

Lithium

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Mineral SUK Centre for sustainable mineral development

Definitions, mineralogy and deposits

Definitions and characteristics

Lithium is a silvery-white to grey alkali metal with a metallic lustre when fresh, but it is also highly reactive and in air quickly tarnishes to a dull silvery-grey and then black. It is the lightest metal, the least dense of all the elements that are not gases at 20°C and can float on water.

In common with the other alkali metals (sodium, potassium, rubidium, caesium) lithium is very soft, with a hardness that is less than talc (which has a hardness of 1 on Mohs scale) and can therefore be cut with a knife. In its elemental form, lithium reacts easily with water, albeit with less energy than the other alkali metals, and is potentially explosive. It is also inflammable in oxygen and may ignite when exposed to moist air. However, it is not found in nature in elemental form and its compounds are non-flammable.

Lithium has excellent electrical conductivity (i.e. low resistivity) and it is also the most electronegative metal, which is one of the properties that make it ideal for use in batteries. The addition of lithium imparts high mechanical strength and thermal shock resistance in ceramics and glass. Other physical properties are summarised in Table 1.

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).

Published information relating to lithium can be confusing because of the different terminology used to describe the quantities involved. Figures can be quoted as lithium content (Li), lithium oxide content (Li_2O , also known as lithia content) or lithium carbonate content (Li_2CO_3). Lithium also forms a wide range of chemical compounds and production quantities of these are often expressed as 'lithium carbonate equivalent' or LCE. Conversion factors between these various forms, and other common compounds, are shown in Table 2.

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Symbol	Li	
Atomic number	3	
Atomic weight	6.94	
Density in solid form @20°C	534	kg m ⁻³
Melting Point	180.54	°C
Boiling Point	1342	°C
Crystal Structure	Body centred cubic	
Hardness	0.6	Mohs scale
Electrical resistivity	9.5	m Ω cm
Thermal conductivity	85	W m ⁻¹ K ⁻¹

Table 1Selected properties of lithium.

Mineralogy

Lithium does not occur in elemental form in nature because of its reactivity. However, there are more than 100 known minerals that may contain lithium, although only a few of these are currently economic to extract. The most common lithium-bearing minerals found in economic deposits are shown in Table 3 and described briefly below. Lithium is also extracted from various types of brines and these are discussed further in the next section.

Spodumene

Spodumene (Figure 2) is the most abundant lithium-bearing mineral found in economic deposits. It occurs as prismatic, lath-shaped, crystals in granites and pegmatites often



Figure 1 Lepidolite in pegmatite from the Archaean Rgueïbat Shield, western Mauritania, specimen from the BGS collection, image number PJW0882, BGS © NERC.

			To convert to:	
To convert from:	Chemical formula	Lithium content	Lithium oxide content	Lithium carbonate equivalent
			Multiply by:	
Lithium	Li		2.153	5.323
Lithium oxide	Li ₂ 0	0.464		2.473
Lithium carbonate	Li ₂ CO ₃	0.188	0.404	
Lithium chloride	LiCI	0.163	0.362	0.871
Lithium bromide	LiBr	0.080	0.172	0.425
Lithium hydroxide mono- hydrate	LiOH.H ₂ O	0.165	0.356	0.880
Butyllithium	C₄HgLi	0.108	0.233	0.576

 Table 2
 Conversion factors for lithium and selected compounds.

Mineral name	Chemical formula	Lithium content (Li %)	Appearance (colour and lustre)
Spodumene	LiAISi ₂ 0 ₆	3.7	White, colourless, grey, pink, lilac, yellow or green; vitreous
Lepidolite	K ₂ (Li,AI) ₅₋₆ {Si ₆₋₇ AI ₂₋₁ O ₂₀ } (OH,F) ₄	1.39–3.6	Colourless, grey/white, lilac, yellow or white; vitreous to pearly
Petalite	LiAISi ₄ O ₁₀	1.6-2.27	Colourless, grey, yellow or white; vitreous to pearly
Eucryptite	LiAISiO ₄	2.1–5.53	Brown, colourless or white; vitreous
Amblygonite	LiAI[PO ₄][F,OH]	3.4–4.7	White, yellow or grey; vitreous to pearly
Hectorite	Na _{0.3} (Mg,Li) ₃ Si ₄ O ₁₀ (OH) ₂	0.54	White, opaque; earthy
Jadarite	LiNaSiB ₃ O ₇ (OH)	7.3	White; porcellanous

 Table 3
 The most common lithium-bearing minerals found in economic deposits.



intermixed with quartz. Spodumene has a hardness of 6.5 to 7 on Mohs scale and a density of 3.1–3.2 kg m³. It has a pronounced longitudinal cleavage and decomposes to kaolinite and montmorillonite on weathering. Some varieties, known as kunzite or hiddenite, are considered to be of gem quality (Kunasz, 2006; Garrett, 2004).

Lepidolite

The variability expressed in the general chemical formula in Table 3 stems from a structural complexity attributed to a mixture of polymorphs. Lepidolite (Figure 1), an uncommon form of mica that is found in pegmatites, has a hardness of 2.5–3 on Mohs scale and a density of 2.8–3 kg m⁻³. It has a lamellar cleavage, giving its crystals a book-type structure. Lepidolite can also contain potassium, rubidium and caesium, which may provide valuable by-products (Kunasz, 2006; Garrett, 2004).

Petalite

Petalite is a monoclinic mineral with two cleavage directions. It often occurs with lepidolite in pegmatites

Figure 2 Spodumene from the Walnut Hill pegmatite, Huntington, Hampshire County, Massachusetts, USA. (Author: Rob Lavinsky, iRocks.com – CC-BY-SA-3.0).

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and in some cases there is evidence that it alters to spodumene. Petalite has a hardness of 6 on Mohs scale and a density of approximately 2.4 kg m⁻³ (Kunasz, 2006; Garrett, 2004).

Eucryptite

Eucryptite was formerly an important ore of lithium, worked in Zimbabwe, but deposits are relatively rare and it is now of little economic importance. It has a hardness of 6.5 on Mohs scale and a density of 2.6 kg m⁻³ (Kunasz, 2006; Garrett, 2004).

Amblygonite

Amblygonite was also formerly extracted for lithium in Zimbabwe. Again deposits are uncommon and it is now of little economic importance. It has a hardness of 5.5 to 6 on Mohs scale and a density of approximately 3 kg m⁻³ (Kunasz, 2006; Garrett, 2004).

Hectorite

Hectorite is a trioctahedral smectite clay mineral formed from the alteration of volcaniclastic rocks by hydrothermal or hot spring activity. The lithium substitutes for magnesium within the lattice structure of the mineral. It has a hardness of 1–2 on Mohs scale and a density of 2–3 kg m⁻³. Although not currently extracted for lithium, it is expected to be developed in future. (Kunasz, 2006; Western Lithium, 2016; Bacanora Minerals, 2016).

Jadarite

A new mineral discovered in Serbia in 2007, jadarite is a monoclinic, white borosilicate mineral with a hardness of 4 to 5 on Mohs scale and a density of 2.45 kg m⁻³ (Stanley et al, 2007). It is not currently extracted for lithium but has the potential to be a significant source in the future (Mills, 2011).

Brine chemistry

The term 'brine' refers to any fluid containing a high level of dissolved solids. Usually these solids are composed of sodium (Na) and chloride (Cl⁻) (i.e salt), but also commonly contain calcium (Ca), potassium (K), magnesium (Mg) and carbonate (CO_3) (Rodinia Minerals, 2009).

Lithium is known to occur in many brines or waters, but usually at low concentrations. For example, seawater contains an average 0.18 ppm Li (from total dissolved solids of approximately 35 000 ppm). However, lithium content can be significantly increased, particularly in high temperature geothermal waters, as the element is leached or scavenged from surrounding rocks. To become economic, however, these lithium-bearing brines generally need to be further concentrated by evaporation. A selection of typical lithium-bearing brine compositions is shown in Table 4.

Deposits

Lithium is extracted from two main categories of deposits: minerals and brines. In terms of minerals, currently lithium is extracted only from pegmatite deposits but future sources are likely to include deposits of hectorite and jadarite. Extraction from brines primarily occurs from continental brine deposits, but extraction from geothermal and oilfield brines has been demonstrated in recent years, albeit not yet on a commercial scale. Key characteristics of these deposit types are set out below and summarised in Table 5. Selected locations are shown on Figure 3.

Major deposit classes and extractive operations *Pegmatites*

Pegmatites are defined as "essentially igneous rock, mostly of granitic composition that is distinguished from other igneous rocks by its extremely coarse but variable grain size or by an abundance of crystals with skeletal graphic,

	Clayton Val- ley, USA	Salar de Atacama, Chile	Salar de Hombre Muerto, Argentina	Salar de Rincon, Argentina	Zhabuye Salt Lake, China	Qaidam Basin Salt Lakes, China		
	All figures in weight per cent							
Li	0.02-0.04	0.11-0.31	0.05-0.06	0.03	0.05-0.10	0.01-0.03		
К	0.53–1.00	1.80-2.97	0.52-0.62	0.62-0.66	2.64-3.83	0.60-0.66		
Mg	0.03-0.06	0.82-1.53	0.05-0.09	0.28-0.30	0-0.001	0.47-3.51		
Са	0.02-0.05	0.02-0.04	0.05-0.09	0.04-0.06	0-0.01	0.02-0.42		
В	0-0.01	0.06-0.07	0.02-0.04	0.04	0.29-1.46	0.03-0.05		
Na	6.20-7.50	1.03–9.10	9.79–10.30	9.46–9.79	10.66–10.81	6.20-6.84		
CI	10.10-11.70	2.03-18.95	15.80–16.80	15.80	12.16-12.31	9.20-20.42		

Table 4Selected typical lithium-bearing brine compositions (Sources: Evans, 2014; Garratt, 2004; Pavlovic and Fowler,2004; King, 2010; Shengsong, 1986). Other elements and compounds may also be present.Li, lithium; K, potassium; Mg, magnesium; Ca, calcium; B, boron; Na, sodium; Cl, chlorine

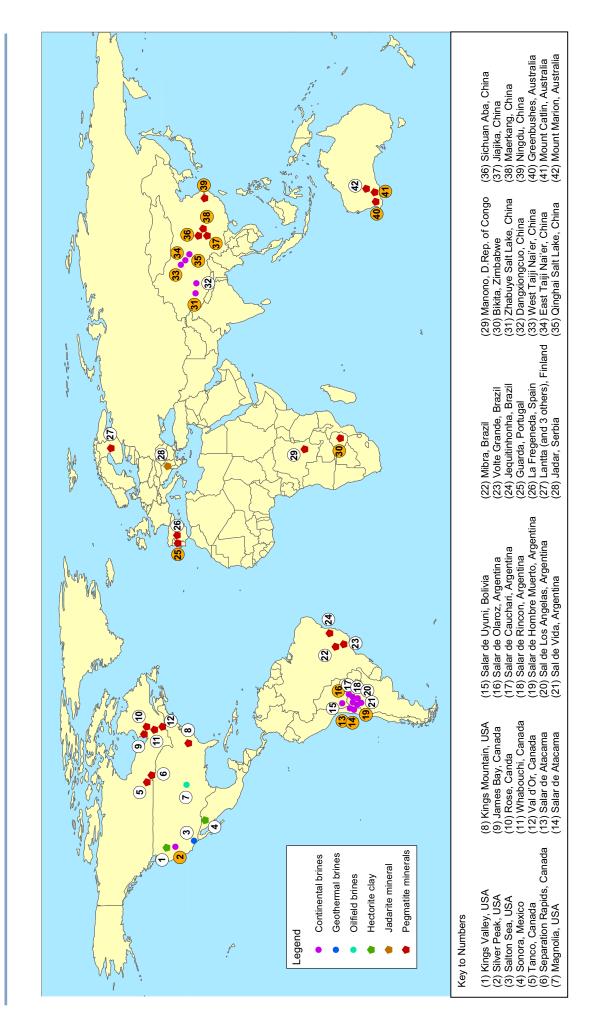


Figure 3 Location of selected lithium deposits. Labels coloured orange are the sites known or believed to be producing lithium, as at May 2016. (Some locations shown on the map are in production but not for lithium)

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or other strongly directional growth habits" (London, 2014). They typically form lenses, dykes or veins that are usually found close to, or in association with, large plutonic intrusions. The coarse grain-size of crystals observed in a pegmatite is largely controlled by the presence of fluxes and volatiles (for example boron, fluorine, chlorine or water), which decrease nucleation rates (i.e. a reduction in the number of nuclei available to form crystals), but increases rates of ion diffusion (i.e. allowing ions to migrate further within a crystal lattice). This results in the formation of fewer, larger crystals. Many pegmatites form by the extended fractional crystallisation of a fluid-rich, fertile (i.e. metal-enriched) parent magma.

Although pegmatites are not particularly unusual, lithiumbearing ones are relatively rare (Evans, 2014). Despite this they have been the predominant source of lithium for many decades and it is only the development of continental brine operations, particularly in South America, that has in recent years reduced the share of lithium supply sourced from pegmatites.

