

Sulfate 170 Anomalies in Cenozoic Volcaniclastic Deposits in the Northern High
Plains, North America

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Project Summary

It has been proposed that a series of extreme dry fogs probably delivered a large quantity of sulfate to the northern High Plains, North America, during the peak of the Great Basin volcanism ~ 28 million years ago (Bao et al., 2003, *Geophysical Research Letters*). The hypothesis is based on a unique type of stable isotope signature, an array of positive sulfate ^{17}O anomalies found in a particular volcanic ash bed in the Oligocene volcanoclastic deposits in this region. This discovery and the proposed interpretation have generated interest, as well as debates on the possibility of past abnormal atmospheric events being recorded by rocks versus alternative explanations of the sulfate ^{17}O anomalies. Examination of modern and ancient playa sulfate, as well as the volcanic ash beds exposed in extremely arid and old surfaces (e.g., ash beds in the Atacama Desert or in the Antarctica Dry Valleys), does not support some of the alternative explanations on the origin of the anomalous sulfate in the Oligocene ash bed. Furthermore, more ash beds have been found to have distinct sulfate ^{17}O anomalies, and these may extend from ~ 33 Ma to ~ 7 Ma in age in this region. Given the wide implications of this discovery in Earth sciences, the PI proposes to further test the dry-fog hypothesis through the following tasks: (1) Map out the spatial heterogeneity of sulfate deposition and isotope compositions at the type locality of the Gering Formation, (2) Understand the sedimentological, mineralogical, and diagenetic factors that resulted in the preservation of the anomalous sulfate in the Gering Formation, (3) Establish a temporal pattern of volcanic sulfate deposition in Badlands National Park, South Dakota, (4) Examine a depositional sequence of normal playa sulfate at Wolf Butte, Nebraska, (5) Date the Gering ash beds, and (6) Prepare to sample dry fogs.

The intellectual merit of this proposal lies in the new prospect that ancient dramatic sulfate aerosol events may be preserved and can be studied in rock records. By studying the little known, but potentially frequent, volcanic sulfur emission events using the novel $\Delta^{17}\text{O}$ parameter, this project will reveal and partially fill critical gaps in our understanding of the oxidation pathways of volcanically emitted sulfur gases in the atmosphere, as well as the effects of volcanic eruption on global climate and on local environment.

This proposed study has broader impacts on education in particular and on humanity in general. We have a hypothesis in place that offers explanation for the mysteriously anomalous sulfate in ancient ash beds. To fully test it, a learning-by-doing approach has been designed to break down the big puzzle into several small pieces of puzzles. In the end, each of the students (two graduate students and several undergraduate students) will have to know how his or her own piece of the puzzle fits into the whole problem. This project will provide students a unique opportunity to learn a broad spectrum of Earth science, including field mapping, stratigraphy, depositional environment, geochronology, temporal trend of Cenozoic volcanisms, volcanic sulfur emissions/oxidation/transport, atmospheric chemistry, stable isotope geochemistry, paleoclimate, and post-depositional diagenesis. The project will initiate and nurture research activities on atmospheric chemistry at LSU. It will provide an exciting educational opportunity for the general public, as most of the research sites are at popular national monuments and parks and our results can be effectively displayed in the parks. On the point of humanity, if the cause of the massive ^{17}O -anomalous sulfate deposits is indeed a series of extreme dry fogs that were linked to the volcanic eruptions in the west, we ought to find out the origin, frequency, and potentially devastating environmental and biological consequences of these fogs. If it happened before, it will happen again. Studying these unusual geological events will help civilization prepare for the next big one.

TABLE OF CONTENTS

For font size and page formatting specifications, see GPG section II.C.

| | Total No. of Pages | Page No.* (Optional)* |
|--|-----------------------|--------------------------|
| Cover Sheet for Proposal to the National Science Foundation | | |
| Project Summary (not to exceed 1 page) | 1 | |
| Table of Contents | 1 | |
| Project Description (Including Results from Prior NSF Support) (not to exceed 15 pages) (Exceed only if allowed by a specific program announcement/solicitation or if approved in advance by the appropriate NSF Assistant Director or designee) | 15 | |
| References Cited | 4 | |
| Biographical Sketches (Not to exceed 2 pages each) | 2 | |
| Budget (Plus up to 3 pages of budget justification) | 6 | |
| Current and Pending Support | 1 | |
| Facilities, Equipment and Other Resources | 1 | |
| Special Information/Supplementary Documentation | 2 | |
| Appendix (List below.) (Include only if allowed by a specific program announcement/ solicitation or if approved in advance by the appropriate NSF Assistant Director or designee) | | |
| Appendix Items: | | |

*Proposers may select any numbering mechanism for the proposal. The entire proposal however, must be paginated. Complete both columns only if the proposal is numbered consecutively.

PROJECT DESCRIPTION

Results from Prior NSF Support

1. NSF IF-EAR (Instrumentation and Facility -- Earth Sciences):

Award No. EAR-0129793,

Title: **"Acquisition of a CO₂-Laser Fluorination System and a Mass Spectrometer System for Multiple Stable Isotope Analyses"**

Duration: March 1, 2002 to Feb. 29, 2004

I have completed the construction of a CO₂-Laser Fluorination line and the setup and calibration of a Mass Spectrometer System (Finnigan MAT 253) at LSU Oxy-Anion Stable Isotope Center (OASIC). Both systems are functioning in excellent condition and have generated > 500 oxygen isotope data. Most of the preliminary data reported in this proposal were generated at LSU.

The CO₂-Laser Fluorination line was designed and constructed to generate molecular oxygen (O₂) for both $\delta^{18}\text{O}$ and $\delta^{17}\text{O}$ analyses for sulfate (as barite). User can analyze 12 to 18 samples per working days on the line. I have trained one technician (Margarita Khachatryan) and two graduate students (Kathryn Jenkins and Tao Fang) to operate the system. Our laboratory O₂ reference gas (LSU-O₂) has been calibrated with UWG-2, a garnet distributed by Dr. Valley's group at University of Wisconsin -Madison [Valley *et al.*, 1995]. The result of this independent calibration matches the working standard at Dr. Thiemens' laboratory at University of California San Diego within analytical precision.

Currently, we are in the process of adding a Thermal Combustion-Elemental Analyzer (TC-EA) with conflo-III interface to the existing MAT 253 system to measure the $\delta^{18}\text{O}$ of sulfate and nitrate as well as the $\delta^{15}\text{N}$ of nitrate. This upgrade will establish the LSU OASIC as one of the few in the world that can measure both the $\delta^{18}\text{O}$ and the $\Delta^{17}\text{O}$ of various oxianions accurately.

2. NSF OPP (Office of Polar Program)

Award No. OPP-0125842

Title: **"Collaborative Research: Multiple Isotope Analyses of Soil Sulfate and Nitrate in the Antarctic Dry Valleys"**

Duration: April 1, 2002 to March 31, 2005

We have successfully accomplished two major tasks of this project: field expedition and the development of analytical capability for nitrate stable isotope analyses. A total of 9 team members from co-PI Dr. Marchant's group and my group camped out at the Asgard Range and the Olympus Range and completed fieldwork. We sample 54 soil pits of a variety of age, elevation, parent materials, and distance to the ocean. All samples arrived at LSU in April, 2003.

Analytical preparation, particularly the measurement and separation of a variety of water-soluble salts (sulfate, nitrate, iodate, and perchlorate) have been tested on surface salt deposits that I collected from the Atacama Desert, Chile, in 2001. The work on Chilean soils has provided valuable experience and spared potential mistakes that could otherwise occur when analyzing the precious Antarctica samples (see [Bao *et al.*, submitted]). One of the ash beds from the Taylor Valley also gives us an opportunity to study a situation when a volcanic ash bed merely serves as a matrix for accumulation of atmospheric sulfate, a case pertinent to this proposal (see [Bao, submitted]).

The successful setup of the CO₂-Laser Fluorination line and the Mass Spectrometer System at LSU OASIC has laid down a solid analytical support essential for the project. Also, we recently

have successfully set up a line for nitrate $\delta^{18}\text{O}$ and $\delta^{17}\text{O}$ measurement. $\Delta^{17}\text{O}$ values as large as +32‰ are found common for Antarctica soil nitrate. Two manuscripts are in preparation.

1. Introduction

Dry fogs are one of the unusual atmospheric or climatic events associated with volcanic eruptions [Camffo and Enzi, 1994; Grattan and Pyatt, 1999; Stothers, 2000]. One of the best documented events occurred in the summer of 1783 in Europe [Demaree et al., 1998; Stothers, 1996; Thordarson and Self, 2003].

