Lithium

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3-A. Crystal Chemistry

The most important common characteristic of the alkali elements is the single electron in the outermost energy level of their atoms. As shown by the spectroscopically determined ionization energies, these electrons can be easily detached. The cores remaining after the first ionization have the same electronic configuration as the immediately preceeding noble gases in the periodic table, and this fact explains the very high second ionization potentials. The aptitude of the alkali metals to be transformed into positively charged ions results in their extremely reactive chemical character. Lithium exhibits many similarities with the other alkali metals, although the small size of the Li atom and the Li^+ ion does lead to some remarkable differences; in many respects its behavior constitutes a transition between the group of the alkali metals and that of the alkaline earth metals, especially magnesium. Characteristic properties for lithium are: the low solubilities of various salts e.g. the fluoride,

Table 3-A-1. *Lithium minerals*

Compound		References
Cryolithionite	$Na_3Al_2[Li^{[4]}F_4]_3$	MENZER (SB 1930, 498)
Lithiophosphatite	$Li_3^{[4]}[PO_4]$	ZEMANN (SR 1960, 397)
Triphylite	$Li^{[6]}(Fe, Mn)[PO_4]$	DESTENAY (SR 1950, 319)
Amblygonite	$Li^{[5]}Al(F, OH)[PO_4]$	BAUR (SR 1959, 429)
Eucryptite	$Li^{[4]}Al[SiO_4]$	WINKLER (SR 1953, 562)
Spodumene	$Li^{[6]}Al[Si_2O_6]$	CLARK *et al.* (1969)
Bikitaite	$Li[AlSi_2O_6] \cdot H_2O$	HURLBUT (SR 1957, 436)
Petalite	$Li^{[4]}[AlSi_4O_{10}]$	LIEBAU (SR 1961, 505)
Neptunite	$Li^{[6]}KNa_2Fe_2Ti_2O_2[Si_8O_{22}]$	CANNILLO *et al.* (1966)
Holmquistite (Li-amphibole)	$Li_2^{[4]}Al_2(Mg, Fe)_3(OH)_2[Si_4O_{11}]_2$	WHITTAKER (1969)
Lepidolite (Li-mica)	$KLi_2Al(F, OH)_2[Si_4O_{10}]$	RADOSLOVICH (1963)
Zinnwaldite (Li-mica)	$KLiFeAl(F, OH)_2[AlSi_3O_{10}]$	RADOSLOVICH (1963)
Cookeite (Li-chlorite)	$LiAl_4(OH)_8[AlSi_3O_{10}]$	BROWN and BAILEY (1962)
Elbaite (Li-tourmaline)	$Na(Al, Li, Mg)_3^{[6]}(OH, F)_4[BO_3]_3[Si_6O_{18}]$	ITO and SADANAGA (SR 1951, 310)
Lithiophorite	$(Al, Li)^{[6]}MnO_2(OH)_2$	WADSLEY (SR 1952, 266)

carbonate and phosphate, the tendency towards covalent bond formation, and solvation — all of which are due to the high polarizing power of Li^+, the highest of all the alkali ions.

Because of the small size of Li^+ with respect to that of the next alkaline ion Na^+, we can expect only rather limited substitution of lithium for sodium in crystals. A possible diadochy between Li^+ and Al^{3+}, Fe^{2+} and especially Mg^{2+}, owing to the radius similarity of these ions, may take place in the late phases of magmatic crystallization and affects the compositions of some minerals, e.g. clinopyroxenes and micas. There are, however, a few independent lithium minerals, which are listed in Tables 3-A-1 and 3-D-1.

With the exception of cryolithionite, $Na_3Al_2[LiF_4]_3$, and lithiophorite, (Al, Li) $MnO_2(OH)_2$, lithium occurs in nature mostly in silicates or phosphates. Therefore, the present crystallochemical review concerns only lithium-halogen and lithium-oxygen bonds.

I. Li Halides

From alkali halides a set of effective ionic radii for the alkali ions can be derived. The value for Li^+ is 0.78 Å (see this handbook, Vol. I, Table 12—8, p. 390).

In the Li-halides which show the NaCl structure type, the Li^+ ions is in 6-fold coordination with Li-halogen bond lengths as follows: Li—F, 2.014 Å; Li—Cl, 2.570 Å; Li—Br, 2.751 Å; Li—I, 3.000 Å (after Systö, 1969). Very similar bond lengths for Li octahedrally coordinated by fluorine are found in $Li[SbF_6]$ (Burns, 1962) namely Li—F, 2.032 Å. Distorted octahedral coordination occurs in Li_6BeZrF_{12} (Sears and Burns, 1964) with average Li—F bond lengths of 2.08 Å and 2.04 Å respectively for the two crystallographically non-equivalent LiF_6 octahedra.

Other fluorides show Li in tetrahedral coordination. In $Li_2[BeF_4]$ (Burns and Gordon, 1966), whose structure is isotypic with phenakite, the average Li—F distances for the two independent LiF_4 tetrahedra are 1.875 and 1.861 Å; the mineral cryolithionite is isostructural with garnets, with LiF_4 replacing SiO_4 tetrahedra, (Menzer, SB 1930, 498). Li also has tetrahedral coordination in Li_2NiF_4, which belongs to the family of inverse spinels (Rüdorff and Kandler, SR 1957, 267).

Concerning distances between Li and the other halogens, Jacobi and Brehler (1969) report two independent $Li(H_2O)_2Cl_4$ octahedra in $Li_2ZnCl_4 \cdot 2\,H_2O$ with average Li—Cl bond lengths of 2.75 Å, significantly longer than those in LiCl.

II. Oxygen-containing Li Compounds

In structures where lithium is coordinated to oxygen, Li^+ usually exhibits the coordination numbers four or six, in the form of more or less distorted tetrahedra and octahedra.

The occurrence of such different coordination numbers arises from the fact that the crystal structure of most of the oxygenated compounds, containing no other large ion, can be explained by close packing of oxygen atoms. The lithium ions can be accomodated in the tetrahedral and octahedral sites of this packing.

Tables 3-A-2a and 3-A-2b list Li^+—O bond lengths for 4- and 6-coordination respectively.

The tetrahedral coordination occurs more frequently than the octahedral one. As with the fluorides the $Li^{[4]}$—O distances are shorter than the $Li^{[6]}$—O distances. The average value for $Li^{[4]}$—O is 1.97 Å, while the average $Li^{[6]}$—O bond length is 2.14 Å. These values can be compared with 1.82 Å reported by Akišin and Rambidi (SR 1958, 282) for the Li—O bond length from electronic diffraction data on Li_2O vapour. Solid Li_2O has an "anti-fluorite" structure, with a $Li^{[4]}$—O bond length of 2.00 Å (Zintl *et al.*, SB 1934, 283).

An intermediate coordination number was found (Baur, SR 1959, 429) in the mineral amblygonite, $LiAl(OH,F)[PO_4]$, in which Li^+ is coordinated in the form of a distorted trigonal bipyramid by four oxygen atoms of PO_4 groups (at distances 2.12 ± 3, 2.05 ± 3, 2.11 ± 3, and 2.14 ± 3 Å) and one (OH, F) ion (at a distance of 1.95 ± 3 Å). The average $Li^{[5]}$—O bond length is 2.07 Å, intermediate between the values found for tetrahedral and octahedral coordinations. In $Li[BO_2]$ the Li^+ ion also binds four oxygen atoms at an average distance of 1.967 Å and one more oxygen atom at 2.473 Å (Zachariasen, 1964). In $Li[AsO_3]$ (Hilmer and Dornberger-Schiff, SR 1957, 391) one lithium ion shows tetrahedral coordination, and a second one has four neighboring oxygen atoms at an average distance of 1.99 Å and two more oxygen atoms at 2.54 Å. In these last cases the lithium coordination number can be described as $(4+1)$ and $(4+2)$ respectively. The structure of $Li[AsO_3]$ closely resembles the structure of diopside $CaMg[Si_2O_6]$.

The diopside atomic arrangement is present also in $LiNa[BeF_3]_2$ (Hahn, SR 1953, 336) and in spodumene, α-$LiAl[Si_2O_6]$ (Warren and Biscoe, SB, 1931, 527).

Several structures containing LiO_4 tetrahedra can be related to SiO_2 structure types; in $KLi[SO_4]$ (Bradley, SB 1925, 376), Li tetrahedra share the four vertices with different SO_4 tetrahedra to form a tridymite-like framework. In tetragonal γ-$LiAlO_2$ (Marezio, 1965a; Bertaut *et al.*, 1965), AlO_4-tetrahedra share corners to build a cristobalite-like framework. The Li^+ ions are accomodated in tetrahedral holes and each LiO_4 tetrahedron shares an edge with an AlO_4 tetrahedron.

Some Li-silicate structures can be considered to be derivatives of SiO_2 structures. In β-$Li[AlSiO_4]$ (Winkler, SR 1948, 474), the small Li^+ ions are accomodated in the empty channels of an atomic arrangement where Al, Si and oxygen atoms occupy the same sites as in the high-quartz. The hexagonal form of spodumene (γ-spodumene, $Li[AlSi_2O_6]$-III) (Li, 1968), also has the high-quartz structure with the Li^+ ions randomly situated in tetrahedral interstitial holes on equipoints of rank 3; additional tetrahedral sites are also possible for Li^+ in the structure.

The framework of β-spodumene, $Li[AlSi_2O_6]$-II (Li and Peacor, 1968), is isotypic with keatite and the four lithium ions per unit cell are randomly distributed among four sets of paired eight-fold equipoints with $^1/_2$ occupancy in tetrahedral oxygen environment. Several additional distorted tetrahedral sites are available; furthermore, Li may occupy octahedral positions at higher temperature.

