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First sulfur isotope measurements in central Greenland ice cores along the preindustrial and industrial periods

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[1] Sulfur isotopes of sulfate have been measured in a discontinuous set of polar ice core samples from Summit, central Greenland, covering the preindustrial (from the fourteenth to the eighteenth century) and industrial (from 1872 to 1969 A.D.) periods. Results have been used to estimate the different source contributions to the deposited sulfate and their evolution along the last centuries. They indicate that the preindustrial background sulfate budget is slightly dominated on a year-round average by marine biogenic emissions, amounting to close to half of the non-sea-salt sulfate (49%). The second contribution is provided by continental sources of secondary sulfate, including background volcanism and, to a lesser extent, continental biota (44% of the non-sea-salt sulfate). Sulfur emitted by relatively weak eruptions is found to be largely depleted in ^{34}S compared to bulk volcanic S, suggesting an efficient washout of the heavier isotope during the tropospheric transport. The impact of human-driven emissions on the sulfate deposited in central Greenland ice is visible in isotope data as early as 1870 A.D. The isotopic signature of anthropogenic sulfur deposited during the twentieth century is found to be constant ($\delta^{34}S \approx + 3.0 \pm 1.5‰$), regardless of the changes of dominant source regions and emission processes. This signature is slightly but measurably lighter than the one reported for Arctic haze pollution events. *INDEX TERMS:* 0325 Atmospheric Composition and Structure: Evolution of the atmosphere; 0368 Atmospheric Composition and Structure: Troposphere—constituent transport and chemistry; 9315 Information Related to Geographic Region: Arctic region; *KEYWORDS:* sulfur isotopes, Greenland, pollution transport

1. Introduction

[2] Sulfur is strongly involved in the atmospheric chemistry and the climate system. Sulfate is a major component of submicron particles in marine as well as most continental atmospheres, at least for present-day. These fine particles are relatively resistant to mechanical atmospheric sinks (wet or dry deposition) and strongly interact with incoming solar radiation, thus increasing the optical depth of the atmosphere. They can also act as cloud condensation nuclei, enhancing the radiative role of clouds [*Bates et al.*, 1987; *Charlson et al.*, 1987]. Sulfuric acid, the main ultimate compound of the atmospheric sulfur chemistry, is responsible for most of the free acidity in the atmosphere [*Charlson and Rodhe*, 1982].

[3] The present-day sulfate budget is highly dominated by man-induced sulfur emissions, which, on the global scale, exceed the natural sources. According to recent models and inventory estimates, anthropogenic emissions represented ~75% of the global gaseous sulfur emissions, and accounted for 84% in the Northern Hemisphere, during the 1980–1990 decade [*Bates et al.*, 1992; *Spiro et al.*, 1992]. Important uncertainties remain on the natural part of the sulfur cycle and therefore on the assessment of the climate forcing due to anthropogenic sulfur emissions. Indeed, direct observation of the natural budget of sulfur in the Northern Hemisphere is hampered by pollution on the regional scale, even in the most remote areas. The involvement of the sulfur cycle in the atmospheric chemistry and the Earth's climate and the impact of human activities on its budget make it mandatory to assess as accurately as possible the natural variability and the anthropogenic contribution to this cycle.

[4] The Greenland ice sheet record helps reconstruct the evolutions of the past atmospheric chemistry of the Northern Hemisphere. Chemical studies of impurities trapped in polar ice cores have permitted qualitative evaluations of the impact of anthropogenic emissions on the chemistry of the atmosphere over the last 150 years (see *Legrand and Mayewski* [1997, and references therein] for a review). The growing impact of human activities on the sulfate budget has been detected by the change of sulfate levels in Greenland ice cores, which rose rapidly since the end of the nineteenth century [*Neftel et al.*, 1985; *Mayewski et al.*, 1986, 1990]. It can be assumed that preindustrial sulfate primarily originates from sea spray and dust particles or results from the oxidation of sulfur emitted by the marine biota (mainly as dimethyl sulfide, DMS) and by the volcanic activity (mainly as SO_2). Comparing Greenland sulfate ice records with SO_2 emission estimates for the United States and Eurasia, *Fischer et al.* [1998b] concluded that Greenland sulfate levels were mainly controlled by North American emissions in the first half of the twentieth century, whereas the major increase of levels detected after 1950 was largely governed by Eurasian emissions. The growing

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Table 1. Description of Ice Samples Analyzed for S Isotopes

Sample	Depth, m	Date,[a] A.D.	Core	Ice Weight, g	$[SO_4]$,[b] ng g^{-1}	SO_4 Content, μmol
I	12.10–13.20	1966–1969	GRIP 93b	1778	102.2	1.89
H	25.25–26.35	1931–1934	GRIP 93b	2166	92.3	2.08
G	33.00–34.10	1902–1906	Eurocore	2337	63.5	1.55
F	38.50–40.15	1885–1889	Eurocore	3153	47.9	1.57
E	42.90–44.55	1872–1877	Eurocore	3598	35.2	1.32
D	85.25–86.35	1705–1710	Eurocore	3170	30.7	1.01
C	100.65–101.75	1642–1646	Eurocore	3377	33.4	1.18
B	155.70–157.35	1395–1402	Eurocore	5644	26.3	1.55
A	176.00–177.65	1303–1311	Eurocore	5675	25.8	1.53

[a] Date estimates are based on calcium and ammonium ions seasonal variations and a few identified volcanic horizons [*Legrand and De Angelis*, 1996; *Savarino*, 1996; *Savarino and Legrand*, 1998].
[b] Average concentration is measured on total melted samples.

emissions result from coal burning, ore smelting, and oil consumption.

[5] The source apportionment to the sulfate budget can be examined by comparing past sulfate variations with changes of other chemical species. However, such an approach remains qualitative most of the time since there are no straightforward indicators of the various sources contributing to the sulfur cycle (e.g., halogenated acids for volcanic emissions or methane sulfonic acid (MSA) for marine biota emissions [*Legrand and Mayewski*, 1997]). Isotopic analysis of deposited sulfur, together with chemical tracers, may help toward an accurate quantification of the relative natural and anthropogenic contributions and their changes over the past. The isotopic ratio $^{34}S/^{32}S$, or the associated notation $\delta^{34}S$, is a good tracer of sulfur sources when their isotopic signatures are sufficiently distinct from one another [e.g., *Nielsen*, 1974; *Herut et al.*, 1995; *Mayer*, 1997]. This tool has been used in particular in the study of the long-range transport of anthropogenic emissions toward the Arctic atmosphere [*Nriagu et al.*, 1991; *Li and Barrie*, 1993; *Norman et al.*, 1999].

[6] The experimental procedure that we developed for isotopic measurements of sulfur in Antarctic ice at the micromolar level [*Patris et al.*, 2000a] has been applied to a discontinuous set of ice samples from central Greenland cores, spanning the last few centuries, including the preindustrial era and the twentieth century. The aim of this work is to provide new insights to our knowledge of the natural sulfur budget in the Northern Hemisphere and to document the history of the pollution during the last century with original isotopic data.

2. Sampling and Methods

2.1. Ice Coring

[7] The samples analyzed in this study are firn and ice sections from two cores extracted near Summit, central Greenland, in the frame of the EUROCORE and Greenland Ice Core Project (GRIP) European projects. The Summit site is located at the most elevated point of the Greenland ice sheet (72°34′N, 37°38′W, 3240 m above sea level (asl). The EUROCORE 305-m-long main core was extracted in 1989 and has been thoroughly used to investigate past atmospheric chemistry changes that have occurred at high northern latitudes over the last millenium [e.g., *Blunier et al.*, 1993; *De Angelis and Legrand*, 1994; *Savarino and Legrand*, 1998]. The GRIP firn core used here was extracted in 1993 and was nearly 70 meters long, covering the last two centuries [*Legrand and De Angelis*, 1996]. Ice cores were cut in 55-cm-long pieces, packed in sealed polyethylene bags, shipped, and stored at −25°C until processing.

