Year-round record of size-segregated aerosol composition in central Antarctica (Concordia station): Implications for the degree of fractionation of sea-salt particles

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[1] The origin of sea-salt aerosol that reaches the high Antarctic plateau and is trapped in snow and ice cores remains still unclear. In particular, the respective role of emissions from the open ocean versus those from the sea-ice surface is not yet quantified. To progress on this question, the composition of bulk and size-segregated aerosol was studied in 2006 at the Concordia station (75°S, 123°E) located on the high Antarctic plateau. A depletion of sulfate relative to sodium with respect to the seawater composition is observed on sea-salt aerosol reaching Concordia from April to September. That suggests that in winter, when the sea-salt atmospheric load reaches a maximum, emissions from the sea-ice surface significantly contribute to the sea-salt budget of inland Antarctica.

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1. Introduction

[2] At the global scale, the presence of sea-salt aerosol in the marine atmosphere is mainly related to bubble bursting and wave crest disruptions. Recently, it was shown that in coastal Antarctic regions the primary source of sea-salt is not the open ocean but the sea-ice surface [*Wagenbach et al.*, 1998; *Rankin et al.*, 2002]. This finding rises the key question of the source of atmospheric sea-salt aerosol reaching the high Antarctic plateau (open ocean or sea ice) since numerous sea-salt records have been obtained from deep ice cores extracted there. These ice records have shown larger concentrations of sea-salt during past cold climates than at present. These changes were first attributed to enhanced storminess over open ocean and transport inland during cold climate in spite of the greater distance of the open ocean from Antarctica [*Legrand et al.*, 1988; *Petit et al.*, 1999]. Such an explanation was also invoked to explain the present-day well-marked maximum of sea-salt content of snow and aerosol observed in winter at inland Antarctic sites [*Legrand and Delmas*, 1984; *Bodhaine et al.*, 1986]. However, model simulations of the sea-salt produced from the open ocean failed down to reproduce the larger sea-salt concentrations over inland Antarctica during cold climates [*Reader and McFarlane*, 2003]. More recently, it was proposed that the sea-ice surface, not the open ocean, which had been extended during cold climate, was the main source of sea-salt over Antarctica at that time [*Wolff et al.*,

2003]. This assumption is now persistently used to discuss deep ice core records by using sodium as a proxy of sea-ice extent [*Wolff et al.*, 2006; *Fischer et al.*, 2007].

[3] The chemical composition of sea-salt aerosol varies, specially the sulfate to sodium ratio, depending on the involved emission process. The sulfate to sodium mass ratio of sea-salt aerosol emitted by the open ocean is similar to that in seawater (0.25). Newly formed sea-ice is covered by highly saline brine and frequently by fragile salty frost flowers. Below −8°C mirabilite ($Na_2SO_4 \bullet 10\ H_2O$) starts to precipitate leading to a depletion of sulfate relative to sodium in sea-salt aerosol emitted from sea-ice compared to sea-salt aerosol emitted from the open ocean. At coastal Antarctic sites in winter, where the sea-ice surface is the dominant source of sea-salt aerosol, *Wagenbach et al.* [1998] estimated that the sulfate to sodium mass ratio in sea-salt aerosol is close to 0.07 at Neumayer (70°S, 85°W) and 0.10 at Dumont d'Urville (66°S, 140°E) based on examination of bulk aerosol samples. This estimation was done by examining the relationship between the non sea-salt sulfate ($nssSO_4^{2-}$) content calculated by using the seawater ratio of sulfate to sodium ($[nssSO_4^{2-}] = [SO_4^{2-}] - 0.25\,[Na^+]$) and sodium. A more straightforward approach to quantify the sulfate depletion of sea-salt aerosol is to examine the size-segregated composition of particles collected on an impactor. A size-segregated aerosol composition study performed at Dumont d'Urville (coastal Antarctica) has shown that sea-salt aerosol present in supermicron modes is depleted in sulfate relative to sodium (sulfate to sodium ratio of 0.13) from May to October [*Jourdain and Legrand*, 2002].

[4] Such a source dependant chemical composition of sea-salt aerosol can be used to apportion the two sources of sea-salt aerosol. This was done at South Pole by *Harder et*

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Table 1. Mean Blank Values Observed in the Extract of Bulk Filter and Impactor Plates and Estimated Atmospheric Detection Limit[a]

		MSA	SO_4^{2-}	Na^+	Mg^{2+}
Bulk Filters	blank, ng g^{-1}	0.6 ± 0.5	2.8 ± 1.3	5.6 ± 3.2	0.8 ± 0.2
	DL, ng m^{-3}	0.07	0.2	0.4	0.03
Impactors	blank, ng g^{-1}	0.002 ± 0.006	0.2 ± 0.1	2.3 ± 0.5	0.8 ± 0.2
	DL, ng m^{-3}	0.001	0.006	0.05	0.02

[a]DL defined as three times the blank standard deviation for a typical sampling volume of 215 m^3 (STP) for bulk filters and 200 m^3 (STP) for impactor runs.

al. [2000] who found that in one bulk aerosol sample collected in September and having a high sodium content the estimated sulfate to sodium ratio was close to 0.12. Examination of bulk aerosol filters collected at the high Antarctic plateau station of Dome Fuji (77°S, 40°E) suggested a larger sea-salt fractionation (sulfate to sodium ratio of 0.07, *Hara et al.* [2004]). Finally the bulk aerosol study carried out at Kohnen station (75°S, 0°E) by *Weller and Wagenbach* [2007] did not allow to decide to what extent sea-salt aerosol at central Antarctica has been fractionated. From these studies based on examination of bulk aerosol composition, it can be concluded that the present-day source apportionment of sea-salt over inland Antarctica remains unclear.

[5] Composition of bulk and size-segregated aerosol was studied over the course of winter 2006 at the Concordia station. In contrast to the situation at coastal sites where primary sea-salt and biogenic sulfate are present in very different size modes (mainly from 1 to 10 μm for sea-salt, 0.3 μm for biogenic sulfate, *Jourdain and Legrand* [2002]), it is expected that inland Antarctic the two sulfate fractions lie in more similar size modes. We therefore deployed a 12 stage impactor for which the segregation between the size modes at 0.3 and 1 μm would be still accurate enough.

