

Lithium

Chapter K of

**Critical Mineral Resources of the United States—Economic and
Environmental Geology and Prospects for Future Supply**



Professional Paper 1802–K

**U.S. Department of the Interior
U.S. Geological Survey**

Periodic Table of Elements

1A 1 H hydrogen 1.008																	2 He helium 4.003
3 Li lithium 6.94	4 Be beryllium 9.012											5 B boron 10.81	6 C carbon 12.01	7 N nitrogen 14.01	8 O oxygen 16.00	9 F fluorine 19.00	10 Ne neon 20.18
11 Na sodium 22.99	12 Mg magnesium 24.31	3B	4B	5B	6B	7B	8B			11B	12B	13 Al aluminum 26.98	14 Si silicon 28.09	15 P phosphorus 30.97	16 S sulfur 32.06	17 Cl chlorine 35.45	18 Ar argon 39.95
19 K potassium 39.10	20 Ca calcium 40.08	21 Sc scandium 44.96	22 Ti titanium 47.88	23 V vanadium 50.94	24 Cr chromium 52.00	25 Mn manganese 54.94	26 Fe iron 55.85	27 Co cobalt 58.93	28 Ni nickel 58.69	29 Cu copper 63.55	30 Zn zinc 65.39	31 Ga gallium 69.72	32 Ge germanium 72.64	33 As arsenic 74.92	34 Se selenium 78.96	35 Br bromine 79.90	36 Kr krypton 83.79
37 Rb rubidium 85.47	38 Sr strontium 87.62	39 Y yttrium 88.91	40 Zr zirconium 91.22	41 Nb niobium 92.91	42 Mo molybdenum 95.96	43 Tc technetium (98)	44 Ru ruthenium 101.1	45 Rh rhodium 102.9	46 Pd palladium 106.4	47 Ag silver 107.9	48 Cd cadmium 112.4	49 In indium 114.8	50 Sn tin 118.7	51 Sb antimony 121.8	52 Te tellurium 127.6	53 I iodine 126.9	54 Xe xenon 131.3
55 Cs cesium 132.9	56 Ba barium 137.3	*	72 Hf hafnium 178.5	73 Ta tantalum 180.9	74 W tungsten 183.9	75 Re rhenium 186.2	76 Os osmium 190.2	77 Ir iridium 192.2	78 Pt platinum 195.1	79 Au gold 197.0	80 Hg mercury 200.5	81 Tl thallium 204.4	82 Pb lead 207.2	83 Bi bismuth 209.0	84 Po polonium (209)	85 At astatine (210)	86 Rn radon (222)
87 Fr francium (223)	88 Ra radium (226)	**	104 Rf rutherfordium (265)	105 Db dubnium (268)	106 Sg seaborgium (271)	107 Bh bohrium (270)	108 Hs hassium (277)	109 Mt meitnerium (276)	110 Ds darmstadtium (281)	111 Rg roentgenium (280)	112 Cn copernicium (285)	113 Uut (284)	114 Flerovium (289)	115 Uup (288)	116 Lv livermorium (293)	117 Uus (294)	118 Uuo (294)
Lanthanide Series*		57 La lanthanum 138.9	58 Ce cerium 140.1	59 Pr praseodymium 140.9	60 Nd neodymium 144.2	61 Pm promethium (145)	62 Sm samarium 150.4	63 Eu europium 152.0	64 Gd gadolinium 157.2	65 Tb terbium 158.9	66 Dy dysprosium 162.5	67 Ho holmium 164.9	68 Er erbium 167.3	69 Tm thulium 168.9	70 Yb ytterbium 173.0	71 Lu lutetium 175.0	
Actinide Series**		89 Ac actinium (227)	90 Th thorium 232	91 Pa protactinium 231	92 U uranium 238	93 Np neptunium (237)	94 Pu plutonium (244)	95 Am americium (243)	96 Cm curium (247)	97 Bk berkelium (247)	98 Cf californium (251)	99 Es einsteinium (252)	100 Fm fermium (257)	101 Md mendelevium (288)	102 No nobelium (259)	103 Lr lawrencium (262)	

element names in **blue** are liquids at room temperature
 element names in **red** are gases at room temperature
 element names in **black** are solids at room temperature

Modified from Los Alamos National Laboratory Chemistry Division; available at <http://periodic.lanl.gov/images/periodictable.pdf>.

Cover. Lithium-brine evaporating ponds at Clayton Valley, Nevada. The dark rectangular pond at the upper center of the image is 1.7 kilometers long. Photograph by Doc Searls/CC-BY-2.0 (http://commons.wikimedia.org/wiki/File:Chemetall_Foote_Lithium_Operation.jpg).

Lithium

By Dwight C. Bradley, Lisa L. Stillings, Brian W. Jaskula, LeeAnn Munk, and Andrew D. McCauley

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Edited by Klaus J. Schulz, John H. DeYoung, Jr., Robert R. Seal II, and Dwight C. Bradley

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U.S. Department of the Interior
U.S. Geological Survey

U.S. Department of the Interior

RYAN K. ZINKE, Secretary

U.S. Geological Survey

William H. Werkheiser, Acting Director

U.S. Geological Survey, Reston, Virginia: 2017

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Conversion Factors

International System of Units to Inch/Pound

Multiply	By	To obtain
Length		
angstrom (Å) (0.1 nanometer)	0.003937	microinch
angstrom (Å) (0.1 nanometer)	0.000003937	mil
micrometer (µm) [or micron]	0.03937	mil
millimeter (mm)	0.03937	inch (in.)
centimeter (cm)	0.3937	inch (in.)
meter (m)	3.281	foot (ft)
meter (m)	1.094	yard (yd)
kilometer (km)	0.6214	mile (mi)
Area		
hectare (ha)	2.471	acre
square kilometer (km ²)	247.1	acre
square meter (m ²)	10.76	square foot (ft ²)
square centimeter (cm ²)	0.1550	square inch (in ²)
square kilometer (km ²)	0.3861	square mile (mi ²)
Volume		
milliliter (mL)	0.03381	ounce, fluid (fl. oz)
liter (L)	33.81402	ounce, fluid (fl. oz)
liter (L)	1.057	quart (qt)
liter (L)	0.2642	gallon (gal)
cubic meter (m ³)	264.2	gallon (gal)
cubic centimeter (cm ³)	0.06102	cubic inch (in ³)
cubic meter (m ³)	1.308	cubic yard (yd ³)
cubic kilometer (km ³)	0.2399	cubic mile (mi ³)
Mass		
microgram (µg)	0.0000003527	ounce, avoirdupois (oz)
milligram (mg)	0.00003527	ounce, avoirdupois (oz)
gram (g)	0.03527	ounce, avoirdupois (oz)
gram (g)	0.03215075	ounce, troy
kilogram (kg)	32.15075	ounce, troy
kilogram (kg)	2.205	pound avoirdupois (lb)
ton, metric (t)	1.102	ton, short [2,000 lb]
ton, metric (t)	0.9842	ton, long [2,240 lb]
Deposit grade		
gram per metric ton (g/t)	0.0291667	ounce per short ton (2,000 lb) (oz/T)
Pressure		
megapascal (MPa)	10	bar
gigapascal (GPa)	10,000	bar
Density		
gram per cubic centimeter (g/cm ³)	62.4220	pound per cubic foot (lb/ft ³)
milligram per cubic meter (mg/m ³)	0.0000006243	pound per cubic foot (lb/ft ³)
Energy		
joule (J)	0.0000002	kilowatthour (kWh)
joule (J)	6.241×10^{18}	electronvolt (eV)
joule (J)	0.2388	calorie (cal)
kilojoule (kJ)	0.0002388	kilocalorie (kcal)

International System of Units to Inch/Pound—Continued

Multiply	By	To obtain
Radioactivity		
becquerel (Bq)	0.00002703	microcurie (μCi)
kilobecquerel (kBq)	0.02703	microcurie (μCi)
Electrical resistivity		
ohm meter ($\Omega\text{-m}$)	39.37	ohm inch ($\Omega\text{-in.}$)
ohm-centimeter ($\Omega\text{-cm}$)	0.3937	ohm inch ($\Omega\text{-in.}$)
Thermal conductivity		
watt per centimeter per degree Celsius ($\text{watt/cm } ^\circ\text{C}$)	693.1798	International British thermal unit inch per hour per square foot per degree Fahrenheit ($\text{Btu in/h ft}^2 \text{ } ^\circ\text{F}$)
watt per meter kelvin (W/m-K)	6.9318	International British thermal unit inch per hour per square foot per degree Fahrenheit ($\text{Btu in/h ft}^2 \text{ } ^\circ\text{F}$)

Inch/Pound to International System of Units

Length		
mil	25.4	micrometer (μm) [or micron]
inch (in.)	2.54	centimeter (cm)
inch (in.)	25.4	millimeter (mm)
foot (ft)	0.3048	meter (m)
mile (mi)	1.609	kilometer (km)
Volume		
ounce, fluid (fl. oz)	29.57	milliliter (mL)
ounce, fluid (fl. oz)	0.02957	liter (L)
Mass		
ounce, avoirdupois (oz)	28,350,000	microgram
ounce, avoirdupois (oz)	28,350	milligram
ounce, avoirdupois (oz)	28.35	gram (g)
ounce, troy	31.10 348	gram (g)
ounce, troy	0.03110348	kilogram (kg)
pound, avoirdupois (lb)	0.4536	kilogram (kg)
ton, short (2,000 lb)	0.9072	ton, metric (t)
ton, long (2,240 lb)	1.016	ton, metric (t)
Deposit grade		
ounce per short ton (2,000 lb) (oz/T)	34.285714	gram per metric ton (g/t)
Energy		
kilowatthour (kWh)	3,600,000	joule (J)
electronvolt (eV)	1.602×10^{-19}	joule (J)
Radioactivity		
microcurie (μCi)	37,000	becquerel (Bq)
microcurie (μCi)	37	kilobecquerel (kBq)

Temperature in degrees Celsius ($^\circ\text{C}$) may be converted to degrees Fahrenheit ($^\circ\text{F}$) as follows:

$$^\circ\text{F} = (1.8 \times ^\circ\text{C}) + 32$$

Temperature in degrees Celsius ($^\circ\text{C}$) may be converted to kelvin (K) as follows:

$$\text{K} = ^\circ\text{C} + 273.15$$

Temperature in degrees Fahrenheit ($^\circ\text{F}$) may be converted to degrees Celsius ($^\circ\text{C}$) as follows:

$$^\circ\text{C} = (^\circ\text{F} - 32) / 1.8$$

Datum

Unless otherwise stated, vertical and horizontal coordinate information is referenced to the World Geodetic System of 1984 (WGS 84). Altitude, as used in this report, refers to distance above the vertical datum.

Supplemental Information

Specific conductance is given in microsiemens per centimeter at 25 degrees Celsius ($\mu\text{S}/\text{cm}$ at 25 °C).

Concentrations of chemical constituents in soils and (or) sediment are given in milligrams per kilogram (mg/kg), parts per million (ppm), or parts per billion (ppb).

Concentrations of chemical constituents in water are given in milligrams per liter (mg/L), micrograms per liter ($\mu\text{g}/\text{L}$), nanograms per liter (ng/L), nanomoles per kilogram (nmol/kg), parts per million (ppm), parts per billion (ppb), or parts per trillion (ppt).

Concentrations of suspended particulates in water are given in micrograms per gram ($\mu\text{g}/\text{g}$), milligrams per kilogram (mg/kg), or femtograms per gram (fg/g).

Concentrations of chemicals in air are given in units of the mass of the chemical (milligrams, micrograms, nanograms, or picograms) per volume of air (cubic meter).

Activities for radioactive constituents in air are given in microcuries per milliliter ($\mu\text{Ci}/\text{mL}$).

Deposit grades are commonly given in percent, grams per metric ton (g/t)—which is equivalent to parts per million (ppm)—or troy ounces per short ton (oz/T).

