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The mechanism of sulfate aerosol formation: Chemical and sulfur isotopic evidence

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### Journal

Geophysical Research Letters, 10(7)

### ISSN

00948276

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### Publication Date

1983-07-01

### DOI

10.1029/GL010i007p00513

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Peer reviewed

THE MECHANISM OF SULFATE AEROSOL FORMATION:  
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## Abstract

In order to study the mechanism of aerosol sulfate formation, weekly samples of SO<sub>2</sub> and aerosol SO<sub>4</sub><sup>=</sup> were collected at Hubbard Brook Experimental Forest, West Thornton, New Hampshire from July to December, 1980. Samples were analyzed for concentration and sulfur isotopes (δ<sup>34</sup>S). Late summer-early fall samples are characterized by high, variable SO<sub>4</sub><sup>=</sup> levels and low SO<sub>2</sub> levels, while late fall - early winter samples exhibit low SO<sub>4</sub><sup>=</sup> and high SO<sub>2</sub> levels. These trends suggest that the oxidation rate varies seasonally, with faster oxidation during warmer months. The sulfur isotopic fractionation between aerosol SO<sub>4</sub><sup>=</sup> and SO<sub>2</sub> is intermediate between that expected from homogeneous and heterogeneous reactions, indicating that both processes can be important. The isotopic data suggest that homogeneous oxidation reactions are more important than solution reactions, particularly during warm months.

## Introduction

The current concern about ecological damage resulting from acid precipitation has focused considerable interest on the conversion of SO<sub>2</sub> to sulfate aerosol in the atmosphere. Laboratory studies have revealed a multitude of potentially important oxidants and oxidation pathways. Though many of the major processes are known, quantification of the various oxidation mechanisms in the environment remains elusive because such a large number of parameters must be specified in order to model actual field conditions. As a result, it is not yet known whether SO<sub>2</sub> oxidation occurs primarily in gas phase, in cloud droplets, or on the wetted surfaces of aerosol particles. The purpose of this study is to provide information about the relative importance of homogeneous and heterogeneous reactions in the formation of tropospheric sulfate aerosol in the non-urban northeastern United States.

## Experimental Techniques

Weekly samples of aerosol SO<sub>4</sub><sup>=</sup> and SO<sub>2</sub> were collected simultaneously by drawing air through a two-stage filter cassette with a high volume air pump. The upper aerosol filters were untreated Whatman 41 filters. The lower filters, also Whatman 41, were pretreated with K<sub>2</sub>CO<sub>3</sub> and glycerol to collect SO<sub>2</sub>. The trapped SO<sub>2</sub> oxidized to SO<sub>4</sub><sup>=</sup> during collection and storage. Filter SO<sub>4</sub><sup>=</sup> blanks were less than 1% of SO<sub>4</sub><sup>=</sup> collected. The air flow through the filters was determined by measuring the pressure drop across a calibrated orifice which was located downstream from the air pump.

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Paper number 3L0714.

0094-8276/83/003L-0714\$03.00

SO<sub>4</sub><sup>=</sup> was extracted from the filters with three Milli-Q water washes and the resulting solutions were filtered through Millipore filters. Aliquots of these solutions were analyzed for SO<sub>4</sub><sup>=</sup> by ion chromatography. BaSO<sub>4</sub> was precipitated from the remainder of the filter extracts by acidifying with HCl, heating, and adding BaCl<sub>2</sub>. The precipitate was washed free of Cl<sup>-</sup>, dried, weighed (10-20 mg) into quartz combustion tubes and heated to 800°C in a muffle furnace. The BaSO<sub>4</sub> was then converted to SO<sub>2</sub> by thermal decomposition under vacuum (Holt and Engelkemeir, 1970). The gas produced was allowed to react with hot Cu (500-600°C) to reduce any SO<sub>3</sub> present to SO<sub>2</sub> (Bailey and Smith, 1972). Yields of 95-100% were obtained using this procedure. The sulfur isotopic composition of SO<sub>2</sub> was measured on a Micromass 602 ratio mass spectrometer. The raw data was corrected for the oxygen isotopic composition of the sample and standards by measuring both 66/64 (SO<sub>2</sub>) and 50/48 (SO) ratios. The results are reported in the notation as per mil deviation from the CDT standard, where

$$\delta^{34}\text{S} = \left( \frac{(34/32)_x}{(34/32)_{\text{Std}}} - 1 \right) \times 10^3$$

