Distribution and Isotopic Composition of Li in the Salton Sea Geothermal Field

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ABSTRACT

The behavior of Li during interactions between geothermal brine and the host rocks of the Salton Sea Geothermal Field (SSGF) are poorly constrained. Because of this, the total size of the recoverable Li reservoir after a Li-depleted brine is reinjected into the SSGF and interacts with the reservoir rocks at depth is uncertain. Here, we present bulk rock and brine Li concentration ([Li]) and δ^7Li along with in situ [Li] measurements of rocks and minerals from the deep portions of the California State 2-14 scientific drilling core and a few commercial wells in the SSGF to (1) characterize the dominant mineral hosts of Li and (2) constrain the behavior of Li during brine-rock interaction at depth.

Li concentrations are highest in authigenic chlorite and [Li] in chlorite decreases with increasing depth (270-580 ppm at ~2358 m, 70-100 ppm at ~2882 m); groundmass containing chlorite has up to 250 ppm Li at ~2358 m. Chlorite from ~2358 m depth is observed to encase pyrite in anhydrite-bearing rocks, indicating that specific brine-mineral reactions are important to fixing Li in the rocks at these depths. Metasediments have δ^7Li (relative to Li-SVEC) = +1.8 to +7.9‰. Below 1.5 km depth, there is a positive correlation between depth (and temperature) and δ^7Li such that rocks from the chlorite-calcite metamorphic zone have δ^7Li = +2.0 to +4.3‰ and rocks from the deeper, hotter biotite metamorphic zone have δ^7Li = +4.3 to +7.9‰. Conversely, whole rock [Li] decreases with depth from ~80 ppm (~2358 m) to ~10 ppm (~2882 m). The geothermal brines have δ^7Li = +3.7 to +4.7‰. The values of the rocks and brines overlap with the known δ^7Li of many Li-bearing fluids and solid Earth reservoirs of Li, obscuring the origin of Li in the SSGF. The difference in [Li] and δ^7Li between chlorite-bearing rocks at depth suggests that the partitioning of Li in chlorite between the brine and rock is temperature dependent – lithium becomes more incompatible in chlorite in the biotite metamorphic zone, indicating an important control of temperatures above and below 325°C on the behavior of Li.

1. Introduction

There is a steadily increasing demand for Li as a component in batteries for short term power storage and electric vehicles (Ambrose and Kendall, 2020). Currently, lithium mining, refining, and battery assembly is an environmentally damaging process that requires energy- and water-rich mining and processing techniques and long distances for international supply chains (Sun et al., 2017; Olivetti et al., 2017; Liu and Agusdinata, 2020; Kelly et al., 2021; Chordia et al., 2022). With efforts to combat climate change focusing on decarbonization and renewable energy resources, demand for Li-batteries as an efficient means for short term power storage has increased, along with interest in establishing large, reliable domestic sources of lithium ores. Lithium is thus considered a critical mineral by the United States Department of Interior (U.S.G.S., 2022).

Hypersaline brines from the Salton Sea Geothermal Field (SSGF) contain ~200 ppm Li (Skinner et al., 1967; Helgeson, 1968; Maimoni, 1982; Williams and McKibben, 1989; McKibben and Hardie, 1997). While there has long been interest in recovering Li from these brines (e.g., Maimoni, 1982), until recently it was not considered cost-effective given the substantial challenges of managing these metal-rich brines at near-boiling temperatures. Given the demand of the green energy transition and interest in developing domestic sources of Li, plans to extract Li from these brines are now moving forward. Beyond developing a domestic supply, this process would also have a smaller physical footprint and environemental impact compared to the traditionally employed methods (less water consumed and carbon released; Liu and Agusdinata, 2020; Kelly et al., 2021; Chordia et al., 2022; Kumar et al., 2022).

As one of the lightest elements on the periodic table, Li has a large relative difference in the mass between its two stable isotopes, ^6Li and ^7Li (~17%), which leads to larger fractionations at low temperatures (<250°C; e.g., Chan et al., 1994; Wunder et al., 2007; Millot et al., 2010). This fractionation occurs during fluid-rock interactions because of the preferential incorporation of ^7Li into lower coordination environments (e.g., Wunder et al., 2007; Penniston-Dorland et al., 2017 and references therein). When a fluid containing Li interacts with a rock to precipitate new Li-bearing minerals, ^6Li will partition preferentially into the mineral host (octahedral coordination) and leaves the fluid (tetrahedral coordination) enriched in ^7Li. When the fluid and mineral share the same coordination environment (e.g., quartz), the fractionation of Li isotopes is minimized (e.g., Schauble, 2004; Penniston-Dorland et al., 2017 and references therein).

