

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

R. Weller,¹ F. Traufetter,^{1,2} H. Fischer,¹ H. Oerter,¹ C. Piel,¹ and H. Miller¹

Received 26 September 2003; revised 18 February 2004; accepted 24 February 2004; published 1 April 2004.

[1] We quantified postdepositional losses of methane sulfonate (MSA^-), nitrate, and chloride at the European Project for Ice Coring in Antarctica (EPICA) drilling site in Dronning Maud Land (DML) (75°S , 0°E). Analyses of four intermediate deep firn cores and 13 snow pits were considered. We found that about $26 \pm 13\%$ of the once deposited nitrate and typically $51 \pm 20\%$ of MSA^- were lost, while for chloride, no significant depletion could be observed in firn older than one year. Assuming a first order exponential decay rate, the characteristic e -folding time for MSA^- is 6.4 ± 3 years and 19 ± 6 years for nitrate. It turns out that for nitrate and MSA^- the typical mean concentrations representative for the last 100 years were reached after 5.4 and 6.5 years, respectively, indicating that beneath a depth of around 1.2–1.4 m postdepositional losses can be neglected. In the area of investigation, only MSA^- concentrations and postdepositional losses showed a distinct dependence on snow accumulation rate. Consequently, MSA^- concentrations archived at this site should be significantly dependent on the variability of annual snow accumulation, and we recommend a corresponding correction. With a simple approach, we estimated the partial pressure of the free acids MSA , HNO_3 , and HCl on the basis of Henry's law assuming that ionic impurities of the bulk ice matrix are localized in a quasi-brine layer (QBL). In contrast to measurements, this approach predicts a nearly complete loss of MSA^- , NO_3^- , and Cl^- . **INDEX TERMS:** 0322 Atmospheric Composition and Structure: Constituent sources and sinks; 0330 Atmospheric Composition and Structure: Geochemical cycles; 0365 Atmospheric Composition and Structure: Troposphere—composition and chemistry; 1827 Hydrology: Glaciology (1863); 1863 Hydrology: Snow and ice (1827); **KEYWORDS:** postdepositional loss, snow chemistry, methane sulfonate

Citation: Weller, R., F. Traufetter, H. Fischer, H. Oerter, C. Piel, and H. Miller (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.*, 109, D07301, doi:10.1029/2003JD004189.

1. Introduction

[2] Polar ice cores represent an extraordinary archive of climate proxies from which information about temperature, precipitation, and composition of the paleo atmosphere can be derived in high temporal resolution [e.g., *Legrand and Mayewski*, 1997]. For example ionic impurities stored in the ice matrix are the result of atmospheric trace compound deposition and are potential proxies for the interaction between biogeochemical cycles and climate [e.g., *Yang et al.*, 1997], as well as atmospheric circulation. Unfortunately, for certain ionic species, deposition seems to be reversible. For volatile acids HA (with A^- = formate, acetate, fluoride, chloride, nitrate, and methane sulfonate) postdepositional losses are partly well documented and described, especially for low accumulation sites in Antarctica and central Green-

land [*De Angelis and Legrand*, 1995; *Legrand et al.*, 1996; *Wagnon et al.*, 1999; *Röthlisberger et al.*, 2002, 2003; *Delmas et al.*, 2003]. These previous investigations revealed that the mentioned acid species are not archived conservatively in the firn, complicating an interpretation of their profiles in ice cores. Concerning the physicochemical processes leading to postdepositional losses, there is some evidence that in acidic firn layers, the more or less volatile free acids HA are re-emitted to the firn air from which they are readily mixed within the atmospheric boundary layer by eddy diffusion [*Wagnon et al.*, 1999]. Thus, as deduced by *Wagnon et al.* [1999] polar ice caps act as a source for once deposited volatile trace compounds, complicating not only the interpretation of their firn but also their atmospheric concentrations in polar regions. Mainly the strong and nonvolatile sulfuric acid, a dominant component in Antarctic snow and ice [*Legrand and Mayewski*, 1997] acts as potential H^+ donor for the anions A^- . In the special case of nitrate/ HNO_3 , photolysis seems to be an additional and efficient loss mechanism within the upper firn layer [*Dibb et al.*, 2002; *Wolff et al.*, 2002] leading to significant NO_x emissions into the stable boundary layer above the snow

¹Alfred Wegener Institute for Polar and Marine Research, Bremerhaven, Germany.

²Now at Prinsengracht 596/II, Amsterdam, Netherlands.

surface [Honrath *et al.*, 1999; Jones *et al.*, 2001]. This mechanism is thought to have a dramatic impact on local photochemistry [Davis *et al.*, 2001]. Previous investigations carried out in continental Antarctica revealed that loss of volatile acids is mainly restricted to the upper few meters in the firn [Wagon *et al.*, 1999], however, loss rates linked with this process have not yet been evaluated. In addition, while the influence of accumulation rate, firn acidity, and temperature on the firn concentrations of acid species has been described in several previous investigations [e.g., Legrand *et al.*, 1996; Wagon *et al.*, 1999; Röthlisberger *et al.*, 2002], quantification of total postdepositional losses are scarce [De Angelis and Legrand, 1995; Wagon *et al.*, 1999].

[3] In view of the present deep ice core drilling activities on Amundsenisen in the framework of the European Project for Ice Coring in Antarctica (EPICA), a characterization of postdepositional losses of the most prominent anions at the drilling site is obviously of basic importance. Accordingly, we focused our interest to provide a representative quantification of postdepositional losses and loss rates of methane sulfonate (MSA^-), nitrate (NO_3^-), and chloride (Cl^-) in the upper firn layers at the EPICA drilling site in Dronning Maud Land (EDML). Furtheron, we try to assess the dependence of the observed losses on snow accumulation rate and address the question to what extent ionic concentration profiles archived in the EDML ice core are influenced by the varying annual snow accumulation. To meet this aim, analyses of four intermediate deep ice cores and 13 snow pits were considered. Finally we will speculate about the physicochemical processes which may be responsible for the observed findings.

2. Site Selection, Sampling, and Analyses

[4] In the framework of EPICA, several comprehensive pre-site surveys have been carried out on Amundsenisen [Oerter *et al.*, 1999, 2000]. Data from 13 snow pits and 4 intermediate-depth firn cores recovered during the field campaigns 1997/1998 and 1999/2000 are presented here (Figure 1). All drill sites are located in the Atlantic sector of the East Antarctic plateau more than 500 km away from the coast at an altitude range between 2600 and 3160 m above sea level (a.s.l.), i.e., well above the marine boundary layer. The mean annual snow accumulation (about $50\text{--}100\text{ kg m}^{-2}\text{ yr}^{-1}$) is rather low but varies by a factor of two between individual sites. Details on the location, altitude, dating of the cores and snow pits as well as sampling procedure and analysis can be found in the work of Göktas [2002] and Göktas *et al.* [2002]. In general, samples were analyzed for MSA^- , Cl^- , NO_3^- , SO_4^{2-} , Na^+ , NH_4^+ , K^+ , Mg^{2+} , and Ca^{2+} by ion chromatographic (IC) analysis. In short, the uncertainty for the measured ionic concentrations discussed in this study was approximately 3–5% for the main components MSA^- , Cl^- , NO_3^- , SO_4^{2-} , Na^+ , increasing to between 10% and 20% for the minor species NH_4^+ , K^+ , Mg^{2+} , and Ca^{2+} .

