Final Technical Report: G10AP00056 - Lithium Brine Resources: A Predictive Exploration Model

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Abstract

Lithium is a scarce and technologically important element. Ubiquitous use of Li-ion batteries for energy storage has put increasing demands on the resource. Lithium brine deposits hold the majority of easily produced Li as compared to pegmatites which are also mined for Li and Li-rich clay (hectorite) deposits. Therefore, understanding the formation of lithium brine deposits is essential for developing exploration tools and models for the identification and development of these deposits. Clayton Valley, Nevada, USA is the location of the sole Li brine in production in North America. It is located in a closed-basin system with an arid climate. The Li-rich brines are currently being produced from six different aquifers in the playa. The brines have formed from a complex process involving evaporation, mixing, and halite, and hectorite (dissolution, precipitation, ion exchange and sorption). Climate fluctuations in Clayton Valley, NV over time (at least since ~ 1Ma) have played a role in the preservation of Li in clays (hectorite).

Introduction

Lithium is a scarce and technologically important element produced primarily from brines and pegmatites. Although it is a non-renewable resource, it is used in conjunction with renewable energy technologies and hybrid automobiles, primarily in the form of Li-ion batteries. Now the most used form of batteries in many electronics. The consumption of lithium carbonate is on the rise and so far global production has kept pace. It is essential, however, that a predictive exploration model for lithium brines be developed to help meet future demand. This study focuses on geochemical aspects to determine the origin of the brines.

Clayton Valley is located in Esmeralda County, Nevada, USA approximately 180 km north of Death Valley, CA and is the location of the only Li brine deposit in production in North America (Fig 1). Clayton Valley is a closed basin with an area of 1,342 km^2 and a playa surface of 72 km^2. The basin lies in the eastern rain shadow of the Sierra Nevada and is arid with an annual average precipitation of 13 cm, average evaporation rates of 142 cm/yr and an average temperature of 13^{o}C. The elevation of the valley floor is 1298 m, lower than any of the basins in the region.

Methods

Subsurface brines, groundwater, springs, and meteoric water (snow) were collected in February and May, 2010. Brines were collected by pumping water from existing wells in the Chemetall Foote well field. Brine was allowed to run from the well head into a 5 gallon bucket until pH and T stabilized before containing the samples. Water samples for dissolved elemental and anion analysis were filtered in the field using a plastic 60 mL syringe and 0.45 µm syringe filter into 30 mL HDPE bottles. The samples were acidified at the end of each day with ultra-pure nitric acid. Water samples for total elemental analysis and hydrogen and oxygen isotope analysis were collected into 30 and 15 mL bottles respectively and the sample for total elemental analysis was acidified at the end of each day. Water samples for Li isotope analysis were collected in pre-cleaned 125 mL bottles and were kept cool until returned to the UAA Geochemistry Laboratory where they were filtered through 0.45 µm filters, acidified and shipped to Rutgers University where they were analyzed for Li isotopic composition. All elemental and anion analyses were performed by ICP-MS at the UAA ASET lab. Hydrogen and oxygen isotope analysis were completed at the UAF soils lab. Lithium concentrations in rocks were determined by ICP-MS after a 2-acid microwave digestion and dilution process. Clays were separated from bulk samples of the ancient lacustrine deposits and from drill core cuttings and analyzed for hydrogen isotopic composition by methods outlined in Horton and Chamberlain (2006 and references within) at Stanford University.

Laboratory weathering/leaching experiments were modified after Munk et al. (2006). Nine polycarbonate flasks were prepared with 0.50g of the pulverized sample in 150 mL of snow melt collected from Clayton Valley. The flasks with air-permeable membranes were put on a shaker table for 60 days. Solutions were extracted from the flasks on days 1, 2, 5, 10, 20, 30, 40, 50, and 60 and prepared for analysis via ICP-MS and IC for major and trace elements including lithium, and anions respectively. pH was measured throughout the duration of the experiment.

Geology of the Basin

The basement consists of late Neoproterozoic to Ordovician carbonate and clastic rocks that were deposited along the ancient western passive margin of North America. During late Paleozoic and Mesozoic orogenies, the region was shortened and subjected to low-grade metamorphism. Granitoids were emplaced at ca. 155 and 85 Ma. Extension commenced at ca. 16 Ma and has continued to the present, with changes in structural style. A metamorphic core complex just west of Clayton Valley was exhumed from mid-crustal depths during extension. The basin is bounded to the east by a steep normal fault system toward which basin strata thicken. Tuffaceous lacustrine facies (Esmeralda Formation) deposited during the Late Miocene or Pliocene, contain up to 1300 ppm Li and average 100 ppm Li (Kunasz, 1974; Davis and Vine, 1979). Late Miocene or Pliocene felsic tuffs and rhyolites along the basin's eastern flank have Li concentrations reported by Price et al. (2000) to be as high as 228 ppm, however, this study indicates that the highest Li concentrations in these volcanic rocks is actually an order of magnitude less (~22 ppm). Multiple wetting and drying periods during the Pleistocene resulted in the formation of alternating lacustrine deposits, salt beds, and Li-rich brines. Hectorite in the playa sediments contains from 350-1171 ppm Li (Kunasz, 1974). Prior to development of the brine resource, a salt flat and brine pool existed in the north part of the basin, but groundwater pumping has eliminated the surface brine pool.

