

Multiple oxygen and sulfur isotopic analyses on water-soluble sulfate in bulk atmospheric deposition from the southwestern United States

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[1] Sulfate is a major component of bulk atmospheric deposition (including dust, aerosol, fog, and rain). We analyzed sulfur and oxygen isotopic compositions of water-soluble sulfate from 40 sites where year-round dust traps collect bulk atmospheric deposition in the southwestern United States. Average sulfur and oxygen isotopic compositions ($\delta^{34}\text{S}$ and $\delta^{18}\text{O}$) are 5.8 ± 1.4 (CDT) and 11.2 ± 1.9 (SMOW) ($n = 47$), respectively. Samples have an oxygen 17 anomaly ($\Delta^{17}\text{O}$), with an average value of $1.0 \pm 0.6\text{‰}$. Except for a weak positive correlation between $\delta^{18}\text{O}$ and $\Delta^{17}\text{O}$ values ($r^2 \approx 0.4$), no correlation exists for $\delta^{18}\text{O}$ versus $\delta^{34}\text{S}$, $\Delta^{17}\text{O}$ versus $\delta^{34}\text{S}$, or any of the three isotopic compositions versus elevation of the sample site. Exceptional positive $\Delta^{17}\text{O}$ values (up to 4.23‰) are found in samples from sites in the vicinity of large cities or major highways, and near-zero $\Delta^{17}\text{O}$ values are found in samples close to dry lakes. Comparison of isotopic values of dust trap sulfate and desert varnish sulfate from the region reveals that varnish sulfate has average isotopic values that are $\sim 4.8\text{‰}$ lower for $\delta^{18}\text{O}$, $\sim 2.1\text{‰}$ higher for $\delta^{34}\text{S}$, and $\sim 0.3\text{‰}$ lower for $\Delta^{17}\text{O}$ than those of the present-day bulk deposition sulfate. Although other factors could cause the disparity, this observation suggests a possibility that varnish sulfate may have recorded a long-term atmospheric sulfate deposition during the Holocene or Pleistocene, as well as the differences between sulfur and oxygen isotopic compositions of the preindustrial bulk deposition sulfate and those of the industrial era. **INDEX TERMS:** 0305 Atmospheric Composition and Structure: Aerosols and particles (0345, 4801); 0345 Atmospheric Composition and Structure: Pollution—urban and regional (0305); 1040 Geochemistry: Isotopic composition/chemistry; **KEYWORDS:** atmospheric deposition, sulfate, stable isotopic compositions, O-17 anomaly, desert varnish, dust

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1. Introduction

[2] Sulfate (SO_4^{2-}) is one of the main aerosol particles in the atmosphere, a major component of cloud condensation nuclei in the atmosphere, and a major contributor of acid rain. Sulfate has an important role in tropospheric and lower stratospheric chemistry [Adams *et al.*, 1999; Cadle, 1972; Fegley *et al.*, 1980; Tie *et al.*, 1994; Toon *et al.*, 1987]. Biogenic sulfur gases, (e.g., dimethylsulfide and hydrogen sulfide), volcanic sulfur gases (mostly sulfur dioxide), and anthropogenic sulfur emission (mostly sulfur dioxide) are ultimately oxidized in the atmosphere and become sulfate. The biogenic and volcanic sources provided nearly 100% of the total sulfur gases in the preindustrial atmosphere. At present, about 70% of the total sulfur emissions are from anthropogenic sources [Seinfeld and Pandis, 1998], including the primary sulfate that is the product of direct sulfur

oxidation by air O_2 at high-temperature vents in many factories [Holt and Kumar, 1984; Jamieson and Wadleigh, 2000]. Additional sources of atmospheric sulfate include sea salt and mineral dust. Sulfate can precipitate onto existing particle surfaces or can become aerosol particles through gas particle conversion in the atmosphere. Desert dust can be coated with sulfate through surface chemical reactions while passing over polluted areas [e.g., Dentener *et al.*, 1996; Xiao *et al.*, 1997]. Large particles will fall out as dry deposition. Atmospheric sulfate is also extremely soluble in water and can be scavenged by rain droplets. The dry and wet atmospheric deposition of sulfate onto the Earth's surface is the ultimate sink for atmospheric sulfur gases. Atmospheric deposition described in this paper includes both dry and wet depositions such as settling dust, aerosol fallout, rain, and dew.

[3] Atmospheric sulfate contributes significantly to the total sulfate budget in some continental environments. In moist regions, if not adsorbed onto soil minerals the atmospheric sulfate can easily be leached out of soils into

streams and lakes, and some of the sulfate can be reduced back to sulfides (hydrogen sulfide or sulfide minerals) by microbial activities. In arid regions, however, atmospheric sulfate tends to be retained longer or even accumulated in soil or on rock surfaces, due largely to the low precipitation amounts [Bao *et al.*, 2000a; Bao *et al.*, 2001b; Eckardt and Spiro, 1999]. Transport of eolian dust can mix and redistribute sulfate produced by different sources with potentially different isotope compositions throughout the world. Bulk atmospheric deposition constitutes an important source of sulfate for arid regions. Plants require sulfate to manufacture certain amino acids [e.g., Weber *et al.*, 2000]; thus a shift in the amount or source of atmospheric sulfate may be reflected in plant growth, especially in the desert where oxidation of organic matter is rapid. There is increasing interest in the origin of the vast salt deposits found in some of the driest deserts in the world. The sulfate deposits in the Central Namib Desert, the Atacama Desert, and the Antarctic Dry Valleys all have long-term atmospheric input as a major origin (including dust transported from local sources) [Bao *et al.*, 2000a; Bao *et al.*, 2001b; Bohlke *et al.*, 1997; Eckardt and Spiro, 1999]. Analyses of bulk atmospheric deposition are more representative of the bulk deposition sulfate than analyses of one or two atmospheric deposition types (e.g., aerosol, rain, fog, or dust) for a region.

