## Part 1 Lithium

#### GEOLOGY

Lithium is a comparatively rare element, although it is found in many rocks and some brines, but always in very low concentrations. The average amount in the earth's upper crust has been estimated to be about 20 ppm by Vine (1980), although others have quoted values as low as 7 ppm (Bach *et al.*, 1967; igneous rocks 6 ppm, sedimentary rocks 11.5 ppm) and as high as 60 ppm (Deberitz, 1993; 27th in rank of elemental abundance). Even with these small numbers, however, there are a fairly large number of both lithium mineral and brine deposits, but only comparatively a few of them are of actual or potential commercial value. Many are very small, others are too low in grade or located in remote areas, or too expensive to recover and process. Some of the better-known deposits are roughly located in Fig. 1.1, and estimates of the lithium reserves of various deposits (or countries) are listed in Table 1.1.

The deposits have been formed because of lithium's higher solubility than most other cations, so it sometimes has concentrated in flowing and cooling magma and/or its accompanying aqueous fluids, as well as in evaporating brines. Thus, its minerals are generally found in the latter stages of alkaline magma flow, intrusion and crystallization, as occurs in pegmatite formations. There are about 145 minerals containing lithium as a major component (>200 with >0.002% Li<sub>2</sub>O), and about 25 contain over 2% Li<sub>2</sub>O (Deberitz, 1993). Forty-three of the better known of these minerals are listed in Table 1.2.

The high-lithium brines usually have obtained most of their lithium from geothermal waters, with perhaps some of the lithium coming from surface leaching of volcanic ash, clays or other rocks. However, lithium is very difficult to leach from the lattice structure of all rocks and minerals, so little is dissolved unless the water is very hot. Experimental studies have shown that at ambient temperatures, only 55–170 ppb dissolves from extended contact with granitic rocks, but at 275–600°C 0.25–2.4 ppm Li can be extracted in the same agitated, long contact-period (Dibble and Dickson, 1976). Analyses of cores into deep-ocean rift or subduction zones



Figure 1.1 Location and reserve estimate of some of the world's lithium deposits (Anstett et al., 1990; reserves: R1 proven, R2 probable).

Geology

Estimated Lithium Reserves of Various Lithium Deposits, 1000 mt Li

Reserves
$5000^{a}$
$0^{b}(4300-4600)^{j}$
$800^{c}$
$.4^{a}(115-382)^{g,h}$
$1000^{c}$
$1000^{c}$
$1000^{c}$
526 <sup>c</sup>
31.6 <sup>a</sup>
$1000^{c}$
2000 <sup>c</sup>
14,718
$> 0.3^{a}$
$23^{b}$
$26^d$
309 <sup>a</sup>
$9.8^{e}$
$0.2^{a}$
$150^{b}$
$10^a$
3.3 <sup><i>a</i></sup>
$240.5^{a}$
73 <sup><i>a</i></sup>
139 <sup>a</sup>
$500^{d}$
$10^{c}$
130 <sup>a</sup>
44.3 <sup>a</sup>
$71^c$

<sup>a</sup> Anstett *et al.* (1990). <sup>b</sup> USGS (2002). <sup>c</sup> Garrett (1998). <sup>d</sup> Lloyd (1981). <sup>e</sup> Kesler (1960). <sup>f</sup> Ide and Kunasz (1989). <sup>g</sup> Kunasz (1994). <sup>h</sup> Dillard and McClean (1991).

have shown that lithium is adsorbed on, rather than leached from near-surface rocks (up to 1.8 km in depth), and only significantly leached from deeper rocks at temperatures greater than  $300-350^{\circ}$ C. Based upon the isotopic analyses of lithium in the upper rocks there is some exchange by adsorption and simultaneous leaching in

#### Table 1.2

Formula and Group of Some of the Lithium Minerals (Vine, 1980)

Name and formula	Mineral group or series
Amblygonite (Li,Na)AlPO <sub>4</sub> (F,OH)	Amblygonite
Bertossaite (Li,Na) <sub>2</sub> (Ca,Fe,Mn)Al <sub>4</sub> (PO <sub>4</sub> ) <sub>4</sub> (OH,F) <sub>4</sub>	_
Bikitaite LiAlSi <sub>2</sub> O <sub>6</sub> ·H <sub>2</sub> O	Zeolite (?)
Bitvite Ca(Al,Li) <sub>2</sub> [(Al,Be) <sub>2</sub> Si <sub>2</sub> (O,OH) <sub>10</sub> ]·H <sub>2</sub> O	Margarite
Brannockite KLi <sub>2</sub> Sn <sub>2</sub> Si <sub>12</sub> O <sub>30</sub>	
Cookeite (Li,Al <sub>4</sub> )Si <sub>3</sub> AlO <sub>10</sub> (OH) <sub>8</sub>	Chlorite
Cryolithionite Li <sub>2</sub> Na <sub>2</sub> Al <sub>2</sub> F <sub>12</sub>	
Eckermannite $Na_2(Mg Li)_4(Al Fe)Si_8O_{22}(OH F)_2$	Amphibole (asbestos)
Elbaite Na(Li Al) ALBaSicOat(OH F).	Tourmaline
Enhesite $Na(LiAl_2)(Al_2Si_2)O_1O(OH)_2$	Margarite
Euroventite LiAlSiO.	
Euclyptic $Ei(HOO_4)$ Eerghanite $LiH(HO_4/OH)_{(VO_4)_{22}}$ 2H <sub>2</sub> O	
For $r_{i}$ sicklarite (Li, Fe <sup>3+</sup> Mn <sup>2+</sup> )PO	Sicklerite
Constlavite (Na Li) As Sh S $6H O$	Siekienie
Heatorite Na $(M_{\alpha}, Li)_4 As_2 Si_8 Si_7 O II_2 O$	Smaatita
Holmanistita Li (Mg Ee <sup>2+</sup> ) (A1 Ee <sup>3+</sup> ) Si O (OH)	Amphibale
Holmquistite $Li_2(Mg, re)_3(Ai, re)_2Si_8O_{22}(Off)_2$	Ampinoole
$ \begin{array}{l} \text{Installightanke Ca_{3}Ll_{2}De_{3}(SIO_{4})_{3}F_{2} \\ \text{Isometry } \left[ \left( F_{1} + A_{1} \right) + \left( F_{1} + F_{1} + F_{1} + F_{1} \right) + \left( F_{1} + F_{1} + F_{1} + F_{1} + F_{1} + F_{1} \right) + \left( F_{1} + F_{1} $	
Lepidonie K(Li,Ai) <sub>3</sub> (Si,Ai) <sub>4</sub> $U_{10}(F,OH)_2$	Mica
Liberite $Li_2BeSiO_4$	
Lithiophilite Li(Min <sup>-</sup> ,Fe <sup>-</sup> )PO <sub>4</sub>	Litniophilite-triphylite
Lithiophorite (AI, Li)MnO <sub>2</sub> (OH) <sub>2</sub>	—
Lithiophosphate Li <sub>3</sub> PO <sub>4</sub>	
Manandonite <sup>a</sup> LiAl <sub>4</sub> (AlBSi <sub>2</sub> O <sub>10</sub> )(OH) <sub>3</sub>	Chlorite
Montebrasite (Li, Na)Al(PO <sub>4</sub> )(OH,F)	Amblygonite
Nambulite $LiNaMn_8Si_{10}O_{28}(OH)_2$	—
Natromontebrasite (Na, Li)Al(PO <sub>4</sub> )(OH,F)	Amblygonite
Palermoite (Li, Na) <sub>2</sub> (Sr,Ca)Al <sub>4</sub> (PO <sub>4</sub> ) <sub>4</sub> (OH) <sub>4</sub>	
Petalite LiAlSi <sub>4</sub> O <sub>10</sub>	—
Polylithionite KLi <sub>2</sub> Al(Si <sub>4</sub> O <sub>10</sub> )(F,OH) <sub>2</sub>	Mica
Rankamite (Na,K,Pb,Li) <sub>3</sub> (Ta,Nb,Al) <sub>11</sub> (O,OH) <sub>30</sub>	—
Regularly interstratified montmorillonite-chlorite	—
Sicklerite $Li(Mn^{2+},Fe^{3+})PO_4$	_
Sogdianite (K,Na) <sub>2</sub> Li <sub>2</sub> (Li,Fe,Al,Ti) <sub>2</sub> Zr <sub>2</sub> (Si <sub>2</sub> O <sub>5</sub> ) <sub>6</sub>	_
Spodumene LiAlSi <sub>2</sub> O <sub>6</sub>	Pyroxene
Swinefordite	Smectite
Taeniolite KLiMg <sub>2</sub> Si <sub>4</sub> O <sub>10</sub> F <sub>2</sub>	Mica
Tavorite LiFe <sup>3+</sup> PO <sub>4</sub> OH	
Tosudite	
Triphylite $Li(Fe^{2+},Mn^{2+})PO_4$	Triphylite-lithiophilite
Virgilite	
Zinnwaldite K(Li,Al,Fe) <sub>3</sub> (Al,Si) <sub>4</sub> O <sub>10</sub> (OH,F) <sub>2</sub>	Mica
More recently determined lithium minerals <sup>b</sup>	
Diomignite $Li_2(B_4O_6)O_7$ ?	—
Liddicoatite (end member of the group) CaLi <sub>2</sub> Al <sub>7</sub> B <sub>3</sub> Si <sub>6</sub> O <sub>27</sub> (OH) <sub>4</sub>	Tourmaline
Chlorite, boron-bearing (end member) Li2Al5BSi2O14·4H2O	Chlorite

 $^{a}$  Manandonite is listed by some as the same formula with 2H<sub>2</sub>O.  $^{b}$  Garrett (1998).

5

the temperature range of  $50-350^{\circ}$ C, but little net change (James *et al.*, 2003; Chan *et al.*, 2002b,c; You and Gieskes, 2001). Other rocks or higher temperature leaching conditions must allow a greater amount of lithium to be removed, since some geothermal springs have lithium values of 6-50 ppm, but in all cases the lithium concentration is still very low. When these dilute geothermal waters are concentrated by the evaporation occurring in arid climate, closed, reasonably impervious basins, comparatively strong lithium brines have resulted in a few large playa deposits. Many large medium-concentration lithium brines have also been formed in various oil or gas field waters, potash deposit end-liquors (seawater only contains about 0.17 ppm Li), and a number of miscellaneous sources such as the Salton Sea geothermal brine and end-liquors from various commercial solar pond operations.

#### **Brine Deposits**

As with minerals, many brines and waters contain some lithium, but as noted above it is usually found in extremely low concentrations. There are a few exceptions, but as of 2003 only three brine sources had become actual commercial operations, and each had comparatively high levels of lithium (although one only contained  $\sim$  160 ppm Li), appreciable lithium reserves and good solar ponding conditions (the Salar de Atacama, Chile; Salar de Hombre Muerto, Argentina; and Clayton Valley, USA). Their brines were obtained from the porous strata under the surface of playas, and each appears to have lithium-containing hot springs as their principal source of the lithium. By-product lithium has also been recovered from Searles Lake, but its concentration in the lake brine is only 50-80 ppm Li. Because of the very dilute lithium concentration in even the best of brine deposits, they all owe their value to the availability of solar evaporation ponds to inexpensively further concentrate the lithium. Again, as an exception to this, Searles Lake used plant evaporation, but even with multiple products it became too expensive, so their lithium recovery has ceased. At the Salar de Hombre Muerto alumina-adsorption may be used to first fairly selectively separate the lithium from the other salts in the brine, but then solar evaporation would still be needed to concentrate the eluted dilute lithium solution. The projected reserves of lithium in the world's few potential or actual commercial brine deposits has been roughly estimated as about 15 million metric tons of Li (Table 1.1), but the practical recovery of the lithium from many of these deposits would be very difficult. The more important lithium-brine deposits are separately discussed in the following sections.

### Clayton Valley (Silver Peak), Nevada

This relatively small 83 km<sup>2</sup> (O'Neill *et al.*, 1969; 100 km<sup>2</sup>, Davis *et al.*, 1986) dry lake (playa) is about 16 km long and 6.4 km wide, and has a drainage basin area of about 1300 km<sup>2</sup> (Fig. 1.2). It is located in central Nevada about 87 km southwest of Tonopah, 274–282 km from Reno and Las Vegas, and 40 km east of the Nevada–California border. Its elevation is 1300 m, and in the porous strata under its



Figure 1.2 Location map of Clayton Valley and its surrounding mountains (Davis et al., 1986).

surface there is a fairly concentrated sodium chloride brine with comparatively high amounts of potassium and sulfate, but very little magnesium and other ions (Table 1.3). It also has a fairly high content of lithium in a brine pool with about a 54 km<sup>2</sup> area and an average deposit depth of about 460 m. Originally the central area contained 100-800 ppm Li, and the discovery well at 229 m depth contained

			Barret and C	D'Neill (1970)		Davis (1	.986)		
	First well <sup>a</sup>	Anon. (1966)	Feed	Product	Kunasz (1974)	Well <sup>b</sup>	Springs*	Brown and Beckerman (1990)	Garrett (1996)
Na	8.16	7.50	6.20	7.80	6.62	6.37	9010	6.20	4.69
K	1.17	1.00	0.80	4.80	0.77	0.80	892	0.80	0.40
Li*	678	400	400	5000	380	230	36	200	163
$Mg^*$	533	600	400	70	600	360	51	200	190
Ca*	407	500	500	40	560	450	372	200	450
Sr*	_	_	_	_	_	179	_	_	_
Ti*	_	_	_	_	_	211	_	_	_
Rb*	50	_	_	_	_	20	_	_	21
Mn*	_	_	_	_	_	42	_	_	_
Zn*	_	_	_	_	_	18	_	_	_
Ni <sup>*</sup>	_	_	_	_	_	7	_	_	_
$V^*$	_	_	_	_	_	5	_	_	_
As*	0.7	_	_	_	_	_	_	_	_
Cl	13.11	11.70	10.10	16.10	9.50	10.00	13,850	10.06	7.26
$SO_4$	1.12	0.75	0.71	2.90	1.11	0.66	545	0.71	0.34
$CO_3^*$	233	_	_	_	_	$650^{c}$	609 <sup>c</sup>	_	74
$B^*$	70	_	_	$2000^{d}$	_	90	_	50	67
$F^*$	_	_	_	_	_	90	4.2	_	_
$\mathbf{P}^*$	0.7	_	_	_	_	57	_	_	_
Br*	28	_	_	_	_	31	_	20	23
$NO_3^*$	_	_	_	_	_	29	_	_	_
$SiO_2^*$	_	_	_	_	_	11	46	_	_
$\delta^2 H$	_	_	_	_	_	_	-105	_	_
Density	1.180	_	_	1.25	_	1.079	_	_	1.058
Temperature	_	_	_	_	_	19.5	36.5	_	_
рН	_	_	_	_	_	7.1	7.3	_	_
Depth (m)	229	—	—	—	—	158, 218	—	213	—

#### Table 1.3

Various Analyses of the Clayton Valley Brine, wt.% (or \*ppm)

 $^{a}_{b}$  Garrett (1960). And others of about the same year, including Davis and Vine (1979).  $^{c}_{c}$  HCO<sub>3</sub>.  $^{d}_{d}$  Brown and Beckerman (1990).

Geology

678 ppm when pumped at 450 gpm (Garrett, 1960). The average brine analysis when commercial production of lithium carbonate began in 1966 was about 400 ppm. Since that time it has been slowly declining, and in 1998 the concentration was about 100–300 ppm Li (averaging 160 ppm, Harben and Edwards, 1998). In 1990 the average depth of the brine production wells was 213 m. The basin has a fairly limited rainfall (89–127 mm/yr) and a very high (water) evaporation rate of 760–1370 mm/yr (Dillard and McClean, 1991). The sediments in the basin are primarily Quaternary alluvial gravel, sand, silt and clay (partly derived from the alteration of volcanic glass or pumice; Vine, 1980), with some gypsum and calcite and several halite layers. At a 35 m depth the sediments' age is 26,900 years (Fig. 1.3), and there is one zone of 6.9 million year old volcanic ash. It is one of the major brine aquifers (Davis *et al.*, 1986). The sediments tilt, and have several fault lines, which apparently trap the more concentrated lithium brine (Fig. 1.4). The general structure of the sediments in Clayton Valley compared to two other lithium brine deposits is shown in Fig. 1.5 (Vine *et al.*, 1979; Gadsby, 1967).

The lithium (and potassium) in the deposit apparently originated from currently flowing hot springs along the Silver Peak Fault, with the current brine composition being a blend of evaporated water from these springs and surface and ground water that drains into the basin. During several periods of evaporation halite was crystallized, forming occasional beds in the alluvial, ash-fall or stream-carried insoluble sediments. The springs flow at 10–20 gpm and contain 9280–10,000 ppm Na, 786–826 ppm K and 24–43 ppm Li (Table 1.3). The unusually high temperature of the brine in some areas of the deposit (up to 44°C at fairly shallow depth [25.5 m]) would also tend to support the theory of a geothermal origin for the lithium. In the playa sediments there are limited beds of the lithium clay hectorite



**Figure 1.3** Several drill core sections from Clayton Valley, and their possible age correlation with Searles Lake (Davis *et al.*, 1986) (see Fig. 1.47 for the core locations).





Figure 1.4 General cross section of Clayton Valley with its fault planes and possible groundwater flow (Davis *et al.*, 1986).



SILVER PEAK, NEVADA

Figure 1.5 The salt structure in three basins containing high-lithium brine (Kunasz, 1980; reprinted with permission of the Northern Ohio Geological Society).

(analyzing up to 1700 ppm Li) that appear to have been formed by a reaction of the brine's lithium with volcanic ash. The brine is highly supersaturated with hectorite (assumed from its solubility product), indicating that the lithium was deposited from the brine, and not leached from the mineral (Anon, 1981, 1979; Barrett and O'Neill, 1970).

There is one very small Tertiary high-lithium pegmatite dike (with lepidolite; Kunasz, 1974), a zone of moderately high-lithium exposed ancient lake-bed sediments, and some Tertiary extrusive volcanic rocks in the playa's drainage basin (Davis and Vine, 1979; O'Neill et al., 1969). However, such rocks have not created lithium playas elsewhere in the world from normal run-off water leaching, and in the relatively brief lifetime of the Clayton Valley brine it is unlikely that either hectorite, volcanic ash, the old lake-bed sediments or the pegmatite contributed much lithium to this basin by normal-temperature water leaching (see the temperature-solubility data noted above). Waters accompanying the pegmatite, or very hot rock-leaching during vulcanism could have left a high-lithium brine, but it is doubtful that it could have survived the 6-50 million year period from their occurrence to the present. The Silver Peak Fault geothermal waters, however, do appear to have leached deep, hot, high-lithium containing rocks. The total lithium reserves in Clayton Valley were originally estimated to be about 115,000 mt Li, along with 30 million tons of potash (Kunasz, 1994), but have also been estimated as 382,000 mt of Li (Dillard and McClean, 1991).

#### Salar de Atacama, Chile

This Salar is stated to be the third largest playa in the world (Jordan et al., 2002), and is located in Northern Chile about 200 km east of Antofagasta (Figs. 1.6 and 1.9; 280 km by road and rail) in an upper plateau on the western slope of the Andes mountains (Fig. 1.7). The playa has an area of 3000 km<sup>2</sup>, it is 85 km long with a maximum width of 50 km, and in its southern central section is a 1700 km<sup>2</sup> "halite nucleus" of massive salt (Fig. 1.8; Jordan et al., 2002). Its drainage basin area is about 11,800 km<sup>2</sup>, and its elevation 2300 m. The Cordillera de Domeyko with its extensive Tertiary halite and gypsum outcrops (the Cordillera de la Sal) borders the Salar on the west, the high Andes mountains closely border its east side and more distantly the north. A tall (5,200 m), active volcano (Volcan Lascar; also called Cerro Miniques, with smoke frequently emitting from its cone top) and lower hills border the south. Mud flats dominate the northern part of the salar (Fig. 1.9), and there is a small perennial lake where the Rio San Pedro enters from the north. Several other small lagoons or wet areas are usually present in the mud flats further south and along the eastern side of the salar. This northern area acts as a settling, precipitating (calcite, gypsum, borates, etc.) and brine concentrating area for the Salar, allowing fairly pure halite to crystallize in the south.

The large, highly mineralized El Tatio geyser field lies further to the north, and discharges brine containing up to 47 ppm Li (Table 1.4) into the Rio Salado, which joins the Rio San Pedro (Fig. 1.9) and then flows into the Salar. Some small

11



Figure 1.6 Map showing some of the Andean high-lithium salars and their connecting roads.

intermittent streams enter the Salar from various canyons on its eastern side, but there are essentially none from the western mountains with their salt and gypsum outcrops. The average flow of the San Pedro River is 1000 liter/sec, and the intermittent eastern rivers which enter the Salar primarily through alluvial fans (and not on the surface) have maximum spring flow rates (as liter/sec) of: Vilama 218, Aquas Blancas 134, Tulan 59, Honar 50, Peine 17, and Camar 3 (Ide and Kunasz, 1989).

The southern "nucleus" of the playa consists of massive salt, and in areas that are frequently flooded (the eastern side) the surface salt has a beautiful clear white-topink color, and is uniformly fractured into polygonal patterns (usually pentagonal or



**Figure 1.7** The sequence of elevations of the Andean salars, and their highly faulted plateaus (Vila, 1990; reprinted from Stratabound Ore Deposits in the Andes by permission from Springer-Verlag GmbH & Co. KG).

hexagonal)  $\sim 0.6$  m on a side and 1.5-2 m across. All of these salt polygons have developed expansion cracks at their edges, and then capillary evaporative crystallization of additional salt in the cracks has caused an uneven heaving of the polygon edges up to 0.3 m in height. The salt in most of the central area, however, appears to only have been flooded in rare events (such as 50-100 year



**Figure 1.8** Typical salt surface of the central section of the Salar de Atacama (SQM, 2001, courtesy of SQM S.A).



**Figure 1.9** Surface structure of the Salar de Atacama, and its adjacent rivers and streams (Ide *et al.*, 1983; reproduced with permission of the Salt Institute).

storms). It has a silty brown color and its surface is fairly flat in profile (Fig. 1.8), but composed of very rough, jagged and sharp salt. There are no flat surfaces, making walking on the salt very difficult, and driving impossible, although the salt can be bulldozed to a smooth surface. The salt is very porous (30, 20, 15 and 5% at 0-0.5,

		Typical	Thatyses of Se	Verai Elunani Containi	ing Geotherman Di	ines (ppin	)		
		Cerro	Prieto			Stean Spr	n Boat ings		
	Salton Sea <sup>a,b</sup>	From power plant	From salt pond	El Tatio Springs, Chile <sup>c</sup>	Paradox Basin, CO	СО	NV	Yellowstone, Norris, WY	Typical volcanic springs
Na	50,000-70,000	8700	70,000	4460	25,200	682	653	439	815
Κ	13,000-34,200	1700	36,000	523	26,700	103	71	74	101
Mg	700-5700	_		_	30,900	0.3	0.8	0.2	
Ca	22,600-39,000	400	9400	15.4	43,500	6.8	5.0	5.8	_
Fe	1200-3700	0.94	0.4	_	1380	0.3	_		
Mn	1000-2000	0.64	1.8	_	(260)	_	_		
Sr	540-2000	15.7		_	1300	_	1.0	_	_
Zn	500-700	0.2	1.7	_	50	_		_	_
$HN_4$	504-650	_		_	(1090)	_	<1	0.1	_
Te	520	_	4.0	_	_	_	_	_	_
As	312	1.20	6.5		(20)	2.7	2.7	3.1	_
Li	100-400	16	393	46	$110^{d}$	7.1	7.6	8.4	9.4
Ва	200	9.73	17.0	_		_	_	_	_
Pb	90-210	_	6.7	_	6	_	—	_	_
Rb	25-100	9.4	_	6.6	95	_	—	_	_
Cs	24	3.5		15.5	16	_	_	_	
Cu	0.5 - 20	0.12	0.6	_	8	_	—	_	_
Ag	0.5 - 2	_	0.8	_	A1 (66)	_	_	_	_
Sb	—	_	3.3	—	_	0.5	0.4	0.1	_
U	—	_	31.0	_	_	_	_	_	_
Cl	142,000-209,000	15,610	159.000	8050	201.100	952	865	744	1255
CO <sub>3</sub>	_	_		_	(800)	_	0	0	17
									(

#### Table 1.4

Typical Analyses of Several Lithium-Containing Geothermal Brines<sup>a</sup> (ppm)

(continues)

Table	1.4
-------	-----

(continued)

		Cerro F	Prieto			Steam Spri	Boat ngs		
	Salton Sea <sup><i>a</i>,<i>b</i></sup>	From power plant	From salt pond	El Tatio Springs, Chile <sup>c</sup>	Paradox Basin, CO	СО	NV	Yellowstone, Norris, WY	Typical volcanic springs
HCO <sub>3</sub>	_	_	_	45	(882)	246	305	27	177
SO <sub>4</sub>	42-50	_		32	(227)	125	100	28	53
В	400-500	12		179	1690	67.5	49	11.5	36
Br	109-200	20.5		_	1960	_	0.2	0.1	_
Si	40	_	2.1	102	(10)	145	137	247	_
S	15-30	_		_	_	6.9	4.7	0	_
F	4.6 - 10	_		_	(25)		1.8	4.9	7.2
Ι	0.5	_		_	(264)	_	0.1	< 0.1	_
$PO_4$	1.5	_		_	(1000)	0.8	_	_	_
TDS	_	_			359,000	2,500	2360	1890	2850
Density	1.18 - 1.26	_	1.250	_			_	_	_
pH .	4.6-5.5	_		7.4	(6.2)	_	7.9	7.45	8.1
Temperature (°C)	100 - 400	—	—	85	_	—	89.2	84	93

() Limited number of analyses. Reprinted from Borates: Handbook of Deposits, Processing, Properties and Use, Table 5.6, pages 248-249 © 1998, with permission from Elsevier.

<sup>a</sup> Garrett (1998).

<sup>b</sup> Christopher *et al.* (1975). Also, as ppm: Ce 10, Mo 10, Zr 8, Ta 6, As 3, Se 2.5, Ti 2.5, Cr 2, Ge 1, Cd 0.9, Al 0.6, Ga 0.5, Ni 0.5, V 0.3; 500–3000 m depth. <sup>c</sup> Cusicanqui *et al.* (1975). Located 80 km east of Calama; elevation 4250 m; erupting brine near the boiling point. Power production wells at 550–1800 m depth; maximum temperature (263°C) at 800–1000 m. Surface source water  $\delta D - 74$  to -78;  $\delta^{18}O - 10.5$  to -11.0.

<sup>d</sup>Li range 66–173 ppm.

0.5-2, 2-25 and >25 m depth, respectively; average  $\sim 18\%$  for the upper 25 m), and brine-filled from about 0.6-35 m. The porosity then decreases rapidly to nearly zero after about 35-40 m.

The salt's average depth is about 800 m (with one area up to 1400 m), but the depth varies greatly. Based upon a few drill holes and fairly complete seismic data it appears that the Salar has experienced major faulting (Fig. 1.10) during its basinfilling period, forming large escarpments that have later been filled with additional salt. The major fault (SFS) starts at the lower end of the Salar in about its center and extends in a NNW direction through much of the halite nucleus. The escarpment that it formed resulted in a deep zone to the east of the fault, and made the halite in the east be on average about 240 m thicker than in the west, or about 640–960 m thick (average  $\sim$  720 m) west of the SFS Fault, and 1400–620 m thick (average  $\sim$  960 m) to the east (Fig. 1.10). The age of the basement rock in the basin appears to be about 5.1 ma (million years old), and the lower  $\sim$  500 m of sediments do not contain halite. They are about -5.1 ma old based upon uranium-thorium age dating of ignimbrites (consolidated ash flows, welded tuff or recrystallized ash) within or at the edges of the deposit. A second major fault (the Peine Fault) in the Salar occurs near its eastern edge, running in an NNE direction. Detailed stratigraphic sections of three halite cores, age dating and the estimated environment of the Salar during each period are shown in Fig. 1.11 (Jordan et al., 2002; Bobst et al., 2001).

Brine can be pumped from the Salar's near-surface salt mass at relative high rates, such as >31.5 liter/sec (500–1000 gpm) without appreciable draw-down, although such high pumping rates would hasten the short-circuiting of brine from nearer the surface and from other areas of the Salar. The brine is saturated with salt, and contains variable concentrations of lithium, potassium, magnesium, sulfate and borate in different locations in the Salar (Tables 1.5 and 1.6; Fig. 1.12). The lithium concentration varies from about 1000–4000 ppm, and averages over 1500 ppm for the two commercial operations on the Salar. The total lithium



**Figure 1.10** Thickness of the halite on both sides of the Salar de Atacama's Salar Fault (Jordan *et al.*, 2002, courtesy of the Geological Society of America).



**Figure 1.11** Stratigraphy and age dating of three halite cores in the Salar de Atacama (Jordan *et al.*, 2002, courtesy of the Geological Society of America).

reserves have been estimated at 4.3-4.6 million mt of Li (Anon., 1998, 1995, 1981; Kunasz, 1994; Coad, 1984).

Brine from the El Tatio geyser field contains 28–47 ppm Li (Cusicanqui *et al.*, 1975), and is probably the major source of the Salar's lithium, boron and potassium (and perhaps the magnesium; Tables 1.4 and 1.13), while the majority of the salt and sulfate must have come from the Cordillera salt–gypsum mass. The ratio of lithium and potassium in the Salar are roughly the same as in the El Tatio run-off waters, and the mineralization from this geyser field alone, based upon current surface flow rates, could have supplied the Salar's lithium and potassium in 250,000–360,000 years. Since the Salar's salt mass and arid evaporating climate has existed for much longer than that period, it would appear likely that the geyser's flow and mineral

		Commette	CODEO	Vergara-Edwards	Bro Beckern	wn and nan (1990) <sup>c</sup>	Orrego <i>et al.</i> (1004) <sup><math>d</math></sup>
	Minsal <sup>a</sup>	(1998)	(1981)	$(1983)^b$	Brine	Product	(1994) product
Na	6.50	9.10	8.00	7.60	7.17	770*	570*
K	3.13	2.36	1.84	1.79	1.85	$190^{*}$	$160^{*}$
Mg	1.30	0.965	0.93	1.00	0.96	1.29	1.92
Li	2420	1570	1500	1600	1500	63,000	60,000
Ca*	530	450	300	245	310	530	_
Cl	17.30	18.95	15.90	15.66	16.04	34.46	35.10
$SO_4$	0.80	1.59	1.70	1.90	1.46	166*	$220^{*}$
$B^*$	556	440	600	685	400	7300	6270
$\operatorname{Br}^*$	_	_	_	_	50	_	_
$HCO_3^*$	600	230	_	_	_	_	_
Density	1.227	_	_	1.226	_	1.250	1.252
pH	—	—	_	—	—	6.50	_

Table 1.5

Various Salar de Atacama Brine Analyses, wt.% or \*ppm

<sup>a</sup>Estimated.

<sup>b</sup> Km-20 brine.

<sup>c</sup> Patent assigned to Foote.

<sup>d</sup> Final solar pond brine.

input might also have existed for that long. Also, subsurface flow from El Tatio through the region's many aquifers and faults must have been appreciable, and would have greatly reduced this formation time. Alonso and Risacher (1996) have estimated that 63.4% of the Salar's annual water input at present enters through subterranean flow, but that 85.2% of the yearly lithium addition enters in this underground flow. If these values are correct it would reduce the estimated Salar's lithium input time to as little as 44,000–68,000 years. Since a considerable amount of lithium must have been adsorbed on clay particles while traveling in the river or underground (as occurred in the Owens River feeding Searles Lake), the true age of lithium accumulation is probably somewhere between these two estimated ranges. These authors also estimated that a considerable lithium input came from the small streams flowing from the eastern mountains. However, considering the major uncertainties in their annual flow rate, the amount flowing underground, and the loss by adsorption (which has been very high in studies on deep sea vents, the Owens River and Mono Lake), their lithium contribution was proabably fairly small.

One of the mysteries with this formation theory, however, is what has happened to the borate content of El Tatio's brine? Based on the Salar's lithium and potassium analyses only about one-tenth of the El Tatio boron is now in the Salar's brine. As a related question, why are there not beds of ulexite, colemanite or other calcium borates in the Salar as there are in all of the Puna regions' other lithium-containing,

		21	•								
Salar	pН	Dissolved solids	Na	K	Mg	Ca	Li	Cl	$SO_4$	HCO <sub>3</sub>	В
Aguas Calientes	7.7	81,436	25,460	1183	1361	2538	152	46,690	3154	0	474
Ascoton	7.8	153,600	45,000	3500	5125	920	186	70,000	25,000	2900	783
		47,022	13,870	1670	827	1195	82	24,000	4693	0	595
Atacama	6.6	370,000	91,000	23,600	9650	450	1570	189,500	15,900	230	440
		310,000	85,800	13,000	6350	1100	940	163,900	8540	280	360
		190,000	45,100	9000	5330	900	520	83,780	18,170	240	360
		73,000	18,220	4220	1810	360	290	36,750	3430	320	100
		62,000	14,840	2900	1930	1080	190	27,500	7900	100	88
		40,100	10,280	1690	750	1160	130	20,300	2160	92	61
Bellavista, Pintados	10.4	170,300	50,000	5403	3665	5935	85	100,600	2720	178	225
Huasco	6.0	150,100	38,000	10,000	1750	840	130	83,600	13,600	_	2200
Lugunas	6.8	390,000	126,800	14,280	3630	110	412	176,600	47,770	406	979
Punta Negra	7.1	271,900	86,000	10,000	2620	2080	320	164,500	4480	_	2230
Pujsa	8.6	89,298	28,500	1295	653	375	137	27,660	28,110	0	675
San Martin	_	102,138	28,160	2614	6252	1566	187	60,050	2490	625	426
Surire	7.5	167,200	54,000	8700	1250	750	340	79,800	20,300	90	1820
Hot Springs <sup>a</sup>	7.8	4357	1210	200	28	135	8.3	1905	534	150	47
Rivers <sup>b</sup>	7.7	152	23	2.8	4.3	1.0	0.1	22	20	33	0.7
Soil <sup>c</sup>		—	2.2	0.3	1.8	13.5	65	1.2	22.9	3.1 CO <sub>3</sub>	3.1

 Table 1.6

 Typical Analyses of Various Lithium-Rich Brines in Northern Chile, ppm (Garret, 1998)

Reprinted from Borates: Handbook of Deposits, Processing, Properties and Use, Table 4.3, pp. 201, ©1998, by permission of Elsevier.

<sup>*a*</sup> Also SiO<sub>2</sub> 129, NO<sub>3</sub> 7.4.

<sup>b</sup> Also SiO<sub>2</sub> 45,

<sup>c</sup> South-center of playa, average 6.1 m depth. Also As 158 ppm.



Figure 1.12 Isopach map showing the lithium, potassium and sulfate concentrations in the Salar de Atacama (After Ide and Kunasz, 1989; CORFO, 1985).

geothermally fed salars? The borates are usually found as nodules (like potatoes) buried in the playas' near-surface muds to a depth of 0.2-1.3 m, although some nodules can be much deeper, and some playas have formed layered deposits. Most of these playas have been commercially mined for their borates in the turn of the century, and quite a few still are (Garrett, 1998). However, no large-scale borate deposits have ever been noted in the near-surface of the Salar de Atacama. This probably implies, since the El Tatio geyser field almost certainly supplied most of the Salar's lithium content, and the Salar's sediments are so old that there probably are deeply buried borate deposits in the northern non-halite zone of the Salar. Most of them would have deposited prior to the last ice ages 10,000-21,000 years ago, and then been buried by the sediments carried into the Salar with the massive ice age water flows. This would make their depth below 18-20 m (Fig. 1.11), and indicate that there should be over 114 million tons of ulexite (NaCaB<sub>5</sub>O<sub>9</sub>·8H<sub>2</sub>O; 15.2 MMmt B) buried in the Salar's San Pedro de Atacama mudflats. The ulexite would have slowly formed as the Rio San Pedro water met the high-calcium sulfate run-off water from the Cordillera de la Sal, since ulexite is much less soluble than gypsum (but also

much slower to crystallize). Based upon the hydrodynamics of the other salars most of it would be in the mud flats close to the Cordillera. This reaction, in turn would have liberated the sulfate from the Cordillera's dissolved gypsum, and would account for the high sulfate content in the salar's brine.

Ide and Kunasz (1989) have reported that there are zones of high-lithium sedimentary rocks (up to 470 ppm Li) in the basin's run-off area, and considerable masses of low-lithium volcanic ash and rocks. They made some tests indicating that the rocks could be rapidly leached by water at ambient temperatures to yield 1-15 ppm Li solutions. However, no one else has ever reported such simple low-temperature lithium leaching, as the leach solutions at ambient temperatures from other researchers contained less than 0.01-0.04 ppm Li, and temperatures > 300°C were required to leach that much lithium from the rocks tested. Further, if low-temperature leaching could generate such lithium solutions from volcanic and sedimentary rocks, there should be far more high-lithium brine deposits of this type, since there are many playas in the Andes and elsewhere in the world with similar rocks. However, the only similar (but smaller and/or less concentrated) lithium deposits occur where there are known high-lithium hot springs feeding into closed basins to form playas (Garrett, 1998).

The evaporation rate of water at the Salar is relatively high, even with its high altitude and cold winters and evenings, since there is usually some-to-moderate wind, and the humidity is very low (usually only 5–10%). These conditions allow even the Salar's very hygroscopic MgCl<sub>2</sub> or LiCl solutions to evaporate and crystallize salts. The evaporation rate for water is in the range of 3200 mm/yr, compared with 2300 at Hombre Muerto and 1800 at the Great Salt Lake and Clayton Valley. The area's average rainfall is 10–50 mm/yr (average 10–15; Hombre Muerto 55–70, Clayton Valley 230 and Great Salt Lake 330 mm/yr; Harben and Edwards, 1998). Ide and Kunasz (1989) list the Salar de Atacama's rain at 10–30 mm/yr (average near 10 mm/yr), the solar radiation 630 langleys/day ( $6.3 \times 10^6$  cal/m<sup>2</sup>/day), the temperature range from  $-5^{\circ}$ C (winter) to 35°C (summer), and the brine level generally 50–70 cm from the surface. They also state that there are two confined aquifers in the mud flat area of the Salar that cause some springs to form in both the mud and the edges of the halite zones.

There are also a number of smaller, but similar fairly high-lithium salars throughout the Puna region of Chile, Argentina, Bolivia and Peru as seen in Tables 1.6–1.8, and Fig. 1.6. For example, the Salar de Surrie in Chile contains a brine with 389 ppm Li, 1334 ppm B and 1120 ppm K. It has an area of 150 km<sup>2</sup>, an altitude of 4480 m, 5 and 18°C average winter and summer temperatures, and has an 80°C hot spring in its southeast corner (Garces, 2000). In this high Andean plateau area with its many volcanoes and geothermal springs each of the salars appeared to have originated from the region's hot springs. As the groundwater from rain and snow percolates through the region's many faults it would be heated by contact with rock still hot from the recent or active vulcanism, and in some cases leach both lithium and boron (always an accompanying mineral in these salars). This is the

			Dimein	ang ses at	ine suiu	de moni	ore muerto (pp.	(ou				
	Na	K	Ca	Mg	Li (ppm)	Cl	$SO_4$	B <sub>2</sub> O <sub>3</sub> (B) (ppm)	Total solids	Density (g/cc)	pH	Conductivity (µmho/cm)
Initial brine in the Catal Lagoon (ppm)	15	76	210	72	2.1	900	1100	25 (7.77)	3500	1.001	7.5	—
Catal Lagoon brine at NaCl saturation (wt.%)	9.45	0.55	0.02	0.16	930	15.8	1.06	1400 (435)	28	1.22	7.2	_
Average brine in the top 1 m of sediments (wt.%)	10.1	0.519	0.088	0.054	521 <sup><i>a</i></sup>	16.0	0.846	750 (233)	27.8	1.204	6.9	1.74
Range (wt.%)	9.9– 10.3	0.24– 0.97	0.068- 0.121	0.018– 0.141	190– 900	15.8– 16.8	0.53-1.14	260–1590 (87–535)	27.2–29.4	1.199–1.212	6.5-7.2	1.68-1.80

Table 1.7

Brine Analyses at the Salar de Hombre Muerto (ppm or wt.%) (Garrett, 1998)

Reprinted from Borates: Handbook of Deposits, Processing, Properties and Use, Table 5.1, p. 232 @1998, by permission of Elsevier.

<sup>*a*</sup> As well as 29 ppm Rb and 33 ppm Cs.

theory for the much-studied El Tatio geyser field, and it probably holds true for all of the region's high-lithium salars.

#### Salar de Hombre Muerto, Argentina

This medium sized (565 km<sup>2</sup>) playa (Fig. 1.13) lies about 240 km SE of Antofagasta, Chile (as the crow flies; 565 km by road and rail), 395 km from Salta, Argentina and 1300 km NW of Buenos Aires, in the remote altiplano area of the Andes Mountains. The nearest large town is Salta in the Andes foothills to the northeast (Fig. 1.6). The Salar is at an altitude of 4300 m (4100 and 3964 m have also been reported) with a small mountain-peak island in its western center, and its surface is always partially flooded (from the Catal Lagoon in the southeast corner; Fig. 1.14) and partially dry. The Salar's surface near the Lagoon often floods in the winter from the perennial Los Patos river, and thus after the water evaporates is usually covered with smooth white salt, while most of the other areas have a dirty,



**Figure 1.13** Surface structure of the Salar de Hombre Muerto (Garrett, 1998; reprinted from Borates; Handbook of Deposits, Processing, Properties and Use, Fig. 5.1, p. 228, ©1998 by permission of Elsevier).



Figure 1.14 Areal view of the Salar de Hombre Muerto's Catal Lagoon, with the northwestern section of the Salar in the background.

very uneven salt-clay surface as in most of the Salar de Atacama (Fig. 1.8). A >50 m thick massive salt body underlies much of the Salar, and contains a highlithium brine in its porous upper section. Its lithium content averages 521 ppm, but varies from 190–900 ppm (Fig. 1.15 and Table 1.7), and the brine is estimated to contain 800,000 mt of lithium, 1.1 million mt of B<sub>2</sub>O<sub>3</sub> and 80 million tons of potassium. The Salar's average air temperature has a high of 7°C and a low of  $-6^{\circ}$ C, with a maximum and minimum of 13 (also noted at 28°C) and  $-32^{\circ}$ C, respectively. The average rainfall is 60–80 mm/yr, and the evaporation rate about 1500 mm/yr. The algae in the Catal Lagoon support a large colony of pink flamingoes, and wild burros and domesticated llamas graze on the bunch grass near the Salar.

The brine in the Salar is usually within 20 cm of the surface, and it appears to be relatively constant in composition with depth to at least 15 m. The analyses listed above were taken from samples mostly at a depth of 0.7-0.9 m, and in these holes the average amount of insolubles in the salt was 1-11%. The average porosity of the salt to 15 m was about 15%, there appeared to be some circulation of the brine in the salt mass, and there was capillary evaporation from the surface. Most of the calcium, and some of the magnesium and sulfate in the Los Patos river water precipitated as it advanced to the edges of the Catal Lagoon and into the main brine body. About 32% of the Salar's near-surface crust contained on average 12.7 cm of cotton ball ulexite



**Figure 1.15** Brine analyses across the Salar de Hombre Muerto, g/liter (Garrett, 1998; reprinted from Borates; Handbook of Deposits, Processing, Properties and Use, Fig. 5.4, p. 231, © 1998 by permission of Elsevier).

(much of it as large nodules like potatoes), starting at an average depth of 80 cm and extending to a depth of several meters. The total ulexite would appear to be about 7 million tons of  $B_2O_3$ , and in the early 1900s some of it had been commercially harvested (Garrett, 1998).

In a 40 m core sample uranium-thorium age dating on layers of ash indicated that the bottom was about 82,000 years (82 kyr) old. At a 6.4 m depth the age was about 8000 years. The amount of mud in the halite from 8-26 kyr indicated that the weather had been comparatively dry, as at present, followed by a brief period of wetter weather. During the period from 64-82 kyr the Salar appeared to have been a saline lake, and the weather was much wetter (Lowenstein *et al.*, 1998).

#### Salar de Uyuni, Bolivia

The Salar de Uyuni is located in central Bolivia fairly near its western border with Chile, about 190 km from Iquique, Chile and the Pacific Ocean (660 km by rail; Fig. 1.6). It lies within the Puna region of the Andes Mountains, a very high, large and arid valley region within the Andes that extends from central Argentina to Peru. The Salar is the world's largest saline playa, with its surface area having been estimated at  $9000-10,500 \text{ km}^2$  (its longest dimension is 120 km; Fig. 1.16), and the



**Figure 1.16** Map of the Salars de Uyuni, Coipasa and Empexa, and the ancient Lago Minchin (Ericksen *et al.*, 1978; reprinted from Energy, Vol. 3, No. 3, © 1978 with permission of Elsevier).



**Figure 1.17** Brine concentration map of Salars de Uyuni, Empexa and Coipasa (Ericksen *et al.*, 1978; reprinted from Energy, Vol. 3, No. 3, © 1978 with permission of Elsevier).

smaller but quite similar Salars de Coipasa and Empexa are adjacent to it (Fig. 1.17). Its altitude is 3653 m, and much of its northern surface is hard, smooth and flat, similar to the Bonneville salt flats in Utah (used for very high speed racing). There are occasional algal reefs up to 75 m high, as well as much lower algal terraces, indicating that the playa was once a much larger and deeper lake (called Lago Minchin). It apparently started to reduce to its present size about 10,000 years ago, and the evaporation was completed about 3520 years ago based upon the age of near-surface organic matter. The Salar's average depth is 121 m, and it has a 0.1-20 m thick salt mass (average 3-6 m) in its central area in the form of 11 porous (20-30% void space) halite beds separated by layers of mud and sand. In the southern section there is a small perennial lake, the surface crust is much more irregular and the near-surface sediments contains significant amounts of ulexite (NaCaB<sub>5</sub>O<sub>9</sub>·8H<sub>2</sub>O; Garrett, 1998).

The Rio Grande de Lipez river flows into the Salar from the south, forming an extensive delta area and the perennial lake. The Salar floods from 0-75 cm deep during the rainy season, but most of the playa usually dries completely in the summer. However, beneath the surface the Salar is filled with brine, and it is always within 5-20 cm of the surface. The brine contains 80 to 1150 ppm of

lithium, and averages 321 ppm Li, but one limited area in the southeast corner averages 625 ppm (Table 1.8 and Fig. 1.17). There are many thermal springs feeding into the Rio Grande river (and thus the Salar) that have a high lithium (4-30 ppm) and boron content, and they are probably the major source of the Salar's minerals. As an example of the Salar's concentrating effect on the springs' water, the Rio Grande river enters the Salar with 11 ppm boron (B is about 2/3 the Li value), but by the time it has passed through the Salar's delta system its concentration is 520 ppm B. The surface crust in this southern area is being mined for its ulexite content (in 1996 at a rate of 5000 mt/mo), and salt has been mined from the central area since the 1500's. It has been estimated that the Salar contains 13 km<sup>3</sup> of brine with 5.5 million mt of lithium, 110 million mt of potassium and 3.2 million mt of boron. The average rainfall in the area varies from 20–50 cm/yr, while the evaporation rate is about 150 cm/yr. There are a number of smaller high-lithium salars at a higher elevation (4000–5000 m) and to the south of Uyuni (Table 1.8; Garrett, 1998).

#### Searles Lake, California

Searles Lake is a medium sized playa located about 200 km north of Los Angeles in the Mojave Desert. Its surface area is about  $100 \text{ km}^2$ , the center of which consists of massive halite that is about 8 m thick. The halite is 3500 years old at the surface and 6000 years old at its base (Fig. 1.3). Beneath the halite are two zones consisting of many saline minerals (halite, trona, hanksite, borax, thenardite, etc.), with a 5 m thick clay layer in between (Fig. 1.18). Both salt masses are very porous ( $\sim$  35%) and filled with a high-density ( $\sim$  1.30 g/cc) brine (Table 1.9). In the central section of the Lake the brine contains an average of 50-80 ppm Li, which grades to about 10-70 ppm Li near the edges of the deposit. The massive, porous halite in the center grades to an overburden consisting of clay at the edges. Under the halite is about 13 m of the massive Upper Salt (1.05 km<sup>3</sup> of salts), the clay layer, and finally 14 m of the Lower Salt (with alternate layers of salts and mud;  $\sim 0.5 \text{ km}^3$  of salts) that extends to a depth of about 40 m. Beneath the Lower Salt is about 30 m of clay, and then a mixed zone which has layers of clay alternating with layers of varying purity sodium carbonate and sodium sulfate minerals with halite.

The source of the various salts in Searles Lake, including the lithium has been fairly positively determined. First, as seen in Fig. 1.19 Searles Lake received most of its water and minerals from the Owens River. The Lake was usually the lowest and the final basin to receive Owens River water after it had accumulated the runoff and spring water from about 420 km along the east side of the Sierra Nevada Mountains. Water could overflow from Searles Lake into the Panamint Valley, and from there into Death Valley, but apparently when this occurred during the peak of the glacial periods the lake had stratified, and only fresh water overflowed. During the interglacial periods the water could evaporate, and for two periods it crystallized the upper salts. This succession of dry and then pluvial periods lasted

									Pastos Grandes	Salar <sup>a</sup>
	S	Salar de Uyu	ni	Salar de l	Empexa <sup>b,c</sup>	Salar de	Coipasa <sup>c</sup>	Но	ot Springs	
	1	2	3	2	4	2	4	Edge <sup>d</sup>	Playa	Subsurface brine
Na	8.2	8.72	7.06	5.4	6.7	7.51	71	317	0.448	7.72
Κ	0.66	0.72	1.17	0.27	0.52	1.10	1.21	43	0.05143	0.891
Mg	0.64	0.65	1.25	0.68	0.32	1.36	1.36	4.5	67 ppm	0.174
Ca (ppm)	456	463	306	209	410	156	227	10.2	212	1440
Li (ppm)	321	349	625	172	253	350	243	5.2	69	1800
Sr (ppm)	_	14	_	_	_	17	_	_	_	_
Cl	14.8	15.71	5.0	9.7	14.8	15.10	16.5	560	0.876	15.67
$SO_4$	1.08	0.85	_	2.8	_	2.46	_	36.5	0.014	0.932
HCO <sub>3</sub> (ppm)	_	333	_	347	_	747	_	106	539	608
B (ppm)	187	204	525	176	_	786	_	2.0	26	376
Br (ppm)	_	49	_	_	_	142		_	_	_
F (ppm)	_	10	_	_	_	33	_	_	_	_
SiO <sub>2</sub> (ppm)	_	7	_	_	_	10	_	39	37	7.1
pН	_	7.25	7.3	—	_	7.23	_	6.55	6.30	7.14
Density	—	1.21	1.19	—	—	1.231	—	1.001	1.013	1.194

 Table 1.8

 Average Analyses of Various Lithium-Rich Bolivian Brines wt.% or ppm (Garrett, 1998)

1; an average of 40 Salar de Uyuni samples, 2; a more detailed individual sample analysis, 3; an average of the eight highest-lithium samples, found in a narrow band in the southern half of the eastern lobe of the salar, 4 is an average of four Salar de Empexa or Coipasa samples.

Reprinted from Borates: Handbook of Deposits, Processing, Properties and Use, Table 4.2, p. 198, © 1998 by permission of Elsevier.

<sup>*a*</sup> This salar is slightly southwest of Uyuni, in Bolivia. There is also a Pastos Grandes in Argentina.

<sup>b</sup> Total dissolved solids (TDS), 19.3.

<sup>c</sup> Adjacent to Uyuni.

<sup>d</sup> All analyses as ppm.



Figure 1.18 Summary of stratigraphic units in Searles Lake evaporite sequence (Smith, 1979).

		Searles Lake	e <sup>a,b</sup>	Gre	eat Salt Lake		Dead	Sea		Bonn	eville <sup>b</sup>
	Upper	Lower	Evaporated	South <sup>c</sup>	Mg Plant <sup>d</sup>	$\mathrm{GSL}^e$	Sea <sup>f</sup>	Conc. <sup>f</sup>	Sua Pan <sup>b</sup>	Brine	Conc.
Na	11.08	11.84	8.32	3.7-8.7	0.5	0.118	3.01	0.38	6.00	8.3	0.2
K	2.53	1.57	10.62	0.26 - 0.72	0.8	0.058	0.56	0.22	0.20	0.5	0.3
Mg	_		_	0.50 - 0.97	7.5	8.55	3.09	7.01		0.4	8.3
Ca	16*		_	0.026-0.036		$50^{*}$	1.29	2.65		$290^{*}$	$88^*$
Li*	54 <sup>g</sup>	60	139	$18^h$	600	1160	12	23	20	57	980
$As^*$	144	_	3480	138		_		_		_	_
$W^*$	22	32	_	_				_		_	_
Fe*	14		_	184		10		_		_	_
Sb*	5		_	_				_		_	_
Cu*	_		_	156				_		_	_
$Zn^*$	_		_	46		_		_			_
$Cr^*$			_	23				_		_	_
Cl	12.30	10.81	13.55	7.0-15.6	20.3		16.10	25.60	7.09	14.0	23.0
$SO_4$	4.61	4.44	1.06	0.94 - 2.00	4.4	2.46	0.061	_	0.83	_	_
CO <sub>3</sub>	2.72	3.84	3.56	5*				_	1.17	_	_
HCO <sub>3</sub> *	_		_	600			190	_	$0.62^{i}$	60	_
B*	2990	4120	14810	$18^h$	540	700	30	_		_	_
Br*	846	537	7390	55		2120	3760	_	200		_
$S^{=*}$	330	1560	2840	_				_		_	_
$P^*$	300	190	2400	_				_		_	_
$F^*$	54	20	_	1.7	_	50		_		_	_
$I^*$	12	20	360	_				_		_	

# $\label{eq:Table 1.9} Table \ 1.9$ The Analyses of Several Lithium-Containing Lakes or Brines, wt.% or \*ppm

(continues)

Geology

#### Table 1.9

(continued)

		Searles Lak	les Lake <sup><i>a,b</i></sup> Great Salt Lake				Dead	Sea		Bonne	
	Upper	Lower	Evaporated	South <sup>c</sup>	Mg Plant <sup>d</sup>	$\mathrm{GSL}^e$	Sea <sup>f</sup>	Conc. <sup>f</sup>	Sua Pan <sup>b</sup>	Brine	Conc.
$SiO_2^*$	_	_	_	_	_		11			_	_
$N^*$	_		_	1.8	_			_	_	_	
Density	1.29	1.30	1.34	$\sim 1.1$	_	1.344	1.198	—	1.124	$\sim 1.2$	$\sim 1.3$

<sup>*a*</sup> Gale (1945).

<sup>b</sup> Garrett (1996) (Searles Lake, Upper and Lower Structure brine; Sau Pan, Botswana; Bonneville Salt Flats, Utah, brine and solar pond end liquor).

<sup>c</sup> Strum (1980) (South arm of lake; dilute values unless a range is given).

<sup>d</sup> Toomey (1980) (product from the magnesium plant's solar ponds).

<sup>e</sup> Nelli and Arthur (1970) (maximum evaporated brine from the GSL solar ponds).

<sup>f</sup>Tandy and Canfy (1993) (Sea brine or end liquor from potash plant's solar ponds).

<sup>*g*</sup> Other authors list 70–80 or 150 ppm Li.

<sup>*h*</sup> North arm 42 ppm Li and B.

<sup>*i*</sup>Wt.%; brine to the soda ash plant's solar ponds.



**Figure 1.19** Location of Searles, Bristol and Cadiz Lakes, showing the flow paths to and from the lakes (Ver Planck, 1957, courtesy of the California Division of Mines and Geology).

for about 50,000 years, flushing the concentrated brine and deposited salts from the intermediate basins (Owens Lake, China Lake, etc.) during each wet cycle into Searles Lake, with the last flushing occurring 3500 years ago. This is the age of the surface salts in Searles Lake, and the age of all of the salts in Owens Lake.

#### 34 Part 1 Lithium

It appears that most of the minerals in the lake, other than much of the halite, came from a cluster of geothermal springs in the Owens Valley area (primarily in the Long Valley). After the Los Angeles Metropolitan Water District (MWD) purchased the water rights to the Owens River in the early 1920s its water initially killed several orange groves in the Los Angeles area because of its high boron content. This caused the MWD to analyze the various water sources into the river, and they found that the problem was the hot springs near the Long Valley Caldera, and some hot springs in the White Mountains on the eastern side of the Owens Valley. Using the MWD's data on flow rate and analysis for a 10 year period from these springs, Garrett and Carpenter (1959) made a material balance for the annual tonnage of minerals from the springs, the tonnage of salts in Searles Lake, and the age of the deposit. There was a very close balance for most of the major ions (carbonate, borate and sulfate), as well as the minor ions (tungsten, iodine and fluorine), but the springs were low in Na, Cl and lithium. Later Smith (1976) made a much more detailed material balance using Owens River water for a later period, and each of the two salt beds separately. His results were similar, but generally indicated somewhat less contribution from the River. However, both calculations would appear to definitely indicate that these springs did supply most of Searles Lake's salts except halite, and that there had been considerable loss of lithium from the springs, presumably because of it reacting with, or being adsorbed onto clays and volcanic rocks that the water contacted as it flowed to Searles Lake. This loss is similar to the apparent reaction of volcanic ash or smectite clay to form hectorite (a lithium clay) in the Clayton Valley, and the near-surface adsorption of lithium from the brine in deepocean rift or subduction zones.

The large scale recovery of products from Searles Lake began in 1916, with brine being pumped to large plant evaporators, followed by a succession of processing facilities to recover most of the brine's individual components. In 1936 facilities were installed to remove the very fine crystals of dilithium phosphate that crystallized with the burkeite in the evaporators, and became an impurity in the soda ash and salt cake products. These "licons," containing about 20% Li<sub>2</sub>O were at first sold to Foote Minerals, but in 1951 a plant was built to produce lithium carbonate and phosphoric acid from them. When the plant to process the burkeite was closed in 1978, the lithium operation was also discontinued (Garrett, 1998; Vine, 1976).

*Mono Lake* is one of the lakes that drained into Searles Lake during the ice age periods, and it has been studied for its lithium isotopic composition in a series of papers (Tomascak *et al.*, 2003, 2001, 2000). The current flow of water into the lake comes from streams (75%) and springs, although almost all of the lithium enters from a few thermal springs. The lake water contains 10 ppm Li with a  $\delta^7$ Li of 19.5, while groundwater and stream water  $\delta^7$ Li is variable but up to 31 and 29, respectively, and the thermal spring water  $\delta^7$ Li is 8.4. The volcanic rocks in the area have a  $\delta^7$ Li of 3.8, indicating that their high-temperature leaching is the source of the thermal spring's lithium.

### **Potential Deposits**

#### Great Salt Lake, Utah

The Great Salt Lake is one of the larger inland lakes in the world (Fig. 1.20), and contains a seawater-type brine. Far more than  $5.7 \text{ km}^2$  of solar ponds have been constructed in the north end of the lake in the broad Bear River mud flat estuary, and



**Figure 1.20** Map of the Great Salt Lake showing distribution of most common types of sediments (Gwynn and Murphy, 1980; reprinted from The Great Salt Lake by permission of the Utah Department of Natural Resources).



**Figure 1.21** The limited-permeability railroad causeway across the Great Salt Lake, Utah (Gwynn, 1980; reprinted from The Great Salt Lake by permission of the Utah Department of Natural Resources).

on the west side of the lake to produce potassium sulfate, salt (NaCl), magnesium chloride brine and previously sodium sulfate. Here the brine can be drawn from the lake's more concentrated zone north of the semi-permeable railroad causeway (Fig. 1.21). Solar ponds have also been constructed in the southern part of the lake for salt and magnesium metal production. The solar ponds produce an end-liquor which is much more concentrated in lithium than the original lake brine (Table 1.9), and thus has been considered for commercial lithium recovery. Although the lake's brine concentration varies widely with the climate cycle, the southern brine has contained from 18 to 43 ppm Li, and the northern brine from 40 to 64 ppm Li (Whelan, 1976). The magnesium plant's solar pond end-liquor often contains about 600 ppm Li, while the potassium sulfate plant has achieved values from 700-1600 ppm Li (Toomey, 1980; Nelli and Arthur, 1970). If the latter end-liquor's lithium were recovered it could amount to over 41 mt/yr of Li. Extensive tests have been conducted on both solvent extraction (with a ferric chloride-organic solvent mixture), and a plant evaporation-selective crystallization process to recover this lithium. However, neither appeared to be sufficiently economical to be competitive with other deposits. The Great Salt Lake is estimated to contain 526,000 mt of lithium.

The subsurface brines of the nearby *Bonneville Salt Flats* are of a simpler type with very little sulfate and bromine, and contain 20–60 ppm Li (Table 1.9). The Bonneville brine is also commercially evaporated in solar ponds to produce potassium chloride (potash) and a concentrated magnesium chloride brine that is sold for road de-icing and other uses. This end-liquor has been further concentrated
than that produced at the Great Salt Lake, so it has a higher lithium content of 2000–4000 ppm, and averages 3000 ppm Li. It might be capable of yielding up to 20 mt/yr of lithium (Whelan, 1976).

## Salton Sea Geothermal Brine, California

In the most southern part of California, in about its central section is the large Salton Sea. South of it and extending into Baja California, Mexico is a very large geothermal brine field in the porous sediments at a depth of about 500-3000 m. The brine is a hot ( $100-400^{\circ}$ C) concentrated solution of predominately sodium and calcium chloride, with a very large array of metals and other uncommon ions, including from 100-400 ppm Li (200 ppm average, Vine, 1980; Table 1.4). Geothermal power is obtained from these brines in both the USA and Mexico, and many studies have been made on the possible recovery of lithium from the plants' effluent brine. At the southern end of the Salton Sea district, Cerro Prieto, Mexico contains equally hot, but much more dilute brine with a lithium content of 5-100 ppm. Pilot plant solar ponds have been operated that concentrated the brine to about 400 ppm Li after a potash recovery process, but no attempt was made to recover the lithium (Garrett, 1996; Vine, 1980; Berthold and Baker, 1976).

The origin of the Salton Sea geothermal brine is believed to be meteoric water (based upon  $\delta D$  and  $\delta^{18}O$  values) from the nearby Chocolate Mountains flowing through fault lines deep into the earth, where it is heated by hot rocks or magma. The brine composition might indicate that the descending water dissolved high-magnesium potash salts that had been formed in this former seawater estuary area (from the present Sea of Cortez [Gulf of Baja California]). Then this brine underwent the very common dolomitization reaction (see Chapter 2) by reacting with calcite and converting most of its calcium content to magnesium. Later, when the brine was heated it became highly corrosive to other rocks, and dissolved the wide array of metal ions that it now contains. There is no present indication of a buried potash deposit or of a high temperature rock source, but it is on the very active San Andres fault line and the plunging Pacific Plate, so the heat source might be at considerable depth. The brine could be a concentrated rift vent brine, but its low bromine content, the terrestrial  $\delta D$  and  $\delta^{18}O$  values, and the lack of dolomite and gypsum beds in the formation or nearby makes this very unlikely (Garrett, 1996).

Dead Sea, Israel and Jordan

The Dead Sea is one of the world's largest and lowest inland lakes, containing a concentrated calcium-magnesium-sodium-potassium chloride brine, with about 10 ppm Li (Table 1.9) and reserves of about 2 million tons of Li. The brine is commercially evaporated in large solar ponds to produce potash in both Israel and Jordan, and their pond end-liquors often contain about 30 ppm Li. Some of this brine is processed for bromine and magnesia recovery, but most of it is merely returned to the sea. Because of its ready availability and potential value several laboratory studies have been made on lithium recovery from it, but without economic success.