2.2. Selection of Samples

[8] On the basis of the examination of the temporal evolution of sulfate concentration in the Summit ice [*Legrand et al.*, 1997], nine Greenland ice samples were selected for this study, four of them depicting the preindustrial conditions and five covering the industrial period. Material from the main EUROCORE core was only available below ∼30 m depth, corresponding to ∼1920 A.D. Thus two additional samples were taken from a small GRIP core at shallower depths. Details of the selected samples are given in Table 1.

[9] The choice of the four preindustrial samples was based on the detailed continuous ion analysis and dating achieved by *Savarino* [1996]. This work was performed on 5-cm-long lamellae cut along the core. Sulfur isotopes were analyzed on the remaining part of the section. The sulfate concentration baseline observed between 1200 and 1770 A.D. was rather constant, at ∼30 ng g^{-1}, with lowest values around 20 ng g^{-1} [*Savarino*, 1996]. The four deeper samples were all taken between 80 and 180 m (i.e., between deposition dates 1731 and 1293 A.D.), from intervals where sulfate concentration variability was minimum. Each of them represents 4–8 years of deposition. Sulfate concentrations in samples A and B range between 9 and 50 ng g^{-1} (Figure 1). This ensured that these samples are representative of background conditions. The two other sections showed slightly higher sulfate concentration and variability (from 10 to 124 ng g^{-1} and from 12 to 61 ng g^{-1} in samples C and D, respectively).

[10] The five EUROCORE and GRIP samples covering the industrial period were selected after checking the detailed continuous chemical analysis of the GRIP core [*Legrand et al.*, 1997]. Marked volcanic layers have been carefully discarded from the selected samples. Each of them spans 3–5 years of deposition. The deepest of these sections, dated around 1875 A.D. (∼44 m deep), is just at the threshold of the sulfate level increase (mean $[SO_4^{2-}] \approx 35.2$ ng g^{-1}). Other industrial samples, dated around 1887, 1904, 1932, and 1967, show progressively higher sulfate concentrations (Table 1). Figure 1 shows the detailed $[SO_4^{2-}]$ profile of the two GRIP sections (samples H and I) completed during this work and the $[SO_4^{2-}]$ measured on melted samples E–G.

2.3. Preparation of Samples

[11] Because of their very low sulfur content, the samples are highly sensitive to contamination. Great care was taken during all preparation steps to minimize any risk of contamination and to optimize the yield. All tools and glassware used were thoroughly cleaned in ultrapure conditions (use of particulate-free rooms, laminar airflow benches, and 18.2 MΩ ultrapure water). The mechanic decontamination of pieces of ice was done under a laminar airflow bench at −15°C, by removing the outer layers of the core with a band saw and a clean stainless steel blade [*Legrand et al.*, 1993]. Decontaminated samples were allowed to melt overnight at room temperature in glass beakers placed in sealed polyethylene bags. The bulk meltwaters were aliquoted for accurate ion chromatographic analysis and were slowly evaporated in a rotary evaporator until the volume of the concentrated solution was

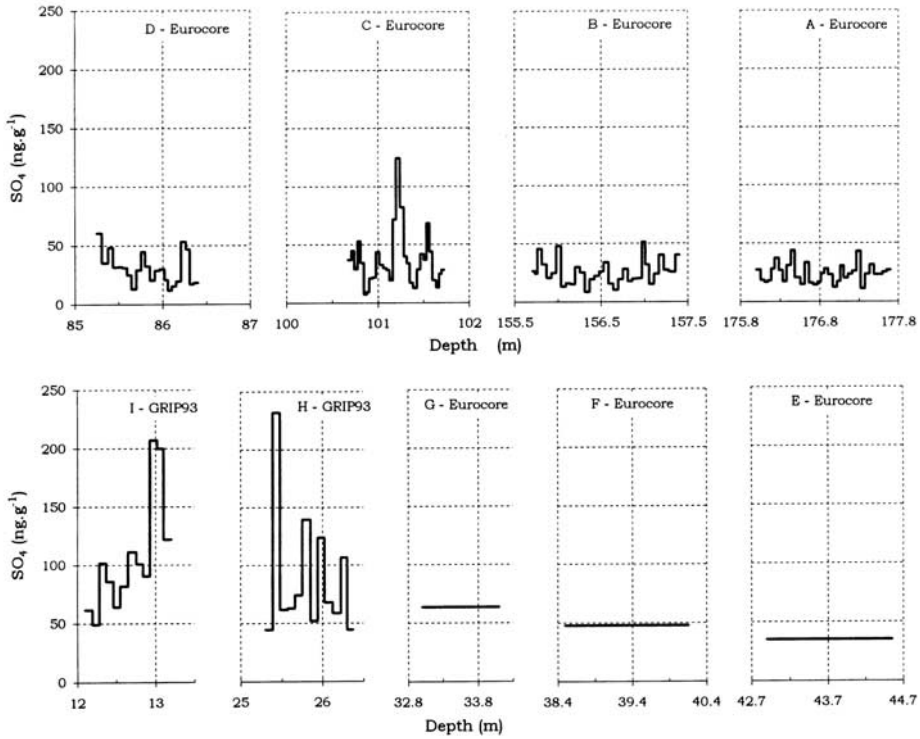

Figure 1. (top) Sulfate concentration along the preindustrial samples (A to D) measured by *Savarino* [1996]. (bottom) Sulfate concentration measured along the samples H and I (this work) and average sulfate concentration measured on melted samples E–G.

~10–20 mL. The evaporation was continued under a pure argon stream, and the last few milliliters were dried out in heated tin capsules used for pyrolysis. Details of the preparation procedure are given by *Patris et al.* [2000a, 2000b]. Ion chromatography (IC) was performed using commonly employed working conditions detailed by *Legrand et al.* [1993] for which the accuracy of IC determinations is typically 5%.

2.4. Isotopic Analysis

[12] Continuous Flow-Isotope Ratio Mass Spectrometry (CF-IRMS) was performed on a Finnigan MAT252 mass spectrometer connected to a Carlo Erba NC-2500 elemental analyzer. Dried sulfate samples put into compacted tin capsules were flash combusted at 1800°C in a pulse of oxygen, yielding SO_2 and SO_3. Sulfur trioxide was reduced into SO_2 on hot reduced copper wires. Evolved gases were desiccated on anhydrite and separated on a gas chromatographic column (Porapak S, 0.8 m long) at 80°C. Under these conditions, SO_2 was separated from the other gases (N_2 and CO_2) formed during the combustion. A split interface at the vent of the elemental analyzer allowed direct introduction of SO_2 in the source of the mass spectrometer via a silica capillary, together with the carrier gas He.