“During several of the summer months of the year 1783 . . . there existed a constant fog over all Europe and great part of North America. This fog was of a permanent nature; it was dry, and the rays of the sun seemed to have little effect towards dissipating it ...” (Benjamin Franklin, 1784 Paris)

“On the 24th, the fog was very dense and accompanied by a very strong smell of sulphur, especially in the morning, although it was still noticeable in the afternoon... asthmatics suffered to an even greater degree ... the fog caused a great extermination of insects ... On the morning of the 25th, the land offered an aspect of severe desolation, the green colour of the plants had disappeared and everywhere the leaves were dry. . . . in a moment, the colour could change from green to brown, black, grey or white. . . Afterwards, a great quantity of leaves fell. --- (Brugmans, 1787)

“The thick dry fog . . . seems to have spread over the whole surface of Europe; ... in the day time, it veils the sun and towards evening it has an infectious smell; in some places, it withers the leaves, and almost all the trees on the borders of the Ems have been stripped of theirs in one night.” – (The Ipswich Journal, Aug. 9, 1783).

The culprit of this troubling sulfuric aerosol event is the 1783 Laki basalt eruption in Iceland, the largest basaltic outpouring in historical times. According to [Thordarson and Self, 2003], this flood lava eruption “emitted similar to 122 megatons (Mt) SO_2 into the atmosphere and maintained a sulfuric aerosol veil that hung over the Northern Hemisphere for > 5 months. The eruption columns extended to 9-13 km and released similar to 95 Mt SO_2 into the upper troposphere/lower stratosphere (i.e., the polar jet stream), enforcing a net eastward dispersion of the plumes which reacted with atmospheric moisture to produce similar to 200 Mt of H_2SO_4 aerosols”.

The 1783 Laki eruption and its dry fogs had dramatic social, economic, and environmental impacts on Europe [Demaree et al., 1998; Durand and Grattan, 2000; Stothers, 1996]. 75% of all livestock and 25% of the human population in Iceland died, and mostly caused directly by toxic fogs. The dry fogs nearly led to the evacuation of Iceland. It also brought about short-term severe winters in Europe and North America, and the annual mean surface cooling was 1.3 °C for 2-3 years [Thordarson and Self, 2003].

There were overall ~ 175 Mt of H_2SO_4 aerosols precipitated to the surface as the form of dry fogs in the summer of 1783 in Europe, according to [Thordarson and Self, 2003]. There is no known sedimentary record, however, of these sulfuric aerosols any where. In this proposal, we will test a hypothesis that, in the Cenozoic, dry fogs occurred frequently in the northern High Plains in North America. The magnitude of several of the dry fogs in the Oligocene and Miocene could be hundreds or even thousands of times higher than the 1783 event. This hypothesis is primarily based on the anomalous sulfate ^{17}O signatures measured in the laboratory and the sheer volume of the deposited aerosol sulfate minerals seen in the field. [Thordarson and Self, 2003] predicted that eruptions and dry fogs of 1783 Laki magnitude will occur again, and if it were to occur today, “one of the most likely immediate consequences would be disruption to air traffic over large portions of the Northern Hemisphere”. However, the impact of an extreme (intense and prolonged) dry fog event, such as the one at ~ 28 Ma, could incur a much greater destruction to the civilization. To convince you the importance of the discovery and the reason behind the

proposed interpretation, I will first present you one of the best-studied occurrences, the mid-Gering ash bed.

2. Geological Background

Volcaniclastic deposits, which include eolian, alluvial, and fluvial sediments, dominate the Oligocene and Miocene continental deposits (the White River and the Arikaree Groups) in the northern High Plains, North America [Terry *et al.*, 1998]. In northwestern Nebraska and eastern Wyoming, fine-grained volcaniclastic sandstones of the Gering Formation (Arikaree Group) rest on volcaniclastic siltstones of the Upper Oligocene Brule Formation (White River Group) (Fig. 1). The Gering Formation represents typical arid to semi-arid deposits that are dominated by fluvial and playa sediments [Loope, 1986; Swinehart *et al.*, 1985].

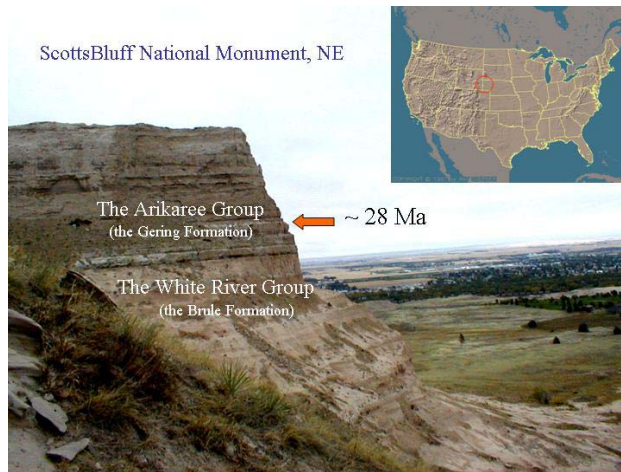


Fig.1. Late Oligocene stratigraphic sequence exposed on the south side of Scotts Bluff National Monument. The arrow points to the position of the mid-Gering ash bed.

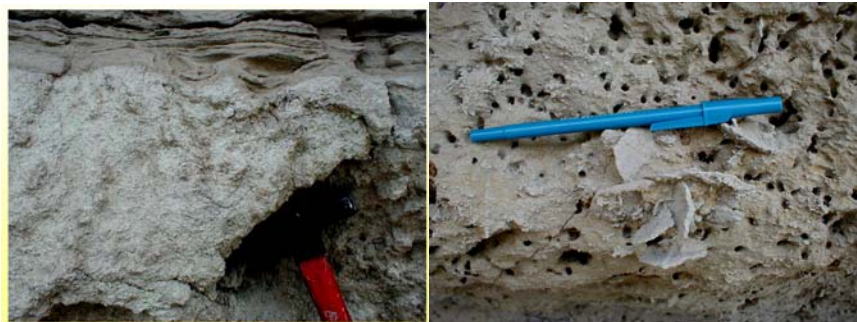


Fig.2. Two types of calcite pseudomorphs after gypsum in the Gering Formation, Scotts Bluff National Monument. The lenticular (left) and rose-like (right) gypsum pseudomorphs occur within and beneath the ash bed, respectively.

Our study initially focused on one of the ash beds in the Gering Formation. We name it the “mid-Gering ash” because it occurs at ~ 10 m above the base of the ~ 20 m-thick Gering Formation at the Scotts Bluff National Monument. We can trace the mid-Gering ash bed in several different localities in western Nebraska and eastern Wyoming. The ash is mainly rhyolitic to dacitic in composition. It is best exposed on several cliff faces at Scotts Bluff National

Monument, Nebraska (Fig. 1). Abundant calcite pseudomorphs after gypsum are seen in the whitish ash layer as well as in the reddish sandstone beneath the ash (Fig. 2).

Estimated sulfate quantity in the mid-Gering ash bed -- The mass of gypsum represented by the pseudomorphs provides an estimate of the quantity of volcanic sulfate that could have been present in pore waters beneath the playa floor around the time the ash bed was deposited. On the basis of the quantity of calcite pseudomorphs after gypsum in the uppermost 20-30 cm of the tephra zone, [Loope *et al.*, in review] estimates that the average sulfate deposition across the playa and its catchment could exceed 100,000 kg km⁻². For comparison, Thordarson and Self (2003) estimate that sulfuric acid deposition from Laki was about 1000 kg km⁻², averaged over the Northern Hemisphere north of 30° N.

Age and possible source of the mid-Gering ash -- Oligocene volcanism in the western United States generated an immense volume of tephra, and the specific source for the mid-Gering ash exposed at Scotts Bluff has not been identified. An earlier attempt to date the mid-Gering ash by J.B. Swinehart, as well as our recent attempt in collaboration with colleagues at USGS, was unsuccessful due to a lack of sanidine. Magnetostratigraphic studies of the Gering Formation at Scotts Bluff, however, place the ash beds described here within a reversed zone at the base of Chron 9, suggesting deposition took place within a time interval of about 300,000 years that ended at ~ 28 Ma [Tedford *et al.*, 1996]. On the basis of characteristic mineral suites, geochemistry, grain-size, and Ar/Ar ages, Larson and Evanoff [1998] concluded that the fine-grained volcanoclastics of the underlying White River Group were erupted 35.5 - 30 Ma from sites in the Great Basin of western Utah and eastern Nevada, which reached its peak activity also at ~ 28 Ma [Best *et al.*, 1989].

