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The Terrestrial Biogeochemical Cycle of barium: A proposed study to examine barium flux in Mojave Desert dust

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The Terrestrial Biogeochemical Cycle of barium
A proposed study to examine barium flux in Mojave
Desert dust

A Thesis Presented
by

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Of Claremont McKenna, Pitzer, and Scripps Colleges
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Abstract

Barium is a relatively abundant element in the crustal environments, Ba quantities can range from anywhere between 200ppm to 900ppm. Most common forms of Ba-minerals found in the environment are barite (BaSO_4), witherite (BaCO_3) and hollandite ($\text{Ba}_2\text{Mn}_8\text{O}_{16}$). Ba is a useful element; it is used in various industries as a component in drilling fluids, in medical research and in manufacturing of various substances such as glass, ceramics, printing paper etc. However high quantity of Ba can be potentially toxic for the human body and can impair plant growth. It is therefore, important to review the terrestrial biogeochemical cycle of Ba, which is less studied and less understood than the oceanic biogeochemical cycle of Ba. Additionally, terrestrial systems face a diverse climate and are not as stable as the oceanic systems. Due to this the terrestrial biogeochemical cycle of barium is continuously changing and is more dynamic than the oceanic cycle. By studying one part of the cycle, i.e. the interaction of Ba in the atmosphere with the geosphere in the Mojave desert, NV, I propose a study to test the hypothesis that occurrence of, Ba-mineral, barite, in desert soils is mainly driven by dust flux. The proposal includes methodology for dust collection, sample analysis using XRF, XRD and SEM.EDS techniques and potential budget and timeline. Evidence supporting this claim would suggest that dust transports such minerals, affects the soil chemistry of desert soils and the interaction of various terrestrial systems.

Introduction and Scope of the study

The objective of my thesis is to review the global terrestrial biogeochemical cycle of barium, including the influence of anthropogenic sources, which alter the cycle more rapidly than many natural sources. Extensive research has been done on the oceanic biogeochemical cycle of barium however, I will reflect on the terrestrial biogeochemical cycle, which is less studied and less understood. Although Ba-minerals can be potentially toxic for the human body and in some cases adversely affect plant growth, my thesis is not focused on examining the toxicology of barium in detail. Instead, I study the way in which barium moves in the terrestrial systems. Generating the terrestrial biogeochemical cycle of barium allows me to study the interaction between the two spheres, atmosphere with geosphere, in depth.

In part II of my thesis, I focus on atmospheric dust fluxes of Ba-minerals, mainly in the form of silt to clay-sized barite and other minerals, in soluble salts and arid soils (Brock-Hon *et al.* 2012) in Mormon Mesa. The presence of barite crystals in petrocalcic horizons at Mormon Mesa, Nevada is thought to be driven by the transport of barium in dust to soil surfaces, and its subsequent dissolution by infiltrating water (Brock-Hon *et al.* 2012). A competing theory is that Ba-minerals precipitate after Ba is weathered out of soil parent materials that include volcanic glass and primary silicate minerals in which Ba is a trace constituent. Subsequently, I propose a study to test the hypothesis proposed by Brock-Hon

et.al. (2012) and Robins *et.al.* (2012) that barite crystals in Mormon Mesa, Mojave desert form mainly due to dust fluxes from nearby sources such as playas and alluvial fans. The study site, Mormom Mesa, Mojave desert, NV is approximately 5 million years old therefore results from this study would also shed light on the climatic changes taking place in this region over millions of years.

Part I. Background: The Terrestrial Barium Biogeochemical Cycle

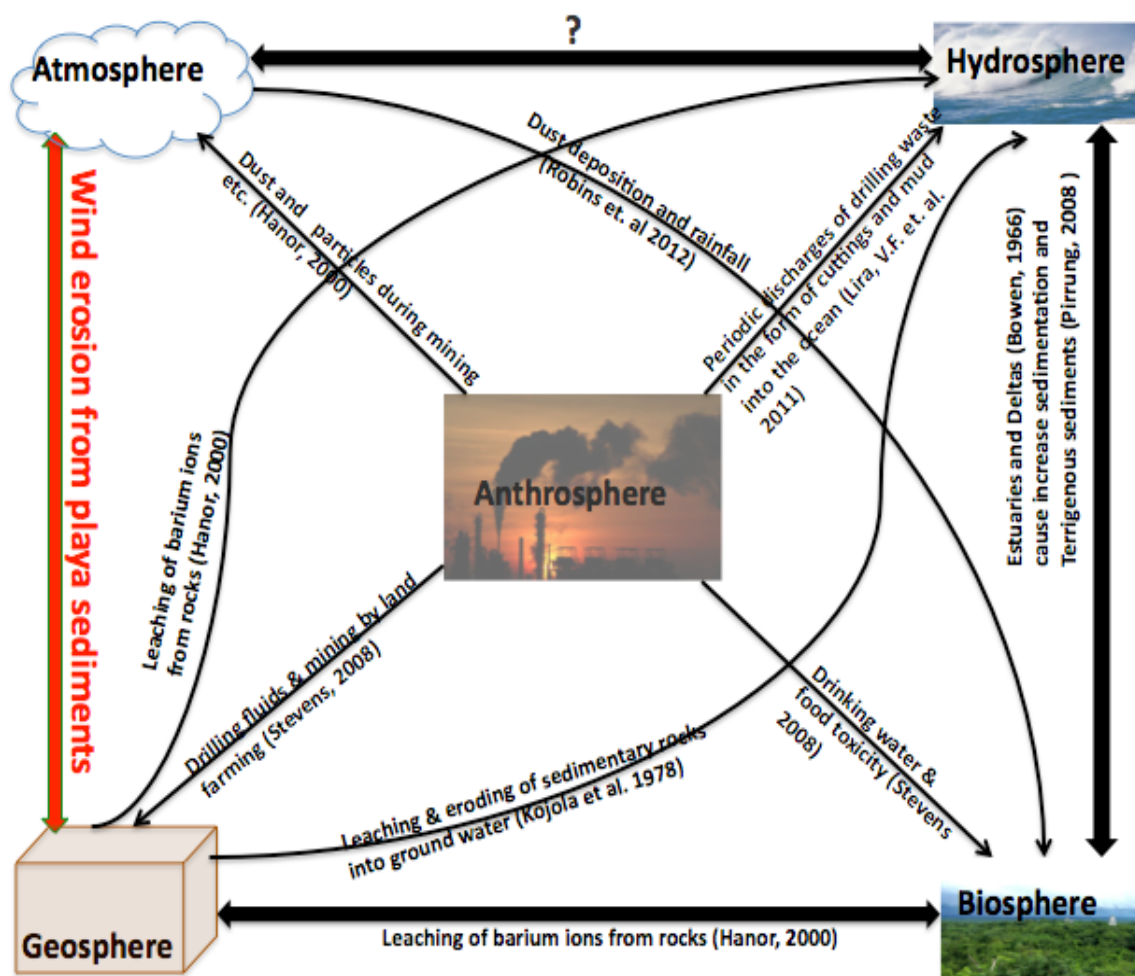
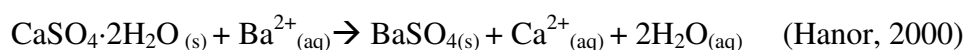


