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## Caliche as a geological repository for atmospheric sulfate

Katie J. Howell<sup>1</sup> and Huiming Bao<sup>1</sup>

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[1] Recent studies demonstrate that important information on sulfur source, oxidation pathway, transport pattern, and reaction kinetics of atmospheric oxidation of sulfur gases can be uncovered by measuring multiple isotope compositions of the oxidation product — secondary atmospheric sulfate (SAS). SAS from Earth's distant past, however, is rarely preserved in the rock records because of its high solubility and small quantity. We report here from the measurement of 47 modern and fossil caliche samples that caliches contain variable amounts of carbonate-associated sulfate (CAS), and the  $\Delta^{17}\text{O}$  values of the CAS range from  $-0.12$  to  $+2.32\text{‰}$  with most values higher than the background value of  $-0.05\text{‰}$  for seawater sulfate, indicating the presence of an SAS component derived from the oxidation of sulfur gases by atmospheric ozone or related oxidants. This study demonstrates that caliche, a pedogenic carbonate common in the geologic record, could serve as a repository for ancient SAS. **Citation:** Howell, K. J., and H. Bao (2006), Caliche as a geological repository for atmospheric sulfate, *Geophys. Res. Lett.*, *33*, L13816, doi:10.1029/2006GL026518.

### 1. Introduction

[2] Oxidation of sulfur gases in the atmosphere has been ongoing since Earth's beginning, although the mode of oxidation may have shifted profoundly since  $\sim 2.5$  Ga when  $\text{O}_2$  started substantially accumulating in the atmosphere. This secular transition may be represented by the change in the dominant formation pathway of secondary atmospheric sulfate (SAS) from  $\text{SO}_2$  UV-photolysis to  $\text{SO}_2$  oxidation by  $\text{O}_3$ ,  $\text{H}_2\text{O}_2$ , or  $\cdot\text{OH}$  before and after the formation of an  $\text{O}_3$  layer that requires a certain pressure of free  $\text{O}_2$  ( $>10^{-5}$  times the present atmospheric level) in the atmosphere [Farquhar and Wing, 2003; Pavlov and Kasting, 2002; Savarino et al., 2000]. Meanwhile, short-lived but massive releases of sulfur gases (mainly  $\text{SO}_2$ ) associated with continental volcanism or bolide impacts have been blamed for a series of atmospheric, climatic, and biological consequences throughout geologic history. It has been speculated that these events may have brought about the destruction of the stratospheric  $\text{O}_3$  layer [Kump et al., 2005], climate cooling due to a thick cloud of sulfuric aerosols [Pope et al., 1997], or massive acid rain [Maruoka et al., 2003; Pope et al., 1997], but the exact chemistry of these transient sulfur-oxidation events is not known. One major reason that these events remain in speculation is the lack of preservation of ancient atmospheric deposits. SAS is the ultimate oxidation

product of sulfur gases in the atmosphere. It is commonly in the form of  $(\text{NH}_4)_2\text{SO}_4$ ,  $\text{NH}_4\text{HSO}_4$ , or  $\text{H}_2\text{SO}_4$  and is highly soluble and rarely preserved in rock records. If we had a preserved ancient SAS sample from the time of interest, we could reveal the source of sulfur, oxidation pathways, transport pattern, and even reaction kinetics by analyzing sulfate's multiple sulfur and oxygen isotope compositions, i.e., the  $\delta^{34}\text{S}$ ,  $\delta^{33}\text{S}$ ,  $\delta^{36}\text{S}$ ,  $\Delta^{33}\text{S}$ ,  $\Delta^{36}\text{S}$ ,  $\delta^{18}\text{O}$ ,  $\delta^{17}\text{O}$ , and  $\Delta^{17}\text{O}$ .