2. Methods

[6] Year-round aerosol samplings were conducted in 2006 at the Concordia Station (central Antarctica, 75°06′S, 123°20′E, 3220 m above sea level) located 1100 km away from the nearest coast. Bulk aerosol samples were collected on Gelman Zefluor (47 mm diameter, 0.5 μm pore size) filters by sucking air at a flow rate of 1.3 m^3 STP (25°C, 1013 hPa) h^{-1}. Filder holders were positioned outside at 2.5 m above the snow surface. They were prepared prior sampling under laminar flow hood and sent to the sampling site in polyethylene bags. After sampling, filters were stored frozen in 20 mL polycarbonate vials sealed in polyethylene bags until extraction with ultrapure water/methanol solution and analysis in Grenoble. 40 samples were collected in 2006 between 17 January and 27 December on a weekly basis

(mean sampled air volume of 215 m^3 STP). 19 blank filters were performed along this period. Mean blank values in the extracted samples and corresponding atmospheric detection limits (taken as three times the blank standard deviation) are summarized in Table 1. Blank values become significant for sodium only and a blank correction was applied for this species.

[7] A study of the size-segregated aerosol composition was carried out on 9 samples collected at Concordia between March and September 2006 by using a small deposit area impactor equipped with a 20 μm cut-off inlet and positioned outside. The used sampling protocol is similar to that described by *Maenhaut et al.* [1996]. Polycarbonate films were used as particle impaction substrates (poreless film from Nuclepore Inc., thickness 10 μm). They were coated with Apiezon L-vacuum grease (dissolved in toluene) to reduce the bounce-off of particles. The sampling interval was 2 weeks. The cut-off sizes of the impactor for Concordia were obtained by moving the cut-off sizes for 1013 hPa and 23°C [*Maenhaut et al.*, 1996] to Concordia mean conditions (640 hPa, −60°C) using Stokes law [*Hinds*, 1998] (Table 2). Loaded polycarbonate plates were kept frozen and extracted in Grenoble in 6 mL of ultrapure water. Blank values are reported in Table 1.

[8] The determinations of Na^+, $CH_3SO_3^-$ (hereafter denoted MSA) and SO_4^{2-} were made by ion chromatography under working conditions summarized by *Minikin et al.* [1998] and *Wagenbach et al.* [1998]. For atmospheric levels of a few to several tens of nanograms per cubic meter the uncertainty is mainly determined by the ion chromatography accuracy, which is typically 5%. In the case of sodium levels close to one nanogram per cubic meter the uncertainty becomes larger due to the blank variability.

3. Seasonal Cycle of Sea-Salt at Concordia

[9] The seasonal change of Na^+ concentrations observed in 2006 at Concordia is reported in Figure 1 for the continuous bulk filter samplings. As discussed by *Legrand and Delmas* [1988] and *Röthlisberger et al.* [2002], Na^+ present in aerosol over the high Antarctic plateau is, for

Table 2. Cut-Off Sizes of the Impactor at 1013 hPa and 23°C [*Maenhaut et al.*, 1996] and for Typical Temperature and Pressure Conditions Encountered at Concordia Station in Winter (640 hPa and −60°C), Obtained by Moving the Cut-Off Sizes for 1013 hPa, 23°C, and a Flow Rate of 0.678 m^3 STP h^{-1} to Concordia Conditions Using Stokes Law[a]

Stage No.	12	11	10	9	8	7	6	5	4	3	2	1
Dp (μm) 1013hPa, 23°C	8.55	4.46	2.69	1.68	1.07	0.81	0.58	0.36	0.22	0.14	0.085	0.044
Dp (μm) 640hPa, −60°C	7.45	3.50	2.29	1.40	0.87	0.64	0.46	0.26	0.15	0.089	0.047	0.028

[a]The flow rate at Concordia converted to 1013 hPa and 25°C is 0.58 m^3 STP h^{-1}.
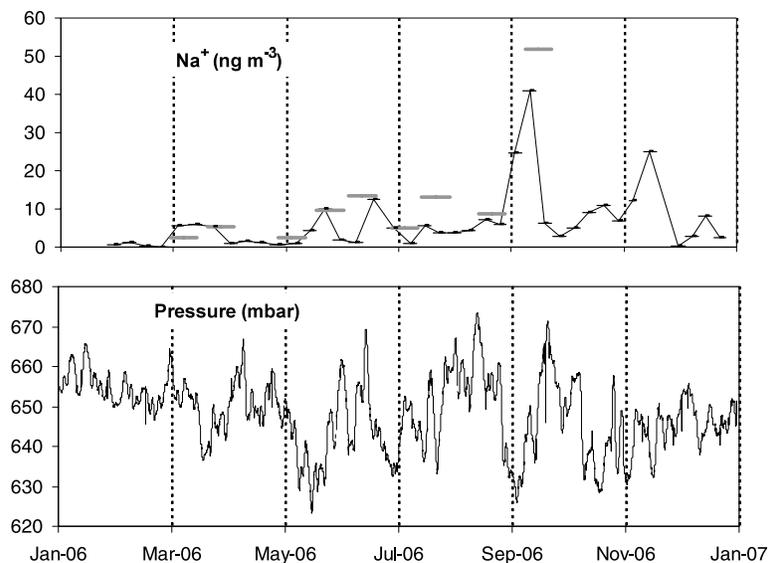
Figure 1. (top) 2006 year-round record of sodium from bulk filters (in black) and of the sum of concentrations observed on the 12 stages of the impactor (in grey). (bottom) Local atmospheric pressure at Concordia. Horizontal bars reported on the sodium curves refer to the sampling time interval. Pressure data are from the Concordia Automatic Weather Station (AWS 8989) of University of Wisconsin-Madison (available on the ftp address: ftp://amrc.ssec.wisc.edu/pub/aws/).

present climatic conditions, mainly related to sea-salt aerosol, while the contribution of leachable sodium relative to continental dust aerosol remains insignificant (~2%). Very low levels of Na^+ are observed in summer, 2.4 ± 2.3 ng m^{-3} from January to March. At that season sea-salt accounts only for less than 10% of the total mass of inorganic aerosol which is dominated by sulfate (not shown). The Na^+ concentrations increase in winter (9.1 ± 9.1 ng m^{-3} between July and November) reaching a maximum (35 ng m^{-3}) in September. Because of the concomitant decrease of sulfate (not shown), sea-salt represents the dominant (~80%) of the total inorganic aerosol load in winter. As seen in Figure 1, the Na^+ peak in September coincides with a large decrease of the atmospheric pressure at Concordia, likely related to a large low pressure system advecting air from the ocean surrounding Antarctica. Although less continuous, impactor samplings reveal a similar temporal change with higher levels after May than before and a maximum in September.