Figure 1. Schematic representation of the terrestrial biogeochemical cycle of barium

Barium in the Geosphere

Barium is an abundant element in the Earth's crust, it is a major component in many igneous and siliciclastic rock types and is typically present in concentrations between 200-900 ppm (Hanor, 2000). Most barium in the Earth's surface exists as impurities in K-bearing minerals such as K-feldspar and K-micas (such as muscovite). This is because Ba^{2+} ions have a similar ionic radius and electronegativity to K^+ ions, and can substitute for K^+ in many minerals. However, some barium also substitutes for calcium ions in Ca-silicates (Hanor, 2000). Barium can also be found forming oxides in igneous rocks, and as hydroxides in weathering products (Kabata-Pendias, 2011). Reactions of barium ions with anhydrite, CaSO_4^{2-} makes barite a replacement mineral of gypsum ($\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$) or anhydrite, via the mechanism:



Clays in sedimentary strata can also favor barium adsorption. The relative closeness of barium to strontium compared to calcium on the periodic table suggests why barite, BaSO_4 , is able to form complete solid solutions with celestine, SrSO_4 , and incomplete solid solutions with anhydrite, CaSO_4 , (Hanor, 2000). Even though there is a significant difference in ionic radii between Ba^{2+} and Sr^{2+} ions of 1.34\AA and 1.18\AA , barite and celestine still form complete solid solutions (Hanor, 2000).

Barium is released from the chemical weathering of sedimentary rocks into both marine and terrestrial systems (Figure 1). There is a degree of overlap between precipitation of barium in oceanic system and in terrestrial systems. However, it is important to look at both the terrestrial and oceanic cycles separately. This is because after precipitation, barium behaves differently in oceans compared with soils.

Barium Geochemistry in the Oceans

Barium is incorporated into the ocean when cold, dense seawater above the ocean floor sinks deep into the crust and reacts with lava, magma, or fresh basaltic rock (Hanor, 2000). Barium also enters ocean through precipitation from pore waters, i.e. the water contained in spaces between sediment particles (Church 1972). Infiltrating seawater moves along permeable faults and fractures in the seafloor (Hanor, 2000). This water is heated and pressurized, which facilitates the dissolution and leaching of ions including Ba^{2+} from crustal rocks. When this hot, hydrothermal seawater eventually rises and is vented back into the colder seawater column, precipitation (crystallization) of ions into various minerals occurs (Hanor, 2000). This is perhaps why marine barite deposits occur in extensional faults in most divergent margins.

Once in the ocean, dissolution of barium, in the form of hydrated divalent cations is rapid. However, re-precipitation of barium from aqueous solutions depends on the types of

ions present in water. Reactions of barium with strontium and sulfate produce insoluble salts such that Ba, Sr and sulfate tend to not persist together when dissolved in seawater (Hanor, 2000). This causes re-precipitation of barium from aqueous solutions in the form of insoluble salts like barium sulfate and barium carbonate. For example, in strontium-barium solutions, a small equilibrium constant is observed between K_{Sr-Ba} at low temperatures, which leads to a strong preferential partitioning of barium into the solid phase and that of strontium into the aqueous phase (Hanor, 2000).

