

Spatial variability of the major chemistry of the Antarctic ice sheet

R. MULVANEY AND E. W. WOLFF

British Antarctic Survey, Natural Environment Research Council, Cambridge CB3 0ET, England

ABSTRACT. A compilation of reliable data for sodium, nitrate, chloride and sulphate has been made. NO_3^- concentrations are remarkably consistent across Antarctica, though there appears to be some correlation with altitude and accumulation rate. Post-depositional loss of NO_3^- is important at low-accumulation sites. Cl⁻ concentration (either measured directly or calculated from Na^+ via the sea-salt ratio) decreases with distance from the coast, though the decline is less rapid if the coastal topography is not steep or mountainous. Excess sulphate (xs SO_4^{2-}) concentration (here calculated from normal sea-salt ratios with Na^+ or Cl⁻) also declines with distance from the coast, though less quickly than Cl⁻. Fractionation of sea-salt ions makes the calculation of xs SO_4^{2-} uncertain.

1. INTRODUCTION

Over the last three decades, ice cores have been drilled at numerous locations in Antarctica. They have ranged from cores of 10 m or less to the deepest core at Vostok, which is now 2546 m long and spans 220 000 years. Soluble ionic chemistry has been measured in many of these cores, and temporal variations have been interpreted in terms of changing atmospheric sources and transport. However, both sources and transport are poorly understood even under current conditions, as is the air-snow transfer function, and this hinders temporal interpretations.

One approach to understanding these factors better is to investigate how chemical concentrations vary spatially and seasonally within Antarctic snowfall. Ideally, this would be done with year-round surveys of atmospheric chemistry at many sites. However, aerosol sampling has been conducted at only a very few sites, often for only part of the year, and sometimes too close to manned stations, so that the results are not representative of the regional background. Exceptions to this are the excellent aerosol records from Neumayer (Wagenbach and others, 1988) and Mawson (Savoie and others, 1992).

The spatial distribution of chemistry in the snowpack can be used as a surrogate for the atmosphere. The ITASE (International Trans-Antarctic Scientific Expedition) sample collections planned for the next few years will provide an excellent data network for doing this. However, much data already exist. It is likely that closer study of them may highlight more clearly some of the questions that ITASE activities need to pursue. Compilations have been made previously for some parameters such as accumulation rate (Giovinetto and Bull, 1987; Giovinetto and others, 1990) and oxygen-isotopic ratios (Morgan, 1982). In this paper, we compile for the first time all the existing and reliable data for soluble chemistry and provide an interpretation of their spatial variability.

2. CHEMICAL SPECIES

The major soluble impurities in Antarctic ice are:

- (1) Sea-salt ions (part of Na^+ , Mg^{2+} , K^+ , Ca^{2+} , Cl^- , SO_4^{2-}).
- (2) H_2SO_4 , derived from oxidation of marine biogenic emissions of DMS and from volcanism (both background and sporadic events).
- (3) HNO_3 , probably derived from the stratosphere and from tropical lightning (Legrand and Kirchner, 1990). At this time, significant anthropogenic contributions are not discernible in Antarctic snow (away from stations) for either sulphate or nitrate.
- (4) H_2O_2 , a product of photochemical processes in the atmosphere.
- (5) Terrestrial input, represented by elements such as Al and Ca, as well as by insoluble dust.

More minor components that have been measured include methanesulphonic acid (MSA) (Legrand and others, 1992), NH_4^+ , organic acids (Legrand and Saigne, 1988) and other trace metals (Görlach and Boutron, 1992; Suttie and Wolff, 1992).

The minor components have been measured only at a few sites and a spatial survey is not yet appropriate. One of the more interesting species may be MSA, because it has only one known source (oxidation of biogenically produced DMS). Current knowledge of MSA has been summarized by Legrand and others (1992). H_2O_2 has also been measured at only a few sites and interest in it continues to grow. The terrestrial elements have been reported in a number of ways (particle numbers, dust concentrations, Al and Ca) and it is difficult to produce a widespread or coherent spatial survey, although this would be valuable. In this paper, we therefore concen-

trate on the first three categories of soluble species.

Large amounts of data exist for Cl^- , NO_3^- and SO_4^{2-} concentrations across Antarctica. We can supplement the Cl data at other sites where Na^+ has been measured by converting to Cl^- using a sea-salt ratio. This procedure ignores the documented cases where Na^+ and Cl are not in sea-salt ratio but, generally, the discrepancy for these two elements is at most a few per cent. Since we do not attempt to look at the fractionation of other sea-salt elements, which requires detailed study of data from single sites or single snowfalls, we have not used Mg^{2+} , K^+ or Ca^{2+} data.

In summary, this paper will compile data for the first three components of the soluble ionic components, using Cl^- (and Na^+), NO_3^- and SO_4^{2-} data. For SO_4^{2-} , we calculate xsSO_4^{2-} from normal sea-salt $\text{SO}_4^{2-}/\text{Cl}^-$ or $\text{SO}_4^{2-}/\text{Na}^+$ ratios, i.e.:

$$\begin{aligned} \text{xsSO}_4^{2-} &= \text{SO}_4^{2-} - 0.103\text{Cl}^- \text{ or} \\ \text{xsSO}_4^{2-} &= \text{SO}_4^{2-} - 0.120\text{Na}^+ \text{ where all species are in} \\ &\quad \mu\text{eq l}^{-1}. \end{aligned}$$

This means that xsSO_4^{2-} here is in effect the sum of two factors: (i) acidic sulphate and (ii) the deficit (or excess) of sulphate in sea-salt aerosol. The latter factor may be significant at near-coastal sites. Minikin and others (1994) have pointed out that negative xsSO_4^{2-} values are often found at coastal sites, implying that a different ratio is appropriate for marine aerosol, at least for some periods of the year. Therefore, they calculated xsSO_4^{2-} using lower ratios. Because we cannot say what ratio might be appropriate for each site, we use the normal sea-salt ratio to quote xsSO_4^{2-} for all sites, except for those of Minikin and others where we have used their xsSO_4^{2-} values. In Table 1, we have also shown the effect of the conventional calculation using normal sea-salt ratios on their values.