[10] The seasonal change of sea-salt observed at Concordia, characterized by a winter maximum is consistent with previous studies conducted at inland Antarctic sites (Table 3). The winter sea-salt level in the Concordia atmosphere in 2006 is however lower than at other inland sites (40 ng m^{-3} at Kohnen in 2003–2005 [*Weller and Wagenbach*, 2007], 60 ng m^{-3} in 1997 at Dome Fuji [*Hara et al.*, 2004]). Measurements made at Concordia in 2005 (not shown) indicate a mean winter value of 15 ng m^{-3}. No definitive conclusion can be drawn from these intersite differences since the different studies do not cover the same years and *Tuncel et al.* [1989] has shown that the mean winter level of sodium at the South Pole can vary from year to year by up to a factor of three (from 20 to 60 ng m^{-3}). If confirmed by multiple year round studies, the relative low sea-salt winter level at Concordia would suggest less frequent advections of marine air at Concordia which faces

the Indian Ocean than at the two other sites which face the Atlantic Ocean. An alternative possibility for the low Na^+ winter concentrations at Concordia could also be the winter sea-ice cover in the Atlantic Ocean sector which is larger than the one in the Indian sector.

4. Amplitude of the Depletion of Sulfate Relative to Sodium in Sea-Salt Particles Collected on the Impactor

[11] The size-segregated composition of aerosol sampled at Concordia is reported in Figure 2 for March and September. The mass size distribution of sea-salt depicted by sodium is dominated by a mode between 0.6 and 3 μm. The size of sea-salt aerosol at Concordia is therefore smaller than that at coastal Antarctic sites (a mode peaking between 6 and 8 μm, *Jourdain and Legrand* [2001], *Hillamo et al.* [1998]). This change of the sea-salt size distribution between coastal and inland Antarctica is expected in relation with the lost of coarse sea-salt particles during transport from the coast towards inland Antarctica. Similarly to what is observed at coastal Antarctic sites [*Jourdain and Legrand*, 2001; *Teinilä et al.*, 2000], MSA is mainly present in submicrometer particles (from 0.09 to 0.5 μm, Figure 2). As seen in Figure 2, the mass size distribution of sulfate exhibits either a preponderant submicrometer mode similar to the MSA one (March 2006) or a double mode at 0.3–0.4 μm and 0.9–1.5 μm (September 2006). Therefore the separation of the two sulfate modes (biogenic and sea-salt) appears to be less straightforward at Concordia than at coastal sites in relation with the presence of fine sea-salt aerosol there.

[12] The chemical composition of particles deposited on the top stages of the impactor, where sea-salt dominates, indicates, except in March, SO_4^{2-}/Na^+ values (denoted R)

Table 3. Sea-Salt Aerosol Data at Inland Antarctic Sites

Site	Position Elevation Distance From the Coast	Season	Na^+ Level, in ng m^{-3} Mean (Std. Dev)	Observed Degree of Sea-Salt Fractionation	Sampling Dates	References
South Pole	90°S 2841 m	S W	5.1 (1.7) 40 (31)		1971, 1975–1976, 1978 1975–1976	*Cunningham and Zoller* [1981]
South Pole	*1300 km*	S W	<11 20–60		Feb 1982 Jun–Aug 1982	*Bodhaine et al.* [1986]
South Pole		S W	8.7 (3.2) 31 (14)		1979–1983	*Tuncel et al.* [1989]
South Pole		S W	0–40	R = 0.12	Jul–Dec 1992	*Harder et al.* [2000]
South Pole		S W	45 n.d.		Dec 1998	*Arimoto et al.* [2001]
South Pole		S W	<17 n.d.		Nov 2000 to Jan 2001	*Arimoto et al.* [2004]
Dome Fuji	77°S 39°E 3810 m 1000 km	S W	10.12 62.1	R = 0.07	Feb–Apr and Dec 1997; Jan 1998 May–Nov 1997	*Hara et al.* [2004]
Kohnen	75°S 0°E 2892 m 520 km	S W	12.0 (6.7) 2.4 (1.9) 5.9 (5.3) n.d.		Jan–Feb 2000 Jan–Feb 2001 Jan–Feb 2002	*Piel et al.* [2006]
Kohnen		S W	8.7 43.3	Not conclusive	Jan–Mar 2000–2005 Jun–Aug 2003–2005	*Weller and Wagenbach* [2007]
East Antarctic Plateau	78°S 139°E 2849 m 600 km	S W	6.2 n.d.		Dec 1990 to Jan 1991	*de Mora et al.* [1997]
Concordia	75°S 123°E	S W	4.95 n.d.		Dec 2000 to Jan 2001	*Udisti et al.* [2004]
Concordia	3233 m 1100 km	S W	2.4 (2.4) 6.0 (5.8)	R = 0.16–0.24 R' = 0.07–0.12[a]	Jan–Mar 2006 Jun–Aug 2006	This work

S, Summer; W, Winter; n.d., no data.
[a]See text.

below the seawater value of 0.25. The case of September corresponds to the time period over which the highest level of sea-salt was recorded in 2006 (Figure 1). The absence of evidence of a sea-salt fractionation in March is not really surprising since in March, the sea-ice extent is very limited in the coastal regions and indeed no fractionation has been observed in March at the coastal station of Dumont d'Urville, 1200 km from Dome C [*Jourdain and Legrand*, 2002]. Note that SO_4^{2-}/Na^+ ratios higher than 0.25 seen in the sea-salt mode in March (Figure 2, left) can be explained by the heterogeneous conversion of SO_2 on sea-salt aerosol as discussed by *Jourdain and Legrand* [2002]. Uncertainties of the SO_4^{2-}/Na^+ ratio are mainly related to the blank variability for low load samples and to the accuracy of ion chromatography (typically 5%) for high load samples and has been calculated as following:

$$(\Delta R/R)^2 = \left([\Delta SO_4^{2-}]/[SO_4^{2-}]\right)^2 + ([\Delta Na^+]/[Na^+])^2 \quad (1)$$

[13] Whereas sea-salt exhibits a significant depletion of sulfate relative to seawater (R = 0.16 ± 0.01) in late winter, a weaker fractionation or an absence of fractionation is suggested for midwinter conditions (R = 0.20 ± 0.02 in late July, R = 0.24 ± 0.05 in early July).

