

SULFUR AND OXYGEN ISOTOPE
CHARACTERIZATION OF AN EOCENE PLAYA
DEPOSIT, NORTHERN HIGH PLAINS, AND
RAINWATER SULFATE, BATON ROUGE, USA

A Thesis

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ABSTRACT

This thesis is composed of two independent chapters which are linked through the application of multiple stable isotope measurements of sulfate.

Chapter 1 compares two Cenozoic playa deposits in the northern High Plains. Anomalous playa sulfate was discovered at Scotts Bluff which is speculated to have originated via the oxidation of volcanically emitted reduced sulfur gases. A question arises, then, is a volcanic origin of sulfate common for other Cenozoic playa deposits in the region. A complete stable isotope characterization was performed on the gypsum sulfate collected at Wolf Butte (nearby apparent playa setting) to determine if the sulfate has a similar origin to that in the Scotts Bluff playa.

No ^{17}O anomaly was found in the sulfate at Wolf Butte and the $\delta^{34}\text{S}$ values range from +12.2 to +14.8‰. Potential sources of sulfate at Wolf Butte include weathering of Cretaceous shale and leaching of volcanic ashes. It is concluded that Scotts Bluff and Wolf Butte represent two different playa gypsum deposits that existed during the Cenozoic in the High Plains.

Chapter 2 looks into atmospheric chemical reactions that form tropospheric sulfate in Baton Rouge area. Multiple stable isotope compositions of atmospheric sulfate in La Jolla, California (Lee 2001) revealed competing oxidation pathways exist between ozone (O_3) and hydrogen peroxide (H_2O_2). To elucidate the source and origin of atmospheric sulfate in Baton Rouge air shed, oxygen and sulfur isotopic compositions were analyzed.

The outcome of this survey found that the sulfate isotopic composition data range

from 0.25 to 1.43‰ and 11.8 to 19.3‰ for $\Delta^{17}\text{O}$ and $\delta^{18}\text{O}$, respectively, and -1.4 to 3.8‰ for $\delta^{34}\text{S}$. High $\Delta^{17}\text{O}$ values were not favored in the winter season as was seen in the study performed in California (Lee 2001). The sulfate $\delta^{34}\text{S}$ appear to be slightly depleted with respect to those in La Jolla rainwater and may be due to a predominately anthropogenic ($\delta^{34}\text{S} \sim 0\text{‰}$) rather than marine ($\delta^{34}\text{S} \sim +9.9\text{‰} \pm 6\text{‰}$) source of sulfate. Also, sulfate concentrations in rainwater were more than twice that measured in two nearby Louisiana monitoring stations, which may be due to the sampling site's close proximity to oil refinery facilities.

CHAPTER 1.

SULFUR AND OXYGEN ISOTOPE CHARACTERIZATION OF AN EOCENE PLAYA DEPOSIT, NORTHERN HIGH PLAINS, USA

INTRODUCTION

An Oligocene playa located in northwest Nebraska (Scotts Bluff National Monument) exhibits an isotopic signature ($\Delta^{17}\text{O}$) incomparable to sulfate-rich deposits found in other arid regions of the world. It was discovered that the oxygen isotopic composition of sulfate extracted from a volcanic ash bed at Scotts Bluff did not lie on the terrestrial fractionation line (Bao 2000). Instead, the sulfate has highly positive $\Delta^{17}\text{O}$ anomalies that reach 5.8‰. To appreciate the peculiarity of the Scotts Bluff playa sulfate deposit, I explain briefly the stable isotope concepts below.

The terrestrial fractionation line follows a mass-dependent fractionation process:

$\delta^{17}\text{O} = 0.52 \times \delta^{18}\text{O}$, or in logarithmic format,

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

in which δ (‰) = $(R_{\text{sample}}/R_{\text{standard}} - 1) \times 1000$, where $R = \delta^{18}\text{O}/\delta^{16}\text{O}$, $\delta^{17}\text{O}/\delta^{16}\text{O}$. The ^{17}O anomaly is reported as $\Delta^{17}\text{O}$, in which $\Delta^{17}\text{O} = \delta^{17}\text{O} - 0.52 \times \delta^{18}\text{O}$, or

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

Positive $\Delta^{17}\text{O}_{\text{sulfate}}$ values are acquired in the troposphere during oxidation of reduced sulfur species (SO_2 , H_2S) by a $\Delta^{17}\text{O}$ anomalous compound such as ozone ($\Delta^{17}\text{O} \sim 35\text{‰}$) (Savarino 2000a). Thus, the oxygen-17 anomaly in sulfate is indicative of an atmospheric origin. It is known that volcanic activity in the Great Plains region during the Cenozoic released large quantities of ash, sulfur dioxide, and hydrogen sulfide into the atmosphere. Sulfate hazes might have formed in the atmosphere via the oxidation of the reduced sulfur gases (Bao 2003; Bao 2005). With the onset of a semi-arid climate during the Early Cenozoic, closed-deflationary basins containing playa lakes were a copious surface feature in the Plains region, much as they are today. The basins may have served as repositories where hazes accumulated sulfate. The record of this process may have been preserved through incorporation of sulfate into evaporite minerals. However, sulfate in most playas studied so far has negligible or no observable ^{17}O anomalies. Therefore, considering the common occurrence of Cenozoic playa deposits in the northern High Plains, is the Scotts Bluff playa an exception or commonplace in terms of the anomalous oxygen isotope composition? If it is indicative of the conditions within the High Plains, then general Cenozoic volcanic processes and the associated climatic conditions were probably responsible for its formation. However, if Scotts Bluff is unique, then determining the nature of that eruption event should be the focus of future research. The purpose of this paper is to examine whether other ancient playa deposits in the region exhibit similar $\Delta^{17}\text{O}$ signatures to that of Scotts Bluff, and to infer if volcanic release of sulfur dioxide, followed by subsequent oxidation to sulfate in the atmosphere, and deposition of sulfate aerosols were a common source of sulfate to playa systems in the region during the early Cenozoic Era.

With the help of H. LaGarry at the Conservation and Survey Division, University of Nebraska, a gypsum-rich Eocene deposit was located at Wolf Butte, approximately one hundred miles north of Scotts Bluff National Monument (Figure 1.1). The Wolf Butte sequence is dominated by sandy-siltstones with two distinct volcanic ash layers and massive gypsum layers. The green and tan siltstone succession at Wolf Butte is typical of deposits of ephemeral lakes in a semi-arid or arid climate (Arakel 1994; Chen 1993). The aerial extent of the Wolf Butte gypsum deposits is not known, but it may represent a small surface-water discharging playa. With its abundant volcanic deposits, the Wolf Butte playa is a good candidate for examining the potential heterogeneity of sulfate geochemical signatures for inland playas in the region.

Oxygen and sulfur stable isotopic compositions of sulfate are indicative of its origin and history, i.e., enriched $\delta^{34}\text{S}$ or $\delta^{18}\text{O}$ can be linked to bacterial sulfate reduction or seawater intrusion, whereas lower $\delta^{34}\text{S}$ or $\delta^{18}\text{O}$ values may be due to the addition of sulfate derived from pyrite oxidation (Fritz 1989; Habicht 1997). The origin of sulfates in lacustrine or playa settings has been studied extensively (Arakel 1994; Arenas 1999; Bao 2000; Bao 2005; Bao 2001; Bao 2003; Chen 1997; Chen 1993; Chivas 1991; Pueyo 2001; Raab 1997; Rech 2003; Rosen 1999; Sanz 1994; Yang 1999). Arakel (1994), Arenas (1999), Chen (1993, 1997), and Sanz (1994) measured no isotope compositions; Chivas (1991), Nakai (1975), Pueyo (2001), and Rosen (1999) measured only $\delta^{34}\text{S}_{\text{sulfate}}$ values; (Yang 1999) measures only $\delta^{18}\text{O}_{\text{sulfate}}$ values; Raab (1997) and Rech (2003) include $\delta^{34}\text{S}$ values of sulfate together with strontium data, Bao 2001 measures $\delta^{18}\text{O}$ and $\delta^{17}\text{O}$ values of sulfate, and Bao (2000, 2003) measure $\delta^{34}\text{S}$, $\delta^{18}\text{O}$, and $\delta^{17}\text{O}$ values of sulfate. The values of $\delta^{18}\text{O}$ and $\delta^{34}\text{S}$, however, often overlap among



Figure 1.1: Map of Nebraska, USA. Wolf Butte lies approximately 85 miles to the north of Scotts Bluff National Monument

sulfate of different origins (Table 1.1). Because the $\Delta^{17}\text{O}$ value of sulfate is unique to sulfate of atmospheric origin, it can be a powerful tool for tracking the source of sulfate in playa settings, even though its end-member values are less well defined at this time (Bao 2001). In this study, multiple stable isotope compositions of the Wolf Butte playa sulfate were measured, including $\delta^{18}\text{O}$, $\Delta^{17}\text{O}$, and $\delta^{34}\text{S}$ values, to compare to those from the Scotts Bluff playa.

LOCATION AND STRATIGRAPHY

The lithologic nomenclature and stratigraphic divisions used in northwest Nebraska have changed over the years (LaGarry 1997). This paper follows the renaming of units by Terry and LaGarry (1997).

The northwest-southeast sloping topography of the High Plains is marked by rolling hills and deep depressions within carbonaceous and non-carbonaceous shale deposits (Gautier 1987) of the Upper Cretaceous Niobrara and Pierre Groups (Gill 1961). The Western Intercontinental Seaway made its initial transgression during the mid-Cretaceous. A second transgression, the Claggett Transgression (Gill 1961), was characterized by the deposition of the organic-rich Pierre Shale (Gautier 1987), which underlies much of the state of Nebraska. Geologic uplift of the Rocky Mountains during the late Cretaceous resulted in slight uplift of the Pierre Shale (Wright 1987). During the Early Cenozoic the Great Plains were still experiencing volcanism that began in the late Mesozoic, and these eruptions led to the deposition of large quantities of volcanic ash.

Table 1.1: Worldwide playa sulfate with SO_4^{2-} source and isotopic values; and various shale deposits and isotope values. (Bao 2003)¹, (This study)², (Yang 1999)³, (Rosen 1991)⁴, (Rech 2003)⁵, (Pueyo 2001)⁶, (Bao 2001)⁷, (Chivas 1991)^{8,9}, (Lu 2001)¹⁰, (Nakai 1975)¹¹, (Raab 1997)¹², (Strauss and Schieber 1990)¹³

Location	Playa Type/Age	SO_4^{2-} Source	$\delta^{18}\text{O}$ value (‰) SMOW	$\delta^{34}\text{S}$ value (‰) CDT	$\Delta^{17}\text{O}$ value (‰)
Scotts Bluff, NE	Continental/Oligocene	Volcanic ash	+1.7 to +14.2 ¹	+0.3 to +8.2 ¹	+0.19 to +5.84 ¹
Wolf Butte, NE	Continental/Eocene	Oxidation of pyrite plus later reduction	+16 to +18.5 ² SMOW	+12.2 to +14.8 ²	0
Death Valley, CA	Continental	Atmosphere, spring flow, groundwater	+8.4 to +22.7 ³	+7 to +21 ³	no data
Bristal Dry Lake, CA	Continental	Groundwater	-0.4 ± 0.9 ⁴	+6 - 9 ⁴	no data
Atacama Desert, Chile	Continental	Groundwater, marine aerosol	no data	+2.9 to +8.7 ⁵	no data
Atacama Desert, Chile	Continental	Major volcanic influence	no data	+4.5 to 9 ⁶	
Central Namib Desert, S. Africa	Transition	Marine sea spray, weathered bedrock	+8.3 to +13.3 ⁷	no data	+0.06 to 1.11 ⁷
Western Australia	Transition	~55% to ~ 100% marine source, weathered bedrock	no data	+13.4 to +23.1 ⁸	no data
Southern Australia	Transition	~55% to ~ 100% marine source, Cretaceous Shale	no data	+9.5 to +20.1 ⁹	
Lake Vanda, Antarctica	Marine	Seawater	no data	+14.1 to +20.3 ¹⁰	no data
Central Jordan Valley, Israel	Marine	Seawater	no data	+17.8 to 19.9 ¹¹	no data
Nijjar Basin, Spain	Marine	Seawater	+10-17 ¹²	+21-24 ¹²	no data
Pyrite, Newland fm, MT		Pyrite oxidation	no data	+14 to +18 ¹³	
Pierre Shale Pyrite, Malone		Pyrite oxidation	no data	-33.0	
Pierre Shale Pyrite, Moore		Pyrite oxidation	no data	-15.4	

Wolf Butte

Wolf Butte, Nebraska, lies in the northwest region of the state located at 42°57' N latitude 103°24' W longitude. Gypsum-rich playa deposits within the lower Chadron Formation of the Lower White River Group (Eocene) outcrop at Wolf Butte. The lower Chadron Formation consists of two subunits, the upper Big Cottonwood Creek Member (BCCM) and the lower Peanut Peak Member (PPM) (Terry 1997). BCCM is composed of tan, silty-claystone deposits with prominent gypsum accretions. A volcanic ash layer tops the section at Wolf Butte. PPM is composed of olive colored claystone with abundant gypsum and is delineated by a distinct volcanic ash layer at the base (Figures 1.2). The PPM is underlain by the Chamberlain Pass Formation (CPF), a clayey-siltstone deposit with sandy cross-cutting channel deposits and abundant selenite. The CPF is underlain by Late Paleocene Yellow Mounds Paleosol Series, which is composed of red, yellow, and brown shales with abundant selenite rosettes. Yellow Mounds Series is underlain by Cretaceous Pierre Shale and the contact between the two formations is unconformable.