The subsurface Li-brines are pumped from six aquifer units. Volcanic glass in the main ash aquifer (MAA) shares strong compositional affinities with the ~750 ka Bishop Tuff. However, this ash bed could also be correlated with some of the 0.8-1.2 Ma tuffs of Glass Mountain (Sarna-Wojcicki et al. 2005). In Clayton Valley, this aquifer system ranges between 5–20 m thick. Other aquifers include the salt aquifer system (SAS) comprised of thick bedded halite deposits interbedded with silt [30-100m]; the tufa aquifer system (TAS), a localized aquifer of consolidated travertine in the upper basin [6-20m]; the lower ash system (LAS), an extensive zone of thin-bedded volcanic ash deposits, interbedded with silt and sand [10-90m]; the margin gravel aquifer (MGA), a localized aquifer of mixed gravel, sand, and silt [10-70m]; and the lower gravel aquifer (LGA), a poorly sorted deposit of coarse to fine gravel, sand, and silt [50-100m].

Geochemistry of Waters in the Basin

Waters sampled in Clayton Valley include springs, groundwater, subsurface brines, and snow (meteoric). The brines are classified primarily as Na-Cl waters. The springs and groundwater have a mixed composition and are more dilute than the brines. The $\delta^{18}O$ and δD signatures of the water are illustrated in Fig. 1. Meteoric water collected as snow plots on the GMWL (global meteoric water line) as does precipitation from nearby Tonopah, Nevada (Friedman et al. 2002). The groundwater brines form an evaporation path from the GMWL with the water from the SAS (the most isotopically enriched brine water, Fig. 2). This trend could also represent a mixing line between freshwater and brine. Fig. 2 also illustrates results from an evaporation experiment of brine that was allowed to evaporate at the surface in Clayton Valley. The results indicate that if the brine evaporates to 100% at the surface, the $\delta^{18}O$ and δD signatures become notably more enriched than those of any of the sampled subsurface brines.

The Na and Cl chemical signature of the waters indicates that there are dilute inflow waters (springs) that are concentrated in Na and Cl through halite dissolution and/or evaporation (Fig. 3). However, based on the brine evaporation trend in Fig. 2, further explanation is necessary.

Figure 4 illustrates that the inflow waters (springs) and non-brine groundwaters are likely affected by water-rock interactions, increasing the $\delta^{18}O$ signature; some of the brines, however, appear to be more strongly influenced by evaporation. Because the most enriched brine (SAS) has a $\delta^{18}O$ and δD that is less than that of the fully evaporated brine (Fig. 1), we suggest that the SAS brine has subsequently undergone dilution from meteoric water. Therefore, we return to the hypothesis that the "evaporation" line in Fig. 2 could represent a mixing line between the SAS and the meteoric/dilute spring waters. Investigating the problem further, Fig. 5 indicates that there is an increase in Na concentration as δD increases for most of the brine samples. Note that most of the non-brine (inflow) waters show an increase in Na at relatively constant δD indicating little evaporation of that water. Some of the spring waters have a slight isotopic enrichment, which is expected because of evaporation through capillary draw. The brines indicate an increase in Na with increase in evaporation.

The Li content of the waters in Clayton Valley ranges from less than 1 µg/L in the snow sample up to 406.9 mg/L in the LAS aquifer. The cold springs surrounding Clayton Valley have Li concentrations of less than 1 mg/L. The one hot spring in the area located east of Clayton Valley near Alkali contains 1.6 mg/L Li. Lithium content of the groundwater from the freshwater well that extracts water from an alluvial fan located near SilverPeak, NV is less than 1 mg/L. The hot groundwater well located northeast of Silver Peak in Clayton Valley contains 40.8 mg/L Li. Interestingly, water collected from a deep geothermal drill rig operating about 20 miles north of Silver Peak in May 2010 had water with only 4.9 mg/L Li. Fig. 5 indicates that the inflow waters and some of the brines have Li concentrated by evaporation and other brines have relatively constant Li with increasing Cl. Davis et al. (1986) proposed that the Li was concentrated by the same processes as Cl and therefore must have been trapped as a Li-rich bittern when the halite formed. The comprehensive data set presented here supports that hypothesis for the formation of the SAS brine, but other processes were likely involved in the formation of other brines. (Further work is underway to use the $\delta^{18}O$ and δD of clays from core samples in the basin to understand the climate history and past periods of Li enrichment). However, because the average Li content of SAS brine is lower than the Li content of the LAS and the MAA-East, there are other sources and/or processes that contribute Li. Fig. 6 indicates that there is another source of Li to the LAS brine because of variable Li concentrations at nearly constant δD, and there is an obvious diversion from the dilute inflow water-SAS mixing line. The likely explanation(s) is that Li is leached from hectorite ($NaO_3(Mg,Li)_3Si_4O_{10}(F,OH)_3$) associated with the volcanic ash, transported from the Esmeralda Formation (east), and/or from authigenic hectorite in the basin.

The range in δ^7Li values (Fig. 7) indicate multiple sources of Li to the subsurface brines; the one hot spring sampled to the east of the valley has the most depleted δ7Li signature, indicating water that has interacted with clay minerals. Further isotopic analyses of the inflow waters and brines are necessary.

δD_{SMOW}, and Climate Record

Clays were separated from reverse circulation drill rock chip samples obtained from a core from Chemetall Foote Corporation. The clays were analyzed for δD_{SMOW} in order to develop an understanding of the past climate record in Clayton Valley, NV. Additionally, clays were separated from ancient lake deposits (Esmeralda Fm) flanking the east side of the Clayton Valley Basin. X-ray diffraction was also performed on the clay fraction (in intervals that contained enough clays) in order to identify mineral phases. Hectorite along with smectite was identified in most of the intervals with clays present. Figure 9 illustrates the δD_{SMOW} results from clays from the core 387X and clays from the Esmeralda Fm. The signature from the clays as a function of depth indicate fluctuations in climate over time between warmer and cooler periods, but without age control on the core it is not possible to know the scale of the fluctuations. The only age control that exists in the basin is the probably occurrence of the Bishop Tuff indicating a marker bed of 750ka. This volcanic ash layer manisfests itself as the Main Ash Aquifer (MAA) in the basin. However, what is striking is that the range of δD_{SMOW} values in the Esmeralda Fm. overlaps more or less the same range of δD_{SMOW} values throughout the sediment core. This may indicate that the clays are genetically related and the clays found in the core in the east part of the basin were transported during basin filling.