The source of the Dead Sea appears to be a blend of hot end-liquor dolomitization brine (such as is found in many springs near the Dead Sea) that has traveled along

#### 38 Part 1 Lithium

fault lines from potash deposits under the Red Sea (Folle and Beutel, 2000), and surface water entering from the Jordan River. Neither seawater nor the river source has a high lithium content, making the lithium concentration unusually low for such a strong brine. However, the Dead Sea is very large, as are the two solar pond potash operations, making the total reserves very large. Even though the Dead Sea is located in one of the lowest valleys in the world, and in a very hot desert, the wind and humidity conditions are not sufficiently favorable to evaporate the brine to crystallize calcium and magnesium chloride salts as at the Salar de Atacama. If they were, then further solar evaporation could appreciably concentrate the lithium, and make its recovery more practical (Epstein *et al.*, 1981).

#### Chinese Dry Lakes

In the high mountainous region of Tibet (Xizang) there are more than 57 highlithium playa lakes similar to those in the Puna or altiplano region of Argentina, Bolivia, Chile and Peru (Fig. 1.22). Geothermal springs with a high lithium content flow into most of the playa lakes, and it has been stated that 37 different ionic species are found in them, along with 27 different minerals in the playas (including many forms of borates). Several of the individual lake analyses are listed in Tables 1.10 and 1.11, and the shape and surface structure of others is shown in Fig. 1.23. Another group of these lakes is in the Qaidam Basin, containing brine with an average of



Maihai; 2, Da Qaidam; 3, Xiao Qaidam; 5, Pengyan-Co; 6, Geerkunsha;
 Xia Caka; 8, Zhacang-Caka; 9, Nieer-Co; 10, Calaka; 11, Zabuye-Caka;
 Laguo-Co; 13, Guojialin; 14, Yagedong-Co; 15-16, Banguo-Co.

**Figure 1.22** Map showing the location of some of the high-lithium lakes in the Qinghai-Xizang (Tibet) Plateau (Dapeng and Bingxiao, 1993; reprinted from the Seventh Symposium on Salt [ISBN 0444891439], Vol. 1, p. 178, Fig. 1, © 1993, with permission from Elsevier).

			Concentration (µmol/l unless noted)									
Lakes	Salinity (g/l)	pН	Na	К	Mg	Ca	Li	$SO_4$	$CO_4$	HCO <sub>3</sub>	$B_2O_3$	Cl
Zabuye Caka												
Surface brine <sup>a</sup>	282.63	8.3	4065.42	543.18	1.37	3.39	90.34	361.98	698.92	_	182.94	3449.21
wt.%			7.29	1.66	26 ppm	106 ppm	489 ppm	2.71	3.27	_	0.99	9.53
Interstitial brine	434.47		10.66	3.83	_	_	660 ppm	2.19	3.75	0	0.45	12.30
Bangkog Cuo												
Lake I surface brine	68.52	8.7	1130.74	109.08	5.45	_	14.98	183.90	76.90	26.55	38.28	675.39
Lake II interstitial brine	119.20	8.6	1562.62	99.88	3.07	0.01	35.30	994.16	124.49	69.90	45.31	561.25
Lake III surface brine	221.88	8.7	2696.38	200.57	4.53	—	18.30	18.87	221.64	201.51	78.66	1118.63
Guogaling Cuo												
Surface brine	114.17		1761.35	87.32	0.41	_	16.14	892.14	207.42	53.50	42.70	459.94
Interstitial brine	125.97	8.8	2217.99	200.85	2.64	—	21.61	769.51	396.29	3.07	106.54	1165.32

# Table 1.10

Chemical Composition of the Brines in Various Alkaline Lakes in the Xizang (Tibet) Plateau, China (Garrett, 1998)

Reprinted from Borates: Handbook of Deposits, Processing, Properties and Use, Table 5.3, pages 238–239, © 1998, with permission from Elsevier. <sup>*a*</sup> Na<sub>2</sub>CO<sub>3</sub> (After subtracting the equivalent Ca, Mg, and Li) 5.36 wt.%; Na<sub>2</sub>SO<sub>4</sub>, 4.01 wt.%; Na<sub>2</sub>B<sub>4</sub>O<sub>7</sub>, 1.11 wt.%; KCl, 3.15 wt.%; NaCl, 13.51 wt.%.

39

			-	- 1	
. I. O	hL	•			
1 4	.,,,,,,,,,,,,,,,,,,,,,,,,,,,,,,,,,,,,,,	<b>C</b>			

	Analyses of Several Lithium-Rich Lakes in the Qaidam Basin, China, wt.% or ppm (Garrett, 1992)													
	Na	K	Mg	Ca	Li (ppm)	Cl	$SO_4$	HCO <sub>3</sub>	CO <sub>3</sub>	$B_2O_3$	Br (ppm)	Total salts	pН	Density (est.)
Da Qaidam														
Intercryst.	5.63	0.44	2.02	0.02	310	13.42	3.41	0.06	0.02	0.20	58	25.05	7.3	1.234
Surface	7.77	0.36	1.17	0.03	182	14.16	2.04	0.21	—	0.26	80	25.68	7.4	1.240
<i>Kiao Qaidam</i> Surface	5.43	0.13	0.39	0.08	38	12.14	3.57	0.004	_	0.19	16.6	21.76	_	1.203
<i>Mahai</i> Intercryst.	8.08	0.16	0.96	0.07	51	10.84	2.33	_		434 ppm	_	22.38	_	1.208
Qinghai Lake <sup>a</sup>	3.93	0.16	0.79	0.01	0.84	5.79	2.35	0.68	0.52	15 ppm	1.5	14.23	_	1.133

<sup>*a*</sup> Also (ppm): Si, 0.93; P, 0.50; Al, 0.26; Cr, 0.12; Ni, 0.092; Fe, 0.067; U, 0.042; Sr, 0.04; Ba, 0.02; Cu, 0.016; Mn, 0.016; Ti, 0.01; I, 0.004; Zn, 0.0021.



Figure 1.23 Several of the high-lithium Chinese Lakes, and their surface composition (Dapeng and Bingxiao, 1993; reprinted from the Seventh Symposium on Salt [ISBN 0444891439], Vol. 2, p. 179, Fig. 1, © 1993, with permission from Elsevier).

41

(as ppm if not noted): 320 Li, 542 B, 6.2% Na, 0.66% K, 0.47% Mg, 159 Ca, 6.7 Sr, 5.4 Rb, 1.9 Cs, 1.7 As, 9.2% Cl, 2.8% SO<sub>4</sub>, 0.12% CO<sub>3</sub>, 948 HCO<sub>3</sub> and 113 F. The age of the lakes is estimated to be 5600-20,000 years. Several of these lakes are quite large, and the Qinghai playa was being prepared for commercial potash production in 2001, with its 8-13 ppm Li brine to be sent to solar evaporation ponds. The final potash end-liquors with about 120 ppm Li were being considered for the production of lithium (Qian and Xuan, 1983).

Lake Zabuye Caka has an especially complex brine, somewhat resembling Searles Lake, but with higher concentrations of all of the alkali metals (K, Li, Rb and Cs; Tables 1.10 and 1.12). The lithium content in its brine varies from 500 to 1000 ppm, and the brine has been extensively studied for potential multiple mineral production. The brine is saturated with both salt and potassium sulfate, and during solar evaporation the lithium starts to crystallize at about a two-fold concentration (Table 1.12; Garrett, 1998, 1992). This lake has also been reported as being developed for lithium production (USGS, 2001).

## Other Geothermal Brines

Brines in the *Reykjanes, Iceland* geothermal field contain modest concentrations of lithium (7.4 ppm), and several studies have been made on its potential recovery. At current flow rates the production of perhaps as much as 500 mt/yr of lithium (as lithium compounds) might be possible. Similar brine and studies have been conducted at the *Wairakei, New Zealand* geothermal area. Their brine contain 12 ppm Li, and their flow rate of 3.785 million l/hr might allow the production of 2400 mt/yr of lithium carbonate. Studies have also been made on the potential recovery of lithium from the geothermal brines of *Cesano, Italy; Cronembourg, Alsace, France*; and the *Hatchobaru* and *Othake* areas of *Kyushu, Japan* (Pauwels *et al.*, 1990). Many other geothermal waters have a lithium content in the range of 1–10 ppm (White *et al.*, 1976), and a few have slightly higher values as indicated in Tables 1.4, 1.13 and 2.6.

The East Pacific Rise *deep-ocean thermal vents* (Fig. 1.11) contain 7.2 ppm Li, have a pH of 3.5, and most of the other ocean thermal vents have a similar relatively high-lithium content. These vents have been extensively studied to determine their lithium source, including the extent of leaching from the rift zone rocks, or the adsorption of lithium onto the clay and other sediments on the ocean floor. For instance, the East Pacific Rise had a volcanic eruption at  $9-10^{\circ}$ C N latitude in 1991. It was noted that the vents' brine greatly decreased in their lithium content near the eruption for several weeks, presumably because of the formation of new and shallower (and thus cooler and briefer) travel paths for the seawater to circulate in the Rise's fracture patterns. Then the lithium slowly increased over the next 6 years (Bray, 1998). The North Fiji Basin vents also have a relatively high lithium content, along with appreciable methane and hydrogen sulfide. These vents are cold, and appear to be seawater-diluted hot vents that have had most of their heavy metal content precipitated by the hydrogen sulfide (Koschinsky *et al.*, 2002). Laboratory studies have been made to simulate the rock-leaching by the Juan de Fuca Ridge

Sample no.	Density	pН	Total salts	Κ	Na	Li	Rb	Cs	CO <sub>3</sub>	$SO_4$	Cl	Br	1	В	Conc. ratio
1	1.3047	10.86	428.56	50.00	139.11	0.87	0.000	0.034	42.13	28.52	160.54	0.965	0.0013	5.90	1.0
Wt.%			32.85	3.83	10.66	$667^{*}$	69*	$26^{*}$	3.25	2.19	12.31	$790^{*}$	$1.0^{*}$	1.46	
2	1.3226	_	433.01	55.15	142.44	1.08	0.000	0.043	40.03	29.65	156.12	1.04	0.0024	6.81	1.25
3	1.3333	10.83	442.58	59.00	142.44	1.26	0.090	0.054	52.33	25.56	151.67	1.29	0.0030	8.40	1.52
4	1.3573	10.38	462.82	65.10	146.15	1.44	0.140	0.066	70.33	23.09	144.55	1.49	0.0021	9.87	1.67
5	1.3630	10.67	465.13	62.50	146.15	1.48	0.140	0.069	80.20	22.19	139.81	1.78	0.0021	10.81	1.76
6	1.3703	10.75	469.82	62.50	155.06	1.50	0.180	0.081	82.33	20.99	132.09	2.07	0.0028	13.01	2.18
7	1.3762	_	473.54	62.50	158.77	1.51	0.180	0.085	88.78	20.21	126.16	2.07	0.0011	13.25	2.23
8	1.3880	10.92	456.88	59.00	162.25	1.63	0.240	0.100	76.93	19.76	121.41	2.34	0.0024	15.22	2.73
9	1.3851	10.98	481.45	59.00	156.91	1.65	0.240	0.100	105.02	18.54	121.69	2.41	0.0025	15.89	2.77
10	1.3987	11.11	473.74	55.15	160.18	1.50	0.240	0.104	97.34	19.55	118.15	2.56	0.0021	16.66	2.85
11	1.4168	11.36	491.73	55.15	173.60	1.82	0.360	0.113	116.35	19.86	107.17	3.33	0.0026	15.97	3.66
12	1.4120	11.22	488.63	56.00	173.61	1.62	0.480	0.180	111.44	18.11	106.93	4.92	0.0038	15.34	5.31
13	1.4155	11.12	505.92	63.00	173.61	1.56	0.720	0.225	116.30	19.92	108.47	5.84	0.0064	16.27	7.31
14	1.4214	11.22	497.44	56.00	181.02	1.64	0.880	0.290	106.82	20.02	105.39	6.78	0.0071	18.59	9.16
15	1.4367	11.08	507.76	56.00	181.02	1.46	1.240	0.450	113.66	19.76	103.73	9.35	0.0074	22.08	13.51
16	1.4409	11.13	524.24	93.35	178.13	1.26	1.800	0.633	107.02	19.76	99.09	13.37	0.0144	22.08	19.31

 Table 1.12

 Solar Evaporation of Zabuye Caka Lake Brine (g/l) (Garrett, 1992)

Concentration of Mg, Ca, Sr, HCO<sub>3</sub> all  $\sim$  0. \*ppm.

Reproduced from Natural Sada Ash: Occurrences, Processing, and Uses, Table 5.12, pp. 184-185, ©1992 with kind permission of Kluwer Academic Publishers.

Geology

Table	1.13
-------	------

	Cesano <sup>a</sup> (mg/l)	$\text{Cronembourg}^b \text{ (mg/l)}$	Wairakei <sup>c</sup> (ppm)	El Tatio <sup>d</sup> (ppm)	Puga Valley <sup>e</sup> (ppm)
Li	350	220	12	38	5.9
Na	63,570	32,200	1200	3620	588
Κ	21,370	3978	185	357	57
Mg	12	145	_	2.2	2.1
Ca	43	4600	18	252	7.3
As	_	_	4.5	45	_
Fe	0.7	5.2	_	0.13	_
Cs	_	_	2.5	11.3	10.5
Rb	_	_	2.5	4.2	0.9
$NH_4$	12	_	_	_	_
Cl	37,010	61,415	2100	6470	375
$SO_4$	91,010	508	32	36	128
$HCO_3$	1900	305	18	46	816
В	13,800	_	28	145	135
F	100	4.6	_	2.9	12
SiO <sub>2</sub>	130	235	560	184	_

Analyses of Various Geothermal Brines

<sup>a</sup> Italy (Pauwels et al., 1990).

<sup>b</sup> Alsace, France (Pauwels et al., 1990).

<sup>c</sup> New Zealand (Rothbaum and Middendorf, 1986).

 $^d$  Chile, average of 12 samples. Also: Sb 40, Sr 1.13, Mn 0.38, Pb < 0.06, Ti < 0.06, Ni < 0.03, Cu < 0.02, Ag < 0.005, Zn < 0.004, S $^{2-}$  18, CO<sub>3</sub> 5.8, pH 7.2, temperature 84.6°C (Cusicanqui et al., 1975).

<sup>e</sup> India (Garrett (1998)). Also: Ba 20, Cu 2.0, Sr 0.22, TDS 2202, pH 7.9.

thermal vents, indicating that lithium is not removed from basaltic rocks below about 150°C, and based upon  $\delta^7$ Li data, at that temperature some lithium is adsorbed by the basalt, and some is leached. Terrigenous sediments can have some of their lithium leached and vent brine lithium re-adsorbed at 50°C, but most of their lithium is not leached until the temperature is over 350°C (James *et al.*, 2003).

An ocean drilling program at the Costa Rica Rift showed that the upper ~ 1.8 km of sediments were enriched in lithium (5.6–20.8 ppm Li) due to the adsorption of lithium onto the clays that were present, and that this lithium had a heavier  $\delta^7$ Li value (6.6–20.8) because of that zone's relatively higher seawater circulation. At greater depth the rock's lithium content was depleted to 0.6 ppm, and its  $\delta^7$ Li values were – 0.8 to 2.1, typical of basaltic or magmatic rocks (Chan *et al.*, 2002b,c). Other laboratory studies have been conducted on the leaching or adsorption of lithium from rocks obtained by the Nankai Trough drilling program. Some of the rock's lithium began to be leached at a temperature of 150°C with considerable isotopic fractionation, and the leaching was nearly completely at temperatures over 300°C. At higher temperatures there was considerable albitization of calcic plagioclase (You and Gieskes, 2001). Various studies have also been made on the lithium

isotopic distribution of unaltered island arc lavas and Mid Ocean Ridge basalt. The Central American arc lava has a  $\delta^7$ Li value of -4.5, and the Kurile arc (eastern Russia), Sunda arc (Indonesia) and the Aleutian arcs averaged from +2.1 to +5.1, thus indicating no partitioning of lithium in these lava flows (Tomascak *et al.*, 2002). Table 1.14 lists the lithium isotopic data for various other lithium rocks or waters.

#### **Oil Field Waters**

A few of the world's oil field waters have a medium-high lithium content, with limited areas of the extensive Smackover brines in the US Gulf Coast states perhaps being the highest. One zone in both Arkansas and Texas has high-sodium and calcium chloride brines with lithium contents of 50-572 ppm. The Texas brine has an average of 386 ppm Li, and the Arkansas brine averages 365 ppm Li (Table 1.15). All of the Smackover oil field brines appear to be concentrated seawater dolomitization brines (because of the high Ca and Br; see Chapter 2), and the high-lithium areas must have had additional geothermal input to supply the Li, B and many of the other trace ions. The brine is found at depths of 1800-4800 m, and its formation thickness is up to 213 m of oolitic limestone with an average porosity of about 5%. Smackover brines are commercially processed to recover bromine in Arkansas, and several studies have been made on the potential recovery of lithium from them. Various other oil field brines have medium-high lithium values such as is indicated in Table 1.15 (e.g., some Texas Cretaceous reservoirs have 132-333 ppm Li (Table 2.5), North Dakota Devonian formations 100-288 ppm Li and the German Altmark gasfield 263 ppm; Holdorf et al., 1993; Chan et al., 2002a; Burkowsky et al., 1991; Collins, 1976).

## Other Lithium Brines

There are many other medium-high lithium brines in the world, with one type being most of the high-calcium chloride brines, which includes those in the Salton Sea geothermal field, the Dead Sea, some groundwaters (i.e., in Germany with 290 ppm Li) and some of the oil field and geothermal brines noted above. Most of the marine *potash deposit end-liquor brines* have a high to medium-high lithium content, such as the Angara-Lena basin, Russia's 1600–1900 ppm, the Paradox Basin's 66–173 ppm Li (Tables 1.4 and 2.2), the Michigan Basin's Sylvania Formation's 36–72 ppm (Table 2.4), and the English Zeichstein Formation's 7–65 ppm, etc. (Table 2.12). However, some end-liquors have only a nominal lithium contents, such as from the Saskatchewan, Canada potash deposits (Bottomley *et al.*, 1999). A few calcium chloride lakes also have medium-high values, such as the Don Juan Pond's 235 ppm, Bristol Lake's 30–108 ppm, Cadiz Lake's 20–67 ppm, and Lake Vanda's 27 ppm (Tables 2.9–2.11).

There are other potential high-lithium brine sources that were initially mediumlithium brines extensively evaporated to recover other minerals (such as at the Great Salt Lake, Bonneville Salt Flats, the Dead Sea and the Qinghai playa noted above). The Sua Pan in Botswana (Fig. 1.24), for example contains brine with about 20 ppm Li (Table 1.9), and it is evaporated in solar ponds to produce soda ash. The endliquors should contain from 200 to 400 ppm Li, and could be further concentrated as

	$\delta^6$ Li values	$\delta^7$ Li values
Sea water	$-31,^{b}-32,^{c}-32.3^{d}$	$+32^{e}$
Potash end liquor	$(-32.1 \text{ to } -36.3)^d$	
Oilfield brine, Israel	$(-26.3 \text{ to } -17.9)^c$	
River water	$(-32.2 \text{ to } -6.0)^{b}$	$(+11 \text{ to } +29)^{f}$
Lakes, fresh water	· _ /	$+32^{e}$
Great Basin closed lakes	_	$(+16.7 \text{ to } +23.7)^g$
Walker Lake, Nevada	_	$+24^{e}$
Great Salt Lake, Utah	_	$+16^{e}$
Lakes, brine (Mono Lake)	_	$+19.5^{g}, +20^{f}$
Springs, fresh water, Mono Lake basin		$+31^{e}$ , $(+7.4 \text{ to } 31)^{f}$
Salt crusts, Mono Lake basin	_	$+32^{f}$
Springs, thermal, Mono Lake Basin	_	$+8.4^{f}$
Deep ocean vent brine	$(-11.5 \text{ to } -2.6)^b$	_
Costa Rica rift	—	$(-0.8 \text{ to } +2.1)^h$
Marine clastic sediments	$(-14.7 \text{ to } -0.9)^b$	_
Near sea floor sediments	—	$(+6.6 \text{ to } +20.8)^h$
Marine carbonates	$(-40 \text{ to } +12)^{b}$	_
Orinoco River sediments		
Volcanic	$(-30 \text{ to } -22)^i$	_
Sedimentary	$(-22 \text{ to } -7)^{i}$	_
Volcanic rocks, Mono Lake watershed		$+3.8^{f}$
Mid Ocean Ridge basalt	$(-4.7 \text{ to } -3.4)^{b}$	_
OIB basalt	$(-6.6 \text{ to } -4.7)^{b}$	_
BABB basalt	$(-2.9 \text{ to } -0.7)^{b}$	—
Costa Rica Rift dyke complex	—	$(-1.7 \text{ to } +7.9)^{j}$
Aleutian Arc lava	—	$(+2.1 \text{ to } +5.1)^{j}$
Central American Arc	$-4.5^{h}$	
Arcs, Costa Rica to Guatemala	$(-4.5 \text{ to } -6.4)^{h}$	
Metabasalt, Canadian Shield	$(-14.7 \text{ to } -15.6)^d$	—
Glass inclusions in olivine, Sicily	,	$(-3.4 \text{ to } +1.2)^k$
Meteorites	$-10.0^{\circ}$	$+16^{l}$

The  $\delta^7$ Li and  $\delta^6$ Li Values of Various Lithium-Containing Materials<sup>*a*</sup>

 ${}^{a}\delta^{7}\text{Li} = 1000 ([{}^{7}\text{Li}/{}^{6}\text{Li}]_{\text{sample}}/[{}^{7}\text{Li}/{}^{6}\text{Li}]_{\text{standard}} - 1)$ , while  $\delta^{6}\text{Li}$  has the  ${}^{6}\text{Li}$  and  ${}^{7}\text{Li}$  reversed. The standard is 92.48%  ${}^{7}\text{Li}$  and 7.52%  ${}^{6}\text{Li}$ , so  $[{}^{7}\text{Li}/{}^{6}\text{Li}]_{\text{standard}}$  is 12.29787, and the inverse is 0.081315. Thus if a sample had  ${}^{6}\text{Li} = 7.3038\%$ , the  $\delta^{7}\text{Li}$  would be + 32.0, while  $\delta^{6}\text{Li}$  would be - 31.0, making the two values of opposite sign and somewhat different. Since most other isotopic data is based upon the higher molecular weight atom, it would appear that that  $\delta^{7}\text{Li}$  should become the satandard notation for lithium.

- <sup>b</sup> Kuidong and Shaoyong (2001).
- <sup>c</sup> Chan et al. (2002a).
- <sup>d</sup> Bottomley et al. (1999).
- <sup>e</sup> Tomascak et al. (2001).
- <sup>f</sup>Tomascak et al. (2000).
- <sup>g</sup> Tomascak et al. (2003).
- <sup>h</sup>Chan *et al.* (2002b).
- <sup>*i*</sup> Huh *et al.* (2001).
- <sup>*j*</sup> Chan *et al.* (2002c).
- <sup>k</sup>Guerenko and Schmincke (2002).
- <sup>1</sup>Ustinova (1998).

			High	ithium <sup>a</sup>
	Collins (1976)	Dow (1984) <sup>b</sup>	Texas	Arkansas
Li*	146	170	386	365
Na	5.69	6.70	5.49	5.98
Ca	2.91	3.45	_	_
Mg	0.29	0.35	_	_
K	0.24	0.28	0.59	0.51
Sr	0.16	0.19	_	_
Fe*	35	41	_	_
Mn*	25	30	_	_
Ba*	19	20	_	_
Rb <sup>*</sup>	_	_	$21^c$	11.2
Cs*	_	_	$21^c$	6.1
Cu*	0.9	1.1	_	_
Cl	14.45	17.17	_	_
Br	0.263	0.313	_	_
$SO_4^*$	375	450	_	_
SiO <sup>*</sup> <sub>2</sub>	_	200	_	_
$B^*$	123	134	_	366
I*	21	25	_	_
F*	_	_	_	4.6
Density	1.180	_	1.171	1.229
No. of Samples	71 Li; 64-284 others		6	11

 Table 1.15

 Various Analyses of Smackover Oilfield Brines, wt.% or ppm\*

<sup>a</sup> Collins (1976). Maximum Li 572 ppm.

<sup>b</sup> Several patents on lithium recovery ion exchange resins.

<sup>c</sup> Only one sample.

other salts crystallize. Lake Abijdata in Ethiopia has similar brines and solar ponds, but is a much smaller soda ash operation. The Sebka El Adhibate, Tunisia has about a 16 ppm Li concentration in a seawater-type brine, and after solar evaporation for potential potash production the end-liquor would contain 250–340 ppm Li (Hamzaoui *et al.*, 2000). There are several other solar evaporation or mineral recovery projects throughout the world with end-liquors that might also be considered for potential lithium recovery.

## **Ore Deposits**

## Theory of Origin

The predominant type of lithium mineral formation is that of high-lithium pegmatites, although a few micas, clays and other minerals have been reported with a comparatively high lithium content. "Pegmatites are an exceptionally coarse-grained



**Figure 1.24** Location of the Sua Pan, Botswana Soda Ash Plant, and a sketch of its solar ponds (Low *et al.*, 2000; reprinted from the Eighth Symposium on Salt [ISBN 0444500650], Vol. 1, p. 523, Fig. 1, ©2000, with permission from Elsevier).

igneous rock with interlocking crystals, normally found as irregular dikes, lenses or veins, especially at the margins of tremendously large bodies of (solidified) magma (flow). Most grains are 1 cm or more in diameter, and the pegmatite's composition is usually that of granite" (-type rocks; Bates and Jackson, 1976). If a large mass of

magma were induced to flow, such as by the extensive shifting of crustal plates or to balance large lava eruptions, and it traveled into a zone where it could slowly cool and crystallize as it flowed, some fractionation of its components would usually occur. During any crystallization of multi-component mixtures where there is at least some circulation (such as by mixing, thermal gradient currents or diffusion) the least soluble compounds will crystallize first, followed by a sequence of minerals crystallizing based upon their solubility. For example, in the evaporation of seawater calcite, gypsum, halite, epsomite, kainite, etc., crystallize somewhat separately and in a sequence as listed. Upon cooling seawater there is a crystallization sequence of ice, hydrohalite, mirabilite, schoenite, etc. When magma was slowly cooled with some mixing the high manganese, iron and magnesium silicates would usually crystallize first and deposit predominately at the upper, cooler surface, or partially segregate as a more viscous fluid that was more available for lava flow. This would tend to leave a granitic-type composition in the remaining magma.

The salts dissolved in any accompanying fluids such as super critical water, carbon dioxide or methane would also crystallize in a sequence, but the solubility of salts above the fluids' critical point does not change much during cooling, and the critical point of water (and most gases) is much lower in pressure and temperature than the melting point of the magma constituents. Thus the accompanying aqueous fluid would usually not crystallize most of its salts until toward the end of the magma's solidification. Further slow cooling of the low-iron, manganese and magnesium magma would form the large crystals characteristic of granite-type rocks, and if there was continued flow and/or circulation the lithium and other "rare elements" that might be present would concentrate in the final (liquid) magma and aqueous fluid (if any were present). The need for these favorable circumstances and the scarcity of lithium has resulted in only a small fraction of the world's pegmatites having a high lithium content, but there are so many pegmatites throughout the world that there are still a large number of lithium pegmatites.

Lithium is one of the more soluble cations in any magma, and its silicate compounds also have comparatively low-melting temperatures and greater fluidity (i.e., they have a lower viscosity) than the Na, K, Al, etc., silicates that would make up the bulk of the granitic magma. Also, most of the other rare metals (if present) would not be sufficiently concentrated to crystallize early in the cooling process. Thus, as the granitic melt continued to cool and crystallize with some internal mixing, the near-final melt (and the aqueous fluid, if any) would become enriched with lithium and many of the other rare elements that may have been present in that particular magma. This remaining fluid would tend to be in the warmest lower or central section of the flowing magma. Then, as the previously solidified granitic-type rock suffered contraction or seismic fractures, or as the flowing magma fractured other overlying rock, because of the greater pressure with depth much of the remaining fluid would be forced into these fractures to form pegmatites. For that portion of the final magma that had experienced sufficient fractionation to concentrate the lithium and other rare metals (if present) the pegmatites would be of

the lithium type. The various components of the magma forced into the pegmatite would then crystallize, and it would usually be in a sequence or zoned pattern depending upon their concentration, solubility and the other components in the magma (and aqueous fluid). If there had been less lithium fractionation, and/or the magma cooled more rapidly in the pegmatite (as at a much shallower depth) the number of zones would be fewer, or it could even be non-zoned. Many of the lithium pegmatites occur in a scattered cluster of barren pegmatites with only a small fraction of them containing lithium, and occasionally some of the other pegmatites would contain predominantly other rare metals.

The depth (pressure), temperature and amount of water present in the lithium pegmatites as they intruded into the overlying fractures and cooled is not known, although considerable laboratory experimental work has been done to help determine these factors. Since spodumene has the highest melting point (1423°C; eucryptite 1397°C and petalite 1356°C; quartz is <1425°C) of the commercial lithium compounds, it might be expected to be the first lithium mineral to have crystallized and be the most common, as it is. This appears to have been the case with the "non-zoned" deposits and those containing massive primary spodumene. However, for the secondary spodumene deposits London (1984) has established phase data with quartz, slightly impure minerals, very high pressures and considerable water (9%) that indicates that spodumene does crystallize first above about 4 kbar pressure and 700°C, but that β-spodumene crystallizes below that pressure (and at 700–900°C). The data further indicates that the  $\beta$ -spodumene would then undergo a "solid-state" conversion to petalite as it cooled below 680°C, and that petalite, in turn, could decompose to  $\alpha$ -spodumene and quartz as the temperature dropped to 320°C and the pressure was reduced from 4 to 1.6 kbar. Below that temperature and burial depth the data showed that petalite could transform into eucryptite and quartz (Fig. 1.25). These pressures correspond to depths of 25,500-10,200 m, respectively, assuming an overburden density of 2.5 g/cc. Normal (low) thermal gradients would reach these temperatures.

At least the petalite conversion aspect of this data appears to be confirmed in some deposits, since after the entire pegmatite was solidified much of the petalite appeared to have been transformed into spodumene and quartz, and occasionally some eucryptite and quartz. The spodumene was in the form of psuedomorphs after petalite, and its very low iron content was similar to that of petalite, and much lower than that of most primary spodumene. However, this phase data and these reactions do not appear to have general applicability, since: (1) solid phase reactions do not occur without the solid being remelted or dissolved, at least on a molecular scale, and then recrystallized after the reaction has taken place. (2) The data shows  $\beta$ -spodumene being stable at 680°C, whereas at atmospheric pressure the change in form from  $\alpha$  to  $\beta$ -spodumene only occurs in ore concentrates above about 1000°C. Also,  $\beta$ -spodumene has never been found in a lithium deposit, and  $\alpha$ -spodumene's melting point is shown as 700°C compared to its atmospheric value of 1423°C. (3) Changes in pressure normally have only a relatively minor effect upon a solid's



**Figure 1.25** Experimental phase diagram for the petalite-spodumene-quartz fields at high pressure and 9% water (with 89% petalite; London, 1984; reprinted from the American mineralogist, courtesy of the Mineralogical Society of America).

melting point, and can not cause chemical reactions, so pressure alone is unlikely to be the reason for these "solid-state" changes, or for the much lowered temperatures. Furthermore, it is hard to visualize how the deposit would be remelted in the long intervening period (presumably with the water having escaped) as the pressure was reduced by the deposit being raised or the surface eroded. (4) The pressures indicated by these tests would require an extreme burial depth of 10,200-31,900 m (33,500-83,700 ft), which is very hard to reconcile with so many deposits now near or outcroping on the surface. (5) The laboratory tests were made with 9% supercritical water (water becomes critical at pressures greater than 0.22 kbar and temperatures above 374°C), but no physical evidence of water's presence has been reported in any of the spodumene-to-petalite deposits. The materials used in the tests beside the water were 45.5% petalite (89% purity) and 45.5% quartz of unknown purity. The impurities should have only slightly lowered the melting points, implying that the super critical water reduced the melting or transformation temperatures dissolved enough of the surface of the minerals to let the solid phase reactions take place. It then slowly worked its way into all of the crystals and back out and if this is what happened, perhaps the presence or absence of water explains why only a few petalite deposits converted to spodumene, and others did not. (6) The temperatures are unbelievably low for any flowing magma.

Most of the pegmatite deposits, including the much-studied Tanco deposit in Canada have a very low water content, and yet the 9% water in these tests is a substantial amount. There are no highly crystallized adjacent cracks or passage ways, even though the escaping magma water would contain many salts, and should have deposited at least some of them. When presumably similar magma water cools or evaporates it deposits large amounts of solids, such as the many veined mineral deposits, and the skarns that formed large massive ore bodies. Even the Salton Sea geothermal brine deposits silica, silver, barium, boron and many other elements as its pressure is released. It has been speculated that aqueous fluids reacted with the wall rock and outer pegmatite zones to form the modest amounts of tourmaline at Tanco, but the tourmaline more likely crystallized from the melt, since almost all lithium sources contain some-to-considerable boron, and very little has been reported elsewhere in the deposit. Also, the very small amounts of water found in lithium mineral inclusions do not predict that there had been a major aqueous phase present during crystallization, since similar inclusions are rather common in many other mineral deposits (see the Calcium Chloride chapter). Finally, other experimental data has shown that with water and lithium minerals heated to  $275-600^{\circ}$ C only 0.25-2.4 ppm solutions result, making the presence of water at reasonable pressures (and burial depths) very unlikely to have caused the petalite-to-spodumene reaction.

As an alternate theory to the super-pressure, low temperature, high water content hypothesis, perhaps a re-heating of the deposit (caused by a nearby magma or pegmatite flow, intruding dikes, or even the heat of crystallization from an adjacent mineral phase) allowed sufficient softening and localized melting of the few transformed deposits for the solid phase reactions to occur (without the need for much water to have accompanied the pegmatite). Also, with this theory the magma would have been at a temperature somewhat above its atmospheric melting point, such as are observed in modern volcanic lava flows (often ~ 1000°C or higher). Without assuming the need for water and high pressures, the high-lithium magma flow more logically would have been at a much shallower depth. This would much better explain why so many thousands of lithium pegmatites are now at, or very near the surface.

#### Structure

In most lithium pegmatites there are several zones rich in different lithium minerals, and zones with varying amounts of quartz, feldspar, mica, albite, apatite and other granitic minerals, as well as zones with other rare minerals such as those containing tantalum, niobium, tin, tungsten, cesium, rubidium, boron, fluorine and other elements. As many as 18 zones have been reported in the Bikita lithium pegmatite, with each rich in specific minerals. The lithium minerals are usually found in the intermediate-to-late (core) zones of the pegmatite, and pegmatites vary widely in the number of zones and different mineralization. As an example of the various minerals that may occur in separate zones of a pegmatite, in the early days of its production the Bikita deposit produced the wide array of minerals

Geology 53

#### Table 1.16

Mineral products	S. tons	Approximate range of contents
Lepidolite	393,000	3.5-4.3% Li <sub>2</sub> O
Petalite	177,000	3.6-4.7% Li <sub>2</sub> O
Spodumene	24,000	4.0-4.7% Li <sub>2</sub> O
Amblygonite	5000	7.5-9.5% Li <sub>2</sub> O
Eucryptite	2000	5.5-6.5% Li <sub>2</sub> O
Beryl	565	10-12% BeO
Tantalite	29	
Microlite	9	
Cassiterite	5	70% Sn

Mineral Production from the Bikita lithium deposit from 1952-1960 (Symons, 1961)

listed in Table 1.16. The *Big Whopper* mine in Kenora, Ontario, Canada in 2002 anticipated the production of (as mt/yr): 21,200 high grade petalite concentrates (the ore contains about 1.3% Li<sub>2</sub>O), 25,400 petalite–feldspar mix, 46,200 sodium feldspar, 9400 potassium feldspar, 8400 spodumene, 22,000 mica and 12.6 tantalum minerals (Saller and O'Driscoll, 2000). By contrast, an example of a sparsely-zoned (even called non-zoned) lithium pegmatite is the North Carolina Tin Belt pegmatites which contain predominantly a fairly uniformly mixture of ~20% spodumene, 41% feldspar, 32% quartz, 6% muscovite and 1% various rare minerals, with no significant amount of secondary minerals or phase transformations (Anstett *et al.*, 1990). There is a zonation of grain sizes in these pegmatites (Table 1.25), but very little of separate minerals.

All of the commercial pegmatite deposits initially owed their value to the minerals being susceptible to hand-sorting because of their large crystal size and/or distinctive color, and now they are dependent upon the selective separation ability of flotation, heavy media and magnetic force to concentrate and purify the lithium minerals. The first commercial lithium flotation process (on spodumene) began in the late 1930s (Singleton, 1979; Manser, 1975).

There are literally thousands of lithium pegmatites throughout the world, but most of them are small and not of potential commercial quality, making the actual number of large, developed deposits relatively small. There are also many lithiumcontaining minerals of potential commercial interest as seen in Table 1.2, but again, only a few have ever been mined on a large scale. Most of the lithium pegmatites are quite old, such as in Precambrian shield areas that are from 600–3000 million years of age (Vine, 1980). Several of the largest lithium deposits are: the very large and complex lepidolite, petalite and other lithium minerals deposit at Bikita, Zimbabwe; the Gwalia Greenbushes primary spodumene deposit near Bunbury, Western Australia; the pegmatite zone that includes Tanco's low-iron spodumene deposit at Bernic Lake, Manitoba, Avalon Ventures Ltd.'s Big Whopper petalite deposit at Kenora, Ontario, and Emerald Field Resources Big Mack petalite deposit near Kenora, Canada; and the now-closed Tin-Spodumene Belt of Foote and FMC in North Carolina, USA. There are large commercial deposits in China, Russia and Zaire (the latter with limited lithium production), and medium-sized ones in Brazil, Namibia, Portugal, Finland and Afghanistan (the latter two not yet mined in 2002; Saller and O'Driscoll, 2000). In the past, and a few at present, of the smaller deposits throughout the world have had limited mining, such as in Rwanda, South Africa and Europe. The major commercial lithium minerals in these deposits are described in the following section.

### **Commercial Lithium Minerals**

#### Spodumene

The most abundant of the lithium minerals is spodumene (LiAlSi<sub>2</sub>O<sub>6</sub>), a lithium pyroxene containing up to 3.73% Li (8.03% Li<sub>2</sub>O), with high-grade deposits usually ranging from 1.35 to 3.56% Li (2.9–7.7% Li<sub>2</sub>O) and 0.007–0.03% Fe<sub>2</sub>O<sub>3</sub>, and the lower-grade deposits 0.5–1.0% Li (1.0–2.2% Li<sub>2</sub>O) and 0.6–1.5% Fe<sub>2</sub>O<sub>3</sub>. Spodumene has been classified into three types. (1) Secondary that has been formed by the conversion of petalite to spodumene (LiAlSi<sub>4</sub>O<sub>10</sub>  $\rightarrow$  LiAlSi<sub>2</sub>O<sub>6</sub> + 2SiO<sub>2</sub>). It is comparatively fine-grained, usually high grade and white, and has a very low iron content (0.01–0.04% Fe<sub>2</sub>O<sub>3</sub>). (2) Primary and zonal, with variable-sized laths of large crystals in well-zoned pegmatites. It is very pure, comparatively low in iron and usually white. (3) Primary and unzoned or phenocrystic, where the crystals are usually relatively small and the spodumene low in grade, high in iron, and fairly uniformly mixed with other minerals. Its color is commonly greenish, and the deposits may be quite large (Table 1.17).

Spodumene is often intermixed (or intergrown) with quartz (Fig. 1.26) and sodium or potassium feldspar, most of which can be removed by flotation and/or gravity separation to produce higher grade lithium concentrates with a lower iron content (in the US 2.3–2.8% Li (5.0–6.0% Li<sub>2</sub>O) and about 0.1% Fe<sub>2</sub>O<sub>3</sub>; Bach et al., 1967). The commercial product is sold at grades ranging from 2.2-3.5% Li (4.5-7.5% Li<sub>2</sub>O), and with 0.01-0.1% Fe<sub>2</sub>O<sub>3</sub>. Spodumene's hardness is 6.5-7 on the Mohs scale, and its density 3.13-3.20 g/cc. Its crystals are monoclinic prisms with a pronounced longitudinal (110) cleavage, causing it to form lath-shaped particles upon being broken. Giant crystals have been found up to 14 m in length, but the dominant size range is 1.3-30 cm long and 0.3-5 cm wide. Its color is usually pale green to white, but it varies from nearly clear white to dark green when it has a high iron content. Some clear spodumene crystals are considered to be gem stones in colors of deep green (hiddenite) or yellow and lilac (kunzite). It decomposes by surface weathering to kaolinite and/or hydrous mica. Several ore analyses are listed in Table 1.18, and some of the larger spodumene deposits are in: Greenbushes, Australia; Ontario and Manitoba, Canada; North Carolina, USA; Bikita, Zimbabwe; Minas Gerais, Brazil; the Chita Region, Russia; and the Altai Mountains, China (Heinrich et al., 1977; Kesler, 1960).

		Iron c	ontent	
Location	Color	FeO (%)	Fe <sub>2</sub> O <sub>3</sub> (%)	Spodumene's description
Kings Mountain, NC	Greenish, semi-vitreous	0.08-0.10	0.70-0.80	Pegmatites are essentially unzoned. Disseminated uniformly in fine-grained quartz-microcline- muscovite <sup>a</sup>
Etta mine, Black Hills, SD	Buff, dull	0.02	0.03	Well-zoned pegmatite. Giant crystals in quartz-rich intermediate zone <sup><i>a</i></sup>
Harding mine, Dixon, NM	White-pale buff, dull-vitreous	0.01	0.01-0.03	Complex horizontally zoned pegmatite. Laths with quartz directly below quartz core <sup>a</sup>
Strickland Quarry, Portland, CT	Pale pink, vitreous	0.02	0.03	Complexly zoned pegmatite. In lepidolite-cleavelandite- quartz-tourmaline rock <sup>b</sup>
Pala, CA	Pink, gem quality	0.10	0.02	Well-zoned pegmatites. Very coarse-grained, with quartz <sup>a</sup>
Bernic Lake, Manitoba (Tanco)	White to pinkish, vitreous	0.01-0.02	0.02-0.04	Complex horizontally zoned pegmatite. Spodumene-quartz with zones of lepidolite and some amblygonite <sup>b</sup>

## **Table 1.17**

Examples of Various Types of Spodumene Deposits (Heinrich et al., 1977)

<sup>a</sup> Primary spodumene.

<sup>b</sup> Secondary spodumene.



**Figure 1.26** Typical crystals of lithium ore: left, zinnwaldite; right, spodumene; both with quartz (Deberitz, 1993, courtesy of Chemetall GmbH).

		Lep	idolite			Spodumer	ne		
		China	6						
	India <sup>a</sup>	Ore	Conc.	South Dakota <sup>c</sup>	Tanco <sup>d</sup>	Green. <sup>e</sup>	Wek. <sup>f</sup>	Afg. <sup>g</sup>	Port.h
Li <sub>2</sub> O	3.70	1.63	4.65	3.76	7.28	2.53	6.60	7.56	7.65
K <sub>2</sub> O	10.69	2.98	8.35	7.00	0.15	1.50	1.50	0.05	_
Na <sub>2</sub> O	1.12	5.12	1.13	1.24	0.15	2.57	0.27	0.16	0.01
Al <sub>2</sub> O <sub>3</sub>	33.17	18.91	23.64	29.14	26.00	13.94	26.70	27.42	27.20
Fe <sub>2</sub> O <sub>3</sub>	2.90	0.17	1.29	0.37	0.045	0.94	1.29	0.24	0.23
SiO <sub>2</sub>	47.57	68.84	55.33	49.18	_	73.74	64.60	64.39	65.09
MgO	_	0.01	_	_	_	0.16	0.07	0.06	_
CaO	_	0.06	_	_	_	0.45	0.02	0.06	_
MnO	_	0.12	_	_	0.03	_	0.14	0.05	0.01
Rb <sub>2</sub> O	_	0.33	1.18	_	_	0.32	0.24	_	_
Cs <sub>2</sub> O	_	_	0.20	_	_	0.04	0.04	_	_
F	_	1.86	1.11	2.30	0.015	_	0.23	_	_
$P_2O_5$	_	0.49	_	_	0.20	0.20	_	0.01	0.06
As <sub>2</sub> O <sub>3</sub>	_	_	_	_	_	79 ppm	_	_	_
CuO	_	_	_	_	_	_	_	_	_
H <sub>2</sub> O	_	_	_	1.35	_	_	_	0.06	_
Acid Insol.	_	_	_	_	_	_	_	_	_
Volatile, 400°C	_	_	_	_	—	_	—	_	_
		Petalite		Eucryptite					
	Brazil <sup>i</sup>	BigWhopp. <sup>j</sup>	Port. <sup>h</sup>	Bikita. <sup>k</sup>		Montebrasite <sup>h</sup>	Licons <sup>1</sup>		
Li <sub>2</sub> O	4.35	4.67	4.49	11.49		8.87	20.30		
K <sub>2</sub> O	< 0.01	0.01	_	< 0.05		_	0.59		
Na <sub>2</sub> O	< 0.01	0.01	0.01	0.05		0.01	22.13		
AlaOa	17.06	16.24	16.75	40.40		35.07	_		

Analyses of Various Lithium Ores, wt.%

(continues)

Table	1.18
-------	------

(continued)

	Petalite		Eucryptite				
	Brazil <sup><i>i</i></sup>	BigWhopp. <sup>j</sup>	Port. <sup>h</sup>	Bikita. <sup>k</sup>	Montebrasite <sup>h</sup>	Licons <sup>1</sup>	
Fe <sub>2</sub> O <sub>3</sub>	< 0.01	0.01	0.05	0.08	_	0.14	
SiO <sub>2</sub>	78.37	77.93	78.91	47.92	_	_	
MgO	< 0.01	0.00	_	_	_	_	
CaO	< 0.02	0.02	_	0.09	_	0.54	
MnO	< 0.01	0.01	0.03	< 0.01	_	_	
Rb <sub>2</sub> O	_	_	_	_	_	_	
Cs <sub>2</sub> O	_	_	_	_	_	_	
F	_	_		_	0.04	_	
$P_2O_5$	< 0.01	_	0.05	< 0.01	49.75	46.40	
As <sub>2</sub> O <sub>3</sub>	_	_	_	_	_	0.41	
CuO	_	_		_	_	0.01	
H <sub>2</sub> O	0.13	_	_	0.23	0.55	3.39	
Acid Insol.	_	_	_	_	_	0.08	
Volatile, 400°C	_	_	_	_	_	2.25	

<sup>a</sup>Lepidolite from Bihar, Rajasthan, India (Vyas et al., 1975).

<sup>b</sup> Lepidolite from Yichun, Hunan, China. Conc. (Xu *et al.*, 1998); Also in the ore: FeO 0.15%, TiO<sub>2</sub> 0.06%; as ppm: Ta 137, Nb 68.9, Zr 18.7, Sr 6.9, Ce 2.52, Nd 1.63, Sm 0.95, La 0.94, Gd 0.84, Eu 0.11 (Yin *et al.*, 1995). The concentrate has had one stage of flotation and roasting (reducing its fluorine).

<sup>c</sup> Lepidolite from the Black Hills, South Dakota (Page, 1953).

<sup>d</sup> Spodumene concentrates, Tanco, Canada (Burt et al., 1988).

<sup>e</sup> Spodumene ore from Greenbushes, Australia; Also: TiO<sub>2</sub> 0.19%, as ppm: Sn 179, Ta<sub>2</sub>O<sub>5</sub> 86, Be 74, Nb<sub>2</sub>O<sub>5</sub> 61, Sr 34, Ni 12, Zr 11.5, U 6.2, Th 3.1 (Partington *et al.*, 1995).

<sup>f</sup>Spodumene from Wekusko Lake, Manitoba (Dresler et al., 1998).

<sup>g</sup> Spodumene from Nuristan, Afghanistan (London, 1984).

<sup>h</sup> Petalite from Minas Gerais, Brazil; also 0.02% TiO<sub>2</sub> (London, 1984).

<sup>i</sup> Spodumene, petalite and montebrasite from the Covas de Barroso district, Portugal (Charoy et al., 2001).

<sup>*j*</sup> Petalite from the Big Whopper deposit, Separation Rapids, Ontario, Canada (Pearse and Taylor, 2001).

<sup>*k*</sup> Eucyrptite from Bikita, Zimbabwe; also <0.01% TiO<sub>2</sub> (London, 1984).

<sup>1</sup>Licons from Searles Lake, California (Stenger, 1950).

#### 58 Part 1 Lithium

*Petalite* (LiAlSi<sub>4</sub>O<sub>10</sub>) has a monoclinic crystal habit with a framework silicate structure, and its cleavage is in two planes 114°C apart. It has a density of 2.4 g/cc, and a hardness of 6. Its color is white, grayish white and more rarely pinkish, with a theoretical lithium content of 2.27%(4.88% Li<sub>2</sub>O), while the commercial deposits vary from 1.4-2.2% Li (3.0-4.7% Li<sub>2</sub>O; Kesler, 1960) and the standard sales grade is 2.0% Li (4.3% Li<sub>2</sub>O). The petalite crystal does not accommodate very much iron, so its deposits have a very low iron content. In some deposits it has been transformed to quartz and spodumene, as noted above. Various larger deposits of petalite occur in: Bikita, Zimbabwe; Kenora, Ontario, Canada; Karibib, Namibia; Aracuai, Brazil; Londonerry, Australia; the Transbalkin area of Russia; and at Uto, Sweden.

Lepidolite  $[K_2(Li,Al)_{5-6}(Si_{6-7}Al_{1-2}O_{20})(OH,F)_4]$  or  $[K_2Li_2Al_4Si_7O_{21}(OH,F)_3]$ or [KLiAl<sub>2</sub>Si<sub>3</sub>O<sub>10</sub>(OH,F)<sub>3</sub>] is a mica with a complex and variable formula. Its lithium concentration ranges from 1.39% (3.0% Li<sub>2</sub>O) to a theoretical maximum of 3.58% Li (7.7% Li<sub>2</sub>O). Its density is 2.8–3.0 g/cc, it has lamellar cleavage, and its crystals have a book-type structure. The books range in size from microscopic to about 5 cm in thickness. Normal lithium concentrations in commercial deposits range from 1.4-1.9% Li (3.0-4.1% Li<sub>2</sub>O), although in the early days of shipments from Rhodesia (now called Zimbabwe) the ore was hand-sorted (based upon its beautiful violet-colored crystalline clusters), and the lithium percentage was at or higher than theoretical. This was probably because of the presence of some of the higher grade range of the series such as *zinnwaldite* (Fig. 1.26), polylithionite or protolithionite (Kesler, 1960). Lepidolite also contains a high, but variable concentration of potassium, rubidium and cesium, which made a valuable by-product for the former American Potash & Chemical Co. plant at San Antonio. Several analyses of lepidolite samples are shown in Table 1.18. The major commercial deposits of lepidolite are in: Bikita, Zimbabwe; Bernic Lake, Manitoba, Canada; Karibib, Namibia; Mina Gerais, Brazil; and Sociedad Mineria de Pegmatites, Portugal.

Amblygonite (LiAl[PO<sub>4</sub>][F,OH]) is the fluorine-rich end member of a lithium aluminum phosphate group, and *montebrasite* is the hydroxyl-rich end member. Amblygonite's color is generally white or creamy, although it can vary from colorless to many other pale colors. It resembles potassium feldspar, but with a bluish or grayish tint instead of feldspar's cream or salmon tint. It is usually found as fine anhedral and compact crystals, but it is sometimes found as short prismatic, tabular or equant (lath-shaped) crystals. It can also occur with polysynthetic twinning in two directions at 90°C. It has a vitreous, greasy or pearly luster on its cleavage planes, and cleaves in all four directions with non-right angles. The crystals have a density of 2.98-3.11 g/cc and a hardness of 5.5-6. Its theoretical lithium content is 4.76% (10.2% Li<sub>2</sub>O), but most commercial ores contain 3.5-4.4% Li (7.5-9.5% Li<sub>2</sub>O). It has been mined in Canada, Brazil, Surinam, Zimbabwe, Rwanda, Mozambique, Namibia, South Africa and the Black Hills and Pala Districts in the United States (Kesler, 1960).

*Eucryptite* (LiAlSiO<sub>4</sub>) has a theoretical Li content of 5.53%, (11.84% Li<sub>2</sub>O) and its ores average 2.1-3.0% Li (4.5–6.5% Li<sub>2</sub>O). The only large deposit is at Bikita, Zimbabwe with an average grade of 2.34% Li (5.0% Li<sub>2</sub>O), and much of the impurity is quartz (Kunasz, 1994). In the early days of the lithium industry eucryptite and amblygonite were the favored minerals, since the lithium could be leached directly (without roasting) by strong acids. However, their deposits are fairly uncommon, and those that were initially worked were quite small. Several of the more well-known present or formerly operated lithium deposits are listed in the following sections.

#### Gwalia Consolidated Ltd. (Greenbushes), Western Australia

The Greenbushes lithium pegmatite deposit is located about 300 km south of Perth (220 km, Tambourakis *et al.*, 1990) and 80 km southeast of the port of Bunbury in the center of a 100 km<sup>2</sup> pegmatite field. The main lithium zone of the pegmatite is 3.3 km long and up to 230 m wide in a 7 km long north–south band of pegmatites that are up to 1 km long (Figs. 1.27 and 1.28). The only lithium mineral is a low-iron primary spodumene (Table 1.18), but there are also major amounts of tin, tantalum (stated to contain half of the world's tantalum reserves; Partington *et al.*, 1995) and niobium, as well as kaolin in the deposit's weathered overburden. The pegmatite has intruded into a gigantic granitoid mass, with the contact minerals



**Figure 1.27** Top and side views of the Greenbushes pegmatite (Partington *et al.*, 1995; reprinted with permission from Economic geology, Vol. 90:3, p. 620, Fig. 3, Partington, G. A., McNaughton, N. J. and Williams, I. S., 1995).



**Figure 1.28** Schematic plan of the zoning in the Greenbushes pegmatite (Partington *et al.*, 1995; reprinted with permission from Economic Geology, Vol. 90:3, p. 621, Fig. 4, Partington, G.A., McNaughton, N. J. and Williams, I.S. 1995).

being foliated greenstone and dolerite. The hanging wall dips to the west  $40-50^{\circ}$ C, and the footwall 55–60°C west. The spodumene is relatively pure (about 50%, or 4.01% Li<sub>2</sub>O), and has an unusually high rubidium content. The main accessory mineral is quartz (about 49%), together with minor amounts (~1%) of feldspar, mica, tourmaline, apatite and beryl.

The pegmatites were formed as a series of linear dikes, varying greatly in their width and length (Fig. 1.27). The main lithium zones are in the hanging and footwalls (Fig. 1.28), with the hanging wall lithium decreasing in thickness to the south and eventually disappearing. The hanging wall lithium is generally richer with up to 5% Li<sub>2</sub>O(2.32% Li; 60–80% spodumene), but the footwall is laterally more continuous. At the top of each zone the spodumene consists of coarse-grained euhedral crystals (many over 5 cm in width) intergrown with quartz, and with a lustrous white or pink color. The crystals are finer-grained in the center of each zone, and are intergrown with quartz and potassium feldspar. The central area also has some lenses of quartz-albite or microcline, and all of the spodumene contains various impurities of apatite, tourmaline, muscovite, beryl and tantalite. There are also some zones of spodumene in the centers of albitic pegmatite dikes and pods to the north of the main lithium pegmatite. It is speculated that the footwall spodumene crystallized soon after the initial pegmatite intrusion 2527 MyrBP (million years before the present; Archean age), while the hanging wall crystallized

slightly later (perhaps as much as 7 Myr). The granitoid host rock may have formed about 90 Myr before the main pegmatite intruded into it. London's (1984) phase data (Fig. 1.25) would indicate that foot and hanging wall temperatures would be 770 and 690°C, and the pressure 5.5 and 5 kbar, respectively. However, this would mean burial depths of over 32,000 m and a thermal gradients of only 2.14°C/m (1.18°F/ft) despite the magma flow being a high temperature event. More logically the temperatures were much higher than this, and the pressures (and depth) much lower. The pegmatite was later cut by a swarm of near-vertical, generally east–west trending dolerite dykes (Partington *et al.*, 1995; Tambourakis *et al.*, 1990).

The Gwalia mine on this deposit is the largest producer of lithium mineral concentrates in the world, with ore reserves to a 220 m depth estimated to be 42 million tons averaging 1.36% Li. The mining zone in 1993 had reserves of at least 7.9 million mt of ore containing 2.02% Li (4.35% Li<sub>2</sub>O) and 0.12% Fe<sub>2</sub>O<sub>3</sub>, as well as 3.63 mm mt of 1.58% Li (3.40% Li<sub>2</sub>O), 0.27% Fe<sub>2</sub>O<sub>3</sub> ore. The cut-off point for high grade ore is above 4.0% Li<sub>2</sub>O (i.e., about 50% spodumene) and 0.1% Fe<sub>2</sub>O<sub>3</sub>, and the low grade ore averages about 3.0-4.0% Li<sub>2</sub>O (37.5-50% spodumene; Flemming, 1993).

Other much smaller occurrences of lithium ores in Australia have also been noted, including the Coolgardie District with petalite, spodumene and amblygonite; Ravenstrope's spodumene; Wodgina's lepidolite; and Euriowie, New South Wales' amblygonite (Harben and Edwards, 1998; Kunasz, 1994).

#### Bikita Minerals, Zimbabwe

A large pegmatite area occurs about 75 km east (69 km ENE; Cooper, 1964) of Fort Victoria and 64 km NE of Masvingo, Zimbabwe, extending for 1700 m and varying in width from 30-70 m (average 64 m; Figs. 1.29-1.31). It generally dips from  $14-45^{\circ}$ C east, but at the  $1800 \times 60$  m outcrop it strikes north, and dips  $35^{\circ}$ C. Because of the dip the true deposit thickness is about 23 m, and in 1964 it had been worked to a depth of 60 m and drilled to 152 m. The deposit's age is about 2650 million years, and thus from the Archean period. The pegmatite area is divided into the Al Hayat, Bikita, Southern and Nigel sectors, and it is distinctly zoned. Table 1.19 lists the general order of zoning in the two sectors, and compares them with a general zoning model for many of the North American pegmatites that had been explored during the same period. The deposit has an unusual variety and tonnage of commercial lithium minerals, as well as tantalum, tin, beryl and pollucite (a cesium mineral). Its proven reserves were 6 million ton at 1.35% Li in 1961 (Cooper, 1964), 12 million mt with an average grade of 1.4% Li in 1979, and 23 million mt in 2002.

The pegmatites outcrop into the area's granite and ironstone (laterite) rocks, and the first commercial operations were for tin, tantalum and microlite from their weathered surfaces, but these alluvial deposits were soon depleted. The wall



Figure 1.29 Map of the Bikita pegmatite and the surrounding area (Symons, 1961).

rocks of the lithium pegmatites are massive Precambrian greenstone (finely banded quartz-amphibolite schist) containing occasional zones of black tourmaline (some with up to 7.5 cm crystals) and biotite. The Li Cs minerals in the pegmatites are distinctly zoned and originally contained in order of abundance: petalite, lepidolite, spodumene, pollucite ( $H_2O\cdot2Cs_2O\cdot2Al_2O_3\cdot9SiO_2$ ), beryl ( $Be_3Al_2(SiO_3)_8$ ), eucryptite (LiAlSiO\_4), amblygonite and bikitaite ( $H_2LiAlSi_2O_7$ ).





Figure 1.30 Geology on 900 ft level horizon, Al Hayat and Bikita sectors (Symons, 1961).

The accompanying minerals include quartz, muscovite, microcline and albite, with very little tourmaline being present. As an example of this highly zoned (and thus easily recoverable) mineralization, Table 1.16 lists the products shipped from the deposit between the years 1952–1960.

The largest deposits of petalite occur in the Al Hayat sector (Fig. 1.30) where very large crystals of low-iron  $(0.03\% \text{ Fe}_2\text{O}_3)$  petalite occur with massive microcline (potassium feldspar) in a matrix of fine-grained albite, muscovite and lesser amounts of quartz. Often there are roughly equal amounts of petalite, microcline and the matrix. The petalite occurs as laths up to 1.8 m long and 46 cm wide with a pronounced platy cleavage, and the laths are often oriented at right angles to the walls of the pegmatite. The laths size and quantity decrease toward the footwall of the deposit, but all of the petalite crystals are quite pure, with essentially no feldspar or other intergrowths. There are also zones of petalite–feldspar in which both minerals occur in giant crystals up to 2.4 m in length in a matrix of albite, quartz and muscovite. The microcline could be white, cream colored or grey, with occasional pale lilac flakes of lepidolite. Typical analyses of the petalite and other lithium minerals found in the deposit are shown in Table 1.20.

The Bikita sector has dimensions of about  $427 \times 29$  and 64 m deep, and lepidolite was originally its dominant lithium mineral (most of it has now been mined), but there were also major amounts of spodumene, petalite and amblygonite. The lepidolite was associated with quartz (but no feldspar) in three distinct zones: (1) A lepidolite–quartz shell on the upper side and the ends of the deposit with about



Figure 1.31 Mineral zonation in the 900 and 1000 ft levels in the Bikita pegmatite (Cooper, 1964). Reproduced with permission of the Geological Society of South Africa.

64

## Table 1.19

Typical Lithium Pegmatite Zones at Bikita and in North America (Cooper, 1964)

A. Zones o	- HW contact	
Border zone	Selvedge of plagioclase, quartz, muscovite	- H.W. contact
Wall zones	Mica band	
	Hangingwall felspar zone	
Intermediate zones	Petalite-felspar zone	
	Spodumene zone	
	Felspathic lepidolite zone	
	Pollucite zone	
	All-mix zone (felspar, quartz,	
	muscovite, lepidolite, etc.)	
Wall zone	Footwall felspar zone	
		- F.W. contact
	Footwall greenstone	
B. Zones	of the Bikita sector	
	Hangingwall greenstone	- HW contact
Border zone	Selvedge (plagioclase, quartz)	II. W. conduct
Wall zones	Muscovite band	
	Hangingwall felspar zone	
Intermediate zones (upper)	Petalite and felspar	
	Spodumene	
	(i) massive	
	(ii) mixed	
	Pollucite	
	Felspar-quartz	
-	"All-mix" zone	
Core zones	Massive lepidolite	
	(1) high grade core	
	(11) near solid	
	Lepidolite-quartz shell	
	(1) lepidolite	
	(11) amblygonite	
intermediate zones (lower)	Cobble Zone	
33.7 11	Feispathic lepidolite	
wall zone	Footwall telspar zone	
	(1) rnythmically banded beryl zone	
	(11) muscovite band	
	(iii) spotted dog	
		- F.W. contact
	Footwall greenstone	

(continues)

#### **Table 1.19**

(continued)

C. The American classification of zones
Border zones
Relatively fine-grained selvedge, generally only a few inches thick.
Wall zones
Coarser and much thicker. Both wall and border zones are more continuous and more constant in thickness than those which follow.
Intermediate zone
Any zone between the wall zones and the core is termed intermediate. Such zones are very variable in shape, size, and continuity.
Core zone
The innermost or central zone, commonly elongate or as a series of disconnected segments
(or lenses).
Reproduced with permission of the Geological Society of South Africa.