The most proximal candidate for the tephra beds within the Gering Formation at Scotts Bluff is the San Juan Volcanic Field of southwestern Colorado. With an estimated volume of 5,000 km³, the Fish Canyon Tuff (~ 28 Ma) arguably records the Earth's largest known volcanic eruption. Although silicic volcanic eruptions are considered to contain little sulfur, volcanism in the San Juans is sulfur-rich [Parat *et al.*, 2002]. The Fish Canyon Tuff has normal remnant magnetic polarity [Lipman, 1975], however, and cannot be the source of the tephra in the Gering Formation unless there exists an unrecognized short-term reversal in Chron 9. Thus, further effort in radiometric dating is critical in identifying the source of eruption and in correlating the equivalent ash beds in the region.

3. Why are the sulfates in the mid-Gering ash bed “abnormal”?

We can measure sulfate's multiple stable isotope ratios, ³⁴S/³²S, ³³S/³²S, ¹⁸O/¹⁶O, and ¹⁷O/¹⁶O. When normalized to international standards, the δ values, as well as the deviations of the δ values from a mass-dependent fractionation line, can be obtained. In this case, we can get $\delta^{34}\text{S}$, $\delta^{33}\text{S}$, $\delta^{18}\text{O}$, and $\delta^{17}\text{O}$ values, as well as the $\Delta^{17}\text{O}$ ($= \delta^{17}\text{O} - 1000 \times [(1 + \delta^{18}\text{O}/1000)^{0.52} - 1]$) or $\Delta^{33}\text{S}$ ($= \delta^{33}\text{S} - 1000 \times [(1 + \delta^{34}\text{S}/1000)^{0.515} - 1]$) values. We conducted a survey of these isotope compositions for sulfate leached out of the mid-Gering ash bed (with abundant calcite pseudomorphs after gypsum) from several different localities in western Nebraska and eastern Wyoming (Fig. 3). A total of 16 samples from the mid-Gering ash bed in the region were analyzed (see Table 1 in [Bao *et al.*, 2003]). No ³³S anomaly (i.e., $\Delta^{33}\text{S} = 0$) was found for any of the sulfate samples that we checked using the SF₆ method (see Table 2 in [Bao *et al.*, 2000b] for the $\delta^{34}\text{S}$ data). The sulfate $\delta^{18}\text{O}$ and $\delta^{17}\text{O}$ values, however, revealed a striking feature that most terrestrial sulfate minerals do not possess [Bao *et al.*, 2000b], the distinct ¹⁷O anomalies or positive $\Delta^{17}\text{O}$ values (up to 5.84‰) (Fig. 4).

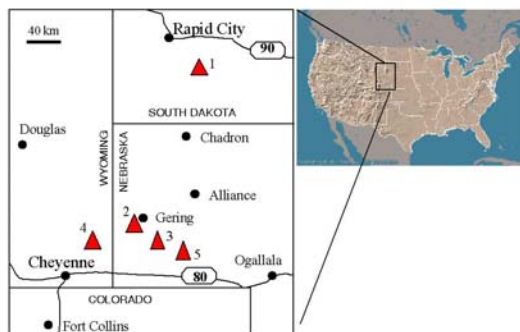


Fig. 3. Map of mid-North America, showing Badlands National Park, South Dakota (1), Scotts Bluff National Monument, NE (2), Chimney Rock, NE (3), Hawk Springs, WY (4), and Broadwater, NE (5). The mid-Gering ash bed can be traced at site 2, 3, and 4.

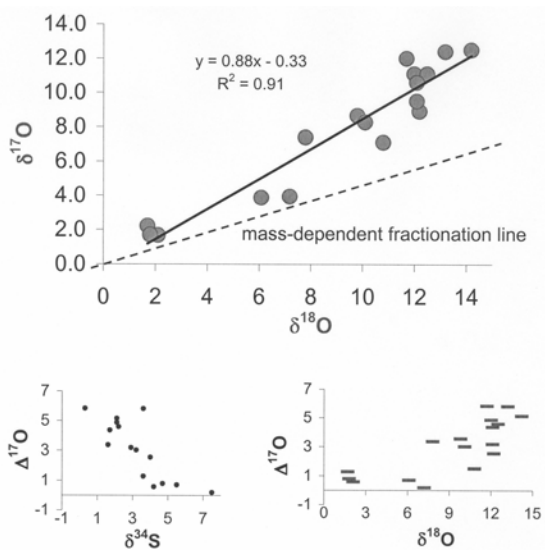


Fig.4. Relationships among oxygen and sulfur isotopic compositions for water-soluble and acid-soluble sulfates extracted from the mid-Gering ash bed and its underlying sand/siltstones. Samples were taken from site 2, 3, and 4 in Fig. 4.

The only processes that can produce ^{17}O -anomalous sulfate – So far only sulfate formed from the oxidation of sulfur gases by O_3 or H_2O_2 possesses an ^{17}O -anomaly [Savarino *et al.*, 2000]. Other oxidation pathways, such as oxidation by air O_2 at high temperature or at particle surfaces by metal catalysts, or gas-phase oxidation by $\bullet\text{OH}$, do not produce an ^{17}O anomaly in the product SO_4^{2-} , measured by $\Delta^{17}\text{O}$ value. In the oxidation of sulfur gases by O_3 or H_2O_2 , the ^{17}O -anomaly in product SO_4^{2-} is not generated by the reaction itself, which is mass-dependent, but is transformed from oxidants O_3 or H_2O_2 that have $\Delta^{17}\text{O}$ values. The ^{17}O -anomalous sulfate is pervasive in atmospheric aerosols, rainwater, snow, dust depositions, building surfaces, as well as surficial deposits from some extremely arid regions such as the Central Namib Desert, the Atacama Desert, and the Antarctica Dry Valleys [Bao *et al.*, 2000a; Bao *et al.*, 2001a; Bao *et al.*, 2000b; Bao *et al.*, 2001b; Johnson *et al.*, 2001; Lee and Thiemens, 2001]. These anomalous sulfates mainly originate from tropospheric oxidation of sulfur gases of anthropogenic or biogenic origin.

Volcanic ashes do contain high content of water-soluble sulfate -- It has been known that fine volcanic ashes carry hundreds to tens of thousands ppm [SO_4^{2-}] when they fall from the sky (e.g., [Armienta *et al.*, 1998; Rose, 1977; Taylor and Stoiber, 1973; Varekamp *et al.*, 1984]).

Although in a few cases (e.g., [Rye *et al.*, 1984]) magmatic sulfate as anhydrite phenocrysts contribute part of the sulfate, some of the water-soluble sulfates carried by ashes can be the product of SO₂ oxidation in the atmosphere after eruption.

(However) No sulfate ¹⁷O anomaly has been found in any of the fresh ash leachates –

We published the first attempt to measure the multiple sulfur and oxygen isotopic compositions for sulfate from fresh ash leachates [Bao *et al.*, 2003]. It was found that all of the 11 samples of various eruption types, particle sizes, and distances from eruption centers lack an ¹⁷O anomaly. Meanwhile, neither the anhydrite phenocrysts from Pinatubo pumice, nor the sulfates derived from elemental sulfur oxidation near an active fumarole have an ¹⁷O anomaly, as expected for sulfate of magmatic origin or of surface oxidation, respectively. Note that, like one of the end-members for the mid-Gering ash bed (Table 2 in [Bao *et al.*, 2003] and Fig. 4), the modern ash leachates lack an ¹⁷O-anomaly, but have higher δ³⁴S values and lower δ¹⁸O values than those of the ¹⁷O-anomalous sulfates.

Since later leaching, transport, or diagenetic alteration can not change or create the sulfate Δ¹⁷O values [Bao, submitted; Bao *et al.*, 2000b], sulfate carried by volcanic ashes can not be the source of the ¹⁷O-anomalous sulfate. Where did the ¹⁷O-anomalous sulfate in the mid-Gering ash bed come from?

4. The hypothesis of dry-fog origin

Apparently, O₃ or H₂O₂ was not involved in the production of the sulfate leached from fresh ashes, and the sulfate in the ~ 28 Ma mid-Gering ash bed has to have a different origin.

