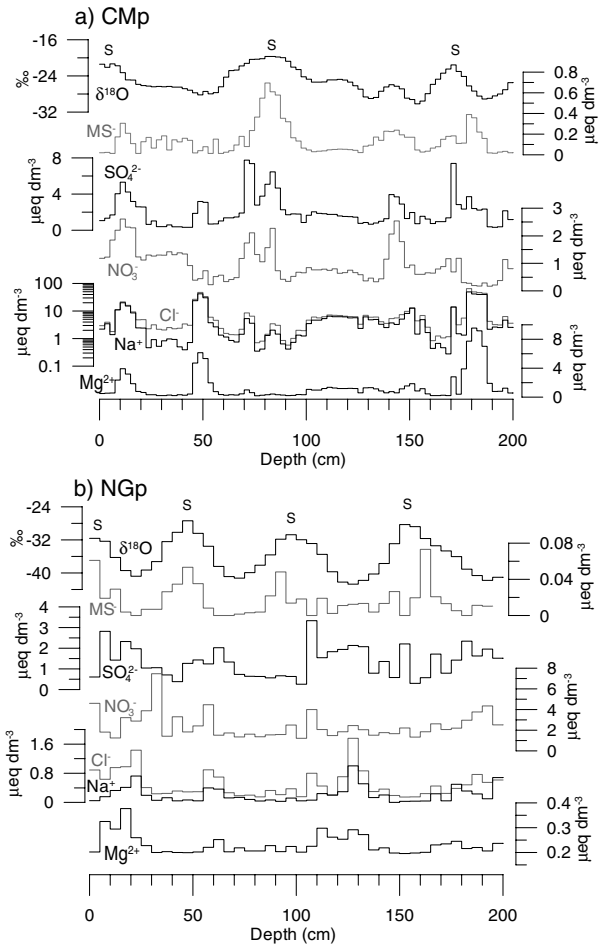

Fig. 1. Depth profiles showing $\delta^{18}O$ and concentrations of MS^-, SO_4^{2-}, NO_3^-, Cl^-, Na^+ and Mg^{2+} from snowpit CMp, Antarctica, (a) and NGp, Greenland (b). S marks what is interpreted as summer snow layer.

profiles were sampled with 5-cm resolution and the rest with 50-cm resolution. The sampled surface consisted of a soft and homogeneous snow layer. The snow pit (NGp) was dug and sampled with a 5-cm depth-resolution down to 2-m and according to the $\delta^{18}O$ variations it contained almost four years of accumulation (Fig. 1b).

All samples were analysed for concentrations of major ions ($CH_3SO_3^-$ or MS^-, Cl^-, NO_3^-, SO_4^{2-}, Na^+, NH_4^+, Mg^{2+}, Ca^{2+}) and water oxygen isotope composition ($\delta^{18}O$). All analyses were made on aliquots of the same sample. Ion concentrations were analysed with ion chromatography on a Dionex IC25 system using AS17/CS12 2-mm column, ASRS/CSRS-ultra suppressor and gradient KOH/MSA-eluent for anion/cation analysis. The analytical reproducibility was from analyses of standard solutions was determined to be within 15% for the full sample concentration range for MS^-, Mg^+, Cl^- and SO_4^{2-}, and on concentrations higher than 0.5 μeq dm^{-3} for Ca^{2+}, Na^+ and NH_4^+, and higher than 0.25 μeq dm^{-3} for NO_3^-, but increasing significantly with decreasing concentration on concentrations lower than the stated limit. Analyses of $\delta^{18}O$ were made on a Finnigan Delta Plus mass spectrometer and the $^{18}O/^{16}O$ ratio is expressed in ‰ related to the SMOW-standard. The analytical error was determined to ±0.1 ‰.

Calculations of the sea-salt (ss) and non-sea-salt (nss) fraction of SO_4^{2-} and Ca^{2+} were performed according the following equations:

$$[\mathrm{ssX}] = \mathrm{k}[\mathrm{A}], \tag{1}$$

$$[\mathrm{nssX}] = [\mathrm{X}] - (\mathrm{k}[\mathrm{A}]), \tag{2}$$

where [X] is the concentration of the concerned species, k is the ratio by equivalents in standard sea water of X to A, where A is a species that in principle have sea-salt as sole source. Na^+ is preferred as reference species A over Cl^- for tracing the sea-salt contribution in Antarctica, since sea-salt Cl^- may be lost as gaseous HCl (Legrand and Delmas, 1988). Therefore Na^+ is used on the samples collected at CM. On the samples from NG Cl^- is used as A due to the higher influence of continental sources on Greenland, which could contribute significantly to Na^+ budget. The k-values used were: Ca^{2+}/Cl^- 0.04, SO_4^{2-}/Cl^- 0.10, Ca^{2+}/Na^+ 0.04. A special case is the k value used to calculate $nssSO_4^{2-}$ at CM. The aerosols at coastal Antarctic sites have been found to be depleted in SO_4^{2-} compared to standard sea water (Minikin et al., 1994; Hall and Wolff, 1998; Wagenbach et al., 1998). SO_4^{2-} depletion is most likely also present at CM (Jonsell et al., 2005) and $nssSO_4^{2-}$ concentrations were therefore calculated with a lower ratio than the standard sea-water ratio (0.04 by equivalents instead of 0.12) as suggested.

4. Results and discussion

The snow chemistry of the NG and CM sites are due to their location different in several aspects, as detected from the ion concentration records (Fig. 2, Table 1). The more proximate location to the sea of CM gives a larger influence of both MS^- (an oxidation product of di-methyl sulphide, DMS, produced by marine phytoplankton) and sea-salt ions (mainly Na^+ and Cl^-). The more proximate location to ice free continents is seen as a higher influence of the dust-proxy $nssCa^{2+}$ at NG. NO_3^- is dominating the ion budget of the NG samples, whereas in the CM samples the relative contribution of NO_3^- is limited. The $ssSO_4^{2-}$ contribution to the total SO_4^{2-} concentration is on average in all sample sets relatively small (CMs 14%, CMp 7%, NGs 5%, NGp 3%).

