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Isotopic composition of sulfur in size-resolved marine aerosols above the Atlantic Ocean

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Abstract. Sulfur isotope measurements were performed on size-segregated aerosols collected during the Albatross oceanographic campaign from 61°N to 35°S above the Atlantic Ocean in October and November 1996. Results obviously showed the dependence of the sulfur isotope ratio upon particle size, the finest particles being depleted in ³⁴S compared to coarse particles, suggesting a heavier continental influence in the fine mode. In the coarse mode, 50–90% of the excess sulfate in both hemispheres was found to be of biogenic origin. In the fine mode a different picture was obtained. In the Northern Hemisphere the contribution of biogenic sulfur was found to be less than 35% of the excess sulfur even in relatively clean air masses. On the other hand, in the Southern Hemisphere the participation of biogenic sulfur was about 60% of the excess sulfur in purely marine air. The contribution of continental sulfur to the fine fraction in the Southern Hemisphere was up to 40 ± 25% even under pure oceanic conditions and far more in the Northern Hemisphere. These results attest to the possible importance of long-range transport of fine sulfate particles or SO₂, possibly through the free troposphere, or the importance of anthropogenic emissions due to shipping.

1. Introduction

It is well established that aerosols and especially fine particles play an important climatic role since they can scatter the solar radiation and they can act as cloud condensation nuclei (CCN), thus influencing the Earth's albedo and subsequently climate [Intergovernmental Panel on Climate Change (IPCC), 1995]. Sulfur is one of the major components of fine aerosol particles over continental areas and the most important in the marine atmosphere [Heintzenberg, 1989; Quinn and Coffman, 1998]. The oxidation of atmospheric dimethylsulfide (DMS) emitted from the oceans is proposed to be the main source of sulfur in fine aerosols in the remote marine atmosphere [Charlson et al., 1987; Bates et al., 1992b; Pandis et al., 1994]. However, its ability to produce new particles is still unclear. Savoie and Prospero [1989] claimed that one of the factors that complicates a clear assessment of climate effects of non-sea-salt sulfate (nss-SO₄, or "excess sulfate") is the non-uniform distribution of its sources. Indeed, continental sources are known to produce important amounts

of submicronic nss-SO₄²⁻ (at least 2 to 3 times more than the biogenic ones). In addition, submicronic aerosols due to their lifetime (of the order of a few days to a week) can influence the atmospheric composition not only in the regions downwind of industrialized areas, but even in remote areas of the world [Polian et al., 1986]. Thus defining the relative contribution of biogenic and continental sources to the sulfur budget, especially above large oceanic areas, should highlight the potential climatic roles of biogenic and anthropogenic sulfur emissions.

One method to estimate the relative contributions of biogenic and continental sources is based on the MSA/nss-SO₄²⁻ ratio. Methanesulfonic acid (MSA) is known to be derived exclusively from the oxidation of biogenic compounds (predominantly DMS). As MSA and nss-SO₄²⁻ have similar physical and chemical properties, they could be subject to similar removal mechanisms and rates. On the basis of the MSA/nss-SO₄²⁻ ratio, Savoie and Prospero [1989] estimated that the biogenic source accounts for about 80% of the annual average nss-SO₄²⁻ over the midlatitude North Pacific. Several authors followed the same procedure to estimate the relative contributions of continental and biogenic compounds to nss-SO₄²⁻ [see, e.g., Prospero et al., 1991; Ayers and Gras, 1991]. However, the lack of knowledge on the exact mechanisms of MSA production and on the reasons of the latitudinal dependence of MSA/nss-SO₄²⁻ ratio prohibits a very confident use of this ratio [Barone et al., 1995; Legrand and Pasteur, 1998].

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Another approach in estimating the relative contributions of continental and marine biogenic sources is the use of sulfur isotopes. Sulfur isotopes have been successfully used in the past for several geochemical implications and for source tracing of sulfur compounds in precipitation [e.g., *Wakshal and Nielsen*, 1982; *Wadleigh et al.*, 1994; *Ohizumi et al.*, 1997] and aerosols [*Calhoun et al.*, 1991; *Li and Barrie*, 1993; *McArdle et al.*, 1998; *Norman et al.*, 1999]. For the northern Atlantic region, *McArdle and Liss* [1995] have shown, by analyzing bulk aerosol samples collected at a marine site (Mace Head, Ireland), that about 30% of the non-sea-salt sulfate during summer was derived from DMS oxidation. Sulfur isotopic composition is useful in distinguishing between overall continental (anthropogenic, biogenic, volcanic, or mineral) and marine (sea-salt or biogenic) sources. Sulfur isotope ratios are presented in the usual delta notation (equation (1)), in the Vienna-CDT (VCDT) scale [*Coplen and Krouse*, 1998]:

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

where the reference is the meteoritic sulfur from the Cañon Diablo Troilite (CDT).

Isotopic domains representative of main sulfur sources can be defined along the VCDT scale: continental sulfur emissions mostly range between 0‰ and +7‰ [e.g., *Nielsen et al.*, 1991; *Nriagu et al.*, 1991; *McArdle et al.*, 1998; *Norman et al.*, 1999]. Sea-salt sulfate is enriched in the ^{34}S isotope, and the isotopic ratio is well defined at $\delta^{34}\text{S} = +21‰$ [*Rees et al.*, 1978]. The isotopic signature of the marine biogenic sulfate is still not well constrained. The theoretical range is +14 to +22‰ [*Calhoun et al.*, 1991], and the few measurements yet achieved cover almost the whole predicted range [*Calhoun et al.*, 1991; *McArdle and Liss*, 1995; *Patris et al.*, 1999].

