

Major Ionic Species in a Snow Pit in Livingston Island, Antarctica

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ABSTRACT. Snow samples were collected at a snow pit, 5 km inland a coast of Livingston Island (60°37'W, 62°37'30"S) down to 1.5 m depth with intervals of about 5 cm in December 1998. Samples were estimated to represent snow falls accumulated during at least austral winter in 1998. Concentrations of major ions, MSA (Methanesulfonic Acid), Cl⁻, NO₃⁻, SO₄²⁻, Na⁺, NH₄⁺, K⁺, Mg²⁺, and Ca²⁺ showed ranges of 0.003-0.066 μg/g, 0.17-26.94 μg/g, 0.01-0.24 μg/g, 0.03-4.88 μg/g, 0.14-13.85 μg/g, nd-0.07 μg/g, 0.01-3.14 μg/g, 0.01-1.81 μg/g, nd-0.48 μg/g, respectively. The results showed that the major ionic compositions of snow were remarkably similar to those of sea water, with much higher concentrations. While concentration levels of all ionic species measured sharply increase at depths of 30 cm, 60 cm and 130 cm, the oxygen isotope ratios do not indicate any distinct seasonal variation. These layers of high ions could be attributed to either one or combining acts of three factors: dry depositions, wet depositions, and partial melting and movements of ionic species with depth. The mean molar ratio (R) of MSA/nss-sulfate (non sea salt sulfate) was 0.11, which was approximately 20-30 % higher than those in remote open ocean, but it was about one third of those in inland Antarctica

Key Words: snow pit, major ions, cations, anions, DMS(Dimethyl Sulfide), MSA (Methanesulfonic Acid)

Introduction

Over the last three decades, our understanding in the behaviors of soluble ionic species in the Antarctic ice cores have been significantly improved (Legrand and Delmas 1985; Legrand and Delmas 1986; Artaxo *et al.* 1992; Suttie and Wolff 1992). Since the Antarctica is regarded as the most remote and pristine background environments, the temporal variations of soluble ionic species in ice cores are expected to represent the global atmospheric changes. In particular, the analysis of sulfate and Methanesulfonic Acid (MSA) in ice cores and snow has provided the useful tools to investigate the vari-

ability in marine biological activities and its related climatological changes in the past.

Atmospheric MSA is solely derived from the oxidation of Dimethyl Sulfide (DMS). DMS is the most dominant species of naturally occurring reactive sulfur compounds in the atmosphere. Its precursor is produced by phytoplanktons in the ocean and transformed into DMS, then released to the atmosphere (Andreae and Raemdonck 1983). DMS in the marine boundary layer is readily oxidized to sulfate and lower amount of MSA. Sulfate and MSA produced by oceanic DMS have been hypothesized to affect the Earth's radiation balance through the formation of cloud condensation nuclei (CCN) which are critical to cloud formation (Charlson *et al.* 1987). It has been widely proposed that measurements of non sea salt (nss) sulfate and MSA in snow and ice cores in

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the Antarctic could provide the key to elucidate the historical variability of marine DMS emission and to investigate the historical links between oceanic productivity and climate. The recent MSA analysis in the Antarctic ice cores revealed the natural variability in marine phytoplankton productivity. In addition, it was also found that the long-term and short-term variation of MSA and nss-sulfate ratios reflected climatological and ENSO changes in Antarctic ice cores, respectively (Legrand *et al.* 1985; Legrand *et al.* 1992; Legrand 1995). While molar ratios of MSA to nss-sulfate observed in marine remote at mid and low latitudes were less than 0.1 (Saltzman *et al.* 1983, 1986), this ratio seems to increase at higher latitudes. Increase in the ratio could be attributed to colder temperature favoring the formation of MSA or the changes in the transport patterns (Legrand *et al.* 1992). However, several studies showed that ratios of MSA to nss-sulfate were often influenced by the sulfate transported from various sources, such as anthropogenic, volcanic, and even stratospheric origins (Legrand and Delmas 1986; Prospero *et al.* 1991; Artoxo *et al.* 1992; Genthon 1992; Guerzoni *et al.* 1992; Suttie and Wolfe 1992). It is, therefore, important to extend our understanding of sulfur chemistry through examining all the possible major sulfur sources in the Antarctic area.