[4] It has been hypothesized that the growth of rock varnishes in an arid region such as southern California and Nevada could have recorded long-term (several thousand to hundreds of thousand years) bulk deposition sulfate signatures [Bao *et al.*, 2001a]. The dominance of anthropogenic sulfate in the atmosphere is a very recent phenomenon (less than 300 years). Most anthropogenic sulfur is derived from fossil fuel (e.g., petroleum and coal). The isotopic compositions for anthropogenic sulfate are likely different from those of the natural or preindustrial background atmospheric sulfate that is dominated by biogenic and volcanic sources. If the total water (and weak acid)-soluble sulfate from desert varnishes can provide a proxy for the bulk deposition sulfate for a time duration given by the age of the varnish, a preindustrial bulk deposition sulfate isotopic composition could be deduced for a region. Such information could potentially be used to reconstruct past atmospheric sulfate deposition and changes with time.

[5] The isotopic ratios $\delta^{34}\text{S}$, defined as $\left(\frac{{}^{34}\text{S}/{}^{32}\text{S}}{({}^{34}\text{S}/{}^{32}\text{S})_{\text{standard}}} - 1\right) \times 1000\text{‰}$, and $\delta^{18}\text{O}$, defined as $\left(\frac{{}^{18}\text{O}/{}^{16}\text{O}}{({}^{18}\text{O}/{}^{16}\text{O})_{\text{standard}}} - 1\right) \times 1000\text{‰}$, have been studied extensively in atmospheric sulfate and are useful in delineating the relative contribution of various sulfur sources and oxidation pathways [Holt *et al.*, 1981; Jamieson and Wadleigh, 2000; Jedrysek, 2000; Ohizumi *et al.*, 1997; Patris *et al.*, 2000; Turekian *et al.*, 2001]. The main limitations of the sulfur isotope ratio have been the broad range of $\delta^{34}\text{S}$ values for anthropogenic sulfur, and the $\delta^{34}\text{S}$ itself is not effective in tracking oxidation pathways. Recently, a new and independent isotopic parameter, the oxygen 17 anomaly ($\Delta^{17}\text{O} = \delta^{17}\text{O} - 0.52 \times \delta^{18}\text{O}$), has been demonstrated to have a specific advantage in discriminating sulfate formed by atmospheric oxidation of reduced sulfur gases from sulfate of other origins [Bao *et al.*, 2000a, 2000b; Johnson *et al.*, 2001; Lee and Thiemens, 2001; Savarino *et al.*, 2000]. Most terrestrial oxygen-bearing compounds have a fixed correlation between $\delta^{18}\text{O}$ and

$\delta^{17}\text{O}$, i.e., $\delta^{17}\text{O} \approx 0.52 \delta^{18}\text{O}$. The $\Delta^{17}\text{O}$ value indicates the degree of deviation from this relation. Positive $\Delta^{17}\text{O}$ values are observed for sulfate derived from the oxidation of reduced sulfur gases in the atmosphere, and the anomalies are transferred from ozone or hydrogen peroxide in the troposphere [Savarino *et al.*, 2000]. Sea salt sulfate and ancient marine evaporites do not have ^{17}O anomalies. No ^{17}O anomaly has yet been measured in sulfate derived from the oxidation of sulfide minerals (e.g., marcasite and pyrite) or black shale [Bao *et al.*, 2001a, 2000b].

[6] The goal of this study is to determine the three stable isotopic compositions ($\delta^{34}\text{S}$, $\delta^{18}\text{O}$, and $\Delta^{17}\text{O}$) for bulk deposition sulfate collected in the southwestern United States (Figure. 1), to explore links between the magnitude of bulk deposition sulfate ^{17}O anomaly and its geographic location, and to compare isotopic data between varnish sulfate and dust trap sulfate.

2. Sampling and Analytical Methods

2.1. Sampling Sites and Approaches

[7] The U.S.G.S. dust trap network consists of about 40 sites in southern California and southern Nevada. Each dust trap consists of an angel-food cake pan that is mounted on a steel fence post 2 m above the ground. Crossed metal straps coated with Tanglefoot Bird Repellent (use of trade names by the U.S.G.S. does not constitute an endorsement of the product) arch above the pan to prevent birds from roosting. Glass marbles inside the pan minimize deflation of dry dust from the trap. Detailed information on the trap design and sampling is given by Reheis and Kihl [1995]. These traps were initially established to study the rate of deposition, grain size, and mineralogical and chemical (major and trace elements) composition of dust being added to soils. The dust traps collect not only mineral (soil) dust and aerosol, but also wet deposition such as rain and snow of the sampling period. The dustpan holds at least 7 cm of water, and is unlikely to overflow in the arid climate regime of the study area, since 7 cm is rarely reached even in the total monthly precipitation [Reheis *et al.*, 2002]. Wet deposition dries out and leaves behind ions in the trap. Because samples were retrieved from the dust traps by washing the glass marbles, screen, and pan with about 1 L of distilled water, the solution integrates ions from both dry and wet depositions.

[8] Previously published studies of these samples [Reheis and Kihl, 1995; Reheis, 1997; Reheis *et al.*, 2002] mainly focused on residual samples that were washed clean of soluble salts. Individual anion concentration in solutions containing these soluble salts was measured on only a few samples. This study focuses on the sulfate in solutions from new samples collected at the same sites. Samples from within Owens Valley (T62–T68, Figure. 1) represent 6 months of deposition from November 1998 to April 1999. All other sites represent about two years of deposition and were collected in 1999. Therefore the sulfate in the solution represents an integrated value for modern deposition of bulk deposition sulfate around the site.

