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INTRODUCTION

Lithium is used to treat depression and this accurately described the state of the industry a decade ago when supply exceeded demand by a wide margin. Since then the industry's personality has undergone a major transformation as expanding demand has been happily supplied by an increasing array of lithium mineral and chemical products. An ongoing transition is away from the hard-rock mining of pegmatites in North America to the extraction of lithium-rich brines in South America. Spodumene producers in Canada and Australia have countered with specialty grades focused on the glass industry.

CONSUMPTION

Lithia (Li_2O) is used commercially either in the form of a lithium chemical such as lithium carbonate or as a spodumene, petalite, or lepidolite concentrate. For example, a high-grade spodumene concentrate contains a minimum of 7.5% Li_2O , and less than 0.1% Fe_2O_3 and a petalite concentrate has a minimum of 4.40 Li_2O and a maximum of 0.05% Fe_2O_3 . Lithia added to glass and ceramics acts as a strong flux, improves the forming properties, and influences many of the properties of the resulting product. For example, lithia imparts the remarkably low coefficient of expansion required in pyro-ceramics such as oven-to-table ware, and improves the stability and electrical properties of glass exposed to radiation such as in black and white TV face plate glass. Adding the lithia as a glass-grade mineral concentrate (glass-grade spodumene has a minimum of 5% Li_2O and less than 0.2% Fe_2O_3) is generally cheaper and has the advantage of con-

tributing alumina to the batch; however, a synthetic chemical such as lithium carbonate has considerably less impurities such as iron.

The main end use of lithium carbonate is in aluminum reduction cells where it improves the conductivity of the molten bath and so reduces the operating temperature, increases the efficiency of power and carbon anode and cryolite use, and decreases fluorine emissions. It is the principle feedstock in the manufacture of a vast array of lithium chemicals used in a great variety of industries (Figure 100). For example, lithium acetate is used in organic synthesis, medicines, and as a catalyst; lithium amide is a constituent in fragrances and anti-histamines; lithium bromide

Consumption of lithium carbonate and concentrates in the United States
(tonnes contained lithium)

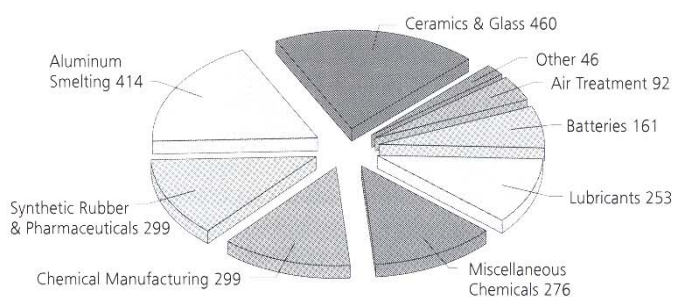


Figure 100

Source: USBM (1993)

Table 89 Minerals Containing Lithium						
Minerals	Formula	Color/Luster	SG	H	Crystal system/ habit	Occurrences
Amblygonite Greek amblys = dull, obtuse and gonia = angle, in ref. to cleavage angle	$\text{LiAlPO}_4(\text{F},\text{OH})$ Ore: 7.5-9% Li_2O	white to grayish, colorless, yellowish, pinkish, tan, greenish, bluish; transparent - translucent; vitreous - greasy	3	$5\frac{1}{2}$ - 6	triclinic; equant to short prismatic xls; in large cleavable masses	granite pegmatites, often in masses and xls of very large size
Bikitaite Bikita deposit, Zimbabwe	$\text{LiAlSi}_2\text{O}_6 \cdot \text{H}_2\text{O}$	white to colorless; transparent; vitreous	2.29-2.34	6	monoclinic; prismatic, pseudo-orthorhombic; massive	assoc. with eucryptite, quartz, stilbite, calcite, and allophane at Bikita
Eucryptite Greek eu = good, and concealed for its occurrence embedded in albite	LiAlSiO_4	colorless, white, and tan; transparent, vitreous	2.65	$6\frac{1}{2}$	trigonal; large single euhedral xls, usually in massive granular aggregates	alteration product of spodumene
Lepidolite Greek lepis = scale and lithos = stone because of its micaceous structure	$\text{K}(\text{Li},\text{Al})_3(\text{Si},\text{Al})_4\text{O}_{10}(\text{F},\text{OH})_2$ Ore: 3.28-8% Li_2O	rose-red, violet-gray, lilac, pink and purple, yellowish, grayish white, and white; transparent to translucent; pearly	2.8 - 3.3	$2\frac{1}{2}$ - 3	monoclinic; tabular xls, hexagonal; thick cleavable masses, coarse - fine scaly aggregates	granite pegmatites, less commonly in granites, aplites, and high-temperature tin-bearing veins
Montebrosite Montebros, Creuse, France	LiAlPO_4F 7% Li_2O	white to grayish white, colorless, yellowish, pinkish, greenish, bluish; vitreous to greasy	2.98 - 3	$5\frac{1}{2}$ - 6	triclinic; equant xls to short prismatic, commonly with rough faces	granite pegmatites often in masses of large xls; may be confused with amblygonite
Petalite Greek petalon = leaf and lithos = stone in ref. to its leaflike cleavage	$\text{LiAlSi}_4\text{O}_{10}$ Ore: 3.8-5.2% Li_2O	colorless, white, gray, yellow; transparent to translucent; vitreous to pearly	2.3 - 2.5	6 - $6\frac{1}{2}$	monoclinic; euhedral xls, usually massive as cleavable blocky segregations	in granite pegmatites
Spodumene Greek spodoun = to reduce to ashes to its ash-gray color	$\text{LiAlSi}_2\text{O}_6$ Ore: 2.9-7.6% Li_2O	colorless, white, gray, yellowish, greenish, emerald green, pink, violet; transparent to translucent; vitreous to dull	3 - 3.2	$6\frac{1}{2}$ - $7\frac{1}{2}$	monoclinic; prismatic xls, often flattened and vertically striated	in granite pegmatites assoc. with quartz, feldspar, muscovite.
Zinnwaldite Zinnwald, Bohemia, named for the local tin (German Zinn) veins	$\text{KLiFe}^{+2}\text{Al}(\text{AlSi}_3)\text{O}_{10}(\text{F},\text{OH})_2$	gray, brown, sometimes dark green; transparent; vitreous	2.9 - 3.3	$2\frac{1}{2}$ - 4	monoclinic; short prismatic or tabular xls; disseminated scales or scaly aggregates	mainly in greisens, high-temperature quartz veins, and in granite pegmatites.