Tetrahedral lithium coordination occurs in some layer or chain silicates and in structurally related germanates; in these structures chains or layers form the structure and are linked together by Li ions in a three-dimensional framework. In $Li[SiO_3]$ (Seemann, SR 1956, 404), Li tetrahedra share all vertices with other LiO_4 tetrahedra. In $Li_2[Si_2O_5]$ (Liebau, SR 1961, 506) and $Li_2[(Si_{0.25}Ge_{0.75})_2O_5]$ (Völlen-

KLE *et al.*, 1968), LiO_4 tetrahedra are linked together in pairs by sharing edges; these doublets share vertices to form complex chains which run parallel to the *c* axes. In the first case these chains bind two adjacent Si sheets; in the second case they connect different chains built up by $(Si, Ge)O_4$ tetrahedra and running parallel to the Li chains. In the mineral petalite, $Li[AlSi_4O_{10}]$ (LIEBAU, SR 1961; 506), Li ions share opposite edges with Al tetrahedra forming Li—Al—Li—Al chains running along the *b* axis and connecting two sheets of SiO_4 tetrahedra in a three-dimensional framework.

Several structures of artificial Li compounds consist of vertex-linked tetrahedra frameworks similar to that of phenakite; typical examples are $Li_2[WO_4]$ (ZACHARIASEN and PLETTINGER, SR 1961, 391), $LiAlGeO_4$, $LiGaGeO_4$, $LiZnVO_4$ (BLASSE, 1963), eucryptite (α-$Li[AlSiO_4]$) (WINKLER, SR 1953, 562), and $Li_2[BeF_4]$. In $LiGaO_2$ (MAREZIO, 1965b), connections between LiO_4 and GaO_4 tetrahedra occur through vertices, each oxygen atom being shared by four tetrahedra, two Ga-centered and two Li-centered; $LiGaO_2$ has the arrangement of a wurtzite-like structure. In lithiophosphatite, low-temperature $Li_3[PO_4]$ (ZEMANN, SR 1960, 397), LiO_4 tetrahedra share edges and vertices with each other and are linked by corners to PO_4 tetrahedra; the resulting structure can be described as a distorted hexagonal close-packing of oxygen atoms, where Li and P atoms occupy tetrahedral sites. Comparison of x-ray powder data and i.r. spectra of the low- and high-temperature forms of $Li_3[PO_4]$ suggests that important structural rearrangements are not involved in the transition (TARTE, 1967).

In $(NH_4)Li[SO_4]$ (DOLLASE, 1969) and in $(N_2H_5)Li[SO_4]$ (BROWN, 1964), each LiO_4 tetrahedron shares the four corners with four different SO_4 tetrahedra and vice-versa to form a three-dimensional network with four- and six- and four- and eight-membered rings respectively. Rings of four and eight tetrahedra Li- and S-centered are present in the framework of $Li_2[SO_4] \cdot H_2O$ (LARSON, 1965) where each Li tetrahedron shares corners with different Li and S tetrahedra. In $Li_2[C_2O_4]$ (BEAGLEY and SMALL, 1964), the vertices of the LiO_4 tetrahedra are connected by $C_2O_4^{2-}$ ions into sheets which form the crystal structure.

Coordination octahedra around Li^+ can occur either separately or linked together in various ways. Isolated octahedra, for example, occur in α-spodumene, where Li^+ is in sixfold coordination in contrast to the arrangement observed in β- and γ-spodumene. Recent x-ray studies (CLARK *et al.*, 1969) have shown that Li-pyroxenes, due to the small size of the cation in position M2, do not maintain the symmetry of the space group C2/c (corresponding to M2 site occupied by Na or Ca), the true symmetry being C2. However, since deviation from C2/c occurs for a few weak reflections, refinement in this space group represents a reliable average structure. Coordination around the cation, which is irregularly eightfold when M2 is occupied by Na or Ca, becomes sixfold in Li-pyroxenes because the two most distant oxygen atoms are removed from coordination polyhedron. In the synthetic pyroxene, $(Li_{0.85}Fe^{2+}_{0.03})(Fe^{3+}_{0.95}Fe^{2+}_{0.05})[Si_2O_6]$, Li is still in octahedral coordination but two Li-O distances are significantly longer (CLARK *et al.*, 1969).

Isolated octahedra occur also in neptunite (CANNILLO *et al.*, 1966). In $LiMn[PO_4]$ (GELLER and DURAND, SR 1960, 399), the synthetic analogue of the manganous compound of the mineral triphyline, Li octahedra are linked by sharing edges to

Table 3-A-2a. *$Li^{[4]}$—O bond lengths*

Compound	Distances (Å)		Mean	References
LiOH (by neutron diff.)	1.96 (4)		1.96	Dachs (SR 1959, 330)
LiOH · H_2O	1.96 (2)	1.98 (2)	1.97	Rabaud *et al.* (SR 1957, 240)
γ-$LiAlO_2$	2.06 ± 2 (2)	1.95 ± 2 (2)	2.00	Marezio (1965a)
$LiGaO_2$	2.00 ± 3 2.00 ± 2	2.00 ± 2 1.95 ± 2	1.99	Marezio (1965b)
$Li_2[CO_3]$	1.96 1.96	1.97 2.00	1.97	Zemann (SR 1957, 394)
$Li[BO_2]$	1.964 ± 8 1.945 ± 8	1.952 ± 8 2.007 ± 5	1.967	Zachariasen (1964)
$Li_2[B_4O_7]$	1.97 ± 2 2.07 ± 2	2.02 ± 2 2.14 ± 2	2.05	Krogh-Moe (1968)
$Li_2[SO_4]$ · H_2O	1.917 ± 5 1.969 ± 6	1.950 ± 8 2.001 ± 7	1.959	Larson (1965)
	1.907 ± 6 1.937 ± 9	1.942 ± 6 1.953 ± 6	1.935	
$LiNa[SO_4]$	1.87 ± 4 2.08 ± 4	1.88 ± 4 2.09 ± 4	1.98	Morosin and Smith (1967)
$Li(NH_4)[SO_4]$	1.89 ± 10 1.98 ± 3	1.89 ± 4 1.90 ± 2	1.91	Dollase (1969)
$Li(N_2H_5)[SO_4]$	1.96 ± 4 1.97 ± 4	1.95 ± 4 1.88 ± 4	1.94	Brown (1964)
$Li_2[WO_4]$	1.87 ± 8 1.80 ± 8	2.10 ± 8 1.80 ± 8	1.89	Zachariasen and Plettinger
	1.88 ± 8 2.00 ± 8	1.98 ± 8 2.02 ± 8	1.97	(SR 1961, 391)
$Li_3[PO_4]$	2.00 ± 5 1.90 ± 5	1.97 ± 5 1.95 ± 5	1.96	Zemann (SR 1960, 397)
	1.98 ± 5 (2) 1.98 ± 5	2.00 ± 5	1.99	
$LiK_2[P_3O_9]$ · H_2O	1.96 ± 3 1.93 ± 3	1.94 ± 3 1.97 ± 3	1.95	Eanes and Ondik (1962)
$Li_2[Si_2O_5]$	1.85 1.99	2.04 1.88	1.94	Liebau (SR 1961, 506)
β-$Li[AlSiO_4]$	2.01 (4)		2.01	Winkler (SR 1948, 474)
$Li[AlSi_4O_{10}]$ petalite	1.92 (2)	1.99 (2)	1.95	Liebau (SR 1961, 506)
$Li_2[(Si_{0.25}Ge_{0.75})_2O_5]$	2.01 ± 7 1.93 ± 7	1.93 ± 7 1.90 ± 7	1.94	Völlenkle *et al.* (1968)
$Li_4[GeO_4]$	1.94 ± 5 (2)	1.92 ± 5 (2)	1.93	Völlenkle and Witt-
	2.02 ± 5 (2) 2.14 ± 5	1.94 ± 5	2.03	mann (1969)
$Li_2[C_2O_4]$	2.076 ± 4 1.999 ± 4	2.033 ± 4 1.935 ± 4	2.011	Beagley and Small (1964)

form linear strings, in a structure which is related to chrysoberyl. Similar connections occur in $Li_{1+x}V_3O_8$ (Wadsley, SR 1957, 301); in this compound additional Li atoms are probably randomly distributed in tetrahedral sites. Connections through edges occur also in rhombohedral double oxides with the general formula $LiXO_2$ (where X is V, Ni, Co, Al, Cr, Rh, Nb) (Wyckoff, 1964) with the structure of the $NaHF_2$ type, that is with each LiO_6 octahedron sharing six edges with neighboring octahedra to form planes having hexagonal packing. In $Li[IO_3]$ (Rosenzweig and Morosin, 1966) and $LiSbO_3$ (Edstrand and Ingri, SR 1954, 444), Li octahedra share opposite faces to form infinite chains. A similar arrangement is observed in $Li[ClO_4] \cdot 3H_2O$ (Datt *et al.*, 1968) and $Li[MnO_4] \cdot 3H_2O$ (Ketelaar, SB 1935, 447); the most interesting feature of these structures is that Li is coordinated only by oxygen atoms of water molecules forming $[Li^{[6]}(H_2O)_3]$-chains linked to the framework by hydrogen bonds. Many synthetic Li compounds show the atomic arrangement of spinel (Wyckoff, 1965). In all these structures Li^+ ions show octahedral coordination. $LiFe_5O_8$ (Kato, SR 1952, 325), $LiAl_5O_8$ and $LiGa_5O_8$ also have a spinel-like structure, but show an ordered low-temperature and a disordered high-temperature form. This feature occurs also in lithium ferrite $LiFeO_2$ (Kato, SR 1958, 325) which, after quenching from high temperature, has an NaCl structure in which Li^+ and Fe^{3+} ions are randomly distributed among the positions of the metallic atoms in NaCl. By annealing at 570°C lithium and iron become segregated into a fully ordered tetragonal structure.

