



Geochemistry of lithium-rich brines in Clayton Valley, Nevada, USA

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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. Therefore, understanding the formation of lithium brine deposits is essential for exploration. Clayton Valley, Nevada, USA is the location of the sole Li brine in production in N. 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 and precipitation.

Keywords. lithium, brine, Nevada

1 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 100 miles north of Death Valley and is the location of the only Li brine deposit in production in North America. Clayton Valley is a closed basin with an area of 1342 km² and a playa surface of 72 km². 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°C. The elevation of the valley floor is 1298 m, lower than any of the nearby basins.

2 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 as high as 228 ppm (Price 2000). 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 [30-100 m]; the tufa aquifer system (TAS), a localized aquifer of consolidated travertine in the upper basin [6-20 m]; the lower ash system (LAS), an extensive zone of thin-bedded volcanic ash deposits, interbedded with silt and sand [10-90 m]; the margin gravel aquifer (MGA), a localized aquifer of mixed gravel, sand, and silt [10-70 m]; and the lower gravel aquifer (LGA), a poorly sorted deposit of coarse to fine gravel, sand, and silt [50-100 m].

3 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 $\delta^{18}\text{O}$ 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. 1). This trend could also represent a mixing line between freshwater and brine. Figure 1 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 $\delta^{18}\text{O}$ 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. 2). However, based on the brine evaporation trend in Figure 1, further explanation is necessary.

Figure 3 illustrates that the inflow waters (springs) and non-brine groundwaters are likely affected by water-rock interactions, increasing the $\delta^{18}\text{O}$ signature; some of the brines, however, appear to be more strongly influenced by evaporation. Because the most enriched brine (SAS) has a $\delta^{18}\text{O}$ 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 Figure 3 could represent a mixing line between the SAS and the meteoric/dilute spring waters. Investigating the problem further, Figure 4 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 $\mu\text{g/L}$ 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. Figure 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.

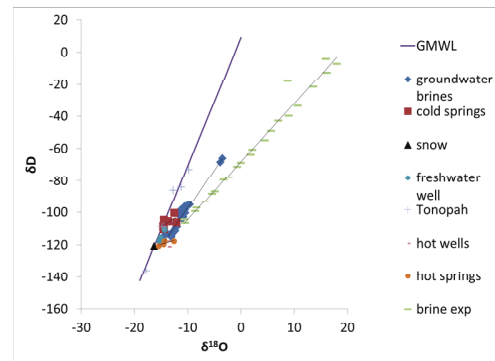


Figure 1. $\delta^{18}\text{O}$ vs. δD for water in Clayton Valley, NV and the brine evaporation experiment.

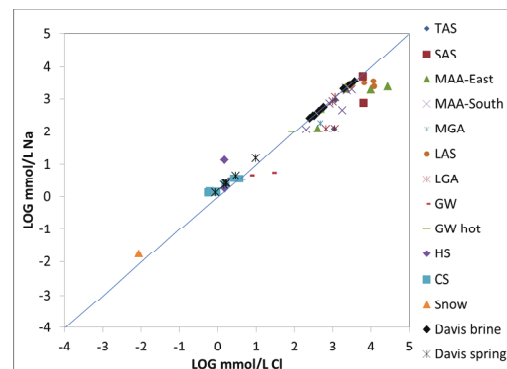


Figure 2. Log-Log plot of Cl vs Na including data from Davis et al. (1986). GW = groundwater, GW hot = hot groundwater, HS = hot springs, CS = cold springs, other aquifer designations in text

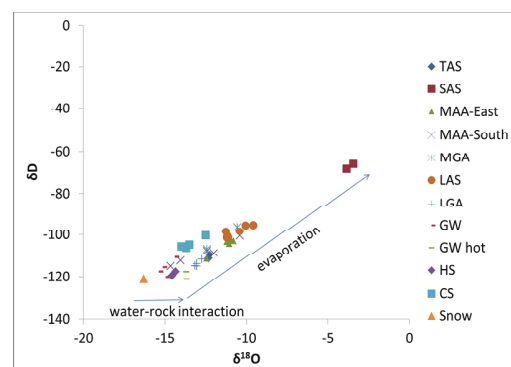


Figure 3. $\delta^{18}\text{O}$ vs. δD for snow, springs, groundwater and brines (Figure 2 for symbols).

