Tellus (1986), *38B*, 375-379

Methanesulphonate in Antarctic ice

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(Manuscript received November 8, 1985; in final form May 21, 1986)

ABSTRACT

Methanesulphonate was investigated as a potential contributor to the sulphur budget and to the acidity of Antarctic ice from Law Dome (66°30′S, 113°00′E). The anion was found to be present at a mean concentration of 0.08 μeq/l and ranged between 0.006 and 0.28 μeq/l. Although methanesulphonate was only a minor anion in comparison with chloride and sea salt sulphate, it was comparable with nitrate and excess sulphate. The concentration of methanesulphonate in the ice did not correlate significantly with excess sulphate nor was there a simple seasonal dependence such as is found for non-sea salt sulphate.

1. Introduction

The analysis of the anionic composition of precipitation from remote areas provides a useful perspective against which anthropogenic influences can be compared (Delmas and Gravenhorst, 1982; Galloway et al., 1982, 1984). Change in composition may reflect global changes in the atmospheric environment with consequences for climatic change. The anionic composition also gives insight into the natural cycling of nitrogen, sulphur and carbon containing atmospheric constituents, and in the case of glacial ice, can assist in the understanding of past climatology (Legrand and Delmas, 1984).

In comparison with studies in urban and industrial areas there has been relatively little work on unpolluted precipitation from remote areas. Despite this, two findings have emerged that give insight into the natural sulphur cycle. They are (1) dimethylsulphide gas is an important contributor to the atmospheric sulphur budget and a significant source of aerosol sulphur in the marine atmosphere (Barnard et al., 1982; Saltzman et al., 1983) and (2) methanesulphonic acid, a relatively stable product of the atmospheric photo-oxidation of dimethylsulphide (Grosjean, 1984; Hatakeyama et al., 1985; Saltzman et al., 1983; Ayers et al., 1986) has been found in maritime aerosol samples from low and southern-mid latitudes.

Antarctic precipitation is arguably as remote from urban and industrial influence as it is possible to be. To date, the acidity and anionic composition of Antarctic ice has been interpreted in terms of a sea salt contribution plus trace quantities of nitric and sulphuric acids that are ubiquitous in the atmosphere (Legrand and Delmas, 1984). In this note we report the results of chemical analysis of 62 ice core sections from Law Dome, Antarctica, spanning two 2.5 year periods of deposition near 1920. The particular aims of this work are to ascertain: (1) the existence or otherwise of methanesulphonate in the ice, (2) the importance of this anion in comparison with sulphate and sulphite as a potential source of ice acidity and sulphur, (3) any apparent correlation between methanesulphonate concentration with that of non-sea salt sulphate.

2. Experimental

Ice cores were collected as part of the Australian National Antarctic Research Expedition (ANARE) glaciology research program at Law Dome (66°30′, 113°00′E) approximately 120 km east of Casey Base, an

Australian Antarctic coastal station. The two ice cores were cut into equal depth sections which, owing to the variation in annual accumulation layer thickness, resulted in annual accumulations being represented by ten or up to twelve sections. Part of each section was used to determine the oxygen isotope profile which was then used to define which sections fell within each annual accumulation. The two lengths of core were each found to represent approximately 2.5 years of deposition. There was also a discontinuity between the two cores where a similar 2.5 year length of core was used for another purpose (carbon dioxide measurements).

Each section was trimmed to leave approximately 200 g of the inner part of the core. 25% of this was then removed by washing repeatedly in distilled deionized water (resistivity > 18 Mohm/cm^2) and a further 25% by allowing the section to melt in a precleaned polyethylene funnel. Problems were experienced earlier with gaseous contaminants contributing nitrate and nitrite to the exposed ice melting in a clear air cabinet. To prevent this occurring the air exposed to the melting ice was purified by passing it through an acid gas adsorption tube of Ascarite prior to particle filtration (0.45 μm).

Samples treated in this way were found to have no detectable levels of nitrite, and nitrate levels were reduced. After about half of the samples had been prepared in this way, blank frozen distilled water began to show traces of sodium, possibly from Ascarite particles penetrating the filter. The procedure was then changed so that 50% of the original ice was removed by multiple washing in distilled deionized water and the remainder allowed to melt in a sealed polyethylene bag (Whirlpak). The meltwater was analysed without delay.