Mobility of Ba^{2+} in Oceans

The solubility of barium in the oceans, in alkaline soil or groundwater solutions, depends on various factors including pH, the concentration of other ions such as carbonate, chloride, and sulfate and on organic complexes formed (Church, 1972). Barium solubility increases as pH decreases from pH 11 to pH 7 and at $pH < 7$ barium solubility is approximately constant (Neubrand, 2000). At higher pH, pH 8 or above (Neubrand, 2000), and depending on the presence of other ions, the solubility of barium decreases and it precipitates in different forms. At pH of 9.3 or less, crystallization of barium sulfate typically limits the concentration of barium in water (Bodek *et al.* 1988). At pH 9.3 or higher, the presence of carbonate may make Ba-minerals like witherite the dominant species (Singer 1974; Bodek *et al.* 1988). However, ions like chloride, nitrate and carbonate can increase the

solubility of barium sulfate in soils, seawater and groundwater below pH 9.3 (Yee-Wan, 2012). Oxidation of elements like Sulfur can increase SO_4^{2-} concentrations, promoting reactions between barium and sulfate ions, and the rapid precipitation of barite. This phenomenon is especially likely in areas with an excess of sulfate such as seawaters (Church 1972). If the solubility of barium decreases it causes sedimentation. Increased sedimentation may increase the risk of accumulating high amounts of barium, which could form hazardous organic compounds and heavy metal salts (Manahan, 2003). The extent to which such accumulation can be hazardous is discussed in the anthrosphere section below.

Estuaries and deltas are also important areas that contribute to the addition of barium into the ocean (Figure 1). Precipitation of barite specifically is accelerated at the point where rivers empty into the ocean; this is due to the high content of sulfate in oceans of approximately 905 mg/L (Bowen, 1966). The combination of different ions and minerals in the estuaries makes it the area of excessive precipitation and biological activity. Precipitation of barite and other minerals occurs because estuaries form a region of estuarine turbidity maximum, ETM, (Greyer, 1993). ETM regions are seen where there is a landward limit of salt intrusion in estuaries (Greyer, 1993). In the ETM region, high levels of suspended particulate matter exist due to the presence of tidal variation in estuarine circulation (Greyer, 1993). A strong tidal force perhaps pushes saline water upriver beneath the flowing river

water and we see tidal re-suspension and sedimentation trapping, which is the horizontal convergence of sediment (Greyer, 1993). Greyer developed a numerical model that supports the hypothesis that an increase in stratification reduces turbulence and increases the rate at which trapping of suspended sediment occurs at the ETM. Along with precipitation, most barium found in marine surface waters comes from terrigenous sediments instead of having biogenic origins (Pirrung, 2008). Terrigenous sediments are sediments that originate in terrestrial environments by erosion of rocks on land (Pinet, 1996) and are transported into the ocean mainly by rivers, but ice and wind also play a part in its displacement.

Mobility of Ba²⁺ in Soil Solutions

It is important to understand mobility of barium in soil solutions (soil water with dissolved ions), rivers and estuaries as part of the terrestrial systems. Once barium is released via weathering of rocks and minerals its mobility depends on the soil's cation exchange capacity and its calcium carbonate content (Yee-Wan, 2012). Cation exchange is a process by which metal ions including Ba²⁺ are taken up by plants in exchange for hydrogen ions (Manahan, 2000), and it is chiefly dependent on the type and abundance of clay minerals and soil organic matter present. Increase in clay minerals and soil organic matter leads to temporary adsorption of barium ions to clay minerals. The rate of adsorption depends on the charge in the solution and the type of phyllosilicates; increase in charge of ions increases the

strength of adsorption (Dixon & Weed, 1898; Brady & Weil 1999). Soils with high cation exchange capacity and high calcium carbonate content have limited barium mobility (Yee-Wan, 2012). This is perhaps because high cation exchange means higher adsorption of barium to plants, which decreases mobility of barium in soils. However, soils with high chloride content and/ or low pH increase barium mobility (Yee-Wan, 2012).

The decay of organic matter also affects the mobility of barium in soil in complex ways. This is because the process of decay is a common oxidation-reduction reaction occurring in soil; it increases the levels of CO₂ dissolved in groundwater, which lowers pH and adds to weathering of carbonates (Manahan, 2000) including witherite (barium carbonate). Lowering of pH due to an increase in dissolved soil CO₂ would increase barium mobility; acidic soils particularly make it easier for plants to take up barium (Pendias, 2011).

Possible mechanism for Ba uptake by plants:



However, increased weathering of carbonates like calcite would reduce acidity thereby decreasing mobility. High amounts of dissolved Cl⁻ ions or Mg²⁺ ions may increase barium mobility in soil (Robins *et al.* 2012; Hanor 2000). It is important to identify such interactions of ions with decaying organic matter because the way in which ions and organic

matter affect barium mobility in soil solutions allows us to better understand how Ba moves and interacts with the terrestrial systems.

Barium in the Biosphere

Barium is found in the biosphere because of biomineralization by microorganisms and because Ba ions leached from rocks and minerals are made available to plants and animals via soil solutions or by seawater (Figure 1). Authigenic barium minerals, i.e. Ba-minerals occurring where they originate, are less abundant in terrestrial environments, but they do form in soils, playas, and groundwater systems according to the same chemical principles that drive barium geochemistry in the oceans. In soils, barium is found in two general types of environments, namely, in extremely wet, saturated soils and in alkaline, dry, desert soils. Reduction of barite is especially favored in soils that have low partial pressure of oxygen, f_{O_2} and high H^+ . However, barium minerals have also been reported from alkaline desert soils with completely different chemistries (Brock-Hon *et al.* 2012; Robins *et al.* 2012). In soils that have developed in the presence of excess water, weathering releases barium as part of a geochemical equilibrium between soil solutions and minerals (Manahan, 2000). The nature of the saturated, subsurface B and C soil horizons provide favorable conditions for weathering because the soil can repeatedly swell and shrink as it hydrates and drains. The recurring pattern of swelling - shrinking perhaps increases the rate of chemical weathering

and the rate of physical abrasion of mineral grains. This in turn releases barium from minerals into the soil in the form of barium ions. These ions usually associate with SO_4^{2-} , and precipitate as barite (BaSO_4). It is essential to understand the chemical form of barium in soils and dust because it affects the availability of Ba for uptake by humans via the gastrointestinal tract (Shock *et al.* 2007) and by plants via cation exchange.