Geologic ages are expressed in mega-annum (Ma, million years before present, or 10^6 years ago) or giga-annum (Ga, billion years before present, or 10^9 years ago).

For ranges of years, “to” and (or) the en dash (“–”) mean “up to and including.”

Concentration unit	Equals
milligram per kilogram (mg/kg)	part per million
microgram per gram ($\mu\text{g}/\text{g}$)	part per million
microgram per kilogram ($\mu\text{g}/\text{kg}$)	part per billion (10^9)

Equivalencies

part per million (ppm): 1 ppm = 1,000 ppb = 1,000,000 ppt = 0.0001 percent

part per billion (ppb): 0.001 ppm = 1 ppb = 1,000 ppt = 0.0000001 percent

part per trillion (ppt): 0.000001 ppm = 0.001 ppb = 1 ppt = 0.000000001 percent

Metric system prefixes

tera- (T-)	10^{12}	1 trillion
giga- (G-)	10^9	1 billion
mega- (M-)	10^6	1 million
kilo- (k-)	10^3	1 thousand
hecto- (h-)	10^2	1 hundred
deka- (da-)	10	1 ten
deci- (d-)	10^{-1}	1 tenth
centi- (c-)	10^{-2}	1 hundredth
milli- (m-)	10^{-3}	1 thousandth
micro- (μ -)	10^{-6}	1 millionth
nano- (n-)	10^{-9}	1 billionth
pico- (p-)	10^{-12}	1 trillionth
femto- (f-)	10^{-15}	1 quadrillionth
atto- (a-)	10^{-18}	1 quintillionth

Abbreviations and Symbols

°C	degree Celsius
g	gram
HMIS	Hazardous Materials Identification System
ISMI	International Strategic Minerals Inventory
kg	kilogram
km	kilometer
km ²	square kilometer
LC ₅₀	lethal concentration 50 (concentration that kills 50 percent of test population within a given timeframe)
LCT	lithium-cesium-tantalum
m	meter
Ma	mega-annum
mg	milligram
mg/d	milligram per day
mg/kg	milligram per kilogram
mg/L	milligram per liter
NFPA	National Fire Protection Association
ppm	part per million
USGS	U.S. Geological Survey

Lithium

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Abstract

Lithium, the lightest of all metals, is used in air treatment, batteries, ceramics, glass, metallurgy, pharmaceuticals, and polymers. Rechargeable lithium-ion batteries are particularly important in efforts to reduce global warming because they make it possible to power cars and trucks from renewable sources of energy (for example, hydroelectric, solar, or wind) instead of by burning fossil fuels. Today, lithium is extracted from brines that are pumped from beneath arid sedimentary basins and extracted from granitic pegmatite ores. The leading producer of lithium from brine is Chile, and the leading producer of lithium from pegmatites is Australia. Other potential sources of lithium include clays, geothermal brines, oilfield brines, and zeolites. Worldwide resources of lithium are estimated to be more than 39 million metric tons, which is enough to meet projected demand to the year 2100. The United States is not a major producer at present but has significant lithium resources.

Introduction

Historical Overview

Lithium (from the Greek *lithos*, for stone) is the first metal in the periodic table. It was recognized as an element in 1817 when the Swedish chemist Johan Arfvedson analyzed the mineral petalite. Useful amounts of lithium metal were first isolated in 1855 by August Matthiessen and, independently, by Robert Bunsen, after whom the Bunsen burner was named (Emsley, 2011). By this time, lithium had been found in other silicate minerals (lepidolite and spodumene) and had been detected in trace quantities in plants, seawater, spa waters, and the human body (Emsley, 2011). In 1869, Dmitiri Mendeleev correctly positioned it adjacent to the alkali metal sodium in his then-revolutionary periodic table of elements.

Petalite, lepidolite, and spodumene are found in granitic pegmatites. The first significant lithium mining began in 1898 at the Etta pegmatite in South Dakota. In the early 1900s, other pegmatite mines in California, South Dakota, and New Mexico also began lithium production, and the

United States dominated the global supply (Norton, 1973). The process of extracting lithium from brine was also first developed in the United States. The earliest production of lithium from brine took place in 1938 as a byproduct of sodium carbonate production at Searles Lake, California. A larger lithium-brine deposit at Clayton Valley, Nevada, began production in 1966. Today, brine resources dominate the lithium industry.

In the 1970s, when the U.S. Geological Survey (USGS) published Professional Paper 820, “United States Mineral Resources” (Brobst and Pratt, 1973), lithium was a relatively obscure mineral commodity that did not even warrant an entire chapter of its own (Norton, 1973). Since then, the global resource picture for lithium has changed considerably. In 1973, the United States was still the world’s leading lithium producer; today, U.S. production lags far behind that of Chile, Australia, and several other nations. Additionally, two new classes of ore deposits—lithium clays and lithium zeolites—have been recognized. Between 1975 and 2005, world lithium production increased by a factor of about five (fig. K1), and more growth is anticipated.

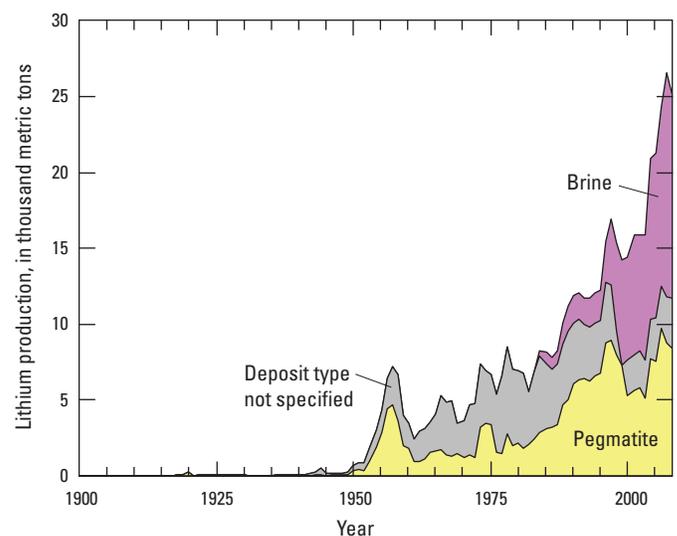


Figure K1. Graph showing world lithium production from 1900 to 2007, by deposit type and year. The layers of the graph are placed one above the other, forming a cumulative total. Modified from Mohr and others (2010).

K2 Critical Mineral Resources of the United States—Lithium

Many advances in understanding lithium geology were spurred by the 1973 oil embargo. Lithium was—and still is—seen as a strategic mineral commodity that could contribute toward U.S. energy independence. At that time, the USGS launched a major research effort on lithium resources that lasted for several years and involved dozens of researchers. Initial results were presented in a multichapter USGS Professional Paper (Vine, 1976), and final results were summarized by Vine (1980). After about 1980, national concerns about energy self-sufficiency ebbed, and studies in lithium-resource geology fell into neglect for more than a quarter century.

A recent revival of interest in lithium has been driven by the threat of global warming from the burning of fossil fuels, combined with the recognition that a transition to electric and hybrid vehicles, which are powered by lithium batteries, could substantially reduce the Nation's carbon footprint and its reliance on foreign oil (U.S. Department of Energy, 2010). Recent summaries of the global lithium resource picture include those by Evans (2008, 2012, 2014), Yaksic and Tilton (2009), Mohr and others (2010), Gruber and others (2011), and Kesler and others (2012).

Lithium as a Critical Element

Lithium has been listed as one of the critical or near-critical elements in various recent studies based largely on its importance in green technologies. It was one of the 15 mineral commodities studied by participating countries in the International Strategic Minerals Inventory (ISMI) of the 1980s and 1990s (Anstett and others, 1990). The National Research Council (2008) concluded that lithium, although not critical at the time of the 2008 assessment, could potentially become critical depending on the level of growth of new uses, such as hybrid vehicle batteries. In the U.S. Department of Energy's Critical Materials Strategy (2010), lithium is included as 1 of 16 key elements. The 2011 joint report of the American Physical Society Panel on Public Affairs and the Materials Research Society on energy-critical minerals included lithium as 1 of 29 key elements for green technology.

Uses and Sources

Lithium has many uses. Worldwide lithium consumption in 2013 by end use was estimated to be as follows (fig. K2): ceramics and glass, 35 percent; rechargeable batteries, 29 percent; lubricating greases, 8 percent; continuous casting mold flux powders, 6 percent; air treatment, 5 percent; and polymer production, 5 percent; primary batteries, 2 percent; primary aluminum production, 1 percent; and other uses, 9 percent (Merriman, 2014).

Ceramics and glass are expected to continue to be the leading end uses for lithium for years to come. In glassmaking (Garrett, 2004), lithium makes the process more economical by reducing the melting point and decreasing viscosity.

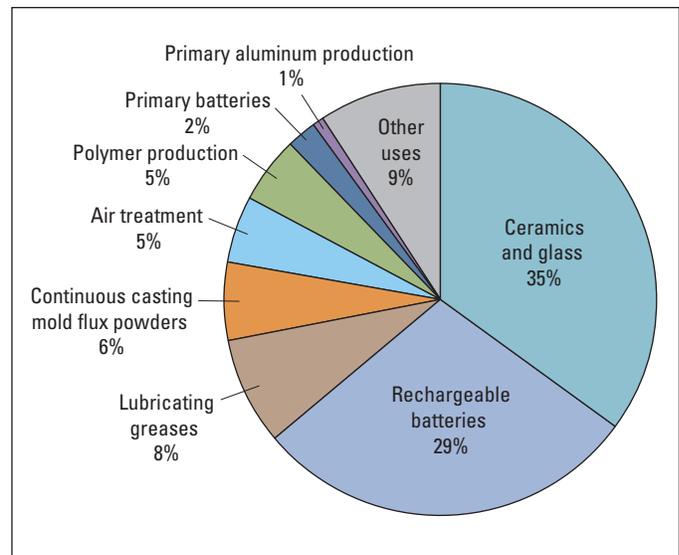


Figure K2. Pie chart showing major end uses of lithium as a percentage of world consumption in 2013. Data are courtesy of David Merriman, Roskill Information Services, Ltd., written commun., May 2014.

The addition of 0.1 to 4 percent lithium oxide (Li_2O), to various glasses increases hardness and reduces thermal expansion. A common application is in glass stovetops; where ordinary window-glass would shatter, lithium-bearing glass can withstand large temperature swings and rough use. In the ceramics industry, lithium is used to make porcelain enamels, glazes, and tiles; as in glassmaking, a small amount of lithium lowers the melting temperature and reduces thermal expansion in the resulting ceramic product (Garrett, 2004).

Production of batteries, which currently rank second among the end uses of lithium, will likely see increased production in the next few years as the production of electric and hybrid vehicles increases. Production will result in increased capacity utilization of the vehicle battery plants that are currently being built worldwide. Battery manufacturing has the largest growth potential of any sector of the lithium industry; several major automobile companies are developing lithium-ion batteries (fig. K3H). Demand for rechargeable lithium batteries now exceeds that of rechargeable nonlithium batteries for use in cellular telephones, cordless tools, MP3 players, and portable computers and tablets. Nonrechargeable lithium batteries are used in calculators, cameras, and watches (Jaskula, 2013).

Other uses of lithium are not widely appreciated by consumers. Lithium is a minor but key ingredient in the electrolytic refining of aluminum. Lightweight lithium-aluminum alloys have applications in the aerospace industry. For example, the fuel tank of the NASA space shuttles used an aluminum-lithium alloy (Garrett, 2004). Lithium, as lithium stearate or similar compounds, is widely used as a high-performance lubricant in automotive, aircraft, industrial, marine, and military applications (Garrett, 2004). As of 1993, 60 percent of all industrial lubricants contained lithium, typically at concentrations of 1 to 2 percent. Lithium chloride and bromide are among the best available

substances for absorbing water; thus, these salts are used in air conditioning systems to reduce humidity while simultaneously cooling the air. Since the 1940s, pharmaceuticals containing lithium compounds have been used to control bipolar disorder. Finally, the lighter of two lithium isotopes, ${}^6\text{Li}$, was used in the production of tritium (${}^3\text{H}$) after World War II by the U.S. Atomic Energy Commission and later by the U.S. Department of Energy in the production of nuclear weapons (Garrett, 2004).

