



## Project Summary

# Oxygen-18 Study of SO<sub>2</sub> Oxidation in Rainwater by Peroxides

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**This study was conducted to examine the usefulness of oxygen isotope ratio measurements in assessment of the importance of peroxide oxidation of SO<sub>2</sub> to SO<sub>4</sub><sup>2-</sup> (hence to acid rain) in the atmosphere. A new analytical method was developed by which the oxygen isotope ratio in peroxide (ppb range) in rainwater could be determined. Supplies of H<sub>2</sub>O<sub>2</sub> of differing isotope ratios were then generated, and, using these supplies to oxidize SO<sub>2</sub> to SO<sub>4</sub><sup>2-</sup>, a comprehensive isotopic relationship was established among H<sub>2</sub>O<sub>2</sub>, H<sub>2</sub>O, and SO<sub>4</sub><sup>2-</sup>. With this relationship, the isotopic quality of sulfate that might be formed in the atmosphere from aqueous-phase oxidation by peroxide was calculated. By comparing calculated to measured isotopic data for sulfates in rainwater, and assuming that this sulfate was formed by either metal (or carbon) catalyzed oxidation or by oxidation by peroxides, it was concluded that 40% or more of atmospheric sulfates in the summer rains in the northeastern U.S. are formed by peroxide oxidation.**

***This Project Summary was developed by EPA's Atmospheric Sciences Research Laboratory, Research Triangle Park, NC, to announce key findings of the research project that is fully documented in a separate report of the same title (see Project Report ordering information at back).***

### Introduction

Considerable interest has been shown in the possibility of using oxygen isotopy to elucidate the role of H<sub>2</sub>O<sub>2</sub> in the oxidation of SO<sub>2</sub> to sulfates in the

atmosphere. Aqueous-phase oxidation of SO<sub>2</sub> to H<sub>2</sub>SO<sub>4</sub> probably accounts for a major fraction of the observed SO<sub>4</sub><sup>2-</sup> in the precipitation occurring in the northeastern United States. The key reactants responsible for this oxidation are not well known, although a large number of possible catalysts and oxidants exist in the atmosphere, including carbon, transition metal ions, hydroxyl and organic free radicals, hydrogen peroxide (including organic peroxides), and ozone. Of these, the last two are the only ones believed to be present in sufficient quantity to produce the observed amounts of SO<sub>4</sub><sup>2-</sup> in wet deposition. It has been postulated that the atmospheric oxidation of SO<sub>2</sub> is limited by the availability of one or both of these oxidants, rather than by the availability of SO<sub>2</sub> itself. This is the so-called phenomenon of nonlinearity between the concentration (and, by implication, the emission) of SO<sub>2</sub> in the atmosphere and the conversion of this SO<sub>2</sub> to H<sub>2</sub>SO<sub>4</sub>. If such is indeed the case, it is important to determine if peroxides have a pivotal role in acid formation and deposition from the atmosphere.

Oxygen isotopic studies are useful in distinguishing between the different oxidation mechanisms effective in the atmosphere. We have previously shown, by laboratory simulation of several different atmospheric reaction sequences, that the oxygen isotope ratio in the product SO<sub>4</sub><sup>2-</sup> is uniquely related to the reaction pathway followed in its formation. The present work was undertaken to determine if atmospheric peroxide is responsible for significant oxidation of

SO<sub>2</sub> to sulfate and if it limits the aqueous-phase formation of sulfuric acid. The results of such studies can have significant implications for energy technology, particularly if they indicate that, because of the nonlinearity in SO<sub>2</sub> conversion discussed above, it may be more important to reduce the ambient concentrations of H<sub>2</sub>O<sub>2</sub> than of SO<sub>2</sub>.

In the 1981 JASON Committee Report to the U.S. Department of Energy, some recommendations for further research were based, at least in part, on our earlier work on SO<sub>2</sub> oxidation by laboratory reagent-grade H<sub>2</sub>O<sub>2</sub>. According to results of our earlier work, the  $\delta^{18}\text{O}$  [deviation in parts per thousand (‰) of the  $^{18}\text{O}/^{16}\text{O}$  ratio of the sample from that of the standard reference material, Standard Mean Ocean Water (SMOW)] of sulfates produced by H<sub>2</sub>O<sub>2</sub> oxidation were significantly lower than the  $\delta^{18}\text{O}$  of sulfates found in rainwater. However, the  $\delta^{18}\text{O}$  of the reagent-grade H<sub>2</sub>O<sub>2</sub> used in those experiments was not known (although it has been found, in our current work, to be very different isotopically from atmospheric peroxides). It became evident that there was a need for isotopic analysis of H<sub>2</sub>O<sub>2</sub> in dilute solutions and for a methodology in which the  $\delta^{18}\text{O}$  values of H<sub>2</sub>O<sub>2</sub>, H<sub>2</sub>O, and SO<sub>4</sub><sup>2-</sup> in rainwater could be compared to assess the importance of H<sub>2</sub>O<sub>2</sub> in the formation of sulfate-constituted acid rain.