[13] The isotopic ratio $^{66}(SO_2)/^{64}(SO_2)$ was integrated along the whole SO_2 peak coming out of the elemental analyzer line. The high linearity of the source of the spectrometer is essential for the continuous-flow analyses. The homogeneity and large excess of oxygen used for the combustion guaranties the reproducibility of the oxygen isobaric interference on SO_2. Isotopic results are presented in the usual delta notation $\delta^{34}S$,

$$\delta^{34}S = \left(\frac{\left(^{34}S/^{32}S\right)_{\text{sample}}}{\left(^{34}S/^{32}S\right)_{\text{reference}}} - 1 \right) \times 1000. \qquad (1)$$

The reference used for the $\delta^{34}S$ scale is the troilite from the Cañon Diablo meteorite and is very close to the mean isotopic composition of terrestrial sulfur. The combustion of standard materials of known isotopic composition (IAEA-S1, IAEA-S2, and NBS-127) was used to perform the calibration between measured δ^{66} (SO_2) and corrected $\delta^{34}S$. The overall experimental uncertainty for nonrepeatable measurements was better than ±1‰.

3. Natural Sulfur Cycle at High Northern Latitudes

[14] Previous glaciochemical studies of central Greenland ice showed that human activities had hardly any measurable impact on sulfate deposition before the second half of the nineteenth century [*Mayewski et al.*, 1990; *Legrand et al.*, 1997], as opposed to the budget of, for instance, several heavy metals [*Hong et al.*, 1996]. The budget of the sulfur deposited in the ice before 1850 A.D. was likely dominated by the two main secondary sulfate contributors, volcanism and marine biota, depending on the transport pathways between the respective source regions and the Greenland ice cap. The Greenland ice sheet culminates above 3000 m asl and can be regarded as a free tropospheric site where the representation of atmospheric signals is of a large geographic scale.

[15] Quantitative assessment of the different source contributions to the central Greenland ice sulfate budget can be performed at the light of chemical species. Sea-salt sulfate can be evaluated from the ice concentration of Na^+, taken as a conservative element of sea spray. Terrigenous sulfate (mainly gypsum) can be derived from the non-sea-salt (nss) Ca^{2+} level, taking into consideration the mean SO_4/Ca mass ratio in the soils. As discussed by *Legrand* [1995], calcium carbonates emitted from continental areas can also be converted into calcium sulfate by reaction with sulfuric acid during their atmospheric transport toward Greenland. However, this

Table 2. Sulfate, Sodium, and Nss-Sulfate Concentrations and Isotopic Composition of Total and Nss Sulfate[a]

Sample	Mean Date, A.D.	$[SO_4^{2-}]$, ng g^{-1}	$[Na^+]$, ng g^{-1}	f_{ss}, %	[nss SO_4^{2-}], ng g^{-1}	δ_{tot}, ‰	δ_{nss}, ‰
			Industrial Times				
I	1967	102.2	4.1	1.0	101.2	3.8	3.6
H	1932	92.3	32.6	8.8	84.1	6.1	4.6
G	1904	63.5	10.1	4.0	60.9	5.7	5.0
F	1887	47.9	5.6	2.9	46.5	6.1	5.7
E	1875	35.2	4.9	3.5	34.0	8.0	7.6
			Preindustrial Times				
D	1708	30.7	12.4	10.1	27.6	10.1	8.9
C	1644	33.4	6.7	5.0	31.8	7.1	6.4
B	1398	26.3	6.0	5.7	24.8	11.7	11.1
A	1307	25.9	6.1	5.9	24.3	11.3	10.7

[a] Precise depth intervals and estimated dates are given in Table 1. Concentrations of total sulfate and sodium are measured on total melted samples. Uncertainties on δ_{tot} are ±1‰. See text for details on [nss SO_4^{2-}], f_{ss}, and δ_{nss} calculations.

process should not affect the terrigenous sulfate source estimation from the Ca^{2+} level. Since methanesulfonic acid (MSA) is only produced in the atmosphere by the oxidation of dimethyl sulfide (DMS) emitted by marine biota, the MSA concentration or the MSA fraction (defined as R = MSA/(nss SO_4 + MSA)) represent potential tracers of the marine biogenic contribution. However, numerous recent studies have shown our present poor understanding of the parameters controlling the relative production of MSA versus sulfate during the atmospheric oxidation of DMS. The apparent sensitivity of the MSA/sulfate branching ratio to meteorological conditions is still largely unexplained, which makes the use of this tracer delicate [*Hansson and Saltzman*, 1993; *Whung et al.*, 1994; *Legrand and Pasteur*, 1998]. Moreover, MSA levels in the ice might not have direct atmospheric significance owing to the poor stability of this compound in the ice matrix [*Mulvaney et al.*, 1992; *Wagnon et al.*, 1999]. The continental biota contribution to the northern high-latitude sulfate budget is minor compared to the marine source: The estimated areal volatile sulfur flux from boreal continental biotopes is generally much lower than the oceanic one (for soils and vegetation) or is in the same range but much less widespread (for lakes or coastal waters) [*Adams et al.*, 1981; *Richards et al.*, 1994; *Levasseur et al.*, 1997; *Sharma et al.*, 1999a, 1999b]. It has also been shown that boreal biomass burning events do not affect the concentration level of sulfate in the present-day central Greenland atmosphere and precipitation [*Dibb et al.*, 1996; *Jaffrezo et al.*, 1998] as well as in preindustrial ice [*Savarino and Legrand*, 1998]. The total contribution of continental biota (freshwater, soils, and plants) and biomass burning does not exceed 10% of the oceanic sulfur emissions on a zonal average north of 65°N [*Bates et al.*, 1992]. The remaining part of the sulfate preindustrial budget is generally attributed to background volcanism [*Legrand et al.*, 1997], including the noneruptive degassing and the weakly eruptive degassing too dilute to be identified as such in the ice. The eruptive volcanic contribution is obvious in well-defined layers impacted by important eruptions. In that case, high acidity and nss-sulfate levels well above the background line are unambiguous [*De Angelis and Legrand*, 1994; *Clausen et al.*, 1997]. By studying seasonal variations of these different chemical species (SO_4, MSA, Na, and Ca) in Summit ice from the preindustrial background period (i.e., a decade around 1280 A.D. free of apparent volcanic spike), *Legrand et al.* [1997] could estimate the mean annual background volcanic contribution to represent 47% of the nss sulfate, whereas the marine biogenic and the terrigenous contributions amounted to 36 and 17%, respectively.

[16] The isotopic composition of sulfur is used here to test this previous conclusion on the source apportionment for the natural sulfate budget in Greenland. The isotopic signature of the seawater sulfate is known to be constant throughout the open oceans and is precisely defined at δ_{ss} = +21.0‰ [*Rees et al.*, 1978]. Sea-salt sulfate is expected to be transferred without isotopic fractionation in sea-spray particles, precipitation, and, ultimately, into the ice sheet. Marine biogenic sulfate is, on the basis of theoretical calculation, thought to be moderately fractionated relative to seawater sulfate (δ_{mb} between +14 and +22‰ [*Calhoun et al.*, 1991]). Isotopic measurement of sulfur in aerosols above the Pacific and the Atlantic Oceans [*Calhoun et al.*, 1991; *Patris et al.*, 2000b], as well as particulate sulfate in north European coastal areas [*McArdle et al.*, 1998], yielded values of δ_{mb} within the theoretical range. But values close to the lower limit of this range could possibly be somewhat influenced by isotopically lighter continentally derived sulfur [*Patris et al.*, 2000b]. The isotopic analysis of background sulfate in South Polar snow layers, which are mainly of marine biogenic origin and isolated from continental influences, gave a value at the center of the theoretical range, i.e., slightly depleted in ^{34}S relative to seawater sulfate (δ_{mb} = +18.6 ± 0.9‰ [*Patris et al.*, 2000a]). This latter value could be used as the marine biogenic signature in Greenland ice, where potential local variabilities on δ_{mb} are averaged by regional-scale atmospheric transport, as is the case in central Antarctica. Volcanic S gaseous emissions have, on average, $\delta^{34}S$ values around 0 to +5‰ [*Nielsen et al.*, 1991]. Crustal or sedimentary sulfur cover a much wider isotopic range, depending highly on the location and the chemical nature of the surface. A mean isotopic signature for continental primary aerosols is thus far more complicated to define than for volcanic or marine biogenic sources. Most of sedimentary sulfates have positive $\delta^{34}S$ [*Nielsen et al.*, 1991]. The continental biogenic source covers a $\delta^{34}S$ range similar to the volcanic one (i.e., around 0‰), with a larger local variability [*Newman et al.*, 1991; *Trust and Fry*, 1992]. The absence of any specific tracer for either of them, and the large dominance of the volcanic term over the biogenic one in the regional budget, make it difficult to distinguish between these two contributors. The continental biogenic member will hereinafter be included together with the background volcanic one under the term "secondary continental source."