Sodium and magnesium were determined by atomic absorption spectroscopy. Methanesulphonate, chloride, nitrite, nitrate, sulphate and sulphite were analysed by ion chromatography. The column used to separate the anions was a Dionex AS3 column, and the eluent was 0.0007 M sodium bicarbonate for methanesulphonate and chloride. The eluent for nitrite, nitrate and sulphate was 0.002 M sodium carbonate. Sulphite, as the hydroxymethanesulphonate adduct, was eluted with an eluent of 0.0009 M sodium bicarbonate containing 0.2% formaldehyde (Davies and Ivey, in press). Replicate analysis indicated that the analytical precision was within 10% for all species. Detection limits for most anions were 0.005 μeq/l using a 5 ml injection volume (signal/noise of 3). A typical chromatogram showing separation of methanesulphonate from chloride is shown in Fig. 1. Full analytical details will appear elsewhere (Ivey and Davies,, 1986).

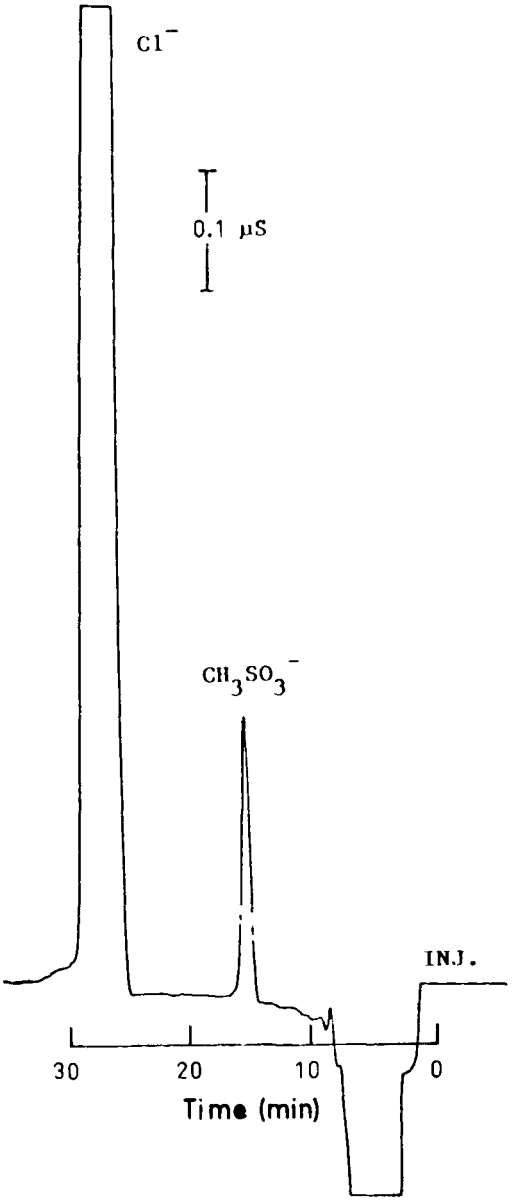

Fig. 1. Typical ion chromatogram of methanesulphonate and chloride in Law Dome ice at respective concentrations of 0.17 and 8.7 μeq/l.

3. Results

The mean concentration and annual deposition of the ions determined are shown in Table 1. Only the 44 results from the two annual cycles in each core have been considered. The range values are from the complete data. The two extra winters that occur in the 62 samples have been excluded to prevent bias in the calculated value for annual deposition. The mean number of samples for a year was calculated on the basis of the isotope profile and the slice width normalized so that the data were reduced to a single annual cycle. A cubic spline function with four points averaging and smoothing was fitted by interpolation (Fig. 2).

Non-sea salt sulphate was calculated for each sample by subtraction of a "sea salt" component from the observed sulphate concentration. The sea salt component is usually estimated by assuming that sodium and magnesium originate from sea salt aerosol only and that the molar ratio of 0.06030 for sulphate to sodium or 0.5305 for sulphate to magnesium (Millero, 1974) is maintained in the salt aerosol. As in some samples an excess over the sea water ratio of sodium to magnesium was noted, we have chosen to use the magnesium content to calculate excess sulphate. The use of the magnesium ratio resulted in fewer negative non-sea salt sulphate values. The remaining negative non-sea salt sulphate results are within a reasonable measure of the cumulative analytical uncertainty (20% of total sulphate concentration).