In this paper we report on the isotopic composition of sulfur in size-segregated aerosols collected during the Albatross oceanographic campaign conducted in the Atlantic Ocean along the 30°W meridian between 61°N and 45°S in October and November 1996. Using the size segregation of aerosols, this work aims at (1) the study of the relative contributions of biogenic and anthropogenic sources to particulate sulfur along the Atlantic and (2) the estimate of the extent to which continental sulfur sources can impact remote marine regions. This information will contribute to the assessment of climatic effects of anthropogenic sulfur emissions.

This is the first attempt to our knowledge to characterize the isotopic composition of sulfur in size-segregated aerosols. This has been made possible by the use of the Continuous Flow-Isotope Mass Ratio Spectrometry (CF-IRMS) technique, allowing precise stable isotope measurements at the micromole level.

2. Experiment

Size-segregated aerosols were collected on Whatman-41 filter paper aboard the German icebreaker R/V *Polarstern* during the Albatross campaign. Figure 1 presents the ship track as well as the location of analyzed samples. The cruise was conducted from Bremerhaven (Germany) to Punta Quilla

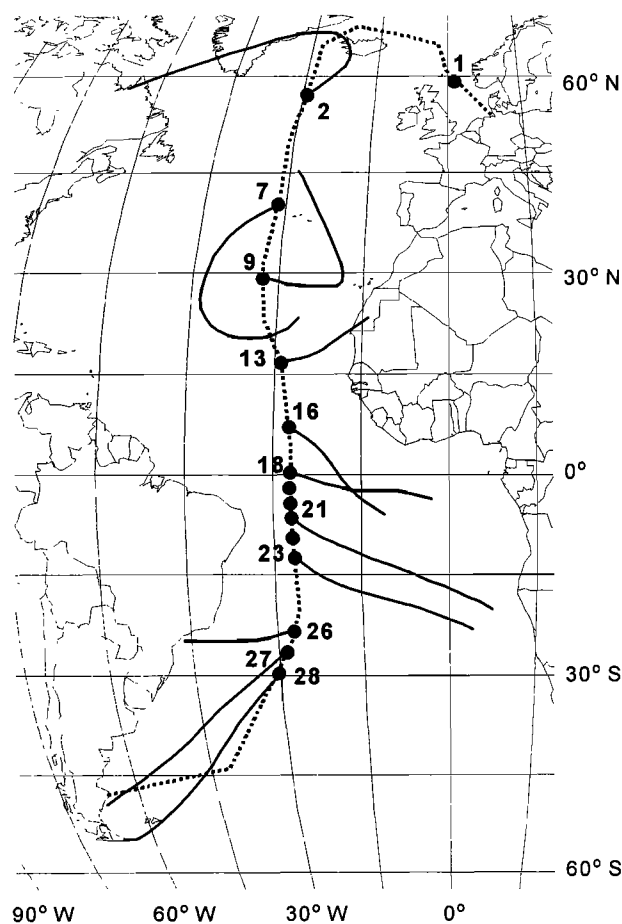


Figure 1. Ship route with sampling positions and 5-day air mass back trajectories.

(Argentina) from October 5 to November 11, 1996. The sampling time ranged from 12 to 24 hours, and the size-segregation was achieved by means of a six-stage cascade impactor (Sierra-Andersen, Model 235). The cascade impactor was operated at a flow rate of $85 \text{ m}^3 \text{ h}^{-1}$, and at this flow rate separated the particles into the following aerodynamic equivalent diameter (D_p) ranges: Stage 1: $>6.40 \mu\text{m}$, stage 2: $2.67\text{--}6.40 \mu\text{m}$, stage 3: $1.33\text{--}2.67 \mu\text{m}$, stage 4: $0.84\text{--}1.33 \mu\text{m}$, stage 5: $0.44\text{--}0.84 \mu\text{m}$. Particles with diameters lower than $0.44 \mu\text{m}$ were collected on the backup Whatman-41 filter (stage 6). The particle size fractions were determined using the empirical equations reported by *Willeke* [1975] and *Fuchs* [1978] which relate D_p to the flow rate and are derived from a similar type of impactor. The sampling was performed at the working deck at the front of the ship about 25 m above sea level, and was not directionally controlled. However, our reported nss- SO_4 values agree very well with those reported by *Krischke et al.* [this issue] during the same cruise, for which a directionally controlled sampling system was used.

The filters were extracted in 20 mL of Milli-Q water for 45 min in ultrasonic bath. The extraction efficiency with this method was higher than 98% for all compounds of interest. In sample extracts, 50–100 μL chloroform were added as a biocide, and all the extracts were analyzed for their ionic composition (including SO_4^{2-} and MSA) within a week using ion chromatography. Cations (sample volume: 10 and

100 mL) were determined with isocratic elution at 1.0 mL min^{-1} of a 20 mM MSA eluent. The separation column was a Dionex CS12 with CSRS-I suppressor in autosuppression mode of operation. Details on the analysis of inorganic and organic anions, the detection limits, and the overall experimental precision for all ionic species are given by *Baboukas et al.* [this issue].

The amount of total sulfur contained in the impactor stages as revealed by ion chromatography ranged from 0.3 up to a few micromoles. Isotope analyses were carried out on the stage filters that contained approximately $1 \mu\text{mol}$ or more of total sulfate. The technique used is specifically adapted to micromolar samples. Special attention was directed to contamination prevention and yield optimization at each step of the procedure. Stringent washing techniques were followed for the decontamination of the experimental equipment in a particulate-free room. Glassware were cleaned in successive heated bathes of nitric acid diluted in ultrapure water ($18.2 \text{ M}\Omega$), thoroughly rinsed in ultrapure water, and dried in an oven.