40% lepidolite, which was in 0.3-3.1 m diameter masses separated by barren quartz layers. (2) A zone with 60-70% coarse grained lepidolite (with quartz) that was easily hand-sorted. And (3) a central core of almost pure (>90%) fine-grained lepidolite that was a beautiful mauve color, and very dense and tough. It often contained small amounts (less than 1%) of microscopic-sized topaz. Near the ends of the lepidolite deposits there were giant (0.3-6.2 m across) masses of white, irregular crystalline amblygonite in a grey quartz. It had sharp contacts to the lepidolite, and contained no intergrowths.

In addition to the lepidolite core there were other lepidolite-containing zones such as the "all mix zones" in which microcline, coarse lepidolite and quartz occurred in spectacular arrangements, sometimes surrounding laths of microcline, petalite or spodumene. Lepidolite could also occur in a "cobble zone" where fairly pure boulders or lenses of lepidolite were found in a matrix of fine albite. In a "felspathic lepidolite" zone the mixture consisted of fine-grained albite, quartz and variable amounts of disseminated lepidolite. In the "wall zone", and particularly the footwall there were rhythmically banded layers of fine grained lepidolite and albite, with irregular and wedge-shaped beryl crystals lying across and through the banded layers. The layers varied from 2.5 mm–10 cm in thickness, and often the lower edge of the lepidolite had a sharp boundary with the albite, while its upper edge graded into the albite. The layers undulated and were occasionally contorted.

In the Bikita sector spodumene occurred in both massive and mixed zones as acicular intergrowths with quartz, and in the form of blocks or laths from 5 cm to 5.5 m in length. In the more massive zones the blocks were separated by 2-5 cm of

	Petalite	Eucryptite	Spodumene-quartz intergrowth	Lepidolite	Amblygonite	Pollucite
SiO <sub>2</sub>	76.79	73.98	76.50	56.24	1.62	47.09
$AI_2O_3$	16.85	18.15	17.09	24.65	33.36	17.41
Li <sub>2</sub> O	4.36	4.98	4.12	3.64	8.60	0.41
Rb <sub>2</sub> O	0.00	0.00	0.00	2.71	ND	0.91
Cs <sub>2</sub> O	0.00	0.00	Trace	0.31	0.00	26.60
K <sub>2</sub> O	0.00	0.23	0.71	7.20	0.20	2.00
Na <sub>2</sub> O	0.46	0.51	0.94	0.26	1.00	3.02
CaO	0.31	0.23	0.36	ND	0.00	0.00
MgO	0.21	0.07	Trace	ND	0.72	0.00
$P_2O_5$	0.00	0.00	0.08	ND	43.97	0.30
F	0.02	0.02	ND	5.10	3.48	ND
Fe <sub>2</sub> O <sub>3</sub>	0.05	0.06	0.017	а	а	а
TiO <sub>2</sub>	0.00	0.00	0.00	ND	ND	0.00
MnO	0.04	0.12	ND	ND	0.03	ND
BeO	0.006	0.01	ND	ND	ND	ND
Loss on ignition	0.65	1.56	0.64	1.12	6.24	2.20
Total	99.75	99.92	100.46	101.23	99.22	99.94

 Table 1.20

 Typical Analyses of the Lithium Minerals in the Bikita Pegmatite, wt.% (Cooper, 1964)

ND, not determined.

Reproduced with permission of the Geological Society of South Africa.

<sup>*a*</sup> These samples contained metallic iron introduced during sample preparation.

Geology

a lepidolite–quartz mixtures. The lepidolite appeared as radiating aggregates with their centers near the walls of the spodumene blocks. In the mixed spodumene zone the percentage of spodumene–quartz laths was lower, and they were usually accompanied by darker lepidolite, along with albite and cleavendite. The pollucite zone of the deposit was massive and had little apparent crystal faces or other indication of grain size, although some cleavage planes indicated crystals 15 cm or so in width. The pollucite was randomly honeycombed by veins of lepidolite 6 mm or so in width that divided the mass into a mosaic pattern with each section 7.5–30.5 cm in size. The lepidolite veins stopped abruptly at the boundaries with other minerals. The cesium content of the pollucite was about 25% Cs<sub>2</sub>O, compared to pure pollucite with about 30% Cs<sub>2</sub>O. The impurity, other than lepidolite appeared to be very fine particles of quartz and some other minerals. The pollucite ore body enclosed a mass of petalite 1.5 m wide, a similar mass of microcline, and a 6.2 m wide lens of lepidolite. In each case the boundaries were sharp between the different minerals.

Other minor lithium mineralization in Zimbabwe occurs in the Insizia, Matobo, Mazoe, Mtoko, Salisbury, Umtali and Wankie districts (Kunasz, 1994; Cooper, 1964; Symons, 1961; Kesler, 1960).

## Tantalum Mining Corp. (Tanco); Bernic Lake, Manitoba, Canada

This high-lithium pegmatite deposit also contains tantalum, cesium, rubidium and beryllium. It occurs about 180 km NE of Winnipeg (Fig. 1.32) in the Cat Lake-Winnipeg River district, with the plant on the northeastern shore of Bernic Lake, and most of the deposit under the Lake (Fig. 1.33). The 2.55-2.65 billion year old pegmatite has intruded into the Archean age Bird River greenstone belt in the Canadian Shield of southeast Manitoba, and is zoned in a complex manner with several lithium ores, tantalum, cesium and other industrial minerals (Tables 1.21 and 1.22). It is lens-shaped with a maximum length of 1990 m, a width of 1060 m and it is up to 100 m thick (Fig. 1.34;  $1440 \times$  up to 820 m by >100 m depth, Crouse *et al.*, 1984; 2400–3,000 long  $\times$  820 m wide, dipping west 7–12°C, Cerny and Lenton, 1995). In 1984 it was probably the second largest known complex-zoned lithium deposits after the Bikita pegmatite, with an unusually large number of minerals (about 100) having been identified in the deposit (Table 1.23). The primary lithium mineral is spodumene, occurring in two separate zones, but there is also considerable petalite, lepidolite and amblygonite (typical analyses are given in Table 1.24). The proven spodumene reserves were estimated to be 7.4 million mt of ore in 1984 with an average of 1.34% Li (2.88% Li<sub>2</sub>O), and the three lepidolite areas had lithium concentrations ranging from 0.87 to 1.31% Li (1.87-2.82% Li<sub>2</sub>O; Vanstone et al., 2002; Harben and Edwards, 1998; Kunasz, 1994; Burt et al., 1988; Crouse et al., 1984).

The Tanco pegmatite appears to have been formed in a series of faults in the overlying granite or basalt that allowed the intruding pegmatite magma to spread and lift the overlying rock, thus forming its somewhat horizontal, lens-like shape



**Figure 1.32** Location of the Tanco and Separation Rapids pegmatites (Pearse and Taylor, 2001; figure first published in the CIM Bulletin, Vol. 94, No. 1049. Reprinted with permission of the Canadian Institute of Mining, Metallurgy and Petroleum).

(Vanstone et al., 2002). It is composed of nine different mineral zones (Table 1.23), with the different ores of commercial interest, tantalum, spodumene, cesium and rubidium, each occurring primarily in separate zones. Most of the spodumene is in the Upper Intermediate Zone and to a lesser extent the Lower Intermediate Zone (Fig. 1.34). The Upper Intermediate Zone is a lens up to 24 m thick, and overlying the central portion of the pegmatite. It appears to have initially crystallized as coarse-grained petalite and potassium feldspar, with crystals of each up to 13 m long. There were also some coarse-grained primary spodumene blades in quartz, albite and other minerals. After the original cooling process most of the petalite and potassium feldspar was transformed into intergrowths of fine-grained spodumene and quartz, in the form of psuedomorphs after the original minerals. Very little of the petalite or potassium feldspar remained unchanged. Since petalite crystals appear to not be able to incorporate much iron, the resulting spodumene has an unusually low iron content (less than 0.05% Fe<sub>2</sub>O<sub>3</sub>; Table 1.24). Small amounts of eucryptite and several other minerals appear to have also formed from a more extensive transformation of the petalite-potassium feldspar mixture or from the secondary spodumene.

Only the Border and Wall Zones of the Tanco deposit occur as concentric shells around the entire pegmatite, although when combined the Lower and Upper



**Figure 1.33** Areal view of the Tanco pegmatite showing the extent of the Upper Intermediate Zone (Burt *et al.*, 1988) (this figure appeared in Industrial Minerals No. 244, January 1988, p. 54. Published by Industrial Minerals Information, a division of Metal Bulletin plc, UK. © Metal Bulletin plc 2003).

Intermediate spodumene zones also form a fairly uniform shell. The normally central Quartz Zone is only central in the western portion of the pegmatite, while the Border Zone is relatively thin (2-30 cm) and composed mainly of fine-grained albite and quartz. The hanging Wall Zone contact is relatively sharp and characterized by the presence of brick-red perthite and schrol, with considerable tourmaline and other minerals, as well as some unaltered petalite-potassium feldspar. The Upper Intermediate Zone is in contact with the hanging Wall Zone, and usually the Lower Intermediate Zone is in contact with the up to 35 m thick lower Wall Zone. In the upper 2 m of the Upper Intermediate Zone the potassium feldspar is a pinkish color, decreasing in intensity from the contact to about 2 m depth. As it mixes with spodumene the spodumene attains a greenish color, which decreases in intensity with depth. Most of the spodumene is in the form of "SQUI" (or squi; spodumene-quartz intergrowths that are psuedomorphs after primary petalite with a very large crystal size). The zone also contains some large blades of primary spodumene (up to 7-13 m long), as well as areas of quartz and amblygonite.

The up to 25 m thick Lower Intermediate Zone has a footwall contact that is more gradual, with a decrease in grain size and the amount of SQUI, although some crystals are up to 2 m long. There is an increasing content of other minerals as the contact is approached, including some 0.5-2 m quartz pods with spodumene and

## Table 1.21

Zone	Main constituents	Characteristic subordinate (accessory), and (rare) minerals	Textural and structural characteristics	Geochemically important major and (minor) elements
Exomorphic unit	Biotite, tourmaline, holmquistite	(Arsenopyrite)	Fine-grained reaction rims and diffuse veins	K, Li, B (P, F)
(1) Border zone	albite, quartz	Tourmaline, apatite, (biotite) (beryl, triphylite)	Fine-grained layers	Na (B, P,Be,Li)
(2) Wall zone	Albite, quartz, muscovite, Li-muscovite, microcline-perthite	Beryl (tourmaline)	Medium-grained, with some giant K-feldspar crystals	K, Na (Li, Be, F)
(3) Aplitic albite zone	<u>Albite</u> , quartz (muscovite)	Muscovite, <u>Ta</u> , <u>oxide minerals</u> , beryl, (apatite, tourmaline, cassiterite) (ilmentie, zircon, sulfides)	Fine-grained undulating layers, fracture fillings, rounded blebs, diffuse veins	Na (Be, Ta, Sn, Zr, Hf, Ti)
(4) Lower intermediate zone	Microcline–perthite, albite, quartz, spodumene, amblygonite	Li-muscovite, lithiophilite (lepidolite, petalite, Ta-oxide minerals)	Medium- to coarse-grained, non-homogeneous	K, Na, Li, P, F (Ta)
(5) Upper intermediate zone	Spodumene, quartz, amblygonite	Microcline-perthite, pollucite, lithiophilite (albite, Li-muscovite), (petalite, eucryptite, Ta-oxide minerals)	Giant crystal size of major and most of the subordinate minerals	Li, P, F (K, Na, Cs, Ta)
(6) Central intermediate zone	Microcline – perthite quartz, albite, muscovite	Beryl, ( <u>Ta-oxide minerals</u> ), (zircon, ilmenite, spodumene, sulfides, lithiophilite, apatite, cassiterite)	Medium-to coarse-grained	K (Na, Be, Ta, Sn, Zr, Hf, Ti)
(7) Quartz zone	Quartz	(Spodumene, amblygonite)	Monomineralic	Si (Li)

Zonation and Location of the Economic Minerals in the TANCO Pegmatite (Crouse et al., 1984)

Geology

 $\underline{1}$ 

72

## Table 1.21

#### (continued)

Zone	Main constituents	Characteristic subordinate (accessory), and (rare) minerals	Textural and structural characteristics	Geochemically important major and (minor) elements
(8) Pollucite zone	Pollucite	Quartz, spodumene (petalite, muscovite, lepidolite, albite, microcline, apatite)	Almost monomineralic	Cs (Li)
(9) Lepidolite zone	Li-muscovite, lepidolite, microcline-perthite	Albite, quartz, beryl, ( <u>Ta-oxide minerals,</u> cassiterite), (zircon)	Fine-grained	Li, K, Rb, F (Na, Be, Ta, Sn, Zr, Hf, Ga)

Underlined minerals occur in economic quantities in the zones indicated. Table published in the Geology of Industrial Minerals in Canada. Reprinted with permission of the Canadian Institute of Mining, Metallurgy and Petroleum.
Zones <sup>a</sup>	(1)	(2)	(3)	(4)	(5)	(6)	(7)	(8)	(9)	Bulk <sup>b</sup>
Biotite	0.1									< 0.01
Quartz	28.7	36.0	27.0	38.0	29.0	15.0	94.9	5.5	10.0	36.07
Albite	66.0	40.7	67.0	25.0	7.0	20.0	0.1	5.0	8.0	25.56
K-feldspar		15.0		24.0	25.0	50.0	2.0	2.5	10.0	22.05
Muscovite	1.0	3.0	3.0	1.0	0.1	12.0		2.0		2.97
Li-Muscovite		3.0		2.0	0.1				70.0	3.00
Lepidolite			0.1	0.5	0.1	0.1		7.0		0.27
Spodumene				6.4	33.0	0.1	2.6	1.7		6.41
Eucryptite					2.0					0.26
Apatite	2.0	0.1	0.4	0.2	0.1	0.2		0.5	0.1	0.15
Lithiophilite	0.1	0.1	0.2	0.5	1.0	0.5			0.2	0.38
Amblygonite		0.5	0.1	1.5	1.0		0.4	0.5	0.5	0.77
Beryl	0.2	0.5	1.0	0.1	0.1	1.0			0.5	0.37
Pollucite				0.5	1.0			75.0		1.28
Tourmaline	2.0	1.0	0.5	0.1	0.1	0.1				0.38
Cassiterite		0.01	0.02	0.02	0.01	0.02			0.02	0.01
Rutile			0.02		0.02	0.02				0.01
Ferrotapiolite			0.02		0.102	0.01				< 0.01
										(continues)

## Table 1.22 Estimated Distribution of the Major Minerals in the Tanco Pegmatite, wt.% (after Cerny et al., 1998)

(continued)										
Zones <sup>a</sup>	(1)	(2)	(3)	(4)	(5)	(6)	(7)	(8)	(9)	Bulk <sup>b</sup>
Columbite group		0.02	0.03	0.02	0.02	0.01			0.01	0.02
Wodginite group			0.05		0.02	0.05		0.03	0.03	0.01
Microlite group			0.02	0.02	0.02	0.03		0.01	0.02	0.01
Simpsonite						0.01				< 0.01
Uraninite					0.005	0.005			0.005	< 0.01
Zircon			0.02		0.01	0.02			0.02	< 0.01
Totals	100.00	99.93	99.48	99.76	99.71	99.18	100.00	99.74	99.41	100.00

**Table 1.22** 

Courtesy of the International Mineralogical Association. <sup>a</sup> See Table 1.21 for the zone designations. <sup>b</sup> Percent of total pegmatite.





**Figure 1.34** Three representative north-south cross sections, and a longitudinal east-west section of the Tanco pegmatite (Crouse *et al.*, 1984). Figure published in the Geology of Industrial Minerals in Canada. Reprinted with permission of the Canadian Institute of Mining, Metallurgy and Petroleum.

amblygonite, and some cloudy pink primary spodumene columns up to 18 cm long. In both spodumene zones there is very little disseminated tournaline. The Lepidolite Zone is up to 18 m thick in the form of two elongated sheets within part of the Central Intermediate Zone. It is in contact with the Upper Intermediate Zone, and consists of fine-grained lithian muscovite and lepidolite with an unusually high rubidium content. It also has a moderate amount of tantalum minerals, for which it is mined (Table 1.22; Vanstone *et al.*, 2002; Cerny *et al.*, 1998; Burt *et al.*, 1988; Crouse *et al.*, 1984).

# North Carolina Tin-Spodumene Belt; Chemetall GmbH (Foote Minerals originally, and Cyprus Foote until 1998)

The combined spodumene reserves in different sections of this 60 km long, > 1.6 km wide belt (Fig. 1.35) make it one of the world's large lithium deposits, containing 185,000 mt of Li that was proven, and perhaps twice that in total ore averaging 0.7% Li (1.51% Li<sub>2</sub>O). All of the ore had a fairly high iron content, such as often about 0.6–0.9% Fe<sub>2</sub>O<sub>3</sub> (Henderson, 1976). Numerous pegmatites had intruded to the surface in this area, with the lithium pegmatites up to 1000 m long, 90 m wide, and more than 200 m deep. They usually did not have the typical zoned structure, and spodumene was essentially the only lithium mineral except for a little

#### Table 1.23

		various iviniera	is round in the raneo reginance (Cerny	<i>ci ui.</i> , 1996)		
Native elements			Oxides	Carbonates		
Lead	PbS	Cassiterite	SnO <sub>2</sub>	Calcite	CaCO <sub>3</sub>	
Bismuth	Bi	Rutile	(Ti,Fe,Ta,Nb)O <sub>2</sub>	Rhodochrosite <sub>3</sub>	MnCO	
Arsenic	As	Ferrotapiolite	FeTa <sub>2</sub> O <sub>6</sub>	Dolomite	CaMg(CO <sub>3</sub> ) <sub>2</sub>	
Copper (?)	Cu	Ferrocolumbite	$(Fe > Mn)(Nb > Ta)_2O_6$	Zabuyelite	Li <sub>2</sub> CO <sub>3</sub>	
Antimony	(Sb»Bi)	Manganocolumbite	$(Mn > Fe)(Nb > Ta)_2O_6$		Borates	
Stibarsen	SbAs	Manganotantalite	$(Mn > Fe)(Ta > Nb)_2O_6$			
Sulfides	s and sulfosalts	Wodginite	Mn(Sn > Ta,Ti,Fe)(Ta > Nb) <sub>2</sub> O <sub>8</sub>	Diomignite	$Li_2B_4O_7$	
		Ferrowodginite	$(Fe > Mn)(Sn > Ta, Ti, Fe)(Ta > Nb)_2$		Silicates	
Galena	PbS	Titanowodginite	$(Mn > Fe)(Ti > Sn,Ta,Fe)(Ta > Nb)_2O_8$			
Sphalerite	(Zn,Cd)S	Ferrotitanowodginite	$(Fe > Mn)(Ti > Sn,Ta,Fe)(Ta > Nb)_2O_8$	Quartz	SiO <sub>2</sub>	
Hawleyite	(Cd,Zn)S	Lithiowodginite	LiTaTa <sub>2</sub> O <sub>8</sub>	Albite	Na(AlSi <sub>3</sub> O <sub>8</sub> )	
Pyrrhotite	$Fe_{1-x}S$	Simpsonite	Al <sub>4</sub> Ta <sub>3</sub> O <sub>13</sub> (OH)	Microcline	K(AlSi <sub>3</sub> O <sub>8</sub> )	
Pyrite	FeS <sub>2</sub>	Stibiotantalite(?)	SbTaO <sub>4</sub>	Sanidine (adularia)	K(AlSi <sub>3</sub> O <sub>8</sub> )	
Marcasite	FeS <sub>2</sub>	Microlite	(Na,Ca)2Ta2O6(O,OH,F)	Rb-feldspar	(Rb,K)(AlSi <sub>3</sub> O <sub>8</sub> )	
Arsenopyrite	FeA <sub>s</sub> S	Uranmicrolite	(Na,Ca,U)2Ta2O6(O,OH,F)	Biotite	K(Mg,Fe) <sub>3</sub> (AlSi <sub>3</sub> O <sub>10</sub> )(OH) <sub>2</sub>	
Molybdenite	$MoS_2$	Cesstibtantite	(Sb,Na)2Ta2(O,OH)6(OH,Cs)	Muscovite	KAl2(AlSi3O10)(OH)2	
Cosalite	PbBiS <sub>2</sub>	Rankamaite-Sosedkoite	(Na,K)3-xAl(Ta,Nb)10(O7OH)30	Lithian muscovite	K(Al,Li)2(Al,Si)4O10(OH,F)2	
Gladiate	CuPbBi <sub>5</sub> S <sub>9</sub>	Ilmenite	(Fe,Mn)TiO <sub>3</sub>	Lepidolite	(K,Rb)(Li,Al)2(Al,Si)4O10(OH,F)2	
Pekoite	CuPbBi11S16	Uraninite	UO <sub>2</sub>	Illite	(K,H2O)Al2(AlSi3O10)(OH, H2O)2	
Gustavite	Pb3Ag3Bi11S24	Manganite	MnO(OH)	Montmorillonite	(Na,Ca)(Mg,Al)2(Si4O10)(OH)2·nH2O	
Tetrahedrite	(Cu,Fe,Ag)12Sb3S13			Cookeite	LiAl <sub>4</sub> (AlSi <sub>3</sub> O <sub>10</sub> )(OH) <sub>8</sub>	
Freibergite	(Ag,Cu,Fe)12Sb3S13		Phosphates	Eucryptite	LiAl(SiO <sub>4</sub> )	
Bournonite	PbCuSbS <sub>3</sub>			Spodumene	LiAl(Si <sub>2</sub> O <sub>6</sub> )	
Dyscrasite	Ag <sub>3</sub> Sb	Fluorapatite	(Ca,Mn)5(PO4)3(F)	Petalite	Li(AlSi <sub>4</sub> O <sub>10</sub> )	
Pyrargyrite	Ag <sub>3</sub> SbS <sub>3</sub>	Carbonate	Ca <sub>3</sub> (PO <sub>4</sub> ,CO <sub>3</sub> ) <sub>5</sub> (OH)	Foitite	$Fe_2^{2+}AlAl_6(Si_6O_{18})(BO_3)_5(OH)_4$	
Miargyrite	$AgSbS_2$	Hydroxyapatite		Schorl	NaFe32+Al6(Si4O18)(BO3)5(OH)4	

(continues)

Part 1

Lithium

Table	1.23
-------	------

(continued)

Sulfides			Phosphates		Silicates		
Cubanite	CuFe <sub>2</sub> S <sub>3</sub>	Lithiophosphate	Li <sub>3</sub> PO <sub>4</sub>	Elbaite	NaLi1.5Al1.5Al6(Si6O10)(BO3)5(OH)4		
Chalcopyrite	CuFeS <sub>2</sub>	Lithiophilite	$Li(Mn > Fe)PO_4$	Rossmanite	LiAl2Al6(Si6O10)(BO3)5(OH)4		
Stannite	Cu <sub>2</sub> FeSnS <sub>4</sub>	Amblygonite	LiAlPO <sub>4</sub> (F,OH)	Feruvite	CaFe <sub>3</sub> <sup>2+</sup> Al <sub>5</sub> Mg(Si <sub>6</sub> O <sub>18</sub> )(BO <sub>3</sub> ) <sub>5</sub> (OH) <sub>4</sub>		
Kesterite	Cu2ZnSnS4	Montebrasite	LiAlPO <sub>4</sub> (OH,F)	Dravite	NaMg3Al6(Si6O10)(BO3)5(OH)4		
Cernýite	Cu2CdSnS4	Tancoite	LiNa2HAl(PO4)2(OH)	Beryl	$Be_3Al_2(Si_6O_{10})$		
	Halides	Whitlockite	$Ca_3(PO_4)_2$	Topaz	Al <sub>2</sub> SiO <sub>4</sub> (F,OH)		
		- Fairfieldite	Ca <sub>2</sub> (Mn,Fe)(PO <sub>4</sub> ) <sub>2</sub> ·2H <sub>2</sub>	Pollucite	(Cs, Na)(AlSi2O6).nH2O		
Fluorite	CaF <sub>2</sub>	Crandallite	CaAl <sub>3</sub> H(PO <sub>4</sub> ) <sub>2</sub> (OH) <sub>6</sub>	Cesian analcime	(Na,Cs)(AlSi2O6).nH2O		
		Overite	Ca <sub>3</sub> Al <sub>3</sub> (PO <sub>4</sub> ) <sub>5</sub> (OH) <sub>6</sub> ·15H <sub>2</sub> O	Holmquistite	$Li_2Mg_3Al_2(Si_6O_{22})(OH)_2$		
		Dorfmanite	Na <sub>2</sub> HPO <sub>4</sub> ·2H <sub>2</sub> O	Zircon	(Zr,Hf)(SiO <sub>4</sub> )		
		Switzerite	(Mn,Fe) <sub>3</sub> (PO <sub>4</sub> ) <sub>2</sub> ·7H <sub>2</sub> O	Thorite	ThSiO <sub>4</sub>		
			Sulfates	Coffinite (?)	USiO <sub>4</sub> ·(OH) <sub>4</sub>		
				Garnet (?)	(Mn,Fe) <sub>3</sub> Al <sub>2</sub> Si <sub>3</sub> O <sub>12</sub>		
		Barite	$BaSO_4$				

Courtesy of the International Mineralogical Association.

Typical Analyses of Lithium Minerals from the TANCO Mine, wt.% (All from the Upper Intermediate Zone, Except as Noted) (Cerny et al., 1998)

	Spodumene <sup>a</sup>	SQI	Petalite <sup>b</sup>	Amblygonite <sup>c</sup>	Montebrasite <sup>d</sup>	Lithiophilite <sup>e</sup>	Eucryptite <sup>f</sup>	Lepidolite <sup>g</sup>	Lithian muscovite <sup>h</sup>
Li <sub>2</sub> O	7.87	4.48	4.55	9.90	9.52	9.13	11.03	4.70	4.57
SiO <sub>2</sub>	63.45	77.08	77.83		_	_	45.18	47.85	43.89
$Al_2O_3$	27.40	16.57	16.58	32.86	35.10	_	43.79	26.02	36.01
Na <sub>2</sub> O	0.114	0.253	0.054	0.047	0.139	0.05	_	0.16	0.23
K <sub>2</sub> O	0.038	0.048	0.050	0.004	0.005	0.01	_	8.52	9.85
CaO	0.16	0.09	0.008	0.132	0.085	1.00	_	_	_
MgO	0.012	0.015	0.028	0.002	0.003	0.51	_	_	_
Fe <sub>2</sub> O <sub>3</sub>	0.053	0.13	0.007	_	_	8.83 <sup>i</sup>	_	0.11	0.40
MnO	_	_	_	_	_	34.39	_	0.55	0.15
Rb <sub>2</sub> O	0.002	0.012	_	_	_	_	_	4.29	1.92
Cs <sub>2</sub> O	0.001	0.008	_	_	_	_	_	0.93	0.25
F			_	6.30	1.40	_	_	4.54	0.38
$P_2O_5$	0.02	0.05	_	49.26	49.11	44.95	_	_	_
$H_2O^j$	0.41	0.37	0.41	3.27	5.32	_	_	1.76	_
Insol.		_	_	_	—	0.07	—	—	_

<sup>a</sup> Log-shaped white crystals. SQI is a spodumene, quartz and feldspar mixture resulting from the decomposition of petalite and feldspar; white crystals.

<sup>b</sup> Grey or white crystals.

<sup>c</sup> White crystals.

<sup>d</sup> Lower Intermediate Zone; secondary; brownish crystals.

<sup>e</sup> Grey at the wall contact; pale brown or orange-pink below the wall.

<sup>*f*</sup>Pale pink crystals.

<sup>g</sup> Lepidolite zone; plus 0.04% TiO<sub>2</sub>.

<sup>h</sup>Lepidolite zone; plus 0.06% TiO<sub>2</sub>.

<sup>*i*</sup> Analyzed as FeO, not Fe<sub>2</sub>O<sub>3</sub>.

<sup>*j*</sup> The OH is included in the  $H_2O$  analysis.

Part 1

Lithium



Figure 1.35 Map of the Kings Mountain, North Carolina pegmatite area (Kesler, 1976).

amblygonite as microscopic crystals. The deposit's average composition was about 15-20% spodumene as fine-grained crystals, 41% feldspar (27% albite and 14% microcline), 32% quartz, 6% muscovite (as small flakes) and 1% rare minerals such as beryl (finely disseminated crystals; often ~0.5% of the pegmatite), cassiterite, columbite, lithiophilite and tantalite. There was also minor amounts of apatite, pyrite, rhodochrosite and sphalerite. The spodumene crystals reached a maximum length of 0.91 m (3 ft), but averaged less than 0.15 m (6 in.; Table 1.25). The spodumene was fairly evenly distributed in the ore, making it comparatively easy to mine and process (Kesler, 1976, 1960).

The Foote Mineral deposit is located about 1.6 km SW of the town of Kings Mountain and had been mined periodically since the early 1900s, but only on a large scale since Foote purchased the deposit and completed exploratory drilling in 1956. Their mining was from a cluster of eight nearly vertical pegmatite dikes that could be recovered from a single open pit. More extensive drilling later outlined ore reserves in the northern part of this area of 29 million mt with an average grade of 0.7% Li. Inferred reserves in the remainder of the area might be about 14 million mt (Kunasz, 1994). The deposit is comparatively young for a lithium pegmatite, with its age initially estimated to be about 260–375 million years

	Typical Grain Size of the Minerals in the North Carolina Lithium Pegmatite (Spanjers, 1990)									
Rock type	Spodumene, % (grain size)	Beryl, % (grain size)	Microcline, % (grain size)	Albite, % (grain size)	Muscovite, % (grain size)	Quartz, % (grain size)	Comments			
Medium- grained pegmatite	20 (0.2–25 cm)	0-2 (0.05-2 cm)	15 (0.2–25 cm)	35 (0.01–1.0 cm)	5–10 (0.01–1.0 cm)	25 (0.01–2 cm)	Most prevalent rock type; dominates major ore bodies and in peripheral dikes			
Coarse- grained pegmatite	30 (1-40 cm)	0	40 (1-50 cm)	5 (0.01–1.0 cm)	5 (0.01–1 cm)	20 (0.01–2 cm)	Between aplite (at wall rock contacts) and medium-grained pegmatite			
Aplite (spodrich)	20-30 (0.01-0.5 cm)	0-2 (0.01-0.2 cm)	0-10 (0.02-0.2 cm)	20–50 (0.01–0.2 cm)	5–10 (0.01–1 cm)	20-40 (0.01-0.1 cm)	One end member of layered aplite; occurs locally within medium-grained pegmatite			
Aplite (spodpoor)	0-2 (0.01-0.5 cm)	0-2 (0.01-0.2 cm)	0-5 (0.02-0.2 cm)	50-80 (0.01-0.2 cm)	5–10 (0.01–0.1 cm)	15-35 (0.01-0.1 cm)	Other end member of layered aplite; often occurs adjacent to wall rock contact			

## Table 1.25

08

(Vine, 1980), and later to be middle or late Paleozoic, or only about 250 MYBP (Spanjers, 1990).

#### North Carolina Tin-Spodumene Belt; FMC

In 1969 Lithium Corporation of America (Lithco or LCA; later purchased by FMC) began to mine their Cherryville, Hallman-Beam spodumene pegmatite deposit in the Long Creek area of North Carolina (Fig. 1.36). They had begun operation in Minnesota processing ore from South Dakota, but moved to Bessemer City, North Carolina in 1954 to utilize the ore purchased from other local operators, and later Foote Minerals' nearby Kings Mountain mine. The LCA deposit had proven and probable reserves of about 27.5 million mt of ore recoverable by open pit mining, containing an average of 0.70% Li (Kunasz, 1994).

The ore on average contained 20% spodumene, 33% albite, 25% quartz, 15% potassium feldspar, 6% muscovite and 1% other minerals (apatite and beryl, with rare cassiterite, columbite and tantalite). It was rhythmically zoned with four components: (1) low-spodumene apalite, which usually occurred adjacent to the pegmatites' wall rock; (2) coarse-grained high-spodumene ore next to the low-grade apalite; (3) medium grained high-spodumene rock, the dominant component of the ore and (4) high-spodumene apalite that occurred locally within the medium-grained spodumene (Table 1.25). The deposit contained about 80% of the large and medium-grained spodumene pegmatite dikes, with a swarm of small spodumene dikes in various orientations filling the joints of the central section. Numerous barren dikes and a few ore dikes from 0.2-10 m thick occurred along the periphery of the deposit, and appeared to be of the same age. The spodumene and microcline crystals were usually perpendicular to the apalite borders in the coarse-grained ore, and more randomly orientated in the medium-grained ore.



Figure 1.36 Top view of the Lithium Corporation's North Carolina Pegmatite (Spanjers, 1990).

#### 82 Part 1 Lithium

It has been speculated that flowing magma that was being cooled and mixed by density and viscosity gradients was slowly being fractionated by solubility differences, and reached this area with a relatively low lithium content. Some of this magma was forced into existing fracture planes in the overlying brittle amphibolite and rapidly cooled, forming thin, fairly contorted low-lithium pegmatite dikes. The remaining magma, which by then had fractionated to a higher lithium content, was finally forced in a series of pulses with a little of the remaining apalite into the now weakened and fractured host rock. This resulted in much more extensive displacement, and made much larger dikes. There was a longer period between some of the pulses, allowing slower cooling and larger crystals in the larger dikes. The variation in pulses helped to form the various lithium zones, but in all cases the cooling of the pegmatites was comparatively rapid to prevent further fractionation and more complex zoning. The temperature and pressure of the pegmatites may have also been influenced by saturated, super critical water that possibly accompanied the molten magma (Spanjers, 1990).

#### Smaller United States Deposits

One of the first lithium pegmatites operated in the United States was from 1900 to 1927 at the Stewart mine in the *Pala district*, San Diego county, Southern California. This very small, but high-grade lepidolite deposit (Fig. 1.37) also contained some amblygonite and small amounts of the unusual kunzite variety of spodumene (Kesler, 1960). Slightly earlier (1898), and extending for much longer the Keystone and other districts of zoned pegmatites in the *Black Hills of South Dakota* became the country's major lithium producers. The limited early US demand for lithium increased considerably during World War I when the use of lithium in alkaline storage batteries required larger supplies. The demand for lithium products greatly increased again during World War II for rescue devices (inflated by



Figure 1.37 Side view of the Stewart Mine's lepidolite pegmatite, San Diego County, California (O'Neill *et al.*, 1969).

hydrogen from lithium hydride), lithium hydroxide for the absorption of carbon dioxide in submarines and for multi-purpose greases. The Black Hills deposits filled most of these needs, with the largest operation being the Etta mine (after 1908 owned by the Maywood Chemical Co.). It supplied spodumene somewhat intermittently for almost 50 years, and there was additional production from many smaller operators.

The Black Hills lithium district consists of a very large number of small pegmatites that intruded into Precambrian rocks in a 710 km<sup>2</sup> area about 1715 million years ago. There are over 200 pegmatites in the main 16 km<sup>2</sup> lithium area (Fig. 1.38), and over 1500 in an adjacent 34 km<sup>2</sup> area with less lithium. However, of these pegmatites only 43 were known to contain from traces (R) to abundant (A => 15%) lithium minerals, with two containing abundant spodumene (33 Rare[R]–A), two abundant lepidolite (5 R–A) and five with fairly common (C) amblygonite (24 R–C). Many other pegmatite minerals such as beryl, cassiterite, columbite–tantalite, feldspar, mica, microlite, pollucite and quartz were also mined in the district, but not in the lithium mines. The lithium production to 1944 totaled: 7127 mt of lepidolite, 7678 mt of amblygonite, 22,619 mt of spodumene, and 100 mt of triphylite (LiFePO<sub>4</sub>).

The spodumene in the Etta deposit had unusually large crystals, with some up to 14 m long, and the average length was about 3 m. It, like most of the Black Hills lithium pegmatites was distinctly zoned, with as many as 12 zones, but among these there were only three lithium mineral zones. Most of the lithium occurred in the intermediate or core zones, accompanied or surrounded by perthite, quartz and albite. The ore grade of spodumene varied widely from 0.5-3% Li, with the amblygonite containing the most, 1.18-2.15% Li (after the initial period it was usually mined as a by-product). In several mines lepidolite was the dominant mineral, with the Bob Ingersoll Mine being by far the largest producer. Their ore averaged 5-20% lepidolite, 40-50% quartz and 40-45% cleavlandite, but the center of the core contained massive, fairly pure lepidolite with high concentrations of the other alkali metals (Table 1.18; Tuzinski, 1983). Its crystals were usually small lilac or purple flakes, about 3 mm wide, and arranged in felted aggregates. Amblygonite was found in an intermediate zone, often in light grey spherical masses about 1.8 m in diameter, but one mass measured  $9 \times 1.2 \times 100$  m. For each of the minerals hand sorting had originally been employed to obtain a fairly high-grade product, but later flotation was used to concentrate each of the ores. Figure 1.39 shows the mineralization in one of the larger South Dakota lithium pegmatites (Page, 1953).

Sirbescu and Nabelek (2001) studied quartz inclusions from the Tin Mountain, South Dakota lithium pegmatite, and found indications of both solid and aqueous (with CO<sub>2</sub> and NaCl) phases. Based upon the average boiling point of the aqueous phase, they came to the conclusion that the deposit formed at 340°C and 2.7 kbar pressure. This estimated depth of >11,000 m and that low temperature would



Figure 1.38 Outline of several of the South Dakota lithium pegmatites (Page, 1953).

appear to be unlikely, and implies that the inclusions formed from supercritical water and carbon dioxide.

Other areas in the US with small lithium pegmatite deposits include the western part of Arizona from Phoenix to Lake Mead. In the White Picacho district distinctly zoned pegmatites range up to 610 m in length by 60 m in width, with zones

Geology 85



Figure 1.39 Geologic maps and sections, northwest part of the Beecher Lode pegmatite, Custer County, South Dakota (Page, 1953).

of 8–23% spodumene, amblygonite or lepidolite. The Harding and Pidlite mines operated for a brief period in New Mexico, and there are several smaller lithium pegmatite areas in Colorado, Connecticut, Maine, Massachusetts, New Hampshire, Utah and Wyoming (Kunasz, 1994; Vine, 1980; O'Neill *et al.*, 1969; Kesler, 1960).

#### The Big Mack and Big Whopper Deposits, Ontario, Canada

The Separation Lake metavolcanic belt of northwestern Ontario (Fig. 1.32) contains the Separation Rapids pegmatite group, with its large number of lithium and rare metal pegmatites. In this group there are more than 37 major rare metal pegmatites and many smaller ones, including two of the world's very large lithium deposits, the Big Mack and Big Whopper. The Separation Rapids formation (Figs. 1.32 and 1.40) is to the east and adjacent to the Winnipeg River-Cat Lake formation in Manitoba that contains the Tanco deposit (60 km to the west of the Big Whopper), and has a very similar age (2646 compared to 2740–2844 Ma), geological setting and mineralization. This makes it appear that they are closely related to each other, although the Separation Lake lithium pegmatites are primarily of the petalite-type while spodumene predominates in Manitoba. There is some evidence that the Separation Rapids pegmatite group originated from the Treelined Lake granitic complex in the adjacent English River Subprovince to the north. The Separation Lake area also contains pegmatites of the beryl-type, along with a few containing mostly lepidolite. Various tantalum and other rare metals are common in most of these pegmatites (Tindle and Breaks, 2000).



Figure 1.40 Some of the lithium pegmatites in the Separation Lake area, Ontario, Canada (Tindle and Breaks, 2000; Zoning: H = homogenous, O = oscillatory, P = patchy; courtesy of the Ontario Geological Survey).

The *Big Whopper* deposit consists of five pegmatite lenses that are  $6 \times 56$ – $12 \times 122$  m in size, and swarms of 1–10 m thick pegmatites adjacent to the lenses (Fig. 1.41). The area is 1350 m long and up to 160 m wide, with the largest lens, the Big Whopper, 350 m long and up to 60 m thick. The pegmatites are nearly vertical, with an unknown depth, and composed of two sections: (1) the majority of the deposit contains alternating zones of potassium feldspar with on average 37% petalite, and lenses of fine-grained muscovite aplite. (2) contains 2–4 cm thick pink petalite layers in orange garnet–quartz–muscovite–albite aplite. The majority of the deposit appears to have been modified by ductile deformation and recrystallization, forming a polygonal net-like mosaic of medium to coarse-grained petalite crystals. They are a translucent light pink color, and very pure, containing about 4.74% Li<sub>2</sub>O with very little iron (Table 1.18; Tindle and Breaks, 2000).

The 842 ha (2080 acre) Big Whopper deposit is owned by Avalon Ventures, and located 60 km north of Kenora on the English River. It has estimated reserves of 11.6 million mt of ore averaging 0.62% Li (1.33% Li<sub>2</sub>O, or 25  $\pm$  5% petalite), and one 5.6 million mt area contains 0.46-0.66% Li ore (0.99-1.42% Li<sub>2</sub>O; Saller and O'Driscoll, 2000). Pearse and Taylor (2001) describe the deposit as being 1.5 km long and usually 10-80 m wide, with 3.2 mt of ore in a  $55 \times 400$  m zone that is amenable to open pit mining. The rock in which the pegmatite intruded is dark green to black amphibolites, and the entire formation appears to have undergone northsouth compression. This has produced foliation, folding and ductile shear zones in the deposit, and made it more homogenous. Some zoning remains, however, with usually a thin albitite or lepidolite-albite-petalite wall zone, and the later minerals also occur in separate thin dykes parallel to the main pegmatite. There is one Rb-Kfeldspar, low-petalite zone, and the other zones are less distinct, being based upon petalite's color (white, blue, grey or pink), as well as variations in the content of Rb-K-feldspar, albite, mica and quartz. Pearse and Taylor (2001) characterized the deposit as containing about 25% petalite (LiAlSi<sub>4</sub>O<sub>10</sub>), 11% albite (NaAlSi<sub>3</sub>O<sub>8</sub>), 10-15% Rb-K-feldspar ([K.Rb]AlSi<sub>3</sub>O<sub>8</sub>), up to 15\% muscovitic mica, 3-5%spodumene, and lesser amounts of lepidolite (with up to 4% Rb<sub>2</sub>O), tantalite minerals (predominately columbite-tantalite), cassiterite (0.04% Sn) and many other minerals.

The *Big Mack* pegmatite system lies to the west of the Big Whopper, and is owned by the Emerald Fields Resource Corp. It consists of a swarm of beryl and petalite-type pegmatites within an area 3 km long and an average width of 200 m. The swarm contains the Big Mack pegmatite which is about  $30 \times 200$  m in size, nearly vertical and of an unknown depth. Its mineralogical features are similar to the Big Whopper, consisting primarily of K-feldspar and petalite, with minor amounts of quartz and muscovite. It contains a thin border zone of fine-grained garnet– quartz–albite aplite with some blue cordierite, and a small 2–3 cm thick core zone of mafic metavolcanic rock. In addition to the petalite the deposit contains small amounts of spodumene, eucryptite, bikitaite and many other minerals (Tindle and Breaks, 2000). The initially estimated ore reserves were greater than 300,000 mt of

#### 88 Part 1 Lithium





(b) Geology of the Big Whopper pegmatite system. Access road English River CAMP N LEPIDOLITE DYKE - [ 700W Area of Cs 600W anomaly in PETALITE ZONE A to D: S metasomatic A - petalite (white) k-feldspar quartz albite 400W selvedges 10000 B - petalite (pink) k-feldspar albite ( > 1000 ppm Cs ) 300W C - petalite (blue-grey and pink) albite mica 1.1.1.1 200W D - petalite lepidolite albite 100W albitite wall zone 100 200 amphibolite host rocks Ι section line 4+60 W (Figure 4) Property Boundary 175 m East metres

**Figure 1.41** The Big Whopper lithium pegmatite (Pearse and Taylor, 2001; figure first published in the CIM Bulletin, Vol. 94, No. 1049. Reprinted with permission of the Canadian Institute of Mining, Metallurgy and Petroleum).

petalite, and consideration was being given to the production of 15,000 mt/yr of this product (USGS, 2000).

#### Other Canadian Lithium Deposits

In *Ontario* the area from Beardmore to Lake Nipigon, including an area 140 km south of Georgia Lake also contains many zoned and unzoned pegmatites, with at least 6 million mt of predominantly spodumene ore. Other areas in Ontario with lithium pegmatites are Dryden, Falcon Lake, Fort Hope, Gull Lake, Lac La Croix, O'Sullivan, Pakeagama Lake, Quetico Park, Root Lake, Superb Lake, Wekusko Lake and Tashota Lake (Kunasz, 1994; Kesler, 1960). The mineral and chemical analysis of an outcrop sample of the unzoned, very small-crystal Wekusko Lake spodumene deposit, averaging 0.79% Li (1.70% Li<sub>2</sub>O) is shown in Table 1.18. A similar outcrop sample from the Pakeagama Lake pegmatite analyzed 0.62% Li (1.34% Li<sub>2</sub>O; in its spodumene), 0.90% Rb<sub>2</sub>O, 0.20% Cs<sub>2</sub>O, 0.038% Ta<sub>2</sub>O<sub>3</sub>, 0.014% Nb<sub>2</sub>O<sub>3</sub>, 0.0076% Sn, 0.0047% Ga and 0.0029% Tl (www.hustonlakemining.com 1999). In 1960 there were considered to be nine lithium pegmatite areas in Ontario, extending from Georgia Lake (137 km NE of Port Arthur) to SE of Lake Nipigon. Both zoned and unzoned spodumene deposits had been located (Kesler, 1960).

#### Quebec; Quebec Lithium Corp

In the Preissac-Lacorne district of western Quebec, half way between the towns of Val d'Or and Amos there is a lithium-rich pegmatite district with dikes containing primarily spodumene and small amounts of lepidolite and other lithium micas. There are also other non-lithium ores such as beryl, pollucite, molybdenite and minor amounts of columbite and tantalite. The district is in a "T" shape extending about 33 km east-west and 20 km north-south. The lithium pegmatites appear to have intruded into this Precambrian Shield area perpendicular to a greenstonegranodiorite contact at shallow depth, and are richest near the contact zone (Fig. 1.42). The largest deposit was owned by Quebec Lithium Corp. with reserves of 15-20 million mt of ore averaging 0.56% Li (0.51-0.93%; 1.21% Li<sub>2</sub>O), and they produced spodumene from the deposit from 1955-1965. Many smaller deposits have also been found in this area, including in Montainier and Delbreuil Townships, and within the Abitibi greenstone belt in Steele and Lowther Townships (Flanagan, 1978; Kunasz, 1976; Kesler, 1960). In the Abitibi region Raymor Resources was considering the development of a spodumene operation on their La Motte property in 1997. The deposit was stated to have reserves of 4.55 million mt of ore containing 0.50% Li (1.07% Li<sub>2</sub>O) to a 100 m depth, and ore with >1.16% Li (>2.5% Li<sub>2</sub>O) below that. The pegmatite was amenable to surface mining (USGS, 2000, 1997).

In *Manitoba* the East Braintree-West Hawk, Gods Lake, Herb Lake and Cat Lake–Winnipeg River (see Tanco) areas all contain lithium pegmatites. Spodumene is the principal lithium mineral, with some petalite, lepidolite and amblygonite. The small Buck and Pegli lithium deposits were also found in the latter area (Cerny and Lenton, 1995). In 1958 the lithium ore reserves were about 8 million tons in the



**Figure 1.42** Side view of the Quebec Lithium Corporation's spodumene pegmatites (Flanagan, 1978; reprinted from Energy, Vol. 3, No. 3, ©1978 with permission of Elsevier).

Winnipeg River area, and 2 million tons in the Herb Lake area, 137 km east of the town of Flin Flon. In the *Northwest Territories* there are also many pegmatites in this Precambrian Shield area, such as an extensive area (13,000 km<sup>2</sup>) north of the Great Slave Lake and the Yellowknife-Beaulieu area. However, of the 500 pegmatites examined by 1960, only 30 contained lithium. Spodumene was the principal lithium mineral, although amblygonite was a prominent constituent of some ore zones. The spodumene was often high grade with a large crystal size, and accompanied by tantalite–columbite, beryl and cassiterite. Both the Moose No. 2 and Best Bet openpit mines have produced lithium ore in this area (Kesler, 1960). The age of these deposits is about 2.2 billion years (Lasmanis, 1978).

#### **Other Countries**

In *Brazil* commercial lithium-bearing pegmatites have been operated for many years in the Jequitinhonha River basin of the Aracuai–Itinga area in northern Minas Gerais province. As an example of this, in 1978 1600 mt of petalite, 1200 mt of lepidolite, 1000 mt of amblygonite (for conversion to lithium chemicals) and 800 mt of spodumene were mined for domestic consumption, and 2500 mt of petalite were exported. Some cassiterite, tantalite and beryl that accompanied the lithium in the pegmatites was also recovered, with the reserves in the Precambrian Brazilian Shield region of that state at that time being about 25,000 mt of Li (Afgouni and Silva Sa, 1978). In 2001 Brazil was the sixth largest lithium producing country.

Small amounts of spodumene and amblygonite have also been mined in the states of Paraiba, Rio Grande do Norte and Ceara (Solonopole and Quixeramobim). The pegmatites dip steeply, are up to 300 m in length and 30 m wide, and distinctly zoned. At least eight contained appreciable spodumene, and 20 some amblygonite (Kesler, 1960). In the province of Goias a number of lepidolite pegmatites have been prospected, with one area about 1 km long and 100-150 m wide. The ore varied from 3-6% Li<sub>2</sub>O, and was colorless to several shades of pink (Petruk and Sikka, 1987). As the demand for lithium minerals increased (particularly petalite) further exploration has resulted in the discovery of other important petalite pegmatites, such as one that contained 100,000 mt of petalite with a 2% Li grade. Spodumene reserves in 1990 were estimated at 300,000 mt, but the richer lepidolite deposits in the country appeared to be nearly exhausted. The most important mining company was Arquena de Minerios e Metais Ltd., mining all of the above-listed minerals. They also supplied spodumene to Companhia Brasileria do Litio, who in 1991 produced about 1500 mt/yr of lithium carbonate with some government assistance in a nearby town. In Argentina there are lithium-bearing pegmatites in the western part of Sierras Pampaneas province in the San Luis, Cordoba and Catamarca areas. The pegmatites are zoned and contain about 18,000 mt of spodumene reserves (Kunasz, 1994). In Bolivia there are also lithium pegmatites in the Bolivian tin belt.

#### Zaire

One of the largest lithium pegmatite deposits in the world occurs in the Manono and adjacent (2.4 km away) Kitotolo deposits in Zaire. Each deposit is 5 km long, 120–425 m wide, proven to a 125 m depth (up to 50 m from the surface is kaolinized), and appear to be zoned. From 1929 to at least 1991 only columbite and cassiterite were being mined, and that from the weathered surface rock of the Manono pegmatite. The near-surface ore of the zoned pegmatites contain 10-25% spodumene in microcline, albite and mica. The deposits face the almost insurmountable problem that the nearest shipping port is at Lobito, Angola, about 2200 km away. The construction of a 10 million lb/yr lithium carbonate plant had been planned for 1980, but was not built (USGS, 1991; Kunasz, 1976; Kesler, 1960).

## Namibia, Other African Deposits

Lithium minerals have been periodically produced by a number of different companies from the Karibib-Omaruru district, Namibia, approximately 190 km from Walvis Bay. The area has several strongly zoned pegmatites containing lepidolite, petalite and smaller amounts of amblygonite. A flotation plant had been installed to process the 20-50% lepidolite ore, based upon reserves of about 1 million mt of ore. There are also an estimated 200,000 mt of petalite ore in the deposit (Kunasz, 1994; Kesler, 1960). In the Alto Ligonha area of *Mozambique* lepidolite, amblygonite and spodumene occur in small zoned pegmatite bodies. The lepidolite has been commercially mined, but the amblygonite is rare, and the spodumene has been altered to kaolinite. In *Rwanda* large amblygonite masses have been found in the pegmatite district west of the capital city Kial. This district is 5.6 km long by 46–760 m wide, and though mined primarily for tin, it is said to

contain 10-25% spodumene and other lithium minerals. The Bougouni area of *Mali* had limited production of spodumene and amblygonite concentrates from 1956–1970, with reserves of about 266,000 mt of 3.02% Li<sub>2</sub>O ore. In the Noumas and Norrabees areas of the Cape Province in *South Africa* spodumene pegmatites occur that contain about 30,000 mt of lithium. Other reports of lithium minerals have been noted in the Ivory Coast, Malagasy Republic, Sudan and north of Kampala, Uganda (Kunasz, 1994; Anstett *et al.*, 1990; Kesler, 1960).

In China lithium minerals (such as petalite) and lithium chemicals are produced from the Altai Mountains in Mongolia, 600 km north of Urmchi, and several other pegmatite deposits in the Hunan, Sichuan and Xinjiang-Uygur provinces. In the latter province the large zoned Koktokay pegmatite has produced spodumene and lepidolite (as well as tantalum, niobium and cesium) since 1946. Its reserves are stated to be over 5 million mt of 0.7% Li ore, and from 2110-7332 mt of Li<sub>2</sub>CO<sub>3</sub> were produced from the deposit each year from 1984-1988. A major low-grade deposit is also operated in southwestern Jiangxi Provence, South China, where the Yichun open pit mine produces lithium, tantalum and niobium. The ore is characterized as a lepidolitetopaz granite, consisting of lepidolite (Table 1.16), albite and quartz, with lesser amounts of topaz, potassium feldspar and amblygonite. The accessory minerals are zircon, monazite, pollucite, columbite-tantalite, microlite and tantalum-rich cassiterite (Fig. 1.43). The pegmatite has intruded through the Yashan granite batholith in the form of a small sheet-like body, which now outcrops and has been weathered to an unknown extent. The lepidolite-topaz granite contains from 15-20% lepidolite (0.74-1.63% Li<sub>2</sub>O) as up to 3 mm crystals in a 40-60% albite lath structure, with Ta-Nb mineralization disseminated throughout the mass. The lepidolite contains relatively high amounts of fluorine, phosphorous and rubidium, and the deposit's age is estimated as 178 MyrBP (Yin et al., 1995).

There are many small lithium pegmatites in *Europe*, and in the early days of the industry several of them were commercially operated. Significant spodumene pegmatites have been found in southern Austria by Minerex, and exploratory underground mining and separation procedures have been conducted. The large Koralpe spodumene deposit is estimated to contain 10 million mt of 0.77% Li ore. A large lithium pegmatite has also recently been discovered in *Finland*, and in 2001 petalite production from it was being considered (USGS, 2002). Previously only the small Viitaniemi, Eraejaervi, central Finland lithium pegmatite containing mostly lithium phosphate minerals had been discovered (Volborth, 1954). Lithium pegmatites also occur in France, but none appear to be of sufficient size or grade to be commercial deposits. At Beauvoir in the Allier province of the French Massif Central a lithium phosphate pegmatite containing lepidolite and amblygonite, with tin and tantalum mineralization has been studied (Raimbault et al., 1995). One of the minor lithium pegmatites that has also been extensively studied is the Varutrask pegmatite in Sweden. It is in the form of a "C" with a shallow dip, and is zoned somewhat as the Tanco pegmatite in Canada. The Inner Intermediate Zone contains amblygonite, spodumene-quartz pseudomorphs after petalite, and petalite



Figure 1.43 Simplified geologic map and cross section of the Yashan Batholith (Yin *et al.*, 1995). Reprinted with permission from Economic Geology, Vol. 90:3, p. 578, Fig. 1 Yin, L., Pollard, P. J., Shoux, H. And Taylor, R. G. 1995.

remnants. Some of this zone is replaced by lepidolite, and in the eastern limb of the "C" it also extends into the Outer Intermediate and Wall zones. The deposit was mined periodically to 1950, and very little of the reserves remain (Heinrich, 1976).

In *Portugal* there are many lithium pegmatites, with the Barroso-Alvao area of northern Portugal being perhaps the most studied (Fig. 1.44). This area has at least 10 good-sized lithium pegmatites containing spodumene with some petalite, amblygonite and montebrasite. Most of the spodumene consists of laths up to 30 cm long, but there are zones where it is in the form of poeciltic aggregates. The major component of the deposits is aplite, and the spodumene is primary and comparatively uniform (similar to the North Carolina, USA deposit). When petalite is present it is usually in the form of a thin continuous coating on spodumene crystals, or as blades with quartz in pseudo-vugs. There is some alteration of the spodumene to albite ( $\pm$  muscovite), and of the petalite to K-feldspar and/or eucryptite (but not spodumene). The bulk samples of the ore vary from 0.80–1.65% Li<sub>2</sub>O, and trace amounts to 0.81% Fe<sub>2</sub>O<sub>3</sub>. Crystals of spodumene contain about 0.23% Fe<sub>2</sub>O<sub>3</sub> (Table 1.16; Lima *et al.*, 1999).

Charoy et al., (2001) have further studied three of the pegmatites in the eastern part of this district, the Covas de Barroso area, and found primary spodumene and small amounts of the secondary minerals noted above. However, they also noted that in the western area the deposits contained only primary spodumene. Their lithium pegmatites outcropped in a swarm of dykes over a 0.1-1 km distance, and were 2-10 m wide with a gentle to steep dip. Most of the spodumene occurred as long blades of euhedral to subhedral crystals, pearly in color, up to 15 cm long and averaging about 5 cm. It contained almost no inclusions, and usually petalite could only be detected by microscope in thin sections of the spodumene's edges, except in one deposit where there were a few angular voids in the spodumene containing needles of petalite with quartz. Some of the petalite had been altered to brownish microcrystals of eucryptite. Aplite was the dominate matrix material, with some Narich plagioclase and quartz, and very little K-feldspar and muscovite. The Li<sub>2</sub>O content of the pegmatites averaged 1.55%, and the composition of three of the lithium minerals in the deposits is given in Table 1.18 (Charoy et al., 2001). In the Guarda area of Portugal a lepidolite and amblygonite deposit has been mined on a small scale for many years (Anstett et al., 1990). At Goncalo, Beira Alta province there is also a lepidolite deposit.

India has a number of small lithium pegmatites (the lepidolite in one is listed in Table 1.18), including the lithium phosphate deposit in the Sewariya batholith of the South Delhi Fold. This leucogranite structure may have been intruded by a volatilerich magma at about 484°C and 500–700 bars pressure, based upon the phosphate minerals that are present (Pandit and Sharma, 1999). In the Govindpal area of Madhya Pradesh there is a zoned pegmatite containing lepidolite, zindwaldite, amblygonite, spodumene and tantalite of unknown size and grade. Sizable lithium deposits exist in *Russia*, with the Zavitaya, Chita Oblast spodumene district in the Ural Mountains having received the most attention, and in 1979 was Russia's largest producer. In the



**Figure 1.44** Map of the Covas de Barroso lithium pegmatites (with names), and other pegmatites in Northern Portugal (Charoy *et al.*, 2001, courtesy of the Canadian Mineralogist). (1) Syntectonic two-mica granites; (2) post-tectonic (post- $D_3$ ) biotite granites. Insert: regional geology for location of the Régua-Verin fault system.

95

Ukrainian Shield's Archean Kirovograd Block there are also a number of lithium pegmatites, including fine-grained petalite in the Polohov deposit, and spodumene and petalite in the Lipnyazhka pegmatite field. The ores are accompanied by microcline, albite, apatite, muscovite, etc. (Eremenko *et al.*, 1996). In the Kola Peninsula's Baltic Shield an unusual lithium–cesium deposit occurs in an andalusite–biotite–quartz schist that is separated from, and may not be part of nearby pegmatites (Nagaytsev and Belyaev, 1995). A number of other Russian lithium pegmatites have also been mentioned, as well as high-lithium granitoids in the Altai (Fig. 1.45) and Transbaikal regions. These Li–F granites also contain appreciable amounts of various rare metals. In the western Kirovogard Block of the Ukrainian Shield there are lithium pegmatites high in petalite, with no minerals containing volatile components, little quartz, and highly disordered K-feldspar. Inclusion evidence indicates that the pegmatites formed at greater than 1100°C and 87 MPa pressure, in the presence of CO<sub>2</sub>-rich fluids. Some petalite later recrystallized in the presence of CO<sub>2</sub>-rich fluids at 680°C and <46 MPa (Voznyak *et al.*, 2000).



**Figure 1.45** Location of rare-metal Li- and F-rich granitoids in the Altai. (1) Li-F-type granitoids: (1) vicinity of Ust'-Kamenogorsk, (2) Kalguta pluton, (3) Dzhulalyu pluton, (4) Alakha pluton, (5) Belokurikha pluton, (6) Ust'-Tulatin pluton, (2) Late Paleozoic and Early Mesozoic Li-rich granitoids: (A) Kalba, (B) Kalguta, (C) Chindagatui, (D) Belokurikha, (E) Karakol, (F) Shchebetin, (G) Sinyushin and Kolyvan, (H) Tigirek; (3) granitoids of the Kalba and Monastyr complexes with unspecified Li and F contents; (4) other granitoids; (5) major faults (Dovgal *et al.*, 1998).

Other lithium production has been obtained from the Tro San Zhen district of the former Russian province of *Kirgiztan*, which is stated to contain significant spodumene and petalite reserves (USGS, 1979). In *Uzbekistan* the Chatkal-Kurama region of central Tien-Shan contains a cluster of pegmatites that includes the Shavaz lithium deposit, the Sargardon tungsten deposit and the Shabrez fluorite deposit (Akhundzhanov, 1997). In *Afganistan's* Hindukush Mountain Range in the Nilau-Kulam and Parun areas there is a potentially large spodumene deposit where much of the ore mined to 1990 was of gem quality (Anstett *et al.*, 1990).

Lithium pegmatite occurrences have also been noted in many other countries, including Bolivia, Chile, Czechoslovakia (lepidolite in the Rozna area in Moravia province), Ireland, Japan (Nagatare, Fukuoka Prefecture), Korea, Sicily (Guerenko and Schmincke, 2002) and Spain (Kunasz, 1994; Deberitz, 1993; Anstett *et al.*, 1990).

#### High-Lithium Clays (Hectorite); Other Rocks

The range of the lithium content in igneous rocks is often about 6–28 ppm Li, but it can vary widely from zero to much higher values, such as the exceptionally Li-rich igneous rock found in the McDermitt Caldera in Nevada and Oregon containing up to 0.35% Li. Sedimentary rocks often contain high lithium values, such as from 10–53 ppm Li, but again the range is considerable, from zero to the medium-rich shales (often 20–100 ppm) to the lithium clays (Table 1.26). The latter includes the high-magnesium-lithium end member of the smectite group *hectorite* [Na<sub>0.33</sub>(Mg,Li)<sub>3</sub> Si<sub>4</sub>O<sub>10</sub>(F,OH)<sub>2</sub>] with a lithium concentration range of from 0.24–0.53%. It is found in a large deposit at Hector, California, 120 km east of the large geothermal

Phy	sical and	Chemical P	roperties of	Some Lithi	um Clays (Vine, 1980)	
	Li	i Al	Mg	F		
Mineral name		(percent or r	elative amo	Relative dispersion of clay in water	Relative Li solubility in water	
Hectorite <sup>a</sup>	0.5	Trace	Major	5.0	Very high	Low
Li-Stevensite <sup>b</sup>	0.4	Low	Major	5.0	Variable	High
Li-smectite <sup>c</sup>	0.7	Medium	Low	Low	Poor	Low
Li-bearing high- alumina clay <sup>d</sup>	0.5	High	None	None	Very poor	Very low

Table 1.26

<sup>a</sup> Type material from Hector clay pit, San Bernardino County, California.

<sup>b</sup>Representative material from Kirkland area, Yavapai County, Arizona.

