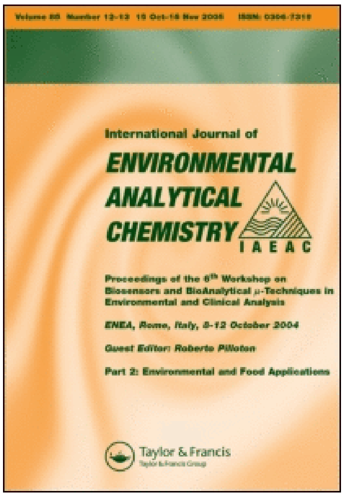

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Seasonal Variations of Oxygen-18 in Atmospheric Sulfates†‡

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Oxygen-isotope analyses were made on samples of aerosol sulfates, SO_2, water vapor, precipitation water, and precipitation sulfates collected over a two-year period near Chicago, Illinois, U.S.A. The purpose of this isotopic study was to help to elucidate the mechanisms of sulfate formation in the atmosphere.

Oxygen-18 enrichments in precipitation sulfates varied seasonally and in phase with the corresponding enrichments in precipitation water. The ratio of the amplitudes of the enrichment-vs.-time curves indicated isotopic equilibration between SO_2 and atmospheric water prior to oxidation.

Oxygen-18 enrichments in aerosol sulfates appeared to vary randomly with season, but averaged about the same as precipitation sulfates. If aerosol sulfates and precipitation sulfates were formed by the same hydrolysis-oxidation mechanism in clouds, relatively long residence times and transport distances of sulfate aerosols may have provided sufficient mixing to obscure seasonal effects such as were observed in the short-residence precipitation sulfates.

KEY WORDS: Sulfate aerosols, precipitation sulfates, atmospheric pollution, oxygen-18.

INTRODUCTION

Atmospheric sulfates, particularly in acid forms, are generally considered to be detrimental to health, vegetation and acid-sensitive materials in the environment. The determination of oxygen isotope ratios in these sulfates, and in the components from which they are formed (SO_2, H_2O, air, etc.), is a unique method for studying the mechanisms of their formation. Information on such mechanisms is pertinent to assessing the transfor-

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mation and transport of atmospheric sulfates, and ultimately to their control as pollutants.

The two widely accepted mechanisms by which SO_2 is transformed to sulfate are aqueous solution of the SO_2 followed by oxidation (hydrolysis-oxidation),[1-4] and gas-phase oxidation of the SO_2 followed by hydrolysis (oxidation-hydrolysis).[5,6] These two mechanisms yield sulfate products of distinguishable oxygen-18 content, although made from the same atmospheric components (i.e., SO_2, H_2O, and oxidants).[7] This is because the two paths of transformation inherently provide different conditions for isotopic fractionation and exchange.

For example, in the hydrolysis-oxidation sequence of reactions, atmospheric SO_2 [in the parts-per-billion (ppb) range] dissolves in a relatively large excess of water (cloud droplets, rain drops, aqueous films on suspended solid particles, etc.) and the oxygen isotopes in the SO_2 equilibrate rapidly with those in the water.[8] The HSO_3^- and/or SO_3^{2-} ions, which are intermediate species between the solvated SO_2 and the subsequently formed SO_4^{2-} ions, are each composed of three oxygen atoms, the average isotopic enrichment of which the water contributes to heavily because of its relatively large excess. That is, isotope-fractionation effects allow the ^{18}O content of the sulfate ion to approach a condition equivalent to three oxygen atoms originating from the water and one oxygen atom from the air oxidant (O_2, O_3, etc.), depending on the relative rates of the isotope-equilibration and subsequent oxidation reactions.

In contrast, the oxidation-hydrolysis sequence of transformation of SO_2 to sulfate provides an entirely different set of conditions for oxygen-isotope fractionation and exchange. The gaseous SO_2 reacts with atmospheric species such as OH, HO_2, O_3, etc., producing oxidized gaseous compounds which are then hydrolyzed by atmospheric water to form sulfuric acid.