3. CRITERIA FOR INCLUDING DATA

For data to be included in this compilation, they must be of good quality and representative of the chemistry at the site.

Good-quality data require careful, accurate analysis and non-contaminating sample collection. In recent years, scientists have become more aware of the need to collect samples in clean bottles without adding contamination. The introduction of ion chromatography has made analysis of ions (particularly anions) much easier and analyses should, in careful hands, be accurate to 5% or so. We have accepted data where ion chromatography (or, for Na^+ , atomic-absorption or equivalent methods) has been used, and where suitable sample-collection techniques are believed to have been used. Where there are no other data for a site, we have accepted (mainly older) data not explicitly meeting these criteria but caution that the accuracy of some of these data is uncertain.

It is very important to use data that represent the site in question. For that reason, we have attempted to exclude data from any sporadic events (such as volcanic eruptions) where they significantly affect the mean concentration. Since no significant pollution trend has so far been observed in Antarctic snow for the species we

have compiled, we do not need a totally common time-scale between sites to achieve comparability, but have generally used data from short cores covering only recent decades. Since there can be large seasonal variations, data should only be accepted where they cover complete years or average many years. However, we have not excluded the French D-sites, where many of the samples cover only 3 years (Legrand and Delmas, 1985). Additionally, at least for nitrate, there is mounting evidence that post-depositional changes occur in concentrations in the surface layers (Neubauer and Heumann, 1988; Mayewski and Legrand, 1990; Wolff, in press). For both these last two reasons, data from collections of only near-surface snow cannot be used to infer a background annual mean and cannot be compared to data from other sites. This is unfortunate, as such data are available from large areas of the continent where no other data exist (Kamiyama and others, 1989; Dac and others, 1992) but we have had to exclude them. Because of the near-surface loss of nitrate evident particularly at low-accumulation sites such as Vostok, data from below 1 m depth are used where possible but this is discussed later.

4. DATA AND DISCUSSION

The data accepted by the above criteria are listed in Table 1 and illustrated in Figures 1–3. The major factors likely to influence concentrations are the distance from the coast, altitude and snow-accumulation rate (listed in Table 1). Secondary factors such as temperature, sunlight received, typical wind speeds and seasonality of deposition may also strongly affect the average concentrations. A problem with analysing the data according to these variables is that many of them vary together. For example, across most of Antarctica, as distance from the coast increases, altitude also increases while temperature and accumulation rate decrease. We discuss each of Cl^- , NO_3^- and SO_4^{2-} in the light of these factors.

4.1. Cl^-

Cl^- (here sometimes measured directly but at some sites calculated from Na^+) is derived mainly from sea spray. Even where HCl is apparently present, it is mainly derived from the reaction of NaCl and H_2SO_4 (Legrand and Delmas, 1988a). We therefore expect that distance from the sea and, to some extent, altitude, will be crucial factors. We calculate distance ignoring sea ice, because this is highly variable and seasonal, and there are normally shore leads providing at least some open water at the coast. In Figure 4 we present Cl^- data from three data sets: the French chain of D sites, the Ross Ice Shelf and the Filchner–Ronne Ice Shelf (FRIS), including Berkner Island and the nearby Coats Land region. Herron (1982) has previously calculated an exponential relationship for Cl^- against altitude for the Ross Ice Shelf, while Minikin and others (1994) have calculated an exponential relationship against distance for the FRIS. As explained earlier, altitude generally increases with distance from the coast in Antarctica, so either approach may be valid, depending on the topography. For ice