2.2. Analytical Techniques

[9] Solutions and dust mixture obtained by washing the glass marbles, screen, and pan with distilled water were

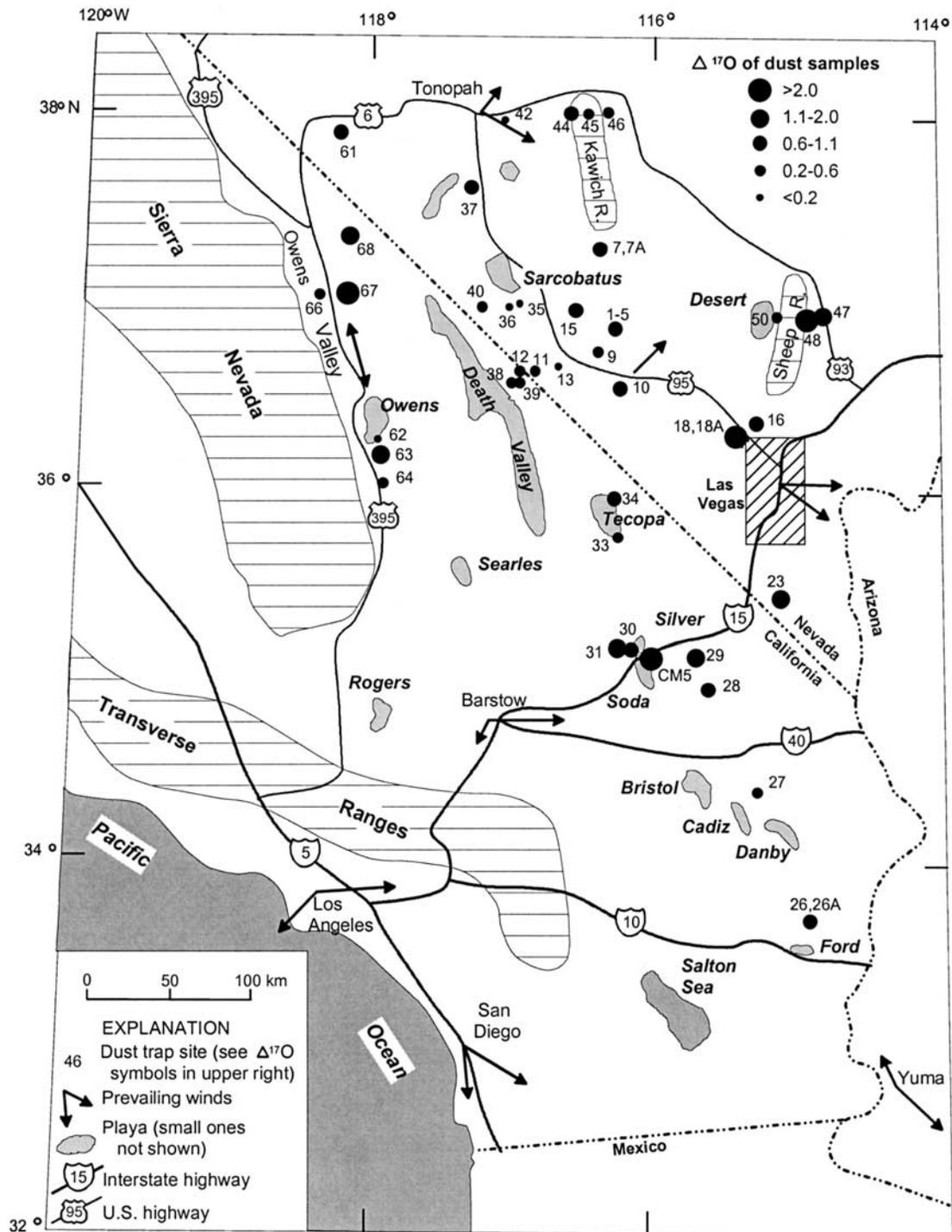


Figure 1. Regional map showing dust trap locations and corresponding $\Delta^{17}\text{O}$ value of dust sulfate.

evaporated to dryness in the laboratory. The dried dust samples, usually 1 g or less in weight, were placed in 40 mL of distilled water (1:40 soil-water ratio) and shaken for 30 min. According to standard protocols for electroconductivity analysis, this degree of dilution is sufficient to ensure complete dissolution of fine-grained water-soluble components, including gypsum (recommended dilution is 1:5 for soils containing less than about 1.5% gypsum by weight [e.g., Bower and Huss, 1948]). After the separation,

the solutions have been kept for weeks to months before sulfate extraction. Each solution was treated with prewashed active carbon to remove organic matter. The solution was evaporated down to 40 mL on a hot plate, followed by filtration through a 0.22 μm filter. After further evaporation, the solution was acidified and saturated BaCl_2 droplets were added to precipitate BaSO_4 . Supersaturated solutions and short heating time (<30 min.) after the addition of BaCl_2 facilitate the precipitation of fine-grained BaSO_4 . The

precipitates were rinsed with deionized water twice and oven-dried for later oxygen and sulfur isotopic analyses. Sulfate is a nonlabile oxy-anion that does not readily exchange its oxygen with ambient water at our experimental conditions (brief heating, basic, or neutral to weak acidic solution) [Zak *et al.*, 1980].

[10] We were concerned that the presence of organic matter in some of the solution bottles might permit bacterial sulfate reduction, which would result in the increase of both $\delta^{34}\text{S}$ and $\delta^{18}\text{O}$ values for the remaining sulfate during storage. Bacteria normally will not, however, use sulfate as an electron acceptor for metabolism if there is nitrate present in the same environment [Achtmich *et al.*, 1995]. Since sufficient nitrate was still present in the solutions (G. Michalski, University of California, San Diego, written communication, 2001), microbial sulfate reduction was probably inhibited and the sulfate isotopic compositions are unaltered by sample storage.