3. Results

[5] Measured MSA^- and NO_3^- concentrations vs. depth profiles for this region are presented in Figure 2. Surprisingly, none of the snow pits showed a significant Cl^- loss

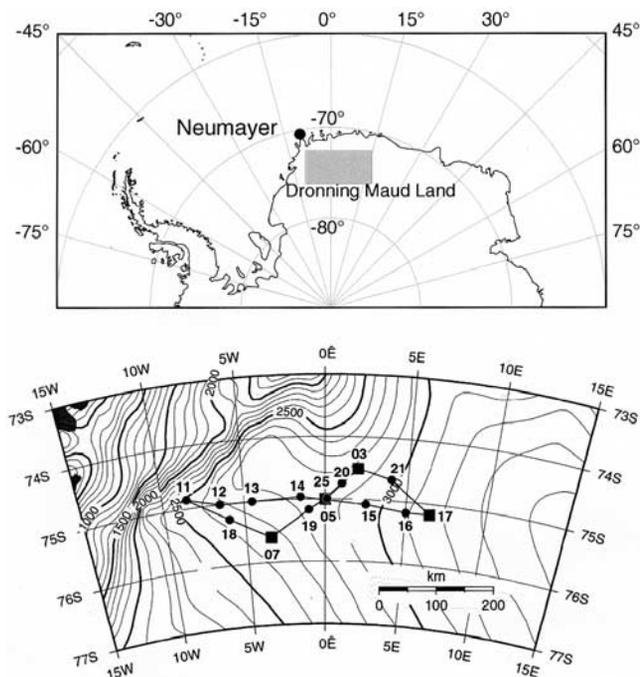


Figure 1. Area of investigation in Dronning Maud Land, Antarctica. The locations of the excavated snow pits are marked with dots, those for the medium depth firn cores by squares. The EPICA-DML drilling site is adjacent to site 05.

(Figure 3). Moreover, even for the Cl/Na ratio, which is a measure for excess chloride (i.e., HCl), we could not ascertain a significant decrease, neither for the Cl/Na maxima, nor for the mean values (Figure 3). MSA^- and NO_3^- loss rates $1/\tau$ [yr^{-1}] were calculated assuming a first order exponential decay according to:

$$[A^-]_t = [A^-]_{t_0} \exp\{-\Delta t/\tau\},$$

where $[A^-]_t$ and $[A^-]_{t_0}$ denote the annual mean concentrations in a firn layer corresponding to the year t , and within the top layer of the snow pit at the year $t_0 = 1997$, respectively, with $\Delta t = t_0 - t$. Table 1 summarizes the results from all 13 snow pits, while in Figure 4 and Figure 5a and 5b the mean values comprising all snow pits are presented. In summary 9 (8) from 13 snow pits showed a distinct NO_3^- (MSA^-) decay vs. depth. There is no obvious explanation for the lack of NO_3^- or MSA^- loss in the other pits. Note, however, that in each snow pit at least either a NO_3^- or MSA^- decay was observed (Table 1). Based on our results we recommend an e -folding time of 6.4 ± 3 years for MSA^- ($r^2 = 0.69$) and 19 ± 6 years for NO_3^- ($r^2 = 0.97$) being representative for the area of investigation on Amundsenisen. The quoted uncertainties refer to Figure 5 and represent the variability between years averaged over the whole region. No significant correlation of loss rates with snow accumulation rate could be derived.

[6] We quantified the total loss of MSA^- , NO_3^- , and Cl^- by relating $[A^-]_{t_0}$ to the 100 years mean concentrations $[A^-]_{100}$ retrieved from the firn cores (Table 2; starting from 1970 AD back to 1870 AD to exclude postdepositional impacts within the upper firn layers). Within the latter

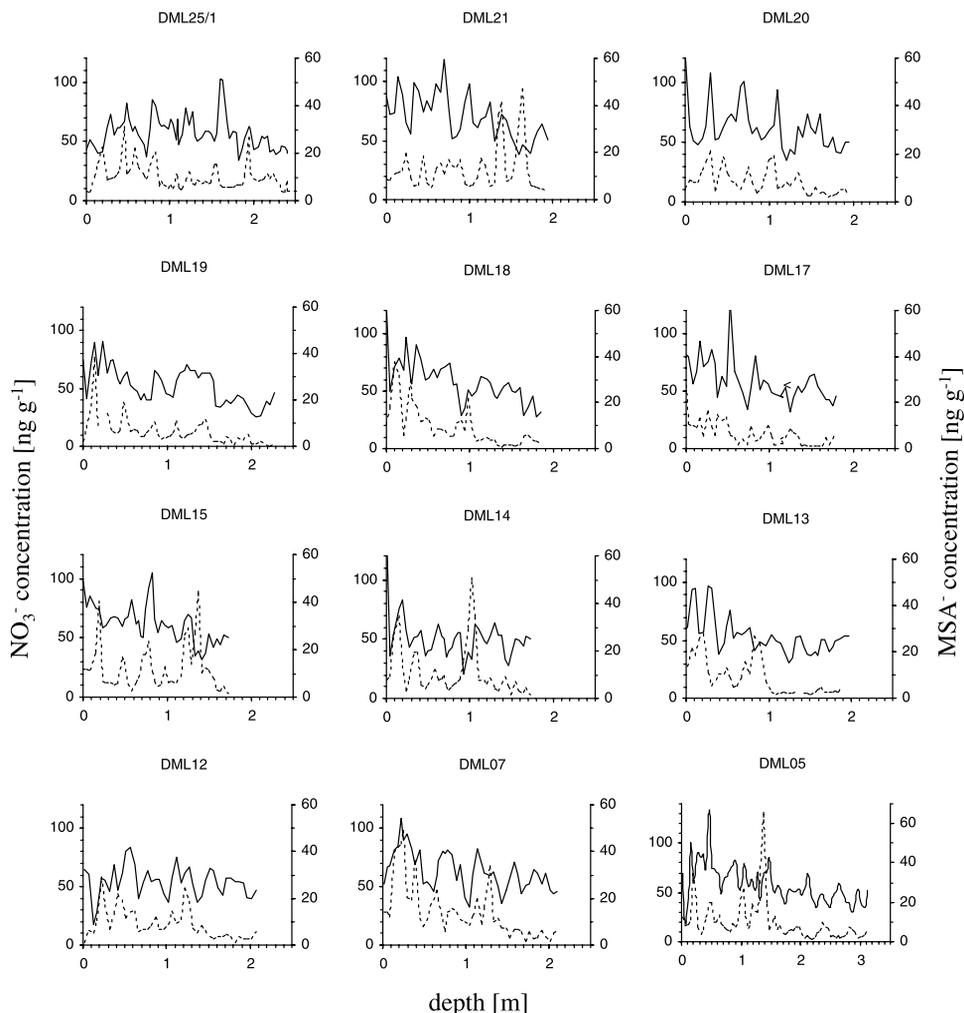


Figure 2. Nitrate (solid line, left-hand scale) and MSA^- (dashed line, right-hand scale) concentrations as a function of depth, measured in 12 snow pits (results from pit DML25/8 are shown in Figure 8).

interval, long-term trends in the corresponding concentration profiles are not detectable. We emphasize that we did not use fresh snow or surface snow concentrations of A^- as a reference point to calculate the total loss. These concentrations turned out to be highly variable [Piel, 2004] and would not provide a robust benchmark. Ideally, $[\text{A}^-]_{t0}$ in a given snow pit has to be compared with the long term mean of a core taken at the same site. In our case, only four medium deep cores are available for such an analysis. Within the given (small) range of snow accumulation rate in the area of investigation ($55\text{--}97 \text{ kg m}^{-2} \text{ yr}^{-1}$), the loss rates and the mean MSA^- , Cl^- , and NO_3^- concentrations found in the snow pits exhibited no significant dependence on the snow accumulation rate ($r^2 < 0.1$ in all cases). In contrast, for $[\text{A}^-]_{100}$ a dependence on snow accumulation rate is observed (Figure 6 and Table 2). Here, MSA^- and NO_3^- concentrations in firm indicated less depositional losses at higher accumulation rates [Göktas *et al.*, 2002], while Cl^- concentrations showed the reverse relation. The influence of the snow accumulation rate (accu) on MSA^- concentrations can be quantified by the following expression:

$$[\text{MSA}^-] = (0.12 \times \text{accu} - 0.87) \text{ ng g}^{-1} \quad r^2 = 0.98.$$

For $[\text{NO}_3^-]$ and $[\text{Cl}^-]$ the linear regressions given in Figure 6 are not significant (F test below a significance level of $\alpha = 0.1$).