The PPM contains many gypsum-rich horizons, which is why it was chosen and extensively sampled for this study (20 samples over a ~15 m section) (Figure 1.4). Massive gypsum rich layers (Figure 1.3) define both the base and top of Peanut Peak Member. An additional four horizons are found throughout PPM alternating between beds of olive claystone (LaGarry 1997). A silicified massive gypsum rich layer defines the top of the PPM. A white volcanic-ash layer is located near the base of PPM (Figure 1.4, G25-2). Chert nodules are found throughout samples G25-7 to G25-15 (Figure 1.4). The spatial distribution of these deposits is unknown at this time. However, thorough

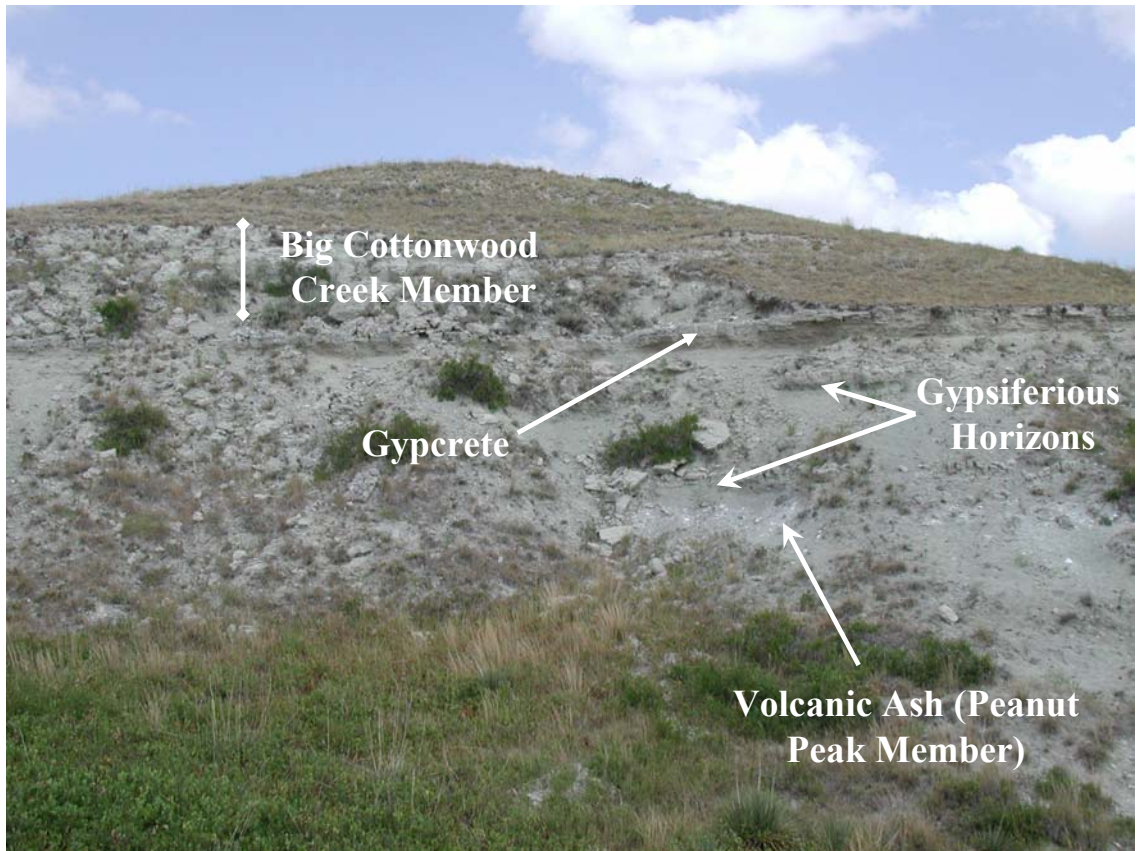


Figure 1.2: Sample section front view, Wolf Butte, NE, USA.



Figure 1.3: Massive gypsum layer at Wolf Butte, NE.

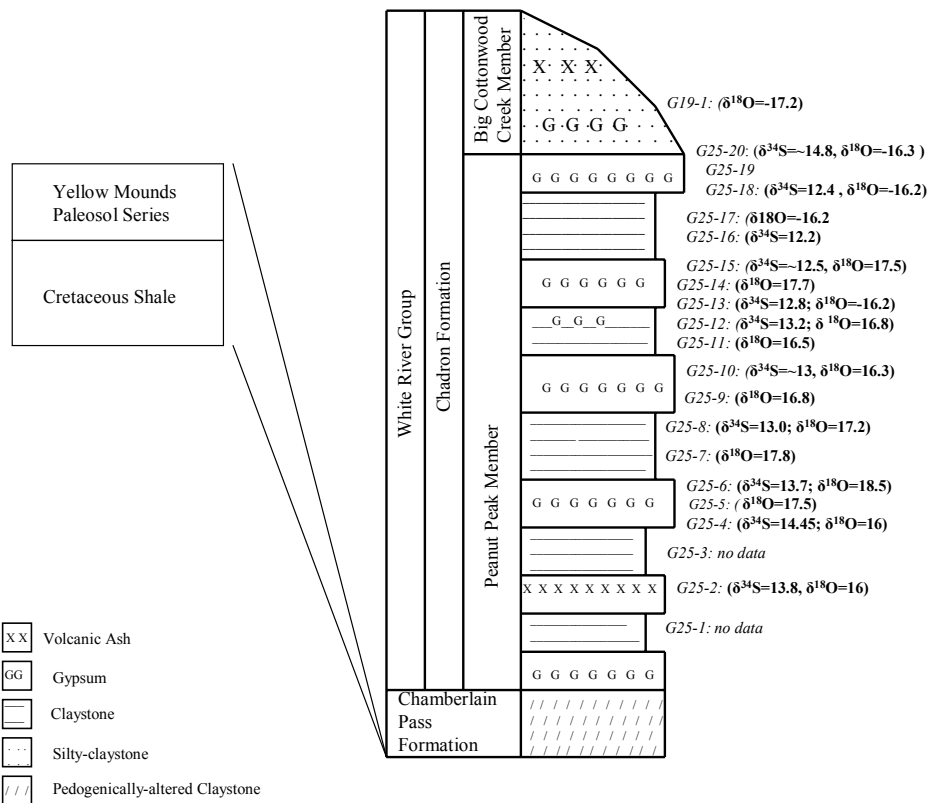


Figure 1.4: Stratigraphic log of Wolf Butte, NE, USA. Includes isotopic compositions of individual gypsum samples at respective sampling horizons. (Column adapted from Terry and LaGarry, 1997).

observation and sampling of adjacent outcrops show no evidence of similar deposits and it is postulated they are not widespread. Future study of this system will consist of mapping the lateral extent of the deposits.

Two Pierre Shale samples were collected from colleagues for $\delta^{34}\text{S}_{\text{pyrite}}$ measurement from the Mancos member of the Pierre Shale, Green Mountain Lake, Colorado (northwest region of northern High Plains) and an unknown member from Chamberlain, South Dakota (south-central region).

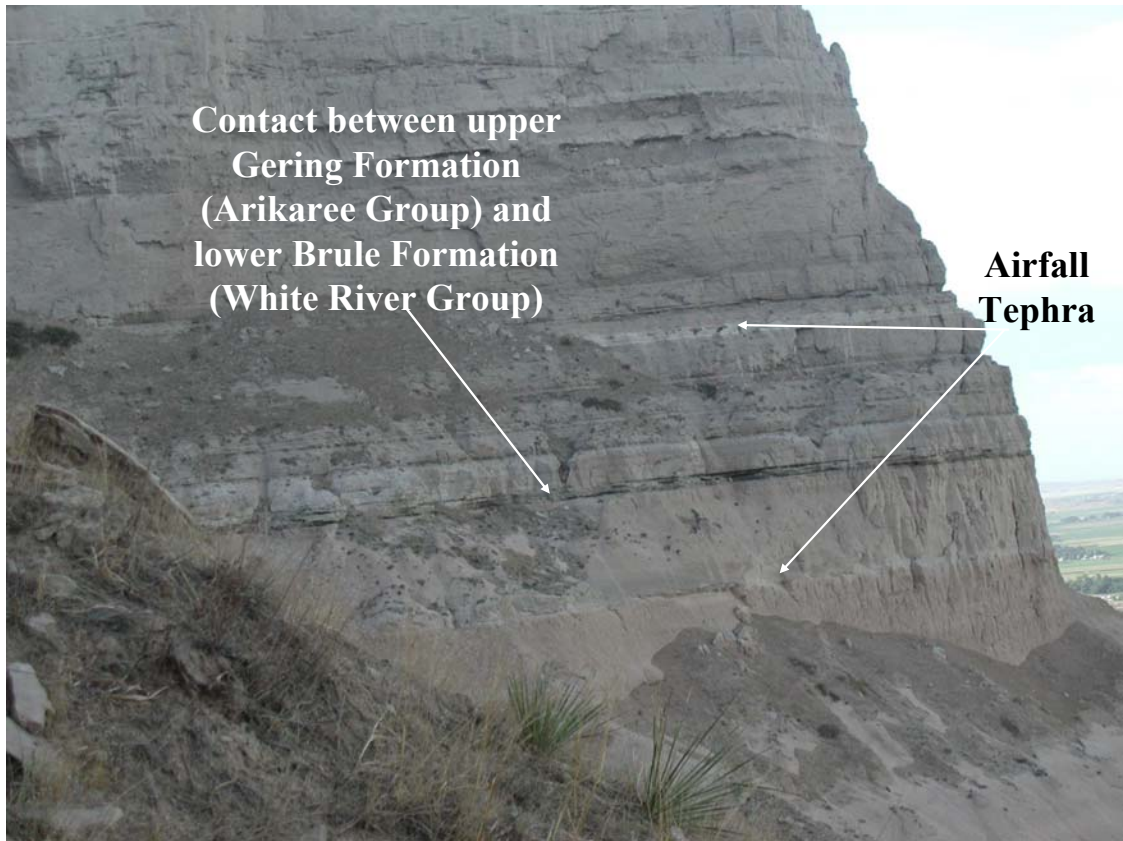
Scotts Bluff

Approximately 100 miles southwest of Wolf Butte (Figure 1.1), the deposits of a continental interior playa at Scotts Bluff, Nebraska, have been described by (Loope 1986; Loope 2005). Calcite pseudomorphs after gypsum are found within the Gering Formation at Scotts Bluff, which is the lowest member of the Arikaree Group. Stratigraphically, the Gering Formation sits unconformably on the Brule Formation (top of the White River Group) (Figure 1.5). The Brule Formation consists of massive siltstone deposits containing volcanic tephra, and the Gering is comprised of volcanoclastic sandstone deposits, which also contain layers of volcanic tephra.

ANALYTICAL METHODS

Mineralogy

An X-ray diffraction analysis was performed with Bruker/Siemens D5000 automated powder X-ray diffractometer with Rietveld analysis software to determine if the rosette crystals in underlying paleosols were gypsum.



Contact between upper
Gering Formation
(Arikaree Group) and
lower Brule Formation
(White River Group)

Airfall
Tephra

Figure 1.5: Gering Formation, Scotts Bluff National Monument, NE.