The variation in ion concentrations recorded for species with a dominant sea-salt contribution (Na^+, Cl^-, Ca^{2+}, Mg^{2+}) is much larger in CMp compared to CMs due to a few high concentration samples in the depth profile (Fig. 1a), which probably are caused

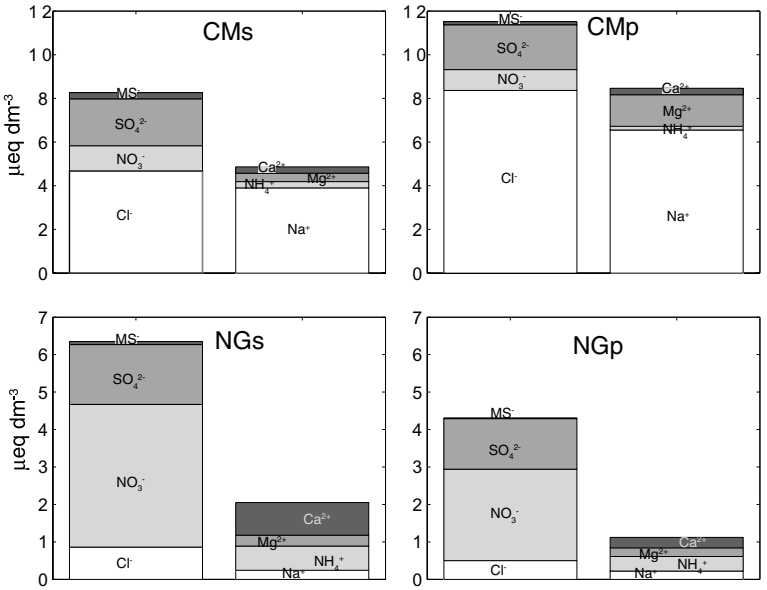

Fig. 2. Mean concentrations of measured ions in the NG and CM surface (s) and pit (p) samples separated in anion and cation stacks.

by efficient transport of sea-salt during storm events. For all other ion species both the mean concentration and standard deviations in CMs are similar or exceeds the corresponding figures in CMp. A similar relation between surface and pit samples is found for all measured ion species in the NG data sets. Such large variation within a small surface area opposes the idea of snow layers with uniform snow chemistry that can be represented by a single sample in a depth profile.

Concentrations of the two major sea-salt species (Na^+, Cl^-) in CMs are strongly correlated (r = 0.98), though the regression coefficient in Table 2 is partly driven by one high concentration sample and becomes lower (r = 0.76) if only considering samples with Na^+ concentrations below 6 μeq dm^{-3} (Fig. 3a). The Cl^-/Na^+ ratio in CMs is close to that of standard sea water (1.16) and the two observations together indicate that sea-salt was transported to the site jointly in particles with no *en route* loss of Cl^-, as has been reported to be significant in other studies performed in Antarctica (Legrand et al., 1988; Wagenbach et al., 1998; Kerminen et al., 2000; Jourdain and Legrand, 2002). Thus, the sea-salt concentration difference among the CMs samples is caused by uneven distribution of sea-salt particles. There is no strong correlation between Na^+ and Cl^- among the NGs samples. We realize that the analytical uncertainty on the low Na^+ concentrations among the NG samples may deteriorate any correlation between Cl^- and Na^+. Though, the mean Cl^-/Na^+ ratio is much higher (6.26) than the standard sea-water ratio, suggesting an excess or additional source of Cl^-. This phenomenon is also reflected in the NGp samples, though the mean Cl^-/Na^+ ratio is smaller (3.84). Since Cl^- is used reference species A in equation 1 and 2, the nssSO_4^{2-} contribution may be underestimated, but will not affect the forthcoming interpretation of the data.

4.1. $\delta^{18}O$ and concentrations of non-sea-salt anions

The range in $\delta^{18}O$ among the surface samples at both CM and NG are large compared to the seasonal variability detected in the snow pit. In NGs the range covers about the upper half of the corresponding range found among the NGp samples, which is consistent when considering that NGs samples were collected in a summer snow layer. At CM, the $\delta^{18}O$ range among the surface samples (CMs) cover almost the whole range recorded in corresponding snow pit samples (CMp).

The $\delta^{18}O$ values of the surface samples are correlated with the concentrations of certain ions. In CMs positive correlations are found between $\delta^{18}O$, MS^-, nssSO_4^{2-} and NO_3^- (Fig. 4, Table 2), whereas in NGs only NO_3^- shows a strong correlation to $\delta^{18}O$ (Fig. 5, Table 2). The correlation between MS^- and nssSO_4^{2-} concentrations among CMs is particularly strong and the samples are rather evenly spread over the concentration range (Fig. 3b), i.e. the correlation is not forced by a few outliers.

As we will now discuss, the ions correlating with $\delta^{18}O$ were possibly all deposited mainly as acids, which had gaseous precursors. In both CMs and NGs the sum of anions exceeds the sum of cations (Table 1). In CMs, Cl^-, nssSO_4^{2-} and NO_3^- dominate the anion budget. While Cl^- is balanced by other sea salt species (mainly Na^+), nssSO_4^{2-} and NO_3^- must be balanced by a not measured cation, which is expected to be H^+. In CMs the calculated H^+ concentration is similar to the concentration sum of NO_3^- and nssSO_4^{2-} and suggests that these anions were mainly deposited as acids; HNO_3 and H_2SO_4, respectively. In the NGs samples the contribution of Cl^- is smaller and the anion budget is dominated by NO_3^- and nssSO_4^{2-}. The concentration of nssSO_4^{2-} balances rather well the concentration sum of nssCa^{2+}, NH_4^+ and Mg^{2+} to which nssSO_4^{2-} also

Table 1. Ion concentrations (μeq dm^{-3}), δ^{18}O (‰), ion balance and Cl^-/Na^+ ratio for the surface and snow pit samples from NG and CM, respectively.

