

## Sulfate oxygen-17 anomaly in an Oligocene ash bed in mid-North America: Was it the dry fogs?

Huiming Bao,<sup>1</sup> Mark H. Thiemens,<sup>2</sup> David B. Loope,<sup>3</sup> and Xun-Lai Yuan<sup>4</sup>

Received 2 January 2003; revised 2 June 2003; accepted 11 July 2003; published 21 August 2003.

[1] The oxygen and sulfur isotope compositions of sulfate, particularly the oxygen-17 anomaly, provide clues to the origin of sulfate. We report a variable oxygen-17 anomaly for water- and acid-leached sulfate from an Oligocene volcanic ash bed in the northern High Plains, U.S.A. We find no sulfate O-17 anomaly, however, in freshly collected ashes from recent eruptions around the world. The Oligocene paleoclimatic and sedimentary evidence argues against a hyperarid condition in the High Plains, thus a long-term background atmospheric sulfate accumulation is less likely the origin. Combining sulfur isotope data, we suggest that the anomalous sulfate was associated with volcanic eruptions in the west, but was not directly carried by ash-falls. Extreme dry-fog (sulfate haze) events resulting from tropospheric oxidation of volcanic sulfur gases might provide a viable explanation for the sulfates in the ash bed that carry the oxygen-17 anomaly. **INDEX TERMS:** 1040 Geochemistry: Isotopic composition/chemistry; 0370 Atmospheric Composition and Structure: Volcanic effects (8409); 8404 Volcanology: Ash deposits; 0305 Atmospheric Composition and Structure: Aerosols and particles (0345, 4801). **Citation:** Bao, H., M. H. Thiemens, D. B. Loope, and X.-L. Yuan, Sulfate oxygen-17 anomaly in an Oligocene ash bed in mid-North America: Was it the dry fogs?, *Geophys. Res. Lett.*, 30(16), 1843, doi:10.1029/2003GL016869, 2003.

### 1. Introduction

[2] The effect of volcanic eruptions on global climate has been a topic of considerable interest in paleoclimatology, atmospheric chemistry, and global climate modeling [Pinto *et al.*, 1989; Robock, 2000]. The key components in the process are the surfaces of fine ash particles and sulfate aerosols derived from the oxidation of volcanic SO<sub>2</sub>. Potential oxidation pathways for volcanic SO<sub>2</sub> include oxidation by air O<sub>2</sub> on catalyzed particle surfaces, aqueous oxidation by H<sub>2</sub>O<sub>2</sub> or O<sub>3</sub>, and gas-phase oxidation by the •OH radical [Bekki, 1995; Harrison and Larson, 1974; Liang and Jacobson, 1999]. Once in the stratosphere, SO<sub>2</sub> could also be photolyzed to generate SO<sub>3</sub>, which hydrates to form sulfate. In order to assess the climatic effect of

volcanically released SO<sub>2</sub> and sulfate aerosols, it is important to estimate the roles of the various sulfur oxidation processes subsequent to eruption. Both oxygen and sulfur isotopic compositions of sulfate, i.e., δ<sup>18</sup>O or δ<sup>34</sup>S = (R<sub>sample</sub>/R<sub>standard</sub> - 1) × 1000‰ (where R is ratio of <sup>18</sup>O/<sup>16</sup>O or <sup>34</sup>S/<sup>32</sup>S, respectively) have been applied to delineate SO<sub>2</sub> oxidation pathways (e.g., [Holt and Kumar, 1991; Newman *et al.*, 1991; Tanaka *et al.*, 1994]). However, success has been limited as a result of overlapping values or the lack of isotopic data differentiating different reaction pathways. There have been few isotopic measurements on collected ash leachates (with notable exceptions [Castleman *et al.*, 1974; Rye *et al.*, 1984]). Little is known about where, when, and how SO<sub>2</sub> was oxidized and deposited after eruption.