[11] Water-soluble sulfate in rock varnishes was extracted by submerging varnished rock chips in acidic (pH \sim 4) solution for 2–3 days as described by Bao *et al.* [2001a]. Some samples were subjected to a second extraction of sulfate by submerging the same rock chips into another batch of acidic solution after the first extraction. It is assumed that the acidic solution resulted in a slight dissolution of the Fe-Mn oxyhydroxides on the surface layers of the varnishes and the release of water-soluble sulfate trapped within the varnish into solution. The solution was raised to neutral or slightly basic pH state by adding NaOH droplets to reduce the adsorption of sulfate on mineral surfaces. This weakly basic solution also prevented potential oxygen isotopic exchange between sulfate and water during the subsequent hot plate evaporation. Sulfate contribution from parent rocks is possible but should be minimal. Most of the varnish samples are from granite. One unvarnished granite boulder was tested and found to have little water-soluble sulfate in it. We have not tested other types of rock in the region. The positive ^{17}O anomaly also suggests that sulfate from parent rock or from the oxidation of sulfur in parent rock is not significant since sulfate of these origins does not have ^{17}O anomalies. The sulfate extraction experiment was done by Bao *et al.* [2001a]. We only measured the sulfur isotopic composition of varnish sulfate in this study.

[12] Measurement of the oxygen isotope ratio on BaSO_4 followed the method of Bao and Thiemens [2000], in which \sim 2–10 mg BaSO_4 was loaded into a reaction chamber and was heated by a CO_2 laser beam in a BrF_5 atmosphere. Among the reaction products (including S-O-F compounds), O_2 is the only gas noncondensable in liquid nitrogen. O_2 was collected in a sieved (13 \times) sample tube and transferred to an isotopic ratio mass spectrometer (IRMS) for analysis. Both $^{18}\text{O}/^{16}\text{O}$ and $^{17}\text{O}/^{16}\text{O}$ ratios are reported in the δ notation ($\delta^{18}\text{O}$ and $\delta^{17}\text{O}$) with respect to the Standard Mean Ocean Water (SMOW). The measurement was done on a Finnigan MAT 251 at the University of California, San Diego. Analytical precision for duplicate samples during the laser fluorination experiment is \pm 0.7 for $\delta^{18}\text{O}$, \pm 0.3 for $\delta^{17}\text{O}$, and \pm 0.07 for $\Delta^{17}\text{O}$. Co variation between $\delta^{18}\text{O}$ and $\delta^{17}\text{O}$ greatly reduces the $\Delta^{17}\text{O}$ error during analysis.

[13] The sulfur isotope ratio ($^{34}\text{S}/^{32}\text{S}$) was measured on a Micromass Isoprime mass spectrometer utilizing continuous

flow inlet systems coupled with high temperature combustion ovens and gas chromatographic separation. BaSO_4 samples (\sim 200 μg) were weighed and folded into small tin cups that were sequentially dropped with a pulsed O_2 purge into a catalytic combustion furnace operating at 1050 $^\circ\text{C}$. SO_2 was separated from other gases with a 0.8-m PTFE GC column packed with Porapak 50–80 mesh heated to 90 $^\circ\text{C}$. The $^{34}\text{S}/^{32}\text{S}$ ratio of SO_2 was determined by comparing integrated peak areas of m/z 66 and 64 for the reference and sample SO_2 pulses relative to the baseline. Isotopic results are expressed in the δ notation with respect to the Canyon Diablo Troilite (CDT) standard. The measurement was done at A. J. Kaufman's laboratory at University of Maryland. Analytical precision for $\delta^{34}\text{S}$ is \pm 0.3%.

3. Results

[14] We have analyzed a total of 47 solution samples that represent atmospheric deposition samples from 40 different sites. Although sulfate content varies among sites, all solutions from the samples contained water-soluble sulfate (as well as nitrate). Table 1 presents data on sample sites and sulfate $\delta^{34}\text{S}$, $\delta^{18}\text{O}$, and $\Delta^{17}\text{O}$ values. The spatial distribution of sample sites in the region and their sulfate $\Delta^{17}\text{O}$ data are displayed in Figure 1. Water-soluble sulfate in modern bulk atmospheric deposition in the southwestern United States has $\delta^{34}\text{S}$, $\delta^{18}\text{O}$, and $\Delta^{17}\text{O}$ values ranging from 1.7 to 10.7‰, from 5.6 to 16.8‰, and from 0.02 to 4.23‰, respectively. Average values of $\delta^{34}\text{S}$, $\delta^{18}\text{O}$, and $\Delta^{17}\text{O}$ are $5.8 \pm 1.4\text{‰}$, $11.2 \pm 1.9\text{‰}$, and $1.0 \pm 0.6\text{‰}$ ($n = 47$), respectively. There are no simple correlations of isotopic compositions with elevation or latitude. Except for a weak positive correlation between $\Delta^{17}\text{O}$ and $\delta^{18}\text{O}$ of the sulfate ($r^2 \approx 0.4$), there are no correlations among $\delta^{18}\text{O}$, $\Delta^{17}\text{O}$, and $\delta^{34}\text{S}$ in general (Figure 2).

[15] Most samples are clustered around the mean isotopic compositions. There are three outliers that give highly positive $\Delta^{17}\text{O}$ values: T18, T18A, and T48. T18 and T18A are samples from a single site on the Kyle Canyon alluvial fan, northwest of Las Vegas (Figure 1). The two sites are near busy traffic flow and within the Las Vegas metropolitan area. T48 is in a relatively remote area, \sim 80 km north of Las Vegas, but near a heavily traveled U.S. highway. Both sites also have higher concentrations of SO_4^{2-} and NO_3^- compared to the rest of the sample sites (an average 5 times higher $\text{NO}_3^-/\text{Cl}^-$ ratio and 7 times higher $\text{SO}_4^{2-}/\text{Cl}^-$ ratio in the three traps than the other traps: G. Michalski, Univ. Calif. San Diego, written communication, 2001). Figure 1 also shows that several other sites with $\Delta^{17}\text{O}$ values greater than 1.3 lie (1) near interstate highway I-15 connecting Los Angeles and Las Vegas, and (2) in and near Owens Valley, a heavily traveled narrow valley bounded by steep mountain ranges. All the sites where sulfate $\Delta^{17}\text{O}$ values are $>1.5\text{‰}$ are within 12 km of major highways (Figure 3).