We do not have experimental data that allow isotopic comparison of sulfates which were clearly formed by the two paths of transformation in the atmosphere. However, we postulate that sulfates formed by the hydrolysis-oxidation sequence should be less enriched in oxygen-18 than sulfates formed by oxidation-hydrolysis, because atmospheric water is considerably less enriched in oxygen-18 than is air oxygen. [The del value, $\delta^{18}O$, which is the deviation in units of parts per thousand (‰) of the $^{18}O/^{16}O$ ratio of the sample from that of Standard Mean Ocean Water, for air oxygen is about +23‰; the average del values for precipitation water and water vapor (at Argonne) are about −8‰ and −18‰, respectively.] Furthermore, sulfates formed by either mechanism do not undergo appreciable isotopic exchange with water;[9] therefore, the isotopic content of a given sulfate remains uniquely characterized by its mechanism of formation. These two phenomena, i.e., the characteristically different enrichments for air and water and the isotopic stability of sulfate, form the bases for the use of the oxygen-isotope method to establish constraints in the assessment of the relative importance of the two mechanisms of formation for a given sample of atmospheric sulfate.

This report gives the results obtained from oxygen-isotope analyses of samples of particulate sulfates, sulfur dioxide, water vapor, precipitation water, and precipitation sulfates. Most of the samples were collected during 1975 and 1976 at Argonne, Illinois, about 30 km southwest of Chicago. Some of the 1975 data were reported previously,[7,10] but they are included here in combination with subsequent data to complete the two-year survey.

Isotopic relationships between the particulate sulfate and precipitation sulfate, and between each type of sulfate and atmospheric water, are discussed; conclusions about sulfate formation mechanisms, based on these relationships are suggested; and the uncertainty in the validity of the isotopic data for sulfur dioxide is briefly described.

The oxygen isotopies of precipitation water and sulfate dissolved in precipitation water have been studied by other investigators.[11,12,13] Dansgaard[11] accounted for the seasonal variations in the ^{18}O content of precipitation water in a mid-latitude climate (such as Chicago) as being effects of temperature and amount of precipitation. The temperature effect predominates during the winter months, and the effect of the amount of precipitation during the other seasons. Mizutani and Rafter[12] and Cortecci and Longinelli[13] compared the $\delta^{18}O$ of precipitation sulfates with that of the precipitation water in which they were dissolved. Cortecci and Longinelli observed a seasonal variation in $\delta^{18}O$ for both the sulfate and the rain water; they attributed the correlation of $\delta^{18}O$ (H_2O) and $\delta^{18}O$ (SO_4^{2-}) to isotopic exchange, prior to atmospheric oxidation.

It is not understood precisely how the sulfur that is eventually collected as precipitation sulfate becomes incorporated into the precipitation water. That is, uncertainties exist about whether entry occurs by in-cloud or below-cloud scavenging and whether the sulfur is scavenged predominantly as SO_2 or as particulate sulfate or both. Moreover, the lack of information about the species scavenged obviously precludes estimation of the relative amounts of each.

Particulate sulfate has also been studied by sulfur-isotope analysis,[14,15] but little if any work has been reported on the application of oxygen-isotope analysis to the study of sulfate aerosols. As discussed above, the oxygen-isotope method should be uniquely applicable to the characterization of the following atmospheric sulfates, according to their origins: (1) primary sulfates, which are emitted directly into the atmosphere from power plants, automobiles, etc.; (2) secondary sulfates that are formed in the atmosphere by hydrolysis-oxidation processes; and (3) secondary sulfates that are formed by oxidation-hydrolysis processes.