Table 1. Data used in this analysis

Site	Lat.	Long.	Altitude	Dist. - coast	Accumulation	Sodium	Chloride	Nitrate	vs SO ₄ ²⁻	Reference	
			m	km	mm a ⁻¹	μeq l ⁻¹	μeq l ⁻¹	μeq l ⁻¹	μeq l ⁻¹		
Dome C	74°42' S	124°04' E	3240	910	36	0.90	0.40	0.31	1.50	Legrand and Delmas, 1988b	
South Pole	90° S		2880	1270	85	0.60	1.30	1.40	1.40	Legrand and Delmas, 1984	
Vostok	78°28' S	106°48' E	3488	1300	22	1.20	0.50	0.25	2.60	Legrand and others, 1988	
D10	66°42' S	139°48' E	270	4	153	19.00	22.14*		0.37	Delmas and others, 1982	
D10	66°42' S	139°48' E	270	4	153			0.32		Legrand and Delmas, 1985	
D23	66°47' S	139°40' E	580	16	445	5.70	6.64*			Boutron and Lorius, 1977	
D24	66°48' S	139°39' E	500	17		2.70	3.00	0.65	1.30	Legrand and Delmas, 1985	
D33	66°51' S	139°33' E	730	26	380	5.70	6.64*			Boutron and Lorius, 1977	
D40	66°54' S	139°29' E	600	33		2.70	3.10	0.15	0.30	Legrand and Delmas, 1985	
D42	67°03' S	139°15' E	100	53	520	2.90	3.38*			Boutron and Lorius, 1977	
D46	67°20' S	138°48' E	1450	93	390	1.00	1.17*			Boutron and Lorius, 1977	
D47	67°23' S	138°43' E	1300	100		0.90	1.20	0.93	0.50	Legrand and Delmas, 1985	
D50	67°37' S	138°20' E	1700	130		1.00	1.10	0.67	0.40	Legrand and Delmas, 1985	
D52	67°47' S	138°07' E	1800	150		0.40	0.40	0.32	0.20	Legrand and Delmas, 1985	
D55	68°01' S	137°47' E	2028	180	70	0.30	0.40		0.40	Legrand and Delmas, 1985	
D55	68°01' S	137°47' E	2028	180	70			0.53		Legrand and Delmas, 1986	
D57	68°11' S	137°33' E	2050	200	410	1.00	1.10	0.66	0.40	Legrand and Delmas, 1985	
D58	68°15' S	137°27' E	2100	210		0.60	0.70	0.50	0.30	Legrand and Delmas, 1985	
D59	68°21' S	137°19' E	2220	223	296	0.50	0.58*			Boutron and Lorius, 1977	
D61	68°39' S	137°07' E	2300	240		0.70	1.00	1.40	0.80	Legrand and Delmas, 1985	
D64	68°41' S	136°48' E	2300	270		0.40	0.50	0.42	0.30	Legrand and Delmas, 1985	
D66	68°51' S	136°34' E	2400	290		0.20	0.40	1.10	0.50	Legrand and Delmas, 1985	
D70	69°09' S	136°05' E	2400	330		0.60	0.80	0.90	0.40	Legrand and Delmas, 1985	
D72	69°20' S	135°48' E	2360	353	232	0.40	0.47*			Boutron and Lorius, 1977	
D73	69°24' S	135°43' E	2400	360		0.60	0.80	1.20	0.80	Legrand and Delmas, 1985	
D77	69°44' S	135°10' E	2400	400		0.90	1.10	0.70	0.40	Legrand and Delmas, 1985	
D80	70°01' S	134°43' E	2130	430	237	0.44	0.70	0.89	0.70	Legrand and Delmas, 1986	
D100	71°34' S	139°59' E	2810	633	126	0.20	0.23*			Boutron and Lorius, 1977	
D110	72°19' S	130°24' E	2960	733	104	0.45	0.52*			Boutron and Lorius, 1977	
D120	73°04' S	128°44' E	3010	833	82	0.40	0.47*			Boutron and Lorius, 1977	
A-3	66°41' S	139°56' E	220	2	450	41.00	22.00			Lorius and others, 1969	
A-5	66°41' S	139°55' E	230	2	450	20.00	13.80		4.50	Lorius and others, 1969	
Cap Prudhoe G1	66°41' S	139°57' E		2		26.00	22.00		6.30	Lorius and others, 1969	
Law Dome	66°30' S	113°00' E		115		5.80	6.10	0.48	0.39	Ivey and others, 1986	
Law Dome (BHQ)	66°43' S	112°50' E	1375	130	650	9.10	10.60*			Yun-gang and others, 1988	
Beethoven Peninsula site 1	71°52' S	074°30' W	580	16				40.10	0.36	1.52	This paper
Beethoven Peninsula site 2	71°36' S	073°00' W	607	32			22.80	0.43	1.50		This paper
Dolleman Island	70°35' S	060°55' W	398	20	390		11.76		3.50		Mulvaney and Peel, 1988
Dolleman Island	70°35' S	060°55' W	398	20	390			0.52			Mulvaney and Wolff, 1993
Dyer Plateau	70°39' S	065°01' W	1943	190		1.19	1.47	0.50	0.86		This paper
GAP St 25	70°53' S	064°57' W	1835	170	460	1.80	1.70				Mumford and Peel, 1982
Gomez Nunatak	74°01' S	070°38' W	1130	135	880		2.35		0.50		Mulvaney and Peel, 1988
Gomez Nunatak	74°01' S	070°38' W	1130	135	580			0.31			Mulvaney and Wolff, 1993
James Ross Island, Dome Dalinger	64°13' S	057°38' W	1660	24	490	7.50	8.74*	0.40	1.90		Aristarain and others, 1982
Puppis Pikes	71°14' S	066°09' W	1356	270			3.82	0.27	1.02		This paper
Rowley Corridor	71°31' S	067°17' W	500	240			7.55	0.39	1.37		This paper
Siple	75°55' S	084°15' W	1054	230	560		2.50	0.45	0.51		Mosley-Thompson and others, 1991
Stephenson Nunatak	72°00' S	069°07' W	300	130			4.71	0.51	1.40		This paper
Temnikov Nunatak	70°34' S	064°15' W	1606	160			1.48	0.19	1.64		This paper
Mizuho	70°42' S	044°20' E	2230	310		0.65	1.10	0.90	0.89		Osada and Higuchi, 1990
Dronning Maud Land	75°00' S	002°00' E	2900	555	77	0.59	0.68	0.88	1.21		Personal communication from E. Isaksson
Dronning Maud Land	71°48' S	004°00' E		200		4.30	3.70		0.90		Gjessing, 1989
Dronning Maud Land	71°58' S	004°00' E		220		2.90	2.10		1.10		Gjessing, 1989
Dronning Maud Land	70°04' S	004°00' E		8		124.00	140.00		-5.00		Gjessing, 1989
Dronning Maud Land	70°00' S	004°00' E		0		360.00	420.00		-30.00		Gjessing, 1989
Roi Baudouin	70°26' S	024°19' E	0	12		84.00	66.00				Brocas and Delwiche, 1963
S-122	70°01' S	043°07' E		215		2.30	2.68*				Murozumi and Nakamura, 1974
Y-135	71°27' S	047°22' E		430		0.50	0.58*				Murozumi and Nakamura, 1974