[16] Three sample sites give very low $\Delta^{17}\text{O}$ values ($<0.1\text{‰}$): T35, T36, and T62. Sites T35 and T36 are close to the south edge of Sarcobatus Flat, a large alkaline playa. T62 sits on the south end of the Owens (dry) Lake; samples from this site in some seasons contain 40% or more soluble salt, values much higher than samples from other sites [Reheis, 1997].

Table 1. Sulfur and Oxygen Isotopic Compositions of Water-Soluble Sulfate Collected in Dust Traps and Geographic Locations^a

Sample	$\delta^{18}\text{O}$ (SMOW)	$\Delta^{17}\text{O}$	$\delta^{34}\text{S}$ (CDT)	Latitude, °N	Longitude, °W	Elevation, m
CM5	13.1	2.40	N. D.	35.22	116.07	282
T1	11.9	0.99	6.3	36.89	116.36	1235
T2	13.5	1.05	2.3	36.89	116.36	1235
T3	12.8	0.67	6.8	36.89	116.36	1237
T4	13.0	1.14	7.8	36.90	116.36	1238
T5	12.2	0.95	7.5	36.89	116.35	1238
T7	11.9	0.88	4.5	37.46	116.35	2138
T7A	11.3	0.63	7.6	37.46	116.35	2138
T9	10.0	0.54	3.8	36.79	116.46	952
T10	12.4	0.93	2.9	36.52	116.11	805
T11	12.2	0.48	4.4	36.63	116.74	903
T12	11.2	0.45	3.3	36.64	116.78	1098
T13	9.1	0.17	N. D.	36.67	116.67	793
T15	13.6	0.80	5.2	37.87	116.62	1171
T16	13.8	0.95	6.8	36.38	115.32	839
T18	14.0	3.59	6.5	36.31	115.44	1318
T18A	15.9	4.23	5.8	36.31	115.44	1318
T23	13.5	1.47	5.0	35.54	115.07	1327
T26	10.7	0.68	5.5	33.74	115.93	190
T26A	12.7	1.03	4.5	33.74	115.93	190
T27	7.8	0.52	6.3	34.42	115.29	403
T28	10.5	0.92	6.3	34.95	115.61	921
T29	14.3	1.12	5.0	35.26	115.73	1257
T30	11.5	0.70	1.7	35.32	116.12	290
T31	12.4	1.69	5.4	35.31	116.14	366
T33	10.6	0.85	8.3	35.82	116.20	512
T34	9.4	0.44	7.2	35.97	116.23	525
T35	8.5	0.02	7.7	37.04	116.87	1244
T36	8.1	0.09	6.5	37.02	117.01	1424
T37	10.5	1.03	6.2	37.69	117.26	1928
T38	9.1	0.35	3.5	36.56	116.88	79
T39	9.5	0.44	4.9	36.58	116.84	177
T40	11.8	0.57	6.5	36.99	117.34	830
T42	5.6	0.17	7.3	38.09	117.11	1629
T44	10.6	0.71	10.7	38.15	116.63	1815
T45	14.2	0.51	4.4	38.18	116.54	2277
T46	11.1	0.38	6.2	38.18	116.42	1760
T47	11.2	1.48	8.8	36.99	115.00	793
T48	16.8	3.47	5.5	37.04	115.05	906
T50	11.9	0.42	N. D.	36.98	115.16	1208
T61	5.9	0.66	7.7	37.87	118.18	1431
T62	8.2	0.07	4.8	36.36	117.94	1087
T63	13.5	1.42	7.3	36.22	117.95	1262
T64	6.5	0.23	5.0	36.03	117.92	1021
T66	8.3	0.33	6.4	36.97	118.31	1590
T67	9.3	2.42	5.1	37.02	118.17	1609
T68	10.0	1.29	N. D.	37.35	118.18	2609

^aN. D. = no data. T1-T5 are multiple traps located a few meters apart at same site. Traps with same number (e.g., 26 and 26A) are also multiple traps at the same site. The $\delta^{17}\text{O}$ value is not listed since it is best reflected by the $\Delta^{17}\text{O}$ value (the deviation of $\delta^{17}\text{O}$ from the terrestrial $\delta^{17}\text{O}$ - $\delta^{18}\text{O}$ relationship).

[17] We have analyzed the $\delta^{18}\text{O}$ and $\Delta^{17}\text{O}$ values for water-soluble sulfate (in weakly acidic solution) in rock varnishes from southern California (mostly sampled from the vicinity of Death Valley National Park, Figure 1 [Bao *et al.*, 2001a]). For comparison to the dust samples, most of these varnish sulfates were further analyzed for their $\delta^{34}\text{S}$ values. Figure 2 shows that the varnish compositions are mostly within the overall data ranges of the modern atmospheric deposition data, but average values of the two sample sets are different. The varnish sulfate has average values for $\delta^{18}\text{O}$ of $6.4 \pm 1.1\text{‰}$ ($n = 17$), $\Delta^{17}\text{O}$ of $0.7 \pm 0.1\text{‰}$ ($n = 17$), and $\delta^{34}\text{S}$ of $7.9 \pm 0.9\text{‰}$ ($n = 16$). Average varnish $\delta^{18}\text{O}$ is $\sim 4.8\text{‰}$ lower, $\delta^{34}\text{S} \sim 2.1\text{‰}$ higher, and $\Delta^{17}\text{O} \sim 0.3\text{‰}$ lower than the modern average values of bulk deposition sulfate as deduced from the dust trap deposited sulfate. For the same desert varnish sample, there is a consistent decrease in the $\delta^{18}\text{O}$ and $\Delta^{17}\text{O}$ values of varnish sulfate from the 1st extraction to the 2nd extraction. Although the differences are

small, those for $\Delta^{17}\text{O}$ are larger than the analytical error (Table 2).

[18] Some dust trap samples came from sites very close to the varnish sample sites: T38 and T39 are within Death Valley National Park, and T-68 is on the crest of the White Mountains close to the location of the “Barcroft” varnish sample. Comparisons of these data (Tables 1 and 2) shows that varnish $\delta^{18}\text{O}$ and $\Delta^{17}\text{O}$ ratios are significantly lower (differences are $>2\sigma$ analytical error) and $\delta^{34}\text{S}$ significantly higher than the isotopic ratios for nearby atmospheric deposition samples.

