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THE MECHANISM OF SULFATE AEROSOL FORMATION: CHEMICAL AND SULFUR ISOTOPIC EVIDENCE

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Abstract

In order to study the mechanism of aerosol sulfate formation, weekly samples of SO_2 and aerosol $SO_4^=$ were collected at Hubbard Brook Experimental Forest, West Thornton, New Hampshire from July to December, 1980. Samples were analyzed for concentration and sulfur isotopes ($\delta^{34}S$). Late summer-early fall samples are characterized by high, variable $SO_4^=$ levels and low SO_2 levels, while late fall - early winter samples exhibit low $SO_4^=$ and high SO_2 levels. These trends suggest that the oxidation rate varies seasonally, with faster oxidation during warmer months. The sulfur isotopic fractionation between aerosol $SO_4^=$ and SO_2 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_2 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_2 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 $SO_4^=$ and SO_2 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_2CO_3 and glycerol to collect SO_2. The trapped SO_2 oxidized to $SO_4^=$ during collection and storage. Filter $SO_4^=$ blanks were less than 1% of $SO_4^=$ 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.

$SO_4^=$ 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 $SO_4^=$ by ion chromatography. $BaSO_4$ was precipitated from the remainder of the filter extracts by acidifying with HCl, heating, and adding $BaCl_2$. The precipitate was washed free of Cl^-, dried, weighed (10-20 mg) into quartz combustion tubes and heated to 800°C in a muffle furnace. The $BaSO_4$ was then converted to SO_2 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_3 present to SO_2 (Bailey and Smith, 1972). Yields of 95-100% were obtained using this procedure. The sulfur isotopic composition of SO_2 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_2) and 50/48 (SO) ratios. The results are reported in the notation as per mil deviation from the CDT standard, where

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

The working standard used in this study was reagent grade $BaSO_4$ which was calibrated against the CDT and OGS standards. The $\delta^{34}S$ value obtained for OGS was 20.3°/oo ± .1°/oo relative to CDT.

Results and Discussion

A. $SO_4^=$ and SO_2 Concentrations

The concentration of aerosol sulfate at Hubbard Brook Experimental Forest, West Thornton, New Hampshire ranged from .9 to 6.5 μg/m^3, with a mean value of 2 μg/m^3. SO_2 levels ranged from .2 to 6.5 μg/m^3, with a mean value of 2 μg/m^3 (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; Altshuller, 1973).

The concentration data show a definite seasonal trend. Late summer-early fall samples are characterized by low SO_2 and high, variable $SO_4^=$ concentrations. Late fall-early winter samples exhibit high SO_2 and low $SO_4^=$ levels. The molar oxidation ratio, $SO_4^=/(SO_2 + SO_4^=)$, clearly demonstrates these relationships (see Fig. 2).

One factor which may contribute to the high summertime $SO_4^=$ levels is local biological production of volatile sulfur compounds, such as H_2S, CS_2, DMS, DMDS. However, the oxidation of these compounds involves SO_2 as an important intermediate during conversion to sulfate (Thiemens, 1977; Hatekeyama et

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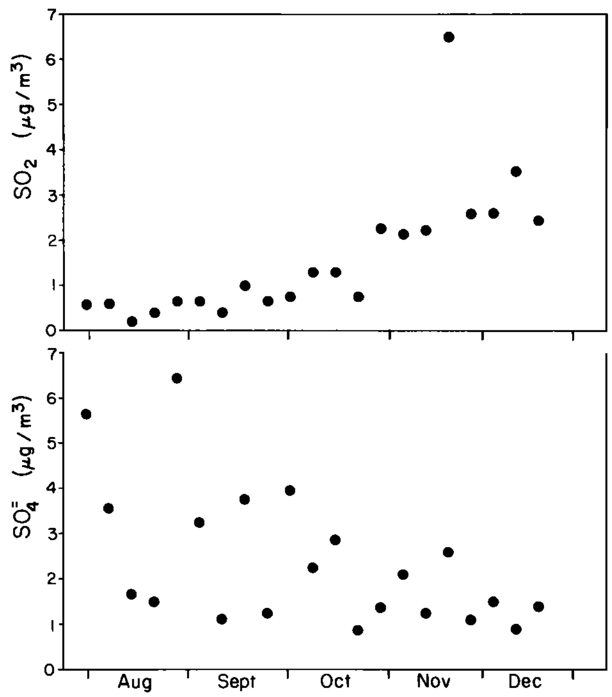

Figure 1. SO_2 and $SO_4^=$ concentrations in weekly samples collected at Hubbard Brook during 1980.

al., 1982; Bonsang et al., 1980). Thus, if the high summertime sulfate levels were due largely to biological emissions, 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 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 (SO_2 + $SO_4^=$) during the late fall and early winter. However, this effect is certainly too small to explain the 400% increase is 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 SO_2 during transport.

