Reports

Primary Sulfates in Atmospheric Sulfates: Estimation by Oxygen Isotope Ratio Measurements

Abstract. *The relative amounts of primary and secondary sulfates in atmospheric aerosols and precipitation can be estimated from measurements of the stable oxygen isotope ratios. The oxygen-18 content of sulfates formed in power plant stack gases before emission into the atmosphere is significantly higher than that of sulfates formed from sulfur dioxide after emission. Results show that 20 to 30 percent of the sulfates in rain and snow at Argonne, Illinois, are of primary origin.*

A knowledge of the relative amounts of primary sulfates (formed within point sources before emission into the atmosphere) and secondary sulfates (formed from gaseous sulfur compounds, principally SO_2, by atmospheric conversion processes) is needed for the formulation of effective control strategies. (i) Such information can be used to infer the relative importance of local versus distant sources. In a given air mass, as SO_2 is gradually converted to sulfate, the fraction of primary sulfates decreases. Thus, if the sulfate content in the primary fraction at a given receptor site is relatively low, the sulfates are likely to be the result of transport from distant sources. On the other hand, a relatively high fraction of primary sulfates would indicate that the corresponding emission sources are within the region of the receptor site. (ii) Such information is needed to determine the linearity of the relationship between SO_2 control and sulfate concentration. Wet scrubbers are not nearly as effective at removing primary sulfate as they are at removing SO_2 (*1*). Therefore, the emissions of primary sulfates will not necessarily decrease linearly with SO_2 reductions. (iii) If primary sulfates are important, new control methods may need to be developed that will effectively remove sulfuric acid mist.

We have developed a method, based on measurements of the stable oxygen isotope ratios ($^{18}O/^{16}O$) in atmospheric sulfates and water, by which locally obtained samples may be used to estimate the relative amounts of primary and secondary sulfates at a given receptor location. This technique can aid in identifying the source regions that lead to polluted precipitation at a given site.

The oxygen isotopy of sulfates prepared from SO_2 in laboratory experiments by eight different methods has been examined. Three of these methods involved aqueous-phase preparations (*2*), four nonliquid preparations in humidified air (*3*), and one high-temperature (400° to 500°C) platinum-catalyzed preparations (*4*). The high-temperature preparations were made to simulate primary sulfate formation; all the other preparations were intended to simulate secondary sulfate formation. The following reactions, corresponding to these preparations, yielded the isotopic results (*5*) displayed in Fig. 1 as the correspondingly numbered curves 1 through 8.

The four aqueous-phase reactions were as follows:

$$SO_2 + H_2O(\ell) \rightleftarrows SO_2 \cdot H_2O(aq) \rightleftarrows HSO_3^- + H^+ \tag{A}$$

$$HSO_3^- \xrightarrow[Fe^{3+}]{\text{air}} SO_4^{2-} \tag{1}$$

$$HSO_3^- \xrightarrow[\text{charcoal}]{\text{air}} SO_4^{2-} \tag{2}$$

$$HSO_3^- \xrightarrow{H_2O_2} SO_4^{2-} \tag{3}$$

The following nonliquid-phase reactions (*6*) were used:

$$SO_2 + H_2O(g) \rightleftarrows SO_2 \cdot H_2O \tag{B}$$

$$SO_2 \cdot H_2O \xrightarrow[\text{electric spark}]{\text{air}} H_2SO_4 \tag{4}$$

$$SO_2 \cdot H_2O \xrightarrow[NO_2]{\text{air}} H_2SO_4 \tag{5}$$

$$SO_2 \cdot H_2O \xrightarrow[\gamma\text{-ray}]{\text{air}} H_2SO_4 \tag{6}$$

$$SO_2 \cdot H_2O \xrightarrow[\text{charcoal}]{\text{air}} H_2SO_4 \tag{7}$$

The elevated-temperature reaction sequence was as follows:

$$SO_2 + \frac{1}{2} O_2 \xrightarrow[\text{Pt}]{400^\circ \text{ to } 500^\circ\text{C}} SO_3 \tag{C}$$

$$SO_3 + H_2O(g) \rightarrow H_2SO_4 \tag{8}$$

As indicated by Eqs. A and B, SO_2 equilibrates with water rapidly in both aqueous-phase and nonliquid-phase reactions, allowing isotopic equilibration to go essentially to completion prior to oxidation of the SO_2 (*2, 3*). Since the molar ratio of H_2O to SO_2 is very high in the atmosphere (~ 10^6), the $\delta^{18}O$ of SO_2 in the atmosphere is dynamically controlled by the $\delta^{18}O$ of atmospheric water; therefore, the initial $\delta^{18}O$ of emitted SO_2 has no appreciable effect on the $\delta^{18}O$ of secondary sulfates formed in the atmosphere.