Sulfate extraction from playa deposits

Samples were collected from one section (Figure 1.2) at the site and taken from bottom to top of ~ 15 m section. Rock samples (poorly cemented) were crushed in the laboratory to a powder texture to enhance sulfate dissolution. Approximately 100mg aliquots were dissolved in distilled and deionized water (DD H₂O). They were then placed in a shake machine (Mistral Multi-Mixer) for one hour to help dissolution. After 10 minutes of centrifugation (Fisher Centrifig© Centrifuge) to separate water soluble sulfate in solution from sediment, the supernatant was filtered (0.2 µm polyethersulfone Millex Millipore filters) into 250 ml beakers. The filtered solution was then heated on a hot plate for 15-20 (Corning PC-35) at setting 5 to evaporate the sample to ~30ml. Once reaching this volume, clean 1 M HCl (36.5 to 38% assay, Fisher) was added to the solution and heated for an additional 10 minutes to release any carbonates in solution. The samples were removed from heat and saturated BaCl₂ (100% assay, J.T. Baker) solution was added to precipitate the previously dissolved sulfate as BaSO₄.

Converting sulfide to Ag₂S

Pyrite (FeS₂) from Cretaceous shale samples was converted to silver sulfide for delta sulfur-34 isotopic analysis. Sulfide for sulfur analyses was generated by a modified method of Canfield (1986). In this method, samples were crushed into fine powder. The crushed sample was placed in a vacuum-sealed flask containing ~2ml ethanol. The sample was subjected to a constant flow of N₂ gas over low heat to purify the air in reaction flask. Reduced chromium was needed to react with the iron in the pyrite in the sample. To produce this 50 ml of 1 M chromic chloride (CrCl₃) solution was reduced by

reaction with granulated zinc in a vacuum. The chromium solution changed from green to blue, indicating the reduction was complete. Next, 10 ml of concentrated HCl was added to the newly formed Cr^{2+} to form CrCl_2 . The CrCl_2 was injected into the sample flask and reacted with the sample for one hour on low stir. The N_2 transported the H_2S gas generated from the sample into a trap flask of 3% zinc acetate through evacuated tubing, at a bubble rate of 1-2 bubbles/second. Ag_2NO_3 solution was added to the Zn_2S solution and Ag_2S precipitated, sat over night, and was washed three times with deionized and distilled water the following day.

Isotope ratio measurements

1. $\Delta^{17}\text{O}$

The oxygen in barite for $\Delta^{17}\text{O}$ analysis was generated offline on a CO_2 -laser fluorination vacuum system at Oxy-Anion Stable Isotope Center (OASIC) at Louisiana State University. The vacuum system consists of a metal line and a glass line, with multiple liquid nitrogen traps. Oxygen gas (O_2) was generated in the metal line and collected in the glass line. Barite samples were weighed to ~ 5-8 mg and placed into small wells within a stainless steel plate, which holds 12 samples. Oxygen gas was generated as barite samples were subjected to laser beam and bromine pentafluoride gas (BrF_5). Standard runs consisted of settings of 3000 μm laser beam diameter, laser setting at continuous wave, and laser intensity between ~3.5 and 5 Watt. For lasing, BrF_5 (~ 80 Torr) is loaded into lasing chamber and samples bombarded for ~2 minutes, which typically generates ~3 Torr gas. The generated gas is then passed through 3 liquid nitrogen traps in the metal line, and an additional 2 traps in the glass line. Glass sample

tubes for the collection of oxygen gas containing molecular sieve (1/16" pellets, Mallinckrodt) heated at 200°C for ~20 minutes before oxygen collection. Oxygen gas (~0.2 to 0.7 Torr) is then collected in sample tubes with molecular sieve, submerged in liquid nitrogen. Samples were collected for 8 minutes.

The oxygen was then transferred to a 253 MAT Finnigan Ratio Mass Spectrometer for isotope measurements. The sample tube heated for ~10 minutes at 80°C before run. A typical voltage reading for mass 32 of oxygen was ~2000mV.

2. $\delta^{18}\text{O}$

The barite-oxygen for $\delta^{18}\text{O}$ was produced by Thermal Conversion Elemental Analyzer coupled with a 253 MAT Finnigan Ratio Mass Spectrometer at OASIS. Approximately 220ug barite was loaded into 3.5 x 5 mm silver capsules. TCEA was run at continuous flow with oven temperature 1450 °C, column temperature 90°C, and flow rate of 85ml min⁻¹.

3. $\delta^{34}\text{S}$

$\delta^{34}\text{S}$ analyses of sulfate were performed at the University of Maryland by Jay Kaufman using a Micromass Isoprime mass spectrometer with continuous flow inlet systems and high-temperature combustion ovens for gas chromatographic separation.

Standards and Notations

Oxygen and sulfur compositions of sulfate were expressed using the standard δ notation: δ (‰) = $(R_{\text{sample}}/R_{\text{standard}}-1) \times 1000$; where $R = \delta^{18}\text{O}/\delta^{16}\text{O}$, $\delta^{17}\text{O}/\delta^{16}\text{O}$, or $\delta^{34}\text{S}/$

$\delta^{33}\text{S}$. The international standards Vienna Standard Mean Ocean Water (VSMOW) and Vienna Canyon Diablo Triolite (VCDT) were used for oxygen and sulfur stable isotope compositions, respectively.

RESULTS

Mineralogy

Wolf Butte gypsum sequence is composed almost entirely of lacustrine deposits of mudstone and silty-claystone with massive and micro-crystalline gypsum, volcanic-clastic silty-sandstones, and capped by silicified gypcrete. The gypcrete is a horizon consisting almost entirely of gypsum, silica cemented, and up to a meter thick (Figure 1.3). The gypsum throughout the profile (Figure 1.2) beneath the gypcrete is found as elongated microcrystalline form in Peanut Peak Member and XRD pattern analysis of the apparent gypsum crystals in the underlying Yellow Mounds Paleosol Series confirms the mineralogy.

Stable isotope data

20 gypsum samples from Wolf Butte were analyzed for $\Delta^{17}\text{O}$, $\delta^{18}\text{O}$ and $\delta^{34}\text{S}$ compositions of sulfate. $\Delta^{17}\text{O}$ values are essentially zero for all samples, with an analytical error of $\pm 0.05\text{‰}$. The $\delta^{18}\text{O}$ ($n=13$) varies from $+16\text{‰}$ to $+18.5\text{‰}$ ($\pm 0.5\text{‰}$) and the sulfur ($n=11$) $+12.2\text{‰}$ to 14.8‰ ($\pm 0.3\text{‰}$) (Figure 1.6). $\delta^{18}\text{O}$ and $\delta^{34}\text{S}$ values for a selenite crystal in the Yellow Mounds Paleosol Series are 16.1‰ ($\pm 0.5\text{‰}$) and 1.2‰ ($\pm 0.3\text{‰}$), respectively. Two members of Pierre shale were analyzed for sulfide- $\delta^{34}\text{S}$ values

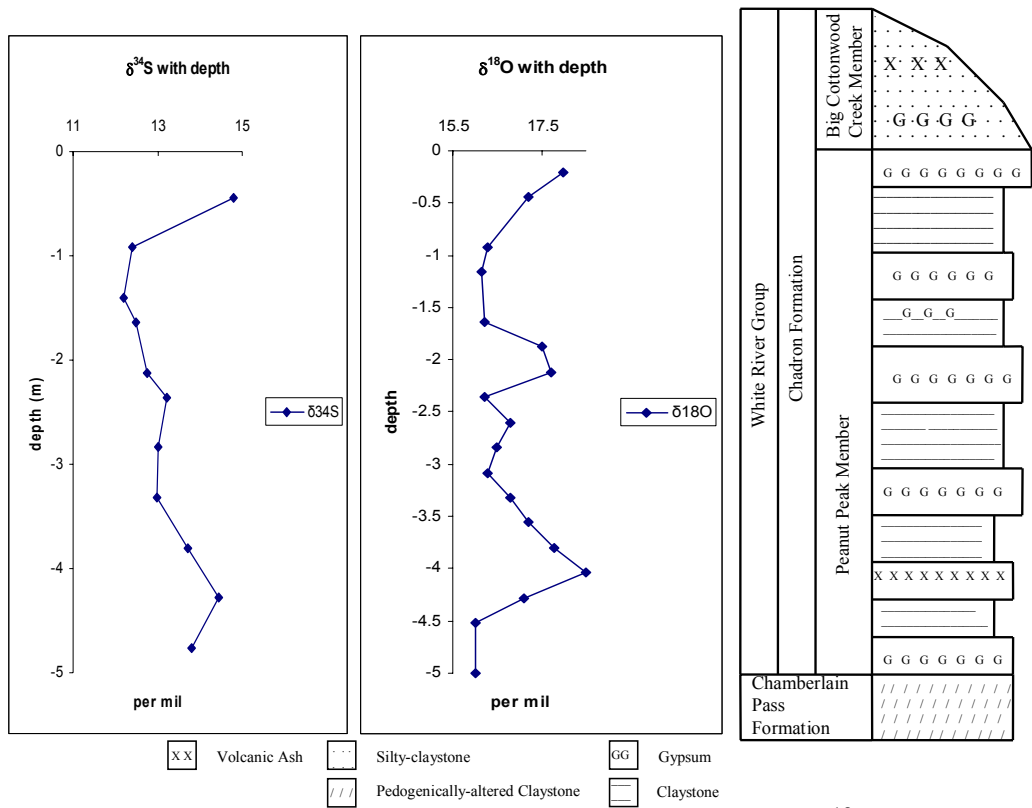


Figure 1.6: Stratigraphic log of Wolf Butte, NE, USA, including $\delta^{18}\text{O}$ and $\delta^{34}\text{S}$ values with depth in sampled sequence.

and have isotopic compositions of -33‰ to -15.4‰, for the unknown member and Mancos Member, respectively.

DISCUSSION

Lithology

Playa deposits in the Gering formation at Scotts Bluff consist of fine-grained massive volcanoclastic sandstone and a prominent volcanic ash layer. Gypsum occurs as calcite pseudomorphs in rosette and lenticular (8 cm diameter (Loope 1986)) form and is restricted to the top zone (~30 cm) of the tephra and the contact between the tephra and the sandstone (Figure 1.5). Gypsum formed displacively in the tephra and by encasement and replacement of sand grains within the sandstone (Loope 2005). This suggests gypsum in the sandstone developed from a sulfate-rich solution, likely originating from saturation of the volcanic tephra. The gypsum-layer does not possess a siliceous component. Massive siltstone lies beneath the Gering Formation; however, no dominantly clay-sized deposits are found at Scotts Bluff. The preserved primary sedimentary structures suggest sedimentation was continuous and uninterrupted by periodic playa desiccation (Loope 2005).

In contrast to Scotts Bluff, Peanut Peak deposits at Wolf Butte consist entirely of claystone, excluding one volcanic ash layer near the base. Gypsum occurs as massive horizons (the uppermost layer contains a siliceous component), and as micro-lenticular crystals within clay deposits. The massive gypsum structures likely formed during periods of low rainfall when groundwater levels fell and gypsum formed from evaporation. The lenticular gypsum crystals may have formed interstitially at the

brine/sediment interface during evaporation such as those identified by (Chen 1997), or may have originated as detrital material through reworking of massive gypsum by aeolian processes (Sanz 1994). Gypsum is not concentrated in the ash layer, as is seen in Scotts Bluff. Thus, sedimentologically, Scotts Bluff and Wolf Butte playa deposits are quite different.

Stable isotope compositions of sulfate

1. $\Delta^{17}\text{O}$

The Scotts Bluff gypsum contains highly positive $\Delta^{17}\text{O}$ values, ranging 0.19 to 5.8‰, whereas the Wolf Butte bears no discernable ^{17}O anomaly (i.e., $\Delta^{17}\text{O} = 0$) (Figure 1.8).

2. $\delta^{18}\text{O}$

Delta oxygen-18 values are very different at Wolf Butte than at Scotts Bluff. $\delta^{18}\text{O}_{\text{sulfate}}$ values of samples from Scotts Bluff range in value from $\sim +2$ to 14‰ (average value ~ 10 ‰) and are consistent with the involvement of ozone (O_3) or hydrogen peroxide (H_2O_2) during the atmospheric oxidation of reduced sulfur. H_2O_2 and O_3 are enriched in $\delta^{18}\text{O}$, $\delta^{18}\text{O}_{\text{H}_2\text{O}_2} = \sim 22$ ‰ to 53‰ and $\delta^{18}\text{O}_{\text{O}_3} = \sim 100$ ‰ and transfer their signal to product sulfate during oxidation. The $\delta^{18}\text{O}$ values of gypsum at Wolf Butte are, however, generally higher (~ 58 ‰) than those of Scotts Bluff, averaging 16.8‰ (Figure 1.7, 1.8).

