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THE FIRST GREENLAND ICE CORE RECORD OF METHANESULFONATE AND SULFATE
OVER A FULL GLACIAL CYCLE

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Abstract. Methanesulfonate (MSA) in ice cores has attracted attention as a possible tracer of past oceanic emissions of dimethylsulfide (DMS). After sulfate MSA is the second most prevalent aerosol oxidation product of DMS, but in contrast to sulfate, DMS oxidation is the only known source of MSA. The hypothesis by Charlson et al., [1987] of a climate feedback mechanism with sulfur emissions from marine phytoplankton influencing the cloud albedo adds to the interest in establishing long records of MSA and non-seasalt sulfate spanning large climatic changes. Records of MSA and non-seasalt sulfate covering time periods from a few years to thousands of year have been extracted from antarctic ice cores [Ivey et al., 1986; Saigne and Legrand, 1987; Legrand and Feniet-Saigne, 1991; Mulvaney et al., 1992] but only the record from the Vostok ice core [Legrand et al., 1991] covers a full glacial cycle. The concentrations of MSA and non-seasalt sulfate in Antarctica have been found to increase under glacial conditions. Here we present the first Northern Hemisphere record of MSA, and the first continuous record of non-seasalt sulfate, both extracted from the Renland ice core, East Greenland. The records are extending from the Holocene to the Eem interglacial 130,000 years B.P. The contrast to the Southern Hemisphere records is striking, with a decreasing concentration of MSA with the advance of glaciation but an increasing concentration of non-seasalt sulfate. A strong linear relationship is found in the Renland ice core between the ratio of MSA to non-seasalt sulfate and the temperature, with higher ratios associated with warmer climatic stages, while the opposite relationship to temperature is found in the Vostok ice core. A more complicated picture is emerging of the use of MSA in ice cores as a quantitative tracer which suggests that previous interpretations can have been overly simplistic.

Sampling and measurements

The Renland ice core [Johnsen et al., 1992a] is the third surface-to-bedrock ice core drilled on Greenland. It was recovered from a small isolated ice cap, only a few hundred meters thick on a high elevation plateau in Scoresbysund Fjord, East Greenland (71.2°N, 26.4°W), during a joint Nordic project in 1988. The drill site conditions (e.g. -18°C in mean annual temperature and 50 cm of ice per year in mean annual accumulation rate) are similar to those on the

Greenland ice sheet. The altitude of 2,340 m a.s.l. minimizes the local marine influence. The Renland ice core is only 324 m long. The record of the glacial period and the previous interglacial is compressed into the deepest 20 m, but is well preserved [Johnsen et al., 1992b].

The ice core was cut with a stainless steel microtome knife under clean room (class 100) conditions into 5 cm samples as follows: 55 continuous samples were cut between 86 and 89 m depth representing the time period A.D. 1812-1820 and 374 continuous samples were cut in the deepest 20 m of the ice core representing approximately 10-145 ka B.P. [Johnsen and Dansgaard, 1992]. The samples were analyzed by chemically suppressed ion chromatography. Major anions (Cl^- , NO_3^- , SO_4^{2-}) and cations (Na^+ , NH_4^+ , K^+ , Mg^{2+} , Ca^{2+}) were determined on an integrated Dionex (4000i/2000i) system using AG5A/AS5A5 μ and Cationfastsep I/II columns, respectively. MSA was determined in the same samples but on an other system using AG4/AS4 columns. The uncertainty in the analyses (1 sigma) are estimated at less than $\pm 10\%$ for all major ions and $\pm 30\%$ for MSA. The seasalt component of the sulfate (based on sodium) is on average 10% of the total sulfate.