Lithium is traded in three forms: mineral concentrates, mineral compounds, and refined metal. Lithium minerals—mainly spodumene, petalite, and lepidolite—are mined from pegmatites and are used mostly as feedstock for glasses and ceramics. Most lithium compounds (for example, lithium carbonate, lithium chloride, and lithium hydroxide) are obtained from brines. Lithium metal (fig. K3G) is obtained by electrolysis from lithium chloride.

The prices of lithium metal and lithium compounds are not published; however, approximate values can be gleaned from a variety of industry sources. Battery-grade lithium carbonate is currently valued at between \$6,500 and \$7,000 per metric ton. In 2010, Japan imported lithium metal valued at \$33.36 per pound, or \$73,546 per metric ton.

Lithium is the element of choice in the various applications listed above. Substitutes do exist, however, in batteries, ceramics, greases, and manufactured glass. For example, calcium and aluminum soaps can substitute for stearates in greases; calcium, magnesium, mercury, and zinc can be used as anode materials in batteries; sodic and potassic fluxes can substitute for lithium in ceramics and glass manufacturing; and composite materials of boron, glass, or polymer fibers can be used in place of aluminum-lithium alloys (Jaskula, 2013).

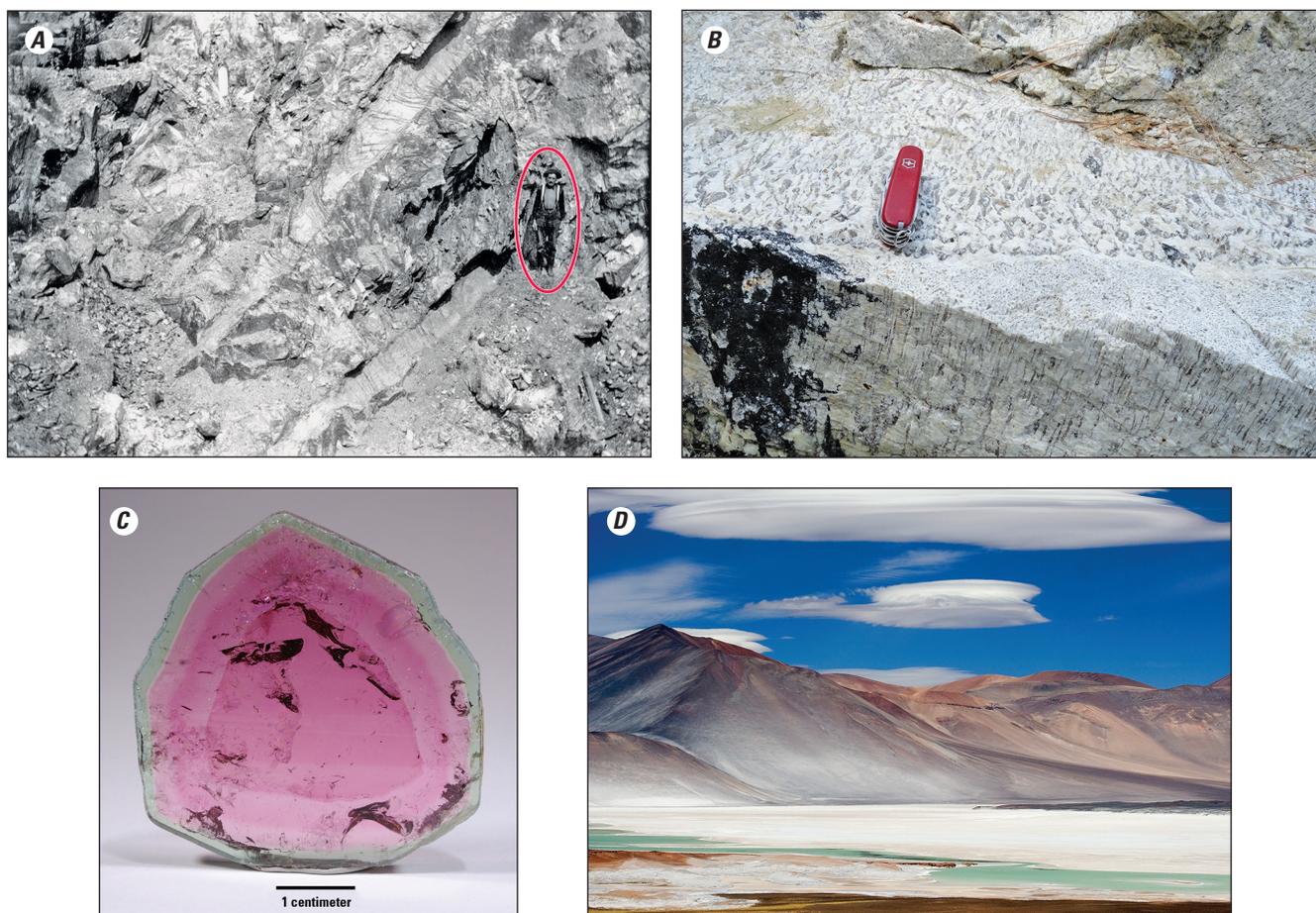


Figure K3. Photographs showing some sources and uses of lithium. *A*, Molds of giant spodumene crystals in the Etta lithium-cesium-tantalum (LCT) pegmatite, Black Hills, South Dakota; note miner for scale. From Schaller (1916). *B*, Graphic granite, which is an intergrowth of quartz and feldspar that is characteristic of pegmatites. This granite is part of the Havey pegmatite in Maine. By Dwight C. Bradley. *C*, Elbaite, also known as watermelon tourmaline, which is a lithium-bearing gemstone. In 1973, a single gem-filled pocket in a pegmatite in Maine produced about 2 metric tons of tourmaline that would be valued today (for gems and mineral specimens) at about \$40 million. This sample is from the Dunton Mine in Newry, Maine. Courtesy of the Mineralogical & Geological Museum at Harvard University (speciman number MGMH 125525. Dunton Mine, Newry, Maine. Copyright 2012. President and Fellows of Harvard College; all rights reserved). *D*, Salar de Atacama in Chile, where lithium brines are pumped from the shallow subsurface. By Luca Galuzzi (www.galuzzi.it/)/CC-BY-SA-2.5 (http://commons.wikimedia.org/wiki/File:Miscanti_Lagoon_San_Pedro_de_Atacama_Chile_Luca_Galuzzi_2006.jpg).

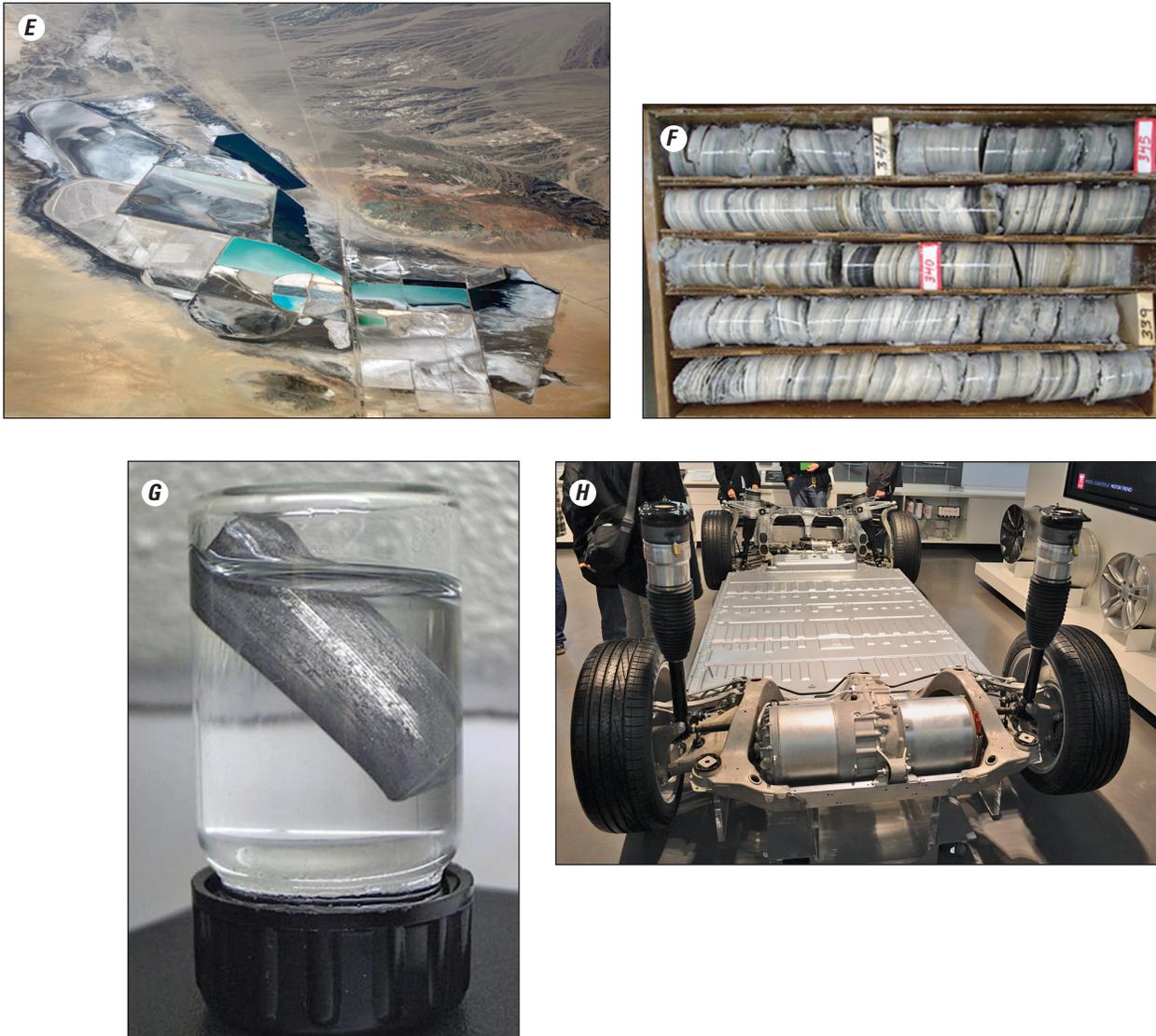


Figure K3.—Continued *E*, Lithium-brine evaporating ponds at Clayton Valley, Nevada. The dark rectangular pond at the upper center of the image is 1.7 kilometers long. By Doc Searls/CC-BY-2.0 (http://commons.wikimedia.org/wiki/File:Chemetal_Foote_Lithium_Operation.jpg). *F*, Drill core through a sequence of Pliocene-age lake sediments containing lithium clay (hectorite) from Fish Lake Valley, Nev. (for location, see fig. K5, inset). Markers indicate depth in feet below the ground surface. Hectorite is present in the tan and gray layers of siltstone and claystone. By Lisa L. Stillings. *G*, Lithium metal is so light that it floats in oil, and so reactive that it cannot be stored in air or water. By W. Oelen/CC-BY-SA-3.0 (http://commons.wikimedia.org/wiki/File%3ALithium_element.jpg). *H*, View into a Tesla Model S® electric car showing the lithium-ion battery covering much of the chassis. Various battery configurations in electric vehicles use between about 10 and 22 kilograms of lithium. By Oleg Alexandrov/CC-BY-SA-3.0 (http://commons.wikimedia.org/wiki/File:Tesla_Motors_Model_S_base.JPG).

Geology

Geochemistry and Mineralogy

In most geologic settings, lithium is found only as a trace element, measured in parts per million (ppm). Earth's mantle contains 1.6 ppm lithium and the oceanic crust contains 4.3 ppm (Sun and McDonough, 1989). The upper continental crust (that is, rocks typically at Earth's surface on land) contains an average of 20 ppm lithium (McLennan, 2001); at this abundance, lithium ranks about 30th among the elements, behind copper but ahead of lead, tin, and silver.