## Approach

The plan of the investigation was to develop a method for the determination of the  $\delta^{18}\text{O}$  of H<sub>2</sub>O<sub>2</sub> in dilute aqueous solutions (simulating rainwater); to prepare solutions of H<sub>2</sub>O<sub>2</sub> of various  $^{18}\text{O}$  enrichments; to use the freshly prepared solutions of H<sub>2</sub>O<sub>2</sub> to oxidize SO<sub>2</sub> to SO<sub>4</sub><sup>2-</sup> for evaluation of the relationship between  $\delta^{18}\text{O}_{\text{SO}_4^{2-}}$  and  $\delta^{18}\text{O}_{\text{H}_2\text{O}_2}$ ; and to apply this relationship to the measured  $\delta^{18}\text{O}_{\text{H}_2\text{O}_2}$ ,  $\delta^{18}\text{O}_{\text{SO}_4^{2-}}$ , and  $\delta^{18}\text{O}_{\text{H}_2\text{O}}$  in precipitation water, for assessment of the importance of H<sub>2</sub>O<sub>2</sub> in the atmospheric transformation of SO<sub>2</sub> to sulfate.

## Results

A new analytical method was successfully developed for the determination of the  $\delta^{18}\text{O}$  of H<sub>2</sub>O<sub>2</sub> (ppb range) in rainwater. The procedure that was finally adopted after many developmental experiments follows. Rainwater, collected in 25-L plastic bottles by four funnels (inverted plastic skylights, each of 1 m<sup>2</sup> catchment, connected to the bottles by plastic hose), was acidified

and kept refrigerated until the time of analysis for effective prevention of peroxide decomposition. A 20-L sample of the rainwater was degassed of dissolved air by a process of combined evacuation, ultrasonic agitation, and helium sparge (VUS). The dissolved peroxide was then oxidized to O<sub>2</sub> by KMnO<sub>4</sub>; the O<sub>2</sub> was removed from the water sample by the VUS treatment and conducted through a bed of charcoal and platinum, where it was quantitatively converted to CO<sub>2</sub>. The CO<sub>2</sub>, containing the same oxygen atoms as the peroxide from which it was derived, was analyzed mass spectrometrically for its  $\delta^{18}\text{O}$ . Measurement of the amount of CO<sub>2</sub> also yielded information on the concentration of peroxide in the atmosphere.

Since there was no commercial source of H<sub>2</sub>O<sub>2</sub> solutions of various  $^{18}\text{O}$  enrichments, solutions were prepared in the laboratory. Using a high-voltage method, water vapors of various  $\delta^{18}\text{O}$  were subjected to a corona discharge that caused the formation of OH radicals; the OH radicals were condensed on a cold surface, where they combined to form H<sub>2</sub>O<sub>2</sub>; the H<sub>2</sub>O<sub>2</sub> was diluted with water and preserved by refrigeration.

These stock solutions of H<sub>2</sub>O<sub>2</sub> of different  $\delta^{18}\text{O}$  values were then used to oxidize SO<sub>2</sub> to SO<sub>4</sub><sup>2-</sup>. A linear relationship was established between the  $\delta^{18}\text{O}$  of the sulfate and the  $\delta^{18}\text{O}$  of the H<sub>2</sub>O<sub>2</sub>. This relationship, combined with one we had previously determined between the  $\delta^{18}\text{O}_{\text{SO}_4^{2-}}$  and  $\delta^{18}\text{O}_{\text{H}_2\text{O}}$ , gave a comprehensive one:

$$\delta^{18}\text{O}_{\text{SO}_4^{2-}} = 0.57 \delta^{18}\text{O}_{\text{H}_2\text{O}_2} + 0.43 \delta^{18}\text{O}_{\text{H}_2\text{O}} + 8.4\%.$$

This relationship could then be used to calculate the  $\delta^{18}\text{O}_{\text{SO}_4^{2-}}$ , when both  $\delta^{18}\text{O}_{\text{H}_2\text{O}_2}$  and  $\delta^{18}\text{O}_{\text{H}_2\text{O}}$  were known.

The relationship was used to compare calculated values to measured values of  $\delta^{18}\text{O}_{\text{SO}_4^{2-}}$  in rainwater samples, in which all three isotopic quantities,  $\delta^{18}\text{O}_{\text{H}_2\text{O}_2}$ ,  $\delta^{18}\text{O}_{\text{H}_2\text{O}}$ , and  $\delta^{18}\text{O}_{\text{SO}_4^{2-}}$ , were experimentally determined. It was found that the measured  $\delta^{18}\text{O}_{\text{SO}_4^{2-}}$  in rainwater samples from four collection sites (Argonne, IL; Research Triangle Park, NC; Whiteface Mountain, NY; and Dearborn, MI), in the late spring and summer of 1985, ranged consistently between the corresponding calculated values for peroxide oxidation and for metal-catalyzed aqueous oxidation, indicating that the sulfate in the rainwater was a mixture of sulfates formed by the two mechanisms.

## Conclusions

Relative deviations of the measured  $\delta^{18}\text{O}_{\text{SO}_4^{2-}}$  values from the corresponding calculated values of the two competing mechanisms (peroxide oxidation and metal-catalyzed aqueous oxidation) indicated that at least 40%, and probably more, of the sulfate was formed by peroxide oxidation. Thus, the isotopic data obtained by our investigation indicate that peroxide oxidation of SO<sub>2</sub> is a major source of sulfate in rainwater and, therefore, that investigations of the origin and possible means of control of atmospheric peroxides are of prime importance.

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**Marcia C. Dodge is the EPA Project Officer (see below).**

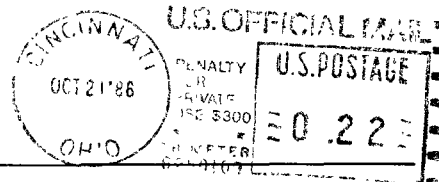
**The complete report, entitled "Oxygen-18 Study of SO<sub>2</sub> Oxidation in Rainwater by Peroxides," (Order No. PB 86-216 751/AS; Cost: \$9.95, subject to change) will be available only from:**

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