

Where is lithium found?



In South America, lithium bearing brines sit in underground aquifers, deep beneath the earth's surface. The brines are pumped up into the desert where they sit in vast pools while the sun evaporates the water off leaving mineral rich salts. This takes between 18 and 24 months and is followed by a secondary process which entails the use of 500,000 gallons of fresh water to produce 1 tonne of lithium carbonate or lithium hydroxide. Water which should be supplying local villages and agriculture. Whilst most of the world's lithium is obtained in this way the whole process is slow, environmentally damaging and unsustainable.

In China and Australia lithium is derived from hard rock ore dug from the ground by traditional open cast mining. Mountains of mine "tailings" scar the countryside. The secondary process of treating the ore with hydrochloric acid to produce lithium chloride is hugely damaging to the

environment. Waste discharged into Chinese rivers has left them full of dead fish and the riverbanks strewn with dead yaks.

It is known that the earth's supply of lithium is finite and may well be exhausted even before the world has converted to electric vehicles. Attempts to promote alternative sources of power for electric vehicles including hydrogen fuel cells and batteries based around cobalt, nickel, graphene, zinc, sodium, magnesium and potassium lag behind lithium for a variety of different reasons. For the foreseeable future lithium remains the most viable battery metal.

It is clear though that a sustainable supply of lithium of lithium needs to be found, one that can be extracted in an environmentally responsible way.

Lithium in saline geosystems: Lake brines and clays

Introduction

Historically, until the electronic revolution, lithium located near the top of the periodic table, was of little economic interest.

With an atomic number of 3 and an atomic weight of 6.9, lithium is exceptionally small and light, with a high charge/radius ratio. Estimates of the average crustal abundance of lithium vary, but it is likely to be approximately 17–20 parts per million (ppm). In igneous rocks, the abundance is typically 28–30 ppm, but in sedimentary rocks, it can be as high as 53–60 ppm (Evans, 2014; Kunasz, 2006). Lithium-prone hypersaline brines can attain values as high as 6000 ppm, but such high levels are unusual.

Lithium compounds are consumed in the production of ceramics, lubricants, glass, and primary aluminium (Figure 1). Its high specific heat capacity makes lithium ideal in heat transfer technology where it is used in welding and metallurgical applications. Its light weight and its high electrochemical potential (it is most electronegative metal known) and its high electrical conductivity make it amenable to battery applications requiring low weight and high storage potential

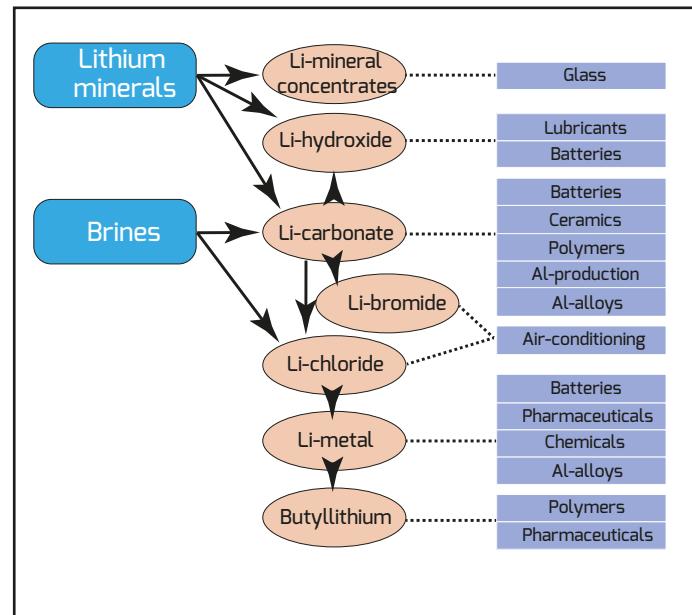


Figure 1. Uses of Lithium (after Ziemann et al., 2012)

Compared to nickel metal hydride batteries, the type of battery currently powering most hybrid electric vehicles, Li-ion batteries are lighter, less bulky, and more energy efficient. Lithium batteries have three times the energy of

Deposit type	Source	Brief description	Typical grade	Examples
Pegmatites	Magmatic fluids	Coarse-grained igneous rock formed during late-stage crystallisation of magmas	1.5-4% Li ₂ O	Greenbushes, Australia; North Carolina, USA; Bikita, Zimbabwe
Hectorite	Saline brine	Lenses of saline lacustrine smectite clay in association with volcanic centres	0.4% Li ₂ O	Kings Valley, Nevada, USA; Sonora, Mexico
Jadarite	Saline brine	Hydrothermally-altered borosilicates in sediments of an enclosed saline lacustrine basin	1.5% Li ₂ O	Jadar, Serbia
Continental	Saline brine	Salt pans or salars in enclosed basins with lithium enrichment likely to be from hot springs	0.04-0.15% Li	Clayton Valley, USA; Salar de Atacama, Chile; Salar de Hombre Muerto, Argentina
Geothermal	Saline hydrothermal brine	Elevated levels of lithium contained in steam at geothermal power stations	0.01-0.035% Li	Salton Sea area, California, USA
Oilfield	Basinal saline brine	Elevated levels of lithium contained in waters or brines produced in oilfields	0.01-0.05% Li	Smackover oilfield, Arkansas, USA Foxcreek, Canada

Table 1. Types and origins of lithium deposits

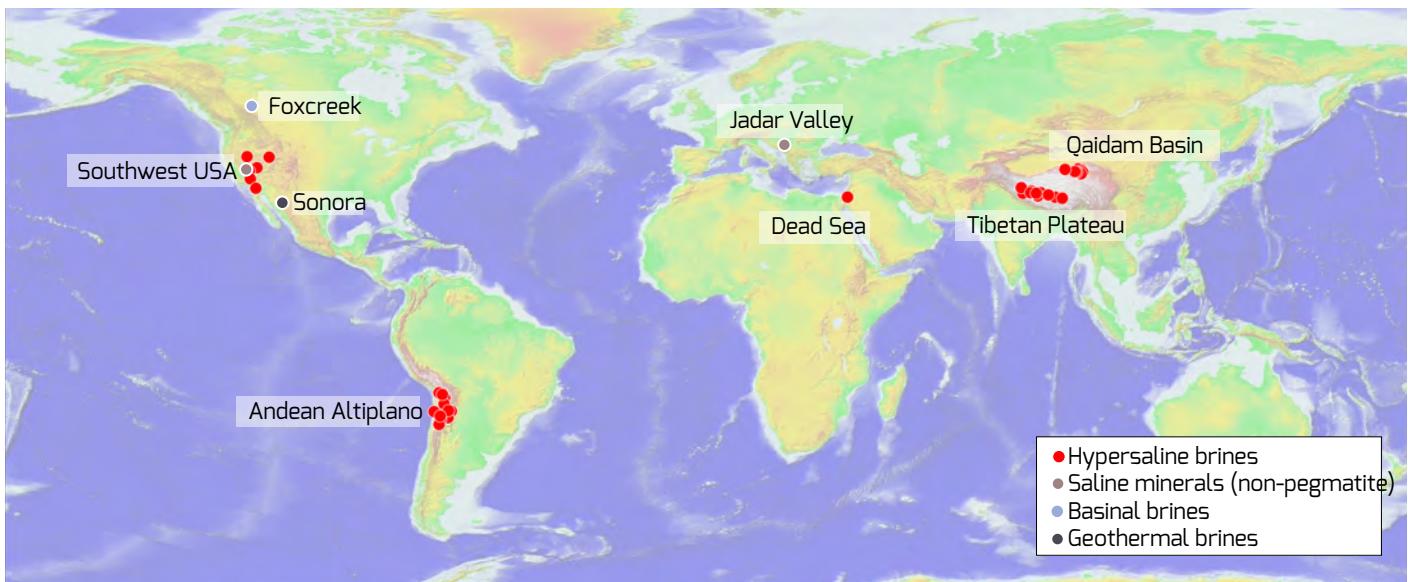


Figure 2. Lithium occurrences in saline sedimentary settings, see Table 1 for detail (extracted from SaltWorks® database version 1.7)

nickel hydride at one-third of the weight, and they operate at very low temperatures with a longer battery life. The use of Li-ion

batteries in electric cars and electronic devices has increased the global demand for lithium, a trend that is likely to continue.

Currently, lithium-rich saline brines are the most economically recoverable Li source on the planet. (Kesler et al., 2012; Grosjean et al., 2012).

