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Do Geothermal Systems Play a Role in Lithium Brine Enrichment in Nevada Playas?

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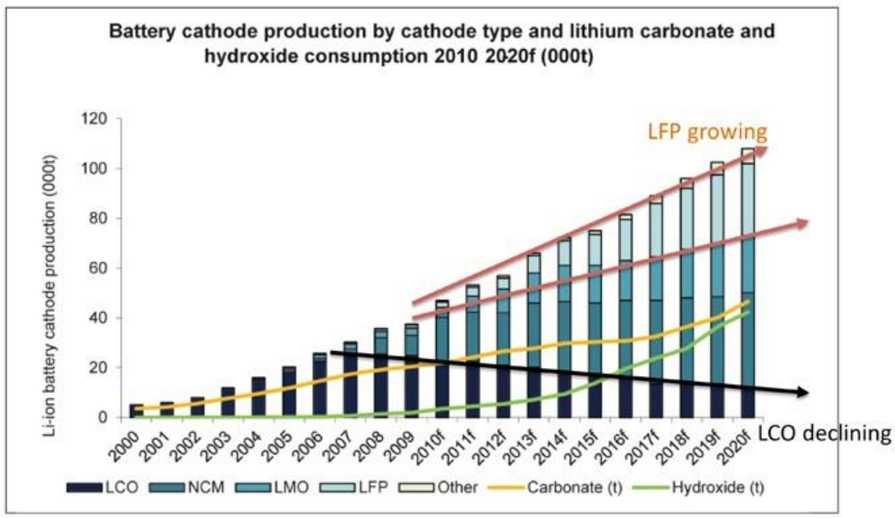
ABSTRACT

Exploration for economic deposits of lithium to be processed for use in batteries to power electric vehicles has become supercharged in the past three years. Numerous companies have entered the race to identify deposits and many are focused on potential brine deposits within the internally drained basins that make up the Basin and Range covering the western US and Nevada and Utah in particular. Only one operating lithium brine mine exists in the US, and it is found in Clayton Valley, Nevada. The question remains as to what other lithium brine deposits exist in the US. In general, lithium brine deposits are pre-request on a set of geological and climatological factors: 1) a source of lithium, 2) an extraction mechanism, 3) a transport mechanism, 4) a trap (closed basin), 5) a suitable solar evaporation rate, and 6) scale (mass flux of lithium and limited dissolved salt competition). Geothermal fluids may contribute to more efficient and selective extraction of lithium from basin sediments and basement rocks; they may help transport the enriched fluids due to thermal upwelling; and finally provide long term mass flux that over sufficient time leads to significant endowment in basins. The basins of western Nevada have many of these prerequisites, but are dominated by clastic sediments and have relatively high subsidence and sedimentation rates. For these reasons it is likely that lithium-enriched brines are deeper than in the mature basins of South America. Since few basins in Nevada have had deep drilling, paleo-brines may remain to be discovered at depths not yet investigated by exploration companies.

1. Introduction

Exploration for lithium from brine and hard rock sources has grown significantly over the past three years with companies targeting many localities on the globe. Brines are currently receiving a lot of attention due to their lower development costs, and Nevada is one of the places receiving a lot of this attention. The increased interest has also led to increased research into the origin of lithium brines in the United States and elsewhere.

The accelerated need for lithium is linked to a global shift away from internal combustion engines to electrically powered vehicles (EVs). The shift to EVs is coupled with increasing use of batteries for power storage and management as grids accommodate increased non-base load renewable generation. In 2016 the percentage use of lithium in ion batteries (39%) exceeded its use in ceramics and glass (30%) for the first time ever. Projections for the use of lithium (stated as “Lithium Carbonate Equivalent” LCE) are expected to more than double in the next five years (Figure 1).



Source: Roskill Consulting

Figure 1: Projected use of lithium in batter production. (http://www.criticalinvestor.eu/lithium accessed May 29, 2017).

Against this backdrop has been a remarkable proliferation of junior exploration companies focusing on exploration for lithium from both brine and hard rock sources. Lithium is moving from a niche commodity to the mainstream. Brine sources remain the easiest and most economical to extract and purify to the levels required by battery manufactures (standard battery grade Li_2CO_3 99.5%). Nevada is the center for this new exploration rush, encouraged by the successful long-term Rockwood Silver Peak lithium brine mine in Clayton Valley developed in 1966 by Foote Mineral Company and now owned by Albemarle Corporation.

Lithium brines commercially exploited today occur as shallow saline lakes (China) and/or as saline aquifers beneath dry lakes (North and South America, i.e., “playas” (English terminology) or “salares” (Spanish terminology)). These lakes or playas occur in closed basins without external drainage, in dry desert regions where evaporation rates exceed stream and groundwater recharge rates, preventing lakes from reaching the size necessary to form outlet streams or rivers. Evaporative concentration of surface water over time within closed basins leads to residual concentration of dissolved salts (Bradley et al., 2013) to develop saline brines enriched in one or more of the following constituents: sodium, potassium, chloride, sulfate, carbonate species, and, in some basins, metals such as boron and lithium. When lithium concentrations exceed 100-200 mg/L, the “lithium” brines can be processed through a two-step process of 1) evaporative concentration in surface solar ponds, and 2) treatment in a chemical processing plant (e.g., Davis et al., 1986).

Currently, new technologies are being developed that may circumvent the solar pond step and enable extraction of lithium with higher efficiencies and at lower concentrations. These are generally termed “direct extraction” methods as lithium is removed from the brine directly and then the spent brine is reinjected. Although to date most lithium brine plants rely upon traditional evaporation ponds, an increasing number of companies are working on direct extraction technologies that are able to extract and purify lithium from brines without the need for evaporative pre-concentration.

2. Lithium Exploration Model

Most playa waters do not have economic concentrations of lithium. But there are some areas of the world where favorable conditions for the development of lithium-rich brines are found. These conditions include: 1) an arid climate, 2) a closed (internally drained) basin with a playa (or salar), 3) tectonically driven subsidence, 4) associated igneous or geothermal activity, 5) suitable lithium source rocks, 6) one or more adequate aquifers, and 7) sufficient time to concentrate a brine (Bradley et al., 2013). The Basin and Range physiographic province of the western US (Figure 2) provides the closed basins, arid climate, and many of the other factors noted as important for brine formation.

