

SULFUR ISOTOPE MEASUREMENTS OF SUBMICROMETER SULFATE  
AEROSOL PARTICLES OVER THE PACIFIC OCEANJulie A. Calhoun<sup>1</sup>

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**Abstract.** The climatic importance of atmospheric submicrometer sulfate aerosol particles necessitates a thorough understanding of the various sources of sulfur to the marine atmosphere [Charlson et al., 1987; Coakley et al., 1987; Charlson et al., 1990]. Over the remote ocean, the primary source of atmospheric non-seasalt (NSS) sulfate is thought to be marine emissions of dimethylsulfide (DMS) [Charlson et al., 1987]. Here we report the results of a study which used stable sulfur isotopes to test this hypothesis. NSS sulfate in submicrometer aerosol particles over remote parts of the South Pacific Ocean had an average  $\delta^{34}\text{S}$  value of  $+15.6 \pm 3.1\text{‰}$ , relative to the Canyon Diablo standard. The sulfur isotopic composition of these particles was 5.5‰ lighter than sulfate derived directly from seawater, but isotopically heavier than sulfate derived from most continental sources. This observed isotopic fractionation between seawater sulfate and NSS sulfate is consistent with the isotopic fractionation predicted for the transformation of seawater sulfate to atmospheric NSS sulfate via a DMS pathway ( $-1$  to  $+7\text{‰}$ ) and hence supports the hypothesis that DMS can be the source of the NSS sulfate.

## Introduction

Atmospheric submicrometer aerosol particles directly affect the earth's climate by backscattering solar radiation [Shaw, 1983; Charlson et al., 1990] and by influencing the albedo of marine clouds [Charlson et al., 1987]. Over the oceans, these aerosol particles are composed primarily of sulfate [Bonsang et al., 1980; Andreae, 1982; Bigg et al., 1984]. The origin of these particles has been of great interest [Charlson et al., 1987; Schwartz, 1988] not only because of the need to incorporate aerosol particles and clouds into global climate models [Albrecht, 1989; Cess et al., 1989], but also to assess the impact of anthropogenic sulfur emissions on the natural atmospheric biogeochemical sulfur budget [Charlson et al., 1991].

The ocean is a potential source of atmospheric aerosol particles through oceanic emissions of DMS. Evidence to

date in support of the ocean-DMS source hypothesis has been mainly circumstantial. Early global sulfur budgets required the ocean to be a net source of reduced sulfur to the atmosphere [Eriksson, 1963; Granat et al., 1976]. DMS has since been measured in ocean surface water and the overlying atmosphere and has been calculated to contribute 0.5 to 1.0 Tmoles of sulfur per year to the marine troposphere [Andreae, 1986; Bates et al., 1987]. This calculated oceanic flux of DMS to the atmosphere is sufficient to support the concentrations of various oxidized atmospheric sulfur species, based on box models using simultaneous measurements of the key oceanic and atmospheric sulfur species [Andreae et al., 1988; Berresheim, 1987; Bates et al., 1990; Berresheim et al., 1990] and laboratory determined DMS photo-oxidation rates [Hynes et al., 1986]. However, the continents are another potential source of submicrometer aerosol particles and long-range transport of sulfur from continents has been used to

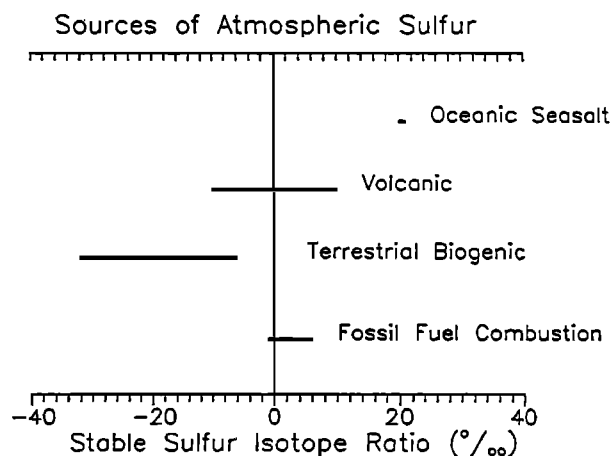


Fig. 1. The range of  $\delta^{34}\text{S}$  values for different sources of atmospheric sulfur reviewed by Nielson [1974].  $\delta^{34}\text{S}$  values are reported in per mil (‰) relative to standard Canyon Diablo meteoritic sulfur according to the relation:

$$\delta^{34}\text{S} = [(R_{\text{sample}} / R_{\text{standard}}) - 1] (1000)$$

where R is the ratio of the two most abundant stable isotopes of sulfur ( $^{34}\text{S}/^{32}\text{S}$ ). It should be noted that  $\delta^{34}\text{S}$  values measured for coals and crude-oils can encompass an even wider isotopic range ( $-20$  to  $+30\text{‰}$ ) and, therefore, the isotopic composition of atmospheric sulfur derived from the combustion of these fossil fuels is expected to vary regionally.