3.1. Chemical and S Isotope Data

[17] A summary of chemical analyses performed on the melted Greenland ice samples and isotopic measurements are presented in the lower part of Table 2. As previously mentioned, non-sea-salt sulfate is calculated from the sodium content,

$$\left[nss - SO_4^{2-}\right] = \left[SO_4^{2-}\right] - \left[ss - SO_4^{2-}\right] = \left[SO_4^{2-}\right] - k[Na^+], \quad (2)$$

where k = 0.25 represents the bulk seawater (SO_4^{2-}/Na^+) mass ratio. The sea-salt fraction of sulfate f_{ss} is then defined as

$$f_{ss} = \frac{[ss - SO_4^{2-}]}{[SO_4^{2-}]} = \frac{k[Na^+]}{[SO_4^{2-}]}. \quad (3)$$

The isotopic composition $\delta^{34}S$ of total sulfate is denoted as δ_{tot}. The isotopic composition of nss sulfate is denoted δ_{nss} and is calculated as

$$\delta_{tot} = f_{ss}\,\delta_{ss} + (1 - f_{ss})\delta_{nss} \quad (4)$$

$$\delta_{nss} = \frac{\delta_{tot} - f_{ss}\,\delta_{ss}}{1 - f_{ss}}. \quad (5)$$

[18] The sea-salt fraction of sulfate is constant for the three deeper sections, at 5.5 ± 0.5% of the total sulfate, and reaches 10.1% in sample D. MSA concentrations of the four ice samples (mean value 1.4 ± 0.7 ng g^{-1}) are well below the levels usually reported at Summit for the last millenium (~3.0 ± 1.5 ng g^{-1} [*Legrand et al.*, 1997]). The mean MSA fraction *R* found here (5.0 ± 2.8%) is also lower than previously reported values. A similar effect has been observed for the Vostok (Antarctica) ice core when measuring MSA in the ice core after a storage period of several years in cold rooms at −15°C (M. Legrand, unpublished data, 1998) without convincing explanation for this observation.

[19] A detailed ion analysis with a high resolution (on 5-cm-long lamellae, i.e. ~4–8 analyses per year) was performed by *Savarino* [1996] between 1200 and 1775 A.D. and is therefore available for our four preindustrial samples (A–D). The corresponding total sulfate profiles are presented in Figure 1. These sections are representative of the background situation as far as sulfate is concerned ($[SO_4^{2-}]$ <80 ng g^{-1}), except section C, which is marked by a transient sulfate spike, likely of volcanic origin.

[20] The isotopic compositions of the total SO_4 and nss SO_4 for the two deeper sections (A and B) are almost identical at +11.5‰ and +10.9‰, respectively (Table 2). Those two samples also exhibit quite similar total SO_4, nss-SO_4, and MSA concentrations (~26 ng g^{-1}, ~24.6 ng g^{-1}, and 2 ng g^{-1}, respectively). As seen in Figure 1, sulfate levels never exceed the seasonal variability generally observed in preindustrial Summit ice (roughly from 10 to 60 ng g^{-1}, with a mean $[SO_4^{2-}]$ of 27 ng g^{-1} [*Legrand et al.*, 1997]) along the two core sections. They can therefore both be considered as representative of background conditions at the scale of a few years. Samples C and D exhibit slightly higher mean sulfate levels (33.4 and 30.7 ng g^{-1}, respectively). The suspected volcanic deposition around 101.3 m detected in the detailed chemical profile of sample C is confirmed by the isotopic composition of this sample (δ_{tot} = +7.1‰ and δ_{nss} = +6.4‰), which is noticeably lighter than the isotopic composition of the two typical background samples A and B. Sample D shows both intermediate sulfate level and isotopic values.

3.2. Sporadic Sulfur Contributions

[21] Figure 2 shows preindustrial δ_{nss} values plotted against the inverse of nss-SO_4^{2-} concentrations. The linear relationship observed between the two parameters suggests the assumption of a binary mixing of one constant and one variable contribution, as exposed by *Krouse* [1980]. In that case, the isotopic signature of the varying member is given by the intercept of the regression line with the ordinates axis (−8.8 ± 5.6‰). The large uncertainty is due to the limited number of data and to the rather low variability of the nss-SO_4^{2-} concentrations in the set of samples, which together bring a large uncertainty on the slope of the regression line. Nonetheless, this signature is noticeably lighter than the usual

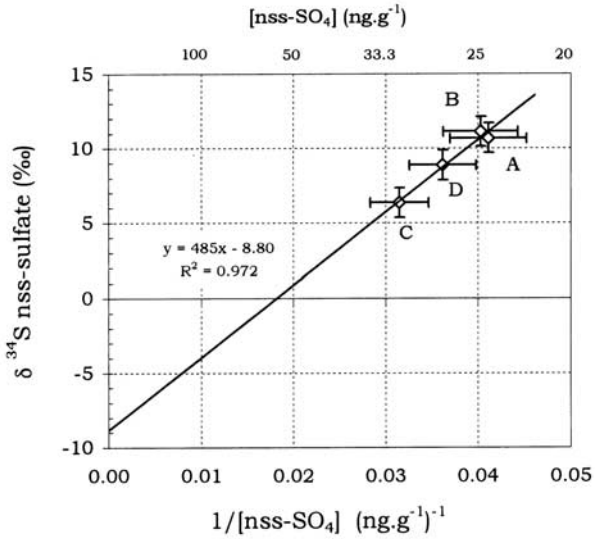

Figure 2. Isotopic composition of nss SO_4 for the preindustrial samples, given as a function of $[\text{nss } SO_4]^{-1}$. Corresponding $[SO_4]$ scale is displayed at the top of the graph.

sulfur volcanic emissions considered after large-scale atmospheric mixing. This value typically suggests a continental source, although it is not representative of terrigenous (crustal or pedospheric) sulfates, and is below the isotopic domains quoted for volcanic gaseous effluents, except for reduced sulfur emissions [*Nielsen*, 1979]. It fits in the range of reduced continental or coastal biogenic emissions on a local scale [*Newman et al.*, 1991; *Trust and Fry*, 1992]. Nevertheless, the shape and chemical characteristics of the acidic sulfate peak at 101.3 m (~2-months-long event and no concurrent presence of any biomass burning chemical tracers) point toward a highly probable volcanic origin. The fact that sample D stands exactly on the regression line suggests that this very ^{34}S-depleted varying contribution does not result from a singular event, but rather corresponds to a situation recurring over a larger timescale.