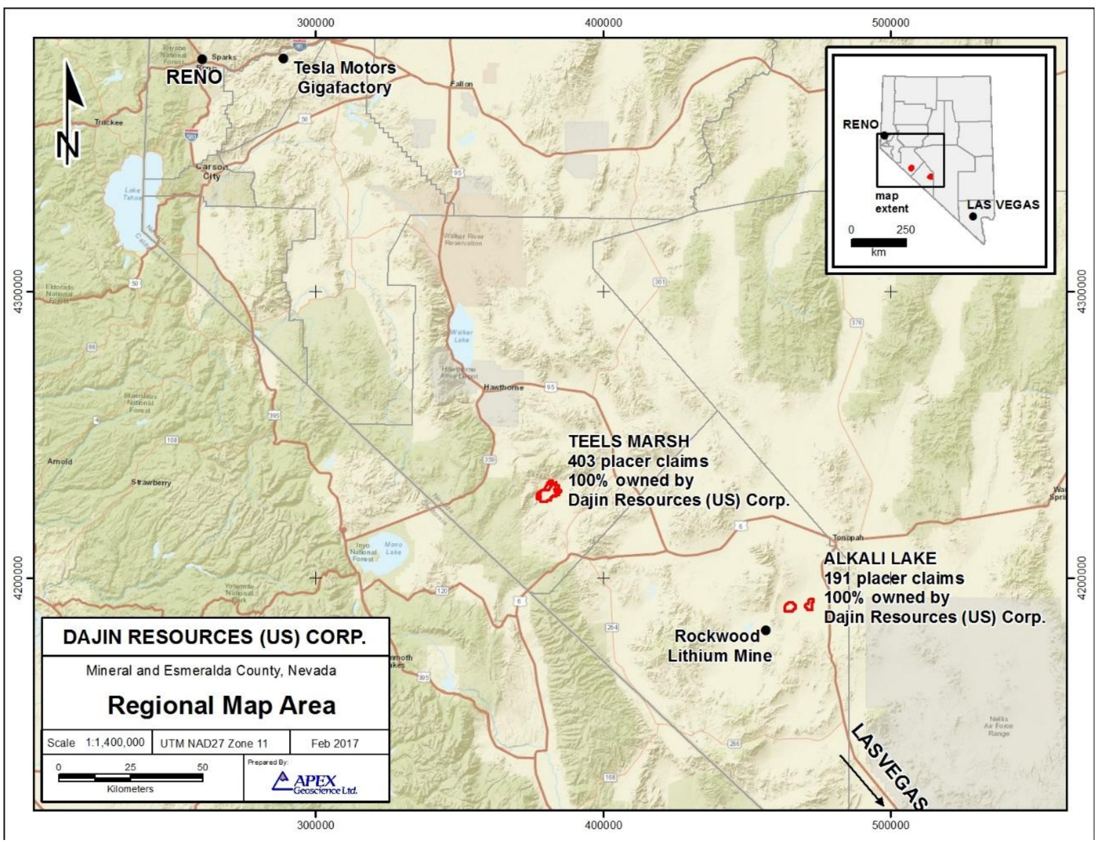


Figure 2: Basin and Range region of Nevada, showing Dajin Resources Corps’ Teels Marsh and Alkali Lake properties as well as the Rockwood Silver Peak lithium brine mine in Clayton Valley.

Despite the large number of closed basins within the Basin and Range, and despite at least two rounds of increased exploration interest since the Clayton Valley discovery more than 50 years ago, the Rockwood Silver Peak mine remains the only operating lithium brine mine in the US. However, economic concentrations of lithium in brines at Silver Peak were reportedly not discovered until drilling was initiated (Davis et al., 1986). As discussed in this paper, brines saturated in dissolved salts are denser than fresh water and thus have the potential to sink and displace less-dense fluids below the surface. Most playas in the Great Basin have not been tested at depth for the presence of lithium brines; therefore, significant potential remains for finding undiscovered resources.

Ultimately, suitable brine enrichment depends on a number of factors such as the mass flux of lithium in incoming groundwater and surface water sources, the weighted average lithium/salt ratios in that water, and a solar evaporation rate high enough that the fresh water component can be removed. Once a dense brine forms it will likely sink within the sedimentary column of the basin until downward movement is impeded by an aquitard or by impermeable basement rocks at the bottom of the basin. Sealing of the upper surface and development of aquitards within the basin are likely the result of weather related flood events significant enough to wash large quantities of fine grained material into the basins. Wind-blown material during drying periods may also have been prevalent as forests died off leaving barren slopes exposed to wind and water erosion.

In west-central Nevada the presence of thick volcanic ash deposits may be an important factor in lithium concentration. Felsic ash is relatively high in lithium relative to other bed rock sources and the glassy ash shards are highly reactive with groundwater and may be especially so when subjected to heated geothermal water. The presence of a thick volcanic tephra layer (the Bishop Tuff) deposited during the eruption of the Long Valley caldera 0.76 Ma ago blankets much of west-central Nevada (Figure 3). This tephra layer forms the largest single lithium brine aquifer at Clayton Valley, where it ranges from 5 to 30 feet (1.5 to 9.1 metres) thick and occurs at depths ranging from 60 to 230 metres (200 to 750 feet)(Zampirro, 2004).

2.1 Aquifers

Within rapidly subsiding closed basins, sedimentation is typically dominated by clastic layers of silt, sand, or gravel in addition to volcanic ash deposits from both local and distal sources. The closed basins of west-central Nevada, including Clayton Valley and Teels Marsh, fall into this category, termed “immature basins” by Houston et al. (2011) to distinguish them from “mature basins”, where chemical sedimentation (halite) is more important. The type of basin has an impact on subsurface exploration potential, because clastic-rich aquifers in immature basins can maintain permeability at depth, whereas salt aquifers tend to lose permeability quickly with depth because of the plastic behavior of salt under pressure (Houston et al., 2011). Conceptually, the presence of viable aquifers at depth in immature basins provides the opportunity for lithium-rich, relatively dense saline brines to descend into the basin where drilling is required to find them. To the authors’ knowledge, the deepest lithium aquifers in the world from which lithium is being produced are at Clayton Valley, where surface concentrations of lithium are inferred to have been lower than in the subsurface (Davis et al., 1986).