[3] Recently, a mass-independent oxygen isotopic signature has been found in sulfate that forms specifically from the oxidation of sulfur gases by O<sub>3</sub> or H<sub>2</sub>O<sub>2</sub> [Savarino *et al.*, 2000]. Other oxidation pathways, such as oxidation by air O<sub>2</sub> at high temperatures or at particle surfaces by metal catalysts, and gas-phase oxidation by •OH, do not produce the O-17 anomaly in product SO<sub>4</sub><sup>2-</sup> (measured by Δ<sup>17</sup>O = δ<sup>17</sup>O - 0.52 × δ<sup>18</sup>O). In the oxidation of sulfur gases by O<sub>3</sub> or H<sub>2</sub>O<sub>2</sub>, the O-17 anomaly in product SO<sub>4</sub><sup>2-</sup> is not generated by the reaction itself, which is mass-dependent, but is transformed from oxidants O<sub>3</sub> or H<sub>2</sub>O<sub>2</sub> that have anomalous O-17 composition. δ<sup>17</sup>O-anomalous sulfate is pervasive in atmospheric aerosols, rainwater, snow, dust depositions, building surfaces, as well as surficial deposits from some extremely arid regions such as the Central Namib Desert, the Atacama Desert, and the Antarctica Dry Valleys [Bao *et al.*, 2000a, 2001a, 2000b, 2001b; Johnson *et al.*, 2001; Lee and Thiemens, 2001]. These anomalous sulfates mainly originate from tropospheric oxidation of sulfur gases of anthropogenic or biogenic origin.

[4] Bao *et al.* [2000b] reported sulfate O-17 anomalies in a few volcanic ash beds of late Oligocene age in Nebraska and South Dakota, USA. This discovery led to the possibility that volcanic sulfur gases, the only other major source of sulfur compounds in the atmosphere [Seinfeld and Pandis, 1998], may have also left a distinct O-17 anomaly in the rock record. It has been known that fine volcanic ashes carry hundreds to tens of thousands ppm [SO<sub>4</sub><sup>2-</sup>] when they fall from the sky (e.g., [Armienda *et al.*, 1998; Rose, 1977; Varekamp *et al.*, 1984]). Although in a few cases (e.g., [Rye *et al.*, 1984]) magmatic sulfate as anhydrite phenocrysts contribute part of the sulfate, some of the water-soluble sulfates carried by ashes can be the product of SO<sub>2</sub> oxidation in the atmosphere after eruption.

[5] The goal of this study is to use both sulfur and oxygen isotope data (including the Δ<sup>17</sup>O) to test the hypotheses that the sulfate in the Oligocene ash beds was originated from volcanic eruptions and that the isotopic data

<sup>1</sup>Department of Geology and Geophysics, E235 Howe-Russell Geoscience Complex, Louisiana State University, Baton Rouge, Louisiana, USA.

<sup>2</sup>Department of Chemistry and Biochemistry, University of California San Diego, California, USA.

<sup>3</sup>Department of Geosciences, University of Nebraska Lincoln, Lincoln, Nebraska, USA.

<sup>4</sup>Nanjing Institute of Geology and Palaeontology, Academia Sinica, Nanjing, People's Republic of China.

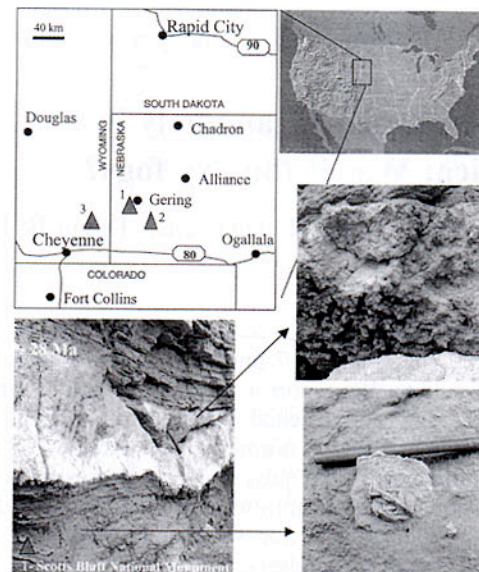
are consistent with those from modern fresh ashes. We carried out a survey of one particular ash bed in the northern High Plains where we previously found extremely high sulfate O-17 anomalies. It is one of the ash beds in the Gering Formation of the Arikaree Group. We name it the “mid-Gering ash” because it occurs at  $\sim 10$  m above the base of the  $\sim 20$  m-thick Gering Formation at the Scotts Bluff National Monument, where it can be seen most distinctly. The Gering Formation represents typical arid to semi-arid deposits that are dominated by fluvial and playa sediments [Loope, 1986]. The ash is mainly rhyolitic to dacitic in composition and often has lenticular and rose-like gypsum pseudomorphs within and beneath the ash bed, respectively. The ash may have come from an eruption in southern Utah and Nevada, where the Great Basin volcanism peaked at  $\sim 28$  Ma [Larson and Evanoff, 1998]. The mid-Gering ash bed can be easily traced in the vicinity (Figure 1). For comparative study, we obtained fresh volcanic ash samples (not leached by rainwater) from colleagues around the world. These recent samples represent different eruption types, particle sizes, and distances from the eruption centers. This is the first systematic analysis of sulfur and oxygen isotope compositions (including the  $\Delta^{17}\text{O}$ ) of the sulfate leached from fresh volcanic ashes.