	CM surface samples (CMs)					CM snow pit samples (CMp)				
	Mean	SD	Min	Max	Range	Mean	SD	Min	Max	Range
$\delta^{18}O$	–24.9	2.1	–28.4	–18.3	10.1	–25.2	2.8	–30.2	–19.7	10.5
MS^-	0.28	0.16	0.07	0.79	0.71	0.14	0.14	0.01	0.70	0.68
Cl^-	4.68	2.15	2.63	14.78	12.15	8.36	12.58	0.59	65.98	65.39
NO_3^-	1.15	0.60	0.46	3.07	2.61	0.96	0.60	0.17	2.61	2.44
SO_4^{2-}	2.15	1.21	0.65	6.25	5.60	2.05	1.67	0.30	7.75	7.44
$nssSO_4^{2-}$	1.98	1.20	0.54	6.00	5.46	1.77	1.61	0.20	7.52	7.32
Na^+	3.90	2.69	1.62	17.20	15.58	6.55	10.72	0.28	49.25	48.98
NH_4^+	0.29	0.10	0.12	0.53	0.40	0.17	0.10	0.04	0.47	0.43
Mg^{2+}	0.38	0.15	0.20	0.88	0.68	1.45	2.00	0.19	9.55	9.35
Ca^{2+}	0.29	0.23	0.03	1.04	1.01	0.29	0.43	0.02	1.79	1.77
$nssCa^{2+}$	0.13	0.23	–0.29	0.94	1.23	0.01	0.22	–0.57	1.28	1.85
Ion balance[1] / H^+	3.15	2.44	–2.50	10.93	13.43	2.02	2.12	–2.82	8.71	11.53
Cl^- / Na^+	1.31	0.29	0.85	2.02	1.17	1.41	1.19	1.01	8.77	7.76
	NG surface samples (NGs)					NG snow pit samples (NGp)				
	Mean	SD	Min	Max	Range	Mean	SD	Min	Max	Range
$\delta^{18}O$	–31.6	2.0	–35.7	–27.9	7.8	–36.0	4.5	–42.7	–27.4	15.3
MS^-	0.08	0.04	0.03	0.17	0.15	0.02	0.02	0.00	0.07	0.07
Cl^-	0.86	0.38	0.30	3.30	3.00	0.50	0.36	0.15	1.76	1.61
NO_3^-	3.81	1.06	1.86	6.09	4.23	2.44	1.26	1.21	7.47	6.27
SO_4^{2-}	1.60	0.73	0.29	2.94	2.65	1.35	0.74	0.30	3.30	3.08
$nssSO_4^{2-}$	1.51	0.72	0.23	2.83	2.60	1.30	0.72	0.24	3.26	3.02
Na^+	0.24	0.30	0.01	2.82	2.81	0.22	0.22	0.03	1.00	0.97
NH_4^+	0.65	0.29	0.14	1.22	1.09	0.39	0.15	0.21	0.84	0.63
Mg^{2+}	0.29	0.08	0.20	0.58	0.39	0.23	0.04	0.20	0.38	0.18
Ca^{2+}	0.87	0.72	0.02	2.80	2.77	0.28	0.49	0.02	2.80	2.73
$nssCa^{2+}$	0.84	0.72	0.00	2.74	2.74	0.26	0.48	0.00	2.73	2.73
Ion balance[1] / H^+	4.44	1.63	–1.10	7.90	9.00	3.37	1.70	1.08	8.42	7.34
Cl^- / Na^+	6.26	4.85	0.52	25.60	25.08	3.84	3.34	0.71	12.65	11.94

[1]Ion balance is calculated as Σ[Anions] – Σ[Cations], which also represents the calculated H^+ concentration.

Table 2. Correlation matrix of measured ion concentrations and δ^{18}O in surface samples from CM in Dronning Maud Land, Antarctica (CMs) and NG on Greenland (NGs). Correlation coefficients (r) in bold are significant on the 0.01 level. If nothing else is stated, r-values in brackets on NGs samples are not significant when one group of samples (20 out of 115) collected within 1 meter are omitted.

CMs/ NGs	$nssSO_4^{2-}$		MS^-		NO_3^-		Cl^-		Na^+		NH_4^+		Mg^{2+}		$nssCa^{2+}$	
	CMs	NGs	CMs	NGs	CMs	NGs	CMs	NGs	CMs	NGs	CMs	NGs	CMs	NGs	CMs	NGs
$\delta^{18}O$	**0.83**	(0.47)	**0.84**	(–0.45)	**0.81**	**0.82**	0.23	(0.28)	0.09	–0.13	**0.49**	(0.62)	**0.41**	0.20	–0.01	0.13
$nssSO_4^{2-}$			**0.98**	**–0.85**	**0.87**	(0.43)	0.18	**0.38**	0.04	0.01	0.38	**0.87**	**0.56**	**0.84**	–0.02	**0.68**
MS^-					**0.83**	(–0.30)	0.28	(–0.31)	0.16	–0.02	**0.41**	**–0.74**	**0.63**	**–0.75**	–0.09	**–0.67**
NO_3^-							0.27	**0.41**	0.07	–0.12	**0.54**	(0.61)	(0.51)[1]	0.18	0.09	0.07
Cl^-									**0.96**	(0.62)[1]	**0.42**	**0.37**	**0.53**	0.24	–0.17	0.21
Na^+											0.38	0.02	**0.47**	**0.50**	–0.26	**0.44**
NH_4^+													0.40	**0.74**	–0.18	**0.59**
Mg^{2+}															0.20	**0.84**

[1]Becomes insignificant if one sample is omitted.