[7] To simplify matters, we related $[\text{A}^-]_{100}$ of the cores to $[\text{A}^-]_{t0}$ of pits with comparable snow accumulation rates (accu): Core DML03 with pits DML13,14,19–21 (accu = $78\text{--}98 \text{ kg m}^{-2} \text{ yr}^{-1}$); core DML05 with pits

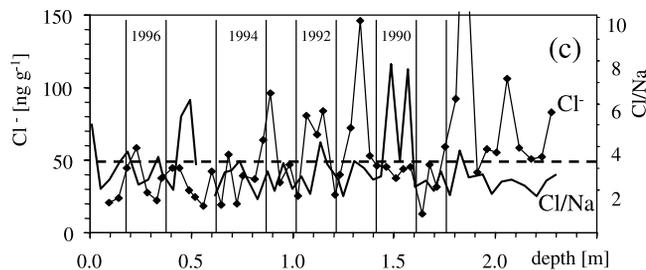


Figure 3. Chloride concentration and Cl/Na ratio as a function of depth, measured in a snow pit excavated at the site DML19. The Cl/Na ratio for seawater is about 1.8. The horizontal broken line represents the corresponding 100 year mean ($[\text{Cl}^-]_{100}$) of the firm cores.

Table 1. Summary of the Results From 13 Snow Pits, Including Mean Snow Accumulation Rates and the Number of Years Covered by Each Snow Pit^a

Snow Pit Site	Accumulation Rate, kg m ⁻² yr ⁻¹	Number of Years	MSA ⁻ , ng g ⁻¹	Cl ⁻ , ng g ⁻¹	NO ₃ ⁻ , ng g ⁻¹	1/τ _{MSA⁻} , yr ⁻¹	1/τ _{NO₃⁻} , yr ⁻¹	Δ[MSA ⁻] _{total} , ng g ⁻¹	Δ[Cl ⁻] _{total} , ng g ⁻¹	Δ[NO ₃ ⁻] _{total} , ng g ⁻¹
DML25/1	72	9	9.8 (17.2)	45.9 (36.4)	59.2 (50.7)	0.08	(*)	-10.7	+9.7	-3.7
DML25/8	72	9	11.8 (20.5)	38.9 (35.3)	64.8 (56.0)	0.08	(*)	-14.0	+10.8	-9.0
DML18	55	10	9.1 (24.5)	57.3 (50.3)	59.2 (81.3)	0.24	0.076	-19.5	+8.4	-40.3
DML07	62	10	13.9 (27.5)	70.7 (84.5)	62.2 (77.0)	(*)	0.060	-21.8	-28.6	-24.0
DML19	78	11	7.1 (16.4)	50.7 (36.9)	55.0 (69.5)	0.18	(*)	-6.6	+10.4	-15.5
DML05	71	10	10.6 (9.9)	47.6 (62.0)	56.6 (58.3)	(*)	0.022	-3.4	+15.9	-11.3
DML20	97	8	8.6 (11.8)	26.5 (37.8)	60.3 (73.1)	0.15	0.022	-2.0	+9.5	-19.1
DML21	83	9	14.1 (11.9)	37.6 (36.2)	68.5 (82.1)	(*)	0.088	-2.1	+11.1	-28.1
DML17	63	14	6.2 (16.2)	37.9 (50.3)	57.2 (72.2)	0.16	0.065	-10.5	+5.6	-19.2
DML15	71	8	13.0 (18.9)	33.4 (57.0)	60.9 (81.5)	(*)	0.089	-12.4	-10.9	-34.5
DML14	81	9	12.0 (18.6)	42.7 (34.7)	50.1 (79.4)	(*)	0.055	-8.8	+12.6	-25.4
DML13	80	10	9.4 (17.8)	48.6 (116)	55.1 (83.2)	0.24	0.099	-8.0	-68.7	-29.2
DML12	68	9	9.5 (11.7)	64 (77.5)	54.8 (47.1)	0.09	(*)	-5.2	-31.4	-0.1

^aMean concentrations of the ions are presented along with the annual mean values of the top layer, [A⁻]₁₀₀ (in parentheses); (*) indicates that no decay could be detected in the snow pit samples, while usually there is a loss Δ[A⁻]_{total} relative to the cores. For definition of first order loss constants 1/τ_{anion} and the total loss Δ[A⁻]_{total} is about ±(15–20)%.

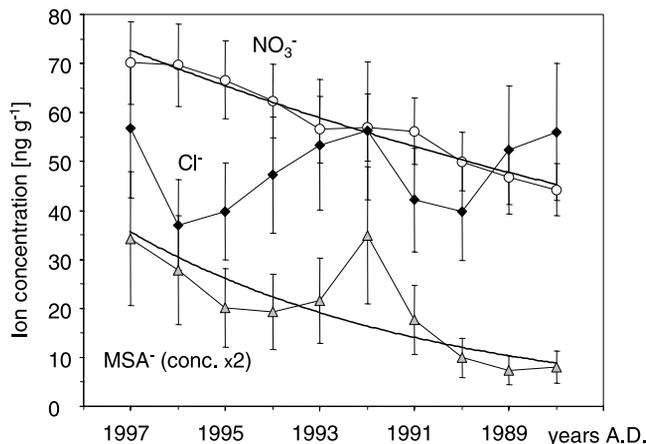


Figure 4. Averages of the annual mean MSA⁻ (gray triangles; note different scale), Cl⁻ (diamonds), and NO₃⁻ (circles) concentrations from 13 snow pits as a function of firm age. The error bars indicate the standard deviations of the values.

DML05,12,15,25 (accu = 62–72 kg m⁻² yr⁻¹); core DML07 with pits DML7 and DML17 (accu = 59–63 kg m⁻² yr⁻¹); core DML17 with pit DML18 accu = 47–55 kg m⁻² yr⁻¹). Finally, the total losses Δ[A⁻]_{total} were defined as follows (Table 1):

$$\Delta[A^-]_{total} = [A^-]_{100} - [A^-]_{t0}$$

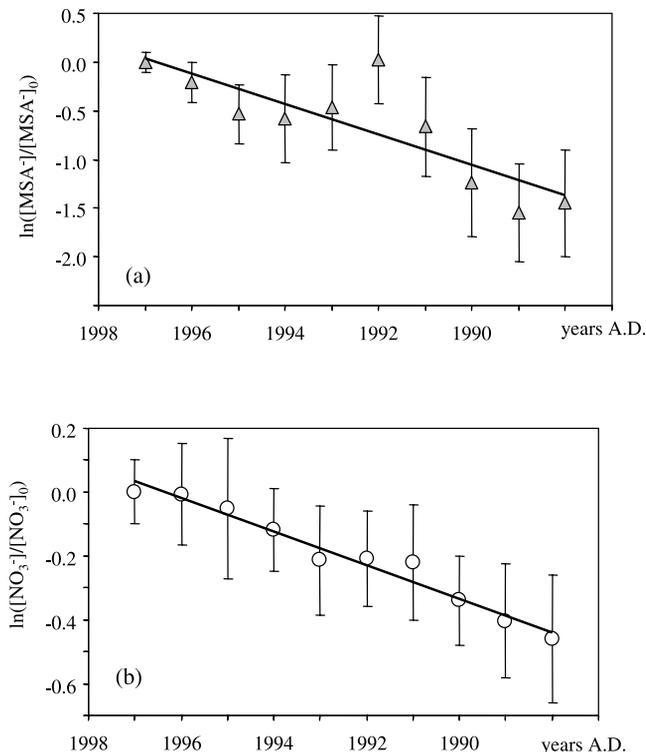


Figure 5. Mean first-order exponential decay of MSA⁻ (a) and NO₃⁻ (b) derived from all 13 snow pits. Error bars represent the corresponding standard deviations (±std) of the annual mean values from the different snow pits.