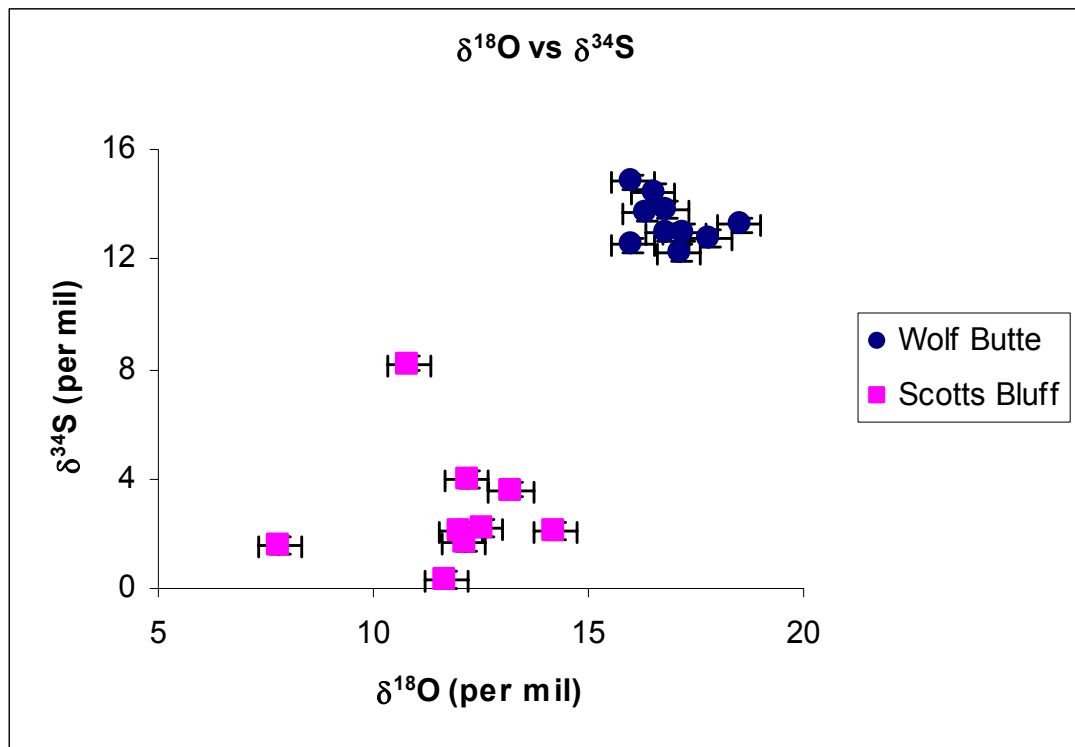


Figure 1.7: δ¹⁸O vs. δ³⁴S at Wolf Butte and Scotts Bluff, NE.

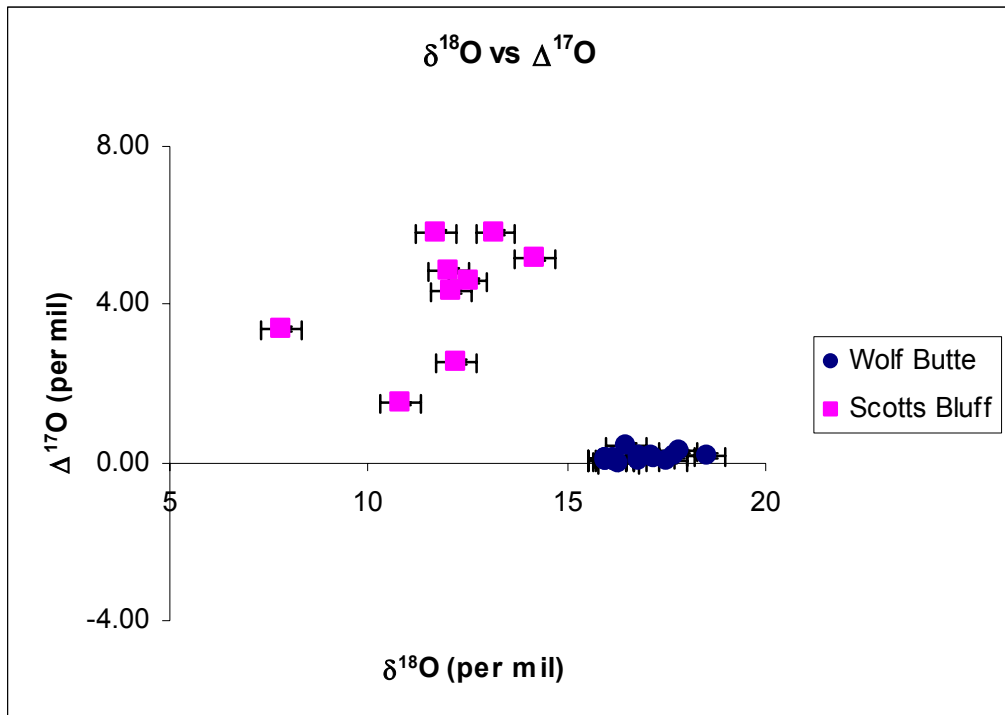


Figure 1.8: $\delta^{18}\text{O}$ vs. $\Delta^{17}\text{O}$ at Wolf Butte and Scotts Bluff, NE. Wolf Butte values ~ 0 and Scotts Bluff highly positive values suggest different sulfate origins.

3. $\delta^{34}\text{S}$

Sulfate-sulfur ($\delta^{34}\text{S}$) values of gypsum are much lower at Scotts Bluff than at Wolf Butte. Scotts Bluff values range from ~ 0 to $+8\text{‰}$ and are consistent with the source of reduced sulfur gases derived from volcanic emissions. The $\delta^{34}\text{S}_{\text{sulfate}}$ values at Wolf Butte have a narrow range (12.2 to 14.5‰) with a mean value of $+13.3 \pm 0.8\text{‰}$. This $\delta^{34}\text{S}$ value is much higher than those of Scotts Bluff, which may be due to post-depositional microbial recycling processes in the Wolf Butte playa. Two members of Pierre shale were analyzed for sulfide- $\delta^{34}\text{S}$ values and have isotopic compositions of -33‰ to -15.4‰ , for the unknown member and Mancos Member, respectively.

Comparison of the Scotts Bluff and Wolf Butte Playas

Oxidation of reduced sulfur gases by O_3 or H_2O_2 is the speculated origin of the ^{17}O -anomalous sulfate at Scotts Bluff. A likely scenario suggested by Bao (2003) is that massive volcanic sulfur emissions were transported to the Northern High Plains and were subsequently oxidized by tropospheric O_3 or H_2O_2 , which formed a persistent sulfuric aerosol haze. Once sulfate settled in a playa setting, the anomalous oxygen signature was preserved because of relatively rapid (Bao 2005) formation of gypsum crystals. Had the anomalous sulfate been subjected to water-saturated playa settings for a longer period of time, microbial reduction and oxidation processes would have attenuated the $\Delta^{17}\text{O}$ signature.

In contrast to Scotts Bluff, the gypsum sulfate at Wolf Butte has no distinct ^{17}O anomaly. This is thought to be typical of most playa sulfate seen around the world (Bao 2005). The absence of a sulfate ^{17}O anomaly in Wolf Butte playa suggests several

possibilities: 1) ^{17}O -anomalous sulfate aerosol was not deposited at Wolf Butte and was not a source of sulfate to the playa system; or 2) anomalous sulfate aerosol was deposited at Wolf Butte, but was later essentially erased by microbial recycling of sulfur. Either case is possible in terms of the isotopic data. In the following section, the Wolf Butte sulfate $\delta^{18}\text{O}$ and $\delta^{34}\text{S}$ data are discussed to constrain its source(s) of sulfate during the Eocene.

Both delta sulfur-34 ($\delta^{34}\text{S}$) and delta oxygen-18 ($\delta^{18}\text{O}$) values measured from samples of the Wolf Butte sulfates are higher than those of the Scotts Bluff sulfates. Possible origins for higher sulfate $\delta^{34}\text{S}$ or $\delta^{18}\text{O}$ values include: marine evaporates ($\delta^{34}\text{S} = \sim 21\text{‰}$ for modern seawater sulfate), volcanic ash leachates ($\delta^{18}\text{O}$ reaching 14.2‰, (Bao 2003)), and the residual sulfate after microbial sulfate reduction ($\delta^{18}\text{O}$ reaches approximately 19.1‰ or higher during sulfate reduction, (Fritz 1989)). No marine evaporite deposits (such as gypsum or halite) have been located in the vicinity; therefore a marine evaporite source can be safely excluded from the pool of possible origins for the Wolf Butte gypsum sulfate. Another possible source of sulfate at Wolf Butte could have come from volcanoclastic deposits, which were common in Northern High Plains during the late Eocene (Terry 2001). Sulfate carried by volcanic ashes (as ash leachates) can be a potential source of the sulfate in the playa. Another important source of sulfate is probably the oxidative weathering of pyrite-bearing Cretaceous shales in the region. The Cretaceous Pierre shale is ubiquitous in the Great Plains and underlies the Wolf Butte deposits (Figure 1.4).

One of the problems associated with concluding that ash leachates and shale weathering are sources of the sulfate signature is that neither initially possessed the high

sulfate $\delta^{34}\text{S}$ and $\delta^{18}\text{O}$ values observed at Wolf Butte. An extensive survey of sulfate leached from fresh volcanic ashes indicates they exhibit a range from -3.4 to 9.6‰ for $\delta^{34}\text{S}$ and 3.9 to 11.3‰ for $\delta^{18}\text{O}$ (Bao 2003), which are both lower than the Wolf Butte sulfate. Moreover, the sulfate derived from pyrite oxidation in Pierre Shale should have a much lower initial sulfate $\delta^{34}\text{S}$ value. This is because the pyrite's $\delta^{34}\text{S}$ values are extremely negative (-15 to -33‰) and oxidation processes do not result in much fractionation in sulfur stable isotopes between pyrite and sulfate. Therefore, the initially precipitated sulfate underwent a secondary fractionation processes in order to achieve the high $\delta^{34}\text{S}$ and $\delta^{18}\text{O}$ values observed at Wolf Butte. The most likely ^{34}S and ^{18}O enrichment process is microbial sulfate reduction in groundwater or within the Wolf Butte playa lake itself. The sedimentological evidence suggests a wet and more water-saturated playa environment existed for Wolf Butte than for Scotts Bluff, which is also consistent with the preservation of the $\Delta^{17}\text{O}$ signature in sulfate at Scotts Bluff. The intermediate sulfate $\delta^{34}\text{S}$ value (1.2‰) for gypsum crystals from the underlying paleosol horizon (Yellow Mound) in Wolf Butte may suggest a successive ^{34}S enrichment process for sulfate from the initial shale weathering (pyrite oxidation), to Yellow Mound gypsum, and then to the overlain Wolf Butte playa.

CONCLUSIONS

Wolf Butte and Scotts Bluff playas represent two distinctly different, end-member playas that existed in the Northern Great Plains during the Eocene and Oligocene. The isotopic data from Wolf Butte greatly differs from Scotts Bluff playa. The highly positive

$\Delta^{17}\text{O}$ values and $\delta^{34}\text{S}$ values near zero are accordant with a secondary atmospheric origin of sulfate for Scotts Bluff. At the same time, $\Delta^{17}\text{O}$ values of zero, and highly positive $\delta^{34}\text{S}$ and $\delta^{18}\text{O}$ sulfate values, at Wolf Butte indicate microbial processes may have altered initial sulfate values. In contrast to Scotts Bluff's atmospheric origin of sulfate, the likely major sources of Wolf Butte sulfate are volcanic-ash leachates and pyrite oxidation from Pierre Shale. Subsequent bacterial sulfate reduction in groundwater and playa water is required to explain the high $\delta^{34}\text{S}$ and $\delta^{18}\text{O}$ values for Wolf Butte sulfate.

FUTURE WORK

At present, the Scotts Bluff playa is an exception in terms of the sulfate oxygen isotopic composition. This suggests that a volcanic origin of sulfate to playa settings was not common in the High Plains during the Cenozoic. This study indicates the Wolf Butte playa may represent a playa of normal origin (groundwater, surface weathering processes) existing in the High Plains during the same era. Future work in this area should include multiple sulfate isotopic compositions of additional Cenozoic playa settings to further establish that the Scotts Bluff playa is truly unique.

CHAPTER 2.

