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Sulfate oxygen-17 anomalies in desert varnishes

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Abstract—Rock varnishes are ubiquitous in arid regions on Earth, and are believed to be commonly present on Mars. Here we report high water-soluble sulfate and nitrate contents in desert varnishes from the Death Valley region of southwestern U.S.A., and that sulfate in varnishes possess $\delta^{17}O/\delta^{18}O$ ratios that do not fall on terrestrial mass-dependent fractionation line. Sulfate from wet and dry atmospheric deposition is probably the source of the $\delta^{17}O$ anomalies. The anomalies are only moderately lower than that of aerosol sulfates collected from the greater Los Angeles area, indicating probably more than half of the sulfate in desert varnish is supplied by atmospheric deposition. This finding suggests that Earth surface environments are constantly accumulating $\delta^{17}O$-anomalous sulfate from the atmosphere; arid and stable conditions facilitate the preservation of these atmospheric signatures. This finding also indicates that different $\delta^{17}O/\delta^{18}O$ ratios found in different components in the Martian meteorites may result from atmospheric chemical processes. *Copyright © 2001 Elsevier Science Ltd*

1. INTRODUCTION

Rock varnish, a seemingly insignificant dark coating on many rock surfaces in arid regions, has been for years a puzzling yet fascinating subject for scientists interested in its origins (Dorn, 1984; Dorn, 1998; Fleisher et al., 1999; Perry and Adams, 1978; Potter and Rossman, 1977). There are numerous studies concerned with mineralogical compositions (Potter and Rossman, 1979), biological origins (Dorn and Oberlander, 1981; Grote and Krumbein, 1992; Nagy et al., 1991), and geomorphology (Oberlander, 1994; Watson and Nash, 1997). Studies of desert varnish are applied to archaeological dating (Dorn and Dragovich, 1990; VandenDolder, 1992), paleoclimatology (Dorn et al., 1987; Liu et al., 1998), exobiology (Mancinelli and White, 1996), and Martian surface studies (Guinness et al., 1997; Israel et al., 1997; King, 1988). Recently, there are renewed interests in varnishes regarding material input from the atmosphere, growth rate, and dating potential (e.g., Fleisher et al., 1999; Liu and Broecker, 2000).

Rock varnish is mainly composed of clay minerals that are cemented to rock by oxyhydroxides of manganese and iron. Sulfate has not been measured in previous compositional studies on varnish. There exist only a few measurements of sulfur content (total S) in desert varnish and its substrate rocks (Dorn, 1998; Dragovich, 1984; Dragovich, 1998; Drake et al., 1993; Glasby et al., 1981; Johnston et al., 1984; Perry and Adams, 1978; Reneau et al., 1992). In general, these measurements indicate that the sulfur content is 5–10 times higher in varnish than in the substrate rock. Windblown inorganic salts or sulfur derived from substrate rock through capillary precipitation are suggested as sources of these sulfur compounds (Hayashi and Miura, 1989; Johnston et al., 1984). However, wet and dry sulfate deposition derived from atmospheric oxidation reactions remains a potential sulfate source that has not been investigated. Nitrate is another major atmospheric species that is closely associated with sulfate in atmospheric deposition, and nitrate accumulation in desert varnish has not been examined. Arid climate and stable surfaces, such as rock and boulder surfaces that accumulate desert varnish, may provide suitable conditions for the preservation of atmospheric signatures, as indicated by a recent finding of ^{137}Cs and excess ^{210}Pb in varnishes (Fleisher et al., 1999).