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balance the sulfur cycle in the marine troposphere [Andreae et al., 1988]. Direct methods are needed to distinguish the relative importance of the various sources of these particles.

The relative abundances of the stable isotopes of sulfur ( $^{34}\text{S}$  and  $^{32}\text{S}$ ) appear to be source dependent (Figure 1) and their study has proven useful for identifying sulfur sources in the past [Kaye, 1987; Nriagu et al., 1991]. However, their application in remote marine regions has been severely limited by the lack of data [Calhoun and Bates, 1989]. Since seawater sulfate provides the sulfur utilized by phytoplankton in proposed DMS production pathways [Andreae, 1986], the isotopic composition of DMS and its atmospheric oxidation products [sulfur dioxide ( $\text{SO}_2$ ), methane sulphonate (MSA), and NSS sulfate] should reflect the isotopic composition of the seasalt sulfate and the fractionation associated with the various steps in the pathway. The end result should be submicrometer aerosol particles which are isotopically heavier than sulfate particles originating from most continental sources [Kaye, 1987; Calhoun and Bates, 1989; Nriagu et al., 1991].

### Methods

Samples were collected aboard the NOAA ships *Oceanographer* in April of 1988 and *Discoverer* in March of 1989 along the  $105^\circ\text{W}$ ,  $140^\circ\text{W}$  and  $170^\circ\text{W}$  latitudinal meridians between  $20^\circ\text{N}$  and  $60^\circ\text{S}$  (Figure 2). Air-mass back trajectories were used to define the history of the sampled air masses (Figure 2). Aerosol particle samples were collected on filters ( $1.0\ \mu\text{m}$  pore size Millipore) downstream of a cyclone separator. The cyclone had a particle diameter cut-size of  $0.6\ \mu\text{m}$ , which minimized the amount of the coarse seasalt particles reaching the Millipore filters [Quinn and Bates, 1989]. Six sample filters and one blank filter were mounted in parallel on a boom extending 5 m upwind of the ship's flying bridge and 20 m above the sea surface. Air

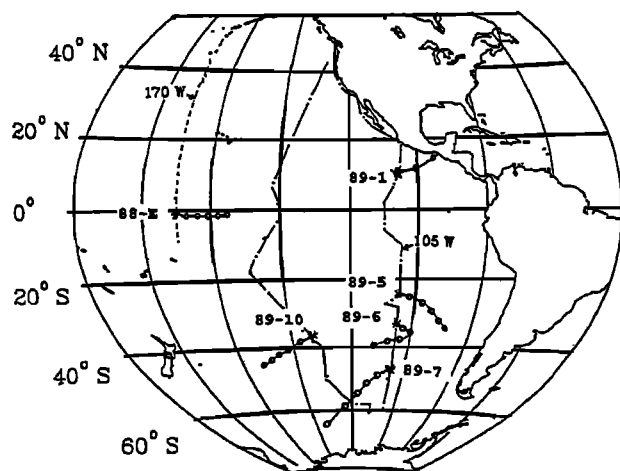


Figure 2. Cruise tracks and sample locations for *Oceanographer* in April/May 1988 ( $170^\circ\text{W}$ ) and *Discoverer* in February/March of 1989 ( $105^\circ\text{W}$  and  $140^\circ\text{W}$ ). Included in the figure are air-mass back trajectories calculated for the ship's position along  $105^\circ\text{W}$  and  $140^\circ\text{W}$  (J. Harris) and  $170^\circ\text{W}$  (D. Covert). All trajectories are indicated by symbols (o) at 24-hour intervals from the midpoint of the sampling period.

passed over the sample filters for an average of three days at flow rates of 80 standard liters per minute. A computer sector controller driven by a wind vane and anemometer was used to limit sample collection to periods when winds were forward of the ship's beam and when wind speeds were greater than 5 m/sec to prevent contamination of the samples from the ship's stack gases. Blank filters were used to account for any contamination acquired during sample handling and/or sample storage.