[22] If one does not question the volcanic origin of the visible peak in section C, and of the moderate perturbation of the section D sulfate profile, the very negative isotopic value obtained needs to be discussed. *Nielsen et al.* [1991] made a comprehensive compilation of isotopic measurements of sulfur from volcanogenic material. A clear pattern emerges from the data set: Direct gaseous emissions from noneruptive activities usually have values very close to the mean terrestrial sulfur ($\delta^{34}S \approx 0$‰), whereas sulfate collected on erupted ashes has on the whole noticeably higher $\delta^{34}S$ (typically around +5 to +10‰). The sulfur gases emitted during an eruption undergo isotopic fractionation as they oxidize to form sulfate, the oxidized species being enriched in the heavier isotope. The oxidation occurs at least partly as a heterogeneous process on the ashes' surface, which favors the presence of enriched ^{34}S sulfate in the particle phase, similar to what was observed in industrial effluents [*Forrest and Newman*, 1977]. The resulting ^{34}S depletion of the remaining gaseous burden could be more and more pronounced as the volcanic plume ages, particularly at high latitudes where meteorological conditions can significantly increase the SO_2 lifetime. The low temperatures prevailing in the Arctic region could also favor the enhancement of the isotopic fractionation [*Saltzman et al.*, 1983]. Whether such a process could cause the nearly 10‰ depletion needed to match the observed fractionation remains to be tested, but seems plausible.

[23] The isotopic study of the sulfate deposition peak in South Pole ice following the 1963 Agung eruption [*Patris et al.*, 2000a] led to the conclusion that volcanic sulfur was essentially unfractio-

nated when integrated over the whole chemistry-transport-deposition process. Nonetheless, *Castleman et al.* [1974] described very large isotopic fractionations of S in stratospheric sulfate particles during several months after this eruption. The positive (up to +16‰) and then negative shifts of $\delta^{34}S$ (down to −24‰) were explained by the more efficient transfer of ^{34}S in the new sulfate particles and by its consecutive depletion in the remaining gaseous load. The volcanic material was transported through the stratosphere and deposited preferentially on the Antarctic ice sheet by subsidence during winter, thus averaging to zero the isotopic fractionation in the deposited sulfate layer. Unlike the stratospheric event, the erupted volcanic material in our Greenland samples was likely transported within the troposphere, as suggested by the narrowness of the deposition peak (a few months). It may therefore have been progressively washed out along the trajectory. Very ^{34}S-depleted deposition in Greenland ice could then correspond to a relatively aged erupted volcanic material.

3.3. Preindustrial Background

[24] The sporadic volcanic sulfate inputs are superimposed on a background sulfate level that dominates the ice sections A and B. The likely sources for this preindustrial nss sulfate comprise primary continental, marine biogenic, and steady secondary continental sulfate sources. Their relative contributions to the background sulfate can be estimated considering that the isotopic signature of nss sulfate is $\delta_{nss} = f_T\ \delta_T + f_{mb}\delta_{mb} + f_C\delta_C$, where δ_T, δ_{mb}, and δ_C are isotopic signatures of the terrigenous, marine biogenic, and secondary continental contributions, respectively, and f_T, f_{mb}, and f_C are the mass fractions of these three contributions to nss SO_4 ($f_T + f_{mb} + f_C = 1$). Table 3 summarizes the ion concentrations and other chemical parameters of these two samples.

[25] The terrigenous SO_4 source can be assessed from the nss-calcium content of the ice. Indeed, sulfate in dust particles is mainly associated with calcium or magnesium as $CaSO_4$ or $MgSO_4$. Here, estimation of f_T is based on nss-Ca^{2+} concentrations that are larger than magnesium (and known with higher accuracy), and on the mass ratio ($SO_4/Ca \approx 0.18$), representative of soils or dust emissions [*Legrand et al.*, 1997]. This ratio is representative of gypsum among dust emissions, not of the calcium sulfate content of the ice that is partly controlled by the reaction of sulfuric acid on calcium carbonate during the transport, as previously pointed out. The terrigenous source is calculated to account for 1.8 ± 0.3 ng g^{-1} of sulfate, which represents f_T = 7.4% of the nss SO_4. The possible main source regions of dust reaching the Arctic, depending on the season, are arid areas located in North America and Central Asia [*Li and Winchester*, 1990; *De Angelis et al.*, 1997; *Zdanowicz et al.*, 1998]. Unfortunately, no constraint on the isotopic signatures for this source (δ_T) can be proposed, as of now, better than the range from 0 to +20‰ covering most sedimentary sulfate values [*Nielsen et al.*, 1991]. The isotopic uncertainty on this contributor adds an error to the background assessment, which can be overestimated to ±0.74‰ on δ_{nss} in the extreme case where δ_T is 10‰ apart from the remaining nss-SO_4 composition ($f_{mb}\delta_{mb} + f_C\delta_C$). This error is inferior to the experimental uncertainty on δ_{tot}. (Because of the low sea-salt content of those samples, the uncertainty on δ_{nss} is equivalent to that on δ_{tot}.)

[26] All the samples cover several years of snow accumulation. The marine biogenic source exhibits a well-marked seasonal cycle in these regions and is characterized by a double peak in spring and late summer following the bioproductivity of the surrounding oceanic regions [*Li et al.*, 1993; *Jaffrezo et al.*, 1994]. It has also been observed that the year-to-year variability in the ice record is rather limited [*Legrand et al.*, 1997]. We can therefore assume that the marine biogenic input is equivalent in each preindustrial sample. Assuming that both variabilities of the marine biogenic and secondary continental sources are small in background conditions, we can estimate their relative contributions considering their respective isotopic signatures δ_{mb} = +18.6 ± 0.9‰ and δ_C = +2.5 ± 2.5‰:

$$f_C\delta_C + f_{mb}\delta_{mb} = \delta_{nss} - f_T\delta_T \cong \delta_{nss} - (0.74 \pm 0.74‰), \quad (6)$$

with

$$f_C + f_{mb} = 1 - f_T = 0.926. \quad (7)$$

In (6) the term δ_{nss} has its own uncertainty, which adds to the error given by the terrigenous member. The numerical calculation gives f_{mb} = 48.8% and f_C = 43.8%, with the uncertainty ±12.7% calculated taking into account all uncertainties (on δ_{nss}, δ_{mb}, δ_C, and δ_T). The main part of the uncertainty on f_{mb} and f_C estimates is coming from the experimental error on δ_{nss}, the terrigenous contributor accounting for only 10% of the total uncertainty. Reducing the likely range for the typical δ_T is therefore not a prime factor to improve this estimate. The raw figure presented here nevertheless suggests a short predominance of the year-round marine biogenic contribution over the secondary continental one, especially over the background volcanic source. The suggested source apportionment (49%, 44%, and 7% for the marine biogenic, secondary continental, and terrigenous contributions, respectively) is in slight disagreement with the estimate proposed by *Legrand et al.* [1997] (36%, 47%, and 17% for the same contributors, neglecting the continental biota). Apart from the dust contribution, which is likely to vary on a short timescale (typically on an event basis), the main difference stands in the relative importance of f_C and f_{mb}. *Legrand et al.* [1997] based their estimate on the examination of seasonal variations of total sulfate deposition, considering that the marine biogenic component is canceled during winter, as suggested by MSA levels close to zero in the corresponding ice layers. Several studies of sea level aerosols in the Arctic actually suggested that the MSA production from DMS oxidation may be strongly reduced during polar winter months but that the sulfate resulting from marine biogenic emissions could still represent a significant portion of particulate SO_4^{2-}, partly due to an enhanced poleward transport [*Li and Barrie*, 1993; *Hopke et al.*, 1995]. Should this transport take place in the free troposphere, the marine sulfur compounds are likely to reach central Greenland in winter. Direct studies of the natural part of Arctic aerosols are

Table 3. Preindustrial Background Concentrations and Chemical Assessment of Sulfate Sources[a]

	Sample	
	A	B
$CH_3SO_3^-$	1.9	2.1
Cl^-	12.6	11.0
NO_3^-	66.1	60.3
SO_4^{2-}	25.9	26.3
Na^+	6.1	6.0
NH_4^+	8.0	5.4
Mg^{2+}	1.6	1.7
Ca^{2+}	11.9	8.7
Nss SO_4^{2-}	24.3	24.8
Nss Ca^{2+}	11.6	8.5
Cl/Na mass ratio	2.1	1.8
R = MSA/(MSA + nss SO_4)	0.07	0.08
Contributions to Sulfate		
sea-salt SO_4^{2-}	1.5	1.5
terrigenous SO_4^{2-}	2.1	1.5
biogenic + volcanic	22.2	23.3

[a] All terms are given in ng g^{-1} except Cl/Na mass ratio and MSA fraction R, which are dimensionless. MSA concentration and R have presumably been altered during sample storage (see text).