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

and δD of clays from core samples in the basin to understand the climate history and past periods of Li enrichment).

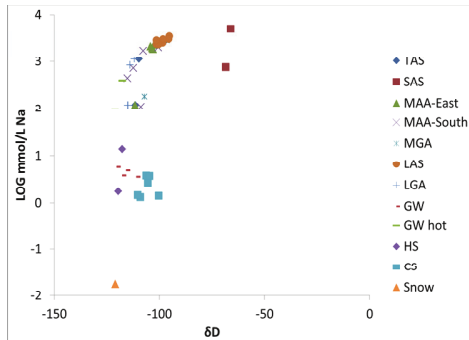


Figure 4. δD vs. LOG Na for snow, springs, groundwater and brines. (Figure 2 for symbols).

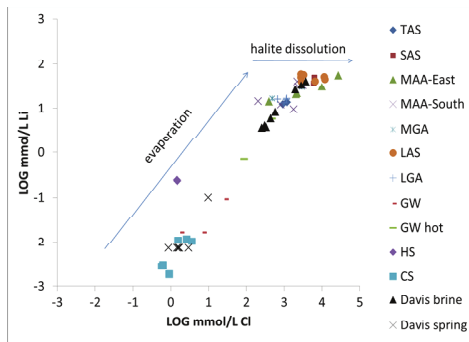


Figure 5. Log-Log plot Cl vs. Li for springs, groundwater and brines. (Figure 2 for symbols).

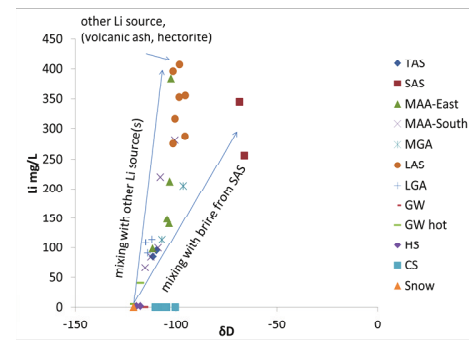


Figure 6. δD vs. Li for springs, groundwater and brines. (Figure 2 for symbols).

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. Figure 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 ($\text{NaO}_3(\text{Mg},\text{Li})_3\text{Si}_4\text{O}_{10}(\text{F},\text{OH})_3$) associated with the volcanic ash, transported from the Esmeralda Formation (east), and/or from authigenic hectorite in the basin.

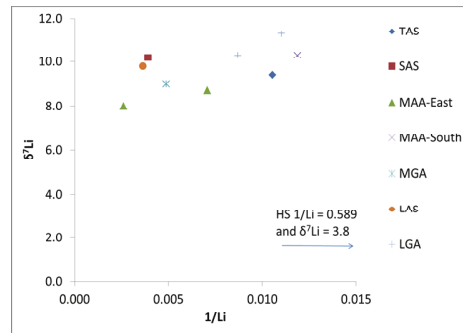


Figure 7. $1/\text{Li}$ vs. $\delta^7\text{Li}$ for the brines, and one hot spring (HS plots off to the right), (Figure 2 for symbols).

The range in $\delta^7\text{Li}$ 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 $\delta^7\text{Li}$ signature, indicating water that has interacted with clay minerals. Further isotopic analyses of the inflow waters and brines are necessary.

4 Conclusions

The Li brine at Clayton Valley, NV, USA has formed from a complex process of evaporation, mixing, and halite and hectorite dissolution and precipitation. The SAS brine appears to be an older brine that has mixed and been diluted with fresh inflow waters. However, the Li, δD , and $\delta^7\text{Li}$ indicate that there is another source(s) of Li to the brines, likely hectorite. The Li sources, accumulation, and storage in the basin are under further investigation.

Acknowledgements

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