Replicate filters were combined to obtain 1–3  $\mu\text{mole}$  sample sizes. The sample sulfate was reduced to  $\text{H}_2\text{S}$  using a concentrated mixture of hypophosphorous acid, hydriodic acid and HCl (61:125:205 by volume) [Thode et al., 1961]. The  $\text{H}_2\text{S}$  gas was trapped in an  $\text{As}^{3+}\text{-NH}_3$  solution cooled in an ice-water bath and solid arsenic-III-sulphide ( $\text{As}_2\text{S}_3(\text{s})$ ) was precipitated with the addition of HCl. MSA which was also present on the Millipore filter did not convert to  $\text{As}_2\text{S}_3$  in the above method. To measure the isotopic composition of the total sulfur (MSA plus sulfate), the sample was placed in a concentrated mixture of nitric acid and HCl inside a sealed tube [Paulsen and Kelly, 1984] to convert the MSA to sulfate prior to reduction to  $\text{As}_2\text{S}_3$ . Samples 89-5 and 89-7 were divided, and one half was analyzed for the isotopic composition of the sulfate only and the other half was analyzed for the MSA plus sulfate. Samples 89-5 and 89-7 had MSA/NSS-sulfate ratios of 5% and 24%, respectively, as determined by ion chromatographic (IC) analysis. Details of the IC analysis were reported by Quinn et al. [1990].

Isotopic analysis by thermal ionization mass spectrometry (TIMS) was performed at the National Institute for Standards and Technology (NIST) using the method of Paulsen and Kelly [1984].  $\delta^{34}\text{S}$  values are reported relative to the standard Canyon Diablo sulfur (see caption, Figure 1). The analytical uncertainty in the TIMS analysis was 9% based on multiple analysis of seawater sulfate ( $+21.1 \pm 1.9\%$ , number of samples = 7,  $\pm$  standard deviation). The isotopic composition of the NSS sulfate ( $\delta^{34}\text{S}_{\text{NSS}}$ ) was calculated from the isotopic composition of the sample's total sulfate ( $\delta^{34}\text{S}_{\text{measured}}$ ) using the equation:

$$\delta^{34}\text{S}_{\text{NSS}} = (1/f_{\text{NSS}}) \times [\delta^{34}\text{S}_{\text{measured}} - (f_{\text{SS}} \delta^{34}\text{S}_{\text{SS}})]$$

where  $\delta^{34}\text{S}_{\text{SS}}$  is the measured or accepted  $\delta^{34}\text{S}$  value for seawater sulfate, and  $f_{\text{NSS}}$  and  $f_{\text{SS}}$  are the fractions of NSS sulfate and seasalt sulfate in the sample, respectively. These fractions are estimated using measured sodium concentrations from ion chromatographic analysis and the  $(\text{SO}_4^{2-})/(\text{Na}^+)$  mass ratio in seawater of 0.252 [Holland, 1978]. Seasalt sulfate was always less than 7% of the NSS sulfate collected on the Millipore filter. Thus, isotopic corrections for seasalt were less than 0.4%. The total uncertainty in sample collection, conversion and TIMS analysis was 14% based on the analysis of replicate samples.

### Results and Discussion

Analysis of air-mass back trajectories (Figure 2) and the atmospheric sulfur chemistry of the region [Calhoun and Bates, unpublished data] suggested that air-masses sampled south of the equator contained "background" marine aerosol particles, while the air-mass sampled north of the equator had