The latter examples show that diadochy between Li^+ and other cations may occur only under special conditions. Replacement of octahedral Li^+ by Fe^{3+} is reported for a cubic Li tungstate with the crystallochemical formula $(Li_{0.92}Fe_{0.08})^{[6]}_{12}[(WO_4)_3W_4O_{16}]$ (Borisov *et al.*, 1969). From a crystal structure determination of the mineral lithiophorite, $(Al, Li)MnO_2(OH)_2$ (Wadsley, SR 1952, 266), it appears that lithium ions randomly occupy one-third of the octahedral aluminium sites in a layer of the brucite type. In tourmalines, where Mg and Al in octahedral coordination are located at different crystallographic sites, a partial substitution of Mg ions by Li and Al ions is observed, one particular example being elbaite (Ito and Sadanaga, SR 1951, 310). In such Li-rich micas as lepidolite and zinnwaldite, Li in octahedral sites replaces Mg and Al (Radoslovich, 1963). In petalite, spodumene and amblygonite, no random distribution of Al—Li has been observed. In holmquistite, $Li_2Al_2(Mg, Fe)_3(OH)_2[Si_4O_{11}]_2$ (Whittaker, 1969), Li^+ ions are confined to a single crystallographic position. In such a case, the preferential entry of Li into its particular site can be explained by electrostatic ordering effects. Holmquistite, isotypic with anthophyllite $Mg_7(OH)_2[Si_4O_{11}]_2$, is a typical example of the substitution of $(Li^+ + Al^{3+})$ for 2 Mg^{2+} ions.

Triphylite, $Li(Mn, Fe)[PO_4]$ (Destenay, SR 1950, 319), exhibits a completely ordered arrangement of the cations. This mineral belongs to a series of natural compounds such as sicklerite and iron sicklerite, with the general formula $Li_{1-y}Mn^{2+}_{1-x}Fe^{2+}_{x-y}Fe^{3+}_y[PO_4]$, the other end of the series being represented by the mineral heterosite, $Fe^{3+}[PO_4]$. Close analogies in the unit cell parameters and x-ray powder data suggest an essentially similar structure. Probably the mechanism of the valence compensation during oxidation causes Li^+ ions to be removed from their octahedral sites, until in heterosite these sites are completely empty. This confirms the peculiar role of lithium as interstitial component in close-packed arrangements.

Table 3-A-2b. *$Li^{[6]}$—O bond lengths*

Compound	Distances (Å)		Mean	References
$LiNiO_2$	2.04 (6)		2.04	Dyer *et al.* (SR 1954, 424)
$LiVO_2$	2.14 (6)		2.14	Rudörff and Becker (SR 1954, 424)
$LiSbO_3$	2.01 (2) 2.07 (2)	2.07 (2)	2.05	Edstrand and Ingri (SR 1954, 444)
$Li[IO_3]$	2.04 ± 6 (3)	2.22 ± 6 (3)	2.13	Rosenzweig and Morosin (1966)
$Li[ClO_4] \cdot 3\,H_2O$ (neutron diffraction)	2.18 (3)	2.08 (3)	2.13	Datt *et al.* (1968)
$LiMn[PO_4]$	2.22 ± 1 (2) 2.16 ± 1 (2)	2.11 ± 1 (2)	2.17	Geller and Durand (SR 1960, 399)
$LiAl[Si_2O_6]$ α-spodumene	2.105 (2) 2.251 (2)	2.278 (2)	2.211	Clark *et al.* (1969)
$Li_{1+x}V_3O_8$	1.99 2.28 (2)	2.08 2.33 (2)	2.25	Wadsley (SR 1957, 301)
$LiKNa_2Fe_2^{2+}Ti_2O_2[Si_8O_{22}]$ neptunite	2.13 ± 2 (2) 2.04 ± 2 (2)	2.15 ± 2 (2)	2.11	Cannillo *et al.*

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References: Section 3-A

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3-B. Stable Isotopes in Nature

The isotope geochemistry of lithium was reviewed by Rankama (1954) and additional references given by Heier and Adams (1964). Svec and Anderson (1965) summarized the existing data on the relative abundances of the lithium isotopes, Table 3-B-1.

Table 3-B-1. *The relative abundances of the lithium isotopes.*
(From Svec and Anderson, 1965; Krankowsky and Müller, 1967;
Balsiger *et al.*, 1968)

^{7}Li/^{6}Li	^{6}Li/^{7}Li	Method	Reference
12.00 ± 0.02	0.08333 ± 0.00014	Atomic wt. determ.	Richards and Willard (1910)
12.0	0.0833	Mass spec.	Bondy and Vanicek (1936)
11.6; 12.52	0.0862; 0.07987	Mass spec.	Brewer (1936)
12.29 ± 0.20	0.08137 ± 0.00132	Mass spec.	Lu (1938)
11.6 ± 0.2	0.0862 ± 0.0015	Mass spec.	Hintenberger (1947)
12.5 ± 0.2	0.0800 ± 0.0013	Mass spec.	Hintenberger (1947)
12.54 ± 0.38	0.07974 ± 0.0024	Mass spec.	Inghram (1947)
12.70 ± 0.7	0.0787 ± 0.0044	Mass spec.	White and Cameron (1948)
12.35	0.08097	Neutron activ.	Kaplan and Wilzbach (1954)
11.53	0.08673	X-ray density	Hutchinson (1954)
12.47 to 12.72	0.08019 to 0.07862	Mass spec.	Cameron (1955)
12.2	0.0820	Mass spec.	Gillieson and Thorne (1955)
12.5	0.0800	Spectroscopy	Gillieson and Thorne (1955)
12.48	0.08013	Mass spec.	Higatsberger (1955)
12.48	0.08013	Mass spec.	Ordzhonikidze and Shyutse (1955)
11.32	0.08834	Mass spec.	White, Collins and Rourke (1956)
13.5	0.0741	Spectroscopy	Brody, Fred and Tomkins (1954, 1957)
12.2	0.08182	Mass spec.	Svec and Anderson, Jr. (1965)
12.17 ± 2%		Mass spec.	Krankowsky and Müller (1967)
12.51 ± 1.75%		Mass spec.	Balsiger *et al.* (1968)

The relatively large mass difference between the two lithium isotopes seems favorable for their separation in nature. Taylor and Urey (1938) found a change of 25 per cent of the normal ^{7}Li/^{6}Li ratio when solutions of LiCl percolate through a column of Na-lepidolite; thus fractionation of Li isotopes could be expected during weathering processes that involve cation exchange. Svec and Anderson (1965) found low ^{6}Li/^{7}Li ratios in evaporite Li_2NaPO_4 from Searle's Lake and reagent Li_2CO_3 (0.07957 and 0.07926 respectively). Since both materials involve crystallization from solution this is in agreement with the greater solubility of the ^{6}Li compound and is consistent with the findings of Cameron (1955) concerning chemical fractionation of the isotopes. Wagner and Pely (1955) produced a change in the ^{7}Li/^{6}Li ratio from 12.48 to 14.03 through repeated precipitation of Li_2CO_3. Bowen (1956) found that ^{6}Li was metabolically more active than ^{7}Li in studies involving yeast. Crystallization of the Li-bearing minerals in the Montgary Pegmatite studied by Svec and Anderson (1965) was in the order: spodumene, amblygonite, lepidolite, with the latter being formed by some replacement mechanism. It appears that ^{6}Li is relatively concentrated in the early minerals and the ^{6}Li/^{7}Li ratios of these samples were 0.08117, 0.08077 and 0.08049 respectively. This is consistent with data given by Cameron (1955) showing a concentration of ^{6}Li in a silicate phase formed when LiI was fused in glass.

The ratio of ^{7}Li/^{6}Li in meteorites is of interest in connection with the nuclear synthesis of the light elements. The production of ^{7}Li by $^{10}B(n, \alpha)^7Li$ could result in variable ^{7}Li/^{6}Li ratios in uranium minerals and meteorites. Ordzhonikidze (1960) found variable Li isotope ratios in uranium minerals. Shima and Honda (1963) reported a ^{7}Li/^{6}Li ratio of 10.5 in lithium samples isolated from the Bruderheim, Harleton and Ehole chondrites, compared with a value of 12.0 in terrestrial rock samples determined under identical experimental conditions (mass spectrometry). This difference of about 15% could not be verified by Dews (1966), who found the ^{7}Li/^{6}Li ratios for Bruderheim and Bjurbøle meteorite chondrules, whole-rock Bruderheim, and standard granite G-1 to be identical within 3.3% (at the 95% confidence level). Their values of the ^{7}Li/^{6}Li ratio were in the range of 12.26 to 12.67. Krankowsky and Müller (1964, 1967) found meteoritic and terrestrial ^{7}Li/^{6}Li ratios to agree within 2 per cent. Poschenrieder *et al.* (1965) used an ion-microprobe mass spectrometer which permitted analysis of very small sample surfaces without chemical preparation. They studied Li in the Holbrook meteorite with this technique and found not only that the abundance of Li was extremely variable over the surface but also that the mass-peak heights of ^{7}Li/^{6}Li varied between 9.5 and 27.5. A sample of terrestrial hornblende analyzed by the same technique did not deviate by more than ± 8 per cent. Balsiger *et al.* (1968) conclude from their studies that no systematic difference can be found between meteorites and terrestrial Li, and that, if Li-isotope variation occurs at all, it must be of local and sporadic character.