Lithium in Rocks from the Basin

Table 1. lists the bulk Li concentrations for various rock types including two samples from alluvial fans collected in the Clayton Valley basin. The concentrations range from below detection (<LOD) to 21.4 ppm (a gray volcanic tuff in the east part of the basin). This is an order of magnitude less than what Price et al. (2000) report for the same volcanic tuff collected in the same location. Figure 10 illustrates the results from leaching (weathering experiments) conducted on three of the rock samples from Clayton Valley, NV. Rock sample CV2R has the greatest amount of Li (22 ppm) and released the highest concentration of Li (~8 µg/L) into solution compared to the two alluvial fan samples 10DW22 with 14 ppm Li and releasing ~6 µg/L Li into solution and 10DW21 with 4.5 ppm Li and releasing ~1 µg/L Li into solution. Alluvial fan sediment sample 10DW21 has approximately 30% less Li than 10DW22. The ratios of Li in the rock (Li_r) to Li released into solution (Li_w) are (Li_r/Li_w) for CV2R = 2750:1, 10DW22 = 2330:1, and 10DW21 = 4500:1. Since 10DW21 is located down drainage (west) from CV2R and is an alluvial fan sediment sample it probably has less Li because it has been weathered (leached) from the original source rock area in Clayton Ridge. This area of the basin also has no detectable surface water in springs or otherwise, unlike the other parts of the basin. Additionally there is a NE-SW trending normal fault that exists in the area near 10DW21 which may act as a conduit for subsurface water to be transported into the basin. This could be a primary mechanism by which Li is brought into the deeper parts of the basin.

Predictive Exploration Model and Next Steps

The sub-surface Li-rich brines in Clayton Valley, NV exist due to a combination of geologic process. The volcanic rocks and alluvial fans surrounding Clayton Valley, NV contain up to 22 ppm Li and Li-rich clays from ancient lake deposits contain up to ~1000 ppm Li (Kunasz, 1970). These Li source-rocks (volcanics and ancient lacustrine deposits) undergo leaching (perhaps low temperature and geothermal) by which Li is removed and transported through the subsurface where it is concentrated through evaporation. Water-rock interaction is also apparent from the $\delta^{18}O$ signature of some of the brines which could mean that heat from the geothermal activity in the subsurface enhances the effects of evaporative concentration of the brines. The fact that Clayton Valley is the lowest topographic point in the region is important because it likely means that there are intrerbasin groundwater contributions. Perhaps Li is even transported from areas beyond Clayton Valley which is part of the focus of the next phase of this research (2011 MRERP grant proposal submitted by Munk and Hynek) along with dating the brines and determining the recharge and regeneration timeframe of the brines.

Conclusions

The Li brine at Clayton Valley, NV, USA has formed from a complex process of evaporation, mixing, and halite and hectorite dissolution, precipitation and ion-exchange/sorption. The SAS brine appears to be an older brine that has mixed and been diluted with fresh inflow waters. However, the Li, δD, and $\delta^{7}Li$ indicate that there is another source(s) of Li to the brines, likely hectorite that accumulated in the basin either from the weathering of the Esmeralda Fm. (ancient lake deposits) flanking the basin. The Li sources, accumulation, and storage in the basin are under further investigation and a new proposal has been submitted to the USGS MRERP 2011 RFP to help support this future work.

Acknowledgements

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Publications Resulting from this Work

Munk, L.A., Bradley, D.C., Hynek, S.A., and Godrey, L., 2011. Geochemistry of Li-rich Brines in Clayton Valley, NV, USA. Society of Geology Applied to Ore Deposits Bi-Annual Meeting, Antofagasta, Chile.

Munk, L.A., Bradley, D.C., Hynek, S.A., and Chamberlain, C.P. 2011. Origin and Evolution of Li-rich Brines at Clayton Valley, Nevada, USA. American Geophysical Union Annual Meeting.

Jochens, H.J., and Munk., L.A., 2011 Understanding Li-bearing Rocks as Potential Sources to Brine, Clayton Valley, Nevada. Alaska Miners Association Annual Meeting, Anchorage, AK.

Jochens, H.J., and Munk, L.A., 2011. Experimental Weathering of Lithium-Bearing Source Rocks Clayton Valley, Nevada, USA. Society of Geology Applied to Ore Deposits Bi-Annual Meeting, Antofagasta, Chile.