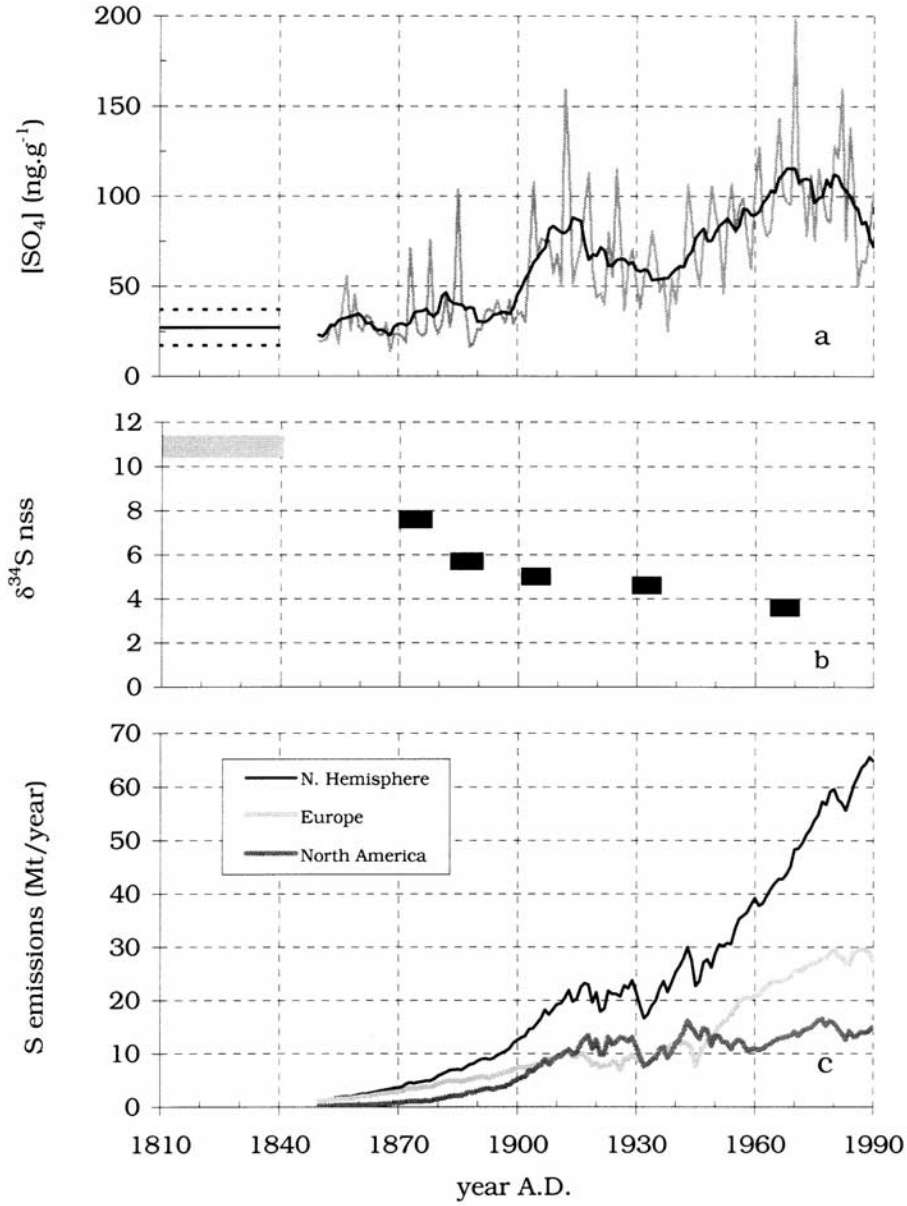

Figure 3. (a) Sulfate profile in Greenland Ice Core Project ice core along the industrial era (annual means and 9-year running average). Data are from *Legrand and Mayewski* [1997]. (b) Isotopic composition of nss-SO_4 for samples E–I. (c) Sulfur emissions for the same period for the Northern Hemisphere, North America (Canada, USA, and Mexico), and Europe (including Russia or USSR). Data are from http://www.asl-associates.com [*Lefohn et al.*, 1999]. Sulfate concentration (27 ± 10 ng g^{-1}) and δ_{nss} (+10.9‰), representative of preindustrial background, are shown for comparison before 1840 on Figures 3a and 3b.

nevertheless hampered at present by predominant anthropogenic sulfur, especially during the winter months.

[27] It may be objected that the volcanic isotopic signature taken for the background assessment (dominating δ_C = +2.5 ± 2.5‰) is a lot different from the one found for erupted material (−8.8 ± 5.6‰). As mentioned in section 3.3, the latter value is not directly representative of volcanic effluents. The hypothesis of isotopic fractionation expressed above involves a large particle surface area on which SO_2 could be heterogeneously oxidized to sulfate, as well as a progressive washout of this isotopically heavy sulfate, especially by sedimentation. The atmospheric aerosol concentration and size distribution required to produce this effect may only be reached within an erupted volcanic plume, as opposed to the situation in the background atmosphere, especially at high latitudes.

4. Industrial Period

[28] A noticeable rise of the sulfate concentration baseline is observed in deposited ice at the turn of the last century, as well as an enhancement of the variability of the concentration [*Mayewski et al.*, 1990; *Legrand et al.*, 1997]. This increase only concerns nss sulfate, whereas sea-salt and continental dust contributions remain essentially constant over this period, as revealed by the absence of changes in Na^+ and Ca^{2+} mean concentrations from preindustrial to industrial-time ice [*Legrand et al.*, 1997]. The nss-sulfate level rose

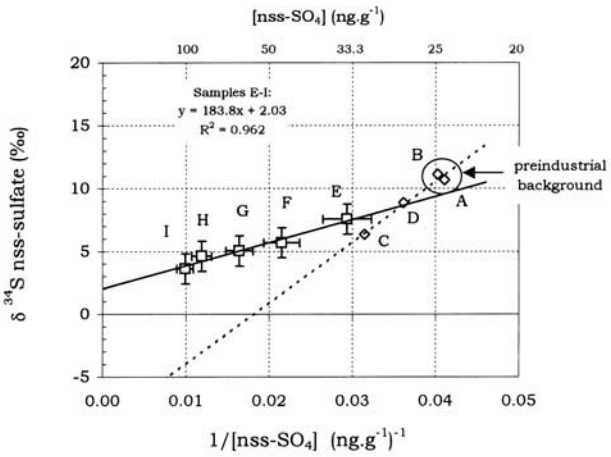

Figure 4. Isotopic composition of nss SO_4 for all the samples: diamonds, preindustrial; squares, industrial. Regression lines for the two sets of samples are shown (solid line, samples E–I; dotted line, samples A–D).

from ~50 ng g^{-1} in 1900 up to ~100 ng g^{-1} in present-day snow, episodically reaching over 150 ng g^{-1}. At the same time, a sharp increase of the nitrate content of the snow has been noted. Human activities are doubtlessly the main driving cause of the evolution observed in Greenland snow chemistry.