The origin of lithium in pegmatites, and the reason why some are enriched in lithium while others are not, has been the subject of research and debate for many years. Their formation processes are considerably more complicated than the relatively simple effects of fractional crystallisation from a granitic magma and they are likely to involve the melting of an enriched source material which ultimately defines the composition of the pegmatite, mixing of magmas and metamorphism (Norton, 1973; Stewart, 1978; O'Connor et al, 1991; Simmons & Webber, 2008; Shaw et al, in press). In addition, variations in pressure and temperature conditions during their formation, combined with the evolution in the composition of the magmas, determine what combination of elements are found in a pegmatite. A classification scheme for pegmatites in general identified five 'classes', which are subdivided into ten 'sub-classes', with some of these further subdivided into 'types' and even 'sub-types' (Černý & Ercit, 2005). Three of the identified 'sub-classes' are potentially lithiumbearing. Černý & Ercit (2005) also divide pegmatites into two 'families' according to the chemical composition; these are NYF (containing niobium, yttrium and REE, and fluorine) and LCT (containing lithium, caesium and tantalum).

The three largest lithium-bearing pegmatite deposits occur in North Carolina, USA, at Manono in the Democratic Republic of Congo (DRC) and at Greenbushes in Australia, although only the latter has produced lithium in recent years.

The lithium-bearing pegmatites in the Kings Mountain district of North Carolina, USA were originally identified as early as 1906 (Carpenter et al, 1995) but were only worked sporadically at first. From the 1950s mining became much larger in scale and for many years the region was the principal area for world lithium production. The pegmatites outcrop on the west flank of the Kings Mountain shear zone which separates the Inner Piedmont high-grade metamorphic rocks from the Kings Mountain belt where the rocks are metamorphosed to a lower grade. The ores are reported to contain an average of 1.5% Li₂O and the pegmatites also contain cassiterite (Carpenter et al, 1995). Undeveloped resources in the region are still believed to exceed 2.5 million tonnes of contained Li (Evans, 2014). However, the commencement of brine operations in South America, at lower production costs, resulted in the closure of both North Carolina's spodumene mines by 1998.

Although, the Manono pegmatite in the DRC is believed to contain in excess of two million tonnes of contained Li (Evans, 2014), it has only been worked in the past for cassiterite and columbite. The deposit is approximately five km long, up to 400 metres wide and the near-surface zoned pegmatite ore contains 10-25% spodumene (Garrett, 2004).

The world's largest operating mine for lithium minerals is at Greenbushes in Western Australia. Here the pegmatite is approximately five km in length and up to 300 metres wide. It lies within the Donnybrook-Bridgetown Shear Zone and intrudes rocks of the Balingup Metamorphic Belt in the south of the Yilgarn Craton, although it is largely obscured by Tertiary sediments and laterite. The pegmatite consists of five mineralogically distinct zones: a contact zone; a potassium feldspar zone; an albite zone; a mixed zone; and a spodumene zone (Ingham et al, 2012). Overall, spodumene represents 26 per cent of the total pegmatite, but in the spodumene zone it can be up to 50 per cent. The September 2012 resource estimate includes measured resources of 0.6 million tonnes at an average of 3.2% Li₂0, indicated resources of 117.9 million tonnes at 2.4% Li₂O and inferred resources of 2.1 million tonnes at 2.0% Li₂O (Ingham et al, 2012).

The first mining operations at Greenbushes began with the open pit extraction of tin in 1888 and this was followed in the 1940s by the production of tantalum. The mine's output of tantalum has expanded many times over the decades and the increasing demand by the 1990s led to the decision to extend the mining operations underground, which commenced in 2001. Lithium was discovered in the unweathered portion of the Greenbushes pegmatite in the late 1940s (Evans, 2014) but lithium mining did not commence until 1983. The lithium processing plant was upgraded in 2011/12 to a production capacity of 740 000 tpa (Ingham et al, 2012). The Greenbushes lithium operations are operated by Talison Lithium Pty Ltd, which is owned jointly by Chengdu Tianqi Industry Group (51%) and Albemarle Corporation (49%) via subsidiaries.

Also in Australia, Galaxy Resources commenced production at its Mount Cattlin mine in late 2010. Located in the Ravensthorpe greenstone belt, the pegmatite here is described as relatively flat lying, typically less than 30 metres below the surface, although deeper mineralisation has been identified, and up to 20 metres thick (Snowdon Group, 2010). The most recent resource estimate, dated March 2011, includes measured resources of 2.5 million tonnes at 1.2% Li_2O , indicated resources of 9.5 million tonnes at 1.06% Li_2O and inferred resources of 4.3 million tonnes at 1.07% Li_2O (Galaxy Resources, 2016). The mine was placed on care and maintenance at the end of July 2012 but restarted mining spodumene at the end of March 2016.

Other well known pegmatite deposits include those at Bikita in Zimbabwe and Tanco in Canada. The Bikita pegmatite has an exposed length of 1700 metres and variable width of up to 70 metres. This is a complex zoned pegmatite with possibly as many as 13 different mineral zones and considerable variation along its length (Černý et al, 2003). It also contains most of the major lithium minerals including spodumene, petalite, lepidolite, eucryptite and amblygonite (Von Knorring & Condliff, 1987). Historically it has been a major producer of lithium and has also been worked in the past for beryl, cassiterite and tantalum. Production in 2014 amounted to approximately 44 000 tonnes of lithium minerals at an average content of 4.2% Li₂O.

The Tanco pegmatite, part of the Bernic Lake group of pegmatites, in Manitoba, Canada (owned by the Tantalum Mining Corporation, a subsidiary of the Cabot Corporation) is another complex zoned pegmatite with over 100 different minerals present including petalite, spodumene, eucryptite and lepidolite. It is approximately 1520 metres long, 1060 metres wide and up to 100 metres thick but does not outcrop at the surface. Lithium production ceased in 2010 and the underground mine is now focused on extracting caesium (Cabot Corporation, 2001; Martins et al, 2013).

Lithium minerals are also extracted from pegmatites in the Jequitinhonha Valley of Minas Gerais State in Brazil

(mainly spodumene), at Gonçalo in Guarda, Portugal and at La Fregeneda in Salamanca, Spain (both mainly lepidolite). Several other locations are known to have lithium-bearing pegmatites (Figure 3), and a number of new projects are being developed.

Hectorite

Deposits of hectorite clay are rare but may result from at least three distinct geological processes: the alteration of volcanic ash or glass; precipitation from lacustrine waters; or the incorporation of lithium into existing smectite clay deposits (Asher-Bolinder, 1991). All three processes require an arid environment and are associated with alkaline waters, volcanic rocks and hot springs which are commonly depositing travertine or fine-grained silica (Zientek & Orris, 2005).

Although hectorite is known to occur in Arizona and is believed to be extracted in California (including at Hector from where the deposit type derives its name), it is not considered to be a lithium resource in these states and the clay is used in oil and gas drilling applications. Lithium Americas Corporation (formerly known as Western Lithium Corporation) is developing the Lithium Nevada project (formerly known as the Kings Valley Lithium Project) based on hectorite clay in the McDermitt Caldera complex close to the border between Nevada and Oregon. Five separate areas of lithium mineralisation have been identified here and the most recent resource estimate from 2011 includes measured resources of more than seven million tonnes at 0.457% Li, indicated resources of more than eight million tonnes at 0.435% Li and inferred resources of more than seven million tonnes at 0.416% Li, at a cut off of 4000 ppm Li (Schneider et al, 2012). A Preliminary Feasibility Study has been completed and a pilot plant has been established in Germany. In early 2015 the company commenced a commercial speciality clay business marketing hectorite and bentonite to the oil and gas drilling industry and later that year merged with Lithium Americas Corporation (Western Lithium, 2016). In March 2016 the company changed its name to Lithium Americas Corporation (Lithium Americas, 2016).

Resources of hectorite have also been reported at the Sonora lithium project, 11 km south of Bacadehuachi in the Sonora state of northwest Mexico. The resource statement of April 2016 reports 839 000 tonnes of contained lithium in the indicated category and a further 515 000 tonnes in the inferred category, within two distinct clay units (Pittuck and Lepley, 2016). A pre-feasibility study has been completed which proposes a two phase open-pit mine with lithium carbonate 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 (Bacanora Minerals, 2016)

Jadarite

Jadarite is a new mineral that has so far only been identified within the Jadar Basin of Serbia. The basin is composed of oil shales, dolomicrites, pyroclastic sediments and evaporites which are believed to have accumulated in a montane 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). It is currently believed that jadarite may be formed by an interaction between clastic sediment, either tuffaceous material or clay minerals, and brine, possibly of hydrothermal origin (Kesler et al, 2012).

Jadarite was discovered in 2007 by Rio Tinto and the Jadar deposit, near the town of Loznica, contains an inferred resource of 125.3 million tonnes at a weighted average of 1.8% Li_2O , in addition to an inferred resource of boron minerals. The Jadar project is currently at the prefeasibility stage which includes further research into the deposit, pilot-testing of recovery and processing methods, environmental studies and socioeconomic analysis (Rio Tinto, 2011). Other companies have commenced exploration for jadarite in the region.

Continental brines

These deposits occur in endorheic basins where inflowing surface and sub-surface waters are moderately enriched in lithium. Economic deposits of this type usually occur in areas where high solar evaporation results in a further increase in lithium concentration. Typically these basins contain salt lakes or salt pans and the lithium is often coproduced with other minerals such as potassium or boron (Evans, 2014).

Extraction of lithium chloride from Clayton Valley, Nevada, USA (where the current operation is known as Silver Peak) began in 1966. This playa lake covers an area of 72 km² with a closed drainage basin of 1342 km² (Munk et al., 2011). Average lithium contents at the time commercial extraction began were approximately 400 ppm, although these have subsequently declined (Garrett, 2004). The geological history of the area is complex including periods of compression and metamorphism followed by extension and faulting. High lithium values have been identified in volcanic tuffs, rhyolites and lacustrine deposits (Munk et al., 2011) but are believed to have been further concentrated by the action of hot springs flowing along the Silver Peak Fault (Garrett, 2004). Lithium-bearing brines are pumped from six distinct sub-surface aquifers, each with a slightly different geochemical signature. Munk et al (2011) concluded that the lithium in the brine resulted from a complex history which includes periods of evaporation, mixing of water sources and both halite and hectorite dissolution and precipitation.

One of the most significant regions for lithium-bearing continental brine deposits is the salt lakes and salt pans of the central Andes in South America, known locally as salars (Figure 3). Here a major subduction zone has resulted in the uplift of the Altiplano-Puna plateau and the formation of a volcanic arc. This has formed a series of endorheic basins bounded by volcanoes on the west and highlands on the east and divided from each other by volcanic rocks, block faulting or alluvial fans (Alonso et al, 1991). The area of internal drainage is reported to be approximately 400 000 km² and there are about 150 basins, with more than 100 salt lakes and pans (Ericksen and Salas, 1987). The arid climate in this region has led to the formation of evaporite deposits, such as halite and gypsum, because evaporation exceeds fluid inflow (Alonso et al, 1991). The precise nature of these evaporite deposits varies depending on the hydrological history of each basin. Additional variation is caused by changes to the clastic sediment content and by differing degrees of porosity, which in some cases is partly due to fractures in the evaporites. The reasons for the high lithium content in the brines associated with many of these basins are not clear. However, it is likely that the ultimate source of the element is the Altiplano-Puna Magma Body located at depth beneath the region (Houston et al, 2011).

One of the most notable continental brine deposits in this region, in terms of lithium extraction, is the Salar de Atacama in Chile. Production began in the southern part of this salar in 1984 with a second development in the northern part commencing in 1996 (Evans, 2014). This playa lake is one of the largest in the world, covering an area of approximately 3000 km² and with a drainage basin of approximately 11 800 km² (Garrett, 2004). The northern part is dominated by mud flats and small pools which encourage the precipitation of certain minerals thereby concentrating the brine and enabling pure halite to crystallise further south. The major conduit for the lithium appears to be the El Tatio geyser field to the north, which discharges geothermal fluids, with a reported content of 28–47 ppm Li, into the Rio Salado and from there into the salar via the Rio San Pedro. However, additional lithium is believed to enter the salar through subterranean water flow and from the small intermittent streams on the eastern flank. The lithium concentration varies between 1000–4000 ppm

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Li and averages over 1500 ppm at the two commercial extraction operations (Garrett, 2004).

Lithium is also extracted from the Salar de Hombre Muerto in Argentina, a playa lake of 565 km². The surface of this salar is partially flooded and partially dry but beneath this surface is a massive body of salt up to 50 metres thick. The lithium-bearing brine occurs mainly in the upper, more porous section of this salt body and typically contains 500–600 ppm Li, although concentrations in the range 190–900 ppm Li have been reported (Garrett, 2004).

In November 2014, production commenced at the Salar de Olaroz in Argentina (Orocobre, 2015), a salt lake that is approximately 25 km from north to south and 20 km from east to west at its widest point. It is located in the northern part of the Olaroz-Cauchari basin, which is approximately 6000 km² in area. The brine from this salar is reported to contain up to 1200 ppm Li, with a mean concentration of approximately 500 ppm Li (Houston and Gunn, 2011). Other parts of the same basin are incorporated into the separate Cauchari-Olaroz project operated by Minera Exar S.A., a subsidiary of Lithium Americas (now merged with Western Lithium). The feasibility study for this project describes proven reserves of lithium of 37 000 tonnes, probable reserves of 477 000 tonnes, measured resources of 576 000 tonnes and indicated resources of 1 650 000 tonnes, at a cut off of 354 mg/L (King et al., 2012). The company is examining options for funding the development of extraction facilities (Western Lithium, 2016).