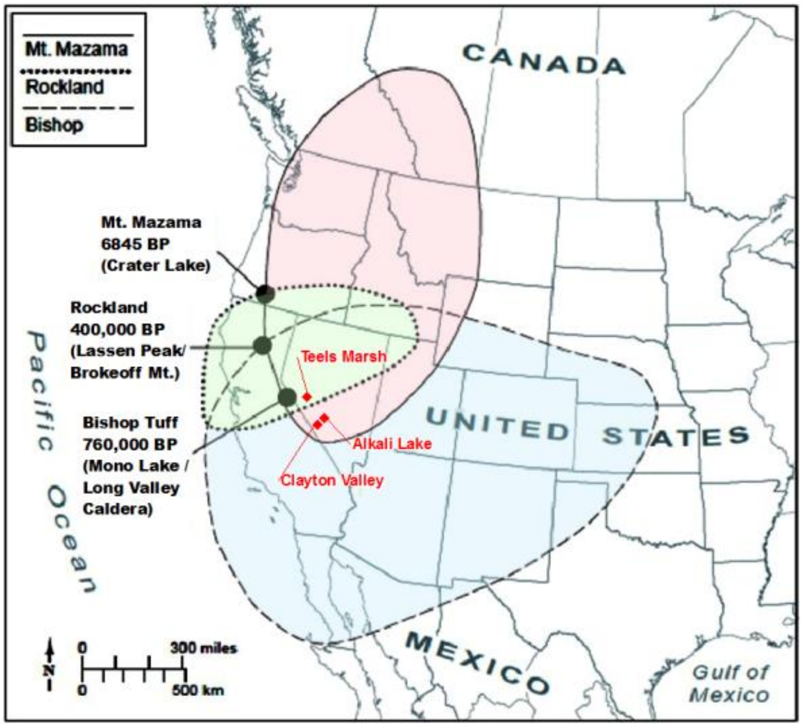


Figure 3: The eruption of the Long Valley Caldera covered much of the western United States under a thick layer of ash (tephra or tuff, shown in blue on the diagram). This ash is a source of lithium as well as a potential aquifer. These ash layers have proven to be the most productive brine sources at the Rockwood Silver Peak mine in Clayton Valley (figure adapted from Zampirro, 2004).

2.2 Climate and Flooding

The tectonic regime in the Basin and Range has led to long term subsidence of basins for millions of years and the development of independent closed basins. The present climatic conditions of the Basin and Range are such that evaporation exceeds precipitation. During the Quaternary and late Tertiary, the climate has alternated between wet and dry. A notable event during the geologically recent history of the Basin and Range is widespread flooding by Lake Lahonton (Figure 4). The lake persisted from 54,000 y.b.p. to 12,000 y.b.p and several wet and dry periods during this period are recorded in the sediments in the basins (Benson et al. 1995, Bradbury et al., 1988). During the wet periods the emergent land was covered with forests similar to the present day Sierra Nevada Mountains.

The waters of Lake Lahonton had a significant impact on ground waters in the region (Benson et al. 1995) leading to widespread recharge. During dry cycles and since the Wisconsin glaciation, the periods where the basins evaporated to dryness left silt and salt deposits that characterize the basins' present day surfaces. During periods of high stand, it is likely that recharge of the aquifers led to dilution of the subsurface brines. Whether dissolution of lithium from near surface volcanic ash deposits was accelerated during this time period remains unknown. During dry periods, precipitation of lithium bearing minerals such as hectorite or searlesite occurred, and the surfaces of many playas, including Clayton Valley, Fish Lake Valley, and Teels Marsh, have elevated lithium values in sediments (Figure 5).

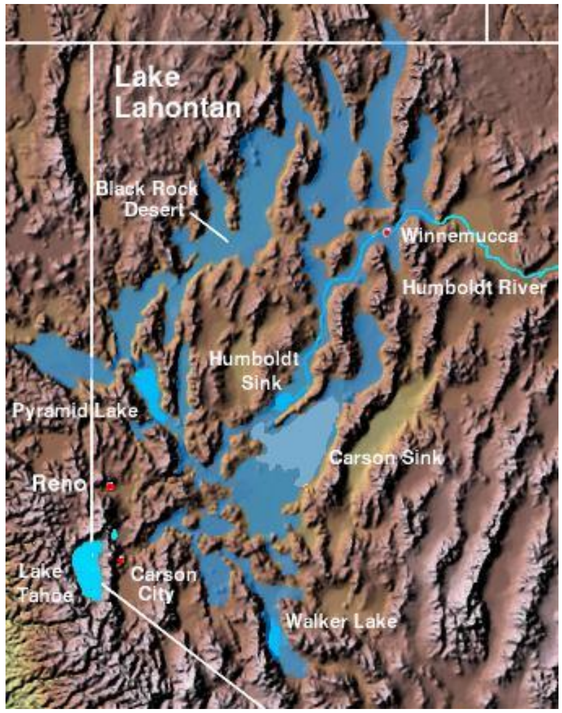


Figure 4: Extent of glacial Lake Lahonton from Decumanus at en.wikipedia, CC BY-SA 3.0 (https://commons.wikimedia.org/w/index.php?curid=11123512 (accessed May 28, 2017).