Also plotted in Fig. 1 are the isotopic data obtained for samples of precipitation water (rain and snow) collected at Argonne, Illinois, during the period October 1976 to March 1978 (*7*). The $\delta^{18}O$ of the sulfate dissolved in the precipitation water is plotted versus the $\delta^{18}O$ of the associated atmospheric water. All of the precipitation samples contained sulfates higher in $\delta^{18}O$ than the sulfates formed by any of the secondary sulfate mechanisms that we tested by using laboratory methods of preparation (curves 1 through 7) (*8*).

It appears from this comparison that the precipitation sulfates were not formed solely by these secondary sulfate mechanisms in the atmosphere, either singly or in combination. Since the $\delta^{18}O$ values for the laboratory-prepared primary sulfates (curve 8) were considerably higher than those of both laboratory-prepared secondary and precipitation sulfates, we conclude that primary sulfates contribute to the composition of the precipitation sulfates and that their relative amounts can be estimated.

In addition to isotopic data on laboratory-prepared primary sulfates, we measured the $\delta^{18}O$ on primary sulfates sampled from the boiler stacks of large coal- and oil-fired power plants (*9*). The $\delta^{18}O$ of five sets of in-stack samples, consisting of metal sulfates and of the sulfuric acid in the probe, coil, and backup filter of the sampling apparatus (*10*), ranged from 35 to 40 per mil. Like the laboratory-prepared primary sulfates, these in-stack sulfates were higher in $\delta^{18}O$ by several parts per mil than those of precipitation and aerosol sulfates, the seasonal ranges of which were about 5 to 15 per mil at Argonne (*7*).

The results of these studies indicate that it is possible to estimate the relative amounts of primary and secondary sulfates in both precipitation and aerosol sulfates. The estimates can be based on the reasonable approximations that the $\delta^{18}O$ of primary sulfates is ~ 40 per mil (curve 8 in Fig. 1) and that the $\delta^{18}O$ of the secondary sulfates can be calculated from the $\delta^{18}O$ of the atmospheric water with which it is associated if one uses an average linear curve that represents the relationships between the $\delta^{18}O$ sulfate and the $\delta^{18}O$ of liquid water in Fig. 1. In

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doing this, one would use measured data on the $\delta^{18}O$ value of precipitation water for precipitation sulfates and data on the $\delta^{18}O$ value of ambient water vapor for aerosol sulfates. The percentage of primary sulfate, x, can then be found from

$$x\delta^{18}O_p + (100 - x)\delta^{18}O_s = 100\,\delta^{18}O_a \qquad (9)$$

where $\delta^{18}O_p$ is the value (~ 40 per mil) for primary sulfates, $\delta^{18}O_s$ is the value for secondary sulfates (calculated from the Fig. 1 relationship and the measured $\delta^{18}O$ value of the associated atmospheric water), and $\delta^{18}O_a$ is the measured value of the atmospheric sulfate.

Equation 9 was used to estimate the primary sulfate fraction in the aerosol and precipitation sulfates collected at Argonne from January 1977 to March 1978 (*7*). Specifically, 2-month running averages of the values of $\delta^{18}O$ for precipitation and aerosol sulfates were used as $\delta^{18}O_a$ in this equation. The values of $\delta^{18}O_s$ were estimated from an average curve based on curves 1 and 2 in Fig. 1. along with 2-month running averages of the measured $\delta^{18}O$ values for the appropriate associated atmospheric water.