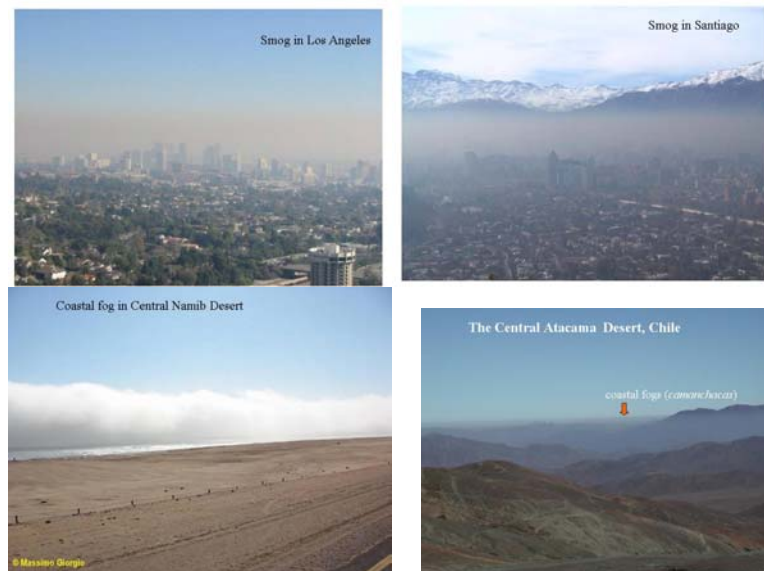


Fig.5. City smog (anthropogenic) and coastal fogs (natural) that contain ¹⁷O-anomalous sulfate

The reduced sulfur gases in our current atmosphere are dominated by anthropogenic emissions. Biogenic and volcanic emissions are only ~ 1/4 to 1/3 of the total budget [Seinfeld and Pandis, 1998]. When anthropogenic sulfur gases are oxidized in the troposphere, the final product sulfate falls back to surface through dry (aerosol) and wet (rainwater) depositions. Sulfate collected from current atmospheric depositions always carries an ¹⁷O anomaly [Bao *et al.*, 2001a; Johnson *et al.*, 2001; Lee and Thieme, 2001]. Similarly, when biogenic DMS emissions occur near the coast of the Central Namib Desert or that of the northern Chile, they are also oxidized and transported as fogs into continental sites, where the hyperarid and stable conditions permit the

accumulation of a massive ^{17}O -anomalous sulfate deposit [Bao *et al.*, submitted; Bao *et al.*, 2001b].

In both the anthropogenic and the biogenic cases, sulfate-rich fogs are observed in nature as smog or coastal fogs (Fig. 5). Fogs or smog are, however, not a necessary condition for the oxidation of reduced sulfur species in the atmosphere, but they are often the indication that a large quantity of sulfate is forming in the atmosphere.

We proposed a scenario based on similar tropospheric chemistry to account for the origin of the ^{17}O -anomalous sulfate in the mid-Gering ash bed. During and after a series of sulfur-rich eruptions in the west, volcanic ashes were carried by Westerly winds and deposited in the High Plains. The sulfate carried by ash particles was mostly formed by SO_2 oxidation on particle surfaces and did not possess an ^{17}O anomaly. However, following the ash fall, dry fogs (clouds of volcanic sulfate aerosols trapped in the planetary boundary layer), derived from SO_2 oxidation in the troposphere, hung over the Great Plains for months, years, or even longer periods. These sulfate aerosols, with a distinct ^{17}O anomaly and a residence time of only a few days, were constantly settling and were incorporated into surface volcanoclastic sediments. The ^{17}O -anomalous sulfate could thus become a significant portion of the total sulfate in ash beds. A quick formation of gypsum minerals ($\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$) prevented the sulfate from a complete leach-out in the volcanoclastic sediments. Figure 4 displays the different mixing of two end-member sulfates in the ash bed in different localities.

(1) *Sulfate from dry fogs*: highly positive $\Delta^{17}\text{O}$ values, high $\delta^{18}\text{O}$, and low $\delta^{34}\text{S}$ values

(2) *Sulfate from ash leachates*: no ^{17}O anomaly ($\Delta^{17}\text{O} = 0$), low $\delta^{18}\text{O}$ and high $\delta^{34}\text{S}$ values.

The highly positive $\Delta^{17}\text{O}$ values (up to 5.8‰) for some ash layers suggest that O_3 ($\Delta^{17}\text{O} \sim 30\text{‰}$) rather than H_2O_2 ($\Delta^{17}\text{O} \sim 1.7\text{‰}$) was the dominant oxidant in many of those cases, since only O_3 has a $\Delta^{17}\text{O}$ value high enough to produce the anomalies we observed in the Oligocene sulfate [Johnston and Thiemens, 1997; Lyons, 2001; Savarino and Thiemens, 1999]. It further indicates that the oxidation of SO_2 may have occurred in neutral to alkaline conditions [Lee and Thiemens, 2001]. The $\delta^{34}\text{S}$ value for the $\delta^{17}\text{O}$ -anomalous sulfate is much lower than the normal sulfate end-member (Fig. 4), suggesting that for a particular eruption event, the SO_2 oxidized on ash particle surfaces was preferentially enriched in ^{34}S relative to the SO_2 remaining in the atmosphere.

5. Examining alternative explanations

I will present in this section the work that my research group is doing currently. The purpose is to show that the dry-fog hypothesis deserves to be and can be evaluated and tested against alternative hypotheses.

Alternative 1 – *Groundwater or later diagenetic processes brought the ^{17}O -anomalous sulfate to the mid-Gering ash bed*

It has been the experience of volcanologists that nearly all the water-soluble sulfates carried by ashes are leached out by rain into a surface hydrologic system. It seems that the dry-fog sulfate would have to face the same fate after deposited onto surface environments. Thus, the preservation and later diagenetic conditions of the ash bed need to be addressed. [Loope *et al.*, in review] studied the evidence from sedimentology, mineralogy, and geochemistry of the ash bed and its associated deposits in detail. They concluded that the semi-arid alkaline playa setting and the early formation of gypsum crystals in a Ca^{2+} -rich pore water facilitated the preservation of sulfate in the ash bed. The groundwater table has never been high enough to completely leach out the initial sulfates. Meanwhile, we have measured the $\Delta^{17}\text{O}$ values of tens of groundwater sulfate samples, including those from semi-arid South Dakota and the Texas Panhandle [Bao, submitted].

None of them show any ^{17}O anomaly. The groundwater and diagenetic processes may have redistributed the sulfate in the volcanoclastic deposits, but they can not generate sulfate ^{17}O anomaly. Thus, the question of the origin of the ^{17}O anomaly still remains.

We also ruled out the possibility of recent anthropogenic sulfate contamination on the outcrops, because similarly exposed outcrops have little sulfate in them and the sulfate content and the $\Delta^{17}\text{O}$ values for the mid-Gering ash bed are highly variable.

Alternative 2 -- The mid-Gering ash bed was exposed for a prolonged time in a hyperarid climatic condition, so that the ever-present biogenic and volcanic background sulfate in the atmosphere, although minuscule and invisible (unlike the dry fogs), could accumulate to a significant quantity, just like the case for the Antarctica Dry Valleys and the Atacama Desert

The only deposits where we have found high sulfate $\Delta^{17}\text{O}$ values are the salts in hyperarid surfaces like the Antarctica Dry Valleys [Bao *et al.*, 2000a] and the Atacama Desert [Bao *et al.*, submitted]. The origin of the ^{17}O -anomalous sulfate in these settings has been contributed to non-sea-salt sulfate (mainly biogenic sulfate) that deposited from the atmosphere. Therefore, why could not the atmospheric background sulfate, consisting of sulfate from both the biogenic and the volcanic origin, be the dominant source of the ^{17}O -anomalous sulfate in the Oligocene ash bed in the northern High Plains?

We have located an ignimbrite/ash bed deposited in a small playa setting in the central Atacama Desert (13.6 ± 1.7 Ma by K-Ar dating) [Chong-Díaz, 1973] and an ash bed (lens) in Taylor Valley of the Antarctica Dry Valleys (~ 10.1 Ma) [D. Marchant, personal communication]. If the anomalous sulfate in the Oligocene mid-Gering ash bed had a similar origin, we should expect to find similar sedimentological and geochemical features among them. And if it is true, the dry-fog hypothesis is *unnecessary* in interpreting the observed sulfate ^{17}O anomaly in the mid-Gering ash bed.

