

Lithium Brines: Origin, Characteristics, and Global Distribution

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Abstract

Over the past two decades, considerable attention has been focused on lithium as a critical mineral resource. This is driven primarily by the unprecedented need for this element in moving the energy transition forward because of its utility in lithium-ion batteries for electric vehicles and energy storage. Lithium resources are found in three main types of deposits, but closed-basin brines are known to currently contain most of the global resources. Lithium resources are also present in sedimentary-basin (oil field) and geothermal-basin brines, although these are emerging and not yet produced at a commercial scale. Here we provide an update on the global state of lithium brine resources by type but with a focus on updating the ore deposit model for closed-basin lithium brines and introducing a seventh important characteristic for the formation of closed-basin lithium brines. This characteristic is hydro(geo)ology, which refers to the coupled role of hydrological basin characteristics and subsurface hydrogeological properties and their structure and distribution. Emerging lithium brine types are incorporated into our updated conceptual model, and case studies of two globally important lithium brine systems are also presented. Pegmatite and volcano-sedimentary lithium deposits are compiled to complete the lithium resource picture. Lastly, we consider lithium production over time and some guidelines for the exploration of closed-basin brines.

Introduction

Lithium is a critical and technologically essential element that has gained enormous attention in the last decade because of its demand, particularly for batteries in electric vehicles and energy grid storage. Reduction in the use of internal combustion engines in transportation is critical to achieving global carbon neutrality, and this transition revolves around lithium and other battery critical elements. Lithium is not a scarce element on a global scale, yet it is predicted that there may be an undersupply because of the unprecedented global demand—a trend that is projected to continue for at least the next two decades. Although the exploration for and discovery of new lithium deposits has seen an overall upswing in the last decade, these activities will require more resources and focus to address the undersupply projections, even with advanced lithium-ion battery recycling. Fluctuations in the market value of lithium further complicate the supply chain. It is predicted that 74 new lithium mines/plants will be needed to meet the projected demands over the next decade (Benchmark Mineral Intelligence, 2024). Lithium sourced from closed-basin (CB) lithium brines is important globally because they host most of the world's lithium supply, are the most economically recoverable lithium source, and have the lowest carbon and freshwater footprint of any currently producing lithium de-

posit type (Kelly et al., 2021; Vera et al., 2023). Therefore, it is important to continue to advance the genesis models of these deposits to develop efficient extraction techniques and exploration models for maximizing recovery and continued discovery of new deposits. In addition to an update of the CB (salar) brine deposits, the current work will briefly address two types of emerging brines that contain lithium but to date are not at commercial production scale. These include sedimentary-basin (SB; e.g., oil field) and geothermal-basin (GB) sources. These emerging deposits leverage existing infrastructure from the oil and gas industry (SB) and the geothermal industry (GB), respectively, but face technological recovery challenges.

Lithium exists globally in three main types of deposits: (1) hard rock (pegmatite/spodumene/granite), (2) brines, and (3) sedimentary-volcanic (Fig. 1). Subcategories of brines include (1) closed basin (e.g., salar), (2) sedimentary basin (e.g., oil field), and (3) geothermal basin (Fig. 2). No preexisting consistent nomenclature for these three brine categories exists in the literature. Therefore, we establish the names for the three main types of lithium brines and offer that these be adopted by the lithium community. These are (1) closed basin (CB), (2) sedimentary basin (SB), and (3) geothermal basin (GB). CB brines can have a modern lake such as Great Salt Lake (USA), Tres Quebradas (Argentina), or Zhabuye Salt Lake (China), or they may be characterized by only a dry crystallized salt surface (playa) that had an ancient lake (Salar de Atacama, Chile, Clayton Valley, Nevada, Salar de Uyuni, Bo-

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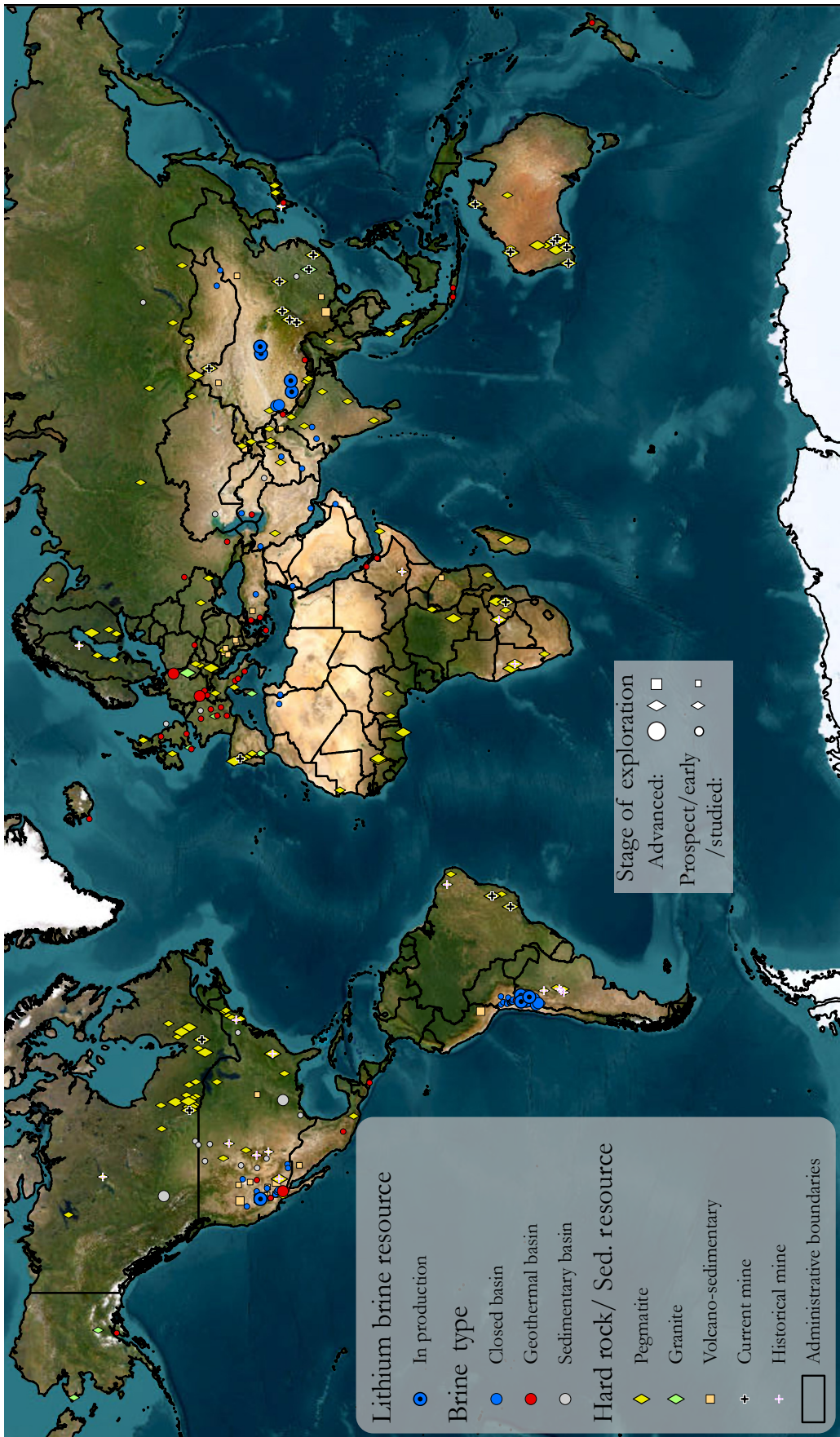


Fig. 1. Global compilation of lithium resource deposit locations by type. Brines including closed basin, sedimentary basin, geothermal basin, hard rock (granite and pegmatite), and clay (volcano sedimentary) are included. Current and historical mines as well as projects in the exploration stage (advanced and prospect/early/studied) are considered.

livia, and numerous other salars in Argentina). The temperature range of sedimentary basins is considered not to exceed about 100°C, whereas high-temperature geothermal brines are typically between 100° and 150°C but can have reservoir temperatures exceeding 150°C.

The lithophilic geochemical behavior of lithium dictates its concentration in low- and high-temperature settings across deposit types. For example, in the evolution of CB brines there is compelling evidence that evaporative concentration is a primary driver of concentrating lithium in brines (Munk et al., 2018) and that hydrothermal inputs and geothermal influence may also contribute. These concentrating processes are effective for lithium because it is incompatible and geochemically conservative. Recovery of lithium from CB brines primarily relies on evaporation ponds with a few projects implementing direct lithium extraction (DLE) at the commercial or precommercial scale. Other CB lithium brine projects are planning and testing DLE as the main suite of technologies to extract lithium from brines, and this group of technologies appears to be the primary future technology plan for lithium extraction for CB, SB, and GB lithium brines (Vera et al., 2023).

The initial brine composition determines the production process. Most CB, SB, and GB lithium brines are of Na-Cl or Na-Cl-SO₄ variety. They contain varying amounts of other major cations and anions, minor and trace elements, and gases including CO₂, CH₄, noble gases, etc. The composition of the source rocks, inflow waters, and the resulting brine composition dictate how the brine will evolve once it undergoes evaporation and mineral precipitation (Eugster and Jones, 1979; Eugster, 1980). These brines typically contain variable amounts of Li, B, Ba, Sr, Br, I, and F, and in the case where lithium is concentrated on the order of hundreds of milligrams per liter, these deposits can be classified as having potential economic viability for lithium extraction (Munk et al., 2016).

CB lithium brine deposits account for about 75% of the world's known lithium resource, although current production is dominated by hard-rock (pegmatite) deposits (U.S. Geological Survey, 2023). In the last decade, many CB-type lithium brines have been discovered, and additional advanced exploration activities are underway globally, but there is only one additional salar lithium brine that has gone into production (Cauchari-Olaroz).

Munk et al. (2016) noted that there are also occurrences of closed basins with abundant saline ground and surface waters not enriched in lithium. These include the ephemeral lakes of southwestern Australia, many of which may have occupied closed basins since the Eocene and are hosted by diverse and highly weathered igneous and metamorphic rocks of the Archean Yilgarn craton (Benison and Bowen, 2006). These waters have salinities that are 5 to 10 times greater than seawater (Bowen and Benison, 2009) and are Na-Cl and Na-Mg-Cl-SO₄ brines, the majority of which have a pH < 4. Another example of low-lithium brines is from the chotts of eastern Algeria (Zatout et al., 2020), which are interpreted to be sources from dissolution of ancient evaporites. Although extreme weathering and evaporation have taken place and the climate and hydrology of these environments may be favorable for concentrating lithium, there seems to be a lack of lithium sources and/or other concentrating mechanisms.

Lithium has also been recognized in deep oil field brines (SB lithium brines) such as those associated with the Smackover Formation in the Gulf Coast of the United States (Collins, 1976; Davari et al., 2024) or the Devonian strata of the Appalachian Plateau of Pennsylvania (Dresel and Rose, 2010; Phan et al., 2016). Some brines are reported to contain hundreds of milligrams per liter of lithium and are usually greater than 1 km deep, which prevented historical development (Gruber et al., 2011), but these brines are now considered an emerging lithium resource type (Butler et al., in press). Additionally, projects in the Smackover Formation from Arkansas to Texas, USA, and the Leduc Formation, Alberta, Canada, are at advanced field pilot to precommercial stage.

Lithium is also present in GB lithium brines in North America (Dobson et al., 2023) and Europe (Gourcerol et al., 2024, and references within), Indonesia, and the Himalayas (Herdianita et al., 2019; Wang et al., 2021; Wahyudi et al., 2023). These brines can have up to several 100 mg/L lithium content and can be produced from reservoirs up to 5,000 m deep.

