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USE OF OXYGEN ISOTOPY IN THE STUDY OF TRANSFORMATIONS OF SO_2 TO SULFATES IN THE ATMOSPHERE*

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The measurement of oxygen isotope ratios in atmospheric water and atmospheric sulfates is a useful analytical method for studying mechanisms of sulfate formation. As a part of the extensive research that has been conducted by many workers in recent years on the world-wide problem of atmospheric sulfates of anthropogenic origin [1,2,6,10,18,19,26,28,29,30], particularly as it relates to acid precipitation [3,20,25], methods of oxygen isotopy have been used in pinpointing the sources of acid sulfates that are damaging to the environment [4,23,24], and in investigating the predominant mechanisms of formation of sulfates in precipitation water and in aerosols [11-14]. Oxygen isotopy is suited to these applications because the ^{18}O contents of sulfates that are formed from SO_2, water and oxidants of known ^{18}O contents differ, depending upon the mechanism by which they are formed (*e.g.*, aqueous air-oxidation, aqueous H_2O_2-oxidation, surface oxidation, homogeneous gas-phase oxidation, etc.). Once formed, the sulfates are extremely stable with respect to isotopic exchange with water in which they are dissolved (21).

Much is known about the oxygen isotopy of atmospheric water and factors that influence it, such as geographical location, season, plant transpiration, etc. [5,8,9,27]. The SO_2 in the atmosphere is probably in isotopic equilibrium with liquid-phase atmospheric water because of the extremely high reaction rates in the hydrolysis equilibration,

$$SO_2 + H_2O \rightleftarrows SO_2 \cdot H_2O \rightleftarrows HSO_3^- + H^+ \quad [1,7]$$

Also, because of this fast reaction, the bisulfite ion, which is the predominant form of S(IV) in precipitation water of pH 3-6 [1], is isotopically dominated by the water (in large excess) in which it is dissolved. Essentially all of the isotopic contribution of the SO_2 is lost in the equilibration [15]. The ^{18}O content of air oxygen is essentially constant at 23.5‰ [17]. The ^{18}O contents of other atmospheric oxidants (such as O_3, H_2O_2 and NO_x), and of free radicals (such as OH, HO_2, etc.) have not been determined, so far as we know.

Previous experimental results have indicated that the $^{18}O/^{16}O$ ratios in water vapor, precipitation water and sulfate contained in precipitation water vary seasonally (higher in summer, lower in winter), while the $^{18}O/^{16}O$ ratio in atmospheric particulate sulfate appears to vary randomly with season [11,12]. These earlier results for water vapor and particulate sulfate were obtained on 24-hour field samples, collected on three consecutive days in each month during 1975 and 1976, ~6 m above ground level, at the Argonne meteorological tower. The samples were arbitrarily intermittent and therefore did not necessarily represent continuous, temporal variations of the oxygen isotopes, except during the three-day sampling period within each month. It was postulated on the basis of the data obtained, that since the two-year averages of ^{18}O content in particulate sulfate and precipitation sulfate were about equal, both were probably formed by the same aqueous oxidation mechanism in clouds. Relatively long residence times and transport distances of particulate sulfates

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probably provided sufficient mixing to obscure the seasonal influence that was observed in the relatively short-residenced precipitation sulfates.

During 1977, sequential seven-day samples of water vapor, particulate sulfate and sulfur dioxide were continuously collected throughout the four seasons. Samples of rain and snow were also collected for most of the precipitation events during this period. The results obtained from this more intensive sampling program are now available for an alternative and possibly more accurate interpretation of the apparent lack of agreement between the isotopic qualities of precipitation and particulate sulfates. The purpose of this paper is to report and discuss these new results.

Experimental

The normal methods of sample collection [11-13] and analysis [14] have been described. The sampling procedures were slightly modified to accommodate the seven-day samples in 1977. The hi-vol air sampler, loaded with a cassette of two filters (the top fiber-glass filter to collect particulate sulfate, and the bottom filter, pretreated with K_2CO_3 and glycerol, to collect SO_2), was maintained at a relatively low flow rate of $\sim$14 m^3/hr. The cold trap used to sample water vapor from the atmosphere was maintained at $\sim$-50°C and an air flow rate of 0.012 to 0.024 m^3/hr.

Results and Discussion

Sequential One-Week Samples

The isotopic results obtained from the 1977 continuous sampling program are plotted versus time in Fig. 1. The data are given in units of $\delta^{18}O$, which is the deviation in parts per thousand (‰) of the $^{18}O/^{16}O$ ratio of the sample from that of Standard Mean Ocean Water (SMOW).

