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Ice-core record of oceanic emissions of dimethylsulphide during the last climate cycle

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making it hydrophobic. This surface-hydrophilic rubber film, however, remained completely water-wettable even after many days of rinsing. The amphiphilic block copolymer responsible for the wettability is attached quite firmly (probably covalently) to the rubber surface. The bulk of the material remained totally hydrophobic: there was no detectable swelling of the film by water.

Further evidence that the amphiphilic block copolymer is attached to the rubber surface and not dissolved in the water is obtained by transferring water that has been spread over the hydrophilic rubber onto an ordinary hydrophobic film. The water beads up in a manner similar to that shown in Fig. 1*a*, indicating that the surface tension of the water has not been substantially reduced. When it is placed back on the hydrophilic rubber, the same water spreads again. This procedure can be repeated many times, and demonstrates that the spreading of water over the rubber film is due to the surface hydrophilicity of the film rather than lowering of the liquid's surface tension. □

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Ice-core record of oceanic emissions of dimethylsulphide during the last climate cycle

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THE Vostok ice core in Antarctica has provided one of the longest climate records, enabling the stable-isotope, major-ion and gas composition of the atmosphere to be reconstructed over many thousands of years. Here we present depth profiles along this core of methanesulphonate and non-seasalt sulphate (produced by the atmospheric oxidation of dimethylsulphide), which provide the first historical record of biogenic sulphur emissions from the Southern Hemisphere oceans over a complete glacial–interglacial cycle (160 kyr). Those measurements confirm and extend some previous observations made on a very limited data set from the Dome C ice core in Antarctica, which indicated increased oceanic emissions of dimethylsulphide during the later stages of the glacial period, compared with the present day[1]. The observed glacial–interglacial variations in methanesulphonate and non-seasalt sulphate confirm that the ocean–atmosphere sulphur cycle is extremely sensitive to climate change.

During initial attempts to remove surface contamination from the outer part of the ice-core sections, we washed the core with ultrapure water at a temperature of ~20 °C. This method has been used successfully for the analysis of mineral species[2], and to study methanesulphonate (MSA) content over the past 30 kyr in the Dome C ice core[1]. Vostok data obtained using this procedure are compared with Dome C data for the same climate periods (Table 1). Although the non-seasalt (n.s.s.) sulphate increases from stage A to stage B by a factor of two in both cases, the MSA content at Vostok remains fairly constant during the climate change whereas the Dome C core exhibits an increase by a factor of five from the warm to the cold stage. Such a difference is difficult to understand because Vostok (located 600 km from Dome C on the high Antartic plateau) has similar geographical and meteorological characteristics (elevation, mean annual temperature). Laboratory experiments indicate that extensive rinsing of Vostok ice leads to mobility of MSA, which does not occur with other ions. This effect may be related to the fact that the Vostok core was drilled with kerosene drilling fluid, whereas the Dome C core was drilled dry. In addition, the Vostok core sections were stored for 24 hours at −3 °C before washing, to prevent breakage of the core.

TABLE 1 Non-seasalt sulphate and MSA in the Vostok and Dome C ice cores

	Dome C		Vostok	
	MSA (ng g^{-1})	n.s.s. SO_4^{2-} (ng g^{-1})	MSA (ng g^{-1})	n.s.s. SO_4^{2-} (ng g^{-1})
Holocene	2.5 (W)	70 (W)	4 (W)	108 (W)
(Stage A, 0–10 kyr BP)			5 (L)	102 (L)
Glacial age	13 (W)	136 (W)	5 (W)	230 (W)
(Stage B, 18–30 kyr BP)			31 (L)	222 (L)

W, data obtained by washing the ice-core sections. L, data obtained by subcoring with a lathe (see text). Vostok data, this work; Dome C data, ref. 2.

Subsequently, we designed an ice-core lathe equipped with a stainless-steel knife to mechanically remove the outer part of the core (until 95% of the volume was removed). The MSA content of successive fractions from the outer to the inner part of the core (not reported here) is constant, indicating the reliability of the procedure. Using this method, the increase in MSA during the glacial age in the Vostok core (Table 1) is similar in magnitude to that at Dome C. We prepared 47 ice sections in this manner, each representing approximately six years of accumulation. These sections were cut from the core at roughly 40-m intervals over the length of the 2,080-m core[3].