Table 2. Summary of the Results From the Firm Cores^a

Core Site	Accumulation Rate, kg m ⁻² yr ⁻¹	Number of Years	[MSA ⁻] ₁₀₀ , ng g ⁻¹	[Cl ⁻] ₁₀₀ , ng g ⁻¹	[NO ₃ ⁻] ₁₀₀ , ng g ⁻¹
DML03	91.4 ± 30	200	9.8	47.3	54.0
DML05	62.4 ± 12	1833	6.5	46.1	47.0
DML07	57.7 ± 12	1533	5.7	55.9	53.0
DML17	46.1 ± 12	200	5.0	58.7	41.0

^aMean snow accumulation rates within the period 1970–1870 AD (±std), total number of years covered by each core, and 100 year mean concentrations of the considered anions [A⁻]₁₀₀ (period 1970–1870).

[8] Again, considering all snow pits, a significant Cl⁻ or excess chloride loss could not be found (2 ± 33%), while in contrast about 26 ± 13% of the once deposited NO₃⁻ and 51 ± 20% of MSA⁻ were not preserved in firm. Only for MSA⁻ the quantified relative loss ΔMSA_{rel} [%] showed a distinct correlation with the snow accumulation rate (r² = 0.69, Figure 7):

$$\Delta\text{MSA}_{\text{rel}}[\%] = -(1.6 \pm 0.3) \times \text{accu} + (168 \pm 24) \quad r^2 = 0.69. \quad (1)$$

[9] Below a characteristic depth Δz of around 1.2 ± 0.2 m and 1.4 ± 0.2 m the mean MSA⁻ and NO₃⁻ concentrations, respectively, reached the 100 year mean concentrations of the cores. The threshold depth Δz was derived from the calculated mean first order loss rates and the observed mean total losses, assuming a firm density of 0.35 g cm⁻³ and an average snow accumulation rate of 75 kg m⁻² yr⁻¹ [Oerter *et al.*, 1999]. Note that data presented by Delmas *et al.* [2003, Figure 2] from Vostok indicate that postdepositional losses of nitrate ceased beyond a depth of around 1.5 m, while for MSA the situation appears less clear.

4. Discussion

4.1. Comparison With Previous Results From Antarctica

[10] The higher total postdepositional loss of MSA⁻ and NO₃⁻ observed at Vostok (78°28'S, 106°48'E, 3490 m a.s.l., annual mean temperature T = -56°C) and Dome C

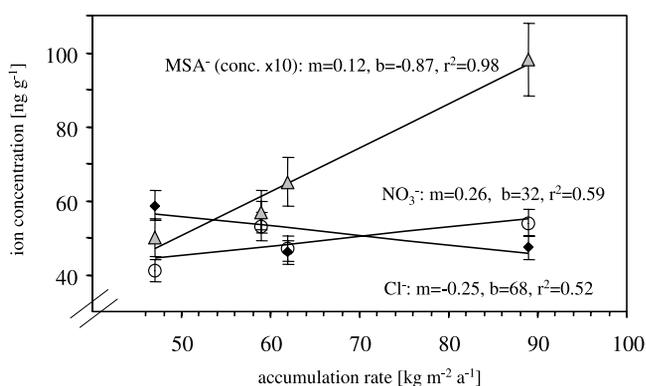


Figure 6. Dependence of the MSA⁻ (triangles; note different scale), NO₃⁻ (circles), and Cl⁻ (diamonds) concentrations found in 4 firm cores (100 year means from 1970 to 1870 AD) on the snow accumulation rate. In contrast to the results from the snow pits in each case a significant correlation is given (m = slope [10⁻⁹ yr kg⁻¹ m⁻²], b = intercept [ng g⁻¹]).

(74°39'S, 124°10'E, 3240 m a.s.l., T = -53.5°C) compared to our findings may be attributed to the much lower accumulation rate at these sites (Table 3). Röhrlisberger *et al.* [2000] found a pronounced temperature dependence of nitrate concentrations archived at different Antarctic sites with higher concentrations at lower annual mean temperature. This tendency may partly compensate the impact of snow accumulation rate. However, Table 3 reveals that the latter factor is clearly dominant (note that annual mean temperature at EPICA DML is -46°C).

[11] The lack of a postdepositional Cl⁻ loss at DML05 remains peculiar. Although our fresh and surface snow samples taken from this site during austral summer showed high Cl/Na ratios between 6 and 12 [Piel, 2004], Cl/Na was around 2.3 ± 1 in the snow pits and firm cores, close to the seasalt ratio of 1.8. These fresh and surface snow samples further indicate that most of the excess chloride (HCl) and about 50% of nitrate, were typically lost within a few weeks [Piel, 2004]. In contrast MSA⁻ postdepositional depletion seemed to occur more gradually. In contrast, at Vostok the Cl/Na ratio decreased from a value of 5 in the upper 2 m to about 0.3–0.4 at greater depth [Wagnon *et al.*, 1999]. Recently Röhrlisberger *et al.* [2003] observed significant Cl⁻ deficits relative to Na⁺ below a threshold accumulation rate of about 40 kg m⁻² yr⁻¹ in EPICA Dome C ice core. Results from Wagnon *et al.* [1999] revealed a distinct positive correlation between Na⁺ and non sea salt sulfate concentrations, but not with Cl⁻, indicating that Na⁺ was associated with sulfate due to the reaction of sulfuric acid aerosol with NaCl. In contrast, our findings clearly showed the contrary relation, suggesting that deposited seasalt was persistent. These differences may be attributed to the different location and precipitation regime. While DML, which is about 500 km away from the coast, is subject to cyclonic activity and receives about 80% of its precipitation from frontal clouds [Reijmer *et al.*, 2002], low accumulation

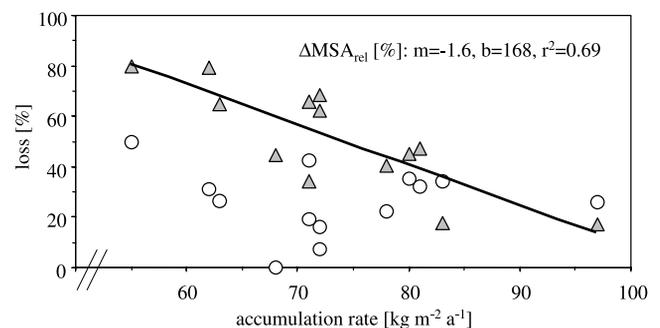


Figure 7. Dependence of the relative MSA⁻ (triangles) and NO₃⁻ (circles) losses on the snow accumulation rate (m = slope [yr kg⁻¹ m⁻²], b = intercept [%]).

Table 3. Summary of Reported Postdepositional Losses of MSA^- , NO_3^- , and Cl^- Found in Snow Pits or Firn Cores Drilled at Vostok, Dome C, South Pole, and DML05 (This Work) With the Corresponding Snow Accumulation Rates in Parentheses

Anion	Vostok, ^a 22 kg m ⁻² yr ⁻¹	Dome C, ^b 35 kg m ⁻² yr ⁻¹	South Pole, ^c 85 kg m ⁻² yr ⁻¹	EPICA–DML, 62 kg m ⁻² yr ⁻¹
MSA^-	90% ^d	-	-	61 ± 13%
NO_3^-	90% ^{a,d}	72% ^c 97% ^e	no trend ^c	30 ± 15%
Cl^-	80% ^d 52% ^a	≈70% ^f	no trend ^b	5 ± 32%

^aFrom *De Angelis and Legrand* [1995].