4. Discussion

[19] The following discussion focuses on 1) the spatial distribution and average isotopic compositions of modern atmospheric sulfate deposition (including redistributed dusts), and 2) the disparity in isotopic compositions be-

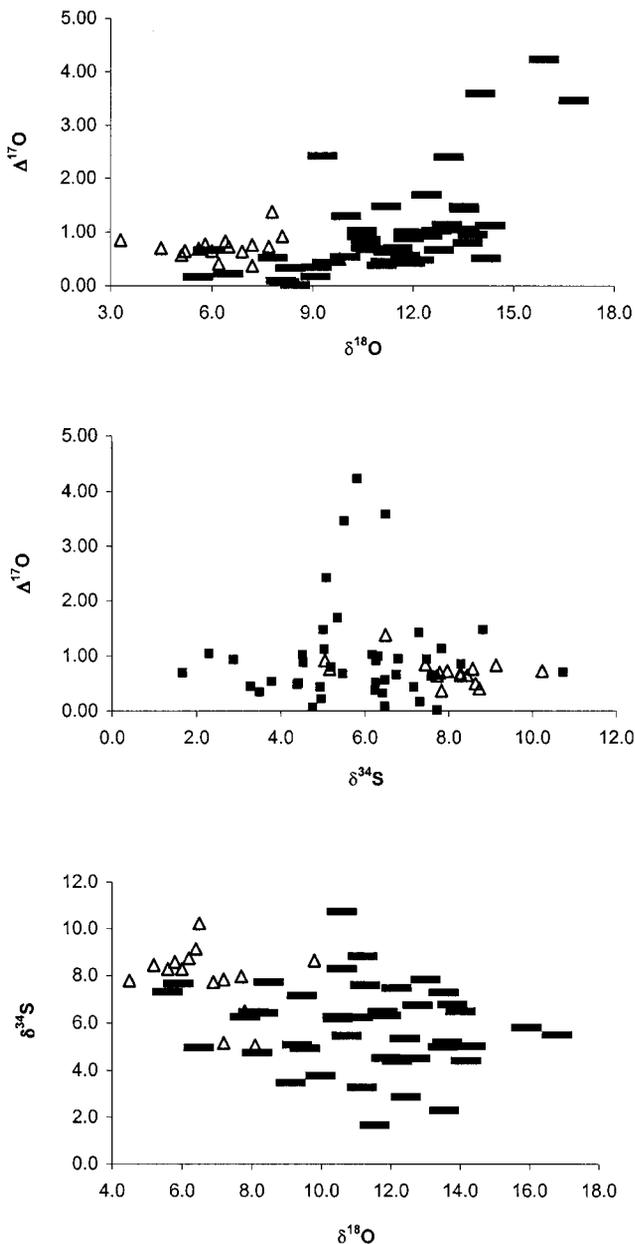


Figure 2. Diagrams showing (a) $\Delta^{17}\text{O}$ versus $\delta^{18}\text{O}$, (b) $\Delta^{17}\text{O}$ versus $\delta^{34}\text{S}$, and (c) $\delta^{34}\text{S}$ versus $\delta^{18}\text{O}$ for water-soluble sulfate from dust traps (data in Table 1). The open triangles (Table 2; oxygen isotope data from *Bao et al.* [2001a]) are water-soluble sulfate extracted from desert varnishes from the region.

tween varnish sulfate and dust trap sulfate, with possible implications for a historical record of bulk deposition sulfate in the region.

4.1. Sources of Sulfate in Bulk Atmospheric Deposition in Southwestern United States

[20] Water-soluble sulfate in the dust traps comes from three major sources: (1) wind-blown sulfate minerals from surface soils, dry washes, or playas, (2) dry aerosol deposition, and (3) rainwater. Sea salt sulfate is insignificant in the study area because of the great distance to the ocean

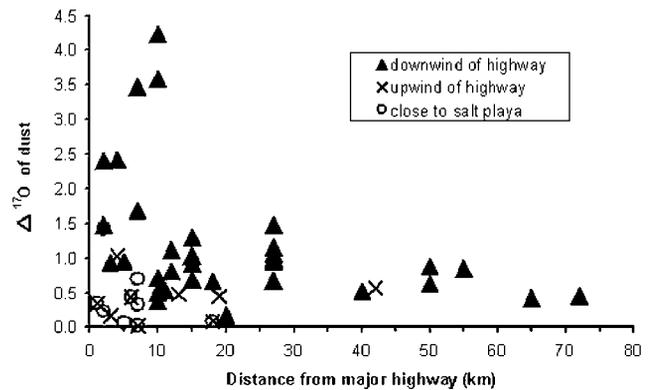


Figure 3. Relation between $\Delta^{17}\text{O}$ value of dust sulfate and the proximity of the dust trap to major highways. A circle with superimposed cross denotes a site that is both upwind of a major highway and close to a salt playa.

plus the rain shadow effect, as also shown by the concentrations of SO_4^{2-} , Cl^- , and Na^+ in the rainwater from several sites in the region (National Atmospheric Deposition Program/National Trends Network, <http://nadp.sws.uiuc.edu/nadpdata/>). Therefore wind-blown dusts that contain sulfate minerals derived from regional surface sediments (soils, dry washes, and playas) together with anthropogenic sulfate are the two major sulfate sources collected in the dust traps. The former can be a mixture of local sources and average regional surface deposits [*Reheis et al.*, 2002]. The latter source mostly represents the oxidation of reduced sulfur gases emitted from industrial activities.