The following treatment took place in a class 100 laminar flow bench to avoid particulate contamination. Evaporation of 20 to 30 mL solutions was conducted in small glass containers under gentle heating, in a pure argon stream to avoid possible gas contamination. The last 2 to 4 mL were picked up with a polypropylene syringe checked free of sulfur contamination (i.e., no measurable sulfate discharge in 5 mL of ultrapure water after 48 hours storage). The final drying step was carried out in a glass tube placed on a heated aluminum base supporting tin capsules. A pure argon stream was maintained in the tube during evaporation. Samples were introduced drop by drop in the heated tin capsules containing acid-washed Chromosorb resin, on which CF-IRMS blank tests demonstrated the absence of sulfur. Sulfate precipitated in the capsule as the solution dried out. The tin foil was then wrapped up and compacted, ready to be introduced in the elemental analyzer (Carlo Erba NC-2500) for on-line CF-IRMS analysis [*Giesemann et al.*, 1994; *Patris et al.*,

1999]. Tin encapsulated samples were combusted in a flash of oxygen at temperature reaching locally 1800°C . Sulfate was thermally decomposed to SO_2 and SO_3 . Sulfur trioxide was reduced to SO_2 on hot reduced copper wires. Evolved gases were carried by pure helium through a desiccating trap, separated by gas chromatography, and introduced in the source of the Finnigan MAT-252 mass spectrometer via a silica capillary.

The isotopic ratio $^{66}\text{SO}_2/^{64}\text{SO}_2$ was integrated along the whole SO_2 peak detected by the mass spectrometer. Isotopic composition of the sample is compared to that of international standards processed the same way. The homogeneity and the large excess of the oxygen gas used for sample combustion assure reproducibility of oxygen isotopic interference on SO_2 . The combustion of standards of known $\delta^{34}\text{S}$ composition (IAEA-S1, S2, and NBS-127) was used to perform the calibration between measured $\delta^{66}(\text{SO}_2)$ and corrected $\delta^{34}\text{S}$. The procedure employed does not allow replicate measurements. The mass spectrometer was not at optimum configuration while these analyses were done which mainly reduced signal sensitivity. The experimental uncertainties quoted here ($\pm 1\%$ on $\delta^{34}\text{S}$ values) take this fact into account, but are most probably overestimated.

Excess sulfate isotopic signature (denoted δ_{nss}) has been retrieved from the measured value for total sulfate (δ_{tot}), considering the well defined sea-salt component (taking sea-salt sulfate isotopic signature $\delta_{\text{ss}} = +21\%$ and mass fraction $f_{\text{ss}} = k [\text{Mg}^{2+}]/[\text{SO}_4^{2-}]$, where k is the seawater (SO_4/Mg) mass ratio). Mg^{2+} has been used instead of Na^+ to calculate the excess sulfate due to the much lower and more reproducible blanks compared to Na^+ :

$$\delta_{\text{tot}} = f_{\text{ss}}\delta_{\text{ss}} + (1-f_{\text{ss}})\delta_{\text{nss}} \quad (2)$$

or

$$\delta_{\text{nss}} = (\delta_{\text{tot}} - f_{\text{ss}}\delta_{\text{ss}})/(1-f_{\text{ss}}) \quad (3)$$

Owing to error bars divergence when f_{ss} is close to 1, only samples with sea-salt sulfate component under 90% of total sulfate have been calculated for δ_{nss} . This was generally the

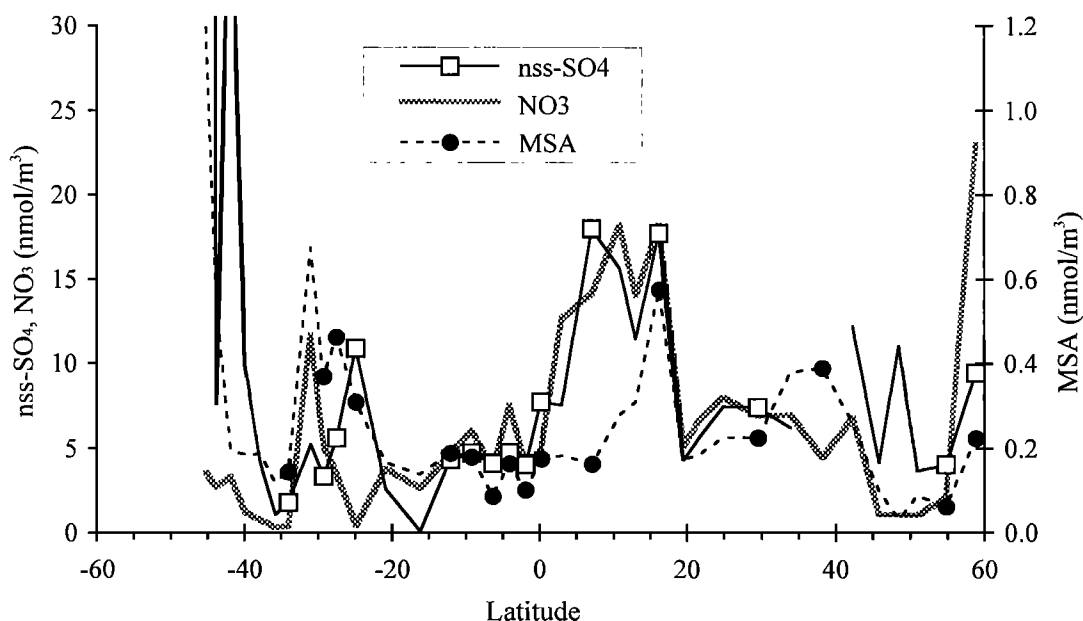


Figure 2. Measurements of total nss- SO_4 , NO_3 , and MSA (sum of the six stages of the cascade impactor) during the campaign. Symbols indicate the samples analyzed for $\delta^{34}\text{S}$.