Curve A in Fig. 1 shows the temporal variation of $\delta^{18}O$ in atmospheric water vapor, collected $\sim$6 m above ground level. Data points representing consecutive one-week samples are connected by solid lines. Broken lines connect points interrupted by missing or improperly processed samples. Besides the strong seasonal quality, it may be noted that the integrated weekly value for $\delta^{18}O$ was sometimes essentially constant for several weeks, *e.g.*, August and September; occasional perturbation spikes occurred, as near the end of October; and the transitions between winter and the other three seasons of the year were comparatively abrupt.

Curve B gives the corresponding results for atmospheric water that was sampled as rain and snow. The open circle data points represent rain and the crossed circle points represent snow. The shape of the plot approximates that of water vapor, the average level being about 9‰ higher because of the isotopic separation that is characteristic of the two-phase system. The abrupt change between winter and the warmer seasons and the spike at the end of October were in phase with the same features in the water vapor curve.

Shown as Curve C are the $\delta^{18}O$ values for the sulfate contained in the rain (open circles) and snow (crossed circles). The seasonal variation strongly indicates the influence of the precipitation water on the $\delta^{18}O$ of the dissolved sulfate. As previously observed [11], the amplitude of the wave curve for the dissolved sulfate is roughly 3/4 of that of the solvent water, indicating isotopic equilibration via the precursor ion, SO_3^{2-} or HSO_3^-. The three results that appear to be low values in the period of June-August were from storms on days of southwest resultant wind direction. The only other storm in 1977 on a day of southwest resultant wind direction was on March 4. These four points are designated by arrows. A large power plant is located about 8 km southwest of our sampling site and large complexes of oil refineries and storage tanks are located a few km farther southwest. It is uncertain which, if any, emissions from these industrial areas contributed to the apparent summer perturbations in $\delta^{18}O$.

Curve D gives the $\delta^{18}O$ for particulate sulfates collected continuously through 1977. In agreement with previous results obtained from the three 24-hr samples per month in