At the Salar de Rincon in Argentina production commenced with a pilot plant in early 2011 (Evans, 2014). This playa lake is approximately 500 km² in area with a salt body covering 260 km². Lithium content of the brine is reported as 330 ppm (Pavlovic and Fowler, 2004).

Another significant area for the production of continental brines is the Tibetan plateau in China, where extraction takes place from the Zhabuye Salt Lake and the Xi Taiji Nai'er and Dong Taiji Nai'er salt lakes in the Qaidam Basin. The basins in the plateau were created during the formation of the Himalayas, an area with a complex history of faulting and deformation, as described by Zhuan et al (2011) as well as many others.

The Zhabuye salt lake is located in the western part of the Tibetan plateau, at an elevation of 4421 metres above sea level and is surrounded by mountains up to 6500 metres. It has both wet and dry areas, and the salt pan covers an area of more than 240 km². The area is both arid, with evaporation loss more than three times greater than pre-

cipitation, and cold with an average annual temperature of just 1°C (Zheng et al, 2007).

The Qaidam Basin, towards the north of the plateau, covers an area of 90 000 km², with a catchment area of approximately 250 000 km². It contains 28 separate salt lakes, in addition to brackish lakes, one freshwater lake and numerous dry playas (or salt pans). The salt lakes and playas cover more than a quarter of the total area of the basin. The climate is extremely arid with evaporation rates that are many times greater than precipitation. The Xi Taiji Nai'er (or West Taiji Nai'er) Lake and the Dong Taiji Nai'er (or East Taiji Nai'er) Lake are at around 2800 metres above sea level and have surface areas of 82 km² and 116 km² respectively. Located towards the centre of the basin these two lakes are aligned on a north-west trending zone which is reported to have greater lithium enrichment, mainly as a result of reduced levels of dilution from water inflow (Chen & Bowler, 1986; Shenasona, 1986).

Geothermal brines

Elevated levels of lithium, in the range of 12 to 350 ppm Li, have been reported in a number of geothermal areas including: Reykjanes, Iceland; Wairakei, New Zealand; Cesano, Italy; Alsace, France; Kyushu, Japan; and, in particular, the Salton Sea in California, USA. They have also been observed at deep ocean thermal vents such as those along the East Pacific Rise and in the North Fiji Basin (Garratt, 2004). Many of the continental brines extracted from salt lakes or from beneath salt pans, as described above, are likely to be enriched in lithium as a result of geothermal activity and it has been suggested therefore that the geothermal areas themselves could be a future source of lithium on a co- or by-product basis alongside renewable energy generation.

The Salton Sea Known Geothermal Resource Area in California, USA has a total of 11 geothermal power stations, generating more than 370 MW of electricity. The first 10 plants opened between 1982 and 2000; the 11th plant opened in 2012 and further plants are planned (CalEnergy, 2012; Energy Source, 2012). Naturally-occurring water heated underground by a high geothermal gradient in host rocks is brought to the surface by drilling and converts to steam due to the reduced pressure. This steam is used either directly to turn turbines which generate the electricity or is used to heat other water to steam for the same purpose. Once cooled the resulting water is reinjected through additional wells.

The water used in the Salton Sea area's geothermal plants contains various metals such as lithium, manganese and zinc, with lithium values reported in the 100–200 ppm

range. The production of steam in a geothermal power station increases the concentration of dissolved constituents, such as lithium, in waste waters thus potentially enabling mineral by-production (Maimoni, 1982; Kesler et al, 2012). Simbol Materials entered into an agreement with Energy Source to use the brine from their geothermal power plant as a source for the lithium extraction facility (Germani, 2012). Simbol commenced operations at its demonstration plant, using a proprietary process, in 2010, opened a high purity lithium carbonate plant in 2011 and demonstrated the production of lithium hydroxide through electrolysis in 2013 (Simbol Materials, 2014). Unfortunately the company was effectively closed down in early 2015 (Roth, 2015).

Oilfield brines

The process of extracting oil and gas from wells will inevitably also extract water or brine from the underground formations. In a few oilfields these waters or brines have a medium to high concentration of lithium together with other elements such as bromine. In most cases the water or brine produced in oilfields is considered a waste product and it is usually reinjected underground in order to avoid subsequent pollution risks.

Brine from the Smackover oilfield in Arkansas, USA has one of the highest concentrations of lithium with contents reported to be up to 500 ppm Li from depths of 1800–4800 metres below the surface (Garratt, 2004). The oil and brine are pumped from the Smackover Formation, which consists of oolitic limestone up to 213 metres thick, overlying a salt basin containing thick layers of halite, anhydrite and gypsum. Collins (1976) concluded that the lithium in the waters from the Smackover Formation originated from volcanic rocks of Triassic age in the Gulf Coast area, but noted that it must have been concentrated by the repeated influx of spring or sea water and several periods of evaporation. This brine has been used as a source of bromine at the Magnolia facility in Arkansas since 1969. The Albemarle Corporation, which owns the Magnolia plant, has developed proprietary technology for extracting lithium from the same brine in a laboratory setting, and through a pilot plant, to produce lithium carbonate (Albemarle Corporation, 2011).

Extraction methods and processing

Lithium is produced from two sources: brines and hard rock (pegmatites). Historically lithium was entirely sourced from traditional hard rock mining but more recently extraction from brine deposits has become increasingly common because, in general, this source has lower production costs.

Extraction methods

Extraction methods for lithium vary according to the type of deposit. Hard rock deposits are mined using similar techniques to many other metals using surface (open-pit) or sub-surface (underground) methods. Brines, because they are liquids, are extracted by pumping from wells.

Hard rock deposits

Surface mining

Open-pit mining methods are used for deposits that are near to the surface (usually less than 100 metres). This generally involves removing the overburden, digging the ore or blasting with explosives, then removing the ore by truck or conveyor belt for stockpiling prior to further processing. Material is removed in a series of layers, leaving horizontal benches at the sides of the surface mine to enable the vertical 'faces' to be worked at a safe height. This gives the surface mine a characteristic 'stepped' appearance. The height of the working faces depends on the stability of the rock being worked.

	Deposit type	Brief description	Typical grade	Examples			
Minerals	Pegmatites	Coarse-grained igneous rock formed during late-stage crystallisation of magmas	1.5–4% Li ₂ 0	Greenbushes, Australia; North Carolina, USA; Bikita, Zimbabwe			
	Hectorite	Lenses of smectite clay in association with volcanic centres	Kings Valley, Nevada, USA; Sonora, Mexico				
	Jadarite	Altered sediments in an enclosed basin	Altered sediments in an enclosed basin 1.5% Li ₂ O				
Brines	Continental	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	Elevated levels of lithium contained in steam at geothermal power stations	0.01–0.035% Li	Salton Sea area, California, USA			
	Oilfield	Elevated levels of lithium contained in waters or brines produced in oilfields	0.01–0.05% Li	Smackover oilfield, Arkansas, USA			

Table 5 Key features of lithium deposit types.

Surface and underground mining are sometimes combined at a single mine, and may take place simultaneously in order to access shallow and deeper parts of an ore body. For example, both methods have been used at Talison Lithium's Greenbushes Mine in Western Australia (Figure 4) and the Bikita Mine in Zimbabwe (Garrett, 2004).

The Greenbushes Mine was developed for lithium extraction in 1983 and is the world's leading producer of hard rock lithium minerals (Talison Lithium, 2014). When production began the deposit was overlain by an average of 20 metres of weathered clay-bearing material that was initially extracted using front-end loaders or excavators (Garrett, 2004). Spodumene ore is mined from the unweathered zones in the pegmatite that are exposed in open pits. The rock is drilled and then blasted on either five or ten metre benches using explosives. The broken material is removed using a hydraulic excavator and dump trucks and the ore is taken to two nearby processing plants; one producing low iron concentrates for the ceramics and glass industries and the other producing lithium concentrates suitable for chemicals. The waste material is used within the site as part of the company's rehabilitation plan (Talison Lithium, 2014).

The Bikita Mine is one of the world's oldest lithium mineral producers and extracted mainly lepidolite and petalite, as well as amblygonite in smaller quantities. Open-pit operations at the mine included two pits: the Bikita Pit, which was developed for lepidolite, and the Al Hayat Pit for petalite. Overburden, consisting of weathered greenstone rock with feldspar, quartz and mica, was removed at an average ratio of 1:1 overburden:ore. The ore was transported to the processing plant by narrow gauge railway (Garrett, 2004).

Underground mining

Underground mining methods are used when openpit mining is, or becomes, prohibitively expensive. For example, if the deposit is too deep or if its form is such that underground mining is more efficient. Underground access is through an adit (horizontal), a shaft (vertical) or a decline (at an angle). Ore is mined in stopes on a number of roughly horizontal levels at various depths below the surface.

Early operations at the Bikita Mine used underground methods where a 610 metre long adit was used to access the workings. Wagons were loaded through overhead chutes and then taken to the processing plant by diesel locomotives (Garrett, 2004).



Figure 4 Aerial photograph of Greenbushes Mine, Western Australia. Photograph supplied by Albemarle Corporation. © Hugh Brown 20121203.

The pegmatite at Cabot Corporation's Tanco Mine in Manitoba, Canada, is accessed by both a shaft and a 20° decline from the surface and is mined using the room and pillar underground mining method (Cabot Corp, 2001). This is where mining progresses in a near horizontal direction by opening multiple stopes or rooms leaving pillars of solid material for roof support. Ore is blasted using explosives then transported to the shaft using an underground rail system, dump trucks or a conveyor belt. Old workings are backfilled with waste material in some mines to improve ventilation by forcing air to travel through only those areas that are being worked, as well as providing more roof support.

Lithium-bearing clay deposits

Lithium-bearing clays (e.g. hectorite) are generally found near to the surface so open-pit methods are likely to be used for their extraction. However, as they are relatively soft materials, it is likely that no blasting will be necessary. The preliminary feasibility study for Lithium America Corp's Lithium Nevada project envisaged the mine working on a single bench, due to the shallow depth of the deposits, with a 41° maximum slope angle for the pit walls and a maximum slope height of 90 metres. Its calculations are based on using a surface miner with a rotating cutting drum and short feeder conveyor directly loading dump trucks, although a hydraulic excavator may be required to remove overburden (Schneider et al, 2012).

Lithium brines

Lithium-bearing brines are found underground in porous rocks at varying depths and with varying porosity. To access these brines wells, or boreholes, are drilled into the brine aquifer and pumps are used to bring the liquid to the surface. The number, location and spacing of these wells will depend on the characteristics of the brine aquifer, such as its geometry, size, porosity, depth and the required flow rate of the brine.

In general, figures for these parameters are not published. However, Garrett (2004) quotes the Clayton Valley location in Nevada, USA as having 30 wells in 1969 with a flow rate that was approximately 500 litres per second, while SQM at the Salar de Atacama had 40 production wells in the late 1980s with a flow rate that equated to more than 1400 litres per second. It is not clear whether these rates are continuous or only for short periods of time. Figures quoted by Orocobre, when the evaporation ponds at their Salar de Olaroz project were in the process of being filled, indicated a flow rate of 180 litres per second with the possibility of increasing this to 220 litres per second with the addition of larger pumps for their southern well field (Orocobre, 2014). For geothermal or oilfield brines the extraction of lithium would be a by- or co-product of existing operations and consequently the well spacing and flow rates would usually be determined by the requirements of those other operations.

Processing

Hard rock deposits

The first phase of processing the lithium ore involves physical beneficiation to increase the lithium content. Concentration is normally undertaken at, or close to, the mine site and involves crushing the ore and separating lithium and gangue minerals, using a range of physical and chemical processes. The concentrate then undergoes chemical beneficiation to recover the lithium.

Physical beneficiation

After mining, the lithium ore is crushed and the lithium minerals separated on the basis of their physical, electrical and magnetic properties to form a concentrate. Physical separation processes used include wet and dry screening and separation by gravity, magnetic, electrostatic and magnetohydrostatic methods depending on the properties of the ore and gangue materials. Further lithium concentration is achieved by froth flotation, dense media separation (DMS) or a combination of the two methods (Grammatikopoulos et al., 2011).

Froth flotation involves using water, chemicals and compressed air to separate the lithium minerals. First water is added to the powdered ore to produce a suspension. Air is blown upwards through the tanks then chemicals are added which make specific minerals water repellent and cause air bubbles to stick to their surfaces. Consequently, these minerals collect in a froth at the surface and are removed. DMS uses heavy liquids of a suitable density, so that the minerals lighter than the liquid float and the denser ones sink (Wills, 1997). If the deposit is coarse grained, flotation may not be necessary and a concentrate can be produced using only gravity separation methods (Evans, 2014).

At the Greenbushes mine (Figure 5) the ore is put through four stages of crushing (utilising one jaw crusher and a series of cone crushers) before entering one of two separate processing plants. The Technical Grade Plant (TGP) is fed with spodumene containing less than 0.1 per cent iron oxide which enables the production of a low iron concentrate for the ceramics and glass industries. After wet grinding in two ball mills the material is treated in a series of gravity, magnetic separation and flotation stages and then filtered and dried (Ingham et al, 2012).

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Figure 5 Processing plant at Greenbushes Mine, Western Australia. Photograph supplied by Albemarle Corporation. © Hugh Brown 20121203.