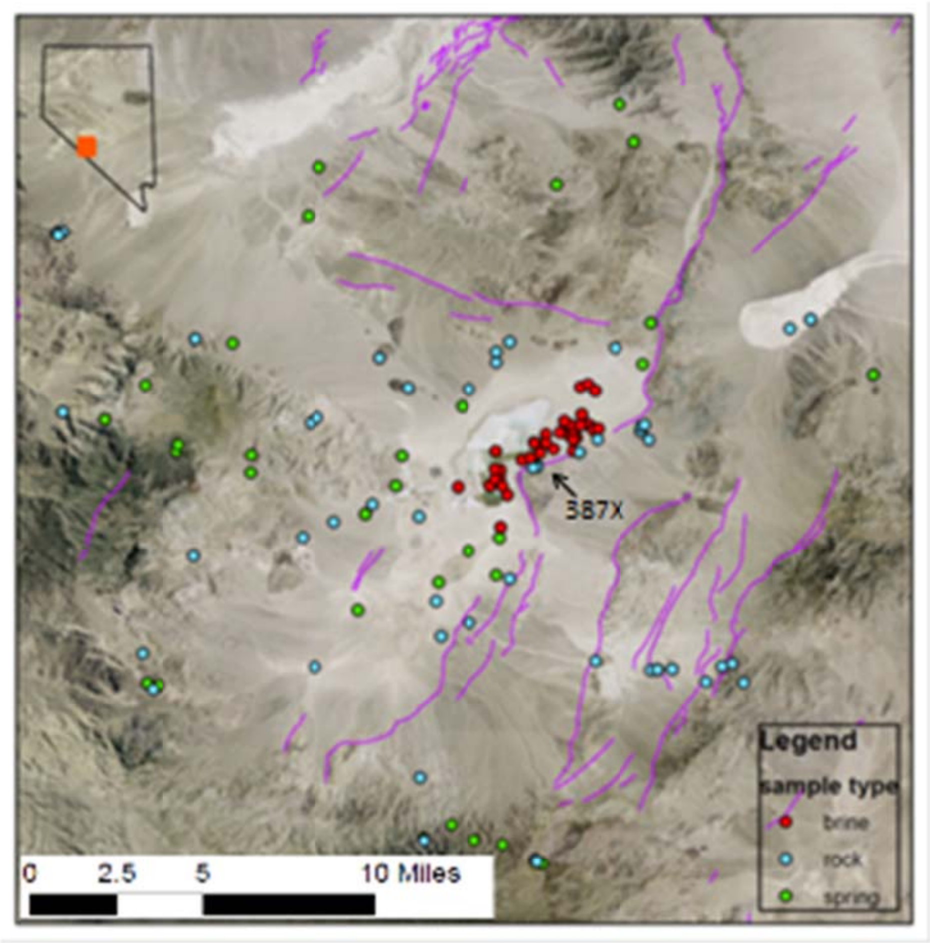

Figure 1. Clayton Valley, Nevada field area showing locations of brine, spring, and rock samples collected in Clayton Valley, NV. The approximate location of drill core 387X is also indicated. The evaporation ponds which hold the pumped subsurface brines are located near the middle of the figure where the brine samples are. Purple lines are mapped faults in the area.

Table 1. Bulk Li concentrations in rocks from Clayton Valley, NV

Sample	**Li (ppm)**	**rock type**
CV-2R	21.4	volcanic tuff
CV-3R	10.8	volcanic tuff
CV-4R	19.9	rhyolite
CV-6R	9.0	volcanic tuff
CV-7R	1.4	volcanic tuff
CV-11R	5.8	obsidian
CV-14R	<LOD	volcanic tuff
10DW1	<LOD	granite
10DW7	1.7	orthogneiss
10DW21	4.5	alluvial fan
10DW22	14.0	alluvial fan
10DW35	1.9	volcanic tuff

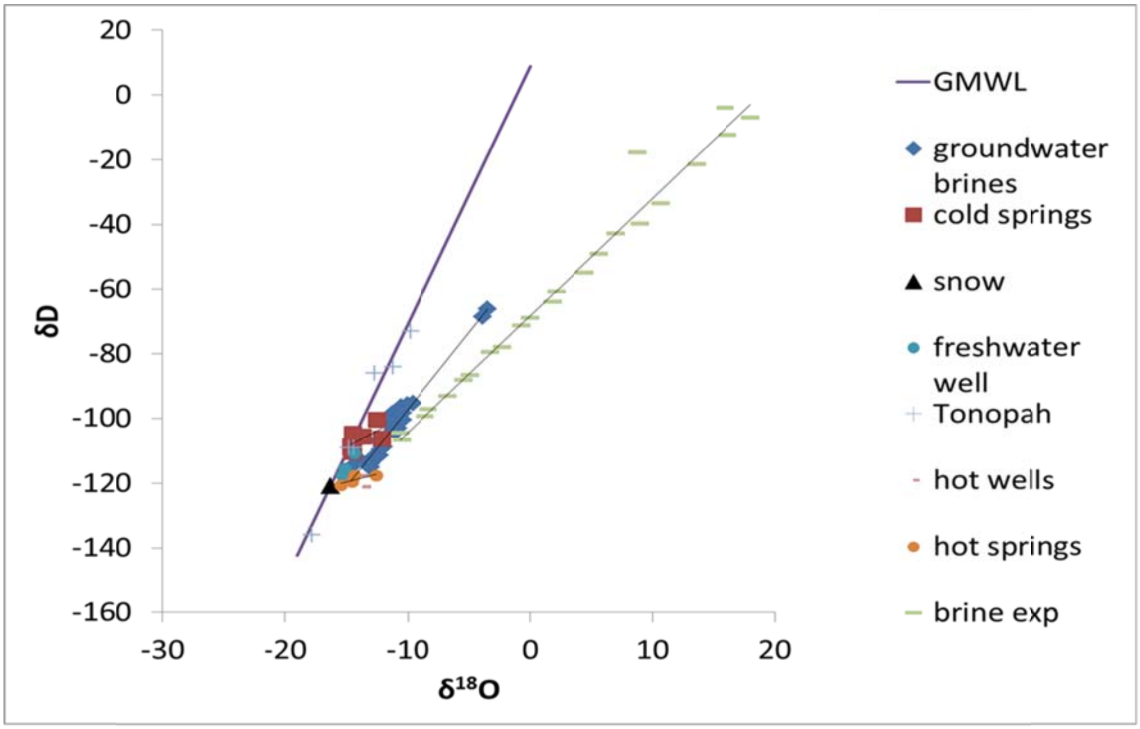

Figure 2. $\delta^{18}O$ vs. δD for water in Clayton Valley, NV and the brine evaporation experiment.