For each sample, the concentrations of Na^+, Ca^{2+}, SO_4^{2-} and $CH_3SO_3^-$ were determined by ion chromatography. MSA and sulphate were determined using an AS5 separator column, a gradient pump system (Dionex 4000i) and an integrator with an accuracy of 5% (at the 95% confidence level). Cations were measured using working conditions reported elsewhere[4]. In a previous Vostok ice-core study[5], it was established that the calcium content mainly reflects the terrestrial input to the Vostok ice and that it is feasible to estimate the marine component of Na^+ (denoted Na_m^+) from determinations of Ca^{2+} and Na^+. It is then possible to calculate the content of non-seasalt sulphate by subtracting seasalt sulphate from the total sulphate.

The profile of n.s.s. sulphate (Fig. 1*b*) shows moderate glacial–interglacial changes from 98–102 ng g^{-1} during interglacial stages (G and A, respectively) to 208–240 ng g^{-1} during cold stages (B, D and H) (see Table 2). This picture is very similar to that from previously published data[5,6]. Between 1,200 and 1,300 m three samples exhibited unusually high levels of n.s.s. sulphate (>400 ng ml^{-1}). By comparison with data previously obtained at similar depth[5], it seems that these high concentrations are not related to the long-term pattern of sulphate deposition. Instead, they reflect short-term changes associated with volcanic eruptions which sporadically perturb the background level of sulphuric acid in the Vostok precipitation[7]. At these three levels no significant changes in the MSA content is observed. We therefore neglect these values here. The variations in the MSA profile, like those of n.s.s. sulphate, strongly correlate with climate conditions, changing from 5 ng g^{-1} during inter-

TABLE 2 Mean concentrations of MSA and n.s.s. SO_4^{2-} in the Vostok core

Stage	Depth (m)	MSA (ng g^{-1})	n.s.s. SO_4^{2-} (ng g^{-1})	R (%)	MSA′ (ng g^{-1})	n.s.s. $SO_4^{2-\prime}$ (ng g^{-1})	S'	$Q_{s'}$
A	0–275	5±2	102±11	5±1.5	5±2	102±11	107±13	1
B	325–550	31±3	222±7	14±1.5	20±2	146±5	166±5	1.55
C	575–850	22±6	168±14	13±4	16±4	120±9	136±10	1.27
D	875–975	32±2	242±17	13±1	21±1	162±9	183±9	1.70
E	1,000–1,475	13.0±4	139±20	10±4	11±3	109±18	120±17	1.1
F	1,500–1,600	19±3	148±7	13±2	13±2	105±5	118±7	1.1
G	1,625–1,875	5.5±3	98±17	5.4±2	5.5±3	100±11	106±13	1.0
H	1,925–2,080	25±1	208±50	12.5±3	16±1	136±31	152±30	1.4

R is the weight ratio of MSA to n.s.s. SO_4^{2-}. Primed values MSA′ and n.s.s. $SO_4^{2-\prime}$ are concentrations corrected for variations in accumulation rate. S' is the sum of MSA′ and n.s.s. $SO_4^{2-\prime}$ and Q' is the ratio of S' in each stage to S' in stage A.

glacial stages (A and G) to 25–31 ng g^{-1} during very cold stages (B, D and H).

One of the notable features of the record is the similarity of the general trends in MSA and n.s.s. sulphate. Because oceanic sulphur is an important source of MSA, this covariance strongly suggests that n.s.s. sulphate in the precipitation over the central Antarctic is primarily derived from oceanic emissions. It is also possible that sources of non-marine sulphate covary with the marine component. Given recent evidence regarding productivity limitation by aerosol-transported nutrients such as iron[8,9], it is perhaps possible that the marine emissions of dimethylsulphide (DMS) from the southern ocean and the long-range transport of continental-derived sulphate might correlate over long timescales and large variations in climate.