<sup>c</sup> Representative material from Montana Mountains, Humboldt County, Nevada.

<sup>d</sup> Representative material from Missouri fire-clay district, Mint Hill area, Osage County, Missouri. Probably a mixture of kaolinite, cookeite, and possibly diaspore. spring-formed borax deposit at Boron (that also contains high-lithium shales; 0.2-0.4% Li). At Hector it occurs as a massive deposit with some travertine-like calcite, and associated rocks of sandy to bentonitic clay and volcanic ash. It is partly covered by a younger basalt flow, leading to the suggestion that it may have been formed by a reaction with the existing volcanic ash and high-lithium thermal spring waters that accompanied the basalt. A large deposit of bentonitic clay 90 km further east containing 0.2% Li perhaps indicates some relationship between these three high-to-medium lithium content clay deposits (Kesler, 1960). Smaller amounts of hectorite have also been found in Clayton Valley, McDermitt, and the Lake Mead area, Nevada; near Wickenburg, Arizona; Socorro, New Mexico; Lincoln, Montana; and a number of other locations with lithium contents of up to 0.11-0.19 (Anon., 1979).

Hectorite is usually white, with swelling characteristics that at one time gave it some use in cosmetics as an adsorbent for facial oil, as a paint thickener and a beer clarifier. Extensive tests on the commercial processing on hectorite have indicated that the recovery of lithium is both expensive and difficult. The US hectorite reserves have ben estimated as 15.1 million tons of Li (Kunasz, 1994). In a limited number of locations several other types of high-lithium clays have also been found, such as the flint clays in Missouri, Kentucky and Pennsylvania with up to 0.5% Li (Vine *et al.*, 1979; Anon., 1979). An estimate of the average abundance of lithium in some of the other comparatively high-lithium members of common rocks and waters has been made by Vine (1980) and White *et al.* (1976), as ppm: shales 60–66, pelagic clay 57, granite 30-40, basalt 10-17, sandstone 15, carbonates 5 and geothermal water 1-10. Seawater is 0.17, and Vine (1980) estimates the earth's average crust at 20 ppm Li.

#### Lithium Isotopes

Since the late 1990s there has been a growing literature on lithium isotopes, as indicated in Table 1.14. Both  $\delta^6$ Li and  $\delta^7$ Li have been reported, since a standard nomenclature has not yet been established. This is quite unusual in isotopic work, and makes the values of different investigators difficult to compare. Nevertheless, the studies have been quite useful in determining the origin of some brines, the amount of lithium adsorbed on clays or other rocks, and on various other physical or chemical changes.

#### PROCESSING

#### History of the Lithium Industry

Lithium was discovered by the Swedish geologist, Arfvedson in 1817, who separated it from petalite found in Sweden's Uto pegmatite, and named it after the Greek word lithos, meaning stone. It was first isolated as a metal in trace amounts by Sir Humphrey Davy and Brande in 1818, in larger quantities by Robert Bunsen and

Mathiessen in 1854, and the metal was first prepared as a commercial product in 1925 by Metallgesellschaft in Langelsheim, Germany. They utilized zinndwaldite recovered from the Zinndwald, Germany base metal tailing dumps, and this company has remained in continuous production of lithium compounds from purchased ore concentrates or lithium carbonate since 1923. Lithium products were first commercially produced in the US by Maywood Chemical Co. in New Jersey in 1927, and then by the Foote Mineral Co. in the late 1930s, both using their own South Dakota or purchased ore concentrates. LCA later started operation near Minneapolis, Minnesota, and the US Government sponsored the Solvey Process Co. in the late 1940s to initiate mining at the large Kings Mountain, North Carolina spodumene deposit. Foote bought the mine in 1951, and in 1953 started lithium hydroxide production from this ore at Sunbright, Virginia. Also in 1953 the US Government let three contracts for the purchase of lithium hydroxide to Foote, LCA and American Potash, with the contracts expiring in 1960. The latter two companies built new plants in Bessemer City (1955 using their own North Carolina ore) and San Antonio (1956 using purchased Southern Rhodesia [Zimbabwe] lepidolite), respectively.

In 1960 the industry's over-capacity only allowed operation at about 20% of capacity, and Maywood ceased the production of lithium compounds. LCA closed their Minneapolis plant in 1959 (and canceled their long-term ore contract with Quebec Lithium), while American Potash & Chemical Co. closed their Texas plant in 1963. American Potash's Searles Lake lithium operation had started in 1951 and closed in 1978. Quebec Lithium in turn started producing lithium chemicals, but closed their plant in 1965. The production of ore from South Dakota stopped in 1969, and sanctions against Southern Rhodesia (still one of the world's major suppliers) curtailed their ore imports from 1965–1980. Foote's Clayton Valley brine operation commenced in 1966, and LCA started mining spodumene in North Carolina in 1968. Foote's Salar de Atacama operation started in 1984, while SQM's started at the Salar de Atacama, and FMC's (formerly LCA) at the Salar de Hombre Muerto in 1997. Both of the North Carolina mines closed after their brine operations had been well established, and FMC essentially closed their Hombre Muerto plant in 1998 because of SQM's greatly reduced lithium carbonate pricing.

Some of the first large-scale uses of lithium were in lithium batteries, lithium hydroxide in lithium greases, the absorption of carbon dioxide in submarines in World War II, and the filling of balloons with hydrogen made from lithium hydride. During 1955-1960 lithium began to be used much more extensively in ceramics and glass, and <sup>6</sup>Li was employed to produce tritium for hydrogen bombs. In the late 1950s lithium bromide began to be used in air conditioning on a large scale, and in 1961 *n*-butyl lithium began to be used as a catalyst for synthetic rubber. Lithium carbonate began to be employed in aluminum reduction cells in the second half of the 1960s, and from 1972 onwards many new uses for lithium were developed.

#### **Brine Processing; Solar Ponds**

Because of the very dilute concentration of lithium in even the most favorable brines, and the expense of directly recovering the lithium in a processing plant, solar evaporation of the brine to further concentrate it has been a necessary first step in all of the world's current lithium brine operations. Intrinsically solar evaporation is a very simple and inexpensive operation, but it does have a number of demanding requirements, and can have many problems. Since it relies upon solar radiation for the energy to evaporate water from the brine, the pond areas must be very large and the land comparatively flat and inexpensive. Most of the highest-lithium brines are found in dry lakes (playas), so this requirement is easily met, but it would not be with most of the oilfield, geothermal, potash deposit end-liquor or similar brines. The pond area must also have good evaporating conditions, which again is usually the case with most dry lakes but not with most other brines. The rate of evaporation depends upon the amount of solar radiation (sunlight), the humidity, wind and temperature, and these conditions vary widely. This effects the pond size, the final brine concentration, the cost of the ponds and their operation, and the final brine treatment methods and cost. The ponds require careful construction, operation and control, with adequate provisions for product brine storage during the winter and periods of unusual weather.

To be most cost-effective the ponds must be divided into many segments to maximize the overall evaporation rate (the rate decreases with the brine concentration), so that each of the salts in the brine may crystallize in separate ponds, and that ponds may be taken out of service to periodically remove (harvest) these salts (after the entrained brine has been thoroughly drained) without undue disruption to the entire system. There must be as much gravity flow between the ponds as possible, and the banks must be protected from wave erosion. Then, the most important of the pond design factors is for them to be reasonably free from leakage. If the ponds are constructed of soil a careful soil survey must first be made of the entire pond area to be sure that there is a continuous layer of adequately impermeable clay under the pond, at least at a reasonable depth. If there are occasional zones of permeable soil it must be removed and back-filled with clay. If the clay layer occurs at depth, then the outer pond walls must be cut with a trench and back-filled with clay to prevent the upper porous zones from leaking laterally. Meandering former sandy stream beds must also be sealed with these clay "cut-off walls." In cases where the soil permeability is of border-line value canals may be built adjacent to the outer walls and filled with a more dilute brine at a higher level than in the ponds to form a "hydraulic seal." In this case the ponds are usually operated with the feed brine at the outer edges of the pond system, and the product brine in the center. With most of the world's large playas sufficient areas of impermeable soil can be found to form a solar pond system with a reasonably low amount of leakage. However, without the soil testing and the cut-off walls the ponds may leak excessively, as did at least the initial ponds at Clayton Valley.

As an alternative to clay-sealed ponds they can be lined with an impermeable plastic membrane. For the most demanding ponds (or pond areas) one of the most popular membranes is 25 mil reenforced Hypalon. It is highly puncture-resistant, has a very long service life (>25 years) with low-to-moderate concentrations of magnesium chloride in the brine, and it is quite resistant to ultra-violet oxidation. For the bulk of the ponds a much less expensive, but less rugged membrane might be used such as 20-40 mil PVC (polyvinyl chloride) or polypropylene. Although theoretically the membranes can make a leak-free pond, in practice this is often far from the case. The problem is that the plastic sheets can only be produced with a limited width in the factories, and they may have some-to-many small holes in them as they are formed. Also, the membranes are very heavy, further limiting the size of each piece. This means that strips of membrane must be joined together (sealed) to from the desired pond size when actually laid out on the floor of the pond. The Hypalon sheets are joined with a glue, while the polypropylene, PVC and most other membranes can be heat-sealed. Both jobs are difficult, and the chance for imperfect seals is always present, as well the possibility of punctures from underlying rocks, or tears as the membrane is stressed. Careful visual inspection, as well as some electric testing can find some leaks at this time, and after the membrane has been formed the ponds may initially be filled with water, with moisture or conductivity sensors in the soil, and other leaks found and repaired before the ponds are placed in service. There are a number of articles on solar pond design and operation, such as by Garrett (1966).

Because of the low concentration of the lithium in the original brine, leakage prevention, just as the recovery of as much as possible of the entrained brine from harvested salts, is very important. Many methods have been suggested to determine leakage in both clay and membrane-lined ponds, but they have had very limited success. The simplest is that shown in Fig. 1.46 utilizing the difference in pressure between the brine in the pond and the moist soil underneath (Lee and Cherry, 1978), while various electrical measurements can also be used to detect moisture in the soil. Piezometers (small open-ended tubes to measure the hydrostatic pressure) are sometimes employed, but the most positive type of detector is the use of small porous tubes placed under the surface of the ponds, where actual samples of the leaked brine can be withdrawn by vacuum. In all cases, once a leak is detected it is still very difficult to find the exact hole, and then repair that area of the membrane. However, despite these problems, if very carefully constructed and maintained, membrane linings can provide a most satisfactory brine retention barrier, and even though relatively expensive, in general be superior in performance to clay-lined solar ponds. The various commercial operations, and other suggested processing methods for lithium recovery will be reviewed in the following sections.

#### Clayton Valley (Silver Peak), Nevada; Chemetall

Production of lithium from this deposit was initiated in 1966 by the Foote Mineral Co. in a \$2 million plant with a capacity of 14 million lb/yr of lithium



**Figure 1.46** An example of a solar pond leakage detection meter (Low *et al.*, 2000; reprinted from the Eighth Symposium on Salt (ISBN 0444500650), Vol. 1, p. 524, Fig. 1.4, ©2000, with permission from Elsevier).

carbonate (that could be extended to 18 million lb/yr for a 2-year period). Foote was acquired by Cyprus Minerals Co. in 1988 (and then called Cyprus Foote Mineral), and it in turn by Chemetall in 1998. The Clayton Valley operation, as are all of the lithium brine deposits, is dependent upon solar evaporation to concentrate the brine from the playa (as discussed above) to a value where lithium can be precipitated with sodium carbonate. In the ponds (Figs. 1.47 and 1.48) as the brine (Tables 1.3 and 1.27) evaporates it first crystallizes small amounts of calcite and gypsum (Garrett, 1960), and then salt at a rate to deposit a layer about 0.3 m thick per year. The evaporation rate of water in the area usually varies from 760–1200 mm (30–40 in.)/yr, and the rainfall is often less than 130 mm (5 in.)/yr.

In 1969 the operation pumped 100-300 gpm of brine from each of 30 0.3 m (12 in.) diameter gravel-packed wells, perforated for their entire depth, and surrounded by 15 cm (6 in.) of gravel. They were 90-240 m (300-800 ft) deep with multi-stage centrifugal pumps at their base, powered by 50 HP engines on the surface. The brine level was sometimes as low as 15-76 m (50-250 ft) beneath the playa floor, and it contained an average of 400 ppm Li. The brine was sent through transite pipes to the initial 308 ha (760 acre) pond. The total area of the nine solar evaporation ponds in use at that time was 642 ha (1587 acre), and brine was advanced from pond to pond as it concentrated (Fig. 1.49) to minimize the entrained brine lost in the crystallized salts. Salt did not crystallize in the first pond, but it did in ponds 2, 3 and 4 (520, 90 and 86 acre, respectively). Slaked lime was added to the brine leaving the fourth pond after it had been evaporated for about 10 months, and it



**Figure 1.47** Map of Clayton Valley and its early solar ponds and wells (Davis and Vine, 1979; reprinted courtesy of the Rocky Mountain Association of Geologists).



**Figure 1.48** Photograph of the more recent Clayton Valley solar ponds in 1991 (courtesy of Rocky Mountain PAY DIRT).

			Maxim conte	um lithium ent (ppm)	
Well number	Elevation at surface (m)	Total depth penetrated (m)	Brine	Sediment	Comments
CV-1	1302.4	120.4	60	310	Gravel below 300 ft (91 m)
CV-2	1303.0	120.4	55	930	
CV-2A	1304.5	83.8	100	390	Gravel below 235 ft (72 m); bottom hole temperature 44°C
CV-3	1304.2	187.5	160	640	Maximum 33°C at 415 ft (126 m)
CV-4	1301.5	242.3	190	1700	
CV-5	1301.5	146.3	110	770	Mostly in gravels
CV-5A	1301.5	224.0	640	960	Penetrated thick sequence of salt beds

 Table 1.27

 UISGS Logs for the Clayton Valley Drill Holes Shown in Fig. 1.47 (Vine. 1980)

precipitated gypsum and hydrated magnesia (reducing the Mg content of the brine to 2-3 ppm) in the fifth 19 ha (46 acre) pond (also listed as two 12 ha [30 acre] ponds). The resultant magnesium hydroxide and calcium sulfate were periodically dredged (Fig. 1.50) from the ponds and sent to a sludge-containment reservoir. Since the brine was then basic, much of the remaining calcium precipitated with absorbed carbon dioxide in pond 6 (17 ha; 41 acre) with a mixture of sodium and potassium chloride (sylvinite). The sylvinite was harvested and stockpiled separately for possible future potash recovery. Salt and glaserite (K<sub>3</sub>Na[SO<sub>4</sub>]<sub>2</sub>) crystallized in pond 7 (17 acre), while in ponds 8 (5 ha; 13 acre) and 9 (6 ha; 14 acre) salt, potassium chloride and glaserite all precipitated.

The final brine to be sent to the plant contained 5000 ppm Li, and it was stated that if the final concentration were over 6500 ppm Li, lithium-potassium sulfate would crystallize and be lost (Gadsby, 1967). Because of lithium carbonate's appreciable residual solubility when precipitated in the plant, this rather low lithium concentration required that a high percentage of the end-liquor brine from the plant be recycled back to the ponds. From 75–90% of the pond evaporation occurred during the months of April through October, so the final pond held enough brine to service the plant throughout the year and to help smooth-out the yearly weather fluctuations. Brine was initially pumped primarily from an unconsolidated volcanic ash aquifer, and later some was also pumped from porous halite (although it tended to dissolve, causing the upper sediments to cave-in) and sand or gravel beds (Gadsby, 1967).

In 1970 it was noted that the average brine concentration had dropped to 300 ppm Li, the well field covered an area of  $5.2 \text{ km}^2$  (2 mi<sup>2</sup>), and that 10 of the 30 wells, and



**Figure 1.49** (a) Solar pond and pumping station at Clayton Valley (Deberitz, 1993, courtesy of Chemetall GmbH). (b) Pumping brine between ponds at Clayton Valley (Dillard and McClean, 1991, courtesy of Rocky Mountain PAY DIRT).

the No. 9 pond had been added during the first expansion in 1967. Twenty new wells were to be drilled from 1970–1971 in a second expansion. The new wells were spaced on 610 m (2000 ft) centers, not perforated in their upper 12.2 m (40 ft) to minimize the entry of more dilute near-surface water, and the wells pumped at



Figure 1.50 Dredge removing loose salts from the Clayton Valley solar ponds (Dillard and McClean, 1991, courtesy of Rocky Mountain PAY DIRT).

50-500 gpm. The brine in the ponds varied in depth from 0.9-1.2 m for the larger ponds to about 0.3 m for the smaller ponds. The 23 km (14 mi) of pond dikes were constructed of granular dolomitic limestone or a gravel-silt-clay mixture, and had an inner clay core to minimize leakage. There were also 27 km of access roads and 16 km of power lines. Pumping was required between ponds 1 and 2, 5 and 6 (Fig. 1.49), and from 9 to the plant, but all of the other interpond flow was by gravity, since the land sloped at about 0.19-0.38 m/km(1-2 ft/mi). By 1970 pond 5 was full of gypsum and magnesium hydroxide, so it was abandoned and the lime slurry added to pond 6 (Anon., 1970; Barrett and O'Neill, 1970).

In 1991 there were 40–60 wells that were 150–300 m deep (average 213 m), and they pumped several million gallons per day of brine from the playa. There were 22 ponds covering 1620 ha (4000 acre), subdivided into about 30 sections. The well construction was a variation of typical water wells, and both submersible and turbine pumps were used. The salt was only periodically removed (Fig. 1.51) from 61 ha (150 acre) of the smaller ponds as they became too full, and the dikes were raised on the larger ponds instead of removing the salt. The final ponds were plastic-lined (Fig. 1.48) to improve the pond efficiency, since the initial earthen ponds suffered considerable leakage. The entire evaporation process took 16–24 months time, compared to 12–18 months in 1966–1970 (Dillard and McClean, 1991). By 1993 the piping had been changed to PVC, and in 2001 the initial brine averaged 160 ppm Li, the final brine 6000 ppm Li, and there were 16 km<sup>2</sup> of solar ponds (Kunasz, 1994).



Figure 1.51 Hauling salt from Clayton Valley solar ponds with a scraper-carrier (Dillard and McClean, 1991, courtesy of Rocky Mountain PAY DIRT).

From the final pond the concentrated brine (Table 1.3) with a density of about 1.25 g/cc was pumped nearly 4.8 km (3 mi; 1.5 mi in 1967, Gadsby, 1967) to the processing plant in the town of Silver Peak. The plant had been converted from a silver ore cyanide-leach plant that had operated there from 1864-1961. In the conversion all of the tanks and settlers were rubber lined to reduce iron contamination in the product, and considerable new equipment was added. The solar pond brine was first reacted with lime to remove most of the residual magnesium and some of the sulfate and borate ions, and then a small amount of soda ash was added to precipitate most of the calcium from the lime reactions. The slurry from these operations was settled and filtered, and the overflow solution sent to storage tanks. From there the brine was pumped through filter presses to be totally clarified, and then heated to 93°C (200°F; lithium carbonate has an inverse solubility) and reacted with dry soda ash and hot wash and make-up waters to precipitate the lithium carbonate product. Extra water was added to prevent salt from crystallizing, since the pond brine was saturated with salt. The lithium carbonate slurry was thickened in a bank of cyclones, and the underflow fed to a vacuum belt filter where it was washed and dewatered. The cyclone overflow and filtrate were returned to the solar ponds, since they still contained at least half of the feed brine's lithium.

The filter cake was sent to a stainless steel rotary steam-tube drier, and the  $\sim 99\%$  pure product was then air-conveyed to a storage bin. The product was considered a "commercial" grade since it still contained about 400 ppm B, and its major impurities were sulfate, sodium and potassium, with lesser amounts of calcium, magnesium and moisture. These impurities made it unsuitable for metal production or other demanding uses (Brown and Beckerman, 1990). From Silver Peak it was shipped by truck 89 km to the rail station at Mina, Nevada in either bulk or bags as a white, granular, free-flowing product. In 1970 plans were being considered to ship some of the product in a pellet form for the aluminum industry. Part of the lithium carbonate was also converted into lithium hydroxide at the plant (Anon., 1970; Gadsby, 1967).

Foote hired contractors (Target Construction Co. in 1991) for the maintenance of the solar pond's dikes and the 320 km (200 mi) road system. For this work Target used four 12 yard dump trucks, five 30 yard bottom dumps, a 6 yard loader, and employed nine people. In 1991 Foote employed 62 workers with a payroll of about \$2 million and combined taxes of about \$1 million (Kunasz, 1994; Dillard and McClean, 1991; O'Neill *et al.*, 1969). In 1981 their capacity was 8000 mt/yr, and in 1997, 5700 mt of lithium carbonate were produced from the deposit. The output from the plant was shipped to Germany or their conversion plants in Pennsylvania, Tennessee and Virginia (USGS, 1997; Lloyd, 1981).

### Salar de Atacama, Chile

Two of the world's four commercial lithium brine recovery operations are located on the Salar de Atacama (Fig. 1.52). The mineral rights to the Salar are owned by the Chilean government, and in the late 1970s to mid-1980s their development agency, Corporacion de Fomento de la Produccion (CORFO) and their contractor, Saline Processors of the USA conducted exhaustive tests on the Salar to explore its mineral reserves and to develop economic methods of recovering the minerals. A brine sampling and drilling program initially established the halite's porosity and permeability, and then the area, depth and composition of the Salar's brine. This allowed isopach maps to be made of each of the important ions in the brine, as shown in Fig. 1.10 for lithium, potassium and sulfate. There is a considerable shifting in the ratios and concentrations of these ions, as well as boron and magnesium, within different areas of the Salar. Detailed meteorological data was gathered, including solar evaporation rates for different concentrations of brines to establish solar pond sizing. Typical evaporation rates for the brine as it concentrates are listed in Table 1.28. The average evaporation rate of water was about 3000-3300 mm/yr, the rainfall about 10-25 mm/yr, the average relative humidity about 10%, and there was frequently a moderate wind. Temperatures ranged from a minimum of  $-20^{\circ}$ C in June to  $9-28^{\circ}$ C in January, but because of the low humidity and the wind there was excellent evaporation capability even in the


**Figure 1.52** Map of Northern Chile showing the location of the Salars de Atacama and Carmen (Harben and Edwards, 1997; this figure appeared in Industrial Minerals No. 353, February 1997, p. 29. Published by Industrial Minerals Information, a division of Metal Bulletin plc, UK. ©Metal Bulletin plc 2003).

### 110 Part 1 Lithium

	Original brine <sup>a</sup>			To sylvinite pond			To sulfate pond			From carnallite pond
Cl	192.0			205			195			292
$SO_4$	23.3			45			88			23
$H_3BO_3(B)$	4.4 (0.77)			9.2 (1.61)			18 (3.15)			50 (8.74)
Na	93.2			72.0			40			4.0
Mg	12.3			23.7			46			92
ĸ	22.0			46.8			37			4.0
Li	1.96			3.66			7.07			8.9
H <sub>2</sub> O	873			856			860			867
Density	1.227			1.258			1.284			1.323
Evaporation		Summer	Winter		Summer	Winter		Summer	Winter	
Rate (mm/day)		8.0	4.0		7.3	3.7		5.7	3.0	
Salts cryst.		Halite			Sylvinite			Sulfates, Carnallite		

#### Table 1.28

Typical Brine Analysis in the Salar de Atacama Experimental Solar Ponds (g/liter) (Garrett, 1998)

<sup>a</sup> Also containing, as wt.%: Ca 0.03, NO<sub>3</sub> 0.012, CO<sub>3</sub> 0.003, I trace; KM-20 brine.

winter with such normally hygroscopic salts as bischoffite. The periphery of the Salar was also examined for impervious clay that could be used to locate and construct inexpensive solar ponds. Only two areas were found that were adequate in size and impermeability, but the southwestern area had the unusual feature of frequent tunnels as might be formed by small rodents or moderately sized roots that had totally decayed. However, the mid-salar area appeared to have reasonably uniform and impermeable clay (Fig. 1.53). Finally, laboratory and solar pond studies were made to determine the phase chemistry of the different brine types upon being evaporated (Crozier, 1986; CORFO, 1985; Saline, 1985).

These studies allowed CORFO to establish the most economical processes for the production of each of the potential products from the Salar's brine: lithium carbonate, lithium chloride, lithium sulfate, potassium chloride, potassium sulfate, boric acid, magnesium chloride and magnesium sulfate. In most of the experimental studies brine was taken from the location Km-20 (Fig. 1.53), which contained somewhat of an average of the Salar's brine composition. When solar evaporated in the summer a sequence of salts crystallized as the brine concentrated (Table 1.28), initially being salt (halite, NaCl); then halite and sylvite (KCl that forms a mixture with the NaCl called sylvinite); then halite, sylvite and potassium lithium sulfate (KLiSO<sub>4</sub>); then halite, kainite (KCl·MgSO<sub>4</sub>·2.75H<sub>2</sub>O) and lithium sulfate (Li<sub>2</sub>SO<sub>4</sub>·-H<sub>2</sub>O); then halite, carnallite (KCl·MgCl<sub>2</sub>·6H<sub>2</sub>O) and lithium sulfate; then primarily bischoffite (MgCl<sub>2</sub>·6H<sub>2</sub>O), and finally primarily bischoffite and lithium carnallite (LiCl·MgCl<sub>2</sub>·7H<sub>2</sub>O; Vergara-Edwards and Parada-Frederick, 1983).



**Figure 1.53** Location of the Chemetall Salar de Atacama Lithium and Potash Leases and Buffer Zone (Coad, 1984). (This figure appeared in Industrial Minerals No. 205, October 1984, p. 28. Published by Industrial Minerals Information, a division of Metal Bulletin plc, UK. ©Metal Bulletin plc 2003.)

## 112 Part 1 Lithium

Because of the unusually low humidity and the prevailing winds at the Salar the brine can be evaporated to precipitate all of these compounds, in contrast to most places in the world where carnallite would be the final salt crystallized in the solar ponds. With the above-noted salts deposited in separate solar ponds the harvests could be halite, then sylvinite to produce potash (KCl, using a flotation separation from halite), then carnallite to produce coarse potash (Garrett, 1975), and then the potassium, lithium and sulfate salts could be harvested together. They could be converted to lithium and potassium schoenite (K<sub>2</sub>SO<sub>4</sub>·MgSO<sub>4</sub>·6H<sub>2</sub>O), these salts removed from the halite by flotation, and then the schoenites converted into potassium sulfate. The lithium salts would dissolve in the schoenite conversion liquor and be sent back to the ponds to join the end-liquor from the potash and lithium salts pond. This process is in commercial operation on the Great Salt Lake (but without the lithium salts; Garrett, 1970, 1967), and its equal viability with mixed potassium-lithium salts was demonstrated by CORFO. Later the same separation and conversion with salts quite similar to those formed at the Salar de Atacama has been conducted in China and at the Salar de Uyuni (Ramos and Kirigin, 2000). All of the brine's lithium and boron could then be simply recovered from this end-liquor (Vergara-Edwards et al., 1985, 1983; Garrett, 1985; Pavlovic-Zuvic et al., 1983; Garrett and Laborde, 1983).

# Salar de Atacama, Chile; Chemetall

The company Sociedad Chilena del Litio (SCL) was formed in 1982 as a 55% Foote Mineral (now Chemetall) joint venture with the Chilean government agency CORFO to produce lithium and potash from the Salar de Atacama. They received a 30 year concession from CORFO that would be renewable for 5 year periods until 200,000 mt of lithium equivalent had been produced, which might take 40-45 years. The concession covered 16,720 ha (41,315 acre), with a 6850 ha strip of land adjacent to the concession guaranteed not to be leased to any one else (Fig. 1.53). They would also have an exclusive right to recover lithium from the Salar for 10 years. SCL then constructed a solar pond system and lithium carbonate plant costing \$56 million, and with 14 million lb/yr (6350 mt/yr) of lithium carbonate equivalent (LCE) capacity. The pond location at the Salar de Atacama was called Chepica del Salar, and the concentrated brine from the ponds was shipped to a lithium carbonate (Li<sub>2</sub>CO<sub>3</sub>) plant on the Salar de Carmen near Antofagasta and the small town of La Negra. Production started in 1984, and in 1986 Foote purchased CORFO's share of the operation. The original plant capacity was soon raised to 24 million lb/yr of LCE, and in the early 1990s potash also began to be recovered as a by-product from the sylvinite harvested from their solar ponds. By 1991 they shipped 11,800 mt of lithium carbonate, and in 1995 they were exporting 28 million pounds of LCE, and selling their byproduct potash to SQM's large Chilean potassium nitrate operation.

The process that Sociedad Chilena de Litio Ltd. uses is presumably similar to that used by Foote at Clayton Valley, except that the brine initially had about

a 1500-1900 ppm Li content and a much higher magnesium to lithium ratio (Tables 1.5, 1.6 and 1.28). Foote located their brine wells in a position on the lake where the sulfate content was comparatively low (see Figs. 1.10 and 1.53), and yet there was still a high lithium concentration. Based upon their initial announcements they then planned to precipitate most of the sulfate and part of the borate from the brine leaving the halite ponds with calcium chloride (Anon., 1984a,b). The resulting low-sulfate brine would produce a larger crop of sylvinite, followed by halite-carnallite and then halite-bischoffite to remove most of the magnesium. As the evaporation proceeded to about 4% Li, there would finally be a period when bischoffite and lithium carnallite crystallized together. To obtain the highest yields this mixture could be leached to dissolve the lithium and leave most of the bischoffite, with the leach-brine recycled to the bischoffite ponds. The mixture could also be harvested and sold, or discarded as desired. In any case the final brine from the ponds would contain up to 6% Li and be a nearly saturated lithium chloride solution. It would have a comparatively low magnesium, sodium, potassium and sulfate content. As far as is known, the Salar de Atacama, a few other Andean salars and the Tibetan region of China are the only places in the world where the humidity is low enough to allow bischoffite and lithium salts to be crystallized in solar ponds on a commercial scale.

At the Foote operation the initial solar pond system had an area of 89 ha (220 acre; 100 ha, Coad, 1984), but was soon expanded to 130 ha (320 acre). In 1993 there were  $1.5 \text{ km}^2$  (150 ha; 371 acre) of solar ponds (Fig. 1.54; Deberitz, 1993). Initially there were nine ponds varying in size from 2.2–14 ha, with three of the ponds divided into two parts to make a total of 12 sections. The ponds were constructed on a flattened and smoothed area of the Salar's salt surface, and lined with 0.5 mm (20 mil) PVC plastic sheet. The lining was made from 1.5 m wide strips that weighed about 1 t, and they were sealed together in the ponds. This required 61 km (38 mil) of carefully-made seams that then had to be both manually, and later when the ponds contained ~20 cm of brine, electrically examined for leaks. Initially the brine in the ponds was maintained at a 25–40 cm depth, and the brine flowed by gravity or was pumped from pond to pond. After the final pond the brine was pumped to a 0.7 ha deep storage reservoir with a floating cover to prevent further evaporation (Anon., 1984a).

Their area's evaporation rate was 1270-1780 mm (50-70 in.)/yr, and the rainfall very little most years (10-30 mm), but on rare occasions there were heavy storms. The solar radiation in the area was  $6.3 \times 10^6 \text{cal/m}^2/\text{day}$ , the relative humidity as low as 5%, and moderately intense winds arose in the afternoons. Brine was initially pumped at 1000 gpm from three wells that were 30 m (100 ft) deep to fill the ponds to an average 38 cm depth (Anon., 1984a). After the halite ponds the brine was mixed with calcium chloride and end-liquor from the processing plant to precipitate gypsum and some of the boron, with the precipitate being washed to recover some of the entrained liquor's lithium content. The salt was harvested from the halite ponds once per year and placed in stockpiles, while



**Figure 1.54** Chemetall solar ponds at the Salar de Atacama (Deberitz, 1993, courtesy of Chemetall GmbH).

the salts from the sylvinite ponds were harvested more frequently and processed in a plant on the Salar to produce potassium chloride. The plant at Chepica (at the southeastern end of the Salar de Atacama) employed 51 people, 32 of whom came from the nearby village of Peine, where all of the employees lived. They worked on an 11-day schedule, with 4 days off, allowing them time to travel by road or light plane to the larger towns of Antofagasta or Calama (450 km away), if they desired. The plant maintained a modern quality control laboratory (Coad, 1984; Anon., 1984a).

The pond's final brine (Table 1.5) was removed from the holding pond at a concentration of 4.3-6% Li, trucked about 80 km (90 km, Coad, 1984) south to a new railroad station at Pan de Azucar (Fig. 1.6; initially at a rate of 100 m<sup>3</sup>/day), and then shipped by rail cars about 170 km further to La Negra (a small town south of Antofagasta on the Salar de Carmen and the Pan American highway) for final processing (Fig. 1.55; Kunasz, 1994; Crozier, 1986; Anon., 1984a). The process employed in the plant at La Negra has not been described, but is thought to follow



**Figure 1.55** Aerial view of the Chemetall Lithium Carbonate Plant at La Negra (near Antafagasta Chile, courtesy of Chemetall GmbH).

the steps of the Clayton Valley operation and one of their patents. The large amount of boron (~8000 ppm) in the brine must be removed to avoid serious contamination of the product, and this can be easily done by solvent extraction. In an acidic brine all long-chain alcohols in an insoluble solvent can extract boron fairly selectively with a moderate extraction coefficient, and with all brines (including very basic ones) multi-carbon diols have a more selective and much higher extraction coefficient (Garrett, 1961, 1963). Foote's boron-removal patent follows the patent of Folkestad et al. (1974) (removing boron from strong MgCl<sub>2</sub> solutions) and suggests using a simple 7–12 carbon alcohol such as iso-octanol or 2-ethyl hexanol in about a 20% mixture with kerosene. The brine is first brought to a pH of 2 with hydrochloric acid, and then contacted with a ratio of about four volumes of the solvent to one part of brine. Under these conditions the solvent has an extraction coefficient ranging from 6-14, so when mixed with the brine and settled in four stages of counter current contact the residual brine should contain less than 5 ppm of boron (Table 1.29; but also suffer a 5-10% lithium loss in the solvent). The loaded solvent can then be stripped of its boron and lithium content with water or dilute caustic in several other mixer-settler stages, and be ready for reuse (Brown and Beckerman, 1990). The amount of solvent loss was not mentioned in the patent, but with strong magnesium chloride solutions Folkestad et al., (1974) estimated that the stripped

#### Table 1.29

Brine and Product Analyses of a Boron Extracti	ion Process with	n Lithium Chloride	Crystallization (Brown
and Be	eckerman, 1990	))	

Chemical species	Brine	Brine after B removal	Chemical species	With B removal evap. crystallized, 90% recovery <sup>a</sup>
Li	6.30	6.03	LiCl (dry basis)	99.2%
Na	0.077	0.073	Na	0.17
К	0.019	0.018	К	0.0015
Mg	1.29	1.29	Mg	0.075
Ca	0.053	0.051	Ca	0.004
В	0.73	0.0001	В	< 0.0001
$SO_4$	0.016	0.019	$SO_4$	0.004
Cl	5.86	34.46	Cl	82.9
			H <sub>2</sub> O	0.4

Boron extraction with four parts of 20% isooctanol in kerosene to one part of brine, and four mixersettler stages.

<sup>a</sup> 90% of the lithium chloride input is recovered.

brine would contain at least 200 ppm of solvent, and the boron eluting solution 2000 ppm of solvent.

The purified brine might then be treated as at Clayton Valley, with lime to precipitate most of the magnesium and sulfate, followed by a reaction with a small amount of soda ash to precipitate the remaining magnesium and calcium. After the precipitates were removed by settling and filtration the brine could be heated and lithium carbonate formed by the reaction with soda ash. When thoroughly washed and dried this would form an excellent product for most uses. Alternately, however, to form lithium chloride directly, or for higher purity lithium carbonate, the brine following the lime, minor soda ash additions and filtration steps could be evaporated at about 110°C to crystallize lithium chloride. Some of the slurry would be continuously removed, thickened, filtered, the solids washed at 130°C, and the lithium chloride dried at 170°C. The high-lithium filtrate and wash water could be returned to the solar ponds. This should produce a 99.2% LiCl product (Table 1.29). To produce a 99.9% lithium chloride product the previous crystals could be dissolved and re-crystallized, or further washed with, or dissolved in isopropanol and then recrystallized. Also, the lithium chloride could be dissolved and reacted with soda ash to precipitate a high-purity lithium carbonate. The plant at La Negra initially employed 63 people, and Foote's lithium carbonate was either sold directly, or some of it compacted into granules (Anon., 1984a). In 1998 lithium chloride production was also initiated using lithium carbonate as the raw material (Crozier, 1986; Coad, 1984). If it is assumed that sulfate is still precipitated from the brine, the general flowsheet shown in Fig. 1.56 should roughly illustrate the Chemetall process.



Figure 1.56 A general flowsheet for obtaining lithium carbonate from Salar de Atacama brine (Wilkomirsky, 1998).

### 118 Part 1 Lithium

### Salar de Atacama, Chile; SQM S.A (Formerly SQM Chemicals or Minsal)

In 1986 CORFO formed a consortium called Minsal where they had a 25% ownership, Amax Exploration had a 63.75% participation, and Molymet 11.25%. The objective was to establish a multi-product operation on the Salar, and they were granted mineral rights on 1586 km<sup>2</sup> of the Salar, with water rights to 240 liter/sec. The central 820 km<sup>2</sup> of the concession to a depth of 40 m was estimated to contain 26 million mt of K, 1.7-1.8 million mt of Li (or 20 billion pounds of LCE), 22 million mt of sulfate, and 0.7 million mt of boron. Amax initiated additional drilling and a new feasibility study, but in 1992 sold their interest in the venture to SQM, as did Molymet in 1993. SQM had been a purchaser of considerable potassium chloride to be converted into potassium nitrate at their large nitrate operations fairly close to the Salar (at Maria Elena, Cova Sur and Pedro de Valdivia; Fig. 1.6), making it the product of their greatest initial interest. They planned to add lithium, potassium sulfate and boric acid later in a sequence of expansions using the end-liquor from the potash ponds as the feed material for the lithium, and new brine for the other products (Table 1.30). In 1995 SQM purchased CORFO's then 18% interest in the venture for \$7 million, becoming the sole owner of the company, and their 300,000 mt/yr, \$55 million potash plant started production. In December, 1996 lithium carbonate also began to be produced as a by-product in a 40 million lb/yr LCE, \$51 million pond system and plant.

SOM, as Foote, initially selected a brine extraction location for its well field where the brine had the maximum potassium and the least sulfate for potash and lithium production, and later a location with the maximum sulfate content for potassium sulfate production (Fig. 1.57). Because of this the plants could initially use the simplest processes and have the lowest capital and operating costs. In the initial operation brine with up to 3400 ppm Li was pumped from the Salar in 40 wells, 28 m deep on a 200–500 m grid, which delivered up to 5280 m<sup>3</sup>/hr of brine to the solar ponds. There were also 13 monitoring wells to follow any changes in the brine concentration and its depth from the surface. The ponds were lined with flexible PVC or reinforced hypalon membranes, and the brine flowed through the sections of the pond system in series. The initial salt ponds had an area of 1.16 million  $m^2$ , followed by 3.36 million  $m^2$  for the sylvinite ponds, and later 1 million  $m^2$  of ponds were installed for lithium production. The plant employed 184 people, of which 120 were hired from the sparsely populated local area. Contractors were used to drill and maintain the wells, harvest the salts, transport them to their respective stockpiles, and reclaim the sylvinite to feed the potash plant's conveyor belt. They also provided all of the miscellaneous trucking needed at the Salar, and transported the potash to Coya Sur or Maria Elena and the concentrated lithium chloride brine to the Salar de Carmen. SQM unloaded the brine and potash, and stacked the later material at its nitrate plants (Harben and Edwards, 1997).

In the solar ponds (Fig. 1.58) salt (halite) crystallized immediately as the brine evaporated, and with the low-sulfate brine utilized by SQM, much of the potassium

	Capacity (mt of product)	Capital expenditure (\$MM, US)	Start-up date
Stage 1			
Potash	300,000	55	October 1995
Stage 2			
Lithium carbonate	18,000	51	December 1997
Stage 3			
Potassium sulphate	250,000	150	January 1998
Boric acid	20,000		
Total investment		\$256	

Table 1.30

Initial Schedule for SQM's Salar de Atacama Plant Construction (Harben and Edwards, 1997)

This table appeared in Industrial Minerals No. 353, February 1997, p. 35. Published by Industrial Minerals Information, a division of Metal Bulletin plc, UK. ©Metal Bulletin plc 2003.



Figure 1.57 Location of the various pond and plant operations on the Salar de Atacama (SQM, 2001, courtesy of SQM SA).



Figure 1.58 Aerial view of SQM's potash-lithium solar ponds at the Salar de Atacama (SQM, 2001, courtesy of SQM SA).

then crystallized as sylvinite. In the initial operations when the ponds were adequately full of salt or sylvinite crystals they were drained for about 1 week, the crystal mass broken and windrowed to drain for 4 weeks, the crystals then loaded and carried to the stockpiles for 4 weeks, and 1 week was spent smoothing the pond floor and re-flooding it to commence another cycle. A permanent 30 cm thick floor of crystals was maintained in the ponds to protect the membrane during harvesting, and the thickness of the deposited crystals was built-up to a minimum of 35 cm before being removed. During harvesting (Fig. 1.59) the crystal bed was first lifted from the floor and broken by Caterpillar or Rahco modified pavement-breakers



Figure 1.59 Harvesting salts at SQM's solar ponds on the Salar de Atacama (SQM, 2001, courtesy of SQM SA).

controlled by lasers to cut the harvested crystals exactly to the permanent crystal floor. An average pond produced 35,000 m<sup>3</sup> ( $\sim$  35,000 mt) with each harvest, using ten 20 mt trucks, two bulldozers and seven 3 m<sup>3</sup> front-end loaders (Harben and Edwards, 1997).

The harvested salt was sent to large storage piles (Fig. 1.60), or some could also be used to reinforce the solar ponds' walls or make internal baffles in the ponds to better control the brine flow. The sylvinite was taken to the potash plant (Fig. 1.61) and crushed and ground to its sylvite liberation size (about 6 mm), and then the potassium chloride was separated from the mixture in froth flotation cells. The potash was next thickened, centrifuged, washed and trucked about 250 km to their potassium nitrate plants as a  $\sim 95\%$  KCl (on a dry basis) slightly moist product. The salt from the flotation cells was also centrifuged, washed and sent to disposal stockpiles, while a bleed stream from the flotation brine was returned to the sylvinite solar ponds. The brine leaving the sylvinite ponds contained about 1% Li, and was sent to the lithium ponds to be concentrated to about 6% Li (38% LiCl, or essentially LiCl's saturation point), 1.8% Mg and 0.8% B. A portion of this brine to produce the desired amount of lithium carbonate was trucked 250 km to near Antofagasta at the Salar de Carmen, and the remainder allowed to seep into the Salar for potential future use (Harben and Edwards, 1997). A very brief outline of the Salar operations is given in Fig. 1.62.



Figure 1.60 One of SQM's salt (halite) solar ponds, with a salt disposal pile in the background (courtesy of SQM SA).



**Figure 1.61** SQM's potassium chloride plant at the Salar de Atacama, with a solar pond in the foreground (SQM, 2002, courtesy of SQM SA).



**Figure 1.62** General flow sheet of SQM's Salar de Atacama process (Harben and Edwards, 1998). Figure published in the Forum on the Geology of Industrial Minerals. Reprinted with permission of the Canadian Institute of Mining, Metallurgy and Petroleum.

In 2002 the brine was delivered from 92 wells that were equipped with submersible pumps powered by diesel or electric motors. All of the wells were 40 m deep, with perforated casings and no gravel-pack because of the structural strength of the halite. Their pumping rate varied considerably because of the differences in salt porosity, and the wells' useful life depended upon how rapidly the brine composition changed to an undesirable composition. There were 17 pond strings on the Salar, with 3 for lithium production, and 14 for the potash and potassium sulfate–boric acid plants. The total pond area was 15 million m<sup>2</sup> (1500 ha or 3710 acre), including 150 ha for the lithium ponds, and all of the ponds were lined with plastic membranes. Brine averaging 1500-2000 ppm Li and 1.85% K was gathered from wells along an 8 km canal (Fig. 1.63) for the potash–lithium ponds, and was then pumped from the canal to the halite ponds (Fig. 1.58). These ponds had an average size of 120,000 m<sup>2</sup>, and crystallized about 2 million tons of salt per year. The salt was periodically harvested and disposed of in nearby piles that were limited to a 10 m height (Fig. 1.60).

When the brine in the halite ponds became saturated with potassium chloride it was pumped to  $\sim 100,000 \text{ m}^2$  sylvinite ponds where it was joined by brine from a few wells that were already saturated with potash. The sylvinite ponds were also periodically taken out of service, drained and harvested, and their salts sent to the potash plant storage–drainage piles (Fig. 1.61). In 2002 the total of the potash plant's capacity was 650,000 mt/yr, and the KCl was hauled to Coya Sur in covered



Figure 1.63 The brine canal for SQM's potash-lithium solar ponds (courtesy of SQM SA).

dump trucks to be converted to potassium nitrate (also with a plant capacity of 650,000 mt/yr).

Brine from the sylvinite ponds next went to the carnallite ponds (Fig. 1.64), and from there to the 500,000 m<sup>2</sup> bischoffite ponds (Fig. 1.65). These two series of lithium ponds were also periodically taken out of service to harvest predominantly carnallite from the first ponds, and bischoffite from the later ponds. These minerals were stockpiled separately, with some of the bischoffite sold as magnesium chloride (with a capacity of 450,000 mt/yr), and the carnallite saved for later conversion to potash. The six carnallite ponds were divided into two groups of three, with the higher sulfate brine directed to one group, and then its end-liquor was returned to the Salar by being flooded onto its porous surface. The final brine from the bischoffite ponds contained 6.0-6.1% Li, and was sent to 40,000 m<sup>2</sup>, about 3 m deep holding ponds to await truck shipment to the lithium carbonate plant. The plant had a capacity of 22,000 mt/yr of Li<sub>2</sub>CO<sub>3</sub> in 2002, to be raised to 28,000 mt/yr in 2003 (Moura, 2002; Etchart, 2002; Nakousi, 2003).

The potassium sulfate and boric acid plants (Fig. 1.66; with capacities of 250,000 and 16,000 mt/yr, respectively) started production in 1998 using a separate brine supply and solar evaporation system. After the brine had left the initial halite ponds all of the potassium and sulfate salts were allowed to crystallize and be harvested together from one set of ponds. In 2002 the first processing step was to leach its halite content, and then convert the residue to schoenite with return liquor from



**Figure 1.64** One of SQM's carnallite solar ponds with a typical mild wind-rippled surface (courtesy of SQM SA).



Figure 1.65 Bischoffite draining prior to harvesting from one of the final lithium solar ponds (courtesy of SQM SA).

the potassium sulfate crystallizers. The schoenite was next reacted with potash and converted to potassium sulfate (Fig. 1.67; Ramirez, 2002). In other potassium sulfate plants the harvested salts are first converted to fairly large crystals of schoenite, and the halite then removed by flotation. The harvest salts could also be initially floated



Figure 1.66 SQM's potassium sulfate plant at the Salar de Atacama (SQM, 2002, courtesy of SQM SA).



**Figure 1.67** A general flowsheet for the production of potassium sulfate and boric acid at the Salar de Atacama (Harben and Edwards, 1997; this figure appeared in Industrial Minerals No. 353, February 1997, p. 31; published by Industrial Minerals Information, a division of Metal Bulletin plc, UK. ©Metal Bulletin plc 2003).

to remove the halite, but the liberation size of most of the potassium sulfate compounds from solar ponds is very small, and the yields are poor. The final brine from the sulfate ponds is acidified with sulfuric acid to crystallize ("salt-out") boric acid. Lithium sulfate and magnesium sulfate could also be readily recovered from the boric acid end-liquor if desired (CORFO, 1985).

A flowsheet for the Salar de Carmen (Antofagasta) lithium carbonate plant in 2002 is shown in Fig. 1.68. Brine is first unloaded from tank trucks bringing it from the Salar de Atacama, and sent to storage tanks. It is a sparkling clear, bright yellow color with a boron content of about 8000 ppm B. The boron was first removed from the brine to a 2 ppm B level by contacting it in four stages with an alcohol–kerosene mixture in a liquid–liquid extraction plant. After extraction the brine was colorless, indicating that the color may have been from a metal or organic borate, since alkali borates are colorless. The boron was removed from the solvent in stripping cells with a dilute sodium hydroxide solution, and this sodium borate–lithium chloride solution was returned to the Salar. Pictures of the plant are shown in Figs. 1.69 and 1.70.

A Chilean laboratory study by Orrego *et al.* (1994) (based upon the Folkestad *et al.*, 1974 patent), had suggested using iso-octanol as the boron solvent in a 50 vol% mixture with kerosene. In their study the solvent contacted the acidified brine ( $\sim 0.1 \text{ N H}^+$ ) in a one-to-one (by volume) ratio in four countercurrent liquid–liquid extraction stages to reduce the boron in the brine to less than 5 ppm B (Table 1.31). The solvent could then be regenerated by three stages of water wash or with a 0.02 N NaOH solution. The aqueous wash would contain a significant amount of boron (the equivalent amount at SQM in 2002 would be 3500 mt/yr H<sub>3</sub>BO<sub>3</sub>), and



Figure 1.68 Flowsheet for SQM'S lithium carbonate plant at the Salar de Carmen (SQM, 2002, courtesy of SQM SA).



**Figure 1.69** SQM's lithium carbonate plant at the Salar de Carmen. View from Office to the east, Laboratory on left; Warehouse in middle right; Plant in middle left (courtesy of SQM SA).



**Figure 1.70** Second view of SQM's lithium carbonate plant. Processing building to the right; boron extraction to the left (courtesy of SQM SA).

### Table 1.31

Isotherms at 25°C for Boron Extraction from Salar de Atacama Brine, and Re-extraction in Water (Orrego *et al.*, 1994)

Isoterma de	e Extracción	Isoterma de Reextracción			
[Boro] <sub>ac</sub> (g/liter)	[Boro] <sub>org</sub> (g/liter)	[Boro] <sub>ac</sub> (g/liter)	[Boro] <sub>org</sub> (g/liter)		
6.70	11.46	64.40	2.04		
6.21	11.46	49.05	1.43		
5.56	11.46	29.49	1.41		
4.07	11.35	19.84	1.32		
2.50	10.70	9.82	1.20		
0.58	7.27	5.24	0.77		
0.063	3.89	3.58	0.51		
0.040	2.60	2.19	0.31		
0.031	1.56	1.57	0.23		
0.026	1.12				
0.003	0.78				

Boron extraction with one part of 50% isooctanol in kerosene to one part of brine, and re-extraction with six parts of solvent to one part of water. Reprinted courtesy of Nucleotecnica.

could be returned to the Salar's boric acid plant. Figure 1.71 shows the rapidity of the extraction, and indicates the high lithium loss (in these tests  $\sim 10\%$ ) with the boron based upon the brine's greatly reduced density and viscosity.

After boron extraction the brine was next sent to the "Chemical Area" building where it was first reacted with a fraction of the stoichiometric amount of soda ash needed to precipitate all of the magnesium. The resultant magnesium carbonate was then filtered on two large rotary drum vacuum filters with a traveling cloth filter-and-discharge membrane. The brine was next reacted with lime to remove the rest of the magnesium and much of its sulfate content. This magnesium hydroxide–calcium sulfate precipitate was then filtered in a bank of plate and frame filter presses. The filter cake from both precipitations was next repulped and sent to two solid bowl centrifuges. Their discharge cake contained from 30 to 40% moisture, and was hauled by truck to a local dump. The filtrates from each of the dewatering devices were returned to the brine stream. The purified lithium carbonate product. It was filtered on a belt filter, and washed first with wash water and then with fresh water. The filtrate still contained about 1% Li, so it was recycled to the feed brine to the extent that water and salts had been removed from the system.

The lithium carbonate filter cake was next dried in a direct fired rotary dryer with a multiple cyclone dust collector. The 99.3-99.4% Li<sub>2</sub>CO<sub>3</sub> product then went to a three-tray screen, the oversize was ground and returned to the screen, the middle size became a product grade, and the fines were sent to a compactor to form a  $\sim 20$  mm thick briquette. These granules were ground and fed to a screen to form the desired product sizes, and some of the product was further ground to form a very fine powder. In 2002 they had 18 product grades of different particle size and sulfate content. The products were shipped in 0.5 and 1 t bulk bags; 25 kg, 25 and 50 lb bags; or in plastic lined 100 kg fiber drums. The plant operated on a three shift, 7 days/week basis, had a semi-automatic control system and an analytical laboratory to insure the product quality and assist in the plant operation. There were automatic sprinklers over the liquid extraction mixer-settlers in case of fire, and any off-spec or spilled product was re-dissolved and added to the incoming brine. Only a nominal amount of pilot plant testing had been needed for the plant design and construction, and the start-up operation went very smoothly (Nakousi, 2003; Arqueros, 2002; SQM, 2002; Harben and Edwards, 1998).

The initial offering price that SQM posted for its lithium carbonate was \$0.90/lb, or about half of the then-existing market price. This reduced price considerably stimulated the market for lithium carbonate (sometimes at the expense of lithium ore concentrates), and caused high-cost producers to close their plants. This, in turn, has allowed the price to again slowly rise, but stay below that of higher-cost producers. The SQM plant's nominal capacity was 40 million lb/yr of lithium carbonate in 1998, and they sold 15.4 million pounds. They expected to sell 28.6 million in 1999 and then run at near-capacity of 22,000 mt/yr of lithium carbonate (Schmitt, 1998). In 1999 SQM began selling lithium hydroxide, and later



**Figure 1.71** The rate of extraction and solvent washing, and the density and viscosity of strong lithium chloride brine before and after boron extraction (Orrego *et al.*, 1994; reprinted courtesy of Nucleotecnica).

lithium chloride. In 2002 they were considering installing a butyl lithium plant in Texas (SQM, 2001; USGS, 2000).

### Salar de Hombre Muerto, Argentina; FMC

Production of lithium carbonate and chloride started at the Salar de Hombre Muerto in 1997 utilizing a new process developed by FMC. Although details of the process have not been disclosed, several of their recent patents are based upon selective lithium adsorption onto alumina. In the early stage of their development work 17 wells were drilled in the Salar's central salt mass, from which 678 m of core were obtained to determine the salt's porosity. Brine samples were taken at various depths, and the reserves of the deposit were estimated (Anon., 1984b). Considerable experimental work was then conducted in the laboratory, pilot plants and on the Salar. An extensive infrastructure was next constructed for this remote, high altitude location, and eventually a multiple-well brine-gathering system was installed on the Salar.

In their process patents and announcements the brine to be utilized was assumed to be saturated with NaCl and contain about 600 ppm lithium. In the alumina patents brine would be sent in counter-flow through a series of columns packed with polycrystalline hydrated alumina. The flow rate and number of columns would be adjusted so that the lithium would be almost completely (and fairly selectively) adsorbed from the brine leaving the last (freshest) column. It would then be discharged from the plant and returned to an area of the Salar far from the inlet wells. After the alumina in the first (or oldest) column was nearly saturated with lithium it would be removed from brine flow circuit, and the lithium mostly removed from the alumina (eluted) by a water wash. The resultant solution would contain up to 1% lithium, and could then be concentrated in solar ponds (Fig. 1.72) to the desired concentration for further purification and/or processing. The eluted column would next be given a saturated sodium chloride wash (perhaps containing some lithium) to recover the entrained lithium and to raise the ionic concentration in the alumina.



**Figure 1.72** Solar ponds at the Salar de Hombre Muerto (Chem. Week, 1995 and 1998; reprinted with permission from Chemical Week, November 22, 1995, Chemical Week Associates; reprinted with permission from Chemical Week, December 2, 1998, Chemical Week Associates).

It would then be returned to the brine adsorption system as the last column in the lithium recovery process.

In preparing alumina to have a high lithium capacity for the process it would be necessary to initially react the alumina with lithium chloride in a saturated sodium chloride solution. This would form LiCl/Al(OH)<sub>3</sub> crystals in which the lithium chloride was present in amounts up to a 0.2 mol fraction. The alumina has a strong affinity for the lithium in high-ionic solutions, but the adduct is not stable (i.e., the lithium can be eluted) in dilute solutions. The aluminum hydroxide reacts somewhat as if the lithium chloride were a hydrate [Al(OH)<sub>3</sub>·n H<sub>2</sub>O·LiCl] molecule that was stable (could be attached or removed) depending upon the solution's total ionic strength. If the alumina were first treated with lithium hydroxide followed by hydrochloric acid the LiCl in the LiCl/Al(OH)<sub>3</sub> crystal could be increased up to a 0.33 mol fraction. The lithium adsorption–desorption cycle was stated to be repeatable many times before the lithium-treated alumina had to be regenerated or discarded. Eluate concentrations up to 1.1% Li with comparatively small amounts of impurities, and loadings of 3.6 g Li/liter of alumina were claimed in the process patents (Bauman and Burba, 1997, 1995).

It was announced that the commercial process worked very well, reportedly at a 20% cost saving over the conventional solar evaporation-magnesium and sulfate precipitation process. The initial brine strength varied from 0.22 to 1.08 g/liter Li, and averaged 650 ppm Li. The plant had a capacity of 45 million lb/yr of LCE (although it produced fairly pure LiCl directly from the brine), and cost \$68 million. The product distribution as the plant started in late 1997 was 12,000 mt/yr lithium carbonate and 9650 mt/yr lithium chloride. However, in 1999 after SQM had greatly lowered the price of lithium carbonate they partly closed the plant and contracted to purchase lithium carbonate from SQM. They announced that some lithium chloride would still be produced from the Salar, and then purified and perhaps converted to other products at Guemes, Salta province, Argentina (Fig. 1.6; Harben and Edwards, 1998). In 2002, it was reported that this production was 4729 mt LiCl and 906 mt Li<sub>2</sub>CO<sub>3</sub> (944 mt of Li; USGS, 2002).

Some of the favorable conditions for the operation were that the Argentine government had granted complete ownership of the Salar to FMC, the brine had a relatively high lithium content, there was an adequate area for solar ponds, the evaporation rate was quite high, and there was an excellent fresh water supply. However, if they only produced a crude product at the Salar (the lithium chloride brine from the solar ponds) and shipped it to another plant for final processing, the transportation costs would be very high. The trip to the nearest harbor would require first trucking the product a considerable distance ( $\sim 145$  km) over a tortuous unpaved mountain road, loading it into rail cars, and then shipping by rail down the steep west side of the Andes, across the Atacama desert (420 additional km) to Antofagasta. If the product were to go to a plant near Salta, the same mountain road would have to be traveled, and the rail haul would go down the east side of the Andes

to the plant ( $\sim$  395 km). In either case supplies would have to follow the same difficult routes back to the Salar.

## Searles Lake, California; American Potash & Chemical Co

As Searles Lake brine was evaporated in triple-effect evaporators the lithium concentration reached about 140 ppm Li (Table 1.9). During this evaporation process salt (NaCl) was crystallized predominantly as large crystals, burkeite  $(3Na_2SO_4\cdot Na_2CO_3)$  as medium-sized crystals, and dilithium sodium phosphate (called licons; Li<sub>2</sub>NaPO<sub>4</sub>) as very fine crystals. This allowed most of the salt to be removed from the other crystals by hydraulic classification, and the licons (representing about 40% of the feed brine's lithium) to later be removed by froth flotation. The untreated licons contained about 9.3–10.7% Li, and typical yearly production rates were 200 mt in 1938, 522 mt in 1943 and 765 mt in 1976. Originally the licons were sold to the Foote Mineral Co., but starting in 1951 they were converted to lithium carbonate and phosphoric acid at Searles Lake.

Searles Lake brine had a comparatively high organics content (called "humates"), and coconut oil was added as a froth-control agent in the brine evaporators. Much of these organics were adsorbed onto the burkeite and licons as they crystallized, and these fine salts were separated together from most of the salt crystallized in the evaporator, and then filtered and washed. Next this burkeite mixture was given a hot, partial leach, and in a second step the burkeite was totally dissolved. Most of the licons did not dissolve, leaving the remaining licons with a high proportion of the organics. In the early days of the soda products operation these licon solids contaminated the products, caused slurries to foam, they inhibited filtration, and formed a sticky scum on the top of liquid-filled tanks and on metal surfaces. To reduce this problem in 1936 they began to scrape the scum from the surface of various processing vessels, put it in a small tank and on a campaign basis add water and steam, and then filter and dry it to form their first ~ 20% Li product (Table 1.18) in the amount of about 200 mt/yr.

In 1942 the Government asked companies to increase their lithium production, so at Searles Lake they installed a plant to recover the licons much more effectively, with the first production being in mid-1943. They took advantage of the licons being self-floating (because of their adsorbed organics) by designing a vessel to be aerated, and then collecting the foam. Initially they added some kerosene (to better control the foam) to the burkeite leach tank, and then cooled the  $\sim 0.2\%$  licons slurry of burkeite leach liquor to about 27°C in a multiple-spray cooling tower. The slurry next went to a "conditioning" tank, and then to four parallel 10,000 gal flotation vessels where air was forced at 4–8 psi through porous carbon plates in their base. The foam that was formed was scraped from the top surface, and the clear brine passed on to the soda products plant. Later they found that the kerosene and conditioning could be eliminated, and that instead of porous plates the air could be introduced into the suction of the pumps bringing the licons slurry to the flotation

tanks. They also installed a second stage of flotation with a commercial foam-release separator, and a small amount of additional licons were scraped from the surfaces of several of the soda products plant tanks. The foam was then sent to agitated, heated tanks to dissolve any remaining burkeite (it would also float), filtered, washed and prior to 1951 dried in a steam-jacketed, mixing-type dryer. This product was shipped in 100 lb bags, and in 1945 sold for \$256/mt, f.o.b. Trona (Rykken, 1976; Gale, 1945).

In 1945 they began work on a process to produce their own lithium carbonate, following the patent of May (1952; Fig. 1.73) who noted that lithium sulfate and sodium sulfate had a quite low ( $\sim 1.4\%$  Li) solubility in > 30-40% phosphoric acid. In the commercial process the licons were first roasted to burn off their organics content, and then mixed with 93% sulfuric acid at 115°C to form 45–50% phosphoric acid and a mixture of lithium and sodium sulfate crystals. The phosphoric acid was then evaporated to 78%, which crystallized additional salts, and reduced the lithium content to less than 0.4% Li. The mixed sulfate crystals were centrifuged, washed and re-dissolved, and then soda ash was added to the solution at



Figure 1.73 Flowsheet for the conversion of licons into lithium carbonate and super-phosphoric acid (May, 1952).

 $93^{\circ}$ C to precipitate lithium carbonate. The end-liquor was next treated with a small amount of phosphoric acid and evaporated to nearly sodium sulfate's crystallization point, precipitating trisodium phosphate that was recycled to the licons leach step. The final solution then only contained <0.07% Li instead of its original 0.28% Li, and it was sent to the soda products plant. The operation produced about 900 mt/yr of lithium carbonate, with an overall recovery from the lithium in the brine entering the evaporators of about 30% (Rykken, 1976; Williams, 1976). The operation was terminated in 1978 after 40 years of production when the soda products plant was closed.