Table 1. Description of Aerosol Samples Analyzed for S Isotopes

Samples	Date and Duration of Sampling	Latitudes Spanned	Air Masses Origin	Stages Used for S Isotopes
1	Oct. 6, 1996 (21h)	56°-61°N	North Sea, Great Britain	1, 2, 3, 4, 5, 6
2	Oct. 12, 1996 (23h)	57°-52°N	North Atlantic, Greenland, Iceland	2, 4, 5, 6
7	Oct. 16, 1996 (12h)	40°-37°N	middle North Atlantic, marine air	total
9	Oct. 17, 1996 (21h)	32°-27°N	northeast Atlantic, marine air	1, 2, 3, 4, 5, 6
13	Oct. 20, 1996 (22h)	18°-14°N	east Atlantic, African coast	total
16	Oct. 22, 1996 (26h)	10°-5°N	Guinea basin	1, 3, 5, 6
18	Oct. 24, 1996 (11h)	1°N-1°S	South Atlantic; easterly winds	5
19	Oct. 25, 1996 (11h)	1°-3°S	ID	5+6
20	Oct. 25, 1996 (10h)	3°-5°S	ID	5+6
21	Oct. 26, 1996 (11h)	5°-8°S	ID	5+6
22	Oct. 26, 1996 (12h)	8°-11°S	ID	5+6
23	Oct. 27, 1996 (12h)	11°-13°S	ID	5+6
26	Oct. 29, 1996 (23h)	23°-27°S	southwest Atlantic, Brazilian coast	1, 2, 3, 4, 5, 6
27	Oct. 30, 1996 (11h)	26°-28°S	southwest Atlantic; SW winds	5+6
28	Oct. 31, 1996 (11h)	28°-30°S	ID	5+6
30	Nov. 1, 1996 (11h)	33°-35°S	no data	5

Air masses origins were deduced from 5-day back trajectories. All samples were collected along the 30°W meridian above the Atlantic Ocean, except the first one above the North Sea.

case, except for a few coarse fractions (samples 1 and 2) and one total filter (filter 7). Error bars were calculated taking into account uncertainties on δ_{tot} and on f_{ss} . Uncertainties on δ_{nss} are in some cases substantially higher than on δ_{tot} due to high f_{ss} [Patris, 1999].

3. Results and Discussion

3.1. Ions: Major Features

3.1.1. Sulfur ions. The measurements of total nss-SO₄ (sum of the six stages of the cascade impactor) during the campaign are reported in Figure 2. The mean value of 7.8 nmol/m³ observed during the experiment is among the lowest recorded over the Atlantic Ocean [Sciare *et al.*, this issue], suggesting that pure marine conditions occurred during the major part of the cruise. Total particulate MSA concentrations are also depicted in Figure 2. They ranged from 0.03 to 1.2 nmol/m³ (mean of 0.26 ± 0.22 nmol/m³) and agree well with previous observations above the Atlantic Ocean. More information about the sulfur species measurements and previous studies are given by Sciare *et al.* [this issue].

3.1.2. Nitrate. NO₃⁻ measurements in aerosol phase are shown in Figure 2. In agreement with Prospero *et al.* [1995] we consider our measured NO₃⁻ concentrations on Whatman-41 filters as the sum of gaseous HNO₃ and particulate NO₃⁻. Since no marine source is known for NO₃⁻, it can be used as an excellent indicator of anthropogenic influence. During the campaign, NO₃⁻ concentrations ranged between 0.3 and 23 nmol/m³ (average at 6.1 ± 5.6 nmol/m³). With the exception of three events at the beginning, at the end of the cruise, and around 10°N, which were probably influenced by continental emissions, all other values are among the lowest reported for the Atlantic [Prospero *et al.*, 1995]. More details on the factors controlling the NO₃⁻ and HNO₃ concentrations will be reported elsewhere.

3.2. Sulfur Isotopes

The isotopic composition of sulfur has been measured on five impactor filter series, collected between 61°N and 25°S,

as well as nine fine particle fractions ($D_p < 0.84 \mu\text{m}$) collected between the equator and 35°S. Two bulk aerosol filters were also analyzed, collected at 38°N and 16°N, respectively. Detailed description of the samples analyzed is presented in Table 1. The isotopic results for total sulfur from the impactor series are shown in Figure 3 and numerically presented in Table 2 together with calculated δ_{nss} .

3.2.1. Bulk aerosol. The two bulk aerosol backup filters were sampled in quite different conditions. Sample 7 was exposed during night (October 15, 0910 LT to October 16, 1025 LT) between 39.7°N and 36.7°N. The 5-day back trajectory analysis clearly indicates a marine origin of the air masses, situated within 30°-45°W longitude and 20°-40°N latitude intervals during that time. Sample 13 was collected during 22 hours (October 20, 1115 LT to October 21, 0935 LT) from 18.3°N to 14.2°N. Air masses came from the African coast within the preceding 5 days. Table 3 shows concentrations of ionic tracers of maritime and continental influences, confirming trajectories analysis: major ions of mainly marine origin (sulfate, chloride, sodium, magnesium) are at higher levels in filter 7 than in filter 13; in contrast, nitrate and oxalate ions concentrations are noticeably higher in the latter.

Sulfur isotopic composition of sulfate from filter 7 is quite representative of seawater sulfate (+20.8 ± 1‰). The sea-salt fraction of sulfate determined by chemical analysis is overestimated (110% of total sulfate, as calculated using Mg²⁺ as the sea-salt tracer). Sulfur isotopes and chemical composition consistently show the strong domination of ss-SO₄ in this sample. The very high total sulfate level observed (31 μg/m³, which is 1 order of magnitude higher than average) strongly suggests a very large sea-spray impact on this filter. Excess sulfate content, and therefore its isotopic composition, cannot be defined with acceptable precision.