Result and discussion

The profiles of MSA and non-seasalt (nss) sulfate for the period 10 to 145 ka B.P. are shown in Figure 1. Mean values for the climatic stages (i.e. conventional marine oxygen isotope stages) are presented in Table 1. The MSA concentration is a factor of 2.0-2.5 lower during glacial maximum (stage 2) than in interglacial periods (stage 5e and stage 1, the latter represented by two limited sample series in Pre-boreal and late Holocene). Preliminary results from the GISP2 ice core (ongoing deep drilling in the Greenland Summit area) support the glacial/interglacial MSA trend observed at Renland, suggesting that it is characteristic of the main Greenland ice sheet. The nss sulfate concentration is a factor of 1.9-2.7 higher during glacial maximum in the same comparison as above. This increase in nss sulfate concentration during the glacial period has previously been observed in both the Dye 3 and Camp Century deep ice cores [Herron and Langway, Jr., 1985].

The molar ratio (R) of MSA to nss sulfate in the Renland ice core is strongly related to the climate. The oxygen isotope ratio ($\delta^{18}\text{O}$) indicates the past climate (by a linear relationship to the local mean annual temperature [Dansgaard et al., 1973]) with low $\delta^{18}\text{O}$ values associated with low temperatures. When the data are averaged over different climatic stages, there is a strong linear relationship ($r^2=0.99$) between R and the oxygen isotope ratio $\delta^{18}\text{O}$

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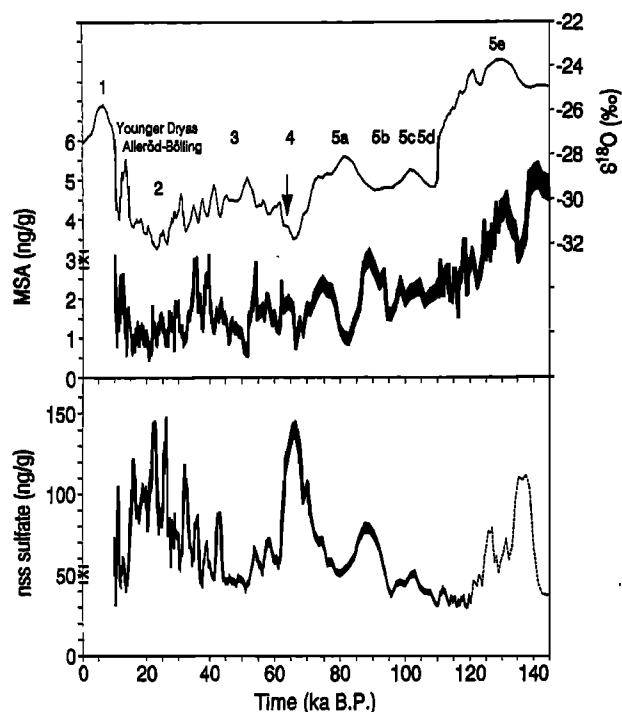


Figure 1. Top: The Renland $\delta^{18}\text{O}$ profile as 10 point running averages of 2.5 cm samples. The different climatic stages are indicated. The arrow indicates the position of the boudinage layer. Mid section: Methanesulfonate (MSA) as 5 point running averages of 5 cm samples in an envelope of calculated standard error of mean. The mean value over seven full years of accumulation (A.D. 1813-1819) is indicated by a cross (\pm s.e.). Bottom: non-seasalt (nss) sulfate presented as for MSA. The seasalt contribution has not been extracted beyond 120 kyr B.P. (dashed line) because of extremely high sodium concentrations in some melt layers.

(Figure 2), with higher R-values associated with warmer stages. R ranges from 0.077 in stage 5e to 0.014 in stage 2. This relationship to temperature is inverse to the temperature dependence of MSA production inferred [Berresheim, 1987]

from laboratory oxidation studies [Hynes et al., 1986] of the reaction of DMS with OH. This latter temperature dependence is thought to be responsible for the observed [Bates et al., 1992a] latitudinal gradient of R, with higher R-values found at higher latitudes. The existence of other factors controlling R apart from temperature (e.g. seasonal transport differences, additional sources of nss sulfate) is indicated by the annual cycle of R measured [Ayers et al., 1991] at Cape Grim, Tasmania, where R decreases during winter. Undoubtedly, the R for different glacial stages obtained at a single site of deposition can be influenced by several processes.