Source: various including Roberts et al., 1990

Table 91 Chemical Analyses of Brines from Salars of the Central Andes (mg/L)

										Dissolved
	Cl	SO ₄	HCO ₃	Li	Na	K	Ca	Mg	B ₂ O ₃	Salts
ARGENTINA										
Salmar Muerto	194,800	11,100	n.d.	914	121,900	9,340	1,000	268	1,455	340,920
Salmar	190,500	15,990	n.d.	350	122,200	6,570	280	2,120	1,609	338,510
Salmar	190,600	7,440	n.d.	97	123,100	3,400	600	1,290	708	326,747
Salmar Grandes	178,700	26,080	n.d.	440	118,200	4,730	740	2,980	2,220	332,560
Salmar	192,700	19,980	n.d.	1,020	112,300	8,170	320	7,550	3,765	343,210
Salmar Grande	148,900	10,610	n.d.	420	92,400	3,710	800	2,600	1,673	259,960
Salmar	190,700	8,260	n.d.	160	119,500	160	760	1,840	138	321,423
BOLIVIA										
Salmar	191,800	13,200	592	700	94,900	13,500	461	11,800	1,136	351,000
Salmar	120,000	34,100	430	213	67,200	3,400	259	8,480	702	239,000
Salmar	186,000	25,300	785	338	100,400	9,080	253	12,120	2,208	368,000
Salmar Grandes	194,000	2,460	n.d.	1,640	101,000	14,200	3,100	3,480	3,041	320,825
Salmar	126,000	17,900	n.d.	712	68,900	12,000	600	1,670	2,011	228,407
CHILE										
Atacama (1)	183,100	16,140	560	760	103,000	12,900	520	6,130	1,705	370,000
Atacama (2)	182,800	25,500	220	1,200	98,000	19,500	300	8,500	1,673	385,000
Atacama (3)	189,500	15,900	230	1,570	91,100	23,600	450	9,650	1,416	370,000
Salmar	131,380	11,430	n.d.	540	73,200	13,200	890	3,830	3,700	235,620
Salmar	172,130	87,990	0	86	60,000	14,960	88	48,640	740	400,000
Salmar	109,630	15,360	620	101	62,200	4,800	820	6,251	1,078	210,000
Salmar	112,980	26,700	n.d.	480	65,000	13,500	610	5,880	2,333	277,270
Salmar Martin	68,000	1,570	415	170	30,100	2,410	8,469	1,646	985	112,960
Salmar	70,000	25,000	2900	186	45,000	3,530	920	5,125	2,520	153,600

n.d. - not determined; Source: Ide and Kunasz, 1989, and various sources cited in the report

For example oilfield brines in the Paradox Basin, Utah, and in the Smackover Formation in Arkansas and Texas (see bromine, page 74). Brines may be concentrated in salars by evaporation in desert regions of the central Andes in South America such as in Chile, Argentina, and Bolivia (Table 91).

In order to produce economic concentrations of lithium, Kunasz (Anon., 1984) suggests that brines must satisfy five basic requirements:

1. occurrence near volcanoes that date from Tertiary or Recent periods — geologically young volcanoes less than 50 million years old;
2. the brines are supplied by volcanic-geothermal activity and must drain into enclosures or basins from which they cannot escape;
3. they are found only in the desert belts of the earth;
4. solar evaporation in the area must exceed precipitation - as the brine loses water to the air, the lithium content increases;
5. for the lithium content to be enriched to the level of commercial value, a period of geologic time — a million years seems a reasonable estimate — must have elapsed in the process of brine accumulation and enrichment.

PRODUCTION

Recent exploration successes and commercial developments have radically changed the lithium supply picture. Operations based on salars in Chile and Argentina have virtually eliminated the supply of lithium from the spodumene deposits of the eastern United States which once accounted for the bulk of world's supply. Production from brines in the United States continues. The

lithium from brines is sold as lithium carbonate whereas the minerals are largely marketed as concentrates. The main producers of lithium minerals are Australia, Canada, Zimbabwe, China, and Russia (Ober, 1996).