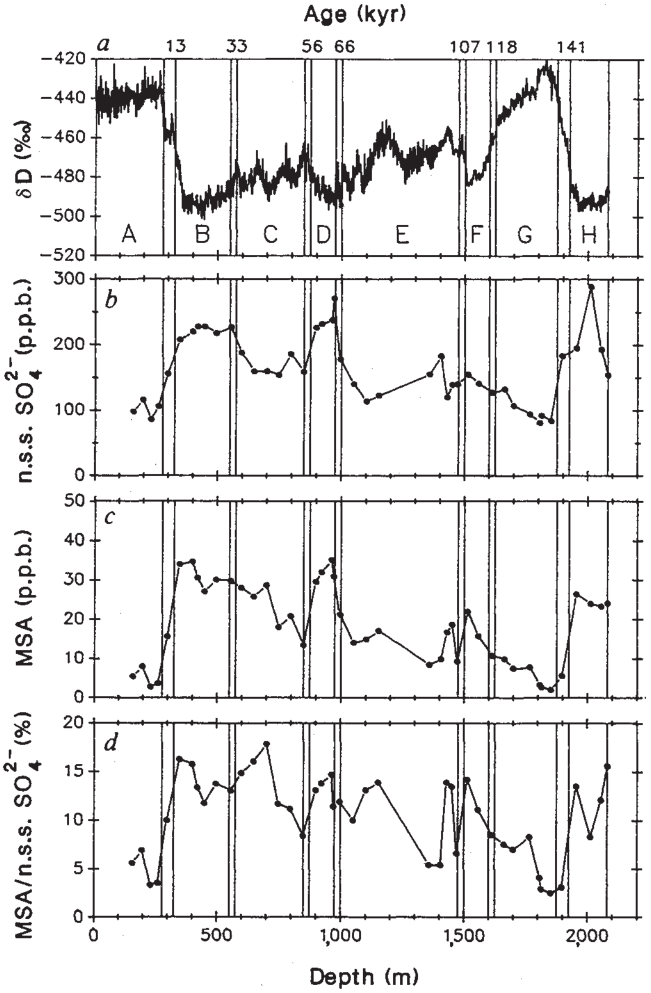

FIG. 1 Depth profiles of *a*, δD, *b*, non-seasalt sulphate, *c*, MSA and *d*, the ratio of MSA to non-seasalt sulphate in the Vostok ice core. Upper and lower stage boundaries are marked by vertical lines. (δD is deuterium isotope profile from ref. 3.)

The relative magnitude of the glacial–interglacial changes in MSA are greater than those of n.s.s. sulphate, resulting in a decrease in the ratio R of MSA to n.s.s. sulphate during warming. During cold stages R is high, with values reaching 14%, and during warm stages R reaches a minimum of 3%. In the present atmosphere, there is a systematic trend of R in marine aerosols, from low ratios in the low and mid-latitudes (2–10%, ref. 10) towards higher ratios at higher latitudes (15–100%; ref. 11). This effect is presumably atmospheric, related to the different temperature-dependence of OH addition and H-atom abstraction in the oxidation of DMS by OH (ref. 12). It is presumed that these different pathways give rise to the two principal products of DMS oxidation, MSA and SO_2 (which is subsequently converted to sulphate). The decrease in R during warming might therefore reflect either increasing temperature in the DMS source region, or a change in the primary DMS source region, with increasing input from long-distance transport from the lower latitudes. Here, we make the implicit assumption that the basic features of the aerosol size distributions of MSA and n.s.s. sulphate (and hence their transport and depositional characteristics) are relatively constant for different climates. This point may bear further investigation in view of recent data indicating that the size distribution of MSA may be dependent on that of the preexisting aerosols[13].

Other possible explanations for the generally low ratios observed in the high Antarctic plateau (for both glacial and interglacial conditions) require the input of a significant non-marine sulphate component. Stratospheric input has historically been considered a possible contribution to the sulphate budget of central Antarctica, but there is now general agreement that this contribution is weak except after sporadic major volcanic eruptions[14–16]. Input of continental-derived sulphate is another possibility, as mentioned above. A significant component of the sulphate present during glacial times, at least, is ionically balanced by calcium and the possibility exists that this sulphate is terrestrially derived. During glacial stages (B, C and D) calcium concentrations in our samples vary widely (more than a factor of three, from 13 to 52 ng g^{-1}), but the ratio R remains essentially constant. This implies that this sulphate was marine in origin and was neutralized in the atmosphere by reaction with calcium carbonate of terrestrial origin.

Because the partitioning between MSA and n.s.s. sulphate seems to be modulated by climate, it is useful to examine the total oxidized sulphur, which we presume to be the sum of MSA and n.s.s. sulphate (Table 2) instead of n.s.s. sulphate alone as in previous studies[5,6]. The higher concentrations of n.s.s. sulphate and MSA found in cold stages are partly due to the reduced accumulation rates during this time. To obtain a more representative picture of the actual atmospheric concentrations in the past, we have corrected concentrations in ice using a method presented elsewhere[6]. We have also assumed that MSA and n.s.s. sulphate have similar deposition processes because both MSA and n.s.s. sulphate are present in the atmosphere as fine particles[10]. The corrected data, shown in Table 2, suggest that the oxidation products of DMS were constant during interglacial stages (stage A and G), but were enhanced significantly during the second part of the glacial age (stage B, C and D). Assuming that inputs of MSA and n.s.s. sulphate over the high Antarctic plateau are related largely to marine DMS emissions at mid-latitudes, our data suggest enhanced productivity from the DMS-producing portion of the oceanic biota between 18 and 70 kyr BP (before present). Whether this increase represents a real increase in oceanic productivity or simply an ecological shift favouring DMS producers is not known. Some workers have suggested that marine sediment cores show evidence for increased productivity between 15 and 70 kyr BP in upwelling areas[17], but this finding remains controversial.