The primary objective of this study was to investigate the composition of major ionic species including MSA in snow falls in Livingston Island, Antarctica. While this island is relatively remote as it is located inside of Antarctic circle and surrounded by oceans with high marine productivity, it is still close to anthropogenic sulfur sources. In this paper, various factors controlling MSA and nss-sulfate concentrations in recent snow fall were investigated.

Experimental methods

Sampling site and sampling procedures

Snow samples were collected from a 1.5 m deep pit at a site (60°15'W, 62°37'30"S) in Livingston Island,

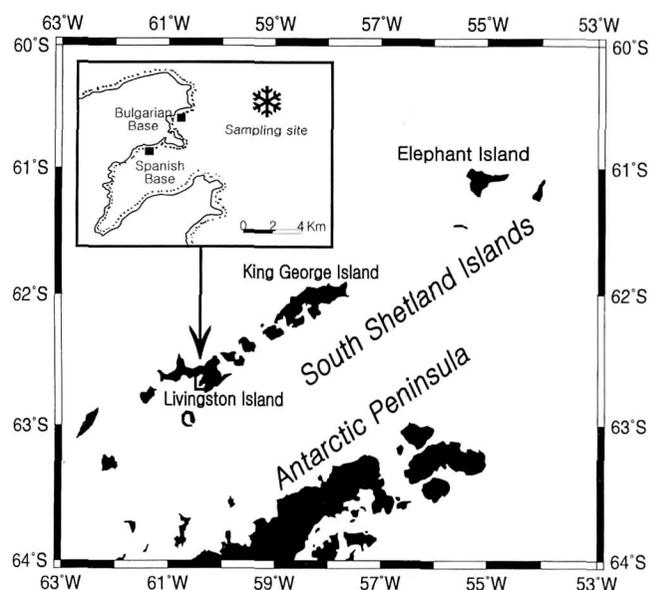


Fig. 1. Location of Livingston Island, South Shetland Islands, showing the sampling site.

South Shetland Islands, near the Antarctic Peninsula, on 18 December, 1998 (Fig 1). The site was located at 450 m altitude, 5 km from the nearest coast and 6 km and 8 km in a straight line from Bulgarian and Spanish bases located on the coast, respectively. Two bases are manned during only summer season (from the early December to the late February each year) and were open several days before our sampling work in 1998. A snow pit was dug using pre-cleaned plastic shovels. The upwind vertical wall was cut with pre-cleaned low density polyethylene (LDPE) scrapers, and 20 successive snow samples were collected from the surface down to a depth of 1 m with intervals of 5 cm. The samples were collected by pushing ultra-clean LDPE vials (160 ml vials with closure from Nalgene, Nalge Company) vertically into the snow. Below 1 m depth, there was a series of thin ice layers between 100-140 cm depth (103.0-103.5 cm, 117.5-117.8 cm, and 138.0-138.4 cm). Because of a possible migration of chemical constituents occurred during melting, 6 samples between ice layers were collected in well preserved snow layers, in which recrystallization of snow grains was not observed (depth intervals collected: 105-110, 110-115, 118-123, 125-130, 130-135, 139-144 cm, respectively). Once collected, samples in vials were sealed in two layers of pre-cleaned LDPE

Table 1. Conditions for ion chromatography operation

	Anion	Cation
Sample loop volume	100 μ l	100 μ l
Separation column	Dionex AS11	Dionex CS14
Guard column	Dionex AG11	Dionex CG14
Eluent	1.5-10 mM NaOH	8 mM MSA
Eluent flow rate	1.0 ml/min	1.0 ml/min
Detector	conductivity	conductivity
Detector output range	0.5	0.5
Suppressor	Solid phase	none
Background	5 μ S	1150 μ S

bags, frozen and transported to laboratory. All plastic items used for sampling were extensively cleaned several times with ultrapure water in a Class 100 clean room as described in detail in Legrand (1985).