To examine potential atmospheric accretion of sulfate onto rock surfaces and subsequent preservation, we adopt an approach that measures both $\delta^{17}O$ and $\delta^{18}O$ values for sulfate in varnish (similar isotopic work on nitrate is in progress). It is known that sulfate from atmospheric deposition deviates from a mass-dependent relation in its $\delta^{17}O/\delta^{18}O$ ratio. The atmospheric sulfate $\Delta^{17}O$ value ($= \delta^{17}O - 0.52 \times \delta^{18}O$), a parameter quantifying the deviation, varies between 0.2 and 3.0‰ (Lee, 1997; Lee et al., 1998). One likely source of these positive $\delta^{17}O$-anomalies is transfer from ozone or hydrogen peroxide during the oxidation of reduced gaseous sulfur compounds in the atmosphere. Atmospheric ozone and hydrogen peroxide are known to have positive $\Delta^{17}O$ values (Johnston and Thiemens, 1997; Krankowsky et al., 1995; Mauersberger, 1987; Savarino and Thiemens, 1999). In contrast, nearly all terrestrial processes involving solid and liquid phase sulfate are known to have $\Delta^{17}O$ values ~ 0 (Bao et al., 2000). Thus, positive $\Delta^{17}O$ values are associated with atmospheric processes. In this paper, we report the first measurements of (1) sulfate and nitrate concentrations and their ratios in desert varnishes; and (2) sulfate $\delta^{17}O$ and $\delta^{18}O$ values in desert varnishes and other desert surface deposits from the southwestern USA. We further quantify the fraction of atmospheric input for varnish sulfate by comparison to aerosol sulfate $\Delta^{17}O$ values collected from the greater Los Angeles area.

2. METHODS AND MATERIALS

We collected samples of desert varnish as well as sediment beneath desert pavement, playa mud, calcrete, surface salt crust, salt core, and brine in the Death Valley region, southwestern U.S.A. (Fig. 1). Sulfate and nitrate contents of 6 selected varnish samples with relatively thick coatings (~50 μm) were extracted in a progressive leaching method, and measured by ion chromatography (Dionex 2001I) (Table 1). We

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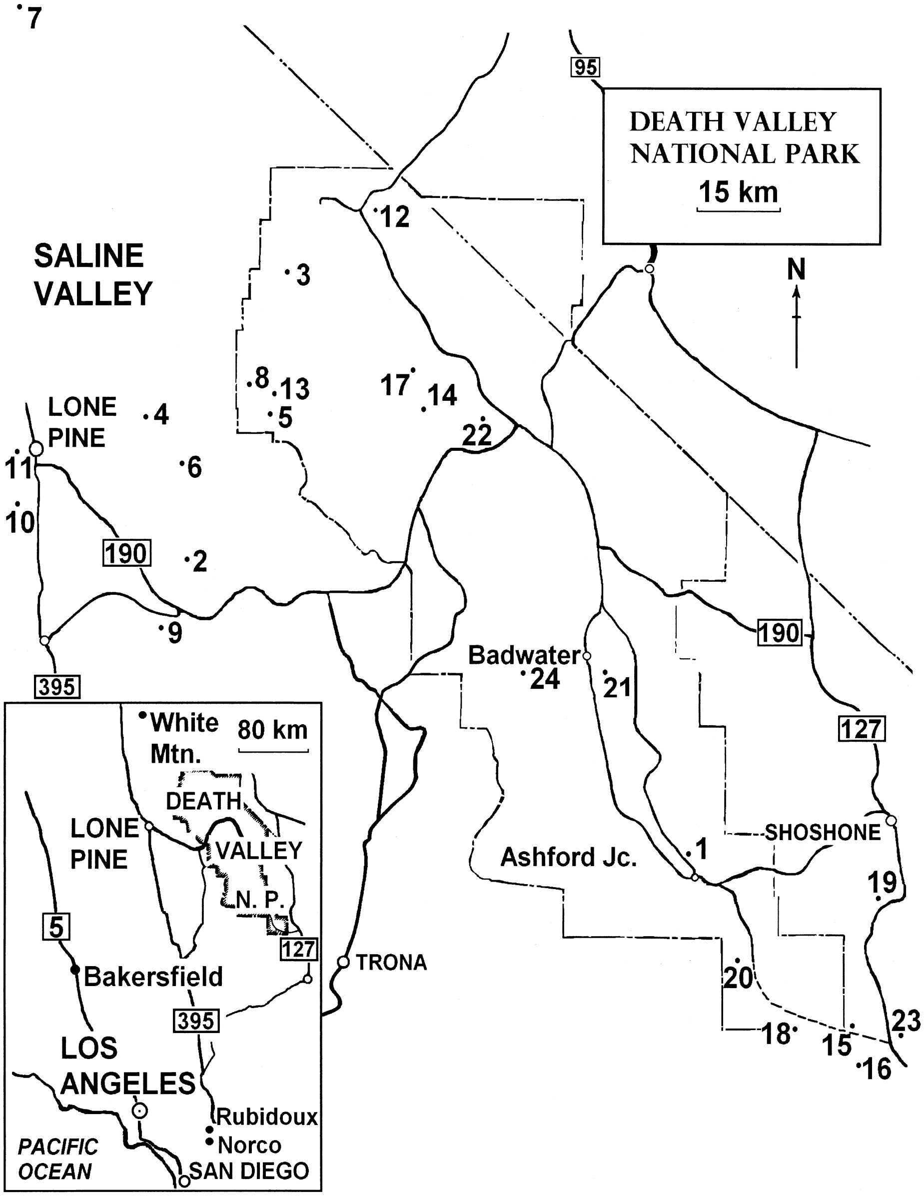