Lithium is classed as a large-ion lithophile element: as a cooling magma starts to crystallize minerals, lithium stays in the remaining melt until near the end. Active plate tectonics over Earth's history have concentrated lithium in the continental crust through the partial melting of the mantle beneath mid-ocean ridges and volcanic arcs. The melt, or magma, rises and then cools to become new rock in Earth's crust, bringing much of the available lithium with it. Among the common rock or sediment types, the highest lithium concentrations are in shales (which average 66 ppm), deep-sea clays (which average 57 ppm), and low-calcium granites (which average 40 ppm) (Faure, 1998 and references therein). These trace concentrations are insufficient for an ore deposit or even for the formation of minerals in which lithium is part of the chemical formula. When present only in trace concentrations such as these, lithium atoms substitute for other metals (typically magnesium) in common rock-forming minerals.

Lithium minerals form only when rare combinations of favorable factors line up. Most of the known lithium minerals are found in coarsely crystalline granites known as lithium-cesium-tantalum (LCT) pegmatites. In terms of lithium resources, the most important minerals are spodumene and petalite (both lithium aluminum silicates) and the pink mica lepidolite (potassium lithium aluminum silicate). The main lithium mineral in sedimentary rocks is the clay hectorite. More information on lithium minerals is provided in table K1.

Lithium is extremely soluble. During weathering of rocks, it tends to be removed in solution and carried to the sea by rivers. Thus, lithium would be expected to have built up in the oceans in the same way that a buildup of sodium has made the oceans salty. Yet, remarkably, seawater contains less than 1 ppm lithium. The likely explanation is that seawater lithium is scavenged in trace quantities by clay minerals and accumulates in sea-floor oozes.

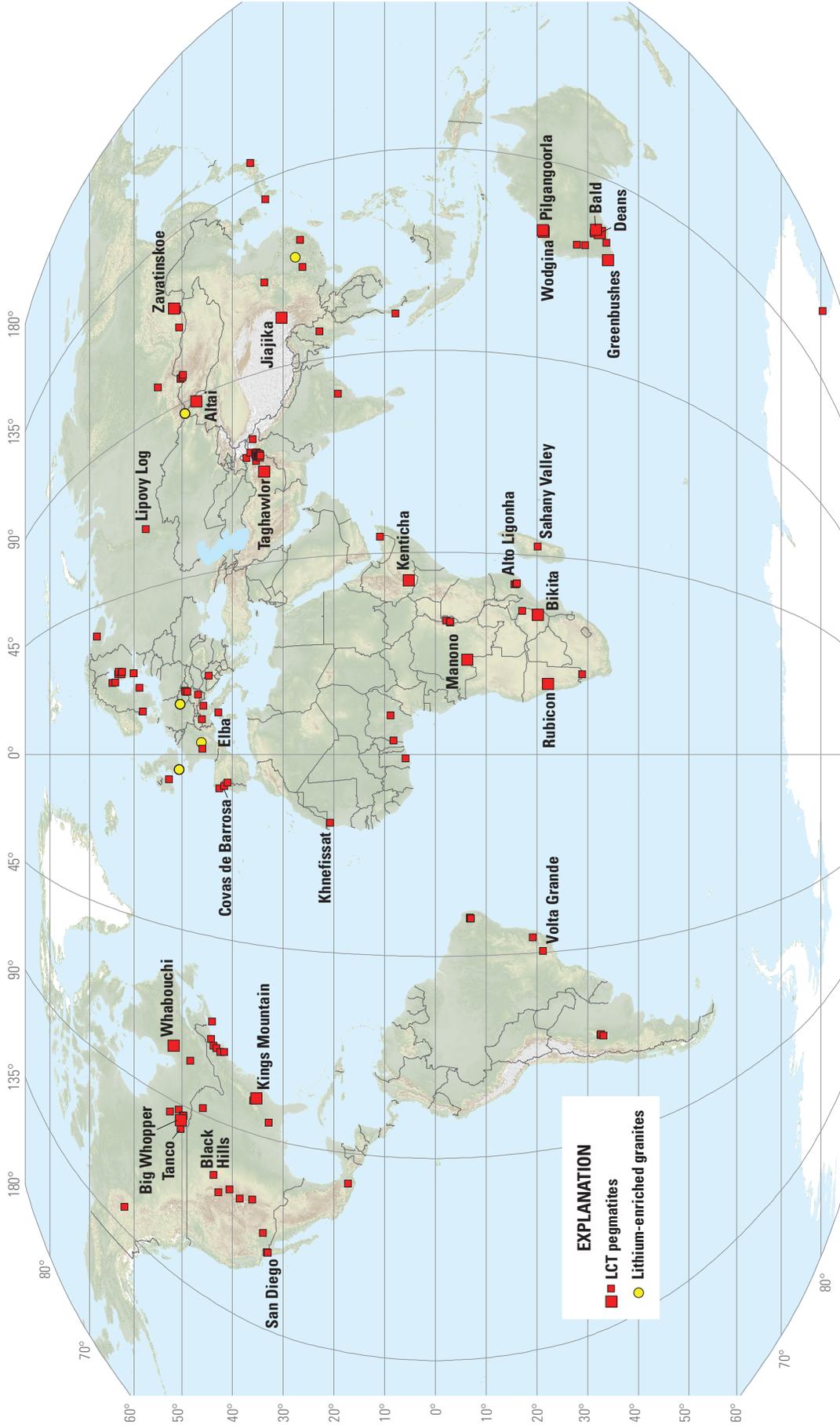
Deposit Types

Present and potential sources of lithium worldwide are broken down by deposit type, as follows: closed-basin brines, 58 percent; pegmatites (including lithium-enriched granites), 26 percent; lithium-clays (hectorite), 7 percent; and oilfield brines, geothermal brines, and lithium-zeolites (jadarite), 3 percent each (Evans, 2012). Figures K4 and K5 show the worldwide distributions of lithium deposits.

Table K1. Commercially and (or) scientifically important lithium-bearing minerals.

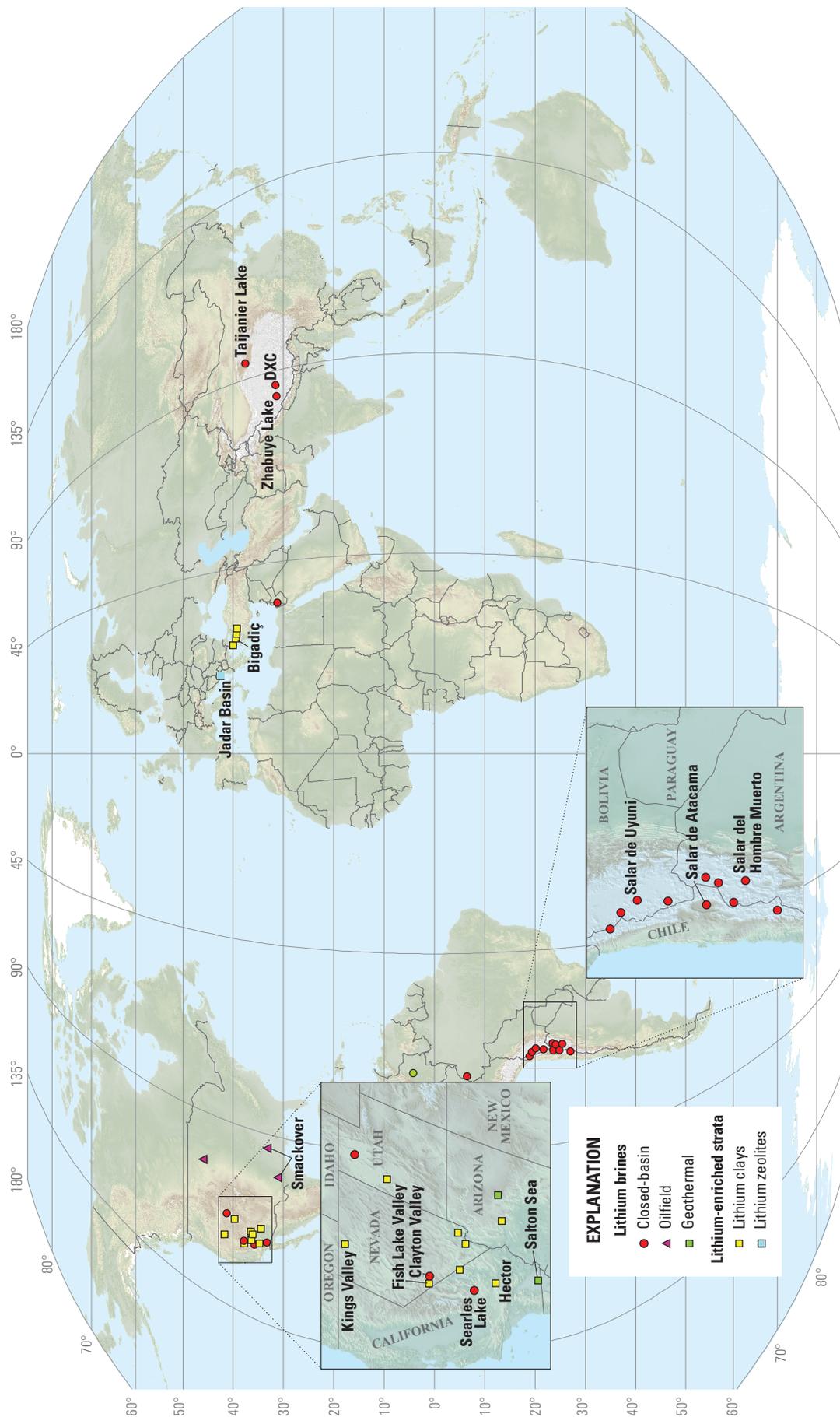
[Chemical compositions are from Barthelmy (2014)]

Mineral name	Chemical formula	Lithium (weight percent)	Geologic setting
Amblygonite	$(\text{Li,Na})\text{Al}(\text{PO}_4)(\text{F,OH})$	3.44	Pegmatite intrusions in orogenic belts; solid solution with montebasite
Elbaite	$\text{Na}(\text{Li,Al})_3\text{Al}_6(\text{BO}_3)_3\text{Si}_6\text{O}_{18}(\text{OH})_4$	1.89	Tourmaline group. Pegmatite intrusions in orogenic belts. Includes the gem form watermelon tourmaline
Eucryptite	LiAlSiO_4	5.51	Pegmatite intrusions in orogenic belts
Hectorite	$\text{Na}_{0.3}(\text{Mg,Li})_3\text{Si}_4\text{O}_{10}(\text{OH})_2$	0.54	Hydrothermal alteration of volcanic ash in arid, closed basins
Jadarite	$\text{LiNaB}_3\text{SiO}_7(\text{OH})$	3.38	Hydrothermal alteration of volcanic ash in arid, closed basins
Lepidolite	$\text{K}(\text{Li,Al})_3(\text{Si,Al})_4\text{O}_{10}(\text{F,OH})_2$	3.58	Pegmatite intrusions in orogenic belts
Montebasite	$\text{LiAl}(\text{PO}_4)(\text{OH,F})$	4.74	Pegmatite intrusions in orogenic belts
Petalite	$\text{LiAlSi}_4\text{O}_{10}$	2.09	Pegmatite intrusions in orogenic belts
Spodumene	$\text{LiAlSi}_2\text{O}_6$	3.73	Pegmatite intrusions in orogenic belts. Gem forms are triphane (yellow), kunzite (pink), and hiddenite (green)
Zabuyelite	Li_2CO_3	18.79	Evaporite mineral (rare)



Base from U.S. Geological Survey Global 30 arc-second elevation data (1998) and from Natural Earth (2014); Robinson projection; World Geodetic System 1984 datum

Figure K4. World map showing locations of selected lithium-cesium-tantalum (LCT) pegmatites and lithium resources. The larger red squares indicate pegmatites containing major lithium and (or) tantalum resources. Adapted from Bradley and others (2016).