Excess sulfate concentration from filter 13 represents 1.7 μg/m³, which is 62% of the total sulfate. The measured $\delta^{34}\text{S}$ for total sulfate is $\delta_{\text{tot}} = +13.8 \pm 1\text{‰}$, and the calculated $\delta^{34}\text{S}$ for excess sulfate is $\delta_{\text{nss}} = +9.4 \pm 2.6\text{‰}$. These values are consistent with results from a previous study by Gravenhorst [1978], where isotopic composition of particulate excess

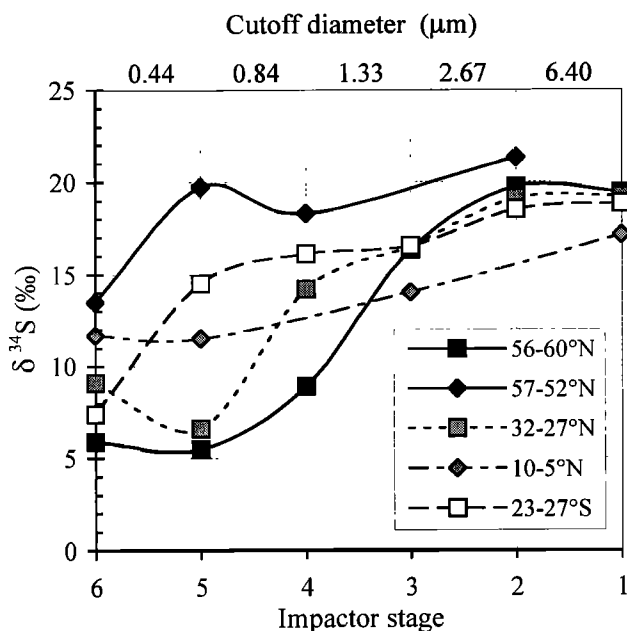


Figure 3. The $\delta^{34}\text{S}$ measured for total particulate sulfate versus impactor stages. Spanned latitudes are displayed in the legend frame. Error bars of $\pm 1\%$ are not shown.

sulfate above the North Atlantic was $\delta_{\text{NSS}} = +7$ to $+9\%$ for samples under direct continental influence, and $\delta_{\text{NSS}} = +11$ to $+13\%$ for aerosols in Sahara trade winds. This $\delta^{34}\text{S}$ range is intermediate between typical continental (up to $+7\%$) and biogenic marine ($+14$ to $+22\%$) signatures, suggesting a balanced mixing of the two terms.

Sulfur isotope results on these two total filters are consistent with meteorological and chemical data. They are a valuable tool for the assessment of atmospheric sulfur sources

and will be used further to study the source distribution of particulate sulfur in relation to the particle size.

3.2.2. Size-segregated aerosols. Coarse particles (collected on stages 1 and 2; cutoff diameter $2.7\ \mu\text{m}$) are primary aerosols, mostly sea-spray produced locally. Their residence time in the marine boundary layer (MBL) strongly depends on meteorological conditions (wind speed, rain events) and is of the order of a few hours to a few days.

As can be seen in Figure 3, coarse particles exhibit rather constant sulfur isotopic compositions through the latitudinal range investigated (from 60°N to 27°S). Chemical analyses showed that approximately 80% of sulfate is of sea-salt origin in these aerosols. The $\delta^{34}\text{S}$ values obtained are close to that of seawater sulfate; however, a shift toward lighter values can be pointed out (close to $+19\%$; see Table 2). Sample 1 was collected above the North Sea in air masses that passed above the British Islands during the last few days before sampling, as deduced from meteorological maps. Nonetheless, isotopic ratios for coarse particles ($+19.5\%$) show a dominant sea-salt source for sulfate in this size range, which is consistent with the short lifetime of these aerosols.

Calculated excess sulfate isotopic compositions for coarse fractions, when sufficient accuracy is reached ($\text{ss-SO}_4 < 90\%$ of total SO_4), show mean values ($+13.7\%$ and $+12.5\%$ for stages 1 and 2, respectively) close to but below the lower estimate of the theoretical signature of DMS-derived sulfate (between $+14\%$ and $+22\%$, as mentioned earlier). Air mass back trajectories do not suggest direct continental influences on these samples (numbers 9, 16, and 26) within 5 days. Sample 9 corresponds to descending air masses from a purely marine area of the North Atlantic (between 20° and 30°W in longitude; 40° and 25°N in latitude), whereas filter 16 sampled air masses coming from the northeastern part of the South Atlantic. Sample 26 was probably influenced by air from coastal areas along the Brazilian shore. Coarse particle analyses show similar S isotope ratios for total sulfate and for

Table 2. Sulfur Isotopic Composition (Measured δ_{tot} and Calculated δ_{NSS}) of Sulfate From Size-Segregated Aerosols

Sample	Stage 6	Stage 5	Stage 4	Stage 3	Stage 2	Stage 1	Sample	Stages 5+6
1	5.9 (5.6 ± 1.0)	5.5 (5.2 ± 1.1)	8.9 (6.5 ± 1.5)	16.3 (10.1 ± 3.8)	19.7	19.4	19	14.3 (13.4 ± 1.3)
2	13.5 (-0.3 ± 6.8)	19.7 (18.8 ± 1.9)	18.3 (14.9 ± 3.0)		21.3		20	13.2 (13.1 ± 1.1)
9	9.1 (1.0 ± 3.1)	6.6 (6.1 ± 1.1)	14.2 (12.8 ± 1.4)	16.5 (12.8 ± 2.5)	19.1 (12.8 ± 7.1)	19.2 (16.7 ± 3.0)	21	14.6 (13.6 ± 1.6)
16	11.7 (11.1 ± 1.1)	11.5 (8.8 ± 1.2)		14.0 (10.1 ± 2.3)		17.1 (11.5 ± 3.8)	22	12.3 (11.5 ± 1.2)
18		11.1 (10.9 ± 1.0)					23	13.7 (13.5 ± 1.1)
26	7.4 (6.3 ± 1.2)	14.5 (13.8 ± 1.3)	16.1 (14.2 ± 1.7)	16.5 (9.7 ± 4.3)	18.5 (12.1 ± 6.4)	18.8 (13.0 ± 6.4)	27	13.6 (13.5 ± 1.1)
30		15.8					28	12.6 (12.6 ± 1.1)
<i>Mean δ_{tot} and Dispersion</i>								
δ_{tot}	+9.5	+12.1	+14.4	+15.8	+19.7	+18.6		+13.5
$\pm \sigma$	3.1	5.0	4.0	1.2	1.2	1.0		0.8
<i>Mean δ_{NSS} and Dispersion</i>								
δ_{NSS}	+4.7	+10.6	+12.1	+10.7	+12.5	+13.7		+13.0
$\pm \sigma$	4.6	5.1	3.8	1.4	0.5	2.7		0.8

Plain text values are for δ_{tot} , and parentheses are for δ_{NSS} . Uncertainties on δ_{tot} ($\pm 1\%$) are not indicated. Dispersion ranges do not take uncertainties into account.