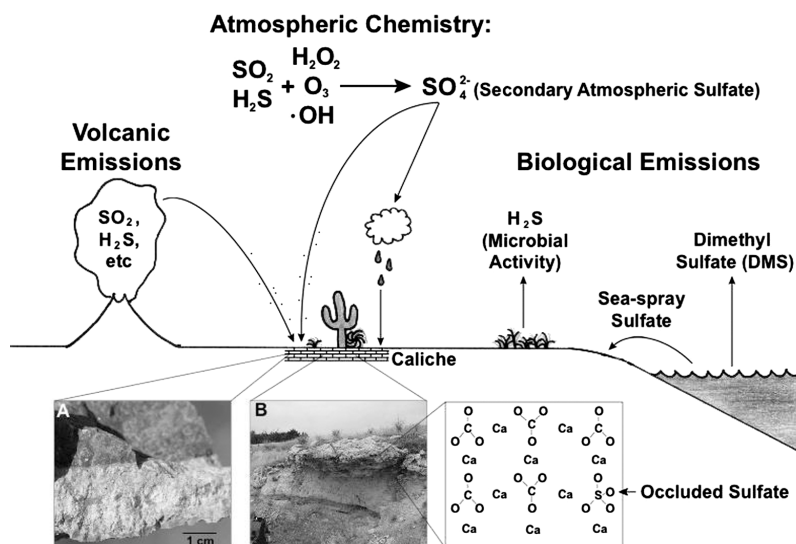
[3] Sulfate's  $\delta^{34}\text{S}$  and  $\delta^{18}\text{O}$  are good tracers of sulfur source and sulfur oxidation pathways despite many uncertainties [Holt and Kumar, 1991; Jamieson and Wadleigh, 2000; Tanaka et al., 1994]. But recent discoveries of multiple oxygen and sulfur isotope compositions, particularly the  $\Delta^{33}\text{S}$  and  $\Delta^{17}\text{O}$  values, add significantly to resolving sulfate-formation mechanisms [Bao et al., 2000b, 2003; Farquhar et al., 2000; Johnston et al., 2005; Savarino et al., 2003]. For example, the presence of a  $^{33}\text{S}$  anomaly suggests that  $\text{SO}_2$  photolysis was a predominant sulfate-formation pathway, a scenario that can only occur without a significant  $\text{O}_3$  shield in the atmosphere [Farquhar et al., 2001; Pavlov and Kasting, 2002]. The presence of an  $^{17}\text{O}$  anomaly in SAS on the other hand may suggest that  $\text{O}_3$  or  $\text{H}_2\text{O}_2$  was the major oxidant involved in the oxidation of  $\text{SO}_2$  in the atmosphere [Savarino et al., 2000]. Oxidation of  $\text{SO}_2$  by oxidants other than  $\text{O}_3$ ,  $\text{H}_2\text{O}_2$ , or possibly stratospheric  $\cdot\text{OH}$  does not produce an  $^{17}\text{O}$  isotope anomaly that is measured by the parameter  $\Delta^{17}\text{O}$ :

$$\Delta^{17}\text{O} = \delta^{17}\text{O} - \left[ (1 + 0.001 \times \delta^{18}\text{O})^{0.52} - 1 \right] \times 1000$$

[4] Preservation of ancient SAS is extremely rare. There are only two known cases where old SAS is preserved. The first is the surficial salt deposits in old, hyperarid deserts like the Central Namib Desert, the Atacama Desert, and the Antarctica Dry Valleys [Bao et al., 2000a, 2000b, 2001]. The second case is the calcite pseudomorphs after gypsum in an Oligocene volcanic ash bed in northwestern Nebraska [Bao et al., 2003]. In both cases, the positive  $\Delta^{17}\text{O}$  signatures indicate an SAS component exists in these deposits. The sulfates in hyperarid deserts, however, are the result of continuous atmospheric deposition and accumulation since Miocene. They are essentially long-term but modern deposits. Similar massive deposits have not been found in the geologic record. In the ash-bed case, the preservation of SAS is attributed to the early formation of gypsum crystals due to high sulfate concentration in a playa setting [Loope et al., 2005], a unique case not yet encountered at other locations or times.

[5] In this study, we test whether caliche, a pedogenic carbonate commonly found in semi-arid to arid settings, is capable of preserving SAS. It is well known that the precipitation of calcite can occlude certain amounts of sulfate from an ambient solution within its crystal structure,

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**Figure 1.** Cartoon depicts the processes involved in the occlusion of carbonate-associated sulfate in caliches, including major sources of sulfur gases and sulfate in the atmosphere and the key formation pathways of secondary atmospheric sulfate. Photo A shows a modern rind caliche growing on a limestone matrix, Texas (sample “Sierra Blanca TX 1”), and photo B shows a massive Miocene caliche developed on a volcanic ash bed in the Ogallala Formation, Nebraska (sample “Broadwater NE 5”). Objects are not to scale.