The working standard used in this study was reagent grade BaSO<sub>4</sub> which was calibrated against the CDT and OGS standards. The <sup>34</sup>S value obtained for OGS was 20.3‰ ± .1‰ relative to CDT.

## Results and Discussion

A. SO<sub>4</sub><sup>=</sup> and SO<sub>2</sub> Concentrations

The concentration of aerosol sulfate at Hubbard Brook Experimental Forest, West Thornton, New Hampshire ranged from .9 to 6.5 μg/m<sup>3</sup>, with a mean value of 2 μg/m<sup>3</sup>. SO<sub>2</sub> levels ranged from .2 to 6.5 μg/m<sup>3</sup>, with a mean value of 2 μg/m<sup>3</sup> (see Fig. 1). These levels are considerably lower than average eastern U.S. values, reflecting the distance between Hubbard Brook and strong urban sources of atmospheric sulfur. In fact, these levels are lower than those reported for other non-urban sites in the eastern United States (Hitchcock, 1976; Altshuler, 1973).

The concentration data show a definite seasonal trend. Late summer-early fall samples are characterized by low SO<sub>2</sub> and high, variable SO<sub>4</sub><sup>=</sup> concentrations. Late fall-early winter samples exhibit high SO<sub>2</sub> and low SO<sub>4</sub><sup>=</sup> levels. The molar oxidation ratio, SO<sub>4</sub><sup>=</sup>/(SO<sub>2</sub> + SO<sub>4</sub><sup>=</sup>), clearly demonstrates these relationships (see Fig. 2).

One factor which may contribute to the high summertime SO<sub>4</sub><sup>=</sup> levels is local biological production of volatile sulfur compounds, such as H<sub>2</sub>S, CS<sub>2</sub>, DMS, DMDS. However, the oxidation of these compounds involves SO<sub>2</sub> as an important intermediate during conversion to sulfate (Thiemens, 1977; Hatekeyama et

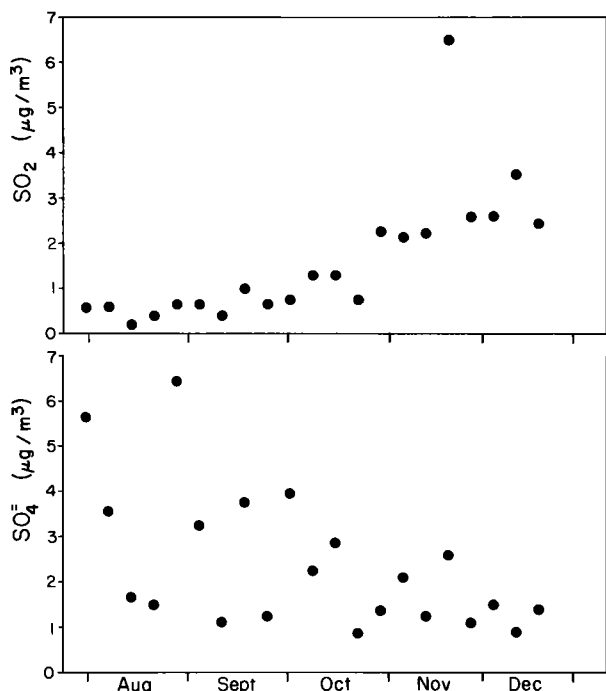


Figure 1.  $\text{SO}_2$  and  $\text{SO}_4^-$  concentrations in weekly samples collected at Hubbard Brook during 1980.

al., 1982; Bonsang et al., 1980). Thus, if the high summertime sulfate levels were due largely to biological emissions,  $\text{SO}_2$  levels should have been high as well, which is clearly not the case at Hubbard Brook.