# **Chinese** Lakes

Plans were announced in 2000 that lithium and various other products would be produced from Zabuye Salt Lake by the Tibet Lithium New Technology Development Co. The lake has a complex mineral content, including over 1 million mt of lithium, along with recoverable amounts of boron, bromine, cesium and potassium (Garrett, 1992). Experimental work had produced a lithium concentrate containing 78% Li<sub>2</sub>CO<sub>3</sub>, and a \$170–240 million, multiple-product plant was proposed to be started in 2003 (Saller and O'Driscoll, 2000). Discussions have also been made on the possible by-product recovery of lithium from the end-liquors (with about 120 ppm Li) of Qinghai Basin's large projected potash plant at Qarhan Lake (Fig. 1.74). A joint venture called Qinghai Lithium Ltd. was formed in 2000 by Pacific Lithium Ltd. of New Zealand and the Chinese government. It was stated that the lake contains 1 million tons of lithium, 1 million tons of boron and greater than 17 million tons of potassium (USGS, 2000; Garrett, 1996).



**Figure 1.74** Structure of Qaidam Basin, China (Sun and Lock, 1990). Legend: (1) mountains; (2) playa surface; (3) major potash deposits; (4) smaller potash deposits; – – –, outline of Qarhan Playa; Q, Qarhan Salt lake; D, Dabuxun Saline Lake. Reprinted by permission of Science Press (China).

### 136 Part 1 Lithium

## Various Proposed Processing Methods

# Liquid Extraction

The selective extraction of lithium from brines has been a much studied but elusive target. Many organic compounds can dissolve some-to-considerable lithium chloride with some selectivity for it compared to sodium and potassium chloride (and perhaps calcium chloride), but usually not magnesium chloride. An example of this is organic alcohols, where often the lithium chloride solubility is greater the lower the molecular weight, and the selectivity improves with greater molecular weight. Based upon these properties Hermann (1966) has suggested that a dry mixture of lithium, sodium and potassium chlorides or sulfates can be dissolved in anhydrous alcohols containing 3-8 carbon atoms (preferably butanol; solubility 10.57 g LiCl/100 g solvent). Almost no sodium (82 ppm) and sulfate dissolves, and very little potassium, so upon partial evaporation of the saturated butanol most of the impurities will crystallize. After they are filtered the lithium chloride can be recovered by further distillation or by re-extraction with water. Brown and Beckerman (1990) more recently suggested doing the same treatment with isopropyl alcohol (solubility 12.2% LiCl, 67 ppm Na), and others have discussed a similar lithium extraction with propanol (16.22 g LiCl/100 g solvent, 152 ppm Na), isobutanol (7.3% LiCl, 113 ppm Na), pentanol (8.1% LiCl, 34 ppm Na), 2-ethylhexanol, isopentanol, amyl alcohol (9.02 g LiCl/100 g solvent), isoamyl alcohol, allyl alcohol (4.36 g LiCl/100 g solvent), tetrahydrofuran (4.6% LiCl, 42 ppm Na) and other alcohols. Morris and Short (1963) noted that 0.001-1.84 M of lithium chloride could dissolve in tri-*n*-butyl phosphate, and that pure solutions had distribution coefficients (D, the concentration of lithium in the solvent/concentration of lithium in the aqueous phase after vigorous contact and settling) of 0.002-0.16, depending upon the initial LiCl concentration.

Despite the appreciable solubility of low-molecular weight alcohols in water or brine, Gabra and Torma (1978) also suggested using butanol to extract lithium from aqueous solutions of sodium, potassium and calcium. The distribution coefficients were very low, but still could allow an extraction with some purification of the lithium (Table 1.32). The use of insoluble carriers (such as kerosene) for the solvent (to lower the solvent loss in the aqueous phase) reduced the extraction to impractical levels. Holdorf *et al.* (1993) suggested such an extraction with amyl alcohol or fermentation alcohol (e.g., 52.1% 2-methylbutanol-1 and 47.9% 3-methylbutanol-1). They preferred 2–2.5 volumes of solvent per volume of brine, six extraction stages and two re-extraction (stripping) stages. They claimed a 95% lithium recovery from a 260 ppm Li gas field brine, with 52% of the magnesium also being extracted, and only a 0.1% solvent loss in the stripped brine. This low solvent loss is difficult to understand with such a low molecular weight alcohol.

Many other organic compounds have been noted that might be able to somewhat selectively extract lithium, but essentially all of them also extract magnesium, and require a drastic pH or composition modification of the brine. For instance some

#### **Table 1.32**

The Extraction of Lithium, Sodium, Potassium and Calcium from a Dilute Brine Containing All Four Chlorides (Gabra and Torma, 1978)

	Distribution coefficient					Separation factor		
	$D_{ m Li}$	$D_{\rm Na}$	$D_{\mathrm{K}}$	D <sub>Ca</sub>	S <sup>Li</sup> <sub>Na</sub>	$S_{\rm K}^{ m Li}$	$S_{\mathrm{Ca}}^{\mathrm{Li}}$	
<i>n</i> -Butanol	0.058	0.023	0.020	0.017	2.5	2.9	3.4	
sec-Butanol	0.044	0.022	0.021	0.020	2.0	2.09	2.1	
Isobutanol	0.018	0.009	0.009	0.005	2.0	2.00	3.6	
Pentanol	0.011	0.008	0.005	0.006	1.38	2.20	1.8	
Isopentanol	0.01	0.006	0.007	0.005	1.66	1.43	2.0	
2-Ethylhexanol	0.004	0.007	0.004	0.006	0.57	1.00	0.7	
2-Ethylisohexanol	0.005	0.006	0.005	0.006	0.83	1.00	0.8	
Octanol	0.005	0.007	0.006	0.006	0.71	0.83	0.8	
2,4-Dimethyl-3-pentanol	0.006	0.007	0.008	0.014	0.86	0.75	0.4	
o-Chlorophenol	0.018	0.0056	0.020	0.013	3.21	0.90	1.4	
p-Chlorophenol	0.0119	0.0049	0.01	0.012	2.43	1.19	1.0	
o-Cresol	0.045	0.019	0.03	0.006	2.36	1.50	7.5	
<i>m</i> -Cresol	0.007	0.014	0.013	0.0008	0.50	0.53	8.8	
p-Cresol	0.011	0.01	0.006	0.0012	1.0	1.83	9.2	
Cresol	0.008	0.019	0.0049	0.009	0.42	1.63	0.9	
Molar sol. of phenol/benzene	0.011	0.003	0.005	0.011	3.67	2.20	1.0	
<i>p-sec</i> -Butylphenol/benzene	0.005	0.017	0.0013	0.009	0.29	3.85	0.6	
<i>p</i> -1,1,3,3-Tetramethyl-(butyl)phenol/benzene	0.002	0.003	0.007	0.003	0.67	0.29	0.7	
<i>p-tert</i> -Butylphenol/benzene	0.012	0.0089	0.008	0.012	1.35	1.50	1.0	

With *n*-butanol the lithium extraction was the same at pH values from 1 to 11, although pH > 8 reduced the calcium extraction. The optimum ratio of solvent to brine was 1/1, among the ratios of 1/5 to 3.2/1 that were tested. As high as a 90% lithium recovery was obtained in four mixer–settler stages from solutions containing from 30-300 g/l lithium.

Reprinted from Hydrometallurgy, Vol. 3, p. 26, Table 1, ©1978, with permission from Elsevier.

diketones can extract lithium and a limited amount of magnesium (to improve the Li/Mg ratio 10 to several 100-fold), but only when the solution is strongly basic. Dipivaloylmethane ( $[CH_3]_3C-C=O)_2-CH_2$  as a 0.7 M solution in ether (as a carrier), with equal volumes of Great Salt Lake (GSL) potash plant end-liquor (Tables 1.9 and 1.33) and the solvent, and with the brine adjusted to 3% NaOH, can extract 90% of the lithium in one stage of mixing and settling. With only 0.3% NaOH the lithium extraction was 20%, and with no caustic, or with the carrier solvent being kerosene, benzene, petroleum ether, acetyl ether, chloroform, carbon tetrachloride, and many other solvents there was no extraction. Dang and Steinberg (1978) have also hypothecated a lithium recovery process for Smackover oilfield brine based upon this solvent. Other diketone extractants such as pivaloyltrifluoroacetone have an extraction coefficient for lithium of 0.1 with and without pH adjustment, 4-methylbenzoyl trifluoroacetone's coefficient is 0.06, and the chelating

agent diacetylmethane 0.043, but in all cases magnesium was also extracted. Other expected lithium solvents such as tri-*n*-butylphosphate, *bis*(2-ethylhexyl)phosphoric acid and mono(octylphenyl)phosphoric acid had no extraction effect on lithium in untreated Great Salt Lake end-liquor. Others have suggested the  $\beta$ -diketones thenoyltrifluoroacetone and dibenzoylmethane, and the acidic organophosphorus compounds di-(2-ethylhexyl)phosphoric acid and 2-ethylhexylphosphonic acid mono 2-ethylhexyl ester as lithium extractants, but their effectiveness is limited.

Many authors have studied lithium extraction processes in which they only attempted to separate lithium from other alkali metals, and sometimes calcium. For the separation from calcium chloride Goodenough and Gaska (1967) used alcohols or ketones and massive amounts of ammonia or urea. Ma and Chen (2000) studied the addition of two organic compounds that acted synergistically together (only LIX54 was a slightly effective solvent by itself) in batch experiments and on a supported liquid membrane. They used the commercial ion exchange chelating agent LIX54 ( $\alpha$ -acetyl-*m*-dodecylacetophenone) and the neutral complexing agent TOPO (tri-octyl-phosphine oxide) in a kerosene solution for the batch experiments or to soak a thin membrane film of Celgard 2500 (37-48% porosity; 0.05-0.19 µm pore size). With the membrane the film was dried under vacuum for 30 min, placed in the extraction cell, and a Li, Na, K solution passed over it. The extraction coefficients were only appreciable at a pH higher than 12, and in the batch experiments LIX54 had a moderate coefficient for lithium, and a lesser one for potassium and sodium. The mixed solvents had a very high coefficient when lithium was alone, but it fell to a moderate value in mixed-salt solutions, and some sodium and potassium were also extracted. The stripping (elution) solution for the solvent or membrane was water at a pH of 0.05-2. The initial solution concentrations were 10-100 ppm Li, 1000-7000 ppm Na and 30-500 ppm K, and with the membrane tests a 90% lithium removal was obtained after 2 hr of recirculated flow, and a 70-75% recovery was obtained from the strip solution in a similar period. The strip solution had about the same lithium concentration as the feed solution, but the reduction in its sodium and potassium content was not noted. Kinugasa et al. (1994) studied the kinetics of this solvent pair, and noted that in their work sodium was not extracted with the lithium. Somewhat similar results have been obtained when crown ethers (such as dibenzo-14-crown-4) and lipophilic anions were incorporated into membranes, with the eluate having a considerable reduction in the divalent cations (Olsher, 1982).

Lee *et al.* (1968) studied the synergistic use of trioctylphosphine oxide (TOPO) again as the adduct former, but with the chelating agent dibenzoylmethane. Their individual extraction coefficients from 0.02 M Li or 0.88 M KCl when in a 0.1 M KOH solution were 0.025 and 0.010, respectively, and 131 for a mixture of LiCl and KCl. When in *p*-xylene as a solvent carrier, *D* was 82.4, in carbon tetrachloride 68.5 and dodecane 49.1, while other solvents greatly reduced the lithium extraction. The selectivity factors ( $D_{\rm Li}/D_{\rm Na}$ ) for Li/Na were 570 and Li/Cs 12,400 in 3 M NH<sub>4</sub>OH solutions, and the lithium extraction was only effective at pH values above about 10.

	Feed	Raffinate	Wash liquor	Strip liquor	Strip recycle	Product
Li	0.116	0.0113	0.305	0.420	0.087	0.360
Na	0.118	0.098	0.120	0.009	0.079	5.86
Κ	0.058	0.042	0.024	0.001	0.001	0.001
Mg	8.55	6.19	1.72	0.02	0.005	0.02
Ca	0.005		_	_	_	0.0002
Fe	0.001	0.010	6.40	5.60	6.20	0.002
$SO_4$	2.46		_	_	_	0.016
Br	0.212		_	_	_	0.006
В	0.070		_	_	_	0.0027
Р	0.005		_	_	_	0.001
HCl	0	0.15	0.20	0.30	0.03	0.03
Density	1.344	1.228	1.240	1.180	1.170	1.130
Pounds	1000	1385	212	294	266	296
Add to the	e brine or sol	vent, as pounds				
	Fe		$H_2O$	H <sub>2</sub> O	$H_2O$	
	1.05		164	241	220	
	HCl			Na	Solvent	
	6.82			17.5	626	
	Solvent			Li	HCl	
	1540			0.071	0.63	

Table 1.33

The Extraction of Lithium by Ferric Chloride in an Insoluble Solvent, wt.% (Nelli and Arthur, 1970)

The only fairly selective liquid extraction process that has been suggested for lithium solutions with a high magnesium content is that by Nelli and Arthur (1970). They employed end-liquor (Table 1.33) from the massive Great Salt Lake (Strum, 1980) potassium sulfate plant's solar ponds. The process involved a quite elaborate series of liquid-liquid extraction steps centered around the substitution of lithium chloride into a ferric chloride complex. In the presence of strong chloride solutions and some hydrochloric acid lithium is nearly all converted into the relatively stable lithium tetrachlorferrate, which can be easily extracted by a number of solvents. In their process (Fig. 1.75 and Table 1.33) about an equal stoichiometric amount of ferric chloride is added to the lithium in the brine, along with enough hydrochloric acid to make the solution 0.04-0.1 N in HCl. This forms the iron complex which is then extracted by 1-2 parts of solvent per part of brine, with the solvent being a 20% mixture of tributyl phosphate and 80% diisobutylketone. This lithium extraction is made in seven countercurrent mixer-settler stages. The exiting brine (raffinate) is depleted of about 90% of its lithium content, but unfortunately, some magnesium is also extracted. This magnesium is recycled back to the initial extraction step (unavoidably along with about 34% of the lithium) by a "washing" step of the solvent with four countercurrent mixer-settlers and just enough water (1 part/10-11



**Figure 1.75** Flow sheet for the ferric chloride extraction process for lithium from high-magnesium brines (Nelli and Arthur, 1970).

parts solvent) to remove all of the magnesium and the minimum of lithium. Then the remaining lithium tetrachlorferrate is "stripped" with more water (1 part/3–7 parts of solvent) in five countercurrent stages and the solvent is ready to be recycled. The strip water is next made about 2 N with sodium chloride, and contacted with a different solvent in six countercurrent stages to remove its ferric chloride content. This solvent is an equal molar mixture of di(2-ethylhexyl)phosphoric acid (20 vol%) and tri-*n*-butyl phosphate (30 vol%) with benzene or a similar non-polar diluent (50 vol%), and its total volume is about twice that of the salt-adjusted strip solution. The raffinate from this step is the product, containing about 0.36% Li, 200 ppm Mg and 20 ppm Fe. The second solvent is then stripped of its ferric chloride with about 0.3 parts of water in six countercurrent stages. The solvent is recycled, and its raffinate joins the feed brine in the first stage as the ferric chloride source.

### Alumina Adsorption

A very large number of articles and patents have been issued on methods to precipitate or adsorb lithium from brines, but by far the most common is the suggested adsorption or co-precipitation of lithium on aluminum hydroxide or alumina. When aluminum chloride is added to a neutral or basic solution containing lithium most of the lithium joins the voluminous aluminum hydroxide gel-like precipitate. In a similar manner, hydrated aluminum hydroxide can adsorb lithium, and a wide range of mixtures with aluminum hydroxide (either in a solid phase or as a co-precipitate) can act in a similar manner. This method was first proposed by Goodenough (1960), with further details provided by Neipert and Bon (1967), and then by numerous investigators in many combinations (i.e., such as with ion exchange resins or other co-precipitants). Many different lithium-containing brines were also tested, such as seawater, geothermal brines from Italy, France and Japan, as well as brines from the Dead Sea, Salton Sea, the Great Salt Lake and various oilfield waters. However, no commercial processes were ever developed utilizing aluminum hydroxide precipitates.

One of the investigated brines was the *Wairakei Geothermal* power plant discharge. In 1986 this highly mineralized (As, B, Li, Si, etc.; Table 1.13) brine was being dumped into the Waikato River, causing considerable pollution. Consequently, studies were made on the recovery of many of the brine's constituents, including an aluminum hydroxide co-precipitation process for lithium, a patented process for the recovery of high-grade colloidal silica, and the recovery of calcium silicate and arsenic. Rothbaum and Middendorf (1986) found that after silica removal a 95% yield of lithium could be obtained by adding sodium aluminate to the brine at a pH of 10, and at 30°C. The lithium could be recovered from the alumina gel (which was claimed to filter well) by washing at 60°C, and the residual alumina could be recycled by dissolving the gel in sodium hydroxide. However, since the gel only contained 3% solids the eluted brine was only four times stronger than the original solution, and did contain some other salts.

With the fairly concentrated *Italian and French geothermal* brines (Table 1.13) at a nearly neutral pH, a modest excess of aluminum chloride, and temperatures from ambient to 80°C there was an almost complete recovery of lithium in the aluminum hydroxide gel. However, there was no practical means to make a product from the lithium chloride–aluminum hydroxide mixture (Pauwels *et al.*, 1990). The Goodenough (1960) and Neipert and Bon (1967) patents were based upon removing lithium from the high-calcium, medium–low magnesium dolomitization brines of the *Michigan Basin's potash end-liquors* (56 ppm Li; Table 2.5), both as-is and concentrated. Their optimum temperature of precipitation was 81°C, the pH 6.8 and using about 0.007 parts of AlCl<sub>3</sub>·6H<sub>2</sub>O/g of brine (with the as-is brine). However, both the optimum temperature and pH varied with the brine's total concentrated or magnesium-precipitated brine. Their recovery was from 80 to 90%, and they suggested removing the lithium from the aluminum hydroxide precipitate with hot water.

With *Salton Sea* brine laboratory tests had apparent technical success (up to 99% recovery), but were not considered to be economically practical. Under optimum conditions aluminum chloride in the amount of 3.0 times the stoichiometric amount of lithium was added to the brine at a pH of 7.5 and a temperature of 75°C. It was noted that if most of the magnesium had been removed lower temperatures (25–50°C) and different pH's would be optimum, but that with magnesium higher temperatures (50–100°C) and lower pH's were required (Berthold and Baker, 1976). *Seawater*, even though it only contains 0.17 ppm Li, has been studied for lithium

### 142 Part 1 Lithium

recovery in many reports, such as by Kaneko and Takahashi (1990). They found that the best adsorbent was a 50 mol% mixture of aluminum hydroxide and magnesium hydroxide, precipitated together and dried to a pore size of 20-30 Å. A 40% lithium recovery was obtained, and when eluted with 0.05 N HCl there was a sevenfold increase in the lithium concentration.

With Dead Sea potash pond end-liquor Pelly (1978) also used aluminum chloride to co-precipitate the brine's 30 ppm of lithium, adding a threefold excess of AlCl<sub>3</sub>, adjusting the pH to 6.8-7.0, heating the brine to about 55°C, and allowing a 4 hr residence time. After the aluminum hydroxide (with about an 80% Li yield) was filtered and washed, the precipitate was dissolved with hydrochloric acid to form a 680 ppm Li solution with the composition shown in Table 1.34. For each ton of lithium recovered it required 73 t of lime for the pH adjustment, 19,000 m<sup>3</sup> of water to wash the precipitate, and 92 t of HCl for the product leaching. Epstein et al. (1981) continued this work, but dissolved the lithium-alumina precipitate in isoamyl alcohol, and then stripped the lithium from the alcohol with water. A 1.7% Li solution was obtained, but it also contained 1.2% Ca and 0.4% Mg, with considerable loss of alcohol and lithium. Bukowsky et al. (1991) proposed concentrating Smackover oilfield brine, precipitating the lithium with aluminum hydroxide, leaching the alumina with iso-amyl alcohol, stripping the alcohol with water, precipitating the solution with soda ash, and carbonating the slurry to form a fairly pure lithium bicarbonate solution after filtration.

Tests have also been made on adsorbing lithium onto alumina from strong potash end-liquor dolomitization brines, such as found in the Angara-Lena basin's Znamenskoe deposit in the Irkutsk oblast. This brine contained, as wt.%: 25.44 CaCl<sub>2</sub>, 9.40 MgCl<sub>2</sub>, 1.49 NaCl, 0.52 KCl, 1640-1870 ppm LiCl, and 37.31% total salts, with a density of 1.34 g/cc. Ryabtsev et al. (2002) followed the work of Bauman and Burba (1997, 1995) and described their aluminum oxide adsorbent as having the formula  $LiCl \cdot 2Al(OH)_3 \cdot m H_2O$ . They noted that it was formed in a layered structure that resulted in a molecular-sieve effect that could only be penetrated by lithium. They further stated that up to 40% of the lithium in this compound could be released by a water wash, and then be replaced (the adsorption reaction) by contact with a lithium-containing strong brine. They prepared their adsorbent by mixing equimolar amounts of crystalline LiCl and Al(OH)<sub>3</sub> with 0.5 m of  $H_2O$ , forming granules, and then drying them. It was stated that their capacity for lithium was 7 mg/g of adsorbent. When the granules were made by using 6-8%PVC as a binder, they had a capacity of 5-6 mg lithium/g of granules. The PVCalumina pellets were ground to various size fractions, placed in columns, and then contacted with brine at various flow rates. It was found that 1-2 mm particles were optimum, and that over a 90% lithium recovery could be obtained from the brine. However, to have a fairly pure lithium product the column needed to be drained of brine, or displaced before the water wash started. This required as much as 2.2 bed volumes of water, and resulted in about a 20% lithium loss, but this wash water could be re-treated in the column. To obtain a higher lithium concentration during

1 abic 1.07	Та	ıble	1.3	4
-------------	----	------	-----	---

# Laboratory Tests on Dead Sea Brine, g/kg (Tandy and Canfy, 1993)

					Ph	osphate process		
	Dead Sea		Alumina	Precipitation		Leaching precipitate (wt.%)		
	Brine	End-liquor	Leach liquor	End-liquor	Precipitate (wt.%)	Original <sup>a</sup>	Final	Brine
Li	11.6 (ppm)	30 (ppm)	680 (ppm)	7 (ppm)	0.40	2600 (ppm)	170 (ppm)	1440 (ppm)
Na	31.5	2.5	0.16	3.2	10.4	11.9	0.5	4.1
Κ	6.4	2.6	_	2.5	1.4	_	_	_
Mg	35.7	63.5	1.25	63.2	2.3	2.4	6.9	0.05
Ca	14.4	26.9	0.29	25.9	3.3	2.0	11.4	_
Al	_	_	16.0	_	_	_	_	_
Cl	184.1	244.8	70.8	237.7	6.5	8.1	_	3.4
$PO_4$	_	_	_	0.02	40.0	40.8	50.8	13.7
$H_2O$	_	658.6	—	667.5	35.7	—	_	—

<sup>a</sup> Same as the precipitate in the previous column, except only one run, while the previous column was an average of seven runs.

the elution (water wash) stage, the more dilute portions of the eluate could be used as the elution water, allowing a lithium concentration in the product of as much as 12-15 g/liter. However, during their runs the average product concentration was about 6-9 g/liter, and the most effective adsorbent capacity 3 mg/g. The decrease in efficiency with repeated adsorption-elution cycles was not discussed, nor was the amount of other ions in the product, although in one run the calcium content was about equal to that of the lithium.

A possible commercial use of similar alumina technology is with FMC's hydrated alumina–lithium chloride granules suggested to be used in countercurrent adsorbent beds for Salar de Hombre Muerto brine, as discussed above. Here the lithium brine to be processed would be maintained saturated with salt as it contacts the alumina–LiCl granules, and the lithium fairly selectively adsorbed. Then the adsorbed lithium would be removed (eluted) from the granules in a second step with low-lithium water in a similar countercurrent manner. The dilute, fairly pure lithium eluate could finally be concentrated in solar ponds, and the resulting strong lithium chloride solution purified and made into the desired products (Bauman and Burba, 1997, 1995).

### Other Processing Methods

Pan et al. (2002) have presented a general review of various methods to recover lithium from brines, and Sprinskiy (2000) made a similar review of methods to recover lithium from Carpathian groundwater. Many other adsorbents for lithium have also been suggested, such as spinel or cryptomelane-type MnO<sub>2</sub>, or antimonates of Sn<sup>+4</sup> or Ti<sup>+4</sup>. Abe et al. (1993) recovered lithium from seawater (at 0.17 ppm Li) with a number of metal oxide adsorbents, and found that granules of  $\lambda$  or  $(\lambda + \gamma)$ MnO<sub>2</sub>·0.18H<sub>2</sub>O, 3.1TiO<sub>2</sub>-Sb<sub>2</sub>O<sub>5</sub>·4.9H<sub>2</sub>O and 1.1SnO<sub>2</sub>-Sb<sub>2</sub>O<sub>5</sub>·4.9H<sub>2</sub>O could all recover up to 99% of the lithium when seawater was slowly passed through packed beds of the oxides. The adsorption preference for the manganese dioxide and tin antimonate was in the sequence of Li > Cs > Rb > K > Na, while with the titanium Cs was preferred over Li. This allowed lithium separations from sodium of  $10^4 - 10^5$  fold, Li from K of about 1/10th that amount, and separations from Mg and Ca only about 10-fold or less. The maximum amount of lithium adsorbed was about 0.003 g Li/g of oxides, and when eluted from the column with 1-5 M HNO<sub>3</sub> the best separation was with  $\lambda$ MnO<sub>2</sub> and a 63% recovery. The peak strength of this eluate (as ppm) was about 6 Li, 4 K and Ca, and 2.4 Na and Mg, with the average eluate being about half that value. No testing was done on the re-use or re-generation of the adsorbents, or of re-treating the eluate.

A subsequent series of reports were made on similar studies with different adsorbents, perhaps culminating with the selection of  $H_{1.6}Mn_{1.6}O_4$  as the preferred adsorbent. It was prepared by heating LiMnO<sub>2</sub> to 400°C to form Li<sub>1.6</sub>Mn<sub>1.6</sub>O<sub>4</sub>, and then reacting it with 0.5 M HCl. In column tests this material was capable of loading from 34 to 40 mg of Li/g of adsorbent from seawater, along with 4.1–6.6 Na, 0.5–1.4 K, 2.3–2.5 Mg and 2.9–4.0 Ca mg/g. The cations could be almost totally removed (eluted) by 0.5 M HCl (along with 2.5–3.5% of the Mn), and in a second
adsorption cycle the recovery and loading were almost the same. The recovery efficiency from the seawater was about 60% (Chitrakar et al., 2001). Umeno et al. (2002) later added the same manganese oxide adsorbent to a polyvinyl chloride polymer to prepare an adsorbent film. Using a specially designed membraneseawater contact box the loading was 10.6 mg/g of membrane for lithium, along with 4.3 Na, 0.4 K, 10.8 Mg, 5.3 Ca and 0.5 Sr as mg/g. It was speculated that the manganese oxide was in the form of an ion sieve with a predominant pore size small enough for lithium, but not sodium, potassium or calcium. The magnesium, with about the same ionic radius has a much higher energy of hydration, and thus needs more energy to become dehydrated and enter the pore space. The larger particle size of the manganese oxide granules in the packed bed accentuated this effect, and thus rejected more magnesium. Other adsorbents that have been suggested include Li<sub>2</sub>Cr(PO<sub>4</sub>)<sub>1.67</sub>, which was claimed to react similarly to lithium-alumina, have a capacity of 9.3 mg/g in seawater, and have a concentration factor of  $3.3 \times 10^4$ . It was most effective above a pH of 6.2, but could be used down to a pH of 3 (Miyai et al., 2001). Activated carbon impregnated with sodium oleate has also been suggested for seawater, along with many types of equipment to facilitate the lithium adsorption.

Precipitating lithium from low-lithium brines with sodium phosphate has also been tested, after the model of licons being precipitated from Searles Lake brine. Tandy and Canfy (1993) studied the precipitation of *lithium phosphate* from *Dead Sea* potash pond end-liquor, and found that perhaps a 70% Li recovery could be obtained. By adding over a 30-fold molar excess of disodium phosphate to the lithium in the brine, adjusting the pH to 6–7, heating to 80°C, and with a 20–30 min residence time about 76% of the lithium would be precipitated along with dicalcium phosphate and the excess disodium phosphate. The precipitate contained about 0.3% Li, and could be leached with water to recover over 90% of the Li, with the remainder being in the residual phosphate precipitate. The filtrate contained about 1440 ppm Li in a sodium phosphate–chloride solution (Table 1.34).

For complex brines where solar ponding is possible, and potash recovery is also desired, a *salting-out process* has been suggested by Garrett and Laborde (1983). Using the brine from the Salar de Atacama as an example, the brine could be evaporated to first crystallize salt and then the bulk of the potash salts as either sylvinite or sylvinite and potassium double salts. Then the brine could be cooled in a plant to about  $-10^{\circ}$ C to crystallize about 50% of the remaining sulfate as magnesium sulfate heptahydrate (epsomite). The residual brine would be further solar evaporated and then again cooled to crystallize additional epsomite. After its removal the brine would again be solar evaporated, and then heated to about  $30^{\circ}$ C (the normal summer pond temperature) and epsomite added to salt-out much of the lithium as lithium sulfate. Boric acid could be precipitated from the residual brine by adding sulfuric acid. To recover the remaining lithium lime could be added to remove the small amount of sulfate that was still present, and the brine evaporated to form a concentrated lithium chloride solution.

Brine from the *Great Salt Lake* is similar to seawater, and it has also been studied for lithium recovery. In the commercial production of potassium sulfate from the Great Salt Lake the end solar pond liquors can contain 1000-1900 ppm Li (average as ppm: Li 1500, B 360, Br 300; as %: Mg 6.9, SO<sub>4</sub> 3.6; Toomey, 1980; Tables 1.9 and 1.33). Upon further evaporation in a processing plant at about 70°C to a Li value of 8000–9000 ppm essentially only magnesium sulfate and sodium and potassium chloride crystallize, and upon continued evaporation bischoffite and the lithium– magnesium double salts would form. Although expensive, presumably the *plant evaporation* of the Great Salt Lake solar pond end-liquor could form the basis of a process similar to that accomplished in the much lower humidity Salar de Atacama solar ponds.

# **Ore Processing**

## Greenbushes, Australia; Sons of Gwalia

The Greenbushes operation of Australia (previously called Gwalia Consolidated Ltd. and then Lithium Australia Ltd.) is the largest producer of lithium mineral concentrates in the world. Production started in 1983, and from 1998 to 2002 they had 150,000 mt/yr of capacity. In 1993 they were mining >4.0% Li<sub>2</sub>O (1.86% Li), low iron ore in an open pit with an average 1.8/1 overburden ratio (Fig. 1.76). They excavated 7000 mt/month of ore by conventional drill-and-blast techniques, employing a contractor's personnel and mining equipment as directed by the Greenbushes' staff. The ore was overlain by an average of 20 m (maximum 60 m) of



Figure 1.76 Side view of the Greenbushes spodumene mine in Western Australia (Flemming, 1993a; reprinted courtesy of the Australasian Institute of Mining and Metallurgy).

weathered clay-bearing material that generally could be removed by a front-end loader or excavator. The massive deposit was also sufficiently homogenous to be easily monitored for grade-control by blasthole sampling. The benches were 5 m high, and the blasted and transported ore was first stockpiled into 8000–10,000 mt piles (equivalent to a single blast) to allow blending to the crushers for a fairly uniform plant feed. The most harmful impurity in the ore was iron, which was partly in the spodumene molecular structure, and partly from contamination by the greenstone and dolerite in the hanging wall, and lateritic mud from the overburden and material spilled on the roads. Great care was taken to prevent iron contamination, as well as selective mining to not mix high and low grade ores in the pit (Flemming, 1993a).

In the nearby plant in 1993 the -800 mm (31.5 in.) ore was reduced in size at a rate of 230 t/hr by being sent through a series of grizzles, screens and two stages of jaw crushers, followed by a cone crusher with a -12 mm (-1/2 in.) discharge (Fig. 1.77). This equipment was used on a campaign basis with either their spodumene or tantalum (which was also mined) ore in batches of 7000-8000 mt.



**Figure 1.77** Crushing section flowsheet at the spodumene ore treatment plant of Gwalia Consolidated Limited, Greenbushes, WA (Flemming, 1993a; reprinted courtesy of The Australasian Institute of Mining and Metallurgy).



**Figure 1.78** Spodumene concentrator flowsheet at the Greenbushes mine of Gwalia Consolidated Limited, Greenbushes, WA (Flemming, 1993a; reprinted courtesy of The Australasian Institute of Mining and Metallurgy).

The -12 mm spodumene ore was sent to a storage bin, and then as needed to a primary screen. From there the +3 mm (+6 mesh) ore was delivered to a wet ball mill in series with a screen to be reduced to a -3 mm size (Fig. 1.78). The ball mill had 75 mm balls, and ran with a slurry density of 75–80%. The -3 mm slurry was pumped to a hydraulic classifier where the  $\sim 250 \,\mu\text{m}$  ( $60 \,\text{mesh}$ ) particles were removed in the overflow stream. The underflow was sent to a vibrating 1700  $\mu\text{m}$  by 800  $\mu\text{m}$  slotted screen and its  $\sim +820 \,\mu\text{m}$  ( $\sim 20 \,\text{mesh}$ ) oversize returned to the ball mill. The screen underflow then went to a second vibrating screen of the same size, and its underflow was sent to rougher spirals to remove the heavy minerals (mainly cassiterite and tantalite). The cleaned classifier overflow solids were filtered and washed on a flat bed filter, the cake sent to a fluid bed dryer, and the dry product was re-screened and passed through a low-intensity magnetic separator to become "Glass Grade Spodumene". When the raw ore contained about 4.35% Li<sub>2</sub>O (2.02% Li), the underflow from the hydraulic classifier (and the final product) contained 4.8–5.0% Li<sub>2</sub>O (2.23–2.32% Li) and < 0.13% Fe<sub>2</sub>O<sub>3</sub>.

The classifier overflow was next sent through two stages of cyclones to remove the  $-20 \,\mu\text{m}$  (<400 mesh) slimes, and the coarser particles sent to flotation cells. The reagent was 700 g of fatty acids per ton of ore, the feed slurry density 35–40% solids, the caustic conditioning time 10-15 min, and the pH 7.1. The rougher concentrate was reprocessed (cleaned) in two stages of additional flotation, with a 45% slurry density and a pH of 6.7. An 88% lithium recovery was obtained in the flotation cells from a feed material with 3.8 Li<sub>2</sub>O (1.77% Li; this is a fairly typical spodumene flotation circuit, Manser, 1975). The flotation tailings consisted primarily of quartz and feldspar, with 0.8% Li<sub>2</sub>O (0.37% Li), and was stored for possible future recovery. The flotation overflow was vigorously washed with sulfuric acid at a pH of 1.5-2.0 to remove the fatty acid (which discolored the spodumene and reduced the subsequent magnetic separation efficiency) and some of the iron and apatite, and then sent to low intensity magnetic separators to remove any tramp iron (from the grinding balls). Next the ore was sent to spirals (gravity separators) to remove more of the heavy minerals (which were further processed), and finally to high-intensity magnetic separators to remove the para-magnetic minerals, which were primarily tourmaline. The remaining material was passed through a 560  $\mu$ m (~28 mesh) screen, and then filtered and washed on a belt filter. The cake was dried in a fluidized bed dryer to form their "Spodumene Concentrate" product. If desired, the dust from the dryer's flue gas cyclone collector could be sold separately as a "Fine Grade" product.

The plant could treat 22 mt/hr of ore in 1993 with an overall lithium recovery of 82% when the ratio of glass grade to concentrate was 3.5/1. The plant operation was on a 24 hr, 7 days/week basis, with two operators and a supervisor (shared with the tantalum plant) on each shift. The products were shipped in bulk from the port of Bunbury, or in bags from Fremantle, and careful quality control was maintained (Harben and Edwards, 1998; Flemming, 1993b). The product could contain up to 1-2% tourmaline (small black specks) with a 14.4% Fe<sub>2</sub>O<sub>3</sub> content and a melting point of 1100°C, but other than the iron, being a borosilicate it did not harm the glass. Quartz was the major impurity in the spodumene products, with 0.5-1% other minerals such as Na- or K-feldspar and tourmaline (Kingsnorth, 1988). Four grades were being produced in 1993, with the main ones being concentrate containing 3.49% Li (7.5% Li<sub>2</sub>O; about 95% spodumene, 5% quartz), 0.10% Fe<sub>2</sub>O<sub>3</sub>, a maximum of  $5\% + 212 \mu m$  (65 mesh), and a minimum of  $60\% + 75 \mu m$  (200 mesh) particles. The glass grade contained 2.23% Li (4.8% Li<sub>2</sub>O; about 60% spodumene, 40% quartz with 0.5–1% other minerals), 0.13% Fe<sub>2</sub>O<sub>3</sub>, zero +820  $\mu$ m (~20 mesh), and a minimum of  $95\% + 105 \,\mu\text{m}$  (150 mesh) particles. Much of their ore concentrates went into the production of container glass, television tubes and pyroceramics (Flemming, 1993a,b).

A "Chemical Grade" product was initiated in 1992 that could be made with either low, or preferably high grade ore. In 1996 they commenced production of lithium carbonate from these concentrates in a small plant, but because of SQM's drastic

reduction in the price of lithium carbonate the next year, and technical problems with the plant it was closed in 1997 (USGS, 1997).

# Bernic Lake, Canada; Tanco

The Tanco operation at Bernic Lake, SE Manitoba was originally (in 1929) a tin prospect because of cassiterite (up to 6.9% Sn) in the pegmatite's outcrop, and subsequent drilling found a large rare element deposit. Over the years the deposit was more extensively drilled, and a limited amount of amblygonite was mined in 1960. A three compartment, 93 m deep shaft was sunk into the pegmatite in 1956, it was deepened to 103 m in 1959, and 1800 m of exploratory mining was done. In 1968 the shaft was again deepened to 169 m, and in 1969 a 400 m long, 20% inclined entry was constructed. From 1969 to 1982 tantalum mining was conducted, and in 1984 a 5 t/hr spodumene pilot plant program began utilizing the idle tantalum mill. Its successful conclusion led to a \$6 million, 15,000 mt/yr spodumene plant being built to begin operation in 1986. Tantalum mining re-commenced in 1988, amblygonite concentrates began to be separated in 1989, and a cesium formate plant opened in 1997 (Vanstone, 2002).

The mining operation in 1988 was on the Upper Intermediate Zone, approaching within about 60 m of the floor of Bernic Lake, with the three-compartment shaft and the  $3.1 \times 4.3 \times 400$  m incline being used for ore hauling and entry, respectively. Room and pillar open stope mining was practiced, and since the mining followed the thickness of the ore the stopes were of variable height. The first entry was made in the upper zone of the ore, and lower entries were made as needed. The principal lithium ore was "squi" (spodumene-quartz intergrowth with considerable potassium and sodium feldspar, and albite), along with occasional laths of primary spodumene and feldspar. Masses of petalite, amblygonite and lepidolite (except when mined for its tantalum content) were avoided unless it was necessary to mine through them to obtain additional squi. The initial pillars were 16 m square, and the rooms 16 m wide, but as additional rock mechanic details were established, in 1988 the standard rooms were 15 m wide with 7.7 m pillars, and on average about 20 m (10-30 m) high (requiring a tall roof-scaling "giraffe" (Fig. 1.79). This allowed an 89% ore recovery, with very little dilution and the minimum of waste rock development. The roofs were arched for greater strength, and seldom needed to be bolted except for some long-term entries. When bolts were used they were 3 m (10 ft) long with a pressure-expandable seal to the rock. By 2002 the room size was increased to 22 m.

In 2002 two-boom hydraulic jumbos performed all of the drilling for drifts, benches and entries, while a single-boom long-hole drill was used for pillar size-reduction. The drill holes were often up to 10 m (30 ft) deep, and it was found that with this very hard rock ordinary steel drills with an abrasive fluid provided the most economical drilling. After blasting the ore was picked up and transported to various ore passes that were located throughout the mine using 3.82, 4.59 or  $5.35 \text{ m}^3$  (5, 6 or 7 yd<sup>3</sup>) load-haul-dumps (LHDs), front end loaders or 20 t trucks. The larger ore



Figure 1.79 Roof scaler "Giraffe" in the TANCO mine (Taylor, 2002, courtesy of the Tantalum Mining Corporation of Canada Limited).

particles were broken to a -300 mm size on grizzlies over the chutes by mobile or stationary pneumatic or electric rock-breakers. The ore then dropped to the 130 m level where it was loaded into 4 t side dump rail cars, and hauled to the shaft loading pockets. From there it was hoisted to the surface in 4 t skips, and stored in 450 mt ore bins before being delivered to the processing plant. The mining rate was about 300 mt/day in 1988 (Vanstone *et al.*, 2002; Burt *et al.*, 1988).

The tantalum and spodumene ores in 2002 each had their own skip pocket and surface storage bins, and their ore was hoisted daily. However, to accommodate the

pollucite ore, one of the pockets and bins was emptied each week, and the pollucite was hoisted and processed on a campaign basis as needed. The extensive diamond drilling of the deposit allowed the mining plan to be made well in advance, and if needed all three ores (spodumene, tantalite and pollucite) could be mined at the same time. Each ore was handled in the same primary crushing equipment (reduced to a -12 mm size), but each type of ore had its own fines storage bin. For the mine ventilation the air entered through the shaft and a vent rise, and exited through the inclined entry at a rate of 5300 m<sup>3</sup> (190,000 ft<sup>3</sup>) per minute. All of the mine maintenance was conducted on-site (Vanstone *et al.*, 2002).

In the plant in 1988 (Figs. 1.80 and 1.81) the spodumene ore was initially crushed in a three-stage operation, first in a jaw crusher, and then by standard and short head cone crushers, both in closed circuits with screens. The ore was crushed to a -12 mm size at a rate of 90 mt/hr in a single shift operation, and then stored in a 450 mt bin. From there the crushed ore was fed to a wet screen at a rate of 14 mt/hr to remove the -0.4 mm particles (0.5 mm in 2002). The -0.4 mm particles were sent to a 150 mm cyclone, with its overflow pumped to the slimes pond, and the underflow joined the heavy media underflow ore. The coarse ore from the screens next went to a two-stage heavy media separator with an effective separation density of 2.65 g/cc. The heavy media was a 70:30 mixture of ferrosilicon and magnetite with a feed density of 2.74 kg/liter. Both of the separator's sink and float discharge streams were drained and thoroughly washed to recover the heavy media, which was thickened in a low-intensity magnetic separator for recycling (the loss was about 0.15 kg/t of ore).



**Figure 1.80** Aerial view of the TANCO mine's surface facilities (Taylor, 2002, courtesy of the Tantalum Mining Corporation of Canada Limited).



**Figure 1.81** Flow sheet for the Tanco spodumene concentration process, Ontario, Canada (after Burt *et al.*, 1988; this figure appeared in Industrial Minerals No. 244, January 1988, p. 58. Published by Industrial Minerals Information, a division of Metal Bulletin plc, UK. ©Metal Bulletin plc 2003).

The light fraction was feldspar which was stored for potential later processing, while the underflow stream and the original -0.4 mm fraction was filtered and sent to a second 500 mt storage bin. From there it was fed at 8.5 mt/hr to a  $2.4 \times 3.7$  m ball mill with 75 mm steel balls, operating in closed circuit in 2002 with two sets of 2 mm primary screens followed by a hydroseparator that only allowed about

 $-150 \ \mu m$  sized (100 mesh) ore to leave the ball mill circuit. Rougher and cleaner spirals also recovered tantalum from the grinding circuit streams, and a 1.5 m diameter low intensity magnet removed the iron produced during the grinding process. The  $-150 \ \mu m$  ore was next deslimed in two stages with 150 and 100 mm cyclones, the final overflow sent to the tailings pond, and both cyclone underflows advanced to froth flotation cells. The heavy media overflow, the cleaner spirals' underflow and the slime streams were processed through several additional stages of density separation by spirals, tables and Falcon separators to recover more of the tantalum as a valuable by-product from the spodumene ore.

The first set of rougher and cleaner flotation cells was used to remove amblygonite, since it would contaminate the spodumene with both phosphate and fluorine, and an amblygonite-spodumene mixture called Montebrasite could be sold as an extra product. The separation was made at a pH of 9.2 with limited amounts of tall oil fatty acid and petroleum sulfonate as the collector, and starch as the spodumene depressant. The floated amblygonite stream was sent through high intensity magnetic separators to remove any weakly magnetic iron minerals, and then the Montebrasite was filtered, dried and packaged for sale. The amblygonite flotation underflow solids were next re-floated in a single stage to remove mica, and thus reduce the K<sub>2</sub>O level in the final product (Vanstone *et al.*, 2002).

The underflow stream from the mica flotation was next de-starched in two stages of cyclones, and the final underflow sent to the main flotation cells to remove the feldspar and quartz. These cells operated at the same pH as the amblygonite cells, with more of the same reagents, and at a pulp density of 35-40%. The underflow went to scavenger cells, and the spodumene overflow to cleaner cells, and then the scavenger overflow and cleaner tails were reground in a  $1.8 \times 1.4$  m ball mill to be returned to the rougher cells.

The flotation concentrate was next passed through a low-intensity magnetic separator, and then acid washed at a pH of 1.5 to remove any iron or it's stains, and to dissolve some of the minor minerals in the ore such as lithiophilite (a lithium phosphate compound). Finally the ore passed through a high-intensity magnetic separator to remove most of the remaining iron and any magnetic minerals such as tourmaline. The spodumene was then washed, thickened, filtered on a belt filter to an 8% moisture content, and dried in a propane-fired rotary drier to less than 0.1% moisture. The spodumene was sent to shift bins for analysis, and when approved to three 180 mt storage bins. From there the product was trucked in bulk or bags 70 km to a rail siding at Moslon, and then by rail to the main line of the Canadian Pacific railroad. Overseas shipments were made from Thunder Bay, one day to the east (Harben and Edwards, 1998; Burt *et al.*, 1988; Crouse *et al.*, 1984).

In 1991 Tanco produced 12,000 mt/yr of low-iron lithium ore, and 160 mt of tantalum ore, and in 2001 Tanco was the largest supplier of lithium, tantalum and cesium (pollucite) minerals to the United States. In addition it sold amblygonite (containing >7% Li<sub>2</sub>O and 20% P<sub>2</sub>O<sub>5</sub>), and potentially could sell feldspar (some containing 0.4% Li<sub>2</sub>O, 9.5% K<sub>2</sub>O and 1.5% Rb<sub>2</sub>O), lepidolite (with an even higher

rubidium content), quartz, mica, beryl, rubidium, gallium, and more than 80 minerals ranging from bismuth to zircon-hafnium (Harben and Edwards, 1998; Kunasz, 1994; Burt *et al.*, 1988).

## Zimbabwe; Bikita Minerals

The famous Bikita mine has been the largest producer of lepidolite and petalite in the world, and is also one of the oldest lithium mineral producers. The mine is located 64 km NE of Masvingo, Zimbabwe (69 km east of Fort Victoria in the former Southern Rhodesia), and is in the largest (1550 m length; 29–64 m width) of a series of pegmatites in the Bikita tin field. The mine was first opened in 1911 to recover tin, and later mined for tantalum, beryllium and lithium. Bikita Minerals first acquired some of the deposit in 1953, and added more in 1959 to form a total area of  $32.5 \text{ km}^2$ . The land varies in altitude from 1097 to 1372 m, and consists of rolling hills and flat, swampy valleys, with the climate being subtropical. The average maximum and minimum temperatures are 34 and  $6.7^{\circ}$ C, respectively, and the annual rainfall 678 mm.

In the early lithium operations prior to 1960 a 610 m adit was used to enter underground workings in the lepidolite deposit at the 61 m level. Cars were loaded through overhead chutes, and then hauled by diesel locomotives to the beneficiation plant 450 m from the adit. The ore was crushed to about a -76 mm size and screened, the waste removed by hand sorting from a conveyor belt, and the waste and fines stockpiled for potential future use. The concentrates were often of almost mineral collector's appearance, and they were trucked to the port at Beira for overseas shipment, and later delivered by the Rhodesian Railways. Petalite was mined in an open pit, and also hand sorted, but amblygonite was only obtained by selective hand mining in outcrop areas (Kesler, 1960).

Lepidolite was the first lithium mineral mined in large quantities (from 1954 to 1959; primarily for the American Potash plant), followed by petalite from a 460 by 46 m zone east of the lepidolite mine, and amblygonite in smaller quantities. Mining was later conducted by open pit operations in both of the two sectors, as shown in the 1960 cross-section drawings of Fig. 1.82. An extensive drilling and underground development program had first been conducted to better define the ore body, and mining plans were developed for both predominantly lepidolite (the Bikita pit) and petalite (the Al Hayat pit). The benches in both pits were 15.2 m high for each development level, and then subdivided into working faces 7.6 m high. Slots 7.6 m wide were initially cut at right angles to the strike, and into the ore bodies to initiate the pits. The average overburden ratio was 1/1, and the overburden consisted of weathered greenstone country rock and low-grade lithium ore, feldspar, quartz and mica, all of which were stockpiled for potential future recovery. If lenses of spodumene, amblygonite, petalite, beryl or cassiterite were encountered in the overburden they were sent to the hand-picking plant for possible recovery. Once the overburden was removed selective mining was employed to recover each type of ore. Also, the lepidolite and petalite ores were mined at different periods on



Figure 1.82 Side view of the Bikita lithium mines in Zimbabwe (Symons, 1961).

a campaign basis so that the same mining, crushing and hand sorting equipment could be used for each ore.

During this period the mined ore was separated by a complex crushing-hand sorting operation (Fig. 1.83). It was hauled to the surface of the pit in trucks, and



Figure 1.83 Flow sheet for the Bikita lepidolite hand-sorting process, Zimbabwe (Symons, 1961).

then transported to the plant (which was about 2100 m away) in narrow gauge rail cars. The first stage of size reduction was a  $91 \times 64$  cm jaw crusher set with a 12.7 cm ore discharge. The crushed ore was screened at a 7.6 cm size, and the oversize was washed and sent to a hand-picking belt. Quartz and feldspar were first removed, then spodumene, and finally mixed ore which was returned to the screen undersize stream. The large ore particles that remained on the belt were rescreened with the oversize sold as a glass maker's product, and the undersize sold for chemical processing.

The -7.6 cm ore from the screen went to a  $76 \times 45.7$  cm jaw crusher set to discharge at 4.45 cm, and the crushed ore was sent to a screen with 3.18 cm openings. The underflow went to a storage pile, while the overflow was washed and rescreened at 4.45 cm and 9.53 mm in a two-deck screen. The underflow went to the reject storage pile, while both oversize fractions were separately hand sorted, and after screening the product stream was passed under a 2537 Å ultraviolet light which caused the eucryptite to glow salmon-pink, allowing it to be seen and removed. Both lepidolite and petalite were handled in this manner, but often the former did not require the amblygonite screening step (Symons, 1961).

Production by the hand-sorting method for the period 1952–1960, when Bikita was the world's dominant lepidolite producer, is shown in Table 1.16. In 1979 mining was done primarily in the Al Hayat sector, producing as mt/yr: 26,400 petalite, 9600 lepidolite, 9600 spodumene and considerable feldspar (separated from the petalite). Hand sorting produced a comparatively high-grade product, but a large fraction of the ore was lost in the rejects and fines. Consequently, detailed (and successful) studies were made on both froth flotation and gravity separations, but they were not cost-competitive at Bikita until the mid-1980s when a 10,000 mt/yr heavy media separator was installed. It has allowed fine petalite to be recovered from the waste stockpile as a 4.4% Li<sub>2</sub>O product, and added 30 years to the mine's life. The deposit's lepidolite by 2002 was nearly depleted except for the reject piles, and in 1994 10,000 mt/yr of spodumene concentrates began to be produced using a flotation separation step (Harben and Edwards, 1998; Symons, 1961).

# North Carolina; Chemetall (Foote)

Foote Mineral Co. purchased its North Carolina spodumene deposit in 1951, and limited mining and milling (327 mt/day capacity) in a somewhat improved plant began in 1952. The mine and processing plant had previously been operated by the Solvey Process Co. under a US Government contract from 1943 to 1946. Their ore averaged 15-20% spodumene, and was mined from an outcropping pegmatite that appeared to be over 305 m long and up to 91 m wide. Strip mining was employed, with the top 1.8-2.4 m of rock being considered as overburden, and the severely weathered ore beneath that somewhat selectively rejected. In the mill the ore was crushed to -7.6 cm in a jaw crusher, and then screened to a -1.9 cm size, with the oversize being further crushed in a cone crusher. The -1.9 cm ore was then fed to two wet pebble mills with granite blocks as the grinding media, working in series

with a 40 mesh screen. The slurry from the screen was deslimed by a hydrocyclone and then sent to Humphrey spirals to remove about 5% of the ore as heavy particles, which were reprocessed and treated as a by-product. The remaining ore was then fed to flotation cells that did the unusual job of floating the waste rock (quartz, mica, feldspar and some hornblende). The silicate minerals collector was a fatty acid amine, the spodumene depressant was dextrine (which works best in an alkaline solution), caustic was the pH regulator (kept below 11.3), and pine oil was the frother. The spodumene underflow was dewatered and sent to storage, while the overflow which contained about 7% spodumene was sent to scavenger flotation cells, then to a gravity separation table, and the recovered spodumene added to the product. An expansion plan to raise the mine and mill capacity to 910–1090 mt/day was being considered in 1953 (Goter *et al.*, 1953).

After an extensive drilling program from 1954 to 1956 a new mine was established, a new mill and ore processing plant was built, and production started on a much larger and more efficient scale. The operation was expanded in 1978 at a cost of \$22 million, and an adjacent processing plant built with a capacity of 12 million lb/yr of LCE. The mine and plant were later de-bottlenecked to 16 million mt/yr by 1984. Ore was obtained from their open pit mine, which then operated on a cluster of eight pegmatites that were 3-62 m thick, but required considerable selectivity in the mining operation. The pit was initially designed to have 10 benches and become 61 m (200 ft) deep, but that could later be expanded to a 122 m depth. The benches were 6.1 m high and 9 m wide since the 10-20 m thick amphibolite and clay overburden in those pegmatites could not support very high vertical walls (Kesler, 1976).

The first stage of mining was to excavate a 53 m slot across the ore, and then typically develop a pit 400 m in diameter and 61 m deep. In 1969 the pit had 11 benches, and usually three benches were mined simultaneously, with a new, deeper bench being opened as the lower ones became exhausted. The exact mining method for each pegmatite depended upon its width, but the barren rock was usually removed first on three sides to minimize contamination of the ore. The lowest side of the pegmatite was then mined first in order to allow the easier down-slope blasting. After the ore had been blasted the larger boulders were moved to one side and broken by 2273–4545 kg Ni-Hard "drop balls" before being hauled to the plant. Maintenance of the mining equipment was done in a nearby service building, and all of the machinery surfaces contacting the ore had to be frequently rebuilt or replaced because of the ore's abrasiveness, which was similar to quartz in hardness (Bach *et al.*, 1967; Johnson, 1958).

In 1960 the maximum haul for the ore to the plant was 800 m, and 670 m for the overburden to the tailings pile. Primary gyratory crushers first reduced the ore to a -15 cm (-6 in.) size, and then it proceeded to a series of size reduction and screening steps until its liberation size had been reached for a flotation separation (in 1960 there was also heavy media separation). Prior to flotation the ore was acid washed and then given an abrasive scrubbing to remove stains on the crystal surfaces



**Figure 1.84** Photograph of Foote's Kings Mountain Spodumene Mine and Processing Plant (Anon., 1976; reprinted with permission from Chemical Week, October 20, 1976, Chemical Week Associates).

(from groundwater penetration) that would block the flotation reagents (Kesler, 1976). The flotation concentrate (now the cells' overflow) was settled and shipped to their plants at Sunbright, Virginia and at Exton, Pennsylvania, while the flotation underflow was filtered, washed and discarded. A picture of the mine and processing plant during this period is shown in Fig. 1.84.

In the processing plant in 1969 the spodumene concentrates were mixed as a slurry with finely ground limestone in the ratio of one part ore, 3.5 parts of limestone, and the slurry was fed into a 3 m diameter, 104 m long  $(10 \times 340 \text{ ft})$  coalfired rotary kiln. It was discharged at a temperature of 1030-1040°C (980°C, Williams, 1976), with limestone first being calcined to form lime, and the spodumene changed from the  $\alpha$  to the  $\beta$  form. The lime then reacted with the  $\beta$ spodumene to form dicalcium silicate and lithium oxide, plus various impurity by-products, with the mixture discharged from the kiln as about 2.54 cm pellets. This "clinker" was next cooled and ground, and leached with hot water in a six-stage countercurrent mixer-settler (thickener) system. The thickener underflow (the dicalcium silicate, etc.) was vacuum filtered, washed and discarded, while the overflow lithium hydroxide solution was pressure-filtered and then concentrated in a three-stage evaporator-crystallizer. A slurry of the crystallized lithium hydroxide monohydrate was continuously withdrawn, settled, centrifuged and dried as the final product, while the remaining liquor and filtrate were further evaporated. This allowed additional recovery of lithium hydroxide crystals, and the production of a saleable 50% solution of sodium hydroxide (Fig. 1.85; Bach et al., 1967).

Foote Mineral also sold spodumene concentrates to LCA prior to their establishing their own mine, and to glass and ceramic producers in three grades: chemical, ceramic and low iron (Stinson, 1981; O'Neill *et al.*, 1969). To produce the low-iron concentrates Foote first converted the concentrates from  $\alpha$  to  $\beta$  spodumene



**Figure 1.85** A general flowsheet for producing lithium hydroxide from spodumene by the lime-roast process (Wilkomirsky, 1998).

by firing them in a kiln at about 1100°C. This material was then cooled to 300°C and contacted with chlorine gas in a pressurized reactor, which formed both FeCl<sub>3</sub> and AlCl<sub>3</sub> vapor. The temperature had to be carefully controlled, since at higher temperatures LiCl would also vaporize, and at lower temperatures the reaction with iron would not be complete. The spodumene from the reactor was typically converted from a 0.67% Fe<sub>2</sub>O<sub>3</sub> to a 0.075% Fe<sub>2</sub>O<sub>3</sub> product (Heinrich *et al.*, 1977).

The recovery of lithium from spodumene ore was discontinued by Foote in 1984 (1986, USGS, 2000) and the mine and plant placed in a "stand-by" condition. It was officially closed in 1991 and the mine and plant dismantled in 1994 (USGS, 1997). However, the Kings Mountain conversion plant (converting lithium hydroxide to other lithium products) continued as a major processor of Clayton Valley and Salar de Atacama lithium carbonate into other lithium chemicals and lithium metal. Butyl lithium was produced at their New Johnsonville, Tennessee and Taiwan plants, and many other lithium chemicals were made at their parent company, Chemetall GmbH's plant at Langelsheim, Germany.

## North Carolina; FMC (Lithium Corporation of America, LCA)

LCA, who were later purchased by FMC, initially were located (as Metalloy Corp. until 1947) in St. Louis Park, near Minneapolis, Minnesota. They purchased

hand-picked ore or concentrates of spodumene or petalite to produce their lithium products, and in the 1940s began to utilize some ore from their South Dakota mines. During this period they also performed extensive experimental work to determine the most favorable spodumene recovery method, and developed a patented sulfuric acid roast process that could also be used with other ores. In their Minneapolis plant concentrates were used as-is, and coarse ore was first crushed to a -2.5 to -5 cm size in a  $23 \times 41$  cm jaw crusher (Fig. 1.86). The ore was next fed to a 12.2 m long, 1.52 m outside diameter, 1.22 m inside diameter fire brick-lined rotary kiln revolving at about 1 rpm, with the ore flowing in a countercurrent manner to the flame and flue gas. The kiln heated 1-2 t/hr of ore to 1050-1100°C, which converted most of the spodumene from the  $\alpha$  to the  $\beta$  form. The changes in the ore from heating allowed the lithium in the spodumene to be more easily dissolved, since  $\alpha$ -spodumene is almost insoluble in even strong acids. The hot ore then went to an adjacent  $0.91 \times 7.9$  m water-cooled rotary (7 rpm) cooler which discharged the ore at 95–120°C. The ore had been decrepitated in the kiln to a -2.5 cm (average 8 mesh) size, and was next ground in an air-flow roll mill to a predominantly -200mesh size.

The fine ore then entered a  $0.3 \times 3.1$  m, 20 rpm screw conveyor along with a 35-40% excess of 66° Be (93%) sulfuric acid, and was mixed and conveyed to a  $0.91 \times 7.9$  m co-current fired steel rotary kiln. The acidified ore was heated to  $250^{\circ}$ C, and then dumped into an 8000 gal ( $2.7 \times 7.9$  m) wooden, air-agitated, batch operated dissolving tank. In this overall reaction from decrepitation to leaching the ore maintained its original structure (it even had very similar X-ray diffraction lines), and merely exchanged lithium for hydrogen:  $Li_2O \cdot Al_2O_3 \cdot 4SiO_2 \rightarrow H_2O \cdot Al_2$ O3:4SiO2. Ground limestone was also added to the leach tank to neutralize the excess sulfuric acid, bring the pH to 6-6.5 and precipitate much of the iron and aluminum that had dissolved. After about 30 min of agitation the slurry (in batches containing 10 mt of ore) was withdrawn, filtered and washed on a vacuum drum filter. The solids with 30% moisture and <1% of the initial lithium were discarded, and the filtrate was treated with lime to a pH of 12. Then a small amount of soda ash was added to remove the remaining calcium, magnesium, iron and aluminum to produce, after filtration, a fairly pure 100 gpl Li<sub>2</sub>SO<sub>4</sub> solution. This solution was adjusted to a pH of 7, evaporated to 200 gpl, activated carbon was added to remove organics, and the mixture filtered. Finally, the solution was maintained at 90°C, soda ash was added to precipitate lithium carbonate, and the slurry was centrifuged. The lithium carbonate cake was then washed and dried to yield about 6000 lb/day of product. The filtrate was cooled to crystallize glauber salt (Na<sub>2</sub>SO<sub>4</sub>·10H<sub>2</sub>O; which was made into a salt cake [Na<sub>2</sub>SO<sub>4</sub>] by-product), and the remaining solution recycled to the evaporator (Fig. 1.86; Ellestad and Clarke, 1955; Hader et al., 1951).

The advantages claimed for the process compared to an alkali or other leach were that: (1) Fine grinding of the ore was not necessary, since  $\beta$  spodumene is porous and even coarse particles react fairly rapidly with sulfuric acid (-200 mesh ore is leached in 3–15 min). (2) The kiln operations only required a short residence time



Figure 1.86 The initial flowsheet for LCA's production of lithium carbonate from spodumene by the acid roast process (after Hader et al., 1951).

since both reactions occurred rapidly. (3) There was no mixing problem with the ore and sulfuric acid, and the subsequent water-leaching was rapid. (4) They felt that the process was the only one amenable to treating low-grade lithium ores directly, without first producing concentrates. In their experience with weathered (outcrop) South Dakota ore the flotation efficiency to form concentrates was only about 45-50%, and the leaching processes about 85% efficient. By contrast, the acid-roasting process could give an 80% yield on 0.7% Li spodumene ore directly, instead of their estimated overall yield of 38-43% with South Dakota concentrates. In 1955 they planned on using it on run-of-mine ore in their Minnesota and new Bessemer City, North Carolina plants (Ellestad and Clarke, 1955; Ellestad and Leute, 1950).