EXPERIMENTAL

Event samples of rain and snow were collected in open areas, well away from buildings and heavily traveled roads. Samples of particulate sulfates and sulfur dioxide were collected on separate filters in a hi-vol air sampler. The first of the two 20 × 25 cm filters (Gelman Spectrograde glass fiber paper) collected the particulate sulfates from the air stream; the second filter (Whatman No. 1 cellulose fiber paper, pretreated with K_2CO_3 and glycerol[16]) collected the SO_2. Simultaneously, water vapor samples were collected from another air stream flowing through a cold trap, maintained at −79°C.

Twenty-four-hour samples of particulate sulfates, SO_2, and water vapor were collected on each of three consecutive days, during each month of 1975 and 1976. The hi-vol unit and the water vapor sampler were located about 6 m above ground level at the Argonne meteorological station.

The SO_2, collected on the alkaline-treated filter, was air-oxidized from sulfite to sulfate before or during the process of leaching it in water for subsequent analysis. The analytical methods used for converting the oxygen in SO_4^{2-} and in H_2O to CO_2 for mass spectrometric determination of the $^{18}O/^{16}O$ ratio are described elsewhere.[17]

RESULTS AND DISCUSSION

Precipitation water and precipitation sulfates

Figure 1 shows the isotopic results obtained for precipitation water and for the sulfates dissolved in the water. The open data points represent samples of rain; the crossed points represent snow. The average temperature for each month is also plotted for comparison.

The temperature effect on the seasonal variation of $\delta^{18}O$ of precipitation water, which appeared to be strongest during winter months, was in agreement with Dansgaard's interpretation of the relative effects of temperature and amount of precipitation.[11]

Two significant features of the precipitation sulfate data are that (1) the $\delta^{18}O$ for the sulfate varied seasonally and in phase with the variations of the $\delta^{18}O$ of the water in which it was dissolved, and (2) the amplitude of the sulfate variation was less than that of precipitation water by a factor of about 0.7. This ratio of amplitudes could result from the isotopic exchange which occurs under the conditions of a hydrolysis-oxidation mechanism, as discussed in the introduction. That is, if three of the four sulfate oxygens were essentially contributed by the water, the seasonal variation of δ^{18}O in the sulfate should be about three-fourths, or less, of that in the water. Therefore, it may be concluded that this relationship (factor of ~0.7) between the amplitudes of the two temporal variations "curves" indicates that the sulfate in precipitation was formed predominantly by the hydrolysis-oxidation mechanism.

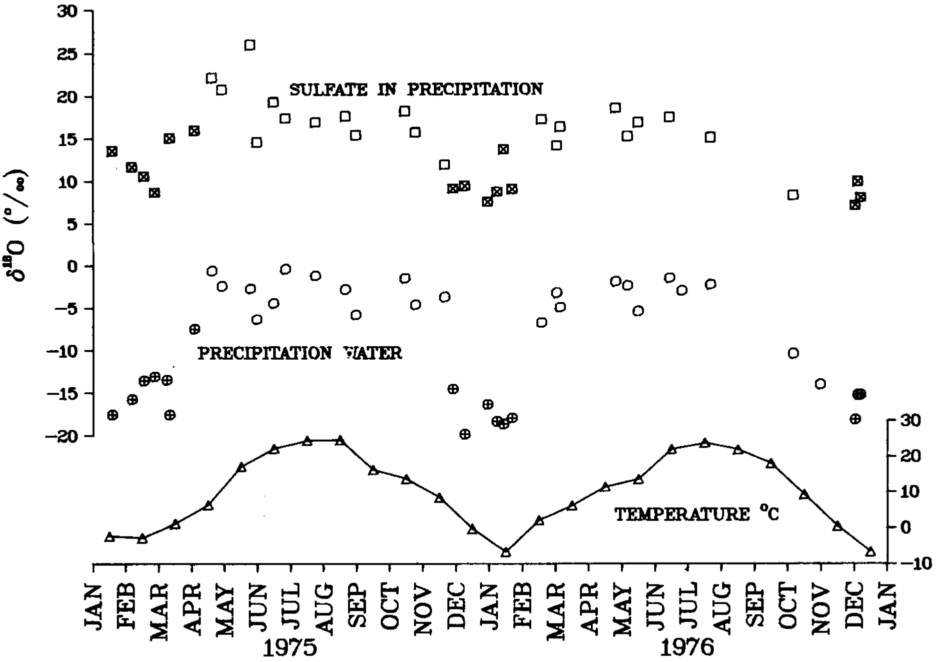

FIGURE 1 Isotopic results for dissolved sulfates and water in precipitation, and average monthly temperatures at Argonne, Illinois, 1975 and 1976. Crossed data points denote snow samples.