[29] The isotopic variability of anthropogenic sulfur at limited scale is high compared to the natural $\delta^{34}S$ range. This is partly explained by the great variety of reservoirs exploited (e.g., soils, H_2S gas, and fossil fuels). Reported values range from as low as ~−40‰ for sulfide smelting activities up to ~+30‰ for oil or gas consumption [*Grey and Jensen*, 1972; *Nielsen*, 1974; *Newman et al.*, 1991]. However, atmospheric measurements of anthropogenic sulfur are now sufficiently numerous and consistent to identify a narrow isotopic range characteristic of average human-induced emissions. Isotopic analyses of atmospheric sulfur downwind of industrialized areas, at a distance allowing regional-scale mixing or in precipitation, yield consistent values between 0‰ and +7‰ [e.g., *Cortecci and Longinelli*, 1970; *Saltzman et al.*, 1983; *Nriagu et al.*, 1987; *Herut et al.*, 1995; *Wadleigh et al.*, 1996; *Ohizumi et al.*, 1997; *McArdle et al.*, 1998; *Pichlmayer et al.*, 1998; *Querol et al.*, 2000].

[30] Sulfur isotopes have also been used during the last decade in the study of the Arctic haze. These pollution events have been occurring in a recurrent manner during winter months for the last 50 years at sea level in the Arctic region [*Barrie*, 1986]. They are attributed by meteorological, tracer, and model studies to the transport of pollutants from Eurasia, mainly [*Barrie et al.*, 1989; *Maenhaut et al.*, 1989; *Christensen*, 1997; *Xie et al.*, 1999]. Sulfur isotopes have been used to try to distinguish between Eurasia and North America as pollution source regions [*Nriagu et al.*, 1991], but this ought to be cautiously done as isotopic signatures of anthropogenic material from these areas largely overlap, not to mention that slight fractionation could occur during atmospheric processing of the sulfur. Nonetheless, identified anthropogenic sulfur in the Arctic atmosphere or in precipitation shows $\delta^{34}S$ values in the 0 to +7‰ range, preferentially closer to the upper limit [*Nriagu et al.*, 1991; *Li and Barrie*, 1993; *Norman et al.*, 1999].

4.1. S Isotope Data

[31] The isotopic compositions of industrial-time samples (E to I) are given in Table 2 for total and nss sulfate. Isotopic ratios are plotted in Figure 3 along the GRIP sulfate profile [*Legrand and Mayewski*, 1997] and sulfur anthropogenic emission estimates (data from http://www.asl-associates.com [*Lefohn et al.*, 1999]). As indicated before, visible volcanic layers were avoided during the sample selection in order to focus our study on the evolution of the background atmosphere during the last 150 years. Isotopic results show a clear progressive trend toward lighter values as the nss-sulfate deposition increases (from δ_{nss} = +7.6‰ around 1875 A.D. to +3.6‰ in ice dated ~1967 A.D.). This drift is consistent with our current knowledge on isotopic distribution of sulfur in anthropogenic emissions. The plot δ_{nss} versus $[\text{nss } SO_4^{2-}]^{-1}$ shown in Figure 4 suggests a quasilinear relationship (r^2 = 0.96), again indicating that the varying member, supposedly mainly anthropogenic, has a roughly constant $\delta^{34}S$ and is superimposed on a steady natural background. The regression line calculated for the samples E to I intercepts the *y* axis at $\delta^{34}S$ = +2.0‰, which is indeed a value characteristic of anthropogenic sulfur emissions on a large scale. However, this overall picture should be more precisely described.

[32] If we assume that an anthropogenic sulfate input with a constant well-defined isotopic signature is superimposed on the preindustrial background sulfate level, the regression line would pass through the preindustrial background point defined by samples A and B ($\delta_{nss} \approx$ +10.9‰ and $[\text{nss-}SO_4^{2-}] \approx$ 24.6 ng g^{-1}). Figure 4 suggests that this is roughly the case, given the experimental uncertainties.

Table 4. Industrial Era Background Concentrations and Chemical Assessment of Sulfate Sources[a]

Sample	E	F	G	H	I
$CH_3SO_3^-$	1.3	1.9	1.4	2.5	2.4
Cl^-	15.4	12.6	23.0	15.3	12.9
NO_3^-	63.7	57.9	64.8	84.0	99.4
SO_4^{2-}	35.2	47.9	63.5	89.1	102.2
Na^+	4.9	5.6	10.1	4.5	4.1
NH_4^+	10.4	5.8	8.9	7.0	9.7
Mg^{2+}	1.1	1.1	1.2	1.1	0.9
Ca^{2+}	11.4	9.7	13.4	5.8	6.7
Nss SO_4^{2-}	34.0	46.5	60.9	87.9	101.2
Nss Ca^{2+}	11.3	9.5	13.0	5.6	6.6
Cl/Na mass ratio	3.1	2.3	2.3	3.4	3.2
R = MSA/(MSA + nss SO_4)	0.04	0.04	0.02	0.03	0.02
		Contributions to Sulfate			
Sea-salt SO_4^{2-}	1.2	1.4	2.5	1.1	1.0
Terrigenous SO_4^{2-}	2.0	1.7	2.3	1.0	1.2
Biogenic + volcanic + anthropogenic	32.0	44.8	58.6	86.9	100.0

[a] All terms are in ng g^{-1}, except Cl/Na mass ratio and MSA fraction *R*, which are dimensionless. MSA concentration and *R* have presumably been altered during sample storage (see text).

Table 5. Anthropogenic Signature δ_A Estimated for Constant and Corrected Marine Biogenic Contributions

Sample	δ_A, ‰	
	I[a]	II[b]
I	+1.3 ± 1.3	+2.5 + 1.3
H	+2.3 ± 1.4	+3.0 ± 1.4
G	+0.9 ± 1.8	+3.0 ± 1.6
F	−0.1 ± 2.3	0.0 ± 2.3
E	−1.4 ± 4.5	−1.4 ± 4.5

[a] Marine biogenic contribution to sulfate is considered constant for all samples and is equivalent to the preindustrial background (12.0 ng g^{-1}).

[b] Marine biogenic contribution is corrected proportionally to MSA ice concentration variations since 1870.

4.2. Anthropogenic Contribution to Greenland Sulfate

[33] As a first approximation, we can consider that the natural contribution to the sulfate deposited in 1870–1970 is similar to the one present in the preindustrial samples. Indeed, the terrigenous contribution to samples E–I is in the same range as for samples A and B (compare Ca^{2+} and Mg^{2+} concentrations in Tables 3 and 4), which indicates that no dramatic change in atmospheric transport patterns occurred during the period. The volcanic and biogenic terms are less easy to evaluate solely from the chemistry of the ice, but their importance could be considered to be close to the preindustrial: for an unchanged accumulation rate, the marine biogenic source would contribute for ~12 ng g^{-1} of sulfate, and the secondary continental source would contribute for ~10.7 ng g^{-1} of sulfate. The anthropogenic signature δ_A can then be calculated for each individual sample. The resulting signatures, presented in Table 5, column I, shift along time from −1.4 ± 4.5‰ for sample E (dated ~1875) up to +2.3 ± 1.4‰ for sample H (~1932).