SULFUR AND OXYGEN ISOTOPE CHARACTERIZATION RAINWATER SULFATE, BATON ROUGE, USA

INTRODUCTION

Combustion of sulfur-containing fossil fuels release large quantities (~70 Tg of sulfur per year) of sulfur dioxide, a sulfate precursor gas, into Earth's atmosphere annually (Smith 2001). Since the industrial revolution, the atmospheric sulfur cycle has been dominated by anthropogenic sources (Seinfeld and Pandis 1998). In the atmosphere, SO₂ is readily oxidized forming sulfate particulates. It has been suggested by (Ghan 1998) the concentration of sulfate, and thus SO₂, in the atmosphere is directly related to the formation of sulfate aerosol. In the atmosphere, sulfate aerosols can function as cloud condensation nuclei (Ghan; Lee 2001; Pirjola 1998; Turco 2000), which directly and indirectly affect Earth's albedo and ultimately climate. This is accomplished by reducing solar irradiance and altering the reflective properties of clouds, respectively (Kogan 1997; Mitchell 1995; Thomas 2003). Although SO₂ has a relatively short lifetime in the atmosphere of days to weeks (Seinfeld 1998), the oxidative pathways affect the lifetime and transport of sulfate aerosols(Charlson 1978). It is known when atmospheric conditions vary (i.e., pH, moisture content, and temperature), different sulfur dioxide oxidative pathways dominate (oxidation by either O₃, O₂, H₂O₂, or ·OH radicals) in the troposphere (Savarino 2000b). In La Jolla, California, Lee (2001) reported SO₂ oxidation by ozone predominates over other pathways during the winter season, while ·OH is the dominant oxidant during the summer. Meteorological, climatic, and atmospheric chemical conditions in the Baton Rouge area are different from those of La Jolla, e.g.,

high humidity, high O₃ concentration in the summer, and less sea-salt influence.

Therefore, the dominant formation pathway for atmospheric secondary sulfate in Baton Rouge might be different from those in other regions. Multiple stable isotope compositions of oxygen-bearing compounds such as sulfate provide insight into atmospheric oxidation processes (Lee 2001; Romero 2003). To determine if seasonal variations in the oxidative pathways of sulfur dioxide occur in Baton Rouge air shed as they have been found in California (Lee 2001; Romero 2003), a complete stable isotope characterization of atmospheric sulfate was performed, which is detailed here.

The origin, formation, and dynamics of atmospheric sulfate have been studied extensively (Botha 1994; Boulaud 1978; Charlson 1978; Friedlander 1978; Leung 2001; Pirjola 1998; Polissar 1998; Ravishankara 1997; Rodriguez 2002; Turco 2000). In addition, extensive studies have investigated isotopic compositions of sulfate to further understand the chemistry of sulfur oxides in the atmosphere (Herut 1995; Holt 1981; Holt 1978; Jamieson 2000; Jedrysek 2000; Lee 2001; Romero 2003). Holt (1981, 1978) measured $\delta^{18}\text{O}_{\text{sulfate}}$ to understand sulfate aerosol formation, and Herut (1995) and Jamieson (2000) analyzed both $\delta^{18}\text{O}_{\text{sulfate}}$ and $\delta^{34}\text{S}_{\text{sulfate}}$ to trace sources of sulfate and sulfur, respectively, in urban and coastal precipitation. Savarino (2000b) investigated the multiple oxygen isotopic compositions of sulfate produced from different oxidative reactions to investigate the origin of mass-independent signatures; Lee (2001) examined anomalous isotopic composition of oxygen in atmospheric sulfate to trace the oxidative pathway; and Romero (2003) documented the non-mass-dependent sulfur isotope composition in atmospheric aerosol sulfate.

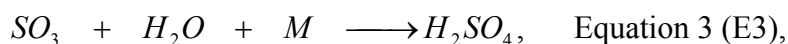
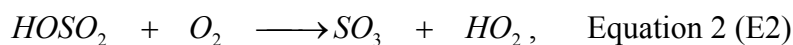
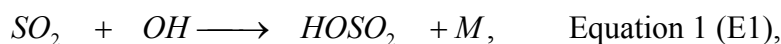
The oxygen-17 anomaly is the deviation of the ratio $\delta^{17}\text{O}/\delta^{18}\text{O}$ from the mass-

dependent fractionation line $\delta^{17}\text{O} = 0.52 \times \delta^{18}\text{O}$ (δ (‰) = $(R_{\text{sample}}/R_{\text{standard}} - 1) \times 1000$, where $R = \delta^{18}\text{O}/\delta^{16}\text{O}$, $\delta^{17}\text{O}/\delta^{16}\text{O}$), which chemical and biochemical processes follow. Only sulfate of atmospheric origin has been found to possess a non-mass-dependent signature characterized by:

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

The anomalous oxygen isotope signature is gained during oxidation of sulfur dioxide by a $\Delta^{17}\text{O}$ -bearing species such as ozone (~35‰) or hydrogen peroxide (~2‰) (Lee 2001; Savarino 2000b). In this reaction either one or more than one, depending on which species is the oxidant, oxygen molecules is transferred to the product sulfate. In this project an investigation is undertaken of the oxygen-17 anomaly coupled with $\delta^{18}\text{O}$ and $\delta^{34}\text{S}$ isotopic compositions of atmospheric sulfate to determine the oxidative pathways of reduced gaseous sulfur species (e.g., SO_2 and H_2S) in Baton Rouge region.

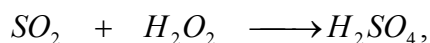
It has been well established that reduced sulfur compounds (e.g., SO_2 and H_2S) undergo both aqueous-phase and gas-phase oxidation in the atmosphere. The specific oxidative pathway depends on atmospheric conditions (i.e., pH or humidity). Gas-phase oxidation of reduced sulfur dominates when humidity is low and the principal oxidants include molecular oxygen (O_2) or the OH radical ($\cdot\text{OH}$). Savarino (2000) proposed the following mechanisms for oxidation by $\cdot\text{OH}$ and O_2 ,



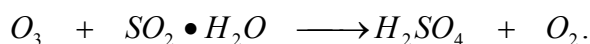
where M is an inert third body molecule. The sulfur and oxygen isotopic compositions

($\delta^{18}\text{O}$, $\Delta^{17}\text{O}$, $\delta^{34}\text{S}$) of product sulfate reflect the compositions of the sulfur source and oxidants (water vapor and gaseous oxidant), respectively. Because none of the chemical species involved in reactions E1-E3 possess an oxygen-17 anomalous signature, no $\Delta^{17}\text{O}$ value is observed in product sulfate.

Ozone (O_3) and hydrogen peroxide (H_2O_2) are the principal aqueous-phase oxidants of SO_2 . Savarino (2000) proposes the following mechanisms for the aqueous-phase oxidation of SO_2 by H_2O_2 when pH is < 5 ,



and by O_3 when pH is ≥ 6 ,



Both H_2O_2 and O_3 possess highly positive $\Delta^{17}\text{O}$ values ($\sim +2\text{‰}$ and $+35\text{‰}$, respectively) and this oxygen-17 signature is transferred to product sulfate during oxidation. The above equation demonstrates one oxygen molecule is transferred from O_3 to product sulfate (SO_4), while two oxygen molecules are transferred to SO_4 when H_2O_2 acts as oxidant. Therefore, the magnitude of the $\Delta^{17}\text{O}$ value in product sulfate reflects the oxidant. Because ozone contains $\Delta^{17}\text{O}$ values as high as 35‰ , highly positive values are expected when ozone is oxidant ($+5$ to $+8\text{‰}$). Because H_2O_2 possesses $\Delta^{17}\text{O}$ values of approximately $+2\text{‰}$, relatively lower values are observed when H_2O_2 is the oxidant ($< +1\text{‰}$).

Over a 1.4 year period, twenty rainwater samples were collected for isotope analyses of total wet and dry atmospheric deposition of sulfate and nitrate. However in the case of nitrate, high levels of organic contamination in rainwater have inhibited the ability to precipitate clean ($> 98\%$ pure) nitrate for isotopic measurements ($\delta^{18}\text{O}$, $\Delta^{17}\text{O}$,

$\delta^{15}\text{N}$) even after several rinses through Supelco Discovery DSC-18 12 ml solid phase extraction filters. A purification method is currently being developed to separate nitrate through the use of an Ion Chromatography Preparation System to obtain reliable isotopic compositions. Therefore, stable isotope data in this report will focus on sulfate only.

METHODOLOGY

Rainwater collection

Rainwater was collected from the roof of Howe-Russell Geoscience Complex at Louisiana State University, using 5 gallon buckets made of polyvinyl chloride. This location is approximately 6.2 miles southwest of one of the largest oil and gas refineries in the world which is located north of downtown Baton Rouge (Figure 2.1). The sampling location is along the main air mass trajectory, ~260 miles northeast of Houston, Texas, where more than fifteen oil and gas refineries are located (Figure 2.2). In this study twenty rainwater samples were collected over a 17 month period. The frequency with which these samples were taken depended on magnitude and timing of rainfall events; during the rainy season (November to February) approximately three samples were collected per month and one sample per six weeks were collected during drier periods. After collection of samples, the rainwater was evaporated in 2 liter beakers on hot plates to concentrate sulfate.

Measurement of major anions and cations in rainwater

Sulfate, nitrate, and chloride concentrations in rainwater were measured using an AS14 Dionex anion column. Sodium and ammonium were measured using a CS14

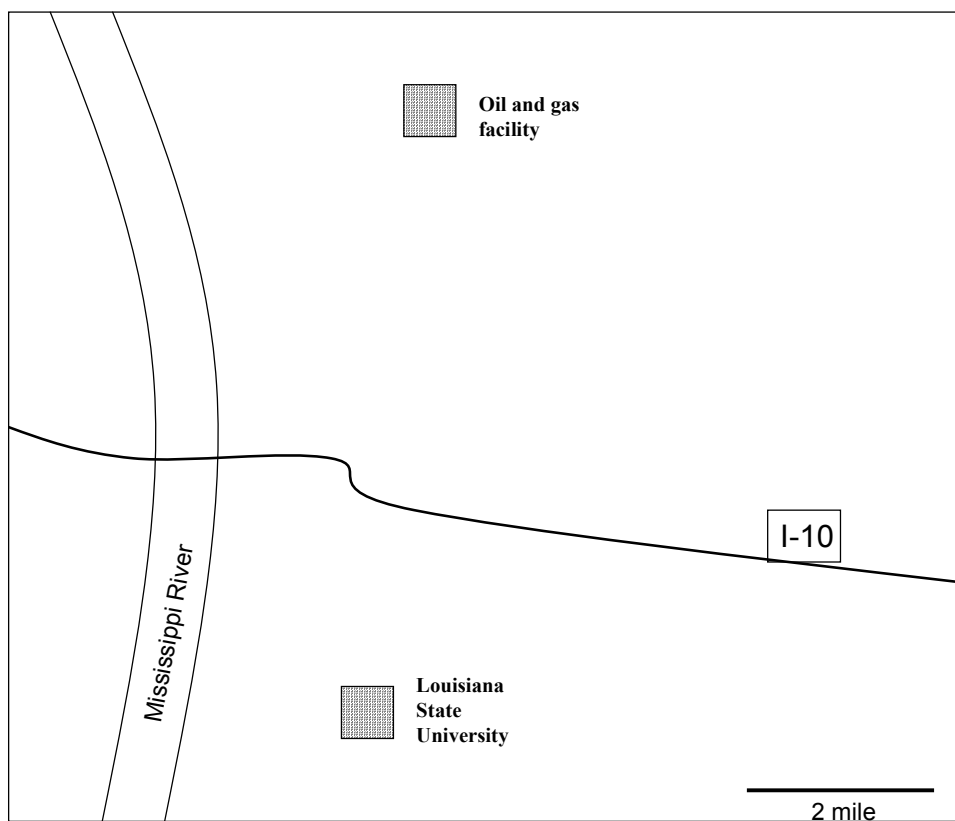


Figure 2.1: Sample location's (Louisiana State University) proximity to a local oil and gas refinery. The refinery may be a minor source of sulfate in Baton Rouge rainwater.