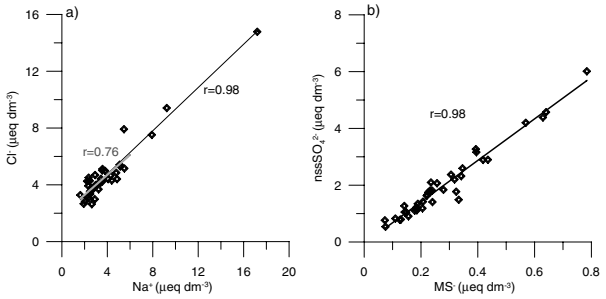

Fig. 3. Scatter plots of CMs concentration data for Na^+ vs. Cl^- (a) and MS^- vs. $nssSO_4^{2-}$, (b). The black lines are linear regressions of the full concentration range. In plot a the grey line is a linear regression restricted to $Na^+ < 6\ \mu$eq dm^{-3}.

shows positive correlations (Table 2) and suggests that deposition of $nssSO_4^{2-}$ was mainly as a neutral salt. To balance the ion budget on NG NO_3^- must have been deposited as HNO3. These conditions are concordant with results from measurements of the central Greenland summer atmosphere where NO_3^- was mainly present as HNO_3(g) while particulate $nssSO_4^{2-}$ dominated the $nssSO_4^{2-}$-budget (Dibb et al., 1994). As a result of its low concentration in the snow, the depositional form of MS^- (as volatile acid or neutral salt) gives no imprint on the ion balance.

Evidence of gaseous precursors of $nssSO_4^{2-}$ and MS^- at CM is the observed dominance of the corresponding particulate aerosols in the submicron mode ($nssSO_4^{2-}$ 90% and MS^- 95%) in the summer atmosphere above Wasa/Aboa-research stations (Kerminen et al., 2000). However, the concentrations of these gas precursors in the air above CM are not known, although they have all been detected in the coastal Antarctic atmosphere (Davis et al., 1998; Jefferson et al., 1998; Jourdain and Legrand, 2001).

The explanation behind the obtained correlations between ion concentrations and δ^{18}O among the surface samples must involve a mechanism that combines concentration control with fractionation of oxygen isotopes and can not be related to seasonality cycles of the species, since all samples are collected on a summer snow surface. The mechanism can not either be related to dry deposition fluxes since the δ^{18}O signal is recorded in the water isotopes.

Though MS^- and $nssSO_4^{2-}$ have a common source in DMS, they are products of different complex oxidation pathways (e.g. Saltzman, 1995) and will not as the sea-salt species be transported jointly as particles from source to deposition. The high

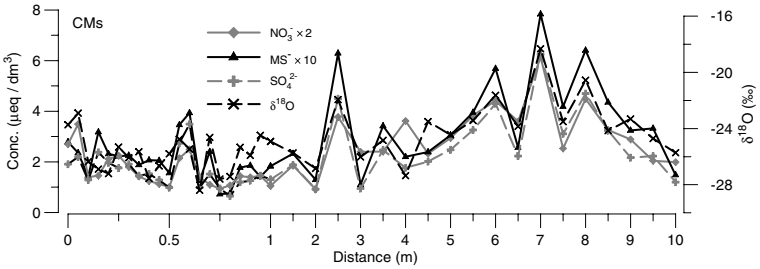

Fig. 4. Length profile of NO_3^-, SO_4^{2-} and MS^- concentrations and δ^{18}O of the surface samples from CM. Note that NO_3^- and MS^- concentrations have been multiplied by a factor 2 and 10, respectively, to enhance the comparability.

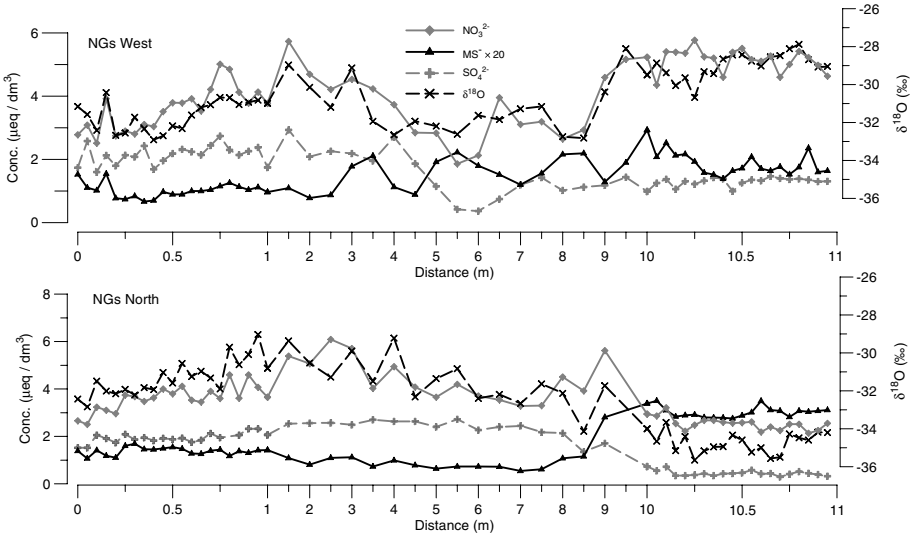

Fig. 5. Length profiles of NO_3^-, SO_4^{2-} and MS^- concentrations and δ^{18}O of the surface samples from NG. Note that MS^- concentrations have been multiplied by a factor 20 to enhance the comparability.

correlation found between MS^- and $nssSO_4^{2-}$ among the CMs samples is not likely to arise solely due to common variations in source strengths or transport efficiency. Moreover, an interpretation based on a common source provides no link to NO_3^- which sources are, although not being clear (Wolff, 1995), not related to DMS oxidation.