Because of these fractionation behaviors, Li isotopes are useful for constraining the extent of interactions between surface and near-surface waters and rocks (Munk et al., 2011; Godfrey et al., 2013; Araoka et al., 2014; Sanjuan et al., 2016; Munk et al., 2018; Garcia et al., 2020; Godfrey and Álvarez-Amado, 2020; He et al., 2020). Generally, studies of surface brines compare measured δ^7Li ($\delta^7Li = [\ (^7Li/^6Li)_{sample}\ /\ (^7Li/^6Li)_{standard} - 1]\ *\ 10^3$) and Li concentration (represented here as [Li]) of the surface reservoir with surrounding aqueous sources feeding the reservoir to narrow down the potential origins of Li in the surface brine along with observations of other elements and isotopic systems (e.g., Munk et al., 2011; Godfrey et al., 2013; Munk et al., 2018; He et al., 2020). Other studies add to these observations with measurements of brines at depth (Garcia et al., 2020) or modeled how fractionation and mixing change the δ^7Li of the surface Li reservoirs (Araoka et al., 2014; Godfrey and Álvarez-Amado, 2020). By constraining the behavior of Li isotopic fractionation for the sources and sinks of Li within saline systems, as is the case in the SSGF, reservoir rocks and brines can provide the record of extent of interactions between surface and near-surface fluids and source rocks in the past. This study combines petrography and analytical

geochemistry to identify the dominant mineral hosts of Li in the source rocks in the SSGF and assess the extent to which interactions between the source rock and brine are recorded in these sources and sinks.

Geologic History
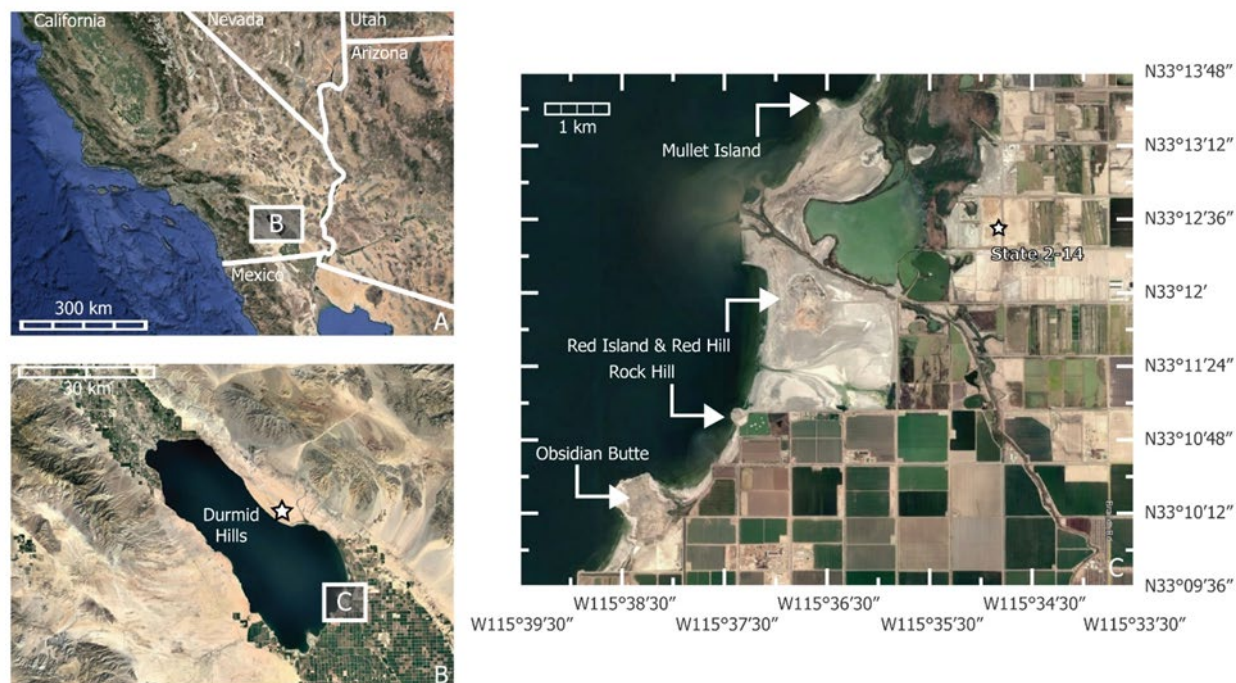
Figure 1. A. Regional map of southern California. B. Map of the Salton Sea. The sampling location for the Durmid Hills is labeled with a star. C. Map of the northern part of the SSGF. Rhyolitic domes are labeled and indicated with arrows. The location of the State 2-14 well is labeled and indicated with a star.