Economically recoverable forms of lithium occur in four types of deposits (Table 1;

Figure 1)

- (1) Pegmatites,
- (2) Continental saline brines,
- (3) Hydrothermally altered saline lacustrine clays,
- (4) Geothermal and basinal brines.

Figure 2 plots known occurrences of lithium in saline deposits. There are four main clusters of hypersaline brine-related lithium occurrences, 1) Andean Altiplano, 2) Tibetan Highlands, 3) Qaidam Basin and 4) Playa brines in the Basin and Range of the south-west USA. Then there are the lesser volumes, as yet un-economic lithium accumulations, associated with lacustrine clays near Hector, California and in the Jadar

Valley, Serbia. Basinal (oilfield) brines are known to entrain elevated levels of lithium in the Smackover Fm, USA and the Fox Creek region of Canada. Geothermal

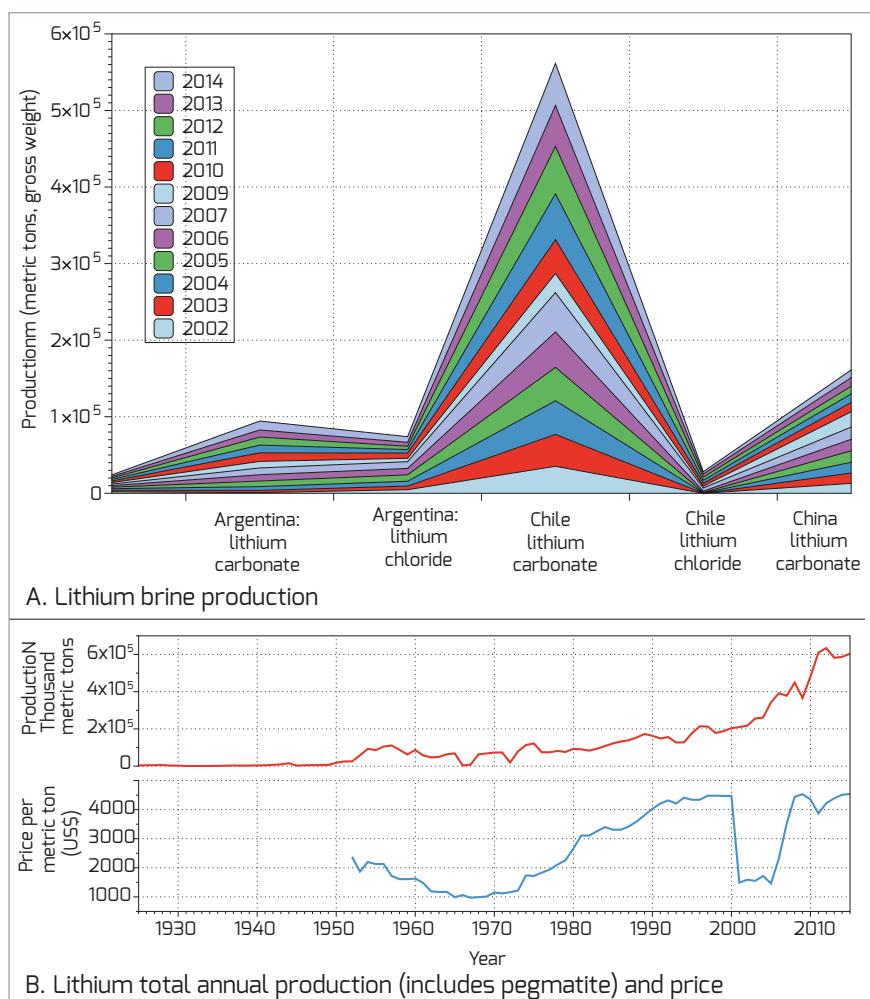


Figure 3. Lithium brine production. A) Cumulative area plot of annual production of lithium salts from brine producing countries in metric tons. USA also produces variable tonnages of lithium from brine, but figures not made public, they are less than other countries listed. B) World production from 1925 - 2015 (metric tons, includes both brine and spodumene sources), C) Price per metric ton in US dollars from 1954 to 2015. Compiled from USGS on-line data tables downloaded from <http://minerals.usgs.gov/minerals/index.html> last accessed June 28, 2017.

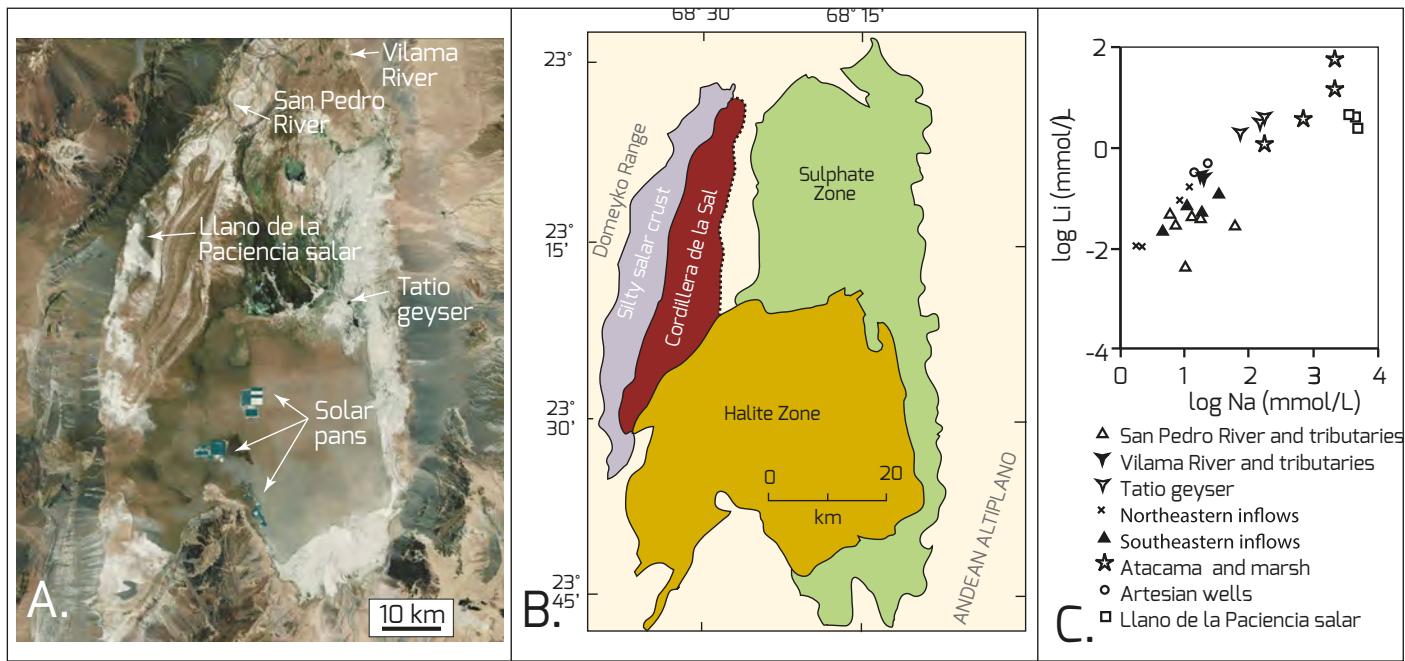


Figure 4. Lithium brines in Salar de Atacama, Chile. A) General overview of Salar de Atacama, Chile, showing centripetal endorheic drainage (Bing® image scaled and mounted in MapInfo). B) Surface geology showing nearby Neogene evaporite outcrops in the Cordillera de la Sal. C) Lithium content of wells in the halite nucleus and other nearby brine sources (after Carmona et al., 2000).

brines below the Salton Sea can also contain elevated levels of lithium.

Lithium-rich continental brine sources account for about three-fourths of the current world lithium production with the remainder from pegmatites (Figure 3; U.S. Geological Survey, 2017). Only the geology of hypersaline brine sources and associated saline sediment hosts, basin brines and clay replacements are discussed in detail in this article. For information on pegmatites and oilfield brines, the interested reader is referred to Garrett (2004), Kesler et al. (2012) and Evans (2014). All three articles contain a broader discussion of occurrences of lithium raw materials and their processing.

In natural brines, most lithium salts are highly soluble and tend to stay in solution until lithium concentrations approach and exceed 6000 ppm. Lithium can be absorbed by saline playa clays at lower concentrations, as in the hectorite beds in Clayton Playa, Nevada or hydrothermally from hypersaline saline waters as formed jadarite nodules in the Jadar Valley, Serbia. Actual lithium carbonate precipitates are highly soluble and so very rare in sedimentary basins; lithium carbonate (zabuyelite) is a natural precipitate from the high-altitude hypersaline waters of Lake Zabuye on the Tibetan Plateau.

