

Sulphate and nitrate concentrations in snow from South Greenland 1895–1978

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An understanding of the phenomenon of acid rain requires the identification of the sources of the species affecting the pH of rainwater, both natural and anthropogenic, and their temporal and spatial development. The scant data concerning the historical development of the acidity in precipitation are from urban regions or their vicinity, where local effects dominate and obscure the hemispherical pattern¹. The Greenland ice sheet allows us to trace the evolution of the acid rain in a remote location that is free from local effects. Sulphuric and nitric acids are the two species that dominate the acidity in precipitation^{2–4}. We report here measurements of $[\text{SO}_4^{2-}]$ and $[\text{NO}_3^-]$ in firn samples spanning the period 1895–1978. Samples, each covering 1 yr, were taken from a 70-m core drilled at Dye 3, South Greenland; $[\text{NO}_3^-]$ and $[\text{SO}_4^{2-}]$ both increased by a factor of ~ 2 during the period. By comparing the recent concentrations of nitrate and sulphate with those resulting from natural sources, we conclude that anthropogenic emissions of the precursors (NO_x , SO_2) had already surpassed natural sources in the late 1950s.

In 1980 a shallow electromechanically drilled core was collected near Dye 3 (65°11'N, 43°30'W) in the frame of the US-Danish-Swiss Greenland Ice Sheet Program. The main purpose of this core was to provide samples for studying the influence of the 11-yr solar cycle on the ^{10}Be concentration in the firn⁵. As a supplementary study, anion concentrations were determined by ion chromatography as possible correction factors to eliminate 'meteorological noise' in the ^{10}Be data. To avoid contamination, the drill site was located 2 km north of the radar station and perpendicular to the main wind direction. In the field, the acidity was qualitatively determined by solid electrical conductivity measurement (ECM)⁶ and a small strip of the core was cut for continuous $\delta^{18}\text{O}$ analysis with a resolution of eight samples per calculated year. After field sampling, the cores were packed in polyethylene tubes and sent back to the laboratory. The volcanic Katmai eruption, which took place in 1912 in Alaska, is clearly visible in the ECM record and served as an internal check on the accuracy of the timescale used. The $\delta^{18}\text{O}$ and ECM results showed the mean snow accumulation rate at Dye 3 to be 50-cm water equivalent yr^{-1} and provided an age/depth relation which allowed us to cut the core into annual samples. To remove external contamination before chemical analysis, the outer layer of the firn was removed with a stainless steel microtome knife. All sample treatment was done in a cold room (-20°C). The samples were melted in a covered polyethylene beaker and aliquots were taken for chemical analysis. To check whether the sampling and melting procedure introduces any noticeable background, we treated ultra-pure water in the same manner as the samples. This water was frozen in the polyethylene beaker in the cold room and re-melted in the laboratory. Blank values were below 8 parts per 10^9 (p.p.b.) (ng per g ice) for the measured species; the reproducibility of the measurements was better than 5%. Figures 1 and 2 show $[\text{NO}_3^-]$ and $[\text{SO}_4^{2-}]$ during the period 1895–1978. To reveal the general trend, a spline-smoothed curve has been drawn through the points. Nitrate and sulphate show an increasing trend with a large year-to-year fluctuation; our measured concentrations can be compared with published data^{7–9}. For the years 1895–1904 we measured a mean sulphate level of 36 p.p.b., which is higher than for the two time periods 1539–1577 and 1773–1791, where the sulphate level was determined by Herron⁷ to be 22 p.p.b.

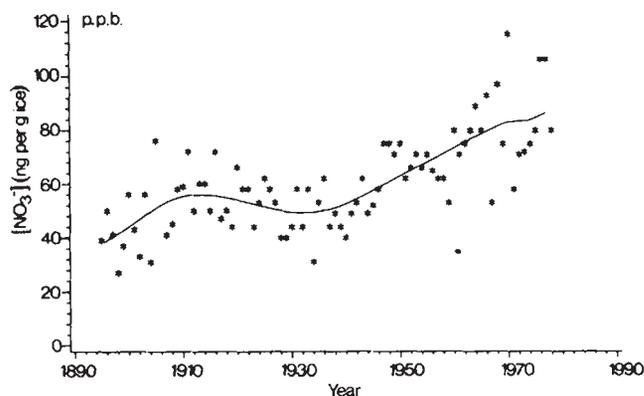


Fig. 1 Annual $[\text{NO}_3^-]$ in a shallow core from Dye 3, South Greenland. The general trend is shown with a spline-smoothed curve.