The CB lithium brines from the Central Andes of Bolivia and northern Chile were comprehensively reported in Risacher and Fritz (2009) and references therein. Moraga et al. (1974), Rettig et al. (1980), F. Risacher (unpub. report, 1999), Risacher et al. (2003), and Risacher and Fritz (1991) report the geochemical composition of hundreds of brine samples. The focus of most of this work was to examine the origin of the salts in the salars. Risacher and Fritz (2009) also provided a general classification for these brines (alkaline, sulfate-rich, and calcium-rich), and indicated that alkaline salars are absent in Chile because of the presence of high-sulfur volcanic rocks that are a major source of hydrogen ions during weathering. The origin of solutes to salars in the Central Andes has been addressed by the major and trace element and isotopic investigations of Alpers and Whitmore (1990), Spiro and Chong (1996), Carmona et al. (2000), and Boschetti et al. (2007). However, none of these studies specifically addressed the origin and accumulation of lithium. López Steinmetz et al. (2018, 2020) compiled a regional-scale geochemical reconnaissance across 12 salars in Argentina with a focus on lithium variability and grades, and López Steinmetz and Salvi (2021) attempted to develop a relationship between basin size and lithium brine grade. Munk et al. (2018) developed the first mass balance approach using chemical fluxes to indicate that the modern hydrogeologic setting of the Salar de Atacama could account for the accumulation of the salts and solutes (e.g., lithium) in the deposit building on the work of Corenthal et al. (2016). This was followed by detailed geochemical modeling of inflow, transition (brackish lagoon), and brine waters to further understand the potential connections among water types in the basin (Munk et al., 2021), which created a framework for interpreting both resource and environmental issues in this basin and beyond.

At Clayton Valley, Nevada, Kunasz (1974), Davis et al. (1986), Price et al. (2000), and Zampirro (2004) provided early ideas on the sources and concentrating processes of lithium in the Clayton Valley brines. Munk et al. (2011), Jochens and Munk (2011), and Coffey et al. (2021) provide the most recent investigation of the origin of lithium in the brines as well as how the lithium is sequestered in the subsurface aquifer

and contributes a sustainable source of lithium over time to the brines. This was followed by a detailed study by Gagnon et al. (2023) of the role of paleoclimate on the accumulation of lithium in authigenic clays through time in the subsurface basin-fill strata of Clayton Valley, Nevada.

Lithium-enriched brines and lakes in China have been reported on more recently (e.g., Li et al., 2023) in the West Kunlun-Karakoram orogenic belt on the northern margin of the Tibetan Plateau. Although this region is gaining more attention, the mechanisms that deliver and concentrate lithium in a large number of lithium-rich salt lakes in the Tibetan Plateau remain a topic of interest (Yu et al., 2013; Wang et al., 2018; He et al., 2020; Miao et al., 2022; Zhang et al., 2022). A detailed account of lithium brines from the Qaidam basin can be found in Zhang et al. (in press).

Bradley et al. (2013) identified common characteristics of lithium-rich continental brines as the basis for an ore deposit model, and these were later expanded on in Munk et al. (2016). In the current contribution we modify and elaborate on the Munk et al. (2016) common characteristics for CB lithium brines and add a seventh characteristic (basin hydro(geo)logy). We provide a comprehensive global distribution of not only lithium brines (App. Table A1; Fig. 2) but also all lithium deposits on a global scale (App. Table A2; Fig. 1) including published lithium resource estimates. This is the most comprehensive compilation of global lithium deposits to date. The discussions of the general geology, hydrogeochemistry, and climate of CB lithium brine systems are also updated with new ideas and research findings since Munk et al. (2016). We offer some updated ideas on exploration for CB lithium brine deposits. Detailed and updated discussions on Clayton Valley, Nevada, USA, and of the Salar de Atacama, Chile are provided as case studies that include all new work and new ideas on these systems. Assessments of water and brine resources are provided in the context of water needed for brine extraction and processing in consideration of environmental water requirements. We also created a new 3-D conceptual geologic model to include CB, SB, and GB lithium brine systems for a global perspective; however, we do not attempt to detail SB or GB lithium brines in this approach, as those are covered in other chapters of this Special Issue or are outside the scope. Our focus is primarily on details and updating of CB lithium brine systems.

Seven Characteristics Common to Closed-Basin Lithium Brines

The lithium-rich brine systems initially compiled in Munk et al. (2016) have been expanded on to include new discoveries and/or projects in CB lithium brines (App. Table A1) and more conceptual details on SB and GB lithium brines (Fig. 3). Here we update and improve the original CB lithium brine ore deposit model from the original six common (global) characteristics by adding a seventh characteristic as well as updating the advancements in understanding of the original six characteristics required to form CB lithium brines. These include: (1) arid climate, (2) closed basin containing a salar (salt crust), a salt lake, or both, (3) associated igneous, geothermal, and/or hydrothermal activity, (4) tectonically driven subsidence, (5) suitable lithium sources, (6) sufficient time to concentrate lithium in the brine, and (7) basin hydro(geo)logy.

Climate is the first characteristic and perhaps the most important, as it is linked to all the others because it (1) contributes to the formation of the salars in a CB setting, (2) is a factor in the concentration of lithium in brines over time, and (3) is essential for the concentration of lithium in evaporation ponds for economic purposes. Appendix Table A1 indicates the classification of the climate for each lithium-rich brine location in terms of hyperarid, arid, semiarid, or dry subhumid.

The second characteristic, shared by all CB lithium brines, is a closed basin with a salar(s) or salt lake(s) or both. This characteristic is controlled primarily by climate and tectonic setting. Salars or salt crusts are common where brines exist in shallow subsurface aquifers. The aquifers may be composed of some combination of salts including halite, gypsum, and carbonate, as well as volcanic ash or ignimbrites, alluvial gravels and sands, and tufa (commonly evidence of modern and/or past hydrothermal activity). Most of the locations in Appendix Table A1 are classified as salars. Salt lakes may also contain enrichments of lithium, although these are typically in the lower range of the lithium concentration spectrum (App. Table A1). Numerous salt lakes do not have commercial lithium production, because they have low concentrations, among other factors (e.g., Great Salt Lake, Utah).

The third characteristic is evidence of geothermal and/or hydrothermal activity. This likely plays a significant role in the formation of lithium-rich brines for several reasons: (1) it provides heat for enhanced leaching of lithium from source rocks; (2) it plays a role in the concentration of lithium through distillation or “steaming” of thermal waters in the shallow subsurface; (3) thermally driven circulation may be an effective means for advecting lithium from source areas to regions of brine accumulation; (4) it can result in the alteration of primary minerals and rocks to lithium-enriched secondary minerals such as clays, which can, in turn, be potential sinks and/or sources of lithium to brines if leaching and transport occur from the clay source; and (5) there may be lithium derived from primary magmatic hydrothermal sources.

A fourth characteristic of all lithium-rich brine deposits is that they occur in basins that are undergoing tectonically driven subsidence. The basins listed in Appendix Table A1 have several different tectonic drivers, including extension, transtension, and orogenic loading. Figure 2 depicts a clear relationship between CB and GB brine locations and tectonically active margins.

The fifth characteristic or requirement for the formation of CB lithium brines is viable sources of lithium. Lithium sources in various basins appear to include high-silica, vitric volcanic rocks such as ignimbrites and ashes, lithium-rich clay minerals, and ancient salar salt deposits. Determining the relative contributions of lithium sources to CB lithium brines is an active area of research and it, along with the time factor discussed below, is now recognized as a key characteristic to be worked out to improve exploration methods for CB (e.g., Munk et al., 2018; Coffey et al., 2021).

The sixth characteristic or requirement for the formation of lithium-rich brines is time. The time it takes to leach, transport, and concentrate lithium in continental brines is not well understood. However, it appears that most lithium brines of economic interest are geologically young (Neogene). Work at Clayton Valley, Nevada, USA, and the Salar de Atacama,

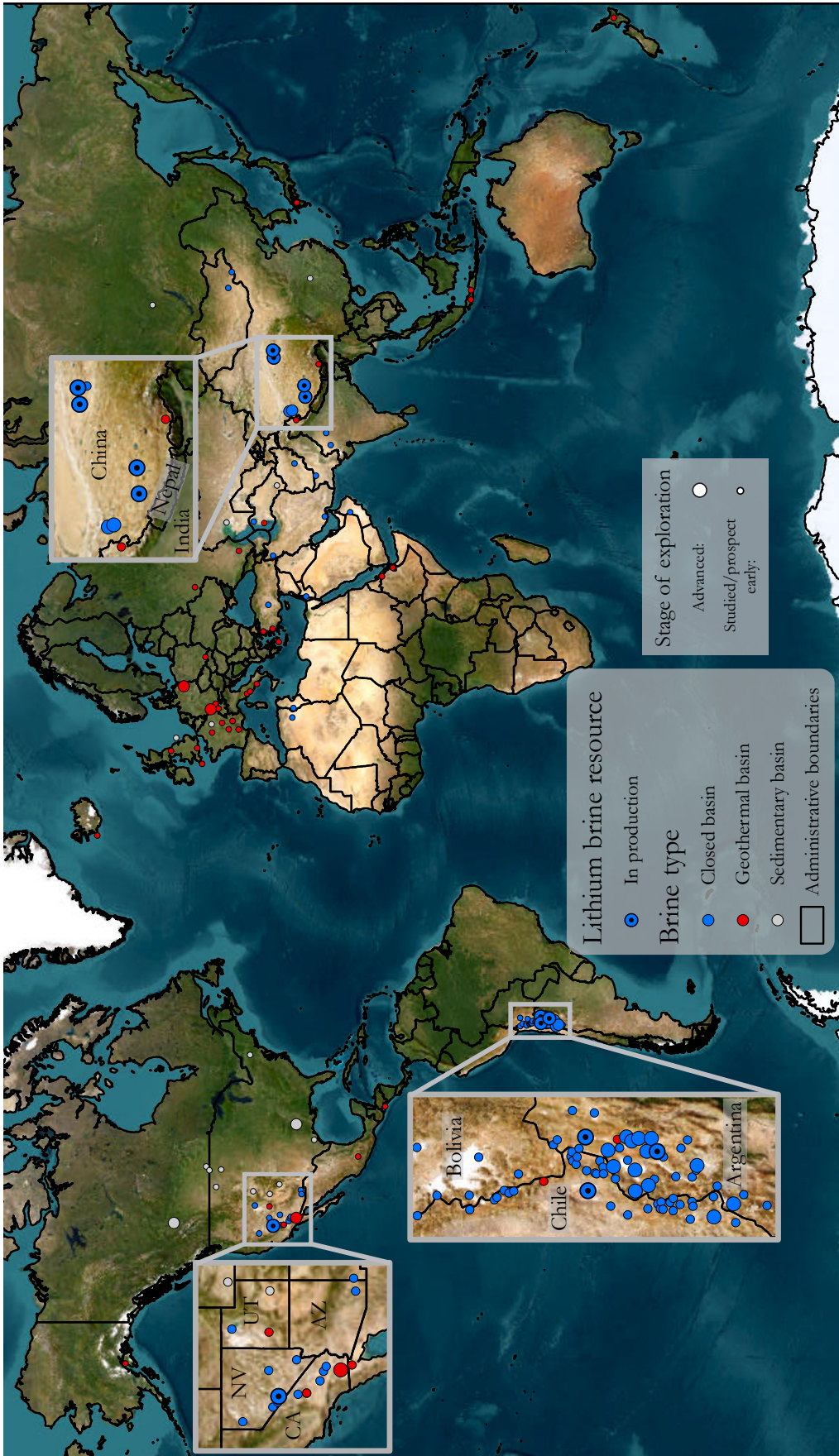


Fig. 2. Global compilation of lithium brine resources and projects. Brines from closed basins, sedimentary basins, and geothermal basins are included as well as current mine sites and exploration sites. Abbreviations: AZ = Arizona, CA = California, NV = Nevada, UT = Utah.