Considering the large concentration difference on the submeter scale and that the process must involve a fractionation of oxygen isotopes, it seems unlikely to be explained by a gradient in postdepositional loss rates. On a much larger spatial scale, compilation of data from Antarctic and Greenland sites showed a temperature dependent loss rate of NO_3^- (Röthlisberger et al., 2002), but gave rise to a negative correlation between NO_3^- and $\delta^{18}O$ (i.e. opposite to here). Furthermore, $nssSO_4^{2-}$ is considered to be a conservative species as no postdepositional loss has been reported.

Having a rougher surface, we have considered that the obtained correlations among CMs are the result of sampling snow layers from different precipitation events with different chemical signals. We did actually find a correlation between the concentrations of the anions (NO_3^-, $nssSO_4^{2-}$, MS^-), but also to sea-salt concentrations (Na^+, Cl^-), in the top part of CMp (25 cm, 10 samples, which could be considered to be representative for the different snow layers possibly emerging at the surface). The correlation between the anions in CMs can therefore not be an effect of sampling different distinctive snow layers, since no correlation exists between the anions and sea-salt ions among the CMs samples (Table 2).

Our tentative explanation is based on a sublimation–redeposition cycle of water vapour. Isotopic fractionation during sublimation is very small due to the low diffusive rate of mixing within the snow crystals and can in practice be ignored (Friedman et al., 1991), whereas the redeposited mass will be enriched with the heavy isotope of oxygen (i.e. $\delta^{18}O$ values become less negative compared to the vapour phase).

Since relative humidity is temperature dependent, a diurnal solar radiation cycle can drive a sublimation–redeposition cycle; day time sublimation and night time redeposition, which will be reflected in the isotopic composition of the surface snow (Moser and Stichler, 1980). An almost analogous mechanism for the isotopic enrichment in depth hoar has been described (Epstein et al., 1965; Sommerfeld et al., 1991). Recordings from automatic weather stations in vicinity of the sampling sites show diurnal cycles in relative humidity during the days prior to sampling (Fig. 6). In addition, a division in local zones of net sublimation and net deposition on the snow surface can arise from wind flows because the microtopography creates local high-pressure and low-pressure areas (Albert, 2002). This mechanism is more likely to give an impact on the snow surface on CM, where the microtopography was more pronounced compared to NG.

Using the equations of isothermal condensation by Dansgaard (1961) put in delta notation, we can express the isotopic signal in the redeposited mass $\delta^{18}O_r$ as a function of the initial signal

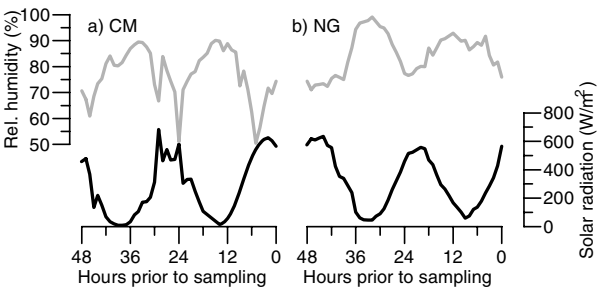

Fig. 6. Relative humidity and solar radiation data from automatic weather stations in the vicinity of the sampling sites; a) 0.7 km from sampling site CM, b) 7 km from sampling site NG.

in the vapour phase of the sublimated snow ($\delta^{18}O_s$);

$$\delta^{18}O_r = (1000+\delta^{18}O_s)(1-\beta^{\alpha})(1-\beta)^{-1}-1000, \quad (3)$$

where β is the remaining vapour fraction and α is the temperature dependent fractionation factor.

The collected surface snow samples can be seen as a mixing of the signal of the original snow and the redeposited mass:

$$\delta^{18}O_{sample} = \delta^{18}O_r c + (1 - c)\delta^{18}O_s, \quad (4)$$

where c is the mixing ratio. If c equals one, the sample consists completely of redeposited mass.

The link between fractionation of $\delta^{18}O$ due to redeposition of water vapour to the control on ion concentrations is provided by reports on effective scavenging of SO_4^{2-} and NO_3^- during rime formation. In reviewing the postdepositional process of NO_3^- in polar snow, Röthlisberger et al. (2002) declared riming as being very effective in scavenging of $HNO_3(g)$ and surface hoar have been demonstrated to have significantly higher NO_3^- concentrations than the buried snow below (Udisti et al., 2004). A similar effect on other volatile acidic gases is conceivable. Studies of scavenging processes in clouds (Puxbaum and Tscherwenka, 1998) indicated that SO_4^{2-} scavenging was enhanced by riming. Modelling (Lamb and Chen, 1990) and laboratory experiments (Iribarne and Barrie, 1995) have also shown considerable oxidation of $SO_2(g)$ (producing SO_4^{2-}) during riming. The scavenging effect on MS^- is less investigated. The presence of $nssSO_4^{2-}$ and possibly MS^- mainly as neutral salts at NG will, in contrast to at CM, limit the gas scavenging of these species at NG.

The obtained coupling between $\delta^{18}O$ and the ion species points at an air–snow transfer process, which significantly alters the ion concentrations and the $\delta^{18}O$ signal of surface snow. With repeated sublimation–redeposition cycles, the net effect on ion concentrations will depend on how well the species are conserved or volatilized during sublimation, but also on the rate of gas adsorption. The sublimation–redeposition cycle will continue until the snow surface is buried by next snowfall and the effect on depth profiles of the proposed mechanism will be small on sites with frequent and extensive snow fall events and largest on sites having few and small snow fall events. From a site with the

latter characteristics (Dome Fuji, Antarctica), minima in SO_4^{2-} concentrations in summer snow layers were suggested to arise form a diurnal sublimation–redeposition mechanism only active during the summer season (Iizuka et al., 2004), since in polar regions the cycle will not be active in winter time due to the lack of a driving radiation cycle. However, the mass transfer of water vapour will be limited in the extreme cold environments because of the exponential relation between saturation vapour pressure and temperature.