Chemical Analysis

In laboratory, the samples were melted, and major anions (MSA, Cl^- , NO_3^- , SO_4^{2-}) and cations (Na^+ , NH_4^+ , K^+ , Mg^{2+} , Ca^{2+}) was analyzed by ion chromatograph (IC) with Dionex column AS 11 for anions and CS14 for cations. Samples were injected into sampling loop (100 μ l) via a sterile inert Acrodisc syringe filter (0.45 μ m). Detailed conditions for IC set up are listed in Table 1. To quantify the levels of contamination during the sampling, storage, transport, and analysis, three field blank samples were prepared and analyzed. The detection limits for MSA and other major ions were around 0.001 $\mu\text{g/g}$ and around 0.01 $\mu\text{g/g}$, respectively. The instrument was well calibrated with working standards, and the linearity was always greater than 0.99 in correlation coefficient. Analytical precision was in the range of 5-10% for all ions. Based upon the concentration of conservative component Na^+ , nss-sulfate was calculated from the following equation.

$$\text{nss-sulfate} = [\text{sulfate}] - 0.24[\text{Na}] \quad (1)$$

Measurement of oxygen isotope

In order to determine source and times of snow accumulations, snow layers must be characterized

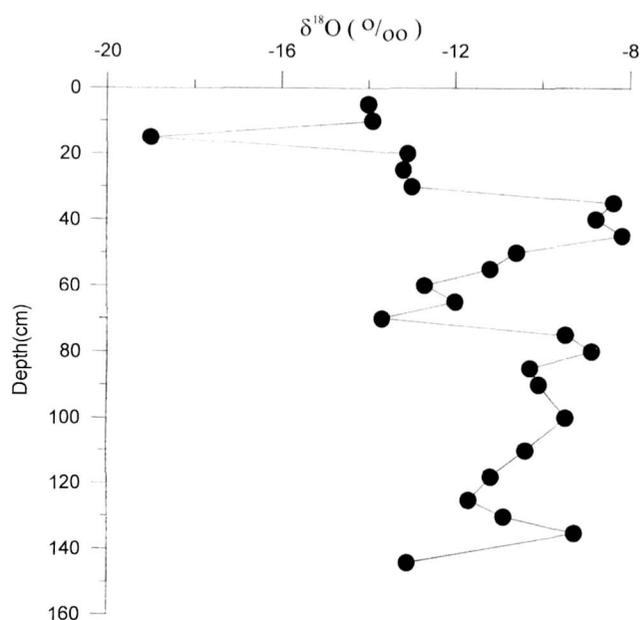


Fig. 2. Vertical profile of the oxygen isotope ratios from the snow samples collected in Livingston Island.

with season. For this, oxygen isotope ratios of our snow samples were measured by stable isotope ratio mass spectrometer (VG Prism II) in Korea Basic Science Institute. As shown in Fig. 2, the vertical variation of the oxygen isotopes does not represent a pronounced winter minimum which is detected at other sites in Antarctica, making it impossible to clearly distinguish between seasons in 1998. It should be noted that our samples do not cover snow layers precipitated in summer 1998, because the melting of significant amount of snow accumulated in Livingston Island occurs in summer when temperature rises above 0°C . Thick ice layer, not be penetrated by a steel skewer, was found to be present at a depth of about 2 m of the sampling site. This ice layer is assumed to have been formed after the summer melting previous to 1998. In addition, considerably thick ice layers were present at the depth interval of 1.5-2 m, indicating the probable fall layers. Although the depth profile of oxygen isotopes does not provide an apparent winter minimum at any depth, it was estimated that our deeper samples covered snow layers deposited in winter and thus corresponded to snow accumulation of at least six months from July to December, 1998.

