I. Abstract

Lithium is recognized as an essential metal in the development of clean energy via lithium-ion batteries. These batteries are becoming extensively used as both energy storage devices as well as for vehicle propulsion. One geologic formation where lithium concentrates is in closed-basin brines, where it can then be economically viable to extract. An example of such a brine is in Clayton Valley, Nevada. This location is optimal for study because it is currently in production, it is not as large as some other deposits, and it is the only lithium-brine in the US. Because lithium brines occur in similar settings worldwide, it is appropriate to research its geochemical and petrological properties to assist in the development of a mineral exploration model.

Samples of suspected lithium source rocks, brine, groundwater, and meteoric water samples will be collected in Clayton Valley. In a laboratory setting, the rocks will be classified using petrological and geochemical techniques. Weathering experiments will be conducted on the source rocks to elucidate the mechanism by which lithium is released into the environment and evaporation experiments will give insights into brine evolution and lithium concentration. All samples from the weathering and evaporation experiments will be analyzed for total and dissolved metals as well as anions. The data generated from this project will be included in a geochemical model to help understand the basic processes lithium brines evolve which can then be used to help in exploration for additional deposits.

II. Specific Aims

Because of the increasing demand for lithium-ion batteries, it is critical that we understand how lithium deposits are formed and how we can use that knowledge to help find more deposits as well as to understand the environmental impacts of extracting this resource. To date, there has been little research focused on this critical and scarce element, which is the underlying motivation for this study.

This study will focus on the continental brine in Clayton Valley, Nevada (the only known lithium brine in the United States). This brine is optimal for study because it is the only economic lithium deposit of its type currently in production and the geologic setting is typical of global continental brines. Therefore the understanding of the release of lithium from the volcanic rocks and its subsequent accumulation through evaporation in Clayton Valley will be transformative to any lithium deposit on the planet.

The goals of this study are to:

1. *Characterize the potential lithium source rocks in Clayton Valley to decipher which geologic formations contribute lithium to the environment.*

2. *Model the geochemical processes that control the release of lithium from source rocks and the subsequent concentration of lithium in the basin through laboratory experiments.*

III. Introduction

The use of lithium has recently emerged as a growing market in alternative energy. The demand for the rechargeable lithium-ion batteries is the main driver as they are extensively used in technologies including smart phones, laptops and have become the primary battery of choice for hybrid vehicles. With the acknowledgement of declining fossil fuel resources on a global scale, a recent initiative from the U.S. Department of Energy Vehicle Technologies Program in Energy Efficiency and Renewable Energy (2010) states that the development of lithium-ion batteries for vehicle propulsion is favorable due to their performance in cold weather, abuse tolerance, and ability to recharge at high rates. This initiative awarded $940 million in grants to lithium battery materials suppliers, manufacturers, and a recycler (USGS Mineral Commodity Survey, 2010). Lithium batteries will also become increasingly important as the global energy supply turns to alternative means such as solar, wind, and hydroelectric which are limited for use on a wider scale due to the problem of efficient energy storage and transport (DOE Critical Materials Strategy, 2010).

Economically important sources of lithium are from two distinct geologic formations: 1) continental brines and 2) lithium-bearing minerals such as spodumene found in pegmatites. Another occurrence of lithium in hectorite, a hydrothermally altered clay, exists but is currently not economic to produce. The production cost of the marketable compound lithium carbonate, from continental brines is lower than production cost from pegmatites by at least $2000 per ton (Roskill, 2009), highlighting its importance as the optimal source of lithium. Availability of continental brines for current production is increasing, although still not great enough to meet current worldwide demand, especially with a growing interest in batteries (Roskill, 2009). This indicates a need for more exploration to find additional lithium resources to help fuel the future of sustainable energy needs.