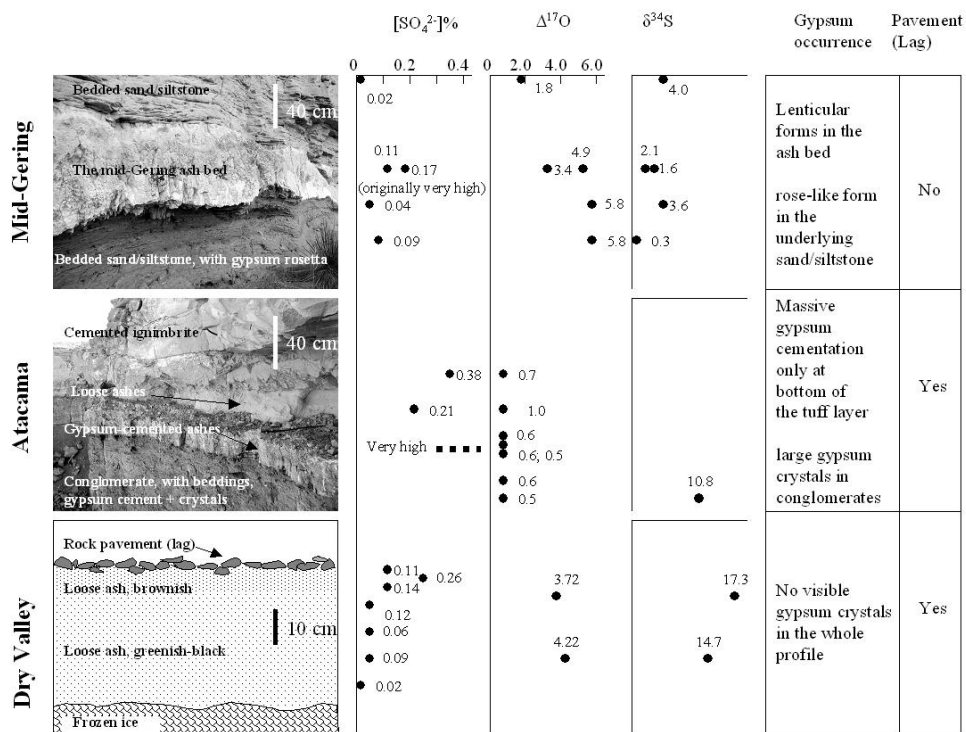


Fig.6. Comparing sulfate content, isotopic compositions, and key sedimentological features of the vertical profiles of three different ash beds

We did comparison on sulfate concentration, isotope data, gypsum occurrence, and sedimentary features of these ash beds (Fig. 6). The two tuff beds in current hyperarid settings represent typical cases where surface ash beds happen to serve as a matrix for the accumulation of a significant amount of atmospheric background sulfate (^{17}O -anomalous) due to the extreme surface aridity and long stability. The sedimentary features (e.g., the absence of a desert pavement and the forms of gypsum crystals), both $\delta^{34}\text{S}$ and $\Delta^{17}\text{O}$ data along a vertical profile, and sulfate concentrations of the mid-Gering ash bed, however, do not fit those of the two volcanic ash beds in modern hyperarid settings. Paleontological and sedimentary data do not support a hyperarid condition in the northern High Plains at $\sim 28\text{Ma}$. The maximum exposure time (magnetostratigraphic data) for the mid-Gering ash bed could be less than a few hundreds of thousands of years. Therefore, time is not sufficient for the accumulation of atmospheric background sulfate to the observed level. A playa setting may concentrate sulfate from the surrounding areas by surface water flow. As we demonstrated below, however, a playa setting, in most cases, tends to erase sulfate's $\Delta^{17}\text{O}$ value.

Alternative 3 -- Playa settings in arid or semi-arid settings accumulate and preserve anomalous sulfate by inflows of steams and formation of evaporative minerals

For continental settings where the climatic condition is not as extreme as the Atacama Desert, the Dry Valleys, or the Central Namib Desert, a brief transport and therefore concentration of sulfate by surface water are possible in a variety of playa settings. Could some of the playas in those regions accumulate atmospheric background sulfate with a high $\Delta^{17}\text{O}$ value? In recent years, our laboratories have accumulated both $\delta^{18}\text{O}$ and $\delta^{17}\text{O}$ data for sulfates in various natural occurrences, especially sulfates from a variety of modern playas. Extensive survey shows that sulfates of non-atmospheric origins have no ^{17}O anomaly. Sulfates from playa settings in arid and semi-arid regions do not have ^{17}O anomalies or have smaller anomalies than those of the surrounding surfaces, which is in contrast to the sulfate data in the mid-Gering ash bed. One of the examples is the spatial distribution of surface sulfate $\Delta^{17}\text{O}$ value in Death Valley (Fig. 7).

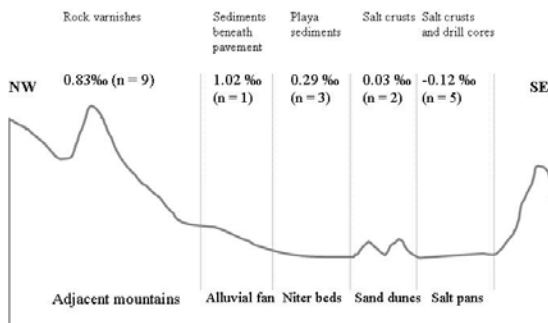


Fig.7. A transect showing the landscape and the sulfate $\Delta^{17}\text{O}$ values in various surface localities in Death Valley, U. S. A. Data are from [Bao *et al.*, 2001a]. Objects are not to scale.

Therefore, the observed ^{17}O -anomalous gypsum deposits in the mid-Gering ash bed is most likely the result of 1) a pulse of intense input of atmospheric sulfate as dry fogs that originated from volcanic eruptions, and 2) the semi-arid environment that facilitated a quick formation of gypsum crystals. Proposed study on radiometric dating and diagenesis in this proposal (see below) will help to further test the hypothesis.

Detailed discussion on these alternative possibilities can be found in [Bao, submitted].

Alternative 4 -- *The anomalous sulfate was mainly from the stratosphere, instead of the troposphere*

An explosive volcanic eruption can send huge amount of SO₂ into stratosphere [Bluth *et al.*, 1997; Cadle, 1980; Evans and Kerr, 1983; Rose *et al.*, 2000; Vedder *et al.*, 1983]. Although data are still scarce, homogeneous oxidation by •OH or heterogeneous oxidation, possibly by O₃, on the existing sulfate aerosol are the main pathways for SO₂ oxidation in the stratosphere [Harrison and Larson, 1974]. Stratospheric •OH, O₃, and even H₂O may have large ¹⁷O anomalies according to measurements and models [Krakovsky *et al.*, 2000; Lyons, 2001], and these do transfer to product sulfate. Recent modeling study [Savarino *et al.*, 2003] indicates that SO₂ photo-oxidation becomes significant for SO₂ greater than few ppmv, and is the dominant pathway for SO₂ greater than tens of ppmv.

A major difficulty of this scenario is, however, that once SO₂ gets into the stratosphere, it would be dispersed all over the globe. The extremely high sulfate content in the Oligocene-Miocene ash beds would require large stratospheric deposition of sulfate onto a specific region, a process that is difficult to accommodate by atmospheric circulation dynamics. Moreover, a distinct ³³S anomaly would be expected for sulfate of SO₂ photo-oxidation origin, on the basis of ice-core records of past volcanic sulfates [Savarino *et al.*, 2003] as well as recent laboratory photo-oxidation experiments [Farquhar *et al.*, 2002]. No ³³S anomaly, however, has been found in 5 of the analyzed Oligocene ash beds (see Table 2 of [Bao *et al.*, 2000b] for δ³⁴S data).

At this time, stratospheric sulfate isotope data are absent and their formation speculative. We will not, therefore, completely reject the possibility of stratospheric sulfate component, and will keep analyzing selected ancient volcanic sulfates for their Δ³³S values.

6. Latest discoveries

One of our newest discoveries in this research area is that the mid-Gering dry-fog event could be just one of the many that have occurred in the Cenozoic in the northern High Plains.

We did a preliminary survey of the volcanoclastic deposits in the White River Group (Eocene to Oligocene) and the Arikaree Group (Oligocene to Miocene) in western Nebraska, eastern Wyoming, and South Dakota. We have located more than a dozen ancient ash beds and calcite-cemented lenses or sand/siltstones within or below the ash beds that have variable sulfate ¹⁷O anomalies. These deposits range from ~ 33 Ma to ~ 7 Ma in age.

- (1) In Badlands National Park, relatively smaller sulfate ¹⁷O anomalies have been found in a few ash beds in the Brule Formation (~ 32 - 33 Ma [Prothero and Swisher, 1992; Swisher and Prothero, 1990]), but higher ¹⁷O anomalies in the Rockyford Ash (~ 30 Ma [Prothero and Swisher, 1992]) and the sediments above.
- (2) In western Nebraska, the upper part of the Gering Formation also has high sulfate content, and the other two major ash beds in the formation and their underlying fluvial deposits all contain ¹⁷O-anomalous sulfate. Several ash lenses in the overlying Monroe Creek-Harrison Formations (late Oligocene and Miocene ages, ~ 27 - 22 Ma [MacFadden and Hunt, 1998]) in Scotts Bluff National Monument also have distinct ¹⁷O anomalies (data not shown here).
- (3) The anomalies are present in the late Miocene Ogallala ashes of the Ash Hollow Formation at Broadwater, NE (~ 13 - 7 Ma [Perkins *et al.*, 1995]).
- (4) An ash bed in the Scenic Member (the Brule Formation, ~ 33 Ma, Badlands N. P.) has high sulfate content but no ¹⁷O anomaly except for a small Δ¹⁷O value (~ 0.56‰) for a cemented layer (sample B00-6) on the top.
- (5) An initial analysis of a gypsum-rich deposit of the Big Cottonwood Creek Member, the Chadron Formation (Eocene), at Wolf Butte, northwestern Nebraska, shows that none of the gypsum sulfate has an ¹⁷O anomaly.