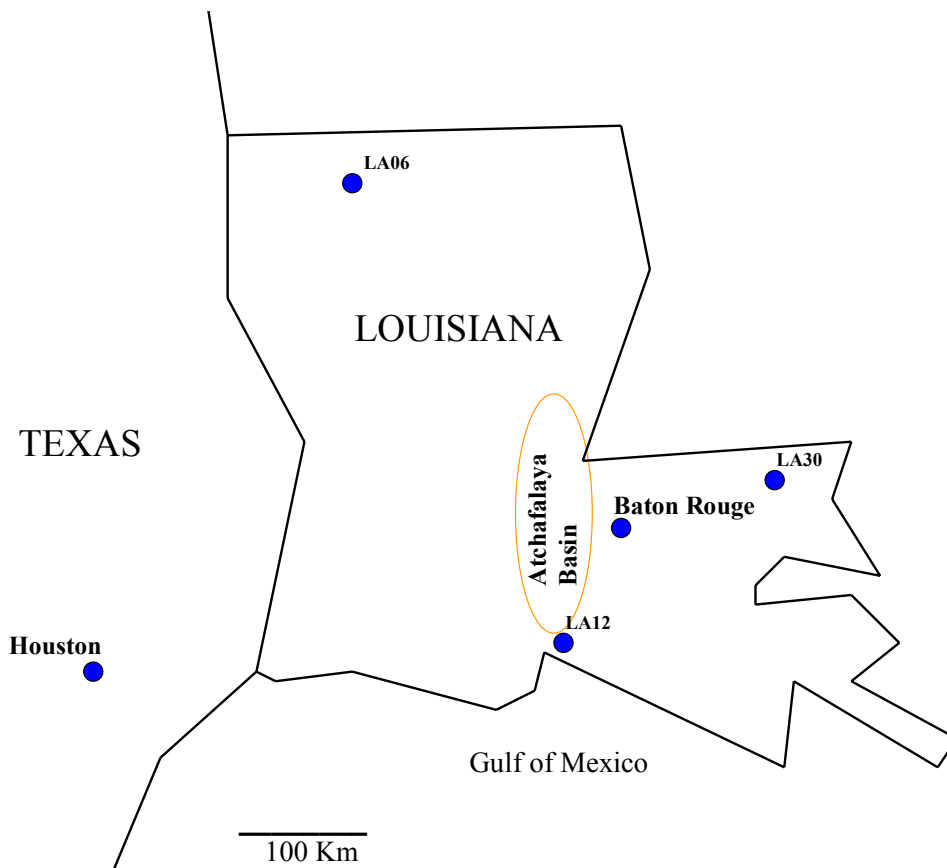


Figure 2.2: Location map for relevant features associated with Baton Rouge rainwater study. The map includes Baton Rouge, La, the Louisiana coast of the Gulf of Mexico, the Atchafalaya Basin, three National Atmospheric Depositional Program monitoring stations, and Houston, Texas.

Dionex cation column. All measurements were conducted on a Dionex ICS-90 Ion Chromatograph.

Estimating sea-salt sulfate in Baton Rouge area

Baton Rouge is located approximately 175 km north of the Louisiana coast of the Gulf of Mexico (Figure 2.2). To determine marine sulfate component of the total atmospheric sulfate measured, sodium concentrations in the rainwater were determined. Because the chloride ion (Cl^-) is volatile when associated with hydrogen in the atmosphere, sodium content was used to correct for sea-salt input using:

$$f_{ss} (\%) = \left(\frac{0.252 \times Na^+}{S^{+6}} \right) \times 100$$

from (Calhoun 1991).

Sulfate Extraction

Rainwater was evaporated down to ~30 ml to concentrate sulfate. After cooling, the solution was run through Supelco Discovery DSC-18 12 ml solid phase extraction filters (Discovery DSC-18 12, Lot No. SP29531) three times using a water-driven vacuum system to draw rainwater solution through filters. The filter was rinsed twice with distilled and deionized water to collect remaining sulfate. The concentrated sample solution was then filtered again excluding material larger than 0.2 μm particle diameter to exclude any particulates. The solution was then placed on a hot plate for an additional ~20 minutes to heat the solution before adding approximately 1-2 ml 1 M HCl to acidify the solution and drive out carbonate ion as CO_2 . The acidified solution was then removed

from heat after 10 minutes. In order to efficiently precipitate barium sulfate (BaSO_4), an aqueous saturated solution of barium chloride (BaCl_2) was added. The BaCl_2 solution was prepared with barium chloride (Fisher Scientific, 99.0% purity), distilled and deionized water, and acidified with HCl solution (1 molar solution prepared from 10 M solution from Fisher, 36.5% assay). For storage pending analysis, the supernatant was poured into a separate centrifuge tube, wrapped in foil, and stored in a refrigerator.

In order to minimize potential nitrate contamination of the samples prior to sulfate isotopic analysis, a second round of processing was performed. This involved redissolved and reprecipitated sulfate second and third times using a Diethylenetriaminepentaacetic acid (98% assay, Fisher) (DTPA) dissolution and reprecipitation method (DDARP method) (Bao 2005, in preparation). The purpose of this step is to minimize nitrate contamination of the precipitated sulfate. The dissolution and reprecipitation solution was prepared using DTPA and 50% weight/weight sodium hydroxide solution (98% assay, Fisher). This resulted in an aqueous solution containing 0.05 M DTPA and 1 M NaOH. Once barite samples were completely redissolved in the DTPA solution, concentrated HCl (10 M) was added to reprecipitate BaSO_4 . The sample was centrifuged, supernatant was poured out and DTPA solution was added a second time. The sample re-dissolved, concentrated HCl was added to reprecipitate BaSO_4 a second time as DTPA-SO_4 . DTPA-BaSO_4 was washed four times with distilled and deionized H_2O and placed in oven for two days.

Nitrate extraction

The supernatant after the first sulfate extraction was neutralized using 2 M NaOH

(98% assay, Fisher) for storage. Later the solution was run through a cation column (CG10 in H⁺ form, Resin Tech) in H⁺ form at a flow rate of approximately 2 ml min⁻¹ to remove remaining cations in solution. Prewashed solid silver oxide (AgO) (99% assay, Alfa Aesar) was added to the solution passed through the column to remove chloride anion from solution. The solution was then filtered using < 1 μm filter paper (Qualitative P4, Fisher) and placed in a freeze dryer (Labconco Freezone© 4.5) to obtain AgNO₃ crystals for oxygen analyses.

Isotope ratio measurements

1. Δ¹⁷O

Oxygen for Δ¹⁷O analysis was generated offline using CO₂-laser fluorination vacuum system at Oxy-Anion Stable Isotope Center (OASIC) at Louisiana State University. Barite samples for analysis were prepared by first weighing portions to ~ 6-10 mg and placing them into small wells within a stainless steel plate. Oxygen gas (O₂) collection tubes with molecular sieve heat at 200°C for ~20 minutes to clean the sieve before sample burning and collection. Standard runs consist of settings of 1450-3000μm laser beam diameter, lasing with continuous wave, and laser intensity between ~3.5 and 5 Watt. Bromine pentafluoride (BrF₅) is loaded into lasing chamber and samples bombarded with laser for ~2 minutes. The generated oxygen gas is then passed through 5 liquid nitrogen traps before O₂ (~0.2 to 0.7 Torr) is collected in sample tubes, submerged in liquid nitrogen. In this process samples for analysis were collected exactly over a 6 minute period.

Oxygen (O₂) was then transferred to a 253 MAT Finnigan Ratio Mass Spectrometer

for $\delta^{17}\text{O}$ and $\delta^{18}\text{O}$ isotope analysis. For this the sample tube (O_2) was heated ~10 minutes at 80°C before the analysis run.

2. $\delta^{18}\text{O}$

The $\delta^{18}\text{O}$ was determined online using Thermal Conversion Elemental Analyzer (TCEA) coupled with a 253 MAT Finnigan Ratio Mass Spectrometer at Oxy-anion stable isotope center (OASIC) at Louisiana State University. For oxygen analysis $220 \pm 20 \mu\text{g}$ aliquots barite were loaded into 3.5 x 5 mm silver capsules. TCEA runs continuous flow with oven temperature at 1450°C , column temperature 95°C , and flow rate of 85 ml min^{-1} with a carrier gas of helium.

2. $\delta^{34}\text{S}$

The $\delta^{34}\text{S}$ measurement of sulfate was performed by Jay Kaufman at the University of Maryland. Micromass Isoprime mass spectrometer using continuous flow inlet systems coupled with high-temperature combustion ovens and gas chromatographic separation were utilized for isotope measurements.

Isotope data are reported using the international standards Vienna Standard Mean Ocean Water (VSMOW) and Vienna Canyon Diablo Triolite (VCDT) for oxygen and sulfur, respectively. The analytical errors are $\pm 0.06\text{‰}$, $\pm 0.5\text{‰}$ and $\pm 0.3\text{‰}$ for $\Delta^{17}\text{O}$, $\delta^{18}\text{O}$, and $\delta^{34}\text{S}$, respectively.

RESULTS

Sulfate and nitrate concentrations

Sulfate concentrations in rainwater varied between 0.64 parts per million (ppm) and 13.3 ppm, nitrate concentrations varied between 0.23 ppm and 2.01 ppm. Sulfate/nitrate ratios varied between 1.15 and 3.82, the higher ratios were observed during longer collection periods (Table 2.2).

Isotopic Compositions

Isotope compositions of rainwater sulfate range from 0.26 to 1.43‰ ±0.05 with an average value of 0.7‰ ± 0.34‰ for $\Delta^{17}\text{O}$; from 11.8 to 19.3‰ with an average value of 14.5‰ ± 2.3‰ for $\delta^{18}\text{O}$; and from -1.4 to 3.8‰ with an average value of 1.3‰ ±1.5‰ for $\delta^{34}\text{S}$, respectively (Table 2.1, 2.2). Figures (2.4, 2.5, and 2.8) indicate a weak correlation between $\Delta^{17}\text{O}$ values and sulfate concentration, $\Delta^{17}\text{O}$ and $\delta^{18}\text{O}$ values, and SO_4/NO_3 ratios and $\Delta^{17}\text{O}$ values, respectively. No correlation was observed for $\delta^{18}\text{O}$ and $\delta^{34}\text{S}$ values (Figure 2.6).

For nitrate, isotope values for one datum (nitrate precipitated from rainwater sample) are 23.4‰ (±0.06‰) for $\Delta^{17}\text{O}$ and 59.6‰ for $\delta^{18}\text{O}$. We will not discuss the implication of these nitrate data. A new method for the extraction of pure nitrate from rainwater is in progress and therefore only sulfate data are discussed in this study.

Seasonal trends

No seasonal variation was observed for $\Delta^{17}\text{O}$ over the 17 month period (Figure 2.7, 2.8). $\delta^{18}\text{O}$ lows (11.3 and 11.8‰) were observed during the winter seasons of 2003

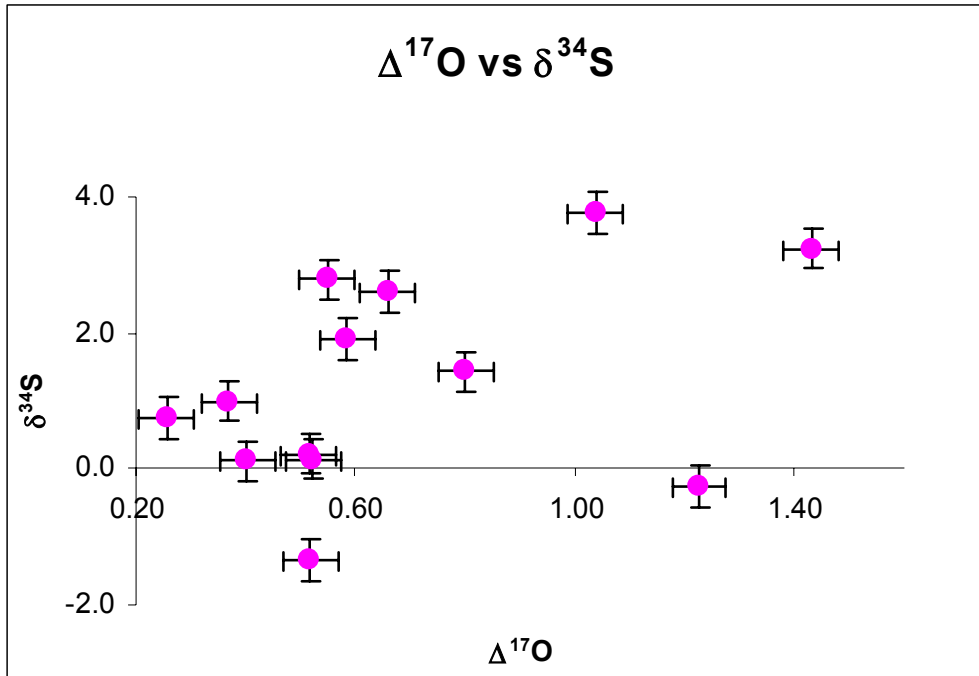


Figure 2.3: Correlation plot for Baton Rouge rainwater sulfate $\Delta^{17}\text{O}$ versus $\delta^{34}\text{S}$. No apparent trend was observed.