## 2. Methods

[6] Rock (often loosely cemented) samples were collected from 4 sections in different localities (Figure 1). A smaller aliquot of the samples was measured for the concentration of sulfate after treated with  $\sim 0.05$  M HCl solution. In a larger aliquot, water-soluble sulfate was extracted and precipitated as barite from solution containing sulfate leached from ashes or volcanoclastic deposits as described in [Bao *et al.*, 2000b]. Some calcite-cemented rocks were treated with  $\sim 1$  M HCl solution to disaggregate the sediments and to release sulfate trapped within the calcite into solution. Molecular oxygen was generated from barite using a direct  $\text{CO}_2$ -laser fluorination method [Bao and Thiemens, 2000] at UC San Diego and at Louisiana State University. The  $\delta^{18}\text{O}$  and  $\delta^{17}\text{O}$  (thus  $\Delta^{17}\text{O}$ ) analyses were conducted at UC San Diego. The sulfate  $\delta^{34}\text{S}$  measurement was conducted at A. J. Kaufman’s laboratory at the University of Maryland. Isotopic results are expressed in the  $\delta$  notations with respect to the Standard Mean Ocean Water (SMOW) for oxygen and to the Canyon Diablo Troilite (CDT) for sulfur. Analytical precisions ( $2\sigma$ ) for  $\delta^{34}\text{S}$ ,  $\delta^{18}\text{O}$ ,  $\delta^{17}\text{O}$ , and  $\Delta^{17}\text{O}$  are  $\pm 0.3\text{‰}$ ,  $\pm 0.7\text{‰}$ ,  $\pm 0.4\text{‰}$ , and  $\pm 0.06\text{‰}$ , respectively. The  $\delta^{18}\text{O}$  value has a larger deviation between replicate analyses in our laser fluorination method than in other methods that have 100%  $\text{O}_2$  yield. It is important to emphasize that experimental fractionation cannot produce the observed mass-independent anomaly. The co-variation between the  $\delta^{18}\text{O}$  and  $\delta^{17}\text{O}$  during any step in the experiment results in the observed small error for  $\Delta^{17}\text{O}$  value. Our laboratories have run numerous marine evaporites and seawater sulfates, and all show, as expected, a  $0 \pm 0.15\text{‰}$   $\Delta^{17}\text{O}$  value.

## 3. Results

[7] A total of 16 samples from the mid-Gering ash bed in the region were analyzed (Table 1). Most of the sulfates



**Figure 1.** Map of the northern High Plains, U. S. A., the mid-Gering ash bed, and the lenticular and rose-like forms of gypsum pseudomorphs. The mid-Gering ash bed was sampled at Scotts Bluff National Monument (1), Chimney Rock (2), and Hawk Springs (3).

leached from the ash bed and the sand/siltstone immediately beneath it have distinct and variable O-17 anomalies (up to 5.84‰). The O-17 anomaly, as well as the sulfate content in the rocks, is extremely variable in space, even within a single outcrop. In contrast, sulfates leached from all of the 11 modern fine ash samples exhibit no O-17 anomaly (Table 2). Neither the anhydrite phenocrysts from Pinatubo pumice, nor the sulfates derived from elemental sulfur oxidation at the surface near an active fumarole have an O-17 anomaly, as expected for sulfate of magmatic origin or from surface oxidation, respectively. Both ancient ash beds and modern fresh ashes contain water-soluble or acid-soluble sulfate of comparable concentrations with large variability. The sulfates in the mid-Gering ash bed and in its underlying volcanoclastic sediments are apparently the mixture of two end-members: one with highly positive  $\Delta^{17}\text{O}$ , high  $\delta^{18}\text{O}$ , and low  $\delta^{34}\text{S}$  values, and the other with no O-17 anomaly, but low  $\delta^{18}\text{O}$  and high  $\delta^{34}\text{S}$  values (Figure 2). Note that, like one of the end-members for the mid-Gering ash bed (Table 2 and Figure 2), the modern ash leachates lack an O-17 anomaly, and have high  $\delta^{34}\text{S}$  values and low  $\delta^{18}\text{O}$  values.