The Chemical Grade Plant (CGP) at Greenbushes treats the ore with higher iron content to produce concentrate suitable for the manufacture of lithium carbonate and other chemicals. This processing circuit includes further crushing, gravity separation and flotation (Ingham et al, 2012). During these processes the lithium is separated from heavy minerals, such as cassiterite and tantalite, by gravity, from quartz and feldspar by flotation, from iron and apatite by acid washing and from para-magnetic minerals, such as tourmaline, by high-intensity magnetic separation (Garrett, 2004; Ingham et al, 2012).

A typical concentrate suitable for lithium carbonate production will generally contain between 6-7% Li₂O (75–87% spodumene) whereas a higher grade concentrate used in ceramics and other applications that require particular chemical specifications contains about 7.6% Li₂O and has lower iron content (SGS, 2012).

Chemical processing

Following physical beneficiation to produce a lithium concentrate, subsequent processing is required to produce lithium chemicals or lithium metal. Many different methods have been suggested to recover lithium from its ores but the most commonly used method is the acid leaching process.

Naturally occurring spodumene (α -spodumene) has a monclinic structure and in this form is chemically unavailable to leaching. Therefore the first stage of both the acid and carbonate leaching methods is to convert it to β -spodumene (which has a tetragonal crystal lattice) by heating in a kiln to 1050°C for about 15 minutes causing a phase transformation. The roasting causes the crystal lattice to expand making the mineral less dense so the lithium can be chemically extracted (Grammatikopoulos et al., 2011).

Following conversion to β -spodumene, the first stage of the acid leaching process is to roast a mixture of finely ground spodumene and sulphuric acid at 250°C to form lithium sulphate. This is followed by a leaching step to separate the lithium. During the sulphation and leaching, impurities such as iron, aluminium and magnesium are also converted to the sulphate form so are leached together with the lithium (Anzaplan, 2012). Removal of these impurities is achieved by dissolution in water of the lithium sulphate followed by liquid-solid separation through filtration, producing a lithium sulphate solution with trace levels of magnesium and calcium as the only significant impurities (Grammatikopoulos et al., 2011). The purified lithium sulphate solution is treated with sodium carbonate to precipitate insoluble lithium carbonate. This product is dried before being sold or used by the producer as feedstock in the production of other lithium compounds (Ober, 1996). Lithium carbonate grades of up to 99.3% can be achieved using this method but for battery grade (99.5% Li₂CO₃) further processing such as bicarbonation is required (Grammatikopoulos, 2011).

An alternative method, known as carbonate leaching, involves first combining the β -spodumene concentrate with water to make a fine-grained slurry. This mixture is then reacted with sodium carbonate at 215°C and 2140 kPa in a pressure vessel and carbon dioxide is added to convert the insoluble lithium carbonate into the more soluble bicarbonate. With appropriate reaction conditions, contaminants such as sodium, aluminium and iron are precipitated out at this stage. Lithium carbonate product is then precipitated by driving off the excess carbonate, which is recycled in the process (Anzaplan, 2012). Both routes are shown schematically in Figure 6.

An alternative processing method is to leach the spodumene with lime (CaOH₂). In this process the spodumene ore is mixed with finely ground limestone and heated in a kiln to 900 to 1000°C. During this process the limestone is calcined to form lime and the spodumene changed from the α to β form (as in the acid and carbonate leaching processes). The lime then reacts with the β -spodumene to form dicalcium silicate and lithium oxide. The resulting clinker is crushed and milled and leached with hot water forming lithium hydroxide which is separated, washed and dried as a final product. The lithium hydroxide can be converted to lithium chloride by reacting it with hydrochloric acid (Garrett, 2004; IOES, 2012).

Lithium-bearing clays

The preliminary feasibility study technical report for the Lithium Nevada project proposes a two-stage process for extracting lithium from hectorite clays. The dry ore preparation stage involves crushing and grinding of the ore and two reagents, anhydrite and dolomite, which are then mixed and combined in a granulator. The resulting granules would be dried, calcined and then cooled. The second stage, a wet recovery process, would involve leaching the calcine with water at 70°C to create a brine from which calcium, potassium sulphate, lithium carbonate and sodium sulphate would be precipitated in turn. The lithium carbonate would be precipitated following the addition of sodium carbonate and the resulting crystals

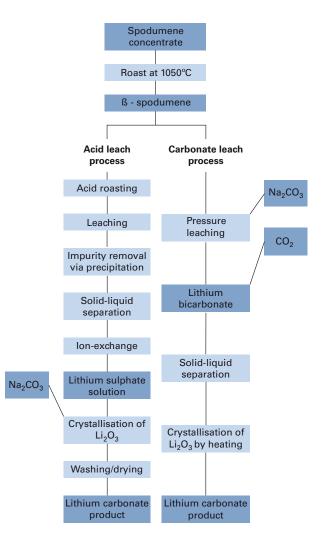


Figure 6 Generalised flow diagram of the acid and carbonate leaching processes for chemical beneficiation of spodumene concentrate.

would be washed, filtered and dried before packing. The lithium recovery rate is estimated to be 87.2% by this route (Schneider et al, 2012).

Continental brine deposits

The methods used to process brines to extract lithium will vary depending on the particular chemistry found at each deposit (Evans, 2014). However, the first step will always involve concentrating the brines, because even the higher-grade brines contain only very low concentrations of lithium. For continental brine deposits this frequently takes place by solar evaporation in a series of surface ponds (Figure 7). Lithium is more soluble than other elements found in the brines and, therefore, compounds such as sodium chloride, potassium chloride or calcium sulphate will precipitate first leaving the brine increasingly concentrated in lithium. Eventually the lithium itself will precipitate as lithium chloride but often the concentrated brine is removed for further processing before that stage. The

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Figure 7 Aerial photograph of a lithium brine operation in the Salar de Atacama, Chile. Photograph supplied by Albemarle Corporation. © 2013 Haroldo Horta.

evaporation process must be carefully monitored to avoid the precipitation of undesirable forms of these compounds, such as potash in the form of carnallite rather than as sylvinite and lithium in the form of a complex salt rather than a simple chloride (Evans 2014).

To make the solar evaporation process economically effective, the pond area must be large and as free from leakage as possible. The ponds can be either sealed with clay or lined with an impermeable plastic membrane. High rates of evaporation are also essential and this is dependent on the amount of solar radiation, humidity, wind and temperature. These factors vary greatly and can have an impact on the pond size, final brine concentration, operating costs and treatment methods (Garrett, 2004).

The brine is pumped through a series of evaporation ponds, as it becomes more concentrated in lithium. In simplified terms the series of ponds is (Evans, 2014):

1. Sodium chloride (common salt) is precipitated first. This can be harvested as a by-product if required.

- 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 sylvinite) is precipitated. These 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). It is then transferred to a recovery plant.

This brine may also be enriched in boron and magnesium. The boron is removed by solvent extraction using kerosene and processed to produce borates and boric acid by-products (Harben and Edwards, 1997). Magnesium has to be removed from the brine as it increases the processing costs of producing lithium carbonate (Evans, 2014). This is done by first adding sodium carbonate to precipitate magnesium carbonate. Lime is then added to precipitate magnesium hydroxide (Harben and Edwards, 1997). The lithium-rich brine is treated with sodium carbonate to precipitate a lithium carbonate slurry. This is filtered then washed with water to remove any residual sodium chloride. Finally this is dried leaving a >99% pure lithium carbonate product. Brines that are not used are injected back into the salars (Harben and Edwards, 1997; Kunasz, 2006).

As previously mentioned, the particular extraction method used varies between deposits. At the Salar de Hombre Muerto in Argentina the extraction process is less reliant on solar evaporation and instead an ion-exchange process is used to selectively extract lithium chloride. At the Salar de Rincon, after a first set of evaporation ponds has raised the lithium content to 2.5 grams per litre, the brine is transferred to a reactor where it is treated with hydrated lime and sodium sulphate in order to precipitate magnesium hydroxide and calcium sulphate. The brine is then pumped to a second set of solar evaporation ponds for further concentration of the lithium (Evans, 2014).

Co-products, such as potash and boron minerals, can also be produced from lithium-bearing brines (Figure 8). The co-products can be very significant contributors to the overall project economics, and in certain cases can significantly offset the cost of producing lithium (Rodinia Lithium, 2011). At the Salar de Atacama, for example, Rockwood Lithium produces potassium chloride (potash) and bischofite (a hydrous magnesium chloride mineral) as well as lithium carbonate and lithium chloride, while SQM produces potassium chloride, potassium sulphate and boron in addition to lithium carbonate (Rockwood Lithium, 2016; Garrett, 2004) Rockwood Lithium is a business unit of Albemarle Corporation.

Other types of brine

The details of processes used to extract lithium from geothermal or oilfield brines are proprietary and have not been published. Simbol Materials reported that its technology used by-products from its geothermal plant, such as carbon dioxide, waste water and condensate, to extract lithium, manganese and zinc (Simbol Materials, 2014). Albemarle announced in 2011 that it had developed new technology to recover lithium from its existing Magnolia bromine facility and was using a pilot plant to optimise the process (Albemarle, 2011).

Further processing

A wide variety of lithium compounds is commercially available although lithium carbonate is the most widely used and accounts for more than 90 per cent of consumption. Other forms of lithium with important industrial uses include lithium hydroxide, butyl-lithium, lithium metal and lithium chloride (Evans, 2014). The majority of the available compounds are obtained by processing lithium carbonate. The notable exception to this is the production of lithium metal and its derivatives (Evans, 2014).

Lithium metal is produced by the electrolysis of a mixture of molten lithium chloride and potassium chloride (usually 40–60% LiCl; Garrett, 2004). Anhydrous lithium chloride is

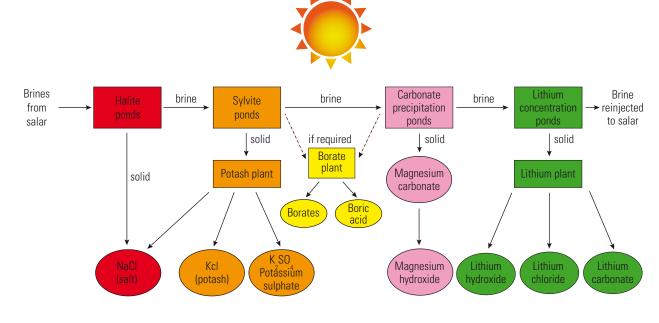


Figure 8 Generalised process for lithium extraction from brine deposits, with associated co-products. N.B. Sequence and exact chemicals produced vary according to each deposit (adapted from Mills, 2010).

the cell feed and the potassium chloride acts as the solvent and supporting electrolyte. The electrolysis cell has a central steel cathode where molten lithium is produced and graphite anodes where the chlorine evolves. The cell may have an exterior ceramic or other insulation. A bellshaped structure is present above the cathode to collect the rising molten lithium and prevent it from reacting with the chlorine gas (Kipouros and Sadoway, 1998). As the lithium flows from the cell, it is poured into ingots and allowed to cool in an inert atmosphere (Garrett, 2004).

Environmental implications

This section provides a brief overview of the main environmental interactions that arise during the life cycle of lithium. The two methods of obtaining lithium (hard rock mining and brine extraction) can have different impacts but also several that are similar, as shown in Table 6.

Toxicity

Lithium is not considered to be toxic to humans, and is used in controlled doses to treat some neurological disorders. However, long-term use or large doses can cause a range of problems including dehydration, diarrhoea, vomiting, blurred vision, tremor, slurred speech, drowsiness, confusion, muscle twitches, fits or unconsciousness (NHS, 2013).

Specifications and uses

Specifications

As described previously, lithium does not occur as a native metal because it is so reactive but pure lithium metal can

be manufactured from chemical compounds. In addition, there are a large number of compounds that contain lithium, some of which occur naturally while others are manufactured in processing plants. The most important of these are:

Lithium oxide (Li₂O)

Lithium oxide, also known as lithia, is an inorganic chemical compound formed by the reaction of lithium atoms with the oxygen in air. It is a white solid that has a density of 2013 kg m³ and a melting point of 1438°C. It reacts with water and steam to form lithium hydroxide. Many mine operators working deposits of lithium minerals will quote their grade figures in terms of the content of lithium oxide.

Lithium carbonate (Li₂CO₃)

Lithium carbonate is an inorganic chemical compound which has a density of 2110 kg m⁻³ and a melting point of 723°C. It has a relatively low solubility in water and this can be exploited in order to extract lithium from minerals and brines. Lithium carbonate is produced from lithium chloride in fluids by the addition of sodium carbonate followed by washing with water to remove the sodium chloride that forms. Lithium carbonate is the precursor that is most frequently used to produce other lithium compounds and products. It is sold in a variety of grades for different uses depending on purity and particle size distribution (Evans, 2014).