Lithium carbonate brines

Production from hypersaline pore brines in South American salars dominates current world lithium brine production, with Chile and Argentina producing some two-thirds of the documented world brine production (Figure 2). Chile has

emerged as the largest lithium carbonate producer from a lake brine, largely through the exploitation of brines in Salar de Atacama. China and Argentina are the other main producers of lithium from saline lake brines (Figure 3).

Lithium in salar brines of the Andes

Salar de Atacama lies on the Tropic of Capricorn at an altitude of 2,300 m in the Desierto de Atacama, some 200 km inland from Antofagasta. In its more central portions this salt-encrusted playa contains a massive halite unit (nucleus) that is more than 900 m thick, with an area ≈ 1,100 km². Fringing saline muds, with an area ≈ 2,000 km², surround the nucleus (Figure 4a, b).

The current salt crust atop this halite nucleus contains a sodium chloride interstitial brine that is rich in Mg, K, Li, and B (Figure 4c; Figure 5; Alonso and Risacher, 1996). Lithium contents of the pore brine range from 200-300 ppm in the marginal zone, some 500-1,600 ppm in the intermediate zone and 1,510-6,400 ppm in the salt nucleus). The nucleus zone averages 4,000 ppm lithium and is asymmetric with respect to the salar centre due to the sump offset via ongoing faulting. Main inflows to the salar drain volcanic formations of the Andean Highlands located to the east of the basin.

Salts dissolved in inflow waters have a double origin. Weathering of volcanic rocks supplies K, Li, Mg, B and, to a lesser extent, Na and Ca. Leaching of ancient halokinetic evaporites sourced in a mother salt layer beneath and piercing the volcanic formations provides additional amounts of Na, Ca, Cl, SO₄ to the most saline inflow waters.

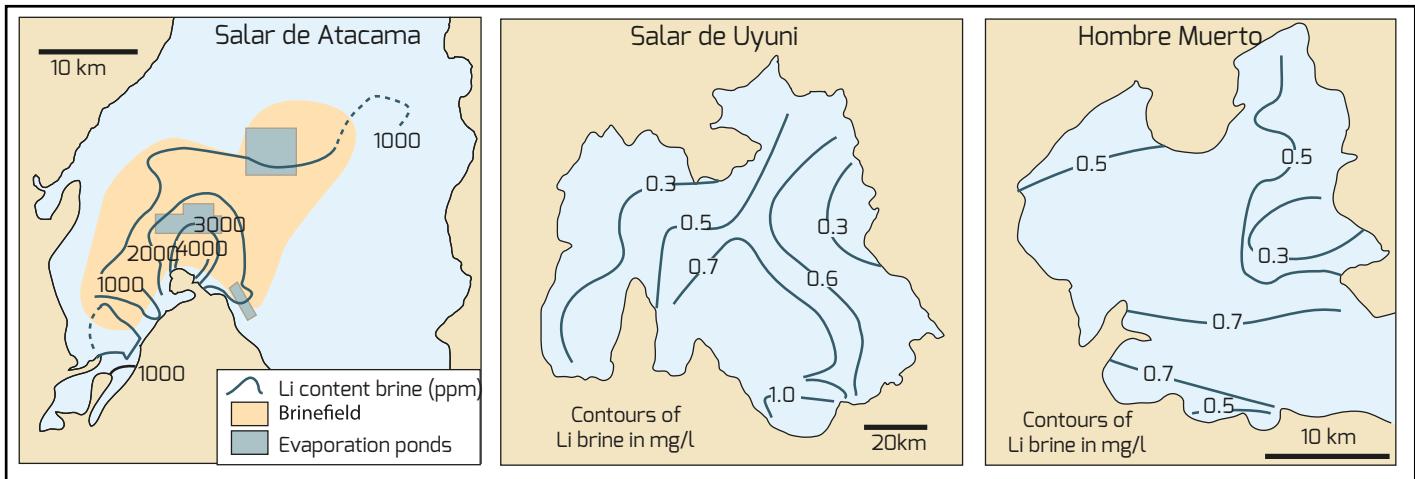


Figure 5. Selected South American salars showing variations in Lithium in near surface pore brines (after Kesler et al., 2012)

The mass-balance of the upper halite nucleus in the salar shows a strong excess of NaCl with respect to the bittern solutes Mg, K, Li, B. According to Alonso and Risacher (1996), this suggests that the nucleus did not originate from evaporation of inflow waters similar to the present groundwaters. Rather, the excess of NaCl is due to NaCl-rich inflow waters that formerly drained the Cordillera de la Sal, a Tertiary-age evaporitic ridge along the western rim of the present-day salar (Figure 4b).

Although annual salt accretion rates in a salar salt nucleus facies in an Andean salar can be as high as 5-6 cm/year (Ruch et al., 2012), the average sedimentation rate of halite in the Atacama lake centre is \approx 0.1 mm/year, based on the age of an ignimbrite interbedded with the salt. This slow aggradation rate implies a climatic setting of long dry periods and inactivity alternating with short wet periods during which large amounts of water, and so large amounts of salt, are first recycled and then accumulate in the halite crusts of the basin sump. The lack of peripheral lacustrine deposits and the high purity of the Atacama salt

also suggest that the main salt unit is not the remnant of an ancient deep saline lake, but originated mostly from evaporation of waters supplied by subsurface and subterranean saline seeps.

Once Li-rich lake brines are pumped to the surface they flow into a series of evaporation pans where three main economic products (halite, potash and lithium salts) are recovered. To achieve this controlled salt-series production, the brines are first pumped from 30 metre deep boreholes that penetrate the porous salt nucleus layer into a series of solar evaporation ponds (Figure 6a). Over the successive passage through the concentrator ponds, liquors are concentrated by a factor of 25, generating a final brine strength of 4.3% Li (Figure 6b). During evaporation and processing for production of halite, potassium chloride and potassium sulphate from lithium precursor brines, the ion ratios are continuously monitored and adjusted to avoid the precipitation of a lithium potassium sulphate salt. This combination of solar concentration and brine processing, proceeds as follows:

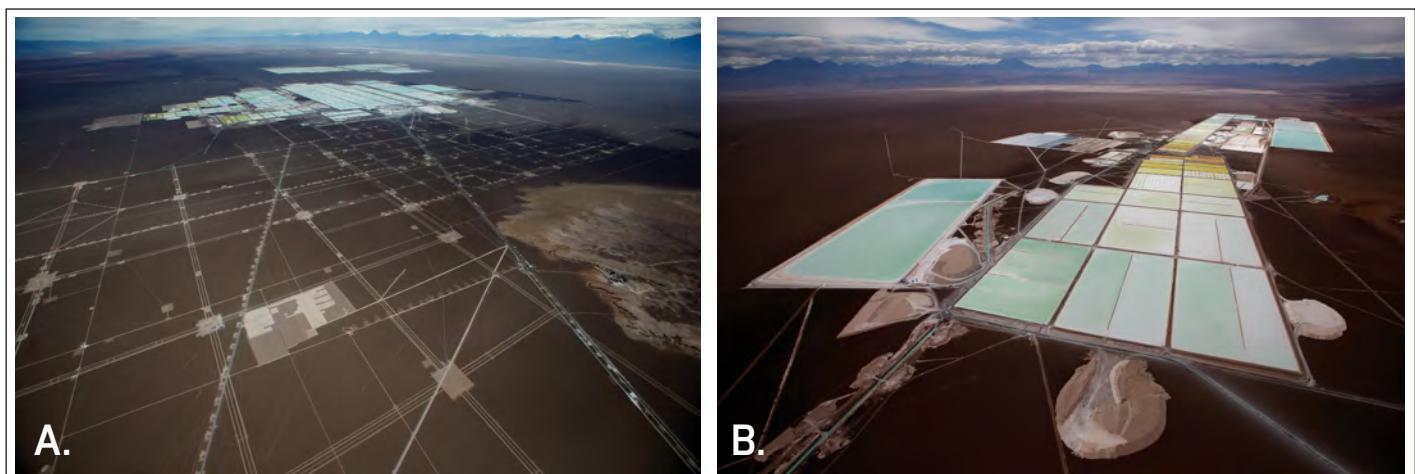


Figure 6. Production at Salar de Atacama. 1) View of a brine field where saline brine is pumped to the surface and into nearby solar evaporation pans. B) Solar evaporation pans, pans showing yellow-green coloration where liquors are approaching lithium carbonate saturation (\approx 6000 ppm) and are ready to be pumped to the brine processing plant.