^bFrom *Legrand and Delmas* [1988].

^cFrom *Mayewski and Legrand* [1990].

^dFrom *Wagnon et al.* [1999].

^eFrom *Röthlisberger et al.* [2000].

^fFrom *Röthlisberger et al.* [2003].

sites like Vostok are extremely remote and diamond dust seems to be the primary way of precipitation. Accordingly, snow formation, hence wet deposition of aerosol, and subsequently recrystallization processes in the snowpack are expected to differ between the two regimes, leading to different aerosol deposition as well as preservation.

[12] Striking MSA^- peaks could be found in nearly all snow pits in 1997 and 1992 AD. These outstanding MSA^- concentration peaks could be retrieved in two snow pits excavated two years later close to this site (Figure 8). We conclude that in spite of distinct postdepositional MSA^- losses, the overall signature of MSA^- concentration profiles remained preserved. However, more subtle (tens of percent) changes in peak concentrations could still be masked by typical accumulation rate changes (Figure 8). To exclude a possible bias by the MSA^- concentration peak in 1996/1997 AD in calculating the first order loss rate, we re-evaluated τ_{MSA} considering only the years from 1995/1996 back to 1990/1989 AD. This results in a slightly, but negligibly lower e -folding time of 6.3 ± 3.5 years ($r^2 = 0.63$). As mentioned by *Göktas et al.* [2002], a migration of MSA^- peaks away from highly acidic H_2SO_4 layers, evident in firn cores from other Antarctic sites [*Minikin et al.*, 1994; *Pasteur and Mulvaney*, 2000; *Curran et al.*, 2002; *Delmas et al.*, 2003] could not be unequivocally verified, even in our high resolution snow pit samples (DML25/8, about 10 samples per year).

4.2. Possible Physicochemical Processes Causing HA Loss

[13] There are two potential physicochemical processes which are most probably responsible for the observed losses: Formation of volatile acids HA in acidic snow layers which are partially re-emitted to the atmosphere [*Wagnon et al.*, 1999], or photochemical reactions of HA or A^- within the firn layer. The latter process is known to act as a significant nitrate/ HNO_3 loss mechanism [*Dibb et al.*, 2002; *Wolff et al.*, 2002]. Even for MSA photo-oxidation could be relevant: *Milne et al.* [1989] measured a rather fast reaction rate of MSA with OH radicals in aqueous solutions ($k_{298\text{K}} = 4.7 \pm 0.9 \times 10^7 \text{ M}^{-1} \text{ s}^{-1}$) and estimated a typical lifetime of MSA in midlatitude cloud droplets of only 1.2–3.5 hours. Applied to our conditions, an average OH concentration in the quasi-brine layer (see below) of around 10^{-16} M would be sufficient to cause the observed MSA decay rate in upper firn layer. However, as stated by *Wolff et al.* [2002] in case of postdepositional nitrate loss, below a

depth of about 10 cm actinic radiation can be expected to become insignificant. Consequently a continuous loss of nitrate and MSA^- down to a depth of 1.2–1.4 m cannot be attributed to photochemistry.

[14] In the following approach, which is mainly drawn upon the proceeding of *Cho et al.* [2002] we will assess whether formation of the volatile free acids is a potential

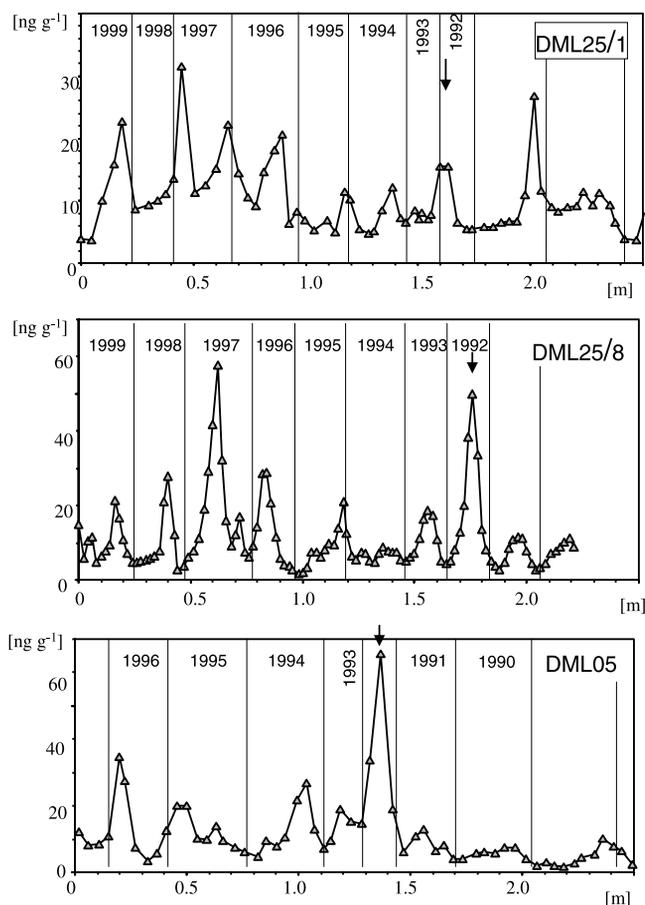


Figure 8. MSA^- concentrations as a function of depth, measured in three snow pits. Snow pits DML25/1 and DML25/8 were excavated two years after DML05 at nearly the same position. The MSA^- peak in 1992 is well represented in both pits. Note that the dating of the pits is based on the Na^+ and nss-sulfate profiles [see *Göktas et al.*, 2002] and thus independent from the MSA^- profile.

Table 4. Molal Ionic Concentrations in Bulk Ice and Within the Quasi-Brine Layer (QBL), Ratios of the Free Acids HA in the QBL, Henry's Law Constants for HA, Corresponding Equilibrium Mixing Ratios of Gaseous HA According to Henry's Law^a

Anion	Bulk Ice, $\mu\text{mol kg}^{-1}$	QBL, mol kg^{-1}	$[\text{HA}]/[\text{A}^-]_{\text{total}}$	$H_{\text{HA}},$ $\text{mol L}^{-1} \text{atm}^{-1}$	p_{HA}/p_0 (Mixing Ratio)	Atmospheric Mixing Ratio of HA
MSA ⁻	0.095	0.26	0.83	8.97×10^{11}	0.36×10^{-12}	5×10^{-15b}
SO ₄ ²⁻	0.83	2.3	-	-	-	-
NO ₃ ⁻	0.79	2.2	0.34	1.55×10^8	7.3×10^{-9}	10×10^{-12c}
Cl ⁻	1.04	2.9	2.4×10^{-5}	30	3.5×10^{-6}	80×10^{-12d}
H ⁺	2.27	6.4	-	-	-	-

^aHere $p_0 = 680$ hPa, i.e., the air pressure at the sampling site, and typical atmospheric HA mixing ratios are presented. For details, see text.

^bFrom Mauldin *et al.* [2001].

^cFrom Weller *et al.* [2002].