Table 2.1: Sulfate isotopic compositions of rainwater and aerosol studied worldwide. (Lee 2001)¹; (Romero 2003)²; (Jamieson 2000)³; (Jedrysek 2000)⁴; (Cortecci 1970; Holt 1978; Jamieson 2000; Jedrysek 2000; Lee 2001; Mizutani 1969; Rafter 1967; Romero 2003) (Cortecci 1970)⁹

Location	Sulfate Type	$\delta^{18}\text{O}$ (‰)	$\Delta^{17}\text{O}$ (‰)	$\delta^{34}\text{S}$ (‰)
Baton Rouge, Louisiana	Rainwater	+11.8 to +19.3 (MV 14.5 \pm 2.3‰, n=15)	+0.25 to +1.43 (MV 0.7 \pm 0.3‰)	-1.3 to +3.8 (MV 1.3 \pm 1.5‰)
La Jolla, California ¹	Rainwater	+7.2 to +15.1 (MV 11.0 \pm 2.3‰)	+0.2 to +1.4	no data
La Jolla, California ¹	Aerosol	+5.3 to +15.2 (MV 8.9 \pm 2.2‰)	+0.4 to +1.4	no data
WMRS, California ¹	Aerosol	+5.2 to +10.1	+1.0 to +1.6	no data
La Jolla, California ²	Aerosol	no data	+0.2 to +1.35	+1.84 to +19.1 (MV 9.9 \pm 6.0‰)
Bakersfeild, California ²	Aerosol	no data	+1.3 to +3.00	+3.05 to +12.32 (MV 5.7 \pm 2.7‰)
WMRS, California ²	Aerosol	no data	+1.3 to +1.4	+4.2 to +4.7 (MV 4.4 \pm 0.4‰)
Wroclaw, Poland ³	Rainwater	+10.9 to +19.6 (MV 14.2‰)	no data	+0.92 to 6.02 (MV 4.26‰)
Eastern Canada ⁴	Rainwater (long-range anthropogenic)	+14.7	no data	+4.4
Eastern Canada ⁴	Rainwater (coastal)	+28.9	no data	+6.8
Eastern Canada ⁴	Rainwater (local)	+12.8	no data	+10
Israel ⁵	Rainwater	no data	no data	0.0 to +15.3
Illionios, USA ⁶	Rainwater	+4.0 to +18 (MV ~14‰)	no data	no data
Gracefield, New Zealand ^{7,8}	Rainwater (near harbor)	MV 11.2‰ (n=3)	no data	MV 9.1‰ (n=17)
Kaitoke, New Zealand ⁷	Rainwater (near mountains)	MV 10.5‰ (n=2)	no data	MV 12.7‰ (n=2)
Pisa, Italy ⁹	Rainwater	+5 to +17‰ (n=71)	no data	-2.5 to +7.1‰ (n=65)

Table 2.2: Rainwater data for Baton Rouge, including ion concentrations, percent sea salt concentrations, and stable isotope compositions. Fraction sea salt (fss) and non-sea salt fraction (nss) contributions were calculated based on both chloride and sodium concentrations in Baton Rouge rainwater.

Collection date	SO4 (mg/L)	NO3 (mg/L)	Cl(mg/L)	Na (mg/L)	NH3 (mg/L)	f%ss(Na)	NSS%(Na)	f%ss(Cl)	NSS%(Cl)	$\delta^{17}\text{O}$	$\Delta^{17}\text{O}$	$\delta^{18}\text{O}$	$\delta^{34}\text{S}$
9/2/2003	2.55	0.90	1.01	0.27	0.82	2.63	97.37	2.54	97.46				1.43
9/25/2003	1.26	0.57	0.33	4.35	0.38	87.00	13.00	1.26	98.74	0.04	0.80	12.10	-1.35
11/3/2003	11.33	9.83	2.13	0.96	0.28	2.14	97.86	11.30	88.70	-1.07	0.52	12.10	0.75
11/18/2003	2.16	1.46	1.36	0.30	0.20	3.48	96.52	2.14	97.86	-1.62	0.26	11.30	0.14
12/1/2003	0.64	0.24	0.35					0.63	99.37	3.47	0.52	19.30	-0.25
12/15/2003	3.53	1.45	1.38					3.51	96.49	0.57	1.23	11.80	0.22
12/29/2003	1.57	0.48	1.09	1.67	1.35	26.86	73.14	1.55	98.45	2.03	0.52	14.50	0.12
1/19/2004	3.95	1.45	1.59	0.54	0.40	3.46	96.54	3.93	96.07	2.09	0.40	15.30	2.79
2/2/2004	1.37	0.37	0.90	0.69	0.29	12.60	87.40	1.36	98.64	0.31	0.55	13.30	3.76
2/11/2004	1.16	0.38	0.55	0.56	0.46	12.08	87.92	1.15	98.85	2.53	1.04	16.10	1.90
2/26/2004	2.02	0.79	0.62					2.02	97.98	2.58	0.59	17.10	
4/28/2004	13.30	3.48	3.48					13.25	86.75				0.99
5/4/2004	1.46	0.70	0.29	0.98	0.40	16.91	83.09	1.46	98.54	2.13	0.37	16.60	3.24
5/19/2004	1.41	0.77	1.27	1.83	0.50	32.83	67.17	1.39	98.61	4.88	1.43	15.70	2.60
6/7/2007	2.54	1.20	2.15				100.00	2.51	97.49			14.50	
6/29/2004	1.36	0.79	0.86					1.35	98.65	2.82	0.66	14.70	
9/10/2004													
10/13/2004	1.32	0.45	0.64					1.32	98.68				

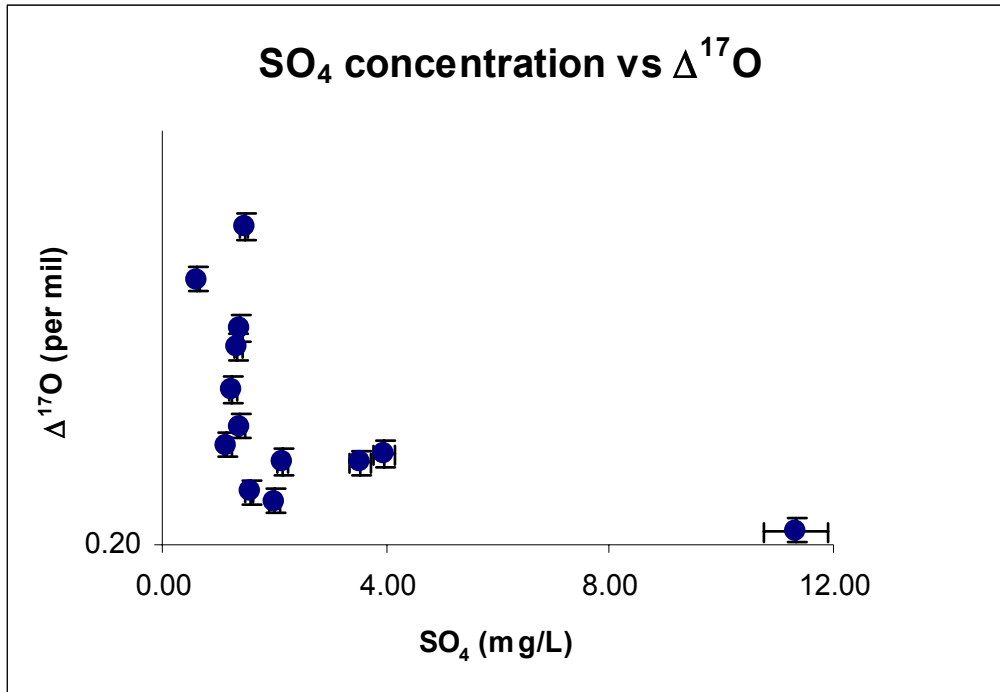


Figure 2.4: Correlation plot for Baton Rouge rainwater sulfate: sulfate concentration versus $\Delta^{17}\text{O}$. $\Delta^{17}\text{O}$ generally decreases with increasing sulfate concentration.

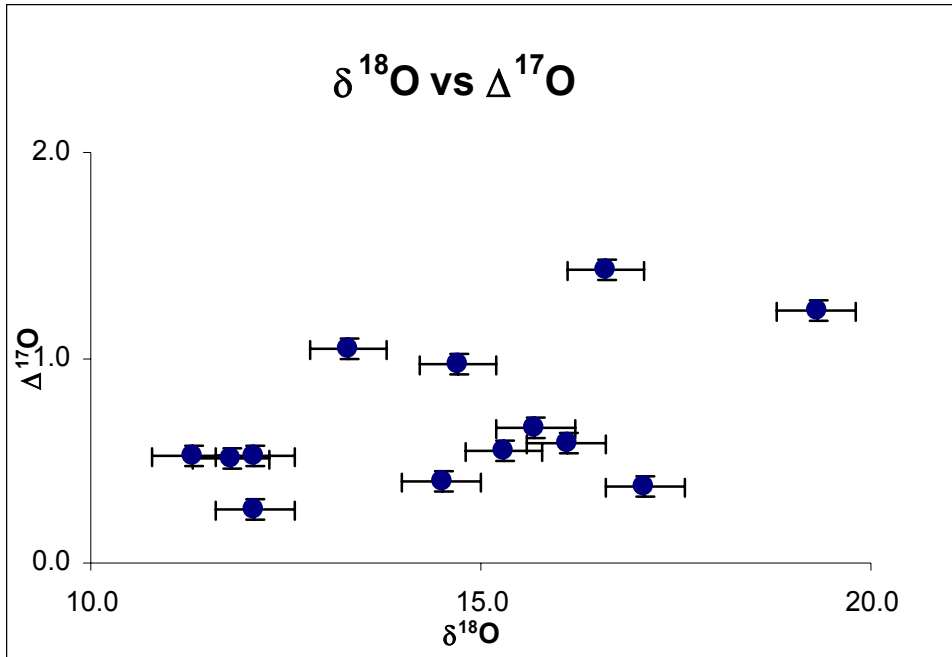


Figure 2.5: Correlation plot for Baton Rouge rainwater sulfate: $\delta^{18}\text{O}$ versus $\Delta^{17}\text{O}$. A weak positive correlation between the two variables was observed.

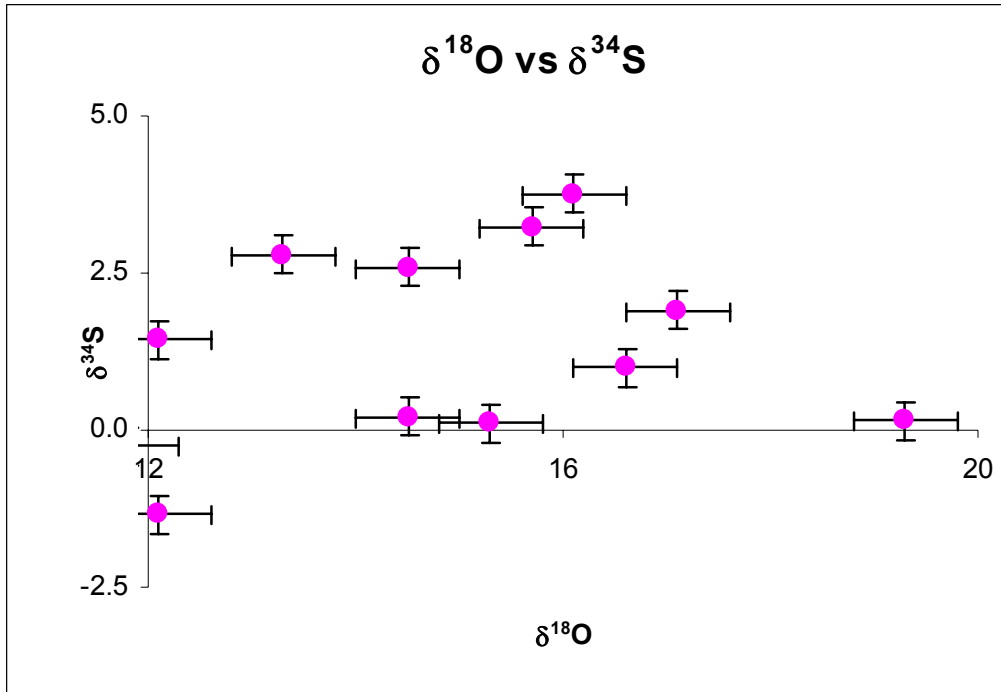


Figure 2.6: Correlation plot for Baton Rouge rainwater sulfate: $\delta^{18}\text{O}$ versus $\delta^{34}\text{S}$. No apparent trend was observed.