Site	Lat.	Long.	Altitude	Dist.— coast	Accumul- ation	Sodium	Chloride	Nitrate	xs SO ₄ ²⁻	Reference
			m	km	mm a ⁻¹	μeq l ⁻¹	μeq l ⁻¹	μeq l ⁻¹	μeq l ⁻¹	
Y-200	71°46' S	048°56' E		490		0.60	0.70*			Murozumi and Nakamura, 1974
Y-300	70°55' S	049°53' E		440		0.50	0.58*			Murozumi and Nakamura, 1974
BAS5	81°28' S	060°36' W		530	92		5.13	0.78	1.16(0.84)	Minikin and others, 1994
BAS6	81°36' S	058°10' W		530	89		5.44	1.15	1.25(0.92)	Minikin and others, 1994
BC90	76°59' S	052°28' W		44	204		27.00	0.78		Graf and others, 1991
Berkner Island	79°36' S	045°37' W	900	150	174		16.08	0.55	1.75(0.77)	Wagenbach and others, 1994
Berkner Island	78°18' S	046°17' W	730	50	226		29.62	0.52	2.33(0.53)	Wagenbach and others, 1994
Coats Land	77°02' S	022°32' W	1862	150	155		3.00	0.71	0.50	Mulvaney and Wolff, 1993
Coats Land	77°34' S	025°22' W	1420	145	59	2.48	3.34		2.16	This paper
D131	76°58' S	054°42' W		55	201		22.48	0.61	1.85(0.48)	Minikin and others, 1994
D136	77°12' S	053°08' W		70	189		22.34	0.48	1.89(0.53)	Minikin and others, 1994
D230	77°22' S	056°06' W	49	120	199		13.65	0.59	1.56(0.73)	Minikin and others, 1994
D231	77°41' S	057°20' W	54	160	185		11.57	0.61	1.23(0.52)	Minikin and others, 1994
D235	77°31' S	054°33' W		123	184		18.70	0.71	1.69(0.53)	Minikin and others, 1994
D236	77°56' S	055°59' W		171	166		14.36	0.73	1.83(0.88)	Minikin and others, 1994
D240	77°52' S	052°48' W	54	110	196		18.28	0.66	1.69(0.58)	Minikin and others, 1994
D330	78°02' S	056°59' W	50	185	176		10.86	0.58	1.55(0.89)	Minikin and others, 1994
D335	78°18' S	056°59' W	51	221	170		11.09	0.93	1.67(1.00)	Minikin and others, 1994
D336	78°43' S	057°51' W		272	156		11.31	0.82	1.64(1.02)	Minikin and others, 1994
D340	78°36' S	055°26' W	56	210	155		10.07	0.79	1.54(0.93)	Minikin and others, 1994
D341	78°57' S	056°50' W	60	255	137		8.94	0.84	1.21(0.67)	Minikin and others, 1994
Filchner Ice Shelf	79°00' S	057°00' W		270	140			0.50		Moser and others, 1990
Georg von Neumayer	70°00' S	008°00' W		0	350			0.30		Moser and others, 1990
Rutford	78°33' S	082°58' W	160	420			4.93	0.86	0.62	This paper
Ski Hi depot	74°58' S	070°46' W	1372	220			2.16	0.94	0.65	This paper
Base camp	82°28' S	166°00' W		450		4.30	5.01*			Warburton and Linkletter, 1977
C-16	81°11' S	170°29' E	70	360	100		4.40	0.60	0.83	Herron, 1982
C-7	78°58' S	176°00' W	0	70		8.50	9.90*			Warburton and Linkletter, 1977
C-7-1	78°30' S	177°00' W		0	130	26.00	30.29*			Herron and Langway, 1979
E-8	84°37' S	169°42' W		670		0.50	0.58*			Warburton and Linkletter, 1977
F-8	84°18' S	172°12' W		640		1.50	1.75*			Warburton and Linkletter, 1977
G-8	83°30' S	171°00' W		580		1.40	1.63*			Warburton and Linkletter, 1977
H-9	83°11' S	168°48' W		520		1.05	1.22*			Warburton and Linkletter, 1977
I-8	82°30' S	165°12' W		460		1.95	2.27*			Warburton and Linkletter, 1977
J-8	82°05' S	165°24' W		400		1.40	1.63*			Warburton and Linkletter, 1977
J-9	82°22' S	168°40' W	55	450	90	4.30	5.01*			Herron and Langway, 1979
L-7	81°23' S	165°00' W		280		2.10	2.45*			Warburton and Linkletter, 1977
Little America V	78°10' S	162°13' W		0		19.00	22.14*			Langway and others, 1974
M-7	80°56' S	164°06' W		230		4.10	4.78*			Warburton and Linkletter, 1977
Q-13	78°57' S	179°55' E	50	130	140			0.70	1.20	Herron, 1982
RIC	80°11' S	161°48' W		150		3.80	4.43*			Warburton and Linkletter, 1977
Roosevelt Island	79°22' S	161°40' W		130		5.70	6.64*			Warburton and Linkletter, 1977
Ross Is Windless Bight	77°45' S	167°00' E		0			12.00	1.00	2.00	Palais and others, 1989
Dominion Range	85°15' S	166°10' E	2780	1100	35			1.60		Lyons and others, 1990
N.Victoria Land E10	72°00' S	165°00' E	1400	130	160	3.60	4.20	0.60	1.00	Allen and others, 1985
N.Victoria Land M1	72°00' S	162°00' E	2305	230	160	3.80	4.60	0.82	1.10	Allen and others, 1985
South Victoria Land	77°32' S	160°35' E		100				1.10		Lyons and others, 1990
Byrd	79°59' S	120°01' W	1530	700	160		1.70	0.65	0.74	Herron, 1982

* Indicates where Cl⁻ values have been calculated from Na⁺ given in the original reference, using normal sea-salt ratios.

Figures in brackets are the xsSO₄²⁻ concentrations for the Filchner–Ronne Ice Shelf calculated in the conventional manner using normal sea-salt ratios.

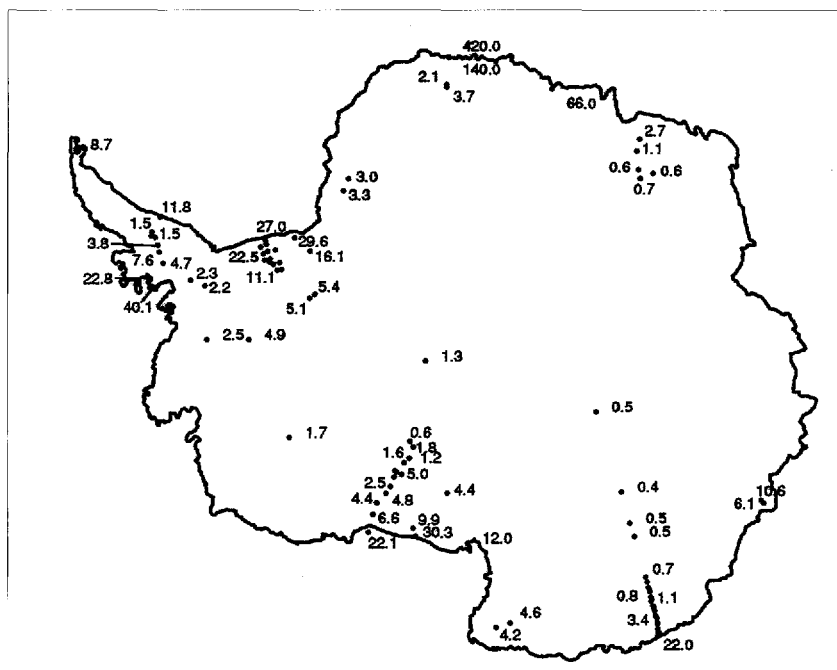


Fig. 1. The spatial distribution of Cl^- data across Antarctica is shown along with Cl^- concentrations in $\mu eq l^{-1}$. In areas where there are a great number of data points, selected concentrations only have been given for clarity.

shelves, distance from the coast varies independently of altitude, so that this factor alone can be investigated.