Lithium chloride (LiCl)

Lithium chloride is the most common lithium-bearing compound found in brine operations. It is a white solid that has a density of 2068 kg m^{-3} and a melting point of 605°C. It

Life cycle stage	Hard rock	Brine			
Mining or extraction	Energy usage (for extraction and transport machinery, crushing, processing); infrastructure development; visual impact; noise; dust; traffic movements; removal of soils and disruption to ecosystems; water usage; waste products (e.g. gangue, oil and lubricants from machinery); mine reclamation requirements. Under- ground mines may also have subsidence or impacts on hydrogeological systems (groundwater).	Lower energy usage if solar energy used to con- centrate brines but energy still needed to operate pumps and machinery; infrastructure development; visual impact; noise; dust; traffic movements; risk of ecological damage to the salar; water usage in pro- cessing stages; potential for chemicals to leak from evaporation ponds; waste products (although a large proportion will be salt that can be safely deposited on the surface of a salar).			
Processing and manufacturing	Energy usage to operate processing and manufac- turing plants; use of acid or other chemicals for leaching; roasting involves heating in a kiln to high temperature which is likely to involve emissions to air; removal of impurities may lead to waste products; water usage; supplies of consumables; transportation.	Energy usage to operate recovery equipment; use of chemical compounds required to separate impurities or to operate an ion-exchange process; some stages may require heating or other processes that could lead to emissions to air; water usage; disposal of waste products; transportation.			
End use	The use of lithium in glass and ceramics reduces the melting point of compounds and thereby reduces the energy requirements of these processes. The use of lithium in batteries has also reduced their weight to energy ratio and thus enables fuel and energy savings. Electric vehicles or hybrid vehicles that use lithium-ion batteries have the potential to significantly reduce carbon emissions.				

 Table 6
 Overview of environmental interactions in the lithium life cycle.

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can be produced from lithium carbonate by treating it with hydrochloric acid. Lithium chloride is the chemical form typically used to produce lithium metal.

Lithium bromide (LiBr)

Lithium bromide is produced from lithium carbonate by treatment with hydrobromic acid. It is a white solid with a density of 3464 kg m⁻³ and a melting point of 552°C. It is extremely hygroscopic, which means that it attracts and holds water molecules, making it very useful as a desiccant particularly in air conditioning systems.

Lithium hydroxide (LiOH)

Lithium hydroxide is an inorganic compound which is available in its anhydrous form or as a monohydrate with the chemical formula of $LiOH \cdot H_2O$. It is produced by a chemical reaction between lithium carbonate and calcium hydroxide. The anhydrous form has a density of 1460 kg m⁻³ and the monohydrate form has a density of 1510 kg m⁻³. Both forms have a melting point of 462°C.

Lithium metal (Li)

Lithium metal is produced by electrolysis from a mixture of lithium chloride and potassium chloride.

Uses

Lithium is probably most familiar in everyday use in the lithium-ion batteries that power modern society's mobile phones and other portable electronic devices. However, lithium has a wide variety of other uses and historically greater quantities have been used in the ceramics and glass industries. The principal uses for lithium are shown in Figure 9. Although the relative proportions of these categories change with time, and vary for different regions of the world, Figure 9 shows the most recently published figures on a global scale.

Ceramics and glass

In 2015, 32 per cent of total lithium consumption was in the ceramics and glass sectors. Lithium oxide is used as a flux in the ceramics and glass industries because it reduces the melting point and viscosity of silica-based compounds, thereby saving energy and reducing costs for producers. As lithium has a low coefficient of thermal expansion (i.e. it expands little as temperature rises), lithiumcontaining glass or glazes on ceramics are more resistant to higher temperatures and enable products to withstand sudden changes in temperature. Glass containing lithium is also more resistant to chemical attack and has improved hardness and shine (SQM, 2012). Lithium combined with copper creates blue coloured glazes, and when combined with cobalt produces pink glazes for ceramics.

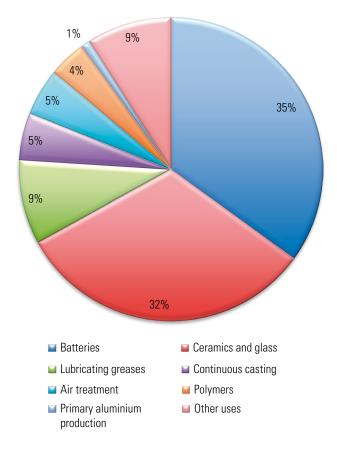
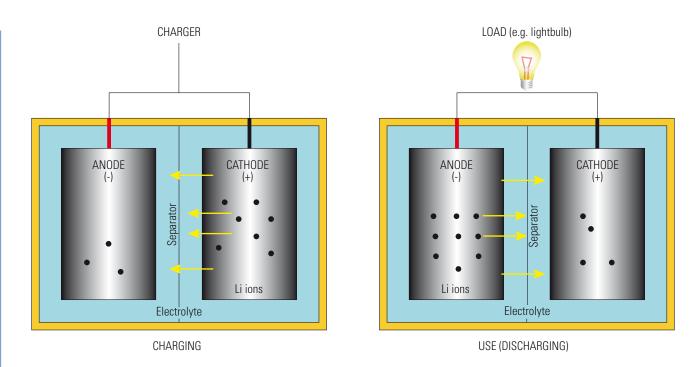


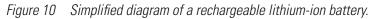
Figure 9 Global uses of lithium (data sourced from Jaskula, 2016).

Batteries

Of total lithium consumption in 2015, 35 per cent was used in batteries. Lithium is used in several different types of batteries, both non-rechargeable and rechargeable. In non-rechargeable forms (also known as disposable batteries) lithium metal or compounds are used for the anode. These batteries have a longer life than most other types of disposable battery but tend to be more expensive. They are often used for applications where long-life is important, for example in medical implanted devices such as pacemakers. They are also often used in watches, clocks and cameras where they have the advantage of reduced size compared to other battery types.

Rechargeable batteries are frequently of the 'lithium-ion' type. In these batteries the lithium is present in the electrolyte and sometimes also as the positive electrode (or cathode). Lithium ions move from the negative electrode, through the electrolyte to the positive electrode during use or discharge, and move in the opposite direction during charging (see Figure 10). The negative electrode (or anode) is typically made of carbon in the form of graphite. The positive electrode can be lithium cobalt oxide, lithium iron phosphate, lithium manganese oxide or a non-lithiumbearing substance.





Lithium-ion batteries have advantages over other types of rechargeable battery because in general they are lighter, they have a high energy density (i.e. they produce more energy per unit of weight), they hold their charge better and they have no 'memory effect', which means they do not have to be completely discharged before recharging. However, they are more susceptible to fluctuations in temperature and they will be ruined if completely discharged. The latter means that a lithium-ion battery pack will also contain a tiny computer to manage the battery and this makes them more expensive than other forms. Safety concerns have also been raised because there is a risk of fire if lithium-ion batteries overheat, a problem that caused the temporary grounding of the Boeing 787 Dreamliner aeroplane in January 2013 (Naik, 2013). However, this risk can be controlled with careful management that prevents short circuits or overheating.

Lithium-ion batteries are used for numerous applications including mobile phones, laptop computers, cameras, and many other consumer electronics, electric vehicles, electricity grid-scale storage and aerospace.

Lubricating greases

A lubricating grease is a type of lubricating fluid that has been combined with a thickening agent which ensures the lubricant is more easily retained where it is needed. Lithium hydroxide, when heated with a fatty substance, produces a lithium soap grease which is one of the most commonly used of all lubricating greases due to its good performance and cost effectiveness (Verdura et al, 2003). Approximately nine per cent of lithium consumption was for this purpose in 2015.

Air treatment

Lithium bromide and lithium chloride are both hygroscopic and are used as desiccants for gas streams, for example in air conditioning systems. Lithium hydroxide and lithium peroxide are used to remove carbon dioxide in enclosed spaces such as submarines and spacecraft by converting it to lithium carbonate. Lithium peroxide is particularly useful in these applications because it releases oxygen during the process.

Metallurgical

Metallic lithium is used as a flux in welding or soldering because it promotes the fusing of other metals and at the same time it absorbs any impurities. Lithium is also alloyed with aluminium, cadmium, copper or manganese in the manufacture of specialised aircraft parts.

Polymers

Organolithium compounds, including butyllithium, are used in the production of polymers and for other similar chemical uses. In these uses the lithium compounds are usually reagents, catalysts or initiators. These chemical processes are used in the production of synthetic rubber and plastics.

Pharmaceuticals

A number of lithium compounds, including lithium carbonate, are used in medicine as mood-stabilising drugs or for the treatment of bipolar disorder. Lithium is sometimes used, in conjunction with other substances, for other psychiatric disorders and has also been used for a range of non-psychiatric illnesses. However, there are concerns that using lithium for certain non-psychiatric conditions can be ineffective or even harmful (Mohandas and Rajmohan, 2007).

Primary aluminium production

Primary aluminium is produced by the electrolytic reduction of alumina which is dissolved in a cryolite bath. The addition of lithium carbonate to this bath reduces its melting point, thereby saving both energy and cost.

Other uses

If artificially grown as a crystal, lithium fluoride is clear, transparent and has a low refractive index which means it is suitable for use in infra-red or ultra-violet optics. Lithium fluoride is also sometimes used in the focal lenses of telescopes. Lithium niobate is used in optics and telecommunications. Metallic lithium and lithium hydrides are used as high energy additives in rocket propulsion. Certain lithium isotopes are also used in nuclear reactors and in nuclear weapons.

New technologies and expanding markets

The most significant growth in the markets for lithium over recent years has been in batteries and this is expected to continue, especially if the demand for electrically-powered cars continues to escalate (Stafford, 2016).

Most portable electronic devices used in the modern world have a rechargeable lithium-ion battery. In an 'ordinary' mobile phone the battery contains between 1 gram and 3 grams of 'lithium carbonate equivalent' (LCE), while a smartphone contains between 2 grams and 3 grams (SignumBOX, 2012). The gradual switch from 'ordinary' mobile phones to 'smart' phones will therefore require more lithium, in addition to the greater demand created by the dramatic increase in the use of mobile phones generally. The use of portable computers is also increasing significantly. A typical laptop computer requires a lithium-ion battery that contains 30-40 grams of LCE, while the battery for a tablet computer requires 20–30 grams of LCE. Cordless power tools have also been developed, and these use a lithium-ion battery that contains 40–60 grams of LCE (SignumBOX, 2012). Other devices that may use lithium-ion batteries include cameras, portable video recorders, MP3 players, cordless telephones, wireless games consoles etc. Consequently, the demand for lithium for battery technology is expanding, even without the introduction of electrically-powered cars.

There are currently three different types of electricallypowered cars, the majority of which use lithium-ion batteries. A hybrid electric vehicle (HEV) has both an internal combustion engine and an electric motor that uses energy stored in a battery, which is recharged by the internal combustion engine and by energy captured during braking. A plug-in hybrid electric vehicle (PHEV) is similar to an HEV except that the battery can also be charged by plugging it into an external power source. An all electric vehicle (EV), sometimes referred to as a battery electric vehicle (BEV), has only the electric motor and no internal combustion engine at all. Each of these types requires different quantities of lithium: an HEV needs between 0.8 and 2 kg of LCE; a PHEV requires between 1 and 10 kg of LCE; and an EV needs between 8 and 40 kg of LCE (SignumBOX, 2012). Various forecasts for lithium demand have been made but clearly their accuracy depends on how significant demand will be for electrically-powered cars. Rockwood Lithium (2013) summarised this variation in a diagram that shows LCE requirements for 'portable batteries', excluding for cars, increasing from approximately 20 000 tonnes LCE in 2010 to 65 000 tonnes LCE by 2025. Adding in a 'low scenario' for electric cars increases this to 155 000 tonnes LCE by 2025, while if a 'high scenario' for electric cars is realised the demand rises further to 350 000 tonnes LCE.

The European Commission (2014a) suggested that the annual growth rate in lithium-ion batteries for hybrid and electric vehicles could reach nearly 15 per cent per year in the period 2011 to 2020, while the growth rate for the lithium market as a whole is forecast to grow by more than 8 per cent per year in the same period.

The US Department of Energy (2011) has also considered future supply and demand scenarios for lithium carbonate in the light of the anticipated increases in demand for lithiumion batteries, particularly for electrically powered cars. In their lowest scenarios they estimate that 200 000 tonnes of lithium carbonate will be required by 2025, their medium scenario indicates that 400 000 tonnes will be needed, while their high scenario suggests demand for lithium carbonate may rise to 900 000 tonnes by 2025. This medium demand scenario is based on increases in electrically powered cars from less than 1 million vehicles in 2010 to 36.6 million in 2025. Despite this significant increase, the US Department of Energy concluded that producers of lithium would be able to increase capacity to meet this demand and consequently considered lithium to be 'not critical' in the short term albeit 'near critical' in the medium term.

A relatively new and potentially growing use for lithiumion batteries is in electricity grid storage systems. These are particularly important where the source of electricity is from renewable sources such as wind or solar power which are intermittent by nature. Batteries are only one method of storing energy (others include pumped-water, or compressed gas) and lithium-ion are only one type of possible batteries that could be used. Where they are used the demand for lithium carbonate is considerable – as much as 600 kg per megawatt of storage capacity (Canada Lithium, 2013). Research is continuing into different types of lithium-containing batteries with the aim of further increasing energy density, reliability and safety for both grid storage and electric vehicles. Research is also examining ways of recycling lithium-ion batteries in order to reuse all the materials contained within them, in addition to the lithium (Owens, 2015).

World resources, reserves and production

Resources and reserves

Global resources of lithium have been estimated by the USGS to be approximately 41 million tonnes, with the

largest resources held by Bolivia, Chile, Argentina, the USA, China and Australia. The USGS also estimates that worldwide reserves of lithium are approximately 14 million tonnes, with the most significant reserves held by Chile, China, Argentina and Australia (Jaskula, 2016).