The Bessemer City plant was thus designed to handle any grade of ore, including ore directly from the mine, and its initial operation in 1956 was with as-mined 1.0-1.5% Li<sub>2</sub>O (0.46-0.70% Li) ore. However, the process in the plant did not run as smoothly as in the pilot plant tests, and many changes had to be made. The conversion of the ore to  $\beta$  spodumene was not complete below about 1100°C, but the impurities in the ore would fuse at temperatures above about 1160°C and considerable lithium would become insoluble. This required very careful operational control of the feed rate and firing temperature. Also, the large amount of fines in the ore caused very high dust losses with the flue gas in the kiln, and the air flowing through the cooler following the kiln. Consequently, an indirect  $3 \times 61$  m rotary water cooled unit was used with a more modest air flow, as well as a fan and dust collector so that the cooling air could be used in the kiln's burner. This also further complicated the kiln and cooler control, and a two-stage scrubber was needed for the kiln's flue gas. The unprocessed ore required considerably more sulfuric acid in the acid roaster, which in turn required that the leach tank be lead and acid brick lined, and the agitator and pump be neoprene lined.

In the new plant, as a process improvement a slurry delivery system was installed for the soda ash instead of the air-slide conveyors used for most of the other solid phase handling. The run-of-mine ore process was utilized for 11 months, but at the end of that time it was felt that the plant capacity could be increased by 180% when operating on concentrates, so that became the permanent feed material, with very little loss in overall recovery (Andrews, 1958). Obviously their South Dakota 45– 50% flotation yield should have been greatly increased in North Carolina, and it is very likely that the low grade ore added impurities to the product.

In the mid 1960s LCA developed their Cherryville open pit spodumene mine, located about 10 km NE of the Foote Kings Mountain deposit (Figs. 1.35 and 1.36). The spodumene contained about 0.7% Li (1.5% Li<sub>2</sub>O), and was first ground to a small particle size and concentrated by flotation (initially by heavy media) to about 3% Li (6.5% Li<sub>2</sub>O; initially 3.73 or 8.0% Li<sub>2</sub>O). After being thickened and filtered the concentrate was sent to the nearby Bessemer City plant with an improved process (Fig. 1.87) and roasted in an 82 m (250 ft) long rotary kiln to  $1075-1150^{\circ}$ C. This changed the molecular structure of the spodumene from the  $\alpha$  to the  $\beta$  form, and increased its surface area by 30%. The converted ore was discharged from the



Figure 1.87 Flowsheet for the acid-roast conversion of spodumene into lithium carbonate (Wilkomirsky, 1998).

kiln, cooled and ground to a -100 mesh size in a ball mill, and mixed with a slight excess (over the stoichiometric amount of lithium) of 93% sulfuric acid. The acid mixture was then heated in a rotary kiln to  $200-250^{\circ}$ C ( $250-300^{\circ}$ C, Bach *et al.*, 1967), and the discharged material leached with water to form a fairly pure lithium sulfate solution. The slurry was neutralized with ground limestone, settled, and the underflow filtered in rotary vacuum filters, washed and discharged. The thickener overflow and filtrate were treated with small amounts of lime and then soda ash to remove the calcium and magnesium, and settled and re-filtered (Howling, 1963).

This purified solution was neutralized with sulfuric acid to a pH of 7–8, and then concentrated to 200-250 g/liter in a five-effect evaporator. The strong solution was treated to remove alumina, again filtered, and then a strong soda ash solution added to precipitate lithium carbonate at  $90-100^{\circ}$ C. The solids were settled, centrifuged, washed and dried as the main product. The remaining solution (thickener overflow and centrate) still contained about 15% of the original lithium, so it was cooled to  $0^{\circ}$ C to crystallize (as the decahydrate) the major impurity, sodium sulfate, and then recycled to the ore leach system. The sodium sulfate decahydrate was centrifuged and washed, and then evaporated to yield sodium sulfate as a by-product. The lithium carbonate was either sold as is, or formed into other products, such as being reacted with hydrated lime to produce lithium hydroxide (Stinson, 1981; Bach *et al.*, 1967; see the Roast, Acid Leach section below for more details on this process).

The processing of ore was discontinued in 1998, following a 3 year \$18 million expansion to 36 million lb/yr LCE in 1981, but the Bessemer City plant adjacent to the mine remained as FMC's major production facility for other lithium chemicals, including the metal and organo-lithium compounds. Some lithium chemicals are

made at Bayport, Texas, butyl lithium and lithium metal are also produced at Bromborough, Mersyside, UK (Lithium Corp. of Europe), and they had a 100 mt/yr battery grade lithium metal operation for lithium batteries as a joint venture (Asia Lithium Corp.) at Kagawa, Japan. In 1981 they produced over 70 lithium compounds at their Bessemer City plant (Lloyd, 1981), and in 1996 \$30 million was spent to modernize and further expand the plant (USGS, 1997).

# American Lithium Chemicals; Bikita Lepidolite

In the mid-1950s the government contracted with the three lithium producers (LCA, Foote and the American Potash & Chemical Co.) for the purchase of lithium hydroxide monohydrate in order to extract most of its <sup>6</sup>Li content. Since American Potash did not have an adequate supply from its brine processing operation (discussed above), they constructed a new plant near San Antonio, Texas, and from 1955 to 1960 imported lepidolite ore from Bikita, Southern Rhodesia (now Zimbabwe) as their raw material. One part of the ore was mixed with three parts of local limestone (one of the reasons for the plant's location) and the mixture wet ballmilled to a -200 mesh size. The slurry was filtered and the wet filter cake then heated in a 3.66 m (12 ft) diameter, 99 m (325 ft) long rotary kiln to about 911°C. The hot discharge was quenched, wet ball-milled again, and leached in a countercurrent mixer-settler system. The underflow slurry was filtered, washed and the solids discarded, while the overflow liquor and filtrate were treated to remove aluminum, pressure filtered and sent to a triple-effect evaporator. In it an impure lithium hydroxide monohydrate was crystallized, which was removed, centrifuged and then dissolved and recrystallized into a pure product. The remaining liquors were further processed and evaporated to first recover more lithium, and the residual concentrated solution sent to storage tanks.

After the contract period ended a new company, San Antonio Chemicals was formed to treat the end-liquors from the process by evaporating them much further to recover saleable caustic soda and an alkali crystalline mixture that contained, after reacting with soda ash: 70% K<sub>2</sub>CO<sub>3</sub>, 23% RbCO<sub>3</sub>, 3% Na<sub>2</sub>CO<sub>3</sub>, 2% Cs<sub>2</sub>CO<sub>3</sub> and 1% Li<sub>2</sub>CO<sub>3</sub>. Plans had been made to separate the mixture into pure products, but the operation was not deemed to be profitable, so the by-product was sold as a mixture and the plant closed (Bach *et al.*, 1967; Symons, 1961).

# Quebec Lithium Corp

Spodumene had been produced from the Preissac-Lacorne deposit by the Quebec Lithium Corp. from 1955 to 1959, supplying ore to LCA's North Carolina plant. Mining was conducted underground, with the initial area developed about 450 m in diameter from a 171 m deep shaft. After mining, the ore was concentrated by flotation (Kesler, 1960) in a mill near the shaft site with a capacity of 2000 mt/day of concentrates. This operation closed when LCA opened their own mine in North Carolina (Kunasz, 1994).

However, in 1960 mining started again to supply ore for the production of lithium carbonate or hydroxide, using the Quebec Government's Archambault-Oliver (1963) spodumene process. In it the ore was first ground to a small size and heated to about 1000°C to convert the spodumene to the  $\beta$  form. After cooling the ore was ground to a finer size, slurried with water and a recycle solution, as well as soda ash in slight excess (such as 10-30%) over the lithium content of the ore. The slurry (9-50 wt.%) was then pumped into an agitated pressure vessel at about 140-300°C (preferably 185-250°C; 50-600 psi) with an ore retention time of about 1 hr. This leached the lithium and converted it to lithium carbonate, while the spodumene remained as a zeolite-type insoluble aluminosilicate. The slurry from the pressure vessel and recycle lithium carbonate precipitation filtrate then went to a carbonation tower operating at 20°C, where carbon dioxide converted the insoluble lithium carbonate and lithium silicate into soluble lithium bicarbonate (0.65-1.8% Li greater than the concentration in the recycle solution). Sodium silicate was also converted into silica, and any soluble aluminum or iron silicates were precipitated. The slurry from the carbonation tower was next thickened and filtered, and the solids washed and discarded (they were claimed to be saleable as a zeolite). The overflow and filtrate were then heated to about 95°C which converted much of the bicarbonate to carbonate, and precipitated the desired lithium carbonate product. The remaining solution and the carbon dioxide formed from the bicarbonate were both recycled to the carbonation (leach) tower. Alternately, the slurry from the bicarbonate tower could be reacted with lime to produce a lithium hydroxide solution and insoluble calcium silicate. After filtering the solids the solution could be evaporated and lithium hydroxide monohydrate crystallized (Archambault and Olivier, 1963).

The process operated commercially for several years, and the production was increased fivefold since it started in 1961 to reach an annual rate of 2 million lb/yr of lithium carbonate. However, after the US Government's purchase of lithium ended the plant could only run at reduced levels because of the intense competition, and closed in 1965 (Flanagan, 1978; Anon., 1967).

# **Other Operations**

# Black Hills, South Dakota

In the early days of the lithium industry in the United States the most heavily developed mining area was in the Black Hills of South Dakota, where the Eta mine was the largest and most long-lived operation. However, there were also many smaller deposits such as those operated by LCA from 1941 to 1953, where they developed mining and mineral processing techniques that were useful for their subsequent North Carolina deposit. They used both open pit and underground large-scale, mechanized mining methods at their Edison, Mateen and Longview-Beecher deposits, with each being a cluster of small outcropping spodumene pegmatites. To process the ore they first used a 12 t/hr heavy media separator with the results shown in Table 1.35, along with a list of the densities of the minerals involved. The yield was reduced because some of the ore was partially altered, which lowered its

#### Table 1.35

Results of LCA's Heavy Media Separation of Spodumene Ore from the Black Hills, SD (Munson and Clarke, 1955)

Product	Weight, Pct	Lithia, Pct	Distribution, Pct	
Sink	7.1	5.36	47.4	
Float	66.5	0.16	13.4	
Fines	26.4	1.19	39.2	
Composite	100.0	0.80	100.0	
	Specific gravity, g/cc			
Spodumene	3.1			
Quartz	2.65			
Microline	2.56			
Albite	2.60			
Muscovite	2.76-3.1			
Apatite	3.2			
Tourmaline	3.0-3.2			
Triphylite	3.4-3.56			

Courtesy of Mining Engineering Magazine; reprinted with permission of Mining Engineering Magazine.

density. Also, only -3.8 cm to 6 mesh ore was used because the acicular cleavage of the spodumene made the smaller particles tend to float. Flotation was next tested, using preliminary desliming, caustic washing, and an anionic fatty acid collector (Fig. 1.88). Standard equipment was used, except for changes caused by the ore's rapid settling and abrasiveness. The results are shown in Table 1.36, and in addition to the spodumene clean mica and feldspar could also be produced by subsequent flotation steps with cationic collectors (Munson and Clarke, 1955).

China's Yichun Li–Ta–Nb mine in 1998 accounted for 90% of the country's recoverable lithium reserves, and its lepidolite was easily obtained as concentrates from the open pit mine's tantalum and niobium processing. However, initially there was only a small amount of lithium carbonate processed from this ore due to the high cost of the lime sintering process (see the American Potash and Chemical Co. Section, above). To reduce these costs a pressurized ammonium chloride leach process has been suggested by Xu *et al.* (1998). In this process lepidolite concentrates (Table 1.18) would be initially partially defluorinated by being heated to 850°C for 20 min, and then ground to a  $-74 \,\mu\text{m}$  (~200 mesh) size. The roasted concentrates would be cooled and made into a 25% aqueous slurry, with 3.5 mol of ammonium chloride being present per mole of total alkaline solids in the concentrate. The slurry would be heated under pressure at 240°C for 90 min, and then cooled, filtered and washed. The process was estimated to leach about 95% of the lithium, but the filtrate would also contain most of the other alkali metals in the ore. The filtrate would consequently be evaporated to crystallize the sodium, potassium,



**Figure 1.88** LCA's spodumene flotation process for Black Hills, South Dakota ore (Munson and Clarke, 1955, courtesy of Mining Engineering Magazine).

rubidium and cesium chlorides, and after they were separated, the high-lithium endliquor would be treated with lime and a small amount of soda ash to further remove impurities. Finally, a lithium carbonate product would be precipitated with ammonium carbonate or soda ash, and the filtrate recycled to the pressure reactor.

Lithium ore has been produced in *Brazil* since the early 1960s, with the initial mining company being Arquena de Minerios e Metals Ltd. They mined a number of lithium minerals (spodumene, petalite and lepidolite) in Aracuai and Itinga, and also supplied amblygonite initially, and then spodumene to Cia Brasileira de Litio. The latter company had built a plant at Aguas Verelhas, Minas Gerais province, and in 1991 produced about 1000 mt/yr of lithium hydroxide and 200 mt/yr of lithium carbonate, with some government assistance (US Bur. Mines, 1992; Afgouni and Silva Sa, 1978). By 2000 Brasileira de Litio was producing its own spodumene concentrates from their underground Cachoeira mine in Aracuai (USGS, 2001), and in 2002 Metallurg was planning to produce concentrates of a lithium-bearing feldspar for domestic use (Tamlin *et al.*, 2002). In *Portugal* the major lithium mining operation

#### Table 1.36

Data from LCA's Spodumene Flotation Process with Black Hills, SD Ore (Munson and Clarke, 1955)

Product	Weight, Pct	Lithia, Pct	Distribution	
No. 1 Partly Altered Spodumene Pe	gmatite			
Concentrate	15.9	4.92	63.5	
Slime	31.8	0.68	17.2	
Tail sand	52.3	0.46	19.3	
Composite	100.0	1.26	100.0	
Flotation efficiency, <sup>a</sup> 75.8 pct				
No. 2 Altered Spodumene Pegmatite	2			
Concentrate	13.1	5.13	57.1	
Slime	38.3	0.75	24.1	
Tail sand	48.6	0.46	18.8	
Composite	100.0	1.21	100.0	
Flotation efficiency, <sup>a</sup> 76.0 pct				
No. 3 Hard Rock with Altered Spod	umene			
Concentrate	14.2	3.94	66.4	
Slime	20.4	0.53	12.8	
Tail sand	65.5	0.27	21.0	
Composite	100.0	0.82	100.0	
Flotation efficiency, <sup>a</sup> 76.0 pct				

Courtesy of Mining Engineering Magazine.

<sup>a</sup>Lithia recovery from deslimed flotation feed.

in 2002 was the Soc. Minera de Pegmatite who sold unprocessed lepidolite ore. In *Namibia* the mining company in 1996 was Intermetmin Ltd who sold petalite and some lepidolite concentrates from their Rubicon mine (Harben and Edwards, 1998). In mid-1998 the company suddenly ceased operating after there had been a fairly rapid succession of owners and a \$2.6 million government loan (USGS, 2000). *North Korea* has produced limited quantities of low-grade spodumene (Tamlin *et al.*, 2002).

## Various Proposed Processes

A detailed laboratory study has been presented by Dresler *et al.* (1998) on the *Roast, Acid-Leach Process* that exactly follows the process previously used by the LCA (now FMC) at their North Carolina deposit. It is reviewed here because of the additional details that it supplies on this very effective spodumene process. Their ore was from Wekusko Lake, Manitoba, which as at LCA's deposit was an unzoned and low-grade (0.79% Li) spodumene ore, but with a very small crystal size. Electron micrographs showed that each of the minerals in the ore (Table 1.18) was present as discrete crystals, but the liberation size was quite small. Consequently, they ground the ore to a  $-212 \,\mu$ m ( $\sim 65 \,$ msh) size, and made into a 23% slurry to be agitated and conditioned with 2 kg of sodium hydroxide/mt of ore for 20 min.

#### Table 1.37

The Lithium Recovery and Li<sub>2</sub>O Content with Rougher and Successive Stages of Cleaner Flotation (Dresler *et al.*, 1998)

Li <sub>2</sub> O (wt.%)	Rougher	Cleaner stages			
	4.40	5.87	6.59	6.80	7.05
Li recovery (%)	96.9 LisCO <sub>2</sub> product impurities $ppm^a$	87.97	76.36	70.36	56.8
Al	24				
Ca	1630				
Fe	15				
K	9.9				
Mg	357				
Na	1007				
S	1323				
Si	209				
Р	15				

<sup>*a*</sup> Starting with 6.6% Li<sub>2</sub>O, 0.9% Fe, 0.2% Na and 0.15% K spodumene concentrates (from a 76% flotation recovery), roasted at 700–1200°C, 50% excess of sulfuric acid added and roasted at 250°C for 15 min (giving a 97% Li recovery after leaching). The product was precipitated with soda ash at a pH of 6.5–11 and 90°C, producing 98% Li<sub>2</sub>CO<sub>3</sub> (Wekusko Lake, Man., Canada spodumene).

This aided in the desliming of the  $-15 \,\mu$ m particles, and resulted in a 4–5% Li loss. The ore was then filtered and washed to remove the NaOH, and further conditioned with 400 g/mt of oleic acid for 3 min. Next, it was again made into a 23% slurry, the pH adjusted to 6.8 with sulfuric acid, Dowfroth 250 added and sent to a rougher flotation cell. The rougher product contained 4.40% Li<sub>2</sub>O (2.04% Li) and had a 96.9% yield, but needed to be cleaned in 2–4 successive flotation steps to reach an acceptable grade, reducing the recovery to 76% (without recycling, regrinding and scavenging flotation steps; Table 1.37). The final concentrate in these tests averaged 6.6% Li<sub>2</sub>O (3.07% Li), 0.9% Fe<sub>2</sub>O<sub>3</sub> (originally 0.94–1.64%), 0.2% Na and 0.15% K.

After the concentrate was filtered, washed and dried it was heated to  $1100^{\circ}C$  for 15 min to form  $\beta$ -spodumene. The roasted ore was then cooled, mildly crushed, a 50% excess of 93% sulfuric acid added and the mixture heated to 250°C for 15 min. The reacted mass was next cooled and then leached with water at room temperature. A 97% yield of lithium in the  $\beta$ -spodumene was obtained, and lime was added to the leach solution to neutralize the excess sulfuric acid, raise the pH to 6.5 and precipitate most of the iron, aluminum and sulfate. The slurry was filtered and the pH raised to 12.0 by the addition of a small amount of soda ash to precipitate the calcium. This mixture was filtered, some activated carbon added to remove organics, the solution was refiltered and the pH reduced to 7.0 with sulfuric acid. The clear solution was then evaporated to 200 g/liter lithium sulfate concentration. Finally, soda ash was added to the strong, hot solution to precipitate lithium carbonate. When filtered, washed and dried analysis showed >98% Li<sub>2</sub>CO<sub>3</sub>, with the impurities listed

in Table 1.37. The lower purity than LCA's product previously made by the same process may have been due to LCA's further process optimization, or the weathered ore (from an outcrop) used in these experiments.

Another of the established lithium ore processing methods was the Roast, Lime or Limestone Leach Process, combining an initial roast with limestone followed by water leaching, or roasting and then leaching with lime. There are a large number of patents and articles on the process, and it was commercially practiced by Foote, American Potash (both are discussed above) and others. Again, it is being further reviewed here to provide additional processing details. One of the early patents was by Nicholson (1946) who suggested grinding spodumene ore to -200 mesh, mixing it with ground limestone and roasting the mixture at 1120°C. The cooled ore would then be reground to -100 mesh and leached with water at 100°C. The roasting temperature was claimed to be low enough to prevent much of the silica and aluminum from reacting with the lime, an excess of limestone improved the lithium leach, and the process resulted in 80% lithium yield. Alternately, the ore could be ground to -100 to -200 mesh, roasted at  $1100-1150^{\circ}$ C to form  $\beta$ -spodumene, and then reacted with lime under 15-250 psi pressure at 194-204°C. After filtration, a 1-4% LiOH solution would be obtained that contained essentially no silica or aluminum. In either case the solution could be purified and lithium hydroxide crystallized, or soda ash added or the solution carbonated with carbon dioxide to form lithium carbonate, as desired.

Research on the *Big Whopper petalite deposit* in the Separation Rapids area of Ontario, Canada has reported a patented process that can produce >4.7% and 4.0% Li<sub>2</sub>O petalite products. It also separates 11.5-12% K<sub>2</sub>O with  $\ge 1.0\%$  Rb<sub>2</sub>O K-feldspar and  $\ge 10\%$  Na<sub>2</sub>O Na-feldspar, as well as concentrates of mica, spodumene, tantalum, cassiterite, garnet and perhaps silica. After crushing, grinding and desliming the spodumene would first be floated with fatty acids, and then petalite with a fatty amine and proprietary reagents. K-feldspar would next be floated, followed by Na-feldspar, and the heavy metals would be recovered by gravity separation at several points in the process (Pearse and Taylor, 2001).

A large number of other processes have been suggested to recover lithium from its ores (over 60 US patents on this subject were issued between 1900 and 1965). In the early days of the industry high-grade ores of lepidolite, amblygonite and zinnwaldite (a lithium-iron mica) were merely heated with *sulfuric or hydrochloric acid*, and the mixture then leached with water, but spodumene could not be leached in this manner. However, the leached solution contained most of the metals in the ore (particularly iron and aluminum), and this required a complex purification process (e.g., Vyas *et al.*, 1975; Gauguin *et al.*, 1961; Siegens and Roder, 1934). Later there were *base-exchange processes* such as roasting finely ground ore, or reacting slurries at high temperatures (100–300°C) with an excess of potassium, sodium, calcium or magnesium sulfate (as pressurized solutions or melts) to form a leachable residue. Lithium sulfate could then be crystallized and the reactant-salt purified, crystallized and recycled (e.g., Lindblad et al., 1943). This again was an expensive and difficult process. Several other process suggestions were based on adding calcium sulfate or calcium chloride to the ore and then roasting it with limestone or lime. Lithium hydroxide with lithium sulfate or chloride would be leached from the roasted mixture and then the separate components crystallized (e.g., Vyas et al., 1975 who roasted lepidolite with limestone and calcium chloride at 950°C. A water leach gave an 80% yield of 4-8% LiCl). In one version of this type of reaction the use of high enough temperatures to volatilize lithium chloride was suggested, and even operated on a small scale by Solvey in North Carolina before Foote purchased their deposit (Bach et al., 1967; Ellestad and Clarke, 1955). As a more novel process Goodenough and Stenger (1958) have suggested contacting very finely divided βspodumene (roasted spodumene ore) with much larger sized strong-cation ion exchange resins (in the hydrogen form) at about 100°C to leach lithium. The resin is then separated from the ore on screens, and lithium recovered by contacting (eluting) the resin with a strong acid. This also regenerates the resin for reuse.

In the early days of the lithium industry considerable attention was paid to the recovery of lithium from moderately *high-lithium Clay*. Lien (1985) noted that in laboratory tests some clays could have as high as an 80% lithium extraction with a simple sulfuric acid leach, but that most required a more complex process. In brief tests a roast at 750°C with two parts of clay and one part limestone, followed by a leach with an excess of 20% hydrochloric acid gave a 70% lithium yield. In a second series of tests five parts of clay, three parts of gypsum and three parts of limestone were roasted at 900°C. A water leach resulted in an 80% recovery of lithium sulfate. In the later process the raw materials were first ground together to a -100 mesh size and then formed into 6.5 mm pellets before being roasted. The pellets reduced the dust loss and increased the particles' contact with the flue gas.

The roasted pellets were next ground to a -100 mesh size and leached with water in an agitated container. The leach liquor contained 2.5–3 g/liter of lithium, considerable sodium and potassium sulfate, some gypsum (0.6 g/liter Ca) and other impurities. Soda ash (in recycle liquor) was added to the leach liquor, and the calcium carbonate that formed was removed by filtration. Then the solution was evaporated nearly to the sodium and potassium sulfate crystallization point (9– 10 g/liter Li, 120 g/liter of both Na<sub>2</sub>SO<sub>4</sub> and K<sub>2</sub>SO<sub>4</sub>), and the near-boiling solution reacted with soda ash to precipitate lithium carbonate. The remaining liquor still contained 4.0–4.5 g/liter of lithium carbonate (~1900–2100 ppm Li), and was then cooled to 0 to  $-3^{\circ}$ C to crystallize glauber salt and K<sub>2</sub>SO<sub>4</sub>, leaving 70 g/liter Na<sub>2</sub>SO<sub>4</sub> and 105 g/liter K<sub>2</sub>SO<sub>4</sub> in solution. After the crystallized salts were removed, the solution could have been further evaporated to crystallize more potassium sulfate, and the remaining solution recycled to the leach liquor evaporator (Fig. 1.89). As a second example of processing clay, Amer and Rashed (2002) processed  $-40 \,\mu$ m El-Fayoum (Egypt) bentonite in an autoclave at 250°C for 90 min with about 50%



**Figure 1.89** Flow sheet for the production of lithium carbonate from clay (Lien, 1985; reprinted form Lithium, Ed. R. O. Bach, Sec. 6, © 1985 by permission of John Wiley & Sons, Inc.).

sulfuric acid. They had fairly good lithium recoveries, but there was also considerable iron, aluminum and other impurities in the leach solution. The low grade of the clays (< 0.60% Li) and the complex processes would make them non-competitive with lithium brines or ore concentrates.

Lithium has also been recovered from *obsolete lithium-containing batteries*. In 1997 the US Navy awarded a \$10.5 million 4 year contract to ToxCo, Inc. to recycle 4400 lithium batteries of 1200 kg that had been used as a back-up power source for the now-abandoned missile silos. Their subsidiary LithChem International had developed a grinding-hand sorting process in 1994 for recycling the lithium, aluminum, nickel and stainless steel, and the batteries began to be processed in a plant at Trail, British Columbia, Canada in 1998. Originally, the lithium was to be sent to Pacific Lithium Ltd in New Zealand to be converted into high-grade lithium carbonate (USGS, 1997), but instead they converted it themselves into lithium carbonate and hydroxide in a plant at Baltimore, Ohio. In 1996 they had also purchased excess lithium hydroxide (containing mostly <sup>7</sup>Li) from the US Government, to be sold to the lithium grease market. In 1999 they purchased a fluorine products company, and began making lithium fluoride, lithium hexafluor-ophosphate and other battery electrolytes (USGS, 2000).

Many other proposals have been made to recover lithium from various sources, such as small *lithium batteries*. For instance, Tanaka and Shimamune, 2003 suggest dissolving the electrode materials, filtering, adjusting the pH to 7-10 to precipitate cobalt, and then recovering lithium. Alternately they propose electro-depositing the

dissolved cobalt, and then forming lithium carbonate after the remaining solution has been purified. An alternative procedure was suggested by Lee and Yang (2001) that involved heating, shredding, calcining, leaching and lithium precipitation. The batteries were heated to 500°C and then shredded, followed by the metal being removed and the remaining powder heated to 800°C for 2 hr. It would next be leached with 2 M sulfuric acid (or 1 M HNO<sub>3</sub>) containing 20% excess hydrogen peroxide as a reducing agent. More than 95% of both the cobalt and lithium were claimed to be solubilized, and could then be separately precipitated. To precipitate LiCoO<sub>2</sub> the Li/Co ratio in the solution was adjusted to 1.1, and then 1 M citric acid was added to form a lithium cobalt gel. It was removed and calcined at 950°C for 24 hr to produce a product with a surface area of 30 cm<sup>2</sup>/liter and a particle size of 20  $\mu$ m. Various recovery methods have also been proposed to recover the lithium used in other batteries, polymerization reactions, lithium zeolites, molten radioactive salt wastes and mixed lithium compounds, among others.

# Lithium Chemicals

A very wide variety of lithium chemicals are sold commercially, as illustrated by Chemetall's "Product Line" in 2002 listing 33 inorganic lithium chemicals and 36 organic lithium compounds, with others available upon request. Their major production facility for these chemicals is in Langelsheim, Germany (Fig. 1.90), and many of the inorganic chemicals are produced from lithium carbonate as the initial



Figure 1.90 Aerial view of Chemetall's Langelsheim, Germany Lithium Chemicals Plant (courtesy of Chemetall GmbH).

lithium source. However, even with this wide diversity, in 1993 about 50% of the total lithium usage was as (unconverted) lithium carbonate, and about 20% as lithium hydroxide.

To produce *lithium hydroxide* either moist lithium carbonate filter cake or the dry product was mixed with about a 5% excess of lime in sufficient recycle wash and make-up water to form a 0.3 lb/gal LiOH solution. The reaction was conducted at near the boiling point in an agitated tank, and the final slurry was then settled. The calcium carbonate solids that were formed were washed in a three-stage countercurrent decantation system, and either recalcined to form the lime used in the hydroxide reaction or discarded. The wash water was returned to the reactor, and the strong overflow liquor filtered and evaporated to a strength of about 1.39 lb/gal at 100°C to be sold as a liquid product, or evaporated further to continuously crystallize lithium hydroxide monohydrate. The concentrated liquor could also be cooled in a crystallizer to about 40°C to form the lithium hydroxide monohydrate. In either case the lithium hydroxide would be centrifuged and dried if an impure grade were desired, or redissolved at near the boiling point and recrystallized to form a purified product. In the latter case small amounts of lime and soda ash, followed by activated carbon would be added to remove impurities, and the slurry then filtered. The purified solution would be recrystallized, centrifuged and then dried (Hader et al., 1951). To produce anhydrous lithium hydroxide the monohydrate could be dehydrated in an inert gas (because of its strong tendency to react with carbon dioxide) dryer, possibly operating under vacuum, and often this product would be pelletized (Fig. 1.91). It has also been suggested by Bruhn et al. (1998) that lithium



Figure 1.91 A general flowsheet for converting lithium carbonate into lithium hydroxide monohydrate (Wilkomirsky, 1998).

hydroxide could be made by the electrolysis of lithium chloride solution in a membrane cell, similar to the production of sodium hydroxide.

Lithium chloride is made in a similar manner, starting with either lithium carbonate as wet filter cake or the dry product. It is reacted with a slight excess of hydrochloric acid (usually 31% HCl) in a rubber lined reactor with a rubber lined agitator, and sufficient reactants are added to bring the solution to a density of 1.180-1.195, or about 3 lb of lithium chloride/gal. Carbon dioxide that is formed is vented from the top of the reactor, perhaps aided by an air stream to control the vigor of its evolution. A small amount of barium chloride is then added to precipitate any sulfate that is present, sulfuric acid is added to remove the excess barium, and the solution is neutralized with lithium carbonate. This slurry is filtered, and the clear solution then evaporated to about 40% LiCl to make a saleable liquid product. To produce a dry product, since the solution's boiling point and solubility are so high, it must be further concentrated by direct contact with flue gas or in a directly fired pot. In the former case, a ceramic lined packed tower can be used with the solution flowing downward, and the flue gas rising to concentrate the solution to near its solidification point. It can then flow to a direct fired ceramic lined dryer to be solidified, with the exit flue gas going to the tower, or it can more easily be solidified on a chilled roll and then sent to a dryer. In either case the lithium chloride that is formed must finally be ground in a hammer mill and screened to the proper size (usually in sizes below 8 mesh), and packaged in air-tight containers (Fig. 1.92). Since lithium chloride is acidic and very corrosive, its solutions are usually neutralized with lithium hydroxide before being shipped or solidified. In both forms it is also very hygroscopic (Hader et al., 1951). Also, as previously discussed lithium chloride may be produced directly from either lithium ores or brines (Brown and Beckerman, 1990; Stenger, 1950).

*Lithium bromide* is made in a very similar manner to lithium chloride, except it is primarily sold as a 54-55% solution. Lithium carbonate is reacted with hydrobromic acid (usually as 45% HBr), with the pH of this solution adjusted to >7. It can also be produced by reacting lithium carbonate or hydroxide with bromine and a reducing agent. With either reaction, lithium hydroxide is then added until the solution has a 0.01 N hydroxide content. This solution is next evaporated to the 54-55% LiBr concentration, and then shipped in 55 gal steel drums. Most of the product is used in air conditioning systems, but a small amount of lithium bromide is also solidified in a manner similar to lithium chloride to be used in organic chemical reactions.

*Lithium hydride* is produced from lithium metal, with the metal first placed under high vacuum (<1 mm pressure) to remove most of the oxygen, nitrogen and moisture. It is then melted, and hydrogen slowly admitted until a pressure of about 5 psi is reached. The reaction is highly exothermic, so no additional heat is required, and the reaction must be carefully controlled. When the reaction is complete, lithium hydride is removed (sometimes dumped from a tapered wall reactor) and ground to size. *Lithium amide* is made by taking the crushed lithium hydride and heating it in an oven containing only ammonia. As the amide is formed hydrogen is evolved, and it is burned as it leaves a vent in the reactor. The amide is widely used in the



Figure 1.92 A typical flowsheet for the production of lithium chloride and lithium metal (after Hader *et al.*, 1951).

pharmaceutical industry (Hader *et al.*, 1951). *Lithium aluminum hydride* (LiAlH<sub>4</sub>) is produced by the reaction of lithium hydride with anhydrous aluminum chloride in dry diethyl ether. The solvent can be boiled-off to produce a dry powder, and the powder can be pelletized. Alternately, it can be sold as a solution, such as 20% in diethyl ether, 10% in tetrahydrofuran or 15% in tetrahydrofuran/toluene. It is used as a versatile reducing agent in many organic reactions (Deberitz, 1993).

*Lithium alkyls* such as *n-butyl lithium* can be prepared by several methods, with one being the reaction of the desired alkyl (or aryl) halide (usually the chloride) with finely dispersed lithium metal in a hydrocarbon solvent (Deberitz, 1993). There is some demand for *purified lithium carbonate* (99.999%), and in 1999 it was produced by various companies, including Lithium Metals Technologies, Inc. (Limtech) at the rate of 300 mt/yr. In 2000 they announced a proposed expansion to 1000 mt/yr (USGS, 2000).



**Figure 1.93** An example of an electrolytic cell used to produce metallic lithium (Averill and Olson, 1977; reprinted from Energy, Vol. 3, No. 3,©1978 with permission of Elsevier).

Lithium metal can be produced by the electrolysis of a molten lithium chloridepotassium chloride mixture, such as 45% LiCl/55% KCl (the range is 40-60% LiCl). At LCA the reduction has been conducted at 460°C, although 420°C was noted for Chemetall, by Deberitz (1993), and up to 500°C has been stated by others. In the simplest form of the cells a steel shell can act as the cathode for the electrolysis (Fig. 1.93). The cell may have exterior ceramic or other insulation, and steel rod supports on the bottom can also be used for cathodes. The anode is constructed of graphite which slowly sloughs-off, and since this corrosion increases the spacing between the anode and cathode, and thus the voltage, usually some means of adjusting this spacing is built into the equipment. The vessel may be heated by gas firing between the outer fire brick and the vessel's inner steel walls. Lithium metal accumulates at the cell's surface where it automatically flows from the cell or is skimmed-off with a ladle. The metal is poured into ingots and allowed to cool under an inert atmosphere. Lithium chloride used in the cell must be quite pure and dry, and the chlorine gas that is generated (about 5 kg/kg Li) is carefully routed away from the molten lithium (LCA, 1968).

Foote's original cell design used 2.54 cm thick steel plate in the form of a  $1.2 \times 1.8$  m box 0.91 m deep. It was placed in a fire box with the flame impinging on the bottom, and had four 20.3 cm diameter graphite anodes 1.8 m long, supported from the top and lowered into the cell as the lower section was corroded-off and the voltage increased. The cathode was the steel box, with a fan on top to exhaust the chlorine under a slight vacuum. The cell ran at about 6–6.5 V and 8600 A (a theoretical 80% energy efficiency) to produce 41 kg/day of lithium. The metal was

periodically withdrawn from the surface and cooled into ingots which were later remelted at 186°C and formed into the desired products. In case of fires lithium chloride was used to smother the flame (Hader *et al.*, 1951).

Initially the typical energy consumption for the electrolysis was about 46 kW hr/kg Li metal (not including the fuel requirement), or about 4000 A hr per kg of lithium at theoretically 3.76 V, with the actual range 6-12 V. The cell voltage is reduced at higher temperatures, but the graphite corrosion rate also increases. In more modern cells the terminal voltage is more typically 6.7-7.5 V, the current 30-60 kA, the current density 6-7 kA/m<sup>2</sup>, the power consumption 30-35 kW hr/kg Li and the LiCl consumption 6.2-6.4 kg/kg Li. The average energy efficiency of the cells was initially about 20-40%, but now it is considerably higher. In the modern cells wire gauze diaphragms may also separate the electrodes and help channel the reaction products (Deberitz, 1993; Cooper *et al.*, 1979; Averill and Olson, 1977).

To produce high-purity lithium metal the lithium and potassium chlorides in the melt must be exceptionally pure, and then the carbon, nitrogen and oxygen that inadvertently enter the metal must be reduced. The liquid metal can be first filtered at 200°C through sintered stainless steel with 5  $\mu$  pores to remove the calcium, carbides, nitrides and oxides of various metals. Also, the liquid lithium can be de-gassed under a high vacuum at temperatures of 20–670°C to remove gaseous impurities. "Getters" such as titanium, zirconium and aluminum can also be added before filtration to form various insoluble compounds. Liquid lithium with 20 ppm nitrogen and 150 ppm oxygen have been achieved (Averill and Olson, 1977; LCA, 1968).

A process utilizing the direct electrolysis of lithium carbonate has been developed by the Lithos Corp. (LithChem International), with claims that it could reduce the cost of lithium metal by 20%. In 1997 they announced the planned construction of a pilot plant to produce 20-30 mt/yr of lithium metal (USGS, 1997). Raymor Industries Inc. also were considering commercializing a process developed by McGill University for the direct electrolysis of spodumene to form lithium metal. They claimed a 25% cost savings for the metal (USGS, 2000). The electrolysis of lithium solutions to form a lithium amalgam with mercury, and then converting the amalgam in a fused salt cell to the metal has also been proposed (Cooper *et al.*, 1979).

Lithium metal is sold in the form of either ingots, rod, wire, shot, sheet, special shapes or dispersions in both a high-sodium and low-sodium grade (LCA, 1968). In addition to the companies previously noted producing lithium metal, it has also been made by duPont in the USA; Yahagi Iron Co in Nagoya, Japan; Metaux Speciaux SA in Plombieres St. Marcel, Savoie, France; China; the former USSR, and various other companies (US Bur. Mines, 1992).

# TOXICOLOGY

Most of the simple inorganic lithium compounds are only moderately toxic, with values such as: (1) lithium carbonate; lowest reported lethal dose, oral  $LD_{LO}$ 

(rat) = 710 mg/kg; lowest reported toxic dose, oral  $\text{TD}_{\text{LO}}$  (human) = 7 mg/kg; (2) lithium chloride; lethal for 50% of the test animals, oral  $\text{LD}_{50}$  (rat) = 751 mg/kg; oral  $\text{LD}_{50}$  (rabbit) = 850 mg/kg; intraperitoneal, ip  $\text{LD}_{50}$  (mouse) = 604 mg/kg (Sax, 1979). Concentrated or solid lithium hydroxide can cause caustic burns, and skin contact with lithium halides can result in skin dehydration. Organolithium compounds are often pyrophoric and require special handling (Kamienski *et al.*, 1993).

Lithium carbonate and citrate also have some very important medical uses within a very narrow range of concentrations, but there are toxic effects beyond that range. They are very effective in the treatment of manic-depressive illness, bipolar disorder, depression, suicide prevention and for a variety of other psychiatric and medical conditions. However, it often causes minor-to-serious side effects, with weight gain and impaired coordination being the most common reasons for patients not taking the drug. Mild hand tremor is the most common side effect, with fatigue and muscle weakness second most common. There can also be lithium intoxication, constant thirst, frequent urination, blurred thinking, short-term memory deficits and the more serious renal, thyroid (endocrine) and cardiovascular complications.

To be most effective, lithium should be taken at monthly intervals throughout the patients life and closely monitored for side effects, which usually immediately (or soon) disappear when treatment is stopped. Doses less than 0.6 mmol/liter of blood serum are usually not effective, and more than 1.5-2 mmol/liter can cause life-threatening reactions. However, the toxic effects usually wear-off fast (lithium is 50% excreted within 24–48 hr), or in severe cases can be treated by vomiting, emesis and close monitoring of the body's fluid electrolyte disturbances. Doses of 0.9-1.4 meq of Li/liter (~0.5 g/day lithium carbonate or citrate) are thus usually prescribed to alleviate the acute manic or other symptoms (Ezzell, 2003; Fieve and Peselow, 1985).

Lithium metal is classified as UN 1415 or "Dangerous when wet" and will react with water to form flammable hydrogen and lithium hydroxide that can be corrosive to the skin and eyes. Lithium metal is easily ignited in the air and once burning, requires special techniques to extinguish (Kamienski *et al.*, 1993).

# USES

Lithium has a wide variety of uses, and the ones that have consumed the largest volume of lithium have varied widely over time. In the early days of the industry, batteries were the largest purchaser of lithium (as metal or chemicals), then atom bombs, followed for many years by grease as the dominant customer. Then glass and ceramics followed for 10-15 years by aluminum reduction furnaces utilizing the most lithium, and from 1990 onwards the market has become very diversified, with
glass and ceramics again being the largest purchaser of lithium chemicals or ore concentrates. Table 1.38 lists examples of the percentage of total US lithium sales by various categories for the period 1951–2000, and the tonnage sold by category from 1975–1985. In the following sections each of the major categories of lithium sales will be separately reviewed.

## Glass

In the glass industry lithium helps to make many types of products, such as borosilicate glass, containers and bottles, fiberglass, flaconnage, internally nucleated glass ceramics, pharmaceutical glass, photochromic glass, soda lime glass, television tubes, thermal shock-resistant cookware (for freezer-to-oven use) and sealed-beam headlights. In preparing glass lithium has many benefits, such as listed in Table 1.39. It increases the melting rate by lowering the viscosity of the glass and reducing the melting temperature. Tests have indicated that as little as 0.1-0.2% Li can increase the productivity of the glass furnace 6-17% (Kingsnorth, 1988) without changing the batch cycle or reducing the glass quality (the density, refractive index, luster and transparency remain the same). The increase in the plants' capacity and production rate with lowered temperatures also increases the life of the furnace lining. Lithium reduces the seed (bubble) count (content) in the glass, lowers its thermal expansion coefficient and provides higher chemical durability to the finished product. Another important benefit is the potential reduction of calcium fluoride (CaF<sub>2</sub>) used as a flux, and the partial or total reaction with any fluorine that may be present in the glass (as well as some of the  $SO_2$  and  $NO_y$ ), thus reducing corrosion and the toxic emissions from the kiln. The lower viscosity and temperature of the glass also increases the speed of the glass-forming equipment as the glass leaves the furnace (Harben and Edwards, 1998). The use of a 0.1-0.5% Li<sub>2</sub>O addition enables container and bottle glass to produce lighter weight, thinner walled products (U.S. Bur. Mines, 1992).

As an example of the reduction in melting point of glass batches, glass containing either 15% Li<sub>2</sub>O, Na<sub>2</sub>O or K<sub>2</sub>O had melting temperatures of 500, 700 or 850°C, respectively. The viscosity reduction is exemplified by a lime–soda–silica glass where the viscosity was  $10^{12}$  poise at 566°C, and the same viscosity was obtained at 500, 544 and 533°C with glass containing an equal amount of lithium, sodium or potassium, respectively. An example of the improvement in the glass furnace capacity is illustrated by the replacement of 1% Na<sub>2</sub>O with 0.48% Li<sub>2</sub>O in zinc alabaster or opal glass causing the reduction of 8.4-10.5% in the melting time, and 18.2% and 23.0% in fining time (removing bubbles), respectively (Fishwick, 1974). Some of the typical amounts of lithium added to various types of glass are shown in Table 1.39.

Either lithium carbonate (or other lithium compounds) or lithium mineral concentrates may be used as the lithium source in many types of glass, with several of the pure ore melting points being: spodumene 1423°C, eucryptite 1397°C and

		6									
	2000	1997	1993	1992	1989	1985	1980	1969	1953	1951	
Glass and	18	18				24					
ceramics	32	20	34	38	46.2	14	32	_	39	31	
Aluminum		2	18	14	16.4	28	33	14	_	_	
Lubricants	18	11	11	11	20.1	17	20	20	47	40	
Batteries	9	7	7	7	4.8	1.5	0.5	_	2	10	
Organics	9	13	13	13	1.9	2.5	1.5	_	2	4	
Chemicals		13	13	13	9.0	7.5	6	_	_	_	
Air conditioners		4	4	4		3.0	4.5	7	2	5	
Other	14	12			1.6	2.5	2.5	—	8	10	
			B. Useage Pat	ttern (mt of	Li) (USGS,	, 1986)					
	1985	1984	1983	1982	1981	1980	1979	1978	1977	1976	1975
Glass and ceramics	730	910	550	410	820	770	820	820	1000	550	640
Aluminum	640	1000	730	550	910	820	910	1090	1360	1320	1270
Lubricants	550	730	410	360	450	500	450	450	450	360	320
Batteries	90	55	45	27	0	0	0	0	0	0	0
Other	270	220	270	470	730	640	730	730	910	320	400
Total	2270	2910	2000	1820	2910	2730	2910	3090	3730	2550	2630
										( <i>co</i> .	ntinues)

	C. Sa	les of various lithin	um chemicals,	million pounds of lithium carbonate equivalent <sup>a</sup>
	1992	1989	1974	
Li <sub>2</sub> CO <sub>3</sub>	48	47.7	35.0	
LiOH·H <sub>2</sub> O	11	20.1	11.4	
LiCl	_	_	1.9	
LiBr	_	_	2.2	
Other salts	_	3.0	_	
Metal	5	4.8	1.2	
n-Butyl lithium	3	1.9	1.2	
Ore concentrates	—	14.9		
Miscellaneous	—	1.5	0.1	
Total	68	79	53	
			D. Sale	s for aluminum <sup>a</sup>
1974	38% <sup>b</sup>	1550 mt Li		
1973	36	1270		
1972	32	960		
1971	30	860		
1970	26	640		
1969	14	270		
1968	9	180		

Table 1.38

(continued)

<sup>a</sup> Various sources.

<sup>b</sup> Percent of total lithium sold.

### (Kingsnorth, 1988)

The benefits of spodumene to glass making
A. Related to lithia content
Reduced melting temperature giving
Reduced energy consumption
Increased furnace refractory life
Reduced glass viscosity in the molten and semi-molten states, leading to
Increased "pull" (production) rates (8–15%)
Better glass forming characteristics, higher "pack"
Improved thermal shock resistance of finished product
Improved strength of glass product
Low cost
B. Mineral form

Reduced rejection rate (0-3%)

Improved glass quality with respect to fewer "seeds" and better thermal shock resistance The GGS alkali content (equivalent to 100 kg of soda per tonne on a molar basis) The GGS alumina content (170 kg of alumina per tonne of GGS)

Application	Method of addition	Typical % Li <sub>2</sub> O (% Li)
TV tubes		
Reduces melting temperatures	Spodumene concentrate	0.1 - 1.0
Improves forming properties Good finish to glass	Petalite and Li <sub>2</sub> CO <sub>3</sub>	(0.05-0.4674)
Pyro-ceramic ware		
Zero coefficient of expansion	Spodumene concentrate	0.4 - 4.0
Improves forming characteristics	Petalite and Li <sub>2</sub> CO <sub>3</sub>	(0.19 - 1.86)
Fibreglass		
Reduced viscosity, improves	Various minerals including	0.1 - 1.0
continuity of fibre production	spodumene concentrate	(0.05 - 0.46)
Safety glasses		
Improved Strength	Various minerals including 0.1 to 1.0 spodumene concentrate	(0.05–0.46)
Vacuum flasks, perfume bottles		
Ease of forming	Various minerals including	0.1 - 0.8
Good finish and strength	spodumene concentrate	(0.05 - 0.37)

Established lithia additions in the glass industry

This table appeared in Industrial Minerals No. 244, February 1988, p. 24. Published by Industrial Minerals Information, a division of Metal Bulletin plc, UK. ©Metal Bulletin plc, 2003.

petalite 1356°C. However, since the commercial products only contain 50–95% of the pure mineral, their actual melting points are somewhat lower than this because of forming eutectic compositions with their feldspar, quartz and mica impurities. Kaolin is often added with the lithium ores, and within limits the aluminum and silica in the ores can be beneficial to the glass. In some cases the ore concentrates further improve the glass by making it slightly more dense than when using lithium carbonate, and the surface hardness may be improved by as much as 20% (Fishwick, 1974). Different minerals may also have advantages over other types of ore for certain glasses, such as having a low degree of expansion upon being melted, or other beneficial physical properties.

Many of the lithium ore concentrates have a low enough iron (or other harmful impurity) content to be used directly in some glass formulations, while other glasses require a higher purity lithium source. In addition, some concentrates, such as highiron spodumene have a more restricted use, or require that the iron content be lowered. Some ores can even be used without being formed into higher-purity concentrates if the lithium content is high enough, and the iron is sufficiently low. An example of this is Glass Grade Spodumene from Australia with a minimum of 4.8% Li<sub>2</sub>O (2.23% Li) and a maximum 0.2% Fe<sub>2</sub>O<sub>3</sub> (usually 0.1%; Table 1.40). In 1988 the ore concentrates only cost about 40% of an equal amount of lithium in lithium carbonate and were quite suitable for uses such as container glass and pyroceram (Kingsnorth, 1988). However, since the lithium carbonate price reduction in 1998, the cost for the lithium in most ores became roughly the same as lithium carbonate, or only slightly lower (Table 1.41). About 50% of the total consumption of lithium in the glass, ceramics and aluminum industries prior to 1998 had been from ores, but since that time the reduced price of lithium carbonate has allowed it to replace some of these ore uses. Ores constituted about 15% of the total lithium market in 1993 (Flemming, 1993a,b), and in 2002 the estimated 3010 mt of contained lithium sold as ore (assuming an average grade of 4.0% Li<sub>2</sub>O) was about 19% of the total (Tamlin et al., 2002).

## Ceramics

Lithium is used in ceramics to make frits and glazes, porcelain enamels (for kitchenware and bathroom fixtures), sanitaryware, shock-resistant ceramics and porcelain tiles. Either alone or combined with other compatible materials such as feldspar and nepheline syenite it produces lower melting temperature mixtures with increased fluxing power. This improves the product quality, plant efficiency and productivity by lowering the firing (vitrification) temperature, reducing the firing cycle time and reducing the "soak" period. It also forms products with lower thermal expansion coefficients (and thus greater shock resistance), lower pyroplastic deformation, more brilliant body and glaze colors, greater glaze adherence and gloss, and more stain resistance. Again, both ores and lithium compounds can be used for this application, and with ores, petalite is usually preferred over spodumene because there is no volume,

			A. C	hemical analysis						
		Typical <sup>b</sup>		,	Tanco		Greenbushes <sup>a</sup>			
							Glass grade concer	trates		
	Glass grade	Ceramic grade	Low iron	Typical <sup>c</sup>	Specifications <sup>d</sup>	Typical	Spec.	Specifications		
Li <sub>2</sub> O	4.8-6.5	7.2	7.1*	7.25-7.30	7.25 ± 0.1	5.01	4.8*	7.5*		
Fe <sub>2</sub> O <sub>3</sub>	1.7	0.9* *	$0.1^{*}$ *	0.04 - 0.05	$0.06 \pm 0.01$	0.12	0.13* *	0.10* *		
K <sub>2</sub> O	0.5	0.27	0.14	0.10-0.20	0.30* *	0.17				
Na <sub>2</sub> O	0.3	0.30	0.35	0.15-0.20	0.36* *	0.09				
SiO <sub>2</sub>	63.0	64.1	64.8	_	-	75.91				
Al <sub>2</sub> O <sub>3</sub>	24.7	26.5	26.3	25-27	24.0*	17.88				
MgO	Trace	Trace	Trace	_	—	_				
CaO	Trace	Trace	Trace	_	_	_				
MnO <sub>2</sub>	_	_	_	0.02 - 0.04	$0.04^{*}$ *	_				
P <sub>2</sub> O <sub>5</sub>	_	_	_	0.15-0.25	0.27* *	0.06				
F	_	_	_	0.01 - 0.02	-	_				
LOI	—	—	_	—	—	0.29				
			В	. Particle size						
		Typical <sup>b</sup>		,	Tanco		Greenbushes <sup>a</sup>			
							Glass grade concen	trates		
	Glass grade	Ceramic grade	Low iron	Typical <sup>c</sup>	Specifications <sup>d</sup>	Typical	Spec.	Specifications		
+20 mesh (841 µm)		_	_	_	0* *	_	nil	_		
+28 mesh (600 µm)		_	_	_	trace	_		_		
$+48 \text{ mesh} (300 \text{ \mum})$		_	_	_	1.0* *	_		_		
+65  mesh (212  µm)		_	_	_		_	95.0*	5.0* *		
$+200 \text{ mesh} (75 \mu m)$		_	_	_	50.0*	_	(105 µm)	60.0*		
(15 µm)					2010		(105 µm)	50.0		

\* minimum; \*\* maximum. *a* Flemming (1993b). *b* Dresler *et al.* (1998). <sup>c</sup> Burt *et al.* (1988). *d* Vanstone *et al.* (2002).

Examples of Lithium Ore Concentrates' Prices, \$/mt (Saller and O'Driscoll, 2000; Tamlin et al., 2002)

	Li <sub>2</sub> O (%)	1998-2000	1992 <sup>a</sup>	1988 <sup>b</sup>	\$/kg Li <sub>2</sub> O, Dec. 2000
Spodumene concentrates <sup>c</sup>	6.9-7.5	330-395	385	340	5.12-6.53
Glass grade spodumene <sup>c</sup>	4.8 - 5.0	215-230	175	160	4.48-4.60
Petalite <sup>d</sup>	3.5-4.6	180-270	230	175	4.18-6.28
Lithium carbonate <sup>e</sup>	40.4	$2068 - 2600^{f}$	4320	3410	5.12-6.53

<sup>a</sup> Kunasz (1994).

<sup>b</sup> Kingsnorth (1988).

<sup>c</sup> Basis, seller's US warehouse.

<sup>*d*</sup> Basis, f.o.b. Durban, Australia.

<sup>e</sup> Basis, bags or drums, delivered in the US.

<sup>f</sup> During January 1999 \$1760–2200 mt<sup>-1</sup>; for year 1999 \$1760–2030 mt<sup>-1</sup>; McCracken and Sheth (1999).

structure or phase change as it is heated, as there is with spodumene. Since lepidolite is the only ore that contains both fluorine and rubidium (which are also good fluxes), it has been preferred in some ceramics and glass applications, but it is no longer as plentiful as the other ores (Anon., 2001; LCA, 1968).

Glazes and enamels utilize lithium to the same extent as ceramics, and for the same reasons. An enamel is a glass-like coating bonded to a metal (steel, cast iron, aluminum, etc.) by fusion at temperatures above about 550°C, causing the metal and the enamel to permanently combine. This gives a product the hardness of glass and the strength of the base metal. Lithium imparts desirable properties to both enamels and glazes, and can allow their use without first forming frits, to make aventurine, corrosion-resistant ("glass") coatings for steel tanks, in high-voltage porcelain because of its low coefficient of expansion, leadless glazes for dinner ware, opaque and crystalline glazes, and to produce whiteware.

Lithium  $(0.5-4\% \text{ Li}_2\text{O})$  is also one of the ingredients that has allowed the production of glass-ceramics, in which glass is forced to crystallize into very fine crystals that form a dense, strong, heat-resistant ceramic material. Examples of this are Pyroceram cookware, stove tops and the nose-cone tiles on space vehicles. The increased surface hardness, and the very low thermal expansion between -73 and about 600°C (e.g.,  $0 \pm 0.05 \times 10^{-6}$ /°C from 0 to 50°C; Deberitz, 1993) has been beneficial for optical glass and large telescope mirrors (Fig. 1.94). Lithium is also used in various applications where improved resistance to sudden temperature change, and a lower coefficient of expansion is important such as some optical glass ceramics or refractories (e.g., specialty brick for furnace linings). There are also many other ceramic-type applications for lithium, such as lithium ferrites (Li<sub>0.5</sub>Fe<sub>2.5</sub>O<sub>4</sub>), which maintain their magnetic properties up to 680°C. Lithium borosilicates can be used as



**Figure 1.94** Examples of glass ceramics for telescopes; left, support; right, 8.6 m diameter (45 mt) mirror (Deberitz, 1993, courtesy of Schott Glass, Mainz/Germany and Chemetall GmbH).

the binder for high-temperature fuzed alumina grinding wheels or refractories, and lithium can act as an accelerator for cement, in mullite formation, to densify magnesium oxide, to make piezoelectric materials or self-curing paints, and many other widely differing uses (Fishwick, 1974). In some cases the lithium is first reacted with other desired metals to form compounds such as cobaltites, manganites, etc., before being added to the ceramic or glaze mixture.

## Aluminum

Lithium is employed in the aluminum industry in amounts such as 1-3% LiF in the bath, or ratios such as 2 kg lithium carbonate/mt of aluminum (the range is usually 1.5–4 kg; Nicholson, 1977). It lowers the electric reduction cells' (Fig. 1.95) temperature ( $\sim 970^{\circ}$ C; the alumina-cryolite melting point), raises the electrical conductivity of the cell (thus lowering the required overvoltage, which reduces the power requirement), and it reduces the fluorine emissions from the electrolytic cells by 25-50% (Table 1.42). Lithium carbonate reacts with the cryolite (Na<sub>3</sub>AlF<sub>6</sub>) "solvent" in the cell to form lithium fluoride, which has a very high fluxing ability, electrical conductivity and low volatility. Lithium is most beneficial for older plants, where it can reduce the energy costs by 5-10%, and bring the cell efficiency up to 90–95%. However, most of the lithium was purchased to initially charge the cells, and the replacement amount is now comparatively small. Also, with the more modern cells the energy efficiency is already at 90-93%, and lithium can only add 1-3% greater efficiency. Thus, the usage of lithium is now less cost effective, and has slowly declined to the point that in the US in 2000 only about 50% of the aluminum mills employed lithium in their cells (Jarvis, 2000).

Lithium alloys with aluminum also find some use, since lithium can impart some very useful properties to the aluminum. For example, one lithium alloy retains a high strength to 204°C in contrast to conventional alloys only being effective to  $121-177^{\circ}$ C. The alloy also increases the modulus of elasticity by about 8%, which



**Figure 1.95** Aluminum electrolytic cells (Deberitz, 1993, courtesy of Hamberger Aluminum Werke (HAW) and Chemetall GmbH).

could facilitate an aircraft flying at speeds of 1300-1600 mph (Kesler, 1960). At the maximum of 2-3%, lithium could reduce the density of an aluminum alloy by 7-10% and raise the modulus of elasticity by 10-15% (Deberitz, 1993). However, lithium also increases the cost of the aluminum alloy by 3-6 fold, and since about 70% of an airplane's weight was aluminum (before the advent of composite fiber and plastic materials) this price increase was prohibitive. There were also some problems with corrosion and fatigue cracking. In addition, lithium is extremely difficult to introduce into alloys, since lithium floats on the molten aluminum, immediately burns, and very little enters the aluminum. Either expensive and hard to manage fluxes must cover the molten aluminum or the lithium must be added to the molten aluminum as it leaves the furnace. In both cases an inert gas must cover the metal ingots as they cool, and water-quenching can not be used. Finally,

Advantages and Disadvantages of Using Lithium in the Aluminum Industry (Nicholson, 1977)

#### Advantages of Lithium

Lowers the melting temperature of the molten electrolyte.

Increases the cell's electrical conductivity.

The above items lower the electricity consumption and other costs, or increase the production for the same unit costs.

Reduces the fluorine emissions.

Reduces the consumption of anode carbons.

Reduces the consumption of cryolite.

#### Disadvantages

The operational control is more difficult and more dependent upon instruments.

Lithium decreases the purity of the aluminum because of the presence of some lithium and perhaps iron in the product.

It sometimes causes difficulties in casting intricate shaped products due to the formation of heavier oxide layers.

Scrap aluminum with lithium is undesirable.

the reprocessing of lithium alloy scrap is quite difficult and hazardous, which adds to the cost of fabrication (Anon., 1998).

A considerable amount of research has been done on lithium–aluminum alloys because of their favorable properties, and in satellite and space applications, plus some of the more demanding aircraft parts, various uses have developed. An example of this is NASA's "Super Light Weight Tanks" for the liquid hydrogen fuel and liquid oxygen used in space shuttle launches. Twenty-five of the tanks were ordered in 1996 to be 47 m long, have an 8.4 m diameter and weigh 26.3 mt (Fig. 1.96). They were made from 5.9 mt ingots that were then rolled into various metal thicknesses for different sections of the tanks. The lithium alloy contained from 0.3-0.5% silver, and had excellent cryogenic properties, strength up to 100,000 psi, and good fatigue, fracture toughness and corrosion resistance. Each 1% Li in the alloy lowered the density of the metal by 3%, and raised the elastic modulus (stiffness) by almost 5%. Another alloy without silver (that was cheaper and 4-5% lighter) was used in the F-16 airplanes for a critical aft bulkhead because of its superior fatigue resistance (Anon., 1998).

## Batteries

Lithium is the most electropositive of all metals, with a standard electrode potential of 3.045 V compared with 2.71 V for sodium and 0.76 for zinc. It thus can generate the greatest electrical power per unit weight or volume of any metal, but it is also extremely reactive and thus potentially dangerous. Special designs and applications





**Figure 1.96** Super light weight aluminum–lithium alloy fuel tank for space shuttle launches (Anon., 1998; reprinted by permission of Light Metal Age).

are thus required, and they have perhaps been best achieved with rechargeable batteries (Fig. 1.97). In 2001 there were four common types of rechargeable batteries: lithium-ion (52% of the market), lithium polymer (4%), nickel metal hydride (27%), and nickel–cadmium (17%). Amongst these, the lithium-ion and lithium polymer batteries could store and deliver the most energy per unit of space, with the commercial batteries producing 3.7 V, or about three times more than the nickel cadmium or nickel metal hydride batteries. They were lighter, had a longer shelf life, and did not have the "memory effect" problem (the amount of energy stored was decreased if the battery was charged before having been fully discharged) of the nickel batteries. They were thus preferred for the newer generations of high-performance applications such as in mobile phones, camcorders, laptop computers,



**Figure 1.97** The general structure of a rechargeable lithium battery (Abraham, 1985; reprinted from Lithium, Ed. R. O. Bach, Sec. 11, ©1985 by permission of John Wiley & Sons, Inc.).

hand-held portable electronic devices, tracking systems, home repair or construction tools, and military and medical devices, even though they were more expensive than some other batteries (Cairns, 2002).

Initially rechargeable lithium batteries used a non-aqueous electrolyte and lithium plates as the anode, allowing lithium to dissolve during use, and to be replated onto the anode when being recharged. This was a conventional oxidationreduction battery with a very high voltage output and capacity, but it required expensive control circuitry to prevent fires or explosions if the batteries overheated (its cell reaction is exothermic). Since lithium metal is very reactive the cells could also be dangerous if water entered the battery, or under certain other conditions. This problem could be somewhat improved if the lithium was alloyed with copper or tin, since the anodes' crystal structure would still not change much during the charge–recharge cycles, and the alloys' lower reactivity could lessen the need for expensive safety switches in the batteries. Even with its problems these batteries were extensively used for large, special situations such as stand-by power sources for missile silos. It is possible that new technology such as the lithium polymer battery design of Fig. 1.98, or the use of a thin-film, polymer-ceramic composite electrolyte may re-establish the use of lithium metal anode batteries (Alper, 2002). An even earlier use of lithium was in the old Edison nickel-iron batteries where lithium salts in the electrolyte provided high conductivity, and prevented freezing down to  $-40^{\circ}$ C.

Uses 193



**Figure 1.98** The lithium polymer battery concept (D'Amico, 1996; reprinted with permission from Chemical Week, March 20, 1996, Chemical Week Associates).