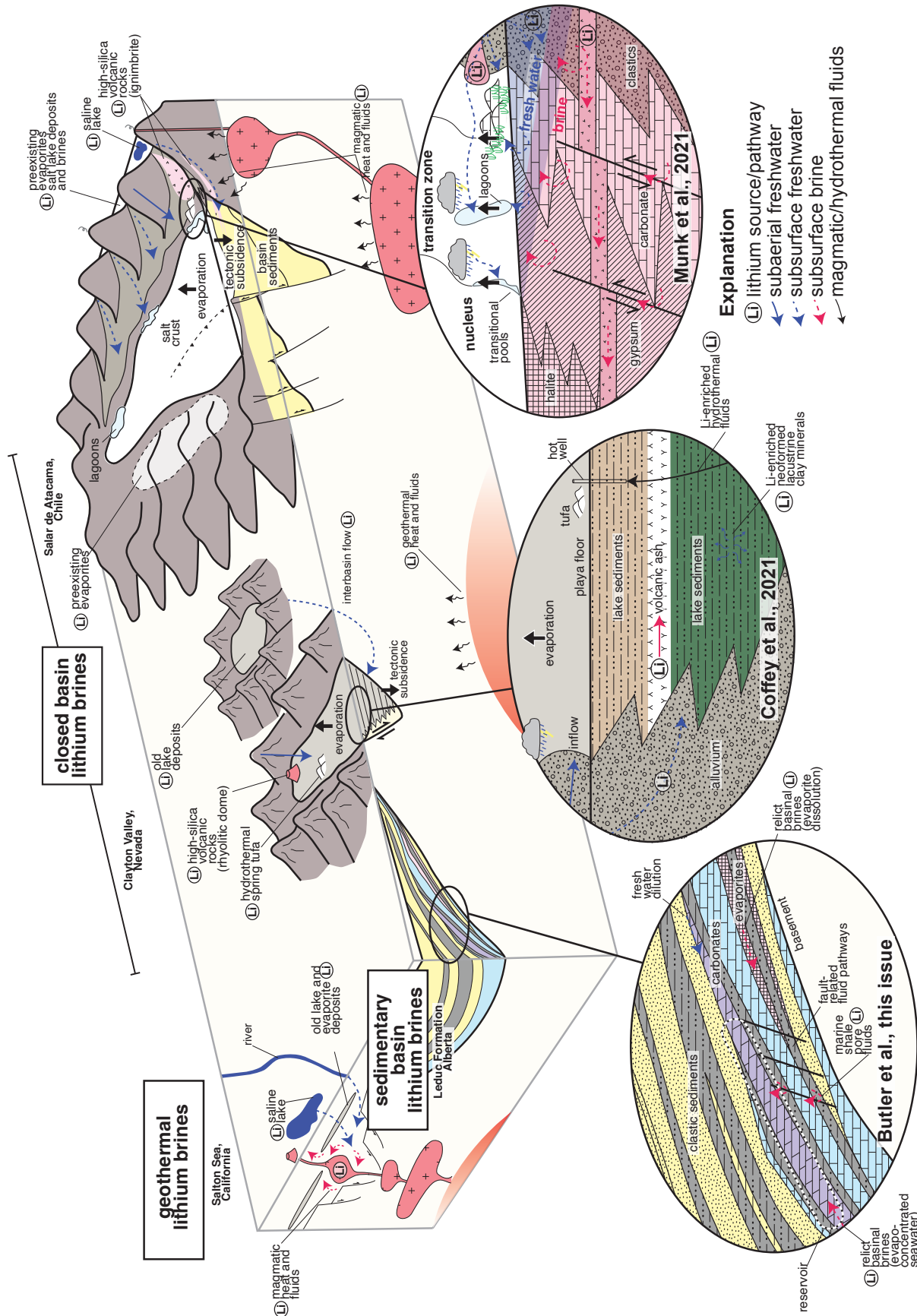


Fig. 3. Lithium brine conceptual model for closed-basin, sedimentary-basin, and geothermal-basin brine genesis. Lithium sources and fluid (fresh and brine water) pathways are broadly depicted. Conceptualization utilized Munk et al. (2016, this study), Coffey et al. (2021), Butler et al. (in press), and Hulen et al. (2002).

Chile, and in the Puna region of Argentina has provided insights into the ages of inflow waters and brines. Detailed investigations of South American basins show that most inflow waters and brine groundwaters are of premodern age (100s to 1,000s years old; Moran et al., 2022, 2024). Studies of Clayton Valley basin inflow waters have similar findings (Kirshen et al., 2022). This is a characteristic feature of these closed arid basins and is likely also an important factor in forming the lithium resource.

The seventh characteristic is the basin hydro(geo)logy. We consider this factor to be the combination of hydrological basin characteristics and subsurface hydrogeological properties and their structure and distribution. Basin hydro(geo)logy reflects the combined processes of streamflow generation, groundwater recharge processes, lithium transport mechanisms in the unsaturated and saturated zones, the functioning of the transition zone between fresh water and brine, and the lithium brine aquifers. Together these factors control the mass flux of lithium to the basin floor as well as the storage, release, and lithium brine deposit size and economic viability. We separate climate from basin hydro(geo)logy for two main reasons. First, hydrological processes mediate and transform precipitation onto the basin into surface and subsurface pathways that have shown to be important for both lithium transport/mobilization and brine recharge. Secondly, hydrogeologic properties and aquifer distribution within the basin place important constraints on lithium brine generation and resource extraction.

General geology of CB lithium brines (basins, tectonics, and stratigraphy)

Figure 2 shows the global distribution of brines that have lithium concentrations reported (including salt lakes) detailed in Appendix Table A1.

Most CB lithium brines are located in the continental arc subduction Altiplano-Puna region of the Central Andes of South America. The collisional Tibetan Plateau, China, also hosts lithium-enriched lakes. Houston et al. (2011) classified the salars in the Altiplano-Puna region of the Central Andes in terms of two end members—"immature clastic" or "mature halite"—primarily using (1) the relative amount of clastic versus evaporite sediment; (2) climatic and tectonic influences, as related to altitude and latitude; and (3) basic hydrology, which controls the influx of fresh water. The immature classification refers to basins that contain alternating clastic and evaporite sedimentary sequences dominated by gypsum and that have recycled salts and a low abundance of halite. These conditions occur in basins with larger and more consistent influxes of fresh water—conditions that occur in wetter climates and often at higher elevations. In the Altiplano-Puna region, these conditions occur more commonly in the north and east of the region because of the regional precipitation gradient. Mature refers to salars in arid to hyperarid climates that occur in the lower elevations of the region, reach halite saturation, and have intercalated clay and silt and/or volcanic deposits. One outlier from this classification is Clayton Valley, Nevada, USA. The subsurface aquifer system is dominated by lacustrine clay-rich deposits up to 1,000 m thick, where the lowermost and marginal areas of the basin fill are clastic sands and gravels (Coffey et al., 2021), but this basin is at a relatively

lower elevation (1,300 m) as compared to the >4,000-m basins on the Puna Plateau.

A key point made by Houston et al. (2011) is the relative significance of permeability, which is controlled by the geologic and geochemical composition of the aquifers. For example, immature salars may contain large volumes of easily extractable lithium-rich brines simply because they are a mixture of clastic and evaporite aquifer materials that have higher porosity and permeability.

Our conceptual geologic model for lithium brines is shown in Figure 3. The model seeks to account for the general sources, sinks, and processes that mobilize, sequester, and concentrate lithium. This model is intended to be conceptual and was developed primarily from the information we have gathered from our extensive investigations over the last decade on the CB brines at Clayton Valley, Nevada, USA, and Salar de Atacama, Chile, Salar de Pastos Grandes, Salar de Antofalla, Salar Tres Quebradas, Cauchari-Olaroz, and others in Argentina as well as new information from SB and GB lithium brines. For CB lithium brine systems, the concepts of Houston et al. (2011), Asher-Bolander (1982, 1991), Coffey et al. (2021), and Munk et al. (2016, 2018) also informed our model.

Effects of geochemistry, climate, hydrogeology, and hydrothermal influence on evolution of CB lithium brines

Geochemical and isotopic characteristics: The minimum, maximum, and average lithium concentrations for the brines and lakes in this study are listed in Appendix Table A1 and summarized in Figure 4. These values are compiled from several sources detailed in Appendix 1. Because some of the basins do not have minimum and maximum lithium concentration data reported in the literature, we use the average lithium concentrations to compare basins. The lowest average lithium concentration is 13 mg/L in the Bam salt plug, Iran, and the highest average lithium concentration is 1,880 mg/L for the brine in Salar de Atacama, Chile. For comparison, average seawater contains 0.2 mg/L lithium. Figure 4 compares the lithium concentrations among CB, SB, and GB brines from our global compilation. CB brines not only contain the majority of the global lithium resource, but they also have the highest overall concentrations of lithium among the three brine types. SB lithium brines have a mean lithium concentration of 99 mg/L as compared to GB lithium brines with a mean of 81 mg/L, but both can have maximum concentrations that approach 500 mg/L.

The potentially important sources of lithium to brines include high-silica volcanic rocks, preexisting evaporites and brines, hydrothermally altered clays, and hydrothermal fluids. Advancements in deciphering the role of lithium leaching from source rocks by low- and high-temperature fluids have been made by Coffey et al. (2021) who showed that most of the lithium in the Clayton Valley, Nevada, USA, lithium brine is sourced from the clay-rich lacustrine aquifer materials themselves. The lithium was sequestered in these clay-rich sediments during precipitation from the ancient lake waters that had hot-spring contributions. Godfrey et al. (2013) reported similar findings from low-temperature leaching of lithium from volcanic rocks near Salar del Hombre Muerto, Argentina. Risacher and Fritz (2009) concluded that lithium and boron in Andean salars are derived from the weathering

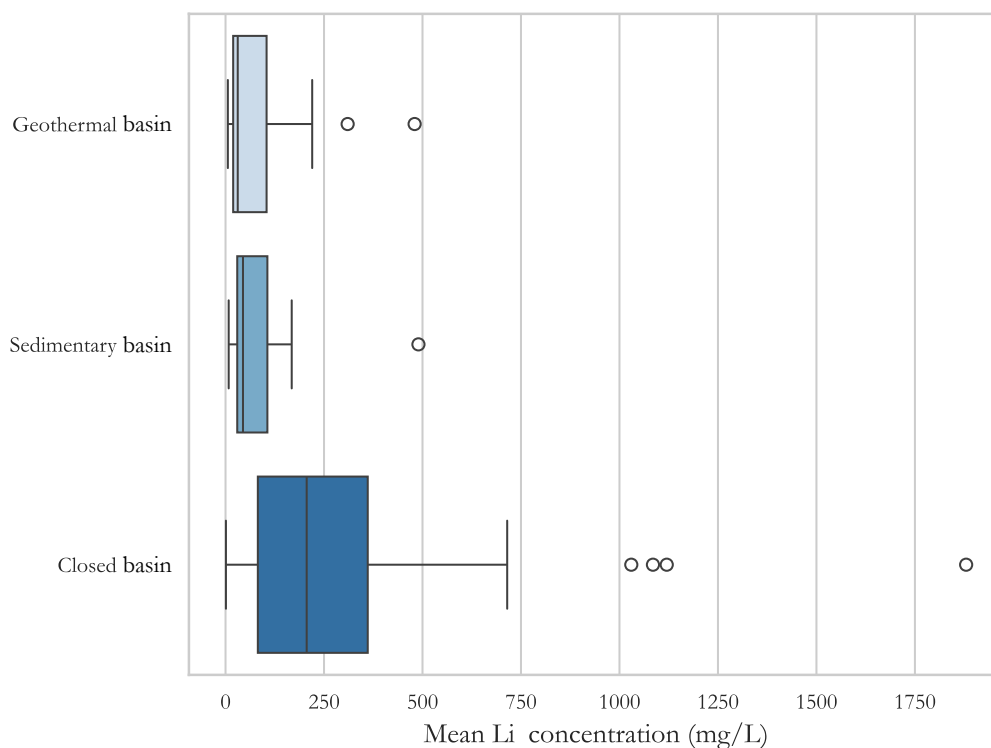


Fig. 4. Lithium concentrations across the three types of lithium brines. Closed-basin brines (dark blue) have the highest mean and maximum concentrations of lithium followed by sedimentary-basin (medium blue) and geothermal-basin (light blue) brines, respectively.

of ignimbrites. Franco et al. (2020) and Garcia et al. (2020) investigated the origin of the CB brine at Salar de Olaroz, Argentina, and determined that volcanic rocks with elevated lithium and geothermal inputs to a major inflow stream combined with secondary concentrating processes all contribute. Yu et al. (2013) demonstrated that playas in the Qaidam basin receive lithium transported by streams that is ultimately sourced from upstream hydrothermal inputs, hypothesizing that the source(s) of lithium are from alteration of volcanic rocks by hydrothermal fluids and/or from direct connection to deeper differentiated magma sourced fluids. Li et al. (2024) utilized lithium and boron isotopes to identify sources and processes contributing to formation of lithium brines from the Qinghai-Tibet Plateau in China and found that deep water-rock interaction and low-temperature, near-surface weathering are the primary mechanisms that contribute to lithium-rich brines and that along transport pathways the formation of secondary minerals increases the $\delta^7\text{Li}$ of fluids. This is similar to the findings of Munk et al. (2018, 2021) for the shallow-water inflow and brine system at Salar de Atacama, Chile, along a flow path influenced by water-rock interaction and evapotranspiration. At the Salar de Pozuelos, Argentina, Meixner et al. (2022) utilized $\delta^7\text{Li}$ and other isotopic systems to attribute the sources of lithium to low-temperature weathering of Cenozoic ignimbrites with little to no input from hydrothermal sources. Orberger et al. (2015) did a chemical and isotopic survey of four salars in Argentina, indicating that most lithium is sourced from low-temperature water-rock interaction. Interestingly, lithium isotopes have also been utilized to trace the origin of lithium in lithium-ion batteries (Desauty

et al., 2022), which, given the complexity of the lithium supply chain, could be a forensic tool for ensuring certification.