We have obtained confirming results in a laboratory experiment (to be reported in a later publication) in which tank SO_2 was dissolved in water supplies of various oxygen-18 enrichments, prior to air oxidation in a closed system. The slope of the linear relationship between the δ^{18}O of the sulfate products and the δ^{18}O of the water was also about 0.75.

Particulate sulfates and water vapor

The isotopic data for particulate sulfates and water vapor, collected at the Argonne site during 1975 and 1976, are presented in Figure 2. The corresponding data for the sulfate concentrations are shown in Figure 3. Figure 4 shows similar isotopic and concentration data for 24-hour hi-vol samples, collected at 10-day intervals at San Diego, California, throughout 1975. (These samples were supplied by the Air and Industrial Hygiene Laboratory, California Department of Health.) In Figures 5 and 6, $\delta^{18}O$ values are plotted vs. concentration for Argonne and San Diego, respectively.

As was found for precipitation water, $\delta^{18}O$ for water vapor at Argonnne also varied seasonally, although at levels about 10‰ lower than the corresponding precipitation water. This difference resulted from the isotopic shift characteristic of the phase change of gaseous to liquid water at ambient temperatures.

The average del value for particulate sulfates (13‰) was close to that of precipitation sulfates (14‰) for the two-year period at Argonne. The variation of $\delta^{18}O$ with seasonal changes, however, was remarkably

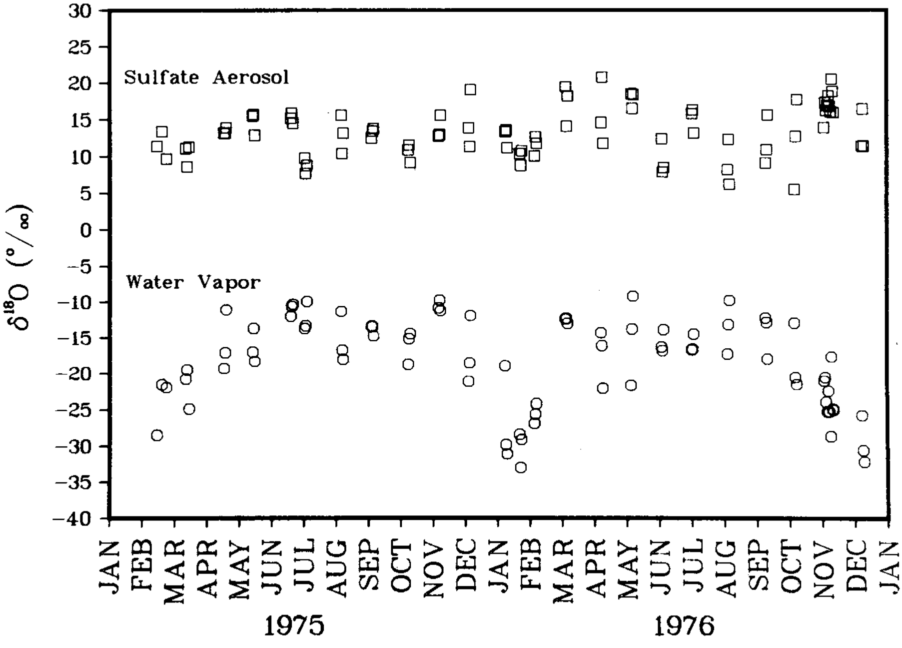

FIGURE 2 Isotopic results for particulate sulfates and water vapor at Argonne, Illinois, 1975 and 1976.