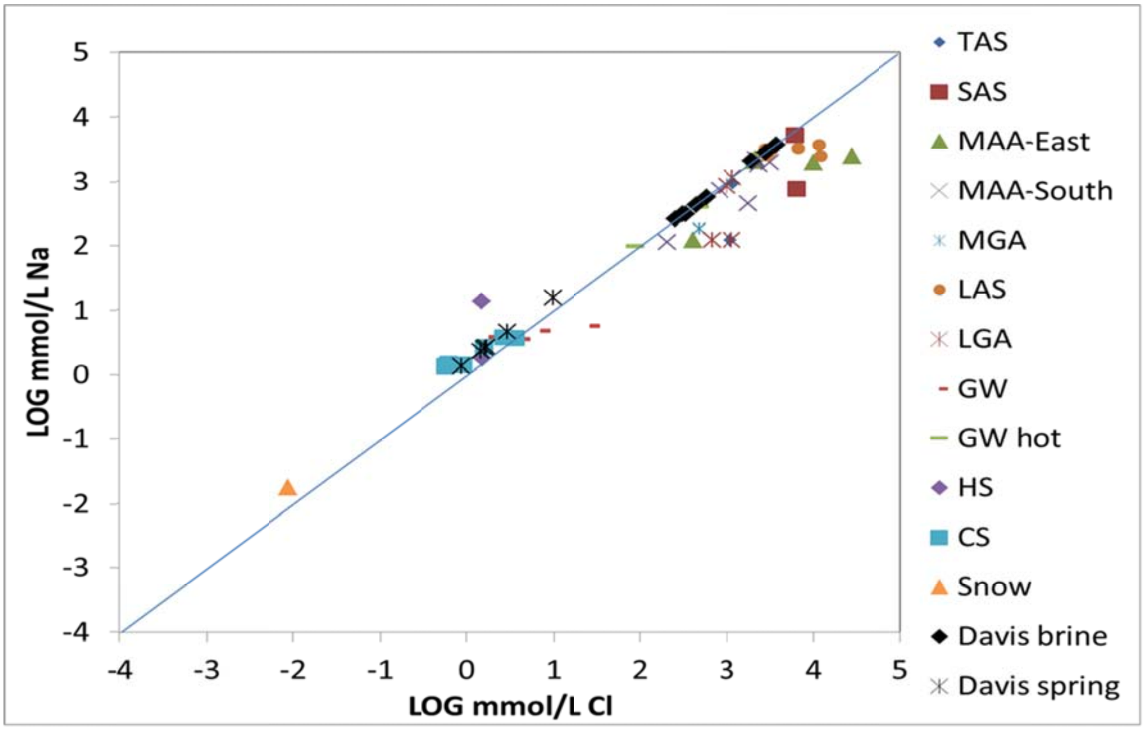

Figure 3. Log-Log plot of Cl vs Na including data from Davis et al., 1986. (GW = groundwater, GW hot = hot groundwater, HS = hot springs, CS = cold springs, other aquifer designations given in text).

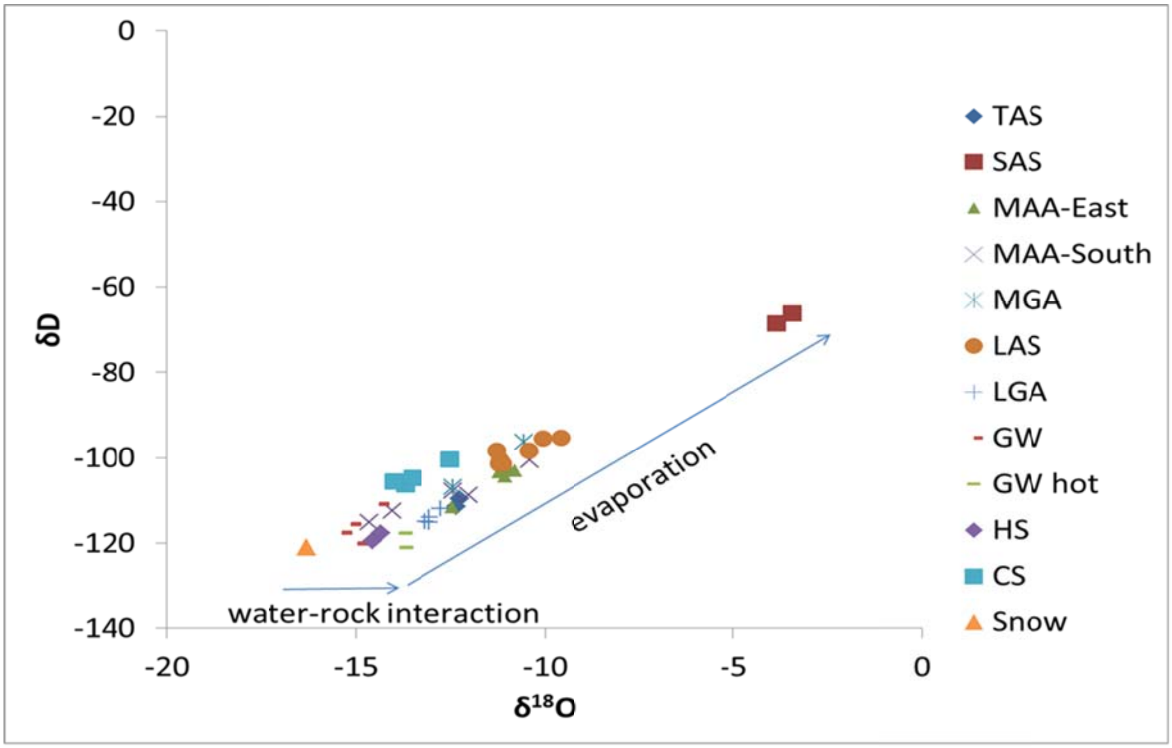

Figure 4. δ^{18}O vs. δD for snow, springs, groundwater and brines (Fig. 3 for symbols).