In Figure 4, we have plotted the data against distance. The much higher Cl^- values near the coast on the Filchner–Ronne Ice Shelf compared to the Ross Ice Shelf are perhaps due to differences in width of fringing sea ice (so that the true distance to a large body of open water is implied to be greater at the Ross Ice Shelf). There would also be an effect if there were greater wind speeds carrying sea spray to the FRIS. The rate of decline in concentration with distance will be controlled by scavenging losses

during transport, which are governed by factors such as wind speed and accumulation rate.

The data from Berkner Island lie within the trend of the FRIS data. The implication is that, at least across open topography as on FRIS, altitude (at least up to 1000 m) has little additional effect on concentrations. However, it is also apparent that at other sites with steep coastal topography (e.g. the line of D sites and Coats Land) there is a much more rapid decrease than on open ice shelves. There is no indication of higher concentrations at low-accumulation sites (Dome C, Vostok) and

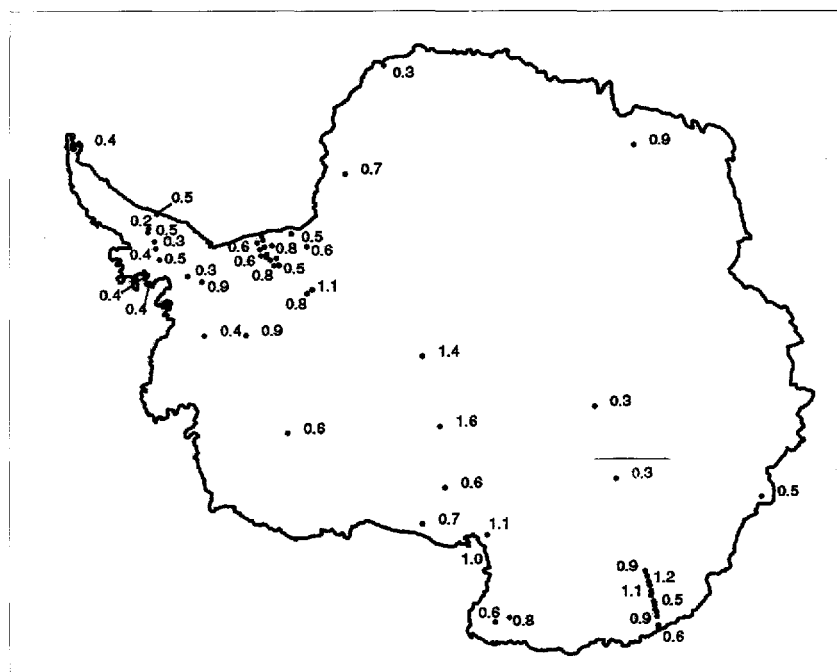


Fig. 2. The spatial distribution of NO_3^- data across Antarctica is shown along with NO_3^- concentrations in $\mu eq l^{-1}$. In areas where there are a great number of data points, selected concentrations only have been given for clarity.

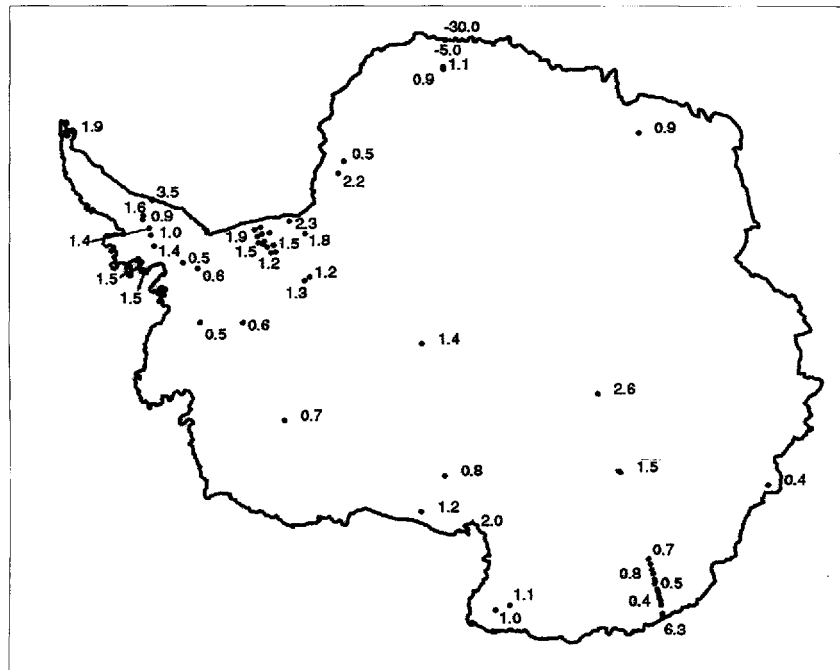


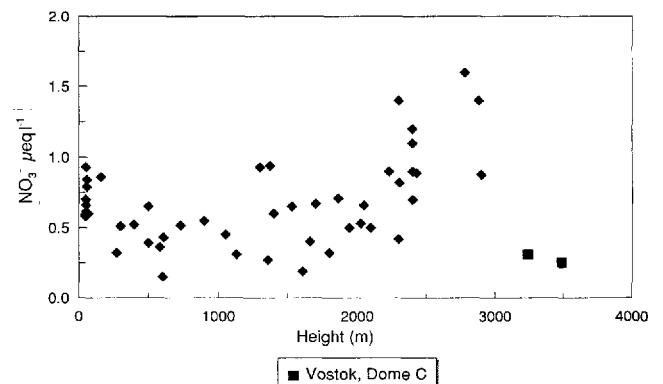
Fig. 3. The spatial distribution of $xs\text{SO}_4^{2-}$ data across Antarctica is shown along with $xs\text{SO}_4^{2-}$ concentrations in $\mu\text{eq l}^{-1}$, calculated as described in the text. In areas where there are a great number of data points, selected concentrations only have been given for clarity.

high-altitude central eastern sites show uniformly low concentrations below $1\ \mu\text{eq l}^{-1}$. Finally, the ratio Cl^-/Na^- is close to the sea-water ratio at most sites, with notable exceptions at very low-accumulation rate sites — Dome C and Vostok. This may imply post-depositional evaporation of HCl, analogous to the effects suggested for HNO_3 (Mayewski and Legrand, 1990; Wolff, in press).