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3-C. Abundance in Cosmos, Meteorites, Tektites and Lunar Materials

I. Cosmic Abundance

Published abundance curves of the elements (e.g. UREY, 1952) show that the abundance of Li (together with Be and B) is abnormally low for its atomic weight. BURBIDGE *et al.* (1957) explain their abnormal position by assigning a different type of synthesizing process.

Estimates by GOLDSCHMIDT (1937), UREY (1952), SUESS and UREY (1956) and ALLER (1961b) give an abundance of 100 Li atoms per 10^6 Si atoms.

The abundance of Li in the sun was given by ALLER (1961a) as $\log N = 0.54$, where N is the number of Li atoms per gram of solar material.

II. Meteorites

The data on Li in meteorites was summarized by HEIER and ADAMS (1964), and it was concluded that chondrites form a very homogeneous group with respect to Li content. STROCK (1936) indicated 3.5 ppm Li, HORSTMAN (1957) assumed 4 ppm Li, and PINSON *et al.* (1953) found a narrow spread between 1.7 and 3.8 ppm (arithmetic mean 2.7 ppm) Li in chondrites. PINSON (1954) indicated 0.5 ppm Li in the Mighei carbonaceous chondrite, and KRANKOWSKY and MÜLLER determined 1.3 ppm in Orgueil. Data on Li in chondrites not included in the review by HEIER and ADAMS (1964) is shown in Table 3-C-1, and it would appear that the average Li content is rather less than reported earlier (i.e. 2.7 ppm). It also appears that achondrites may have lower Li concentrations than chondrites (BALSIGER *et al.*, 1968). However, the concentration of Li in the same meteorite may be extremely variable. POSCHENRIEDER *et al.* (1965) studied the Holbrook meteorite with an ion-microprobe mass spectrometer. They found the Li concentration in general to be below

Table 3-C-1. *Lithium in chondrites and achondrites.*
(Not included in HEIER and ADAMS, 1964)

Class		ppm Li	Analytical method	Reference
CL	Holbrook	< 1	I	POSCHENRIEDER *et al.* (1965)
	Holbrook	2.0	I	BALSIGER *et al.* (1968)
	Bruderheim	1.7	I	SHIMA and HONDA (1963)
	Bruderheim	1.5	I	SHIMA and HONDA (1963)
	Bruderheim	1.1	I	KRANKOWSKY and MÜLLER (1964)
	Bruderheim	0.4	I	DEWS (1966)
	Bruderheim, chondrules	0.267	I	DEWS (1966)

Table 3-C-1 (continued)

Class		ppm Li	Analytical method	Reference
CL	Bruderheim, lath. chondr.	0.089	I	Dews (1966)
	Bjurböle, chondrules	0.134	I	Dews (1966)
	Bjurböle, chondrules	2.3 ± 0.2	I	Balsiger *et al.* (1968)
	Bjurböle	1.8	I	Krankowsky and Müller (1967)
	Bjurböle, matrix 2.0 μ	2.1	I	Balsiger *et al.* (1968)
	Bjurböle, matrix 2.2 μ	3.4	I	Balsiger *et al.* (1968)
	chondrules (s)	1.1	I	Krankowsky and Müller (1967)
	chondrules (m)	0.9	I	Krankowsky and Müller (1967)
	Chainpur, chondrules	1.8	I	Balsiger *et al.* (1968)
	Chainpur, total	1.5	I	Balsiger *et al.* (1968)
	Ehole	1.8	I	Krankowsky and Müller (1964)
	Ehole	1.8	I	Krankowsky and Müller (1964)
	Ehole	1.2	I	Shima and Honda (1963)
	Ehole	1.3	I	Shima and Honda (1963)
	Harleton	1.3	I	Shima and Honda (1963)
	Kunaschak	1.2	I	Krankowsky and Müller (1964)
	Ramsdorf	0.9	I	Krankowsky and Müller (1964)
	Tieschitz, chondrules	1.45	I	Balsiger *et al.* (1968)
	Tieschitz, total	3.1	I	Balsiger *et al.* (1968)
Ce	Abee	1.3	I	Krankowsky and Müller (1964)
Ab	Tatahouine	0.96	I	Krankowsky and Müller (1964)
		1.02	I	Krankowsky and Müller (1964)
		0.53	I	Krankowsky and Müller (1964)
		0.44	I	Krankowsky and Müller (1964)
		1.08	I	Krankowsky and Müller (1964)
Ae	Norton County, total	0.33	I	Balsiger *et al.* (1968)
	Norton County, coarse enstatite	0.23	I	Balsiger *et al.* (1968)
Cc	Essebi	1.6	I	Krankowsky and Müller (1967)
	Essebi, chondrules (1)	1.6	I	Krankowsky and Müller (1967)
	Essebi, chondrules (2)	2.9	I	Krankowsky and Müller (1967)

the detection limit (about 1 ppm); however, some spots were found where the concentration was as high as about 100 ppm Li. It is apparent that much more research is needed in order to estimate the exact Li content in meteorites.

Krankowsky and Müller (1967) found 40 ppb Li in troilite inclusions in the Odessa octahedrite. Li contents in silicates from this meteorite (1.3 and 1.9 ppm Li) are similar to the values measured for chondrites and chondrules.

III. Tektites

The data on Li in tektites was summarized by Heier and Adams (1964) and more recently by Ottemann (1966) who gave the averages: 82 ppm Li in bediasites; 14 ppm Li in moldavites; 42 ppm Li in australites; 40 ppm Li in Pacific tektites. The 82 ppm Li in bediasites must be a printing error in that Chao (1963) gave the average as 18 ppm (range 8–29 ppm). Taylor (1966) reported an average of 42 ppm Li in australites (range 36–52 ppm).

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IV. Lunar Materials

Data on Li in lunar fines and common lunar rock types are given in Table 3-C-2. The highest concentrations are found in Kreep-type rocks and the lowest in anorthosites. The concentration range observed in mare basalts is similar to that of terrestrial basalts.

Analytical techniques used for the determination of Li in lunar materials include emission spectroscopy, neutron activation and isotope dilution mass spectrometry.

The ^{7}Li/^{6} Li ratio of Lunar rocks and soils has been found to agree with the (average) terrestrial abundance within the limits of experimental uncertainties (Eugster, O., Bernas, R. K.: Proceedings of the Second Lunar Science Conference *2*, 1461, 1971. Wanless, R. K., Loveridge, W. D., Stevens, R. D.: Proceedings of the Apollo 11 Lunar Science Conference 2, 1729, 1970).

Table 3-C-2. *Lithium content of lunar rocks and fines* (in ppm)[a]

Rock type	$\bar{x}$	s	Range	n
Mare basalts				
Apollo 11 A	16.7	3.2	12–20	6
Apollo 11 B	12.2	2.9	9–15	6
Apollo 12	6.3	1.4	3.1–10	15
Apollo 15	6.0	0.8	4.6–7.7	16
Apollo 17	8.9	0.3	8.6–9.2	4
Kreep-*type rocks*				
Apollo 12, sample 12013	100			1
Apollo 14 breccias	32.5	7.7	24–46	7
Apollo 14 basalts	23.5		21–26	2
Apollo 15 Kreep	23.7		21–26.4	2
Apollo 16 Kreep	19.3		17–23	4
Apollo 17 noritic breccias	12.1		9.4–15	3

Table 3-C-2 (continued)

Rock type	$\bar{x}$	s	Range	n
Highland rocks				
Apollo 15 anorthositic rocks	10.9		1.8–16	3
Apollo 16 anorthositic rocks $>31\%$ Al_2O_3	1.6		1.3–1.7	4
Apollo 16 25–31% Al_2O_3	9.1	4.6	4.8–18	10
Apollo 16 21–24% Al_2O_3	10.7	1.7	9.4–14	5
Fines				
Apollo 11, sample 10084	11.0			1
Apollo 12	17.0		16–18	3
Apollo 12 high K	24		23–25	2
Apollo 14	29	6.0	22–41	10
Apollo 15	10.5	1.7	8.4–12.5	7
Apollo 16	7.3	1.2	4.5–9.7	27
Apollo 17	9.4	1.2	7.9–11.9	17
Luna 16	8.8	1.2	8.3–10	7
Luna 20	6.1			1

[a] $\bar{x}$ is derived by first averaging all reliable existing data on one sample; the different samples are then averaged (each sample average is given equal weight). Standard deviations (s) are calculated from (n) which is the number of samples for which data exist.

References from which concentration data are obtained:

THE LUNAR SAMPLE PRELIMINARY EXAMINATION TEAM: Preliminary examination of lunar samples from Apollo 11. Science **165**, 1211 (1969).

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WATKINS, C. (ed.): Lunar Science-III, Houston: Lunar Science Institute 1972.

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Lunar Science-V, Houston: Lunar Science Institute 1974.

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3-D. Abundance in Rock-Forming Minerals, Lithium-Minerals

Some of the Li-rich minerals that may occur in pegmatites are listed in section 3-F. The more important minerals which concentrate lithium are given in Table 3-D-1. In common rock-forming minerals, Li differs markedly from the other alkali metals in that it is concentrated in femic silicate minerals where it may replace Mg^{2+}.