There are few reports describing barium toxicity in plants, in some cases excessive barium concentrations have led to stunted growth of barley and beans (Pendias, 2011). Adding Ca, Mg and S salts into the growth media can decrease potential barium toxicity in plants. Formation of witherite and barite due to the addition of the above salts causes complex interactions between these elements (Pendias, 2011) that perhaps reduce barium mobility in soil thereby decreasing uptake of barium by plants.

Biom mineralization is a mechanism by which microbes precipitate minerals. Most organisms lack the ability to differentiate between calcium, strontium and barium ions. However some algae, such as the desmid green algae *Closterium moniliferum*, specifically precipitate (Ba, Sr) SO_4 crystals in terminal vacuoles situated at the cell boundaries because of low solubility of barium relative to SrSO_4 and CaSO_4 (Krejci, 2011). Specific precipitation is accomplished by maintaining a level of under saturation or only slightly super saturation with respect to $\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$ and super saturation with respect to SrSO_4 in their vacuoles. By

preventing nucleation of celestine crystals these organisms preferentially precipitate (Ba, Sr)SO₄. These processes tend to occur via inorganically mediated and biologically mediated sulfate reduction reactions (Hanor, 2000).

In the Earth's crust, at high pressure and temperature, reducing agents of barite i.e. methane, hydrogen, carbon monoxide and solid carbon help barium to precipitate. However, in the biosphere, bacteria are the likely agents. Human activities such as mining of crude barite ore are a way of obtaining barium on a large scale (Yee-Wan, 2004).

Barium in the Atmosphere: Delivery to Soils

In arid soils, as mentioned above, wind erosion from playa sediments is a major source of barium in the atmosphere (Figure 1). Wind erosion and subsequent deposition of minerals as sediments is the process by which elements in the atmosphere deposit on the earth's surface (Manahan, 2000). The addition of barium ions to the soil from the atmosphere occurs via rainfall or dust (Figure 1). This net addition is especially noticeable in arid soils where rainfall combines with alkaline soil and fluctuations in soil moisture increase barium mobility between soil horizons (Robins *et al.* 2012). Interpluvial climate increases the amount of dust, which comes from playa sediments or volcanic rocks (Robins *et al.* 2012) and the alkalinity of the soil, which increases the amount of barium that reaches the soil surface and its mobility in soil. Before deposition to the surface soils, various factors affect

the residence time of barium in the atmosphere such as the size of the particle, its chemical composition and environmental factors like rainfall (Yee-Wan, 2012). Chemical forms of barium present in dust play an important role in its availability for uptake by humans (Shock, 2007). Inhalation of barium particles can cause baritosis in humans, which is discussed in the Anthrosphere section.

Barium in the Anthrosphere: Health Implications of Ba biogeochemistry

Human activities as diverse as drilling, medical research, and explosives manufacture influence the global biogeochemical cycle of barium (Figure 1). Some barium minerals such as barite are useful materials. Barite can easily be crushed into powder form and used for fillers, extenders and weighting agents (Hanor, 2000). Barite and witherite (BaCO_3) are important sources of barium chemicals that are used in manufacturing of glass, ceramics, TV tubes, paint, plastics, photographic print paper etc.(Hanor, 2000). In the health industry, barite is used for gastrointestinal X-ray examinations. It is also a component of drilling fluids and is used to monitor the impact of oil drilling platforms (Yee-Wan, 2012). However, sedimentation of barium in surface waters can accumulate to hazardous amounts (Manahan, 2003).

Evaluating the anthropogenic sources of barium is important because high levels of barium are potentially toxic for the human body. In humans, barium absorption occurs via the

gastrointestinal and respiratory tract. In the body, Ba ions interfere with the signaling mechanism of neurotransmitters by inhibiting Ca^{2+} activated K^+ channels in cell membranes, which can be potentially fatal (Gregus and Klaassen, 1996). Exposure to high levels of barium has an effect on the electrolyte balance, cardiovascular system, neuromuscular system, and gastrointestinal tract in humans (Yee-Wan, 2012). However, most of the barium manufactured for anthropogenic uses is in the form of barium sulfate, which is largely insoluble in the human body. Ingestion of barite (barium sulfate) compounds will not have adverse effects, as the barium is simply removed from the body through the large intestine. However, inhalation of barium sulfate in high concentration may lead to baritosis (Hanor, 2000). Baritosis is one of the benign pneumoconiosis; it lies in the lungs for years without producing symptoms (Doig, 1976).