These recent findings provide us new opportunities to address the following existing and new problems.

7. Proposed work

We propose the following 6 sub-projects that will provide further tests on the dry-fog hypothesis.

(1) Map out the spatial heterogeneity of sulfate deposition and isotope compositions at the type locality of the Gering Formation

We have done a preliminary lateral tracing of the mid-Gering ash bed at three localities in northwestern Nebraska and eastern Wyoming (Fig. 3) [Bao *et al.*, 2003]. Large variations in both gypsum occurrence and sulfate isotope compositions were identified. So far, we have not addressed the lateral variations in detail. We will use the type locality of the Gering Formation to study the relationship between depositional condition (paleo-surface) and volcanic sulfate deposition. There is an apparent variation in lithology and thickness of the Gering Formation from Scotts Bluff to the type locality, 12 to 20 km south and southeast of Scotts Bluff. The type section of the Gering Formation is located at Helvas Canyon, Wildcat Ridge area, where it reaches the maximum thickness of about 45 m [Schultz *et al.*, 1967; Tedford *et al.*, 1996; Vondra *et al.*, 1969], whereas at Scotts Bluff, the Gering is only ~ 20 m. Large pumice pebbles are seen in the type section (Twin Sisters Pumice Conglomerate Bed) but not as noticeable in outcrops at Scotts Bluff. If subtle variation in depositional environment would affect the accumulation and preservation of volcanic sulfate, this site should provide the best opportunity to study the relationship. The Wildcat Ridge area is public land with an excellent exposure of Oligocene and Miocene volcanoclastic deposits. It is an ideal site for students to learn a wide spectrum of Earth science from basic field geology to volcanic-atmospheric sciences (see below). We, with the assistance of Dr. Swinehart (UNL-Conservation and Survey Division), will map, trace, describe, and sample the two members (the Helvas Canyon Member and the Mitchell Pass member) of the Gering Formation in the Wildcat Ridge area and compare the data with the three major ash beds seen at Scotts Bluff National Monument. It is expected that 3 to 4 independent senior and master-degree projects will come out of this site.

(2) Understand the sedimentological, mineralogical, and diagenetic factors that resulted in the preservation of the anomalous sulfate in the Gering Formation

[Loope *et al.*, in review] attributed the exceptional preservation of ancient volcanic sulfate in the ash bed and its underlying strata at Scotts Bluff to the semi-arid alkaline playa setting, where the early formation of gypsum minerals and the arid climate helped in retaining some of the original sulfate. The replacement of these gypsum crystals by calcite, however, indicates that meteoric or possibly occasional groundwater had affected these sulfate deposits after their formation. It is possible that the replacement may in fact contribute to the preservation of some of the sulfate inside the pseudomorphs either as trapped gypsum residues due to incomplete replacement, or as carbonate-associated sulfates (CAS) in a calcite crystal lattice.

We will approach this problem from two directions. First, we will examine the relationships among depositional environment (topographic high or low, playa or stream, fluvial or eolian deposits), gypsum crystal morphology, sulfate concentration in the pseudomorphs, and sulfate isotope compositions. Individual crystals will be dissolved and measured for sulfate and Ca^{2+} concentrations. Second, we will do an extensive survey of the CAS concentration among different types of continental (or freshwater) carbonates, including soil carbonates, lake carbonates,

calcretes near arid soil surface, and stalagmites. Each of the measured samples will be carefully examined for its origin and geological background. Modern and ancient marine sedimentary carbonates generally have CAS concentration ranging from ~ 200 to 24,000 ppm, with the marine skeletal carbonates (e.g., shell, coral) normally having the highest value [Staudt and Schoonen, 1995]. Our preliminary data show that some of the calcite pseudomorphs and cements contain tens of thousands ppm of CAS. Unfortunately, there is no compilation of CAS concentration data for continental carbonates at this time. These data will lay down a background dataset for us to compare with when working on the sulfate-bearing volcanoclastic deposits.

These research topics are well suited for undergraduate senior thesis projects.

(3) Establish a temporal pattern of volcanic sulfate deposition in Badlands National Park (N. P.), South Dakota

This site will provide us opportunity to conduct two research projects. The first one will focus on a basal Arikaree unit, the Rockyford Ash in the park. The second project will survey the sulfate isotope compositions in major ash deposits from the Eocene to the uppermost Miocene exposed in the park.

If the mid-Gering dry-fog event occurred at Scotts Bluff, it should have affected areas in close proximity. We have shown that the same mid-Gering ash bed can be traced at Chimney Rock, NE and Hawk Springs, WY (Fig. 4). Badlands N. P. at S.D. is, however, located ~ 300 km northeast of Scotts Bluff. It has one of the best and most extensive exposure of Cenozoic continental deposits, ranging from the base Cretaceous Pierre Shale and the Yellow Mounds paleosol on top of it, to the Chamberlain Pass Formation (Eocene), the Chadron Formation (Eocene-Oligocene), the Brule Formation (Oligocene), and to the Sharps Formation (Oligocene and Miocene) [Retallack, 1983; Terry *et al.*, 1998]. The Rockyford Ash at the base of the Sharps Formation in Badlands N. P. may be comparable in stratigraphic position to the Gering Formation at Scotts Bluff (Fig. 9). But the Rockyford Ash could be older than the Gering Formation that is probably restricted to a paleovalley along Wildcat Ridge [Swinehart *et al.*, 1985]. Preliminary data indicate that the Rockyford Ash also contains ^{17}O -anomalous sulfates. These sulfates, however, have lower $\Delta^{17}\text{O}$ values than those from Scotts Bluff. The Rockyford Ash can be traced in the park to greater distance. We plan to do a similar study on this ash bed as we did for the mid-Gering ash bed in Nebraska and Wyoming.



Fig. 9. The Rockyford Ash on top of the Poleslide Member of the Brule Formation, Cedar Butte, Badlands N. P.

Thus far, our limited samples from the park indicate that sulfates from ash beds of Eocene and early Oligocene ages have no ^{17}O anomaly or smaller anomalies than those of the late Oligocene and Miocene ages. Our future field survey will focus on confirming this initial finding by sampling sections along Notch Trail, Saddle Pass Trail, and the Pinnacle area in the park. It will give us a complete volcanic sulfate profile ranging from the Late Cretaceous to middle Miocene in age. This sub-project will be part of the thesis for a newly recruited Ph. D student.

(4) Examine a depositional sequence of normal playa sulfate at Wolf Butte (the Chadron Formation, Eocene)

We did a reconnaissance (in collaboration with Dr. LaGarry at UNL-Conservation and Survey) on an apparent Eocene playa sequence at Wolf Butte. This ~ 10-m sequence consists of a mixture of gypsum, clay, and volcanic ashes. It sits on top of the Yellow Mounds paleosol in which selenite crystals are abundant. So far, none of the analyzed sulfate has shown any distinct ^{17}O anomaly, and the $\delta^{34}\text{S}$ values are ~ 14‰ (CDT). This Wolfe Butte site was probably a typical Eocene playa setting in northwestern Nebraska that had sulfate source from the weathering of underlying Pierre Shale, instead of from dry fogs. Therefore, it provides us an ideal case for a comparative study between playas that had accumulated dry-fog sulfate and those that had not.



Fig.10. An ~ 10-m thick evaporite deposits in the Big Cottonwood Creek Member of the Chadron Formation, Wolf Butte, northwestern Nebraska

A Master-degree graduate student, Kathryn Jenkins, is working on this project at this time.

(5) Date the Gering ash beds

Absolute age data on the Oligocene ash beds in the Gering and the overlying Monroe Creek-Harrison formations are absent at this time. We only have a rough idea that this ash bed probably deposited at ~ 28 Ma during Chron 9 [Tedford *et al.*, 1996]. Further dating on the mid-Gering ash bed and several other ash beds up in the sequence will help to constrain the maximum exposure time of the mid-Gering ash before the deposition of the overlying playa/eolian deposits and ashes. Absolute age data will also help to link the mid-Gering ash bed to a specific volcanic eruption event in the west, and to correlate basal Arikaree units in the region.