- 1) Sodium chloride (common salt) precipitates first. If required, this salt can be scrape-harvested as a by-product.
- 2) At the appropriate level of concentration, the brine is transferred to a second set of ponds in which a mixture of sodium chloride (salt) and potassium chloride (potash, in the form of sylvite) is precipitated. These salts usually are harvested and the two components separated in a flotation plant.
- 3) The remaining brine is piped to another set of evaporation ponds where it remains until the concentration increases to 6000 ppm Li (essentially the saturation point of lithium chloride - saturated brines typically show a green colour as visible in Figure 6b). Ripe brine is then transferred to a recovery plant where impurities such as magnesium and boron are removed. When soda ash (sodium carbonate) is added to the ripe brines, lithium carbonate drops out. Brine with low magnesium levels is the preferred feed brine as this makes for simpler processing.

The high initial lithium content of the Atacama brines and the extremely arid setting (3200 mm pan evaporation and <15 mm precipitation) means that only 90 hectares of evaporation ponds are required for one of the current brine operations on the salar, this is only 5% of the area required at Clayton Valley, Nevada with its milder climate and lower Li concentration in the feeder brine (Figure 7). Borate (as perborate) is recovered at levels of 0.84 g/l during lithium extraction at Atacama. Increasing volumes of lithium are also produced by new nearby salar brine processing facilities in Salar de Hombre Muerto, Argentina and Salar de Uyuni, Bolivia. All these salars have lower levels of Li in the primary brine feed than Atacama.

Lithium brines in the USA

Clayton Valley is host to the only commercially producing lithium project in North America, Albemarle's Silver Peak brine

evaporation pond project (Figure 7). Historically, the Clayton Valley playa produced about one-third of the US lithium requirements, but its economic viability suffered from fierce market competition, especially from South America, and a largely depleted brine supply. Originally, the central valley area contained 100–800 ppm Li, and the discovery well at 229 m depth contained 678 ppm when pumped

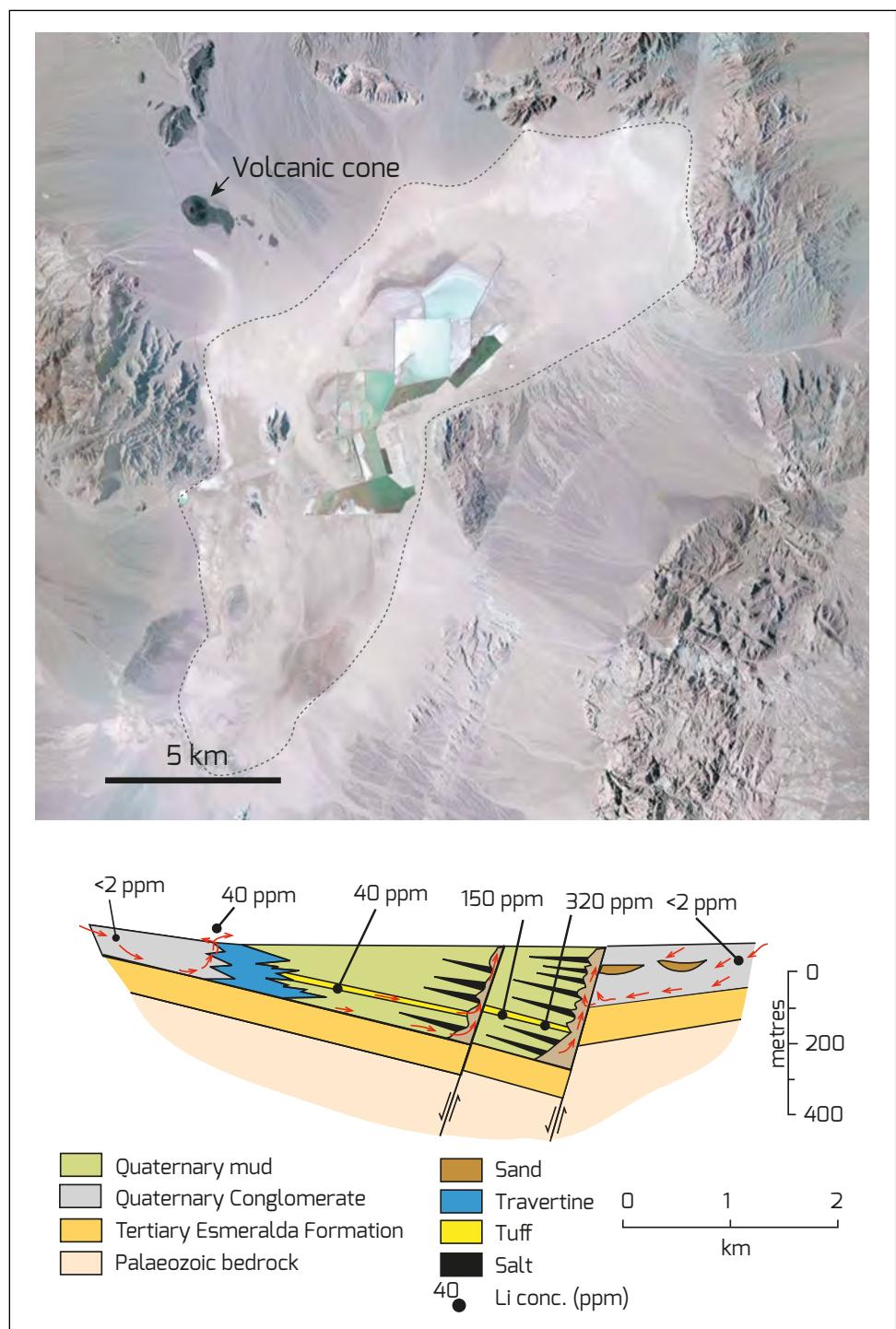


Figure 7. Plan view and generalised cross section of Clayton Valley (Silver Peak) Playa, Nevada. Basin is hydrographically closed with a recent volcanic cone in bajada to northwest of playa depression. Cross section shows the relative position of the major tuff-bed aquifer, inferred directions of groundwater flow and representative lithium concentrations (ppm) in the various aquifers and springs (in part after Davis et al., 1986).

at 450 gpm (Garrett, 2004). The average brine analysis when commercial production of lithium carbonate began in 1966 was about 400 ppm (Figure 7). Since that time the feed concentration of lithium has been slowly declining, and in 1998 the concentration was about 100–300 ppm Li (averaging 160 ppm, Harben and Edwards, 1998).

The Silver Peak Playa has an area of 50 km² and an elevation of 1300–1400 m (Figure 7). It lies in the rain-shadow of the Sierra Nevada, with an annual rainfall ≈ 130 mm and an evaporation rate of ≈ 1380 mm.

Near-surface sediments consist of a mixture of clays (smectite, illite, chlorite, kaolin) and salts (halite and gypsum) and widespread pedogenic calcite. Lithium in the brines is derived from weathering and leaching of volcanics in the Tertiary Esmeralda Formation and Quaternary ash-fall tuffs (Davis et al., 1986). Lithium content is highest on the eastern side of the playa adjacent to the outcropping marls of the Esmeralda Fm. Before it is leached, lithium is held in the clay fraction of the playa sediments and is probably part of the clay structure (hectorite is a widespread but minor component in the Clayton Valley clays – see later)).

Lithium-rich brine feed to the plant averages 0.023% (230 ppm) lithium in a background NaCl concentration of 200,000 ppm, is pumped from depths of 100–300m in the Clayton Valley (Silver Peak) playa via a number of gravel-packed wells. The lithium (and potassium) in the deposit probably originated from hot springs along the Silver Peak Fault, with the current brine composition being a blend of evaporated water from these springs and surface and ground water that drains into the basin (Garrett, 2004).

Modern saline spring

outflows contain

9280–10,000 ppm

Na, 786–826 ppm K

and 24–43 ppm Li.

Unusually high brine temperatures in some areas of the deposit (up to 44°C at fairly shallow depths ≈ 25m) tend to support a volcanic/geothermal origin for the lithium. Some of the brine feeder wells show elevated levels of radon gas.

Pumped brine progresses through a series of fractionating evaporation ponds (Figure 7; Zampirro, 2004). Lithium

concentration in the liquor increases to 6,000 ppm over the course of 12 to 18 months in the solar evaporation pans. When the lithium chloride level reaches optimum concentration, the liquor is pumped to a recovery plant and treated with soda ash to precipitate lithium carbonate, which is then removed by filtration, dried, and shipped.