The SSGF is located in southern California, on the southeastern shore of the Salton Sea (Fig. 1). This region is shaped by a variety of tectonic processes related to the subduction of the Farallon slab (until ~12 Ma) and change to strike-slip and extensional motion in the present (e.g., Atwater, 1970; Mammerickx and Klitgord, 1982; Stock and Hodges, 1989). Upon the opening of the Gulf of California into western North America around 6 Ma (e.g., Matti et al., 1985; Oskin and Stock, 2003; Dorsey et al., 2007), the Colorado River deposited sediments into the Gulf of California, and eventually isolated the northern part of the rift, the Salton Trough, from the remainder of the Gulf of California through creation of a delta by ~4 Ma (e.g., Winker and Kidwell, 1986; Lonsdale, 1989). Periodically the Colorado River is re-routed northwards, filling the Salton Trough with water and sediments from the Colorado Plateau and creating short-lived instances of a lake in the Salton Trough (e.g., Van De Kamp, 1973; Wilke, 1976; Waters, 1983; Philibosian et al., 2011; Tompson, 2016; Rockwell et al., 2022), referred to as Lake Cahuilla, after the Cahuilla people who live in the region (as referenced in MacDougal, 1914). Sedimentation rates have kept pace with rifting related subsidence beneath the Salton Trough (e.g., Lonsdale, 1989), producing thick sections of sedimentary rocks rich in evaporite minerals (2-4 km thick; e.g., Elders and Sass, 1988).

Magmatism associated with rifting have heated this system (Elders et al., 1972; Han et al., 2016), yielding hot, advecting brine and progressive metamorphic grade rocks -for example, in the State

2-14 drill core, these metamorphic grades are a chlorite-calcite zone (610-2,480 m, ~180-325°C), biotite zone (~2,480-3,000 m, ~325-350°C), and a clinopyroxene zone (~3,000-3,180 m, >~350°C; Cho et al., 1988; Sass et al., 1988). Five rhyolitic domes (~2,000-12,000 years old) are located in the SSGF as surface expressions of the heat in this system (Fig. 1.C.; Robinson et al., 1976; Wright et al., 2015; Schmitt et al., 2019). Beneath these domes are a series of buried extrusive and intrusive rhyolites that are ~450,000 years old (~1500 m depth; Schmitt and Hulen, 2008). The repeated episodes of volcanism in this region speak to the long-standing nature of the deep magmatic activity taking place under the SSGF. This unique focus of tectonic, hydrological, and geomorphological events resulted in the sediments, host rocks, and pore waters that exist at depth beneath the Salton Sea today, including the source of the geothermal brines currently being used to power the SSGF (e.g., Coplen, 1976; Rex, 1983; Waters, 1983; McKibben et al., 1988a; Brothers et al., 2022).

Sample Descriptions and Methods

Samples in this study include igneous and sedimentary surface rocks, geothermal brines collected from 22 commercial wells in the SSGF, as well as previously analyzed commercial drill cuttings (Schmitt and Hulen, 2008), newly analyzed commercial drill cuttings, and State 2-14 drill core specimens (e.g., McKibben et al., 1988a; McKibben et al., 1988b; Elders and Sass, 1988; Herzig et al., 1988; Herzig and Elders, 1988). Surface samples were collected from Obsidian Butte and Rock Hill (Fig. 1.C.; Robinson et al., 1976; Herzig and Jacobs, 1994) and the Durmid Hills (Fig. 1.B.; Babcock, 1974). Newly prepared thin sections in this study were prepared by Burnham Petrographics, LLC. Samples were analyzed via Scanning Electron Microscope, Laser Ablation Inductively Coupled Mass Spectrometry, and Inductively Coupled Mass Spectrometry of digested rocks. A more detailed sample description and methods section is available in Humphreys et al. (in review).

Results

Surface Samples

Surface rhyolitic rocks have [Li] dependent on mineralogy (1-91 ppm; Humphreys et al., 2023). The highest [Li] are found in volcanic glass ([Li]$_{Obsidian Butte}$ = 91 ppm) and plagioclase ([Li]$_{Rock Hill}$ = 90 ppm, Humphreys et al., 2023). Whole rock δ^7Li vary by volcano ($\delta^7Li_{Obsidian Butte}$ = +3.5 to +3.8‰, $\delta^7Li_{Rock Hill}$ = +8.1 to +10.3‰; Humphreys et al., 2023). Buried, hydrothermally-altered rhyolitic rocks from depths of 1573 m (5160 ft) – 2655 m (8710 ft; Schmitt and Hulen, 2008) have [Li] from 2-68 ppm and δ^7Li = +6.4 to +7.6‰, with quartz having the highest [Li] (maximum = 68 ppm; Humphreys et al., 2023). Surface sedimentary and evaporitic rocks collected from the Durmid Hills (Fig. 1.B.; Babcock, 1974) also have [Li] and δ^7Li that vary by rock type, with [Li]$_{sandstone}$ = 1-13 ppm and $\delta^7Li_{sandstone}$ = +5.2‰; [Li]$_{mudstone, spot analysis}$ = 142–177 ppm, [Li]$_{mudstone, whole rock}$ = 97-115 ppm (compared to 104-136 ppm; Sturz, 1989), and $\delta^7Li_{mudstone}$ = +1.5‰; (Humphreys et al., 2023); $\delta^7Li_{interbedded mudstone and gypsum}$ = +5.5 to +6.0‰; and [Li]$_{cryptocrystalline gypsum}$ = <1 ppm and δ^7Li = -9.1‰ (Humphreys et al., 2023).