Lithium is a metal with unique geochemical behavior because it tends to remain in solution even under extreme evaporative and concentrated conditions. Continental brines have been formed in desert regions with abundant lithium-rich volcanic rocks. Therefore, the source of lithium is generally agreed to be from the weathering of these rocks and the subsequent concentration in subsurface brines due to evaporation (Davis, 1986; Price et. al., 2000; Kunasz, 1974). Brine deposits with anomalously high lithium content occur in similar geologic settings worldwide, including Bolivia, Argentina, Chile, the United States, Afghanistan, and Tibet.

The Clayton Valley, Nevada lithium brine (Figure 1) has been studied in limited detail (Albers, 1972; Kunasz, 1974; Davis and Vine, 1979; Pantea,1981; Davis, 1986; Price, 2000; Zampirro, 2005) however a *quantifiable* model of the source(s) of lithium and the processes by which it is concentrated has not been well documented (L. Munk, personal communication). However, the basic hypothesis to be tested in our research is is that lithium found in brines may originate from young volcanic rocks and/or a geothermal source.

The scientific understanding of lithium brines has historically evolved with an economic need for the metal. Originally, the only known sources of lithium ore were in pegmatites (an igneous rock that is highly fractionated and contains elevated concentrations of lithium and other associated elements). The discovery of lithium in Searles Lake, California brines opened the door to exploration of other continental brines for anomalous levels (Kunasz, 1973). The Leprechaun Mining Company discovered high levels of lithium in Clayton Valley in 1965 (Kunasz, 1973; Davis & Vine, 1979). Kunasz (1973) originally identified volcanic rocks and geothermal water as possible lithium sources for the brine in Clayton Valley. He evaporated samples of geothermal water in a laboratory setting, which resulted in the same concentration of lithium that was in the natural brine, thus suggesting that the primary source of lithium was in the geothermal water but this did not rule out a volcanic rock source. Davis and Vine (1986) later interpreted that the brine had evolved by evaporation and mineral precipitation within the basin, causing its composition to differ from the natural source waters. They agreed with Kunasz (1973) that the source of lithium was potentially from the tertiary volcanics or geothermal water but suggested that no one source was responsible for the anomalous levels found to be concentrated in the brine. No quantitative study of lithium source or transport has been completed, leaving this to be speculative. Price (2000) analyzed both unweathered and weathered lithium source rocks. He identified the main lithium-bearing source rocks as obsidian, perlite, devitrified rhyolite, and ash-flow tuff. He found that the weathered samples had lost an average of 128 ppm lithium versus the unweathered samples and suggested that this was the main source of lithium for Clayton Valley.

Other research is underway by McKibben (in prep.) to investigate the dispersion rates of lithium from spodumene, a common lithium ore mined in pegmatites. This work along with that proposed here and by L. Munk will help us understand how lithium is released into the environment. Munk et al. (pers. comm.) are currently conducting a large scale project to model the geochemical evolution of the Clayton Valley lithium brine. My research fits directly into this larger project and will contribute to the overall geochemical model and development of an exploration tool for other brines.

Figure 1. USDA Farm Service image of Clayton Valley. The town of Silver Peak is on the left, with evaporation ponds for lithium ore concentration on the right. Clayton Valley is located in Esmeralda County in Nevada near the border with California Image taken directly from Google Earth.

IV. Project Design

This project will be both field and laboratory based. Field work in Clayton Valley, Nevada is required in order to obtain samples of lithium-rich brine and the lithium-source rocks. Laboratory investigations will help elucidate the geochemical processes that release lithium to the environment and the subsequent processes that concentrate lithium in the subsurface brines. Both the field and laboratory methods that will be developed by this project will be transformative to other lithium brine deposits on a global scale. In particular, to date, there have been no laboratory studies conducted in order to understand how lithium is concentrated into economically viable deposits. These laboratory experiments will be the first of their kind to contribute to furthering the understanding of significant geochemical processes that concentrate this element and will assist in locating more of these energy-critical deposits.