The new rechargeable lithium ion batteries totally eliminated the above problems since they do not contain metallic lithium, and instead obtain their power from the concentration difference of lithium ions traveling between the electrodes. The anodes are ultrapure graphite impregnated with lithium ions, one lithium ion to six carbon atoms, and the cathodes are extremely porous lithium–cobalt, nickel or manganese oxides (such as LiCoO<sub>2</sub>). In 2002 polyvinylidene fluoride (PVDF) was used as a binder for both the cathode and anode in 80-90% of the batteries, with a minimum of structural rearrangement to the electrodes during use. The lithium electrolyte has to be non-aqueous, and was usually lithium hexafluorophosphate (LiPF<sub>6</sub>) dissolved in ethylene carbonate, but some LiMnO<sub>2</sub> or other paste compositions were also employed. They allow the lithium ions to transfer fairly freely (but unfortunately with some resistance) between the electrodes during the charge or discharge cycles.

The graphite, or sheets of carbon anodes were loaded with lithium ions, which flow from the anode as the battery discharges, and form a complex with the metal oxide at the cathode. The lithium ions are forced back to the anode when the battery is being charged. The carbon in the anode (negative electrode) was subject to improvements, since it could be flammable, it was slow in taking up the lithium ions, and if lithium became plated onto the electrode it was dangerous. For the positive electrode cobalt oxide was most commonly used with lithium oxide, but cobalt had the problems of being very expensive, a toxic material, and it could overheat upon charging. Manganese oxide ( $Mn_xO_y$ ) with lithium oxide was potentially a much better cathode, but it had a relatively short life in the past because it looses its structural integrity as it is being used. The addition of some chromium extended its life considerably. Iron (or other transition metal) phosphates (such as LiFePO<sub>4</sub>) when doped with aluminum, niobium, zirconium or magnesium had also been proposed as cathodes that were less expensive, less toxic, and had a good electrical conductivity (Anon., 2002; Cairns, 2002; Tullo, 2002; Alper, 2002; Anon., 2000; D'Amico, 1996).

In the lithium polymer batteries a conductive lithium polymer replaced the inorganic-filled organic liquid electrolytes (Fig. 1.98), enabling the use of light-weight plastic cases of various shapes (which could even be flexible) in place of the conventional metal cases. The polymers that could be used in the batteries include PVDF copolymers and fluoropolymers, all of which could help hold the battery together as well as separate the positive and negative electrodes, even at high voltages. Since the lithium polymer technology would replace liquid electrolytes it was claimed to be safer than lithium ion batteries since it could not overheat or explode under some circumstances. It had been expected that these batteries would offer the greatest growth potential for the future, but up to 2002 that had not yet occurred.

Lithium's 47% fraction of the \$3.61 billion rechargeable battery market in 1999s had become 52% and \$3 billion by itself in 2002. Sony Corp. had about 33% of this market, and Sanyo Electric Company 23% in 2000. Sony originally developed the lithium-ion batteries, but in 2000 began converting much of its manufacturing capacity to the more profitable lithium polymer type. Sanyo Electric also produced about 32% of the nickel–cadmium, and 46% of the nickel hydride batteries in 2000 (Lerner, 2001; Jarvis, 2000). Considerable research has been conducted on rechargeable lithium batteries for automobiles, but by 2002 there were still major safety and construction problems.

Non-rechargeable lithium batteries have been used for many years in large electric storage units by the military, and later small batteries (Fig. 1.99) began to be used in calculators, cameras, watches, microcomputers, electronic games, small appliances, toys and other applications where a long life and/or high current density are desired (for instance, pacemakers could last 8-10 years compared to 1 year for conventional batteries). They provide higher energy per unit wight than any other metal, with the electrochemical equivalence of lithium being 3.86 Ahr/g, compared to 1.16 for sodium, 0.5 for silver, 0.48 for cadmium, 0.28 for zinc and 0.26 for lead (Deberitz, 1993). They are more expensive than ordinary alkaline batteries, but have a much higher performance, and in 2002 were the dominant battery type in some countries such as Japan. For certain applications lithium sulfur dioxide batteries have been made with a 10 year life with no reduction in performance, and were included in the Galileo spacecraft for it anticipated 6 year trip to explore the planet Jupiter (U.S. Bur. Mines, 1992). Some of the other cathode materials that have been used with lithium, and their practical energy density as mW/cm<sup>3</sup> are thionyl chloride (SOCl<sub>2</sub>) 700-800; copper oxide (CuO) 550-650; manganese dioxide (MnO<sub>2</sub>) 500-580; carbon fluorine (CF<sub>x</sub>) 450-500; sulfur dioxide (SiO<sub>2</sub>) 400-450; bismuth oxide (Bi<sub>2</sub>O<sub>3</sub>), pyrite (FeS<sub>2</sub>), and lead bismuthate (PbBi<sub>2</sub>O<sub>5</sub>) 350–500. They operate at voltages from 1.5–3.9 V (Deberitz, 1993).





**Figure 1.99** Sketches of various types of lithium batteries (Marincic, 1985; reprinted from Lithium, Ed. R. O. Bach, Sec. 9, ©1985 by permission of John Wiley & Sons, Inc.).

There is a considerable literature on lithium batteries as both technical articles and patents. This includes many on the construction of the batteries themselves, and on each of the battery components. The use of lithium in batteries is not a large market for lithium (about 7% of the total in 2001), but the consumption has grown at an annual rate of 15% from the late 1980s to 2002. Even though the batteries utilize lithium and other metal oxide cathodes, and lithium in the electrolyte, the amount per battery is very small. However, growth should continue, and if the use of batteries in automobiles developed this could greatly increase the sales of lithium in this market. It is also expected that the market will increase when these batteries are produced in standard sizes (as has occurred with the non-rechargeable batteries). In the past many of them have been custom made for each application (Tullo, 2002; Saller and O'Driscoll, 2000; Schmitt, 1999).

## Grease

Considerable lithium hydroxide is used in making greases, and the demand grew at a steady 2% per year for the period 1980–2000. It is used in military, industrial, automotive, aircraft and marine applications, and 55% of all industrial greases contained lithium in 1981 and 60% in 1993. Lithium hydroxide (about 1 pound per 45-100 pounds of grease) is reacted with 12-hydroxy-stearic or other fatty acids, since lithium stearate forms a matrix or sponge-like gel lubricant where the lithium attaches to the metal, and the long-chain multi-hydroxyl end of the stearate molecule extends outward in the form of interlocking spirals to hold the petroleum lubricant and cushion the wearing surface. Mixtures containing 5-10% of the lithium soap are an excellent lubricant for bearing surfaces, since they are almost totally water insoluble, and stable in consistency over a range of shear and temperatures from -55 to +200°C. The gel holds a high volume of oil, resists oxidation and hardening, and if liquefied will reform as a stable grease upon being cooled. Because of these qualities the grease is used over a wide variety of demanding service applications (Deberitz, 1993; Lloyd, 1981).

## Other Uses

### Lithium Metal

The market for lithium metal was growing at about 5% per year in the early 2000s because of its use in making organic chemicals, batteries, alloying and other applications. It is made by the electrolysis of a molten lithium chloride-potassium chloride mixture in specially designed cells, with the molten metal collecting in the top and being periodically withdrawn and cooled as ingots. Most of the ingots are then converted into a wide variety of other shapes and forms, including thin sheets, pellets, powder, etc., for each specific use. Lithium is quite soft (about 0.6 on the Mohs scale), and it can be scratched and cut with a fingernail. Some lithium is alloyed into lithium-aluminum (containing up to 7.5% Li) and lithium-magnesium (up to 13% Li) metals because of their low density (Li weighs 33, Mg 108 and Al 162 lb/ft<sup>3</sup>), high-temperature performance, and improved elasticity, tensile strength and corrosion resistance. Many of the alloys commonly contain 2-3% lithium, and have been used in commercial or military aircraft where they have the potential of reducing the aircraft's weight by as much as 10%. Their usage, however, has been limited by their high cost, the introduction of competitive high-performance fiberplastic compositions, and the difficulty in forming the alloys because of lithium's extreme reactivity (Jarvis, 2000; U.S. Bur. Mines 1992; Anon., 1981). Other uses for lithium metal include its ability in very small amounts to remove oxygen or other gases from many molten metals, its use as an intermediate or raw material in the production of organic compounds, or in batteries, as noted elsewhere in this chapter (Kunasz, 1994).

### Air Conditioning

In air conditioning lithium bromide or chloride are used in the dehumidification of air and other gases because of the very low vapor pressure of their solutions, their low viscosity, high stability, non-toxic properties and low corrosivity (the solutions are made neutral or basic, and corrosion inhibitors are usually added). Both lithium bromide and chloride are extremely hygroscopic, and can dry air or other gases down to a very low moisture content. As they remove water from the air the gas is also cooled (because of water's high heat of vaporization), thus providing a refrigeration effect. Their solutions (such as 54-55% LiBr) are used in very large building air conditioning systems (Fig. 1.100) to remove the desired amount of moisture from the air, and then heat or further cool the air to its most comfortable temperature. A slip stream of the lithium solution is continuously removed from the absorber and evaporated back to its most effective concentration. Small amounts of lithium hydroxide, and perhaps lithium chromate, nitrate or molybdate are added to the recirculating brine as corrosion inhibitors (Deberitz, 1993). The solutions can also be used for absorption-evaporation (chilling), refrigeration or heat-pump systems. Solid lithium chloride or bromide can be used to dry organic liquids, as a desiccant, and in dehumidification applications (Llovd, 1981).

## **Organic Compounds**

Many organic compounds containing lithium have found important industrial, medical and other uses. In these compounds the lithium is usually bonded directly to the carbon atom, and because of the covalent nature of these bonds many of the compounds are liquids or low-melting solids. They are soluble in many hydrocarbons, as well as often being soluble in polar organic solvents such as ethers, alcohols or related materials. Many of the organolithium compounds are reactive with oxygen or air, and they may ignite spontaneously in the pure state or concentrated solutions (Kamienski et al., 1997). The most prominent organolithium compound is normal butyl lithium, which is used as a stereospecific catalyst in the polymerization of butadiene, isoprene and styrene for the production of synthetic rubber, and for the production of other polymers or elastomers. These rubbers are especially useful since the lithium catalysts develop an unusual microstructure in the product that provides various superior physical properties. For example, it can catalyze copolymers of styrene and butadiene for automobile tires that are relatively abrasion-resistant, and thermoplastic rubbers that do not require later vulcanization. The catalysts can also form "castable" elastomers and liquid polymers with a wide range of molecular weights for solventless surface coatings and other uses. Normal butyllithium can be shipped in various forms, including frequently as a 15-20% solution in hexane in special containers (Fig. 1.101).

Other organic lithium compounds are catalysts for polyethylene, polyethyleneterephthalate films and fibers, and various other polymers. Some lithium-organics



**Figure 1.100** An example of a large lithium bromide air conditioning unit (Deberitz, 1993, courtesy of York International GmbH and Chemetall GmbH).



Figure 1.101 Typical container for organolithium compounds (Deberitz, 1993, courtesy of Chemetall GmbH).

(as is lithium metal) are useful in many Grignard-type reactions, and find applications in the pharmaceutical, agricultural and other fields. For example, lithium is used in the preparation of vitamin A, antihistamines, carotenes, some steroids, synthetic penicillins, tranquilizers and many other compounds. Usually lithium metal, carbonate or chloride are used as the starting materials in the synthesis of these organic lithium compounds (Jarvis, 2000; Kamienski *et al.*, 1997; U.S. Bur. Mines, 1992; Lloyd, 1981; LCA, 1968).

## Miscellaneous Uses

One of the main application of lithium carbonate is as the starting chemical to produce a wide variety of other lithium compounds. An example of this is the production of lithium hypochlorite, which finds fairly extensive use in *bleaches, sanitizers and swimming pool conditioners*. It is used in many large-scale laundries as a bleach, and in swimming pools it provides excellent sanitation (by killing bacteria) while minimizing algae growth without the problems of a calcium residue. It sold at the rate of three million pounds per year in 1981, and was one of five major markets for lithium. As a *medicine*, lithium carbonate or acetate has been used since 1949 as a very effective treatment for manic depression (approved by the US Food and Drug Administration in 1969). It is used in very small quantities (e.g.,  $600-900 \text{ mg/day } \text{Li}_2\text{CO}_3$ ), since too much can be toxic and have serious side-effects, and too little will not be effective, hence it is closely monitored in the blood stream of patients (see the Toxicology section). The reason for its effectiveness has remained a mystery, as is the case with some of its modern competitive medicines.

### 200 Part 1 Lithium

In *metallurgy* lithium metal is used to degas (scavenge, or remove gas from) aluminum, copper, bronze (this results in these three purified metals having a higher electrical conductivity), germanium, lead, silicon, thorium and other metals. It may also be used as an alloying ingredient for various metals besides aluminum and magnesium. Lithium chloride is an additive (or flux) to salt baths for dip brazing and open hearth soldering, and lithium carbonate, chloride or fluoride are used as scavengers and cleaners since they form low-melting slags with many metal oxides. They are also used for flux welding powders and welding rod coatings for difficult to weld metals (i.e., steel alloys and aluminum) where they reduce the flux's melting temperature and surface tension, and increase the metal's wetability. In the building industry lithium carbonate is an additive for quick-setting cement, special adhesives and quick-curing floor tile. Lithium hydroxide can reduce the premature deterioration of concrete because of its stronger reactivity with silica (USGS, 1997). The electronics industry uses high purity lithium carbonate and other salts for solid ion conductors and monocrystals. Dyes and pigments employ lithium hydroxide as an additive for dyestuffs to increase their solubility, and for increasing the brilliance of specific pigments. Other lithium salts are used with acid dyes. Lithium chromate can be used as a *corrosion inhibitor* for aggressive aqueous solutions in absorption refrigerators, and lithium hydride as a gas source for air-sea rescue kits. Pellets of lithium hydroxide or carbonate have been used extensively as adsorbents for carbon dioxide in submarines, space vehicles, and portable life-support systems (Fig. 1.102). A mixture of lithium nitrate and potassium nitrate is useful in forming hot melts to vulcanize various plastics such as EPDM, EPT or EPM (Deberitz, 1993).

At some time in the future molten lithium might also be used as a hightemperature heat transfer fluid (it melts at a low temperature [180.5°C], but does not boil until 1347°C). Large amounts of lithium hydroxide monohydrate were purchased from 1953–1960 by the US Government for its <sup>6</sup>Li content, which was converted into tritium for hydrogen bombs. About 75% of the <sup>6</sup>Li was extracted, and the remaining 42,000 mt of lithium hydroxide has been slowly sold for industrial use. The <sup>6</sup>Li also has a high neutron cross section, so it could be useful for reactor shielding, or perhaps much later for nuclear fusion reactors if they were ever to be found feasible. Lithium carbonate or other lithium salts might also have a potential application for molten fuel cells if they were to become popular for powering electric cars or other uses (Saller and O'Driscoll, 2000; Kamienski *et al.*, 1993; U.S. Bur. Mines 1992; Lloyd, 1981; LCA, 1968).

## INDUSTRY STATISTICS

The production of lithium carbonate prior to 1966 came primarily from the processing of lithium minerals (since the 1960s primarily spodumene and petalite), but by 1998 this source became phased out except in China (using lepidolite) and



**Figure 1.102** An example of an air purification, carbon dioxide removal unit (Deberitz, 1993, courtesy of Dornier GmbH and Chemetall GmbH).

Russia, and now most of the world's supply is extracted from various brine deposits. This source, combined with solar evaporation is much more economical, and thus has allowed the price of lithium carbonate to be considerably lowered. Initially the two US producers, FMC (formerly LCA) and Chemetall GmbH (formerly Foote Minerals and then Cyprus Foote) purchased lithium minerals or concentrates, and later mined spodumene from their large North Carolina deposits (Johnson, 1958) and converted it into lithium carbonate. Then in 1966 Foote began to recover lithium from their Clayton Valley (Silver Peak), Nevada brine deposit, and in 1984 from brine in the Salar de Atacama (with the final processing being done near Antofgasta), Chile. In 1997 SQM (originally Sociedad Quimica y Minera de Chile, then SOM Chemicals, and now SOM S.A.) also began to produce lithium carbonate from the Salar de Atacama, and cut the selling price of lithium carbonate roughly in half to gain market share. In 1997 FMC opened a similar operation at the Salar de Hombre Muerto in Argentina, but closed it the next year and contracted to purchase the less expensive SQM product. They continued to produce some lithium chloride from this facility. The Cyprus Foote and FMC spodumene operations were both officially closed by 1998.

The lithium carbonate production capacity of various companies over the years to 2002 is listed in Table 1.43. The primary producers in 2002 were: (1) SQM Chemicals, with a capacity of 22,000 mt/yr of LCE from the Salar de Atacama in Chile. (2) Chemetall GmbH (who acquired the former Cyprus Foote Minerals) with 16,000 mt/yr capacity on the Salar de Atacama, and 5700 mt/yr from Clayton Valley in Nevada. And (3) FMC with 20,000 mt/yr of idle capacity from the Salar de Hombre Muerto, Argentina (Jarvis, 2000; Saller and O'Driscoll, 2000).

During the 1990s there were three major producers of lithium ore concentrates, as indicated by production capacity in Table 1.43 of various mines or countries for several years preceding 2002. Sons of Gwalia owned the largest high-grade lithium (spodumene) pegmatite deposit that was in production during this period, with sufficient capacity to supply all of the world's needs. The other two large producers of lithium concentrates were Tanco in Canada and Bikita in Zimbabwe. The amount of production from China and Russia was unknown but probably substantial, and there was relatively small production in Brazil and Portugal (and until 1998 from Namibia). Two other deposits in Canada, and one in Finland were considering production in 2002, but they faced the problems of heavy competition in an over supplied market. The estimated Western world consumption of these lithium ore concentrates (or raw ore) in the year 2000 was 158,200 mt, with an equivalent lithium carbonate content of about 18,200 mt. The specifications for various ore concentrates is listed in Table 1.40, and the list prices for spodumen and petalite concentrates for 1992–2000 are given in Table 1.41 (Anon., 2001).

The estimated lithium content of lithium carbonate (or chloride) or concentrates (or ore) produced from their own deposits by various countries is listed in Table 1.44. There is a wide variability in the accuracy of these numbers, as some are merely educated guesses, and different sources have estimated quite different numbers. Also, in some years an estimated grade of the lithium ore or concentrates that were sold was made to establish the tonnage of lithium. Even with these inaccuracies, the numbers should be approximately correct, and they indicate that the total market for lithium has grown at about 3-5% per year from 1960-2000. The estimated US import, export, consumption, production, and the list price of lithium carbonate for a number of years is listed in Table 1.45A, as tabulated by the US Geological Survey or Bureau of Mines. The US ore production from 1880-1954 is listed in Table 1.45B. Table 1.46 lists examples of product specifications for lithium carbonate from several producers.

# CHEMISTRY, PHASE DATA, PHYSICAL PROPERTIES

Lithium is the third element in the periodic chart, and the lightest of all metals  $(0.534 \text{ g/cc} \text{ at } 20^{\circ}\text{C})$ . Its atomic weight varies widely with the source from

A. Estimated Lithium Production Capacity, m Lithium carbonate operations from brine	t/yr Li (Various Reported Values)
Salar de Alacama	1094 1096 1100 1000 1260 1001 2220 1006 2560 2000 2720 2002 2010
Chemetall (Foole)	1984–1986, 1190; 1990, 1300; 1991, 2220; 1996, 2300; 2000, 2730; 2002, 3010
SQM S.A.	1997–1998, 5580; 1999, 3410; 2000, 5700; 2002, 4130
Salar de Hombre Muerto	$1000, 27(0, (2100^4), L^2(20, 1/20), L^2(21))$
FMC	1998, 3760 (2120) as $L_{12}CO_3$ ; 1630 as $L_1C1$ )
Clayton Valley (Silver Peak)	1055 1100 1071 1520 1001 1100 1000 1005 1005 1000 1000
Chemetall (Foote)	1966, 1190; 1971, 1530°; 1981, 1190; 1990, 1200; 1996–2000, 1030
Searles Lake"	1945–1978, 169
Pacific lithium <sup>c</sup>	1996, 564
Raymor industries <sup>d</sup>	1999, 56; 2001 <sup><i>c</i></sup> , 188
$Li_2CO_3$ from ores	
Cia Brasileria de Lithio, Brazil	1991, 307; 1996, 188
China	1986, 680; 1992, 1280; 1996, 1500; 2000, 1880
Russia	1986, 1020; 1990, 1350; 1996, 2250
Chemetall (Kings Mountain) <sup>a</sup>	1978, 1020; 1984, 1360; 1991, 1540
FMC (Bessemer City) <sup><math>a</math></sup>	1977, 1100; 1978, 1300; 1981, 2370; 1985, 3070; 1997, 3330
American Potash <sup>a</sup>	1956–1963, 1100
Quebec Lithium <sup><i>a</i></sup>	1961, 34; 1964, 170
Gwalia <sup>a</sup>	1996–1997, 213

(continues)

B. Lithium Ore Concentrates as 1	000 mt of concentrates/yr
Gwalia (Greenbushes)	2002, 150 ( $80^{\circ}$ ); 2001, 150 ( $67.6^{\circ}$ ); 2000, 70 <sup>e</sup> ; 1999, 150 ( $65^{\circ}$ ); 1996, 55 <sup>e</sup> ; 1994, 53 <sup>e</sup> ; 1991, 40 <sup>e</sup> ; 1984, 13.2 <sup>e</sup> ;
	$1983, 5^{e}$
Bikita	2002, 55 (41 <sup>e</sup> ); 2001, 55 (49.6 <sup>e</sup> ); 2000, 50 (37.5 <sup>e</sup> ); 1999, 50 (37.7 <sup>e</sup> ); 1996, 25 <sup>e</sup> ; 1994, 23.5 <sup>e</sup> ; 1993, 18 <sup>e</sup> ; 1992, 12 <sup>e</sup> ;
	$1991, 9.1^e; 1990, 19^e; 1986, 27^e$
Tanco	2002, 21 (15 <sup>e</sup> ); 2001, 21 (15 <sup>e</sup> ); 2000 (18 <sup>e</sup> ); 1999, 21 (19 <sup>e</sup> ); 1996, 22 <sup>e</sup> ; 1994, 20 <sup>e</sup> ; 1992, 18.5 <sup>e</sup> ; 1990, 12 <sup>e</sup> ; 1991, 12 <sup>e</sup> ;
	$1986, 15^{e}$
Russia	$2000, 75; 1996, 63 (40^{e}); 1992, 45^{e}; 1991, 50^{e}; 1990, 55^{e}$
China	$2000, 63; 1996, 50 (16^{e}); 1990, 16^{e}$
Brazil	2002, 6 est.(6 <sup>e</sup> ); 2000, 6 (6 <sup>e</sup> ); 1999, combined with Namibia est. 2 (2 <sup>e</sup> ); 1990–1996, 1.6 <sup>e</sup> ; 1989, 2.1 <sup>e</sup> ; 1986, 39
Namibia <sup>a</sup>	1996, 2 (2.5 <sup><i>e</i></sup> ); 1994, 1.9 <sup><i>e</i></sup> ; 1993, 0.7 <sup><i>e</i></sup> ; 1990–1992, 1.2 <sup><i>e</i></sup> ; 1956, 8.4 <sup><i>e</i></sup>
Portugal	2002 and all other small operators est. 25 ( $20^{e}$ ); 1999, 12.5; 1996, $8^{e}$ ; 1992–1995, $9^{e}$ ; 1991, $10^{e}$ ; 1990, $7.6^{e}$
Quebec Lithium <sup>a</sup>	1955–1959, 2/day
South Dakota <sup>a</sup>	1942, 5 <sup>e</sup> ; LCA 1953, 12 t/hr
Searles Lake <sup><i>a</i></sup> (licons)	1976, 0.765; 1943, 0.522; 1938, 0.200

Table 1.43 (continued)

Conversion ratios: MM lbs/yr lce/11.7346 = mt/yr Li; mt/yr lce/ 5.3228 = mt/yr Li; st/yr lce/5.8673 = mt/yr Li; mt/yr LiCl/ 6.1077 = mt/yr Li.

<sup>*a*</sup> No longer operating. <sup>*b*</sup> Possible for a 2 year period.

<sup>c</sup> Proposed, but not built.

<sup>d</sup> Converts commercial lithium carbonate to 99.999% purity.

<sup>e</sup> Reported sales, not capacity.

204

Part 1

Lithium

Estimated World Production of Lithium Salts or Concentrates, mt of Contained Li (USGS, 2002-1958)

	2002	2001	2000	1999	1998	1997	1996	1995 <sup>a</sup>	
Argentina	200	200	200	200	1130	8	8	8	
Australia	2000	2400	2400	2200	2100	2800	3700	3700	
Brazil	220	—	30	32	32	32	32	32	
Canada	700	700	710	710	700	1600	690	660	
Chile	6800	6757	6732	5674	5326	4551	2700	2600	
China	2400	2440	2440	2346	2440	2909	2800	2800	
Namibia	_	_	—	—	28	40	48	50	
Portugal	200	140	140	140	160	180	160	180	
Russia	2000	2000	2000	2000	2000	2000	800	800	
$US^{b}$	700	700	700	700	700	1070	800	800	
Zimbabwe	700	700	740	700	1000	700	500	520	
Total	15,900	15,700	16,400	15,100	15,400	15,170	11,800	12,150	
	1994 <sup>a</sup>	1993 <sup>a</sup>	1992 <sup>a</sup>	1991 <sup>a</sup>	1990 <sup>a</sup>	1989 <sup>a</sup>	1988 <sup>a</sup>	1987 <sup>a</sup>	
Argentina	8	6	12	6	1	2	2	1	
Australia	3570	3560	2860	2720	2690	1200	900	360	
Brazil	32	32	32	22	22	32	29	36	
Canada	630	590	580	380	380	420	420	140	
Chile	2550	2550	2660	2100	2230	1430	1390	910	
China	2800	2710	2710	2710	2630	260	260	_	
Namibia	36	14	22	23	24	37	44	64	
Portugal	180	180	180	200	150	400	310	14	
Russia	800	800	900	1000	1100	2200	2200	1640	
$US^b$	900	900	900	900	900	1800	_	_	
Zimbabwe	470	360	260	180	380	300	_	—	
Total	11,480	11,700	11,100	10,200	10,500	8081 <sup>c</sup>	—	—	
	1986 <sup>a</sup>	1985	1984	1983	1982	1981	1980	1978	
Argentina	1	1	1	4	3	1	2	18	
Australia	357	363	217	81	3	1		_	
Brazil	33	20	19	43	56	57	58	140	
Canada	16	10	3	—	_	—		_	
Chile	837	847	396	—	_	—		_	
China	835	835	835	555	420	390	390	270	
Namibia	23	36	16	14	19	23	—	230	
Portugal		1	7	4	6	6	7	720	
Russia	1350	1350	1350	1350	1350	1250	1250	1300	
$US^b$	3805	4200	4992	4450	3468	4922	4792	5300	
Zimbabwe	534	530	425	357	194	111	405	900	
Total <sup>c</sup>	7791	8193	8261	6858	5519	6761	6905	8100	

(continues)

				(continu	ued)				
	1975	1974	1973	1972	1971	1970	1967	1966	
Argentina	9	9	9	4.5	4.5	4.5	7.2	17.2	
Australia	27	27	36	36	36	18	26.1	8.7	
Brazil	136	136	136	136	109	54	_	189	
Canada	91	82	82	36	36	36	3.1	5.9	
Mozambique	9	18	18	18	9	9	_	2.1	
Namibia	272	272	227	227	227	91	51.8	66.5	
Portugal	9	36	36	23	18	9	_	_	
Russia	1814	1633	1633	1361	1361	635	—	—	
$US^b$	4990	4717	4536	4082	3629	3266	_	_	
Zimbabwe	862	862	862	862	862	862	—	1590	
Total <sup>c</sup>	6260	6169	5697	5352	4808	4627	_	—	
	1962	1961	1960	1958	1957	1956	1955	1954	1953
Canada <sup>d</sup>	10	63	42	59	77	71	2	_	
Namibia <sup>d</sup>	33	68	_	269	202	169	256	219	311
$\mathrm{US}^d$	_	_	_	_	_	_	_	937	675
Zimbabwe <sup>d</sup>	710	670	1492	2560	3278	3096	2465	1622	589
Total <sup>c</sup>	_	_	_	2906	3656	3462	2843	3083	1911
	1952	1951	1950						
Canada <sup>d</sup>	_	_	_						
Namibia <sup>d</sup>	294	355	294						
$\mathrm{US}^d$	387	322	230						
Zimbabwe <sup>d</sup>	44	79	6						
Total <sup>c</sup>	844	834	596						

Table 1.44

<sup>a</sup> Factored from the 1996 reports of ore tonnage and tons of lithium equivalent.

<sup>b</sup> Estimated based upon the assumed lithium carbonate production from Clayton Valley.

<sup>c</sup> Sum of the listed entries.

<sup>d</sup> Estimated from the tons of lithium ore shipped, and assuming a 2.73% Li content for the ore.

6.94-6.99, but was averaged as 6.941 in 1995 (Coplen, 1997). Its atomic radius is 0.68 Å, while its hydrated ionic radius is 3.40 Å, and the hydration energy 519 kJ/ mol. At high pressure lithium changes to a strange cubic structure not seen in any element. At about 39 GPa it begins to change from its high-pressure, face-centered cubic form to a rhombohedral form. Then at about 45 GPa it converts to a new cubic structure with a large unit cell containing 16 atoms and a reduced conductivity. This form appears to be stable to 165 GPa (Anon., 2000). A comparison of some of the

## Table 1.45A

	2000	1999	1998	1997	1996	1995	1994	1993	1992	1991
Imports for consumption Exports Consumption <sup>a</sup> Price $(\$/k_0)^b$	2880 1310 2800	2640 1330 2800	2590 1400 2800	975 2200 2800	884 2310 2700	1140 1900 2600	851 1700 2500	810 1700 2300	770 2100 2300	590 2400 2600
Li <sub>2</sub> CO <sub>3</sub>	4.47	4.47	4.47	4.47	4.34	4.34	4.41	4.21	4.32	4.21
LiOH·H <sub>2</sub> O Employment <sup>a</sup>	5.74 100	5.74 100	5.74 100	5.74 230	5.51 230	5.62 230	5.62 230	5.71 230	5.53	5.37
	1990	1989	1988	1987	1986	1985	1984	1983	1982	1981
Imports for consumption	790	630	1000	820	640	373	82	32	27	136
Exports	2600	2600	2300	1800	1800	2270	2840	2360	2080	2360
Consumption <sup>a</sup>	2700	2700	2700	2450	2360	2270	2910	2000	1920	2910
Production <sup><math>c</math></sup> Price ( $\$/kg$ ) <sup><math>b</math></sup>	—	—	—	—	3805	4200	4992	4450	3468	4922
Li <sub>2</sub> CO <sub>3</sub>				3.41	3.30	3.39	3.29	3.26	3.10	3.10
LiOH·H <sub>2</sub> O				4.33	4.25	3.39	4.25	4.25	4.05	4.05
Employment <sup>a</sup>				230	265	275	300	300		
	1980	1979	1978	1977	1976	1975	1974	1973	1972	1971
Imports	82	45	9	9	9	82	64	120	27	120
Exports	2270	2180	1820	1640	1450	820	930	836	582	590
Consumption	4153	3871	3900	3483	2540	2620	3420	2870	2440	2340
Government stock pile	0	0	5	230	149	55	391	142	_	_
Production <sup>d</sup> Price $(\$/kg)^b$	6341	6006	5711	5114	3834	3301	3874	3590	3005	2820
Li <sub>2</sub> CO <sub>3</sub>	2.66	2.55	2.24	1.94	1.83	1.69	1.72	1.21	1.14	1.12
LiOH·H <sub>2</sub> O	3.52	3.37	3.08	2.57	2.79	2.60	1.91	1.39	1.39	1.34

Recent United States Lithium Statistics, mt of contained Li (USGS, 1900-2002)

(continues) 207

				Table 1 (contin	<b>.45A</b> wed)					
	1970	1969	1968	1967	1966	1965	1964	1963	1962	1961
Imports Exports	45 890	36 890		875 <sup>e</sup>	232 <sup>e</sup>	281 <sup>e</sup>	676 <sup>e</sup>	562 <sup>e</sup>		
Consumption Production <sup>c</sup> Price (\$/kg) <sup>b</sup>	1595 2440	1146 2000	1520 <sup><i>a</i></sup> 3700	—	—	2500	—	—	—	1500
Li <sub>2</sub> CO <sub>3</sub> LiOH·H <sub>2</sub> O	1.14 1.30	1.01 1.21	0.99 1.19	0.95 1.21	1.01 1.21	1.08 1.19	1.14 1.23	1.17 1.19	1.17 1.19	
	1960	1959	1958	1957	1956	1955	1954	2001	2002	
Imports Exports Consumption <sup>a</sup> Production <sup>c</sup> Price (\$/kg) <sup>b</sup> Li <sub>2</sub> CO <sub>3</sub> LiOH·H <sub>2</sub> O	1600 1.26 1.59	 1.47 1.59	3000 1.47 1.41	 1.47 1.50	— 1.96 1.76	 2.16 1.94	760 907	1990 1480 1400 4.47 5.74	1920 1620 1100	

<sup>a</sup>Estimated.

<sup>b</sup> Year end listed price (perhaps up to 50% higher than the actual price). <sup>c</sup> Anstett *et al.*, 1990.

<sup>*d*</sup> Stinson (1981) 1974–1980; others sum of above items.

<sup>e</sup> Assuming 2.76% Li ore.

				,	Table 1.45	В						
The Ea	arly Producti	on of Lithiu	n Ores in the United	d States, mt o	of ore/yr (J	ohnson, 19	58 through	1920; U.S	. Bur. Min	ies, 1925–	1955, 1958)	
1880–1900 Ve: (mt Li <sup>a</sup> : 1899 4	ry small; 190 0, 1901 130,	00–1917 Avg 1910 40, 19	g.527; 1918–1920 A 021 140)	Avg.5,900;								
1920	1925	1926	1927	1928	1930	1933	1934	1935	1936	1937	1938	1939
10,611	2849	3357	3786	4173	1630	457	652	1047	1126	1231	809	1805
(1000 mt Li <sup>a</sup>		—	—	420	120	—	_	_	—	_	—	—)
1940	1941	1942	1943	1944	1945	1946	1947	1948	1949	1950	1951	
1824	3476	5811	7398	12,083	2,219	2781	2214	3521	4389	8442	11,780	
(210 mt Li <sup>a</sup>		_	_	550	_		210	_	_	330	—)	
1952	1953	1954	1955 →									
14,162	24,712	34,319	Not published									

<sup>a</sup>O'Neill et al. (1968).

MINSAL (SQM) lithium carbonate specifications							
	Powder	Granular					
Li <sub>2</sub> CO <sub>3</sub>	99% min.	99% min.					
Cl	0.02% max.	0.02% max.					
Na	0.12% max.	0.18% max.					
К	3 ppm max.	3 ppm max.					
Ca	0.04% max	0.068% max.					
Mg	0.011% max	0.025% max.					
SO <sub>4</sub>	0.1% max.	0.1% max.					
В	10 ppm max.	10 ppm. max.					
Fe <sub>2</sub> O <sub>3</sub>	0.003% max.	0.003% max.					
H <sub>2</sub> O	0.20% max.	0.2% max.					
LOI	0.7% max.	0.8% max.					
Insolubles	0.02% max.	0.02% max.					

# Typical Lithium Product Specifications (Harben and Edwards, 1997)

Specifications and typical analyses for commercial lithium compounds  $^{a}% =\left( \left( x,y\right) \right) \left( x,y\right) \right) \left( \left( x,y\right) \right) \left( x,y\right) \right) \left( x,y\right) \left( x,y\right) \left( x,y\right) \right) \left( x,y\right) \left( x,y\right) \left( x,y\right) \right) \left( x,y\right) \left( x,y\right) \left( x,y\right) \left( x,y\right) \right) \left( x,y\right) \left( x,y\right) \left( x,y\right) \left( x,y\right) \left( x,y\right) \left( x,y\right) \right) \left( x,y\right) \left($ 

		Impurities (%)
	Maximum	Typical production sample
Lithium carbonate, technical		
Moisture (loss at 110°C)	0.50	0.01
$SO_{4}^{2-}$	0.50	0.35
CaO	0.05	0.04
$Na_2O + K_2O$	0.30	0.18
Fe <sub>2</sub> O <sub>2</sub>	0.005	0.003
Heavy metals	0.002	< 0.001
Chlorides	0.01	< 0.005
Lithium hydroxide monohydrate <sup>b</sup>		
Cl <sup>-</sup>	0.003	0.002
NaOH	0.05	0.01
$SO_4^{2-}$	0.05	0.02
Fe <sub>2</sub> O <sub>3</sub>	0.005	0.001
CaO	0.08	0.05
CO <sub>2</sub>	0.20	0.10
Insolubles	0.01	0.005
Lithium, chloride, technical		
Moisture	1.00	0.60
Alkalinity as Li <sub>2</sub> CO <sub>3</sub>	0.10	0.06
$SO_{3}^{2-}$	0.01	0.01
CaCl <sub>2</sub>	0.15	0.10
NaCl + KCl	0.50	0.40
Fe <sub>2</sub> O <sub>3</sub>	0.006	0.003
BaCl <sub>2</sub>	0.01	0.01
Insolubles	0.025	0.01

(continues)

Table	1	16
I able	1	.40

(continued)

	Specifications and typical analyses for commercial lithiur	m compounds (cont.)
Lithium metal		
Na		0.6
K		0.01
Ca		0.02
N		0.06
Fe		0.001

<sup>a</sup> Kingsnorth, 1988.

<sup>b</sup> Specified minimum assay as LiOH, 53.5%: typical production sample. 55.0%.

#### Table 1.47A

Various Chemical and Thermodynamic Properties of Lithium: A. Lithium Metal<sup>1</sup> (CAS No. 7439-93-2)

Molecular weight: <sup>6</sup>Li 6.015; <sup>7</sup>Li 7.016, Average 6.941 Abundance: 7.42% (<sup>6</sup>Li), 92.58% (<sup>7</sup>Li) Atomic number 3 Electron shells: 1S<sup>2</sup> 2S<sup>1</sup> Atomic radius 1.52 (or 1.55) Å; Mg is 1.60 Å Radius: Ionic 0.68 Å (or 0.60, Mg is 0.65); Hydrated 3.40 Å Covalent 1.23 Å Atomic volume 13.10 cm<sup>3</sup>/mol Density at 20°C 0.534 (33.3lb/ft<sup>3</sup>; Mg = 108; Al =  $162lb/ft^3$ ) Crystal structure: body centered cubic Melting point 180.54°C Boiling point 1342°C(1336–1347°C) Hardness 0.6 on Mohs scale ("it cuts like cheese") Oxidation potential (Standard electrode potential;  $\text{Li} \rightarrow \text{Li}^+$ ) - 3.045 V (3.038); 0.259 g/amp hr Specific heat 0.8 cal/g/°C; at 25°C 0.849 cal/g; 3.56 J/g °C liquid at M.P. 1.05 cal/g/°C Thermal conductivity 84.8 J/m sec °C Electrical resistivity at 20°C 9.446  $\times$  10<sup>-6</sup>; 0°C 8.55 µohm-cm Vapor pressures (°C, mm Hg): 702, 0.49; 802, 2.82; 902, 12.1; 1002, 41.0; 1052, 70.5; 1077, 91.0 Heat of fusion 103.2 cal/g; 3.00(or 2.93) kJ/mol Heat of vaporization 5024 cal/g; 145.92 (135; 148) kJ/mol Ionization energy (kJ/mol): 1st 520.2; 2nd 7394.4, 3rd 11,814.6 Hydrated energy 519 kJ/mol Coefficient of expansion  $6 \times 10^{-5}$  cm/cm/°C; Elastic modulus 11 GPa; Rigidity 4.2 GPa; Youngs modulus 4.9 GPa Thermonuclear reaction:  ${}^{6}\text{Li} + {}^{1}\text{n} \rightarrow {}^{3}\text{T} + {}^{4}\text{He} \quad 4.78 \text{ MeV}$  $^{7}\text{Li} + {}^{1}\text{n} \rightarrow {}^{3}\text{T} + {}^{4}\text{He} - 2.47 \text{ MeV}$ Neutron cross-section 71 barns; <sup>6</sup>Li 945, <sup>7</sup>Li 0.033 barns Characteristic spectrum lines: Red 6708 Å: Orange 6103 Å

<sup>a</sup> Data from Anstett et al., 1990; Lloyd, 1981; LCA, 1968 and others.

### 212 Part 1 Lithium

Table 1.47b
Lithium Solutions
Activity coefficient at various total ionic concentration (mol), 25°C: 0.975 at 0.001 m; 0.965 at 0.002 m 0.948 at 0.005 m; 0.929 at 0.01 m; 0.907 at 0.02 m; 0.87 at 0.05 m; 0.835 at 0.1 m; 0.80 at 0.2 m
Low-solubility salts: carbonate, phosphate, fluoride and oxalate; High-solubility of halides (except
fluoride) in water and polar organic solvents; High solubility of lithium-alkyls in hydrocarbons.

Table 1 47D

Its chemical behavior is often very similar to magnesium.

Solubility in NH<sub>3</sub> 10.17%; Reduction potential in NH<sub>3</sub> - 2.99

#### Table 1.47C

Comparative Atomic, Ionic and Molecular Properties of the Alkali Metals (Lloyd, 1981)

	Li	Na	К	Rb	Cs
Atomic number	3	11	19	37	55
Electronic configuration	2,1	8,2,1	8,8,2,1	18,8,8,2,1	18,18,8,8,2,1
Atomic weight	6.941	22.990	39.098	85.67	132.905
Heat of atomisation from standard (kcal/mol)	39.0	25.9	19.8	18.9	
Heat of formation of molecules from atoms (kcal/mol)	-27.2	-18.4	- 12.6	-11.3	- 10.4
Ionisation potential for gas (kcal)	123.8	117.9	99.7	95.9	-89.4
eV	5.36	5.18	4.41	4.16	3.96
Electronic affinity (eV)	0.54	(3s) 0.74	(4s) 0.7		
Normal electrode potential (V)	3.038	2.71	2.92	2.92	2.93
Electronegativity	1.0	0.9	0.8	0.8	0.7
Ionic radius (Å)	0.68	0.97	1.33	1.47	1.67
Covalent radius (Å)	1.58	1.92	2.38	2.53	2.72
Internuclear distance in molecule (Å)	2.67	3.08	3.91		4.55

properties of the alkali metals is listed in Table 1.47, along with a discussion of lithium's chemistry.

The solubility of lithium carbonate in pure water is listed in Table 1.48, and shown in Fig. 1.103. Lithium carbonate's solubility with sodium chloride present at 25°C is listed in Table 1.49, but the data from various authors is quite variable. Seidell (1965) indicates that the solubility of lithium carbonate in water at 25°C is 5950 ppm Li, and that when both lithium carbonate and sodium chloride are saturated the lithium solubility is 5200 ppm, while Deng *et al.*, (2002) listed the latter value at 980 ppm. There is no saturated NaCl-Li<sub>2</sub>CO<sub>3</sub> data at 100°C, but Seidell's 25°C data would extrapolate to 2500 ppm Li, Deng *et al.*'s, (2002) to about 500 ppm Li, while Lien (1985) found 1900–2100 ppm Li in the system saturated with the three salts Li<sub>2</sub>CO<sub>3</sub>, Na<sub>2</sub>SO<sub>4</sub> and

Table	1.47D
-------	-------

	Li	Na	К	Rb	Cs
Appearance	Silvery white solid	Silvery white solid and liquid, purple vapour	Silvery white solid and liquid, green vapour	Silvery white solid	Silvery white solid
Lattice		-	Body centred cubic		
Hardness (Mohs' scale)	0.6	0.7	0.4		0.2
Specific gravity at 0°C	0.5	0.972	0.859	1.525	1.903
Melting point (°C)	179.5	97.8	63.5	38.7	29.8
Boiling point (°C)	1336	883	762	700	670
Heat of fusion (kcal/g atom)	0.69	0.63	0.57	0.53	0.50
Effective number of free electrons per atom	0.55	1.1	0.97	0.94	0.85

Properties of the Alkali Metals in the Metallic State (Lloyd, 1981)

#### Table 1.47E

Comparative Chemistry of Lithium (Lloyd, 1981)

Lithium is the leading element of the Group 1a series, and as such, exhibits in many of its properties and the same characteristics as the common alkali metals: sodium and potassium. However, in some respects it shows similarities with the alkaline earth metals, in particular with magnesium. This is manifested by

the formation of a normal oxide, rather than peroxide, on reaction with oxygen decomposition of the carbonates on heating direct formation of nitrides and carbides from the elements the very low solubility of the carbonates, fluorides and phosphates the high degree of hydration of the ions solubility of the salts in polar organic solvents, such as methanol and ethers the solubility of the metal alkyls in non-polar organic solvents

The low atomic weight of lithium results in its compounds bearing a higher percentage of the anion than other comparable cations. Thus

the perchlorate LiClO<sub>4</sub> and nitrate LiNO<sub>3</sub> generate a higher proportion of oxygen per unit weight of the compound;

the peroxide Li<sub>2</sub>O<sub>2</sub> and hydroxide LiOH will absorb more carbon dioxide;

the hydride LiH yields more hydrogen per unit weight than any other;

the hypochlorite LiOCl will generate more free chlorine per unit weight;

Li on oxidation evolves more heat — 10.25 kcal/g (Na at 2.16 kcal/g)

the ionisation of Li gives the highest emf per unit weight of all metals

(continues)

### 214 Part 1 Lithium

Table 1.47E (continued)

Also, because of this effect, the lithium salts in either the fused state or the aqueous state deviate most from ideal behaviour. They depress the freezing points of fluid systems. In the fused state they are good fluxes. They reduce surface tension and viscosity and because of this they bring reactants into contact, and enhance reaction rates.

The small ionic radius of the lithium atom means that its compounds with other small atoms and cations are strongly ionic in bond form. The high ionic potential results in a high energy of hydration— the ion is strongly solvated in aqueous solutions, and these show the widest deviations from the ideal. By reason of being the most electro-positive of elements, with its small size it exhibits strong covalency in many compounds. This confers a special place on lithium in the field of organic-metallic chemistry. It also leads to the solvation of the ionic compounds in organic solvents which exhibit high solubilities for the salts. Similarly, the organo-lithium compounds, for example BuLi, are readily soluble in non-polar solvents such as hexane and cyclo-hexane. Even so, the solution has sufficient anionic strength to determine stereo-specific polymerisation of isoprene and butadiene.

 $K_2SO_4$  (May (1952) reported 2800). It would appear that the correct lithium solubility for the  $Li_2CO_3$ -NaCl saturated system at 100°C would be somewhat over 2000 ppm Li (as is encountered in some of the commercial operations). For the system saturated with both  $Li_2CO_3$  and  $Na_2CO_3$  (as an approximation of the Salar de Atacama's precipitated brine), Seidell's three authors found 4490, 4290 and 2740 ppm Li at 25°C (and perhaps about 3500 ppm Li at 100°C). Deng *et al.*'s (2002) saturated NaCl- $Li_2CO_3$  data at 25°C indicated that the solution had a pH of 7.16, a density of 1.2204, a viscosity of 1.9575 Mpa s, and a refractive index of 1.3808.

	Li <sub>2</sub> CO <sub>3</sub> (	g) per 100 g		Li <sub>2</sub> CO <sub>3</sub> (g) per 100 g				
T (°C)	Water	Solution	ppm Li	T (°C)	Water	Solution	ppm Li	
0	1.54	1.52	7062	40	1.17	1.16	5389	
10	1.43	1.41	6551	50	1.08	1.07	4971	
20	1.33	1.31	6086	60	1.01	1.00	4646	
25 30	1.29 1.25	1.28 1.24	5947 5761	80 100	0.85 0.72	0.84 0.71	3902 3298	

Table 1.48

Solubility of Lithium Carbonate in Water (Seidell, 1965)

Density of saturated solution at  $0^{\circ}C = 1.017$ ; at  $15^{\circ}C = 1.014$ . 100°C sat. with NaCl ~ 2900 ppm Li (2500); 100°C sat. with Na<sub>2</sub>SO<sub>4</sub> and K<sub>2</sub>SO<sub>4</sub> 1900–2100 ppm Li (Lein, 1985); 100°C sat. with Na<sub>2</sub>SO<sub>4</sub> and K<sub>2</sub>SO<sub>4</sub> 2800 (May, 1952).



Figure 1.103 The solubility of lithium carbonate in water at various temperatures (Seidell, 1965).

215

	С	omposition o	f liquid pha	se (mass %)			Jãnecke index/(mol/100 mol dry-salt)				
No.	Li <sup>+</sup>	Na <sup>+</sup>	$Cl^{-}$	$CO_{3}^{2-}$	H <sub>2</sub> O	2Li <sup>+</sup>	$2Na^+$	$2Cl^{-}$	$CO_{3}^{2-}$	H <sub>2</sub> O	Solid phase <sup>a</sup>
1	0.20	12.30	0.17	16.77	70.56	5.11	94.89	0.85	99.15	1390.5	$C_A + L_B$
2	0.16	12.38	0.86	16.12	70.48	4.11	95.89	4.32	95.68	1394.6	$C_A + L_B$
3	0.0062	12.14	3.24	13.13	71.49	0.17	99.83	17.28	82.72	1501.7	$C_A + L_B$
4, E	0.092	13.92	8.76	11.15	66.08	2.14	97.86	39.94	60.06	1186.6	$C_A + C_B + L_B$
5	0.044	13.52	8.42	10.71	67.31	1.07	98.93	39.96	60.04	1258.2	$C_A + C_B$
6, F	0.044	13.20	10.66	8.39	67.70	1.09	98.91	51.80	48.20	1295.9	$C_A + L_B + NaCl$
7	0.00048	12.60	8.74	9.05	69.61	0.01	99.99	44.98	55.02	1411.1	$C_B + NaCl$
8	0.09	10.60	15.56	1.05	72.70	2.74	97.26	92.59	7.41	1704.0	$L_B + NaCl$
9	0.098	10.30	15.88	0.43	73.30	3.06	96.94	96.93	3.07	1762.2	$L_B + NaCl$
10	0.16	10.26	16.00	0.54	73.04	4.91	95.09	96.16	3.84	1729.2	$L_B + NaCl$
11	1.91	9.40	23.20	0.89	64.60	40.23	59.77	95.66	4.34	1049.2	$L_B + NaCl$
12, G	7.88	0.084	37.90	2.10	52.03	99.68	0.32	93.84	6.16	507.5	$L_A + L_B + NaCl$
13	8.16	0.086	37.68	3.50	50.57	99.68	0.32	90.10	9.90	476.3	$L_A + L_B$
14	7.36	0.026	36.52	0.95	55.15	99.89	0.11	97.02	2.98	577.1	$L_A + L_B$
15	7.76	0.03	34.70	4.22	53.29	99.88	0.12	87.43	12.57	528.8	$L_A + L_B$
16	7.96	0.082	38.48	1.96	51.52	99.69	0.31	94.33	5.67	497.5	$NaCl + L_A$
17	8.16	0.082	39.60	1.87	50.28	99.70	0.30	94.70	5.30	473.7	$NaCl + L_A$
18, H	6.82	0.00	30.24	3.89	59.05	100.0	0.00	86.79	13.21	667.5	$L_A + L_B$
19, A	0.17	10.15	0.00	13.98	75.70	5.26	94.74	0.00	100.0	1805.0	$C_A + L_B$
20, B	0.00	9.72	8.64	5.37	76.27	0.00	100.0	57.65	42.35	2004.3	$C_A + C_B$
21, C	0.00	11.11	11.34	4.90	72.65	0.00	100.0	66.19	33.81	1670.4	$NaCl + C_B$
22, D	6.56	0.079	33.64	0.00	59.73	99.64	0.36	100.0	0.00	699.4	$NaCl + L_A$

Solubility Data of the Li<sup>+</sup>, Na<sup>+</sup>/Cl<sup>-</sup>, CO<sub>3</sub><sup>2</sup>-H<sub>2</sub>O Systems at 298.15 K (Deng et al., 2002)

<sup>a</sup> L<sub>A</sub>, LiCl·H<sub>2</sub>O; L<sub>B</sub>, Li<sub>2</sub>CO<sub>3</sub>; C<sub>A</sub>, Na<sub>2</sub>CO<sub>3</sub>·10H<sub>2</sub>O; C<sub>B</sub>, Na<sub>2</sub>CO<sub>3</sub>·7H<sub>2</sub>O; letters are invariant points.
217

## Table 1.50

T (°C)	Density of sat. sol.	LiCl (g) per 100g sat. sol.	Solid phase
-2.4		4.0	Ice
-9.0		8.0	Ice
-23.0		14.0	Ice
-36.0		18.0	Ice
-50.0		21.0	Ice
-62.0		24.0	Ice
-66.0		24.4	$Ice + LiCl \cdot 5H_2O$
$-73^{c}$		24.85	$Ice + LiCl \cdot 5H_2O$
$-75.9^{a}$		25.0	$Ice + LiCl \cdot 5H_2O$
$-80^{b}$		25.3	$Ice + LiCl \cdot 5H_2O$
-63.0		26.4	LiCl·5H <sub>2</sub> O
-60.4		28.2	LiCl·5H <sub>2</sub> O
-58.0		29.6	LiCl·5H <sub>2</sub> O
-57.0		30.4	$LiCl \cdot 5H_2O + LiCl \cdot 3H_2O$
$-65.6^{a}$		_	$LiCl \cdot 5H_2O + LiCl \cdot 3H_2O$
$-68^{b}$		28.7	$LiCl \cdot 5H_{2}O + LiCl \cdot 3H_{2}O$
-54.0		30.5	LiCl·3H <sub>2</sub> O
-48.0		30.8	LiCl·3H <sub>2</sub> O
-31.0		33.4	LiCl·3H <sub>2</sub> O
-19.2		36.4	LiCl·3H <sub>2</sub> O
-15.6		37.2	$LiCl \cdot 3H_{2}O + LiCl \cdot 2H_{2}O$
$-20.5^{a}$			$LiCl \cdot 3H_2O + LiCl \cdot 2H_2O$
-20		36.9	$LiCl\cdot 3H_2O + LiCl\cdot 2H_2O$
0	1.268	40.9	LiCl·2H <sub>2</sub> O
5	—	42.0	LiCl·2H <sub>2</sub> O
10	1.279	42.7	LiCl·2H <sub>2</sub> O
15	—	43.8	LiCl·2H <sub>2</sub> O
18.5	1.293	45.35	$LiCl \cdot 2H_2O + LiCl \cdot H_2O$
$12.5^{b}$	—	40.5	$LiCl \cdot 2H_2O + LiCl \cdot H_2O$
$19.0^{a}$	—		$LiCl \cdot 2H_2O + LiCl \cdot H_2O$
19.1 <sup>c</sup>	—	—	$LiCl \cdot 2H_2O + LiCl \cdot H_2O$
25	1.296	45.85	LiCl·H <sub>2</sub> O
30	—	46.3	LiCl·H <sub>2</sub> O
40	1.303	47.3	LiCl·H <sub>2</sub> O
50	1.308	48.3	LiCl·H <sub>2</sub> O
60	—	49.6	LiCl·H <sub>2</sub> O
70	—	51.1	LiCl·H <sub>2</sub> O
80	1.331	52.8	LiCl·H <sub>2</sub> O
90	1.342	54.8	LiCl·H <sub>2</sub> O
96	1.347	56.1	$LiCl \cdot H_2O + LiCl$
93 <sup>c</sup>	—		$LiCl \cdot H_2O + LiCl$
100.5 <sup>b</sup>	—	56.5	$LiCl \cdot H_2O + LiCl$

Solubility of Lithium Chloride in Water (Seidell, 1965)

(continues)

Table 1.50   (continued)				
T (°C)	Density of sat. sol.	LiCl (g) per 100g sat. sol.	Solid phase	
94 <sup>a</sup>	_	_	$LiCl \cdot H_2O + LiCl$	
97	_	56.8*	LiCl·H <sub>2</sub> O	
98	—	57.4*	LiCl·H <sub>2</sub> O	
100	1.347	56.2	LiCl	
110	—	56.7	LiCl	
120	1.344	57.2	LiCl	
130	—	57.6	LiCl	
140	1.339	58.0	LiCl	
160	—	59.2	LiCl	

\*metastable.

 $^{a-c}$  Data from different authors.

## Table 1.51

# The System Lithium Chloride-Sodium Chloride-Water (Seidell, 1965)

		Results	at 25°C <sup>a</sup>		
Grams per 100 g sat. sol.		Grams per 100 g sat. sol.		Grams per 100 g sat. sol.	
LiCl	NaCl	LiCl	NaCl	LiCl	NaCl
45.8	0.0	35.7	0.3	17.4	7.3
45.5	0.5	33.5	0.4	16.9	8.4
41.3	0.4	33.5	0.3	6.5	19.0
40.1	0.2	31.6	0.8	0.0	26.4
36.8	0.3	24.9	2.3		
		Results	at $40^{\circ}C^{b}$		
Grams sat	per 100 g . sol.		Grams p sat.	oer 100 g sol.	
LiCl	NaCl	Solid phase	LiCl	NaCl	Solid phase
47.98	0.0	LiCl·H <sub>2</sub> O	25.48	5.26	NaCl + $\sim 4\%$ LiCl
46.51	0.68	$LiCl \cdot H_2O + NaCl$	17.52	10.13	NaCl + $\sim 4\%$ LiCl
44.76	0.82	$NaCl + \sim 4\%$ LiCl	6.14	19.05	NaCl + $\sim 4\%$ LiCl
41.60	1.04	NaCl + $\sim 4\%$ LiCl	0.0	26.65	NaCl + $\sim 4\%$ LiCl
33.96	3.17	NaCl + $\sim 4\%$ LiCl			

<sup>*a,b*</sup> Data from different authors;  $\sim 4\%$  LiCl is an unknown double salt.

# Chemistry, Phase Data, Physical Properties

219

## Table 1.52

Grams LiCl per 100 g sat. sol.	ns LiCl per 100 g sat. sol. Grams MgCl <sub>2</sub> per 100 g sat. sol.					
Results at -50°C						
31.0	0.0	LiCl·3H <sub>2</sub> O				
29.5	2.0	LiCl·3H <sub>2</sub> O				
28.4	4.0	$LiCl \cdot 3H_2O + DS$				
25.4	6.6	DS				
23.6	8.6	$DS + MgCl_2 \cdot 12H_2O$				
22.6	8.4	MgCl <sub>2</sub> ·12H <sub>2</sub> O				
15.6	7.8	$MgCl_2 \cdot 12H_2O + Ice$				
17.6	6.6	Ice				
18.6	4.8	Ice				
20.4	1.4	Ice				
21.0	0.0	Ice				
	Results at $-30^{\circ}$ C					
34.4	0.0	LiCl·3H <sub>2</sub> O				
33.0	2.2	LiCl·3H <sub>2</sub> O				
32.0	4.0	$LiCl \cdot 3H_2O + DS$				
28.6	7.4	DS				
27.0	10.4	$DS + MgCl_2 \cdot 6H_2O$				
21.0	12.8	MgCl <sub>2</sub> ·6H <sub>2</sub> O				
16.4	15.4	$MgCl_2 \cdot 6H_2O + MgCl_2 \cdot 8H_2O$				
4.4	22.2	MgCl <sub>2</sub> ·8H <sub>2</sub> O				
3.4	22.8	$MgCl_2 \cdot 8H_2O + MgCl_2 \cdot 12H_2O$				
0.0	21.6	MgCl <sub>2</sub> ·12H <sub>2</sub> O				
0.0	19.4	Ice				
7.0	11.6	Ice				
11.0	6.8	Ice				
16.0	0.0	Ice				
	Results at $-10^{\circ}$ C					
8.8	0.0	Ice				
6.4	4.0	Ice				
4.0	7.0	Ice				
0.0	11.6	Ice				
	Results at 0°C					
38.8	0.0	LiCl·2H <sub>2</sub> O				
38.2	2.6	LiCl·2H <sub>2</sub> O				
38.0	4.8	$LiCl \cdot 2H_2O + 1:1:7$				

The System Lithium Chloride-Magnesium Chloride-Water (Seidell, 1965)

(continues)

Grams LiCl per 100 g sat. sol.	Grams MgCl <sub>2</sub> per 100 g sat. sol.	Solid phase
	Results at 0° (cont.)	
32.5	8.6	1:1:7
29.6	11.0	1:1:7
28.0	12.4	$1:1:7 + MgCl_2 \cdot 6H_2O$
23.0	14.2	MgCl <sub>2</sub> ·6H <sub>2</sub> O
18.6	17.0	MgCl <sub>2</sub> ·6H <sub>2</sub> O
13.2	21.6	MgCl <sub>2</sub> ·6H <sub>2</sub> O
5.4	28.6	MgCl <sub>2</sub> ·6H <sub>2</sub> O
0.0	35.0	MgCl <sub>2</sub> ·6H <sub>2</sub> O
	Results at 25°C	
45.65	0.0	LiCl·H <sub>2</sub> O
43.1	2.68	LiCl·H <sub>2</sub> O
40.0	5.74	$LiCl \cdot H_2O + 1:1:7$
40.2	5.68	$LiCl \cdot H_2O + 1:1:7$
38.0	6.99	1:1:7
37.1	7.42	1:1:7
35.4	8.32	1:1:7
33.9	9.34	1:1:7
29.3	13.7	1:1:7
*28.8	14.2	$1:1:7 + MgCl_2 \cdot 6H_2O$
28.0	14.3	MgCl <sub>2</sub> ·6H <sub>2</sub> O
22.0	18.0	MgCl <sub>2</sub> ·6H <sub>2</sub> O
18.9	20.0	MgCl <sub>2</sub> ·6H <sub>2</sub> O
8.4	28.3	MgCl <sub>2</sub> ·6H <sub>2</sub> O
0.0	35.4	MgCl <sub>2</sub> ·6H <sub>2</sub> O
	Results at 30°C	
46.2	0.0	LiCl·H <sub>2</sub> O
39.9	6.27	$LiCl \cdot H_2O + 1:1:7$
39.0	6.81	1:1:17
35.4	8.84	1:1:17
35.3	9.14	1:1:17
34.1	9.93	1:1:17
33.2	10.6	1:1:17
31.7	10.7	1:1:17
29.3	13.5	1:1:17
26.6	15.7	1:1:17

Table 1.52(continued)

(continues)

Grams LiCl per 100 g sat. sol.	Grams MgCl <sub>2</sub> per 100 g sat. sol.	Solid phase
	Results at 30°C (cont.)	
*26.6	16.6	$1:1:17 + MgCl_2 \cdot 6H_2O$
25.7	16.5	MgCl <sub>2</sub> ·6H <sub>2</sub> O
24.8	16.8	MgCl <sub>2</sub> ·6H <sub>2</sub> O
17.1	21.7	MgCl <sub>2</sub> ·6H <sub>2</sub> O
10.1	27.3	MgCl <sub>2</sub> ·6H <sub>2</sub> O
0.0	35.6	MgCl <sub>2</sub> ·6H <sub>2</sub> O
	Results at 70°C	
51.2	0.0	LiCl·H <sub>2</sub> O
46.5	4.58	LiCl·H <sub>2</sub> O
39.4	11.2	LiCl·H <sub>2</sub> O
38.2	12.3	$LiCl H_2O + 1:1:7$
37.3	13.9	1:1:7
36.1	14.5	1:1:7
26.4	20.4	1:1:7
22.3	23.5	1:1:7
21.6	24.1	1:1:7
20.5	24.4	1:1:7
*20.0	26.4	$1:1:7 + MgCl_2 \cdot 6H_2O$
19.0	26.1	MgCl <sub>2</sub> ·6H <sub>2</sub> O
18.8	26.3	MgCl <sub>2</sub> ·6H <sub>2</sub> O
15.3	27.9	MgCl <sub>2</sub> ·6H <sub>2</sub> O
10.2	31.2	MgCl <sub>2</sub> ·6H <sub>2</sub> O
0.0	38.7	MgCl <sub>2</sub> ·6H <sub>2</sub> O
	Results at 102°C	
56.9	0.0	LiCl
30.4	23.4	LiCl
29.2	23.9	LiCl
22.5	29.7	LiCl
19.2	34.1	LiCl
17.4	35.6	$LiCl + MgCl_2 \cdot 6H_2O$
13	39	MgCl <sub>2</sub> ·6H <sub>2</sub> O
9	41	MgCl <sub>2</sub> ·6H <sub>2</sub> O

Table 1.52(continued)

 $1:1:7 = LiCl \cdot MgCl_2 \cdot 7H_2O$ ; DS, Double salt of undetermined composition; \* extrapolated value.