Hofstra et al. (2013) reported that fluid inclusions in quartz phenocrysts from high-silica volcanic rocks in the Great Basin region of the United States contain elevated lithium concentrations relative to their host vitric matrices, suggesting that volcanic glass is a significant and readily available source of lithium released to the environment via weathering processes and that fluid inclusions in erupted volcanic rocks may ultimately be an important lithium source. Ellis et al. (2018) reported that welded ignimbrites from the Yellowstone-Snake River Plain have more lithium in phenocrysts from slowly cooled ignimbrite interiors compared to their quickly quenched and glassy counterparts, attributing this to lithium mobilization post-eruption as groundmass cools. However, no transport and accumulation mechanisms to brines are offered in these models, highlighting the importance of connecting the rock sources to the basin hydrology and geochemical accumulation mechanisms of lithium in brines.

The predictive sequence of evaporite formation in closed-basin salt lakes was established by Hardie and Eugster (1970) and Eugster et al. (1978). Their model indicates that there are three major fluid pathways or “chemical divides” that result during evaporation, which are dictated by the initial ionic composition of the fluid. Eugster and Jones (1979) also proposed five major fractionation mechanisms that could account for brine evolution including mineral precipitation, dissolution of efflorescent crusts and sediment coatings, sorption, degassing, and redox. CB lithium brines as classified here do correspond to the late-stage fluids described by Eugster and

Hardie (1978). An excellent example of this is the CB lithium brine in the Salar de Atacama, which contains thousands of milligrams per liter of lithium and is primarily produced from a halite aquifer with both sulfates and carbonates flanking the basin. Munk et al. (2021) also show detailed equilibrium geochemical modeling from this margin, indicating that the waters in these regions are in equilibrium with various salts as a function of distance from the margin to the halite nucleus and highlighting the importance of mineral precipitation in producing the existing Na-Cl brine that is enriched in lithium.

In addition to evaporative concentration processes as described above, the distillation of lithium from geothermal heating of fluids may play a significant role in concentrating lithium in these brines and perhaps causes prolonged replenishment of brines that are in production. This is likely part of the reason that the lithium brine in Clayton Valley, Nevada, USA, has a sustainability component (Coffey et al., 2021). Since many of the lithium-rich brines exist over, or in close proximity to, relatively shallow magma chambers, it may be that through faults and fractures, the late-stage magmatic fluids and vapors have pathways to migrate into the closed basins. The hydrogeochemistry of inflow waters is a main driver of bringing lithium to CB lithium brines both in settings where it has been shown that long-term ambient weathering is primarily responsible for solute generation (Munk et al., 2018, 2021) and where hydrothermal (Coffey et al., 2021; Gagnon et al., 2023) and/or geothermal (Tan et al., 2012; Alam and Munoz, 2024) influences may aid in enhancing solute generation and transport.

Climatic and hydrologic factors in the generation of lithium brines: Certain climatic characteristics are shared by all closed basins hosting lithium brines. Typically, these basins are in subtropical and midlatitudes where arid climates are expected (Fig. 2). An arid climate is imperative for evaporative concentration of surface and shallow subsurface brines. All of the basins investigated herein have evaporation far exceeding precipitation (App. Table A1, Aridity Index). As a first assessment, an arid climate and a low precipitation/evaporation ratio are very favorable for the development of lithium-rich brines. However, what is critical for generating economic brines is a large flux of water to the basin. For example, at the Salar de Atacama, Chile, evaporation greatly exceeds precipitation, irrespective of whether precipitation estimates are 10 (Jordan et al., 2002a), 25 (Houston et al., 2011), 31 (Boutt et al., 2021), 39 (Table 1; Moran et al., 2022), or anything <50 mm/a (e.g., Bookhagen and Strecker, 2008). Under any scenario, there is a net water deficit on the Salar de Atacama, and evaporative concentration of inflow waters is possible, but without significant inflow water it would not be possible to generate the enormous volume of highly concentrated brine present there. This has been observed in other CB lithium brine basins in the Altiplano-Puna Plateau.

The magnitude of water flux through a lithium-rich brine-generating basin that is necessary for economic brines is dependent, in turn, on the lithium content of the average inflow waters. Economic CB lithium brines typically contain a minimum of 100 mg/L lithium and more commonly more than 500 mg/L and up to thousands of milligrams per liter of lithium, whereas the inflow waters may only contain lithium in the range of 1 to 10 mg/L or less (Munk et al., 2018, 2021).

Given that most lithium-brine-generating basins have many inflows that are low in lithium, it could reasonably be assumed that the average lithium content of inflow waters is less than 1 mg/L. Thus, the combined effects of evapotranspiration and precipitation of evaporite minerals must concentrate inflow waters by many orders of magnitude and the time-integrated flux of water through the basin must be sufficient to create a lithium brine deposit that contains enough total lithium to be economic, irrespective of lithium concentration.

There are a number of ways in which large influxes of water can be combined with high evaporation rates to create favorable conditions for generation of lithium-rich brines (Corenthal et al., 2016; Boutt et al., 2021). One example is that of a seasonal climate where wet seasons alternate with hot and dry conditions. To generate both sufficient inflow and evaporation with seasonal climatic variation, each year must be split between one of these two functions. The recharge area (precipitation) and the concentration area (evaporation) are identical, but they must each serve these functions for only a part of the year, thereby increasing the amount of time required to generate a brine of a given lithium concentration. Similarly, alternating between wet and dry climates on longer timescales is a mechanism for evaporative concentration of large volumes of water in a closed basin. Again, time is the limiting factor in this scenario, as the same land surface must serve both functions. Climatic cycles played an important role in the generation of the lithium-rich brine in Salars de Copiasa and Uyuni, where at least 130 k.y. of climatically driven lake level cycles have been documented on the Bolivian Altiplano (Placzek et al., 2011). Alternatively, recharge and evaporative concentration can operate simultaneously in different areas of the hydrographic basin. As for the Salar de Atacama, precipitation elsewhere in the drainage basin can serve as the lithium influx while the low elevation salar surface can serve to concentrate the inflow waters. Likewise, the nearly 5,900-m-high resurgent dome of the Cerro Galán caldera may be an important recharge area for the Salar del Hombre Muerto at ~4,000-m elevation.

In addition to elevation and topographic relief differences, the size of a drainage basin relative to the salar/playa surface (López Steinmetz and Salvi, 2021) is an important consideration (App. Table A1). The size of the drainage basin is not limited to surface drainage. Regional groundwater flow below topographic divides is one additional factor that can contribute significant amounts of water to a closed basin (Corenthal et al., 2016; Moran et al., 2019). Modern recharge rates appear to be too small to account for water flux leaving these systems. Boutt et al. (2021) documented in the Salar de Atacama basin that the net recharge rate (fraction of precipitation that reaches the groundwater system) must be close to 21% to balance the lower end of discharge rates from the basin floor. This rate is significantly higher than the 4% estimated from geochemical mass balance approaches and much larger than global compilations for arid regions (Scanlon et al., 2006). At Clayton Valley, Nevada, a large regional groundwater flow system contributes the majority of the water flux to the basin (Rush, 1968; Rush and Schroer, 1971; Brooks et al., 2014; Kirshen et al., 2022). Importantly, the imbalance in the modern inflow and outflow of lithium-producing basins is a key attribute of their hydrological system. Subsurface flow paths

provide ample water to aid in the mobilization and evaporative enrichment of lithium within a closed basin and may also provide significant additional sources of lithium.

The climatic condition requisite for the generation of lithium brines is a net water deficit at the basin floor. A wide range of localities satisfy this condition; however, water cannot be evaporated and lithium cannot be concentrated unless there is a sufficient influx of both. For this reason, localities favorable to the generation of lithium-rich brines juxtapose wetter conditions with the hot, dry conditions characteristic of basin floors. This can be accomplished in many ways, including seasonality, climatic cycles, and climatic variation within the surface and/or subsurface drainage basins. Therefore, the role of climate can be complicated by other factors, and these must be assessed for each basin.

Hydrogeology: As discussed above, most known CB lithium brine deposits occur in the shallow subsurface of tectonically active, closed basins in arid regions (Fig. 1). In these settings, basin hydrology and hydrogeology are inextricably linked through depositional and tectonic processes and have important impacts on the geometry and nature of subsurface flow paths. Host aquifers in these systems range from clastic sedimentary units associated with alluvial fans and playa sediments (including volcanic deposits) to halite and other salts. Fresh water enters the system either on the flanks through permeable alluvial sediments and is confined to the more permeable facies (fan gravels, sands), or through subsurface paths from upgradient basins (Houston, 2011; Munk et al., 2021). Fresh water mixes and floats on the denser basin brines and is ultimately diffusively driven upward by a moisture gradient, which is maintained by sufficiently arid conditions. This results in significant loss of water through evaporation and concentration of dissolved constituents.

Hydrothermal influence: The role of hydrothermal fluids and geothermal heating in sourcing and transporting lithium in CB brines has been briefly addressed in a handful of studies (Tan et al., 2012; Coffey et al., 2021; Gagnon et al., 2023; Li et al., 2023; Alam and Munoz, 2024) but is gaining traction as more focus is put into understanding the relative contributions of this factor. Most of the findings point to the importance of hydrothermal inputs—from deep fluids (Li et al., 2023), from riverine inputs to CB salars, or from lakes (Tan et al., 2012; Godfrey et al., 2013)—as potential long-term hot spring-derived sources of lithium to lacustrine settings (Coffey et al., 2021; Gagnon et al., 2023). Other geothermal influences on liberating lithium from geothermal heating (Tan et al., 2012; Alam and Munoz, 2024) have also been reported. However, the relative role of hydrothermal and geothermal influences—either from direct contributions of warm water carrying lithium that is subsequently sequestered in a basin or from geothermal heat accelerating weathering processes—requires much attention to try to quantify the relative contributions and will be an important piece of advancing the ore deposit models of not only CB lithium brines but also SB and GB lithium brines.

Characteristics of SB Lithium Brines

Sedimentary-basin lithium brines occur globally but are most well known in North America. No projects are at commercial-scale production, but several are in the field pilot or precom-

mercial stage. Relatively elevated (>40 mg/L) lithium concentrations have been documented in petroleum basin waters since the 1970s (e.g., Collins, 1976). Diverse terminology has been applied to these fluids, including “sedimentary formation waters,” “oilfield brines,” “basinal brines,” and “lithium-rich groundwaters” (Dugamin et al., 2021, 2023; Davari et al., 2024; Marza et al., 2024). SB lithium brine systems are found in deep (>1 km) pressure-driven (i.e., confined) reservoirs and aquifers and are relatively low temperature (<100°C) fluids characterized by high total dissolved solids (>100,000 ppm) and low (10s mg/L) to moderate (100s mg/L) lithium concentrations (App. Table A1). These brines are commonly geochemically heterogeneous with local variability in lithium concentration (e.g., Butler et al., in press) likely due to the complexity of water sources, rock-water interaction, and other processes impacting the brine composition that are not well documented. Despite their relatively low lithium grade, SB brines are present in large quantities and available as a by-product of hydrocarbon production, i.e., “produced waters,” but also as primary brines where these waters have not been mixed with injected water or impacted in other ways from oil and gas production. With the advent of DLE technologies, SB brines are poised to be a readily available domestic source of lithium for countries that lack CB lithium brines (e.g., the USA and Canada; Kumar et al., 2019) but could also become important in places with an abundance of CB lithium brines, such as Argentina and Bolivia, which have vast oil fields. SB brines may also be more environmentally friendly than traditional lithium resource alternatives, requiring significantly less land use, for example (E3 Lithium, 2024).