and most of the occluded sulfate is structurally substituting for the carbonate ion ( $\text{CO}_3^{2-}$ ) [Takano *et al.*, 1980]. In an arid or semi-arid soil where leaching is limited and microbial sulfate reduction is absent, sulfate introduced into a soil column by dry and wet atmospheric deposition could accumulate and become occluded in a slow-growing calcium carbonate (Figure 1). The most diagnostic isotope signature of SAS formed in the atmosphere is its positive  $\Delta^{17}\text{O}$  value, so we focus our measurement on the  $\Delta^{17}\text{O}$  of carbonate-associated sulfate (CAS) in caliches. Due to the great sample diversity in both parent material and geographic location, the  $\delta^{34}\text{S}$  was not measured. Despite a small fraction derived from the oxidant, the  $\delta^{18}\text{O}$  value of SAS is largely determined by the  $\delta^{18}\text{O}$  of its precursor,  $\text{SO}_2$  or  $\text{HSO}_3^-$  [van Stempvoort and Krouse, 1994], and is related to that of water vapor in the atmosphere and therefore environmental parameters such as elevation, latitude, or climate. Since sorting out environmental factors is not the intended goal of this study, we only report a general range of  $\delta^{18}\text{O}$  values among our geographically diverse samples without further discussion. Similarly, the precise ages of the examined caliche samples are not relevant for the purpose of this study. If CAS in caliches were found to bear positive  $\Delta^{17}\text{O}$  values, caliche’s commonality and early appearance in the geological record [e.g., Harrison and Steinen, 1978; Knauth *et al.*, 2003; Mack and James, 1992; Martini, 1994; McPherson, 1979] allows it to serve as a viable repository for SAS that can be used to reconstruct past secular and transient atmospheric sulfur oxidation events.

## 2. Materials and Methods

[6] The term “caliche” is used in literature in a variety of ways [Machette, 1985; Reeves, 1970]. In this paper, caliche refers to pedogenic carbonate in the form of massive layers, indurated slabs, irregular concretions, encrustations, coat-

ings, and rinds formed near the soil surface in arid to semi-arid environments. We collected a variety of caliche samples (Table 1), and they fall into two major groups: 1) modern caliches actively developing in the southern High Plains of North America (Texas and New Mexico) on diverse parent materials including limestone, volcanic ash, basalt, rhyolite, colluvium, and alluvium, and 2) fossil caliches of Eocene-Miocene ages developed on volcanoclastic sediments from the northern High Plains of North America (northwestern Nebraska). Information pertaining to individual sites and caliche samples are listed in Table 1.

[7] A caliche sample was first analyzed for CAS concentrations using small chips of the caliche (~200 mg). The chips were cleaned in an ultrasonic bath using distilled and deionized (DD) water to remove potential surface contaminants and then dissolved in 0.1 M acetic acid. The solution was evaporated to drive off excess acetic acid and diluted for the measurement of major anion concentrations using an ion chromatograph (Dionex ICS-90). CAS used for isotope analyses was extracted from a large aliquot of cleaned caliche sample using a high-grade HCl (1 M) solution. The solution was filtered and acidified before adding  $\text{BaCl}_2$  droplets to precipitate barite ( $\text{BaSO}_4$ ). The barite was further cleaned by two repeated DDARP treatments, a method using DTPA, a chelating agent, to dissolve previously precipitated barite and to reprecipitate the barite by acidification [Bao, 2006]. The triple-oxygen isotope compositions were determined using  $\text{O}_2$  generated from barite in a  $\text{CO}_2$  laser-fluorination system [Bao and Thiemens, 2000] and run on an isotope-ratio mass spectrometer (Finnigan MAT 253) at the Oxy-Anion Stable Isotope Center (OASIC) at Louisiana State University (LSU). The  $\delta^{18}\text{O}$  value has an error of  $\sim\pm 0.7\text{‰}$  due to non-quantitative yield during laser fluorination and may have unpredictable error if barite is not pure or grain size too coarse. The  $\Delta^{17}\text{O}$  has a much smaller measurement error of  $\pm 0.05\text{‰}$  because of covariance be-