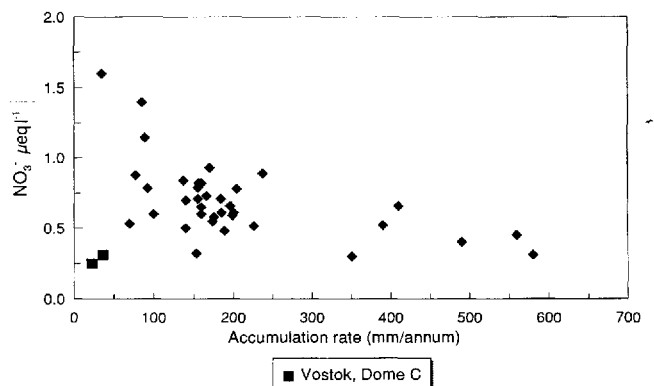
4.2. NO_3^-

The main feature of NO_3^- (present mainly as HNO_3) concentrations across Antarctica is their extraordinary uniformity. The Filchner Ronne Ice Shelf data indicate that there is no effect of distance from the sea (Minikin and others, 1994). Plots of NO_3^- (Fig. 5a and b) against altitude and accumulation rate show that there is a tendency for NO_3^- to increase with altitude but decrease with accumulation rate. There are two outliers — Vostok

and Dome C. Profiles of NO_3^- against depth from these sites show a steady decrease in concentration from the surface to approximately 1 m (Mayewski and Legrand,



a



b

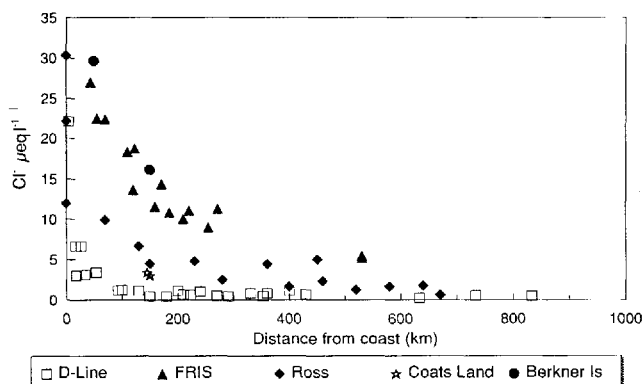


Fig. 4. The concentration of Cl^- from the French chain of D sites, the Ross Sea, the Filchner Ronne Ice Shelf, including Berkner Island, and Coats Land plotted against distance from the coast.

Fig. 5. a. NO_3^- versus altitude; b. NO_3^- versus accumulation range.

1990). This has been explained as resulting from a post-depositional loss of HNO_3 from the snow, either by evaporation or perhaps photolysis, at these sites where it takes a decade or more for 1 m of snow to accumulate (Neubauer and Heumann, 1988; Wolff, in press). For the remaining sites, NO_3^- appears to increase with altitude, though very low-altitude sites do not fit well with this trend. An altitude dependence might imply a NO_3^- source high in the atmosphere, perhaps from the stratosphere. The two major expected sources for NO_3^- (Legrand and Kirchner, 1990) are the stratosphere and tropical lightning, from which NO_3^- may be transported through the stratosphere. Kamiyama and others (1989) and Dahe and others (1992) both noted very high NO_3^- concentrations in surface snow at high-altitude sites. An accumulation-rate dependence would imply a high proportion of dry deposition at central Antarctic sites, or it may be explained by a relatively constant flux of NO_3^- to the surface, with dilution at higher-accumulation sites. It is clear that we do not yet understand fully the deposition mechanism of NO_3^- and further investigation is urgently required.

4.3. xs SO_4^{2-}

Data from both FRIS and the Ross Ice Shelf show xs SO_4^{2-} decreasing with distance from the coast (Fig. 6), while the French line of D sites shows no similar effect. However, it should be pointed out that, when the FRIS data are recalculated using conventional sea-salt ratios, the trend in the data is more similar to that of the D sites. Mulvaney and others (1993) found that the concentration of Cl^- falls off more quickly with distance from the coast than does xs SO_4^{2-} . The data presented here confirm this and the explanation is likely to be a more successful scavenging mechanism for Cl^- than for SO_4^{2-} . xs SO_4^{2-} appears largely independent of both accumulation rate and altitude, though the high concentrations at the central East Antarctic sites is slightly anomalous and may indicate the effect of dry deposition. The high concentration, dominated by large summer peaks, found at Dolleman Island is believed to be due to the close proximity of the biologically produced DMS (Mulvaney and others, 1992). Similar high values for xs SO_4^{2-} are also found at the coastal sites of Cap Prudhoe and A-5, and we can assume that this is also due to the productivity of the nearby ocean.

5. CONCLUSIONS

Cl^- decreases with distance from the sea but the coastal topography is also important, with open ice shelves allowing more sea salt to be carried inland than in areas with coastal mountains. No single formula involving distance from the coast and altitude describes all the data, and more data are needed to define regimes where the two factors (as well as possible post-depositional losses inland) are dominant. This may lead to insights into source areas and transport strengths across the continent. More sophisticated studies will need to look at the variation between sites in different seasons, as the seasonal variability can be huge at some sites.

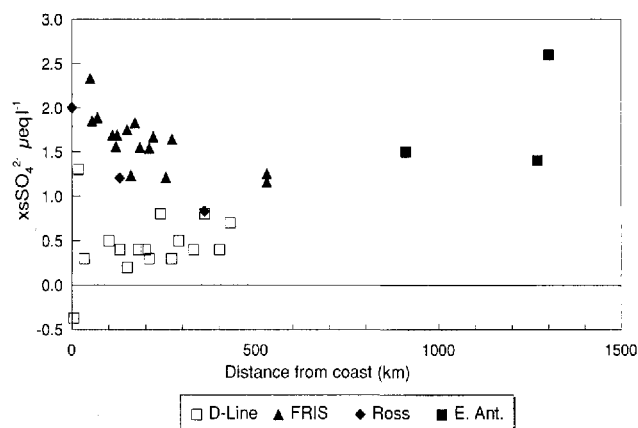


Fig. 6. The concentration of xs SO_4^{2-} from the French chain of D sites, the Filchner–Ronne Ice Shelf, the Ross Sea and the central East Antarctic sites against distance from the coast.