[34] It has been shown that the MSA concentration in Greenland ice followed a significant decrease over the twentieth century [*Whung et al.*, 1994; *Legrand et al.*, 1997]. Interpretation of this profile is delicate as it could possibly reflect (1) a decline in marine bioproductivity at Northern high and midlatitudes [*Roemmich and McGowan*, 1995], (2) a perturbation affecting the DMS production (like the sea-ice cover of Arctic and sub-Arctic regions [*Legrand et al.*, 1997]), (3) a possible shift in atmospheric transport patterns or deposition seasonality, or (4) a change of the MSA/nss-SO_4 branching ratio due to human-driven modifications of the atmospheric chemistry [*Legrand et al.*, 1997]. In the hypothesis that this MSA variation is not essentially driven by a change in the MSA/nss-SO_4 branching ratio, we can speculate that a proportional decrease in marine biogenic sulfate concentration in the ice occurred at the some time. The marine biogenic contribution to deposited sulfate can be corrected proportionally to the [MSA] variation in the ice. A corrected value of δ_A can then be calculated and is reported in Table 5 column II and in Figure 5. (For this estimate, smoothed data of [MSA] from *Legrand et al.* [1997] was used instead of our measurements, which were likely altered by a long storage period, as previously pointed out.) The estimated anthropogenic signature is not significantly different from the uncorrected one for the earlier samples, before the clear decreasing trend of MSA. But the values of δ_A for the three twentieth century samples are in this case higher, standing between +2.5 ± 1.3‰ and +3.0 ± 1.6‰. These estimates are consistent with our knowledge of anthropogenic sulfate emissions. They also indicate that anthropogenic sulfate reaching central Greenland is slightly but measurably isotopically different from that involved in present-day Arctic haze (~ +5.0 ± 0.9‰ calculated by *Norman et al.* [1999]). This difference can possibly be accounted for by a different distribution of the anthropogenic sulfur sources at sea level and on the Greenland ice cap.

[35] The Arctic haze is reported not to reach central Greenland, partly owing to a strong wintertime stratification of the Arctic atmosphere [*Barrie*, 1986]. A modeling study suggested that the relative importance of source regions of Arctic pollution varies with the elevation [*Iversen*, 1989]: According to that model, low-level atmospheric pollution originates mainly from the former Soviet Union, whereas the European and, to a lesser extent, Northern American contributions increase with altitude. Different patterns have also been observed in atmospheric and snow concentrations of several species in Greenland, according to the site elevation [*Jaffrezo et al.*, 1994; *Fischer et al.*, 1998a]. These observations tend to confirm that source region apportionment made for sea level Arctic anthropogenic sulfur might not be directly extrapolated to central Greenland.

[36] The onset of a measurable impact of industrial activities on the sulfate deposited in central Greenland is not easy to determine from the sulfate concentration profile, because of the relatively high natural variability observed in high-resolution analyses. The industrial impact starts to be obvious in Greenland ice in the 1900–1910 decade, during which the mean sulfate concentration nearly doubles (Figure 3a). This is the decade when, according to different estimates [*Dignon and Hameed*, 1989; *Lefohn et al.*, 1999], anthropogenic sulfur emissions began to dominate over volcanic and marine biogenic emissions in the Northern Hemisphere (~13 Tg S per year [*Bates et al.*, 1992; *Spiro et al.*, 1992]). *Dignon and Hameed* [1989] calculated that anthropogenic sulfur was already 30–40% of the natural flux in the decade 1870–1880, which was later confirmed by *Lefohn et al.* [1999]. In agreement with these estimates, the isotopic compositions of our nineteenth century samples confirm that anthropogenic sulfate notably altered the sulfate budget at least as early as 1870 (Sample E, Figure 3b).

[37] The variability of the calculated anthropogenic sulfate signatures is rather limited over the twentieth century. This result was unexpected when considering that the nature of emissions changed through time from predominant coal burning in the first part of the century, progressively replaced by a larger consumption of oil, and that the dominant source regions switched from Europe in the nineteenth century to North America early in the twentieth century and to Eurasia since 1950 [*Lefohn et al.*, 1999]. The isotopic differences reported between the different types of fuels or the different origins of the raw materials [*Nielsen et al.*, 1991] are not apparent in these preliminary ice core results.

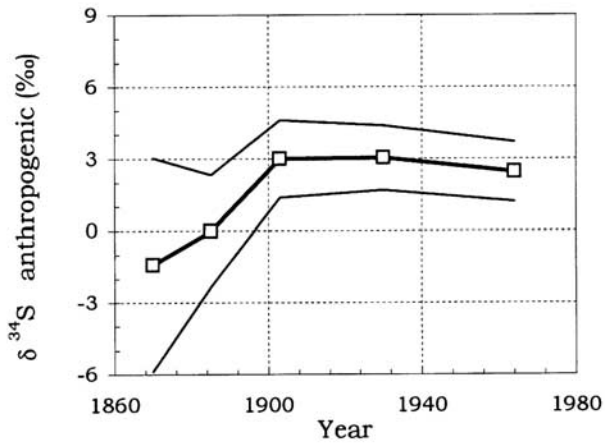

Figure 5. Estimated isotopic signature of anthropogenic sulfur reaching Greenland, taking into account the possible decrease of marine biogenic contribution to the deposited sulfate along the twentieth century.

5. Conclusions

[38] Sulfur isotopes have been measured in Greenland ice along a discontinuous series of samples covering the preindustrial modern period (from the fourteenth to the eighteenth centuries) and the industrial era (from 1872 to 1969 A.D.). Results have been used to quantify the different contributions to the deposited sulfate, representative of the mid- to high-latitude Northern Hemisphere atmospheric sulfate budget.

[39] Two samples with very low sulfate content ($\sim$26 ng g^{-1}), representative of the preindustrial background conditions, have nss-SO_4 isotopic compositions intermediate between marine and continental values ($\delta^{34}S \sim +10.9‰$), showing an equilibrated contribution from the two main sources, marine biota and background volcanism. The preindustrial background sulfate budget is found to be slightly dominated by marine biogenic emissions on a year-round average, amounting to close to half of the nss sulfate (49%). Continental contributions to secondary sulfate (mainly background volcanic activity and, to a lesser extent, the continental biosphere) represent the second source during background conditions (44%), whereas terrigenous sulfate is estimated to be <10% of the total. The above estimates are uncertain by ±13%. The debate on natural background sulfur sources still calls for supplementary data.

[40] Samples marked by a relatively weak eruptive volcanic activity comprise a volcanic sulfur member largely depleted in the heavy isotope ^{34}S compared to bulk volcanic material. It is hypothesized that the isotopic fractionation observed could result from heterogeneous oxidation of SO_2 on large particles within the volcanic plume, leaving the remaining gaseous sulfur proportionally enriched in ^{32}S. This clearly needs to be assessed with further investigations, in particular, with field measurements in volcanic eruption plumes.

[41] Sulfate deposited along the last 150 years is progressively depleted in ^{34}S, as expected considering the growing human-induced emissions characterized by low $\delta^{34}S$. The isotopic signature of anthropogenic sulfur is estimated to be constant in the three samples covering the twentieth century (+3.0 ± 1.5‰) regardless of the changes of dominant source region and emission processes. This signature is slightly but measurably lighter than the one reported for Arctic haze pollution events ($\sim$ +5.0 ± 0.9‰). Supplementary data are required to describe more accurately the time evolution of sulfur emissions, especially the potential changes of natural emissions in response to anthropogenic forcings.

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