CHILE

Chile has emerged as one of the world's major lithium producers through the exploitation of the Salar de Atacama by Sociedad Chilena de Lithio, Ltd. (SCL) and Sociedad Minera Salar de Atacama S.A. (MINSAL) with an annual capacities of 14 million kg and 18 million kg respectively. This salar, some 85 km long and 50 km wide, straddles the Tropic of Capricorn about 280 km inland from Antofagasta in the east-central portion of the Second Region (Figures 101 & 102). The floor lies at 2,300 m above sea level and is bounded on the east by the Andean Cordillera

and on the west by the Domeyko Cordillera; the northern margin is marked by the Rio San Pedro deltaic sediments (Kunasz, 1983). Interpreted as a graben that originated in the Miocene, the basin has a basement of Paleozoic and Mesozoic marine rocks; these in turn are overlain by Tertiary-Quaternary continental sedimentary rocks, in part with abundant saline beds, rhyolitic ashflow tuffs, and andesitic lavas and breccias. Unconsolidated clastic sediments have accumulated as erosion products of the bedrock together with enormous amounts of saline materials accumulating in the salar itself during the late Tertiary and Quaternary. Saline minerals are still amassing in the salar (Ide and Kunasz, 1989).

The Salar de Atacama Basin covers approximately 3,000 km² including the 1,100-km² salt core or nucleus proper which contains brine-saturated, porous to dense halite surrounded by nar-

Table 92 Lithium Minerals and Brine:

World Production (tons)

	1990	1991	1992	1993	1994	1995
Australia (s)	40,000	40,376	42,516	52,900	53,000	55,000
Russia*	55,000	50,000	45,000	40,000	40,000	40,000
Canada (s, m)	12,000	12,000	18,500	18,900	20,000	21,000
Zimbabwe*	19,053	9,186	12,837	18,100	25,300	26,000
China*	15,000	15,500	15,500	15,500	16,000	16,000
Chile (b)	9,082	8,575	10,823	10,400	10,400	10,600
Portugal (l)	7,614	10,000	9,000	9,000	9,000	8,000
United States (s, b)	W	W	W	W	W	W
Brazil (a, p, s)	475	1,560	1,600	1,600	1,600	1,600
Argentina (s, a)	69	287	620	300	400	400
Namibia (a, l, p)	1,190	1,190	1,160	742	1,860	2,610
Total	159,483	148,644	157,138	168,560	172,010	181,210

a - amblygonite; bk - bikitaite; b - brine; l - lepidolite;

m - montebrasite; p - petalite; s - spodumene; *not specified;

W data withheld

Source: USGS

of lithium-rich clays; the El Tatio geothermal waters to the north which contain 28 to 40 ppm lithium; and the saline lakes of the Andean Cordillera to the east (east-west lineaments of Pliocene(?) and Quaternary age may have provided the passageways for lithium-bearing solutions to enter the basin). The area is one of internal drainage with effective basin closure in which evaporation has exceeded precipitation since the Miocene. The salar is constantly being recharged by streams and ground water from the Andes and to a lesser extent rainfall in the center of the basin and in the Cordillera de Domeyko. The basin's own microclimate is intermediate between that of the Andean Highlands to the east and the Atacama Desert to the west — with annual rainfall of 10 to 30 mm, mainly coming between December and March, temperatures ranging from a minimum of -5°C in winter to 35°C in summer, westerly winds blowing predominantly in the afternoon and reaching 100 km/hour, and a low relative humidity of less than 10%. Since skies are generally cloudless with solar radiation of about 630 langley/day (6,300,00 cal/m²/day) and the evaporation rate is 3,000 mm per year, brine concentration through solar evaporation is especially efficient (Ide and Kunasz, 1989).

ARGENTINA

FMC Corp.'s Lithium Division's Salar de Hombre Muerto operation straddles the border between Catamarca and Salta provinces, some 1,300 km northwest of Buenos Aires, Argentina. Lithium carbonate production at the salar began in early 1997. The deposit is reported to contain 130,000 tons of lithium in brine ranging from 0.22 to 1.08 g/l. At approximately 4,300 m above sea level in a region of snow and cold, solar evaporation is less than at the Salar de Atacama in Chile. Consequently, FMC has developed a patented ion exchange process to extract lithium from brines containing on average 0.065% Li. The production capacity is just over 20 million kg/year of lithium carbonate and represents an investment of some \$68 million.

BRAZIL

Lithium-bearing pegmatites are exploited in various parts of Minas Gerais State, in particular near Aracuai where they have mainly been mined for cassiterite, tantalite, and beryl. More recently the spodumene, petalite, lepidolite, and amblygonite have been extracted. The main producer is Arqueana de Minerios e Metais. Other lithium-bearing pegmatites are known in the states of Paraiba, Rio Grande do Norte, and Ceara in the northeastern part of Brazil.

CANADA

Lithium minerals have been identified in Quebec, Ontario, Manitoba, and the Northwest Territories; an unzoned pegmatite in the area of Barraute, Quebec, was mined during the 1950s and 1960s. However, current production is confined to Tantalum Mining Corporation of Canada Ltd.'s (TANCO) mine at Bernic Lake, some 180 km east-northeast of Winnipeg, Manitoba. This one of many such lithium-bearing dikes in the Winnipeg River-Cat Lake-Bernic Lake area of southeastern Manitoba which forms part of the Archean Bird River greenstone belt. The individual deposit is a bi-lobate, north-dipping body with a maximum thickness of 90 m, width of 500 m, and a strike length of 1,200 m. The deposit can be described as a "vertically asymmetrical, but otherwise concentric, crystallization sequence of primary zones carrying the bulk of Si, Al, K, Li, Cs, P, and F, which were attacked by metasomatic processes producing mainly

albite, muscovite, and lepidolite accompanied by minerals of Be, Ta, Sn, Zr-Hf, and Ti" (Crouse et al., 1984). The pegmatite contains a number of unusual minerals including spodumene and petalite grading 2.76% Li₂O, lepidolite containing 2.24% Li₂O, amblygonite, lithiophilite, zinnwaldite, stanniferous tantalite grading 0.216% Ta₂O₅, beryl grading 0.20% BeO, pollucite grading 23.3% Cs₂O, scheelite, rhodochrosite, rubidium and gallium minerals, and more than 60 minerals ranging from native bismuth through feldspar to zircon-hafnium (Andrews, 1993).