Lithium from brine, when the Clayton Valley first produced product in the 1970s, was considered a unique deposit. Its operations established the technology and economic viability of lithium recovery from saline brine, which led to the development of brine production from the salars of South America that now dominate world production of lithium from brine.

Lithium brine in Chinese salt lakes: Zabuye (Zhabei) and Qaidam basins

The lithium brine resource of China is mostly stored in two saline lake regions in high altitude zones, Lake Zabuye region in the Alpine tundra climate zone on the Tibetan Plateau and four salt lakes in the cold arid steppe region of the Qaidam Basin on the Mongolian Plateau (Figure 2). Something like 80% of brine lithium resource found in China is contained in the four salt lakes of the Qaidam: Bieletan, DongTajinaier, XiTajinaier, and Yiliping (Figure 8; Yu et al., 2013). Zabuye lake on the Tibetan Plateau is probably the most geologically interesting as the Li content of the lake waters are so elevated that it is the only known lacustrine location where lithium carbonate, zabuyelite, is a natural brine precipitate (Figure 9. Nie et al., 2009; Gao et al., 2012).

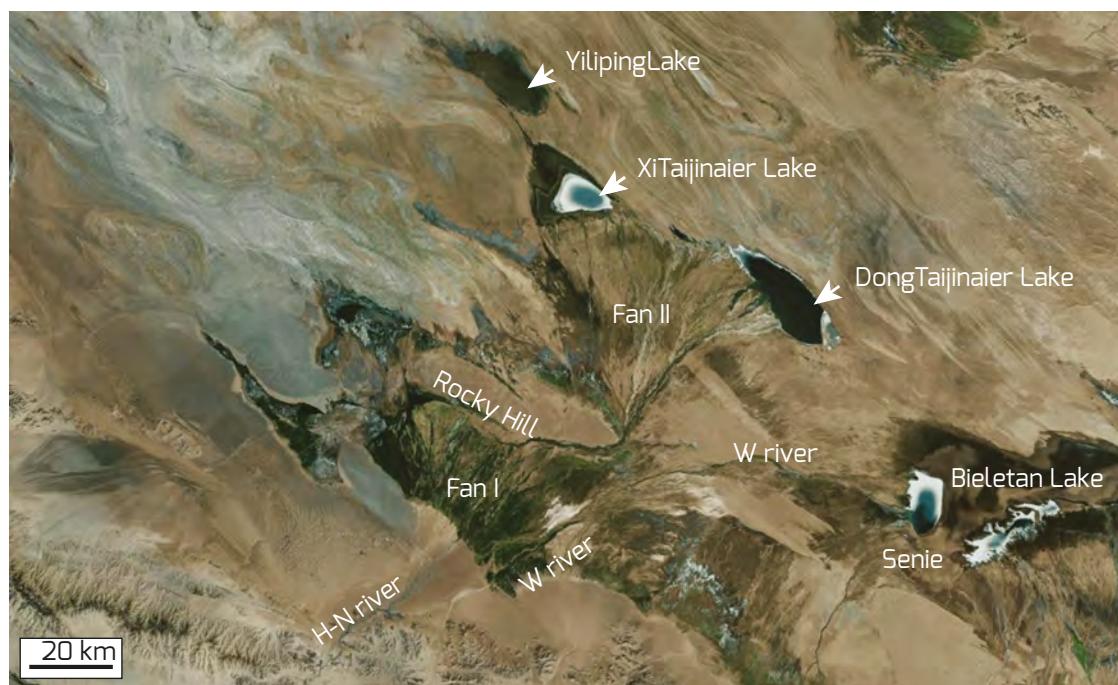


Figure 8. Lithium lakes and supplying rivers and fans in Qaidam Basin (after Yu et al., 2013). The Golmud potash lakes and brine plant lie to the east of Lake Senie.

Qaidam Lakes

Detailed sedimentological and hydrological work in the Qaidam by Yu et al. (2013) has shown that: (1) Some 748.8 tonnes of lithium is transported annually into the lower catchment of the four salt lakes via the Hongshui-Nalinggele river (H-N river in Figure 8), which is the largest river draining into the Qaidam Basin, (2) Li-rich brines are formed only in those salt lakes in the Qaidam that are associated with inflowing rivers with Li concentrations greater than 0.4 mg/l, and (3) the water's Li concentration is positively correlated with elevated levels in both the inflowing river and the associated subsurface brine. Their findings show that long-term input of Li⁺ from the Hongshui-Nalinggele river controls the formation of lithium brine deposits. They conclude that the source of the lithium in the lake brines is ultimately from hydrothermal fields, where two active faults converge in the upper reach of the Hongshui River. These hydrothermal fields are associated with a magmatic heat source, as suggested by the high Li⁺ and As³⁺ content water in geysers in the geothermal field. Based on the assumption of a constant rate of lithium influx, they estimate that the total reserves of lithium in the Qaidam were likely formed since the postglacial period.

Field mapping and coring indicate that lithium reserves in each of the four salt lakes depend on the influx of Li-bearing water from the H-N River. The data also suggest that during the progradation of the alluvial Fan I, the Hongshui-Nalinggele drained mostly into the Bieletan salt lake, until the Taijinaier River shifted its watercourse to the north and began to feed the salt lakes of the DongTaijinaier, XiTaijinaier and Yiliping salt lakes, while also driving Fan II progradation (Figure 8).

One of the Yu et al. (2013) major findings in terms of lithium enrichment models is the importance of the contrasting hydroclimatic conditions between the high mountains containing ice caps and the terminal salt lakes. The greater than 4000 m of relief in the watershed enables a massive amount of ions, such as K⁺, to be weathered and transported, together with detrital material from the extensive, relatively wet alpine regions to the concentration sumps in hyperarid terminal salt lakes, where intense evaporation rapidly enriches the lake water, resulting in evaporite deposition and associated K- and Li-rich brines. It is no surprise that a saline lake at the foot

of the nearby Golmud River fan is one of the few places in the modern world where carnallitite is found (Casas and Lowenstein, 1992).

Lake Zabuye

Lake Zabuye is located some 1000 km west of Lhasa, the Tibetan capital, and lies in the ET Köppen high altitude climate zone of the Tibetan Plateau (Figures 2, 9). The lake is perennial, and water levels can vary by metres each year; in 2008 the water level was some 4422 m above sea level. At this level, the lake's area is approximately 247 km². Salinity varies from 360 to 440 ‰, depending on seasonal differences in water input and evaporation rate. The volume