In an interglacial climate, the marine biogenic sulfur compounds in Greenland precipitation can come from either regional sources (i.e. Greenland coastal waters) or more distant, lower latitude sources. Trajectory analyses of air masses influencing the South Greenland ice sheet [Davidson et al., 1993a] indicate that the influence of different source areas varies with season, favouring the regional sources during summer. In contrast, the regional sources are closed off in a glacial climate due to the sea ice cover. Palaeoceanographic reconstructions [Ruddiman and McIntyre, 1981] place the winter sea ice extent as far south as 45°N during the most advanced glacial stage.

The interglacial R-values (Table 1) found at Renland are lower than R expected for the regional marine boundary layer. Recent time series measurements in Mace Head, Ireland, show summertime R-values of 0.30 (D. Savoie et al., manuscript in preparation) suggesting that pre-industrial R for the marine boundary layer around Greenland should be at least as high. The glacial R-values are lower than R presently measured, on average 0.065 [Savoie and Prospero, 1989], in low and mid latitudes. This may indicate the importance of sulfate of other origin in the Renland precipitation, such as volcanic or other continentally derived sulfate.

Apportioning different natural sources of non-sea salt sulfate in the precipitation of today is difficult, and more so of the past. At present, volcanic sulfur emissions from eruptive and non-eruptive degassing volcanoes in the Northern Hemisphere (NH) have recently been estimated [Bates et al., 1992b] to be of the same order as the biogenic emissions. Other significant non-anthropogenic sources of

TABLE 1. Mean concentrations and standard deviations of MSA and nss sulfate in the Renland ice core

Stage	Depth m	Time ka B.P.	Number of samples	$\delta^{18}\text{O}$ ‰	MSA ng/g	nss SO_4^{2-} ng/g	Molar ratio R
1: Late Holocene	86.60 - 89.05	(A.D. 1813-1819)	49	-27.5	3.0 ± 1.5	50 ± 33^1	0.060
1: Pre-boreal	305.80 - 306.55	10.0 - 10.5	15	-28.0	2.4 ± 1.2	48 ± 14	0.051
Younger Dryas	- 307.30	- 11.8	15	-30.6	1.5 ± 0.9	77 ± 29	0.022
Allerød-Bölling	- 308.35	- 14.4	21	-29.0	1.7 ± 0.9	50 ± 15	0.036
2	- 311.75	- 30.2	67	-31.3	1.2 ± 0.7	97 ± 32	0.014
3	- 315.15	- 57.6	64	-30.2	1.5 ± 0.8	61 ± 24	0.026
4	- 319.85	- 70.0	16	-30.9	1.6 ± 1.2	95 ± 43	0.020
5a-d	- 321.35	- 110.2	30	-29.0	2.0 ± 1.3	54 ± 21	0.040
5e	- 323.05	- 121.6	33	-25.8	2.5 ± 1.3	36 ± 9	0.077
5e (melt layers)	- 324.35	- 144.7	26	-24.4	3.7 ± 1.6	$(68 \pm 43)^2$	
Boudinage layer ³	315.65 - 319.55	63.5 - 64.5	77	-32.2	0.8 ± 0.6	137 ± 27	0.006

1. five samples influenced by the volcano Tambora eruption excluded

2. sea salt contribution not extracted

3. due to a pinch-and-swell instability [Staffelbach et al., 1988]

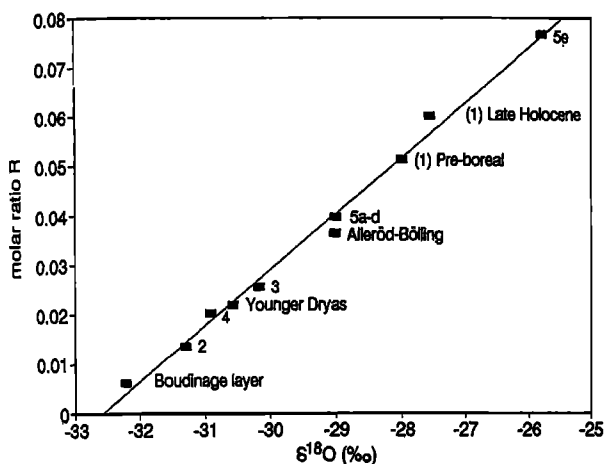


Figure 2. Plot of the molar ratio (R) of methanesulfonate to non-seasalt sulfate against $\delta^{18}\text{O}$ as mean values for the indicated periods ($r^2=0.99$).