4. Discussion

As noted in the introduction we restrict ourselves here to discussion of three specific points. Other questions concerning, for example, the importance of other acids such as hydrochloric and nitric acids will be addressed elsewhere when cores spanning several more annual cycles have been analysed.

The first point concerns the presence of methanesulphonate in the ice cores. Methanesulphonate was detected in all sections of ice core at a concentration between 0.006 μeq/l and 0.28 μeq/l. This compares with reported rainwater concentrations of between 0.06 and 1.56 μeq/l in monthly rainwater samples from Cape Grim, a remote coastal site (Ayers et al., 1986) and, 0.03 to 1.06 μeq/l from Miami (Saltzman et al., 1983) although these latter measurements did not span a full year.

The second point concerns the potential contribution to acidity and the sulphur budget made by methanesulphonate in comparison with sulphate and sulphite. A recent estimate of selected sulphur deposition in the Antarctic (Delmas, 1982) was made by summing the measured sulphate, and sulphur dioxide based on its deposition velocity and concentration in the Antarctic atmosphere. This summation implies that deposited sulphur dioxide is present in the ice as a species other than sulphate, presumably sulphite, or perhaps a more stable aldehyde adduct. Our measurements (Davies and Ivey, 1986) which can detect sulphite or its

Table 1. *Mean concentration, standard deviation, annual deposition and range in the concentration of ions in Law Dome ice. Concentrations in μeq/l. deposition in μeq/m²/yr. Mean annual ice thickness 0.63 m, ice density 0.83 g/ml.*

	Na^+	Mg^{2+}	Cl^-	SO_4^{2-}	NO_3^-	$CH_3SO_3^-$	xs SO_4^{2-}
Arithmetic mean	5.82	1.02	6.08	0.92	0.48	0.077	0.39
Number of Samples	44	44	44	44	44	44	44
Standard Deviation	4.58	0.67	5.25	0.64	0.40	0.06	0.50
Annual Deposition	3040	530	3170	480	250	40	200
Range: max.	22.2	3.4	28.5	4.1	1.69	0.28	2.4
min.	0.74	0.16	1.10	1.15	0.10	0.006	−0.42

All samples (see text). xs = non-sea salt sulphate.