Furthermore, the biological input must be superimposed on the anthropogenic background. Estimates indicate that 10–30% of the total annual anthropogenic  $\text{SO}_2$  emissions are due to space heating during winter (Goffin, 1973; Caulson, 1973). This may be reflected in the Hubbard Brook data, which shows a 35% increase in the total sulfur burden ( $\text{SO}_2 + \text{SO}_4^-$ ) during the late fall and early winter. However, this effect is certainly too small to explain the 400% increase in  $\text{SO}_2$  levels at this time. The total sulfur burden may also be influenced by seasonal changes in depositional processes, i.e. rates of wet and dry precipitation. Meteorological patterns may also shift the sources of sulfur advected to Hubbard Brook and, hence, the amount of time available for oxidation of  $\text{SO}_2$  during transport.

While emission, transport and depositional processes can certainly generate seasonal variations in  $\text{SO}_2$  and  $\text{SO}_4^-$  concentrations it is unlikely that they are of sufficient magnitude to explain the Hubbard Brook data. A more viable interpretation of the data is that the observed oxidation ratios mirror a seasonal change in the oxidation rate of  $\text{SO}_2$ , with faster oxidation occurring during warmer months than during cold months.

### B. Sulfur Isotopes

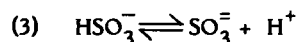
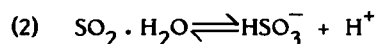
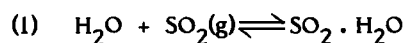
The  $\delta^{34}\text{S}$  of  $\text{SO}_2$  at Hubbard Brook ranged from  $-1.1$  to  $2.3$ ‰ (11 samples) and that of aerosol  $\text{SO}_4^-$  ranged from  $0.8$  to  $3.5$ ‰ (14 samples). Simultaneous  $\delta^{34}\text{S}$  measurements on both  $\text{SO}_2$  and  $\text{SO}_4^-$  were made on 8 samples. From this data and the concentration data, the  $\delta^{34}\text{S}$  of the total atmospheric sulfur burden ( $\delta^{34}\text{S}$ ) at Hubbard Brook can be calculated using the equation

$$\delta^{34}\text{S} = \frac{\text{SO}_2 \delta^{34}\text{SO}_2 + \text{SO}_4^- \delta^{34}\text{SO}_4^-}{\text{SO}_2 + \text{SO}_4^-}$$

(in which  $\text{SO}_2$  is expressed in  $\mu\text{g}/\text{m}^3$  as  $\text{SO}_4^-$ ). The values of  $\delta^{34}\text{S}$  range from  $-0.5$  to  $2.2$ ‰. The isotope data are shown in Fig. 3.

It is not known to what extent the variation in  $\delta^{34}\text{S}$  reflects source variability or isotopic fractionation due to differential removal of  $\text{SO}_2$  and  $\text{SO}_4^-$  during transport. It is interesting to note that  $\delta^{34}\text{S}$  appears to decrease from summer to winter. If a biological source is responsible for this trend, then its  $\delta^{34}\text{S}$  is greater than that of the anthropogenic background. This trend is the opposite of that found in rainwater sulfur in the Great Lakes region (Nriagu and Coker, 1978), where summer rains were several per mil lighter than winter precipitation. However, because of the large (nearly 20‰) variability in the  $\delta^{34}\text{S}$  of anthropogenic emissions, it is impossible to accurately assess the importance of the biological sulfur source from this type of data.