different for the two types of sulfate (Figures 1 and 2). Instead of varying seasonally and in phase with the $\delta^{18}O$ of atmospheric water, as in the case of precipitation sulfate, the $\delta^{18}O$ of particulate sulfate varied randomly with season. The del values for particulate sulfate at San Diego also varied randomly with season and averaged ~4‰ higher than the $\delta^{18}O$ at Argonne. [The sulfate particles in San Diego may have had higher

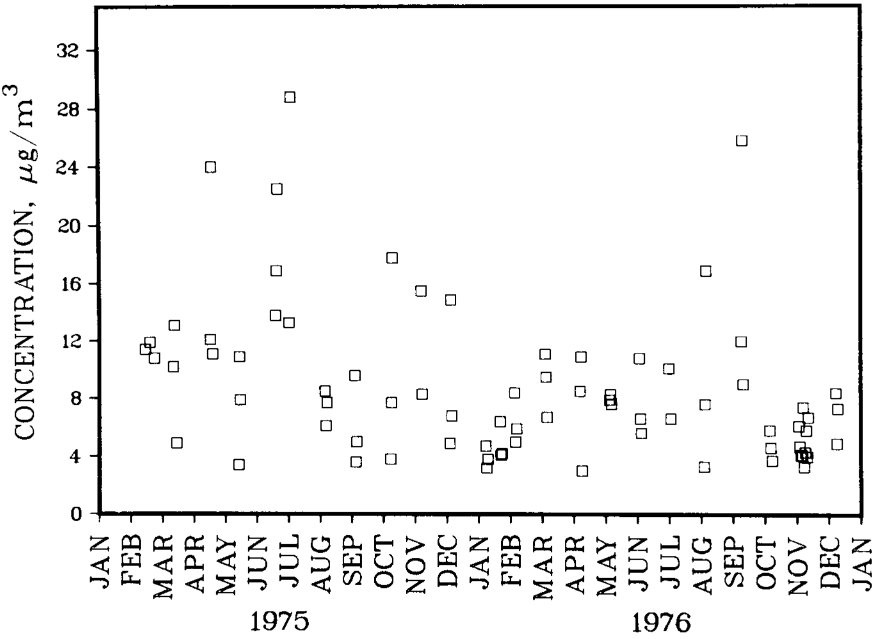

FIGURE 3 Concentration of particulate sulfates at Argonne, Illinois.

average del values than Argonne in 1975 because the lower latitude of San Diego would favor a higher ^{18}O content in atmospheric water.[11] The effect of adding sea-spray sulfate ($\delta^{18}O = \sim 9.5‰$) to the particulate sulfates in San Diego would be to lower their average del value rather than raise it.] Furthermore, the variations of concentrations at both sites (Figures 3 and 4) failed to show distinct seasonal patterns. The correlations of isotopic enrichment with concentration were, in both cases, insignificant (Figures 5 and 6).

An hypothesis has been developed that is consistent with experimental observations that (1) the average $\delta^{18}O$ for precipitation sulfates and particulate sulfates were about equal; (2) the $\delta^{18}O$ did not vary consistently with concentration; and (3) the variability of the $\delta^{18}O$ of precipitation sulfates was closely coupled to the seasonal variability of $\delta^{18}O$ of precipitation water, while the $\delta^{18}O$ of particulate sulfates varied randomly with season. The hypothesis is as follows. Both types of sulfate were formed predominantly by the same hydrolysis-oxidation mechanism in liquid water, but their residence times in the atmosphere were vastly different. The precipitation sulfates remained in the atmosphere for a relatively short period of time after formation and, because of their