Fig. 1. Death Valley National Park.

further analyzed $\delta^{17}O$ and $\delta^{18}O$ compositions of water-soluble sulfate in rock varnishes and other desert deposits collected from 38 localities (Fig. 1; Table 2). For comparison, 21 atmospheric aerosol sulfate samples collected from the greater Los Angeles area were analyzed for their $\delta^{17}O$ and $\delta^{18}O$ values (Fig. 1; Table 3). Water-soluble sulfate was converted to barite. Molecular oxygen was extracted directly from barite by laser fluorination and analyzed by mass spectrometry (MAT 251), following a new approach described in Bao and Thiemens (2000). The procedure has an analytical error of $\pm$ 0.8‰ and $\pm$ 0.05‰ for $\delta^{18}O$ and $\delta^{17}O$, respectively. The high precision of $\Delta^{17}O$ value is due to the co-variation of $\delta^{18}O$ and $\delta^{17}O$ during isotopic analysis. All oxygen isotopic compositions are reported in the standard δ notation as per mil deviation from SMOW.

Water-soluble sulfate was extracted from rock varnishes as follows. Thin layers of varnished rock were chipped off and collected in the field. The chip's inner side is substrate rock, which in our case is mostly granite in composition with little sulfate in it. Chips with a total varnished surface area of 0.05–0.1 m^2 were placed in a large beaker ($>$500 cm) and rinsed twice with Millipore water to remove surface dust and other adhering contaminants. Varnish samples were then soaked in Millipore water (adjusted to pH = 4–5 by HCl solution) for 1 to 2 days, along with periodic ultrasonic treatments to promote the dissolution of Mn-Fe oxyhydroxides on varnish surface. Before collecting the extraction, NaOH solution was added to raise the solution pH above 8. This procedure is important because (1) most sulfates adsorbed on the Mn-Fe oxyhydroxide particle surfaces while in acidic condition will be desorbed into the alkaline solution; and (2) subsequent evaporation in alkaline condition minimizes oxygen isotope exchange between sulfate and water (Hoering and Kennedy, 1957; Lloyd, 1968). Once the solution is evaporated to ~100 ml, pre-washed active carbon is added to remove organic material. After further evaporation, the solution is collected, centrifuged, and filtered. The ~20–50 ml solution is then acidified prior to the addition of $BaCl_2$ solution to precipitate barite ($BaSO_4$). The varnish coating remains

Table 1. Sulfate and nitrate contents of selected varnish samples.

	SO_4^{2-} (% weight)[a]			NO_3^- (% weight)			total SO_4^{2-} (% weight)	total NO_3^- (% weight)	NO_3^-/SO_4^{2-} (molar ratio)
Sample	(1)	(2)	(3)	(1)	(2)	(3)			
Ash-J	1.33	0.81	1.00	0.18	0.07	0.11	3.14	0.36	0.18
Camp-1	0.10	0.07	0.28	0.03	0.12	0.33	0.45	0.48	1.65
G-Stand	0.12	0.37	0.47	0.09	0.13	0.05	0.96	0.27	0.44
M-UF	0.02	0.18	nd[b]	0.02	0.02	nd	0.20	0.04	0.31
Saline	0.16	0.29	0.62	0.07	0.23	0.98	1.07	1.28	1.85
SP-RD	0.09	0.58	0.72	0.02	0.04	0.31	1.39	0.37	0.41

[a] Weight percentages are estimated on the basis of measured varnish area, average thickness of 50 μm, and specific density of 2 g/cm^3. (1) Varnish samples soaked in weakly alkaline solution (HCO_3^--added) for 4 days at room temperature; (2) Varnish samples from (1) further soaked in 0.05 M HCl solution for 5 days at room temperature; (3) Varnish samples from (2) soaked in 0.33 M HCl solution until all varnish dissolved. All estimated weight percentages have 10–20% error.