Figure 2a shows the percentages of primary sulfates in aerosol and precipitation sulfates sampled at Argonne during this period. Primary sulfates appear to constitute from about 10 to 40 percent of the total ambient sulfates, both in aerosol and in precipitation. These values are much higher than what would be estimated on the basis of the percentage of primary sulfates in the total emissions from large point sources. Even if curves 4 through 6 in Fig. 1 are used to calculate $\delta^{18}O_s$, the percentages of primary sulfates are not substantially affected. This result suggests that for this analysis it is immaterial whether the secondary sulfates are formed by aqueous-phase or nonaqueous-phase mechanisms. If oxidation by H_2O_2 is considered to be significant, the percentage of primary sulfates would be even greater than 10 to 40 percent. The primary fraction in aerosol sulfates varied from about 10 percent in the summer to 30 to 40 percent in the winter, whereas the primary sulfate fraction in precipitation sulfates did not show a strong seasonal variation, ranging from 20 to 30 percent throughout most of the period of observation (Fig. 2a). These seasonal variations would be somewhat different if curves other than the average of curves 1 and 2 in Fig. 1 were used to calculate $\delta^{18}O_s$.

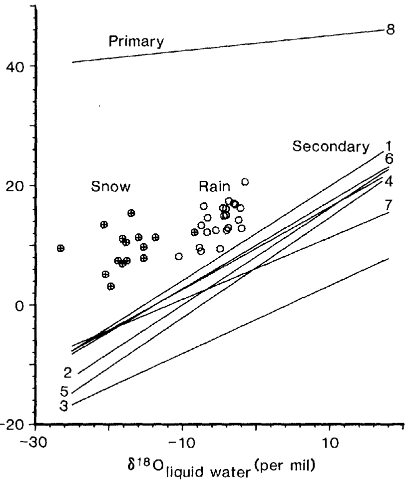

Fig. 1. Isotopic results on sulfates formed by eight different laboratory methods and on sulfates in precipitation at Argonne, Illinois, during the period October 1976 to March 1978.

Figure 2b shows the estimated loadings of primary and secondary sulfates in atmospheric aerosols sampled from January 1977 to March 1978. We derived these values by multiplying the respective primary and secondary fractions by the measured total aerosol sulfate loadings. The primary sulfate loadings in the aerosol are relatively constant on an annual basis, whereas secondary sulfates experience a distinct maximum during the summer months. Corresponding estimates for precipitation sulfates were not possible because of inadequate sulfate concentration data.

The high $\delta^{18}O$ values of about 40 per mil do not necessarily apply to all the sulfates that are normally included in the term "primary sulfate." Results of limited laboratory tests show that these high values of $\delta^{18}O$ are observed only when SO_3 is an intermediate in the formation of the sulfate, such as might be expected in, or very near, the combustion zone of the furnace. However, sulfates are also produced by a variety of heterogeneous SO_2 oxidation processes downstream of the furnace but ahead of emission from the stack. These sulfates are included in the common use of the term "primary sulfate" but have much lower $\delta^{18}O$ values, similar in magnitude to the $\delta^{18}O$ values of the sulfates produced in the atmosphere from SO_2. The presence of varying amounts of these sulfates in a sample obtained from the flue gases would lower the average $\delta^{18}O$ value of the sample, as evidenced by the variability in the ^{18}O content of the in-stack samples. To the extent that sulfates not produced via the SO_3 intermediate are present in the emissions from sources, the calculated results shown in Fig. 2 underestimate the amount of "primary sulfates" in the atmosphere.

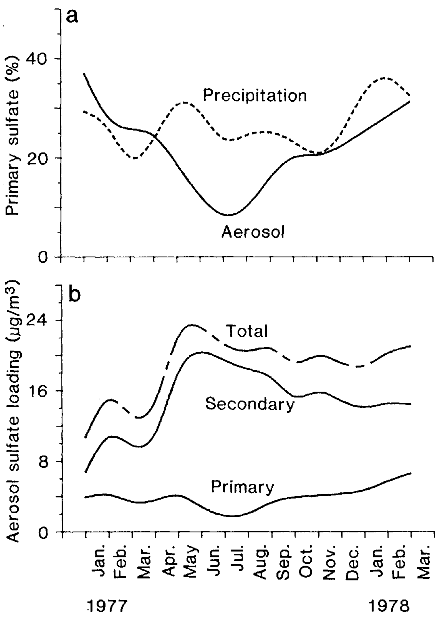

Fig. 2. The percentages of primary sulfate in aerosol and precipitation sulfates (a) and the loading of primary and secondary sulfates in the aerosol (b) at Argonne, Illinois, from January 1977 to March 1978.