While emission, transport and depositional processes can certainly generate seasonal variations in SO_2 and 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 SO_2, with faster oxidation occurring during warmer months than during cold months.

B. Sulfur Isotopes

The $\delta^{34}S$ of SO_2 at Hubbard Brook ranged from −1.1 to 2.3°/oo (11 samples) and that of aerosol $SO_4^=$ ranged from 0.8 to 3.5°/oo (14 samples). Simultaneous $\delta^{34}S$ measurements on both SO_2 and $SO_4^=$ were made on 8 samples. From this data and the concentration data, the $\delta^{34}S$ of the total atmospheric sulfur burden ($\delta^{34}\Sigma S$) at Hubbard Brook can be calculated using the equation

$$\delta^{34}\Sigma S = \frac{SO_2\ \delta^{34}SO_2 + SO_4^=\ \delta^{34}SO_4^=}{SO_2 + SO_4^=}$$

(in which SO_2 is expressed in μg/m^3 as $SO_4^=$). The values of $\delta^{34}\Sigma S$ range from −0.5 to 2.2°/oo. The isotope data are shown in Fig. 3.

It is not known to what extent the variation in $\delta^{34}\Sigma S$ reflects source variability or isotopic fractionation due to differential removal of SO_2 and $SO_4^=$ during transport. It is interesting to note that $\delta^{34}\Sigma S$ appears to decrease from summer to winter. If a biological source is responsible for this trend, then its $\delta^{34}S$ 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°/oo) variability in the $\delta^{34}S$ 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 SO_2 and aerosol $SO_4^=$ 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 SO_2 in aqueous solution occurs by the reactions

(1) $H_2O + SO_2(g) \rightleftharpoons SO_2 \cdot H_2O$

(2) $SO_2 \cdot H_2O \rightleftharpoons HSO_3^- + H^+$

(3) $HSO_3^- \rightleftharpoons SO_3^= + H^+$

A large equilibrium fractionation accompanies the first dissociation (2), with HSO_3^- enriched in the heavier isotope relative to $SO_2 \cdot H_2O$. The fractionation factor α, defined as

$$\alpha = \frac{(^{34}S/^{32}S)_{HSO_3^-}}{(^{34}S/^{32}S)_{SO_2}}$$

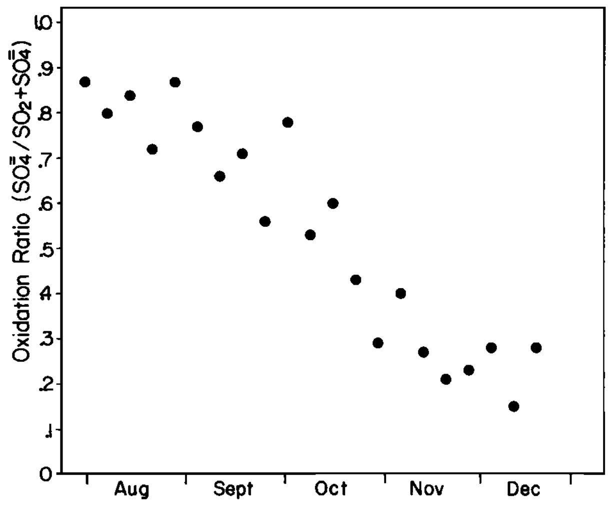

Figure 2. Oxidation ratio of atmospheric sulfur at Hubbard Brook, calculated from the concentration data shown in Figure 1.

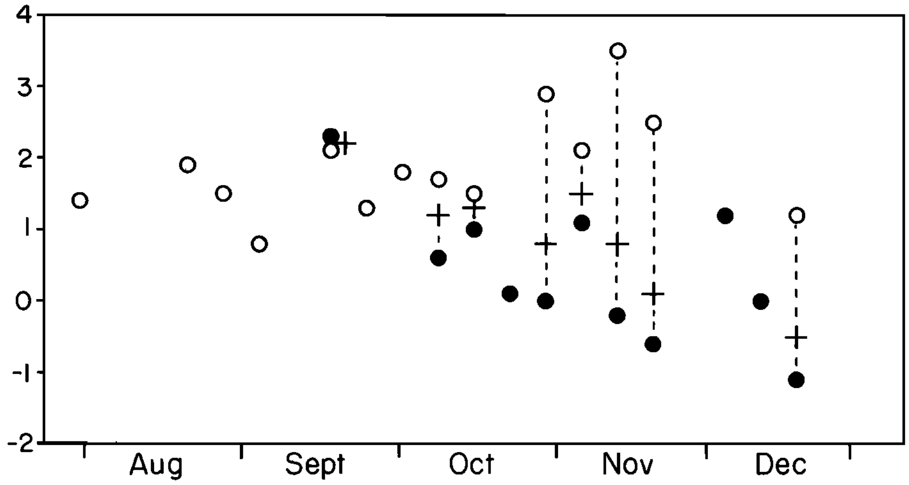

Figure 3. Sulfur isotope ratios ($\delta^{34}S$) of SO_2 (●), $SO_4^=$ (O) and total sulfur (+) at Hubbard Brook. The total sulfur values are calculated using the concentration data shown in Figure 1.