From the oxygen isotope profile, we can assume

Table 2. Simple Statistics of Major Ionic Species

Species	Min	Max	Mean	σ
Na ⁺	0.1347	13.856	2.670	2.986
NH ₄ ⁺	0	0.065	0.007	0.014
K ⁺	0	0.314	0.077	0.866
Mg ²⁺	0.006	1.809	0.321	0.394
Ca ²⁺	0	0.479	0.061	0.105
Formate	0.037	0.019	0.026	0.021
MSA	0.003	0.066	0.019	0.015
Cl ⁻	0.173	26.942	5.962	6.799
NO ₃ ⁻	0.007	0.245	0.033	0.045
SO ₄ ²⁻	0.033	4.877	0.862	1.069
NSS SO ₄ ²⁻	0	1.388	0.201	0.326

unit: $\mu\text{g/g}$

the possible conditions of snow deposition and accumulation at the study site. First, it is likely that heavy snow accumulation may have occurred during several precipitation events, with relatively lower accumulation in winter. Thus, the snow accumulation is not evenly distributed, especially for the depth below about 80 cm in the profile (Fig. 2). Second, the weather conditions from winter to spring were relatively moderate at the study area in 1998. No direct observation of meteorological conditions in Livingston Island are available. However, meteorological data obtained at King Sejong Station of King George Island (Fig 1), about 100 km apart from Livingston Island, could allow us to deduce the weather conditions at the study area. In King George Island, the monthly averaged temperatures in winter were between -7.4 and -1.4°C from July to October in 1998. The temperatures increased slightly over 0°C even in winter months. There is no large difference in temperature between winter and the early spring. The weather condition of Livingston Island is expected to be similar to that of King George Island.

Results and Discussion

It is well known that in near coastal areas relative compositions of ionic species in aerosol reflect those of sea water, with little fractionation. As shown in

Table 3. Mean concentrations of nss-sulfate and MSA measured in aerosols (Prospero et al., 1991)

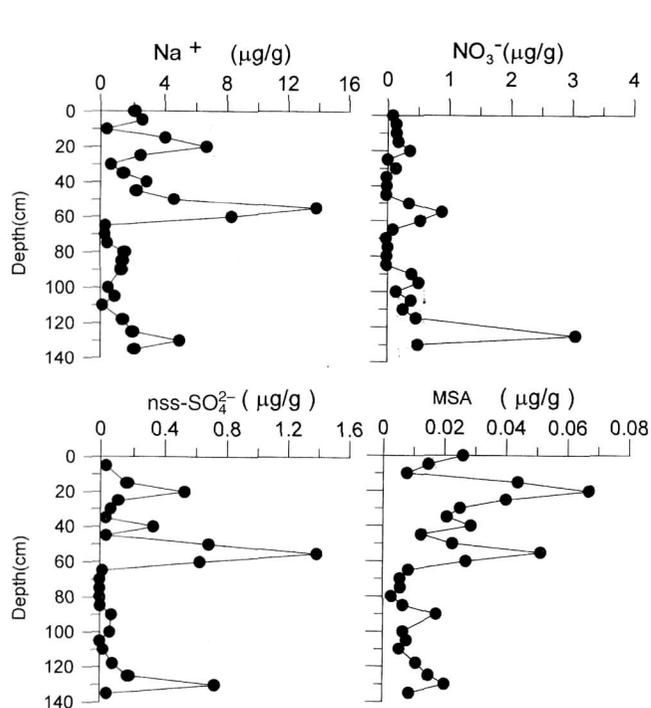
Constituent	Mawson	Neumayer	South Pole	Cape Grim	American Samo
NSS SO ₄ ²⁻	90	71	83	280	360
MSA	20	-	-	18	26