In final, the relative importance of this air-snow transfer process for the total ion chemistry of the depth profiles from the two sites presented here is difficult to assess. We do not obtain similar couplings between the ion species and $\delta^{18}O$ in the depth profiles (Fig. 1) as in the surface snow because the signal from the suggested mechanism active on the surface will be superimposed on the well known seasonality signals of the species (Legrand and Mayewski, 1997). At this stage we restrict our discussion to the identification of the correlations and a suggestion of responsible mechanism. The impact on depth profiles in different environments needs further attention.

We have little direct information on the depositional form of MS^- at the two sites. Following our gas scavenging suggestion, it is implied that MS^- is present as volatile acid at CM but not at NG. We also note that MS^- in NGs, in contrast to the conditions in CMs, is strongly anti-correlated with $nssSO_4^{2-}$ and with its associated cations (NH_4^+, Ca^{2+}, Mg^{2+}), which indicates that the major pathway for MS^- deposition on NG is not associated with SO_4^{2-} containing particles.

5. Summary and conclusions

We have examined the variation in ion concentrations and $\delta^{18}O$ in surface snow at two sites with different site characteristics, one site in near-coastal Antarctica (CM) and the other on the Greenland ice sheet (NG). We find large variations in ion concentration on the submeter scale. For all ions at CM, except ions with a dominating sea-salt fraction (Na^+, Mg^{2+} Ca^{2+}, Cl^-), the horizontal variation in the surface snow is similar or larger than the vertical variation in snow pits although the latter contains a seasonal signal.

Covariations in ion concentrations and $\delta^{18}O$ among the surface samples are revealing information on the depositional characteristics of the species. At CM a strong correlation between Na^+ and Cl^- concentrations implies a joint deposition as sea-salt particles. Correlations between $nssSO_4^{2-}$, NO_3^- and MS^- among the CMs samples cannot be interpreted likewise, due to their different and gaseous origin. Moreover, the concentrations of these three anions correlate with the $\delta^{18}O$ values, while at NG only NO_3^- correlates with $\delta^{18}O$. The reason to these correlations are ambiguous, but we suggest a mechanism that involves redeposition of water vapour (leading to less negative $\delta^{18}O$ values) in the surface snow with simultaneous enhanced gas scavenging. Because of predominant presence of $nssSO_4^{2-}$ and possibly also MS^- as neutral salt at NG, these species are at NG not affected by this mechanism. The mechanism will alter the chemical signal from that of the original precipitation. We still need better constrains on the conditions for redeposition of water vapour and on the scavenging mechanism of the concerned acids to confirm our suggested mechanism. A strong anticorrelation between MS^- and $nssSO_4^{2-}$ is detected in the Greenland surface snow samples. Further studies of this kind are needed to understand the significance of this observation and will contribute towards better interpretations of the signal of ion species in both present and past deposited snow.

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References

Albert, M. R. 2002. Effects of snow and firn ventilation on sublimation rates. *Ann. Glaciol.* **35,** 52–56.

Cunningham, J. and Waddington, E. D. 1993. Air flow and dry deposition of non-sea-salt sulfate in polar firn: Paleoclimatic implications. *Atmos. Environ.* **27**(17–18), 2943–2956.

Dansgaard, W. 1961. The isotopic composition of natural waters with special reference to the Greenland ice cap. *Medd. om Grönland*. **165**(2), 1–120.

Dansgaard, W. 1964. Stable isotopes in precipitation. *Tellus* **16,** 436–468.

Davidson, C. I., Bergin, M. H. Kuhns, H. D. 1996. Atmospheric deposition of chemical species to polar snow. *Chem. Eng. Comm.* **151,** 227–249.

Davis, D., Chen, G., Kasibhatla, P., Jefferson, A., Tanner, D. and co-authors. 1998. DMS oxidation in the Antarctic marine boundary layer: comparison of model simulations and field observations of DMS, DMSO, $DMSO_2$, H_2SO_4(g), MSA(g), and MSA(p). *J. Geophys. Res.- Atmos.* **103**(1), 1657–1678.

Delmas, R. J., Wagnon, P., Goto, A. K., Kamiyama, K. and Watanabe, O. 2003. Evidence for the loss of snow-deposited MSA to the interstitial gaseous phase in central Antarctic firn. *Tellus* **55B,** 71–79.

Dibb, J. E., Talbot, R. W. and Bergin, M. H. 1994. Soluble acidic species in air and snow at Summit, Greenland. *Geophys. Res. Lett*. **21**(15), 1627–1630.

Dibb, J. E., Talbot, R. W., Munger, J. W., Jacob, D. J. and Song, M. F. 1998. Air-snow exchange of HNO_3 and NOy at Summit, Greenland. *J. Geophys. Res.-Atmos.* **103**(3), 3475–3486.

Dixon, R. W., Mosimann, L., Oberholzer, B., Staehelin, J., Waldvogel, A. and co-authors. 1995. The effect of riming on the ion concentrations of winter precipitation. 1. A quantitative analysis of field measurements. *J. Geophys. Res.- Atmos.* **100**(6), 11,517–11,527.

Epstein, S., Sharp, R. P. and Gow, A. J. 1965. Six-year record of oxygen and hydrogen isotope variation in South Pole firn. *J. Geophys. Res.* **70,** 1809–1814.