Current production is more than 20,000 tons/year of spodumene concentrate based on the extraction of some 300 tons/day of ore plus montebrasite.

UNITED STATES

Increased output from low-cost brine operations outside the United States has severely curtailed US lithium production. In fact, by the end of the century the two pegmatite districts in North Carolina will no longer produce spodumene which leaves a solitary brine operation to supply domestic lithium.

KINGS MOUNTAIN, NORTH CAROLINA

The general area of Kings Mountain, North Carolina, can be divided into three northeasterly-striking geological zones — the Inner Piedmont, the Kings Mountain Belt, and the Charlotte Belt. The Kings Mountain Belt includes metasedimentary rocks such as quartzite and marble, and mica schist which is partly of volcanic origin. The belt, which extends for about 80 km from the Catawba River in North Carolina to the Gaffney area of South Carolina, contains an impressive array of mineral deposits including iron ore, gold, lead, barite, and kyanite. However, it is the lithium deposits that have made the area famous. These deposits are contained in the 50-km-long "tin-spodumene belt" extending from Lincolnton, North Carolina, to Gaffney, South Carolina. Part of this belt contains pegmatite bodies of Late Devonian or Early Mississippian age intruded into thin layered amphibolites and mica schists. To the northwest is the Cherryville Quartz Monzonite, which is probably genetically related to the pegmatites (Kesler, 1976; White, 1981). The pegmatites, mostly unzoned, commonly contain spodumene that is uniformly distributed throughout and are found in individual bodies up to 1,000 m long, with a continuous lithology down to about 200 m. The make-up usually averages 32% quartz, 27% albite, 20% spodumene, 14% microcline, 6% muscovite, and 1% trace minerals such as beryl, apatite, rhodochrosite, and sphalerite. The spodumene contains 7.5% Li₂O, and so the crude ore contains about 1.5% Li₂O or 7,000 ppm Li (Kesler, 1976). Although these are classic deposits, they are largely of academic interest since Foote Minerals and FMC Corp. have replaced mined feedstock with supplies from the brines of South America.

CLAYTON VALLEY, NEVADA

In Clayton Valley, Esmeralda County, Nevada, located some 40 km east of the Nevada-California border, lithium-bearing brines occur in an undrained structural depression filled with Quaternary sediments comprising a mixture of clay minerals (including hectorite, smectite, illite, chlorite, and kaolinite), halite, and gypsum, all cemented by calcium carbonate. The area at an elevation of 1,530 m is in the Sierra Nevada rain shadow where evaporation is 140 cm/year compared with a precipitation level of only 13 cm. The lithium content in the surface playa ranges from 350 to 1,171 ppm, whereas core samples contain 260 to 1,713

ppm. Size analysis indicates that concentration is in the clay-mineral fraction, and that the lithium is nonexchangeable, i.e. it is part of the clay structure (hectorite was identified). The brine saturating the sediments is chemically simple — sodium chloride solution containing minor amounts of potassium and sulfate and a little calcium and magnesium. Reserves based on systematic exploration work are 202 million tons of 0.02% Li, or 40,000 tons of lithium. Cyprus Foote Mineral Company currently produces around 5.5 million kg/year of LCE from the brine.

The source of the lithium is thought to be the weathering and leaching of the country rock exposed around Clayton Valley, in particular the Tertiary Esmeralda Formation and an ash-fall tuff. The lithium content of the clays in the playa decreases to the west and north; it is highest on the eastern side of the playa in a zone immediately adjacent to the marls of the Esmeralda Formation. The deposit became enriched in lithium after deposition of a thick ash; faulting then created structural depressions, in which Esmeralda sediments accumulated and hectorite and clinoptilolite were formed in fault zones from the alteration of the volcanic tuff and the sediments supplied from pre-Tertiary country rocks. Renewed faulting in the Quaternary formed a smaller structural basin into which the lithium bearing sediments and interstitial salts of the Esmeralda Formation were recycled.

ZIMBABWE

Production in Africa is dominated by the famous Bikita Mine in Zimbabwe from which Bikita Minerals (Pvt) Ltd. produces around 26,000 tons of various lithium mineral concentrates. The Bikita zoned pegmatite is the largest of a series of pegmatites in the Bikita tin field situated some 64 km northeast of Masvingo, Zimbabwe. The field lies at the northeastern extremity of the Victoria schist belt, and is surrounded by Archean granite and granodiorite of the great Rhodesian assemblage of batholiths. The Bikita pegmatite, 2,360 million to 2,650 million years old, intrudes the Precambrian rocks of the Basement Complex (these are among the oldest rocks found to date). The zoning of the pegmatite indicates crystallization in stages and in a closed system where no addition or loss of material took place. The pegmatite, which strikes NNE with a moderate dip generally to the east, forms a ridge 70 m above the otherwise flat terrain.

The pegmatite is divided into three sectors — Al Hayat; the Bikita Sector, Quarry area; and the Bikita Sector, South East Area. The first two of these are exploited. The easterly dipping Al Hayat Sector has a strike length of 735 m and is 45 to 65 m wide. It has an irregular and patchy intermediate zone containing lithium and cesium minerals, sharp and persistent wall contacts, and a zoning pattern as shown in Table 94 (Cooper, 1964).