The isotopic fractionation between  $\text{SO}_2$  and aerosol  $\text{SO}_4^-$  can be used to assess the importance of aqueous phase oxidation in cloud droplets and in films on the wetted surfaces of aerosol particles. The dissolution of  $\text{SO}_2$  in aqueous solution occurs by the reactions



A large equilibrium fractionation accompanies the first dissociation (2), with  $\text{HSO}_3^-$  enriched in the heavier isotope relative to  $\text{SO}_2 \cdot \text{H}_2\text{O}$ . The fractionation factor  $\alpha$ , defined as

$$\alpha = \frac{(^{34}\text{S}/^{32}\text{S})_{\text{HSO}_3^-}}{(^{34}\text{S}/^{32}\text{S})_{\text{SO}_2}}$$

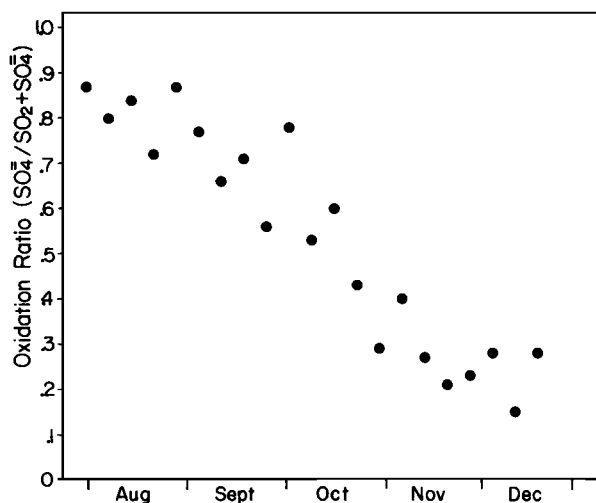


Figure 2. Oxidation ratio of atmospheric sulfur at Hubbard Brook, calculated from the concentration data shown in Figure 1.

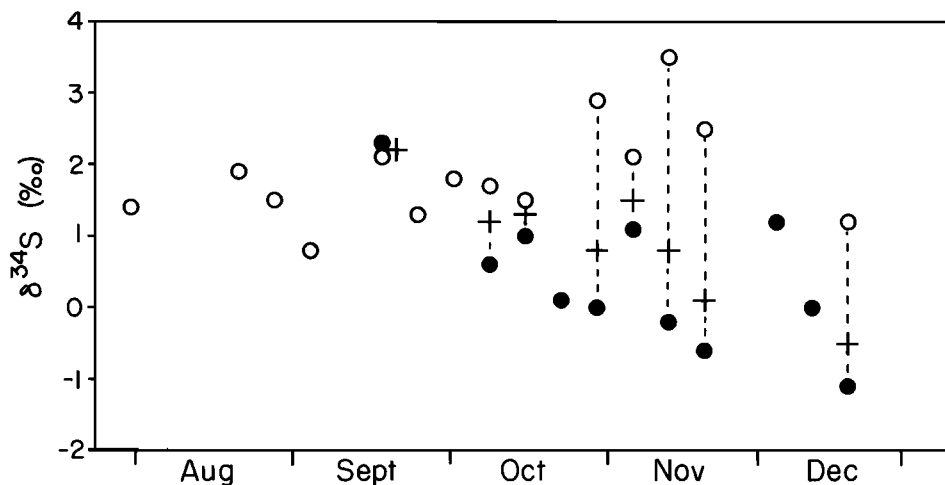


Figure 3. Sulfur isotope ratios ( $\delta^{34}\text{S}$ ) of  $\text{SO}_2$  ( $\bullet$ ),  $\text{SO}_4^-$  ( $\circ$ ) and total sulfur (+) at Hubbard Brook. The total sulfur values are calculated using the concentration data shown in Figure 1.

was experimentally determined to be 1.0165 at 25°C (Egiazarov, 1971).  $\alpha$  increases with decreasing temperature. Extrapolation of measurements at 25, 50 and 70°C yield a value of  $\alpha$  of roughly 1.021 at 0°C, assuming a linear relationship between  $\ln \alpha$  and  $1/T$ . The isotopic fractionation associated with the other reactions (1,3) are considerably smaller, with values on the order of 1.001 (Eriksen, 1972).