## 4. Discussion

[8] The data from recent ashes shown in Table 2 suggest that sulfates carried by ash falls were formed in a pathway likely dominated by surface catalyzed oxidation that involves no  $\text{O}_3$  or  $\text{H}_2\text{O}_2$ . Thus, the modern ash data do not offer explanation on the origin of the Oligocene sulfate that has O-17 anomalies.

[9] The only other terrestrial settings that have sulfate  $\Delta^{17}\text{O}$  value as positive as reported here are the regolith in Antarctica Dry Valleys ( $\Delta^{17}\text{O}$  up to 3.4‰) [Bao *et al.*, 2000a] and the Atacama Desert ( $\Delta^{17}\text{O}$  up to 4.6‰) [Bao,

**Table 1.** Sulfate Concentration and its Oxygen and Sulfur Isotopic Compositions, in the Mid-Gering Ash Bed, the Northern High Plains, U. S. A.

Sample	$\delta^{34}\text{S}$	$\delta^{18}\text{O}$	$\delta^{17}\text{O}$	$\Delta^{17}\text{O}$	$[\text{SO}_4^{2-}] \%$
<i>Southeastern Scotts Bluff, NE</i>					
LB04	0.3	11.7	12.0	5.84	0.088
LB05	3.6	13.2	12.4	5.82	0.041
LB06(1) <sup>a</sup>	1.6	7.8	7.4	3.37	0.169
LB06(3) <sup>a</sup>	2.1	12.0	11.1	4.87	0.114
<i>Northwestern Scotts Bluff, NE</i>					
Loope1 <sup>b</sup>	2.2	12.5	11.1	4.59	n.a. <sup>c</sup>
Loope2 <sup>b</sup>	1.7	12.1	10.6	4.36	n.a.
LB23(1)	8.2	10.8	7.1	1.5	0.038
LB24(1)-S <sup>a</sup>	n.a.	9.8	8.7	3.5	0.03
LB24(1)-R <sup>a</sup>	2.1	14.2	12.5	5.15	n.a.
LB26	4.0	12.2	8.9	2.54	0.007
<i>Chimney Rock, NE</i>					
LB27	3.6	1.7	2.2	1.28	0.069
LB28(1) <sup>a</sup>	4.2	3.0	2.1	0.54	0.069
LB28(2) <sup>a</sup>	4.7	1.8	1.7	0.79	
<i>Hawk Springs, WY</i>					
LB36	2.9	12.1	9.5	3.18	0.117
LB37	3.2	10.5	8.3	2.89	0.041
LB-39-a <sup>a</sup>	5.5	6.1	3.9	0.71	0.034
LB-39-b <sup>a</sup>	7.5	7.2	3.9	0.19	n.a.

Errors are expressed in Method section.

<sup>a</sup>These pairs of samples are different pieces of the same specimen.

<sup>b</sup>From [Bao et al., 2000b].

<sup>c</sup>Not available (due to small sample size).

unpublished data]. The Great Plains was a semi-arid grassland that supported a diverse and abundant vertebrate fauna in late Oligocene [Woodburne, 1987]. The dynamic depositional condition of the Gering Formation is in contrast to the stable, old, and hyperarid surface that is extremely important to the accumulation of significant amount of background sulfate from the atmosphere. Thus, the case for long-term accumulation of background sulfate is difficult to apply here.

[10] If the  $\delta^{17}\text{O}$ -anomalous sulfate is associated with volcanic eruptions, then it is not the sulfate carried by fine ashes, as indicated by data from the modern samples (Table 2).