[b] Non-detectable.

Table 2. Oxygen isotopic compositions of sulfate from varnishes, recent and ancient desert deposits, groundwater, and salt beds.

Sample	$\delta^{18}O$	$\delta^{17}O$	$\Delta^{17}O$	Sample description	Location on Figure 1	Elevation (m)
Varnish						
Ash-J	6.5	4.1	0.73	Varnish on lava flow	1	5
Camp-1	6.9	4.2	0.64	Varnish on lava flow	2	1655
Camp-2	4.5	3.0	0.7	Varnish on lava flow	3	850
Saline	8.1	5.1	0.92	Varnish on granite	4	914
Ulida	6.0	3.7	0.65	Varnish on granite	5	1347
Jackass	7.2	4.1	0.37	Varnish on granite	6	2195
G-Stand	7.8	5.5	1.38	Varnish on granite	8	1235
Barcroft	5.6	3.6	0.69	Varnish on granite	7	3825
Grapevine	7.2	4.5	0.76	Varnish on granite	12	1311
Darwin	9.8	5.6	0.5	Varnish on granite	9	1372
Gunga	9.8	5.9	0.79	Varnish on granite	11	1402
MCT-1	4.6	2.9	0.54	Varnish on granite	10	2652
M-UF-1	7.7	4.8	0.73	Varnish on granite	13	1402
M-UF-2	6.2	3.6	0.41	As above, 2nd extraction	13	1402
MF-3	7.3	4.3	0.54	Varnish on marble	13	122
SP-RD-1	6.4	4.2	0.83	Varnish on marble	15	91
SP-RD-2	5.8	3.8	0.77	As above, 2nd extraction	15	91
MF-1	3.3	2.5	0.85	Varnish on desert pavement	14	122
Camp3-1-1	5.2	3.4	0.65	Varnish on desert pavement	16	408
Camp3-1-2	5.1	3.2	0.57	As above, 2nd extraction	16	408
Recent desert deposits						
Uflat-1	6.2	3.7	0.49	Mud from surface of a playa	13	1402
Niter-5	9.8	5.2	0.18	Calcite nodule from surface of a playa	17	25
Niter-7	5.3	3.1	0.31	Loose sediment, 8–12 cm below playa surface	17	25
Niter-12	6.5	3.7	0.37	Calcrete, 10–40 below playa surface	17	25
R-track-3	7.1	4.3	0.6	Mud from a playa, 3 cm below the surface	8	1230
MF-2	6.9	4.6	1.02	Loose sediment beneath MF-1 pavement	14	122
Domunt	9.5	5.7	0.76	Water-soluble sulfate on aeolian sands	23	122
Ancient desert deposits						
Confid-1	8.6	4.6	0.19	Ancient lake-bed gypsum	20	90
Sara-10	7.4	3.9	0.11	Ancient lake-bed gypsum	18	83
Sara-11	7.7	4.1	0.16	Ancient lake-bed gypsum	18	83
Zam-3	7.0	4.2	0.54	Ancient playa(?)mudstone	19	442
Groundwater and playa salt beds						
Badwater	10.0	5.1	−0.07	Water from Badwater, Death Valley	21	−90
SPD-5	3.1	1.6	−0.06	Salt from flats between sand dunes	22	0
SPD-6	6.7	3.6	0.12	Salt from flats between sand dunes	22	0
DV3	9.3	4.8	−0.07	Salt core, −3.3 m (from surface), Badwater	24	
DV10	9.1	4.5	−0.16	Salt core, −10.5 m (from surface), Badwater	24	
DV131	16.9	8.7	−0.12	Salt core, −131 m (from surface), Badwater	24	
DV143	14.6	7.4	−0.18	Salt core, −143 m (from surface), Badwater	24	

Table 3. Oxygen isotopic compositions of sulfate from aerosols collected in southwestern USA.