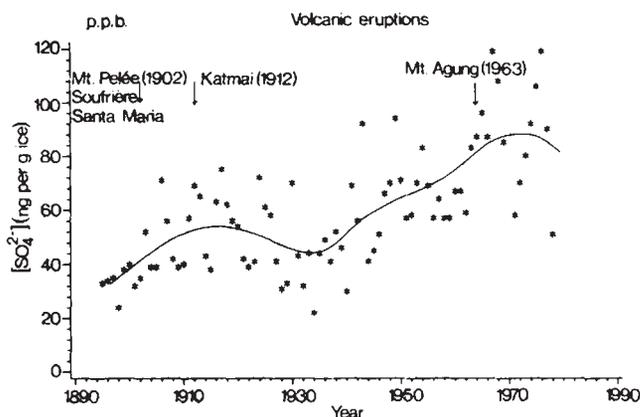


Fig. 2 Annual $[\text{SO}_4^{2-}]$ in a shallow core from Dye 3, South Greenland. The general trend is shown with a spline-smoothed curve.

Under unfavourable meteorological conditions the radar station is a possible source of contamination, especially for sulphate. However, the measured $[\text{SO}_4^{2-}]$ of 90 p.p.b. for the recent time period 1973–1978 agrees well with Herron's level of 85 p.p.b. for the time period 1975–1981, which was determined in a pit study much further from the Dye 3 station than was our drilling site. Furthermore, our sulphate and nitrate data do not show a discontinuity over the year 1961, when the radar station was constructed. We conclude, therefore, that the contamination attributable to emissions from the radar station is small. We found no indication that the occurrence of melt layers in the Dye 3 firn core influences $[\text{NO}_3^-]$ and $[\text{SO}_4^{2-}]$.

The nitrate levels measured by Herron⁷ are generally slightly higher than ours (Herron's 1884–91, 51 p.p.b., our 1895–1904, 44 p.p.b.; Herron's 1975–81, 114 p.p.b., our 1973–78, 86 p.p.b.). The high nitrate value we found for 1906 is surprising; we cannot exclude contamination of this sample, particularly as $[\text{SO}_4^{2-}]$ is also relatively high and in Rasmussen's Dye 3 data⁸, $[\text{NO}_3^-]$ for 1906 is not elevated. As a consequence of the 1908 Tunguska impact in Siberia, Turco *et al.*¹⁰ have calculated that NO_x concentrations in the lower stratosphere would be elevated by an order of magnitude for a period over 1 yr. The years 1908–10 do not, however, show a higher $[\text{NO}_3^-]$, so that the predicted enhancement of $[\text{NO}_x]$, if it occurred, did not penetrate into the troposphere. Similar conclusions were reported by Rasmussen *et al.*⁸, based on their measurements at Dye 3 and Camp Century.

The concentration depends on three factors: the scavenging process, the transport of air masses from the source to the receptor and the source strength. We ascribe the general trend in anion concentrations to increasing source strength and the short-time fluctuations to the variability in transport processes and scavenging.

Although NO_3^- and SO_4^{2-} are mainly incorporated as HNO_3

and H_2SO_4 in the ice¹¹⁻¹³, HNO_3 and H_2SO_4 are not emitted directly into the atmosphere. The precursors for HNO_3 are NO and NO_2 , and for H_2SO_4 are SO_2 , dimethyl sulphide (DMS) and H_2S . All these species are oxidized in the atmosphere, either in the gas phase or in cloud droplets¹⁴ to form the two acids, which are then effectively removed by precipitation. The global sources or precursors of HNO_3 and H_2SO_4 are compiled in Table 1. The range of estimates in the literature is large, especially for the natural sources, which cannot be derived from economic data as can the anthropogenic sources. The volcanic contribution is, of course, subject to extreme fluctuation. During the time period covered by our samples, the volcanic activity was low except for the years 1902, 1912 and 1963¹⁵. With the exception of the already mentioned Katmai explosion, all large eruptions were in the equatorial zone. Their contribution to the sulphate level in our samples is not distinguishable from the scatter.