Evans (2014) provides a detailed breakdown of estimated world resources by mine, or group of mines, that amounts to a similar figure of approximately 40 million tonnes. He notes that some of these resource figures include reserves but does not separately specify what the reserve figures are. Table 7 is a summary of Evans' resources table and Figure 11 is a graphical representation of these statistics. These figures are liable to change as companies continue to develop lithium projects and announce the results from feasibility assessments or additional exploration.

Production

In 2014 there were eight countries known to be producing lithium. Of these, *five* are producing lithium minerals (Aus-

Country	Туре	Number of deposits	Tonnes Li contained
Bolivia	Continental Brines	1	8 900 000
Chile	Continental Brines	3	7 100 000
	Pegmatites	several	2 830 000
	Hectorite	1	2 000 000
USA	Geothermal Brines	1	1 000 000
UJA	Oilfield Brines	1	850 000
	Continental Brines	1	40 000
	Sub-total		6 720 000
Argentina	Continental Brines	6	6 520 000
	Continental Brines	numerous	2 600 000
China	Pegmatites	numerous	750 000
	Sub-total		3 350 000
D.R.Congo	Pegmatites	1	2 300 000
Australia	Pegmatites	3	1 683 500
Russia	Pegmatites	numerous	1 000 000
Canada	Pegmatites	3 + others	977 000
Serbia	Jadarite	1	950 000
Brazil	Pegmatites	2	185 000
Mexico	Hectorite	1	180 000
Austria	Pegmatites	1	134 000
Zimbabwe	Pegmatites	1	56 700
Finland	Pegmatites	1	14 000

Table 7 Estimated world lithium resources (adapted from Evans, 2014).

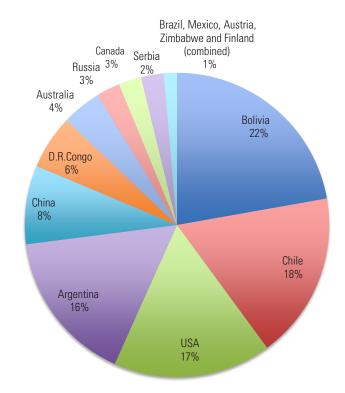


Figure 11 Percentage of estimated world resources held by each country (data from Evans, 2014).

tralia, China, Zimbabwe, Portugal and Brazil) while *four* are extracting lithium from brines (Chile, Argentina, China and USA). China is the only country using both production methods.

It is difficult to compare gross weight production figures between countries that are producing minerals and those producing brine because the lithium content of the two sources are very different. For example, in 2014 Australia produced over 440 000 tonnes of spodumene compared with and estimated 61 000 tonnes of brine produced in Chile and yet in terms of the lithium content Chile was by far the larger producer. In Table 8 the figures have all been converted to lithium content to enable a direct comparison to be made.

Total world production in 2014 of lithium content was 26 100 tonnes; this is an increase of nearly ten per cent from the 23 800 tonnes produced in 2013 tonnes but is still six per cent lower than 2012 (Table 8). There was a 26 per cent decrease in global output between 2008 and 2009; this is believed to have been caused by the economic downturn towards the end of 2008, which reduced demand. However, production bounced back in 2010 and grew by 19 per cent in 2011 compared to 2010 (Brown et al, 2016).

The BGS has been collating production figures for lithium since the 1920s and the increasing trend over that time period is shown in Figure 12. It is interesting to note that global lithium production was relatively flat from the late 1950s through to the early 1980s but since then it has more than quadrupled. This undoubtedly is due to the increase in demand for lithium as mankind has found new uses for the element but is also due to the significant reduction in costs associated with production from brines.

Country	20	10	20	11	20	12	20	13	20	14
	Li content (tonnes)	% of world total								
Chile	9 700	43	12 900	48	13 200	48	11 200	47	11 500	44
Australia	5 600	25	7 800	29	8 400	30	6 800	28	8 300	32
Argentina	3 100	14	2 500	9	2 400	9	2 300	10	2 800	11
China	1 100	5	1 200	4	1 200	4	1 200	5	1 200	5
USA	1 000	4	1 000	4	1 000	4	870	4	900	3
Zimbabwe	800	4	900	3	900	3	900	4	900	3
Portugal	700	3	600	2	300	1	300	1	300	1
Brazil	400	2	200	1	200	1	200	1	200	1
Spain	100	1	0	0	0	0	0	0	0	0
Canada	0	0	0	0	0	0	0	0	0	0
World total	22 600		27 000		27 800		23 800		26 100	

Table 8Lithium producing countries between 2010 and 2014 (figures are estimated Li content)(Adapted from Brown et al, 2016).

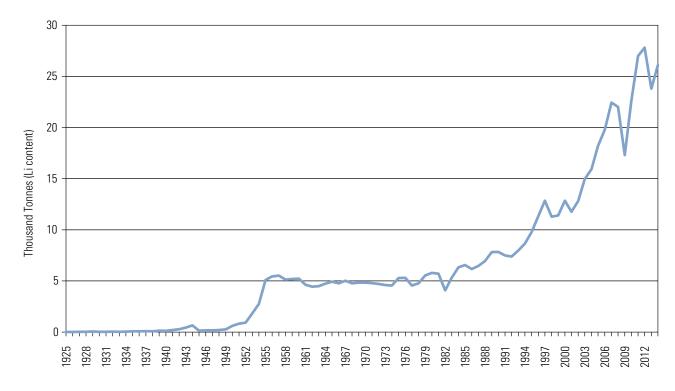


Figure 12 World production of lithium from 1925 to 2014.

World Trade

Lithium is traded globally in a number of different forms, including concentrates, carbonate, oxides and hydroxides, chloride, bromide and metal. Trade data for lithium concentrates are not available using the Harmonised System of trade codes (also known as Combined Nomenclature) because it is combined with many other commodities under code HS260790 for "Other ores and concentrates, not elsewhere specified". However, data are available for lithium carbonate (HS code 283691) and lithium oxides and hydroxides (HS Code 282520). Trade data for lithium in other forms are also not available because they are combined with other elements.

It is known that most of the spodumene produced in Australia is exported as concentrate and that this largely goes to China for processing into lithium carbonate, but the quantities involved cannot be verified from the usual sources due to trade code issues.

Recent trends in global exports of lithium carbonate and oxides/hydroxides are shown in Figure 13. As would be expected from the drop in production figures mentioned earlier, world exports of lithium carbonate showed a significant drop in 2009 but a strong recovery in 2010 and 2011. This fall is also present in the global export figures for lithium oxides and hydroxides but is less dramatic. Both compounds also show a decrease in exports in 2013 when compared to 2012, but a significant increase in 2014. The main exporting countries in 2014 for lithium carbonate and lithium oxides and hydroxides are shown in Figure 14. Although there are some significant exports of oxides and hydroxides, most notably from the USA, and of carbonate, from Argentina for example, all these export figures are dwarfed by the scale of the exports of lithium carbonate from Chile. In 2014 Chile exported 49 387 tonnes of lithium carbonate or nearly 60 per cent of all lithium carbonate exported in that year. This compares to just 14 per cent from the second largest exporter, which was Argentina. The USA was the largest exporter of lithium oxides and hydroxides, amounting to 8 885 tonnes or 35 per cent of the total oxides and hydroxides exported in 2014. China was the second largest exporter of oxides and hydroxides with 24 per cent of the total.

The recent trends in lithium carbonate imports are shown on Figure 15, alongside trends in imports of lithium oxides and hydroxides. As with production and exports, there is a significant drop in imports of lithium carbonate in 2009 but a strong recovery thereafter. Imports in 2011, 2012 and 2013 have exceeded 80 000 tonnes, a 26 per cent increase in 2011 compared to pre-recession 2008, but imports have dropped below 80 000 tonnes in 2014. A similar dip in 2009 is also shown for imports of lithium oxides and hydroxides but, as with exports, it is not quite so dramatic. Imports in 2014 have increased to more than 20 000 tonnes.

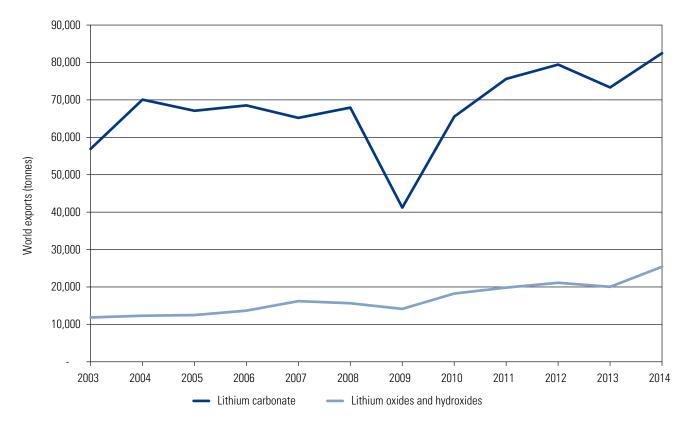


Figure 13 Trends in global exports of lithium carbonate and lithium oxides and hydroxides (data sourced from United Nations, 2016).

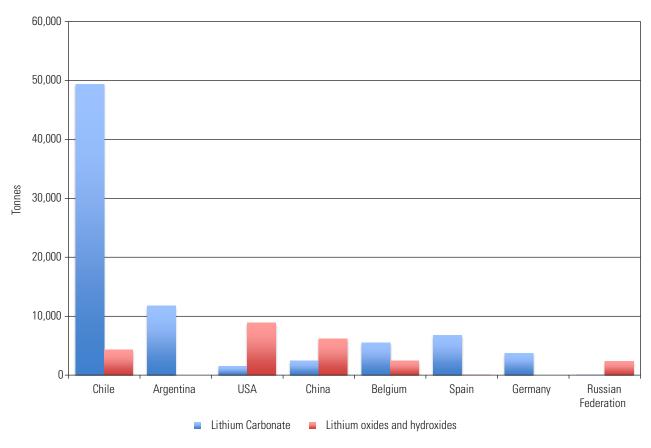


Figure 14 The largest exporting countries for lithium carbonate and oxide/hydroxides in 2014 (data sourced from United Nations, 2016).

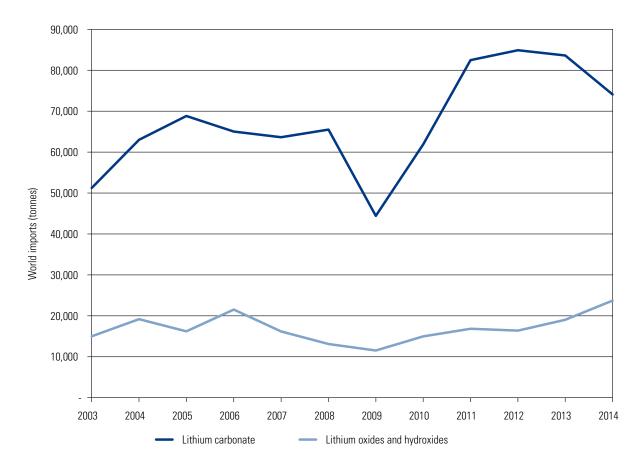


Figure 15 Trends in global imports of lithium carbonate and lithium oxides and hydroxides (data sourced from United Nations, 2016).

The main importing countries in 2014 for lithium carbonate and lithium oxides and hydroxides are shown in Figure 16. Perhaps surprisingly, China was not the largest importer of lithium carbonate in 2013; rather the Republic of Korea was the largest with imports of 14 981 tonnes or 20 per cent of the total lithium carbonate in that year. However, China was the second largest (13 601 tonnes or 18 per cent) followed by the Japan (12 108 tonnes or 16 per cent) and the USA (9 626 tonnes or 13 per cent of the total). The largest importer of lithium oxides and hydroxides in 2014 was Japan, which imported 6 667 tonnes or 28 per cent of the total imported globally, followed by Belgium (2 388 tonnes or 10 per cent) and Republic of Korea (1 965 tones or eight per cent of the total).

Europe is reliant on imports for both lithium carbonate and lithium oxides and hydroxides and received most of its imports in 2014 from Chile. Of the 2 812 tonnes of lithium oxides and hydroxides imported by the 28 members of the European Union (from countries outside the EU), 37 per cent came from Chile while a further 33 per cent came from Russia. Of the 10 664 tonnes of lithium carbonate imported by the EU-28 (from outside the EU), 84 per cent came from Chile.

Prices

Lithium is traded in a number of forms, including lithium spondumene concentrate, lithium spodumene glass grade, lithium carbonate, lithium ore petalite and others. Each form is traded at a different price and many are not published in literature.

Prices for lithium spodumene have not been consistently reported in recent years. However it appears that the price was relatively stable between 2002 and 2006 but since then it has more than doubled from US\$330–350 per tonne in January 2006 to US\$720–770 per tonne in January 2011. In March 2016, prices for spodumene concentrate, with >7.5 per cent Li_2O CIF Asia, were reported as US\$755–780 per tonne.