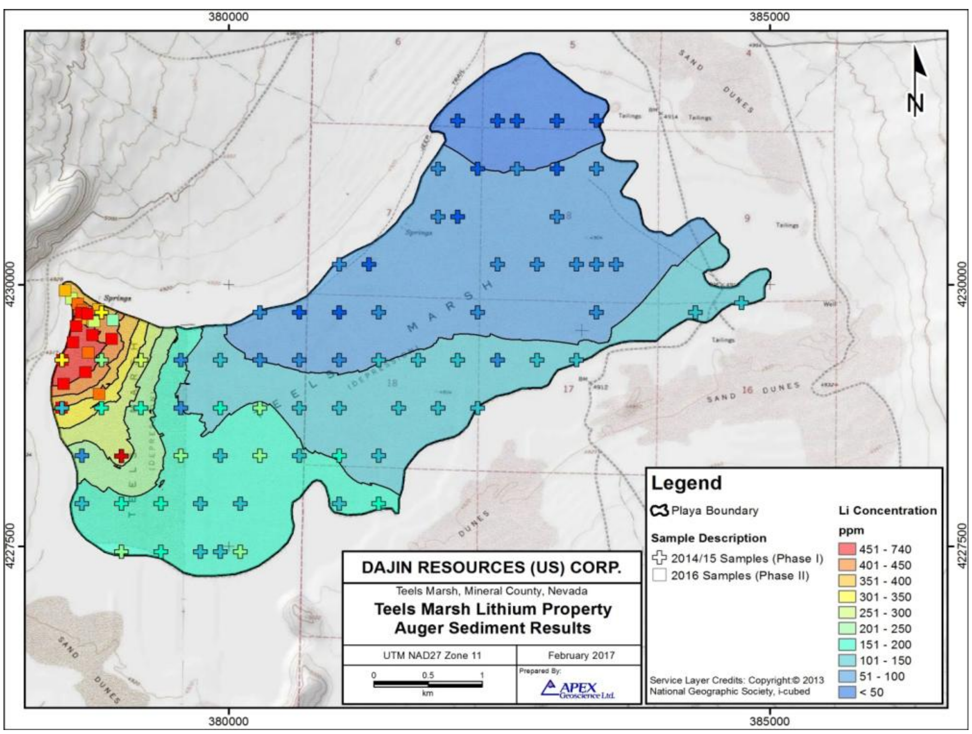


Figure 5: Lithium concentrations in shallow auger sediments sampled by Dajin Resources Corp. at Teels Marsh, Nevada. Ordinary kriging was used to interpolate lithium concentrations using a maximum of 12 input points for each grid cell, after averaging all lithium concentrations for a given auger site (figure taken from Coolbaugh and Hickson, 2017).

During the Pleistocene lakes have filled and desiccated (Figure 6, Reheis 1999) in the tectonically driven pull apart basins of the region in response to climatic, tectonic and geomorphic events. Detailed, multidisciplinary paleolimnologic records from related subbasins are required to separate these processes and understand the lake level history before it can be reliably used to interpret paleoclimatology (Benson et al., 1995, Bradbury et al. 1988). To the best of our knowledge, no work has been done correlating lithium brine deposits in Clayton Valley to paleo-lakes that may have occupied the basin in the past.

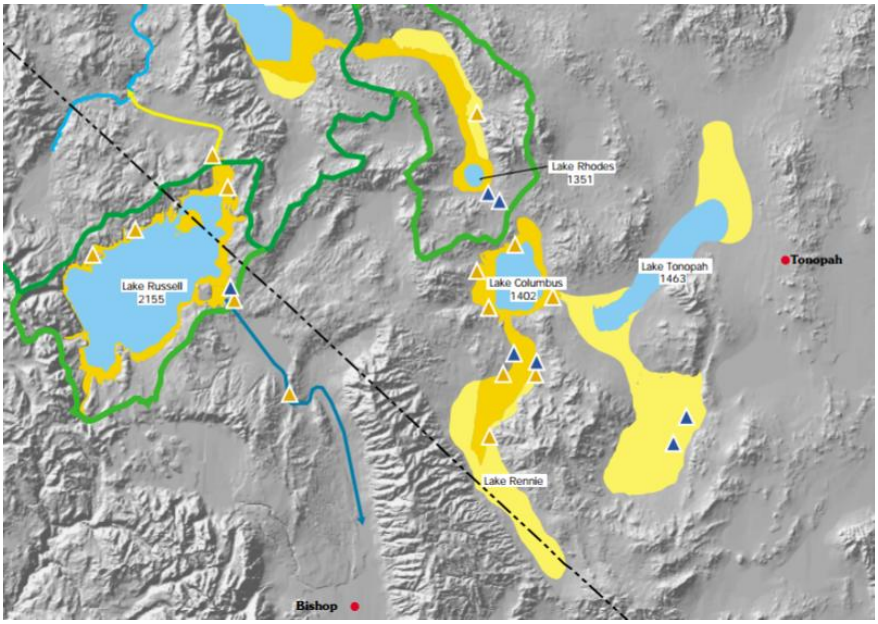


Figure 6: Extent of Pleistocene glacial lakes in the Clayton Valley and Teels Marsh areas (from Reheis, 1999).

3. A Geothermal Connection

In addition to closed basins and climate, there appears to be a good spatial correlation between felsic volcanism, geothermal activity and lithium brines, lithium-enriched clays (e.g. hectorite) and lacustrine sediments containing lithium minerals (e.g. searlesite). A geothermal association is known or suspected at a number of lithium-brine deposits around the world, including Clayton Valley (Davis et al., 1986; NBMG, 2014), Salar de Atacama, Chile (Lowenstein and Risacher, 2009), and the Qaidam Basin, China (Yu et al., 2013).

Geothermal activity may not be a necessary prerequisite for lithium brine formation, because there is evidence that non-thermal devitrification and weathering processes can liberate lithium from volcanic rocks (Price et al., 2000). We argue nonetheless, that thermal groundwater can make the process more efficient by accelerating the dissolution of lithium rich glassy volcanic rocks and by selectively dissolving lithium relative to other constituents. This is demonstrated by abundant empirical data on the composition of geothermal fluids as a function of temperature. These data show that the Li/Mg (Fouillac and Michard, 1981) and Li/Na (Kharaka and Mariner, 1989) ratios systematically increase multiple orders of magnitude as temperature increases; indeed, these correlations form the basis for the Li/Mg and Li/Na geothermometers (Fouillac and Michard, 1981; Kharaka and Mariner, 1989). Houston et al. (2011) observe that many Central Andean brines have elevated Li/Mg ratios, which are difficult to explain under surface weathering conditions in volcanic terrains where groundwater commonly has elevated magnesium concentrations, but easier to understand in the context of a geothermal groundwater history.