**Table 2.** Water-soluble sulfate concentration and its oxygen and sulfur isotopic compositions from freshly collected recent ashes

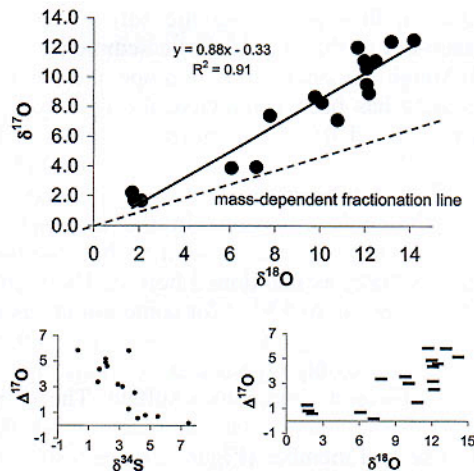
Sample Description	$\delta^{34}\text{S}$	$\delta^{18}\text{O}$	$\delta^{17}\text{O}$	$\Delta^{17}\text{O}$	$[\text{SO}_4^{2-}] \%$
ash, Vesuvius, 1872	-3.4	1.7	0.8	-0.07	0.150
ash, Mt. Spurr, 1992	7.2	3.9	2.1	0.06	0.327
ash, San Miguel, 1970	4.7	10.5	5.4	-0.07	n.a.*
ash, Fuego, 45 km, 1974	8.5	7.2	3.7	-0.08	0.159 <sup>§</sup>
ash, Fuego, 55 km, 1974	8.6	10.5	5.4	-0.03	0.159 <sup>§</sup>
ash, Popocatepetl, 1997	9.6	11.3	5.8	-0.08	0.132
ash, Popocatepetl, 1998	8.3	10.1	5.3	0.03	0.025
ash, Popocatepetl, 1996	7.9	9.9	5.3	0.14	0.575
Santorini, pumice + ash; Minoan Age	n.a.*	6.2	3.3	0.09	0.019
ash, Lascar, 1993	2.6 <sup>+</sup>	10.7	5.5	-0.11	0.165
ash, El Chichon, 1982	8.2 <sup>†</sup>	5.1	2.6	-0.03	n.a.*
anhydrite from pumice, Mt. Pinatubo, 1991	4.8	5.4	2.8	-0.01	
lapilli, Mt. St. Helens, 1980	n.a.*	4.9	2.4	-0.12	
surface near a fumarole, Santorini	6.4	6.1	3.3	0.15	

\*Not available.

<sup>+</sup>[Risacher and Alonso, 2001].

<sup>†</sup>Average value of the three ash sulfate samples from [Rye et al., 1984].

<sup>§</sup>Average value of 31 samples [Rose, 1977].

**Figure 2.** Relationships among oxygen and sulfur isotopic compositions for water-soluble and acid-soluble sulfates extracted from the mid-Gering ash bed and its underlying sand/siltstones. Samples were from site 1, 2, and 3 in Figure 1.

One possible origin for the anomalous sulfate may be that this particular eruption was highly explosive and the  $\text{SO}_2$  plume penetrated deep into the stratosphere. Although data are still scarce, homogeneous oxidation by  $\bullet\text{OH}$  or heterogeneous oxidation, possibly by  $\text{O}_3$ , on the existing sulfate aerosol are the main pathways for  $\text{SO}_2$  oxidation in the stratosphere [Harrison and Larson, 1974]. Stratospheric  $\bullet\text{OH}$ ,  $\text{O}_3$ , and even  $\text{H}_2\text{O}$  may have large O-17 anomalies according to measurements and models [Krankowsky et al., 2000; Lyons, 2001], and these do transfer to product sulfate. A major difficulty of this scenario is, however, that once  $\text{SO}_2$  gets into the stratosphere, it would be dispersed all over the globe. The extremely high sulfate content in the Oligocene ash bed (Figure 1 and Table 1) would require large stratospheric deposition of sulfate onto a specific region, a process that is difficult to accommodate by atmospheric circulation dynamics. Recent study on distal ash fall [e.g., Rose et al., 2003] may indicate possible mechanism for transporting stratosphere sulfate onto surface, but sulfate oxygen-17 anomaly has yet to be documented for distal ash falls.