Two of the better-studied SB brine systems include the Jurassic Smackover Formation brines of Arkansas/Texas (Standard Lithium, USA) and the Devonian Leduc Formation brines of Alberta, Canada (E3 Lithium Ltd.) with measured and indicated resources of 2.81 and 16 Mt lithium carbonate equivalent (LCE), respectively. Although these SB brines are significantly different in resource scale and average lithium concentration (148 and 75 mg/L Smackover and Leduc, respectively), several common characteristics are observed between them, including (1) they likely originate from seawater and/or halite dissolution; (2) the relict fluids are subsequently modified by rock-water interactions, diagenesis, hydrocarbon emplacement, regional-scale groundwater flow, and mixing and dilution processes; (3) present-day brines are geochemically heterogeneous including significant regional variability in lithium concentration; (4) both are hosted in carbonate reservoirs; and (5) both are associated with marine carbonates, shales, and evaporites (Hitchon et al., 1971; Collins, 1976; Moldovanyi and Walter, 1992; Stueber et al., 1994; Huff, 2019; Davari et al., 2024; Marza et al., 2024; Butler et al., in press).

Lithium has also been documented in deep groundwaters of the Siberian sedimentary platform brines to be between 40 and 240 mg/L up to depths of 4,000 m (Shouakar-Stash et al., 2007) and 3.1 to 415 mg/L in the Olenerek artesian basin in a large diamond mine quarry (Alekseeva and Alekseev, 2018).

There are SB brines—including the Sichuan basin, Sichuan Province, with lithium concentrations of 90 mg/L in the west and 32 mg/L in the east; the Jiangnan basin, Hubei Province, with lithium concentrations from 43 to 65 mg/L;

the Jitai basin, Jiangxi Province, with a lithium concentration of 100 mg/L reported—and deep buried (oil field) brines are also found in the Qaidam basin with lithium concentrations of 36 to 983 mg/L (Li et al., 2018, and references within). More details on Qaidam basin lithium brines are given in Zhang et al. (in press).

Characteristics of GB Lithium Brines

Geothermal lithium brines are found primarily in northern Europe, North America, Siberia, and the Tibet Plateau and sparsely in other tectonically active margins. The northern European system is the most well-studied and documented system in terms of lithium sources and distribution. None of these brines or projects are at commercial-scale lithium production, but they represent an emerging lithium brine type and in most cases are in locations with existing geothermal production infrastructure. Complications in developing robust resource models and in extracting lithium from these high-salinity, high-temperature fluids are two of the main limiting factors to their pace of advancement.

Lithium resources associated with GB brines range in lithium concentration from less than 1 mg/L to 480 mg/L in Naples, Italy, with a mean of 81 mg/L across sites included in this study (App. Table A1). Resource estimates are currently limited to the Salton Sea, California, and Upper Rhine River Valley in Europe, which have estimated lithium resources at 0.77 Mt and 1.9 Mt, respectively. Resource estimates are currently not well constrained, because of uncertainties in resource volumes and extents, although some GB brines are predicted to produce 100,000 tonnes of Li/yr.

In Europe (Italy, Germany, France, and the United Kingdom) there are six identified regions where lithium could be extracted from deep fluids containing lithium between 125 and 480 mg/L (Sanjuan et al., 2016, 2022). These are Na-Cl brines with total dissolved solids (TDS) equal to or greater than 56 g/L and a high range between 120° and 380°C, with the UK site having lower TDS and temperatures. They are divided into two general categories by Sanjuan et al. (2022): (1) ultrageothermal systems ($\geq 300^\circ\text{C}$) with lithium concentrations from 250 to 480 mg/L in Mesozoic sedimentary reservoirs in young volcanic environments (Quaternary) where heat is sourced from intrusive magmatic activity and (2) low to geothermal systems (120°–250°C) with no associated magmatic heat source and lithium concentrations from 140 to 210 mg/L in deep tectonic sedimentary basins overlying crystalline basement.

In addition to high-TDS and high-temperature reservoirs, rock type and mineralogy are also important for the formation of GB lithium brines. High chloride concentrations are attributed to evaporated seawater or fresh water, halite dissolution, primary parent fluids, mixing, etc., whereas other solutes are thought to originate from hydrothermal water-rock interaction. The sources of lithium are attributed to white micas and biotite dissolution. The most promising region of the Upper Rhine graben has lithium sourced from a 450-m-thick micaceous continental sandstone (Triassic Buntsandstein) with minor contributions from the granite basement (Sanjuan et al., 2022). The Rhine graben is an intracontinental rift formed from the collision of the European and African plates during the Paleogene. It extends from the North Sea to the Medi-

terranean in western Europe and is underlain by Paleozoic crystalline basement of a massive granite overlain by 4 to 5 km of Mesozoic to Cenozoic sedimentary rocks (Sanjuan et al., 2022).

The Upper Rhine graben region along the France-Germany border has many geothermal projects that are considered promising for geothermal lithium extraction. However, even though the lithium concentrations have been well-documented, resource estimates remain challenging. This is because of the uncertainty associated with production fluid flow rates and injectivity indices, complex fault networks that control deep fluid circulation, and volume and recharge rates of the reservoirs (B. Sanjuan, unpub. report, 2020). At a first order, Pauwels et al. (1991) estimated a lithium resource of 0.3 to 2.2 Mt of lithium. B. Sanjuan (unpub. report, 2020, and references within) suggest an approach to lithium resource estimation in GB brine systems at the scale of individual geothermal sites rather than the regional scale. They point to advantages of better constraints at this scale to include details of the geology, faults, lithium concentrations, hydrodynamic parameters, etc., that are required to reduce uncertainties.

In North America, the Salton Sea geothermal region has received recent attention as a potential resource of lithium from GB lithium brines (Dobson et al., 2023). Historically this region had reports of up to 983 mg/L Li (Werner, 1970; Williams and McKibben, 1989). The Salton Sea geothermal field has averaged about 120 Mt of brine per year since 2004, although most of this brine is recycled because of reinjection. The current resource estimate postulated by Dobson et al. (2023) is 127,000 t of LCE per year. The estimated total resource of the region is 18 Mt of LCE if assumptions for porosity and total reservoir size are increased to what is deemed a larger resource extent (Dobson et al., 2023). Complications and environmental drawbacks to commercial production of this potential resource are documented in Dobson et al. (2023); the reader is referred to that extensive document for those details.

CB Lithium Brine Case Studies

Case study 1: Clayton Valley, Nevada

Clayton Valley, Nevada, USA, in Esmeralda County, Nevada, approximately 160 km north of Death Valley, California, is the only lithium brine deposit in commercial production in North America. Clayton Valley is a closed basin with an area of 1,342 km² and a playa surface of 72 km². The basin lies in the eastern rain shadow of the Sierra Nevada Mountains and is arid with an annual average precipitation of about 120 mm, average evaporation rates of 1,420 mm/yr, and an average temperature of 13°C. The elevation of the valley floor is 1,298 m, lower than any of the adjacent basins.

The basement rock 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 (Oldow et al., 1989). 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 is exposed on the west side of Clayton Valley,

which was exhumed from midcrustal depths during Neogene extension. The basin is bounded to the east by a steep normal fault system toward which basin strata thicken (Coffey et al., 2021; Fig. 3). Late Miocene to Pliocene tuffaceous lacustrine deposits (Esmeralda Formation of older usage from Albers and Stewart, 1972) were documented by Kunasz (1974) and Davis and Vine (1979) as containing up to 1,300 ppm lithium and an average of 100 ppm lithium. More recent work by exploration companies indicates that these outcrops contain up to 3,000 ppm lithium. Miocene silicic tuffs and rhyolites along the basin's eastern flank contain lithium on the order of tens of parts per million Li (Jochens and Munk, 2011) and a subsurface tuff in a deep exploration core (EXP2) has an average of 230 ppm lithium (Coffey et al., 2021). The subsurface basin-fill clay-dominated lacustrine sediments sampled from five deep (610–1,006 m) exploration cores contain up to 1,700 ppm Li (Coffey et al., 2021). Hectorite in the surface playa sediments has been reported to contain 350 to 1,171 ppm lithium (Kunasz, 1974).

At Clayton Valley, brines are pumped from six aquifer units (Zampirro, 2004; Munk et al., 2011), which are the lower gravel aquifer, marginal gravel aquifer, lower aquifer system, main ash aquifer, salt aquifer system, and the tufa aquifer system. Coffey et al. (2021) refined the subsurface sedimentology and stratigraphy of the Clayton Valley aquifer system based primarily on five deep cores. The main units identified are the lower gravel unit, clastic and salt unit, clastic and ash unit, lower clastic unit, main ash unit, and the upper clastic unit. These more or less correspond with the aquifers of Zampirro (2004), but because the total aquifer system is not extensive across the basin and was not intercepted in any of the deep drill core, it is not included. The main ash aquifer has been identified as the Bishop Tuff by $^{40}\text{Ar}/^{39}\text{Ar}$ (Coffey et al., 2021).

The lithium content of the waters in Clayton Valley ranges from less than 1 $\mu\text{g}/\text{L}$ in snow up to 407 mg/L in groundwater from one of the aquifers composed of volcanic ash (Gagnon et al., 2023). The cold springs surrounding Clayton Valley have lithium concentrations of less than 1 mg/L . One hot spring in the area located east of Clayton Valley near Alkali, Nevada, contains 1.6 mg/L lithium. Lithium content of the groundwater from a freshwater well in an alluvial fan located near Silver Peak, Nevada, is less than 1 mg/L . A hot groundwater well located northeast of the town of Silver Peak contains 40 mg/L lithium. Water collected from a geothermal rig operating about 25 km north of Silver Peak in May 2010 had 4.9 mg/L lithium.

Davis et al. (1986) proposed that the lithium at Clayton Valley, Nevada, was concentrated by the same processes as Cl and therefore must have been trapped as a lithium-rich fluid when the halite formed. They also hypothesized that in the last 10,000 years meteoric water entered the basin and dissolved the halite to form brines with evaporative signatures. Munk et al. (2011) indicated that other sources and processes were likely involved in the formation of the brines in the system because nonhalite aquifers produce brine with higher lithium concentrations than the halite aquifer. It may be that a combination of hydrothermal activity and leaching from volcanic ash and rocks is the major source of lithium in the aquifers in Clayton Valley. We found that the main ash unit in the basin, which is the Bishop Tuff, has lithium content in

glass approximately 12 ppm higher (72 ppm) than the Bishop Tuff (Munk et al., 2016). This may be an indication that the volcanic glass in this aquifer exchanges lithium over time.

Coffey et al. (2021) determined that lithium in the subsurface basin fill sediments is released to the modern groundwater (brine) systems by three mechanisms: (1) release of adsorbed lithium, (2) cation exchange of lithium and magnesium, and (3) possible minor release from the silicate structure at elevated temperatures. They calculated that the subsurface basin fill sediments in Clayton Valley (north) contain an estimated 24.4 to 58 Mt of lithium, which provides a continuous supply of lithium (and other solutes) to the subsurface brines, making this deposit the largest lithium accumulation in a CB setting on a global scale.

Gagnon et al. (2023) developed the first paleoclimate record for the Clayton Valley basin and found that carbonate oxygen isotope values covary with paired bulk lithium concentrations across the deepest core in Clayton Valley (EXP2). This pattern is interpreted to be the result of evapoconcentration prior to authigenic clay precipitation in the paleolake water. This suggests that climate is likely a key factor in controlling the accumulation of lithium in authigenic lacustrine clays in terminal basins containing pluvial lake systems.