Table 94 Zoning in the Al Hayat Sector, Bikita, Zimbabwe

Hangingwall greenstone	H.W. contact
Border Zone: Seldedge of plagioclase, quartz, muscovite	
Wall zones: Mica band	
Hangingwall feldspar zone	
Intermediate zones: Petalite-feldspar zone	
Spodumene zone	
Feldspathic lepidolite zone	
Pollucite zone	
All-mix zone (feldspar, quartz, muscovite, lepidolite, etc.)	
Wall zone: Footwall feldspar zone	
	F.W. contact

The main petalite-feldspar zone is the largest intermediate zone in this sector, and a rich source of petalite. Laths of petalite up to 2 m long, together with crystals of microcline, are set in a matrix of fine-grained albite, muscovite, and minor quartz, as is the spodumene in the adjacent zone. The feldspathic-lepidolite zone is made up of lepidolite intergrown with fine-grained albite and quartz, and is adjacent to a zone of pollucite. The all-mix zone contains all the minerals mentioned except for pollucite. Other minerals in the lithium-bearing zone include eucryptite, a lithium aluminum silicate often formed by the alteration of spodumene and bikitaite, a hydrated lithium aluminum silicate. The Quarry Area of the Bikita Sector is a major source of lepidolite, with lesser amounts of spodumene, amblygonite, pollucite, beryl, and petalite. This is an easterly-inclined dike, 30 to 70 m wide, with a strike length of 470 m. The zoning at the 335-m level is as follows shown in Table 95 (Cooper, 1964).

Table 95 Zoning in the Quarry Area, Bikita, Zimbabwe

Hangingwall greenstone	H.W. contact
Border zone: Seldedge (plagioclase, quartz)	
Wall zones: Muscovite band	
Hangingwall feldspar zone	
Intermediate zones: Petalite and feldspar	
(upper): Spodumene (i) massive; (ii) mixed	
Pollucite	
Feldspar-quartz	
All-mix" zone	
Core zones: Massive lepidolite	
(i) high grade core	
(ii) near solid lepidolite	
Lepidolite-quartz shell	
(i) lepidolite	
(ii) amblygonite	
Intermediate zones: Cobble" zone	
(lower): Feldspathic lepidolite	
Wall zone: Footwall feldspar zone	
(i) rhythmically banded beryl zone	
(ii) muscovite band	
(iii) "spotted dog"	
	F.W. contact

The core zone is the main economic unit. It may be divided into subzones based on the relative amounts of the two major minerals, but all are part of the same lithological unit. In general the high-grade zone has a maximum of 10% admixed quartz, the near-solid lepidolite has up to 40% quartz, and the lepidolite-quartz shell contains lepidolite in irregular isolated masses that make up only 40% of the zone. The "cobble" zone is made up of boulders of clean lepidolite in a matrix of albite, and the feldspathic lepidolite is similar, but without cobbles. Beryl and tantalite are found in the wall zone, and the zone referred to as "spotted dog" is fine-grained albite with scattered muscovite and quartz (Cooper, 1964).

NAMIBIA

A series of pegmatites occurs in the vicinity of Karibib, about 190 km from Walvis Bay, Namibia. Of particular interest for their lithium and beryllium content are the Rubicon and Helicon

pegmatites, southeast of Karibib. Mines at these deposits are owned by South West African Lithium Mines. Associated with late intrusive granites, the pegmatites occur in schist, marble, and quartzite of the Damara System, and larger bodies of pegmatitic granite. These occur as bosses, dikes, and irregular masses made up essentially of a matrix of albite-quartz-muscovite with the mineralized portions representing volatile-rich fractions enriched in silica, alumina, alkali metals, lithium, beryllium, columbium, tantalum, and bismuth.

The main orebodies in the Rubicon pegmatite are in a northwest-oriented zone some 1,050 m long. The Helicon pegmatite is a simple structure consisting of an east-west striking lens about 435 m long. The average width is 70 m and there is a 60° to 70° dip to the north (Roering and Gevers, 1964). The petalite has an average Li_2O content of 4.6; pure high-grade lepidolite may contain 4.2% Li_2O . However, the grade of ore as mined is reduced by admixed minerals such as albite. Amblygonite usually contains 7-8% Li_2O .

ZAIRE

Pegmatites occur throughout a 1,600-km-long tin mineral province extending from Kolwezi in Kananga Province, Zaire, into western Uganda and Tanzania. The belt follows the bend of the Kibaran regional folding, and mineralized areas are related to granitic intrusions produced in the later stages of the orogeny. Tin has been exploited for many years, but lithium has gained prominence through the discovery of what is thought to be the world's largest pegmatitic lithium resource, some 560 km north of Lubumbashi, Katanga Province (Singleton, 1979). Twin laccoliths, the Manono in the east and the Kittolo in the west, each 5 km long and 435 m wide, intrude schist and quartzite of the Precambrian Kibaran system. The zoned pegmatites contain orthoclase or microcline, quartz, and muscovite, together with spodumene, lithium mica, tantalite, columbite, apatite, fluorite, zircon and rutile (Pelletier, 1964). Reserves have been put at 300 million tons of ore (Evans, 1978).