Yu et al. (2013) provide a well-documented example of short-term (since the last glacial period) lithium enrichment in several basinal brines currently being mined for their lithium in the Qaidam Basin, China. This lithium originates from lithium-rich hot springs that flow into rivers that eventually feed into the Qaidam Basin after traveling more than 300 km. Mass flux calculations show that the lithium endowment in the Qaidam Basin can be explained by the current flow rates if operating over approximately 6,000 years (Yu et al., 2013).

3.1 Lithium in Groundwater

An extreme case of lithium-rich geothermal fluids is provided by the Salton Sea, where production fluids have lithium concentrations ranging to over 300 ppm (Klein and Gaines, 2011). Most geothermal waters have much lower lithium concentrations, but still much greater than found in typical non-thermal groundwater. Thermal groundwater in Nevada has lithium concentrations that commonly exceed 1 mg/L, but average 0.66 mg/L (638 analyses, GBCGE (2017a). In comparison, average lithium concentrations reported for municipal water supplies in the US are at least an order of magnitude lower (<0.05 mg/L, Durfor and Becker, 1964). Importantly, our studies show that many geothermal waters in the Great Basin, if evaporated to the point of halite saturation, would generate brines with lithium concentrations in the range of several hundreds of mg/L and higher, without the need of further concentration from precipitation of salt minerals. This provides a suggestive fingerprint, pointing to the viability of generating lithium-rich brines over relatively short periods of time in basins where geothermal influx is significant.

3. Teels Marsh Lithium Exploration

As an example of the influence of geothermal activity on lithium-brine formation, we review the links and evidence for lithium concentration in Teels Marsh, Nevada. Teels Marsh, located in west central Nevada (Figure 2), is the target of lithium brine exploration (Coolbaugh and Hickson, 2017)), and provides an example of the influence of geothermal activity on lithium brine formation.

Teels Marsh is a rapidly subsiding basin within the Mina deflection (Figure 7) and has an estimated depth of 2.5 km (Coolbaugh and Faulds 2016). It is located at the western mapped terminus of the Excelsior Mountain fault system (Figure 7 and 8). As mapped by Wesnousky (2005), the Excelsior Mountain fault bounds Teels Marsh basin on its northern and western margins. The stronger development of faulting on the north and west sides of the basin compared to the east and south sides has led to the development of a composite half-graben within the basin. Seismic profiles and detailed gravity modelling document the deep, central half-graben up to 2.5 km deep, lying within an outer half-graben bounded by the Excelsior Mountain fault (Figure 8; Coolbaugh and Hickson 2017).

Numerous geothermal systems are associated with the basins within the Mina Deflection (Figure 7). Several blind systems were identified there by researchers at the University of Nevada, Reno (UNR) (Coolbaugh et al., 2006, 2013). No thermal springs or wells were known to exist in Teels

Marsh basin prior to the UNR work, but the presence of geothermal activity was suspected based on a recognized link in Nevada between young borates and geothermal activity (Coolbaugh et al., 2006). The geothermal exploration work consisted of geochemical sampling of springs and wells to calculate geothermometer temperatures (Coolbaugh et al., 2006), spectral surveys of surface borate occurrences (Kratt et al., 2006), 2-metre temperature surveys (Kratt et al., 2008), and ultimately, Geoprobe drilling in 2010 (Zehner et al., 2012). The Geoprobe drilling encountered temperatures of up to 97°C at a 40 m depth northwest of the marsh (site “A”, Figure 8), and 78°C at 30 m depth southwest of the marsh (site “B”, Figure 8). An additional source of thermal waters to the playa is indicated by the presence of thermal springs (previously undocumented) south of Teels Marsh associated with large travertine terraces.