There is a remarkable uniformity in the spatial distribution of NO_3^- throughout Antarctica but we have noted the importance of post-depositional loss of HNO_3 particularly in low-accumulation areas. There is evidence that NO_3^- concentration is dependent on accumulation rate and/or altitude. A variety of process studies is essential to understand the factors controlling NO_3^- deposition.

The close proximity of biologically productive areas leads to high concentrations of xs SO_4^{2-} during the summer. Further inland, xs SO_4^{2-} decreases, though not as rapidly as Cl^- . It will not be possible to explore further the significance of xs SO_4^{2-} spatial variability until the factors controlling sea-salt fractionation are understood, so that an appropriate method of calculating xs SO_4^{2-} at all sites can be established.

These limited conclusions show the need for collection of additional samples along with carefully designed experiments to investigate post-depositional modification. There are large areas of Antarctica where the data are sparse and it is anticipated that initiatives such as ITASE will rectify this. The maps (Figs 1–3) point out the severe lack of data on the high polar plateau, and even around sites where multi-national deep ice-core drilling has been proposed. Records covering at least years to decades, and several metres of snow, are needed; large numbers of very shallow cores or surface-snow samples are less useful in this respect. Understanding NO_3^- deposition and sea-salt fractionation at the process level is also required. With this in place, the spatial distribution of these species can offer significant insights to sources and transport that will greatly enhance our ability to interpret the temporal records in ice cores.

REFERENCES

- Allen, B., P. Mayewski, W.B. Lyons and M.J. Spencer. 1985. Glaciochemical studies and estimated net mass balance for Rennick Glacier area, Antarctica. *Ann. Glaciol.*, **7**, 1–6.
- Aristarain, A.J., R.J. Delmas and M. Briat. 1982. Snow chemistry on James Ross Island (Antarctic Peninsula). *J. Geophys. Res.*, **87**, C13, 11,004–11,012.
- Boutron, C. and C. Lorius. 1977. Trace element content in East Antarctica snow samples. *International Association of Hydrological Sciences*