IV. a. Field Methods

Water samples including meteoric (rain and snow), hot spring, and subsurface brines will be collected in May 2011 (It should be noted here that Chemetall Corporation which runs the production plant in Silver Peak, NV has given permission for us to collect the brine samples and are part of the consortium of researchers working with Dr. Munk on this project). These samples will serve as compositional end-members that are representative of all water in Clayton Valley. The composition of these waters will be compared to the laboratory weathering results. They will be analyzed for total (unfiltered) and dissolved (filtered) major and trace elements by inductively coupled plasma mass spectrometry (ICP-MS). Total and dissolved samples will be preserved with ultra-pure nitric acid at the time of collection. Anion analysis by ion chromatography (IC) will also be run. All water samples will be run in the UAA ASET lab.

Based on the current research project being conducted by Dr. Munk and previous studies by Price (2000), I will collect representative lithium-source rocks from the Clayton Valley basin. Munk et al. (in prep) and Price (2000) have identified some of the potential lithium source rocks, however, a complete chemical and petrological investigation is lacking. Therefore I will conduct a full petrologic study on the potential source rocks, which will include bulk chemical analysis and petrography. Rock crushing and initial processing will be done in the UAA Geological Sciences Rock Preparation Room and lithium concentrations will be analyzed in the UAA ASET lab by ICP-MS. All other elemental analyses will be completed at the Washington State University Geoanalytical lab using X-ray fluorescence (XRF) and ICP-MS.

IV. b. Laboratory Methods

Characterization of Rocks

Thin sections of rock samples collected in the field will be analyzed using standard techniques with a petrographic microscope. Modal percent of the minerals and volcanic glass found in thin section will be documented with a point counter mounted to the mechanical stage of the microscope. Any observed color, texture, and weathering will also be documented. The petrographic descriptions in conjunction with the bulk chemical analysis by WSU will aid in the interpretation of the whole rock geochemistry data to accurately depict mineral phases. The geochemical behavior of lithium dictates where the mineral will be partitioned in the rock. Only certain minerals have the ability to take lithium into their crystalline structure. These characterizations will not only contribute to the explanation of the rocks' petrogenesis (origin) but also identify which rocks are potential lithium sources to the brine. These methods will provide data to address Goal 1 of this proposal.

Weathering Experiments

Representative rock and alluvial fan samples will be experimentally weathered in the laboratory in order to understand the release of lithium into the environment. Methods of Munk et al. (2002) will be followed. Approximately 0.50 gram aliquots of the crushed and pulverized samples will be placed in nine 250 mL flasks and filled with 150 mL meteoric water from snow melt that has equilibrated with atmospheric carbon dioxide. The pH of the snowmelt will be measured prior to starting the experiment and the pH will be measured at regular intervals throughout the experiment. The flasks will be placed on a shaker table and agitated at 150 rpm. The resulting solutions will be filtered and analyzed for major and trace elements by ICP-MS and for anions by IC after 1 day and then 2, 5, 10, 20, 30, 40, 50, and 60 days respectively. (See Figure 2 in Anticipated Results)

Evaporation Experiments

The purpose of the evaporation experiment is to model brine evolution. As the natural brine undergoes solar evaporation, the potential for saturation of evaporative mineral constituents increases and solid minerals precipitate from solution (Eugster, 1980). These experiments will establish the mineral phases that can potentially form from the brine and these results can be compared to the phases found in Clayton Valley. Clayton Valley has six known aquifers from which lithium brine is extracted (Zampirro, 2004; Davis, 1986). Samples of brine will be collected from each of these aquifers. In the lab, 2 liters of each sample will be exposed to Clayton Valley's approximate mean summer temperature of 90^0F in a convection oven for three weeks. Small aliquots of the evaporative solution will be collected at regular intervals for chemical analysis by ICP-MS and IC to determine the evolutionary concentration of the solution (Alai, 2003). Once all the solution has evaporated the solids that have formed will be identified and quantified. The data gathered from these experiments will give insight as to which mineral phases form and which phases contain the lithium. From this data an evaporation model can be constructed which will identify the order of evaporite precipitation, the rates of the chemical reactions that take place, and concentration factors for important elements. Goal 2 of this proposed research will be addressed with data from the weathering and evaporation experiments.