Inputs from land-based sources to the impurity level in Greenland must travel quite far and must be able to survive in the atmospheric boundary layer, where removal by precipitation is very effective. Sources in the free troposphere or in the ocean surrounding Greenland will contribute more easily to the concentration in the precipitation of South Greenland. Essentially all anthropogenic sources are land-based with the exception of jet airplanes.

Using the estimated source strengths of the different NO_3^- and SO_4^{2-} precursors, one can calculate the percentage of the '1900 level' of $[\text{NO}_3^-]$ and $[\text{SO}_4^{2-}]$ that is derived from land-based sources. Our calculation assumes that the different sources contribute linearly to the impurity level in the snow and are split into continental (land-based) and other (non-land-based) sources. No interhemispherical mixing is assumed. Two time periods, 1895-1901 and 1973-78, were considered, assuming the emission rates indicated in Table 1 and using the mean measured concentration of these time intervals.

The '1900 level' may be expressed as $\gamma P_C + \delta P_O = C_{1900}$; the 'recent level' as $\gamma(P_C + P_A) + \delta P_O = C_{\text{recent}}$, where γ and δ are factors linking emission rates and firm concentration; P_C , P_A and P_O are the land-based (continental), anthropogenic (~1975) and non-land-based (ocean) production rates, respectively; and C_{1900} and C_{recent} are the '1900' and 'recent' firm concentrations, respectively.

This model is no more than a first approximation. Natural

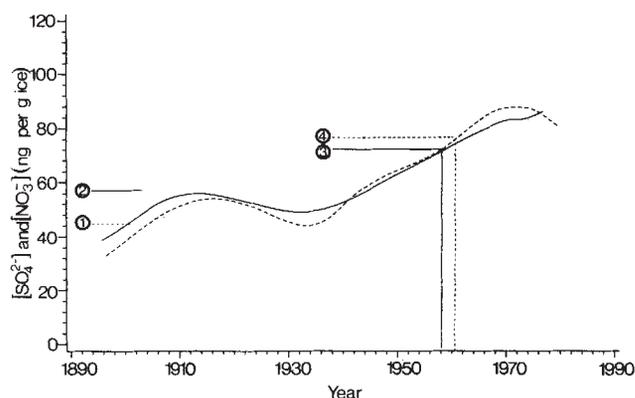


Fig. 3 Time development of atmospheric load with nitrate (—) and sulphate (---). Comparison of anthropogenic and natural input. (1) '1900' $[\text{SO}_4^{2-}] (+1\sigma)$. (2) '1900' $[\text{NO}_3^-] (+1\sigma)$. (3) '1900' $[\text{NO}_3^-] (+1\sigma) + 16 \text{ p.p.b.}$ ($\approx 11 \text{ Tg N yr}^{-1}$ anthropogenic emission) for when anthropogenic N sources were approximately equal to global natural N sources. (4) '1900' $[\text{SO}_4^{2-}] (+1\sigma) + 28 \text{ p.p.b.}$ ($\approx 57 \text{ Tg S yr}^{-1}$ anthropogenic emission) for when anthropogenic S sources were approximately equal to global natural S sources.

sources are diffuse, whereas the anthropogenic components have more the character of point sources. The results of this model calculation give for the 1900 level a contribution of land-based sources to the concentration in the ice of 54% for sulphate and 37% for nitrate. It should be pointed out that this number depends strongly on the emission rates that we have selected in Table 1.

Based on our calculation, 1 Tg yr^{-1} of land-based sulphur source corresponds in the mean annual concentration of the snow in Dye 3 to an additional $[\text{SO}_4^{2-}]$ of $\sim 0.6 \text{ p.p.b.}$, whereas 1 Tg yr^{-1} of land-based nitrogen source corresponds to $\sim 1.4 \text{ p.p.b.}$ of additional $[\text{NO}_3^-]$, respectively. These numbers depend only weakly on the assumed emission rates. Thus, the source distribution and the long-range transport of the sulphur and nitrogen components seem to be different. Our data suggest that the nitrogen component is more easily transported through the boundary layer than is the sulphur component, which seems to be contrary to the calculation published by Rhode *et al.*¹⁶. However, their calculation was based on precipitation data from the European Air Chemistry Network, whereas our data apply to Greenland. The low proportion of the land-based contribution to the pre-industrial $[\text{NO}_3^-]$ supports the idea that NO_x from the stratosphere and produced by lightning are the main sources of the background nitrate in remote regions^{6,17}. Such sources in the free troposphere were also postulated by Huebert and Lazarus¹⁸ to explain their $[\text{HNO}_3]$ measurements in the free troposphere.