Table 3-D-1. *Minerals containing lithium (most important minerals italiced)*

	Silicates
Tourmaline (elbaite) (sorosilicate)	$(Na, Ca)(Mg, Li, Al, Fe)_3(Al, Mg, Fe)_6$ $[(OH)_4 \mid (BO_3)_3 \mid Si_6O_{18}]$
Spodumene (inosilicate)	$LiAl[Si_2O_6]$
Neptunite (inosilicate?)	$LiKNa_2Fe_2Ti_2O_2[Si_8O_{22}]$
Holmquistite (inosilicate)	$Li_2(Mg,Fe)_3Al_2[(OH)_2 \mid Si_8O_{22}]$
Polylithionite (phyllosilicate, trioctahedral mica)	$KLi_2AlSi_4O_{10}F_2$
Li-mica (lepidolite, zinnwaldite)	(phyllosilicate, general formula) $(K, Na, Rb, Cs)(Li_k(Mg, Fe^{2+}, Mn)_n$ $(Al, Fe^{3+})_m[Si_pAl_{4-p}O_{10}](OH, F)_2$ $k = 1$—2; $n =$ up to 3; $m =$ up to 2; $p = 3$—4
Bityite (phyllosilicate)	$CaLiAl_2[Si_2AlBeO_{10}](OH)_2$
Cookeite (phyllosilicate)	$LiAl_4[(OH)_8 \mid AlSi_3O_{10}]$
Eukryptite (tektosilicate)	$Li[AlSiO_4]$
Petalite (tektosilicate)	$(Li,Na)[AlSi_4O_{10}]$
Bikitaite (tektosilicate)	$LiAl[Si_2O_6] \cdot H_2O$
	Phosphates
Amblygonite	$(Li, Na)Al[PO_4](F, OH)$
Lithiaphilite	$LiMn[PO_4]$
Lithiophosphatite	$Li_3[PO_4]$
Montebrasite	$(Li, Na)Al[PO_4](OH, F)$
Palermoite	$(Li, Na)_4SrAl_3[PO_4]_8(OH)_8$
Sicklerite (ferrisicklerite)	$(Li,Mn^{2+},Fe^{3+})[PO_4]$
Tavorite	$LiFe[PO_4](OH)$
Triphylite	$LiFe[PO_4]$

Table 3-D-1. (Continued)

	Halides
Cryolithionite	$Na_3Li_3Al_2F_{12}$
	Borates
Rhodozite	$KNaLi_4Al_4(Be_3B_{10}O_{27})$
	Sulphosalts
Gerstbyite	$(Na, Li)_4As_2Sb_8S_{17} \cdot 6H_2O$

The minerals orthopyroxene — clinopyroxene — amphibole — mica form a series in which there is a regular increase in Li concentration and of the Li/Mg ratio (Rankama and Sahama, 1950; Howie, 1955). There are two reasons for this: (a) the structure of the mica lattice is most favorable for the Li^+ ion, and (b) during replacement of Mg^{2+} by Li^+ the structure suffers a loss in energy and no considerable replacement can take place until at a relatively low temperature.

Li-micas have especially been studied by Ginzburg (1958a, b), Levinson (1953) and Heinrich and Levinson (1953). Foster (1960) reviewed all published analyses of Li-micas.

Li in quartz ranges from 0.5 to 216 ppm (Maxwell, 1953; Siroonian *et al.*, 1959; Stavrov and Znamenskii, 1961; Dennen, 1966, 1967).

The amount of Li which may be admitted into the feldspar structure is restricted. Ahrens and Liebenberg (1945) found that a content higher than 5 ppm Li in a feldspar is exceptional. Heier and Taylor (1959) found that the potassium feldspars from large pegmatites had low or undetectable Li contents. The feldspars from granites and gneisses were generally higher in Li, but only rarely above 5 ppm. Heier (1960) found a maximum of 29 ppm Li in mesoperthites, and potassium feldspars in granulite and the higher part of amphibolite facies frequently contain above 5 ppm Li and may be as high as 12 ppm. A similar range is found in plagioclase feldspars.

Table 3-D-2. *Li distribution in minerals and rocks of the Bugul'min complex (analyses by flame photometry).* (From Vorontsov and Lin, 1966)

Mineral	ppm Li in mineral	% of Li in rock accounted for by given mineral	ppm Li in total rock
Syenodiorite of the apical facies of the Sapkol' massif			
Plagioclase	31	74	
Potassium feldspar	17	22	
Quartz	n.d.	—	
Diopside-hedenbergite	71	8	
Hornblende	43	7	
Total		111	23

Table 3-D-2. (Continued)

Mineral	ppm Li in mineral	% of Li in rock accounted for by given mineral	ppm Li in total rock
Granodiorites of the abyssal facies of the Sapkol' massif			
Plagioclase	7	60	
Potassium feldspar	trace	—	
Quartz	trace	—	
Diopside-hedenbergite	n.d.	—	
Hornblende	33	38	
Total		98	6
Syenodiorite of the upper parts of the apical facies of the Dzhugoyak massif			
Plagioclase	10	31	
Potassium feldspar	12	26	
Quartz	n.d.	—	
Diopside-hedenbergite	37	14	
Hornblende	36	26	
Total		97	14
Syenodiorite of the apical facies of the Dzhugoyak massif			
Plagioclase	7	36	
Potassium feldspar	6	14	
Quartz	n.d.	—	
Diopside-hedenbergite	48	17	
Hornblende	16	12	
Total		89	10
Granodiorite of the apical facies of the Dzhugoyak massif			
Plagioclase	7	50	
Potassium feldspar	trace	—	
Quartz	10	26	
Diopside-hedenbergite	n.d.	—	
Hornblende	20	19	
Total		95	7
Syenodiorite of the Khoroyak massif			
Plagioclase	10	22	
Potassium feldspar	10	13	
Quartz	n.d.	—	
Hornblende	49	17	
Biotite	277	44	
Total		96	23

Table 3-D-2. (Continued)

Mineral	ppm Li in mineral	% of Li in rock accounted for by given mineral	ppm Li in total rock
Quartz diorite of the Michurinsk massif			
Plagioclase	6	13	
Potassium feldspar	10	6	
Quartz	n.d.	—	
Diopside-hedenbergite	21	6	
Hornblende	24	15	
Biotite	198	57	
Total		97	23
Quartz syenite of the abyssal facies of the Bugul'min massif			
Plagioclase	5	11	
Potassium feldspar	5	3	
Quartz	—	—	
Hornblende	—	—	
Biotite	772	100	
Total		114	35
Granite of the apical facies			
Plagioclase	—	—	
Potassium feldspar	13	17	
Quartz	19	13	
Biotite	1,960	66	
Total		96	47

Vorontsov and Lin (1966) studied the distribution of Li (with K and Rb) in the granitoids of the Bugul'min complex (Eastern Sayans) by flame photometry. They gave concentrations in the total rocks and the constituent minerals. The relevant data is presented in Table 3-D-2 and may serve as an illustration of Li concentrations in common rock-forming minerals (see also Kuts and Mishchenko, 1963, for a similar study of Li in plagioclase, microcline, quartz, biotite and muscovite).

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3-E. Abundance in Common Igneous Rock Types and Terrestrial Abundance

I. Ultramafic Rocks

Strock (1936) gave 2 ppm as the average Li content of ultramafic rocks. Horstman (1957, Table 3) lists 26 ppm Li as the average of 2 ultramafic rocks, but this is certainly too high for ultramafic rocks in general. The listed average is that of one amphibolite (38 ppm) and one picritic basalt (14 ppm), and Li appears not to have been detected (or determined) in one limburgitic basalt and two serpentinized peridotites included in the appendix table of his paper. Pinson *et al.* (1953) found less than 0.3 ppm Li in serpentinites, dunites and websterite and Howie (1955) reported 10 and 20 ppm Li in two pyroxenites from the Madras charnockite series of India. Liebenberg (1960, 1961) gives n.d. — 10 ppm Li in pyroxenite; n.d. — 2 ppm in dunite; 0.2—1.4 ppm in harzburgite; and 3—4 ppm Li in anorthosite from the Bushveld igneous complex. Turekian and Wedepohl (1961) estimated 0.X ppm Li in the "average" ultramafic rock, and Vinogradov (1962) indicated 0.5 ppm Li in this material. Basutoland kimberlites analyzed by Dawson (1962) range between less than 4 to 50 ppm Li. Beus (1964) gave 2 ± 1.5 ppm Li in olivine and olivine-pyroxene ultramafic rocks, *vs.* 15 ± 5 ppm Li in pyroxene-amphibole ultramafic rocks.

II. Volcanic and Plutonic Rocks

The small size of the Li^+ ion allows it to replace Mg^{2+} (and Fe^{2+}) in minerals. The geochemistry of Li therefore differs markedly from that of the other alkali metals in that it is contained in the femic silicate minerals. The regular change in Li content and the increase in the Li/Mg ratio occurring with differentiation has been well established. The extensive studies by Nockolds and Allen (1953, 1954, 1956) show the increase in the Li/Mg ratio with differentiation to be a common feature in all magmatic rock series studied. The absolute amount of Li may, however, decrease in the most differentiated rocks, reflecting the decreasing concentration of the Mg host-minerals. Ewart and Taylor (1969) studied trace element abundances in plagioclase phenocrysts from acidic and intermediate volcanic rocks of the Taupo Volcanic zone, New Zealand. Lithium was detected in all plagioclases, but these are depleted relative to groundmass compositions. The Li contents range from 20 to 36 ppm in the rhyolitic plagioclases to 7 ppm in the basaltic plagioclase.

Rocks that are particularly enriched in Li are granitic rocks associated with tin and tungsten mineralization, e.g. some of the Cornish (Bowler, 1958, 1959), German (Strock, 1936; Moenke, 1960) and Russian (Slepnev, 1958) rocks.