Sample	$\delta^{18}O$	$\delta^{17}O$	$\Delta^{17}O$	Sample location and collection time
Norco-9-17	10.8	6.7	1.08	Norco, a week, only one filter
SS1 BU	18.5	12.4	2.76	Bakersfield, 3–6 days, backup filter
SS3 2nd	14.3	9.5	2.09	Bakersfield, 3–6 days, 2nd filter
SS3 3rd	17.2	11.6	2.72	Bakersfield, 3–6 days, 3rd filter
SS3 4th	18.1	12.4	3.00	Bakersfield, 3–6 days, 4th filter
SS3 BU	17.6	11.3	2.18	Bakersfield, 3–6 days, backup filter
SS5-3rd	12.9	8.8	2.09	Bakersfield, 3–6 days, 3rd filter
SS5-4th	15.7	10.8	2.66	Bakersfield, 3–6 days, 4th filter
SS5 BU	17.4	11.1	2.04	Bakersfield, 3–6 days, Backup filter
SS7 BU	18.8	10.9	1.19	Bakersfield, 3–6 days, Backup filter
WRMS-2	6.8	4.8	1.26	White Mtn. (elevation 3825 m), 3 days
Rub-2-2nd	14.3	8.7	1.22	Rubidoux, 1 day, 2nd filter
Rub-2-3rd	17.0	10.3	1.45	Rubidoux, 1 day, 3rd filter
Rub-2-4th	17.4	10.7	1.64	Rubidoux, 1 day, 4th filter
Rub-2-BU	16.1	9.9	1.57	Rubidoux, 1 day, Backup filter
Rub-3-1st	10.2	6.2	0.96	Rubidoux, 1 day, 1st filter
Rub-3-nite-BU	16.5	10.4	1.80	Rubidoux, 9 hrs at night, backup filter
Rub-4-3rd	18.2	11.9	2.43	Rubidoux, 1 day, 3rd filter
Rub-4-4th	21.4	14.3	3.24	Rubidoux, 1 day, 4th filter
Rub-4-BU	19.2	12.9	2.94	Rubidoux, 1 day, backup filter
Sproul-3-4-BU	15.2	8.8	0.92	1 mile off shore, San Diego, backup filter

Aerosol samples were collected using Anderson High Volume Cascade Impactors (Model 1200) at flow rate of 20 cubic feet per minute. The 1st-stage filter collects particle size larger than 10.2 μm, the 2nd between 10.2 and 4.2 μm, the 3rd between 4.2 and 2.1 μm, the 4th between 2.1 and 1.4 μm, and the backup for particle size less than 1.4 μm.

dark-brown in color after the first extraction. Several varnish samples went through a second extraction (Table 2). The dark varnish could all be dissolved in strong acidic solution (e.g., 0.5 M HCl for 3 days). We avoided such treatment because acidic condition accelerates the oxygen isotopic exchange between sulfate and water.

3. RESULTS AND DISCUSSION

3.1. Sulfate and Nitrate Contents

The 6 selected varnish samples have water-soluble sulfate and nitrate weight percents ranging from 0.2% to 3.1%, and 0.04% to 1.3%, respectively (Table 1). The extraction procedure yields a lower limit of sulfate content in varnish, because any sulfate that has already been in form of $BaSO_4$ cannot be extracted. Previous compositional data, mostly from electron microprobe analyses, show that desert varnishes have an average of ~0.2% SO_3 by weight (Dorn, 1998; Dragovich, 1988; Drake et al., 1993; Reneau et al., 1992). Our data suggest a significantly higher sulfate concentration in some varnishes. During sulfate extraction for isotopic analysis, we typically obtain ~25 mg $BaSO_4$ from an area of ~0.1 m^2 varnished surface. Assuming an average varnish thickness of 50 μm and a specific density of 2 g/cm^3, the first extraction yields a SO_4^{2-} weight content of ~0.25%. Due to the great variability of varnish thickness and mineralogy, the sulfate weight content may vary substantially among varnishes.