Our sulphate concentration in the period 1895-1904 is higher than the values given by Herron⁷ for earlier periods. Because volcanic activity was low during 1895-1904, our higher measured concentration indicates that by this time the sulphate level was already considerably elevated over pre-industrial values, possibly reflecting early industrial activity. Our model is inconsistent with the pre-industrial sulphate level given by Herron (22 p.p.b.) and would require a land contribution of over 100%. The most probable explanation is that the natural land-based source used in our model is an overestimate.

Using the relation given above between concentration increase in the ice and source strength, we can deduce the time when anthropogenic sources surpassed the natural source concentration given in Table 1. Figure 3, illustrating this behaviour, shows that the anthropogenic sources started to dominate the total natural sources around 1960. This agrees with the anthropogenic emission data for sulphate given by Möller¹⁹.

Our data suggest that man-made pollution had already started to affect remote regions more than 30 yr ago. The nitrate and sulphate concentrations in Greenland contain information which can ultimately be used to interpret the development and

Table 1 Global emission ranges

		Northern Hemisphere range (Tg S yr ⁻¹)	Southern Hemisphere range (Tg S yr ⁻¹)
Sulphur source			
Natural:	Biogenic sea	14-32	18-40
	Biogenic land	2-74 (32)*	1-36
	Volcanoes	0.6-6 (3)*	0.4-4
Man-made:	(1976)	69-98 (98)*	5-6
Nitrogen source			
Natural:	Soil	0.7-7 (4)†	0.3-3
	Wildfire	0.2-0.6 (0.4)†	0.1-0.3
	Ox. NH ₃	0-3 (1.9)†	0-2
	Biomass burn.	3-8 (5.5)†	
	Lightning	1-4	1-4
Stratosphere	0.15-0.45	0.1-0.45	
Man-made:	Fossil fuel	7-17 (13)†	0.5-1
	Biomass burn.	6-40 (18)†	6-18
	Jets	0.2-0.4 (0.3)†	<0.1

Data compiled from refs 19-24.

* Assumed production for calculations: natural production land-based, 35 Tg yr^{-1} (\approx total land-based production pre-industrial); natural and man-made production land-based, 133 Tg yr^{-1} .

† Assumed production for calculations: natural production land-based, 11.4 Tg yr^{-1} (\approx total land-based production pre-industrial); natural and man-made production land-based, 43 Tg yr^{-1} .

distribution of sources of acid rain, although at the moment our understanding of source strengths and transport is still so rudimentary that the interpretation must remain largely qualitative. More widespread drilling of firn cores in polar regions would allow the historical development of the acid deposition pattern to be established and sophisticated source receptor models to be tested. Nevertheless, the data already show that human activity drastically changed the atmospheric load of the acidic trace species HNO_3 and H_2SO_4 . This fact emerges more clearly in the historical record from remote locations, such as Dye 3, than from direct measurements in populated areas which are influenced by changes in measuring technique and changed local distribution of pollution with time.

We thank W. Bernhard and M. Andrée for assistance during the field work, and W. Dansgaard and H. Clausen from the Geophysical Isotope Laboratory in Copenhagen for the measurements of the $\delta^{18}\text{O}$ samples. M. M. Herron reviewed the manuscript and helped to improve it substantially. This work was supported by the Swiss NSF.

Received 13 November 1984; accepted 5 February 1985.

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Late Eocene microtektites and radiolarian extinctions on Barbados

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A late Eocene microtektite layer has been found in three exposed sections on Barbados, West Indies. These microtektites and associated tektite fragments are compositionally similar to the North American tektites and thus, like the Caribbean and Gulf of Mexico microtektites, may belong to the strewn field of 'North American' microtektites which have been found in deep-sea deposits from the Caribbean Sea, across the Pacific and into the northeastern Indian Ocean^{1,2}. The 'North American' layer has been reported to be approximately synchronous with several radiolarian extinctions^{3,4} and with an anomaly in iridium concentrations⁵⁻⁷, and it has been hypothesized that the microtektites, the extinctions and the iridium anomaly are all related to an asteroid impact. We report here that the radiolarian extinctions predate the microtektite layer and that the highest Ir concentrations apparently coincide with the extinctions. Thus, although the extinctions may be causally related to the Ir anomaly, the microtektites appear not to be.