Base from U.S. Geological Survey Global 30 arc-second elevation data (1996) and from Natural Earth (2014); Robinson projection; World Geodetic System 1984 datum

Figure K5. World map showing locations of selected closed-basin lithium-brine, lithium-enriched oilfield brine, geothermal oilfield brine, geothermal brine, lithium-clay, and lithium-zeolite deposits. The locations of the closed-basin brines are from a tabulation by Munk and others (2016).

Lithium-Cesium-Tantalum Pegmatite Deposits

Granitic pegmatites are igneous rocks distinguished by an extremely coarse but variable grain size and by other unique textures, particularly what are known as graphic intergrowths (fig. K3B; London, 2008). Pegmatites are composed primarily of the major minerals in granite, namely quartz, albite (sodium feldspar), potassium feldspar, and the white mica muscovite, plus smaller amounts of garnet, tourmaline, biotite, and apatite. In addition to the lithium minerals petalite, lepidolite, and spodumene, LCT pegmatites may contain the cesium ore mineral, pollucite; the tantalum ore mineral, columbite-tantalite; the beryllium ore mineral, beryl; and the tin ore mineral, cassiterite. More information on tantalum, beryllium, and tin resources in LCT pegmatites can be found in Foley and others (this volume, chap. E), Schulz and others (this volume, chap. M), and Kamilli and others (this volume, chap. S). LCT pegmatites may also yield gemstones and high-value museum specimens of rare minerals. Gemstones include the beryl varieties aquamarine, emerald, and heliodor; the lithium-bearing tourmaline variety elbaite (“watermelon tourmaline”) (fig. K3C); and the spodumene varieties hiddenite, kunzite, and triphane. LCT pegmatites are also mined for feldspars, muscovite, and ultrapure quartz. The diversity of mineral species in the most complex LCT pegmatites is impressive; at the Tanco deposit in Manitoba, Canada, for example, 105 minerals have been identified (London, 2008). LCT pegmatites are famous among geologists and mineral collectors for their huge crystals. The largest spodumene crystal yet found is 14 meters (m) long (from South Dakota) (fig. K3A); the largest beryl crystal, 18 m; and the largest potassium feldspar crystal, 49 m (Rickwood, 1981). These finds are all the more remarkable because pegmatites are believed to have crystallized in a matter of days to years (London, 2008).

The main producers of lithium from pegmatites are Australia, Brazil, China, Portugal, and Zimbabwe. The world has hundreds of known deposits (fig. K4), and some of these (for example, in Quebec, Canada) contain large reserves of lithium that have not been mined. The United States is not currently producing lithium from pegmatites, although large reserves remain in the Kings Mountain pegmatite district in North Carolina. Other domestic deposits are too small to be viable under current or likely market conditions. Kesler and others (2012) estimated lithium resources for 20 of the world’s most important pegmatite deposits or districts.

Bradley and McCauley (2013) and Bradley and others (2017) have summarized tectonic factors in pegmatite genesis. LCT pegmatites are found in the metamorphic-igneous hinterlands of orogenic belts and are a consequence of plate convergence. Most LCT pegmatites formed during collision between continents or microcontinents and are associated with aluminum-rich granites that originated by melting of metamorphosed sedimentary rocks. Dozens of pegmatites in the Appalachians formed during the protracted collision between Africa and North America that took place 370 million to 275 million years ago.

LCT pegmatites can be dated using isotope geochronology. The age is a function of the ratio of the abundances of a radioactive isotope and its decay product. In pegmatites, the minerals columbite-tantalite, monazite, and zircon are dated by exploiting the decay of uranium-238 to lead-206. LCT pegmatites from six continents have now been dated (Bradley and McCauley, 2013). The oldest one, which is located in Australia, formed at about 2,829 mega-annum (Ma, or million years before present) and the youngest, in Italy, at about 7 Ma (McCauley and Bradley, 2014). The global age distribution is episodic, with a few peak times separated by long intervals of few or no pegmatites (fig. K6). The age peaks at 2,638; 1,809; 962; 485; 309; 274; and 97 Ma correspond to times when Earth’s continents were being assembled into supercontinents (Bradley, 2011).

Even the biggest LCT pegmatites are much smaller than typical granitic plutons, which commonly have areas of greater than 10 square kilometers (km²). The Greenbushes pegmatite in Western Australia, which is large for an LCT pegmatite, is 3 kilometers (km) long and a few hundred meters across (Partington and others, 1995). On a regional scale, LCT pegmatites tend to occur in districts alongside fertile granites, with the highest concentration of lithium and other incompatible elements in the more distal pegmatites (fig. K7). Individual pegmatites take various shapes, ranging from tabular dikes and sills to irregular bodies.

Lithium-Enriched Granites

Some muscovite-bearing granites include zones that are enriched in the elements lithium, tantalum, tin, and fluorine. At the Yichun Mine in Jiangxi Province, China, the top of a biotite-muscovite granite grades into muscovite granite and then into lepidolite granite, which has been mined for lithium and tantalum (Schwartz, 1992). Lithium-enriched granites are closely related to LCT pegmatites, and the two have not been distinguished from one another in recent global assessments of lithium resources (for example, Kunasz, 2006; Evans, 2008; Yaksic and Tilton, 2009; Naumov and Naumova, 2010; and Gruber and others, 2011).

Lithium Brine Deposits in Closed Basins

Closed-basin brine deposits contain an estimated 58 percent of the world’s identified lithium resources (Evans, 2012). Lithium brine deposits are accumulations of saline groundwater that are enriched in dissolved lithium. The locations of the world’s major lithium brine deposits are shown on the map in figure K5. The producing deposits have average lithium concentrations that range from 160 to 1,400 ppm and estimated resources of 0.3 to 6.3 million metric tons of lithium (Munk and others, 2016). The producing deposits are located in Asia, North America, and South America, and lie within the northern and arid latitudinal belts on either side of the equator. These deposits share a number of characteristics, including

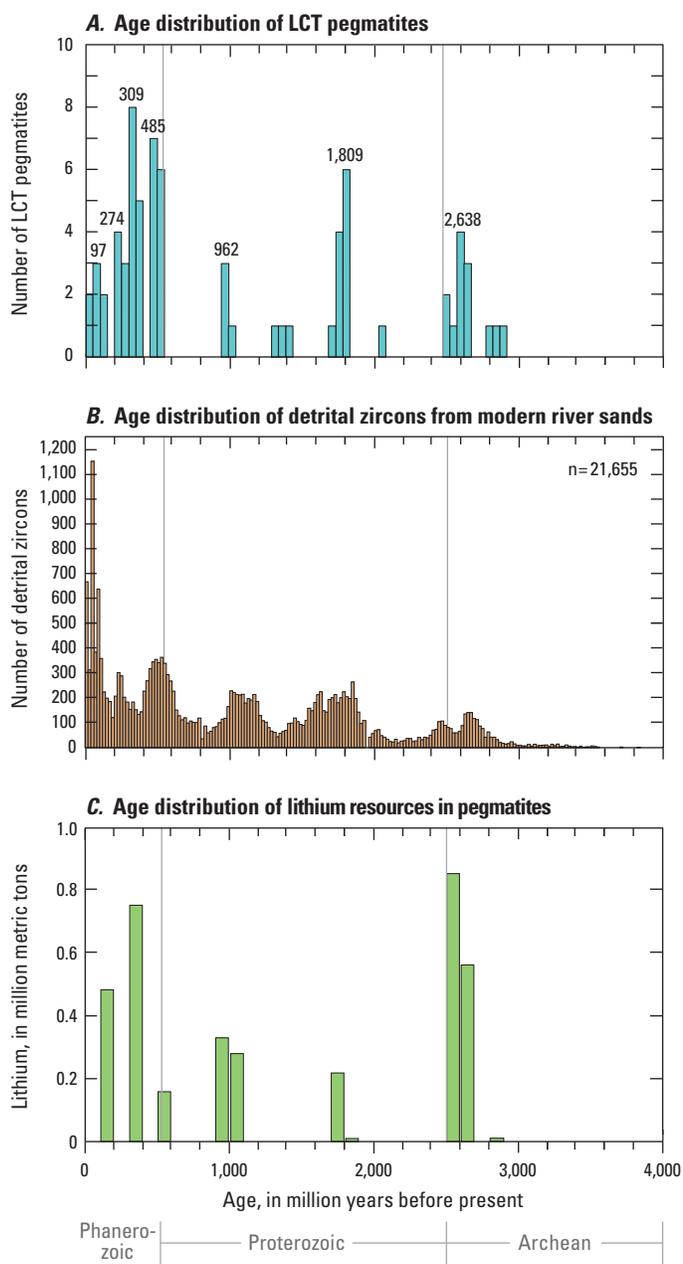


Figure K6. *A*, Histogram of the number of lithium-cesium-tantalum (LCT) pegmatites formed per 50-million-year interval as a function of geologic time showing their episodic genesis (McCauley and Bradley, 2013, 2014). *B*, Histogram showing the age distribution of detrital zircon in modern sand as a function of time. Maxima are interpreted as times when supercontinents were being assembled and minima as times when they were together. LCT pegmatites are thus linked to supercontinent assembly. From Voice and others (2011). *C*, Histogram showing global lithium resource in pegmatites per 100-million-year interval as a function of geologic time. Note the broad correspondence between all three plots. Modified from McCauley and Bradley (2014).

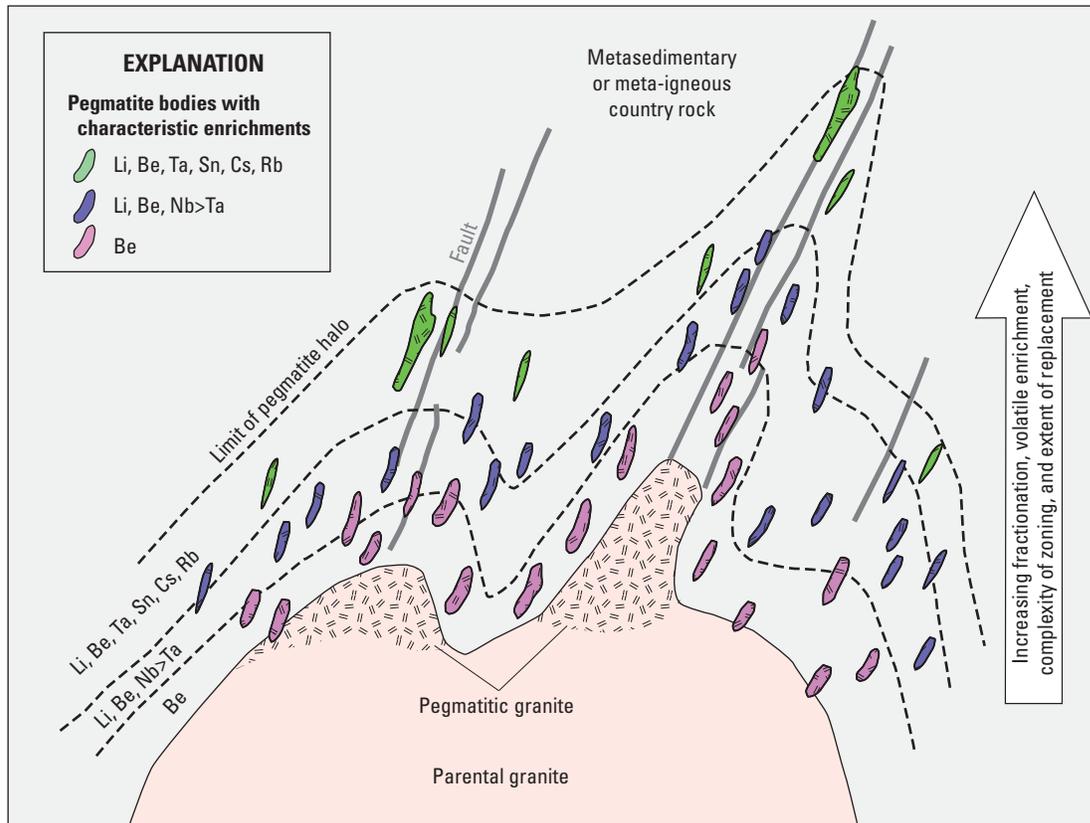
the following: (a) an arid climate; (b) closed basin containing a salt lake or salt flat; (c) tectonically driven subsidence; (d) associated igneous or geothermal activity; (e) lithium-bearing source rocks; (f) one or more adequate aquifers, to host the brine reservoir; and (g) sufficient time to concentrate a brine. Key aspects of the proposed lithium-brine deposit model are shown in figure K8.