Previous studies have not identified the sulfur mineralogy in desert varnishes. The only known example of a sulfate mineral in desert varnish is from the Balchenfjella region, Antarctica, where crystalline jarosite, $KFe_3(SO_4)_2(OH)_6$, mixed with amorphous silica, constitutes a thin yellowish coat on the rock surface (Hayashi and Miura, 1989). They suggested an origin by evaporation of subsurface solution through capillary action, which is different from an origin through biological uptake, input from windblown dust, and other wet and dry atmospheric deposits, proposed for most desert varnishes. Reneau et al. (1992) found that Ba and S are frequently correlated in varnish, suggesting in situ formation of barium sulfate minerals. Our study suggests that a significant amount of water-soluble sulfates exist in varnish. The small quantities, however, pose difficulties for precise mineralogical characterization. Gypsum [$CaSO_4 \cdot 2(H_2O)$], mirabilite [$Na_2SO_4 \cdot 10(H_2O)$], and jarosite are possible mineral phases for the water-soluble sulfates. Alternatively, Mn-Fe oxyhydroxides and clay minerals in varnish possess huge surface areas and are known to adsorb large quantities of sulfate (Ajwa and Tabatabai, 1995; Aylmore et al., 1967; Curtin and Syers, 1990; Parfitt and Smart, 1978). It is probable that most of the water-soluble sulfates exist as adsorbed anions.

Nitrate deposits have been widely found and studied in desert regions (Bohlke et al., 1997; Campbell and Claridge, 1981; Ericksen et al., 1988). Atmospheric deposition is generally believed to be the source of desert nitrate deposits based on their high $\delta^{18}O$ values (up to ~60‰). An organic origin was suggested by Ericksen et al. (1988) for the Clay Hill nitrate deposits in Death Valley. Nitrate has never been measured on rock varnish, but we measured significant nitrate contents in our varnish samples (Table 1). Since HNO_3 is volatile on rock surfaces where the summer temperature can be extremely hot, we believe the nitrate in varnish occurs in neutral species, such as NH_4NO_3 and $NaNO_3$.

The NO_3^-/SO_4^{2-} molar ratio in the 6 varnish samples varies significantly, ranging from 0.18 to 1.85 with an average value of 0.81, which is not significantly different from that of the rainwater in the arid southwestern USA. On the basis of monthly precipitation-weighted means, rainwater at two National Atmospheric Deposition Program (NADP) sites, Bishop, California (CA43) and Smith Valley, Lyon Co., Nevada (NV03) had NO_3^-/SO_4^{2-} molar ratio of 1.44 ± 0.92 (n = 18) and 2.09 ± 1.15 (n = 124), respectively (Network, 1998). The NO_3^-/SO_4^{2-} molar ratio of aerosols in southern California varies depending on location and altitude. Bulk aerosols collected by aircraft over southern California and adjacent areas have NO_3^-/SO_4^{2-} molar ratios of ~1.05 at low-middle altitudes (median altitude 3.1 km) (Li et al., 1997). The large variations of NO_3^-/SO_4^{2-} molar ratios found in different varnishes may result from: (1) preferential loss of nitrate after wet deposition on rock surfaces, by solution or volatilization; and (2) input of sulfate- or nitrate-rich salt dusts.

3.2. Sulfate Δ^{17}O Values in Varnish and Aerosols

Playa salt beds possess no sulfate δ^{17}O anomaly, i.e., $\Delta^{17}O \sim 0$ (Table 2). Some playa and alluvial deposits such as mud, calcrete, or sediment beneath desert pavements show positive sulfate Δ^{17}O values, spreading from 0.1 to 1.0‰. In contrast, the varnish samples exhibit a relatively small range of Δ^{17}O values with an average 0.70 ± 0.22‰ (n = 20) and the highest 1.38‰ (Table 2). Similar amount of sulfate were obtained from the second extractions comparing to those from the first extractions in all three tested varnish samples (M-UF, SP-RD, and Camp3-1). No pronounced δ^{18}O or Δ^{17}O difference was found in these second sulfate extractions (Table 2). Sulfate Δ^{17}O value is not correlated with elevation or type of parent rock of the varnishes, indicating that the source of varnish sulfate is mostly atmospheric. Aerosol sulfates have an average Δ^{17}O value of 2.06 ± 0.71‰ (n = 19, not a weighted mean), most of which were collected in the relatively polluted greater Los Angeles area (Fig. 1; Table 3). Both δ^{18}O and Δ^{17}O values are among the highest for aerosols from the 4th filters. Two bulk aerosol samples "Norco-9-17" (east of Los Angeles) and "WMRS-2" (White Mountain, north of Death Valley National Park), which may represent a reasonable total atmospheric background sulfate, exhibit lower Δ^{17}O values (1.1‰ to 1.3‰) than that of other aerosol fractions. Thus, the largest varnish sulfate Δ^{17}O values, as well as the δ^{18}O values, overlap with the smallest aerosol isotopic values (Fig. 2).