Table 3. Aerosol Ion Concentrations and S Isotopes for Total Filters

	SO ₄ ²⁻	NO ₃ ⁻	Cl ⁻	Na ⁺	Mg ²⁺	C ₂ O ₄ ²⁻	MSA	<i>f</i> _{ss}	δ ³⁴ S
Sample 7	30.9	0.28	276	159	16.1	0.03	0.04	100%	+20.8‰
Sample 13	2.7	1.13	8.4	4.1	0.49	0.14	0.06	38%	+13.8‰

Concentrations are in µg/m³. Sea-salt sulfate fraction *f*_{ss} is determined on the basis of the SO₄/Mg seawater ratio.

excess sulfate when it could have been calculated, regardless of the meteorological and geographic situations encountered. Although the marine biogenic source is expected to represent a predominant supplier to excess sulfate in these mid-ocean coarse particles, results suggest the existence of one supplementary source, depleted in ³⁴S isotope as compared to oceanic sulfur, which should then be continental.

In a general view, micrometric and submicrometric aerosols (stages 3 to 6) feature widely spread δ³⁴S values, showing great sensitivity to local and regional conditions. Calculated δ_{nss} for aerosol sulfate from stages 3 to 5 (i.e., in the 0.44 to 2.7 µm range) show constant mean values around +11‰, but dispersion gets wider as particle size decreases. Excess sulfate from the backup filters exhibits an isotopic signature quite representative of continental S emissions (ranging from -0.3 ± 6.8‰ for sample 2, up to +11.1 ± 1.1‰ for sample 16). Sea-salt sulfate accounts for less than 16% of total sulfate in all fine fractions analyzed, except for one case (sample 2: 57°-52°N) where it represents half of the total SO₄ on both stages 5 and 6.

The two extreme data series (samples 1 and 2, showing lowest and highest δ³⁴S values, respectively, of the data set for particles under 1.3 µm) correspond to samples collected in the same latitudinal range (between 50° and 60°N). As mentioned earlier, impactor 1 sampled air masses above the North Sea that passed over the British Islands, whereas sample 2 was collected in the North Atlantic, where air masses originated from over Greenland or Labrador within the last 5 days.

Excess sulfate isotopic composition for the North Sea particles is rather constant for the three aerosol classes under 1.3 µm and is measured between +5 and +7‰. This value is representative of anthropogenic sulfur emissions in the north of Europe [Nriagu et al., 1991; Pichlmayer et al., 1998] and especially in Great Britain [McArdle et al., 1998]. There is little doubt that nss-sulfate in fine particles collected above the North Sea is predominantly of anthropogenic origin.

On the contrary, sulfate collected on impactor 2 shows a rather high δ³⁴S on the four stages analyzed, ranging from +13.5‰ for stage 6 (<0.44 µm) up to +21.3‰ for stage 2 (between 2.7 and 6.4 µm). Excess sulfate isotopic signatures were calculated for particles under 1.3 µm diameter only (stages 4 to 6). Nss-SO₄ from stages 5 and 4 show high δ_{nss} values, in the marine biogenic range (+19 and +15‰ respectively). However, δ_{nss} calculated for excess sulfate from finer particles (stage 6) is -0.3 ± 6.8‰, which is unequivocally representative of continental sources (anthropogenic or volcanic). Large error bars do not allow us to estimate accurately the marine biogenic contribution in this excess sulfate, but results suggest a strong predominance of continental sources in the finest mode of this sample (>70%). Kruschke et al. [this issue] report the influence of a volcanic plume which could have potentially been crossed by the ship

in the vicinity of Iceland. The sampling for sample 2 started on October 12 in the evening, by the end of the detected volcanic influence. The very low δ_{nss} observed in the finest particle mode of this sampling could possibly be the result of a contamination by volcanic material. In this situation the absence of obvious volcanic influence in other particle modes (*D*_p>0.4 µm) could be the result of the exclusive gas-to-particle conversion oxidation pathway of volcanic effluents within 24 to 48 hours.

Samples specifically analyzed for fine fractions (stages 5+6 together, collected between 1°S and 30°S, *n* = 7) gave rather constant values of δ_{tot}, ranging between +12.3‰ and +14.6‰. Air mass back trajectories show southeastern winds carrying air from marine areas off the South African coasts for samples collected between 1°S and 14°S, and a southwestern influence for samples collected south of this line (air masses from South American coasts, see Figure 1). Calculated δ_{nss} values stand between +10‰ and +15‰, error bars included. There again, isotopic composition is intermediate between continental and marine biogenic sources, though meteorological data suggested a purely marine origin of the air masses for most of these samples.