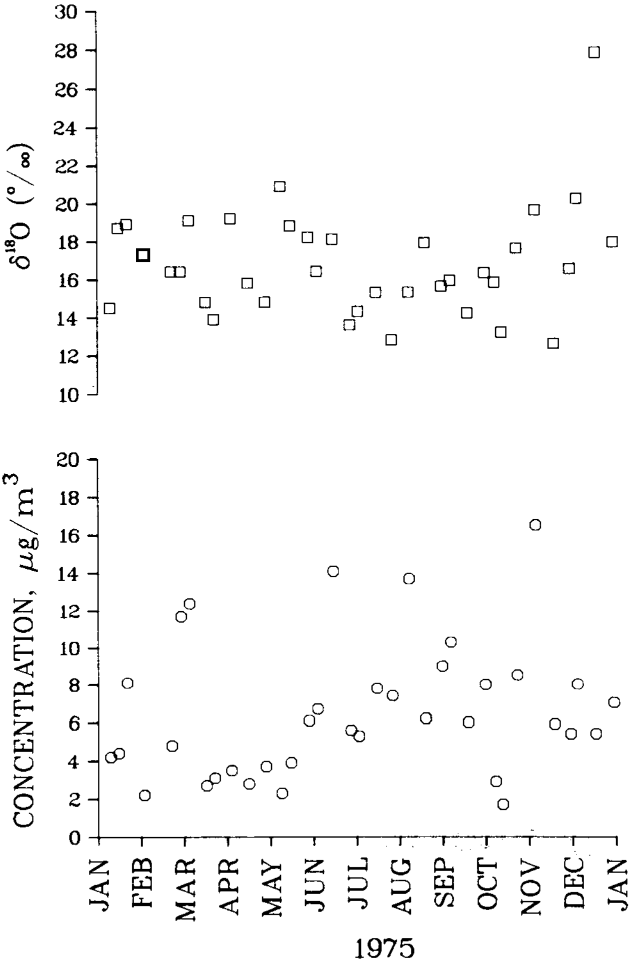

FIGURE 4 Isotopic and concentration results on particulate sulfates at San Diego, California.

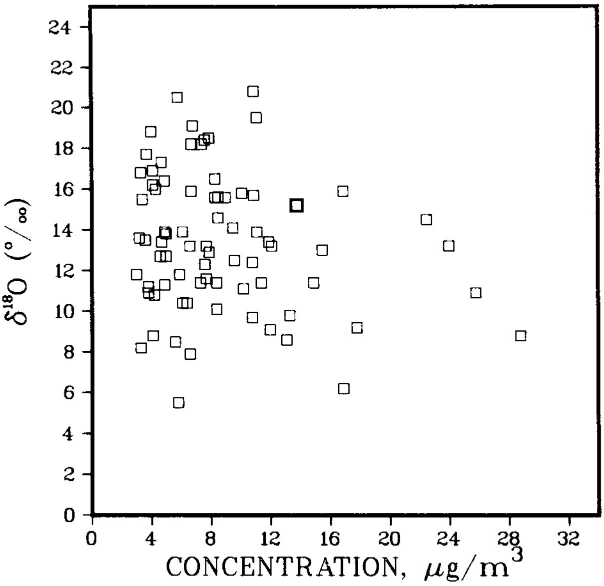

FIGURE 5 ^{18}O enrichment vs. concentration of particulate sulfates at Argonne, Illinois.