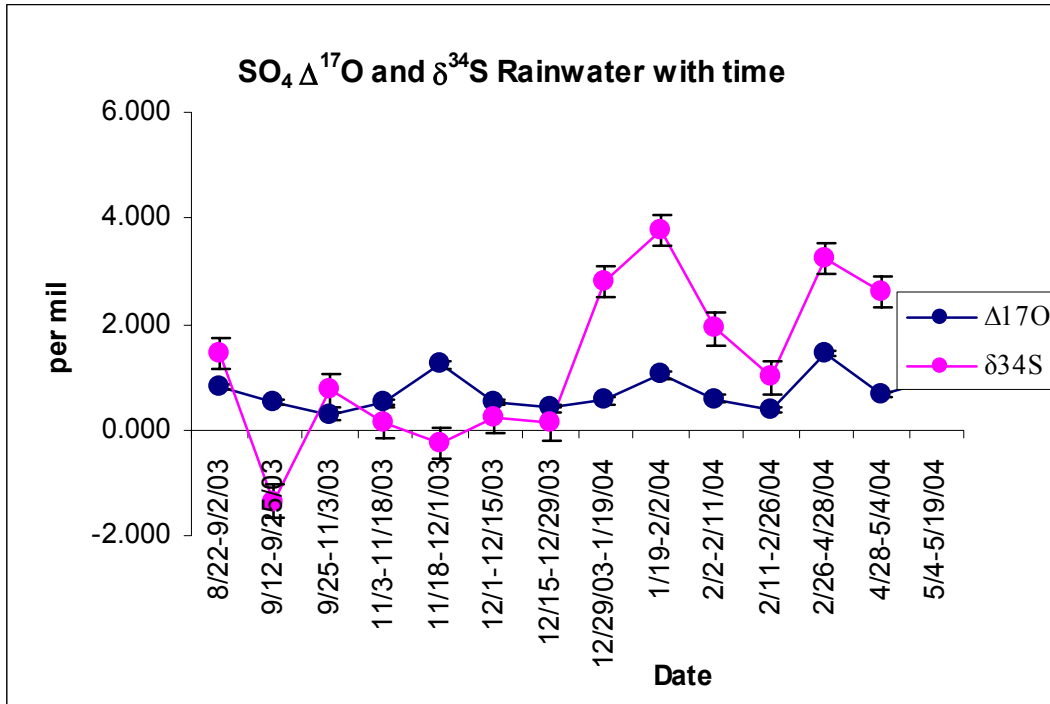


Figure 2.7: $\Delta^{17}\text{O}$ and $\delta^{34}\text{S}$ variation in rainwater sulfate with time.

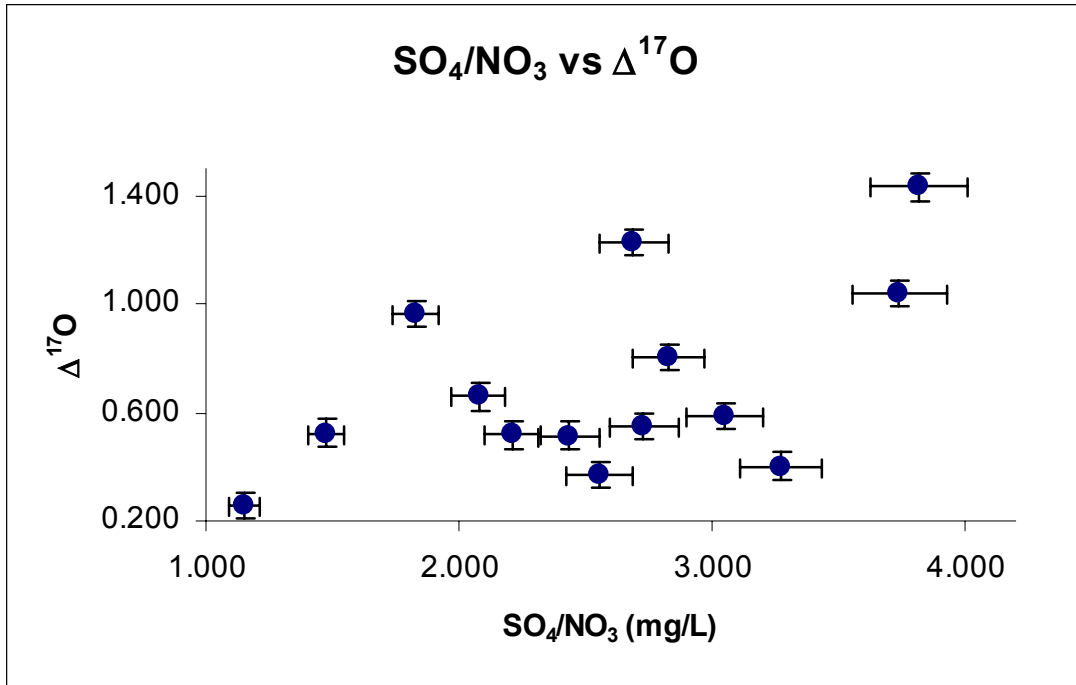


Figure 2.8: Sulfate/nitrate ratio in rainwater versus rainwater $\Delta^{17}\text{O}_{\text{sulfate}}$.

and 2004 (Table 2.1, 2.2; Figure 2.3). $\delta^{34}\text{S}$ peak values were observed during February and May of 2004, and lows during October and December 2003.

DISCUSSION

Previous measurements on oxygen isotope compositions of atmospheric sulfate are potentially erroneous due to the contamination derived from small amounts of atmospheric nitrate occluded in precipitated barite during analytical processing. This small occlusion turns out to be serious because we now know that atmospheric nitrate has extremely positive $\Delta^{17}\text{O}$ and $\delta^{18}\text{O}$ value up to $\sim 25\%$ and 90% , respectively (Michalski 2003). Meanwhile, it has been found that laboratory precipitated BaSO_4 from concentrated rainwater samples can occlude up to 25% nitrate (Bao 2005, in preparation). Therefore, the small quantity of occluded nitrate may obscure the barite's oxygen isotope signatures. We adopted the DTPA dissolution and reprecipitation (DDARP) method to ensure that our $\Delta^{17}\text{O}_{\text{sulfate}}$ is free of nitrate contamination. However, the possibility that nitrate may be occluded into laboratory barite implies that many of the rainwater sulfate oxygen isotope data from previous studies, such as Lee (2001), require revision.

The only multiple stable isotope compositions of atmospheric sulfate measured thus far other than this study, are those from La Jolla, California (Lee 2001). The $\delta^{34}\text{S}$ values of rainwater sulfate are in general higher than ours (mean value $9.9\% \pm 6.0\%$). This can be explained by La Jolla's close proximity to the Pacific Ocean (~ 1 km) which therefore receives a larger portion of sea-salt sulfate contribution in rainwater. The $\Delta^{17}\text{O}$ values are comparable to our results while $\delta^{18}\text{O}$ values are lower than our data. However,

their oxygen isotope data are not further discussed due to uncertainties in possible nitrate contamination.

One of the salient features of Baton Rouge rainwater sulfate data is that sulfate/nitrate ratios in rainwater at the sampling location are on average more than twice the ratios measured in two remote monitoring stations ~75 km to the northeast and ~50 km directly southwest to this study's location. The cause of this elevated sulfate content is unknown. Possibilities include dust input from a nearby construction site and/or downwind transport from emissions derived from an oil and gas refinery facility ~2 miles northwest to the sampling site.

$\Delta^{17}\text{O}$ values varied from 0.26 to 1.43‰ ($\pm 0.06\text{‰}$, $n=14$), and no seasonal variation was observed (Figure 2.1). The positive values are consistent with the dominant oxidative pathway via heterogeneous oxidation by O_3 or H_2O_2 . The small $\Delta^{17}\text{O}$ values ($< 1.5\text{‰}$) also indicate that H_2O_2 is the overwhelming oxidant for atmospheric sulfur oxidation in the region. Atmospheric sulfate formed via oxidation by O_3 should have a much higher $\Delta^{17}\text{O}$ due to the high $\Delta^{17}\text{O}$ of O_3 (up to $\sim 35\text{‰}$). This is consistent with Baton Rouge's meteorological and climatic conditions that are characterized by high humidity and a nearly constant rainwater pH ~ 4.7 year-around (average pH results from three Louisiana National Atmospheric Deposition Program monitoring stations (Figure 2.2)). Lee (2001) showed that at pH < 5 , H_2O_2 is the dominant oxidant, whereas at pH > 6 , O_3 becomes the kinetically favored oxidant for SO_2 oxidation in aqueous phase. However, the higher end of the $\Delta^{17}\text{O}$ value ($\sim 1.4\text{‰}$) exhibited by Baton Rouge rainwater suggests that O_3 still plays a minor role in the oxidation of sulfur in the area. The specific meteorological condition that was related to these high $\Delta^{17}\text{O}$ data points has yet to be

identified.

Estimated sea salt contents conclude that less than two percent of the sulfate in Baton Rouge rainwater had a seawater origin for any given collection period. Therefore, the $\delta^{18}\text{O}_{\text{sulfate}}$ (mean value of $+14.5\text{‰} \pm 0.5\text{‰}$, $n = 15$) should reflect the oxygen signatures of local meteoric water as well as those of oxidants such as O_3 and H_2O_2 . The $\delta^{18}\text{O}$ values lie within the range reported in other regions ($+5.0$ to 19.6‰) where there was little to no sea-salt sulfate contribution (Table 2.1) (Cortecci 1970; Herut 1995; Holt 1981; Jamieson 2000; Jedrysek 2000; Mizutani 1969).

Sulfur $\delta^{34}\text{S}$ values (range -1.4 to 3.8‰ , $n = 13$) are consistent with the spectrum of those reported in other regions (-1.5 to 2.1‰) (Cortecci 1970; Herut 1995; Mizutani 1969) where sea salt contribution is less than 5%. The low $\delta^{34}\text{S}$ values of atmospheric sulfate in Baton Rouge area may be related to oil refinery emissions from multiple refineries (~ 15) in Houston, Texas. Another low $\delta^{34}\text{S}$ source could be the vast swampy areas to the west of Baton Rouge (Atchafalaya Basin, Figure 2.2), where H_2S emission from biogeochemical processes might be significant locally. The prevailing air trajectory in Baton Rouge carries air masses from the southwest (Robert Rohli, personal communication) thus favoring both the transport of refinery emissions in Houston and swamp emissions to our sampling site. Establishing various gaseous sulfur sources and their relative contribution to the Baton Rouge region requires a significantly larger dataset than we currently have.

CONCLUSIONS

The first reliable oxygen isotope data for total atmospheric sulfate together with $\delta^{34}\text{S}$ measurements for a site are presented here. The positive $\Delta^{17}\text{O}$ (mean value $1.3 \pm 1.5\text{‰}$) and the high $\delta^{18}\text{O}$ (mean value $14.5 \pm 2.3\text{‰}$) values measured in Baton Rouge rainwater sulfate suggest that the dominant oxidation pathway for reduced sulfur gases in the atmosphere is aqueous phase oxidation by H_2O_2 , with O_3 as a minor oxidant. The relatively constant pH (4.7) is likely the reason no $\Delta^{17}\text{O}$ seasonal variations are observed. The low $\delta^{34}\text{S}$ values for atmospheric sulfate in Baton Rouge may be related to sulfur emissions from nearby industrial sources and from adjacent swamps, but longer temporal data coverage is needed to determine the contributions of these specific sources.

FUTURE WORK

New Extraction Method for Rainwater Nitrate in Progress

Future work should consist of utilizing a new separation technique currently being developed. Due to the difficulty of excluding dissolved organic matter from rainwater, a new method is being developed for an anion separation technique using a Waters LC 3000 Ion Chromatography Preparation System with Waters 484 Tunable Absorbance Detector to extract clean nitrate from rainwater samples. We use a $3.5\mu\text{M}$ sodium carbonate (Na_2CO_3) and $1.0\mu\text{M}$ sodium bicarbonate (NaHCO_3) (AS14 eluent concentrate in deionized water, $3.5\mu\text{M}$ Na_2CO_3 and $1.0\mu\text{M}$ NaHCO_3 eluent after 100 times dilution, Dionex) eluent. Nitrate absorbs wavelengths near the 270 nm spectrum. Preliminary runs indicate that at a flow rate of 1 ml min^{-1} , nitrate peaks at 6.3 minutes on our system. Once

this method has been validated with additional tests, concentrated rainwater will be processed through the system and collect solution from the column from ~5.8 to ~6.8 minutes for nitrate collection.

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