Nitrate in the marine atmosphere can be used as an indicator of continental influence, being mainly emitted by, or resulting from, human activity. A relationship between nitrate and sulfur isotopic composition in the particle phase cannot be assessed accurately, due to the few data available. Moreover, transport characteristics are different for nitrate and sulfur species. However, a striking similarity exists between data from the three coarser modes (stages 1, 2, and 3) on one hand, and between the three finer modes on the other hand [Patris, 1999]. The δ³⁴S values for particles over 1.3 µm show no sensitivity to nitrate content, the slope of the regression line being almost zero. In contrast, micrometric and submicro-metric aerosol sulfate δ³⁴S drifts toward lighter (i.e., typically "more continental") values as nitrate concentration increases (clearly negative slopes with *r*² = 0.93 (*n* = 4), 0.55 (*n* = 14), and 0.34 (*n* = 12) for stages 4, 5, and 6, respectively). This additional observation tends to confirm the importance of continentally derived sulfate in the fine particle population in the Atlantic boundary layer.

3.3. Discussion

Total sulfur isotopic compositions are presented in Figure 4 as a function of the sea-salt sulfate fraction *f*_{ss}. Except points which exceed 100% for calculated ss-SO₄ contribution, all points lie within a triangle representative of a three-terms blend, similar to the one described by McArdle and Liss [1995] and McArdle et al. [1998], for samples collected in northern Atlantic regions (Ireland, Wales, and Spitzbergen). One apex of the triangle represents seawater sulfate (at *f*_{ss} = 100% and δ³⁴S = +21‰), and the other two lie on the ordinate axis (*f*_{ss} = 0%) and represent the continental

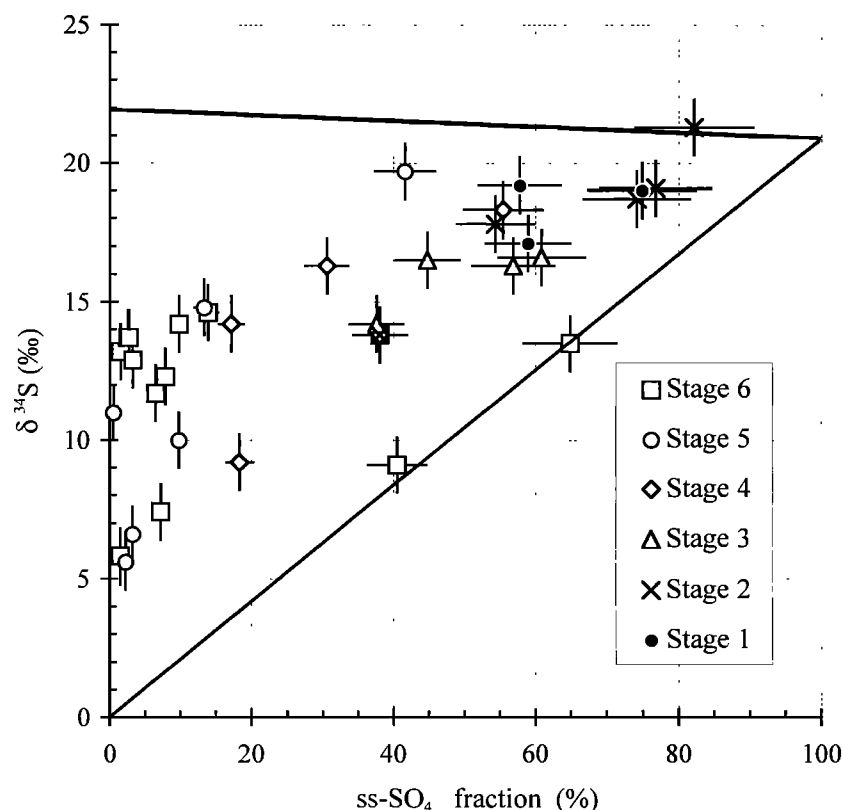


Figure 4. S-isotopic composition of total sulfate as a function of sea-salt sulfate percentage. Sea-salt sulfate is calculated on the basis of Mg concentrations.

($\delta^{34}\text{S} \sim 0\text{‰}$) and marine biogenic ($\delta^{34}\text{S} \sim +22\text{‰}$) contributors. The variety of meteorological and geographic situations undergone during the cruise does not allow precise determination of two excess sulfate end-members. However, results obtained along the wide geographical and meteorological panel covered suggest that the figure described by these authors for coastal areas of the northeastern Atlantic could be extrapolated for most of the Atlantic atmosphere.

Relative contributions of continental and biogenic marine sulfate are difficult to assess with fair confidence, as isotopic signatures of both contributors may vary noticeably at limited

scale. On the basis of their representative isotopic domains we can estimate rough proportions of DMS-derived sulfate (denoted f_{mb}) to overall excess sulfate. For this estimate we consider that continental isotope particularities are partially smoothed after regional-scale mixing and transport, reducing the width of the isotope domain. Marine biogenic sulfur isotopic signature is taken in the center of the predicted range. Values considered for these two contributions are $\delta_c = +3 \pm 2\text{‰}$ and $\delta_{mb} = +18 \pm 2\text{‰}$ respectively. Estimates of the marine biogenic contribution to excess sulfate are presented in Table 4.

Owing to a higher sea-salt content, uncertainties on δ_{NSS} and

Table 4. Fraction of the Marine Biogenic Contribution f_{mb} to Excess Sulfate

Filter	Stage 5+6	Stage 6	Stage 5	Stage 4	Stage 3	Stage 2	Stage 1
1		15 ± 20	15 ± 20	25 ± 20	50 ± 35		
2		0 ± 30	100 ± 15	80 ± 30			
9		0 ± 15	20 ± 20	65 ± 20	65 ± 30	65 ± 50	90 ± 25
16		55 ± 25	40 ± 25		45 ± 30		55 ± 35
18			55 ± 20				
19	70 ± 20						
20	65 ± 20						
21	70 ± 20						
22	60 ± 25						
23	70 ± 20						
26		20 ± 20	70 ± 20	75 ± 20	45 ± 40	60 ± 50	65 ± 45
27	70 ± 20						
28	65 ± 20						