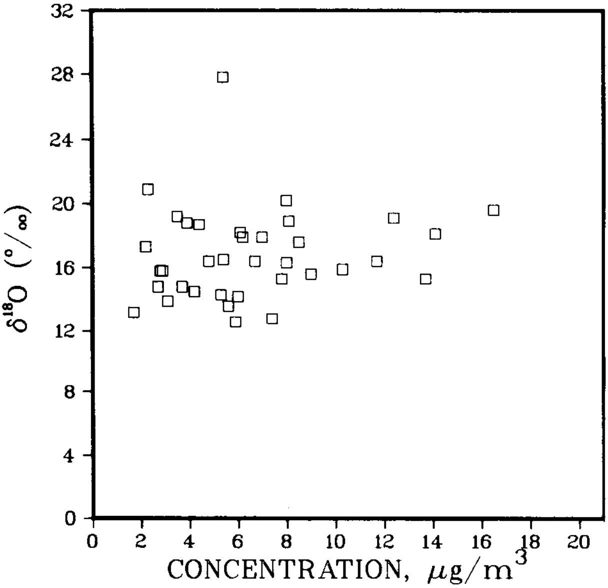

FIGURE 6 ^{18}O enrichment vs. concentration of particulate sulfates at San Diego, California.

prompt removal in rain or snow, their isotopic composition was dominated by that of the ambient atmospheric water. In contrast, the sulfate particles that escaped removal by precipitation, possibly owing to evaporation of the cloud droplets in which they were contained, remained in the atmosphere sufficiently long to become effectively intermixed with particles having different seasonal origins.

Because the residence time of particulate sulfates is believed to be long, the nonseasonal variations of their isotopic composition may also be strongly affected by meteorological conditions. These conditions, which can be strongly cyclic in any season, may allow air masses of different seasonal and latitudinal histories to intermittently reach the stationary hi-vol air sampler where the ambient particulate sulfates are collected for analysis.

Sulfur dioxide

Figure 7 shows the isotopic data for the sulfates formed by collection and oxidation of SO_2 on the alkaline-treated filters. Recent laboratory experiments (to be published later) indicate that the sulfite which is formed on

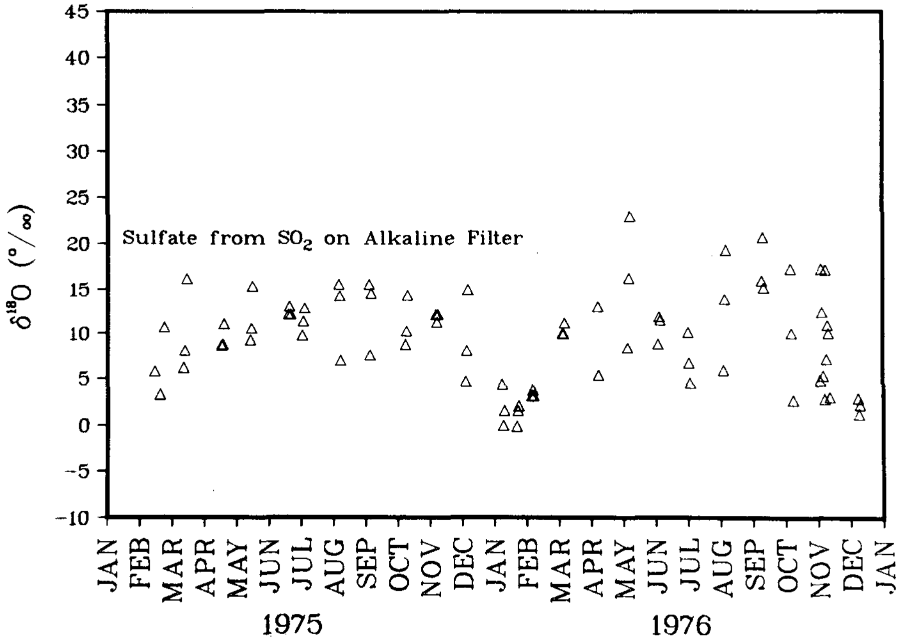

FIGURE 7 Isotopic results for sulfate formed on alkaline filters by atmospheric sulfur dioxide at Argonne, Illinois.

the moist alkaline filter probably undergoes significant, although uncontrolled and as yet undetermined, isotopic equilibration with the reagents (K_2CO_3, glycerol, and ambient water), prior to oxidation to sulfate. The seasonal trends that appear in these data may therefore be caused, at least in part, by isotopic equilibration with the ambient water vapor which is drawn through the sampler during the 24-hour sampling period.

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