[14] In the preceding approach, the small contribution of biogenic sulfate present on the larger fraction of aerosol

(Dp > 0.46 μm) has been neglected. If significant enough the presence of this biogenic sulfate fraction on particles larger than 0.46 μm would have led to an overestimation of the preceding R values. Impactor data permit to characterize the biogenic fraction by checking MSA and sulfate on particles of less than 0.46 μm, where the abundance of sea-salt is weak. For each impactor run the linear relationship between MSA and sulfate present on the 5 lower stages corresponding to particle size smaller than 0.46 μm was examined to derive the mean MSA/SO_4^{2-} mass ratio and its standard deviation (2σ). Biogenic sulfate is then calculated for the whole size distribution using this ratio and subtracted from the total sulfate in order to estimate the sea-salt sulfate to sodium ratio. We here assume that the size distributions of biogenic sulfate and MSA are the same and that the $MSA/nssSO_4^{2-}$ ratio is constant over the entire size distribution. This assumption seems reasonable. For instance on the impactor run in March 2006, for which the sea-salt contribution is very low (5 ng m^{-3} of Na^+) and accounts for 5% of total sulfate, a very good linear relationship ([MSA] = 0.31 [SO_4^{2-}] − 0.014 with r^2 = 0.99) is obtained when the 12 stages of the impactor are considered. A very similar relationship is obtained when only the larger particles (Dp > 0.46 μm) are considered ([MSA] = 0.28 [SO_4^{2-}] − 0.005 with r^2 = 0.98). Later in winter, the sea-salt load becomes more important and we restricted our examination of the relationship between MSA and sulfate to particles below
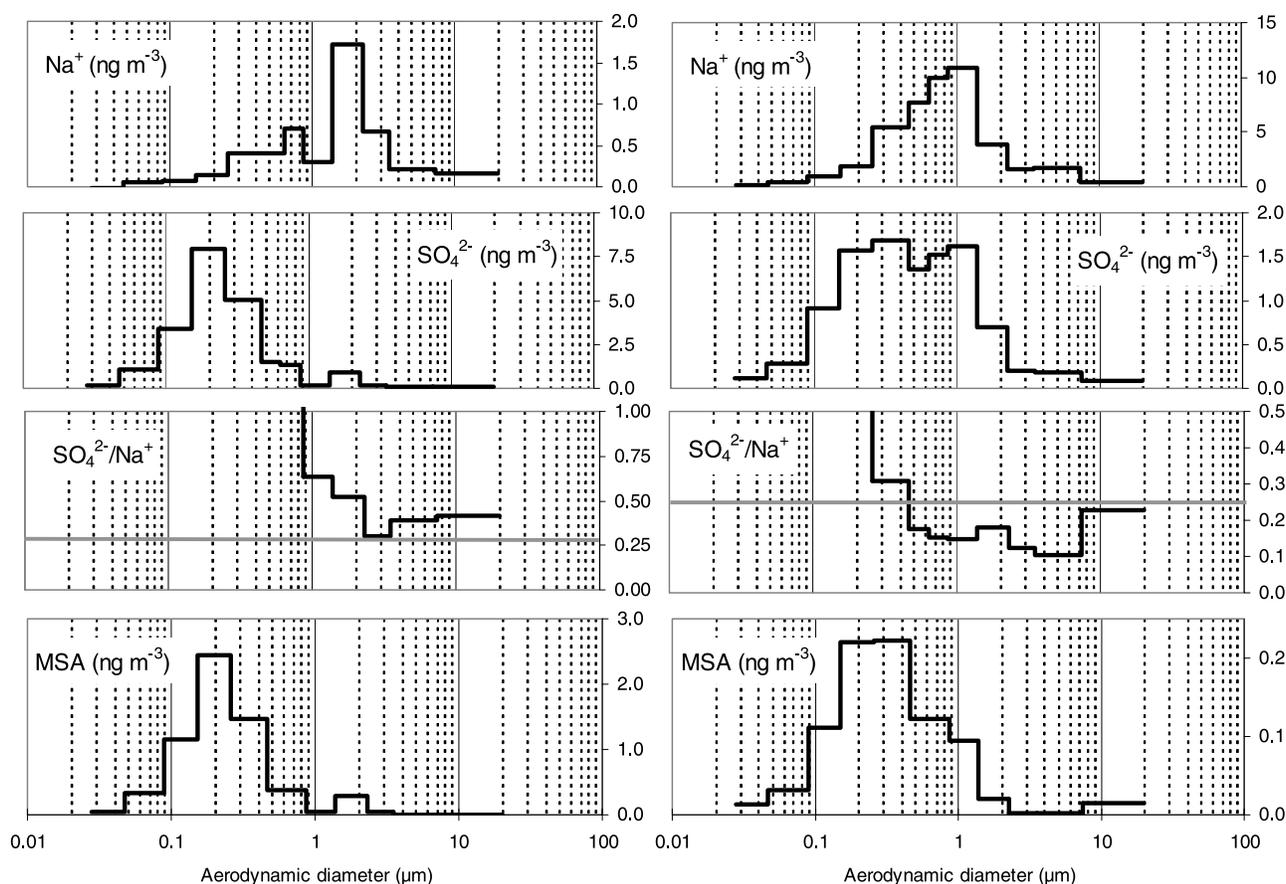
Figure 2. Mass size distribution of Na^+, SO_4^{2-}, and MSA of aerosol sampled at Concordia between 21 March and 4 April 2006 (left) and 9 to 23 September (right). Also reported is the SO_4^{2-}/Na^+ ratio calculated for the larger particles.