Friedman, I., Benson, C. S. and Gleason, J. 1991. Isotopic changes during snow metamorphism. In: *Stable isotope geochemistry; a tribute to Samuel Epstein*. (eds H. P. Taylor Jr., J. R. O'Neil and I. R. Kaplan). Special Publication—Geochemical Society, San Antonio, 211–221.

Ginot, P., Kull, C., Schwikowski, M., Schotterer, U. and Gaggeler, H. W. 2001. Effects of postdepositional processes on snow composition of a subtropical glacier (Cerro Tapado, Chilean Andes). *J. Geophys. Res.-Atmos.* **D106**(23), 32375–32386.

Goto-Azuma, K., Koerner, R. M., Nakawo, M. and Kudo, A. Snow chemistry of Agassiz Ice Cap, Ellesmare Island, Northwest Territories, Canada. *J. Glaciol.* **43**(144), 199–206.

Hall, J. S. and Wolff, E. W. 1998. Causes of seasonal and daily variations in aerosol sea-salt concentrations at a coastal Antarctic station. *Atmos. Environ.* **32**(21), 3669–3677.

Holmlund, P., Gjerde, K., Gundestrup, N., Hansson, M., Isaksson, E. and co-authors. 2000. Spatial gradients in snow layering and 10 m temperatures at two EPICA-Dronning Maud Land (Antarctica) pre-site-survey drill sites. *Ann. Glaciol.* **30,** 13–19.

Iizuka, Y., Fujii, Y., Hirasawa, N., Suzuki, T., Motoyama, H. and co-authors. 2004. SO_4^{2-} minimum in summer snow layer at Dome Fuji, Antarctica, and the probable mechanism. *J Geophys. Res. -Atmos,* **109,** D04307, doi:10.1029/2003JD004138.

Iribarne, J. V. and Barrie, L. A. 1995. The Oxidation of S(IV) During Riming by Cloud Droplets. *J. Atmos. Chem.* **21**(2), 97–114.

Jaffrezo, J. L., Davidson, C. I., Legrand, M. and Dibb, J. E. 1994. Sulfate and MSA in the air and snow on the Greenland Ice Sheet. *J. Geophys. Res. - Atmos.* **99**(1), 1241–1253.

Jefferson, A., Tanner, D. J., Eisele, F. L. and Berresheim, H. 1998. Sources and sinks of H_2SO_4 in the remote Antarctic marine boundary layer. *J. Geophys. Res. - Atmos.* **103**(D1), 1639–1645.

Johnsen, S. J. 1977. Stable isotope homogenisation of polar firn and ice. *Isotopes and impurities in snow and ice. IAHS Publ.* **118,** 210–219.

Johnsen, S. J., Dahl, J. D., Dansgaard, W. and Gundestrup, N. 1995. Greenland palaeotemperatures derived from GRIP bore hole temperature and ice core isotope profiles. *Tellus* **47B,** 624–629.

Jonsell, U., Hansson, M. E., Mörth, C. M. and Torssander, P. 2005. Sulfur isotopic signals in two shallow ice cores from Dronning Maud Land, Antarctica. *Tellus* **57B,** 341–350.

Jourdain, B. and Legrand, M. 2001. Seasonal variations of atmospheric dimethylsulfide, dimethylsulfoxide, sulfur dioxide, methanesulfonate, and non-sea-salt sulfate aerosols at Dumont d'Urville (coastal Antarctica) (December 1998 to July 1999). *J Geophys. Res.- Atmos.* **106**(13), 14391–14408.

Jourdain, B. and Legrand, M. 2002. Year-round records of bulk and size-segregated aerosol composition and HCl and HNO_3 levels in the Dumont d'Urville (coastal Antarctica) atmosphere: Implications for sea-salt aerosol fractionation in the winter and summer. *J. Geophys. Res.- Atmos.* **107**(D22), 4645, doi:10.1029/2002JD002471.

Kärkäs, E., Teinila, K., Virkkula, A. and Aurela, M. 2005. Spatial variations of surface snow chemistry during two austral summers in western Dronning Maud Land, Antarctica. *Atmos. Environ.* **39**(8), 1405–1416.

Kerminen, V. M., Teinila, K. and Hillamo, R. 2000. Chemistry of sea-salt particles in the summer Antarctic atmosphere. *Atmos. Environ.* **34**(17), 2817–2825.

Kreutz, K. J., Mayewski, P. A., Twickler, M. S., Whitlow, S. I., White, J. W. C. and co-authors. 1999. Seasonal variations of glaciochemical, isotopic and stratigraphic properties in Siple Dome (Antarctica) surface snow. *Ann. Glaciol.* **29,** 38–44.

Lamb, D. and Chen, J.-P. 1990. A modeling study of the effects of ice-phase microphysical processes on trace chemical removal efficiencies. *Atmos. Res.* **25**(1–3), 31–51.

Legrand, M. R. and Delmas, R. J. 1988. Formation of HCl in the Antarctic Atmosphere. *J. Geophys. Res. - Atmos.* **93**(6), 7153–7168.

Legrand, M. R. and Mayewski, P. 1997. Claciochemistry of polar ice cores. A review. *Rev. Geophys*. **35**(3), 219–243

Minikin, A., Wagenbach, D., Graf, W. and Kipfstuhl, J. 1994. Spatial and seasonal variations of the snow chemistry at the central Filchner-Ronne Ice Shelf, Antarctica. *Ann. Glaciol.* **20,** 283–290.

Moser, H. and Stichler, W. 1980. Environmental isotopes in ice and snow. In: *Handbook of environmental isotope geochemistry*. (eds P. Fritz and J. C. Fontes). Elsevier, New York, 141–178.

Neumann, T. A., Waddington, E. D., Steig, E. J. and Grootes, P. M. 2005. Non-climate influences on stable isotopes at Taylor Mouth, Antarctica. *J. Glaciol.* **51**(173), 248–258.