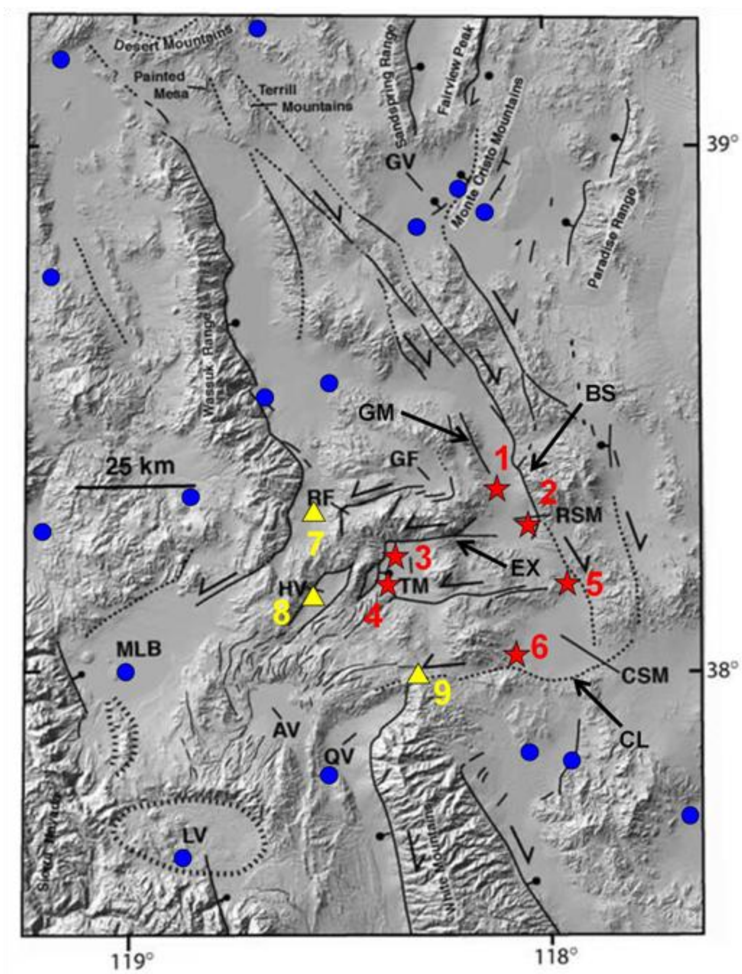


Figure 7: Quaternary faults and geothermal systems in the Mina Deflection. The physical extent of the Mina Deflection encompasses the geothermal areas: 1 = Sodaville, 2 = Rhodes Marsh, 3 & 4 = North & south Teels Marsh, 5 = Redlich, 6 = SW Columbus Marsh; and thermal wells 7, 8, and 9 at Whiskey Flat, Huntoon Valley, and NE of Queen Valley, respectively. RSM = Rhodes Salt Marsh, TM = Teels Marsh, CSM = Columbus Salt Marsh, GF = Garfield Flat, HV = Huntoon Valley, RF = Rattlesnake Flat, MLB = Mono Lake Basin, LV = Long Valley caldera, AV = Adobe Valley, QV = Queen Valley, GV = Gabbs Valley, EX = Excelsior Mountain fault, GM = Gumdrop Hills fault, CL = Coaldale fault, BS = Benton Springs fault. Blue circles are geothermal systems outside the Mina Deflection with measured or estimated temperatures >70°C. Taken from Coolbaugh et al. (2013) and originally adapted from Wesnousky (2005).

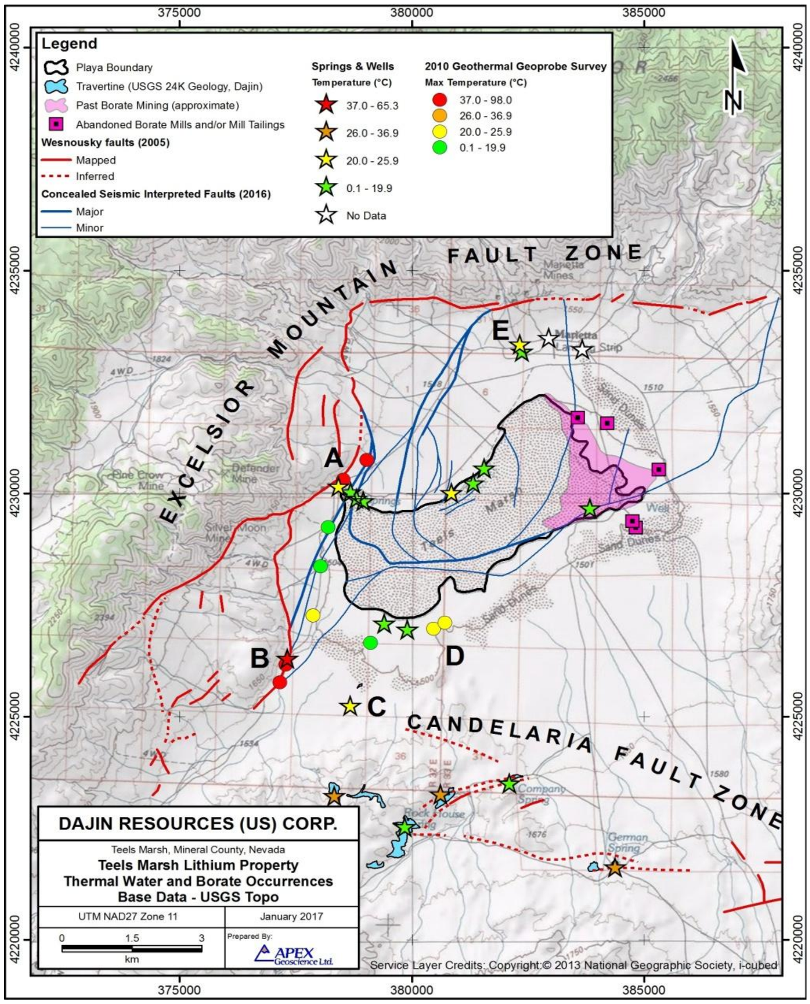


Figure 8: Distribution of known geothermal activity, springs, borates, and travertine at and near Teels Marsh (taken from Coolbaugh and Hickson, 2017).

A reflection seismic survey totaling 19.5 km (12.1 mi) in length was completed by Eagle Exploration Inc. for Dajin in May and June, 2016 at Teels Marsh. The survey consisted of three NW-SE lines that cross the inferred graben at nearly right angles, and one NE-trending longitudinal line that follows the long axis of the graben. The survey was custom-designed for the soft ground conditions and anticipated basin depth of Teels Marsh. The results show a number of reflections in the subsurface as well as clear delineation of the main faults in the basin (Coolbaugh and Faulds, 2016; Figure 9). These structural features may represent aquifers, aquitards or aquicludes or some combination of the three, but their exact nature can't be determined until drilling. However, the consistent WNW-dip of basin sediments in Teels Marsh suggest that geothermal brines may be entering the basin from the west facilitated by the dominant westerly dip, since buoyant thermal fluids should rise upwards and travel outwards away from their presumed source on the western margin of the basin. Relatively dense halite-saturated, and potentially lithium-enriched basin brines might sink in the opposite direction, down-dip in a northwesterly to westerly direction, in a manner similar to that observed at Clayton Valley (Zampirro, 2004).