The atmospheric oxidation of  $\text{SO}_2$  or  $\text{HSO}_3^-$  is irreversible, so isotopic equilibrium with  $\text{SO}_4^-$  is not attained. Instead, oxidation is characterized by a kinetic isotope effect in which the greater reactivity of the isotopically lighter molecules causes them to be preferentially oxidized. Experiments in our laboratory indicate that the kinetic isotopic fractionation involved in the oxidation of  $\text{HSO}_3^-$  by dissolved  $\text{O}_2$  is .996 at 25°C. While the magnitude of this effect may vary with different oxidants and reaction mechanisms, it is probably always considerably smaller than the equilibrium fractionation.

This kinetic isotope effect accompanies oxidation in both the aqueous and gaseous phases. Thus we would expect homogeneous gas phase oxidation of  $\text{SO}_2$  to result in sulfate which is isotopically lighter than the precursor  $\text{SO}_2$  ( $\alpha < 1$ ). Heterogeneous oxidation involves both equilibrium and kinetic effects and the resultant sulfate will be heavier than the  $\text{SO}_2$  it formed from ( $\alpha > 1$ ).

The isotopic fractionation between  $\text{SO}_2$  and  $\text{SO}_4^-$  at Hubbard Brook can be calculated from the measured  $\delta^{34}\text{SO}_2$ ,  $\delta^{34}\text{SO}_4^-$  pairs by the formula

$$\alpha_m = \frac{\frac{\delta^{34}\text{SO}_4^-}{10^3} + 1}{\frac{\delta^{34}\text{SO}_2}{10^3} + 1}$$

The values of  $\alpha_m$  range from .9999 to 1.0037. Because  $\text{SO}_2$  and  $\text{SO}_4^-$  are not in isotopic equilibrium in the atmosphere, reservoir effects may cause the measured isotopic fractionation ( $\alpha_m$ ) to differ from the true isotopic fractionation which accompanies sulfate

formation. Isotope relations in such systems can be modelled using the Rayleigh equation (Broecker and Oversby, 1971)

$$\delta^{34}\text{SO}_2 = (\delta^{34}\text{SO}_2^0 + 10^3) f^{\alpha-1} - 10^3$$

where  $f$  is the fraction of initial  $\text{SO}_2$  remaining (i.e.  $\text{SO}_2/\text{SO}_2^0$ ) and  $\alpha$  is the overall fractionation factor involved in sulfate formation incorporating both equilibrium and kinetic effects.

The extent to which reservoir effects may affect the measured values of  $\alpha$  at Hubbard Brook can be estimated by assuming a closed system and substituting the oxidation ratio and  $\delta\Sigma\text{S}$  for  $1-f$  and  $\delta\text{SO}_2^0$ , respectively in the Rayleigh model equation. A new fractionation factor,  $\alpha_c$ , corrected for reservoir effects can then be calculated from the expression

$$\alpha_c = \frac{\ln \frac{\delta^{34}\text{SO}_2 + 10^3}{\delta^{34}\Sigma\text{S} + 10^3}}{\ln f} + 1$$

The values of  $\alpha_c$  range from .9999 to 1.032 and are plotted with  $\alpha_m$  in Figure 4. This calculation demonstrates that reservoir effects are on the order of .001 or less for the Hubbard Brook samples. The offset between  $\alpha_c$  and  $\alpha_m$  is less than would be expected in a completely closed system. This is not surprising since the air masses at Hubbard Brook undoubtedly have complex histories of  $\text{SO}_2$  input and deposition of  $\text{SO}_2$  and  $\text{SO}_4^-$  during transport.