Case study 2: Salar de Atacama, Chile

The Salar de Atacama is a large, closed continental basin located on the Tropic of Capricorn in the Atacama Desert approximately 200 km east of the Pacific Ocean and immediately to the west of the Altiplano-Puna Plateau. The basin coincides with a sharp bend in the modern Andean volcanic arc, which retreats 60 km east from its regional north-south trend. The salar has a surface area of 3,000 km^2 and a drainage basin flanked on all sides by substantial topography; the Andean volcanic arc dominates recharge to the salar. The salar surface is 2,300 m above sea level (m a.s.l.) and is ~2,000 m lower than the volcanic arc on the western plateau margin. Although precipitation events are rare on the salar surface, they do occur (Boutt et al., 2016), with the Andean Plateau to the east receiving more precipitation but still classified as arid to hyperarid (Strecker et al., 2007). Evaporation at the elevation of the salar varies between 0 and 2.8 mm/d depending on the surface characteristics (Kampf et al., 2005); relative to an estimated mean annual precipitation of 39 mm, the precipitation/evaporation ratio (aridity index) is ~0.033. No evaporation was measured by Kampf et al. (2005) from the rough halite nucleus of Salar de Atacama, which constitutes half of the surface area and hosts the lithium-rich brine at 1-m depth. Surface and groundwater discharge to the Salar de Atacama places important constraints on fresh and brine groundwater extraction (Moran et al., 2022). Boutt et al. (2021) documented that the modern discharge to the salar floor is much larger than modern recharge within the topographic salar watershed. Modeling of regional groundwater flow to the basin suggests that groundwater storage (e.g., Corenthal et al., 2016; Moran et al., 2019, Boutt et al., 2021) is a key driver of modern hydrology and a missing element in many Salar de Atacama conceptual models. Recent work documented in Moran et al. (2022, 2024) suggests that these processes dominate the hydrology of lithium-bearing salars across the Altiplano-Puna Plateau.

The Salar de Atacama basin is characterized by sedimentary, volcanic, and plutonic rocks indicative of its complex geologic evolution during the Paleozoic along the western margin of Gondwana. During the Jurassic and Early Cretaceous this region was an extensional back-arc basin, with inversion and basin-scale tectonic subsidence initiating in the Late Cretaceous and persisting through the Paleogene, transitioning to a forearc basin in the Neogene. Uplift and associated predominantly clastic deposition have been ongoing since the Cretaceous, and during the Plio-Pleistocene, thick evaporite (halite-dominated) deposits have accumulated in the center of the basin that transition to gypsum and carbonate facies with variable fine-grained clastic material near the margins (Munk et al., 2018, 2021).

Some of the key geologic details of the Cenozoic geologic history are important to the lithium system in the Salar de Atacama (Munk et al., 2016). In particular, the Oligocene-Early Miocene normal faulting in a transtensional environment controlled the western margin of the basin and accommodated thousands of meters of strata (Jordan et al., 2007). This sedimentation was accommodated by a normal fault along the western basin margin with as much as 6 km of vertical displacement (Pananont et al., 2004). From ~12 Ma onward the volcanic arc was established east of the Salar de Atacama and shortening resumed, uplifting the intrabasin Cordillera de la Sal and later resulting in development of blind thrust faults within the basin (Jordan et al., 2007). Interpretation of seismic data by Pananont et al. (2004) suggests that the Cordillera de la Sal, a prominent N-S-trending anticlinal feature that separates the Salar de Atacama from the Cordillera Domeyko, results from diapiric flow of Oligocene to Middle Miocene strata initiated in the Miocene and is associated with a deep reverse fault. Uplift of the Altiplano-Puna Plateau is accommodated by monoclinical folding, which is expressed in the geomorphology and westward-tilted strata at the plateau margin (Jordan et al., 2010). Younger Late Miocene and Pliocene ignimbrites derived from calderas on the Andean Plateau were deposited in the Atacama basin. These ignimbrites interfinger with halite deposits that are typically 1 km thick and establish the age of these strata as Plio-Pleistocene with a lower age limit likely to be sometime in the Late Miocene (Gonzalez et al., 2009; Lin et al., 2016). In the southern portion of the salar, these deposits are offset by the salar fault system, which exhibits close to a kilometer of down-to-the-east offset on a reverse fault during this interval (Jordan et al., 2002b; Martinez et al., 2018). The salar fault system can be followed to the south-southwest into the Tilomonte (Tilocalar) Valley as moderate-to high-angle reverse faults, which offset Pliocene ignimbrite and Paleozoic rocks of the eastern Cordón de Lila. Some of the features of this fault system as exposed in the Tilocalar (Tilomonte) Valley suggest the influence of major pre-Andean basement structures (Kuhn, 2002).

Faulting with large (km scale) offset (Salsbury et al., 2011) and the presence of the massive magma chamber associated with the Altiplano-Puna volcanic complex, which contains highly evolved and low-temperature magma at shallow crustal levels with melt inclusion data indicating that magmatic lithium contents of 100 to 1,000 ppm are common in this region (Lindsay et al., 2001; Schmitt, 2001), could be a key combination to the accumulation of lithium in the brines of the Salar

de Atacama. Two important factors may be that the very large magma chamber along the Altiplano-Puna volcanic complex provides (1) a regional geothermal gradient that aids in the leaching of lithium and other solutes from the high-silica high-lithium ignimbrites at or near the surface and (2) possible source of magmatic fluids that transport lithium along faults to the groundwater. Numerous faults exist between the salar and the magmatic arc in the southern half of the Atacama basin, and these could act as fluid conduits. We have observed high dissolved ^3He concentrations in shallow groundwater and brine in the southeastern part of the Atacama basin. These high ^3He concentrations have not been observed in water and brine sampled from the western half of the Atacama basin, and we interpret the ^3He as an indicator of the influence of mantle-derived gases in the southeastern sector of the basin.

The overall geology and rock types of catchments ultimately control the chemical composition of inflow waters, which supply solutes to the groundwater. This water flows toward the basin floor where it recharges the aquifers and can discharge at the surface and undergo evaporation. Corenthal et al. (2016) and Munk et al. (2018) used a mass balance approach to test whether the modern hydrogeologic setting and weathering of the catchment rock types could reasonably explain the accumulation of the evaporites and brines in the Salar de Atacama. Corenthal et al. (2016) first discovered that the amount of Na and Cl in the basin required sourcing solutes outside the topographic watershed. Following this work Munk et al. (2018) divided the watershed of the Salar de Atacama basin into five subwatersheds where shallow groundwater and surface inflows were defined (Boutt et al., 2016; Corenthal et al., 2016). These subwatersheds were further divided into 16 water flux zones, and representative solute concentrations of each were used to calculate a mass balance of lithium and other solutes to the evaporite and brine bodies in the basin (Munk et al., 2018). They found that the total lithium in the evaporites and brines could accumulate in close to 1.9 m.y. The excesses of Na and Cl are attributed to the leakage of these solutes and water from open high-elevation lakes undergoing evaporation but not reaching halite saturation, as documented in Grosjean (1994), and/or from older buried evaporite deposits in the catchment (Rissmann et al., 2015).

Understanding the internal salar hydrogeologic architecture is important for constraining the pathways and rates of subsurface waters. At the Salar de Atacama we have found the following:

1. There is little correlation of hydraulic conductivity to primary lithologic units.
2. To a first order, permeability in the halite nucleus is controlled by secondary processes.
3. Halite has very low permeability and porosity and is largely secondary (dissolution and fracturing).
4. Depth dependence of permeability in the nucleus is due to secondary processes, (compaction and lack of dissolution permeability).
5. The presence of volcanic units, lithologic contrasts (mechanical stratigraphy), clastic and biogenic units, and faulting and fracturing impose strong control on hydraulic properties.

At the Salar de Atacama, it is apparent that secondary dissolution/precipitation of salts is an important factor control-

ling the distribution of porosity/permeability (McKnight et al., 2021). Dissolution/precipitation is not evenly distributed in salars; it is correlated with inflow conditions. The implications of these findings are as follows. There is a strong scale dependence of hydraulic properties. A large amount of heterogeneity in horizontal and vertical directions exists, leading to a poor correlation between core and larger-scale hydraulic tests; core-based measurements are not representative of larger-scale properties. Lithium brine is stored in both matrix and fractures/fissures. The role of dual porosity varies between units (and depths). Transport models (and resource/reserve estimates) must take into account these processes.

Lithium Brine Resources

Lithium production has grown exponentially since the 1950s (Fig. 5). Lithium has multiple uses as an alloy for helping to increase strength to weight in metals. It is used as a coolant in nuclear breeder reactors and as a component of heat-resistant glass, ceramics, and lubricants. It is the key ingredient of drugs used to treat bipolar disease (Garrett, 2004). However, recent lithium demand is driven by its use in rechargeable lithium-ion batteries for electric vehicles and grid storage as well as small electronic devices as the global economy strives for carbon neutrality (Degen et al., 2023). The lithium-ion battery is the premier energy storage choice because it is lightweight and can be efficiently recharged. This is especially key in the transportation sector. The use of lithium-ion batteries is pivotal in the energy transition as the world seeks large-scale ways to reduce greenhouse gas emissions and minimize future global warming impacts, which have reached a new level on the planet over the past few decades. Global

demand for lithium is expected to continue on an exponential trajectory for the coming decades (Benchmark Mineral Intelligence, 2024).

Closed-basin lithium brine resources are located primarily in South America and China, with the United States and Middle East hosting fewer (Fig. 1). Out of the 43 deposits that have resource estimates, only seven are in commercial production. These are Salar de Atacama, Chile; Salar del Hombre Muerto, Argentina; Cauchari-Olaroz, Argentina; Clayton Valley, Nevada, USA; Zhabuye Salt Lake, China; Dangxiongcuo, China; and numerous salt lake resources within and around the Qaidam basin, China. The relationship between mean lithium concentration and total lithium resource indicates that there is a range of acceptable lithium concentrations across projects in production (Fig. 6) and can be used as a guide for exploration for new deposits. However, in addition to the market price, local factors like climate, water availability, access to affordable energy resources, socioeconomic considerations, and other factors also dictate whether a project will go into production.

Exploration for CB lithium brine deposits

Identification of prospective basins: The CB lithium brine basins in Appendix Table A1 are marked by a saline lake or a salar (i.e., a salt flat or salt-encrusted depression). Endorheic closed basins form because of tectonics where inflow waters can only leave by evapotranspiration. If the long-term precipitation to evaporation ratio in a basin increases sufficiently, eventually lake water will overtop some point along the drainage divide and drain, carrying the contained dissolved lithium away. Evidently, the aridity classification must be semiarid or drier, but

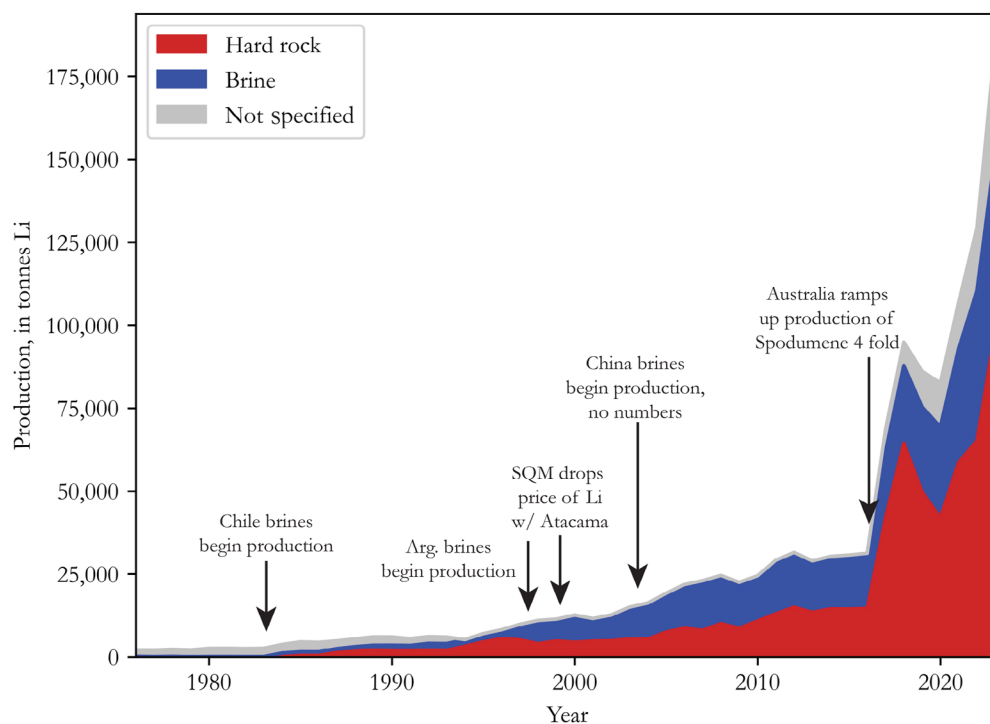


Fig. 5. Total global lithium production based on resource type since before 1980. Major events across brine and spodumene production are highlighted along the timeline.