Manufacturing of barium, its various uses, storage, distribution and disposal release barium into different spheres of the environment. Major sources of anthropogenic release to the biosphere include drilling fluids and agricultural wastes, which may contain dissolved barium (Yee-Wan, 2012). In addition to barium ions obtained from playas as mentioned above, emission of barium particles into the air also occurs due to the release of dust and particulate matter during various anthropogenic activities like mining, refining, and production of barium and barium compounds (Yee-Wan, 2012). In the atmosphere,

barium is mostly present in particulate form as barite, witherite or hollandite, and is also sometimes detected as a trace element in primary silicate minerals. It is then removed from the atmosphere via dry and wet deposition (Yee-Wan, 2012). However, as noted above, the atmospheric flux of ba-minerals is not well understood.

The terrestrial biogeochemical cycle of barium summarized above shows how the biological, geological and chemical factors are involved in the cyclical pathway of this element. It is important to focus more on the terrestrial part of the cycle to get a deeper geological understanding. This is because unlike the stable oceanic biogeochemical cycle, the terrestrial part of the cycle has a constantly increasing amount of barium input from the anthrosphere. Additionally, terrestrial systems face a diverse climate and are not as stable as the oceanic systems; this causes the terrestrial biogeochemical cycle of barium to continuously change thereby making it more dynamic than the oceanic biogeochemical cycle. It is important to understand these modifications to make sure that human activities don't lead to an excessive amount of barium accumulation in the environment. One such modification that I am focusing on is barium deposition on surface soils in arid regions. This is because it is widely accepted that barium leaches out from parent rock however, given the arid conditions, a competing hypothesis suggests that dust deposition of barite perhaps plays an equally if not a more important role on the presence of barium in desert soils.

Part II. Barium in Mojave Desert Dust: Mineralogy & Quantification study

Studies by Robins *et al.* (2012) and Brock-Hon *et al.* (2012) have proposed that the presence of barite, a commonly found Ba-mineral, in desert soils is largely driven by dust flux. However, this hypothesis has not yet been tested. A conceptual model by Robins *et al.* (2012) compares the effects of interpluvial (arid) to pluvial (arid to semi arid) climate change on Ba²⁺ mobility in desert soil. The model suggests that, in arid regions with rare input of water and high ionic strength, Ba²⁺ can leach from dust at the surface and into the soil, where it forms barite. However, in wetter climates, soil has low ionic strength therefore, barite forms crystal complexes that persist in soil while other salts are leached.

To test the above hypothesis, I propose to examine the soil composition and the dust flux at different sites (4 sites) upwind of Mormon Mesa, NV, and compare it with the dust and soil composition of Mormon Mesa (1 site, downwind). Dust will be collected towards the end of the hottest season when rate of evaporation is the highest in playas and on alluvial fans. However, if the experiment does not yield enough samples for analysis or for Ba²⁺ detection, the study might have to be repeated for several years to understand any persisting trends. This proposed research will complement previous studies on dust flux in the Mojave desert (e.g., Robins *et al.* 2012; Reheis 1992,1995, 1997, 2006; Brock-Hon *et al.* 2012; Retallack & Kirby 2007)

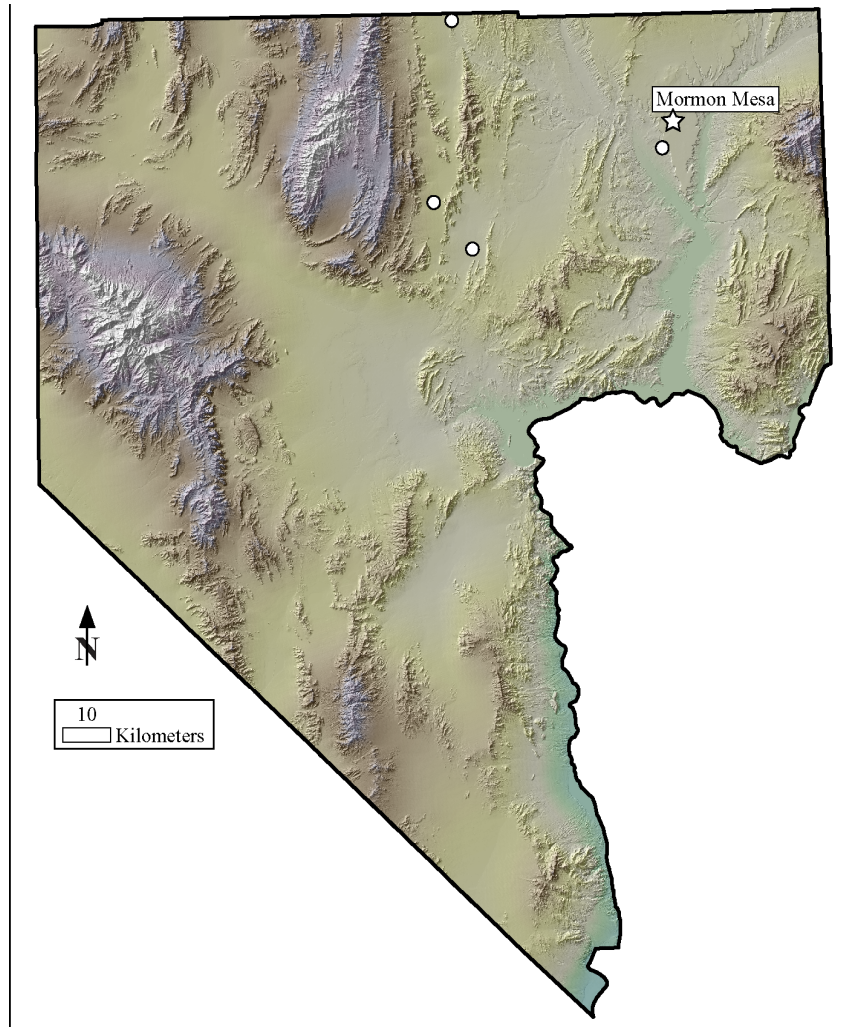


Figure 2. Four representative sites for sample collection (upwind) and one site on Mormon Mesa (downwind). Map & base data from USGS (2005) and Robins (personal communication).