3.3. Implications

The reported sulfate oxygen isotopic compositions should reflect their original signature since alteration or exchange with ambient oxygen-bearing compounds such as water, nitrate, silicates is insignificant under surface conditions (Zak et al., 1980). It is possible that biological sulfate reduction and sulfur oxidation would eventually erase the positive sulfate Δ^{17}O signature in many environments. Sulfate in desert varnish, however, is less likely to become an important electron acceptor in bacterial metabolism, due to the presence of large quantities of Mn-Fe oxyhydroxides and molecular oxygen. Thus, we believe that potential bacterial processes within desert varnish have only minimal effect on sulfate Δ^{17}O signature.

There are three major implications of the present results. First, the large sulfate Δ^{17}O values indicate a major component of atmospheric accretion (dry and wet sulfate depositions) onto desert varnish surfaces, consistent with the ^{137}Cs and excess ^{210}Pb data, which suggest at least part of the varnish materials are supplied from the atmosphere (Fleisher et al., 1999). The fact that the observed Δ^{17}O values are mostly lower for varnish than for aerosols suggests that aerosols are not the only source of sulfate. Other potential sources include (1) aqueous sulfate in rainwater droplets; (2) sulfate from aqueous sulfide oxidation in the substrate rock; and (3) sulfate-bearing aeolian dust from alluvial and playa deposits. It is known that rainwater and aerosol sulfates have positive Δ^{17}O values that likely originated in the atmospheric sulfur oxidation processes (Lee, 1997; Lee et al., 1998). Unfortunately, no Δ^{17}O data for rainwater sulfate from the Death Valley region are available. Sulfate derived from substrate rocks should have near-zero Δ^{17}O values (Bao et al., 2000). Similarly, sulfate formed by the oxidation of reduced atmospheric sulfur compounds (e.g., SO_2) on rock surfaces, if any, should be minimal in quantity and probably zero in Δ^{17}O value. Aeolian dust may be a mixture of playa salts, which mostly have ^{17}O-normal sulfate, and dusts from desert alluvial deposits, which can have zero to positive Δ^{17}O values (as shown in Table 2). Dust deposition is common in the arid southwestern USA (Reheis, 1997; Reheis and Kihl, 1995). Although incorporation into rainwater is limited (Schlesinger and Peterjohn, 1988), dusts can be one of the sources of varnish materials. Assuming that direct atmospheric sulfate (including rainwater and aerosol) in the Death Valley region has a Δ^{17}O value of 1.2‰ on the basis of the average background atmospheric sulfate Δ^{17}O data in adjacent areas, we estimate (based on $\Delta^{17}O = 0.70$‰ for varnish sulfate) that half or more of the sulfate in desert varnishes is derived directly from atmospheric deposition. Here the uncertainty of this estimation comes mostly from the dust components, which can have zero to positive Δ^{17}O anomalies.

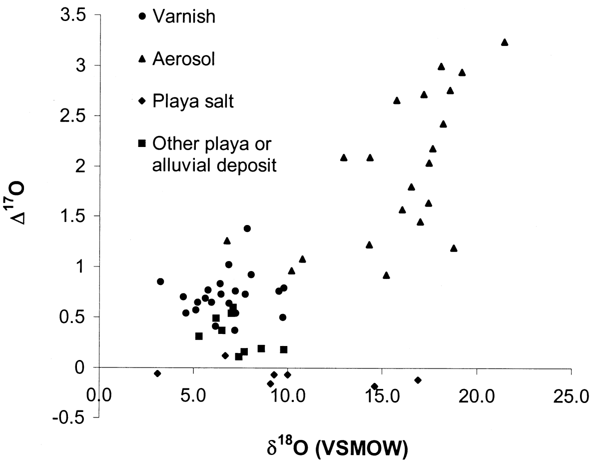

Fig. 2. δ^{18}O vs. Δ^{17}O for varnish, playa, salt core, and aerosol sulfates. The error for Δ^{17}O ($\pm$ 0.05^{18}O ($\pm$ 0.8‰) is not plotted on the diagram.