0.46 μm. From mid-May to late August a good relationship can be observed ([MSA] = 0.06 [SO_4^{2-}] − 0.003 with r^2 = 0.87) for a set of 21 data from 5 impactors. In September the MSA to SO_4^{2-} ratio ([MSA] = 0.14 [SO_4^{2-}] − 0.006 with r^2 = 0.99) for the 5 lower stages of the impactor (Figure 2, right) increases compared to the preceding months, likely due to inceptive biogenic emissions in the Austral Ocean. The potential impact of remaining sea salt on the 0.26– 0.46 μm stage is found to be weak since a similar relationship is observed ([MSA] = 0.14 [SO_4^{2-}] − 0.007 with r^2 = 0.99) on the 4 lower stages. The preceding correlations between MSA and sulfate indicate a change of the slope of the correlation over the season. Such a temporal change has been also observed at coastal sites [*Legrand and Pasteur*, 1998; *Jourdain and Legrand*, 2002] but a discussion on its atmospheric meaning is out of the scope of this paper.

[15] On the basis of the preceding discussions, the SO_4^{2-}/Na^+ ratio attributed to sea salt (R′) was estimated as following:

$$R' = \left(\left[SO_4^{2-} - [MSA]/R_{(MSA/SO42-)Dp<0.46\mu m} \right] \right)/[Na^+] \quad (2)$$

[16] The R′ values (and corresponding estimated uncertainties) are reported for the impactor run in September (Figure 3). The obtained R′ values are almost twice lower than the initially obtained R value. For the total aerosol

mass above 0.46 μm, the new calculated ratio is 0.073 ± 0.024 instead of 0.157 ± 0.013 without taking into account the biogenic contribution (see above). The same calculation applied to some other winter impactor runs gives 0.12 ± 0.084 (instead of 0.243 ± 0.049) in early July and 0.095 ± 0.057 (instead of 0.199 ± 0.022) in late July. In other runs, calculated uncertainties are too large to highlight the discussion. Even underlying an certain uncertainty this calculations show that the initial obtained R values represent an upper limit and may thus underestimate the sea salt fractionation by up to a factor of two.

5. Comparison With Previous Estimates of the Sulfate Depletion Relative to Sodium in Sea-Salt Particles Collected at Other Inland Sites