Tabl	e 1	.53

T (°C)	Li <sub>2</sub> SO <sub>4</sub> (g) per 100 g sat. sol.	Solid phase	T (°C)	$Li_2SO_4$ (g) per 100 g sat. sol.	Solid phase
-1.735	4.072	Ice	30	25.25 <sup>8</sup>	Li <sub>2</sub> SO <sub>4</sub> ·H <sub>2</sub> O
-3.30	7.791	Ice	30	$25.10^{12}$	Li <sub>2</sub> SO <sub>4</sub> ·H <sub>2</sub> O
-5.11	11.30	Ice	31.8	25.47	Li <sub>2</sub> SO <sub>4</sub> ·H <sub>2</sub> O
-7.04	14.33	Ice	35.0	$24.76^3$	Li <sub>2</sub> SO <sub>4</sub> ·H <sub>2</sub> O
-9.67	17.67	Ice	38.0	25.28	Li <sub>2</sub> SO <sub>4</sub> ·H <sub>2</sub> O
-14.65	21.95	Ice	43.7	25.00	Li <sub>2</sub> SO <sub>4</sub> ·H <sub>2</sub> O
-18.45	24.85	Ice	45.6	$24.88^{11}$	Li <sub>2</sub> SO <sub>4</sub> ·H <sub>2</sub> O
-21.4	27.1	Ice	50	24.3 <sup>9</sup>	Li <sub>2</sub> SO <sub>4</sub> ·H <sub>2</sub> O
-23.0	27.9	$Ice + Li_2SO_4 H_2O$	51.6	24.82	Li <sub>2</sub> SO <sub>4</sub> ·H <sub>2</sub> O
-16.0	27.32	Li2SO4·2H2O	52.4	24.71	Li <sub>2</sub> SO <sub>4</sub> ·H <sub>2</sub> O
-13.0	27.24	Li <sub>2</sub> SO <sub>4</sub> ·2H <sub>2</sub> O	55	$24.62^2$	Li <sub>2</sub> SO <sub>4</sub> ·H <sub>2</sub> O
-11.5	27.18	Li2SO4·2H2O	65.7	24.34	Li <sub>2</sub> SO <sub>4</sub> ·H <sub>2</sub> O
-6.5	26.73	Li2SO4·H2O	71.8	$24.2^{10}$	Li <sub>2</sub> SO <sub>4</sub> ·H <sub>2</sub> O
0.0	25.43 <sup>1</sup>	Li <sub>2</sub> SO <sub>4</sub> ·H <sub>2</sub> O	77.0	24.05	Li <sub>2</sub> SO <sub>4</sub> ·H <sub>2</sub> O
0.0	$26.33^2$	Li2SO4·H2O	94.8	23.76	Li <sub>2</sub> SO <sub>4</sub> ·H <sub>2</sub> O
0.6	26.51	Li <sub>2</sub> SO <sub>4</sub> ·H <sub>2</sub> O	94.9	$23.4(1.182)^4$	Li <sub>2</sub> SO <sub>4</sub> ·H <sub>2</sub> O
12.5	$25.98^{6}$	Li <sub>2</sub> SO <sub>4</sub> ·H <sub>2</sub> O	95.2	$24.21^{10}$	Li <sub>2</sub> SO <sub>4</sub> ·H <sub>2</sub> O
14.0	26.07	Li <sub>2</sub> SO <sub>4</sub> ·H <sub>2</sub> O	100.1	$23.5(1.179)^4$	Li <sub>2</sub> SO <sub>4</sub> ·H <sub>2</sub> O
16.7	25.96	Li2SO4·H2O	103.0	23.72	Li <sub>2</sub> SO <sub>4</sub> ·H <sub>2</sub> O
19.6	25.85	Li <sub>2</sub> SO <sub>4</sub> ·H <sub>2</sub> O	104.0	$23.55 (1.176)^4$	Li <sub>2</sub> SO <sub>4</sub> ·H <sub>2</sub> O
20	$25.20^{5}$	Li2SO4·H2O	142.5	22.65	Li <sub>2</sub> SO <sub>4</sub> ·H <sub>2</sub> O
25	$25.50^2$	Li <sub>2</sub> SO <sub>4</sub> ·H <sub>2</sub> O	186	22.7	Li <sub>2</sub> SO <sub>4</sub> ·H <sub>2</sub> O
25	$25.79^3$	Li2SO4·H2O	214	23.0	Li <sub>2</sub> SO <sub>4</sub> ·H <sub>2</sub> O
25	$25.69^{7}$	Li2SO4·H2O	232.8	~23	$Li_2SO_4 H_2O + Li_2SO_4$
27	25.4111	$Li_2SO_4 \cdot H_2O$			

Solubility of Lithium Sulphate in Water (Seidell, 1965)

1 to 12 are data from different authors.

The solubility of lithium chloride in water is given in Table 1.50, and lithium chloride with sodium chloride in Table 1.51. The phase system lithium chloride with magnesium chloride is listed in Table 1.52, and lithium sulfate in water in Table 1.53. The more complex reciprocal salt pair of  $\text{LiCl}-\text{Li}_2\text{SO}_4-\text{MgSO}_4-\text{MgCl}_2$  is plotted in Fig. 1.104. In the evaporation of more complex brines such as from the Salar de Atacama, the solubility data initially follows the seawater evaporation system (see Garrett, 1996) until carnallite crystallizes, and then more closely follows the lithium systems, with or without sulfate and/or magnesium, depending upon the solar pond process being employed. Campbell and Kartzmark (1956–1961) have reported on the five component system: lithium, sodium, potassium, sulfate, chloride and water, and each of its subsystems.



**Figure 1.104** Phase diagram at 0, 35 and 50°C of Li, Mg, Cl,  $SO_4-H_2O$  (Garrett and Laborde, 1983). Reprinted by permission of the Salt Institute.

## REFERENCES

#### Geology

Afgouni, K., and Silva Sa, J. H. (1978). "Lithium Ores in Brazil." Energy 3(3), 247-253.

- Akhundzhanov, R. (1997). "Rare Earth Leucogranite Subvolcanic Analogs from the Chatkal-Kurama Region, Central Tien-Shan." *Uzbekistan Geol. J., Tashkent*, 29–39.
- Alonso, H., and Risacher, F. (1996). "Geochemistry of the Salar de Atacama. Part 1. Origin of its Components and a Material Balance." *Rev. Geol. Chile* 23, 113–122.
- Anon. (1966). "Nevada Brine Supports a Big New Lithium Plant." Chem. Eng., 86-88 (Aug. 15).
- Anon. (1979). "Lithium Investigations in Sedimentary and Volcanic Rocks." USGS Miner. Resour. Invest., 15–17.
- Anon. (1981). "Lithium Producers Gear-Up for a Bright Future." C&EN, 11 (Oct. 26).
- Anon. (1995). "New Lithium Capacity on the Horizon." Chem. Week 157(20), 30.
- Anon. (1998). "New Players and Forces Change Lithium Scene." Chem. Week 160(46), 50.
- Anstett, T. F., Krauss, U. H., Ober, J. A., and Schmidt, H. W. (1990). "Lithium." Int. Strat. Min. Invest. Summ. Rept., U.S. Geol. Survey Circular 930-I, 28 pp.
- Bach, R. O., Kamienski, C. W., and Ellestad, R. B. (1967). "Lithium and Lithium Compounds." Kirk-Othmer Encyclopedia of Chemical Technology, Vol. 12, pp. 529–554. Wiley, New York.

- Barrett, W. T., and O'Neill, J. O. (1970). "Recovery of Lithium from Saline Brines Using Solar Evaporation." *Third Symp. Salt* 2, 47–50.
- Bates, R. L., and Jackson, J. A. (1976). "Dictionary of Geological Terms", 3rd ed., 571 pp. Anchor Press, Garden City, NY.
- Berthold, C. F., and Baker, D. H. (1976). "Lithium Recovery from Geothermal Fluids." Lithium Resources and Requirements by the Year 2000, pp. 61–65.
- Bobst, A. L., Lowenstein, T. K., Jordan, T. E., Godfrey, L. V., Ku, T. L., and Luo, S. (2001). "A 106ka Paleoclimate Record from Drill Core of the Salar de Atacama, Northern Chile." *Paleogeogr. Paleoclimatol. Paleoecol.* **173**, 21–42.
- Bottomley, D. J., et al. (1999). "The Origin and Evolution of Canadian Shield CaCl<sub>2</sub> Brines." Chem. Geol. 155(3–4), 295–320.
- Bray, A. M. (1998). "Controls on Alkali Metal Chemistry in Hydrothermal Vent Fluids for 9–10°N Latitude, East Pacific Rise." Master's Degree, Univ. of New Hampshire, 186 pp.
- Brown, P. M., and Beckerman, S. J. (1990). "Production of Lithium Metal Grade Lithium Chloride from Lithium-Containing Brine." U.S. Patent 4,980,136, 8 pp. (Dec. 25).
- Burkowsky, H., Uhlemann, E., and Steinborn, D. (1991). "The Recovery of Lithium from Gas Field Waters." *Hydrometallurgy* 27, 317–325.
- Burt, R. O., Flemming, J., Simard, R., and Vanstone, P. J. (1988). "Tanco—A New Name in Low Iron Spodumene." Ind. Miner.(244), 55–59 (Jan).
- Cerny, P., and Lenton, P. G. (1995). "The Buck and Pegli Lithium Deposits, Southeastern Manitoba." *Econ. Geol.* 90(3), 658–675.
- Cerny, P., Ercit, T. S., and Vanstone, P. J. (1998). "Mineralogy and Petrology of the TANCO Rare-Element Pegmatite Deposit." Int. Mineral. Assoc. 17th Gen. Mtg., Toronto, Guidebook B6, 74 pp.
- Chan, L. H., Starinsky, A., and Katz, A. (2002). "The Behavior of Lithium and its Isotopes in Oilfield Brines." *Geochim. Cosmochim. Acta* 66(4), 615–623.
- Chan, L. H., Alt, J. C., and Teagle, D. A. (2002). "Lithium and Lithium Isotope Profiles Through the Upper Oceanic Crust." *Earth Planet. Sci. Lett.* **201**(1), 187–201.
- Chan, L. H., Leeman, W. P., and You, C. F. (2002). "Lithium Isotopic Composition of Central American Volcanic Arc Lavas." *Chem. Geol.* 182(2–4), 293–300.
- Charoy, B., Noronha, F., and Lima, A. (2001). "Spodumene–Petalite–Eucryptite in Li-Rich Aplite– Pegmatite Dykes from Northern Portugal." *Can. Mineralogist* 39(3), 729–746.
- Christopher, D. H., Stewart, M., and Rice, J. (1975). "The Recovery of Mineral Values from Geothermal Brines." U.S. Bur. Mines Open File Rept. 81-75, 27 pp.
- Coad, M. (1984). "Lithium Production in Chile's Salar de Atacama." Ind. Miner. 205, 27-33 (Oct.).
- Collins, A. G. (1976). "Lithium Abundance in Oilfield Waters." *Lithium Resources and Requirements by the Year 2000*, U.S. Geol. Survey Prof. Paper 1005, pp. 116–123.
- Cooper, D. G. (1964). "The Geology of the Bikita Pegmatite." *The Geology of Some Ore Deposits in Southern Africa*, pp. 441–461. Geol. Soc. South Africa.
- CORFO (1985, 1981). "Development of the Salar de Atacama." Various reports.
- Crouse, R. A., Cerny, P., Trueman, D. L., and Burt, R. O. (1984). "The Tanco Pegmatite. Southeast Manitoba." *The Geology of Industrial Minerals in Canada*, CIM Spec., Vol. 29, pp. 169–176.
- Cusicanqui, H., Mahon, W. A., and Ellis, A. J. (1975). "The Geochemistry of the El Tatio Geothermal Field, Northern Chile." *Second U.N. Symp. Geothermal Reservoirs* **1**, 703–711.
- Dapeng, S., and Bingxiao, L. (1993). "Origins of Borates in Saline Lakes of China." Seventh Symposium on Salt 1, 177–194.
- Davis, J. R., and Vine, J. D. (1979). "Stratigraphic and Tectonic Setting of the Lithium Brine Field, Clayton Valley, Nevada." *Basin and Range Symp.*, pp. 421–430. Rocky Mt. Assoc. Geol.
- Davis, J. R., Friedman, I., and Gleason, J. D. (1986). "Origin of the Lithium-Rich Brine, Clayton Valley, Nevada." U.S. Geol. Survey Bull. 1622, 131–138.
- Deberitz, J. (1993). "Lithium", 70 pp. Verlag Moderne Industrie AG & Co., Landsberg/Lech., Germany.

- Dibble, W. E., and Dickson, F. W. (1976). "The Behavior of Lithium in Experimental Rock–Water Interaction Studies." *Lithium Resources and Requirements by the Year 2000*, pp. 142–147.
- Dillard, G., and McClean, S. (1991). "Cyprus Foote Mineral Taps a Unique Treasure." Rocky Mt. Pay Dirt, pp. 4A–8A (Sept.).
- Dovgal, V. N., Sabotovich, S. A., and Distanova, A. N. (1998). "Li-F-Type Rare-Metal Granitoid Magmatism in the Altai." *Doklady Earth Sci.* 359A(3), 338–340.
- Dow (1984). "Lithium Recovery by Alumina-Ion Exchange." Lee, J.M., and Bauman, W., 4 pp., U.S. Patents 4,430,311 (Feb. 7); 4,221,756 (Sept. 9, 1980); 4,116,856 (Sept. 26, 1978); others.
- Dresler, W., Jena, B. C., Reilly, I. G., Laffin, S., and Egab, E. (1998). "The Extraction of Lithium Carbonate from a Pegmatite." *Light Metals*, 1303–1308.
- Epstein, J. A., Feist, E. M., Zmora, J., and Marcus, Y. (1981). "Extracting Lithium from the Dead Sea." *Hydrometallurgy* 6, 269–275.
- Eremenko, G. K., Ivanov, B. N., Belykh, N. A., Kuzmenko, A. V., and Makivchuk, O. F. (1996). "Mineralogy and Formation Conditions of Lithium Pegmatites of the Kirovograd Block, Ukrainian Shield." *Mineral. J.* 18(1), 48–57.
- Ericksen, G. E., Vine, J. D., and Ballon, R. A. (1978). "Chemical Composition of Brines in the Salar de Uyuni and Nearby Bolivian Salars." *Energy* 3, 335–363.
- Flanagan, J. T. (1978). "Lithium Deposits and Potential of Quebec and Atlantic Provinces of Canada." *Energy* 3, 391–395.
- Flemming, J. (1993). "Mining Spodumene Ore at the Greenbushes Mine of Gwalia Consolidated Limited, Greenbushes, WA." Australian Mining, Metal., 2nd ed., Vol. 2. Monograph 19, pp. 1417–1419.
- Folle, S., and Beutel, T., (2000). "Overview of Salt Occurrences in the Persian Gulf and Red Sea Region." *Eighth World Salt Symposium* 1, 119–124.
- Gadsby, E. A. (1967). "Lithium from Nevada Brine." Am. Chem. Soc. 3rd Western Regional Meeting; AIChE Meeting, Chicago, 6 pp.
- Gale, W. A. (1945). "Lithium from Searles Lake." Chem. Ind., 442-446 (Sept.).
- Garces, M. (2000). "The Sodium Sulfate and Ulexite Deposits of the Salar de Surie, Chile." *Eighth World Symposium on Salt* 1, 1161–1162.
- Garrett, D. E. (1960). "Lithium Recovery from the Clayton Valley." Personal files.
- Garrett, D. E. (1992). "Natural Soda Ash; Occurrences, Processing and Use", 636 pp. Van Nostrand Reinhold, New York.
- Garrett, D. E. (1996). "Potash; Deposits, Processing, Properties and Uses", 734 pp. Chapman & Hall, London.
- Garrett, D. E. (1998). "Borates; Handbook of Deposits, Processing, Properties and Use", 483 pp. Academic Press, San Diego, CA.
- Garrett, D. E., and Carpenter, L. G. (1959). "Tungsten in Searles Lake." Mining Eng. 11(3), 301-303.
- Guerenko, A. A., and Schmincke, H. U. (2002). "Orthopyroxene-Bearing Tholeiites of the Iblean Plateau, Sicily." *Chem. Geol.* 183(1–4), 305–331.
- Gwynn, J. W. (1980). *Great Salt Lake*. Utah Geol Survey, Bull. 116, 400 pp.; with Murphy, P. J., pp. 83–97.
- Hamzaoui, H. A., M'nif, A., and Rokbani, R. (2000). "Lithium Retention by Sodium Chloride Crystals in Tunisia." *Eighth World Salt Symposium* 1, 517–521.
- Harben, P., and Edwards, G. (1998). "Lithium: Times are Changing." Can. Inst. Mining and Metal., Spec. Vol. 50, pp. 172–182.
- Heinrich, E. W. (1976). "A Comparison of Three Major Lithium Pegmatites; Varutrask, Bikita and Bernice Lake." *Lithium Resources and Requirements by the Year 2000*, pp. 50–54.
- Heinrich, E. W., Salotti, C. A., and Giardini, A. A. (1977). "Processes for the Removal of Iron from Spodumene." *Energy* 3, 273–279.
- Henderson, E. W. (1976). "A Comparison of Three Major Lithium Pegmatites." *Lithium Resources and Requirements by the Year 2000*, pp. 50–54.

- Holdorf, H., Ziegenbalg, G., and Schmidt, B. (1993). "Recovery of Lithium Compounds from Natural Salt Brines." Seventh Symposium on Salt 1, 571–595.
- Huh, Y., Chan, L. H., and Edmond, J. M. (2001). "Lithium Isotopes as a Probe of Weathering; Orinoco River." *Earth Planet. Sci. Lett.* **194**(1–2), 189–199.
- Ide, F. Y., and Kunasz, I. A. (1989). "Origin of Lithium in Salar de Atacama, Northern Chile." Geol. Andes 2, 165–172.
- Ide, F., Vergara-Edwards, L., and Pavlovic-Zuvic, P. (1983). "Solar Pond Design for the Production of Potassium Salts from the Salar de Atacama Brine." Sixth Int. Symp. Salt 2, 367–375.
- James, R., Allen, D. E., and Seyfried, W. E. (2003). "Experimental Study of Alteration of Oceanic Crust and Terrigenous Sediments at Moderate Temperatures." *Geochim. Cosmochim. Acta*, 681–691.
- Jordan, T. E., Munoz, N., Hein, M., Lowenstein, T., Godfrey, L., and Yu, J. (2002). "Active Faulting and Folding Without Topographic Expression in an Evaporite Basin, Chile." *Geol. Soc. Am. Bull.* 114(11), 1406–1421.
- Kesler, T. L. (1960). "Lithium Raw Materials." Ind. Miner. Rocks, Am. Inst. Min. Eng., Sect. 24, 521-531.
- Kesler, T. L. (1976). "Occurrence, Development and Long-Range Outlook of Lithium Pegmatites, North Carolina." *Lithium Resources and Requirements by the Year 2000*, pp. 45–50.
- Koschinsky, A., Siefert, R., Halbach, P., Bau, M., Brasse, S., deCarvalho, L. M., and Fonseca, N. M. (2002). "Geochemistry of Diffuse Low Temperature Hydrothermal Fluids in the North Fiji Basin." *Geochim. Cosmochim. Acta* 66(8), 1409–1427.
- Kuidong, Z., and Shaoyong, J. (2001). "Recent Advances in Research on Lithium Isotopes and its Geological Applications." *Geol. J. China Univ.* 7(4), 390–398.
- Kunasz, I. A. (1974). "Lithium Occurrences in the Brines of Clayton Valley, Esmeralda County, Nevada." Fourth Symp. Salt, N. Ohio Geol. Soc. 1, 57–66.
- Kunasz, I. A. (1980, 1976). "Lithium in Brines." Fifth Symp. Salt, N. Ohio Geol. Soc. 1, 115–117; Ind. Miner. Rocks, 791–803.
- Kunasz, I. A. (1994). "Lithium Resources." "Mono., Ind. Minerals, Rocks". (D. D. Carr ed.), pp. 631–642, Soc. Min. Met. Explor..
- Lasmanis, R. (1978). "Lithium Resources of the Yellowknife Area, Northwest Territories, Canada." Energy 3, 399 pp.
- Lima, A., Noronha, F., Charoy, B., and Farinha, J. (1999). "Exploration for Lithium Deposits in the Barroso-Alvao Area, Northern Portugal." *Mineral Deposits: Processes to Processing*, Vol. 2, pp. 1113–1116. Balkema, Rotterdam.
- Lloyd, J. E. (1981). "Lithium Chemicals." Speciality Inorg. Chem. 40, 98-122.
- London, D. (1984). "Experimental Phase Equilibria in the System LiAlSiO<sub>4</sub>-SiO<sub>2</sub>-H<sub>2</sub>O." Am. Mineralogist 69, 995-1004.
- Low, R., Anderson, D. M., Boak, R. A., and Nkala, G. (2000). "An Investigation of Solar Evaporation Pond Leakage and Possible Remedial Measures at Sua Pan, Botswana." *Eighth World Salt Symposium* 1, 523–528.
- Lowenstein, T. K., Li, J., Hanna, J., Godfrey, L., Jordan, T., Ku, T. L., and Lou, S. (1998). "80,000-Year Paleoclimate Record of the Salar de Hombre Muerto." *Geol. Soc. Am. Abs.* 30, 115–116.
- Manser, R. M. (1975). "Handbook of Silicate Flotation", 196 pp. Warren Spring Lab, Stevenage, England.
- Nagaytsev, Y. V., and Belyaev, A. M. (1995). "Mineralogical, Geochemical and Other Characteristics of a New Genetic Type of Lithium-Cesium Anomaly." *Geokhimiya* 1, 99–107.
- Nelli, J. R., and Arthur, T. E. (1970). "Recovery of Lithium from Bitterns." U.S. Patent 3,537,823, 8 pp. (Nov. 3).
- O'Neill, B. L., Kunasz, I. A., and Wright, L. A. (1969). "The Lithium Production Curve." *Earth Min. Sci., Pen. State Univ.* **30**(6), 45–48.
- Orrego, P., Goldman, C., Reveco, P., Valdes, E., Flores, M. E., Bustos, D., and Jandragholica, D. (1994). "Boron Solvent Extraction from Concentrated Brines of the Salar de Atacama." *Nucleotecnica* **14**(26), 39–46.

- Page, L. R. (1953). "Pegmatites in the Black Hills, South Dakota." U.S. Geol. Survey Prof. Paper 247, 1–206.
- Pandit, M. K., and Sharma, R. (1999). "Lithium Mineralization in Proterozoic Leucogranite, South Delhi Fold Belt, Western India." Anais Acad. Brasileira Ceincias 71(1), 67–77.
- Partington, G. A., McNaughton, N. J., and Williams, I. S. (1995). "A Review of the Geology, Mineralization and Chronology of the Greenbushes Pegmatite, Western Australia." *Econ. Geol.* 90(3), 616–635.
- Pauwels, H., Brach, M., and Foulliac, C. (1990). "Lithium Recovery from Geothermal Waters of Cesano, Italy and Cronembourg, Alsace, France." Proc. 12th New Zealand Geothermal Workshop 12, 117–123.
- Pearse, G. H., and Taylor, R. P. (2001). "The Big Whopper Rare Metals Pegmatite, Separation Rapids, Ontario." CIM Bull. 94(1049), 50–54.
- Petruk, W., and Sikka, D. B. (1987). "The Boanerge Lithium Deposit, Goias, Brazil." *Mining Eng.* **39**(2), 123–127.
- Qian, Z., and Xuan, Z. (1983). "Borate Minerals in Salt Lake Deposits at Chaidamu Basin, China." Sixth Int. Symp. Salt 1, 185–192.
- Raimbault, L., Cuney, M., Azencott, C., Duthou, J. L., and Joron, J. L. (1995). "Geochemical Evidence for a Multistage Magmatic Genesis of Ta–Sn–Li Mineralization in the Granite at Beauvoir, French Massif Central." *Econ. Geol.* **90**(3), 548–576.
- Rothbaum, H. P., and Middendorf, K. (1986). "Lithium Extraction from Wairakei Geothermal Waters." NZ J. Technol. 2(4), 231–235.
- Saller, M., and O'Driscoll, M. (2000). "Lithium Takes Charge." Ind. Miner. 390, 37-47 (March).
- Singleton, R. H. (1979). "Lithium." U.S. Bur. Mines, Mineral Commodity Profiles, 25 pp.
- Sirbescu, M. C., and Nabelek, P. I. (2001). "Pegmatite Melts at 340°C?" Geol. Soc. Am. 33(6), 333 pp.
- Smith, G. I. (1976). "Origin of Lithium in Searles Lake." U.S. Geol. Survey Prof. Paper 1005, 92–103.
- Smith, G. I. (1979). "Subsurface Stratigraphy and Geochemistry of Searles Lake, California." U.S. Geol. Survey Prof. Paper 1043, 122 pp.
- Spanjers, R. P. (1990). "The Hallman-Beam Spodumene Pegmatite Mine, Lithium Corporation of America." *Forum on the Geology of Industrial Minerals*, S. Carolina Geol. Survey, No. 24, pp. 115–119.
- SQM (2002, 2001). "Lithium." SQM S.A., Santiago, Chile, 4 pp.; "SQM," brochure, 35 pp.
- Stenger, V. A. (1950). "Preparation of Lithium Halides." U.S. Patent 2,516,659, 3 pp. (July 25).
- Strum, P. A. (1980). "The Great Salt Lake Brine System." "Great Salt Lake". (J. W. Gwynn ed.), pp. 147-162.
- Symons, R. (1961). "Operation at Bikita Minerals, Southern Rhodesia." *Inst. Mining, Metall. Bull.* 661, 129–172.
- Tambourakis, G., Frost, M. T., and Clynick, G. B. (1990). "Spodumene from the Lithium Pegmatite at Greenbushes, Western Australia." *Aust. Mineralogist* 5, 19–23 (Jan.–Mar.).
- Tandy, S., and Canfy, Z. (1993). "Lithium Production from Highly Saline Dead Sea Brines." Rev. Chem. Eng. 9(3–4), 293–317.
- Taylor, G. (2002). "TANCO, Special Report." Supplement to Trade and Commerce Magazine, 4 pp.
- Tindle, A. G., and Breaks, F. W. (2000). "Tantalum Mineralogy of Rare-Element Granitic Pegmatites from the Separation Lake Area, Northwestern Ontario, Canada." Ontario Geol. Survey, Toronto, Open File Rept. No. 6022, 378 pp.; Mineralogy and Petrology, Vol. 70, pp. 165–198.
- Tomascak, P. B., Widom, E., Benton, L. D., Goldstein, S. L., and Ryan, J. G. (2002). "The Control of Lithium Budgets in Island Arcs." *Earth Planet. Sci. Lett.* 196(3–4), 227–238.
- Tomascak, P. B., Hemming, N. G., and Hemming, S. R. (2003, 2001, 2000). "The Lithium Isotopic Composition of Waters of the Mono Basin." *Geochim. Cosmochim. Acta* 67 (4), 601–611; *Geol. Soc. Am.* 33(6), 351; 32(7), 77.

- Toomey, R. (1980). "Production of Magnesium from the Great Salt Lake." "Great Salt Lake". (J. W. Gwynn ed.), pp. 218–222.
- Tuzinski, P. A. (1983). "Rare-Alkali Ion Halos Surrounding the Bob Ingersoll Lithium Bearing Pegmatite Mine, Keystone, Black Hills, South Dakota." Master's Deg., Kent State Univ., 121 pp.
- USGS (2002–1958). "Lithium." U.S. Geol. Survey Minerals Yearbook; Minerals Commodity Rept., 2–12 pp.
- Ustinova, G. K. (1998). "A Possible Solution to the Problem of the Origin of Li, Be and B." *Doklady Earth Sci.* **358**(1), 124–127.
- Vanstone, P. J., Young, S., Galeschuk, C., Simard, R., and Gibb, A. (2002). "The TANCO Rare-Element Pegmatite, Southeastern Manitoba", 20 pp. Tantalum Mining Corpp., Lac du Bonnet, Man.
- Vergara-Edwards, L., and Parada-Frederick, N. (1983). "Study of the Phase Chemistry of the Salar de Atacama Brine." Sixth Int. Symp. Salt 2, 345–366.
- Ver Planck, W. E. (1957). "Calcium Chloride." Calif. Div. Mines, Geol. Bull. 176, Mineral Commodities of Calif., pp. 101–104.
- Vila, T. (1990). "Salar Deposits in Northern Chile." Stratabound Ore Deposits in the Andes, pp. 703–720. Springer, Berlin.
- Vine, J. D. (1976). "Non-Pegmatite Lithium Resource Potential." U.S. Geol. Survey Prof. Paper 1005, 54–58.
- Vine, J. D. (1980). "Where on Earth is All of the Lithium." U.S. Geol. Survey, Open-File Rept. 80-1234, 107 pp.
- Vine, J. D., et al. (1979). "Lithium in Sedimentary and Volcanic Rocks." U.S. Geol. Survey Prof. Paper 1150, 15–17.
- Volborth, A. (1954). "Phosphate Minerals from the Lithium Pegmatite in the Viitaniemi, Eraejaervi, Central Finland." *Geologica Geographia, Series A3*, 90 pp.
- Voznyak, D. K., Bugaenko, V. M., and Galaburda, Y. A. (2000). "Pegmatites in the Western Kirovograd Block (Ukrainian Shield)." *Mineral. Zhur.* 22(1), 21–41.
- Vyas, M. H., Sanghavi, J. R., and Seshadri, K. (1975). "Lithium Extraction from Indian Lepidolite Ores." *Res. Ind.* 20, 68–70 (June).
- Whelan, J. A. (1976). "Lithium Resources of Utah." *Lithium Resources and Requirements by the Year* 2000, pp. 75–78.
- White, D. E., Thompson, J. M., and Fournier, R. O. (1976). "Lithium Content of Thermal and Mineral Waters." *Lithium Resources and Requirements by the Year 2000*, pp. 58–60.

www.hustonlakemining.com (1999). Pakeagama Lake, 4 pp.

- Xu, S., Xia, J., and Shen, G. (1998). "The Pressure Leaching of Calcined Lepidolite by Ammonium Chloride." *Light Metals*, 1319–1324.
- Yin, L., Pollard, P. J., Shouxi, H., and Taylor, R. G. (1995). "Geologic and Geochemical Characteristics of the Yichun Ta–Nb–Li Deposit, Jiangxi Province, South China." *Econ. Geol., Bull. Soc. Econ. Geol.* 90(3), 577–585.
- You, C. F., and Gieskes, J. M. (2001). "Hydrothermal Alteration of Hemi-Pelagic Sediments." Appl. Geochem. 16(9–10), 1055–1066.

### Processing

- Abe, M., Chitrakar, R., and Tsiyi, M. (1993). "Lithium Recovery from Seawater with Various Inorganic Ion Exchangers." Seventh Symposium on Salt 2, 17–21.
- Afgouni, K., and Silva Sa, J. H. (1978). "Lithium Ore in Brazil." Energy 3, 247 pp.
- Amer, A. M., and Rashed, M. A. (2002). "Hydrometallurgical Extraction of Lithium from Montmorillonite-type Clays." *Inzynieria Mineralna* 3(2), 27–34.
- Andrews, H. J. (1958). "Lithium Extraction from Run-of-Mine Spodumene Ore." Chem. Eng. Prog. 54(1), 54–55.

Anon. (1967). "Soft Route to Lithium." Chem. Week, 20 (June).

Anon. (1970). "Silver Peak Gives Bright Look to Foote Mineral's Lithium Picture." *Eng.*, *Mining J.* **171**(4), 71–73.

- Anon. (1976). "Foote Mineral Company Producing Lithium Carbonate." *Chemical Week*, **32** (Oct. 20). Anon. (1981). "Lithium Producers Gear-Up for a Bright Future." *C&EN*, 11 (Oct. 26).
- Anon. (1984a). "New Lithium Frontier in Chile." Foote Prints (Foote Mineral Co.) 47(1), 2-14.
- Anon. (1984b). "Argentine Project Demonstrates Reserves for Lithium Brines." Mining Eng., 660 (July).
- Archambault, M., and Olivier, C. (1963). "Lithium Carbonate Production." U.S. Patent 3,112,171, 7 pp. (Nov. 26).
- Arqueros, R. P. (2002). Personal Communication, Operations Manager, SQM, S.A., Antofagasta, Chile.
- Averill, W. A., and Olson, D. L. (1977). "Winning Lithium Metal." The Lithium Symp. 3(3), 308-313.
- Bach, R. O., Kamienski, C. W., and Ellestad, R. B. (1967). "Lithium and Lithium Compounds." Kirk-Othmer Encyclopedia of Chem. Tech., Vol. 12, pp. 529–556. Wiley, New York.
- Barrett, W. T., and O'Neill, J. O. (1970). "Recovery of Lithium from Saline Brines Using Solar Evaporation." *Third Symp. Salt* 2, 47–50.
- Bauman, W. C., and Burba, J. L. (2001, 1997, 1995). "Recovery of Lithium Values from Brines." U.S. Patents 6,280,693, 5,389,349 and 5,599,516, ~5 pp. (Aug. 28, Feb. 4 and Feb. 14).
- Berthold, C. F., and Baker, D. H. (1976). "Lithium Recovery from Geothermal Fluids." Lithium Resources and Requirements by the Year 2000, pp. 61–65.
- Brown, P. M., and Beckerman, S. J. (1990). "Production of Lithium Metal Grade Lithium Chloride from Lithium-Containing Brine." U.S. Patent 4,980,136, 8 pp. (Dec. 25).
- Bruhn, G., Cofre, A., Flores, M. E., Lira, S., Parades, C., Vivanco, B., Valdes, E., and Reveco, P. (1998). "Production of Lithium Salts from Salar de Atacama Brine." *Informacion Tecnologica* 9(2), 245–251.
- Bukowsky, H., Uhlemann, E., and Steinborn, D. (1991). "The Recovery of Lithium from Brines Containing more Calcium than Magnesium." *Hydrometallurgy* 27, 317–325.
- Burt, R. O., Flemming, J., Simard, R., and Vanstone, P. J. (1988). "Tanco—A New Name in Low Iron Spodumene." Ind. Miner. 244, 55–59 (Jan.).
- Chem. Week (1998, 1995). "New Lithium Capacity on the Horizon." 160 (46), 50; 157 (20), 30.
- Chitrakar, R., Kanoh, H., Miyai, Y., and Ooi, K. (2001). "Recovery of Lithium from Seawater Using Manganese Oxide Adsorbants." *Ind. Eng. Chem. Res.* 40, 2054–2058.
- Coad, M. (1984). "Lithium Production in Chile's Salar de Atacama." Ind. Miner. 205, 27-33 (Oct.).
- Cooper, J. F., Kirkorian, O. H., and Homsy, R. V. (1979). "Lithium Production by a Lithium Amalgam Electrode." U.S. Patent 4,156,635, 4 pp. (May 29).
- CORFO (1985). "The Commercial Development of the Salar de Atacama." Santiago, Chile, Various reports.
- Crouse, R. A., Cerny, P., Trueman, D. L., and Burt, R. O. (1984). "The Tanco Pegmatite, Southeast Manitoba." *The Geology of Industrial Minerals in Canada*, CIM Spec., Vol. 29, pp. 169–176.
- Crozier, R. D. (1986). "Lithium: Resources and Prospects." *Mining Mag. (London)* **154**(2), 148–152 (Feb.).
- Dang, V. D., and Steinberg, M. (1978). "Preliminary Design of a Lithium Recovery Process with a Selective Solvent." *Energy* 3, 325–336.
- Davis, J. R., and Vine, J. D. (1979). "Stratigraphic and Tectonic Setting of the Lithium Brine Field, Clayton Valley, Nevada." *Basin and Range Symp.*, pp. 421–430. Rocky Mt. Assoc. Geol.
- Deberitz, J. (1993). "Lithium", 70 pp. Verlag Moderne Industrie AG & Co., Landsberg/Lech., Germany.
- Dillard, G., and McClean, S. (1991). "Cyprus Foote Mineral Taps a Unique Treasure." Rocky Mt. Pay Dirt, pp. 4A–8A (Sept.).
- Dresler, W., Jena, B. C., Reilly, I. G., Laffin, S., and Egab, E. (1998). "The Extraction of Lithium Carbonate from a Pegmatite." *Light Metals*, 1303–1308.
- Ellestad, R. B., and Clarke, F. F. (1955). "Extraction of Lithium from its Ores." *Mining Eng.* 7(11), 1045–1047.
- Ellestad, R. B., and Leute, K. M. (1950). "Method of Extracting Lithium Values from Spodumene Ores." U.S. Patent 2,516,109, 5 pp. (July 25).
- Epstein, J. A., Feist, E. M., Zmora, J., and Marcus, Y. (1981). "The Recovery of Lithium from the Dead Sea." *Hydrometallurgy* 6, 269–275.

Etchart, J. P. (2002). Personal Communication, SQM S.A., Process Engineer, Salar de Atacama, Chile. Ezzell, C. (2003). "The Magic of Lithium." *Sci. Am.* **288**(2), 49 pp.

- Fieve, R. R., and Peselow, E. D. (1985). "Lithium Toxicology." "Lithium". (R. O. Bach ed.), John Wiley & Sons, New York, pp. 353–375.
- Flanagan, J. T. (1978). "Lithium Deposits and Potential of Quebec and Atlantic Provinces of Canada." *Energy* 3, 391–395.
- Flemming, J. (1993a,b). "Mining (a) and Treatment (b) of Spodumene Ore at the Greenbushes Mine of Gwalia Consolidated Limited, Greenbushes, WA." Australian Mining, Metal., 2nd ed., Vol. 2. Monograph 19, pp. 1417–1422.
- Folkestad, F. E., Loiten, K. O., Mejdell, G. T., and Torvund, A. (1974). "Method of Removing Boric Acid from Magnesium Chloride Solutions." U.S. Patent 3,855,392, 4 pp. (Dec. 17).
- Gabra, G. G., and Torma, A. E. (1978). "Lithium Chloride Extraction by *n*-Butanol." *Hydrometallurgy* **3**, 23–33.
- Gadsby, E. A. (1967). "Lithium from Nevada Brine." Am. Chem. Soc. 3rd Western Regional Meeting; AIChE Meeting, Chicago, 6 pp.
- Gale, W. A. (1945). "Lithium from Searles Lake." Chem. Ind., 442-446 (Sept.).
- Garrett, D. E. (1963, 1961). "Recovering Boron from Brines by Solvent Extraction." U.S. Patents 2,969, 275 and 3,111,383, 6 pp. (Jan. 24 and Nov. 1).
- Garrett, D. E. (1966). "The Design of Solar Pond Systems." *Second Symp. Salt* **2**, Pond Design, 169–176; Operation, 176–188.
- Garrett, D. E. (1970). "Method of Producing Potassium Sulfate from Sulfate-Containing Brines." U.S. Patent 3,528,767, 7 pp. (Sept. 15); Australian Patent 17,844/67, 31 pp. (Feb. 17, 1967).
- Garrett, D. E. (1975). "Method of Producing Coarse Potash from Carnallite." U.S. Patent 3,895,920, 6 pp. (July 22).
- Garrett, D. E. (1985, 1967, 1960). Personal files.
- Garrett, D. E. (1992). "Natural Soda Ash", 636 pp. Van Nostrand Reinhold, New York.
- Garrett, D. E. (1996). "Potash; Deposits, Processing, Properties and Uses", 734 pp. Chapman & Hall, London.
- Garrett, D. E. (1998). "Borates; Handbook of Deposits, Processing, Properties and Use", 483 pp. Academic Press, San Diego, CA.
- Garrett, D. E., and Laborde, M. (1983). "Salting-Out Process for Lithium Recovery." *6th Int. Salt Symp.* **2**, 421–430; U.S. Patent 4,287,163, 6 pp. (Sept. 1, 1981).
- Gauguin, R., Seine, N. S., and Claus, J. (1961). "Purifying Lithium Salts." U.S. Patent 3,000,699, 3 pp. (Sept. 19).
- Goodenough, R. D. (1960). "Recovery of Lithium." U.S. Patent 2,964,381, 6 pp. (Dec. 13).
- Goodenough, R. D., and Gaska, R. A. (1967). "Recovery of Lithium from Calcium-Containing Brines." U.S. Patents 3,307,922 and 3,306,712, 3 pp. (Mar. 7; Feb. 28).
- Goodenough, R. D., and Stenger, V. A. (1958). "Recovery of Lithium from Lithium-Bearing Ores." Canadian Patent 583,364, 5 pp. (Dec. 30).
- Goter, E. R., Hudspeth, W. R., and Rainey, D. L. (1953). "Mining and Milling of Lithium Pegmatites at Kings Mountain, N.C." *Mining Eng.* 5(9), 880–893.
- Hader, R. N., Nielsen, R. L., and Herre, M. G. (1951). "Lithium and its Compounds." *Ind. Eng. Chem.*, 2636–2646 (Dec.).
- Harben, P., and Edwards, G. (1997). "MINSAL Lithium Carbonate." Ind. Miner., 25-39 (Feb.).
- Harben, P., and Edwards, G. (1998). "Lithium: Times are Changing." Can. Inst. Mining Metal., Spec. Vol. 50, pp. 171–182.
- Heinrich, E. W., Salotti, C. A., and Giardini, A. A. (1977). "Processes for the Removal of Iron from Spodumene." *Energy* 3, 273–279.
- Hermann, J. A. (1966). "Preparation and Purification of Lithium Chloride." U.S. Patent 3,278,260, 4 pp. (Oct. 11).

- Holdorf, H., Ziegenbalg, G., and Schmidt, B. (1993). "Recovery of Lithium Compounds from Natural Salt Brines." Seventh Symposium on Salt 1, 571–595.
- Howling, H. L. (1963). "Purification of Leach Liquors Containing Lithium Values." U.S. Patent 3,099, 527, 3 pp. (July 30).
- Johnson, N. O. (1958). "Kings Mountain Lithium Mining Operations." Mining Cong. J. 44(1), 52-56.
- Kamienski, C. W., McDonald, D. P., and Stark, M. W. (1997). "Lithium and Lithium Compounds." Ency. Chem. Technol., Kirk-Othmer, 1207–1208.
- Kaneko, S., and Takahashi, W. (1990). "Adsorption of Lithium from Sea Water on Aluminum– Magnesium Oxide Gels." Colloids Surf. 47, 69–79.
- Kesler, T. L. (1960). "Lithium Raw Materials." Ind. Miner. Rocks, Am. Inst. Min. Eng., Sect. 24, 521-531.
- Kesler, T. L. (1976). "Occurrence, Development and Long-Range Outlook of Lithium Pegmatites, North Carolina." *Lithium Resources and Requirements by the Year 2000*, pp. 45–50.
- Kingsnorth, D. J. (1988). "Lithium Minerals in Glass." Ind. Miner. (London)(244) (Feb. 28).
- Kinugasa, T., Nishibara, H., Murao, Y., Kawamura, Y., and Watanabe, K. (1994). "Equilibrium and Kinetics of Liquid Extraction by a Mixture of LIX54 and TOPO." J. Chem. Eng. Jpn 27(6), 815–817.
- Kunasz, I. A. (1994). "Lithium Resources." "Mono., Ind. Minerals, Rocks". (D. D. Carr ed.), pp. 631–642, Soc. Min. Met. Explor.
- LCA (1968). "Lithium." Lithium Corporation of America Brochure, 16 pp.
- Lee, D. R., and Cherry, J. A. (1978). "A Field Exercise on Groundwater Flow Using Seepage Meters and Mini-Piezometers." J. Geol. Educ. 27, 6–10.
- Lee, C. K., and Yang, D. H., (2001, 2002). "Recovery of Valuable Metals from Spent Lithium Ion Batteries." Kongop Hwahak 12 (8), 890–895; J. Power Sources 109 (1), 17–21.
- Lee, D. A., Taylor, W. L., McDowell, W. J., and Drury, D. S. (1968). "Solvent Extraction of Lithium." J. Inorg. Nucl. Chem. 30, 2807–2821.
- Lien, R. H. (1985). "Recovery of Lithium from Clay." "Lithium". (R. O. Bach ed.), John Wiley & Sons, New York, pp. 61–71.
- Lindblad, A. R., Walden, S. J., and Sivander, K. A. (1943). "Method of Recovering Lithium from Minerals." U.S. Patent 2,331,838, 3 pp. (Oct. 12).
- Lloyd, J. E. (1981). "Lithium Chemicals." Speciality Inorg. Chem. 40, 98-122.
- Low, R., Anderson, D. M., Boak, R. A., and Nkala, G. (2000). "An Investigation of Solar Evaporation Pond Leakage and Possible Remedial Measures at Sua Pan, Botswana." *Eighth World Salt Symposium* 1, 523–528.
- Ma, P., and Chen, X. D. (2000). "Lithium Extraction from Multicomponent Mixtures Using Supported Liquid Membranes." Sep. Sci. Technol. 35(15), 2513–2533.
- Manser, R. M. (1975). "Handbook of Silicate Flotation", 196 pp. Warren Spring Lab., Stevenage, England.
- May, F. H. (1952). "Process for Producing Lithium Sulfate from Lithium Phosphate." U.S. Patent 2,608, 465, 7 pp. (Aug. 26).
- Miyai, Y., Kanoh, H., Chitrakar, R., and Ooi, K. (2001). "Lithium Adsorptive Properties of a New Type of Ion-sieve, Li<sub>2</sub>Cr(PO<sub>4</sub>)<sub>1.67</sub>." *Nippon Kaisui Gakkaishi* 55(2), 97–102.
- Morris, D. F., and Short, E. L. (1963). "Extraction of Lithium Chloride by Tri-n-Butyl Phosphate." J. Inorg. Nucl. Chem. 25, 291–301.
- Moura, S. (2002). Personal Communication, SQM S.A., Investor Relations, Santiago, Chile.
- Munson, G. A., and Clarke, F. F. (1955). "Mining and Concentrating Spodumene in the Black Hills, South Dakota." *Mining Eng.* 7(11), 1041–1045.
- Nakousi, C. (2003). Personal Communication, SQM S.A., Santiago, Chile.
- Neipert, M. P., and Bon, C. K. (1967). "Method of Lithium Recovery." U.S. Patent 3,306,700, 4 pp. (Feb. 28).
- Nelli, J. R., and Arthur, T. E. (1970). "Recovery of Lithium from Bitterns." U.S. Patent 3,537,823, 8 pp. (Nov. 3).
- Nicholson, C. M. (1946). "Lithium Extraction." U.S. Patent 2,413,644, 4 pp. (Dec. 31).

- Olsher, U. (1982). "Lithium-Selective Membrane." J. Am. Chem. Soc. 104, 4006-4009.
- O'Neill, B. L., Kunasz, I. A., and Wright, L. A. (1969). "The Lithium Production Curve." Earth, Min. Sci., Pen. State Univ. 30(6), 45–48.
- Orrego, P., Goldman, C., Reveco, P., Valdes, E., Flores, M. E., Bustos, D., and Jandragholica, D. (1994). "Boron Solvent Extraction from Concentrated Brines of the Salar de Atacama." *Nucleotecnica* **14**(26), 39–46.
- Pan, L., Zhu, J., and Li, Y. (2002). "Lithium Resources and Progress in their Exploitation Technology." *Kuang. Zong. Liyong* 2, 28–33.
- Pauwels, H., Brach, M., and Foulliac, C. (1990). "Lithium Recovery from Geothermal Waters of Cesano, Italy and Cronembourg, Alsace, France." Proc. 12th New Zealand Geothermal Workshop 12, 117–123.
- Pavlovic-Zuvic, P., Parada-Frederick, N., and Vergara-Edwards, L. (1983). "Recovery of Potassium Chloride, Potassium Sulfate, Lithium and Boric Acid from the Salar de Atacama." *Sixth Symp. Salt* 2, 377–394.
- Pearse, G. H., and Taylor, R. P. (2001). "The Big Whopper Rare Metals Pegmatite, Separation Rapids, Ontario." CIM Bull. 94(1049), 50–54.
- Pelly, I. (1978). "Recovery of Lithium from Dead Sea Bitterns." J. Appl. Chem. Biotechnol. 28, 469-475.
- Ramirez, M. V. (2002). SQM S.A., Process Superintendent, Salar de Atacama, Chile, Personal Communication.
- Ramos, R. O., and Kirigin, J. A. (2000). "Flotation of Potassium Salts from Brines and Magmas of Salar de Uyuni, Bolivia." *Rev. Boliviana Quim.* 17(1), 67–69.
- Rothbaum, H. P., and Middendorf, K. (1986). "Lithium Extraction from Wairakei Geothermal Waters." NZ J. Technol. 2(4), 231–235.
- Ryabtsev, A. D., Menzheres, L. T., and Ten, A. V. (2002). "Sorption of Lithium from Brine into Granular LiCl·2Al(OH)<sub>3</sub>·m H<sub>2</sub>O Sorbent under Dynamic Conditions." *Russian J. Appl. Chem.* 75(7), 1069–1074.
- Rykken, L. E. (1976). "Lithium Production from Searles Valley." Lithium Resources and Requirements by the Year 2000, pp. 33–34.
- Saline (1985). "The Commercial Development of the Salar de Atacama." Ojai, California, Various reports for CORFO by Saline Processors, Inc.
- Saller, M., and O'Driscoll, M. (2000). "Lithium Takes Charge." Ind. Miner. (390), 37-47 (March).
- Sax, N. I. (1979). "Dangerous Properties of Industrial Materials", 1118 pp. Van Nostrand Reinhold Co., New York.
- Schmitt, B. (1998). "New Players in the Lithium Scene." Chem. Week 160(46), 50 (Dec. 2).
- Siegens, H., and Roder, O. (1934). "Process for the Production of Lithium Salts." U.S. Patent 2,040,573, 3 pp. (May 12).
- Sprinskiy, M. I. (2000). "Prospects for the Industrial Utilization of the Carpathian Groundwater Enriched in Lithium." *Geol. Geokhim. Goryuc. Kopalin* 3, 39–51.
- SQM (2002, 2001). "SQM, Lithium." SQM S.A., Santiago, Chile, 35 pp.; SQM Investor Relations, 2 pp.; 2001. "Lithium." SQM Chemicals, 4 pp.
- Stenger, V. A. (1950). "Preparation of Lithium Halides." U.S. Patent 2,516,659, 3 pp. (July 25).
- Stinson, S. C. (1981). "Lithium Producers Expand." C&EN, 11-13 (Oct. 26).
- Strum, P. A. (1980). "The Great Salt Lake Brine System." "Great Salt Lake". (J. W. Gwynn ed.), pp. 147–162. Utah Geological and Mineral Survey, Utah.
- Sun, D., and Lock, D. E. (1990). "Origins of Potash Deposits in the Qaidam Basin." *Sci. China, Ser. B* **33**(2), 198–210 (Feb.).
- Symons, R. (1961). "Operations at Bikita Minerals, Southern Rhodesia." Inst. Mining Metal. Bull. 661, 129–172.
- Tamlin, M., Sheth, A., and McCracken, D. J. (2002). "Lithium." Mining Eng. 54(6), 37-38.
- Tanaka, K., and Shimamune, T. (2003). "Electrolytic Recovery of Cobalt and Lithium from Battery Materials." Japanese Patents 2003031229, 2003027151, 6 pp., 7 pp. (1/31, 1/29).

- Tandy, S., and Canfy, Z. (1993). "Lithium Production from Highly Saline Dead Sea Brines." Rev. Chem. Eng. 9(3-4), 293–317.
- Taylor, G. (2002). "TANCO", 4 pp. Tantalum Mining Corpp., Lac du Bonnet, Man.
- Toomey, R. (1980). "Production of Magnesium from the Great Salt Lake." "Great Salt Lake". (J. W. Gwynn ed.), pp. 218–222. Utah Geological and Mineral Survey, Utah.
- Umeno, A., Miyai, Y., Takagi, N., Chitrakar, R., Sakane, K., and Ooi, K. (2002). "Preparation of Membrane-Type Adsorbents for Lithium Recovery from Seawater." *Ind. Eng. Chem. Res.* 41, 4281–4287.
- U.S. Bur. Mines (1992). "Lithium." U.S. Bureau of Mines, Minerals Yearbook, Minerals Commodity Report, ∼2–10 pp.
- USGS (2002, 2001, 2000, 1997, 1992). "Lithium." U.S. Geol. Survey Minerals Yearbook, Minerals Commodity Report, ~2–10 pp.
- Vanstone, P. J. (2002). "TANCO History", 6 pp. Tantalum Mining Corpp., Lac du Bonnet, Man.
- Vanstone, P. J., Young, S., Galeschuk, C., Simard, R., and Gibb, A. (2002). "The TANCO Rare-Element Pegmatite, Southeastern Manitoba", 20 pp. Tantalum Mining Corpp., Lac du Bonnet, Man.
- Vergara-Edwards, L., and Parada-Frederick, N. (1983). "Study of the Phase Chemistry of the Salar de Atacama Brine." Sixth Int. Symp. Salt 2, 345–366.
- Vergara-Edwards, L., Parada-Frederick, N., and Pavlovic-Zuvic, P. (1985). "Recovery of Lithium from Crystallized Salts in the Solar Evaporation of Salar de Atacama Brines." *Lithium: Current Appl. Sci.*, *Med. Tech.*, pp. 47–59. Wiley, New York.
- Vine, J. D. (1980). "Where on Earth is All of the Lithium." U.S. Geol. Survey, Open-File Rept. 80-1234, 107 pp.
- Vyas, M. H., Sanghavi, J. R., and Seshadri, K. (1975). "Lithium Extraction from Indian Lepidolite Ores." *Res. Ind.* 20, 68–70.
- Wilkomirsky, I. F. (1998). "Extractive Metallurgy of Lithium." Miner. Rev. 53(221), 31-36.
- Williams, T. A. (1976). "Lithium." Eng. Mining J., 40-41 (Mar.).
- Xu, S., Xia, J., and Shen, G. (1998). "The Pressure Leaching of Calcined Lepidolite by Ammonium Chloride." *Light Metals*, 1319–1324.

### Uses

- Abraham, K. M. (1985). "Ambient Temperature Secondary Lithium Cells." "Lithium". (R. O. Bach ed.), pp. 155–175, (Sec. 11). Wiley, New York.
- Alper, J. (2002). "Building a Better Battery." Chemistry, Autumn, Am. Chem. Soc., pp. 11-14.
- Anon. (1981). "Lithium Market to Grow 5-8% per Year." Chem. Marketing Reporter pp. 5 and 20 (Oct. 19).
- Anon. (1998). "Aluminum-Lithium Alloys." Light Metal Age 56(1-2), 102-105.
- Anon. (2000). "New Lithium Battery Design." Sci. News 158, 399 (Dec. 16).
- Anon. (2001, 2002). "Lithium." Mining Eng. 53(6), 44-46 (June).
- Burt, R. O., Flemming, J., Simard, R., and Vanstone, P. J. (1988). "Tanco—A New Name in Low Iron Spodumene." Ind. Miner.(244), 55–59 (Jan.).
- Cairns, E. (2002). "Batteries and Fuel Cells." Newsletter, College of Chem., U. Calif., Berkeley 10(3), 4 (May).
- D'Amico, E. (1996). "Growth Energizes Lithium Ion Interest." Chem. Week 58(11), 46 (Mar. 20).
- Deberitz, J. (1993). "Lithium", 70 pp. Verlag Moderne Industrie AG & Co., Landsberg/Lech., Germany.
- Dresler, W., Jena, B. C., Reilly, I. G., Laffin, S., and Egab, E. (1998). "The Extraction of Lithium Carbonate from a Pegmatite." *Light Metals*, 1303–1308.
- Flemming, J. (1993a,b). "Mining (a) and Treatment (b) of Spodumene Ore at the Greenbushes Mine of Gwalia Consolidated Limited, Greenbushes, WA." Australian Mining, Metal., 2nd ed., Vol. 2. Monograph 19, pp. 1417–1422.
- Harben, P., and Edwards, G. (1998). "Lithium: Times are Changing." Spec. Vol., Can. Inst. Mining Metal. 50, 171–182.
- Jarvis, L. (2000). "Lithium Prices." Chem. Marketing Reporter 257(15), 6 (Apr. 10).

- Kamienski, C. W., McDonald, D. P., and Stark, M. W. (1993). "Lithium and Lithium Compounds." Ency. Chem. Technol., Kirk-Othmer, 1207–1208.
- Kesler, T. L. (1960). "Lithium Raw Materials." *Ind. Miner. Rocks, Am. Inst. Min. Eng., Sect.* 24, 521–531. Kingsnorth, D. J. (1988). "Lithium Minerals in Glass." *Ind. Miner. (London)*(244) (Feb. 28).
- Kunasz, I. A. (1994). "Lithium Resources." "Mono., Ind. Minerals, Rocks". (D. D. Carr ed.), pp. 631–642, Soc. Min. Met. Explor..
- Lerner, I. (2001). "Metal-Based Chemicals for Batteries." *Chem. Marketing Reporter* **259**(22), 9 (May 29).
- LCA (1968). "Lithium." Lithium Corporation of America Brochure, 16 pp.
- Lloyd, J. E. (1981). "Lithium Chemicals." Speciality Inorg. Chem. 40, 98-122.
- Marincic, N. (1985). "High Energy Lithium Batteries." "Lithium". (R. O. Bach ed.), pp. 103–119, Sec. 11. Wiley, New York.
- McCracken, D. J., and Sheth, A. (1999). "Lithium Minerals." Am. Ceram. Soc. Bull. 78(8), 132–134.
- Nicholson, P. (1977). "The Use of Lithium in the Aluminum Industry." Energy 3, 243-246.
- Saller, M., and O'Driscoll, M. (2000). "Lithium Takes Charge." Ind. Miner. (390), 37-47 (March).
- Schmitt, B. (1999). "Chemical Demand for Lithium Batteries." Chem. Week 161(21), 34 (June 2).
- SQM (2002, 2001). "SQM, Lithium." SQM S.A., Santiago, Chile, 35 pp.; SQM Investor Relations, 2 pp.; 2001. "Lithium." SQM Chemicals, 4 pp.
- Tamlin, M., Sheth, A., and McCracken, D. J. (2002). "Lithium." Mining Eng. 54(6), 37-38.
- Tullo, A. H. (2002). "Maintaining a Charge." C&EN 80(28), 25-26 (July 15).
- U.S. Bur. Mines (1992). "Lithium." Annual Commodity Report, Ober, J. A., U.S. Dept. Interior, Bur. Mines, 10 pp. (June 1993).
- USGS (1997, 1986). "Lithium." Annual Commodity Report, Ober, J. A., U.S. Dept. of Interior, Geological Survey, 8 pp.
- Vanstone, P. J., Young, S., Galeschuk, C., Simard, R., and Gibb, A. (2002). "The TANCO Rare-Element Pegmatite, Southeastern Manitoba", 20 pp. Tantalum Mining Corpp., Lac du Bonnet, Man.

#### Statistics

- Anon. (2001). "Lithium." Mining Eng., 44-46 (June).
- Anstett, T. F., Krauss, U. H., Ober, J. A., and Schmidt, H. W. (1990). "Lithium." Int. Strat. Min. Invest. Summ. Rept., U.S. Geol. Survey Circular 930-I, 28 pp.
- Harben, P., and Edwards, G. (1997). "MINSAL Lithium Carbonate." Ind. Miner., 25-39 (Feb.).
- Jarvis, L. (2000). "Lithium Prices." Chem. Marketing Reporter 257(6), 6 (Apr. 10).
- Johnson, N. O. (1958). "Kings Mountain Lithium Mining Operation." Mining Cong. J. 44(1), 52-56.
- Kingsnorth, D. J. (1988). "Lithium Minerals in Glass." Ind. Miner. (London)(244) (Feb. 28).
- O'Neill, B. L., Kunasz, I. A., and Wright, L. A. (1969). "The Lithium Production Curve." Earth, Min. Sci., Pen. State Univ. 30(6), 45–48.
- Saller, M., and O'Driscoll, M. (2000). "Lithium Takes Charge." Ind. Miner. (390), 37-47 (March).
- Stinson, S. C. (1981). "Lithium Producers Expand." C&EN, 11-13 (Oct. 26).
- USGS (or U.S. Bur. Mines), 1900–2002. "Lithium." Commodity Report, U.S. Dept. Interior, ~2–10 pp. each year.

#### Chemistry, Phase Data, Physical Properties

- Anon. (2000). "Lithium's Different Crystal Structure Under Pressure." C&EN 78(46), 20 (Nov. 3).
- Anstett, T. F., Krauss, U. H., Ober, J.A., and Schmidt, H. W. (1990). "Lithium." Int. Strat. Min. Invest. Summ. Rept., U.S. Geol. Survey Circular 930-I, 28 pp.
- Campbell, A. N., and Kartzmark, E. M. (1956). "The Five Component System: Lithium, Sodium, Potassium, Sulfate, Chloride and Water." *Can. J. Chem.* **34**, 672; 1958, **36**, 171; 1959, **37**, 1409; 1958 with Lovering, E. G. **36**, 1511–1517; 1961 with Hutton, H. M. **39**, 1462–1474.
- Coplen, T. B. (1997). "Atomic Weights of the Elements, 1999." J. Phys. Chem. Ref. Data 26(5), 1239-1243.

- Deng, T. L., Yin, H. A., and Tang, M. L. (2002). "Experimental and Predictive Phase Equilibrium of the Li, Na, Cl, CO<sub>3</sub> System at 298.15°K." J. Chem., Eng. Data 47(1), 26–29.
- Garrett, D. E. (1996). "Potash; Geology, Processing, Uses and Phase Data", 734 pp. Chapman & Hall, London.
- Garrett, D. E., and Laborde, M. (1983). "Phase Diagrams at 0°C, 35°C and 50°C of Li, Mg, Cl, SO<sub>4</sub>, H<sub>2</sub>O." Sixth Int. Salt Symp. **2**, 424 pp.
- LCA (1968). "Lithium." Lithium Corporation of America Brochure, 16 pp.
- Lien, R. H. (1985). "Recovery of Lithium from Clay." "Lithium". (R. O. Bach ed.), pp. 61-71.
- Lloyd, J. E. (1981). "Lithium Chemicals." Speciality Inorg. Chem. 40, 98-122.
- May, F. H. (1952). "Process for Producing Lithium Sulfate from Lithium Phosphate." U.S. Patent 2,608, 465, 7 pp. (Aug. 26).
- Seidell, A. (1965). "Solubilities", *Lithium*, Vol. 2, pp. 362–440. American Chemical Society, Washington, DC.