unit : ng/m^3

Table 2, the overall major ionic compositions of snow at the study site were remarkably similar to those of sea water, with much higher concentrations. As the sampling site was located on island and not far from the coast, the composition of snow and aerosol was heavily influenced by sea salt. The mean mass Cl/Na ratio of 2.09 is comparable to the sea water ratio of 1.79, suggesting that there was no chlorine vaporization occurring during the process of transport and deposition. The mean concentrations of MSA, nss-sulfate and their ratio were $0.019 \mu\text{g/g}$, $0.201 \mu\text{g/g}$, and 0.09, respectively. A mass ratio of MSA to nss-sulfate in Livingston Island was slightly higher than that of American Samoa (0.07) and Cape Grim (0.06), as shown in Table 3. Whereas, it was lower compared to that of Mawson (0.22) in the Antarctic (Prospero *et al.* 1991; Harrison *et al.* 1996). If there was no possibility of anthropogenic influence, the difference in ratios could be attributed to the variation in DMS oxidation pathways. The oxidation of DMS in the atmosphere is mainly initiated by the reactions with OH radicals in the remote and clean atmosphere. The oxidation pathways of DMS by either OH addition or abstraction are strongly dependent upon temperature. At cold temperature, OH addition path yielding more MSA than nss-sulfate is preferred. Thus, the summertime mass ratio of MSA to nss-sulfate in Livingston Island could reflect the transient temperature conditions from warm latitude (American Samoa) to cold Antarctic. The molar ratio of MSA to nss-sulfate in Livingston Island also indicated the temperature difference effect on DMS oxidation (Table 4). The mean molar ratio (R) in Livingston Island (0.11) was lower compared to those in Antarctic ice cores (0.16-0.46) (Mulvaney *et al.* 1992), implying the relatively

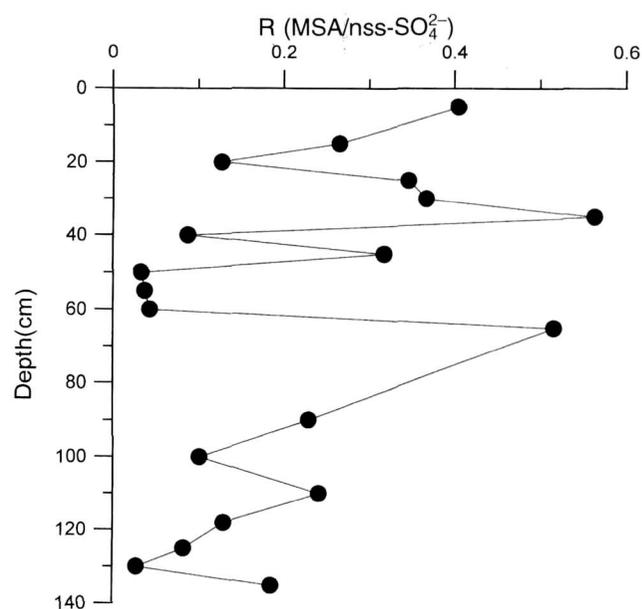
Table 4. Characteristics of the three ice cores and snow pit

	Livingston Island	Dolleman* Island	Gomez* Nunatak	Dyer* Plateau	South** Pole
position	60°37'W, 62°37'S	70°35'S 60°56'W	74°01'S 70°38'W	70°31'S 65°01'W	
date collected	Dec. 1998	Jan.1986	Jan.1981	Jan.1989	1988
Chemical properties					
mean MSA (μM)	0.24	0.85	0.11	0.09	0.10
mean nss- SO_4^{2-} (μM)	2.09	1.86	0.30	0.28	0.63
mean SO_4^{2-} (μM)	8.98	2.55	0.44	0.36	
MSA/nss- SO_4^{2-}	0.11	0.46	0.37	0.32	0.16
nss- SO_4^{2-} / tot SO_4^{2-}	0.23	0.73	0.68	0.78	

* Mulvaney *et al.* 1992** Legrand *et al.* 1992**Fig. 3.** Changes in Na, nitrate, nss-sulfate, and MSA concentrations with depth in the snow pit in Livingston Island.

high temperature DMS oxidation.