IV. c. Data Analysis and Modeling

Standard geochemical and statistical software including PHREEQC and Excel will be used to model the results. Petrological Harker and spider diagrams will be created in Excel to interpret the bulk analysis of the rocks. Piper diagrams will be utilized to interpret the chemistry of both groundwater and surface water.

V. Anticipated Results

Figure 2. illustrates preliminary results of changes in pH of a solution in contact with a lithium-bearing rock from Clayton Valley in a trial run of the outlined weathering experiment. The pH of the solution in contact with one of the suspected lithium source rocks from Clayton Valley changed from 5.55 to 7.26 in 60 days. This preliminary data indicates that the primary minerals from the rock control the pH of the solution over time. Dissociation of primary minerals due to water-rock interactions results in the release of cations and anions to the solution and it is possible that certain elements are in high enough concentration to precipitate as secondary minerals (Brantley, 2008). It is anticipated that lithium will remain in the dissolved phase as it is extremely soluble, even more so than sodium and chloride. Further investigation and bulk water chemistry are required to fully understand the release of lithium and other important elements into the solution.(these chemical analyses will be part of the proposed research).

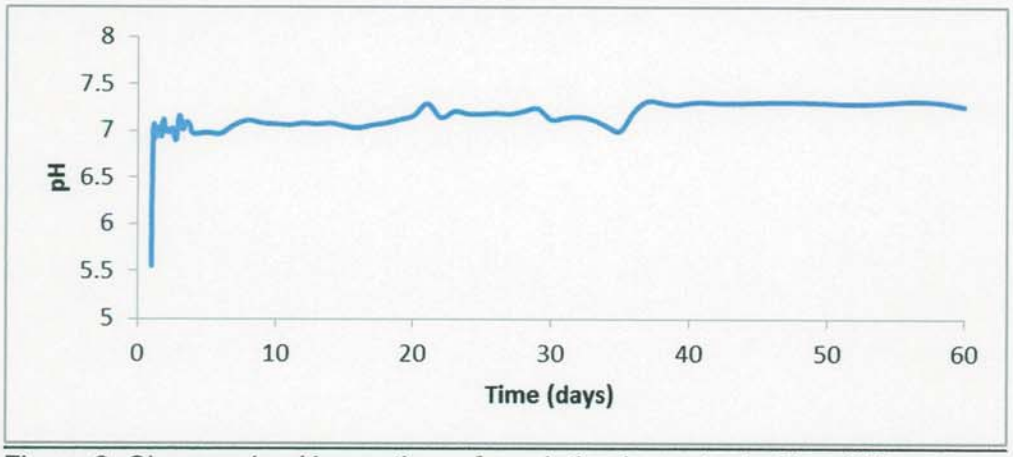

Figure 2. Changes in pH over time of a solution in contact with a lithium-source rock from Clayton Valley, Nevada.

VI. Transformative Aspects

The scope of this project reaches beyond understanding a single brine in Nevada. Because lithium brines of this nature occur in similar settings on a global-scale, modeling the behavior of lithium in Clayton Valley will serve as an excellent indication of what to look for under similar conditions at other prime locations. Although research on lithium deposits had some traction between the 1950s-1980s, modern research on is lacking, especially by US scientists. There is now a critical need for lithium as it is a technologically important element required for optimal energy storage needs. Additionally, there is evidence that fossil fuel production is on the downward part of the global curve (Hubert, 1982). We have also learned much in the past decades about the detrimental effects of fossil fuel burning on the environment and climate (Alley, 2003).

As alternative energy sources become increasingly utilized we also need mechanisms to store and transport that energy. To date, lithium-ion batteries are the most efficient storage mechanisms available, however, because of the large number of batteries required more lithium deposits are needed and must be discovered.

Research on projects such as this one will be transformative within the fields of geology, geochemistry, resource development, and to the future of green energy. With government initiatives promoting clean, safe energy, the collaboration of scientists and resource developers around the world can make a greener future possible.

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