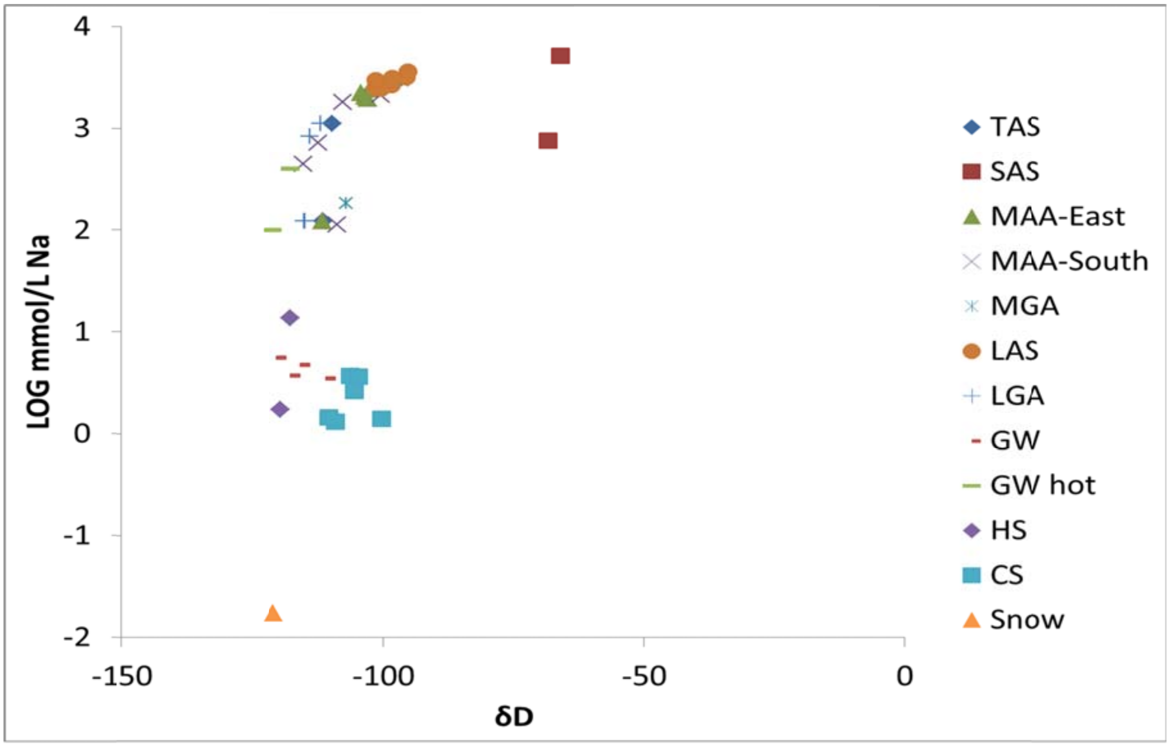

Figure 5. δD vs. LOG Na for snow, springs, groundwater and brines. (Fig. 3 for symbols)

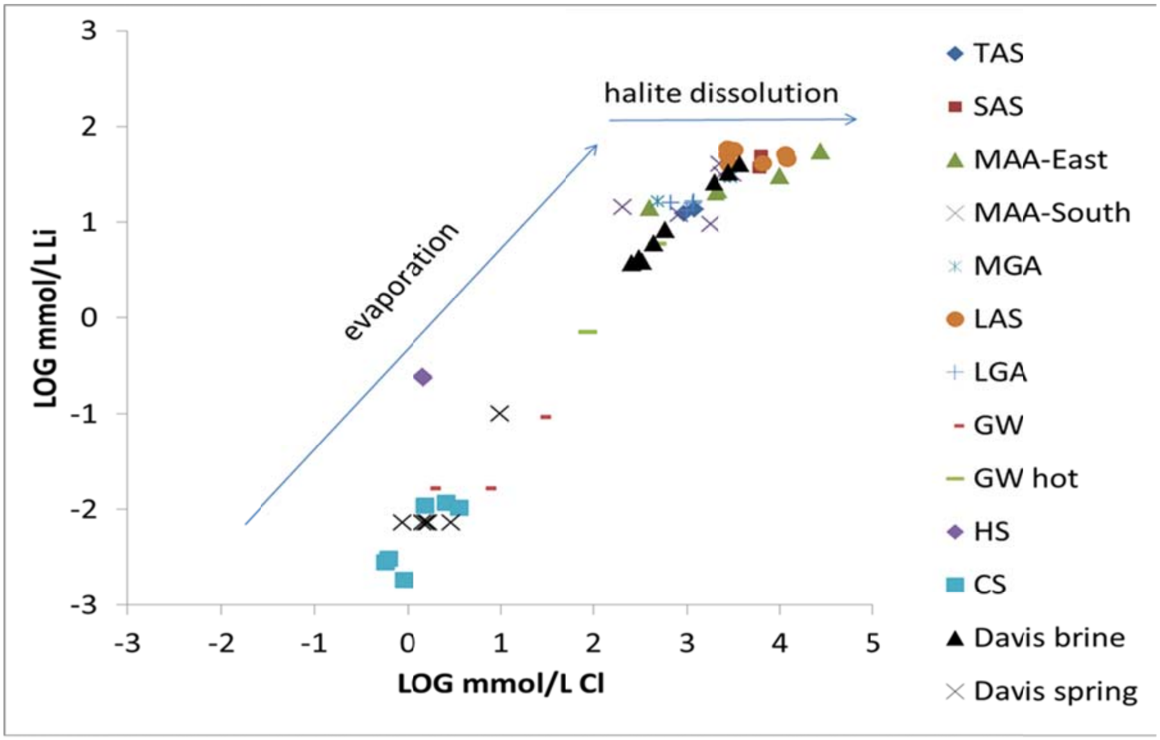

Figure 6. Log-Log plot Cl vs. Li for springs, groundwater and brines. (Fig. 3 for symbols)