^dFrom Piel [2004].

process to explain the observed postdepositional losses. Recent investigations suggest that during snow metamorphosis, ionic impurities are excluded from ice crystals and concentrated in a quasi-brine layer, QBL [Conklin and Bales, 1993; Cho *et al.*, 2002]. Hence we assumed that all ionic impurities are accumulated within the QBL. According to Cho *et al.* [2002] the needed total electrolyte concentration within the QBL to enable a melting point depression ΔT of -30 K, which is typical for summer snow layers in the area of investigation, was estimated by the expression:

$$\ln x_{\text{H}_2\text{O}} = -\frac{\Delta H_{\text{ice}}}{RT_m} \left(\frac{T_m - T}{T} \right).$$

The variables are defined as follows: $x_{\text{H}_2\text{O}}$, mole fraction of H₂O; ΔH_{ice} , the melting enthalpy and T_m , melting point of pure ice. We obtained an enrichment of the ionic concentrations (with $\sum x_i = 1 - x_{\text{H}_2\text{O}}$) in the QBL by a factor of 2.8×10^6 compared to the bulk ice (Table 4). Assuming that an ice grain with a diameter of $200 \mu\text{m}$ is covered by the calculated amount of quasi-brine, the thickness of this layer would be about 0.1 \AA , much less than a molecular monolayer and consequently unrealistic. This indicates that either individual droplets of QBL are distributed inhomogeneously across the crystal surface, or more probably, localized at grain boundaries and triple junctions [Fukazawa *et al.*, 1998; Barnes *et al.*, 2003].

[15] To estimate the equilibrium concentrations of the free acids HA we calculated the concentration of H⁺ from the measured ion balance assuming that the difference between the anion and the cation equivalents corresponds roughly to the H⁺ equivalents ($[\text{ion}]_e$ is given in $\mu\text{eq g}^{-1}$):

$$[\text{H}^+]_e = [\text{MSA}^-]_e + [\text{Cl}^-]_e + [\text{NO}_3^-]_e + [\text{SO}_4^{2-}]_e - [\text{Na}^+]_e \\ - [\text{NH}_4^+]_e - [\text{K}^+]_e - [\text{Mg}^{2+}]_e - [\text{Ca}^{2+}]_e.$$

The ion balance determined from our snow pit samples led to the result that $82 \pm 7\%$ of the cation equivalents are H⁺. Accordingly, the molal concentrations (moles of solute per 1000 g of solvent [mol kg^{-1}]) of the free acids $[\text{HA}]_m$ ($\text{A}^- = \text{MSA}^-, \text{NO}_3^-, \text{and Cl}^-$) were determined by the expression:

$$K_a = \frac{\gamma_{\pm} [\text{H}^+]_m [\text{A}^-]_m}{[\text{HA}]_m},$$

where $K_a(\text{HA})$ denotes the acidity constant of HA, γ_{\pm} is the corresponding activity coefficient, taken from Hamer and Wu [1972] in case of HNO₃ and HCl. For MSA we took the value given by Covington *et al.* [1973]; $[\text{A}^-]_m = [\text{A}^-]_{m,\text{total}} - [\text{HA}]_m$; $\text{p}K_a(\text{MSA}^-) = -1.84$, $\text{p}K_a(\text{HNO}_3) = -1.4$, $\text{p}K_a(\text{HCl}) = -7.0$. The equilibrium partial pressure of gaseous HA can be derived from Henry's law:

$$H_{\text{HA}} \times [\text{HA}]_m = p_{\text{HA}},$$

where H_{HA} is Henry's law constant for HA at 243 K , taken from Schwartz and White [1981], Dean [1992], and from Clegg and Brimblecombe [1985] for HNO₃, HCl, and MSA (only available at $T = 298 \text{ K}$), respectively; p_{HA} = equilibrium partial pressure of HA. The final results of these calculations are summarized in Table 4.

[16] Very clearly, assuming thermodynamic equilibrium conditions with the corresponding atmospheric mixing ratios the volatile acids MSA, HNO₃ and HCl should be re-emitted nearly quantitatively (Table 4). HCl showed the highest supersaturation in comparison with atmospheric mixing ratios, which did not exceed 80 pptv in this region during austral summer [Piel, 2004]. The fact that Cl⁻ concentrations in firn layers older than one year were preserved suggests that the main part of Cl⁻ was located inside the ice crystals. The Cl/Na ratios measured in our samples support the existence of solid seasalt ice condensation nuclei inside ice crystals as found by Kumai [1976] but this point remains controversial [Cullen and Baker, 2001]. MSA showed the lowest supersaturation, provided that gaseous MSA of around $5 \times 10^{-3} \text{ pptv}$ observed at South Pole [Mauldin *et al.*, 2001] are typical in continental Antarctica during austral summer. However, gaseous atmospheric MSA concentrations and Henry's law constant for MSA appear highly uncertain and no temperature dependent measurements of H_{MSA} are available, making a conclusive discussion difficult.

[17] Finally, we have to assess to what extent our simplifications may be responsible for the obvious discrepancies between the model approach and observations. For MSA⁻, temperature dependent activity coefficients and the effect of mixed electrolytes on γ_{\pm} is not available for the ionic composition to be considered here. Measurements performed by Cerquetti *et al.* [1968] indicate that $\gamma_{\pm}(\text{HCl})$ at 243 K should be higher by about a factor of 1.6 compared with the value at 298 K . The impact of mixed electrolytes is complex to assess, but even changing the corresponding activity coefficients by a factor of 10 would only alter p_{HA}

by less than an order of magnitude. Even in this case a nearly quantitative postdepositional loss of HA should be expected. Accordingly, these shortcomings can hardly account for the inconsistency between observations and model approach.

[18] Evidently, our approximation that all ionic impurities are quantitatively accumulated within the QBL is the most critical point. As shown in the extensive work of Gross [1968] the water/ice phase distribution coefficients Γ of ionic impurities are on the order of 10^{-3} to 10^{-5} , hence comparable to the volume ratio QBL/ice. Consequently, only a miniscule part of the ionic impurities may be located in a QBL. Recently $\Gamma(\text{HNO}_3)$ has been determined to be 3×10^{-6} to 1.6×10^{-5} in the temperature range between 265 K and 238 K, respectively [Thibert and Dominé, 1998]. According to Thibert and Dominé [1997, 1998] about 60 $\mu\text{g/g}$ HCl and 1.8 $\mu\text{g/g}$ HNO_3 can potentially be dissolved within the ice lattice, much more than typically found in our samples. In addition, recent scanning electron microscopy studies revealed that most of the chloride in polar ice seems to be located within the lattice [Barnes et al., 2003]. Extrapolating the partial pressure equations given by Thibert and Dominé [1997, 1998] to our conditions ($T = 243$ K, $[\text{HCl}]_{\text{ice}} = 0.79$ nmol g^{-1} , $[\text{HNO}_3]_{\text{ice}} = 0.79$ nmol g^{-1}) result in $p_{\text{HCl}} = 2 \times 10^{-10}$ Pa (i.e., about 3×10^{-3} pptv) and $p_{\text{HNO}_3} = 1.6 \times 10^{-6}$ Pa (i.e., about 22 pptv). Consequently during summer the firm should be highly undersaturated with HCl but roughly in equilibrium for HNO_3 regarding typical atmospheric concentrations (see Table 4). Nevertheless, the QBL approach is consistent with an assessment of H_2SO_4 and HNO_3 concentrations detected in triple junctions of Antarctic ice by scanning electron microscopy and Raman spectroscopy, indicating that these ions are essentially, but probably not exclusively, present in a QBL [Mulvaney et al., 1988; Fukazawa et al., 1998].

[19] Concerning the kinetics of postdepositional MSA^- and NO_3^- losses, several complex physicochemical processes as there are diffusion in ice, firm metamorphosis associated with the formation of quasi-brine layers, electrolyte concentrations in the QBL, transfer velocities QBL-firm air, firm air-atmosphere exchange, and partial adsorption/desorption of HNO_3 and MSA on ice crystal surfaces could be rate determining. Waddington et al. [1996] estimated the timescale for molecular diffusion through the surface layer of ice to be around one hour, while diffusion in ice across a distance of 100 μm would roughly take 60 d for HNO_3 and 230 d for HCl at -30°C [Thibert and Dominé, 1997, 1998]. According to Bales et al. [1995] the timescale of firm air-atmosphere exchange should be on the order of hours to days. Snow metamorphosis, on the other hand, which is mainly driven by temperature gradients is a much slower process. It is most pronounced within the upper firm meter [Gow, 1969] and occurs on the timescale of years. The fact that in our case observed postdepositional losses are negligible beyond a depth of 1.2–1.4 m is consistent with snow metamorphosis associated with QBL formation being a decisive process in determining loss rates and finally the total loss.