AUSTRALIA

The Greenbushes pegmatite deposit, located some 250 km south of Perth, Western Australia, has emerged as a major supplier of lithium minerals and chemicals. According to Gwalia Consolidated Ltd., the deposit contains mining reserves of 7.1 million tons at 4.06% Li_2O , 4.7 millions tons at 0.06% Ta, 10.8 million tons at 0.42% Nb, 4.7 million tons at 0.24% Sn, and 2.3 million

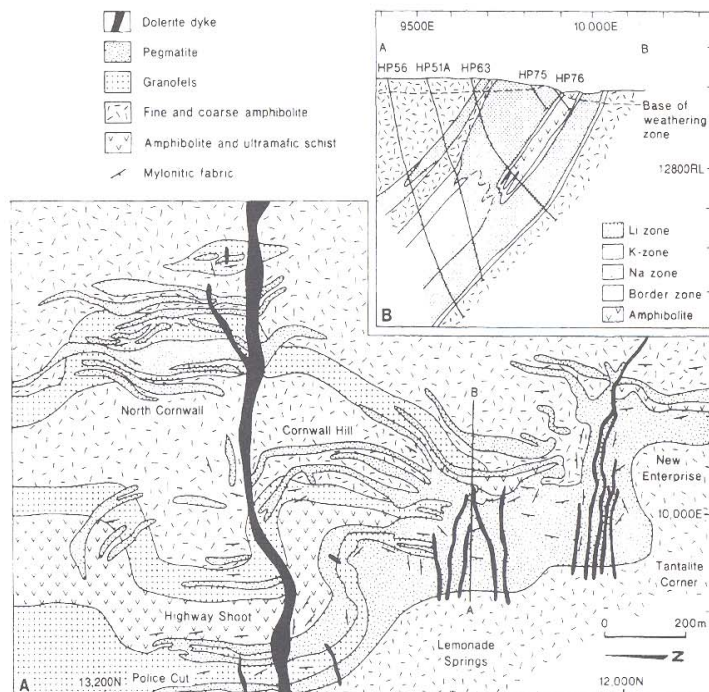


Figure 103 Geologic map of the Greenbushes pegmatite (A) and a cross section illustrating the pegmatite zones (B).

Source: Partington, 1990, and Partington et al., 1995

tons at 30% kaolin. It is claimed that "... Greenbushes has the world's highest grade and largest reserves (in terms of both tons of contained lithium and tons of economic mineralization) of spodumene" (Hatcher and Elliot, 1986); it holds half the world's tantalum resources (Partington et al., 1995). The mine, which started in 1888 as a tin and tantalum operation, currently produces some 55,000 tons/year of spodumene concentrate divided between a high-grade spodumene concentrate (7.5% Li_2O and 0.10% Fe_2O_3) and a glass-grade spodumene ore (4.0% Li_2O) plus lithium carbonate from a 5,000 tons/year capacity plant.

The mineralization at Greenbushes is contained in a giant pegmatite dike swarm that intrudes metasediments and meta-basic intrusives within a 15- to 20-km wide, north to northwest-trending Donnybrook-Bridgetown shear zone. All this is within the Balingup metamorphic belt, one of four major high-grade gneiss and schist belts comprising the Archean western gneiss terrain. The main rocks of the pegmatite district include dioritic gneiss, ultramafic schist, coarse-grained amphibolite, and felsic massive to banded paragneiss (so-called "granofels"). These have been intruded by quartz-biotite-feldspar porphyry dikes, dolerite sills, and dolerite dikes and granitoids that pre-date the intrusion of the mineralized pegmatites. The latter is a series of linear pegmatite dikes that was intruded and crystallized synchronously with deformation (say 2,527 million years ago) and within a medium- to high-temperature (690 - 770°C) and medium-pressure (4 - 5 kbars) metamorphic setting (Han, 1991). The dikes are clustered around an intrusive center in a high-strain area at the boundary between amphibolite and granofels units and have been affected by subsequent deformation and metamorphism.

Overall, the four major compositional zones (Figure 103) and four subsidiary zones that have been recognized are highly unusual — the lithium and other zones that would be expected to crystallize last and at the center of the pegmatite in fact occur as

Table 96 Main Units at Greenbushes, Australia	
Zone	Main minerals
Contact	albite, quartz, biotite, tourmaline, garnet, cassiterite, Ta minerals, zircon, scapolite
Li-zone	spodumene, quartz, apatite, tourmaline, perthite, Ta minerals
K-feldspar	quartz, microcline, perthite, spodumene, tourmaline
Albite	albite, quartz, tourmaline, spodumene, cassiterite, Ta minerals, muscovite, zircon, microcline
Li-zone	spodumene, quartz, apatite, tourmaline, perthite, Ta minerals
Contact	albite, quartz, biotite, tourmaline, garnet, cassiterite, Ta minerals, zircon, scapolite

Source: from Partington and McNaughton, 1994

footwall and hanging-wall marginal zones. This apparent reverse internal zoning plus the unusual ore element distributions may be explained by the fact that tectonic emplacement and crystallization of the pegmatites and metamorphism were synchronous with movement along the Donybrook-Bridgetown shear zone (Partington, 1990; Partington et al., 1995). Intense weathering and laterization typical of the area have kaolinized the feldspar and the spodumene to a depth of as much as 60 m.

The present day pegmatite measures some 6 by 0.5 by 0.4 km equivalent to approximately 1.2 km², which, given the ratio of 70 to 1 for lithium pegmatites suggested by Stewart (1978) means that the parental granitoid postulated to be located beneath Greenbushes has a volume of at least 80 km³. In fact, this is a minimum given the major alluvial deposits which indicate that the pegmatite was at one time considerably larger than today. The main ore shoots occur exclusively in the albite zones in the pegmatite and generally within tourmaline-rich subzones; lithium ore zones are dominated by spodumene, apatite, and quartz with some zones containing up to 5% Li₂O, that is equivalent to 60 to 80% spodumene. The spodumene unit is subdivided into low-grade (+10% spodumene) and high-grade (+25% and over 50% spodumene in places) bodies; the mining of rich extensions of the deposit has allowed the mill-feed grade to be increased from 2.5% to 4.0% Li₂O.