sulfate have yet to be found. Model studies [Langner, 1991] of the distribution of tropospheric sulfate indicate the increasing importance of volcanic sulfate with altitude, and suggest that volcanic sulfate may dominate the mid troposphere at mid and high latitudes in the NH under non-anthropogenic conditions. In the glacial period, the exposure of continental shelves due to the sea level drop and the enhanced aridity on the continents may have added a terrestrial source of non-biogenic sulfate. High concentrations [Johnsen et al., 1992a] of calcium and insoluble dust indicate an increased transport of continental material to the Greenland ice sheet. The difference in nss calcium concentration between interglacial and full glacial conditions is one order of magnitude. The correlation is high ($r^2=0.88$) between nss sulfate and nss calcium in the glacial period. This does not necessarily infer a common source since a high correlation applies to several ions, but may as well indicate the importance of transformation, transport and depositional processes.

The factors controlling the distribution of sulfur compounds in polar ice are complex and can not be unambiguously interpreted in terms of source emissions or atmospheric concentrations. The relative contribution from different sources to the air masses influencing Greenland may have changed as a result of different atmospheric circulation patterns [COHMAP members, 1988] in the glacial period. The precipitation rates at Renland during glacial stages decreased markedly (to a fifth of the present value in stage 2, 3 and 4 [Johnsen and Dansgaard, 1992]) such that the contribution from dry deposition (presently negligible [Davidson et al., 1993b]) may have been significant and at least in part responsible for the increase of nss sulfate. However, the decrease of MSA and R can perhaps be explained in the context of three hypotheses: 1) decreasing input from oceanic DMS emissions, 2) a shift of the marine biogenic sulfur source to regions where the conditions give lower initial R -values, and/or 3) changes in the relative removal rates of MSA and nss sulfate in the glacial atmosphere.

The contrast between Renland and the Vostok ice core MSA records is striking. Glacial conditions at Vostok were characterized by high MSA concentrations, and high R -values; Renland exhibits the opposite trend. Linear

relationships [Legrand et al., 1992] are found in both ice cores between R and isotopic temperature but with opposite signs. It shows that R in polar precipitation can not simply be a function of atmospheric temperatures. However, it would also be remarkable if the strong linear relationship to temperature in the Renland ice core is caused by changing source strengths of two, or more, independent sources of sulfur.

Conclusion

The Renland ice core data suggests a glacial Arctic atmospheric sulfur cycle influenced by low latitude oceanic emissions, possibly decreased, and non-biogenic sources in contrast to Antarctica which appears dominated by increased high latitude oceanic emissions. The isotopic temperature profiles suggest a roughly parallel climatic development [Johnsen et al., 1992a] in Greenland and Antarctica which calls in question the role of marine biogenic sulfate in climate forcing, or otherwise its exclusivity among the atmospheric sulfate aerosols. However, it has to be stressed that it is the composition and size distribution of the total aerosol in the atmosphere that affects the direct radiation balance and the cloud albedo, why records of non-seasalt sulfate alone demand cautious use when discussing climate forcing. The nss sulfate represents less than 5% of the total aerosol mass in the Renland ice core during full glacial conditions. In addition, the apparent influence from changing climatic conditions on the ratio R has to be more understood before using MSA as a quantitative tracer over long time-scales with major climatic changes, either as indicator of the relative strengths of biogenic versus non-biogenic sulfur sources or indicative of changes in the principle source region. Further studies are necessary to take the full advantage of the detailed records that will be available from the two deep ice cores drilled on the Greenland Summit.

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