Subsurface Samples

Like the surface samples, the [Li] and δ^7Li of the metasedimentary rocks vary with mineralogy of the rock and, additionally, depth. Epidotized mudstone has $\delta^7Li_{~1290m}$ = 1.8‰ and mudstone with

hematite veins has $\delta^7Li_{\sim1430m}$ = +5.7 to +6.3‰ (Humphreys et al., 2023). Vein material was not analyzed in either of these metasedimentary rocks, and care was taken to only sample the mudstone in these cores. Monomineralic epidote has $[Li]_{1866m}$ = <1 ppm and δ^7Li_{1866m} = +2.7 to +3.3‰ (Humphreys et al., 2023). Interbedded anhydrite and shale have whole rock $[Li]_{\sim2358m}$ = 79.2–83.9 ppm, spot analysis $[Li]_{\sim2358m}$ = <1–581 ppm with chlorite grains having $[Li]_{\sim2358m}$ = 269-581 ppm (Humphreys et al., 2023). Epidotized metasedimentary rock has $\delta^7Li_{\sim2485m}$ = +2.0 to 4.3‰ with an epidote grain having $[Li]_{\sim2485m}$ = 2.7 ppm (Humphreys et al., 2023). Whole rock interbedded anhydrite and mudstone has $[Li]_{\sim2745m}$ = 34.2 ppm Li with $[Li]_{\sim2745m}$ = <1–87 ppm from spot analyses (Humphreys et al., 2023). An epidotized mudstone has $[Li]_{\sim2819m}$ = <1–18 ppm and $\delta^7Li_{\sim2819m}$ = +6.2 to +7.9‰ (Humphreys et al., 2023). The deepest rocks studied have whole rock $[Li]_{\sim2882m}$ = 6.7–12.3 ppm and $\delta^7Li_{\sim2882m}$ = +4.1 – +5.1‰ with chlorite grains having $[Li]_{\sim2882m}$ = 70-104 ppm, alkali feldspar having $[Li]_{\sim2882m}$ = 2-19 ppm, and groundmass having $[Li]_{\sim2882m}$ = 3-43 ppm (Humphreys et al., 2023). Geothermal brines recovered from multiple geothermal wells in the SSGF have δ^7Li_{brine} = +3.7 to +4.5‰ with previous measurements $[Li]_{brine}$ = 117-245 ppm (Skinner et al., 1967; Helgeson, 1968; Maimoni, 1982; Williams and McKibben, 1989; McKibben and Hardie, 1997).