The fractionation factors at Hubbard Brook are intermediate between those expected from equilibrium and kinetic processes, indicating that both are important. A more quantitative assessment of the relative importance of equilibrium and kinetic processes in sulfate formation would be possible if all the relevant fractionation factors were known. In particular, experimental determinations of  $\alpha$ -kinetic are needed for a variety of oxidants, such as  $\text{O}_3$ ,  $\text{NO}_x$ ,  $\text{H}_2\text{O}_2$ ,  $\text{OH}$ . The seasonality of the data indicates that the importance of heterogeneous oxidation reactions is greatest during cooler months, while they are of only minor importance

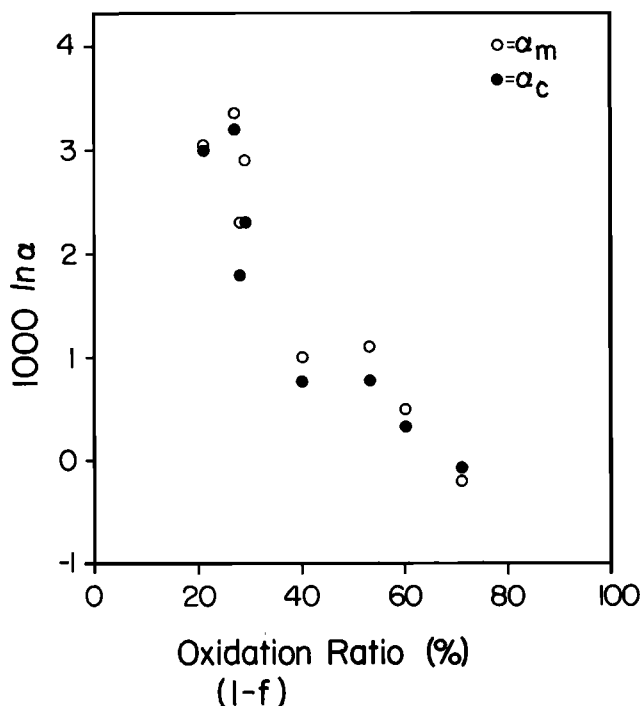


Figure 4. Sulfur isotopic fractionation between  $\text{SO}_4^{2-}$  and  $\text{SO}_2$ ,  $\alpha_m$  plotted against the oxidation ratio (expressed in %).  $\alpha_c$  values are corrected for reservoir effects using the Rayleigh equation.

during warmer months. This is probably due to two factors: 1)  $\text{SO}_2$  solubility increases with decreasing temperature (Johnston and Leppla, 1934) and 2) the photochemical production of gaseous oxidants is probably greatest during summertime. An inverse relationship exists between the fractionation factor and the oxidation ratio, as shown in Figure 4. Taken together, the chemical and isotopic evidence suggests that the overall oxidation rate decreases during cooler months, in spite of the increased role of heterogeneous reactions. From this we can infer that on a yearly, integrated basis, aerosol sulfate is formed primarily by gaseous oxidation.

#### Conclusions

This study demonstrates systematic, seasonal chemical and sulfur isotopic trends in  $\text{SO}_2$  and aerosol sulfate at Hubbard Brook, N.H. These trends can be interpreted in terms of simple chemical models for the oxidation of  $\text{SO}_2$ . The results are as follows:

- 1) Oxidation ratios,  $\text{SO}_4^{2-}/(\text{SO}_2 + \text{SO}_4^{2-})$ , at Hubbard Brook, N.H. are greater during the late summer and early fall than during late fall and winter. This suggests that the oxidation rate varies seasonally, with faster oxidation during warmer months.
- 2) The sulfur isotopic fractionation between aerosol  $\text{SO}_4^{2-}$  and  $\text{SO}_2$  is intermediate between that expected from homogeneous and heterogeneous reactions, indicating that both processes can be important. The isotope data suggest that homogeneous oxidation reactions are more important in the production of aerosol sulfate than solution reactions, particularly during warmer months.

#### Acknowledgments

We wish to thank Dennis Savoie, Ruby Nees, T.G. Snowdon and Albert Castellanos for their assistance in the laboratory, Wayne Martin of the U.S. Forest Service and Don Busso for their assistance in the field, Victor Rossinsky for translation of foreign language manuscripts and M. Thiemens and an anonymous reviewer for helpful comments. This research was supported by NSF grant ATM 79-09239. E.S. wishes to thank Texaco for their support. Contribution of the Rosenstiel School of Marine and Atmospheric Science, University of Miami.

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(Received March 8, 1983;  
accepted March 30, 1983.)