Preliminary work on a small quantity of samples has not identified sanidine minerals; but detrital muscovite, as a sign of contamination, is present in most samples, suggesting that effort is needed to locate pockets of pure ash deposit. We plan to continue our dating effort with Dr. Robert Fleck at USGS in this proposal (see attached e-mail message). We recognize the fact that although we have gained experience in searching for mineral sanidine in the ash deposits, it is not guaranteed that we will find good sanidine crystals for the ash beds in question. Therefore, we are only requesting limited funding for radiometric dating at this time.

(6) Prepare to sample dry fogs

An ultimate test of the dry-fog hypothesis would be to sample and to analyze a real dry-fog event. As demonstrated by our preliminary results [Bao, submitted; Bao *et al.*, 2003; Loope *et al.*, in review], the combination of a sulfur-rich volcanic eruption and a semi-arid climatic and depositional conditions seems to be crucial for both the occurrence of dry fogs and the preservation of the event in the rock records. The preservation issue will be addressed in our proposed work (1), (2), and (4). The actual sampling of dry fogs, however, depends on our preparedness and luck. Although we may not witness a dry-fog event of an equivalent magnitude as the mid-Gering one in our lifetime or even in tens of thousands of years, smaller-scale dry-fog

events are relatively common, as documented historically [Camffo and Enzi, 1994; Durand and Grattan, 2000; Grattan and Pyatt, 1999; Stothers, 1996]. By collecting and analyzing aerosol sulfate derived from dry fogs, we will be able to test one of the crucial observations revealed by the rock record, i.e., the dry-fog sulfates should have positive $\Delta^{17}\text{O}$ values, and their $\delta^{34}\text{S}$ values are lower than those of the sulfates directly carried by ash particles. PI is preparing a separate proposal to NSF *Atmospheric Chemistry Program* to study the atmospheric oxidation chemistry involving the sulfuric acid and sulfates as aerosol particles produced from volcanic SO_2 . Funding for this task is not requested in this proposal.

8. Active involvement of graduate and undergraduate students

Students' roles in the proposal have been specifically mentioned throughout the proposed sub-projects above. One of the most exciting aspects of this proposal is the opportunity of providing students the first hand experience of doing cutting-edge sciences through active researches. The proposed sub-projects offers a rare opportunity where, under a large goal of testing the dry-fog hypothesis, undergraduate and graduate students can learn a broad spectrum of Earth science, including field mapping, stratigraphy, depositional environment, geochronology, temporal trend of Cenozoic volcanisms, volcanic sulfur emissions/oxidation/transport, atmospheric chemistry, stable isotope geochemistry, paleoclimate, and post-depositional diagenesis.

Besides the interdisciplinary nature, a key feature of this proposal is the mysteriousness of the preliminary discoveries. It will take time and effort for the students to really appreciate the "strangeness" of our initial findings. Therefore, the proposal is designed in a way that a big piece of puzzle is separated into many smaller pieces (as sub-projects). Each of the smaller pieces (sub-projects) is itself a problem to solve. Students working on these sub-projects will in the beginning accomplish their own tasks, and then figure out how their works are related to the results from the other sub-projects (worked on by other students), and finally, how all these smaller pieces of puzzles (sub-projects) fit together to solve the big one.

I have learned from my experience that the most effective way of teaching science to undergraduate students is to give them the opportunity to be involved in some unsolved scientific problems that the faculty members themselves are actively working on. By working side by side with the professor, technician, and graduate students, undergraduate students can have a first-hand experience on how science is being done and how new discoveries are made.

I took every opportunity to bring undergraduate students along in fieldwork and get them involved in laboratory experiments. This practice is proven very cost-effective in terms of nurturing students' interest in science and technology. I request funding to support two undergraduate students at LSU (Brandon Laiche and Jennifer Bogan) and a high school student or teacher from Louisiana (unidentified yet) to join our two-week field mapping at Wildcat Ridge, northwestern Nebraska (Proposed work 1). Two minority students from 4-year colleges in the south, sponsored by Geoscience Alliance to Enhance Minority Participation (GAEMP) program (NSF Award #0303138 to LSU), will join the fieldwork and pursue independent research topics.

9. Broader scientific, educational, and social impacts

Scientific -- The effect of volcanic eruptions on global climate has been a topic of considerable interest in paleoclimatology, atmospheric chemistry, and global climate modeling [Pinto *et al.*, 1989; Robock, 2000]. The key components in the process are the surfaces of fine ash particles and sulfate aerosols derived from the oxidation of volcanic SO_2 . Potential oxidation pathways for volcanic SO_2 include oxidation by air O_2 on catalyzed particle surfaces, aqueous

oxidation by H_2O_2 or O_3 , and gas-phase oxidation by the $\bullet\text{OH}$ radical [Bekki, 1995; Harrison and Larson, 1974; Holt and Kumar, 1984; Leung et al., 2001; Liang and Jacobson, 1999; Newman, 1980; Penkett et al., 1979; Saxena and Seigneur, 1987]. Once in the stratosphere, SO_2 could also be photolyzed to generate SO_3 , which hydrates to form sulfate. In order to assess the climatic effect of volcanically released SO_2 and sulfate aerosols, it is important to estimate the roles of the various sulfur oxidation processes subsequent to eruption. Both oxygen and sulfur isotopic compositions of sulfate, i.e., $\delta^{18}\text{O}$ or $\delta^{34}\text{S}$ have been applied to delineate SO_2 oxidation pathways (e.g., [Holt and Kumar, 1991; Newman et al., 1991; Tanaka et al., 1994]). However, success has been limited as a result of overlapping values or the lack of isotopic data differentiating different reaction pathways. There have been few isotopic measurements on collected ash leachates (with notable exceptions [Castleman et al., 1974; Rye et al., 1984]). Little is known about where, when, and how SO_2 was oxidized and deposited after eruption. By studying a little known, but potentially frequent, volcanic sulfur emission events using the novel $\Delta^{17}\text{O}$ parameter, this project will reveal and partially fill critical gaps in our understanding of the effects of volcanic eruption on global climate and on local environment.

Educational -- Undergraduate and graduate students will learn and be trained in various aspects of scientific research (including operation of state-of-the-art equipment) by actively involving in the quest of a largely unknown phenomenon in geological history. Most of the research sites are in popular national monuments and parks and our results can be effectively displayed in the parks. LSU currently has very limited researches going on in topics related to atmospheric chemistry, which is at odd with the No. 1 environmental problem facing the city of Baton Rouge (the capital city of Louisiana): the tropospheric ozone pollution. The operation of this project will provide a ground for faculty and students to expand their research and educational activities in this area.

Social -- A logical next step following this project is to study the impact to life and environment by the proposed extreme dry-fog events in the past. Human society has apparently not experienced atmospheric sulfate deposition of comparable magnitude in terms of density or duration. This study will raise awareness of such a possibility and prepare us for a potentially disastrous dry-fog event in the future.

10. Analytical Method

$[\text{SO}_4^{2-}]$ and $[\text{Ca}^{2+}]$ will be measured on an ion chromatographer (ICS-90 with cation or anion columns) after rocks are treated with weak acid. Water-soluble sulfates will be extracted and precipitated as barite from solutions containing sulfate leached from ashes or volcanoclastic deposits as described in [Bao et al., 2000b]. Some calcite-cemented rocks will be treated with $\sim 1\text{M}$ HCl solution to disaggregate the sediments and to release sulfate trapped within the calcite lattice into solution. Molecular oxygen was generated from barite using a direct CO_2 -laser fluorination method [Bao and Thiemens, 2000]. The sulfate $\delta^{18}\text{O}$ and $\delta^{17}\text{O}$ (thus $\Delta^{17}\text{O}$) analyses will be performed at LSU using the CO_2 -Laser Fluorination line and Finnigan MAT 253 utilizing a dual-inlet system. More accurate sulfate $\delta^{18}\text{O}$ ($\pm 0.3\text{‰}$) will be obtained from a TC-EA system on our existing MAT253. Selected sulfates will be converted to Ag_2S and further to SF_6 for $\Delta^{33}\text{S}$ measurement on the MAT253 using method outlined in [Farquhar et al., 2000; Forrest and Newman, 1977]. The sulfate $\delta^{34}\text{S}$ measurement will be contracted to A. J. Kaufman's laboratory at the University of Maryland. Isotopic results are expressed in the δ notations with respect to the Standard Mean Ocean Water (SMOW) for oxygen and to the Canyon Diablo Troilite (CDT) for sulfur. Analytical precisions (2σ) for $\delta^{34}\text{S}$, $\delta^{18}\text{O}$, $\delta^{17}\text{O}$, and $\Delta^{17}\text{O}$ are $\pm 0.3\text{‰}$, $\pm 0.3\text{‰}$, and $\pm 0.06\text{‰}$, respectively. It is important to emphasize that experimental fractionation cannot produce the observed mass-independent anomaly. Our laboratories have run up to 100 normal marine evaporites and seawater sulfates, and all show, as expected, a zero $\Delta^{17}\text{O}$ value.