The price trend for lithium carbonate for the period 2002 to early 2016 is similar to that for spodumene. The price was relatively stable but it started to rise significantly from 2005 onwards. In January 2005 lithium carbonate was US\$0.95–1.40 per pound whereas by January 2007 the price was US\$2.70–3.00 per pound. Not surprisingly, prices dropped in 2009 due to the effects of the global economic recession, which are also reflected in the

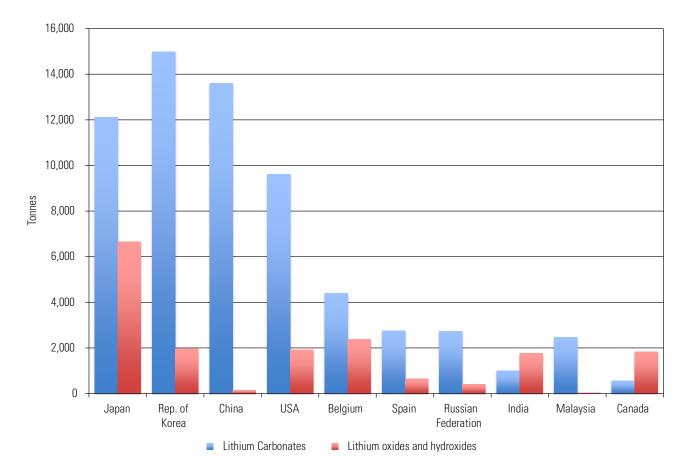


Figure 16 The largest importing countries for lithium carbonate and oxide/hydroxides in 2014 (data sourced from United Nations, 2016).

production figures. However they did subsequently recover, albeit with some volatility, and in April 2016 had reached US\$3.00–3.50 per pound.

Lithium compounds are also sold internationally in a 'spot market' and the prices here can be significantly different, and much more volatile, than the longer-term 'contract' prices quoted above. Prices as high as US\$20 per kilogram for lithium carbonate have been quoted in the trade journals, with lithium hydroxide quoted as over US\$25 per kilogram. High 'spot' prices tend to feed through to higher 'contract' prices with one trade journal quoting contract prices for lithium carbonate as being US\$10–15 per kilogram in April 2016 while lithium hydroxide was US\$14–20 per kilogram (McCormick, 2016).

Recycling and substitution

There is currently little economic need to recycle, or to find substitutes for, lithium because to-date there have been no significant constraints upon supply. The 2009 UNEP report 'Metals Recycling Rates' quotes the end-of-life recycling rate, the global average recycled content and the old-scrap ratio for lithium all as <1 per cent (UNEP, 2009). However, if demand increases as expected due to growing use of electric vehicles, recycling and substitution may begin to play a more important role.

Recycling

For many of the end uses of lithium, recycling does not appear to be carried out at all. This is partly because these end uses are dissipative, as in ceramics and glass, or because the lithium can be reused multiple times, for example when used as a catalyst. Ceramics and glass are themselves recycled extensively and any lithium-containing articles are included within this. The majority of attention in recent years has been devoted to the recycling of lithium-ion batteries.

Although lithium is completely recyclable, and can be recycled repeatedly without loss of performance, the economic incentive to do so from batteries is limited because the process is expensive, the quantities of lithium contained are comparatively small and supplies of primary materials are often more cost effective. Despite this, some recycling of lithium-ion batteries is being undertaken. However, the intrinsic value often comes from the more valuable metals contained in the batteries such as cobalt and nickel rather than the lithium. In some cases the lithium remains in a slag product, which is used as a construction material, rather than being separately recovered (Kumar, 2011). This situation may change if electric vehicles become more common and as a consequence a greater quantity of larger lithium-ion batteries become available for recycling (Hamilton, 2009), albeit this will incur a time-lag due to the lifetime of the batteries. The development of different varieties of batteries, such as lithium iron phosphate, may result in a drastic decline in the economics of recycling due to the absence of the more valuable metals such as cobalt or nickel (Kwade, 2010).

The current drivers to increase battery recycling include the general desire to reduce materials going to landfill, the avoidance of pollution from inappropriate disposal and the risk of fires in landfill sites caused by reactive battery materials. Within Europe, these concerns resulted in the European Union the 'Batteries Directive' (Directive 2006/66/EC), which was adopted in 2006, albeit with subsequent amendments. Amongst other things, this Directive aims to increase the collection and recycling of all types of batteries and fixes targets for these activities (European Commission, 2014b).

Electric vehicle batteries differ from those used in portable electrical devices and not just in terms of their size. They are also different in their energy content, modular structure, cell chemistry and 'battery management system', i.e. the electronic system that protects a rechargeable battery from operating outside is safe parameters. New processes for recycling these are being developed, or existing process are being adapted (Evans, 2014). Most of these processes are proprietary to particular companies and details are therefore scarce. Two published examples are given below.

Retriev Technologies (formerly Toxco Inc) is one of the leading companies in lithium battery recycling with a facility in southern British Columbia, Canada that has been operating since 1992. The company also has recycling facilities in Ohio and in 2009 the US Department of Energy granted it US\$9.5 million to expand its battery recycling operations there (Hamilton 2009). Larger batteries are first disassembled, and more reactive types of lithium battery are pre-treated by cooling to approximately -200°c using a proprietary cryogenic process to avoid the risk of fire or explosion. All the batteries are then crushed under a liquid, both to ensure there are no emissions and to reduce battery reactivity. Metal solids are separated and recycled, while the lithium-rich solution is chemically processed into lithium carbonate for reuse (Retriev Technologies, 2014).

Umicore Battery Recycling, another leading battery recycling company, has developed a closed loop recycling process for lithium-ion batteries. The company reports that this process provides an environmentally sound method, without any potentially hazardous pre-treatment, and returns the lithium, nickel and cobalt metals into cathode materials for new battery applications. Although the dismantling of larger batteries is carried out in Germany and the USA, the main smelting operations take place in Hoboken, Belgium (Umicore, 2016).

An intermediate stage between the use of lithium-ion batteries in electric vehicles and full recycling may be to reuse them as static energy storage. Although electric vehicle batteries are replaced when they fall to 80 per cent of the peak power of a new battery, these requirements do not apply to stationary battery applications and consequently it has been suggested that used electric vehicle batteries could be reconfigured for stationary use before the batteries are eventually fully recycled (Meeus and Scoyer, 2012)

Substitution

Although there are substitutes available for lithium in many applications such as batteries, ceramics, greases, and manufactured glass, in reality there is often little incentive to use substitutes because there has not been a supply shortage and lithium is relatively inexpensive.

Non-lithium fluxes, such as sodium or potassium compounds, can be used in glass and ceramics, but these do not increase the thermal shock resistance to the same degree as lithium carbonate (Evans, 2014). Calcium and aluminium soaps can be used as substitutes for lithium stearates in greases. Composite materials consisting of boron, glass, or polymer fibres in engineering resins can substitute for aluminium-lithium alloys in structural materials (Jaskula, 2016).

There is a very wide range of other, non-lithium, battery types available such as nickel cadmium, nickel-metal hydride and lead acid batteries and new types are being constantly developed. All have advantages and disadvantages compared to lithium-ion types but in general it is the lithium-ion battery that is progressively replacing the other types, particularly where a high-energy density and lightweight battery is required. There is currently no substitute for lithium-ion batteries in most electric vehicles (Evans, 2014), however, the vast majority of vehicles are still powered by oil (petrol or diesel) and other alternatives include natural gas, biofuels and potentially hydrogen. Alternatives to batteries for electrical power grid storage include pumped-storage hydroelectric schemes or compressed air energy storage.

Focus on Britain

There has been limited evaluation of potential lithium resources in Britain (Figure 17). Certain types of granite in the Cornubian Batholith of south-west England have high lithium contents and the St Austell Granite has been investigated as a potential lithium resource.

There are also occurrences of lithium-bearing minerals in Wales, Cumbria and Aberdeenshire, Scotland, but these are not currently economic.

South-west England

The most significant lithium enrichment in Britain is associated with the Cornubian Batholith of south-west England. The Cornubian Batholith is a group of Lower Permian granite intrusions which underlie Cornwall and Devon. It is exposed onshore in five major plutons (Dartmoor, Bodmin Moor, St Austell, Carnmenellis and Land's End) and eleven satellite intrusions (Hemerdon Ball, Hingston Down, Kit Hill, Belowda Beacon, Castle-an-Dinas, Cligga Head, St Agnes, Carn Marth, Carn Brea, Tregonning-Godolphin and St Michael's Mount). The batholith represents the most voluminous igneous manifestation of the Variscan (Hercynian) Orogeny in the British Isles and intrudes a succession of Upper Palaeozoic deformed, Iow-grade, regionally metamorphosed sedimentary and igneous rocks (Chen et al., 1993; LeBoutellier, 2003; Figure 18).

The Cornubian Batholith can be divided into two main groups: biotite granites and lithium-mica-albite-topazgranites. They can be further sub-divided based on grain size, alkali feldspar megacryst size and amount of mafic minerals as shown in Figure 18. Over 90 per cent is made up of a coarse-grained biotite-granite and less than ten per cent is fine-grained biotite-granite. Lithium-bearing granites are restricted to the Tregonning-Godolphin and St Austell plutons and the Meldon Aplite Dyke (Figure 18; Exley and Stone, 1982).

Two types of lithium-bearing granite are present: a lithiummica granite with feldspar megacrysts which is found in the western part of the St Austell Granite and smaller bodies such as Cligga Head, and an equigranular lithiummica granite which is seen in the west-central part of the St Austell Granite and the Tregonning-Godolphin Granite (Exley and Stone, 1982).

The lithium-micas are brown to bronze in colour, sometimes with a lilac tint. Various types of lithium-bearing mica have been identified including zinnwaldite, protolithionite and lepidolite, some containing up to 30 000 ppm lithium (Table 9). Other lithium-bearing minerals are present in the granites such as amblygonite and elbaite (Stone and George, 1977; Weiss, 1994). However, in terms of quantities of lithium involved, the micas are the only ones which have ore mineral potential (Hawkes et al., 1987).

Elevated lithium contents were first identified in these granites in 1825, just eight years after the element was discovered. Values of 2.00 and 4.05 weight per cent LiO_2 were recorded by Turner (1825) in mica samples from unspecified localities (Hawkes et al., 1987). The only lithium extraction in the area was during the 19th century, from the Trelavour Downs pegmatite in the St Austell Granite near St Dennis. Lithium-bearing micas were extracted from the central quartz-feldspar portion of the body for use in firework manufacturing (Sproull, 2006; Hawkes et al., 1987). This working represents the only lithium extraction there has been in Britain.

Tregonning-Godolphin Granite

The Tregonning-Godolphin Granite is located on the south coast of Cornwall and outcrops in an elongate shape covering an area of about 12 km². Most of the pluton consists of medium-grained lithium-mica granite (the Tregonning Granite) with fine-grained biotite-granite in the northern area (the Godolphin Granite). Field relationships indicate that the plutonic history of the complex began with the emplacement of the Godolphin Granite followed by the passive emplacement of the lithium-rich Tregonning Granite. The Tregonning Granite is believed to be derived from the metasomatic alteration and subsequent melting of the Godolphin biotite granite by fluid/rock ion exchange together with the de-anorthitisation of plagioclase feldspar (Stone, 1975).

Exposure of the Tregonning-Godolphin Granite is poor but it has been estimated that the lithium-mica granite covers about four km² and the biotite-granite eight km². Analyses of the Tregonning lithium-mica granite have shown lithium concentrations of up to 2270 ppm. However, the Tregonning-Godolphin Granite has not been assessed for lithium potential as it is located in an Area of Outstanding Natural Beauty (AONB) and the St Austell Granite represents a geologically, technologically and economically more accessible source of lithium (Hawkes et al., 1987).

St Austell Granite

The St Austell Granite outcrops over an area of about 92.5 km² and is made up of coarse-grained biotite-granite, fine-grained biotite-granite and medium-grained lithium-mica granite (Figure 19). The lithium-mica granite covers an estimated area of 8.5 km² and contains about nine per

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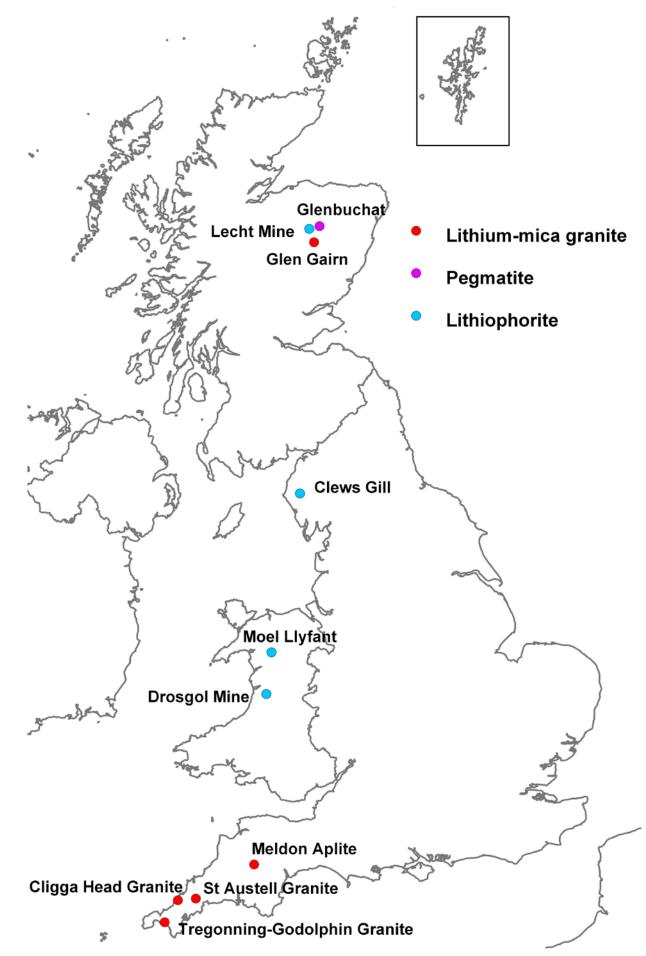


Figure 17 Lithium occurrences in Britain.

hium

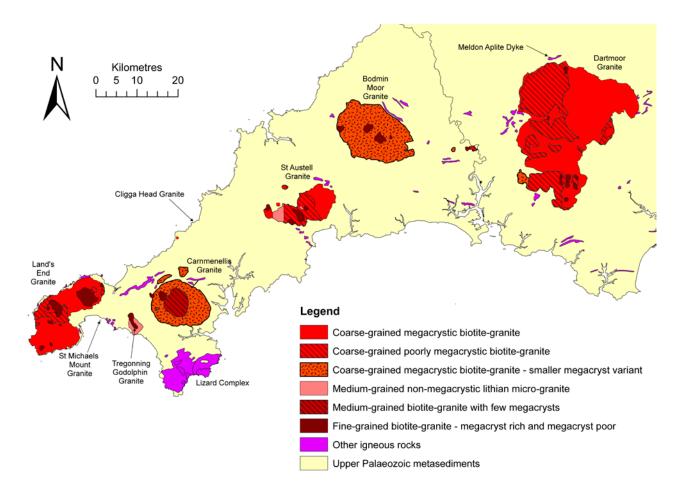


Figure 18 Classification of granites in Cornubian Batholith (adapted from Dangerfield and Hawkes, 1981).