[21] The few exceptionally high $\Delta^{17}\text{O}$ sites are found close to Las Vegas, the major metropolitan area in the region. Other high values are associated with heavily traveled highways, such as Interstate 15 (T29, T31, and CM5), US 395 in Owens Valley (T63, T67, and T68), and US 93 north of Las Vegas (T47, T48). The high $\Delta^{17}\text{O}$ values and the associated high SO_4^{2-} and NO_3^- concentrations

Table 2. Oxygen and Sulfur Isotopic Compositions of Water-Soluble Sulfate Extracted From Samples of Desert Varnishes^a

Sample	$\delta^{18}\text{O}$	$\Delta^{17}\text{O}$	$\delta^{34}\text{S}$	Note
SP-RD-1	6.4	0.83	9.1	1st extraction
SP-RD-2	5.8	0.77	8.6	2nd extraction
M-UF-1	7.7	0.73	8.0	1st extraction
M-UF-2	6.2	0.41	8.7	2nd extraction
Camp3-1-1	5.2	0.65	8.4	1st extraction
Camp3-1-2	5.1	0.57	N. D.	2nd extraction
Ash-J	6.5	0.73	10.2	1st extraction
Camp-1	6.9	0.64	7.7	1st extraction
Camp-2	4.5	0.70	7.8	1st extraction
Saline	8.1	0.92	5.1	1st extraction
Ulida	6.0	0.65	8.3	1st extraction
Jackass	7.2	0.37	7.8	1st extraction
G-stand	7.8	1.38	6.5	1st extraction
Barcroft	5.6	0.69	8.3	1st extraction
Grapevine	7.2	0.76	5.2	1st extraction
Darwin	9.8	0.50	8.6	1st extraction
MF-1	3.3	0.85	7.4	1st extraction

^aThe $\delta^{18}\text{O}$ and $\Delta^{17}\text{O}$ data are from *Bao et al.* [2001a]. N. D. = no data.

suggest that these sites have a dominant input of anthropogenic sulfate.

[22] Several exceptionally low $\Delta^{17}\text{O}$ sites lie close to salt-crustured playa surfaces, such as Owens (dry) Lake and Sarcobatus Flat (Figure 1). Other low values are also associated with playas, such as Cadiz Lake (T27), Tecopa (T33), Desert Dry Lake (T50), and Death Valley (T11-13, T38, and T39). Sulfate from playa salts (including drill core samples) has been shown to have no ^{17}O anomaly [Bao *et al.*, 2001a]. The overwhelming source of sulfate from the oxidative weathering of sulfide minerals and further microbial redox cycling of sulfate in these salt lakes may produce the normal sulfate. In some cases, proximity to a salt-crustured playa may dilute the expected effects of proximity to heavy vehicle traffic. Such mixing may be responsible for the intermediate $\Delta^{17}\text{O}$ values observed at sites adjacent to major highways, such as those found at sites T63, T64, and T66 in Owens Valley, site T30 near Silver Lake, and site T26 near Ford Dry Lake (Figure 1).

[23] The lack of any correlation between geographic location (elevation and latitude) and sulfur and oxygen isotope compositions (Figure 1 and Table 1) suggests that there are no dominant point sources in the region. This result is different from the nearly linear correlation between $\delta^{34}\text{S}$ and latitude observed for the $\delta^{34}\text{S}$ value of sulfate in Rocky Mountain snowpacks at sites in New Mexico, Colorado, and southern Wyoming [Mast *et al.*, 2001]. An elevational gradient in $\delta^{34}\text{S}$ value observed along the slope of the Krušné hory Mountains, Czech Republic was attributed to source dominance of local versus long-distance air pollutions [Groscheova *et al.*, 1998]. Many sulfur isotopic studies show that fossil fuel combustion in North America contributes sulfate with $\delta^{34}\text{S} = 0$ to 5‰ into the atmosphere [Tanaka *et al.*, 1994; Turekian *et al.*, 2001]. Rainwater sulfate has a mean $\delta^{34}\text{S}$ value of 3.9‰ in New Mexico [Popp *et al.*, 1986]. Sulfate in Rocky Mountain snowpacks has $\delta^{34}\text{S}$ ranging from 4‰ to 8.2‰ [Mast *et al.*, 2001]. Overall, our $\delta^{34}\text{S}$ data for bulk atmospheric deposition in southwestern United States are within the reported range of atmospheric sulfate at continental sites.

[24] The weak correlation of high $\delta^{18}\text{O}$ to high $\Delta^{17}\text{O}$ in sulfate from the dust samples is probably related to the atmospheric oxidants O_3 and H_2O_2 , both of which have highly positive $\delta^{18}\text{O}$ and $\Delta^{17}\text{O}$ values [Johnston and Thiemens, 1997; Savarino and Thiemens, 1999].

[25] We note that duplicate traps from the same site and collection period (T1–T5, T7 and T7A, T18 and T18A, and T26 and T26A) have significantly larger variations in sulfate isotopic data than our analytical errors. The variations are particularly notable in values of $\Delta^{17}\text{O}$, whereas the range of values of $\delta^{18}\text{O}$ and $\delta^{34}\text{S}$ among duplicates is within or only slightly larger than the analytical errors. We believe that these variations represent true natural variation in sulfate flux on a fine spatial scale. Similarly large variations in physical properties such as soluble salt concentrations ($\pm 30\%$ by weight from the average) were also observed in samples from the same site (M. Reheis, unpublished data). The cause of these variations is not known at this time. However, the variations raise the question that one or two dust trap sulfate samples collected at certain durations may not be representative of bulk deposition sulfate for a region. The average values of the 47 samples that came

from 40 sites across the region should be statistically a much better representative.

4.2. Have Desert Varnishes Recorded Long-Term, Thus Mostly Preindustrial, Bulk Deposition Sulfate?

[26] In general, the varnish sulfate isotopic data occupy a corner of the broad $\delta^{18}\text{O} - \Delta^{17}\text{O} - \delta^{34}\text{S}$ data field of the bulk deposition sulfate (Figure 2). These disparities could be caused by many potential reasons. However, a distinct possibility is that the varnish sulfate may be a proxy record for the bulk deposition sulfate in the past several to hundreds of thousand years, rather than for the last one or two years that is dominated by anthropogenic sulfate. Before desert varnish can be regarded as an unbiased proxy for long-term bulk deposition sulfate in a region, we have to discuss some of the processes that could also contribute to the observation.