**Table 1.** Concentration, Isotope, and Occurrence Data of CAS Extracted from Caliche Samples<sup>a</sup>

Sample Name <sup>b</sup>	$\Delta^{17}\text{O}$	$\delta^{18}\text{O}$	$[\text{SO}_4^{2-}]$ , ppm	Parent Material	Occurrence
<i>Active Caliches from Southern High Plains</i>					
Marfa TX 3A <sup>c</sup>	+0.68	5.7	126	basalt	rind
Marfa TX 3B <sup>c</sup>	+0.97	7.9	126	basalt	rind
Ozona TX 1	+0.58	12.2	84	limestone	massive
Eagle Nest NM 1A <sup>c</sup>	+0.39	15.7	60	colluvium	concretion
Eagle Nest NM 1B <sup>c</sup>	+0.84	9.7	60	colluvium	concretion
Mentone TX 5	+0.38	10.6	495	limestone	massive
Clayton NM 2A <sup>c</sup>	+0.24	5.5	127	basalt	rind
Clayton NM 2B <sup>c</sup>	+0.18	9.7	127	basalt	rind
Ozona TX 2	+0.20	13.6	83	limestone	rind
Mentone TX 6	+0.12	7.0	402	limestone	massive
Marathon TX 1	+0.12	10.0	117	basalt	rind
Marathon TX 3	+0.07	6.1	98	rhyolite	slab
Mentone TX 2	+0.07	7.8	302	limestone	concretion
Marathon TX 2	+0.06	10.3	339	rhyolite	massive
Garfield NM 1	+0.06	2.7	88	alluvium	encrustation
Magdalena NM 1	+0.05	6.5	111	rhyolite	rind
Marfa TX 2	+0.05	6.0	153	basalt	slab
Magdalena NM 2	+0.04	6.4	220	rhyolite	rind
Mentone TX 8	+0.03	6.0	563	limestone	massive
Sierra Blanca TX 1	+0.02	7.9	37	limestone	rind
Kerrville TX 1	+0.01	14.2	1211	limestone	massive
Mentone TX 1	+0.01	6.0	253	limestone	massive
Socorro NM 1	0.00	3.9	112	alluvium	encrustation
Mentone TX 7	0.00	8.8	397	limestone	massive
Kerrville TX 2	-0.02	15.0	121	limestone	concretion
Mentone TX 4	-0.12	8.3	351	limestone	massive
Clayton NM 1	N.D. <sup>d</sup>	N.D.	43	basalt	rind
Albuquerque NM 1	N.D.	N.D.	58	basalt	concretion
Kerrville TX 3	N.D.	N.D.	60	limestone	massive
Alpine TX 1	N.D.	N.D.	72	basalt	slab
Clayton NM 3	N.D.	N.D.	101	basalt	rind
Tuff Canyon TX 1	N.D.	N.D.	119	ash	massive
Mentone TX 3	N.D.	N.D.	127	limestone	massive
Marfa TX 1	N.D.	N.D.	1113	basalt	concretion
Guadalupe TX 1	N.D.	N.D.	1914	limestone	massive
<i>Pleistocene Caliches on Volcanic Ashes</i>					
Espanola NM 1	N.D.	N.D.	60	ash	slab
Espanola NM 2	N.D.	N.D.	52	ash	slab
<i>Pliocene Soil Carbonate Nodules (B<sub>k</sub> Horizon)</i>					
Belen NM 1	+0.01	5.7	212	paleosol	nodule
Belen NM 2	+0.05	4.2	269	paleosol	nodule
<i>Oligocene-Miocene Caliches from Northern High Plains</i>					
Broadwater NE 4A <sup>c</sup>	+0.37	-1.0	140	ash	massive
Broadwater NE 4B <sup>c</sup>	+0.45	33.8	140	ash	massive
Gordon NE 1A <sup>c</sup>	+0.16	36.4	119	ash	slab
Gordon NE 1B <sup>c</sup>	+2.32	2.6	119	ash	slab
Gordon NE 1C <sup>c</sup>	+0.47	30.1	119	ash	slab
Chadron NE 1A <sup>c</sup>	+0.15	3.9	298	ash	slab
Chadron NE 1B <sup>c</sup>	+0.18	3.6	298	ash	slab
Broadwater NE 1A <sup>c</sup>	N.D.	N.D.	10	ash	massive
Broadwater NE 1B <sup>c</sup>	+1.39	1.4	250	ash	massive
Broadwater NE 2	N.D.	N.D.	11	ash	massive
Toadstool Park NE 1	N.D.	N.D.	12	ash	concretion
Broadwater NE 3	N.D.	N.D.	15	ash	slab
Gering NE 1	N.D.	N.D.	36	ash	slab
Chadron NE 2	N.D.	N.D.	78	ash	slab

<sup>a</sup>Caliche samples were collected during the 2005 field season from the High Plains, North America.