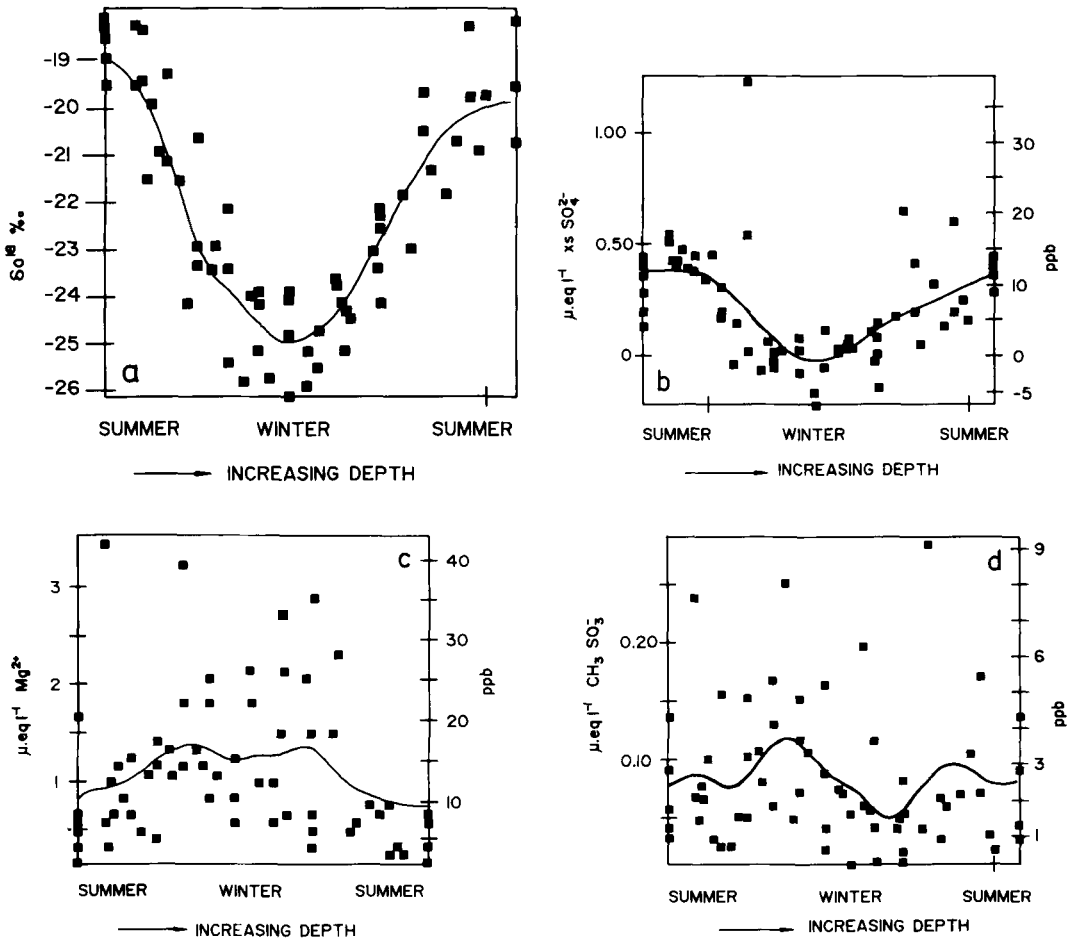

Fig. 2. Annual variations in: (a) oxygen isotope ratio, (b) concentration of non-sea salt [xs] sulphate, (c) magnesium and (d) methanesulphonate in Law Dome ice. The curve fitted through the 62 points is a cubic spline curve with points averaging and smoothing. The concentration units, ppb, are μg/l and as sulphur for methanesulphonate and non-sea salt sulphate.

formaldehyde adduct at a concentration of 0.003 μeq/l, have failed to show that either of these two species is present. This leaves only methanesulphonate and sulphate as potential acid contributors via their protonated parent species. On the asssumption that both were originally present at some stage as their respective acids, it is clear that methanesulphonate is a relatively significant source of acidity contributing 17% of the total sulphur source acidity and thus 29% of sulphur deposition.

Our third point concerns the presence of any interdependency exhibited by methanesulphonate and excess sulphate concentrations in the ice. Such a relationship has been established in aerosol samples collected in the mid-Pacific Ocean (Saltzman et al., 1985). In Fig. 2, the two 2.5 year cycles in the oxygen isotope record, non-sea salt sulphate, methanesulphonate and magnesium have been compounded into a single cycle per ion. Other than the isotope record, only the non-sea salt sulphate concentration shows a simple consistent seasonal variation with a summer maximum. Magnesium concentration, as an indicator of sea salt, shows a minimum in the summer with maximum levels occurring broadly

throughout the winter period. Maximum levels in individual years tend to occur either just before or after the minima in the oxygen isotope profile resulting in the secondary minima in the magnesium cubic spline curve.

The methanesulphonate distribution displayed no simple annual variation. We were unable to establish any significant correlation between the concentration of methanesulphonate and non-sea salt sulphate (correlation coefficient 0.15), although this has been shown for other locations (Saltzman et al., 1985). There are several factors that would be expected to influence the aerosol concentration of methanesulphonate and hence the ice concentration at our site. Among these are: prevailing meteorology and its effect on transport, sea ice extent, the level of marine production of the precursor dimethylsulphide, the rate of reaction of dimethylsulphide in the Antarctic atmosphere and the yield of methanesulphonate from that gas. Whilst a detailed discussion of these factors is premature, we feel that the annual variation exhibited by our results is probably due to seasonal changes in the relative influence of these factors. Further speculation must await aerosol measurements of methanesulphonate and analysis of ice from central Antarctica.

Finally, a point worthy of consideration is that if the annual deposition of methanesulphonate is found to be reasonably consistent, its measurement may well provide a baseline from which changes in other ice consistents due to volcanic or anthropogenic influence can be compared.

5. Conclusion

Methanesulphonate has been found in ice core samples from Law Dome, Antarctica, and represents a significant source of sulphur and acidity deposition in comparison with non-sea salt sulphate. Methanesulphonate concentration in the ice varied independently of non-sea salt sulphate and magnesium (sea salt) concentrations.

6. Acknowledgement

This work was supported with funding from the Australian Department of Science.

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