Discussion

All but one of the rocks measured in this study have $\delta^7Li_{whole\ rock}$ = +1.5 to +10.3‰ (the outlier has δ^7Li = -9.1‰; Humphreys et al., 2023). The δ^7Li_{brine} overlaps with that of the rocks, but with less variation, consistent with previously measured narrow ranges of $\delta^{18}O$ (0 to +3.3 ‰) and δD (-68 to -75 ‰), implying that the brine reservoir is internally convecting and well-mixed (Williams and McKibben, 1989). The geothermal brine samples and host rocks in this study overlap in δ^7Li of many potential source materials (Fig. 2) and Li-rich deposits (Fig. 2). The brines in this study are also heavier in δ^7Li composition than Li-bearing geothermal brines from the Rhine Graben and are lighter in δ^7Li composition than oil field related brines from the Rhine Graben and all brines from the Tibetan Plateau (Fig. 2). Because of this wide overlap between the rocks and brines of the SSGF with global sources and sinks of Li, careful quantitative modeling of isotopic fractionation is necessary to identify the possible source(s) of the Li to SSGF brines.
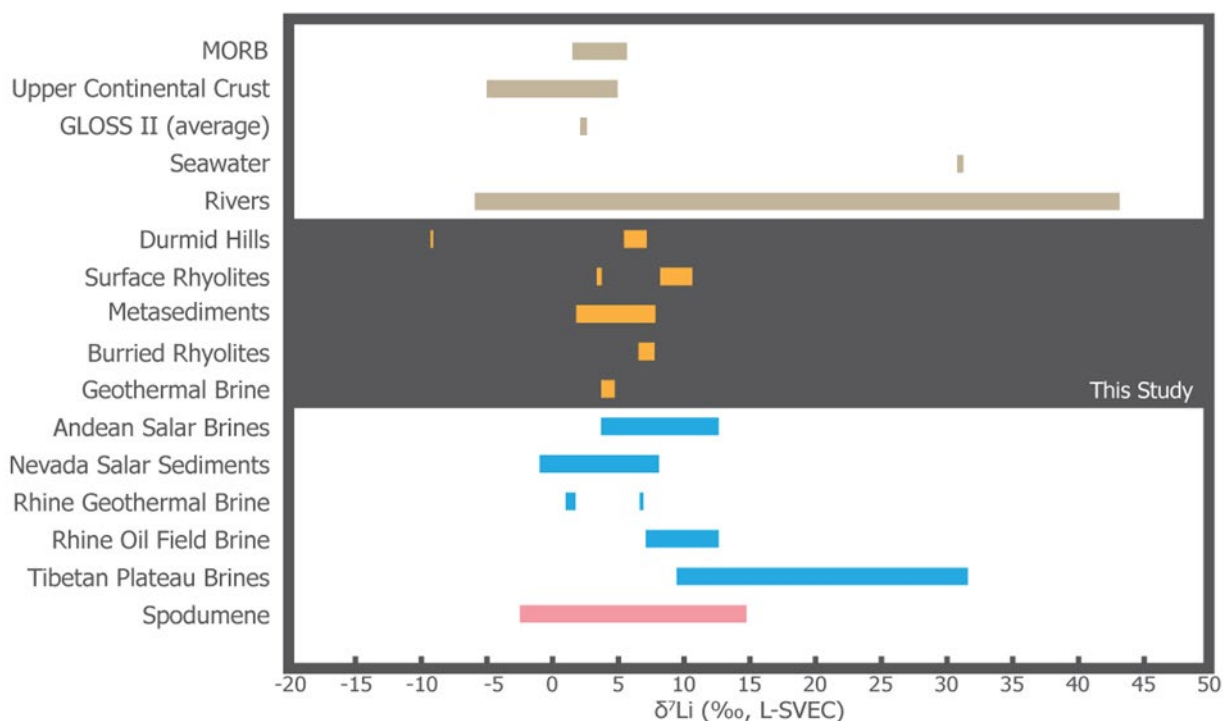
Figure 2. The Li isotopic composition for rocks and brines in this study compared to other Li-bearing reservoirs (modified after Penniston-Dorland et al., 2017). Brown bars represent known global ranges for Mid-ocean Ridge Basalt (Moriguti and Nakamura, 1998; Chan, 2002; Elliott et al., 2006; Nishio et al., 2007; Tomascak et al., 2008), the upper continental crust (Teng et al., 2004; Sauzéat et al., 2015), seawater (Millot et al., 2004), and rivers (suspended and dissolved load; Huh et al., 1998; Huh et al., 2001; Kısakűrek et al., 2005; Pogge Von Strandmann et al., 2006; Vigier et al., 2009; Pogge Von Strandmann et al., 2010; Lemarchand et al., 2010; Liu et al., 2015; Pogge Von Strandmann and Henderson, 2015; Dellinger et al., 2015; Pogge Von Strandmann et al., 2020). Orange bars represent the rock and brine values measured in this study. Blue bars represent known Li-bearing, location specific isotopic data for the Andean salar brines, Nevada salar sediments, Rhine Graben geothermal brines, Rhine Graben oil field brines (Godfrey et al., 2013; Araoka et al., 2014; Sanjuan et al., 2016; Munk et al., 2018; Garcia et al., 2020; He et al., 2020; Godfrey and Álvarez-Amado, 2020; Desaulty et al., 2022). The Pink bar is for the range in known spodumene isotopic values (Magna et al., 2016; Fan et al., 2020; Desaulty et al., 2022).