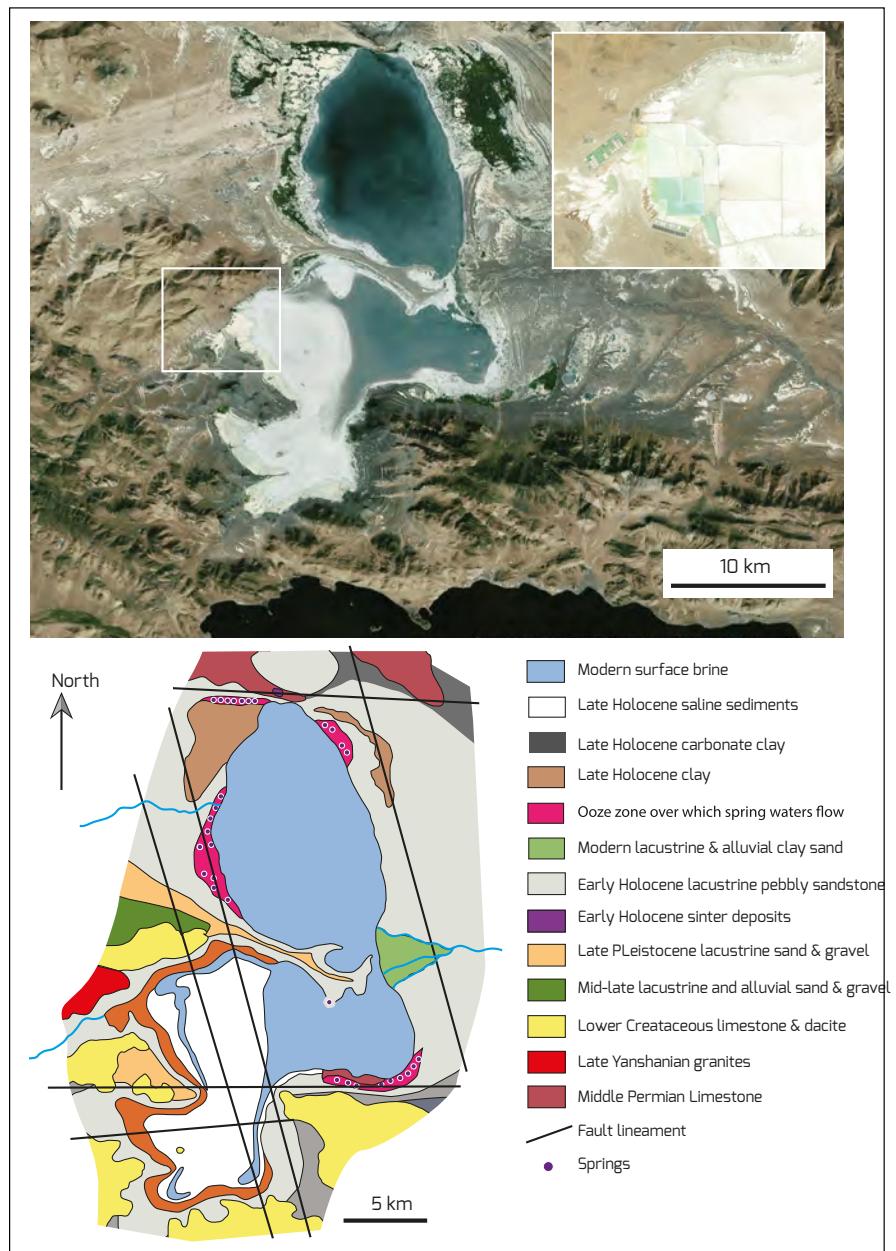


Figure 9. Geology of Zabuye Lake (Zhabei Lake). A) satellite view. B) Geology (after Gao et al., 2012).

of lithium product at the lake is currently limited by the sulphate-rich nature of the primary lake brine, prior to concentration in solar pans (Gao et al., 2012).

When concentrated, the crystallisation sequence of salts from highly concentrated Zabuye lake brine at 25°C is (Figure 10a; Nie et al., 2009):

halite (NaCl) \rightarrow aphthitalite ($3\text{K}_2\text{SO}_4 \cdot \text{Na}_2\text{SO}_4$) \rightarrow zabuyelite (Li_2CO_3) \rightarrow sylvite (KCl) \rightarrow trona ($\text{Na}_2\text{CO}_3 \cdot \text{NaHCO}_3 \cdot 2\text{H}_2\text{O}$) and thermonatrite ($\text{Na}_2\text{CO}_3 \cdot \text{H}_2\text{O}$)

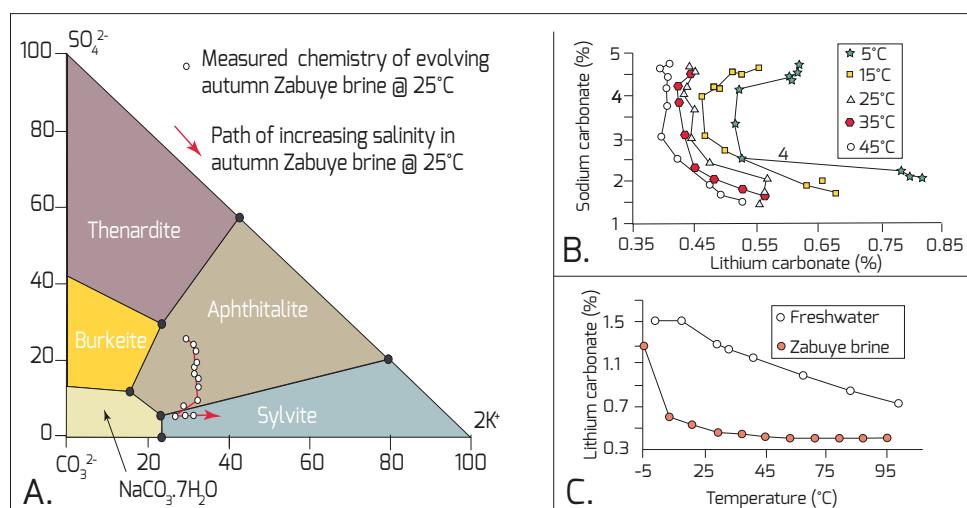


Figure 10. Chemistry of Zabuye Lake brines. A) Brine evolution pathway (after Nie et al., 2009). B) Lithium carbonate solubility with respect to temperature. C) Lithium carbonate solubility with respect to sodium bicarbonate content at various temperatures (after Sha et al., 2009).

The lake's brine is naturally supersaturated with NaCl and other salts, so millions of metric tons of halite, potash, trona, and other minerals have accumulated on the bottom of the lake in the past few thousand years (Zheng and Liu, 2010). Lithium carbonate and sylvite precipitate, via a combination of brine concentration and cooling, and higher levels of lithium carbonate precipitation in the end brine can be induced by the addition of soda ash, as is done in the South American salars (Figure 10b, c).

The problem with the natural lake chemistry of the Zabuye salt lake is that a lithium sulphate salt $\text{Li}_2\text{SO}_4 \cdot 3\text{Na}_2\text{SO}_4 \cdot 12\text{H}_2\text{O}$ precipitates naturally in the early stages of the low-temperature evaporation process, so reducing the levels of lithium carbonate in the end-stage brines. If the brine concentration series in the pans can be artificially held at mirabilite concentration, then the amount of lithium lost to the sulphate salt is reduced, so levels of lithium in the end-stage brines improve (Gao et al., 2012).

Zabuye Lake is of significant economic value as it is a new type of exploited saline lacustrine deposit (compared to the salars of South America) in that contains it precipitates lithium and borate salts in addition to significant volumes of potash, halite, natron and Glauber's salt. Lake waters also retain elevated levels of caesium, rubidium and bromine.

Lithium in minerals soaked in saline brines

Two saline minerals in sedimentary basins known to have significant lithium contents are hectorite and jadarite. Hectorite [$\text{Na}_0.33(\text{Mg},\text{Li})_3\text{Si}_4\text{O}_{10}(\text{F},\text{OH})_2$] is a clay mineral of the smectite group, where the replacement of aluminium by lithium and magnesium is essentially complete. It has a lithium content of more than 1%, a hardness of 1–2 on Mohs scale, and a density of 2–3 kg/m³. To date, an economically viable technology for

extracting lithium from hectorite, rather than from brines that enclose some of these clay deposits, has yet to be developed (Evans, 2014). Jadarite [$\text{LiNaB}_3\text{Si}_0\text{O}_7(\text{OH})$], is a newly recognised mineral with up to 5.7% Li and 14.7% B. Jadarite is a white porcellanous borosilicate mineral with a Mohs hardness of 4–5, and a density of 2.45 gm/cc. It is associated with borate salts such as colemanite in the Oligocene-Pliocene lacustrine host sediments in its type area in the Jadar Valley in Serbia (Stanley 2007). Hectorite is probably associated with crossflows of moderate salinity hydrothermal waters, while jadarite requires a bath of hypersaline hydrothermal waters to form.

Hectorite

Hectorite has a soft, greasy texture, a candlewax-like appearance and feels like modelling clay when squeezed between the fingers. As a colloid, hectorite's unique thixotropic properties for emulsion stabilising, gelling, suspending, binding, bodying and disintegrating, means it sells for more than US\$2,000 a ton, generally as a lubricant to the oil and gas industry. Associated authigenic clays include stevensite and saponite, and in its type area at Hector California lies adjacent to a colemanite deposit.

Hectorite is mined periodically (not as a lithium source) in its type area, the Hector Mine, near Barstow, California. There, hectorite is the main clay mineral in a sequence of altered volcanic ash beds that are interbedded with lake sediments and travertines along an 8 km fault zone (Figure 11; Ames et al., 1958). The hectorite is thought to have formed through hydrothermal alteration of the ash by saline fluids moving up the fault zone (Sweet, 1980). Lithium-bearing volcanic rocks that probably formed in the same way have also been described from Arizona, and the Clayton and King Valleys in Nevada (Brenner-Tourtelot and Glanzman, 1978; Kesler et al., 2012). Hectorite is not considered to be a prime lithium resource in any of these

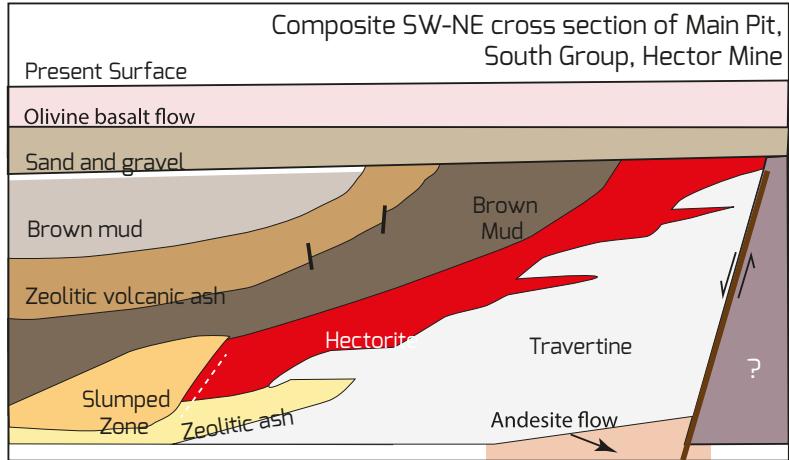


Figure 11. Generalised northeast-southwest cross-section of the geology of the Main Pit, South Group, Hector Mine, California (after Ames et al., 1958)

occurrences. It is, however, considered of co-indicator of the former, or current, presence of Li-rich saline brines and as such is considered a pointer mineral to a possible lithium brine resource.