The concentrations of major ionic species noticeably increased at depths of 20 cm, 60 cm, 90 cm and 130 cm (Fig. 3). If those peaks represented the seasonal variations of deposition, the oxygen isotopic ratio should display a similar variation. However, the oxygen isotope ratio did not show any seasonal variation, as previously discussed (Fig. 2). Thus, it is likely that high ionic concentrations at these layers were the results of either marks of the consistent

**Fig. 4.** Vertical profile of changing ratios (R) of MSA to nss-sulfate in the snow pit in Livingston Island.

and long exposure to air masses originating across the sea (dry deposition), or of snow deposition (wet deposition), or snow melting.

As the study site was close to the sea, the dry deposition of sea salts could contribute more significantly to high ionic concentrations than wet deposition or snow melting did. Determined from the ionic peaks represented, about 4 times of heavy snow accumulation (more than 20 cm) occurred during the relatively short period of time.

As mentioned earlier, the ratio of MSA to nss-sulfate often used to deduce the magnitude of biological sulfur contributions, mainly from DMS. Figure 4

shows the mean molar ratio (R) of MSA and nss-sulfate with depth in a snow pit. Although the ratio fluctuates with depth, there is a trend of increase in the ratio from the bottom to the top. If the DMS oxidation is the key factor controlling the ratio, the increase in the ratio to the top would reflect decrease in temperature. However, it is certain that the snow in the top layer was deposited in the warmer temperature, because the surface samples were taken in December, 1998. Consequently, the increasing ratio to the surface do not support the suggestion that the ratio was solely dependent on DMS oxidation path. The large decrease in ratio (R) was apparently observed at depths of high concentrations of ionic species, even though the MSA concentrations increased at the corresponding depths. The decrease of ratio was mainly due to greater increase in nss-sulfate than those of MSA during high ionic deposition periods. It is not unreasonable to assume that there was the distinct difference in composition between aerosol (dry deposition) and snow (wet deposition). It seems that an additional source of nss-sulfate was predominant during the high ionic deposition periods. The long range transport of anthropogenic sulfur from nearby continents have been reported in the Antarctic (Guerzoni *et al.* 1992; Genthon 1992). Although anthropogenic SO₂ and sulfate from nearby continents might influence ratios of MSA to nss-sulfate, the influence could not be quantified at this study. If layers of snow pit were dated correctly, prevailing air masses, meteorological conditions and the anthropogenic influences could be reconstructed by synoptic meteorological analysis, such as back-trajectory calculations.

Another possibility for a low ratio during the high ionic deposition periods was the temperature difference between layers. Normally, the temperature was much lower during the snow fall than during dry and melting periods. Thus the ratio (R) could decrease selectively by OH abstraction of DMS. However, the oxygen isotope ratios with depth did not firmly support the suggestion of temperature dependency in the ratio.

Although we could not quantify, the anthropogenic influences on aerosol species was most like-

ly and can not be ruled out at this area. The comparisons of chemical composition between aerosol and snow falls will provide the key to solve this question in future study.

Conclusion

Snow samples collected from Livingston Island revealed several interesting characteristics of behaviors of ionic species in aerosol and snow. The extremely high concentrations of major ionic compositions in snow at certain depths suggest that this coastal area periodically receives a large amount of sea salts. Although periodic peaks of ionic species were apparent, the oxygen isotope ratios were not related to those ionic peaks. The layers of high ionic concentrations can be attributed to periods of dry deposition or snow melting, or less likely to the high ionic snow falls. The mean ratio of MSA/nss-sulfate (0.11) measured at the study site was 20-30% higher than those of aerosols in remote open ocean, but lower than those of the inland Antarctic. The low ratios at the high ionic layers implied anthropogenic influences during the dry periods.