State 2-14 rock samples in this study come from the chlorite-calcite (~610-2480 m, ~180-325°C) and biotite (~2480-3000 m, ~325-350°C) metamorphic zones (Cho et al., 1988; Sass et al., 1988). The mineral with the highest measured [Li] of any phase in this study are relatively large chlorite which encases authigenic, skeletal pyrite from ~2358 m in the calcite-chlorite metamorphic zone (269-581 ppm; Fig. 3; Humphreys et al., 2023). Due to the skeletal habit of these pyrite grains, we interpret these pyrites to be in the process of dissolution via reaction with the brine, mobilizing Fe out of the pyrite (McKibben and Elders, 1985) with concurrent hornsfelsic recrystallization of silicate minerals (e.g., quartz and feldspar; e.g., McDowell and Elders, 1980; McKibben and Elders, 1985). Since the appearance of chlorite ($(Mg,Fe)_3(Si,Al)_4O_{10}(OH)_2 \cdot (Mg,Fe)_3(OH)_6$) coincides with the disappearance of dolomite-ankerite ($Ca(Fe,Mg,Mn)(CO_3)_2$) and has been observed replacing feldspar ($KNaCa(AlSi)_4O_8$; McDowell and Elders, 1980; Cho et al., 1988), the combination of these processes provide the necessary elements for the formation of chlorite in this setting.
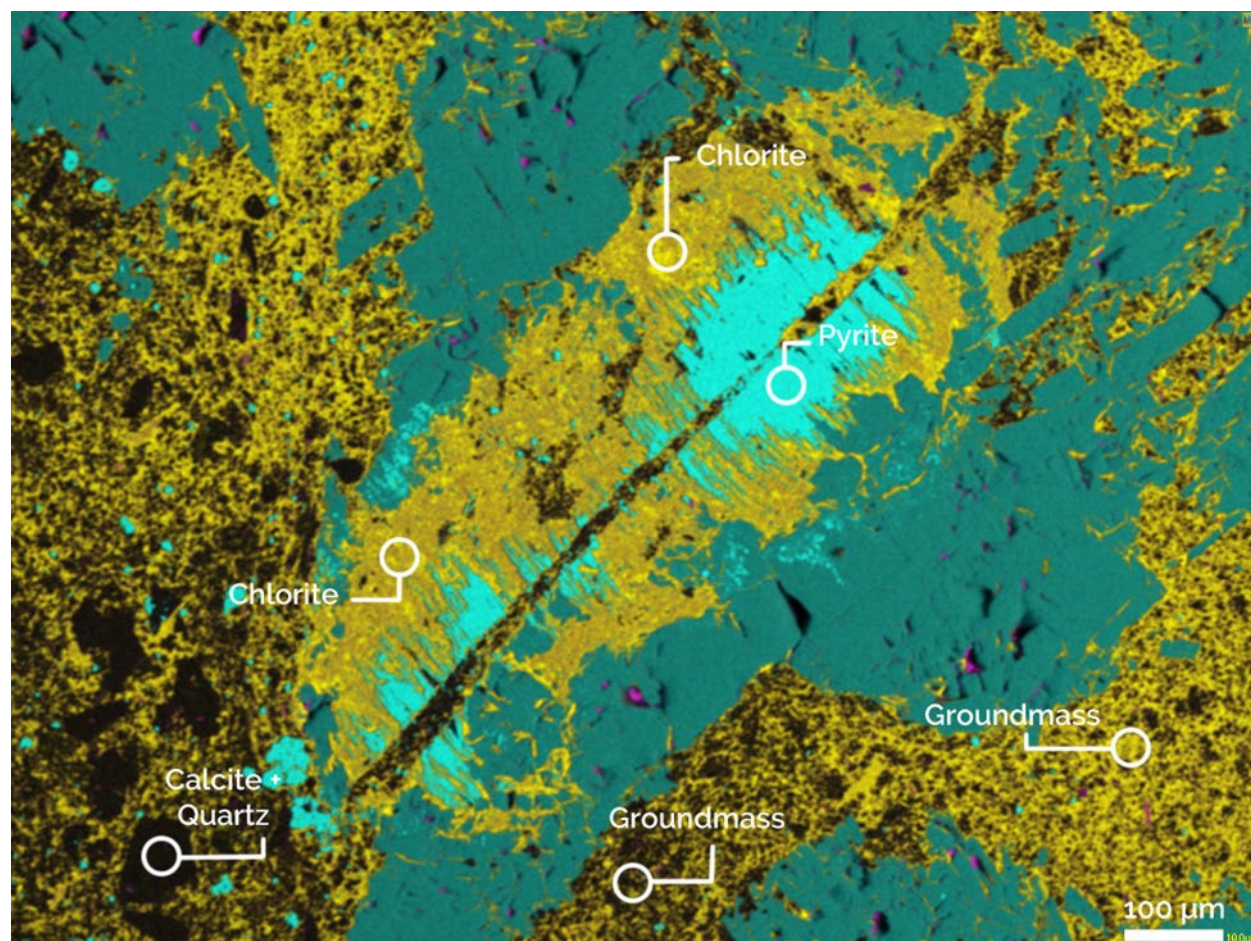
Figure 3. Back Scatter Electron map of metasedimentary anhydrite and mudstone from ~2358 m. Relatively aluminum rich regions are represented by magenta, relatively sulfur rich regions are represented by cyan, and relatively magnesium rich regions are represented by yellow. Anhydrite is the dark cyan mineral that is unlabeled on the sample. Relatively large authigenic chlorite surrounds skeletal pyrite.