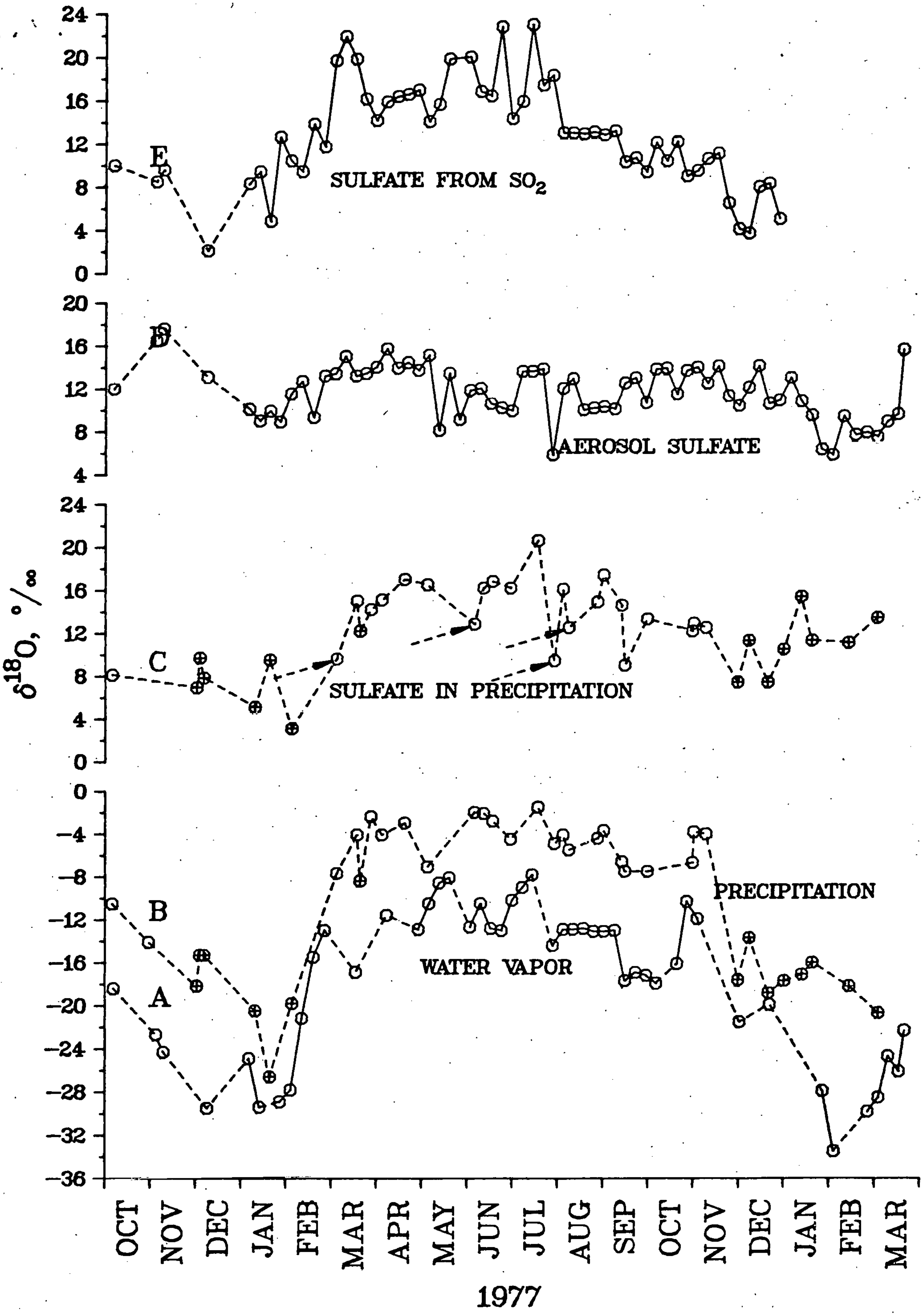

Figure 1. Isotopic results for continuous sequential 7-day samples of water vapor, particulate sulfate, and SO_2, and for event samples of precipitation in 1977.

1975-1976, a distinct seasonal variation like that in precipitation sulfate is not readily evident. However, the possibility that the plot of the 1977 data has a distinguishable wave form, caused by more than one mechanism of sulfate formation, each varying differently with season, is discussed later.

The $\delta^{18}O$ values in Curve E were obtained for sulfates resulting from the collection of sulfate-free SO_2 on K_2CO_3-glycerol treated filters. A seasonal influence on these results is clearly evident, but, as discussed previously [11], it is uncertain how much of this seasonal quality can be attributed to the atmospheric SO_2 and how much to the water vapor that flowed through the filter during sample collection and possibly entered into oxygen-isotope equilibration with the alkaline reagent and sulfite ion. In consideration of this uncertainty, it may be noted that simultaneous constancy of $\delta^{18}O$ occurs in Curves A and E during the month of August. Some concurrent constancy is also seen in Curve D.

In further consideration of the question as to why atmospheric particulate sulfates, collected on inert filters at Argonne and other locations, do not display the same kind of distinct seasonal variation as do sulfates found in precipitation water, Fig. 2 shows averaged monthly data for the 1977, continuously sampled, particulate sulfates, plotted together with monthly averaged intermittent sample data for 1975 and 1976. A broken-line curve is superimposed on the experimental plot for each of the three years to suggest that if the borken-line curve represents hypothetical results from a single mechanism of formation, like that which is operative in the formation of sulfates in precipitation water, the experimental results are substantially accounted for in each year during the late fall, winter, and early spring. Accordingly, the observed experimental results for late spring, summer, and early fall might be attributable to the predominance of an entirely different mechanism which characteristically yields sulfate of lower ^{18}O content.