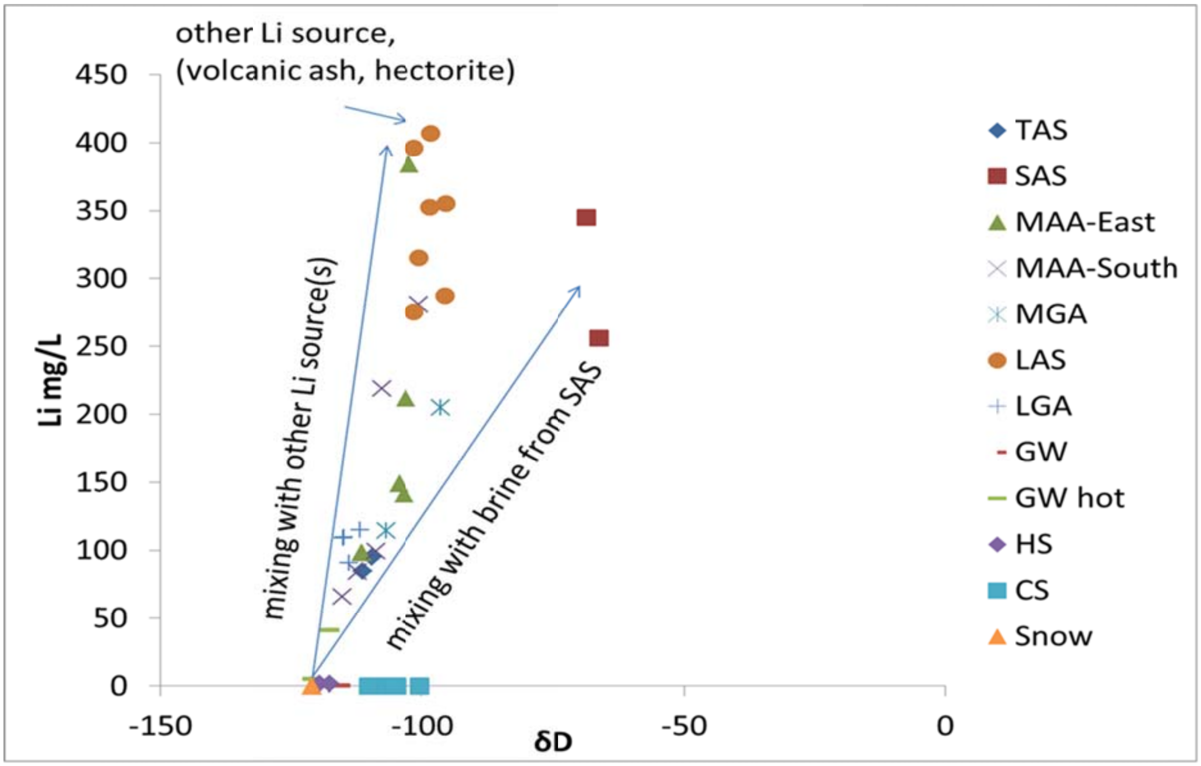

Figure 7. δD vs. Li for springs, groundwater and brines. (Fig. 3 for symbols)

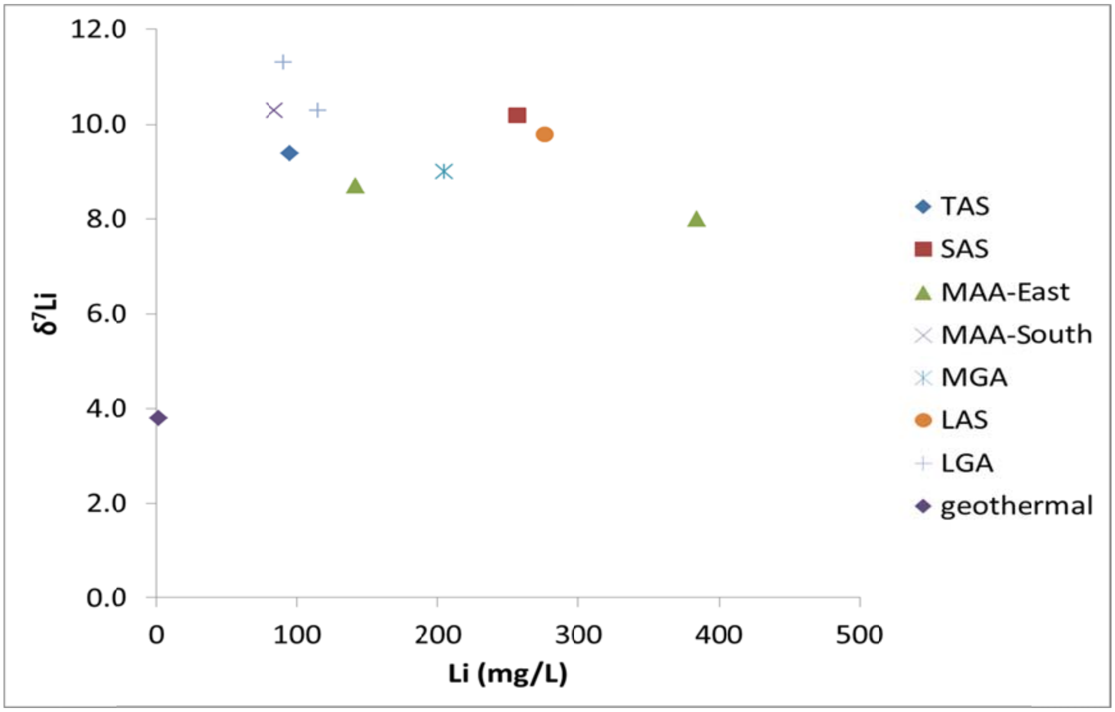

Figure 8. 1/Li vs. δ7Li for the brines, and one hot spring (HS plots off to the right), (Fig. 3 for symbols).