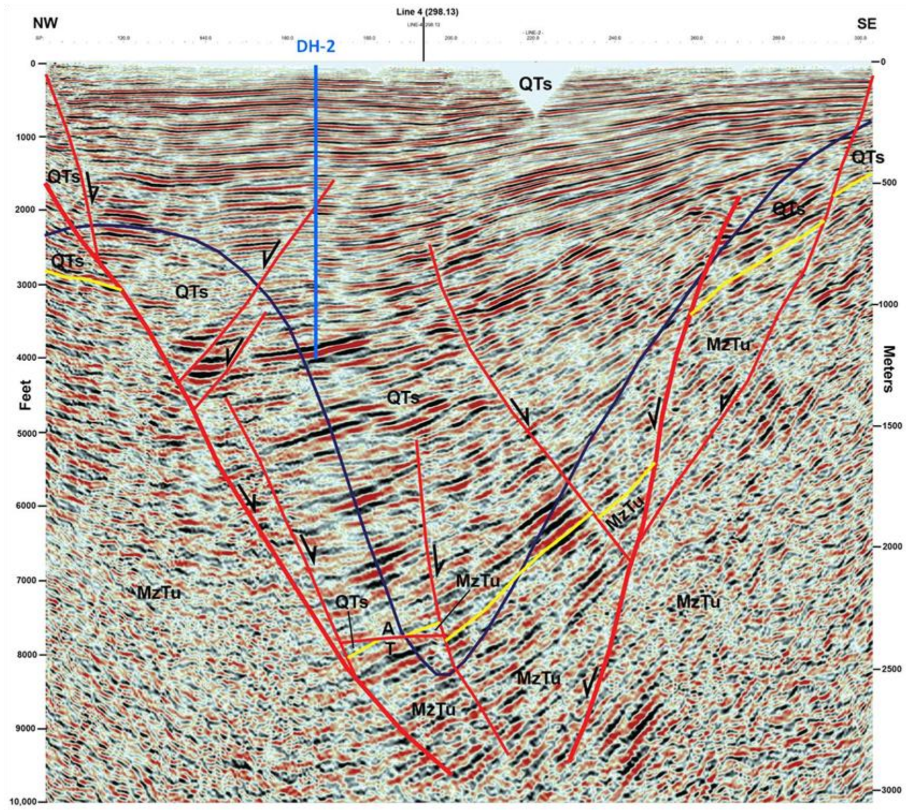


Figure 9: NW-SE seismic reflection profile through Teels Marsh, looking northeast. Red lines are interpreted faults, and the yellow line is the interpreted contact between basin-fill deposits above and rocks below. Gray line is the basin fill-rock contact from the basin-removed topographic elevation model of Wright (2015). Proposed drill-hole 2 is projected to section. QTs = Quaternary and Tertiary sediments, MzTu = undivided Mesozoic and Tertiary rocks. Vertical to horizontal scale is 1:1. (figure taken from Coolbaugh and Faulds, 2016).

At Teels Marsh, elevated lithium concentrations of up to 79 mg/L in brines in the northwest corner of the playa (Figure 10) appear to be related to the incursion of geothermal fluids into the basin. This relationship is inferred on the basis that 1) the highest temperature known geothermal waters in Teels Marsh occur in close proximity to the northwest corner of the playa where lithium concentrations are highest in shallow basin brines, and 2) the solute ratios of the playa brines in this area are different from ratios in most of the Teels playa brines, but quite similar to solute ratios in the nearby geothermal waters (Figure 11).

The lithium-brines in the northwest corner of Teels Marsh provide a hint that perhaps additional lithium brines may be present at depth. The highest concentrations of lithium encountered in auger groundwater come from relatively dilute brines, with sodium and chloride concentrations not exceeding 57,000 and 68,000 mg/L, respectively (Figure 12). If a best-fit evaporation trend in the lithium-bearing brines (Figure 12) is extrapolated to the highest sodium and chloride concentrations observed in the shallow brine data (which are probably at or near halite-saturation), the predicted lithium concentration would be in the range of 140-195 mg/L. It is theorized that as the density of the surface water increases due to natural evaporation, the brines sink below the playa surface.

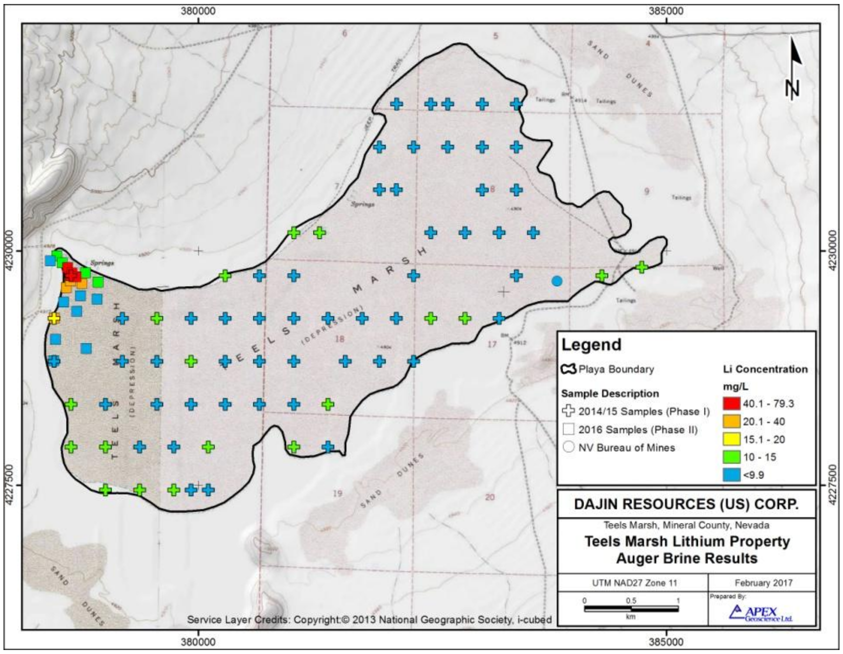


Figure 10: Lithium concentrations in shallow auger groundwater sampled by Dajin Resources Corp. (figure from Coolbaugh and Hickson, 2017).