Hectorite is thought to be a result of the combination of three distinct geological processes: 1) the alteration of volcanic ash or glass; 2) precipitation of authigenic phases from saline lacustrine pore waters; and/or 3) the incorporation of lithium into existing smectite clay deposits (Asher-Bolinder, 1991). To form hectorite, all three processes require an arid environment and are associated with lithium-enriched saline alkaline waters, volcanic rocks and hot springs that can also co-precipitate travertines and fine-grained amorphous silica (Zientek & Orris, 2005).

The same association of processes explains the lithium-rich hectorite clays in King Valley (Nevada Lithium prospects) Nevada. There, layers of hectorite occur in a sequence of sedimentary and tuffaceous rocks in moat sediments along the western side of the McDermitt caldera (Figure 12; Kesler et al., 2012). Volcanic activity at the McDermitt caldera complex has yielded precise $^{40}\text{Ar}/^{39}\text{Ar}$ ages of 16.5 to 16.1 million years ago and was characterised by extrusion of early metaluminous and peralkaline rhyolite, followed by the eruption of a voluminous ignimbrite with peralkaline rhyolite to metaluminous dacite compositions (Carew and Rossi, 2016). After collapse, the central part of the caldera complex was the site of resurgence, and a moat-like lake formed between this resurgent

dome and the caldera walls. The lake was the site of deposition of volcaniclastic sediments that now form a nearly continuous ring within the caldera and host the various hectorite lenses (Figure 11).

Hectorite layers ranging from 1 to 90 m in thickness and have been recognised over a length of about 20 km. Individual layers or groups of layers extending for several km and are annotated as stage 1-5 lenses. The Stage 1 lens of the Lithium Nevada deposit (informally known as the King Valley deposit) has proven and probable reserves of 50 million tonnes, averaging 0.312% Li (Carew and Rossi, 2016).

As in the type area in the Hector Mine in California, hectorite in the various lenses is the

main lithium-bearing clay mineral in a sequence of altered volcanic ash beds. These ash beds are interbedded with saline lake sediments and travertines, and are hosted in the sedimentary moat facies adjacent to an 8 km fault zone. That is the hectorite formed through hydrothermal alteration of volcaniclastic ash in regions where moderately saline hydrothermal fluids moved up a fault zone.

Hectorite clays are also found in the Sonora Lithium Project, 11 km south of Bacadehuachi in the Sonora state of north-west Mexico. The resource statement, in an April 2016 report, lists 839,000 tonnes of contained lithium in the indicated category and a further 515,000 tonnes in the inferred category, within two distinct lacustrine clay units situated below basaltic caprocks (Pittuck and Lepley, 2016). A pre-feasibility study has been completed, which proposes a two-phase open-pit mine with lithium carbon

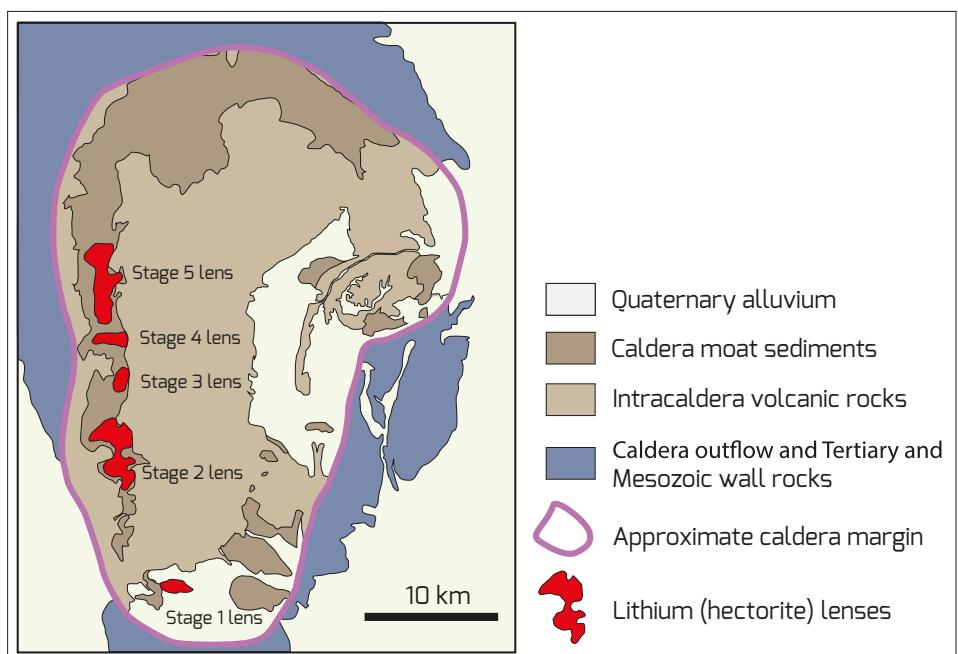


Figure 12. Geology of the King Valley (Nevada Lithium) deposits (after Carew and Rossi, 2016).

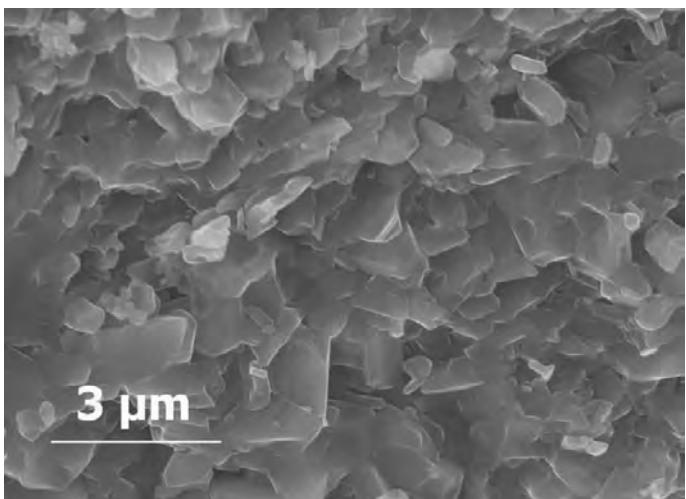


Figure 13. A secondary-electron image illustrating the nature of jadarite (various grey shades). The mineral exhibits a relatively tabular nature and discrete crystallites rarely exceed 5 μm in size. Note the presence of small cavities between the crystallites that give it a pitted appearance when examined in polished section (after Stanley et al., 2007).

ate processing facility and a mine life of 20 years. A pilot plant has also been constructed, and discussions have commenced regarding possible off-take agreements. None of these hectorite occurrences discussed in this article are currently mined as a lithium resource.

Jadarite

Jadarite was discovered in 2007 by Rio Tinto and the Jadar deposit, near the town of Loznica, and at that time was estimated to contain an inferred resource of 125.3 million tonnes at a weighted average of 1.8% Li₂O, in addition to an inferred resource of boron minerals. Jadarite has so far only been identified in significant amounts within the 20km long Jadar Basin of Serbia. The Jadar Basin entrains oil shales, dolomites, pyroclastic sediments and evaporites which are believed to have accumulated in an intermontane lacustrine environment.

The jadarite occurs both in massive form, several metres thick, and also as small nodules within a fine-grained carbonate matrix (Stanley, et al., 2007). At the main Jadar deposit, a layer containing nodular colemanite ($\text{Ca}_2\text{B}_6\text{O}_11 \cdot 5\text{H}_2\text{O}$) overlies three separate layers or lenses containing jadarite $\text{LiNaB}_3\text{SiO}_7(\text{OH})$. Jadarite likely formed via a hydrothermally-facilitated interaction between saline brine and clastic/evaporitic sediment, either in a tuffaceous or clay host (Kesler et al., 2012).