Range estimates are based on isotopic signatures of the marine biogenic and continental sulfate taken at $\delta_{mb} = +18 \pm 2\text{‰}$ and $\delta_c = +3 \pm 2\text{‰}$, respectively. Uncertainties on δ_{NSS} , δ_{mb} and δ_c are taken into account. Units are in percent.

therefore uncertainties on f_{mb} are larger in the coarser modes. However, we can notice that the contribution of marine biogenic sulfur to coarse particles (sized over $2.7 \mu\text{m}$) is centered around 65% of the excess sulfate along the latitudinal range investigated. For medium-range and micrometric particles (2.7 down to $0.8 \mu\text{m}$), f_{mb} stands around 50% on the average. Excess sulfate from fine particles ($<0.8 \mu\text{m}$) present in purely marine air masses from the southern Atlantic is estimated between 50 and 90% to be of marine biogenic origin (samples 18-23), whereas this contribution is generally under 35% in fine particles sampled in the northern Atlantic (samples 1-9).

Our estimates of the biogenic sulfur contribution using S isotope results have been compared to estimates based on the MSA/nss-SO₄ ratio R . The marine biogenic contribution is then estimated by comparing observed R ratios to those expected using the empirical formula from Bates *et al.* [1992a], relating R to the air temperature (following: $R(\%) = -1.5 T(^{\circ}\text{C}) + 42.2$). A reasonable agreement ($\pm 20\%$) was observed in most cases, except for one sample (sample 13), for which trajectory analysis showed that the air mass originated from the middle free troposphere and thus from a cooler environment. We can estimate on the basis of the isotope results that f_{mb} amounts to $45 \pm 25\%$ of the nss-sulfate in this sample; the estimate based on R gives $f_{mb} = 93\%$ (taking $T = 25.8^{\circ}\text{C}$). Consideration of the ambient temperature at the time of sampling tends to underestimate the R ratio and consequently to overestimate the biogenic S contribution.

Excess sulfate present in coarse marine aerosols is thought to get efficiently absorbed in preexisting liquid sea-spray particles, as fine particles or as gaseous species [Pszenny *et al.*, 1989; Sievering *et al.*, 1992; Quinn *et al.*, 1993]. Local washout by sea spray may be a major sink of oxidized biogenic sulfur species in the marine boundary layer [Chameides and Stelson, 1992], thus reducing significantly the lifetime of these compounds in the atmosphere. Air mass back trajectories show that most of the air masses sampled during the campaign came from elevations higher than the boundary layer height, within the preceding 5 days. Subsiding air may convey material, including sulfur compounds, from the free troposphere down to the boundary layer. Raes [1995] proposed that entrainment of newly formed particles from the free troposphere down to the MBL could explain the relatively constant condensation nuclei number concentration near the sea surface. Sulfur present in the free troposphere may therefore be the potential dominant source of secondary sulfate aerosol in the marine boundary layer [Rodhe, 1999].

Continental influence on the nss-sulfate budget in remote marine atmosphere has already been observed [e.g., Prospero *et al.*, 1985]. Thornton *et al.* [1999] carried out extensive measurements of SO₂ above the Pacific Ocean over the years 1991 to 1996 and concluded that the marine biogenic source of SO₂ (via DMS oxidation) is only important in the tropical MBL. These authors showed that anthropogenic SO₂ is of importance in the lower troposphere as far as 1500 km from the source areas, and much further in the mid and upper troposphere in the Northern Hemisphere. They also indicated that background volcanism may control the tropospheric SO₂ budget in the Southern Hemisphere. Recently, Capaldo *et al.* [1999] demonstrated that emissions from ships may also be a significant source of sulfur within the marine troposphere. The ubiquitous presence of continental sulfur in the marine free troposphere, and its apparent involvement in new particle

formation, implies that so-called pristine marine conditions are under significant continental influence as far as the excess sulfur cycle is concerned. The free tropospheric burden appears to be controlled by continental emissions, and is able to replenish the marine boundary layer with fine and ultrafine sulfate particles. The induced radiative impact over the sea surface may be of importance since these particles play an important role in solar radiation backscattering and may act as cloud condensation nuclei inducing albedo increase [Murphy *et al.*, 1998].

4. Conclusion

Sulfur stable isotopes were measured in size-segregated marine aerosols collected above the Atlantic between 61°N and 35°S and were used as sulfur source tracer. A striking feature of the results is the progressive relation linking particle size and S isotope ratios through the whole cruise. The obvious dependence of $\delta^{34}\text{S}$ distributions upon particle size confirms the distinct transport and fate of atmospheric sulfur compounds, according to the characteristics of their emission.

Excess sulfate isotopic signature was calculated, and showed on the whole the clear trend of a more continentally contributed excess sulfate in smaller particles. In the finest mode the lowest continental influences were observed in the Southern Hemisphere as long as sampled air masses did not pass over continents more than 5 days before sampling; the biogenic contribution to fine particulate sulfate accounted in this case approximately for 50-90% of the total nss-sulfate budget. Marine biogenic sulfur in the Northern Hemisphere was less than 35% of the excess sulfur in the fine particles, even when back trajectories showed pure marine origin of the air masses.

Savoie and Prospero [1989] estimated up to 20% of excess sulfate at Midway (North Pacific; 180°W , 30°N) being of continental origin on a yearly average. Our isotope measurements on Atlantic MBL aerosols support the extrapolation of the Pacific atmospheric sulfur budget to the Atlantic atmosphere in general lines. Our results support the hypothesis that continental sulfur could be responsible, via free tropospheric long-range transport and subsidence, or direct ship emissions, for a significant fraction of fine sulfate particles in the MBL, and suggest that continental sulfate may play an important radiative role. This suggestion agrees with the correlation observed by Parungo *et al.* [1994] between anthropogenic sulfur emissions and the marine cloud cover increase during the last few decades, especially in the northern midlatitudes.

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