EXPLORATION AND EXPLOITATION

The most likely areas to host lithium-rich pegmatites are Late Archean and Early Proterozoic fields, with the lower amphibole facies of volcano-sedimentary rocks the main hosts for pegmatites (Cerny, 1991). Likely brine sources are in arid areas such as California (Searles Lake) and Utah (Great Salt Lake) and the various salars of Chile, Argentina, Bolivia, and Peru in South America.

Lithium minerals such as spodumene may be mined by either open-pit or underground methods. At Greenbushes, Western Australia, for example, open-pit mining involves drilling the deposit to a depth of 12 m, blasting, and extracting some 7,000 tons/month of ore. The waste:ore ratio is 2:1. At Bikita, Zimbabwe, mining is also by open pit. In contrast, at Bernic Lake, Canada, extraction is by underground room-and-pillar methods utilizing 15 m wide rooms and leaving 7.7 m square pillars. The extraction rate is 89% with no dilution (Burt et al., 1988).

Processing lithium ore involves crushing and heavy media separation, grinding and classification, flotation and magnetic separation. At Bernic Lake, heavy media separation is used to control the levels of potash feldspar; the sink product is ground and deslimed before passing through a low-intensity magnetic separator to remove abraded iron and iron oxides prior to flotation. Amblygonite is floated off to control P₂O₅ and F levels, and spodumene is further concentrated by reverse flotation of quartz and soda feldspar. After the spodumene is acid leached to remove iron and acid soluble lithiophile, the material undergoes high-intensity magnetic separation, filtering, washing, and drying (Andrews, 1993). At Greenbushes, Western Australia, the heavy media stage is unnecessary. Ore is put through primary and secondary jaw crushing followed by tertiary cone crushing; the product from the ball mill and classification undergoes flotation (to remove tourmaline), gravity concentration (cassiterite and tantalite), low-intensity magnetic separation (abraded iron) and wet high-intensity magnetic separation (tourmaline). The product is filtered and dried (Hatcher and Elliot, 1986). The pro-

cess is simpler at Bikita. Heavy media separation produces a petalite float fraction, and a quartz/spodumene sink fraction which is reprocessed at a higher media density to yield a spodumene concentrate. Petalite and spodumene are dried and ground.

Rather than producing a concentrate, spodumene may be converted to lithium carbonate as proposed at Greenbushes in Australia. The general production method involves mixing calcined and ground spodumene with sulfuric acid in a roasting kiln to form lithium sulfate; this is put into solution, neutralized with limestone, washed, vacuum-filtered, purified with lime, and converted to lithium carbonate by the addition of sodium carbonate (soda ash). The product is finally centrifuged, cooled, and treated with Glauber's salt to form anhydrous lithium carbonate.

Extraction and processing lithium-rich brines are simpler and cheaper than mining pegmatite minerals. For example, at the Salar de Atacama in Chile brines are pumped from a 30-m depth to evaporation ponds. MINSAL maintains a 20-cm thick floor of product on the pond bottoms to protect the liners which yields a 35 cm layer of salt to be harvested by modified pavement profilers utilizing a laser beam to precisely control the depth of the cut while harvesting the salt. On average, each harvest yields 35,000 m³ of product which is equivalent to 35,000 tons. The harvesting fleet consists of ten 20-ton trucks, 2 bulldozers, and seven 3m³ payloaders. Precipitated halite is removed from the NaCl ponds and the remaining brines, enriched in potassium, lithium, and borates, are piped to nearby solar concentration ponds where sylvinite crystals precipitate. These are harvested and trucked to the potash plant to produce a 95% KCl sylvite product. Bitterns remaining after KCl precipitation contain about 1% Li, compared with 0.016% at Silver Peak, Nevada, and 0.068% at the Salar del Hombre Muerto, Argentina. Continued solar evaporation yields a concentration of about 6% Li (38% LiCl₂, therefore it is virtually saturated) plus 1.8% Mg and 0.8% B. This highly concentrated brine is transported some 250 km by contract tank truck to the lithium carbonate plant located just outside of Antofagasta. Here the boron is removed by solvent extraction and the magnesium in a two-step process to precipitate magnesium carbonate and then magnesium hydroxide. The resulting lithium chloride-rich liquor is treated with soda ash to yield a lithium carbonate slurry which is filtered using a belt filter. The precipitate is then washed with water to remove residual NaCl and dried in a rotary drier to yield a 99% pure, fine lithium carbonate powder which is briquetted, ground, and screened to customer specifications (Harben and Edwards, 1997).

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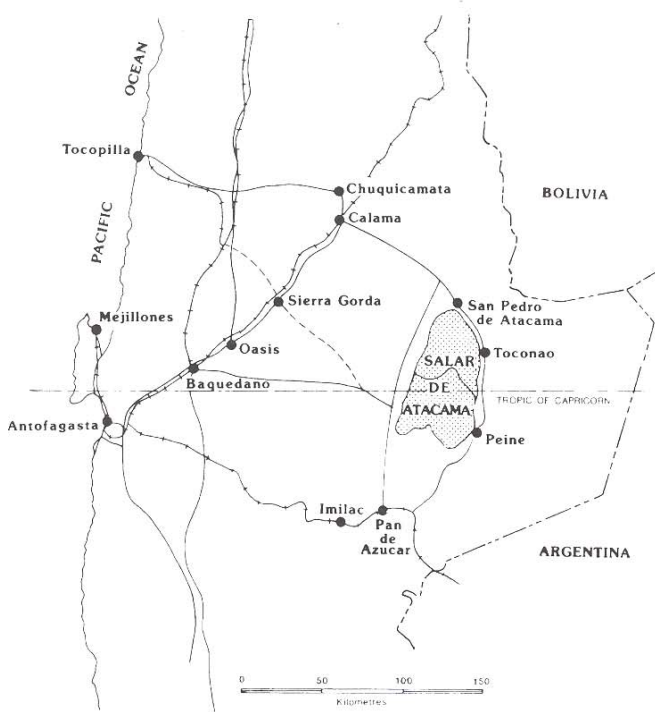


Figure 101 Location of Salar de Atacama in northern Chile. Source: Evans, R. K., 1986.