Five representative sites will be included; one site on Mormon Mesa (downwind) and four, playa, valley-bottom sites upwind of Mormon Mesa will be selected. The composition of dust flux from playa sites upwind of Mormon Mesa (Figure 3) will be measured and compared with the dust composition in Mormon Mesa. From each site, three surface soil

samples and three dust samples will be collected, i.e. a total of thirty samples from these five sites.

Methods

Atmospheric dust will be collected using marble dust collectors (MDCOs). These will be set 2 meters above ground following the methods of Reheis (1995). The dust traps will contain rectangular plastic tray. The tray will be filled with marbles to emulate the effect of a gravel-like surface and prevent the filtered dust from being blown away (Reheis, 1995). Also the marbles should prevent birds from building nests in the tray.



Figure 3. MDCO on a steel fence post 2m above the ground (Reheis 1995).

Figure 3 is an example of a MDCO, the tray in the above figure has Teflon coating (Reheis 1995), which is important part of the dust collector. This is because Teflon is non

reactive and adds no minerals to the sample due to weathering or abrasion. The 2m high pole prevents contributions from heavy, sand-sized particles.

Chemical analysis of dust and soil samples will be performed using several complementary techniques including X-ray fluorescence spectrometry (XRF), X-ray diffraction spectrometry (XRD) and scanning electron microscopy coupled with energy dispersive spectrometry (SEM-EDS). XRF is a procedure that determines chemical composition quantitatively by examining the fluorescent X-ray emitted from a material initially excited by bombarding it with high energy X-rays or gamma rays. Several grams of sample are needed for XRF analysis. In the XRF spectrometer an incident beam passes through the sample, some of the energy from the beam is absorbed by the sample, which in turn energizes or “excites” the sample. The energized sample in turn emits energy of a wavelength characteristic to the element present. Depending on the wavelength, various detectors are used to measure the intensity of the emitted beam.

XRD (X-ray diffraction) is used to determine the non-quantitative mineralogy of the sample, specifically, its crystal structure (lattice spacing) with implications for chemical composition and physical properties. As the x-rays pass through the sample its energy decreases, mainly due to absorption by atoms in crystal lattice (Guinier, 1994). This causes scattering from the crystal lattice and there is interference between the waves scattered,

which causes diffraction patterns to appear that help in determining the crystal structure (Guinier, 1994).

SEM-EDS images and provides a chemical analysis of the sample (dust). In SEM, the sample is positioned beneath an electron beam, which scans the sample surface. Once the electrons strike the sample, different signals are generated, which help in imaging the sample and studying general compositional characteristics such as its mass. When EDS is coupled with SEM the signals that help in determining the elements composition are X-rays, which are emitted from the sample. As the primary beam hits the sample, the sample is energized. The energized sample emits X-rays, which have energy characteristic of the parent element (similar to XRF). Detection of these X-rays via EDS allows for qualitative chemical analysis. Both SEM-EDS and XRF can yield quantitative chemical analysis.

Anticipated Results

XRF and XRD chemical analysis of the dust sample should show the presence of Ba-bearing minerals or compounds by confirming its chemical composition and its chemical structure (lattice spacing). This is because barium originated in the playa sites should combine with the eolian dust and travel upwind to Mormon Mesa. In the dust samples, I expect to find Ba-minerals in high enough concentrations to cause Ba-mineralization.

Additionally, from the SEM analysis I expect to find imperfect, not pristine Ba-mineral structures because traveling from a distance in the wind should weather barite structures.

Study of soil sample from the A-horizon should indicate (1) whether a significant amount of dust is detectable in surface soils and (2) if the mineralogy and chemistry of the surface soil is similar to that of the dust sample collected. Similar mineralogy and chemistry would suggest that Ba-minerals infiltrate from dust into soils. Accumulation of silt, clay and soluble salts support the hypothesis that soil is developing due to dust deposition because parent-rock material contain marginal amounts of silt, clay and soluble salts (Reheis, 1989).

Addition of soluble salts comes from the salt rich dust generated from lake deposition around playas (Reheis, 1997).

Anticipated Implications

It is important to study the implications of dust flux because dust affects the environment in complex ways. Some of the ways in which dust incorporates into the Earth systems is by affecting the global climate, providing nutrients to soil and aquatic ecosystems and by influencing human activity through interfering in visibility and causing health problems (Reheis, 2006). Effects caused by dust are therefore critical because it does not affect the local area but instead travels large distances thereby affecting activity of various ecosystems globally. Dust samples collected by Reheis (1997) traveled up to 40km north and

south of playas. Moreover, dust is comprised of various minerals and compounds that have different effects on various systems. It is therefore important to focus on the different elements and to examine their effects. By focusing on one element, barium in dust, we can examine the interaction of various Earth systems and the effect of barium from the dust flux on soil chemistry in Mormon Mesa, Mojave Desert.

If the sample of dust flux indicates the presence of barium it would support our hypothesis that barium in dust along with other soluble salts is deposited in soil. This would in turn imply the presence of barium compounds not only in bedrocks but also in air. Further implications can be studied like the toxic effects of atmospheric barium on plants and on humans.