Table 3-E-1. *Estimation of the distribution of Li in igneous rocks (nos. in brackets indicate number of samples)*. (From Beus, 1964)

Rock type	ppm Li
Ultramafic rocks, olivine and olivine-pyroxene (6)	2 ± 1.5
Ultramafic rocks, pyroxene-amphibole (15)	15 ± 5
Gabbro (28)	18 ± 5
Mafic intrusives (27)	16 ± 4
Basalts (93)	14 ± 1
Diorites (30)	27 ± 3
Intermediate intrusive rocks (45)	28 ± 3
Andesites (59)	18 ± 3
Granodiorites (35)	38 ± 8
Granites (115)	38 ± 4
Felsic intrusive rocks (150)	38 ± 4
Felsic extrusive rocks (17)	51 ± 12

Table 3-E-2. *Lithium concentrations in volcanic rocks*

Rock type	ppm Li	References
Basaltic rocks	17	Turekian and Wedepohl (1961)
Basaltic rocks	7	Heier and Adams (1964)
Basalt average	10	Taylor (1964)
Oceanic tholeiitic basalts	9 ± 6	Engel *et al.* (1965)
Alkali basalts from seamounts and islands	11 ± 5	Engel *et al.* (1965)
Submarine basalts (8)	15 (3—50)	Gladkikh and Chernysheva (1966)
Olivine basalt, Tahiti (5)	9.6 (5—20)	Gladkikh and Chernysheva (1966)
Basalts, Hawaii (4)	5.5 (4—7)	Gladkikh and Chernysheva (1966)
Basalts, Fiji (2)	10	Gladkikh and Chernysheva (1966)
Basalts, Mont Dore (France) (14)	13 ± 7	Letolle (1965)
Andesites	12	Heier and Adams (1964)
Basic andesites, New Zealand	10 (6.8—14)	Taylor and White (1966)
Andesites, New Zealand	11	Taylor and White (1966)
Andesites, Izu Peninsula (Japan)	6 (4—7)	Taylor and White (1966)
Andesites, Asama (Japan)	12	Taylor and White (1966)
Andesites, New Zealand (6)	22.2 (13—41)	Ewart *et al.* (1968)
Andesites, Mont Dore (France) (16)	25 ± 18	Letolle (1965)
Trachyte	10	Engel *et al.* (1965)
Trachyte (average)	27	LeMaitre (1962)
Trachyte	30	Heier and Adams (1964)
Trachytes, Mont Dore (France) (17)	87 ± 76	Letolle (1965)
Phonolites, Mont Dore (France) (11)	70 ± 30	Letolle (1965)
Rhyolite	50	Heier and Adams (1964)
Rhyolite, Mont Dore (France) (6)	49 ± 15	Letolle (1965)
Rhyolitic ignimbrites, New Zealand (13)	36 (9—100)	Ewart *et al.* (1968)

Average Li concentrations in some major igneous rocks were given by Beus (1964) and reproduced here in Table 3-E-1. Some additional data on Li in volcanic rock types are given in Table 3-E-2. Estimates of average Li concentrations in major plutonic igneous rocks are recorded in Table 3-E-3 which also gives references to more recent papers on Li in granites.

Table 3-E-3. *Concentration of Li in plutonic igneous rocks*

Rock Type	ppm Li	References
Ultramafic rocks	0.X	Turekian and Wedepohl (1961)
Gabbros	10	Heier and Adams (1964)
Diorites	20	Heier and Adams (1964)
Granodiorites	20	Heier and Adams (1964)
High calcium granites	24	Turekian and Wedepohl (1961)
Granites	30	Heier and Adams (1964)
Low calcium granites	40	Turekian and Wedepohl (1961)
Granitic rocks	40	Vinogradov (1962)
Syenites	10	Heier and Adams (1964)
Syenites	28	Turekian and Wedepohl (1961)
Nepheline Syenites	20	Heier and Adams (1964)
Nepheline Syenites, Lovozero Massif	37	Gerasimovskii (1966)
Miascitic Nepheline Syenites	23	Gerasimovskii (1966)

Additional references to recent papers giving data on Li in granites include: Stavrov and Znamenskii (1961), Moenke (1962), Kuts and Mishchenko (1963), Ratiyev (1964), Ivanov (1965), Bowden (1966), Vorontsev and Lin (1966), Kolbe and Taylor (1966).

III. Concentration and Distribution in the Earth

Heier and Adams (1964) used the chondritic model to estimate the distribution of Li in the earth. Based on the average chondrite concentration of 3 ppm Li and reasonable estimates of the Li contents in the continental and oceanic crust, they were forced to consider that the overall Li content of the mantle amounted to 4.2 ppm (Table 3-E-4). This is at least one order of magnitude above the Li content of ultramafic rocks. More recent estimates would put the Li concentration in chondrites closer to 1 ppm. However, the Li content of the continental crust is also almost certainly lower than estimated by Heier and Adams (1964). Taylor (1964) estimated 10 and 20 ppm Li in an oceanic and a continental crust respectively, and his later andesitic model for the overall composition of the continental crust would indicate about 10 ppm Li in this material. In column 4, Table 3-E-4, it is assumed an oceanic crust with 10 ppm Li, an upper continental crust of overall granodioritic composition with about 20 ppm Li, and lower continental crust of medium to high pressure granulite facies affinities containing about 10 ppm Li (Heier, 1960). A chondritic earth composition with 1 ppm Li would still have 1.4 ppm Li in the mantle, which appears high compared with ultramafic rocks.

Table 3-E-4. *Distribution of Li in the earth*

	Approximate Mass fraction in per cent	(1) ppm Li	(2) ppm Li
Core	31.5		
Mantle	68.1	4.2	1.4
lower mantle	57.0		
upper mantle	11.0		
Crust	0.4	25	12
Oceanic crust	0.1	7	10
Continental crust	0.3	32	13
upper ($^1/_3$) continental crust	0.1		20
lower ($^2/_3$) continental crust	0.2		10
Earth	100	3	1
% of Li in continental crust		3	4

(1) HEIER and ADAMS (1963). (2) This paper (see explanation in text).

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3-F. Behavior in Magmatogenic Processes

Lithium is enriched in greisens.

Lithium may be so strongly enriched in some granite and nepheline syenite pegmatites that it forms independent minerals. Lithium is concentrated in these pegmatites with such elements as fluorine, chlorine, phosphorus and manganese. The minerals formed include cryolithionite, $Na_3Li_3Al_2F_{12}$; triphylite, $LiFe(PO_4)$; lithiophilite, $LiMn(PO_4)$; amblygonite, $(Li,Na)Al(PO_4)(F,OH)$; petalite $(Li,Na)(AlSi_4O_{10})$; spodumene, $LiAl(Si_2O_6)$; the lithium micas lepidolite, zinnwaldite, and cookeite; lithium tourmaline, the lithium amphibole holmquistite. The pegmatite minerals amblygonite (8—10% Li_2O), spodumene (4, 5—7.5% Li_2O) and lepidolite (3—10% Li_2O) can be industrial sources of Li.

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3-G. Behavior during Weathering and Abundance in Soils

The Li content of soils is a function of detrital mineralogy, newly formed minerals, organic material, and soil solution composition. The relative amounts of these phases and their specific composition is a function of degree of weathering, time, rainfall, temperature, topography, runoff, and other factors. In this complex dynamic system it is impossible to predict the amount and mobility of Li other than in a general way.

The amount of Li contained in detrital minerals of the soil depends on the parent rock mineralogy (Table 3-G-1).

Table 3-G-1. *Total Li content in Scottish soils derived from different rock types (in ppm).* (From Mitchell, 1964)

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

Lithium content of a peaty gleyed podzol, on granitic till (in ppm). (From Mitchell, 1964)

Depth (in.)	7—9	10—14	17—21	21	21—25	31—36	40—46
Li	20	80	80	150	200	200	200

During weathering, Li is released from the primary minerals to the soil solution as Li^+. It is then removed with the soil solution or incorporated in precipitation clay minerals. For example, in seven soil profiles over arkose, studied by McLaughlin (1955), Li content increased with depth in four profiles and decreased in three profiles. In all cases, both silt and clay fractions contained larger amounts of Li than the parent material. Butler (1953 and 1954) found the same concentration effects featured by silt and clay in soils developing from igneous rocks, with the unexplained exception of an adamellite. Harriss and Adams (1966) attempted to calculate relative mobilities in weathering profiles from granites using Li-soil/Li-parent rock as an index. They concluded that the Li distribution was highly irregular. In podzolic soils and grey forest soils (Table 3-G-1), Li contents tend to increase with depth (Vinogradov, 1959; Mitchell, 1964). In chernozem soils, the reverse trend seems true (Vinogradov, 1959). Lateritic soils are generally lower in Li content which probably reflects both the mafic igneous parent rock and the increase in soil solution leaching and removal typical of areas containing laterites.

The relocation of the Li^+ ion and the effect of soil drainage can be seen in the study of Scottish soils by Mitchell (1964). Mitchell investigated four soils consisting of 75—90% sand, 10—15% silt and 5—10% clay. In freely drained soils, the sand fraction contained most of the Li, but its contribution in poorly drained soils was as low as 20% of the total Li. Lithium was concentrated 5 to 10 times in clays compared to the sand fraction in poorly drained soils but no concentration occurred in clays of freely drained soils.

Data for Li content of soils used in this paper are from Horstman (1957), Vinogradov (1959), Mitchell (1964) and Burridge and Ahn (1965). The mean of 117 samples (this chapter) is 26 ± 2.2 ppm ($s/\sqrt{n}$). The median is 20 ppm. Population statistics for Li in the sedimentary cycle is summarized in Table 3-K-1.