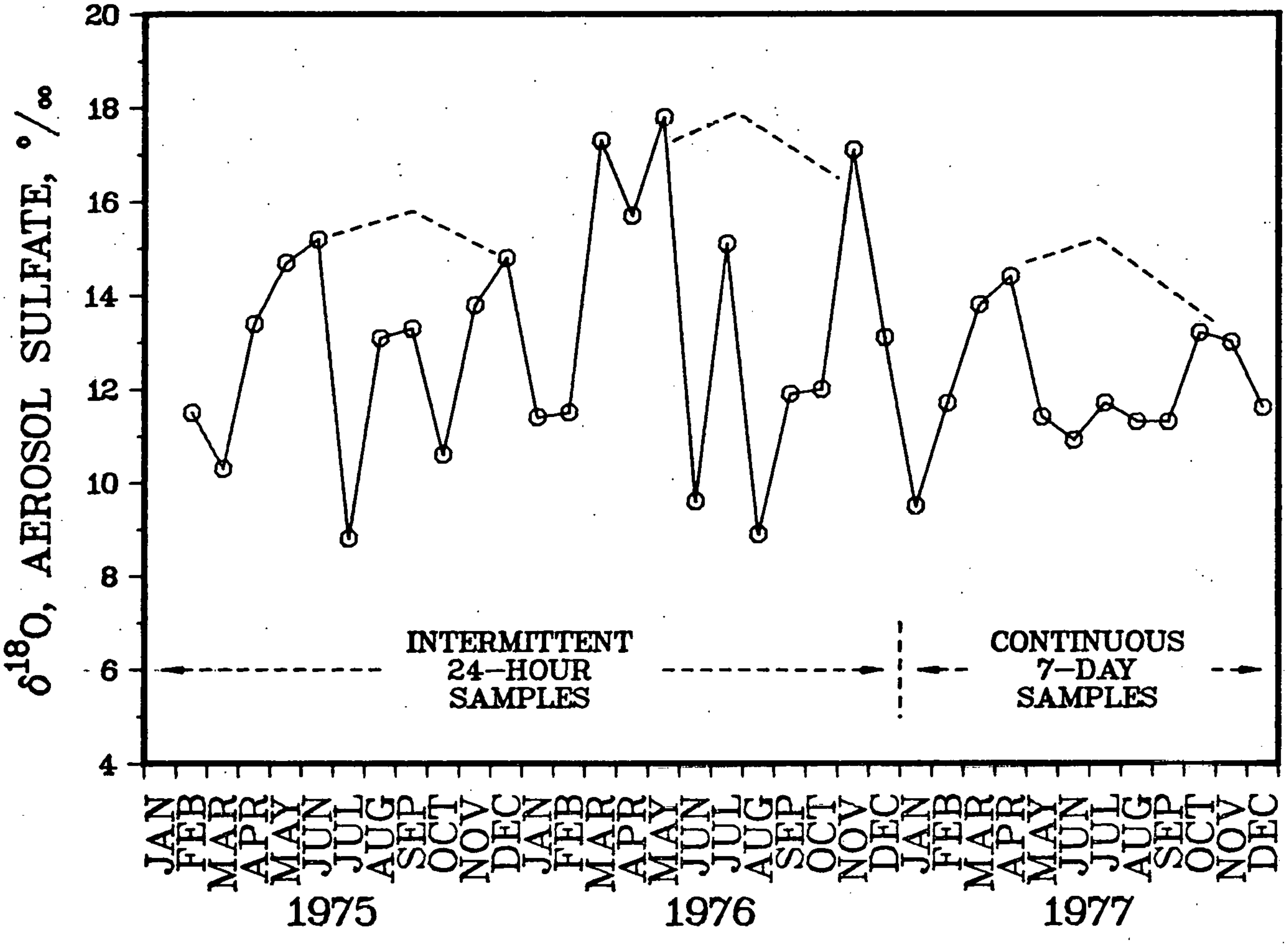

Figure 2. Three-year temporal variation of $\delta^{18}O$ in particulate sulfates at Argonne, IL.

It may be of significance that several of the fluctuations of $\delta^{18}O$ of particulate sulfate in Curve D, Fig. 1, were in antiphase with corresponding fluctuations in average daily minutes of sunshine for the same weeks in 1977 [22], suggesting that increased sunshine corresponds to decreased $\delta^{18}O$ in particulate sulfate. This further suggests that, in a 12-month period, sun-induced mechanism(s) of sulfate formation should be most effective during seasons of greatest insolation (which at the Argonne site reaches a maximum during the summer months).

It may be postulated, therefore, that SO_2 in the atmosphere is converted to sulfate in the late fall, winter, and early spring predominantly by an aqueous oxidation mechanism that yields sulfates isotopically similar, if not identical, to sulfates found in precipitation water: while in the late spring, summer, and early fall, SO_2 is converted predominantly by a sun-induced mechanism that yields sulfates more depleted in ^{18}O. The predominating summer mechanism(s) may involve reactions of SO_2 with OH radicals or other free radicals, or reactions with photochemically produced aqueous-phase oxidants, such as H_2O_2. Either OH radicals or H_2O_2 might be expected to be richer in water oxygen ($\delta^{18}O$ = -5 to 30‰) than in air oxygen ($\delta^{18}O$ = +23.5‰), thus yielding sulfates of lower $\delta^{18}O$. We have not experimentally examined the $\delta^{18}O$ level of sulfates produced by OH-radical reactions with SO_2; we have prepared sulfate by aqueous H_2O_2-oxidation of SO_2, finding it to be ∿12‰ lower in $\delta^{18}O$ than sulfate prepared by aqueous air oxidation [16]. (No comparison was made of the $\delta^{18}O$ of the reagent H_2O_2 used in this experiment with the $\delta^{18}O$ of H_2O_2 that might be naturally produced in the atmosphere.)

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