Proposed Budget

Table 1. Approximate budget for sample collection

	Equipment	Approximate cost of each sample (\$)	Approximate cost total (\$)/year
1.	Travel (gas, dust sampling and conference)	2,400	2,400
2.	Sampling equipment (bags, shovels, labels)	200	200
3.	Dust trap (x15)	100 (x 15)	1,500
4.	Chemical analysis at Pomona college (x 30 sample)	0 (x 30 samples)	0
5.	Chemical analysis at other institutes (x 30 sample)	(40-80)/sample (x 30 samples)	2,400
	Total expenditure (\$/year)		6,500

A budget for the study is presented in Table 1. The cost of carrying out this experiment for a year would be approximately \$6,500 if the chemical analysis were carried out at other institutes. The cost of travel including gas, dust sampling and a conference is approximately \$2400. Equipment including bags, shovels, and labels would be \$200 and setting up three dust trap at each site would be \$1500 (\$100/dust trap). Chemical analysis, if done at Pomona will be free, but at other institutes procedures such as XRF, XRD would cost up to \$(40-80)/sample. For 30 samples one such procedure would be approximately \$2,400/sample.

Further Research

In the future, if results of the proposed study show evidence that supports the presence of Ba-minerals in the dust flux, isotopic studies might be carried out to trace barium sources, which would further strengthen the hypothesis. For example, Van der Hoven and Quade (2002) traced spatial and temporal variation in sources of calcium using strontium isotopes. By using strontium isotopes as a tracer, one might be able to examine whether soil barium can be attributed to dust or instead to the *in-situ* weathering of primary parent materials. If the isotopic signature of Ba and Sr in playas is similar to soil ratios than to the ratios of parent-rock material then the main source of barium is likely to be eolian dust. The isotopic ratios of the samples can be measured using a mass spectrometer.

The location of the study is approximately 5 million years old, a soil profile of the location could give insight into soil development and climate changes over millions of years. If barium in soil is attributed to the dust flux during interpluvial climate then a soil profile could show when, over a span of millions of years, did Mormon Mesa have interpluvial climate and when it had pluvial climates.

Summary

The proposed study will collect and analyze soil and dust samples to test whether a significant amount of dust reaches surface soils and if the mineralogy and chemistry of surface soil is similar to that found in the dust sample. This study could be the basis of future research on atmospheric barium in arid soils and on barium toxicity through aerosol absorption in interpluvial regions. Additionally, detection of increasing quantity of barium in the atmosphere would have further implications on climate change over millions of years, as mentioned above in future research. Data from the MDCOs should be recorded for an extended time period to depict any trends between climate change and barium concentration. Trends of climate changes recorded by MDCOs over decades and those shown by the soil profile could indicate how the climate might change in the future.

Acknowledgements

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References:

Bowen. H. J. M. 1966. Trace Elements 'ii Biochemistry. Academic Press, London, Chap. 5, pp 61-84.

Bates, M H. 1988. Land farming of reserve pit fluids and sludges: fates of selected contaminants. *Water Research*. 22.6: 793-797.

Bodek, I. 1988. Environmental inorganic chemistry: Properties, Processes and Estimation Methods. Elmsford, NY: Pergamon Press.

Brady, N.C. and Weil, R.R. 1999. The nature and properties of soils, twelfth edition. New Jersey: Prentice Hall. 881 pages.

Brock-Hon, A.L; Robins, C.R. Buck, B.J. 2012. Micromorphological investigation of pedogenic barite in Mormon Mesa petrocalcic horizons, Nevada USA: Implication for genesis. *Geoderma*. 179-180.

Church, T.M., and Michel B. 1972: Thorium and Uranium in marine Barite. North-Holland Publishing. 14. 139-144.

Church, T M. and Kenneth W.1972. Marine Barite Saturation. North-Holland Publishing.15. 35-44.

Church, T. M. 1979. Marine Barite. Mineralogical Society of America. 6.175-206.

Capo, R. 1999. Sources of strontium and calcium in desert soil and calcrete. Elsevier. 170. 61-72.

Doig, A. T. 1976. Baritosis: a benign pneumoconiosis. *Thorax*, 31(1), 30-39.

Dixon, J.B. and Weed, S.B., eds. 1989. Minerals in soil environments, 2nd edition. SSSA Book Series 1. Madison, Soil Science Society of America. 1244 pages.

Eylem, C. 1990. Sorption-desorption behavior of barium on clays. *J. Environ. Radioactivity*. 183-200.

Gregus, Zoltán, and Curtis D. Klaassen. 1996. Mechanisms of toxicity. Casarett and Doull's Toxicology: The Basic Science of Poisons, Klaassen, CD (Ed), McGraw-Hill, NY.

Greyer, R. 1993. The importance of suppression of turbulence by stratification on the estuarine turbidity maximum. *Estuarine Research Federation*. 16. 113-125.

Guinier, A. 1994. X-Ray Diffraction: In Crystals, Imperfect Crystals, and Amorphous Bodies. Mineola, NY: Courier Dover Publications. 3-4.

Hanor, J. S. 2000. Barite-Celestine Geochemistry and Environments of Formation. Department of Geology and Geophysics.

Heather D. H. 2003. A Concept-Based Environmental Project for the First-Year Laboratory: Remediation of Barium-Contaminated Soil by *In Situ* Immobilization. Exp.