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3-H. Adsorption Processes Controlling Concentrations in Natural Waters

Experimental evidence indicates that the relative bonding force holding monovalent cations is often, but not always, $Cs^+ > Rb^+ > K^+ > Na^+ > Li^+$ (Schainberg and Kemper, 1967; Krishnamoorthy and Overstreet, 1950). This inverse relationship between ionic hydrated radius (Li: 3.4 Å; Na: 2.76 Å; K: 2.32 Å; Rb, Cs: 2.28 Å; Cotton and Wilkinson, 1966) and exchange capacity is clearly shown by Fig. 3-H-1 (Nachod and Wood, 1945). Boyd *et al.* (1947) determined the free energy changes involved in exchange on a sulfonic acid resin. In cal/mole at 25° C, they found Li^+ (+60), Na^+ (−320), K^+ (−530), Rb^+ (−615) and Cs^+ (−860) in good agreement with the exchange order presented above.

In competition for lattice sites in soil minerals, small amounts of Li seem to have a high bonding energy which has been interpreted as Li substituting in the octahedral position at the edges of the mineral plates (McDowell and Marshall, 1962).

The possibility of Li existing as exchangeable ions on organic matter cannot be ignored (Toth, 1964; Swain, 1963) as such material has a high exchange capacity (240—450 meq/100 g). The replaceability from humic acid systems is, however, similar to that of clays (Li > Na > K).

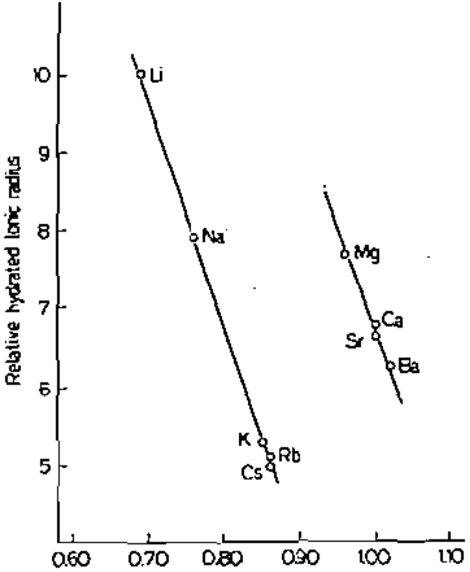

Fig. 3-H-1. Relationship between ionic hydrated radius and exchange capacity for the alkali and alkaline earth ions

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3-I. Abundance in Natural Waters

I. Continental Waters

Population statistics for Li in waters is summarized in Table 3-I-1.

Table 3-I-1. *Population statistics for Li in waters*

	Subdivision						
	$\overline{X}$	s	$s/\sqrt{n}$	n	median	range	concentration
Rivers	23	82	11	56	1	0.1—400	ppb
Sea water	0.190	—	—	—	—	—	ppm
Formation waters (brines)	26	26	2.3	134	19	0.04—100	ppm
Hydrothermal waters	8.2	5.7	0.4	258	8.5	0.01—27	ppm

The concentration of Li^+ in water is primarily controlled by incorporation in clay minerals of soils and sediments and perhaps by biological activity. The latter has been poorly studied.

Feth *et al.* (1964) reported an attempt to determine the Li content of snow in the western United States. They analyzed seven samples but were unable to detect Li above 0.0 ppm.

The variation in chemical composition of river water is exceedingly high. The variation is both geographic and temporal. The temporal variation is primarily the result of fluctuation in the relative amounts of surface runoff and ground water discharge into the rivers. The concentration of dissolved material in rivers usually varies inversely with discharge (Livingstone, 1963). The spatial variation in composition of river water is greatest in upstream areas where the effect of rock and soil types is greatest. As water proceeds downstream, there is a tendency for integration from different tributaries resulting in a more uniform composition.

Galle and Angino (1968) reported a range of Li values, in rivers of the Kansas River Basin, of 0.0 ppm to 0.04 ppm. Durum and Haffty (1963) suggest a median of 1.1 ppb Li for North American rivers. The range of Li concentrations in large North American rivers investigated by Durum and Haffty (1963) was 0.075 to 37 ppb.

Livingstone (1963) found Na/Li ratio in rivers of about 1,500. This ratio is higher than the continental crust ratio of 1,180 (Taylor, 1964), suggesting preferential removal of Li from the water system during weathering and transportation, relative to Na (see discussion of ground water).

The mean Li content of 56 river samples tabulated in the present study is 23 ± 11 ($s/\sqrt{n}$) ppb (data from Durum *et al.*, 1960, and Livingstone, 1963). This is considerably higher than the median of 1 ppb.

Data concerning the Li content of lakes is extremely scarce. Livingstone (1963) presents two older analyses of Lake Tanganyika waters with values of 400 to 800 ppb. These values appear suspiciously high. Cowgill and Hutchinson (1963) report a value of 70 ppb in a Guatemalan Lake. Billings (unpublished data) analyzed twenty-four samples of a small lake in Saskatchewan, Canada. He found a mean of 89 ppb with a range of 85—95 ppb Li. The Li content of lakes appears to be higher than that of rivers.

In lakes participating in the evaporative process, Li appears to concentrate even more than in normal lakes. Livingstone (1963) reports values for what appear to be evaporative lakes of 1,200—8,500 ppb Li. Ratner and Ludmer (1964) report 17,600 ppb Li in the Dead Sea. The Searles Lake deposits of Southern California form an economic source of Li.

Approximately 75% of the 400 California ground water samples analyzed by Bradford (1963) contained less than 50 ppm Li. Billings (unpublished data) found a range of Li values in ground water from Saskatchewan of 15—74 ppb. The mean value of 12 samples was 48 ppb.

II. Sea Water

Chow and Goldberg (1962) determined Li in Pacific Ocean waters by mass spectrometry and reported an average value of 0.170 ppm. Riley and Fongudai (1964) analyzed thirty samples from all the oceans and reported a Li content of 0.183 ppm normalized to a chlorinity of 19.374 ‰. The mg Li/kg per Cl ‰ ratio was $9.39 \pm 0.17 \times 10^{-6}$. Chow and Goldberg (1962) reported a Li/Cl ratio of 8.94 ± 0.12. Angino and Billings (1966) reported an average Li content of 0.194 ppm in 73 samples of Gulf of Mexico and North Atlantic water. Their average Li/Cl ratio was 9.76 and ranged from 8.65 to 10.72 which was a much larger range than previously reported. Their average ratio yields 0.185 ppm in sea water of 19‰ chlorinity. Fabricand *et al.* (1966) reported Li data from one vertical profile in the Atlantic and found an average Li content of 0.169 for water of 35‰ salinity.

Billings *et al.* (unpublished data) have investigated variations in the Li/Cl ratio of Sargasso Sea Water with depth and time. The analytical data of 428 samples show a mean of 0.194 ppm ± 0.008 Li and a mean Li/Cl ratio of 9.73 ± 0.36.

The residence time for Li ranges from 10 to 19 million years depending on the estimate for rate of supply used (Goldberg, 1965). This residence time is long relative to the other alkali elements, except Na, thus illustrating the lower reactivity of Li with the sediments.

III. Subsurface Formation Waters

Billings *et al.* (1969) and Billings (unpublished data) determined the Li content in 134 samples of subsurface brines from the Western Canada basin. The average Li content of the Canadian samples plus twelve oilfield brine analyses from White *et al.* (1963) is 26 ± 2.3 ($s/\sqrt{n}$) ppm. However, the Canadian samples are biased toward extra sampling of high-salt brines. If one recalculates the analyses to weight the relative amounts of various water types (e.g. brines vs. fresher water) in the western Canada basin, one arrives at an average Li concentration of 10.7 ppm. This represents the average for all subsurface water, not just brines, in this particular basin.

The median Li content of the 146 samples was 19.0 ppm. The range in Li content was 0.04 ppm (essentially a potable ground water) to 100 ppm (a brine of 19.3% solids content).

IV. Hydrothermal Waters

The geochemistry of hydrothermal waters has been summarized by ELLIS and MAHON (1964) who suggest that volcanic thermal water compositions can be approached by the hot-water-rock reactions and do not require the presence of "magmatic" water. ELLIS and MAHON (1964) experimented with hot-water-rock reactions up to 350° C for periods up to 300 hours. They found the maximum Li amounts were generally a direct function of temperature.

The mean Li content of 258 samples of hydrothermal waters is 8.2 ± 0.4 $(s/\sqrt{n})$ ppm and the median is 8.5 ppm. The range is 0.01 ppm to 27 ppm. (Data used for these statistics are from ELLIS and MAHON, 1964; ELLIS and WILSON, 1960; GOLDING and SPEER, 1961; and WHITE *et al.*, 1963.)

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3-K. Abundance in Common Sediments and Sedimentary Rock Types

Population statistics for Li in the sedimentary rocks is summarized in Table 3-K-1.

Table 3-K-1. *Population statistics for Li in sedimentary rocks and soils*

	Subdivision						
	$\bar{X}$	s	$s/\sqrt{n}$	n	median	range	concentration
Soils	26	23	2.2	117	20	—	ppm
Dolomites	15.2	20	1.2	292	7.9	—	ppm
Argillaceous sediments	66	24	2.3	105	66	17—207	ppm
Marine shales	76	54	3.7	204	61	4—400	ppm
Fresh-water shales	67	39	5.5	51	68	20—155	ppm
Sandstones	38	25	4	39	31	7—93	ppm

I. Limestones

The clay minerals and detrital silicates should contain most of the lithium in carbonate rocks since substitution for Ca or Mg alkalis is difficult in the carbonate minerals.

Billings and Ragland (1968) analyzed 16 samples of modern reef carbonates containing essentially no quartz or clay. The average Li content was 3.9 ppm. Lithium should be removed from the carbonate lattice during lithification and diagenesis.