[17] At coastal sites, the fractionation of atmospheric sea-salt aerosol can be derived by examining the chemistry of bulk aerosol filters. Following *Wagenbach et al.* [1998], this was done by examining the linear relationship between nonsea-salt sulfate content calculated using the seawater sulfate to sodium ratio ([$nssSO_4^{2-}$] = [SO_4^{2-}] − 0.25 [Na^+]) and the sodium content. Adding the obtained negative value of the slope of this correlation to the seawater mass ratio of 0.25 gives an estimate of the sulfate to sodium ratio in sea-salt particles. This approach done by *Jourdain and Legrand*
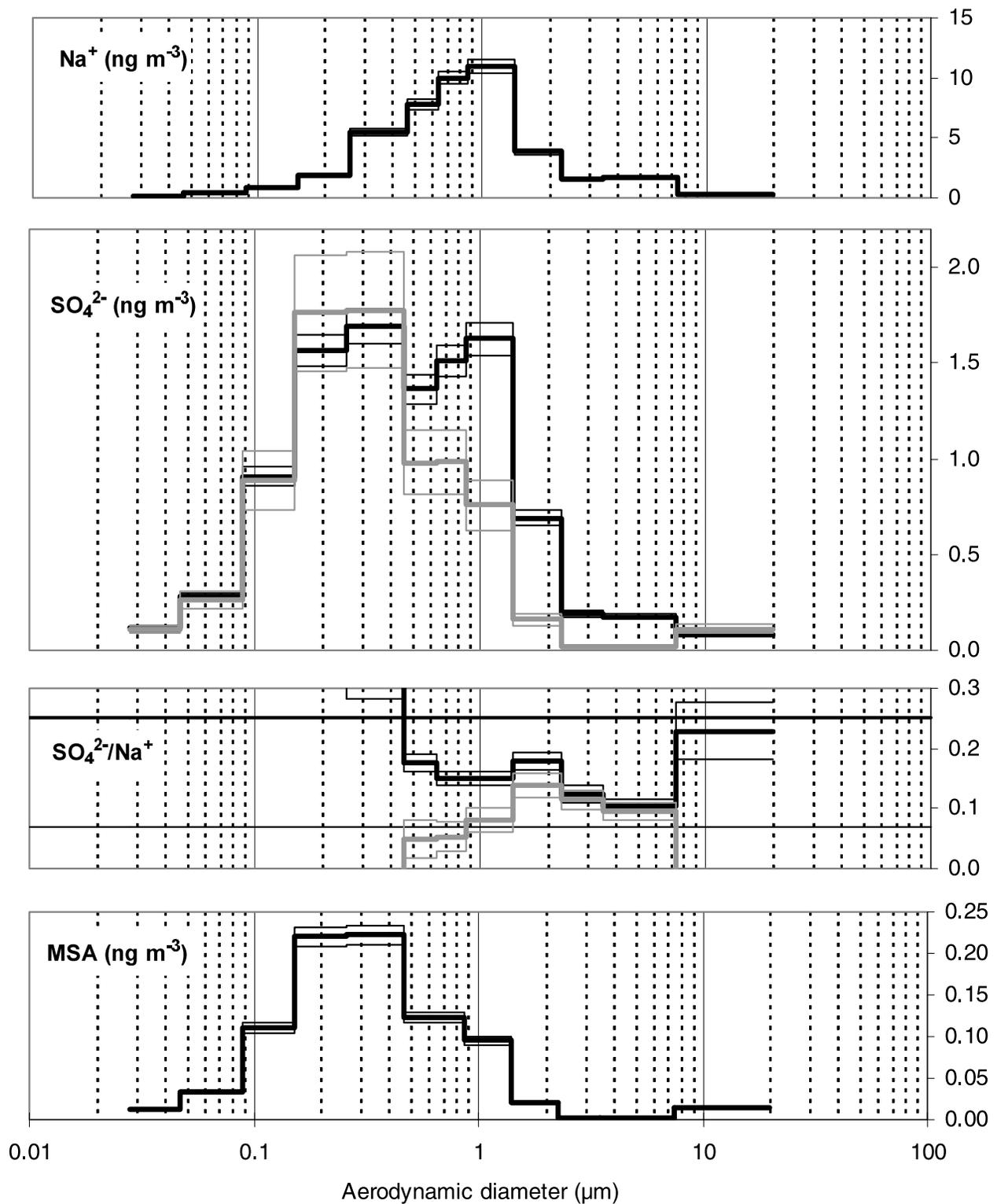
Figure 3. Mass size distribution of Na^+, SO_4^{2-}, and MSA of the aerosol sampled at Concordia 9 to 23 September. Also plotted is the SO_4^{2-}/Na^+ ratio calculated for the larger particles. For SO_4^{2-} levels and the SO_4^{2-}/Na^+ ratio, the grey curves refer respectively to the biogenic fraction of sulfate estimated from MSA (see section 4), and to the ratio R' (see text) corrected from this biogenic fraction.
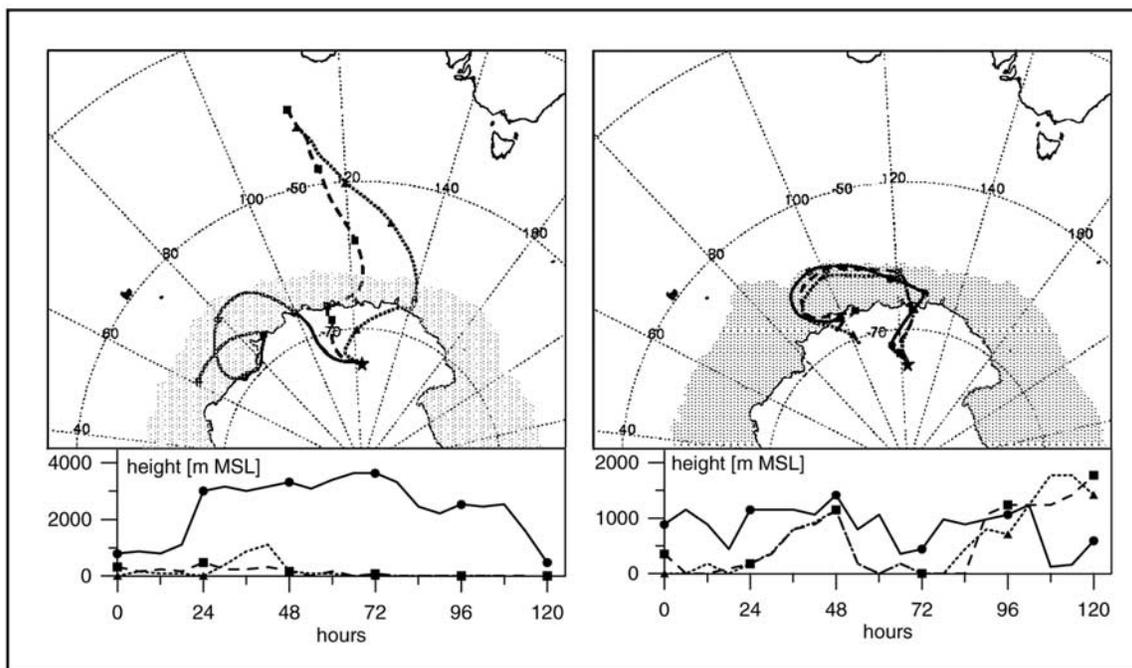
Figure 4.   Example of 5 d backward trajectory in late July (left) and mid-September (right) when a moderate and strong sulfate depletion relative to sodium was observed on sea-salt aerosol at Concordia, respectively. Grey areas refer to the sea-ice cover. Dotted marks indicate the location every day. The plot are combined to corresponding monthly mean satellite derived sea ice map [*Comiso*, 1990, updated 2007] available on the Web at http://nsidc.org/.

[2002] at the coastal site of Dumont d'Urville showed a similar value than that derives from impactor data. This consistency between the two approaches is due to the fact that at coastal site in winter, even if present, biogenic sulfate is far less abundant than the sulfate present on sea-salt particles.

[18]   The lower sea-salt load observed at inland sites compared to coastal sites render the evaluation of the degree of the sulfate depletion relative to sodium by direct examination of the bulk aerosol filter composition less accurate. Conclusions of previous studies conducted at inland sites appear to be strongly site dependant (see Table 3). For instance, at Dome Fuji, *Hara et al.* [2004] estimated the sulfate to sodium ratio of sea-salt aerosol at 0.07. However, this value is mainly driven by two samples containing very high levels of sodium ($\sim$800 ng m^{-3}). Discarding these two extreme values, the slope of the correlation between sulfate (calculated using the seawater sulfate to sodium ratio) and sodium is close to -0.11 leading to a sulfate to sodium ratio in sea-salt of 0.14.

[19]   On the contrary, *Weller and Wagenbach* [2007] were unable to conclude on the degree of sea-salt fractionation at Kohnen since there are too low sea-salt and too high biogenic contents. In order to minimize the effect of biogenic sulfate *Harder et al.* [2000] compare a sample containing a high sodium level (80 ng m^{-3}) at the South Pole with the two samples bracketing it in time and found a sulfate to sodium ratio in sea-salt of 0.14. Examination of bulk aerosol filters collected at Concordia reveals no negative values of the nss-SO$_4^{2-}$ calculated using the seawater sulfate to sodium ratio of 0.25. For most of winter samples,

this is due to a too low sea-salt content, and in September due to the recovery of biogenic sulfate.