Kojola, W.H; Brenniman, G.R and Carnow, B.W. 1978. A review of environmental characteristics and health effects of barium in public water supplies. *Rev Environ Health* 3:79-95.3.

Kabata-Pendias, A. 2011. Trace Elements in Soils and Plants. CRC Press. 4. 142-144.

Krejci, M. R. 2011. Selectivity in biomineralization of barium and strontium. *Journal of Structural Biology*. 176.2 192–202.

- Lagas, P. 1981. Model experiments on the Behaviour of Cyanide and Barium in a Landfill and in the Soil. *Studies in Environmental Science*. 17.539–543.
- Lintern M.J. 2006. The source of pedogenic carbonate associated with gold-calcrete anomalies in the western Gawler Carton, South Australia. *Chemical Geology*. 235. 299-324.
- Lira, V.F; Gap S and Sofie D. 2011. Effects of barium and cadmium on the population development of the marine nematode *Rhabditis (Pellioiditis) marina*. *Marine Environmental Research* 72 : 151-159
- Merefield, J.R.1987. Ten Years of Barium Build-up in the Teign. *Marine Pollution Bulletin*. 18.5 (1987): 220-222.
- Manahan, S.E. 2000. *Toxicological Chemistry and Biochemistry*. 3rd ed. Lewis Publishers.
- González-Muñoz, M.T. 2012. Precipitation of Barite by *myxococcus xanthus*: Possible Implications for the Biogeochemical Cycle of Barium. *ASM Journal*.
- Magalhães, M.O. L. (2012). Effect of variations in the redox potential of Gleysol on barium mobility and absorption in rice plants. *Chemosphere (Oxford)* (0045-6535), 89 (1), p. 121.
- Neubrand, A. 2000. Room•Temperature Solubility Behavior of Barium Titanate in Aqueous Media. *Journal of the American Ceramic Society*. 83.4. 860-864.
- Nogueira, T.A.R; Wanderley, J.D; Ivana, M.F; Marcos O.M and Zhenli H. 2010. Barium uptake by maize plants as affected by sewage sludge in a long-term field study. *Journal of Hazardous Materials* 181.1. 1148-1157.
- Pinet, P.R.1996. *Invitation to Oceanography* St. Paul: West Publishing Company.
- Pichtel, J. 2000. Distribution of Pb, Cd and Ba in soils and plants of two contaminated sites. *Environmental Pollution*. 110. 171-178.
- Pirrung, M; Illner,P; Matthiessen, J. 2008. Biogenic barium in surface sediments of the European Nordic Seas. *Marine Geology*. 250. 89-103.

Reheis, M. 1989. Development Rates of Late Quaternary Soils, Silver Lake Playa, California. *Soil Sci. Soc. Am. J.* 53. 1127-1140.

Reheis, M. 1992. Morphology and genesis of carbonate soils on the Kyle Canyon fan, Nevada, U.S.A. *Geoderma.* 52. 303-342

Reheis, M. 1995. Dust deposition in southern Nevada and California, 1984-1989: Relations to climate, source area, and source lithology. *Journal of Geophysical Research*, 100. 8893-8918

Reheis, M. 1997. Dust deposition downwind of Owens (dry) Lake, 1991-1994: Preliminary findings. *Journal of Geophysical Research*, 102. 25,999-.26.

Reheis, M, 2006. A 16-year record of eolian dust in Southern Nevada and California, USA: Controls on dust generation and accumulation. *Journal of Arid Environment.* 67. 487-520

Retallack, G.J. 2007. Middle Miocene Global change and Paleogeography of Panama. *Palaios.* 22. 667-679.

Robins, C.R; Brock-Hon, A.L; Buck, B.J. 2012. Conceptual Mineral Genesis Models for Calcic Pendants and Petrocalcic Horizons, Nevada. *Soil Science Society of America Journal.*

Stoops, G.J. 1978. Micromorphological Evidence of Barite neoformation on soils. *Geoderma.* 20. 63-70.

Sullivan, L.A and Koppi A.J. 1993. Barite Pseudomorphs after Lenticular Gypsum in Buried Soil from Central Australia. *Aust. J. Soil Res.* 393-396.

Sullivan, L.A. and Koppi. A.J. 1995. Micromorphology of authigenic celestobarite in a duripan from central Australia. *Geoderma* 64. 357-361.

Shock, S.S. 2007. Assessment of the Solubility and Bioaccessibility of Barium and Aluminum in soils affected by mine Dust Deposition. *Environment Science and Technology.* 41. 4813 - 4820.

United States Geological Survey (USGS), 2005. Seamless Data Distribution Digital Elevation Models. US Department of the Interior.

Van der Hoven and Quade, J. 2002. Tracing Spatial and temporal variations in the sources of calcium in pedogenic carbonates in semiarid environments. *Geoderma*. 108. 259-276.

Wongpokhom, N; Kheoruenromne,I; Suddhiprakarn, A; Gilkes, R.J. 2007. Micromorphological properties of salt affected soils in Northeast Thailand. Diss. Kasetsart University, Bangkok 10900, Thailand, Elsevier B.V.

Yee-Wan Stevens; Daphne Moffett; Nickolette Roneyne; Lisa Ingerman and Steven Swarts. 2012 Priority Data needs for Barium.

Zhang, Peng-Chu. 2001. Adsorption of barium (II) on montmorillonite: an EXAFS study. *Colloids and surfaces. A, Physicochemical and engineering aspects (0927-7757)*, 190 (3), p. 239.

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