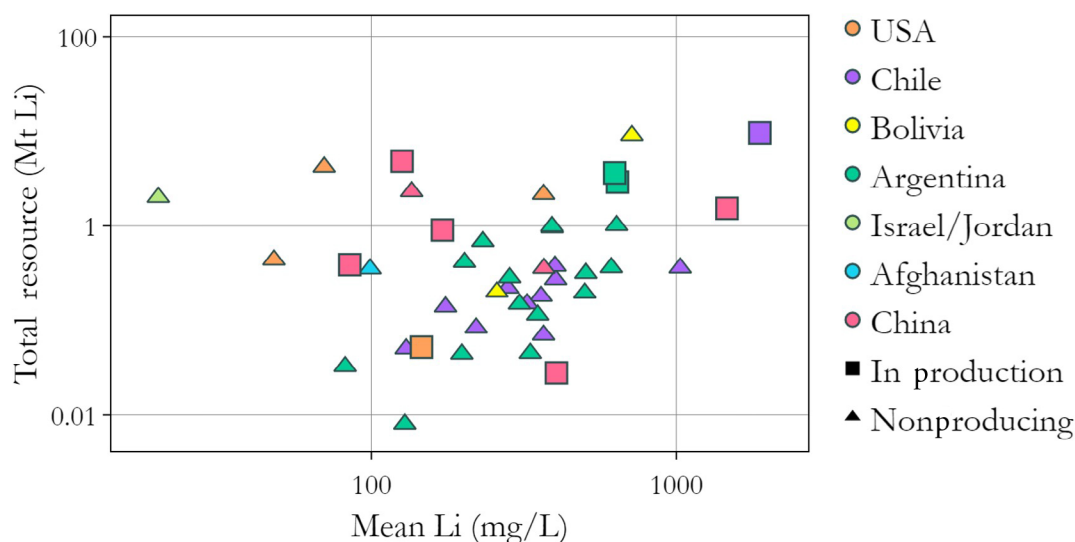


Fig. 6. Mean lithium concentration and total lithium resource for closed-basin lithium brine deposits by country.

the numerical aridity index for the basins in Appendix Table A1 ranges through an order of magnitude, from 0.01 to 0.59. Judging from the present-day distribution of basins, the favorable zones lie between about 19° and 37° north or south (Fig. 1). Rain-shadow effects probably stretch the north-south span of favorable latitudes. Mean annual temperature does not appear to be a critical factor, with values ranging through two orders of magnitude from 0.2° to 22.7°C.

The CB lithium brine basins cataloged in Appendix Table A1 are tectonically active, subsiding basins as evidenced by thick accumulations of Quaternary to Recent sediment and faults. Tectonic settings that favor the accumulation of CB lithium brines include extensional to strike-slip to contractional. The overall tectonic control on basin geometry also seems to be important at the local scale (e.g., Clayton Valley, Nevada). Many but not all the CB lithium-rich brine basins in Appendix Table A1 show evidence for elevated (geothermal) heat flow. The most obvious evidence includes young volcanoes, hot springs, and geothermal resources. Evidence of modern or prior hydrothermal activity is seen in several instances and should be regarded as a favorable characteristic. For example, at Clayton Valley, Nevada, some Miocene to Pliocene basinal deposits were hydrothermally enriched in the lithium that is sequestered in clays. Another example of hydrothermal enrichment of lithium in clays is at Thacker Pass, Nevada (Benson et al., 2023). Lithium-rich concentration halos have been reported from several basins that lack lithium brines in the Basin and Range province (USA; Vine, 1980). In such cases, these may be all that remains of a former brine system that has since leaked away (e.g., Rhyolite Ridge, Reynolds and Chavetz, 2020). In the case of Rhyolite Ridge and other recently discovered lithium-rich clay deposits near Tonopah, Nevada, USA, some of the lithium may have escaped these basins and been transported to Clayton Valley, Nevada, where it was trapped in the younger strata of the basin and the brine. Borate deposits appear to be hybrids involving both hydrothermal and evaporative processes; their presence could also be a favorable indicator for lithium brines past or present. At Salar del Rincón in Argentina, hot-spring

deposits that appear inactive contain residual water with up to 1,500 mg/L lithium (Toledo et al., 2009).

Primary source rocks such as high-silica, vitric tuffs and ignimbrites appear to be a common occurrence in basins that host CB lithium brines. The lithium in these rocks is likely quite mobile in both low-temperature and high-temperature weathering processes. Several studies outlined above have shown that these mechanisms are viable for sourcing lithium to inflow waters to CB lithium brine basins. However, authigenic lacustrine clays that sequester lithium such as those in Clayton Valley, Nevada, also seem to play a role in sourcing lithium to Clayton Valley brines (Coffey et al., 2021). This is likely the case in other CB lithium brine systems of South America, which are currently under investigation.

Physiographic aspects of CB lithium brine basins do not appear to be that important to the existence or size of the resource (Fig. 7). As described above, seven factors control the development of lithium brine resources such that a bivariate or trivariate plot can only explain a portion of the variance in control parameters. Of the basins in Appendix Table A1, basin-floor areas range from 1 to 21,820 km², catchment areas range from 634 to 145,279 km², and basin-floor elevations range from -415 to 4,464 m. A special situation exists at Clayton Valley, Nevada, which may be partly responsible for the size of the resource. Clayton Valley is one of five adjacent closed basins. Although they are hydrologically unconnected at the surface, groundwater ultimately flows into Clayton Valley, the lowest elevation of the five (Coffey et al., 2021). In fact, Clayton Valley may be the end of very long regional groundwater flow paths in the western Basin and Range (Brooks et al., 2014).

Basin-scale exploration: Munk et al. (2016) outlined some essential exploration techniques including the most obvious exploration tool of surface sampling of waters and/or sediments, which is commonly employed by exploration companies. Because many lithium brines are located within 1 m of the surface salt crust, water sampling is easy to use as a general exploration tool. However, deeper brines can be explored with geophysical surveys to identify high-conductivity

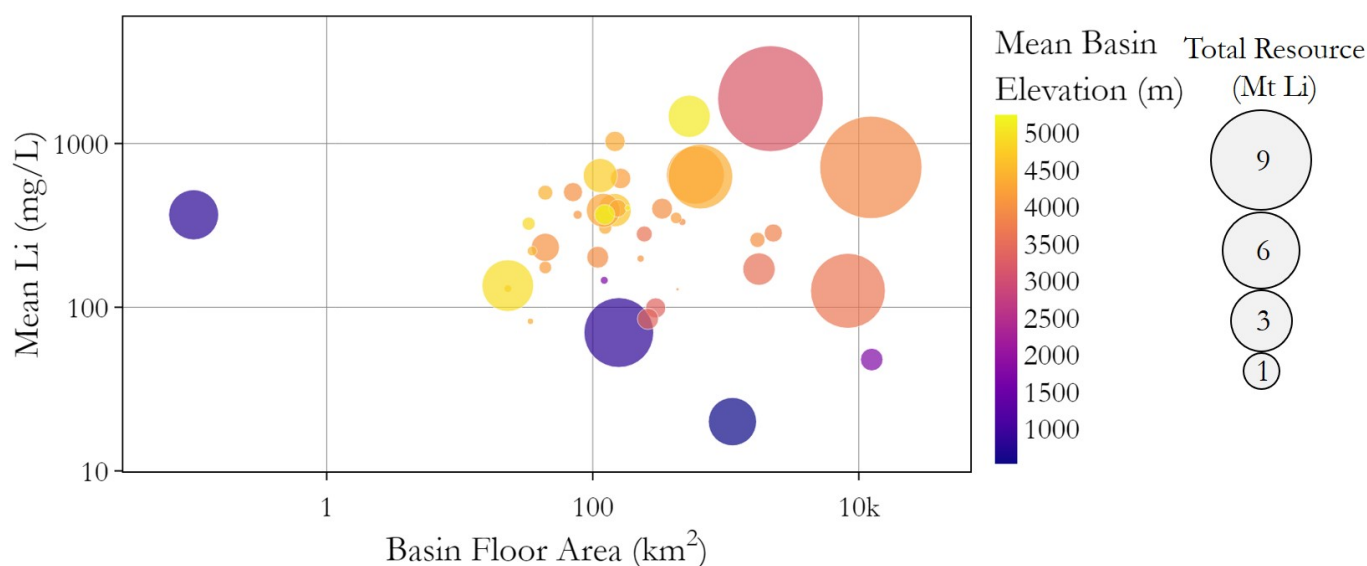


Fig. 7. Mean lithium concentration, basin floor area, and basin floor elevation. The size of the bubble corresponds to the total lithium resource, indicating the overall lack of relationship between the size of the resource and physiographic basin characteristics. However, most resources show a positive relationship between Li concentration and basin floor area.

anomalies that could then be drilled for sampling. Deeper exploration is now common in the salars of Chile and Argentina as more companies realize lithium brines occur at depths below 100 m. Sediment sampling at the surface can also be an indicator of overall lithium enrichment in a given basin but may not be conclusive of a subsurface brine. Many plays in the southwestern United States have been shown to have elevated lithium in soils but no appreciable lithium brine in the subsurface.

Geologic reconnaissance: Several important observations related to the youthfulness of a prospective basin and tectonic, sedimentary, and heat flow characteristics can be assessed with satellite imagery, geologic maps, and field investigations. Basins likely to host CB lithium-rich brines should include young high-silica volcanic rocks, evidence for Quaternary faulting, thick accumulations of clastic and/or evaporite strata, and hot springs or hot-spring deposits. Given the observations of Hofstra et al. (2013) on the lithium content of quartz melt inclusions vs. host rocks, whole-rock geochemistry of vitric rocks may be of limited value for exploration purposes. Rather, if much of this lithium has already been mobilized, an analysis of quartz-hosted melt inclusions and minerals such as biotite, which are known to host lithium and are abundant in many volcanic deposits including ignimbrites and ashes in potential source rocks, may be a better measure of whether the rocks are (were) a potential lithium source. In addition, heat flow can be assessed by estimating the temperatures of formation for hot-spring carbonates or by application of chemical thermometers to hot-spring water. A critical determination to be made is whether the water temperature can be explained by deep circulation of meteoric water with reasonable geothermal gradients or whether a temperature anomaly (e.g., a magma body) might be present at shallow depths. An assessment of tectonics and heat flow over longer periods can be provided by low-temperature thermochronology of bedrock in fault-bounded mountain blocks (Munk et al., 2016).

Mining and production of CB lithium brines

Arid climates promote the formation of CB lithium brines, but this is also a requirement for production, because the first step in processing once the brines are pumped from the subsurface is solar evaporation. Even projects that use DLE typically need some treatment of brines with evaporation ponds. Brines that are pumped to the surface typically carry tens to thousands of parts per million lithium and ideally have a low Mg/Li ratio (<10), as the geochemical behavior of Mg ions can be similar to lithium ions in low-temperature aqueous solution and can interfere with the lithium purification process. In each pond in the chain, brine enters at one end, loses some of its water during the ensuing weeks or months, and is transmitted from the other end into the next pond. Multiple ponds are used to separate the various evaporite minerals that crystallize out in sequence and to compensate for the fact that evaporation rate decreases as TDS increases. This process can take up to two years before concentrating lithium enough for the next processing steps. The concentrate is pumped from the last pond to a chemical plant where various end products such as lithium carbonate, lithium hydroxide, and lithium metal can be produced. Extraction of lithium from SB and GB lithium brines by solar evaporation is not a viable option given the locations of these projects as well as the very large volumes of brine that need to be processed because of relatively low lithium concentrations. DLE is the preferred method for these brines and is likely the future of CB lithium brine production. A comprehensive review of DLE methods is beyond the scope of this work, but more information can be found in Farahbakhsh et al. (2024) and references within as well as in other extensive literature in the field.

Water availability: CB brines are commonly found in arid regions with limited fresh water. Many of the producing lithium from CB, SB, and GB brines require fresh water, so understanding the water budget and hydrologic dynamics of each basin is critical to identify the potential hydrologic im-

pacts of freshwater pumping from mining. Closed basins have no surface water inlet or outlet; all modern freshwater inputs are from streamflow and groundwater recharge sourced from recent precipitation within the topographic or regional watershed. The other potential sources of fresh water are releases from groundwater storage and long flow paths from adjacent basins, although these sources are more difficult to quantify (Moran et al., 2022, 2024). In this section, we discuss the hydrology of CB brines in South America, although our findings can be used to understand the hydrology of other CB deposits and SB and GB brines around the globe.