One must also bear in mind that Argonne is located in a region (near Chicago) in which most of the residential and commercial space heating uses natural gas as the primary fuel, and electric power generation uses mostly coal or nuclear fuels, with a very small fraction of fossil energy deriving from oil combustion. Oil combustion yields higher primary sulfate formation and emissions than an equivalent amount of coal (*11*), and thus the results from other areas, such as the Northeast where much greater amounts of fuel oil are used, are likely to be quite different from our results for Argonne.

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References and Notes

1. J. B. Homolya and J. L. Cheney, *J. Air Pollut. Control Assoc.* **29**, 1000 (1979).
2. B. D. Holt, R. Kumar, P. T. Cunningham, *Atmos. Environ.* **15**, 557 (1981).
3. B. D. Holt, P. T. Cunningham, A. G. Engelkemeir, D. G. Graczyk, R. Kumar, paper presented at the Fourth International Symposium on Stable Isotopes, Jülich, Federal Republic of Germany, March 1981.
4. B. D. Holt, R. Kumar, P. T. Cunningham, unpublished data.
5. The $\delta^{18}O$ is defined as

$$\delta^{18}O = \frac{(^{18}O/^{16}O)_{sample} - (^{18}O/^{16}O)_{standard}}{(^{18}O/^{16}O)_{standard}} \times 1000$$

where the standard is SMOW (standard mean ocean water).
6. The structural form of $SO_2 \cdot H_2O$ (gaseous or surface-adsorbed) is unspecified.
7. B. D. Holt, P. T. Cunningham, R. Kumar, *Environ. Sci. Technol.* **15**, 804 (1981).
8. Although reagent H_2O_2 was used as the oxidant

in Eq. 3, and OH radicals were presumably involved in the γ-ray–induced air oxidation of SO_2 in Eq. 6, the oxygen isotopy of secondary sulfate formation by photochemical processes is not necessarily exhaustively represented by the reactions that we have studied.
9. Samples were supplied by courtesy of R. N. Dietz, Brookhaven National Laboratory, Upton, N.Y.
10. R. N. Dietz, *Brookhaven Natl. Lab. Rep. 27590* (March 1980).
11. J. B. Homolya and S. Lambert, *J. Air Pollut. Control Assoc.* **31**, 139 (1981).
12. This work was conducted under the auspices of the Division of Materials Sciences, Office of Basic Energy Sciences, Department of Energy.

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Juvenile-Adult Habitat Shift in Permian Fossil Reptiles and Amphibians

Abstract. *Among extant large reptiles, juveniles often occupy different habitats from those of adults or subadults and thus avoid competition with and predation from the older animals; small juveniles often choose cryptic habitats because they are vulnerable to a wide variety of predators. Evidence from fossil humeri and femora of Early Permian reptiles collected from sediments of several distinct habitats indicate that similar shifts in habitat occurred. Juvenile* Dimetrodon *seem to have favored cryptic habitats around swamp and swampy lake margins; adults favored open habitats on the floodplains. Similar patterns of habitat shift seem to be present in the reptile* Ophiacodon *and the amphibian* Eryops *and may have been common in fossil tetrapods of the Permian-Triassic.*

A shift in habitat from juvenile to adult is an important adaptation of living reptiles. Unlike the young of most birds and mammals, which enjoy parental protection until they are nearly adult in weight, most reptiles and amphibians act independently of their parents at hatching or shortly after, when the juveniles are a tiny fraction of the adult weight. Among living reptiles, crocodilians have the longest known period of parental care of young, up to 2 years, and yet the young become independent when they are only about 1/50 the weight of a sexually mature adult (*1*, *2*). Competition between successive age classes of one species of reptile can be severe, and subadults and adults may prey on juveniles (*3*). Small juveniles usually have more potential interspecific predators than adults and should prefer more hidden microhabitats. Subadult crocodilians have been observed to be partially segregated ecologically from adults (*1*, *2*); small juvenile crocodilians sometimes seem to prefer cryptic microhabitats, near shore swamps and reedbeds, and it has been suggested that young green turtles (*Chelonia mydas*) spend their first several years hidden within the floating *Sargassum* forests of the Caribbean (*4*). Because of their long independent ontogeny, one species of large reptile may fill the role of a dozen or more species of bird or mammal.