The lithium brine deposit in Clayton Valley, Nev., is a well-studied example that can be used to highlight some of the key characteristics of this kind of deposit. Lithium has been produced from brine in Clayton Valley since the 1960s. It is not a particularly notable basin—it has a relatively small footprint of about 100 km² and a total lithium resource of about 0.3 million metric tons—but it is better understood than the rest.

Clayton Valley is one of about 150 basins in the Basin and Range Province of the Western United States that formed when the western 1,000 km of North America was profoundly reshaped because of interactions with adjacent plates in the Pacific Ocean. A computer animation of this process is available on the Internet (Atwater, 2011). In the past 15 million years, Nevada has been stretched in an east-west direction to about twice its former width. The basins are one of many consequences of this process. The basins are relatively flat regions where the Earth's former surface has subsided over geologic time, and the resulting depressions have been filled with sediment, typically hundreds to thousands of meters thick.

The Basin and Range Province is dry. Its aridity is partly owing to its position in the northerly of Earth's two low-latitude dry belts and partly to a double rain-shadow cast by two of the highest mountain ranges in the contiguous United States (the White Mountains and the Sierra Nevada, the latter of which reaches 4,421 m, or 14,505 feet). The region is so dry that most of the basins are closed; that is, surface waters (mostly snowmelt) can flow in but not out. Inflowing waters bring in dissolved calcium, magnesium, potassium, sodium, and less abundant elements, such as lithium. These elements have built up over time, either in permanent lakes (such as Utah's Great Salt Lake) or in ephemeral lakes that sometimes dry out completely, leaving a salar (salt pan or playa) covered by evaporite minerals. Halite (sodium chloride, or common rock salt) is the best known of these minerals. As a salt lake dries out, lithium behaves somewhat differently than other dissolved metals because it is more soluble. Rather than crystallizing an evaporite mineral, lithium remains in solution and ends up in a bitter-tasting residual brine. This brine is denser than fresh water and sinks into the subsurface where it collects in one or more aquifers (zones or layers of porous and permeable rock or sediment). At Clayton Valley, lithium-enriched brine is pumped from six different aquifers that all lie within a few hundred meters of the surface.

The lithium in Clayton Valley is thought to have come from various sources; some of it was weathered from rocks or sediments by rain, snowmelt, or groundwater, and some



NOT TO SCALE

Figure K7. Schematic cross section showing the concentric arrangement of lithium-cesium-tantalum (LCT) pegmatites (small purple, blue, and green bodies) around a parental granite pluton. In this model, common pegmatites form near the parent, whereas pegmatites with enrichments in incompatible elements (indicated by chemical symbols) and corresponding rare minerals form farther away. Modified from Galeschuk and Vanstone (2005) and Trueman and Černý (1982). Be, beryllium; Cs, cesium; Li, lithium; Nb, niobium; Rb, rubidium; Sn, tin; Ta, tantalum

was brought in by hydrothermal waters that rose from anomalously hot rocks below the basin (fig. K8). Before intense pumping disrupted the groundwater system beneath Clayton Valley, these hydrothermal waters came to the surface at two hot springs.

The arid climate needed to form the brine is also a key to production, because the first step in the extraction of lithium is solar evaporation. In Clayton Valley, brine carrying an average of 160 ppm lithium is pumped to the surface and evaporated in a succession of nine artificial ponds that cover a total area of 16 km² (fig. K3E) (Garrett, 2004). In each pond in the chain, brine enters at one end, loses some of its water during the ensuing weeks or months, and is drained or pumped from the other end into the next pond. Multiple ponds are used so as to keep separate the various evaporite minerals that crystallize out in sequence. It takes nearly 2 years to achieve a concentrate that is both enriched in lithium (to 5,000 ppm) and depleted in other, more abundant, elements. This “mother

liquor” is pumped from the last pond to a chemical plant for production of lithium carbonate and lithium hydroxide. A more complete description of the extraction of lithium from brine is provided in Garrett (2004).

The same general conditions that made the Clayton Valley brines have created even larger deposits in the Andes Mountains of South America and in Tibet in central Asia (fig. K5). The world’s most significant lithium district is the Salar de Atacama, on the Altiplano of Chile (fig. K3D), which is one of the driest places on Earth. The Salar de Atacama is a huge salt flat that covers an area of about 2,100 km², which is roughly two-thirds the size of Rhode Island. It is surrounded by active volcanoes and cut by active faults. The salar is fed by a combination of snowmelt from nearby mountains and hydrothermal fluids from below. At an average of 1,400 ppm lithium, the brine is far richer than at Clayton Valley. The total reserve is more than 20 times greater, at an estimated 7.5 million metric tons of lithium.

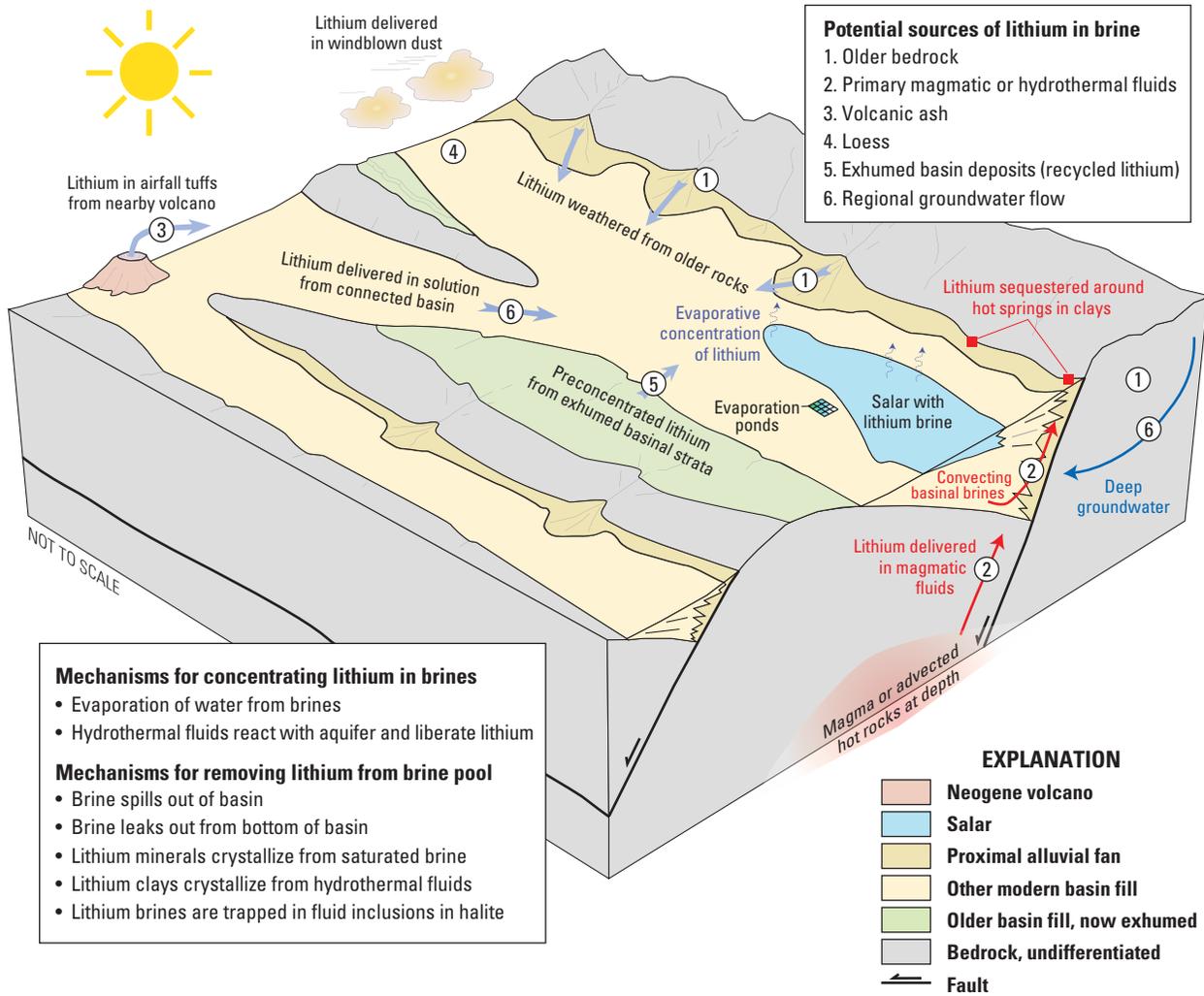


Figure K8. Conceptual ore-deposit model for lithium brine. An extensional basin is shown, but basins in active contractional and strike-slip tectonic settings are also prospective, the requirement being that the basin is closed. From Bradley and others (2013) and Munk and others (2016).

Another notable deposit is the Salar de Uyuni in Bolivia. With an estimated 9 million metric tons of lithium at an average concentration of about 320 ppm (Jaskula, 2013), it is likely the largest accumulation of lithium in the world (Gruber and others, 2011). Despite its size, it is not yet in production. One difficulty is an abundance of dissolved magnesium, which hampers the evaporative concentration of lithium by causing it to precipitate prematurely as an impurity in magnesium salts.

The most noteworthy of several lithium brine systems in China is at Zabuye Lake, Tibet. It is the only known closed basin in which a lithium salt (specifically, Li_2CO_3 , or zabuyelite) precipitates as part of the evaporite mineral sequence, and the only basin in a recent global compilation where volcanism or hydrothermal activity has not been reported (Munk and others, 2016). The brines have an average concentration of 700 ppm and an estimated resource of about 1.5 million metric tons of lithium (Gruber and others, 2011).

Lithium in Other Brines

Deep oilfield brines may contain up to several hundreds of parts per million lithium. Evans (2008) reported high tonnages of lithium contained in oilfield brines in Arkansas, North Dakota, Oklahoma, Texas, and Wyoming, with lithium concentrations of up to 700 ppm. One of the best-known of the oilfield brines is contained in the Smackover Formation in the Gulf Coast area of the south-central United States (Collins, 1976). In some places, the brine contains up to 692 milligrams per liter (mg/L) lithium. The brine occupies pore space in an approximately 200-m-thick limestone at depths of 1,800 to 4,800 m. The brine has been interpreted to be trapped seawater that was subsequently hydrothermally enriched in lithium and other trace elements (Garrett, 2004).

Oilfield brines have two drawbacks as potential lithium resources. First, they typically occur at much greater depths (greater than 1 km) than closed-basin brines. Second, unless they happen to be located in an arid climate, recovery of lithium using the expedient and inexpensive method of solar evaporation will not be feasible (Bradley and others, 2013).

Geothermal brines are another potential source of lithium. These fluids traditionally derive their value from their contained heat, which can be converted to mechanical energy—but some geothermal fluids contain anomalous dissolved metals, including lithium. Reportedly, lithium is now being recovered by Simbol, Inc. from a geothermal brine in the Salton Sea area along the California-Mexico border (Simbol, Inc., 2013).

Lithium-Clay Deposits

A small subset of the world's clay deposits is enriched in lithium. Lithium-bearing clay deposits contain an estimated 7 percent of the world's lithium resources (Evans, 2012).