Each CB deposit is surrounded by a topographic watershed (or basin) with two distinct hydrologic zones: the basin floor and the inflow zone (Fig. 8). The basin floor is topographically flat and often defines the generalized lateral extent of the brine aquifer at the water table, although the brine aquifer extends beneath the fresh water because of density differences. Wetlands and lagoons are commonly found within the basin floor, but this area has limited groundwater recharge or streamflow (McKnight et al., 2023). The inflow zone is the upgradient area that surrounds the basin floor and extends to the basin margins. Almost all the fresh groundwater recharge and runoff from precipitation occurs within the inflow zone then flows downgradient. Streams within these basins can be connected, disconnected, or variably connected to the aquifer below; they can also alternate between gaining and losing to the aquifer along their reach. The general location of the transition from fresh water to brine is at the intersection of these two zones, although this transitional area is dynamic. At the freshwater-brine transition, fresh groundwater discharges above the denser brine (Munk et al., 2021; Fig. 8).

To quantify water availability, we can use results from Kirshen et al. (in press). They estimate availability minus demand (AMD) for 28 active, near-production, or potential lithium producing basins in Chile, Argentina, and Bolivia using the AWARE methodology (Boulay et al., 2018) (Fig. 8). This method calculates the amount of fresh water remaining after human water consumption and environmental water requirements without incorporating water use from lithium mining. The assessment uses region-specific calculations of groundwater recharge and streamflow using the most accurate long-term average precipitation data set available for the region. Mean annual precipitation varies by an order of magnitude across the basins, with a range of 20 to 200 mm. In this region input precipitation largely controls AMD differences in these basins; annual AMD ranges from 1 to 18 mm (Kirshen et al., in press). These AMD values are very low considering the world average is ~160 mm (Boulay et al., 2018). Other factors that control water availability are human water consumption, evapotranspiration, basin elevations, and the frequency and magnitude of large precipitation events. The hydrologic impact of freshwater pumping for lithium mining is variable and depends on the lithium brine processing technology (DLE vs. evaporative technology), lithium production quantity, initial AMD, and inflow zone area (Kirshen et al., in press). Reductions in water availability can reduce streamflow and groundwater discharge to sensitive wetlands and lagoons (Corkran et al., 2024). Quantifying water availability and lithium mining impacts is required to sustainably extract lithium from CB deposits.

Environmental considerations: As with any resource extraction, there are environmental considerations related to CB lithium brine production that are important to identify and mitigate wherever possible. Unlike most traditional mining (oil, coal, Cu, Au, etc.), toxic contamination of land or water is not a major concern, because of the nature of the resource and the minimal required chemical inputs, although salinization of fresh or brackish natural waters with brine from evaporation ponds or pipelines can be an important concern in some cases depending on where a mine is sited. Concerns about impacts center on the use and disruption of water available for society and ecosystems in these systems and energy requirements for the operations. The key concerns can be summarized as (1) freshwater use, (2) brine or brackish water use, (3) land surface disturbance, and (4) energy use or greenhouse gas emissions (Boutt et al., 2023). Of course, the relative importance of each depends on the specific conditions in individual basins, and on the conditions the mine operation needs to economically recover lithium. The risks of environmental harm should be reduced by optimizing operations based on the latest scientific understanding of these hydrogeological systems.

First, an important and often overlooked point is that particularly in these arid closed basins, natural waters cover a large range of salinities from fresh potable water to some of the densest brines on the planet. The dynamics controlling impacts associated with freshwater use are distinct from those of brine or brackish water use. Recent work has shown that one unit of freshwater groundwater abstraction has a substantially larger and more immediate impact on salar hydrological systems than brine groundwater abstraction (Boutt et al., 2023; Corkran et al., 2024). Therefore, when discussing environmental concerns, monitoring, and mitigation, and also when conceptualizing water budgets, it is crucial to separate water use by water type.

The primary concern when it comes to the mining of CB brines is the use and depletion of fresh water. The regions where these brine resources exist are some of the most water-scarce areas in the world; fresh water is precious and uniquely sensitive to impacts from its use (Moran et al., 2022). Particularly, extraction of fresh groundwater upgradient of sensitive salar marginal wetlands has a high risk of impacts due to its importance in providing baseflow to wetlands and streams. Efforts should be taken to reduce as much as possible the use of fresh water by increasing energy use, brine use, or recycling industrial water where appropriate.

The abstraction of brine from salar aquifers creates drawdowns in brine water tables, which risks impacting the position and orientation of fresh-brackish-brine interfaces toward the margins of the basin floors. However, these impacts likely only occur over long timescales, and there appear to be natural processes that buffer impacts from the brine aquifers from migrating into brackish and fresh aquifers at the margins (McKnight et al., 2021; Corkran et al., 2024). These include the influence of large density differences between brine and fresh waters and the reprecipitation of salts and associated changes in permeability (McKnight et al., 2021). Definite evidence of direct impacts from brine drawdowns has not been shown to date, but it's clear that long-term industrial-scale extraction of lithium brine will continue to increase the risk of impacts to salar-marginal wetlands.

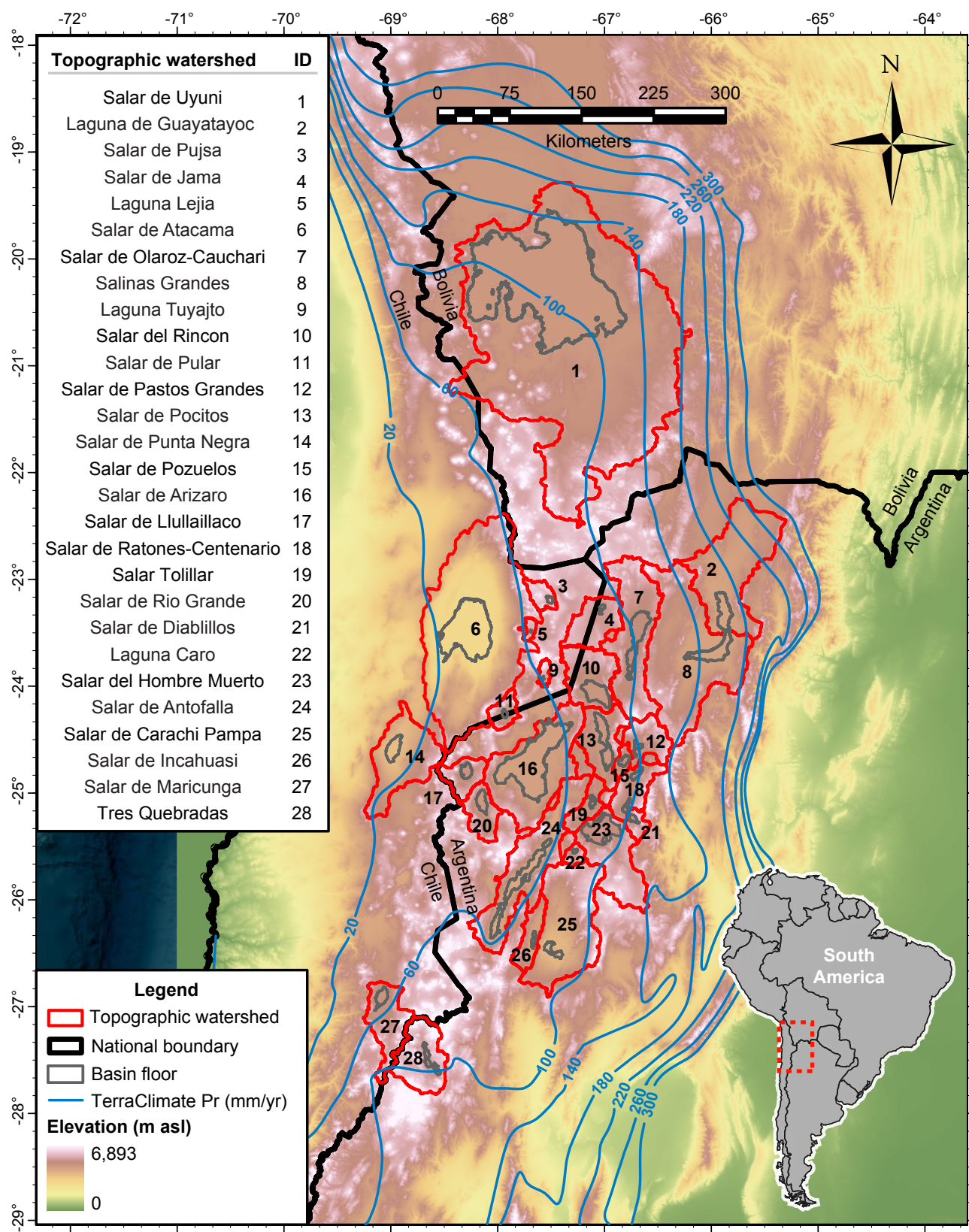


Fig. 8. Map of active, near-production, and potential closed-basin lithium brine-producing basins in Chile, Argentina, and Bolivia. Included are closed basins in red and national boundaries as black lines. The blue contour lines represent the mean annual precipitation between 1958 and 2022 from TerraClimate at 40-mm intervals, and the shaded background shows elevation in meters above sea level (m asl) from the ALOS World 3D DEM. Modified from Kirshen et al. (in press).

Traditional lithium brine mining such as those in the Salar de Atacama requires a large amount of land area for evaporation pond strings, quite clearly seen from satellite imagery of Salar de Atacama. Fortunately, the nature of this resource means that in most cases the infrastructure is built directly on salar surfaces, on top of the brine aquifers. Salar surfaces are naturally quite hostile to life and therefore dramatically reduce the impact of this land disturbance. However, siting evaporation ponds or processing facilities on or near freshwater aquifers or brackish wetlands carries a substantial risk of disturbing natural flow dynamics or salinization of natural waters and should be strongly avoided. As recent work has shown, in these environments there are particular conduits that allow recent rainfall or high-elevation freshwater flows to sustain critical wetlands (Moran et al., 2024). These include streams, springs, and wetland vegetation clusters. The disruption of these natural flows can have rapid and dramatic negative impacts on these hydrologic systems and therefore must be avoided (Boutt et al., 2023).

The final point of concern is the use of on-site energy to produce the resource, which is tied directly to greenhouse gas emissions. Since lithium is a key cog in the energy transition away from fossil fuels, understandably a major focus is on how much greenhouse gas emissions are created from extracting the resource (International Lithium Association, 2024). Currently, traditional methods of mining CB brines are much less energy intensive than hard-rock mining in large part because most of the energy required to concentrate the brine comes directly from the sun. The promise of new DLE technologies that can produce lithium much faster and with greater efficiency has led to a push to supplant or augment traditional brine mining operations. However, it's critical to understand the new inputs required to run full-scale DLE operations, which generally involve substantially higher energy use and freshwater inputs, and what the trade-offs in impacts will be. For instance, does reducing brine drawdowns to net zero with closed-loop systems that reinject brine into the aquifer reduce impacts if freshwater abstraction and or greenhouse gas emissions need to be increased? Important decisions will need to be made about trade-offs between the four concerns discussed here and how to optimize operations in a way that creates the least impact.

Summary

Because of the extensive use of lithium in industrial, manufacturing, and technological applications, the demand for this critical element has been on the rise for the past decade and will continue on this trajectory. CB lithium brines are the most economically recoverable form of lithium deposits and are generally the least carbon intensive. Although current global lithium production is dominated by hard-rock (pegmatite) deposits, CB lithium brines will continue to be a major source of lithium to the global market. Shifts in sources of lithium may occur as emerging lithium brines (SB and GB) and volcano-sedimentary lithium deposits come into production, but that is likely years away. Therefore, continuing to advance the science and understanding of these ore deposits and the critical environmental aspects surrounding their production is paramount to the energy transition. We have identified and outlined the seven common characteristics of

the environments for 110 different basins and their respective brines or salt lakes ranging in mean lithium concentration from 13 to 1,880 mg/L. These characteristics are (1) arid climate, (2) closed basin containing a salar (salt crust) or saline lake, (3) associated igneous or geothermal and/or hydrothermal activity, (4) tectonically driven subsidence, (5) suitable lithium source(s), and (6) ample time to concentrate brine, and (7) hydro(geo)ology. We have improved the framework for future investigations of CB (and other) lithium brines, but much work is still needed to enhance exploration, discovery, and production.

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