5. Conclusions

[20] Our investigations on postdepositional losses of MSA^- , Cl^- , and NO_3^- , based on the analysis of 13 snow

pits and 4 medium depth firm cores provided representative values on total loss and loss rates for the region of Amundsenisen. In contrast to MSA^- , the concentration of the ions Cl^- and NO_3^- exhibited only a marginal dependence on snow accumulation rate in the area of investigation. Moreover, only postdepositional losses of MSA^- strongly depend on snow accumulation rate which is obviously the controlling factor for the observed relation between MSA^- concentrations stored in firm and accumulation rate. Given that even during Holocene the accumulation rate may vary by a factor of two [Oerter et al., 2000], we recommend a correction of MSA^- profiles in firm and ice cores retrieved at this site according to expression (1). We emphasize that the proposed correction is only valid for sites with snow accumulation rates between $50 \text{ kg m}^{-2} \text{ yr}^{-1}$ and $100 \text{ kg m}^{-2} \text{ yr}^{-1}$ and mean annual temperatures around -46°C . At accumulation rates above $100 \text{ kg m}^{-2} \text{ yr}^{-1}$ postdepositional losses become insignificant for all species considered here. In addition loss processes by re-emission of volatile acids should be marginal during glacial periods where high dust entries neutralize strong acids as supported by Röhthlisberger et al. [2000, 2003].

[21] Clearly, more dedicated field and laboratory research is needed to enable a detailed and reliable simulation of the re-emission of volatile acids from firm layers, comparable to recent encouraging progress achieved in modeling the air-snow interaction of HCHO and H_2O_2 [McConnell et al., 1998; Hutterli et al., 2002]. We emphasize the need of laboratory investigations to substantiate the presence of QBLs and to determine electrolyte concentrations in those phases, as well as field measurements to assess firm air concentrations of MSA , HNO_3 and HCl. Such measurements would help to understand the microphysical reason of postdepositional losses and shed some light on the physicochemical processes acting during snow metamorphosis in the upper firm layers.

[22] **Acknowledgments.** This work is a contribution to the “European Project for Ice Coring in Antarctica” (EPICA), a joint ESF (European Science Foundation)/EC scientific program, funded by the European Commission and by national contributions from Belgium, Denmark, France, Germany, Italy, the Netherlands, Norway, Sweden, Switzerland, and the United Kingdom. We also acknowledge the helpful comments of two anonymous referees. This is EPICA publication 91. Financial support by Deutsche Forschungsgemeinschaft (project OE 130/3) is gratefully acknowledged.

References

- Bales, R. C., M. V. Losleben, J. R. McConnell, K. Fuhrer, and A. Neftel (1995), H_2O_2 in snow, air and open pore space in firm at Summit, Greenland, *Geophys. Res. Lett.*, **22**, 1261–1264.
- Barnes, P. R. F., E. W. Wolff, D. C. Mallard, and H. M. Mader (2003), SEM Studies of the morphology and chemistry of polar ice, *Microsc. Res. Technol.*, **62**, 62–69.
- Cerquetti, A., P. Longhi, and T. Mussini (1968), Thermodynamics of aqueous hydrochloric acid from E.M.F.’s of hydrogen-chlorine cells, *J. Chem. Ref. Eng. Data*, **13**, 458–461.
- Cho, H., P. B. Shepson, L. A. Barrie, J. P. Cowin, and R. Zaveri (2002), NMR investigations of the quasi-brine layer in ice/brine mixtures, *J. Phys. Chem. B*, **106**, 1226–1232.
- Clegg, S. L., and P. Brimblecombe (1985), The solubility of methanesulfonic acid and its implications for atmospheric chemistry, *Environ. Technol. Lett.*, **6**, 269–278.
- Conklyn, M. H., and R. C. Bales (1993), SO_2 uptake on ice spheres: Liquid nature of ice-air interface, *J. Geophys. Res.*, **98**, 16,851–16,855.
- Covington, A. K., R. A. Robinson, and R. Thompson (1973), Osmotic and activity coefficients for aqueous methane sulfonic acid at 25°C , *J. Chem. Eng. Data*, **18**, 422–423.