6.   Degree of Fractionation of Sea-Salt Over the Course of Winter at Concordia

[20]   The examination of the size-segregated aerosol composition discussed in section 4 suggests that sea-salt particles reaching Concordia were only during September strongly fractionated. Over July the sulfate depletion relative to sodium appears to be weaker on the average. In order to examine to what extend these data are consistent with the origin of sea-salt, 5-d backward trajectories were performed using Hybrid Single-Particle Lagrangian Integrated Trajectory (HYSPLIT) Model (R. R. Draxler and G. D. Rolph, NOAA Air Resources Laboratory, Silver Spring, Maryland, 2003, available at http://www.arl.noaa.gov/ready/hysplit4. html) twice a day (at 0 and 12 UTC) for two periods: 15 to 30 July and 9 to 23 September corresponding respectively to the late July and September impactor runs. Three atmospheric levels were considered above Concordia as starting point to compute the back trajectories: 3250, 3500, and 4000 m above sea level (respectively 20, 270, and 770 m above Concordia ground). An isentropic vertical motion calculation method was applied to GDAS meteorological data.

[21]   In July most of the backward trajectories show air masses having travelled above continental Antarctica within 5 d. Only 3 d at the end of the sampling period indicate advections from marine areas. Some of the air masses spent up to 2 d above margin Antarctic Ocean but at 1000 to 3000

m above sea level. Other trajectories, on 27 July, indicate that air masses came from the boundary layer of lower latitudes from open ocean areas (Figure 4, left).

[22] In September, the situation is more contrasted: while at beginning and end of the sampling period, air masses spent 5 d above continental areas before arriving at Concordia, between 12 and 17 September , most air masses came from coastal regions. 5-d backward trajectories indicate a travel above the oceanic regions from a few hours to several days at a height between sea level and 1000 m, predominantly near the coast on the sea-ice covered zone (Figure 4, right).

[23] The lower sodium level seen in July than in September is consistent with the persistence of marine air advected to the Concordia site in September. In addition, the strong depletion of sulfate relative to sodium observed in September agrees very well with the relative long time spent by the air just above the sea-ice cover. In July, although the sea-ice cover was similar to that in September, the contact of air masses nearby the marine boundary layer occurred both over open Ocean and to a lesser extend over the sea-ice cover. In addition, since the sea-salt fractionation process should occur on freshly formed sea-ice, we have examined the open water fraction present in the sea-ice cover available at http://www-radar.jpl.nasa.gov/rgps/grid_930408.html (not shown). From September 7th to 8th open water was present and rapidly refroze 10 and 11 September at the time that the air mass arriving at Concordia was in contact with the ice in this sector (from 90° to 120°E). A refreeze of open water also occurred further west (80°E) between 4 September and 6 September. Such rapid changes of the sea-ice were likely induced by a suite of several severe storms that reached Dumont D'Urville between 8 and 23 September (a mean wind speed of 20 m s^{-1} from 13 to 27 September). It therefore appears that the degree of the fractionation of sea-salt in winter strongly depends on the pathway taken by the marine air masses reaching Concordia and of the state of the sea-ice.

7. Summary

[24] Composition of bulk and size-segregated aerosol was studied over the course of winter 2006 at the Concordia station located at inland Antarctica. It is shown that the direct examination of bulk aerosol does not permit to evaluate the sulfate depletion relative to sodium in sea-salt aerosol at this site. Direct examination of the chemistry of large particles collected on a 12 stage impactor reveals a significant sulfate depletion relative to sodium during winter (by more than a factor of two compared to seawater) suggesting that sea-salt emissions from the sea-ice surface contribute significantly to the atmospheric sea salt load at Concordia in winter. These data represent a lower limit of the sea-salt fractionation. An attempt was made to obtain a more accurate estimation of the relative contribution of sea-salt emissions from sea-ice versus open ocean on the high Antarctic plateau, taking into account the biogenic fraction of SO_4^{2-}. Even underlying a not negligible uncertainty due to a significant overlap of the biogenic and the sea salt sulfate mode, originating from the relative fine size of sea-salt aerosol reaching inland Antarctica, this calculation reveals that the sea-salt fractionation estimated without

taking into account the biogenic SO_4^{2-} is underestimated by up to a factor of 2. Using MSA to separate the part of sea-salt and biogenic sulfate, impactor data suggest a strong impact of sea-ice emissions in September and a weaker fractionation during the rest of the winter season. Backward air trajectories suggest that air masses reaching Concordia had a variable contact time with the marine boundary layer and with the sea-ice cover. Furthermore, the appearance of open water in sea-ice followed by a rapid refreeze is likely a key factor in winter. Therefore further multiple-year round size segregated aerosol studies are needed before providing a statistically reliable estimate of the respective contribution of emissions from the open ocean and sea-ice surface. This further work is absolutely mandatory to start a detailed discussion of the time integrated sea salt signal of ice cores.

References

Arimoto, R., A. S. Nottingham, J. Webb, C. A. Schloesslin, and D. D. Davis (2001), Non-sea salt sulfate and other aerosol constituents at the South Pole during ISCAT, *Geophys. Res. Lett.*, *28*(19), 3645–3648.

Arimoto, R., A. Hogan, P. Grube, D. Davis, J. Webb, C. Schloesslina, S. Sagea, and F. Raccah (2004), Major ions and radionuclides in aerosol particles from the South Pole during ISCAT-2000, *Atmos. Environ.*, *38*, 5473–5484.

Bodhaine, B. A., J. J. Deluisi, J. M. Harris, P. Houmere, and S. Bauman (1986), Aerosol measurements at the South Pole, *Tellus*, *38B*, 223–235.

Comiso, J. (1990, updated 2007), *DMSP SSM/I Daily and Monthly Polar Gridded Sea Ice Concentrations*, edited by J. Maslanik and J. Stroeve, September 2006, Natl. Snow and Ice Data Cent., Digital media, Boulder, Colo.

Cunningham, W. C., and W. H. Zoller (1981), The chemical composition of remote area aerosols, *J. Aerosol Sci.*, *12*(4), 367–384.

de Mora, S. J., D. J. Wylie, and A. L. Dick (1997), Methanesulphonate and non-sea salt sulfate in aerosol, snow and ice on the east Antarctic plateau, *Antarc. Sci.*, *9*(1), 46–55.

Fischer, H., et al. (2007), Reconstruction of millennial changes in dust emission, transport and regional sea ice coverage using the deep EPICA ice cores from the Atlantic and Indian Ocean sector of Antarctica, *Earth Planet. Sci. Lett.*, *260*, 340–354, doi:10.1016/j.epsl.2007.06.014.