<sup>b</sup>Samples are named according to their location and categorized in two major groups (see text).

<sup>c</sup>Indicates replicate measurements, which are named with the same label as the original sample plus "A", "B", or "C".

<sup>d</sup>N.D. = no data. Indicates either there was not enough sulfate to be extracted according to measured [CAS] or extractions did not yield sufficient quantities of sulfate for isotope measurements.

tween the  $\delta^{18}\text{O}$  and the  $\delta^{17}\text{O}$ . We also conducted whole-procedure duplicate measurements from rock crushing to isotope measurement on six caliche samples. Oxygen isotope measurement at LSU OASIC has been calibrated against UWG-2 [Bao et al., 2004]. All oxygen isotope compositions are reported with respect to VSMOW.

### 3. Results

[8] A total of 47 samples were analyzed for CAS concentration with values ranging from  $\sim 10$  ppm to  $\sim 2000$  ppm. Among the 47 samples, 29 of them yielded sufficient  $\text{BaSO}_4$  for oxygen isotope measurement. The  $\delta^{18}\text{O}$  values of CAS ranges from  $-1\text{‰}$  to  $+30\text{‰}$  with most values at  $+8.8 \pm 3.4\text{‰}$ . The  $\Delta^{17}\text{O}$  value for CAS ranges from  $-0.12\text{‰}$  to  $+2.32\text{‰}$ . There is no distinct pattern among parent material, caliche occurrence,  $\Delta^{17}\text{O}$  value, or CAS concentration. In addition, the two highest  $\Delta^{17}\text{O}$  values ( $+2.32\text{‰}$ ) are from caliches developed on Eocene-Miocene volcanic ashes in the northern High Plains. Replicate analyses of three samples ("Clayton NM 2", "Broadwater NE 4", and "Chadron NE 1") showed no variation in  $\Delta^{17}\text{O}$  value within the analytical error, but the other three replicate analyses ("Marfa TX 3", "Eagle Nest NM 1", and "Gordon NE 1") were distinct. The largest discrepancy emerged in sample Gordon NE 1, a fossil caliche developed on top of an Eocene ash bed (Table 1).

### 4. Discussion

[9] An extensive survey of seawater sulfate throughout geologic time and sulfate produced via oxidative weathering of sulfide minerals suggests a background  $\Delta^{17}\text{O}$  value of  $-0.05\text{‰}$  for terrestrial sulfate that does not involve atmospheric oxidation or non-mass dependent fractionation processes [Bao, 2005; Bao et al., 2000b]. Among the 29 caliche samples, 28 bear CAS that has  $\Delta^{17}\text{O}$  values higher than  $-0.05\text{‰}$  with the highest anomaly at  $+2.32\text{‰}$ . These data demonstrate that caliche is a geological formation that could retain SAS, confirming our initial prediction.

[10] The ability for carbonate rocks to hold CAS from the time of formation has been confirmed crystallographically [Takano et al., 1980] and empirically on the CAS measurements of many Paleozoic and Precambrian limestones [e.g., Kah et al., 2001]. Contamination by modern sulfate onto an outcrop of fossil caliche is possible only if a significant layer of secondary caliche is forming. If that were occurring, we would have classified the outcrop as a modern active caliche. Considering the high solubility of most sulfate minerals, our analytical procedure plus using only fresh chips should have prevented contamination by modern sulfate.

[11] The magnitude of the  $\Delta^{17}\text{O}$  value of CAS in a caliche sample is determined by two factors. The first is the  $\Delta^{17}\text{O}$  of SAS, which is determined by the relative roles played by  $\text{O}_3$ ,  $\text{H}_2\text{O}_2$ ,  $\cdot\text{OH}$ , or other oxidants during the sulfur-oxidation processes in the atmosphere. The  $\Delta^{17}\text{O}$  value can be quantitatively predicted if necessary atmospheric conditions are given [Alexander et al., 2005; Lee and Thieme, 2001; Lyons, 2001]. In general, the involvement of ozone as an oxidant will increase with increased pH in an aqueous medium [Liang and Jacobson, 1999], which

will result in higher  $\Delta^{17}\text{O}$  values for SAS due to the high  $\Delta^{17}\text{O}$  value of atmospheric  $\text{O}_3$  [Johnson *et al.*, 2000; Johnston and Thiemens, 1997; Krankowsky *et al.*, 2000]. It is therefore expected that the  $\Delta^{17}\text{O}$  of SAS will vary in space and time.