- Cullen, D., and I. Baker (2001), Observation of impurities in ice, *Microsc. Res. Technol.*, *55*, 198–207.
- Curran, A., S. Palmer, T. D. van Ommen, V. I. Morgan, K. L. Phillips, A. J. McMorrow, and P. A. Mayewski (2002), Post-depositional movement of methanesulphonic acid at Law Dome, Antarctica, and the influence of accumulation rate, *Ann. Glaciol.*, *35*, 333–339.
- Davis, D., et al. (2001), Unexpected high levels of NO observed at the South Pole, *Geophys. Res. Lett.*, *28*, 3625–3628.
- Dean, J. A. (1992), *Lange's Handbook of Chemistry*, McGraw-Hill, New York.
- De Angelis, M., and M. Legrand (1995), Preliminary investigations of postdepositional effects on HCl, HNO₃, and organic acids in polar firn layers, in *Ice Core Studies of Global Biogeochemical Cycles, NATO ASI Ser.*, vol. I 30, edited by R. J. Delmas, pp. 361–381, Springer-Verlag, New York.
- Delmas, R. J., P. Wagnon, K. Goto-Azuma, K. Kamiyama, and O. Watanabe (2003), Evidence for the loss of snow-deposited MSA to the interstitial gaseous phase in central Antarctic firn, *Tellus, Ser. B*, *55*, 71–79.
- Dibb, J. E., M. Arsenault, M. C. Peterson, and R. E. Honrath (2002), Fast nitrogen oxide photochemistry in Summit Greenland snow, *Atmos. Environ.*, *36*, 2501–2511.
- Fukazawa, H., K. Sugiyama, S. Mae, H. Narita, and T. Hondoh (1998), Acid ions at triple junction of Antarctic ice observed by Raman scattering, *Geophys. Res. Lett.*, *25*, 2845–2848.
- Göktas, F. (2002), Characterisation of glacio-chemical and glacio-meteorological parameters on Amundsenisen, Dronning Maud Land, Antarctica, in *Reports on Polar and Marine Research*, vol. 425, edited by F. Riemann, pp. 2–41, Alfred-Wegener-Inst. for Polar and Mar. Res., Bremerhaven, Germany.
- Göktas, F., H. Fischer, H. Oerter, R. Weller, S. Sommer, and H. Miller (2002), A glacio-chemical characterisation of the new deep drilling site on Amundsenisen, Dronning Maud Land, Antarctica, *Ann. Glaciol.*, *35*, 347–354.
- Gow, A. J. (1969), On the rates of growth of grains and crystals in South Polar firn, *J. Glaciol.*, *8*, 241–252.
- Gross, G. W. (1968), Some effects of trace inorganics on the ice/water system, in *Trace Inorganics in Water, Adv. Chem. Ser.*, vol. 73, pp. 27–97, Am. Chem. Soc., Washington, D. C.
- Hamer, W., and Y.-C. Wu (1972), Osmotic coefficients and mean activity coefficients of uni-valent electrolytes in water at 25°C, *J. Phys. Chem. Ref. Data*, *1*(4), 1047–1099.
- Honrath, R. E., M. C. Peterson, S. Guo, J. E. Dibb, P. B. Shelson, and B. Cambell (1999), Evidence of NO_x production within or upon ice particles in the Greenland snowpack, *Geophys. Res. Lett.*, *26*, 695–698.
- Hutterli, M. A., R. C. Bales, J. R. McConnell, and R. W. Stewart (2002), HCHO in Antarctic snow: Preservation in ice cores and air-snow exchange, *Geophys. Res. Lett.*, *29*(8), 1235, doi:10.1029/2001GL014256.
- Jones, A. E., R. Weller, P. S. Anderson, H.-W. Jacobi, E. W. Wolff, O. Schrems, and H. Miller (2001), Measurements of NO_x emissions from the Antarctic snowpack, *Geophys. Res. Lett.*, *28*, 1499–1502.
- Kumai, M. (1976), Identification of nuclei and concentrations of chemical species in snow crystals sampled at the South Pole, *J. Atmos. Sci.*, *33*, 833–841.
- Legrand, M., and R. J. Delmas (1988), Formation of HCl in the Antarctic atmosphere, *J. Geophys. Res.*, *93*, 7153–7168.
- Legrand, M., and P. Mayewski (1997), Glaciochemistry of polar ice cores: A review, *Rev. Geophys.*, *35*, 219–243.
- Legrand, M., A. Léopold, and F. Dominé (1996), Acidic gases (HCl, HF, HNO₃, HCOOH, and CH₃COOH): A review of ice core data and some preliminary discussion on their air-snow relationships, in *Chemical Exchange Between the Atmosphere and Polar Snow, NATO ASI Ser.*, vol. I 43, edited by E. W. Wolff and R. C. Bales, pp. 19–43, Springer-Verlag, New York.
- Mauldin, R. L., III, et al. (2001), Measurements of OH, H₂SO₄, and MSA at the South Pole during ISCAT, *Geophys. Res. Lett.*, *28*, 3625–3640.
- Mayewski, P., and M. Legrand (1990), Recent increase in nitrate concentration of Antarctic snow, *Nature*, *346*, 258–260.
- McConnell, J. R., R. C. Bales, R. W. Stewart, A. M. Thompson, M. R. Albert, and R. Ramos (1998), Physically based modeling of atmosphere-to-snow-to-firn transfer of H₂O₂ at South Pole, *J. Geophys. Res.*, *103*, 10,561–10,570.
- Milne, P. J., R. G. Zika, and E. S. Saltzman (1989), Rate of reaction of methanesulfonic acid, dimethyl sulfoxide, and dimethyl sulfone with hydroxyl radical in aqueous solution, in *Biogenic Sulfur in the Environment, Am. Chem. Soc. Symp.*, vol. 393, edited E. S. Saltzman and W. J. Cooper, 518–528, Am. Chem. Soc., Washington, D. C.
- Minikin, A., D. Wagenbach, W. Graf, and J. Kipfstuhl (1994), Spatial and seasonal variations of the snow chemistry at the central Fichner-Ronne Ice Shelf, Antarctica, *Ann. Glaciol.*, *20*, 283–290.
- Mulvaney, R., E. W. Wolff, and K. Oates (1988), Sulphuric acid at grain boundaries in Antarctic ice, *Nature*, *331*, 247–249.
- Oerter, H., W. Graf, F. Wilhelms, A. Minikin, and H. Miller (1999), Accumulation studies on Amundsenisen, Dronning Maud Land, Antarctica, by means of tritium, dielectric profiling and stable-isotope measurements: First results from the 1995–96 and 1996–97 field seasons, *Ann. Glaciol.*, *29*, 1–9.
- Oerter, H., F. Wilhelms, F. Jung-Rothenhäusler, F. Göktas, H. Miller, W. Graf, and S. Sommer (2000), Accumulation rates in Dronning Maud Land, Antarctica, as revealed by dielectric-profiling measurements of shallow firn cores, *Ann. Glaciol.*, *30*, 27–34.
- Pasteur, E. C., and R. Mulvaney (2000), Migration of methane sulphonate in Antarctic firn and ice, *J. Geophys. Res.*, *105*, 11,525–11,543.
- Piel, C. (2004), Variabilität physikalischer und chemischer Parameter des Aerosols in der antarktischen Troposphäre, in *Reports on Polar and Marine Research*, vol. 476, edited by F. Riemann, pp. 91–110, Alfred-Wegener-Inst. for Polar and Mar. Res., Bremerhaven, Germany.
- Reijmer, C. H., M. R. van den Broeke, and M. P. Scheele (2002), Air parcel trajectories to five drilling locations on Antarctica, based on the ERA-15 data set, *J. Clim.*, *15*, 1957–1968.
- Röthlisberger, R., M. A. Hutterli, S. Sommer, E. W. Wolff, and R. Mulvaney (2000), Factors controlling nitrate in ice cores: Evidence from the Dome C deep ice core, *J. Geophys. Res.*, *105*, 20,565–20,572.
- Röthlisberger, R., et al. (2002), Nitrate in Greenland and Antarctic ice cores: A detailed description of post-depositional processes, *Ann. Glaciol.*, *35*, 209–216.
- Röthlisberger, R., R. Mulvaney, E. W. Wolff, M. Hutterli, M. Bigler, M. de Angelis, M. Hansson, J. P. Steffensen, and R. Udisti (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.*, *108*(D16), 4526, doi:10.1029/2003JD003604.
- Schwartz, S. E., and W. H. White (1981), Solubility equilibrium of the nitrogen oxides and oxiacids in dilute aqueous solution, *Adv. Environ. Sci. Eng.*, *4*, 1–45.
- Thibert, E., and F. Dominé (1997), Thermodynamics and kinetics of the solid solution of HCl in ice, *J. Phys. Chem. B*, *101*, 3554–3565.
- Thibert, E., and F. Dominé (1998), Thermodynamics and kinetics of the solid solution of HNO₃ in ice, *J. Phys. Chem. B*, *102*, 4432–4439.
- Waddington, E. D., J. Cunningham, and S. L. Harder (1996), The effect of snow ventilation on chemical concentrations, in *Chemical Exchange Between the Atmosphere and Polar Snow, NATO ASI Ser.*, vol. I 43, edited by E. W. Wolff and R. C. Bales, pp. 173–199, Springer-Verlag, New York.
- Wagnon, P., R. J. Delmas, and M. Legrand (1999), Loss of volatile acid species from upper firn layers at Vostok, Antarctica, *J. Geophys. Res.*, *104*, 3423–3431.
- Weller, R., A. E. Jones, A. Wille, H.-W. Jacobi, H. P. McIntyre, W. T. Sturges, M. Huke, and D. Wagenbach (2002), Seasonality of reactive nitrogen oxides (NO_x) at Neumayer Station, Antarctica, *J. Geophys. Res.*, *107*(D23), 4673, doi:10.1029/2002JD002495.
- Wolff, E. W., A. E. Jones, T. J. Martin, and T. C. Grenfell (2002), Modeling photochemical NO_x production and nitrate loss in the upper snowpack of Antarctica, *Geophys. Res. Lett.*, *29*(20), 1944, doi:10.1029/2002GL015823.
- Yang, Q., P. A. Mayewski, M. S. Twickler, and S. Whitlow (1997), Major features of glaciochemistry over the last 110,000 years in the Greenland Ice Sheet Project 2 ice core, *J. Geophys. Res.*, *102*, 23,289–23,299.

H. Fischer, H. Miller, H. Oerter, C. Piel, and R. Weller, Alfred Wegener Institute for Polar and Marine Research, Am Handelshafen 12, D-27570 Bremerhaven, Germany. (rweller@awi-bremerhaven.de)

F. Traufetter, Prinsengracht 596/II, NL-1017 KS Amsterdam, Netherlands.