[27] A possible source of sulfate on rock varnish could come from in situ oxidation, either by oxidation of sulfur-bearing minerals in parent rock or by SO_2 oxidation on mineral surface. Sulfate derived from oxidation of sulfide minerals have no ^{17}O anomaly as demonstrated by experiments and measurement of natural samples [Bao *et al.*, 2000b]. No experimental data are available for sulfate derived from SO_2 oxidation on mineral surface at this time. Surface-catalyzed SO_2 oxidation, however, does not produce $\delta^{17}\text{O}$ anomalous sulfate, as indicated by data from sulfate carried by fine volcanic ashes [Bao *et al.*, 2003]. Our varnish sulfate has an average $\Delta^{17}\text{O}$ value only 0.3‰ lower than those of the bulk deposition sulfate collected in the same region. Therefore the sulfate contributions from in situ oxidation probably occur, but are not significant for rock varnish.

[28] A preferential accumulation of certain types of sulfate on the varnish surfaces could produce the observed disparities in isotopic data between varnish and current bulk atmospheric deposition. Desert varnishes only form in a limited elevation range; the greater precipitation and thus higher runoff and vegetation cover at higher elevation sites inhibits the development of varnishes [Quade, 2002]. We do not find any correlation between isotopic compositions with elevation at this limited elevation range [Bao *et al.*, 2001a]. Our dust trap samples were collected generally within the same elevation range. This elevation factor therefore should not be one of the causes.

[29] Another possible cause for the difference between varnish and dust sulfates could be that the rock surfaces tend to accumulate sulfate preferentially from wet deposition or from particles of a certain size range from dry deposition. A few preliminary studies have shown that the $\delta^{34}\text{S}$ value increases with the aerosol particle sizes [e.g., Wong *et al.*, 1985; Patris *et al.*, 2000; Turekian *et al.*, 2001]. In the southern California air basin, the $\delta^{34}\text{S}$ ratio varies within 2 to 4‰ for aerosol particles less than 3.5 μm in size, and increases from 5 to 9‰ for particles from 3.5 to 7.5 μm in size [Wong *et al.*, 1985]. Although all these studies dealt with marine or coastal atmosphere, similar size differentiation and isotopic differences are expected for inland site. If the dust traps tend to collect particles of all sizes while the rock varnishes preferentially incorporate the smaller particles from dry deposition, we might expect to see a higher $\delta^{34}\text{S}$ value for dust sulfate and a lower $\delta^{34}\text{S}$

value for varnish sulfate, or the opposite if varnish tends to accumulate the bigger particles. It is not clear if varnish is accumulating bulk deposition sulfate in an unbiased way.

[30] Desert varnish is the product of a slow and long-term accumulation and growth of minerals (clay and oxides) on rock surface, and has probably recorded a lengthy history of dust and atmospheric accumulation in a region [e.g., Bao et al., 2001a; Dorn, 1984; Fleisher et al., 1999; Liu and Broecker, 2000]. If the desert varnish is a good proxy for a long-term (>1,000 years) deposit that mainly incorporated preindustrial atmospheric sulfate, our data suggest that the anthropogenically dominated atmospheric sulfate has higher $\delta^{18}\text{O}$ and lower $\delta^{34}\text{S}$ than that of the preindustrial natural background sulfate. This deduction is consistent with recent $\delta^{34}\text{S}$ data for preindustrial and industrial non-sea salt sulfate derived from polar ice core samples from central Greenland [Patris et al., 2002]. This hypothesis can be further tested if sequential leaching of varnish sulfate from rock surfaces is extracting bulk deposition sulfate samples from a series of progressively older layers. The outermost layers, if forming during the past ~300 years, should have incorporated sulfate from anthropogenic emissions that have lower $\delta^{34}\text{S}$ and higher $\delta^{18}\text{O}$ values, whereas varnish layers that accreted in preindustrial times should show higher $\delta^{34}\text{S}$ and lower $\delta^{18}\text{O}$ values. Unfortunately, the growth of varnish laminae is often uneven on different parts of the rock surface; thus water-soluble sulfate may be released from both younger and older laminae during the same extraction period. Nevertheless, preliminary data indicate consistent decreases for $\delta^{18}\text{O}$ and $\Delta^{17}\text{O}$ values from the 1st extraction to the 2nd extraction (Table 2). Although there are not sufficient $\delta^{34}\text{S}$ data to show a trend, this hypothesis predicts that $\delta^{34}\text{S}$ value should increase from the 1st extraction to the 2nd and to further subsequent extractions.

5. Conclusions

[31] Water-soluble sulfate from modern bulk atmospheric deposition collected by dust traps in the southwestern United States shows large spatial variability in $\delta^{34}\text{S}$, $\delta^{18}\text{O}$, and $\Delta^{17}\text{O}$ values. Highly positive $\Delta^{17}\text{O}$ anomalies are found near metropolitan areas or busy highways, whereas minimal or no $\Delta^{17}\text{O}$ anomalies are found near large saline playas. The lack of correlation between geographical locations (elevation and latitude) and sulfur or oxygen isotope compositions suggests that there are no dominant point sources of anthropogenic sulfate in the region. The sulfur and oxygen isotopic data for water-soluble sulfate in desert varnishes from the southwestern United States are within in the overall data range of the modern bulk atmospheric deposition. However, on average, the varnish sulfate has lower $\delta^{18}\text{O}$ and higher $\delta^{34}\text{S}$ values than that of the modern bulk atmospheric deposition. A likely explanation for the isotopic disparities is the recent dominance of anthropogenic sulfate in the overall sulfate budget in the atmosphere; the varnish sulfate contains a significant portion of preindustrial bulk deposition sulfate. The inferred change in bulk deposition sulfate isotopic data from preindustrial to industrial atmosphere is consistent with recent Greenland ice core data [Patris et al., 2002].

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