Chlorite-rich groundmasses (Fig. 3) in these same metasedimentary rocks (~2358 m) also have elevated [Li] (48-252 ppm) relative to non-chlorite minerals (e.g., anhydrite and pyrite; 0-6 ppm) from similar depths (Humphreys et al., 2023). Combined with elevated [Li] in larger chlorite clasts, this observation confirms hypotheses from Na/Li geothermometry that suggests that chlorite and other octahedral clay minerals are the most likely mineral hosts for Li in the SSGF (Sanjuan et al., 2022). Surface mudstones have somewhat higher bulk [Li] than the chlorite-bearing rocks in the calcite-chlorite zone (Humphreys et al., 2023), suggesting a net loss of Li from the rocks into the brines, and that Li is preferentially incorporated into chlorite. Rocks in the biotite zone have even lower [Li] (7-34 ppm) than those in the chlorite-calcite zone (Humphreys et al., 2023), suggesting that more Li is lost from rocks into the brines at higher temperatures.
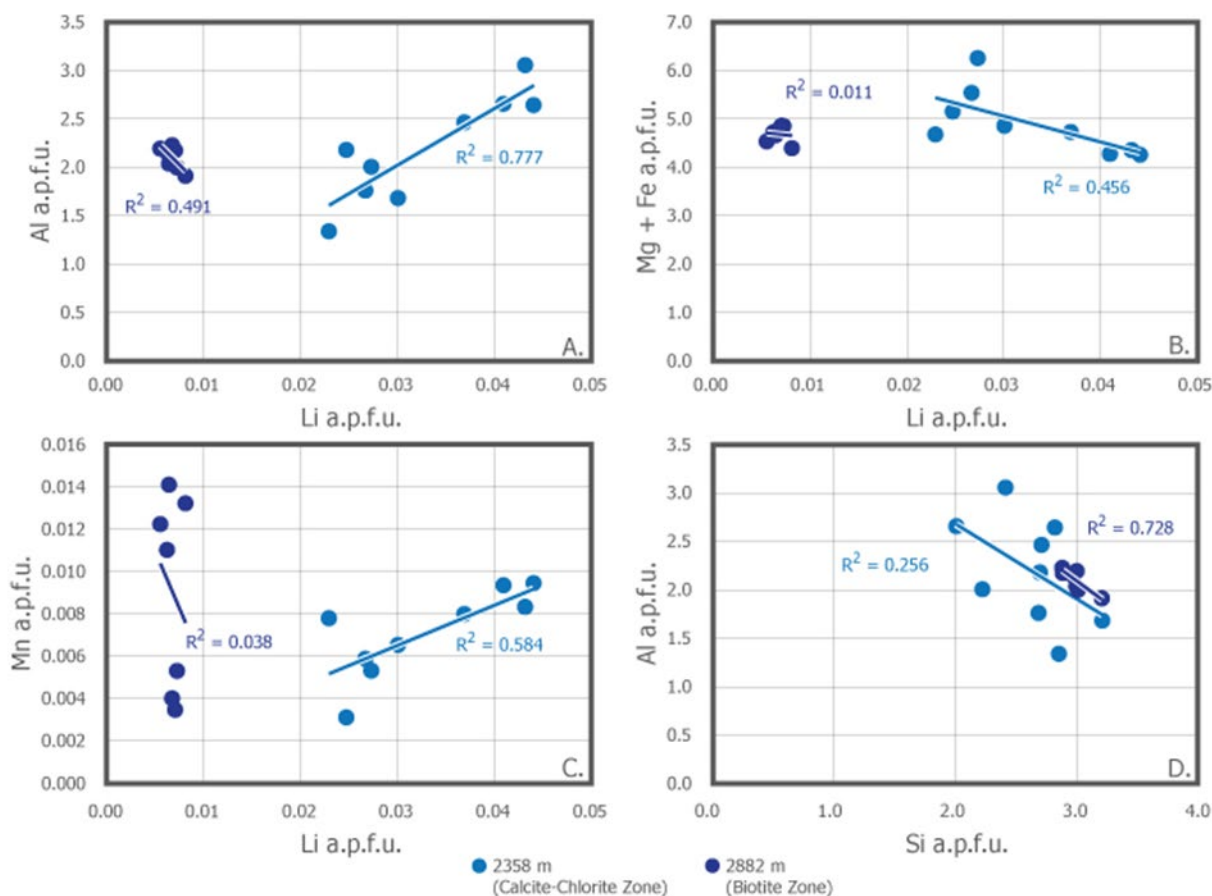
Figure 4. Major element comparison of chlorites in this study with Li and Si atoms per formula unit (a.p.f.u). A. Comparison of Al and Li a.p.f.u. in chlorites found at ~2358 m (blue) and ~2882 m (dark blue). B. Comparison of Mg + Fe (Fe^{2+} + Fe^{3+}) and Li a.p.f.u. in chlorites found at ~2358 m (blue) and ~2882 m (dark blue). C. Comparison of Mn and Li a.p.f.u. in chlorites found at ~2358 m (blue) and ~2882 m (dark blue). D. Comparison of Al and Si a.p.f.u. in chlorites found at ~2358 m (blue) and ~2882 m (dark blue).