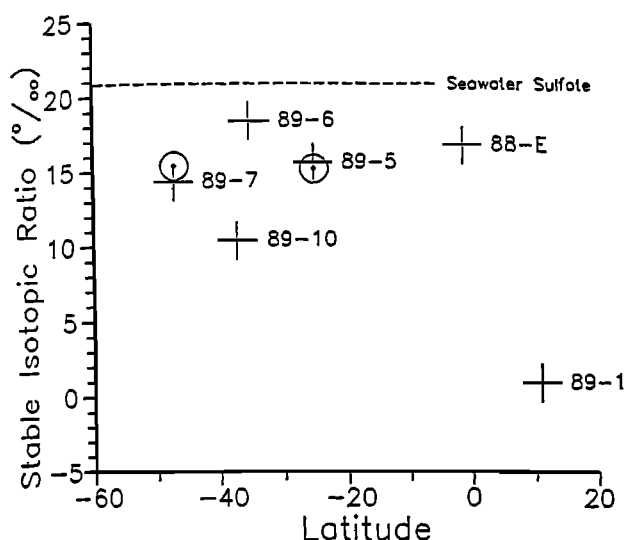


Figure 3. Sulphur isotope measurements of marine submicrometer sulfate aerosol particles collected over the Pacific Ocean as a function of latitude. Crosses indicate  $\delta^{34}\text{S}$  values of the NSS sulfate. Circles indicate  $\delta^{34}\text{S}$  values for the total NSS sulfur (MSA plus NSS sulfate). All  $\delta^{34}\text{S}$  values are reported relative to the Canyon Diablo standard and are corrected for seasalt.

been over the continent within the previous five days and therefore likely contained aerosol sulfate from continental sources. Measured  $\delta^{34}\text{S}$  values for NSS sulfate from the northern and southern hemispheres were significantly different (Figure 3). Sample 89-1, collected in the North Pacific off the coast of Mexico, had a NSS sulfate concentration of  $21 \pm 4.5 \text{ nmol/m}^3$  and a  $\delta^{34}\text{S}$  value of  $+1.0\text{‰}$ . This value is in the mid-range of the  $\delta^{34}\text{S}$  values reported for most continental sources (Figure 1). The samples collected in the southern hemisphere had a mean NSS sulfate concentration of  $3.3 \pm 1.8 \text{ nmol/m}^3$  and mean  $\delta^{34}\text{S}$  value of  $+15.6 \pm 3.1\text{‰}$ .

The sub-micrometer aerosol particles measured during this study were "heavier" (or more enriched in  $^{34}\text{S}$ ) than sulfur from most of the continental sulfur sources and "lighter" than seasalt sulfate (Figure 1). Given the isotopic fractionations associated with assimilatory sulfate reduction by phytoplankton ( $+1$  to  $+4\text{‰}$ ) [Kaplan and Rittenberg, 1964; Chambers and Trudinger, 1979], air-sea transfer of DMS ( $0\text{‰}$ ) and its atmospheric oxidation to sulfur dioxide ( $+2$  to  $+3\text{‰}$ ) [Calhoun and Bates, 1989], and atmospheric oxidation of sulfur dioxide to sulfate ( $-4$  to  $0\text{‰}$ ) [Newman et al., 1975; Saltzman et al., 1983], the overall fractionation between seawater sulfate and NSS sulfate via a DMS pathway should be between  $-1$  to  $+7\text{‰}$ . Considering the uncertainties as a result of limited isotopic measurements [Calhoun and Bates, 1989], the isotopic fractionation observed between seasalt sulfate and NSS sulfate during this study ( $+5.5 \pm 3.6\text{‰}$ ) is consistent with the expected fractionation and therefore supports the hypothesis that DMS can be the source of the NSS sulfate.

Further support for the oceanic-DMS source hypothesis was provided by a comparison of the  $\delta^{34}\text{S}$  values of both the NSS sulfate alone and of the MSA plus NSS sulfate in

samples 89-5 and 89-7 (Figure 3).  $\delta^{34}\text{S}$  values for the NSS sulfate alone and for the MSA plus NSS sulfate were equal within the analytical uncertainty of the MS technique ( $\pm 1.9\text{‰}$ ). This suggests that NSS sulfate and MSA have similar sources and fractionation factors associated with their formation. Since DMS oxidation is the only known source of MSA, these data provide additional support for the hypothesis that DMS can be the source of the background NSS sulfate. However, this argument is limited because of the large analytical uncertainty and the relatively low fraction of MSA-sulfur in these samples. Additional isotopic measurements using more precise analytical methods and samples containing higher proportions of MSA to NSS sulfate are needed.

This study demonstrates that NSS sulfate in remote marine submicrometer aerosol particles has an isotopic composition which is intermediate between seasalt sulfate and most continental sulfur sources. Therefore, measured  $\delta^{34}\text{S}$  values for NSS sulfate can be used to apportion marine and continental sources in a region if the isotopic composition of the local continental sources are known. However, as Figure 1 demonstrates, the isotopic range of potential continental sulfur sources is large and highly variable. Therefore, the utility of the sulfur isotope technique for this purpose is limited to fairly well defined study regions.

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