

Introduction

Lithium is the lightest of the alkali metals belonging to group 1 of the periodic table, along with Na, K, Rb and Cs. The element has an atomic number of 3, an atomic mass of 7, one oxidation state (+1) and two naturally occurring isotopes (^6Li and ^7Li), of which ^7Li is the most abundant at 92.5% of the mass.

Lithium is a lithophile metallic element, occurring predominantly in silicate minerals, and is widely present as an accessory element in K-feldspar, biotite mica, amphibole and clay minerals, such as illite, where it can substitute for K, Na and Mg. It also forms several rather rare minerals occurring mostly in pegmatite, including spodumene $\text{LiAlSi}_2\text{O}_6$ and lepidolite $\text{K}_2\text{Li}_3\text{Al}_4\text{Si}_7\text{O}_{21}$.

During magmatic processes Li^+ can replace Mg^{2+} and Fe^{2+} in pyroxene, tourmaline and amphibole (Ure and Berrow 1982). It may also replace Mg and Al in mica, such as lepidolite and chlorite, but its low charge and small ionic radius (82 pm) limits its ability to compete for lattice sites until the later stages of fractionation. The Li:Mg ratio can, therefore, provide a reliable indicator of magmatic evolution (Nockolds and Allen 1956).

Lithium values in ultramafic rocks are variable; some reports quote values of $<1 \text{ mg kg}^{-1}$ whilst others suggest a value closer to 15 mg kg^{-1} Li. Values for mafic rocks (*e.g.*, basalt) are more consistent and range from 5.5 to 17 mg kg^{-1} . Higher Li contents are observed in more felsic rock types, such as granite, rhyolite and phonolite, where values range from 30 to 70 mg kg^{-1} ; this increase in Li concentration has been associated with both tin and tungsten mineralisation, particularly in Germany and Russia. Lithium concentrations in carbonate rocks are usually low ($\sim 5 \text{ mg kg}^{-1}$), this being attributed to the loss of Li during lithification and diagenesis. Dolomite contains slightly more Li with a reported average of $\sim 8 \text{ mg kg}^{-1}$. Whilst sandstone has a wide range of values for Li content, ranging from 0.5 to 216 mg kg^{-1} , with an average abundance of 1.5 mg kg^{-1} (Chen 1999). Argillaceous marine sediments and marine shale contain by far the highest Li contents, including a maximum reported value of 400 mg kg^{-1} (Wedepohl 1978). The average abundance of Li

in loess is 30 mg kg^{-1} (McLennan and Murray 1999). Elevated Li values are indicative of felsic rocks, possibly of distinctive chemistry and origin.

Lithium is found exclusively in the univalent free ionic form (Li^+) in the natural environment. Despite the stability of the Li^+ (aq) ion, lithium is relatively immobile, because its fluoride, carbonate and phosphate compounds have low solubility. However, Li can be liberated, especially at low pH levels, by the weathering of primary igneous minerals and from secondary clay minerals (Lyons and Welch 1997). Lithium is held less strongly to exchange sites than Na or K, but adsorption to clay and organic matter is significant. The concentration of Li in water can be influenced by biological factors, since it may substitute for K and Na in metabolic activity.

The abundance of Li in soil varies considerably from 1.3 mg kg^{-1} in light organic soil to 56 mg kg^{-1} in calcareous soil. Lower Li contents are reported for light sandy soil, especially those derived from glacial drift in humid climate (6.2 mg kg^{-1} Li). In arid climates, Li follows an upward movement in the soil profile, and may precipitate in the surface horizons along with easily soluble salts of chlorite, sulphate and borate (Kabata-Pendias 2001).

Lithium concentrations in natural water are typically quite low (between 1 and $10 \mu\text{g l}^{-1}$), although is the fourteenth most abundant element in sea water, with a mean value of $170 \mu\text{g l}^{-1}$ (Hem 1992). The quoted average abundance of Li in river particulate matter is 25 mg kg^{-1} (McLennan and Murray 1999).

Lithium is used extensively in industry (Greenwood and Earnshaw 1984). Lithium carbonates are widely used by primary aluminium producers and in the glass and enamel industries. Lithium stearate is used to make automotive greases from oils. The aerospace industry incorporates Li in its low-density Mg and Al alloys and, increasingly, Li-Si alloys are used in batteries. High Li concentrations in streams in mining regions may reflect contamination from mine spoil and colliery wastes.