Table 1 Major oxide composition of selected Barbados microtektites and tektite fragments and North American tektites

Sample no.	SiO ₂	Al ₂ O ₃	FeO	MgO	CaO	Na ₂ O	K ₂ O	TiO ₂
Barbados microtektites								
179-16-2	84.2	10.4	1.48	0.45	0.20	0.60	1.77	0.49
176-16-14	79.4	11.7	3.23	0.61	0.35	1.28	2.54	0.54
173F	78.6	13.0	3.15	0.99	0.63	0.73	1.88	0.61
173E	77.5	12.3	3.67	0.90	0.86	0.83	2.86	0.77
179-16-5	76.0	13.5	3.68	0.96	0.78	1.23	2.78	0.64
Barbados tektite fragments								
173G	81.7	10.2	2.06	0.41	0.94	1.63	2.53	0.43
173H	81.0	10.3	2.71	0.49	0.73	1.56	2.56	0.43
181A	78.9	12.4	3.28	0.56	0.17	1.41	2.04	0.81
173C	78.8	12.6	3.20	0.54	0.46	1.34	2.09	0.60
173D	78.6	12.8	3.18	0.52	0.50	1.31	2.04	0.70
North American tektites								
BM	81.31	10.96	2.43	0.53	0.50	1.50	2.17	0.53
181D	81.0	11.0	2.58	0.60	0.36	0.84	2.61	0.52
181C	78.4	12.5	3.22	0.62	0.41	1.42	2.25	0.66
B-50	78.19	12.35	3.50	0.73	0.65	1.71	2.23	0.74
B-6	76.25	13.49	3.98	0.74	0.74	1.63	2.22	0.74

The data for North American tektite samples BM, B-50 and B-6 are from ref. 14. The rest of the data were obtained by energy dispersive X-ray analysis. A total of 18 microtektites and five tektite fragments from Bath Cliff were analysed.

Microtektites belonging to two Quaternary tektite-strewn fields on land, the Australasian and Ivory Coast, have been found in deep-sea sediment cores taken in the Australasian/Indonesian region and off the Ivory Coast, respectively¹. Much older than the Quaternary group are the late-Eocene North American microtektites, found in a low-latitude band stretching from the Caribbean to the northeastern Indian Ocean. The glassy rounded tektites and microtektites are believed to be produced by impacts^{8,9}. Correlation of late-Eocene microtektites, anomalous Ir, and radiolarian extinctions^{6,7} has been used to suggest a relationship between impacts and extinctions similar to that which has been inferred for the Cretaceous-Tertiary event¹⁰.

Recent detailed biostratigraphical investigations on Barbados¹¹ provided the possibility of locating, on land, the stratigraphical level of occurrence of the microtektites, which had previously been available in only very limited amounts, at scattered localities, in deep-sea cores. The stratigraphical resolution attainable in these land-based sections is 2-10 times greater than that attained in deep-sea sediment cores containing the microtektite layer. For example, the stratigraphical interval separating the earliest occurrence of the radiolarian *Thyrococcytis bromia* and the evolutionary transition of *Lithocyclia aristotelis* to *L. angusta* is 100-110 m at Bath Cliff, 10-20 m at Deep Sea Drilling Project Site 149 (ref. 12), about 10 m at DSDP Site 543 (unpublished data) and 15-45 m at DSDP Site 94 (ref. 13). The microtektites were found in this interval at a single stratigraphical level (10-30 cm thick) in three sections; Bath Cliff, Gay's Cove North and Gay's Cove South.

All three sections were sampled continuously, by taking contiguous samples 5 cm thick. This provided a basis for examining changes in the microtektites throughout their occurrence, and details of the abundances in the uppermost parts of the ranges of radiolarian species as they became extinct. Weighed subsamples of the channel samples were disaggregated and sieved to obtain the >63- μm fraction for investigation of the radiolarians and the microtektites.

Identification of the Barbadian microtektites and tektite fragments as belonging to the late-Eocene horizon which has been called the 'North American' strewn field is indicated by their late Eocene age and by their chemical composition (Table 1). North American tektites are characterized by low lime and magnesia content as compared with tektites from other strewn fields¹⁴, and this is reflected in the composition of the Barbados microtektites and tektite fragments. They have a unimodal size distribution, this being more pronounced in the samples near