Hara, K., K. Osada, M. Kido, M. Hayashi, K. Matsunaga, Y. Iwasaka, T. Yamanouchi, G. Hashida, and T. Fukatsu (2004), Chemistry of sea-salt particles and inorganic halogen species in Antarctic regions: Compositional differences between coastal and inland stations, *J. Geophys. Res.*, *109*, D20208, doi:10.1029/2004JD004713.

Harder, S., S. G. Warren, and R. J. Charlson (2000), Sulfate in air and snow at the South Pole: Implications for transport and deposition at sites with low snow accumulation, *J. Geophys. Res.*, *105*(D18), 22,825–22,832.

Hillamo, R., I. Allegrini, R. Sparapani, and V.-M. Kerminen (1998), Mass size distributions and precursor gas concentrations of major inorganic ions in Antarctic aerosol, *Intern. J. Environ. Anal. Chem.*, *71*(3–4), 353–372.

Hinds, W. C. (Eds.) (1998), *Aerosol Technology*, 2nd ed., 483 pp., John Wiley, New York.

Jourdain, B., and M. Legrand (2001), Seasonal variations of dimethyl sulfide, dimethyl sulfoxide, sulfur dioxide, methanesulfonate, and nonsea-salt sulfate aerosols at Dumont d'Urville (December 1998 – July 1999), *J. Geophys. Res.*, *106*(D13), 14,391–14,408.

Jourdain, B., and M. Legrand (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 aero-

sol in the winter and summer, *J. Geophys. Res.*, *107*(D22), 4645, doi:10.1029/2002JD002471.

Legrand, M., and R. J. Delmas (1984), The ionic balance of Antarctic snow: A 10-year detailed record, *Atmos. Environ.*, *18*, 1867–1874.

Legrand, M., and R. J. Delmas (1988), Soluble impurities in four Antarctic ice cores over the last 30,000 years, *Ann. Glaciol.*, *10*, 116–129.

Legrand, M., and E. C. Pasteur (1998), Methane sulfonic acid to non-sea-salt sulfate ratio in coastal Antarctic aerosol and surface snow, *J. Geophys. Res.*, *103*(D9), 10,991–11,006.

Legrand, M., C. Lorius, N. I. Barkov, and V. N. Petrov (1988), Vostok (Antarctica) ice core: Atmospheric chemistry changes over the last climatic cycle (160,000 years), *Atmos. Environ.*, *22*, 317–331.

Maenhaut, W., R. Hillamo, T. Makela, J. L. Jaffrezo, M. H. Bergin, and C. I. Davidson (1996), A new cascade impactor for aerosol sampling with subsequent PIXE analysis, *Nucl. Instrum. Methods Phys. Res., Sect. B109/110*, 482–487.

Minikin, A., M. Legrand, J. Hall, D. Wagenbach, C. Kleefeld, E. Wolff, E. C. Pasteur, and F. Ducroz (1998), Sulfur-containing species (sulfate and methanesulfonate) in coastal Antarctic aerosol and precipitation, *J. Geophys. Res.*, *103*(D9), 10,975–10,990.

Petit, J. R., et al. (1999), Climate and atmospheric history of the past 420,000 years from the Vostok ice core, Antarctica, *Nature*, *399*, 429–436.

Piel, C., R. Weller, M. Huke, and D. Wagenbach (2006), Atmospheric methane sulfonate and non-sea salt sulphate records at the EPICA deep-drilling site in Dronning Maud Land, Antarctica, *J. Geophys. Res.*, *111*, D03304, doi:10.1029/2005JD006213.

Rankin, A. M., E. Wolff, and S. Martin (2002), Frost flowers-implications for tropospheric chemistry and ice core interpretation, *J. Geophys. Res.*, *107*(D23), 4683, doi:10.1029/2002JD002492.

Reader, M. C., and N. McFarlane (2003), Sea-salt aerosol distribution during the Last Glacial Maximum and its implications for mineral dust, *J. Geophys. Res.*, *108*(D8), 4253, doi:10.1029/2002JD002063.

Röthlisberger, R., R. Mulvaney, E. W. Wolff, M. A. Hutterli, M. Bigler, S. Sommer, and J. Jouzel (2002), Dust and sea salt variability in central East Antarctica (Dome C) over the last 45 kyrs and its implications for southern high-latitude climate, *Geophys. Res. Lett.*, *29*(20), 1963, doi:10.1029/2002GL015186.

Teinilä, K., V.-M. Kerminen, and R. Hillamo (2000), A study of size-segregated aerosol chemistry in the Antarctic atmosphere, *J. Geophys. Res.*, *105*(D3), 3893–3904.

Tuncel, G., N. K. Aras, and W. H. Zoller (1989), Temporal variations and sources of elements in the South Pole atmosphere: 1. Nonenriched and moderately enriched elements, *J. Geophys. Res.*, *94*(D10), 13,025–13,038.

Udisti, R., S. Becagli, S. Benassai, E. Castellano, I. Fattori, M. Innocenti, A. Migliori, and R. Traversi (2004), Atmosphere–snow interaction by a comparison between aerosol and uppermost snow layers composition at Dome C (East Antartica), *Ann. Glaciol.*, *39*, 53–61.

Wagenbach, D., F. Ducroz, R. Mulvaney, L. Keck, A. Minikin, M. Legrand, J. Hall, and E. Wolff (1998), Sea salt aerosol in coastal Antarctic regions, *J. Geophys. Res.*, *103*(D9), 10,961–10,974.

Weller, R., and D. Wagenbach (2007), Year-round chemical aerosol records in continental Antarctica obtained by automatic sampling, *Tellus*, *59B*, 755–765.

Wolff, E. W., A. M. Rankin, and R. Röthlisberger (2003), An ice core indicator of Antarctic sea ice production, *Geophys. Res. Lett.*, *30*(22), 2158, doi:10.1029/2003GL018454.

Wolff, E. W., et al. (2006), Southern ocean sea-ice extent, productivity and iron flux over the past eight glacial cycles, *Nature*, *440*, 491–496, doi:10.1038/nature04614.

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