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Biographical Sketches -- Huiming Bao

Professional Preparation

| | | | |
|--|---|-------------------|-----------|
| Peking University, P. R. China | Geology | B. Sc. | 1982-1986 |
| Nanjing Institute of Geology and Paleontology, Academia Sinica | Sedimentology & Paleontology | M.Sc. | 1986-1989 |
| Princeton University | Stable isotope geochemistry | Ph.D | 1993-1998 |
| University of California San Diego | Atmospheric chemistry & Stable isotopes | Postdoc (3 years) | |

Appointments

| | |
|--------------|--|
| 2001-present | Assistant professor in Geology and Geophysics, Louisiana State University |
| 1998-2001: | Postdoctoral Research Chemist, University of California San Diego |
| 1996-1997: | Research Scientist, University of California, Santa Cruz (in absentia from Princeton University) |
| 1993-1998: | Assistant in Instruction/Research, Princeton University |
| 1989-1993: | Assistant Professor, Nanjing Institute of Geology and Palaeontology, Academia Sinica |

Publications

5 most relevant ones

- Bao, Huiming**, Thiemens, M.H., Loope, D.B. and Yuan, X.-L., 2003. Sulfate oxygen-17 anomaly in an Oligocene ash bed in mid-North America: Was it the dry fogs? ***Geophysical Research Letters***, 30(16): 1843; 10.1029/2003GL016869.
- Bao, Huiming**, and Reheis, M.C., 2003. Multiple oxygen and sulfur isotopic analyses on water-soluble sulfate in bulk atmospheric deposition from the southwestern United States. ***Journal of Geophysical Research, D: Atmosphere***, 108(D14): 4430; 10.1029/2002JD003022.
- Bao, Huiming**, Thiemens, M. H., and Heine, K., 2001, Oxygen-17 excesses of the central Namib gypcretes: Spatial distribution. ***Earth & Planetary Science Letters*** 192. 125-135.
- Bao, Huiming**, Douglas A. Campbell, James G. Bockheim, Mark H. Thiemens, 2000, Origin of sulfate in Antarctic Dry Valley soils as deduced from anomalous ¹⁷O compositions. ***Nature*** 407, 499-502.
- Bao, Huiming et al.** 2000, Anomalous ¹⁷O compositions in massive sulphate deposits on the Earth. ***Nature*** 406, 176-178.

5 other significant ones

- Bao, Huiming**, Greg Michalski, and Mark H. Thiemens, 2001, Sulfate oxygen-17 anomalies in desert varnishes. ***Geochim. Cosmochim. Acta*** 65 (13), 2029-2036.

- Bao, Huiming**, Thiemens, M. H., 2000, Generation of O₂ from BaSO₄ using a CO₂-laser fluorination system for simultaneous $\delta^{18}\text{O}$ and $\delta^{17}\text{O}$ analysis. *Analytical Chemistry* **72**(17), 4029-4032.
- Farquhar, J., **Bao, Huiming** & Thiemens, M. H., 2000, Atmospheric influence of Earth's earliest sulfur cycle. *Science* **289**, 756-758.
- Bao, Huiming**, Koch, P. L., and Rumble, D. III, 1999, Paleocene/Eocene climatic variation in western North America: Evidence from the $\delta^{18}\text{O}$ of pedogenic hematite. *Geological Society of America Bulletin*. **111**, 1405-1415.
- Bao, Huiming** and Koch, P. L., 1999, Oxygen isotope fractionation in ferric oxide-water systems: Low temperature synthesis. *Geochim. Cosmochim. Acta* **63**, 599-613.

Synergistic Activities

1. Being the leader of a research group that consists of one faculty member, one technician, one visiting professor, two graduate students, and two undergraduate students
2. Participating "2003 Workshop for Early Career Faculty in the Geosciences"
3. Panelist of 2003 NSF Antarctica Geology & Geophysics Program

Collaborators during last 48 months

M. C. Reheis (USGS, Denver), S. Xiao (Virginia Tech), A. J. Kaufman (U. Maryland), D. B. Loope (U. Nebraska Lincoln), Chong-Díaz, G (Universidad Católica del Norte, Chile), M. H. Thiemens (UCSD), Gu, B-H. (ORNL), Lowe, D. (Stanford), Jenkins, K and Khachatryan, M (LSU), X.-L. Yuan, Wang, H., and Zhou, C-M (Chinese Academy of Science)

Graduate and Postdoctoral Advisors

MS: Xinan Mu (Chinese Academy of Science),
 Ph. D: P. L. Koch (UCSC),
 Postdoc: M.H. Thiemens (UCSD)

Advisees

Kathryn Jenkins (MS), Tao Fang (PhD)

Facilities, Equipment, and other Resources

The Stable isotope laboratory suite, at LSU Department of Geology & Geophysics, consists of two rooms with a total area of $\sim 1200 \text{ ft}^2$. The suite has three fume hoods, three vacuum-lines, a CO_2 -laser fluorination system, a newly acquired isotope ratio mass spectrometer (IRMS) (Finnigan MAT 253), and two old Nuclide IRMS systems (for parts). The laboratory has a technician (M. Khachatryan) funded currently by Bao's start-up fund from LSU. LSU's strong commitment on PI Bao's future research program is also reflected in providing fund for Bao's new wet-chemistry laboratory and matching fund for the CO_2 -laser fluorination system and the new MAT253 system.

New wet-chemistry facilities (funded by LSU) -- These include an Ion Chromatograph systems (ICS-90), one freeze-dryer, two ovens, one de-ionized water generator, two centrifuges, clean bench with worktops, binocular microscopes, electronic top-loading balance, ultrasonic cleaners, stir & heaters, water bath, desiccation cabinets, corrosives cabinet, filters & apparatus, shaker, evaporation system, rock crusher, etc. LSU has provided sufficient fund to build a fully equipped wet-chemistry laboratory in supporting stable isotope analyses.

A CO_2 -laser fluorination system (funded by NSF and LSU) – It has been built and has analyzed > 500 samples so far. This system (MIR 10, New-Wave Inc.) has a 30-W CO_2 laser that is computer-controlled and easy to operate. The primary purpose of this line is to fluorinate BaSO_4 to get O_2 for the measurement of both $\delta^{18}\text{O}$ and $\delta^{17}\text{O}$ values for sulfate [Bao and Thiemens, 2000]. User can analyze 12 to 18 samples per working day.

Finnigan MAT 253 – As stated in “Results from Prior NSF Support”, this IRMS system has been calibrated and is in excellent working condition. A TC-EA system with conflo-interface has been ordered and is expected to be installed in early 2004. Once installed, LSU stable isotope laboratory will become one of the few in the world that can measure both $\delta^{18}\text{O}$ and $\Delta^{17}\text{O}$ for oxianions (such as sulfate, nitrate, and perchlorate) to the best accuracies.

Other related facilities -- The Department of Geology and Geophysics at LSU is well equipped with analytical facilities that are supportive to this research project. It has ICP-AES (Perkin-Elmer 6500), Dionex 500 ion chromatography system, Perkin Elmer 3300 atomic absorption spectrophotometer and furnace system, JEOL 840 Scanning Electron Microscope w/ EDS x-ray probe, JEOL JXA-733 automated electron microprobe w/WDS & EDS analyzers, with cathodoluminescence detector and digital image analysis system, isotope preparation lab (Class 100 and Class 1000), X-ray powder diffractometers (Siemens and Philips), and computing facilities (e.g., SGI PowerChallenge Server and SGI Indy).

In addition, we have several machine shops and glass shops that serve the college and the University with very reasonable fee.

Subject: Re: need supporting letter

Date: Mon, 27 Oct 2003 14:11:05

From: jswineha@unlnotes.unl.edu

To: Huiming Bao <bao@lsu.edu>

Dear Huiming:

I am looking forward to working with you and your students on the volcanoclastic deposits and ash beds of the White River and Arikaree Groups of the western Nebraska Panhandle as you track the sulfate oxygen-17 anomaly. I think my 30 years of geologic mapping and stratigraphic experience in this region will be of use to the project. I am familiar with many occurrences of ash and gypsum in these strata, especially in the Gering Formation of the Wildcat Ridge.

I am excited about assisting you in further testing of your dry fog hypothesis. It brings a whole new way of looking at volcanic hazards, in both the present and the past.

Looking forward to collaborating with you and your students.

Sincerely yours,

James B. Swinehart
Professor
Conservation and Survey Division
University of Nebraska-Lincoln
Lincoln, NE 68588-0517