Analysis of lithium-enriched clays from several occurrences in the Western United States revealed that they all show enrichments in magnesium, fluorine, and lithium—a combination attributed to hydrothermal processes (Stillings and Morissette, 2012). Hectorite (fig. K3F), which is a member of the smectite family of clay minerals, appears to be the most widespread, but Stillings and Morissette (2012) also found lithium-enriched clays of the illite family, as well as illite-smectite mixtures. Hectorite is a silicate of sodium, magnesium, and lithium and contains about one-half percent lithium (table K1). Lithium-clay deposits, prospects, and occurrences are shown in figure K5.

The most significant lithium-clay resource so far discovered is the Kings Valley hectorite deposit, located within the McDermitt caldera complex, which is an extinct volcanic center in northern Nevada. The McDermitt area had extensive volcanism during the Miocene; at least five collapsed vents and resurgent domes have been recognized within the complex. The lithium clays occur in hydrothermally altered, volcanic-derived sediments of lakes that occupied the caldera (Rytuba and Glanzman, 1979). Recovery of lithium by leaching the clay with sulfuric acid has proven feasible (Eggleston and Hertel, 2008). The deposit is being developed for production, but lithium production has not yet begun (Western Lithium Corp., 2015).

Clays that happen to contain lithium have been mined in Arizona, California, and elsewhere in Nevada. These deposits were or are mined not for their lithium content but rather for their physical properties, which make them good additives to, in order of value, drilling muds, paints, and cosmetics. Hectorite gets its name from such a deposit at Hector, Calif., where lake beds of volcanic ash were altered by hydrothermal fluids that came up along a fault zone (Ames and others, 1958). At least two other deposits in the Southwestern United States have been similarly interpreted (Norton, 1965; Wilkerson and others, 2001). In Turkey, the world-class Bigadiç borate deposit, which formed in the hydrothermally altered sediments that fill a rift-related lacustrine basin, contains associated hectorite (Helvacı and others, 2004).

Lithium-Zeolite Deposits

The only documented lithium-zeolite deposit is from a Neogene basin system in the Balkan region of Eastern Europe (fig. K5). Miocene-age lake beds in the Jadar basin include oil shale, carbonate rocks, evaporites, and tuff (Obradović and others, 1997). These strata have been authigenically overgrown by massive layers of jadarite, which is a recently recognized boron-lithium silicate mineral of the zeolite family (Stanley and others, 2007). The jadarite layers are reportedly several meters thick. This single jadarite deposit contains an estimated 3 percent of the world's lithium resource (Evans, 2012).

Resources and Production

Production

Global annual production of lithium has been increasing since the mid-1900s; in 2012, it was about 37,000 metric tons (fig. K1; Jaskula, 2013). The world has hundreds of lithium deposits, prospects, and occurrences (figs. K4 and K5) but only a few of them are currently producing. The present-day supply of lithium comes from pegmatite deposits and closed-basin brines. The main pegmatite producers are Australia, Brazil, China, Portugal, and Zimbabwe. The main brine producers are Argentina, Chile, China, and the United States. The various other deposit types have potential as future contributors.

The United States imports most of the lithium that it consumes. In 2012, the country's net import reliance was greater than 70 percent (Jaskula, 2013).

Reserves and Other Identified Resources

Global lithium resources total more than 39 million metric tons, which is nearly three thousand times current annual production. Of this resource, the USGS currently estimates there to be approximately 13 million metric tons of reserves; that is, resources that are demonstrated (measured and indicated categories) to be and are currently economically recoverable. These figures have changed in recent years, and various experts have reported a wide range of values based on somewhat different methods and assumptions (Gruber and others, 2011). An important additional aspect of the global lithium outlook is recycling, which was not figured into the above resource estimates. Lithium-ion battery recycling is expected to play a major role in the supply of lithium in the medium to

long term. Lithium can be recycled indefinitely, whereas oil can be used only once. Resources of lithium are expected to satisfy demand into the next century (Evans, 2012).

Although current domestic lithium production is small, the United States is endowed with a substantial lithium resource. Gruber and others (2011) estimated the domestic lithium resource to be about 10.2 million metric tons. This includes the Kings Mountain pegmatite district in North Carolina (5.9 million metric tons of lithium), the Kings Valley hectorite deposit in Nevada (2.0 million metric tons), and various closed-basin, geothermal, and oilfield brines (2.3 million metric tons).

Undiscovered Resources

Exploration for lithium deposits has never been as intense as it has been for other metallic resources, such as gold and copper, so it is likely that large, economically viable lithium deposits remain to be discovered. Now that a potentially very large lithium battery market exists for hybrid and electric vehicles, more exploration is being done, and new deposits will likely be discovered. The USGS contributes to this effort by developing mineral deposit models, which provide a conceptual basis for modern mineral exploration. New models have been developed for both LCT pegmatites (Bradley and McCauley, 2013; Bradley and others, (2017) and lithium brines (Bradley and others, 2013; Munk and others, 2016).

Plots of grade versus tonnage are shown in figure K9 for lithium in pegmatites and brines; these give an indication of the sizes of deposits that might remain to be found. The two parameters, deposit grade and deposit tonnage, vary across a wide range of values for most of the common lithium deposit types.

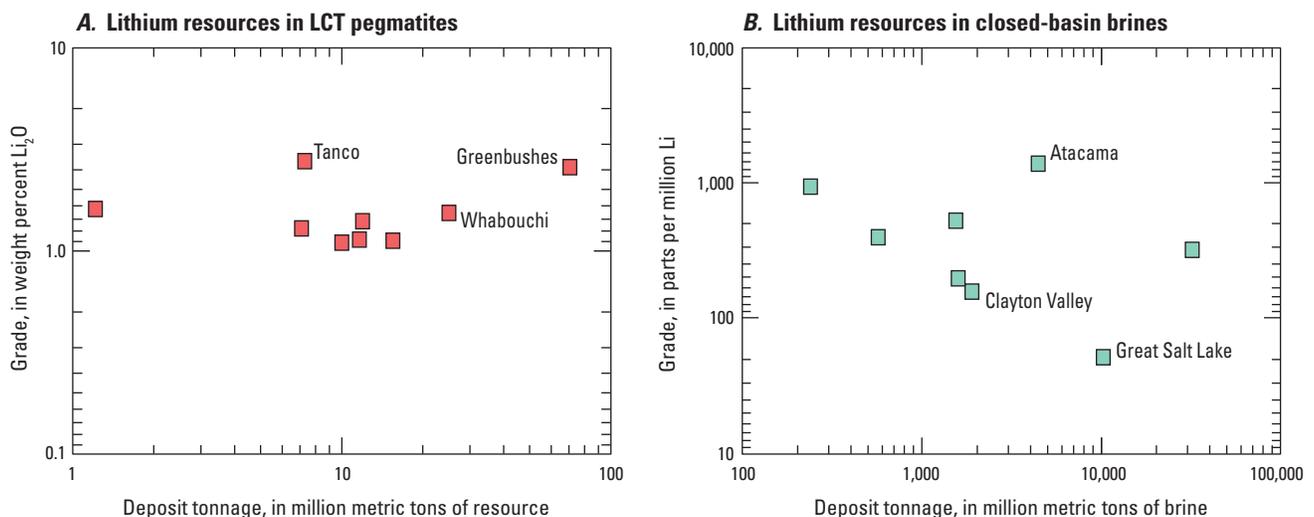


Figure K9. Plots of lithium grade and tonnage for selected world deposits. These plots give an indication of the sizes of deposits that might remain to be found for *A*, lithium-cesium-tantalum (LCT) pegmatites, and *B*, closed-basin brines. Data for the LCT pegmatites are from Bradley and others (2017), and data for the closed-basin brines are from Munk and others (2016). Some of the deposits discussed in the text are labeled.

Exploration for New Deposits

Exploration for Lithium-Cesium-Tantalum Pegmatite Deposits

The search for new LCT pegmatite districts begins with the knowledge that all LCT pegmatites were emplaced into orogenic belts (Bradley and McCauley, 2013). The global age distribution (fig. K6) provides a first-order filter in the search for new LCT pegmatites in unexplored regions. The potential for giant deposits seems greatest in Archean (2,500 Ma and older) collision zones. Most LCT pegmatites intruded metamorphosed sedimentary rocks, typically at conditions of medium pressure and medium to high temperatures (greenschist to amphibolite facies) (Černý, 1992). New deposits are likely to be found within a few kilometers of a “fertile” granite, which generally are large enough (typically several square kilometers in area) to be known already from routine geologic mapping. Fertile granites are identified by the presence of distinctive minerals, such as muscovite, tourmaline, and garnet; by anomalously high concentrations of such trace elements as cesium, lithium, rubidium, tin, and tantalum; and by low concentrations of the major elements calcium, iron, and magnesium (Selway and others, 2005). Around a fertile granite, the more distal LCT pegmatites are more likely to be enriched in lithium (fig. K7). Weathering of LCT pegmatites can result in both soil anomalies and indicator minerals. Smith and others (1987) demonstrated that arsenic, beryllium, antimony, and tin form a 12-by-20-km halo in lateritic soils around the Greenbushes pegmatite; niobium, tantalum, and boron form a smaller, 1-by-5-km halo. Cassiterite, tantalite, elbaite, and spessartine are sufficiently dense and durable to serve as heavy indicator minerals that can be found by panning unconsolidated sediments.

Exploration for Lithium-Brine Deposits in Closed Basins

The most critical factor that determines if a sedimentary basin can accumulate lithium brine is whether or not the basin is closed. All the lithium-brine basins in figure K5 are closed, and all have a saline lake or a salar (that is, a salt flat or salt-encrusted depression). Closed basins form because of tectonic processes, but they are maintained only where, over longer timespans, evaporation exceeds precipitation. If the long-term rate of precipitation in a basin increases sufficiently, lake water will eventually overtop some point along the drainage divide and drain away, carrying with it any dissolved lithium. Mean annual temperature does not appear to be a

critical factor; values range through an order of magnitude from about 0 degrees Celsius (°C) to 23 °C (Munk and others, 2016). Judging from the present-day population of basins, the favorable zones lie between about 19° and 37° north or south latitude (Bradley and others, 2013; Munk and others, 2016). Lithium-brine resources are found in a range of active tectonic settings, from extensional, to strike-slip, to contractional (Bradley and others, 2013; Munk and others, 2016). All but one of the lithium-brine basins show evidence for elevated heat flow, as revealed by the presence of young volcanoes, hot springs, and (or) geothermal resources. Evidence of older hydrothermal activity is seen in several instances and should be regarded as a favorable characteristic. For example, at Clayton Valley, some Miocene to Pliocene basinal deposits were hydrothermally enriched in hectorite; this probably took place a few million years ago, before the lithium-enriched basinal strata were uplifted and exposed. Hectorite concentration haloes have been reported from several basins that lack lithium brines in the U.S. Basin and Range Province (Vine, 1980). In such cases, a hectorite halo may be all that remains of a former brine system that has since leaked away. Like lithium brines, borate deposits appear to be hybrids involving both hydrothermal and evaporative processes; their presence is a favorable indicator for lithium brines. Source rocks, such as felsic, glassy tuffs that have abundant and readily leached lithium, are favorable indicators of a nearby lithium brine deposit (Price and others, 2000).

Exploration for Lithium in Sedimentary Rocks (Clays and Zeolites)

The depositional environments of deposits, prospects, and occurrences in the Basin and Range Province share the following characteristics: they are all found in lake sediments, the sediments contain ash or other volcanic materials, and there is evidence of alteration by hydrothermal fluids (Asher-Bolinder, 1982, 1991). Borate deposits share the same general characteristics, and, accordingly, the presence of borates is a favorable indication for lithium clays. In the Basin and Range Province, borate deposits were extensively prospected in the late 1800s and early 1900s, and many deposits and prospects were found. Lithium clays are not as obvious in these settings as are the common borate minerals; significant lithium resources may thus have been overlooked.

The lithium zeolites at Jadar, Serbia, compose the only known deposit of this type. Accordingly, exploration guidelines must be based on this occurrence, which formed in an extensional tectonic regime and is hosted in Miocene-age lake beds that include oil shale, carbonate rocks, evaporites, oil shale, and tuff (Obradović and others, 1997).