Ohrdorf (1966, 1968) obtained an average of 7.5 ppm for 10 limestones. Turekian and Wedepohl (1961) propose an average for carbonate rocks of 5.0 ppm. Many of the earlier estimates of the Li content of limestones are based on Strock (1936). Ohrdorf (1966) reanalyzed some of the original samples and concluded that Strock's values were high by a factor of about 4. Graf (1960) reported an average of 37 ppm Li in 183 samples of Scottish sedimentary carbonate rocks. Lithium ranged from 1—1,000 ppm.

II. Dolomites

That the Li content of carbonates is primarily a function of the insoluble residue content is demonstrated by the data of Weber (1964), the mean value of 15.2 ± 1.2 ($s/\sqrt{n}$) ppm in the 292 dolomite rocks being higher than the mean value 3.4 ± 0.2 ppm ($s/\sqrt{n}$) of the 174 separated dolomite minerals. The median Li content of dolomite rocks is 7.9 ppm.

III. Argillaceous Sediments

Hirst (1962) found Li concentrated in the muds relative to the sands of the Gulf of Paria. The Li/Al ratio did not vary with sedimentation rate suggesting that Li was incorporated in the clays during weathering and transportation before entering the depositional basin.

The mean Li content of 105 marine argillaceous sediments is 66 ± 2.3 ppm $(s/\sqrt{n})$ (Welby, 1958; Hirst, 1962). The range is 17—207 ppm and the median 66 ppm.

Nicholls and Loring (1962) reported that much of the Li in the shales they investigated is incorporated in illite and apparantly was present in the mineral before deposition.

Keith and Degens (1959) reported that Li (and B) in shales seemed to be suitable indicators of marine vs. fresh-water depositional environment. They found the average Li content of marine shales to be 159 ppm ($s = 26$) and that of fresh-water shales to be 92 ppm ($s = 24$). Each group consisted of fifteen Pennsylvanian-age shales. They reported the same relative results from modern fresh-water and marine muds of Hawaii. Ohrdorf (1966, 1968) investigated 25 samples of Carboniferous shales from Germany. She found the average of marine shales to be 117 ± 15 (s) ppm Li and that of fresh-water shales to be 72 ± 20 (s) ppm Li. It appears that Li may be a useful indicator of depositional environment if restricted to single formations or basins. The absolute amounts quoted above cannot be transferred to other sampling areas as is evidenced by the low average Li content in marine shales from many areas (76 ppm).

The average Li content of 204 shales is 76 ± 3.7 $(s/\sqrt{n})$ ppm with a range of 4—400 ppm. The median Li content is 61 ppm. Data used in the compilation are from Shaw (1954), Horstman (1957), Keith and Degens (1959), Nicholls and Loring (1962), Ohrdorf (1966), Spencer (1966) and Leask (1967).

Lithium contents of fresh-water sediments are given by Gorham and Swaine (1965), Keith and Degens (1959), and Ohrdorf (1966). The mean of 51 samples is 67 ± 5.5 $(s/\sqrt{n})$ ppm Li, the median is 68 ppm and the range is 20—155 ppm. The means of fresh-water argillaceous sediments and rocks are indistinguishable from those of marine argillaceous sediments and rocks.

IV. Sandstones and Other Siliceous Sedimentary Rocks

Dennen (1966) reported the common occurrence of Li in natural quartz. Values reported for Li in quartz range from 0.5 ppm to 216 ppm (Maxwell, 1953; Siroonian *et al.*, 1959; Stavrov and Znamenskii, 1961). Knowledge of the Li content in quartz of sandstones might be useful in studies of provenance and transpotration.

Ohrdorf (1966) reported some anomalously high Li contents for sandstones of a certain Permian bed (885—1,190 ppm). Chemical fractionation of these unusual samples into separate minerals indicated up to 600 ppm Li in the quartz.

The mean Li content of 39 sandstones is 38 ± 4 $(s/\sqrt{n})$ ppm the median is 31 ppm and the range is 7—93 ppm (Horstman, 1957; Hirst, 1962; Ohrdorf, 1966).

Maxwell (1963) discussed the geochemistry of chert and related nondetrital, siliceous sedimentary rocks. The average Li content of 24 samples analyzed by Maxwell was 11 ppm. The Li content ranged from 2 to 36 ppm.

V. Evaporites

Fulda (1939) found that Li was concentrated in the inclusions of residual fluid in potash zones. The maximum Li content of the brine was 19 ppm*. Maxwell (1963) reported that Li occurred in the insoluble residue of salt deposits in amounts up to 93 ppm while the potash contained no detectable Li. Billings (unpublished data) analyzed several sylvite samples from Saskatchewan potash deposits and found no Li above the detection limit of one ppm. Zharebtsova and Volkova (1966) reported that Li did not precipitate with salt minerals. Steward (1963) stated that Li in evaporites is present in the associated clays and clastic materials.

VI. Pelagic Sediments

Pelagic sediments can be assigned to three main types: calcareous oozes, siliceous oozes, and clays.

Ohrdorf (1963) determined the Li content of 11 deep sea clays (Atlantic) which range from 58 ppm to 113 ppm Li with an average content of 91 ppm. She reported a slight increase in Li content with depth in cores of deep sea clays. Other than clay minerals, a potentially large Li contributer which has not been investigated quantitatively is the authigenic zeolite, phillipsite. Goldberg and Arrhenius (1958) analyzed five Pacific pelagic clays and found a range of 49—70 ppm Li with an average of 59 ppm.

Differences between the chemical composition of Pacific and Atlantic pelagic sediments have been pointed out by Goldberg and Arrhenius (1958) for several elements. Comparison of Ohrdorf's data with those of Goldberg and Arrhenius suggests that the Li content of pelagic clays may be higher in the Atlantic than in the Pacific.

No data seem to be available for the Li content of siliceous pelagic sediments such as diatomaceous oozes.

Except for single analyses on composite samples, the only Li analyses available for calcareous globigerina oozes are from Welby (1958). He analyzed nineteen samples which had a range of 21—120 ppm Li with an average of 59 ppm. Horstman (1957) reported a value of 29 ppm Li for a composite of 6 globigerina oozes.

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* Editorial addition in proof: The Li concentration of 22 typical brines with different chemical composition from German Zechstein salt deposits ranges from 1.2 ppm to 270 ppm Li (A. G. Herrmann: Kali und Steinsalz 3, 209—220, 1961).

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3-L. Biogeochemistry

Hutchinson (1943) demonstrated the positive correlation between solubility and biosphere concentration of the elements. When the ionic potential is greater than about twelve or less than about three, the element is relatively soluble and thus relatively available and concentrated in biological material.

Lithium is not known to be metabolically necessary for life (Bowen, 1966) and rarely appears toxic. It apparently is capable of substituting for K^+ or Na^+ in metabolic activities.

Black and Mitchell (1952) suggested an average of 5 ppm (of dry weight) in marine plants. Bowen (1966) suggests an average of 0.1 ppm in land plants, 1 ppm in marine animals, and 0.02 ppm in land animals.

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3-M-N. Abundance in Common Metamorphic Rocks and Behavior in Metamorphic Processes

Lithium concentrations in granites, gneisses and metamorphosed igneous rocks are similar to those of unaltered igneous rocks (Lundegardh, 1947; Howie, 1955, 1958; Heier, 1960).

In a study of the geochemistry of pelitic rocks, Shaw (1954, 1956) found no co-variation with Li and the major elements, nor with Li content and metamorphic grade.

Landergren (1948) found that most Precambrian iron ores and associated rocks in Sweden show a marked deficiency in Li. It would have been reasonable to assume that Li was enriched in these ores which are high in both Mg and Fe. Landergren concluded that the iron ores of central Sweden cannot be of igneous origin.

Evans (1964) studied the changes in minor elements suffered by pelitic hornfelses at Cashel, Connemara, Eire as the result of intrusion of ultramafic or mafic magma. He found that Li, together with the trace elements Ba, Rb, La, and Cs, was lost from the hornfelses together with the major constituents Si, Al, K, Na, and H_2O. In the envelope pelites Li content averages 45 ppm, which is lower than nearly all the analyzed, unhornfelsed pelites. Li is further reduced in the xenoliths and is barely detectable (1 ppm) in the most altered rocks.

Bowler (1959), quoted by Heier and Adams (1964), studied the alkali metals in granite and surrounding sediments, including the contact metamorphic aureole and xenoliths, from south-west England. All the aureoles showed culmination of the trace alkali metals towards the granite contact, rising far above the alkali levels in shales which were not thermally metamorphosed. The data for Li is given in Table 3-M-1.

Table 3-M-1. *Lithium in rocks surrounding intrusive granite in South-west England*

	ppm Li
Xenolith from the Land's End granite	1,650
Schist 10 cm from the contact with the Land's End granite	710
Maximum values for shales are likely to be	250

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3-O. Geochemical Behavior

In atomic abundance Li is the third most abundant of the alkali elements, after Na and K, and it is approximately as abundant as Rb in weight. Some limited substitution by Li for Na may take place in minerals but in general Li substitutes for Mg (and Fe^{2}P) in minerals, and it is distinct from other alkali elements in a geochemical sense. Like the other alkali elements, Li is "oxyphilie", but its upward concentration in the earth is not as pronounced. For the alkali elements, the clarke of concentration in the upper continental crust increases with atomic number.

Lithium is fairly easily determined by optical spectrography in low concentrations and most of the determinations in geological materials have been by this method, and by atomic absorption in waters and sediments.

The geochemistry of Li has been discussed by GOLDSCHMIDT *et al.* (1933, 1934); GOLDSCHMIDT (1954); STROCK (1936); RANKAMA and SAHAMA (1950); HORSTMAN (1957); GINZBURG (1958a) and HEIER and ADAMS (1964).

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