North Greenland Ice Core Project members. 2004. High-resolution record of Northern Hemisphere climate extending into the last interglacial period. *Nature* **431,** 147–151.

Pomeroy, J. W. and Jones, H. G. 1996. Wind-blown-snow: Sublimation and changes to Polar snow. In: *Chemical exchange between the atmosphere and polar snow*. (eds E. W. Wolff and R. C. Bales). NATO ASI Series I Global environmental change, v. 43, Springer-Verlag, Berlin & Heidelberg, 453–490.

Putnins, P. 1970. The Climate of Greenland. In: *Climates of the Polar Regions* (ed S. Orvig). World survey of climatology. Elsevier, New York, 3–113.

Puxbaum, H. and Tscherwenka, W. 1998. Relationships of major ions in snow fall and rime at Sonnblick Observatory (SBO, 3106 m) and implications for scavenging processes in mixed clouds. *Atmos. Environ.* **32**(23), 4011–4020.

Reijmer, C. H. 2001. *Antarctic meteorology. A study with automatic weather stations*. Doctoral Thesis, University of Utrecht, 115.

Reijmer, C. H. and Van Den Broeke, M. R. 2003. Temporal and spatial variability of the surface mass balance in Dronning Maud Land, Antarctica, as derived from automatic weather stations. *J. Glaciol.* **49**(167), 512–520.

Röthlisberger, R., Hutterli, M. A., Sommer, S., Wolff, E. W. and Mulvaney, R. 2000. Factors controlling nitrate in ice cores: Evidence from the Dome C deep ice core. *J. Geophys. Res.-Atmos.* **105**(16), 20565–20572.

Röthlisberger, R., Hutterli, M. A., Wolff, E. W., Mulvaney, R., Fischer, H. and co-authors. 2002. Nitrate in Greenland and Antarctic ice cores: A detailed description of post-depositional processes. *Ann. Glaciol.* **35,** 209–216.

Röthlisberger, R., Mulvaney, R., Wolff, E. W., Hutterli, M. A., Bigler, M. and co-authors. 2003. Limited dechlorination of sea-salt aerosols during the last glacial period: Evidence from the European Project for Ice Coring in Antarctica (EPICA) Dome C ice core. *J. Geophys. Res.-Atmos.* **108**(16), 4526, doi:10.1029/2003JD003604.

Saltzman, E. S. 1995. Ocean/Atmosphere cycling of dimethylsulfide. In: *Ice Core Studies of Global Biogeochemical Cycles* (ed R. J. Delmas). Springer-Verlag, New York, 65–89.

Satake, H. and Kawada, K. 1997. The quantitative evaluation of sublimation and the estimation of original hydrogen and oxygen isotope ratios of a firn core at East Queen Maud Land, Antarctica. *B. Glaciol. Res.* **15**, 93–97.

Sommerfeld, R. A., Judy, C. and Friedman, I. 1991. Isotopic changes during the formation of depth hoar in experimental snow packs. In: *Stable isotope geochemistry; a tribute to Samuel Epstein* (eds H. P. Taylor Jr., J. R. O'Neil and I. R. Kaplan). Special Publication - Geochemical Society, San Antonio, 205–209.

Steffen, K. and Box, J. 2001. Surface climatology of the Greenland ice sheet: Greenland climate network 1995-1999. *J. Geophys. Res.-Atmos.* **106**(24), 33951–33964.

Stenberg, M., Isaksson, E., Hansson, M., Karlen, W., Mayewski, P. A. and co-authors. 1998. Spatial variability of snow chemistry in western Dronning Maud Land, Antarctica. *Ann. Glaciol*. **27,** 378–384.

Udisti, R., Becagli, S., Castellano, E., Traversi, R., Vermigli, S. and co-authors. 1999. Sea-spray and marine biogenic seasonal contribution to snow composition at Terra Nova Bay, Antarctica. *Ann. Glaciol.* **29,** 77–83.

Udisti, R., Becagli, S., Benassi, S., Castellano, E., Fattori, I. and co-authors. 2004. Atmosphere - snow interaction by comparison between aerosol and the uppermost snow layers composition at Dome C (East Antarctica). *Ann. Glaiol*. **39,** 53–61.

van den Broeke, M. R., Reijmer, C. H. and Van De Wal, R. S. W. 2004. A study of the surface mass balance in Dronning Maud Land, Antarctica, using automatic weather stations. *J. Glaciol.* **50**(171), 565–582.

Wagenbach, D., Ducroz, F., Mulvaney, R., Keck, L., Minikin, A. and co-authors. 1998. Sea-salt aerosol in coastal Antarctic regions. *J. Geophys. Res.-Atmos.* **103**(9), 10961–10974.

Wagnon, P., Delmas, R. J. and Legrand, M. 1999. Loss of volatile acid species from upper firn layers at Vostok, Antarctica. *J. Geophys. Res.-Atmos.* **104**(3), 3423–3431.

Weller, R., Traufetter, F., Fischer, H., Oerter, H., Piel, C. and co-authors. 2004. Postdepositional losses of methane sulfonate, nitrate, and chloride at the European Project for Ice Coring in Antarctica deep-drilling site in Dronning Maud Land, Antarctica. *J. Geophys. Res.- Atmos.* **109**(7), D07301, doi:10.1029/2003JD004189.

Wolff, E. W. 1995. Nitrate in polar ice. In: *Ice core studies of global biogeochemical cycles* (ed R. J. Delmas), Springer-Verlag, New York, 195–224.

Wolff, E. W., Hall, J. S., Mulvaney, R., Pasteur, E. C., Wagenback, D. and co-authors. 1998. Relationship between chemistry of air, fresh snow and firn cores for aerosol species in coastal Antarctica. *J. Geophys. Res. - Atmos* **103**(9), 11057–11070.