If the juvenile-adult habitat shift occurred among ancient reptiles and amphibians, recognition of this ontogenetic adaptation would be important in paleoecological reconstructions; otherwise ecological segregation by age in one species might be mistaken for the presence of two distinct species with different adult weights and habitat preferences. The record of ontogenetic habitat shift was studied in fossils from the Early Permian Red Beds of North Central Texas. The fauna of large amphibians and reptiles represents an early stage in the adaptive radiation of reptiles (*5*). The largest samples of single species occur in the Admiral and the overlying Belle Plains Formations. For 70 years, first Case and then Romer (*6*) collected thousands of specimens with good data on locality. Several habitats have been defined by sedimentological and paleontological characters. (i) The Geraldine Bonebed represents swamps choked with logs and other plant debris; sediments are mostly organic-rich clays with pyrite and other sulfides. Flat-bodied bottom-living amphibians which retained gills throughout their life are absent, indicating that the bottom water in this habitat was oxygen-poor, and the only common small aquatic amphibian is *Archeria*, an elongated eellike predator that could swim through a complex habitat of aquatic vegetation and terrestrial plant debris. (ii) The Briar Creek Bonebed represents swampy lakes; sediments are mostly dark mudstones with abundant siderite. Gill-breathing bottom-living amphibians are absent, and *Archeria* is common. (iii) The Rattlesnake Canyon localities represent lakes; sediments are mostly limy mudstones and limestones without plant debris. Gill-breathing amphibians (*Trimerorhachis*) are common, and *Archeria* is rare, suggesting that standing water was well oxygenated and relatively open and clear. (iv) West of William's Ranch represents mixed floodplain, small pond, and stream habitats; sediments are red-green mottled silty mudstones with soil carbonate nodules, lenses of fine dark mudstone, and small channel sandstones with basal mud-clast conglomerates and reworked soil carbonate nodules (*7*). Gill-breathing amphibians are locally common, and *Archeria* is relatively rare; small terrestrial amphibians with well-ossified, stout limbs are common (*8*).

The most commonly preserved elements that can be identified to genus are large limb bones, the humeri and femora. Good skulls are rare, and vertebrae, though numerous, were sometimes not collected. Romer, who recovered 90 percent of the fossils, collected every humerus and femur found in the field (*9*). The average sediment grain size in nearly all sites is in the clay-silt range, and the abundance of small limb bones suggests a low-energy environment with little hydraulic sorting of bones (*10*). All humeri and femora in the Case-Romer collections and in most other Early Permian collections from Texas were recently analyzed (*11*). *Dimetrodon*, a large finback predator, is the most common genus (*12*), and three species—large, medium, and small—are generally recognized. From the published records it appears that the small species preferred swamp and lake habitats, and the largest species preferred mixed floodplain, pond, and stream habitats (*13*). This pattern might in fact represent a shift in habitat of one or more species.

In the limb bones of most Early Permian reptiles and amphibians and extant lower tetrapods, the joint surfaces and the areas of muscle and ligament attachment became progressively better ossified during ontogeny. The fossil sample of the big flatheaded amphibian *Eryops* from the Briar Creek Bonebed shows the most striking case of ontogenetic ossification (Fig. 1A). The largest single sample of *Dimetrodon* bones, also from Briar Creek, is reported to contain bones of all three species. When the femora and humeri from Briar Creek were ordered by increasing size, the collection formed a rather smooth ossification sequence; the smallest size classes show the poorest surface ossification, and the largest size classes have completely ossified articular surfaces and rugosely ossified muscle attachment sites (Fig. 1B). Moreover, the collection showed a continuous allometric relation of femur breadth as a function of length (Fig. 1), and the variance within this allometric relation was no greater than that seen within a growth series of one species of large extant reptile (*14*). *Dimetrodon* specimens from

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