Lithium is not known to be essential in humans; however, it is a biologically active element and Li-based drugs have been used to

treat manic-depressive conditions since the 1950s. It is thought to be involved in metabolic pathways and organ functions, although its specific function is not known (WHO 1996). Lithium can be toxic to plants at concentrations above $60 \mu\text{g l}^{-1}$

(Bradford 1963).

Table 41 compares the median concentrations of Li in the FOREGS samples and in some reference datasets.

Table 41. Median concentrations of Li in the FOREGS samples and in some reference data sets.

Lithium (Li)	Origin – Source	Number of samples	Size fraction mm	Extraction	Median mg kg^{-1}
Crust ¹⁾	Upper continental	n.a.	n.a.	Total	24
Water	FOREGS	807	Filtered <0.45 μm		2.10 ($\mu\text{g l}^{-1}$)
Water ²⁾	World	n.a.	n.a.		2.5 ($\mu\text{g l}^{-1}$)
Stream sediment	FOREGS	797	<0.15	Total (XRF)	20.8
Floodplain sediment	FOREGS	743	<2.0	Total (XRF)	22.5

¹⁾Rudnick & Gao 2004, ²⁾Ivanov 1996.

Li in stream water

Lithium values in stream water range over three orders of magnitude, from <0.1 to $356 \mu\text{g l}^{-1}$, with a median value of $2.1 \mu\text{g l}^{-1}$. Lithium data tend to correlate closely with Na and Sr and, in some areas, to EC, Ca and Mg.

Lowest Li values in stream water ($<1 \mu\text{g l}^{-1}$) are found throughout northern Finland and parts of Sweden and Norway, west Scotland, Ireland, over part of the Massif Central, west Spain, some parts of the Alps, Slovenia and western Croatia, and in northern Albania. Low Li values are associated with a range of rock types.

Enhanced Li concentrations in stream water ($>7 \mu\text{g l}^{-1}$) are found in south-east Britain, the southern and eastern part of the Iberian Peninsula (dry climate with intense evapotranspiration causing concentration of ions in water, enhanced by lithologies containing evaporites and marine sediments in the Baetic Cordillera and the Ebro River basin; thermal water with high Li is known in the Almería region), throughout most of central Germany, parts of the Czech Republic and central Hungary, north-eastern and south-eastern France

and most of central and southern Italy including Sicily. In France, these anomalies are associated with high values of Mg, Ca, Cl, Br, B and SO_4^{2-} and are clearly related to natural or anthropogenic dissolution of evaporate deposits (Keuper and Eocene deposits). High isolated anomalies are seen in eastern France and in north-west England, both possibly associated with post coal mining influence. These high concentrations are principally associated with limestone, dolomite and volcanic rocks. In Italy, high Li values are associated with both alkalic volcanic rocks (Roman Alkaline Province and Vulture) and sedimentary rocks (Sicily, Sardinia and north-western Italy).

The lithium distribution in European stream water can be explained in terms of two major patterns: the “Major-ions” and the “Sea elements” stream water types. The Li distribution closely matches that of electrical conductivity (EC), *i.e.*, of total dissolved solids, as corroborated by the strong correlation coefficient (0.65 with EC, 0.72 with SO_4 and 0.68 with Na).

Li in stream sediment

The median Li content in stream sediment is 20.8 mg kg^{-1} , with a range from 0.28 to 271 mg kg^{-1} .

The Li distribution map shows low Li values in stream sediment ($<9.51 \text{ mg kg}^{-1}$) throughout most

of Finland, all of Norway, northern Denmark, north-east Germany, Poland and Estonia.

A strongly anomalous area of high Li in stream sediment is located along the Pyrenees, explained by several Variscan granitic bodies intruding

Palaeozoic sediments, Lower Palaeozoic black shale, and Triassic clastic rocks containing