[11] We propose here a scenario based largely on tropospheric chemistry to account for the origin of sulfate O-17 anomaly in the mid-Gering ash bed. During and after a series of sulfur-rich eruptions in the west, volcanic ashes were carried by westerly wind and deposited in the High Plains. The sulfate carried by ash particles was mostly formed by  $\text{SO}_2$  oxidation on particle surfaces and did not possess an O-17 anomaly. However, following the ash fall, dry fogs (clouds of volcanic sulfate aerosols trapped in the planetary boundary layer), derived from  $\text{SO}_2$  oxidation in the troposphere, hung over the Great Plains for months, years, or even longer periods. These sulfate aerosols, with a distinct O-17 anomaly and a residence time of only a few days, were constantly settling and were incorporated into surface volcanoclastic sediments. The  $\delta^{17}\text{O}$ -anomalous sulfate could thus become a significant portion of the total sulfate in ash beds. The arid to semi-arid climate in the Great Plains during the Oligocene-Miocene epochs may have facilitated a quick formation of gypsum minerals

(CaSO<sub>4</sub>·2H<sub>2</sub>O), thus preventing the sulfate from a completely leach-out in the volcanoclastic sediments.

[12] Although no direct multi-isotope measurement on dry-fog sulfate has been conducted, the dry-fog sulfate is most likely derived from oxidations involving, at least in part, O<sub>3</sub> and H<sub>2</sub>O<sub>2</sub> as oxidants, because its behavior is similar to that of sulfur gases derived from current anthropogenic or biogenic emissions in the troposphere. An oxygen-17 anomaly has been found to be ubiquitous for tropospheric sulfate, as mentioned before. The highly positive  $\Delta^{17}\text{O}$  values (up to 5.8‰) for some ash layers suggest that O<sub>3</sub> rather than H<sub>2</sub>O<sub>2</sub> was the dominant oxidant in many of those cases, since only O<sub>3</sub> has a  $\Delta^{17}\text{O}$  value high enough to produce sufficiently anomalous sulfate. The  $\delta^{34}\text{S}$  value for the  $\delta^{17}\text{O}$ -anomalous sulfate is much lower than the normal sulfate end-member (Figure 2), suggesting that for a particular eruption event, the SO<sub>2</sub> oxidized on ash particle surfaces was preferentially enriched in <sup>34</sup>S relative to the SO<sub>2</sub> remaining in the atmosphere.

[13] The dry-fog hypothesis can be tested by improved data sets that we are seeking or waiting from recent and future eruption events. The notorious dry-fog events in Europe after the 1783 Laki fissure eruption reflected a typical concentration of volcanic sulfur gases in the lower atmosphere [Stothers, 1996]. However, the high concentration of  $\delta^{17}\text{O}$ -anomalous sulfate in the mid-Gering ash bed suggests that the Oligocene dry-fog events were probably much greater in intensity or duration than the “great dry fog of 1783” in Europe. Our interpretation of the sulfate isotopic data from the Oligocene ash bed from the northern High Plains warns that we have not witnessed dry fogs of similar magnitude. This discovery has revealed our poor understanding of the oxidation chemistry of volcanic sulfur gases from vents to the atmosphere and to subsequent deposition onto surface environments. Such information is crucial in assessing the impact of volcanic eruptions on regional environment and global climate.

[14] **Acknowledgments.** We thank M. Khachatryan, T. Jackson, and A. J. Kaufman for laboratory assistance, J. Swinehart, R. F. Diffendal, Jr., and M. Perkins for field information, Badlands National Park and Scotts Bluff National Monument for access and sampling. U. Sturesson, W. I. Rose Jr., M. A. Armienta, D. Rumble III, F. Risacher, J. Luhr, and M. Couchman provided us recent ash and tuff samples. This project is supported by start-up funds from Louisiana State University and by funding from NSF EAR-IF Program and from Academia Sinica/MSTC.

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- H. Bao, Department of Geology and Geophysics, E235 Howe-Russell Geoscience Complex, Louisiana State University, Baton Rouge, LA 70803, USA. (bao@lsu.edu)
- M. H. Thiemens, Department of Chemistry and Biochemistry, University of California San Diego, MC 0356, CA 92093, USA.
- D. B. Loope, Department of Geosciences, University of Nebraska Lincoln, Lincoln, NE 68588, USA.
- X.-L. Yuan, Nanjing Institute of Geology and Palaeontology, Academia Sinica, Nanjing 210008, Peoples Republic of China.