Environmental Considerations

Sources and Fate in the Environment

Lithium in the environment can be derived from both natural and anthropogenic sources. As noted already, lithium is present in trace quantities in most rocks and natural waters and is a major component only in certain rare pegmatite minerals, clays, zeolites, and brines. Potential anthropogenic lithium sources include mine wastes, and after disposal, the wide range of manufactured products.

In soils, lithium is found in detrital and authigenic minerals and, to a lesser extent, in the organic fraction (Heier and Billings, 1978; Ribas, 1991; Schrauzer, 2002). Its concentration depends upon the parent rock (table K2); a study of Scottish soils shows the highest lithium concentrations are found in soils that develop over claystones and metamorphosed felsic rocks. The top 10 centimeters of a soil profile can be poorer in lithium than lower layers because lithium is leached by weathering solutions and can be incorporated into underlying clay minerals (Mitchell, 1964; Ribas, 1991). Shacklette and others (1973) observed that soils from the Western United States are more enriched in lithium than are those in the Eastern United States, with mean values of 23.3 ppm lithium and 17.3 ppm lithium, respectively. Cannon and others (1975) found a difference between the lithium contents of sediments in hydrologically open and closed basins in the Basin and Range Province of California and Nevada. In open basins, the lithium concentrations are relatively low, ranging from 0 to 150 ppm. In contrast, the range of lithium concentrations in hydrologically closed basins is 30 to 2,000 ppm, and lacustrine clays have a median value of 700 ppm lithium. The difference is owing to hydrological flow patterns; in open basins, dissolved salts are continually carried off by outflowing waters.

Although lithium is not required for the growth of plants, they are known to assimilate it, typically in the range of 0.2 to 30 ppm (Aral and Vecchio-Sadus, 2008). More extreme values have also been reported; for example, matrimony vine (*Lycium barbarum*) from Arizona contained 1,120 ppm lithium (dry weight) (Sievers and Canon, 1973). A study of plants from 20 basins in Nevada and California demonstrated that native plants grown in arid basins absorb more lithium than those in more humid regions. Cannon and others (1975) reported median lithium concentrations of 22.8 ppm (dry weight) from *Magnoliopsida* (also known as dicotyledons)

in arid basins compared with 1.3 ppm from humid regions of the United States (Bertrand, 1952, 1959). Cannon and others (1975) reported that plants growing in hot-spring discharge zones appear to have died from accumulation and precipitation of evaporative salts; these “fossilized root crowns” of salt can contain 1,000 ppm lithium.

Being a highly soluble element, lithium is commonly found as a dissolved species in both groundwater and surface water. This property makes lithium useful as a conservative tracer in hydrogeological studies (Bencala and others, 1990). There is evidence, however, that lithium may be removed from solution through sorption onto suspended clays. For example, in Saline Valley, Calif., 98 percent of lithium is lost from solution during surface flow from the spring to the playa (Lombardi, 1963). Lithium substitutes readily for magnesium in the clay structure because of the similar ionic radii of the two elements, and this isomorphous substitution is likely responsible for the affinity of lithium for clays. Plant uptake is another mechanism by which lithium can be removed from solution, especially soil solution. There is a much greater uptake of lithium by plants in acid soils, as acidity increases the solubility of metals (Schrauzer, 2002; Lenntech, 2007).

The use of lithium batteries is anticipated to increase in the future in response to the increasing demand for electric vehicles. The increased use of lithium in batteries is in turn expected to result in increased recycling of lithium from batteries. Recent press reports of explosions and fires associated with lithium batteries (for example, Mouawad and Drew, 2013) could cause concern about lithium recycling. Spent lithium batteries contain virtually no lithium metal, however, because it has all been converted to lithium oxide by the time the battery stops working (National Electrical Manufacturers Association, 2001). Lithium oxide is unreactive; unlike lithium metal, it does not produce hydrogen gas upon exposure to water, and it does not catch fire. Both HMIS (Hazardous Materials Identification System) and NFPA (National Fire Protection Association) give it a “0” rating for flammability and physical (reactivity) hazard risks (Alpha Aesar, 2012; Sigma Aldrich, 2014). It is a health hazard (a “3” rating by HMIS and NFPA) because it is corrosive and can cause serious eye and skin damage upon contact. Disposal of spent batteries in a modern municipal solid waste facility is not likely to present a lithium hazard, however. Lithium oxide is slightly to moderately soluble—a maximum of 6.67 g of Li₂O can dissolve in 100 g of water (H₂O) at 0 °C (ESPI Metals, 1993).

Table K2. Lithium concentrations (in parts per million) in soils developed on various types of bedrock.

[Sources: Mitchell (1964), as reported in Heier and Billings (1978)]

Igneous			Metamorphic				Sedimentary	
Olivine gabbro	Andesite	Granite	Serpentinite	Quartzite	Granitic gneiss	Quartz mica schist	Shale	Sandstone
30	50	7	30	15	70	200	60	20

Mine Waste Characteristics

Mine-waste characteristics vary with the type of lithium deposit. Only two types of deposits—pegmatites and closed-basin brines—have produced mine wastes.

The mining history of lithium pegmatites may affect the mineralogy of tailings and waste piles that remain. Tin was the original target of mining at Kings Mountain (Kesler, 1942, 1955, 1961), suggesting that lithium-bearing minerals may still remain in dumps from that era. Mineral processing of the pegmatite minerals involved crushing, wet grinding, sieving, gravity concentration, flotation, and collection with fatty acid amines. Tailings were discharged to storage ponds (Garrett, 2004) that likely contain some lithium. In 1969, mineral processing was changed to improve the recovery of lithium. The new process involved calcining (heating) the spodumene concentrate after collection, then leaching the calcine with hot water. Yet even with this newer process, all the lithium still was not recovered.

Another source of lithium to waste and tailings piles can be through dissolution of the lithium minerals in the grinding and sieving steps of processing. For example, spodumene is fairly insoluble in water and dilute acids, but a small amount of dissolution has been observed during ore processing and concentration (Aral and Vecchio-Sadus, 2008). The dissolved lithium will be transported with the processing water and may concentrate in tailings ponds that have concentrations ranging up to 13 ppm.

The production of lithium by evaporation of closed-basin brines produces various evaporite minerals in the sequence of ponds. Details vary among the deposits owing to differences in brine chemistry. Precipitates at Clayton Valley include clay, calcium carbonate, calcium sulfate, hydrated magnesia, potassium-sodium sulfate, and potassium-sodium chloride (Garrett, 2004).

Human Health Concerns

Lithium is not considered an essential element for life, but it is present in most organisms in trace quantities (Léonard and others, 1995; Lenntech, 2007). The normal human intake is about 2 milligrams per day (mg/d) (Léonard and others, 1995), and the human body contains about 7 milligrams (mg). Ingested lithium is absorbed from the intestines and excreted through the kidneys, and the half-life in the body is about 24 hours (Freeman and Freeman, 2006; Aral and Vecchio-Sadus, 2008).

In the realm of human health, lithium is best known as the leading treatment for the debilitating symptoms of bipolar disorder. Modern use of lithium compounds for this purpose dates from pioneering work after World War II in Australia by John Cade (Mitchell and Hadzi-Pavlovic, 2000). About 4 percent of people—or nearly 300 million out of the present world population—will suffer from bipolar disorder at some point in their lives (Ketter, 2010). The number who treat the

condition with lithium is unknown but undoubtedly is in the millions. A typical dosage is 1,800 mg/d of lithium carbonate (Drugs.com, 2013).

Lithium can be toxic. In fact, the United States banned the use of medicinal lithium between 1949 and 1970 for this reason (Strobusch and Jefferson, 1980). Aral and Vecchio-Sadus (2008) summarized the various harmful effects and noted that a dose of 5 g of lithium can be fatal to humans. No lithium poisoning has been reported from industrial applications, however (Aral and Vecchio-Sadus, 2008).

Ecological Health Concerns

Lithium affects metabolism, neuronal communication, and cell proliferation in many organisms in addition to humans. It disturbs the development of invertebrates (Léonard and others, 1995), and, in rats, it has been reported to reduce the number in a litter and the weight of the offspring and to cause incomplete ossification (Domingo, 1994). One of several useful endpoints used in toxicity tests is the concentration that leads to 50 percent mortality (lethal concentration 50, or LC₅₀) after exposure to a substance for a certain amount of time. For earthworms exposed to soil containing lithium, the LC₅₀ value was 70 milligrams per kilogram (mg/kg) after 7 weeks of exposure (Fischer and Molnár, 1997). The sensitivity of fish to lithium was measured in a series of 96-hour tests, which revealed an LC₅₀ value that ranged from 13 mg/L for fathead minnows to greater than 100 mg/L for other fish species. Lithium concentrations of 1.2 mg/L immobilized the tiny crustacean *Daphnia magna* in 64 hours, and a dose of 1.7 mg/L of lithium prevented the formation of embryos in fish eggs (Kszos and Stewart, 2003).

Carbon Footprint

Lithium's potential importance to the world's carbon budget derives from its use in lightweight, rechargeable car batteries. Over the course of a hypothetical lifetime of 150,000 miles (240,000 km), today's average gasoline-powered car will produce about 63,450 kilograms of carbon dioxide based on values from the U.S. Environmental Protection Agency, Office of Transportation and Air Quality (2011). This greenhouse gas will go directly from the tailpipe to the atmosphere, where it will contribute to global warming; some of it will later end up dissolved in seawater, where it will contribute to further ocean acidification, harming or killing fish and shellfish. The carbon dioxide output of an electric car depends largely on the means of charging its battery, but in all cases—even if the electricity comes from a coal-fired powerplant—the output of carbon dioxide is lower than for a gasoline-powered car (Notter and others, 2010). In the best-case scenario, where the battery is recharged from renewable hydroelectric, wind, tidal, or solar power, the carbon dioxide output (beyond infrastructure costs) is negligible.

Problems and Future Research

As is the case for most of the critical elements, lithium resources have not been as thoroughly studied as some conventional metallic resources, such as copper and lead. Basic research on the better-known lithium deposit types (pegmatites and brines) as well as on the newer deposit types (clays and zeolites) would help identify new resources and could ensure that a transition from fossil fuels to renewable energy sources is not limited by the supply of lithium.

For LCT pegmatites, the overarching question is why some orogenic belts are well-endowed with these deposits, whereas other seemingly similar belts are not? The connections between LCT pegmatites and tectonics have yet to be unraveled at the level of detail that would aid in exploration. Although most LCT pegmatites are found in orogenic belts that formed during continental collision, there is no obvious explanation for why particular pegmatites formed where and when they did. To address this problem would require tight geochronology for the pegmatite, for the orogenic belt in which it occurs, and for any associated sedimentary basins. Such an effort is now technologically possible.

A similar question applies to lithium brines—Why have these deposits formed in only a small subset of closed basins in arid regions? In the U.S. Basin and Range Province, for example, about 150 basins share the same basic characteristics, but only a few have lithium brines. Another key question involves the timescale of lithium-brine genesis—Are lithium-enriched brines like fossil fuels, or are they renewable on short time scales?

Lithium-clay (hectorite) and lithium-zeolite (jadarite) deposits have not been systematically studied. Mineral-deposit models would be useful to guide exploration efforts for both types. Lithium-clay deposits, which can be studied at the surface, are also of interest as potential examples of fossil lithium-brine systems that once operated at depth.

Lithium is neither an ecological nor a human health concern when it is present at ambient conditions. As global lithium consumption rises during the next few decades, however, environmental issues related to the production, routine daily use, and disposal of lithium products will warrant additional research.

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Note: All Web links listed were active as of the access date but may no longer be available.

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For more information concerning this report,
please contact:

Mineral Resources Program Coordinator

U.S. Geological Survey

913 National Center

Reston, VA 20192

Telephone: 703-648-6100

Fax: 703-648-6057

Email: minerals@usgs.gov

Home page: <https://minerals.usgs.gov>

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