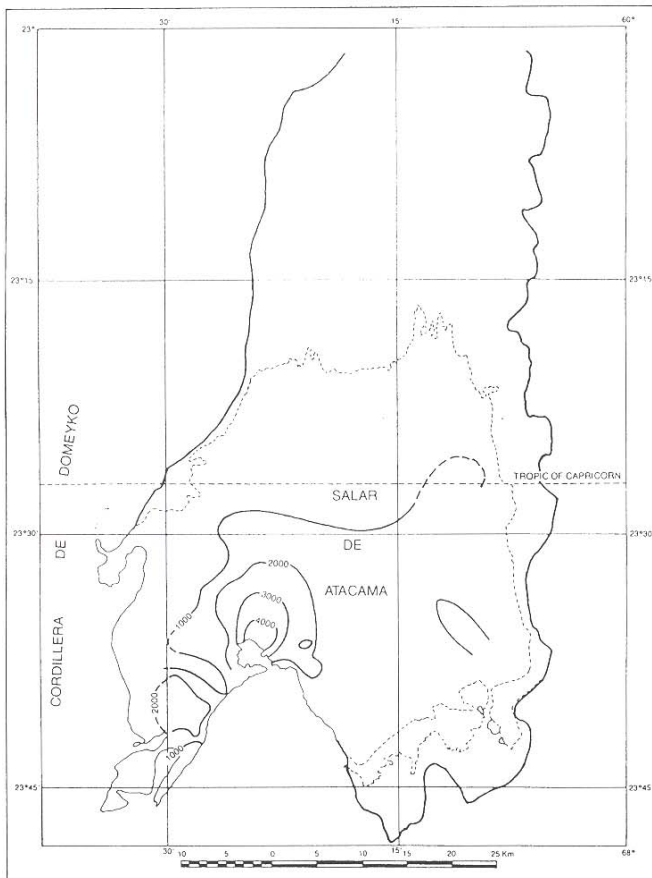


Figure 102 Lithium concentration (ppm) isopleths in the southern part of Salar de Atacama. Source: Ide & Kunasz, 1989

row sulfate and carbonate facies (Ide and Kunasz, 1989; Kunasz 1994). The saline crust may be classified as:

- **silty crust:** comprising silt and sand firmly cemented by halite and underlain by moist to brine-saturated fine-grained silts and sands; this is characteristic of relatively dry marginal areas.
- **sulfate crust:** made up of soft saline efflorescences in marginal zones of the salar where periodic flooding and desiccation takes place; minerals here are mainly sulfates like gypsum and thenardite together with halite and minor ulexite
- **chloride crust:** halite dominates in an environment intermediate between the marginal zones of thin saline crust and the thick salar nucleus; halite is porous and the phreatic brine levels are 50 to 70 cm deep; brines are saturated with NaCl
- **salar nucleus:** consists of relatively pure halite with a density greater than 1.2 g/L and at least 390 m deep; only the top 20 to 30 meters are sufficiently porous to yield Li-rich brines for commercial extraction (below the salt is completely recrystallized into a solid mass devoid of any pores); lithium concentrations are summarized in Table 91.

The thickness of salt in the basin "indicates that saturation with respect to sodium chloride was predominant during most of the subsidence history of this basin. There are no beaches or algae reef complexes that would suggest desiccation from a much larger body of water" (Ide and Kunasz, 1989; Kunasz, 1983).

Both lithium and potassium content increase markedly toward the center of the basin — lithium averaging 200-300 ppm in the marginal zone, 500-1,600 ppm in the intermediate zone, and 1,510-6,400 ppm in the interior halite zone. These figures indicate that this area contains over 36,000 tons of lithium per meter of depth, providing reserves estimated at 2,200m. tons (Evans 1978). The average of 5,000 to 7,000 ppm of lithium in certain areas of the Salar de Atacama is extremely high compared with other salars in the region. This is probably due to the basin having several sources of lithium — the leaching of volcanic rocks and transportation to the salar by stream and groundwater flow; the weathering and leaching of lacustrine sediments (with up to 470 ppm lithium) predating the formation of the salar; leaching

Table 93 Structural Features of Andean Salars

PRIMARY STRUCTURES	
Mineral zoning	Desiccation polygons
Depositional layering	Salt blisters and pressure ridges
SECONDARY FEATURES	
Surface-water flooding	Salt cusps and crenulate margins
	Smooth rock-salt crusts
	Salt channels
Springs	Salt channels
	Brine pools
Rainwater and fog	Rugged rock-salt crusts
	Salt pinnacles, nodules, saucers, and stalactites
Wind	Gypsum dunes
	Gypseous ramparts
Diurnal temperature changes	Chaotic blocks and pressure ridges in silty halite crusts
	Salt-solution tubes
	Salt cones, veins, and sheet
Tectonic deformation	Asymmetric zoning
	Giant oriented polygons
	Faults and fault sag basins

Source: Stoertz and Ericksen, 1974