Clearly, the ocean-atmosphere sulphur cycle exhibits variability that is intimately related to global climate change. It has been suggested that the biogenic aerosols themselves play an important part in forcing climate change either through direct radiative effects or through changes in cloud albedo and distribution[6,18,19]. It may be possible to detect the effects of such climate forcing using high-resolution ice-core records which document the timing of changes in biogenic sulphur levels relative to those in stable isotopes, CO_2 and other chemical tracers during periods of rapid climate change. These studies are currently in progress. □

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Amelioration of subsoil acidity by application of a coal-derived calcium fulvate to the soil surface

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SUBSOIL acidity is a serious problem in many tropical and subtropical soils[1–3]. The high acidity, low calcium contents and often toxic levels of soluble and/or exchangeable aluminium severely impair plant-root development in these soils[1–3]. The relative immobility of surface-applied liming materials limits their ability to reduce subsoil acidity. Recently, the use of gypsum or phosphogypsum has been advocated as an alternative to lime[3–7]. On the other hand, it is well known that humic substances can mobilize and form complexes with metals in soils[8–11]. Here we report that a newly available, coal-derived calcium-fulvate is highly efficient as a carrier of calcium in the soil profile. Moreover, subsoil pH was considerably higher when calcium-fulvate was applied to the soil surface, than when gypsum, calcium-EDTA, $Ca(OH)_2$ or $CaCO_3$ were applied.

Fulvic acid was obtained from the wet oxidation of coal at elevated pressure and temperature, using a recently patented process[12]. This process leads to the formation of a water-insoluble product (oxicoal, containing ~80% base-soluble 'humic' acids) and water-soluble 'fulvic' acids (10–15% yield). The fulvic acids, separated by filtration from the oxicoal, were neutralized to pH 7.2 with $Ca(OH)_2$.

We called the resulting 'solution' (actually a stable suspension because colloidal particles are usually still present) Ca-fulvate. The suspension could be dried to a fine, dark powder but, in our experiments, it was used without further drying. It contained 4.18% total solids and 11.26 g Ca l^{-1}.

TABLE 1 Relevant properties of experimental soils

Soil	Clay (<2 μm) (%)	pH (H_2O)	pH (1 mol l^{-1} KCl)	CEC* (soil) ($cmol_c$ kg^{-1})	Exch.† bases (% of CEC)	Exch.† Ca (% of CEC)
Avalon	6.0	4.68	3.74	1.7	29.0	11.5
Hutton UP	20.2	5.02	4.08	3.2	39.7	18.8
Hutton PR	35.6	4.70	3.97	4.3	28.3	18.0

* Cation exchange capacity (cmol of charge per kg soil).
† Exchangeable.

The downward movement of Ca in soil was studied using cylinders 1 m long × 68 mm inside diameter. Plastic sheeting was used as lining to allow the easy removal of the entire soil column for segmentation and analysis. Care was taken to eliminate micro-channels which may result in preferential flow paths at the soil-liner boundary. Three soil types were used in our experiments (Table 1). The columns were carefully packed with dry soil and leached with two pore volumes of deionized water as a pretreatment to remove free salts. The following substances were then added in 150-cm^3 suspensions to the surface of the water-saturated soil column: H_2O (control), $CaCO_3$, $Ca(OH)_2$ (freshly prepared), $CaSO_4 \cdot 2H_2O$, Ca-EDTA and Ca-fulvate. In the Ca treatments 1.689 g Ca was added in each case; this is equivalent to 20 t ha^{-1} gypsum or 11.6 t ha^{-1} $CaCO_3$. The columns were leached with deionized water at a flow rate of 55 mm h^{-1} until two pore volumes of leachate had been collected in measured fractions. This flow rate is fairly high, but of course lower than the hydraulic conductivity of the columns. The effect of flow rate on Ca distribution may be important, but was not studied. After cessation of water inflow, the columns were allowed to drain. The drainage water was collected as a final leachate fraction. The soil column encased within the lining could easily be removed without disturbance, and was cut into 100-mm-long segments. The segments were dried at 353 K and weighed. The leachate fractions were analysed for Ca, Mg, Na, K, Fe and Al and the pH determined. The soil segments were analysed for the following: total soluble and exchangeable Ca, Mg, Na and K extractable with 1 mol^{-1} l^{-1} ammonium acetate (pH 7) using a 1 : 10 soil/solution ratio; soluble cations in a 1 : 1