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References

- Andreae M.M. and Raemdonck H. 1983. Dimethylsulfide in the surface ocean and the marine atmosphere: a global view. *Science* **221**: 744-747.
- Artaxo P., Rabello M.L.Ç., Willy Maenhaut W., and Grieken R.V. 1992. Trace elements and individual particle analysis

- of atmospheric aerosols from the Antarctic peninsula. *Tellus* **44B**: 318-334.
- Charlson R.J., Lovelock J.E., Andreae M.O., and Warren, S.G. 1987. Oceanic phytoplankton, atmospheric sulfur, cloud albedo and climate. *Nature* **326**: 655-661.
- Genthon C. 1992. Simulations of desert dust and sea-salt aerosols in Antarctica with a general circulation model of the atmosphere. *Tellus* **44B**: 371-389.
- Guerzoni S., Lenaz R., Quarantotto G., Taviani M., Rampazzo G., Facchini M.C., and Fuzzi S. 1992. Geochemistry of airborne particles from the lower troposphere of Terra Nova Bay, Antarctica. *Tellus* **44B**: 304-310.
- Harrison M.R., Peak J.D., and Msibi M.I. 1996. Measurements of Airborne Particulate and Gaseous sulphur and Nitrogen Species in the Area of the Azores, Atlantic Ocean. *Atmos. Environ.* **30**: 133-143.
- Legrand M. 1985. Chimie des neiges et Glaces antarctiques: Un reflet de l'environnement, Thèse Doctorat d'Etat, Univ. Sci. et Méd. de Grenoble, Publ. 478, 439 pp., Lab. de Glaciol. et Géophys. de l'Environ., Saint-Martin d'Hères, France.
- Legrand M. and Delmas R.J. 1985. Spatial and temporal variations of snow chemistry in Terre Adélie (East Antarctica). *Ann. Glaciol.* **7**: 20-25
- Legrand M. and Delmas R.J. 1986. Relative contributions of tropospheric and stratospheric sources to nitrate in Antarctic snow. *Tellus* **38B**: 236-249.
- Legrand M., Feniet-Saigne C., Saltzman E.S., and Germain C. 1992. Spatial and temporal variations of Methanesulfonic acid and non sea salt sulfate in Antarctic ice. *J. Atmos. Chem.* **14**: 245-260.
- Legrand M. 1995. Atmospheric chemistry changes versus past climate inferred from polar ice cores. In: Charlson, R.J. and Heintzenberg, J. (eds), *Aerosol Forcing of Climate*. John Wiley and Sons, Inc., New York. pp. 123-151.
- Mulvaney R., Pasteur E.C., Peel D.A., Saltzman E.S., and Whung P.Y. 1992. The ratio of MSA to non-sea-salt sulphate in Antarctic peninsula ice cores. *Tellus* **44B**: 295-303.
- Prospero J.M., Savoie D.L., Saltzman E.S., and Larsen R. 1991. Impact of oceanic sources of biogenic sulphur on sulphate aerosol concentrations at Mawson, Antarctica. *Nature* **350**: 221-223.
- Saltzman E.S., Savoie D.L., Zika R.G., and Prospero J.M. 1983. Methanesulfonic acid in the marine atmosphere. *J. Geophys. Res.* **88**: 10897-10902.
- Saltzman E.S., Savoie D.L., Prospero J.M., and Zika R.G. 1986. Methanesulfonic and non sea-salt sulfate in Pacific air: regional and seasonal variations. *J. Atmos. Chem.* **4**: 227-240.
- Suttie D.E. and Wolff E.W. 1992. Seasonal input of heavy metals to Antarctic snow. *Tellus* **44B**: 351-357.

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