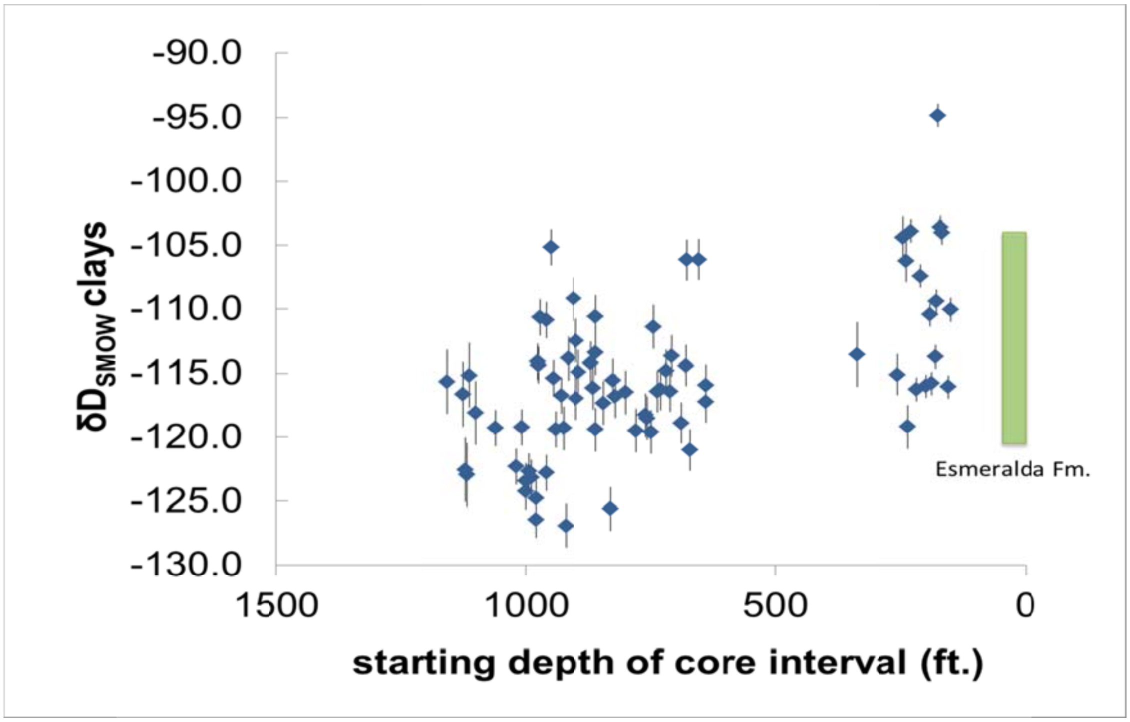

Figure 9. δD_{SMOW} for clays from sediment core and from the Esmeralda Fm. Note the overlap in the δD signature throughout the depth of the core with the clays from the ancient lake deposits of the Esmeralda Fm.

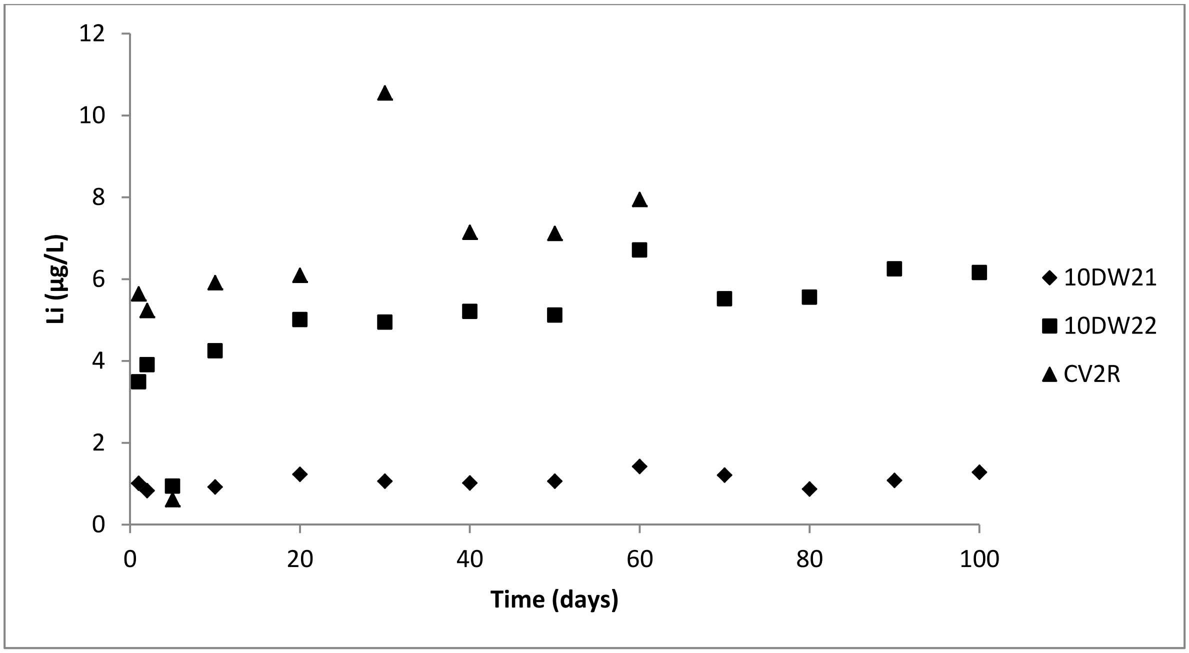

Figure 10. Lithium concentrations resulting from the leaching (weathering) experiments as a function of time. See Table 1 for rock types.

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