In May 2017, Rio Tinto announced that the Jadar area contains one of the largest lithium deposits in the world, lifting their estimate for Lower Jadar's deposits to 138 million tonnes. Extraction is scheduled to begin in 2023, with a projected underground exploitability of 50 years. As of June 2017, construction of a mine has not begun. A jadarite processing plant is also planned next to the mines, that plant will process the ore into lithium carbonate and boric acid.

Summary

Characteristics that appear to be essential to define a potential lithium carbonate brine resource are; i) an arid climate and, ii) a closed, tectonically active basin, with significant elevation and tectonically activity, which can entrain brines with elevated lithium contents (Figure 15; Bradley et al., 2013; Yu et al., 2013; Warren, 2010, 2016). Sources of lithium can be deeply circulated magmatic or recycled basinal fluids. Magnesium levels in the brine should not be too high as this complicates brine processing during lithium carbonate extraction. A co-occurring potash resource, extractable from the same brine, if present can reduce processing costs.

Another possible requirement—or at least a favourable characteristic—is elevated heat flow, as evident from young volcanoes or hot springs and the associated increase in Lirich juvenile waters flushing the surrounding drainage basin, as is occurring beneath the Andean Altiplano. Volcanogenic source rocks in the lake drainage, such as felsic, vitric tuffs that have abundant and readily leached lithium are favourable, but perhaps not essential, since lithium is present in most crustal rocks at tens of parts per million.

Worldwide all the exploited salt lakes have lithium levels in their lake brines that are well above typical (Figure 14). Another possible favourable indication of a lithium brine is the existence of hectorite or jadarite in associated clays in the bajada rims.

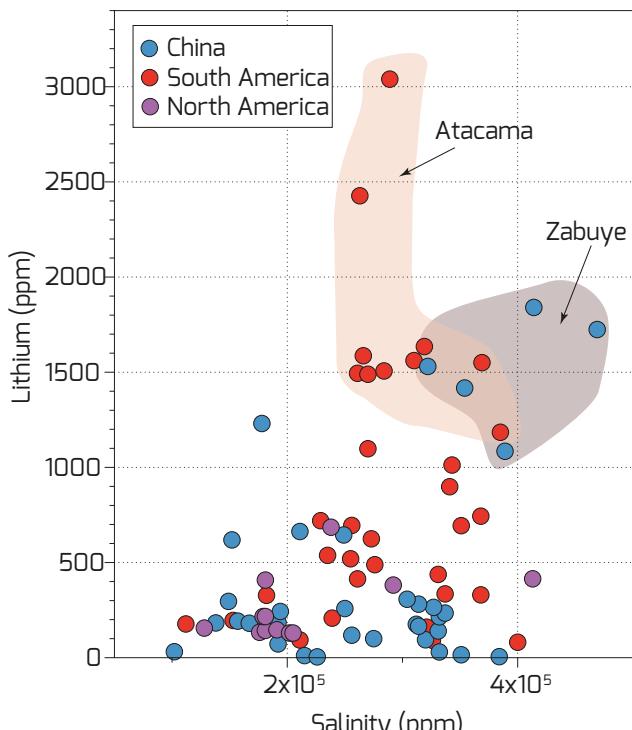


Figure 14. Lithium levels in lake brines and pore waters in various lithium brine lake deposits and prospects in China, South America and North America (plot points extracted from various literature sources compiled in SaltWork® database 1.7)

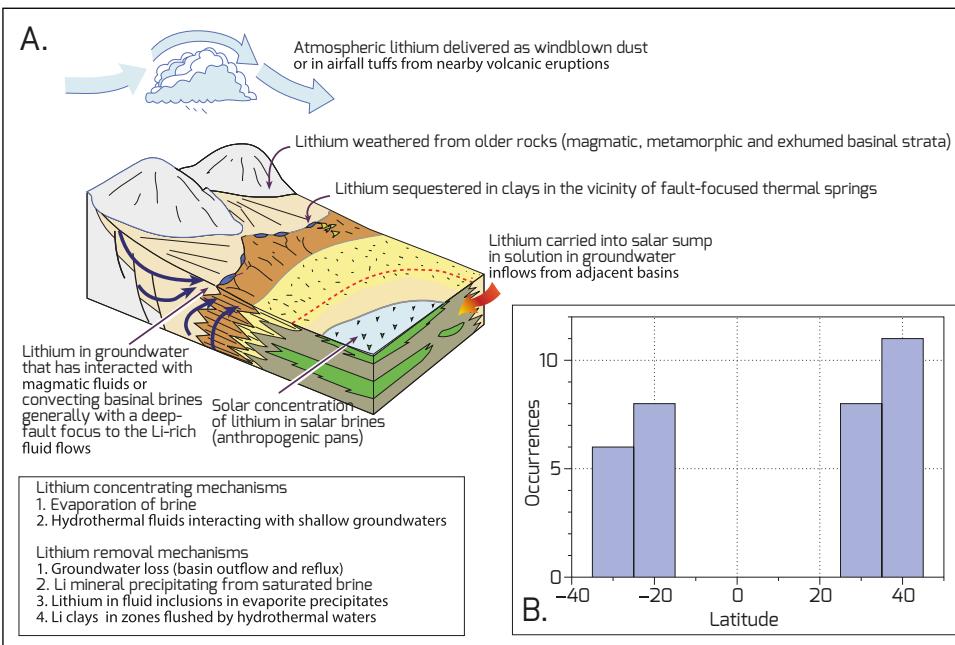


Figure 15. Lithium controls and distribution. A) Summary of mechanisms controlling lithium in a salar setting (after Warren, 2016). B) Latitudinal distribution of modern lithium brine occurrences (replotted with permission from SaltWork database version 1.7 - see also Figure 2)

All known and potential lithium brine deposits are located in arid tectonically active areas, typically in subduction or collision belts with deep-faulted suture systems (Figure 2). At the world scale, lithium-prone saline deposits are latitudinally restricted to cool arid Koeppen climate belts within endorheic brine sumps surrounded by high altitude drainage basins (Figures 2, 15b; Warren, 2010). Borates as evaporite salts are generally tied to the same setting (Warren, 2010).

Active faulting appears to be involved in forming a suitable spring-fed hydrology for all known economic lithium brine basins. Fault-related subsidence also creates accommodation space, without which only a thin veneer of arid basin sediments and brines can accumulate. Thus, a thick basin fill is needed to provide an aquifer of sufficient volume to hold a viable lithium brine resource.

In contrast, saline lakes atop shallow, superficial basins in intracratonic regions such as the Sahara Desert and most inland Australian deserts largely lack active deep-fault control and associated rapid subsidence, and are not known to be prospective for lithium brines.

Salt fills in some lithium basin lacustrine sumps are cut by active intrabasinal faults (known from boreholes and seismic) but have no surface expression due to rapid infill and levelling of the accommodation space by salt precipitation. Significantly, the brine pools in Clayton Valley, Salar de Atacama and the Qaidam sumps are localized along active intrabasinal faults, which also control the distribution of aquifers and influence groundwater movement patterns, as well as the position of maximum stacking of concentrates and brines in the halite nucleus, along with porosity retention levels in the subsurface halite host (Zampirro, 2004; Jordan

and others, 2002). Porosity levels in a host halite aquifer are a major constraint on the potential economics of any salar or salt lake lithium brine resource. Most halite units lose their effective porosity and permeability by depths of 50-60 metres (Warren, 2016; Chapter 1). Thus, most Quaternary lithium brine operations hosted in a halite bed/aquifer will have an economic basement to brine recovery at around this depth. It is unlikely that recovery operations in Salar de Atacama and planned projects in Salar de Uyuni can recover economic brine volumes at much greater depths. There may be a 900m thick halite-dominant succession infilling Salar de Atacama and a number of halite beds to a depth of 120m in Salar de Uyuni, but economic porosities in the halite will likely only be present in the upper portions of the halite fill in both salars.

Postulating likely lithium resources, in a salar of a salt lake, to depths greater than 50-60m should only be done after salar-hydrology-aware drilling has established the presence of economic permeabilities in the hosting halite aquifer and this is likely related to the presence of active faults. Such measurements require drilling and sampling equipment that facilitates reliable "in-situ" determinations of porosity and permeability in the halite mass and Li measurements in the brine that are related to actual content at the level of measurement, with minimal contamination by waters from outside the measured horizon.

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