- Publication 118 (Symposium at Grenoble, 1975 — *Isotopes and impurities in snow and ice*), 164–171.
- Brocas, J. and R. Delwiche. 1963. Cl, K, and Na concentrations in Antarctic snow and ice. *J. Geophys. Res.*, **68**(13), 3999–4000.
- Dahe, Q., E. J. Zeller and G. A. M. Dreschhoff. 1992. The distribution of nitrate content in the surface snow of the Antarctic ice sheet along the route of the 1990 International Trans-Antarctica Expedition. *J. Geophys. Res.*, **97**(A5), 6277–6284.
- Delmas, R., M. Briat and M. Legrand. 1982. Chemistry of South Polar snow. *J. Geophys. Res.*, **87**(C6), 4314–4318.
- Giovinetto, M. B. and C. Bull. 1987. *Summary and analysis of surface mass balance compilations for Antarctica, 1960–1985*. Byrd Polar Research Center, Report No. 1.
- Giovinetto, M. B., N. M. Waters and C. R. Bentley. 1990. Dependence of Antarctic surface mass balance on temperature, elevation, and distance to open ocean. *J. Geophys. Res.*, **95**(D4), 3517–3531.
- Gjessing, Y. 1989. Excess and deficit of sulfate in polar snow. *Atmos. Environ.*, **23**(1), 155–160.
- Görlach, U. and C. F. Boutron. 1992. Variations in heavy metals concentrations in Antarctic snows from 1940 to 1980. *J. Atmos. Chem.*, **14**, 205–222.
- Graf, W. and 6 others. 1991. Isotopic and chemical investigations of 10 m firn cores from the eastern part of the Ronne Ice Shelf, Antarctica. In Miller, H. and H. Oerter, eds. *Filchner-Ronne-Ice-Shelf-Programme, Report No. 5*. Bremerhaven, Alfred Wegener Institute, 45–53.
- Herron, M. M. 1982. Impurity sources of F, Cl, NO₃ and SO₄²⁻ in Greenland and Antarctic precipitation. *J. Geophys. Res.*, **87**(C4), 3052–3060.
- Herron, M. M. and C. C. Langway, Jr. 1979. Dating of Ross Ice Shelf cores by chemical analysis. *J. Geophys. Res.*, **24**(90), 345–357.
- Ivey, J. P., D. M. Davies, V. Morgan and G. P. Ayers. 1986. Methanesulphonate in Antarctic ice. *Tellus*, **38B**(5), 375–379.
- Kamiyama, K., Y. Ageta and Y. Fujii. 1989. Atmospheric and depositional environments traced from unique chemical compositions of the snow over an inland high plateau, Antarctica. *J. Geophys. Res.*, **94**(D15), 18,515–18,519.
- Langway, C. C., Jr. M. Herron and J. H. Cragin. 1974. Chemical profile of the Ross Ice Shelf at Little America V, Antarctica. *J. Glaciol.*, **13**(69), 431–435.
- Legrand, M. R. and R. J. Delmas. 1984. The ionic balance of Antarctic snow: a 10-year detailed record. *Atmos. Environ.*, **18**(9), 1867–1874.
- Legrand, M. and R. J. Delmas. 1985. Spatial and temporal variations of snow chemistry in Terre Adélie (East Antarctica). *Ann. Glaciol.*, **7**, 20–25.
- Legrand, M. R. and R. J. Delmas. 1986. Relative contributions of tropospheric and stratospheric sources to nitrate in Antarctic snow. *Tellus*, **38B**, 236–249.
- Legrand, M. R. and R. J. Delmas. 1988a. Formation of HCl in the Antarctic atmosphere. *J. Geophys. Res.*, **93**(D6), 7153–7168.
- Legrand, M. R. and R. J. Delmas. 1988b. Soluble impurities in four Antarctic ice cores over the last 30,000 years. *Ann. Glaciol.*, **10**, 116–120.
- Legrand, M. R. and S. Kirchner. 1990. Origins and variations of nitrate in south polar precipitation. *J. Geophys. Res.*, **95**(D4), 3493–3507.
- Legrand, M. and C. Saigne. 1988. Formate, acetate and methanesulphonate measurements in Antarctic ice: some geochemical implications. *Atmos. Environ.*, **22**(5), 1011–1017.
- Legrand, M. R., 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**(2), 317–331.
- Legrand, M., C. Feniet-Saigne, E. S. Saltman and C. Germain. 1992. Spatial and temporal variations of methanesulfonic acid and non sea salt sulfate in Antarctic ice. *J. Atmos. Chem.*, **14**, 245–260.
- Lorius, C., G. Baudin, J. Citanova and R. Platzler. 1969. Impuretés solubles contenues dans la glace de l'Antarctique. *Tellus*, **21**(1), 136–148.
- Lyons, W. B., P. A. Mayewski, M. J. Spencer and M. S. Twickler. 1990. Nitrate concentrations in snow from remote areas: implication for the global NO_x flux. *Biogeochemistry*, **9**, 211–222.
- Mayewski, P. A. and M. R. Legrand. 1990. Recent increase in nitrate concentration of Antarctic snow. *Nature*, **346**(6281), 258–260.
- Mimikin, A., D. Wagenbach, W. Graf and J. Kipfstuhl. 1994. Spatial and seasonal variations of the snow chemistry at the central Filchner-Ronne Ice Shelf, Antarctica. *Ann. Glaciol.*, **20** (see paper in this volume).
- Morgan, V. I. 1982. Antarctic ice sheet surface oxygen isotope values. *J. Glaciol.*, **28**(99), 315–323.
- Moser, K., D. Wagenbach and K. O. Münnich. 1990. Nitrate in coastal Antarctic shallow firn cores: comparison of seasonal pattern and of total flux. (Abstract.) *Ann. Glaciol.*, **14**, 349.
- Mosley-Thompson, E., J. Dai, L. G. Thompson, P. M. Grootes, J. K. Arbogast and J. F. Paskievitch. 1991. Glaciological studies at Siple Station (Antarctica): potential ice-core paleoclimatic record. *J. Glaciol.*, **37**(125), 11–22.
- Mulvaney, R. and D. A. Peel. 1988. Anions and cations in ice cores from Dolleman Island and the Palmer Land plateau, Antarctic Peninsula. *Ann. Glaciol.*, **10**, 121–125.
- Mulvaney, R. and E. W. Wolff. 1993. Evidence for winter/spring denitrification of the stratosphere in the nitrate record of Antarctic firn cores. *J. Geophys. Res.*, **98**(D3), 5213–5220.
- Mulvaney, R., E. C. Pasteur, D. A. Peel, E. S. Saltzman and P.-Y. Whung. 1992. The ratio of MSA to non-sea-salt sulphate in Antarctic Peninsula ice cores. *Tellus*, **44B**, 295–303.
- Mulvaney, R., G. F. J. Coulson and H. F. J. Corr. 1993. The fractionation of sea salt and acids during transport across an Antarctic ice shelf. *Tellus*, **45B**(2), 179–187.
- Mumford, J. W. and D. A. Peel. 1982. Microparticles, marine salts and stable isotopes in a shallow firn core from the Antarctic Peninsula. *Br. Antarct. Surv. Bull.*, **56**, 37–47.
- Murozumi, M. and S. Nakamura. 1974. Chemical investigations of polar snow strata. In Kuroiwa, D., ed. *Physical and chemical studies on ice from glaciers and ice sheets*. Sapporo, Hokkaido University, 65–75.
- Ncubauer, J. and K. G. Heumann. 1988. Nitrate trace determinations in snow and firn core samples of ice shelves at the Weddell Sea, Antarctica. *Atmos. Environ.*, **22**(3), 537–545.
- Osada, K. and K. Higuchi. 1990. Transport rates of Na⁺, Cl⁻, NO₃ and SO₄²⁻ by drifting snow at Mizuho Station, Antarctica. *Proc. NIPR Symp. Polar Meteorol. Glaciol.*, **3**, 43–50.
- Palais, J. M., R. Chuan and M. J. Spencer. 1989. Soluble and insoluble impurities in snow samples from Ross Island, Antarctica. *Ant. J. U.S.*, **24**(5), 89–91.
- Savoie, D. L., J. M. Prospero, R. J. Larsen and E. S. Saltzman. 1992. Nitrogen and sulfur species in aerosols at Mawson, Antarctica, and their relationship to natural radionuclides. *J. Atmos. Chem.*, **14**, 181–204.
- Suttie, E. D. and E. W. Wolff. 1992. Seasonal input of heavy metals to Antarctic snow. *Tellus*, **44B**, 351–357.
- Wagenbach, D., U. Görlach, K. Moser and K. O. Münnich. 1988. Coastal Antarctic aerosol: the seasonal pattern of its chemical composition and radionuclide content. *Tellus*, **40B**(5), 426–436.
- Wagenbach, D. and 6 others. 1994. Reconnaissance of chemical and isotopic firn properties on top of Berkner Island, Antarctica. *Ann. Glaciol.*, **20** (see paper in this volume).
- Warburton, J. A. and G. O. Linkletter. 1977. Precipitation-forming mechanisms and the chemistry of precipitation on the Ross Ice Shelf, Antarctica. *International Association of Hydrological Sciences Publication 118* (Symposium at Grenoble, 1975 — *Isotopes and Impurities in Snow and Ice*), 88–94.
- Wolff, E. W. In press. Nitrate in polar ice. In *Global biogeochemical cycles in polar ice*. Berlin, Springer-Verlag.
- Yun-gang, L., Z. Yun-hui, L. Gui-qun and X. Lun. 1988. Analysis of trace elements in the BHQ ice core, Law Dome, Antarctica. (Abstract.) *Ann. Glaciol.*, **11**, 219.

The accuracy of references in the text and in this list is the responsibility of the authors, to whom queries should be addressed.