Mica type	Rock type/locality	Range (ppm) Li
Biotite	Biotite granite	650-1719
Muscovite	Cligga Head pluton	1161-2741
Lepidolite	Meldon Aplite Dyke	16725 - 29733
Lithian biotite	St Austell and Cligga Head plutons	5000-15000
Zinnwaldite	Tregonning-Godolphin and St Austell plutons	15000-20000
Ferroan lepidolite	Tregonning-Godolphin and St Austell plutons	20000-22000

Table 9 Lithium contents of micas (Hawkes et al., 1987).

cent lithium-mica (Hawkes et al., 1987). Field evidence suggests that the lithium-mica granite is intrusive into both the coarse and fine-grained biotite-granites, although it may be metasomatic in origin as in the Tregonning-Godolphin pluton (Stone, 1975).

Studies on the lithium distribution in the St Austell Granite show that high lithium values correlate with the outcrop of

lithium-mica granites (the Nanpean District and Hensbarrow Beacon; Figure 19). The biotite-granites adjacent to the lithium-mica granites also show enrichment in lithium suggesting that they are underlain by lithium-mica granite (Dangerfield et al., 1980). It has been suggested that where lithium values are between 600 and 1200 ppm the contact with the lithium-mica granite may only be between 50 and 100 metres below the surface (Hawkes et al., 1987). Later alteration of the lithium-micas granites by magmatic fluids caused local depletion of lithium (Dangerfield et al., 1980).

The St Austell Granite was assessed for its lithium potential in the late 1980s. An overall resource estimate was made based on a 100 metre thick slab across the four grade zones in the pluton. The whole 92.5 km² area of the St Austell Granite has an estimated lithium content of nearly 16 million tonnes of lithium. However, only the areas where lithium-mica granite outcrops would be capable of yielding ore-grade rock. This roughly eight km² area contains about 3.3 million tonnes of lithium (Table 10; Hawkes et al., 1987).

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Grade zone (ppm Li)	Area (km²)	Estimated Li content for a 100 m thick slab (tonnes)
<600	66.0	8 000 000
600–1200	18.5	4 500 000
1200	7.0	2 800 000
>1800	1.0	490 000
Total	92.5	15 790 000

Table 10Regional resource estimate for the St AustellGranite (Hawkes et al., 1987).

Mineralogical work showed that nearly all the lithium is contained in the various micas with other lithium-bearing phases present in minor amounts. These micas contain a range of lithium values from 0.5 weight percent up to 2.5 weight percent. A large proportion of this mica could be extracted as a by-product of china clay operations in the lithium-mica granites. The waste hard lithium-mica rock could be crushed and milled then a subsequent flotation treatment could yield a two weight per cent Li-concentrate (Hawkes et al., 1987). Further work would need to be carried out in order to determine if the St Austell Granite has economic potential at current prices.

Meldon Aplite

The Meldon Aplite is a sodium-lithium-rich aplite dyke located about one kilometre north-west of the main Dartmoor Granite. Exposure is limited, but the body has a minimum strike length of 3.3 km and is up to 25 metres thick in some areas. The aplite trends north-east to southwest and dips 50° south-east (Worth, 1920). The dyke is contained within Lower Carboniferous slate and quartzite and is thought to be fault controlled (Hawkes et al., 1987).

The aplite is fine-grained, light coloured and is composed mainly of albite, quartz, lithium-mica and orthoclase. It contains numerous accessory minerals including topaz, tourmaline (elbaite), apatite, fluorite and petalite. It has been divided into three aplite types: a marginal chilled facies termed 'blue aplite' which is close to albitite in composition; a 'white aplite' containing albite, quartz and lithium-mica; and a medium to strongly metasomatised 'brown aplite' which is richer in lithium-mica and quartz than the other types. It is cut by a later series of thin potassium- and lithium-rich veins (Chaudhry, 1971; Chaudhry and Howie, 1973).

A range of lithium minerals, including lithium-aluminium micas, amblygonite, spodumene, elbaite, and petalite has been identified in the Meldon Aplite (Von Knorring and

Condcliffe, 1984; Drysdale, 1985; Chaudry and Mahmood, 1979; Chaudhry and Howie, 1973; Chaudhry and Howie, 1976). Petalite and elbaite are the most significant of these although they are not distributed evenly throughout the rock. Petalite content varies and makes up an average of one per cent of the rock, although locally it can be up to 30 per cent (Chaudhry and Mahmood, 1979; Hawkes et al., 1987).

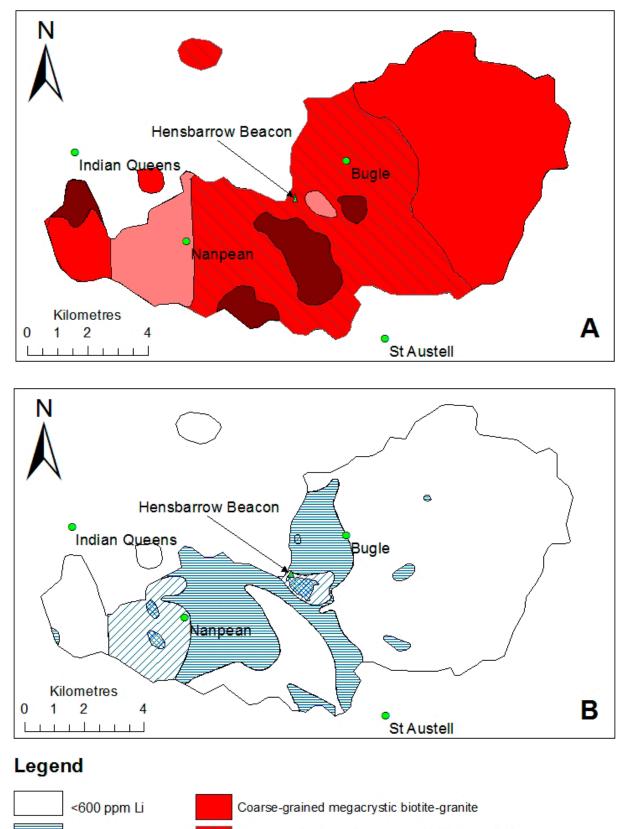
Analyses of a borehole from the aplite have shown it has an average content of 3400 ppm Li with maximum and minimum values of 6000 and 2000 ppm respectively. Samples containing visible petalite gave the highest values and these are generally seen at the Red-a-ven quarries. The mineralogically-banded rocks along the hanging and footwall of the dyke are also enriched in lithium, with values of up to 4000 ppm Li. It has been estimated that the Meldon Aplite contains 45 500 tonnes of lithium, based on an average thickness of 15 metres, length of 3.3 km and depth of 100 metres. It is unlikely, however, that it would ever be extracted because the orientation and narrow width of the dyke would cause open pit working to be expensive. It also has a low grade and is close to Dartmoor National Park (Hawkes et al., 1987).

Scotland

A small body of zinnwaldite-bearing granite outcrops near the centre of the late Caledonian Glen Gairn intrusive complex. The intrusion is compositionally zoned with early, marginal diorites and more evolved central granite. A highly evolved Li-mica bearing granite unit is present in the south-eastern part of the complex and part of the unit at Gairnshiel contains zinnwaldite (Figure 20; Plant et al., 1990; Webb et al., 1992; Hall and Walsh, 1972). The rock is a light coloured, homogenous, fine-grained and is composed of quartz, feldspars, zinnwaldite, muscovite, fluorite and pyrrhotite. The zinnwaldite makes up about five per cent of the rock and appears black in hand specimen (Hall and Walsh, 1972).

In general, lithium-micas are uncommon in Scotland with this manganese-rich variety being particularly rare. It has been suggested that this could mean it is related to the manganese mineralisation at Lecht (15 km to the northwest) and to lead-zinc ores in a calcite-fluorite vein (eight km south-east at Abergairn) which contain manganite and fluorite (Hall and Walsh, 1972).

Gem quality elbaite, a lithium-bearing member of the tourmaline group, has been identified in Glen Buchat, Aberdeenshire. It occurs as transparent prismatic crystals of various shades of pink, green and blue (locally up to 2 cm by 2 mm;





Medium-grained non-megacrystic lithian micro-granite

Fine-grained biotite-granite - megacryst rich and megacryst poor

Figure 19 The geology of the St Austell granite is shown in part A (top) and the distribution of lithium in part B (bottom) (adapted from Dangerfield et al., 1980).

600-1200 ppm Li

1200-1800 ppm Li

>1800 ppm Li

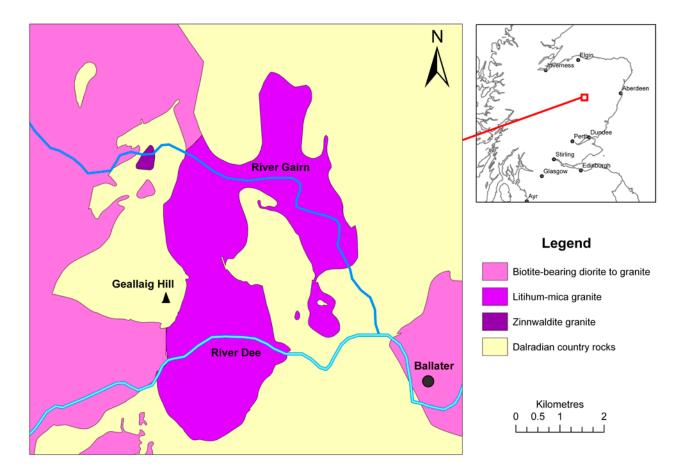


Figure 20 Simplified geological map of the Glen Gairn area showing two major granite divisions and the location of the zinnwaldite granite (adapted from Webb et al., 1992).

Figure 21), closely associated with muscovite and sericite in loose boulders of lepidolite-bearing pegmatite. The pegmatite has limited potential as a gemstone resource due to the small size of the crystals (Jackson, 1982).

Lithiophorite has been identified at the Lecht iron and manganese mines near Tomintoul in Banffshire. Lithiophorite is a lithium-bearing secondary manganese mineral commonly found in the oxidised zones of hydrothermal ore deposits and sedimentary manganese deposits. The Lecht deposit occurs in a brecciated fracture zone extending for about three km within folded Dalradian schists. The lithiophorite generally occurs with cryptomelane in massive, black, finegrained aggregates, sometimes botryoidal in form (Wilson et al., 1970).

Wales

Lithiophorite has been recorded at a few localities in Wales. It has been identified at the disused Drosgol manganese mine in Ceredigion where it is blue-black, botryoidal and typically developed enclosing quartz-coated bleached mudstone fragments within a highly altered vein breccia (Figure 22). Lithiophorite is also present at Moel Llyfant in the Arenig District of Gwynedd. Here it occurs as soft blue-black, feathery masses associated with crypto-



Figure 21 Lithium-bearing pegmatite from Glen Buchat, Aberdeenshire. The main minerals are tourmaline (dark, black), feldspar (pink and white), quartz (clear, glassy) and mica (pale green). BGS collection, image number IMG3672, BGS © NERC.



Figure 22 Botryoidal lithiophorite from a vein outcrop near Drosgol Mine, Central Wales Orefield. National Museum of Wales Collection. © National Museum of Wales.

melane in scree beneath remote trial workings (National Museum Wales, 2011).

Cumbria

Lithiophorite has also been identified in a spoil tip from old haematite workings at Clews Gill, Ennerdale, Cumbria. It occurs as black films or manganese stains on joint surfaces of fragments of the Ennerdale granophyre that has been brecciated by the Red Gill Fault. The lithiophorite is dull black, botryoidal and can be a few centimetres across but never more than one millimetre thick (Clark, 1963).

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