[12] The second factor that determines the  $\Delta^{17}\text{O}$  value of CAS in a caliche is the relative proportion of SAS with respect to sulfates from other sources. For example, marine limestones may have CAS that was inherited from the time of formation [Burdett *et al.*, 1989; Staudt and Schoonen, 1995]. Volcanic ashes may carry magmatic sulfate or may provide surfaces for the formation of sulfate by  $\text{SO}_2$  oxidation [Bao *et al.*, 2003; Zimbelman *et al.*, 2005], and oxidative weathering of sulfide minerals also contributes sulfate to parent materials. All these sulfates bear no  $^{17}\text{O}$  anomaly but can dilute the SAS signature in caliches.

[13] Our modern caliche samples from the southern High Plains should have recorded average  $\Delta^{17}\text{O}$  values of SAS during the last several hundred thousand years — or longer depending on the age of a particular surface. We have recently analyzed year-round  $\Delta^{17}\text{O}$  values for total SAS in Baton Rouge, Louisiana, and Gering, Nebraska, two mid-latitude sites in North America. The yearly average  $\Delta^{17}\text{O}$  is at  $\sim+0.70\%$  [Jenkins and Bao, 2006]. This mid-latitude value is very different from the Antarctic value of  $\sim+2.50\%$  [Alexander *et al.*, 2002; Bao and Marchant, 2006], possibly due to drastically different climate conditions or stratospheric influx. If we use  $+0.70\%$  as the end-member  $\Delta^{17}\text{O}$  value for mid-latitude SAS, the estimated SAS content in caliches of the southern High Plains ranges from 0 to 85% of the total CAS. It should be noted that here we assume the sulfur oxidation chemistry is not fundamentally different between the present atmosphere (dominated by anthropogenic emission) and the past one (dominated by biological and volcanic emissions).

[14] Two of the fossil caliches have  $\Delta^{17}\text{O}$  values at  $+1.39\%$  and  $+2.32\%$ , much higher than data for the other caliches and also higher than the average mid-latitude value of  $+0.70\%$ . In light of the earlier discovery that the sulfate  $\Delta^{17}\text{O}$  values are as high as  $+5.80\%$  in one of the ash beds containing calcite pseudomorphs after gypsum in the Gering formation, Arikaree Group, northwestern Nebraska [Bao *et al.*, 2003], it is conceivable that similar atmospheric sulfur oxidation events (probably dry fogs) associated with other transient volcanic eruptions may have been recorded in the caliches. These extremely positive  $\Delta^{17}\text{O}$  values in the fossil caliches also support that the SAS is preserved from the time of caliche formation and are not modern contamination.

[15] The presence of significant heterogeneity with respect to CAS  $\Delta^{17}\text{O}$  values is manifested by replicate sulfate extractions and isotope measurements within a single caliche sample. The  $\Delta^{17}\text{O}$  differences between replicate analyses range from  $+0.06\%$  to  $+2.16\%$  in some of the modern and ancient caliche samples. Soil is notoriously heterogeneous in space with respect to mineral composition, porosity, and degree of cementation. It is therefore expected that the [CAS] as well as the SAS component of CAS would vary considerably from sample to sample and even within the same sample (e.g. sample “Gordon NE 1”). If the uneven distribution of multiple sulfate end members is responsible for the heterogeneity in the isotope compositions of CAS, multiple sampling of the same caliche outcrop

may help to reveal the individual sulfate end-members and thus their different formation mechanisms.

## 5. Conclusions

[16] Triple-oxygen isotopic analyses of CAS in both modern and ancient caliches show that the carbonate formation typical of arid-climate soils is a good repository for atmospheric sulfate deposition. The sulfate occluded in caliches is a mixture of SAS and background sulfate derived from weathering or inherited from parent materials. Depending on the formation mechanism and the time represented by a caliche sample, the SAS in it holds information on long-term or transient signatures of atmospheric sulfur oxidation. Future work should focus on an effort to delineate multiple sulfate end members occluded in caliches. The inherited heterogeneity of soil caliche formation seems to provide such an opportunity when the  $\Delta^{17}\text{O}$ , together with the  $\delta^{18}\text{O}$  and multiple sulfur isotope compositions, are all measured for CAS. This study alerts the community to a potential repository for ancient atmospheric sulfate so that new research on past atmospheric events can occur.

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