Secondly, it is noticeable that, by comparing the varnish sulfate and the aerosol sulfate Δ^{17}O values, desert varnishes appear to record the minimal Δ^{17}O value of long-term average atmospheric sulfate deposition in a region. A potential implication of this observation is that different regions may have characteristic atmospheric sulfate Δ^{17}O values due to the differences in chemistry of the sources, transport, and mixing.

Desert varnishes or other surface deposits may therefore provide a good record to trace those differences in different regions of the world. The preservation of anomalous sulfate in desert varnishes and some alluvial and playa deposits can be attributed to limited biological sulfur redox activities and the lack of additions from δ^{17}O-normal sulfates in desert environments. As a sedimentary deposit with an extremely slow accumulation rate (several micrometers per 1000 years), desert varnish has the potential to record paleoclimatic information (Liu and Broecker, 2000). Although microlaminations found in many varnishes suggest the presence of a long-term record, the temporal variation of sulfate Δ^{17}O would be difficult to establish at present, due to the low sulfate content in varnishes and the large sample size required for isotopic analysis with current techniques. A rough temporal pattern may be examined by comparing the sulfate data from the first extraction with that from the second, and the third ones or further, assuming sulfate from the subsequent extraction has an older age than does the prior one. The similar values in our three sample pairs suggest perhaps that this low-resolution approach did not pick up any significant variation in overall atmospheric sulfate Δ^{17}O value during the last several to hundreds of thousands of years in the Death Valley region. In addition, because of the special signature of atmospheric sulfate in surface environments, Δ^{17}O and δ^{18}O can provide new natural tracers for interactions of sulfur reservoirs and sulfur biogeochemical cycles. Unfortunately, the survival of desert varnish in geological record is rare (Dragovich, 1984), imposing a limit on its application to the study of ancient land-atmospheric interactions.

Perhaps the most important implication of our findings is in the general planetary science. Although mass-independent isotopic fractionations are known to occur in the Earth's atmosphere, until recently, no examples have been observed in terrestrial solids (Clayton and Mayeda, 1996). Thus, a particular planet or parent body should have a single characteristic value of Δ^{17}O when comparing to terrestrial fractionation line. As shown in this paper, signatures of atmospheric gases can be incorporated into crustal rocks and sediments. The Martian surface is likely covered by rock varnish and dust as suggested by Earth-based and orbital spectroscopy and Viking and Pathfinder landing data (Guinness et al., 1997; Israel et al., 1997; King, 1988; McCord et al., 1982). The abundant ferromagnetic mineral dusts in the Martian atmosphere provide ideal sites for sulfate to adsorb on surfaces or to be incorporated into mineral structures (Burns, 1992; Hviid et al., 1997; Morris et al., 1998). Martian regolith is known to have a high content of sulfate and chloride salts (Bishop et al., 1993; Blaney and McCord, 1995; Burns, 1987; Clark and Van Hart, 1981; Thomas et al., 1999). Nitrate is also a possible component of the Martian regolith (Grady et al., 1995). Recent measurements have demonstrated disparities in Δ^{17}O values among high-temperature silicate minerals, water, calcite, and sulfate within SNC meteorites, which are believed to derive from Mars (Farquhar and Thiemens, 2000; Farquhar et al., 1998; Karlsson et al., 1992). A likely cause of the Δ^{17}O variations may well be the atmospheric chemical processes on Mars, just as observed here on Earth. The cold and dry conditions on Mars are ideal for the preservation of atmospheric depositions. Rock coatings, regolith, and evaporites are therefore potential proxies for current and ancient atmospheric processes on Mars or other planets.

4. CONCLUSIONS

The large positive δ^{17}O-anomalies ($\Delta^{17}\text{O} \sim 0.70‰$) found in sulfate within desert varnishes suggest that (1) a significant portion of the sulfate in varnish comes from the atmosphere (including wet and dry deposition); (2) signatures of atmospheric chemistry can be incorporated into lithosphere; (3) desert environments provide suitable conditions for the preservation of these signatures; and (4) On Earth, oxygen isotopic heterogeneity in surface materials can result from atmospheric chemistry; thus, an atmospheric origin of isotopic heterogeneity on the Martian surface is highly plausible.

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