Chlorite compositions in this study were calculated with $Fe^{3+}/\Sigma Fe = 0.1$ (Dyar et al., 1992) on a 14-oxygen basis and overlap with previous measurements from the SSGF (McDowell and Elders, 1980; Cho et al., 1988). There is a positive correlation between Li and Al ($R^2 = 0.777$; Fig. 4.A.) and Li and Mn ($R^2 = 0.584$, Fig. 4.B), and a moderately negative correlation between Li and Mg + Fe^{2+} + Fe^{3+} ($R^2 = 0.456$; Fig. 4.C.) in chlorite from the chlorite-calcite zone. The relationships between Li and major elements (Fig. 4.A.-C.) and lack of correlation between Li and Si ($R^2 = 0.092$), indicate that Li substitutes into chlorite with Al in the octahedral site (Fig. 4.B.). The partitioning of Li into chlorite is markedly different in the biotite zone - there is no relationship between Si and Al within the calcite-chlorite zone chlorites ($R^2 = 0.256$), but there is a strong negative correlation ($R^2 = 0.728$) between Si and Al in the biotite metamorphic zone (Fig. 4.D.). Additionally, there is a weak negative correlation ($R^2 = 0.491$) between Li and Al within these same rocks (Fig. 4.A.). These relationships suggest that at temperatures >325°C, the incorporation of Al in chlorite switches to the tetrahedral site, and because these chlorites have lower [Li] as well as display a negative correlation between Li and Al (Fig. 4.A.), this substitution is not charge-coupled with Li. Lithium may be more incompatible in chlorite at temperatures >325°C in the State 2-14 rocks. As the partitioning behavior of Li in chlorite depends on fluid and mineral

compositions and temperature, these relationships will be important to constrain and/or test with additional measurements.

Understanding the primary source for [Li] and δ^7Li in the SSGF brines is complex, owing to the variety of geologic processes and length of time in which these processes have been affecting the Salton Trough (~4 Ma to present; Van De Kamp, 1973; Wilke, 1976; Waters, 1983; Winker and Kidwell, 1986; Lonsdale, 1989; Philibosian et al., 2011; Tompson, 2016; Rockwell et al., 2022). Evaporation of Lake Cahuilla likely had little to no effect on the δ^7Li of the evaporating lake waters because salt precipitation does not significantly fractionate Li isotopes (e.g., Tomascak et al., 2003; Godfrey et al., 2013). Also, because Li more readily fractionates at lower temperatures, fractionation is expected to be greatest at shallower to near-surface depths (e.g., Chan et al., 1994; Chan et al., 2002; Millot et al., 2010). Upon burial, incremental hydrothermal metamorphism of these rocks (e.g., Helgeson, 1968; Muffler and White, 1969), would first lead to greater fractionation of δ^7Li between the rocks (lighter δ^7Li) and brine (heavier δ^7Li). With increased depth, fractionation decreases and while the minerals would have progressively heavier δ^7Li compositions in response to the progressively heavier δ^7Li brine compositions, at each stage the metamorphosed clay minerals would still be expected to be lighter in δ^7Li than the equilibrium composition brine. While higher temperatures at depth may have caused the initial release of more Li into the brine from the deeper buried sediments and rocks (e.g., Magenheim et al., 1995; Chan et al., 2002; Millot et al., 2010; Coffey et al., 2021; Ellis et al., 2022), reactive-transport modeling of the SSGF as a whole suggests that the interaction between the rock and brine is slower than is necessary to affect the [Li] of re-injected, Li-poor brines on decadal timescales (Sonnenthal et al., in review).

Conclusions

Lithium concentrations vary with depth and mineralogy within the SSGF. The highest [Li] for rocks and minerals are found within mudstones and decrease with depth, with surface mudstones containing ~106 ppm Li, mudstones at 2358 m containing ~82 ppm Li, and mudstones from 2745 m containing ~34 ppm Li. At depth chlorite has the highest concentration of Li, with values as high as ~580 ppm found at a depth of ~2358 m. Chlorites from deeper in State 2-14 have less lithium within them with a maximum measured concentration of ~104 ppm. Chlorite has been observed to be the primary mineral host of Li at depth.

Lithium isotopic compositions for the rocks vary at depths less than 1.5 km (< ~300°C; Sass et al., 1988) but are consistently lighter than the hypersaline geothermal brine they are in contact with at depths deeper than 1,500 m in the chlorite-calcite zone and heavier than the hypersaline geothermal brine within the biotite metamorphic zone (> 2,480 m and > 325°C). Much like previous hydrogen and oxygen isotopic work done on Salton Sea Geothermal brines (Williams and McKibben, 1989), the δ^7Li composition is narrowly confined ($\delta^7Li_{avg} = +4.1 \pm 0.3$ ‰), indicating a well-mixed brine reservoir.

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