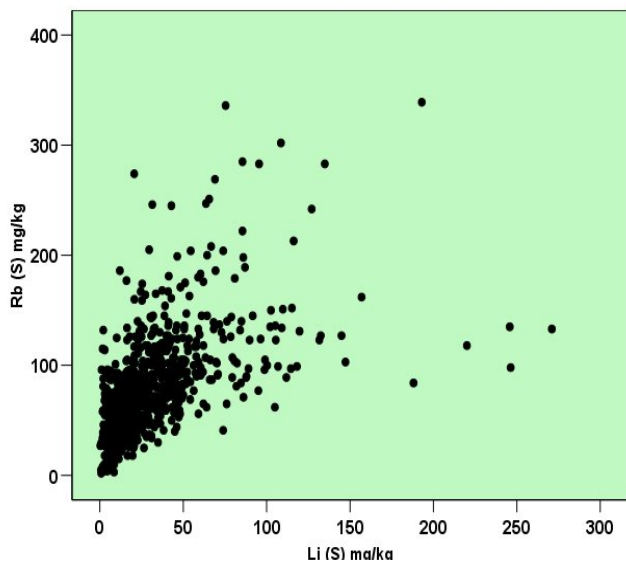


Figure 25. Scattergram of Li and Rb concentrations in stream sediment.

evaporite. High values ($>39.3 \text{ mg kg}^{-1}$) are also located throughout the western Iberian Peninsula, especially in northern Portugal with granitic rocks; England, especially in the north and south-west; central France, south-central Germany, central and southern Italy, Sicily, Sardinia, southern Finland, and a point anomaly in north-west Ireland. Mostly Li is associated with felsic and alkaline rocks in these areas. Black shale and other marine sediments account for high Li values in southern Portugal and Spain, Ireland, central and northern England, and southern Finland.

The affinity of lithium for felsic rocks is confirmed by its good correlations in stream sediment with Rb (0.56), K (0.43), Al (0.54), Ga (0.49) and Be (0.49); a good correlation also exists with As (0.44), Cu (0.41) and Tl (0.41). The scattergram Li-Rb shows good overall correlations, except for a group of samples high in Li but relatively low in Rb, corresponding to the Spanish Pyrenees area (Figure 25).

Li in floodplain sediment

Lithium values in floodplain sediment vary from 0.14 to 302 mg kg^{-1} , with a median of 22.5 mg kg^{-1} .

Low Li values in floodplain sediment ($<9.87 \text{ mg kg}^{-1}$) occur over the glacial drift covered region extending from north Germany, Poland, Lithuania, Latvia to Estonia; the schist, paragneiss, metagreywacke and granulite areas in northern Finland; the granite and amphibolite terrain of northern, central and southern Sweden, and the crystalline rocks of Norway; the crystalline basement of the North West Highlands in Scotland, and the molasse basin of central Austria.

High Li values in floodplain sediment ($>37.0 \text{ mg kg}^{-1}$) are found in mineralised areas associated with felsic rocks in south-west Finland, the Pennines, the Midlands, Wales and the granite of south-west England; an extensive zone from Brittany to Poitou, north Massif Central and the Vosges in France to the Black Forest; Harz Mountains to the Erzgebirge; the border area of

Austria, Slovakia and Hungary; western Croatia; northern Portugal, Galicia, and Cantabrian Mts in Spain; the Pyrenees, and north-east (granite, flysch, Neogene sediments, mineralisation) and southern Greece (limestone, shale, chert).

In floodplain sediment there are three outliers: (a) in northern Portugal (301 mg kg^{-1}) in a basin draining aplo-pegmatitic mineralisations, often with spodumene; (b) another in the western Pyrenees (168 mg kg^{-1}) near Irun, probably caused by Triassic rocks around the Cinco Villas granite, and (c) in south-west England in Cornwall (227 mg kg^{-1}), associated with the St. Austell granite.

Lithium in floodplain sediment shows a strong correlation with Be (0.65), and a good correlation (>0.4) with Al, Ga, Fe, V, Co, Th, Rb, Nb, Y, Ce and La.

In conclusion, the spatial variability of Li in floodplain sediment, and the element associations suggest that it is related to mainly geogenic sources, and the variable lithology of the continent.

Li comparison between sample media

Patterns in Li distribution between stream and floodplain sediments are broadly similar. The main differences are higher Li in floodplain sediment throughout Greece, western Slovakia, coastal Croatia, Brittany in France, and south-western Britain and depleted Li in floodplain sediment in south-western Portugal, Sicily, Sardinia, parts of mainland Italy and northern England. No explanation can be given for these differences. No data are available for Li in soil.

With the exception of Ireland, Fennoscandia and the Baltic states, in which Li is generally low in all sample media, the distribution of Li in stream water is mainly opposite to that observed in sediments. For example, over the Pyrenees and the Variscan parts of the western Iberian Peninsula, stream water Li distributions are quite low compared to sediment data; but in southern and eastern calcareous Spain, Li is high in stream water and low in the sediments.