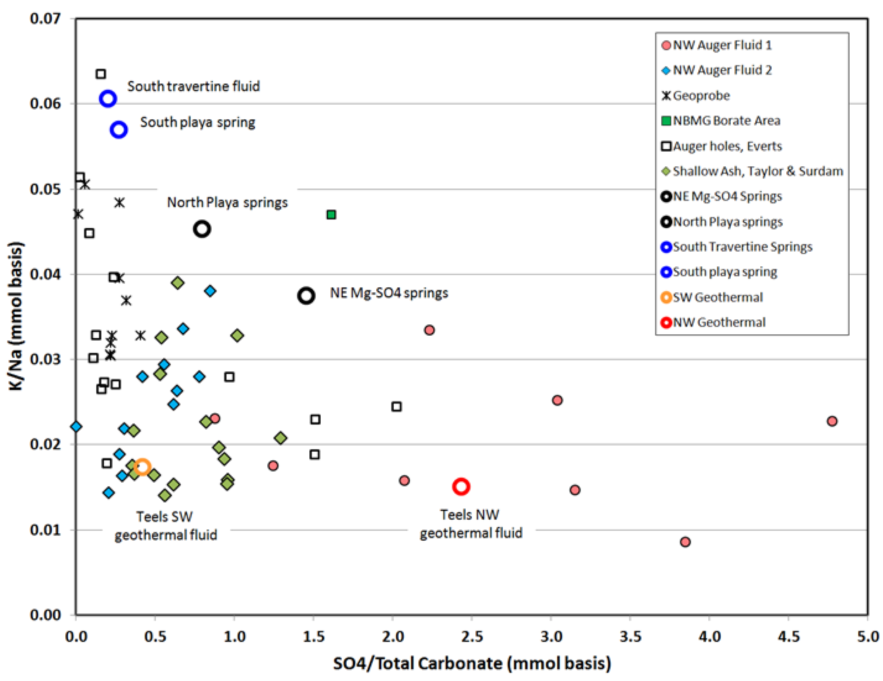


Figure 11: K/Na and SO_4/total carbonate ratios of groundwater and spring samples from within and adjacent to Teels Marsh. Geothermal fluids northwest of the playa (open red circle) have solute ratios similar to that of auger brines in the northwest corner of the playa (small red circles). Auger fluids 1 and 2 are from Dajin's second auger sampling campaign. Shallow ash samples are from Taylor and Surdam (1981) and Everts samples from Everts (1969). North playa, Mg-SO4, and South travertine fluids from Smith and Drever (1976). Teels geothermal fluid and South playa spring samples from Geothermal Development Associates (unpublished data). Figure from Coolbaugh and Hickson, 2017.

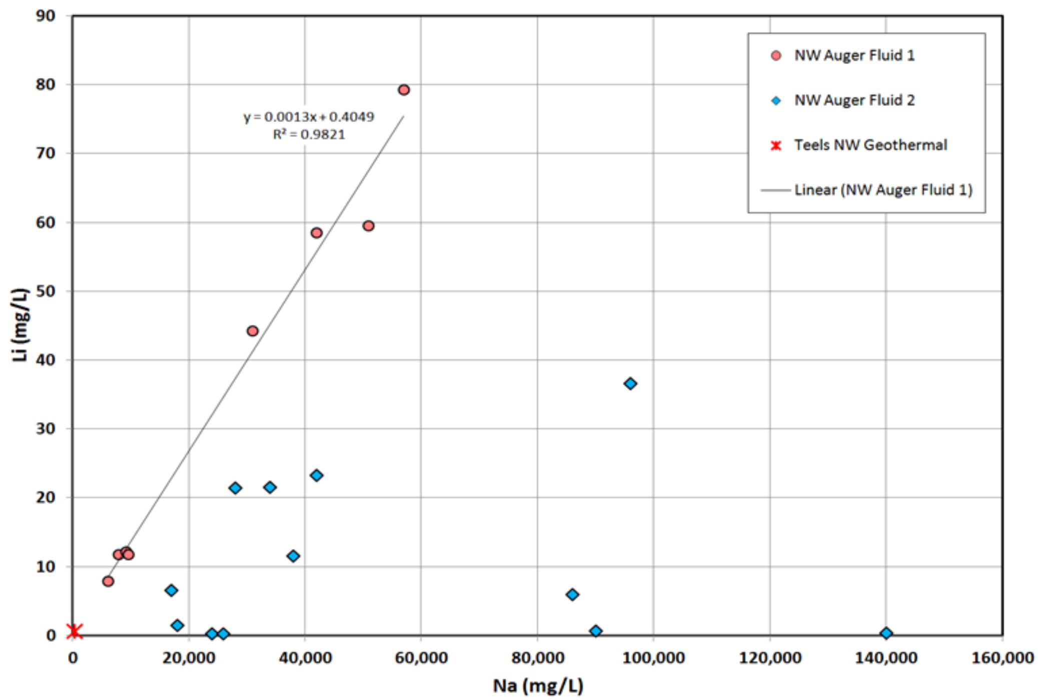


Figure 12: Lithium and sodium concentrations of groundwater sampled during Dajin's second auger drilling campaign. Samples that cluster in the northwest corner of the playa (red circles) fall along a single evaporation trend suggesting that they come from a single source fluid with a lithium/sodium ratio distinct from other auger brine samples. Figure from Coolbaugh and Hickson, 2017.

4. Summary

Without deep drilling and associated geochemical testing for lithium and other elements in the brines it is not possible to determine the total magnitude of lithium enrichment at Teels Marsh caused by geothermal influx. However, our research leads us to believe the following factors are important and are all necessary for successful exploration:

1) a source of lithium,

2) an extraction mechanism,

3) a transport mechanism,

4) a trap (closed basin),

5) a sufficient solar evaporation rate, and,

6) scale: mass flux of lithium and limited dissolved salt competition

Of these factors, we believe that 2, 3, and 6 can be significantly influenced by the presence of geothermal fluids.

The time period of economic brine formation can be short and economic brines might form during one period of basin formation (one dry period), but not in another period in the same basin, depending on mass flux of lithium, exposures of source material to leaching, and level of geothermal activity. Draining of the various basins into each other during water high-stands may also have an impact by depleting upstream basins and enriching downstream ones. This dynamic environment likely forms brines of varying lithium concentrations interlayered within the clastic sediments that fill the basin and suggests that economic brines could exist below aquifers with lower lithium concentrations.

This complex and diverse brine evolution is further complicated by other factors. Some brine may re-mix with incoming fresh groundwater or ephemeral stream water, whereas at other locations and times, salt brines may sink to depths in the playa basin because of their greater density relative to fresher water. Individual tephra layers or clastic sediment layers can serve either as aquifers to transport incoming groundwater and geothermal water, or they can store brines concentrated by evaporation. Faults may act as conduits connecting one subhorizontal aquifer to another, or they can serve as barriers to flow, enabling lithium-bearing brines to accumulate in some structural blocks without contamination from dilute groundwater. Finally, conductive heating by underlying geothermal fluids could potentially induce circulation (analogous to convective overturn) in a portion of basin brines that lie within hydrologically connected regions.

The above-mentioned processes can lead to the development of a heterogeneous subsurface distribution of lithium in closed basins. Only further exploration and deep drilling will unravel the complex history of Nevada's lithium deposits.

5. Acknowledgements

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