was experimentally determined to be 1.0165 at 25°C (Egiazarov, 1971). α increases with decreasing temperature. Extrapolation of measurements at 25,50 and 70°C yield a value of α of roughly 1.021 at 0°C, assuming a linear relationship between ln α 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 SO_2 or HSO_3^- is irreversible, so isotopic equilibrium with $SO_4^=$ 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 HSO_3^- by dissolved 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 SO_2 to result in sulfate which is isotopically lighter than the precursor SO_2 ($\alpha < 1$). Heterogeneous oxidation involves both equilibrium and kinetic effects and the resultant sulfate will be heavier than the SO_2 it formed from ($\alpha > 1$).

The isotopic fractionation between SO_2 and $SO_4^=$ at Hubbard Brook can be calculated from the measured $\delta^{34}SO_2$, $\delta^{34}SO_4^=$ pairs by the formula

$$\alpha_m = \frac{\dfrac{\delta^{34}SO_4^=}{10^3} + 1}{\dfrac{\delta^{34}SO_2}{10^3} + 1}$$

The values of α_m range from .9999 to 1.0037. Because SO_2 and SO_4 are not in isotopic equilibrium in the atmosphere, reservoir effects may cause the measured isotopic fractionation (α_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)

$$\delta^{34}SO_2 = (\delta^{34}SO_2{}^{o} + 10^3)\, f^{\alpha-1} - 10^3$$

where f is the fraction of initial SO_2 remaining (i.e. $SO_2/SO_2{}^{o}$) and α 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 α at Hubbard Brook can be estimated by assuming a closed system and substituting the oxidation ratio and $\delta\Sigma S$ for 1-f and $\delta SO_2{}^{o}$, respectively in the Rayleigh model equation. A new fractionation factor, α_c, corrected for reservoir effects can then be calculated from the expression

$$\alpha_c = \frac{\ln \dfrac{\delta^{34}SO_2 + 10^3}{\delta^{34}\Sigma S + 10^3}}{\ln f} + 1$$

The values of α_c range from .9999 to 1.032 and are plotted with α_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 α_c and α_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 SO_2 input and deposition of SO_2 and $SO_4^=$ 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 α-kinetic are needed for a variety of oxidants, such as O_3, NO_x, H_2O_2, 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

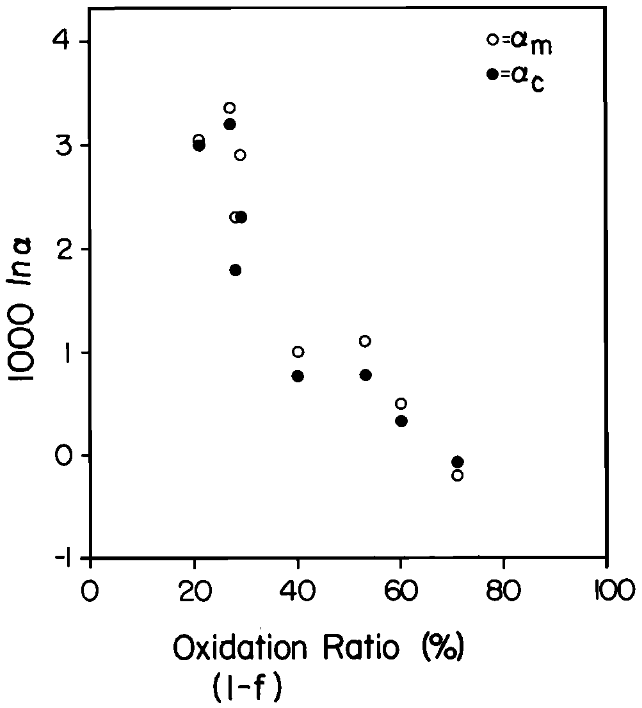

Figure 4. Sulfur isotopic fractionation between $SO_4^=$ and SO_2, α_m plotted against the oxidation ratio (expressed in %). α_c values are corrected for reservoir effects using the Rayleigh equation.

during warmer months. This is probably due to two factors: 1) 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 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 SO_2. The results are as follows:

1) Oxidation ratios, $SO_4^=/(SO_2 + SO_4^=)$, 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 $SO_4^=$ and 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.

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