La – Lanthanum

Introduction

Lanthanum is one of the rare earth elements (REEs), which is a collective term for the elements from lanthanum to lutetium, atomic numbers 57–71, in the periodic table. The element has an atomic number of 57, an atomic mass of 139, one main oxidation state (+3) and two naturally occurring isotopes (^{138}La and ^{139}La), of which ^{139}La is the most abundant at 99.9%.

Lanthanum is a lithophile element forming several minerals, including monazite (Ce, La, Nd, Th)[PO_4SiO_4], which is relatively common, and the rarer cerite $(Ce,La)_9(Mg, Fe)Si_7(O,OH,F)_{28}$. It is also widely dispersed in trace quantities in several rock-forming minerals such as biotite, apatite, pyroxene and feldspar.

Lanthanum has a strong affinity for felsic igneous and a lower affinity for ultramafic rocks (<10 mg kg^{-1}). Mielke (1979) cites La levels in igneous rocks as: basalt 15 mg kg^{-1}; granites 45 to 55 mg kg^{-1}, and an average crustal abundance of 37 mg kg^{-1}. The behaviour of La during metamorphism is not well understood, but partial melting is known to induce La enrichment in the lighter minerals - leucosome - during migmatisation. There is good evidence that La and most other REE may be transported in alkaline hydrothermal solutions (Kosterin 1959).

In sedimentary rocks, a large proportion of the total La content is held in resistate accessory minerals, such as monazite. Feldspar may also contain La and provides an important supply of the element for incorporation into secondary clay minerals during weathering (Ronov *et al.* 1974). Quartzitic sandstone typically has very low concentrations of La (*ca.* 20 mg kg^{-1}) compared with shale or greywacke (*ca.* 50 mg kg^{-1}). In limestone, La is mostly associated with fine clastic impurities, although direct precipitation of La in carbonates has also been recorded (Wedepohl 1978). Mielke (1979) reports levels of La in shale, sandstone and carbonates as 92, 30 and 1 mg kg^{-1} respectively. Diagenetic enrichment of La and other light REE is widely reported in association with hydrous oxide phases in laterite, bauxite and oolitic ironstone (Ure and Berrow 1982). McLennan and Murray (1999) give a value of 35.4 mg kg^{-1} La in loess. Elevated rare-earth element values are generally indicative of felsic rocks, especially intrusives, and the soil and stream sediment derived from them.

Lanthanum is poorly mobile under most environmental conditions. Its release from resistate phases, such as monazite is generally slow, although a small fraction of the total La burden may be held in apatite and biotite, both of which are weathered relatively rapidly at low pH. Its mobility is also limited because of the very low solubility of its phosphate, $LaPO_4$. The La^{3+} ion is only sparingly soluble under normal surface conditions, and its dispersal is typically restricted by adsorption to clay and hydrous oxides (Piper 1974), or by precipitation in authigenic carbonates at high pH (Balashov *et al.* 1964). Hydrolysis products of La^{3+} are also poorly soluble. Calculations using the chemical equilibrium model MINEQL^{+} indicate that dissolved La is complexed mainly to carbonates as $LaCO_3$ and with dissolved organic matter (Moermond *et al.* 2001, ERS 2006). Lanthanum concentrations in river water are very low, typically <1 µg l^{-1} in the United Kingdom (Neal and Robson 2000). The average abundance of La in river particular matter is 46 mg kg^{-1} (McLennan and Murray 1999).

Data on individual REEs in soil are scarce. Their average concentration in soil corresponds most closely to their contents in sedimentary rocks, with the exception of calcareous rocks, where there is an enrichment with respect to the parent rocks. All REEs are reported to be concentrated in alkaline rather in acid soil, probably due to the easy removal of their hydroxide complexes (Kabata-Pendias 2001).

Anthropogenic sources of lanthanum include mining and processing of alkaline rock, petrol production and the disposal of household electrical equipment. La_2O_3 improves the alkali resistance of glass and is used to make special optical glasses. Small amounts of lanthanum are used in the production of nodular cast iron. However, natural sources of La are considered to be more important than anthropogenic ones in the environment (Reimann and de Caritat 1998).

Lanthanum is considered biologically inactive and non-essential. Toxicological data for La, and the REE in general, are relatively scarce, but the toxicity of La is generally considered to be moderate to low. Inhaled REE as dust probably cause pneumoconiosis, and ingested REEs can accumulate in the skeleton, teeth, liver and lungs.

Table 40 compares the median concentrations of La in the FOREGS samples and in some reference datasets.

Table 40. Median concentrations of La in the FOREGS samples and in some reference data sets.

Lanthanum (La)	***Origin – Source***	***Number of samples***	***Size fraction mm***	***Extraction***	***Median mg kg^{-1}***
Crust1)	Upper continental	n.a.	n.a.	Total	31
Subsoil	**FOREGS**	**790**	**<2.0**	**Total (ICP-MS)**	**25.6**
Topsoil	**FOREGS**	**843**	**<2.0**	**Total (ICP-MS)**	**23.5**
Soil2)	World	n.a.	n.a.	Total	35
Humus	**FOREGS**	**367**	**<2.0**	**Total (ICP-MS)**	**1.70**
Water	**FOREGS**	**807**	**Filtered <0.45 µm**		**0.034 (µg l^{-1})**
Water3)	World	n.a.	n.a.		0.05 (µg l^{-1})
Stream sediment	**FOREGS**	**848**	**<0.15**	**Total (XRF)**	**32.5**
Floodplain sediment	**FOREGS**	**743**	**<2.0**	**Total (XRF)**	**24.9**
Stream sediment4)	Canada	26 227	<0.18	Total (INAA)	31

1)Rudnick & Gao 2004, 2)Koljonen 1992, 3)Ivanov 1996, 4)Garret 2006.

La in soil

The median La content is 25.6 mg kg^{-1} in subsoil, and 23.5 mg kg^{-1} in topsoil, with a range from 0.78 to 155 mg kg^{-1} in subsoil, and 1.1 to 143 mg kg^{-1} in topsoils. The average ratio topsoil/subsoil is 0.905.

In subsoil, low La values (<17 mg kg^{-1}) are located in central to northern Finland, central Norway and adjacent Sweden, in glacial drift covered mainland Europe (Netherlands to Poland), central Hungary, and parts of south and east Spain.

Lanthanum in subsoil has high values (>36 mg kg^{-1}) in northern Portugal and Galicia in Spain (crystalline basement of the Iberian Massif), and in the Italian alkaline magmatic province (which contains the strongest anomalies), over the Massif Central, in Brittany, in soil on karst of Slovenia and Croatia, the loess/palaeoplacer area of northern France to Germany, in south-western Norway and in northern Sweden (Salpeteur *et al.* 2005). Point La anomalies in western Greece are in *terra rossa* soil and may be associated with phosphorite and gypsum.

In topsoil, La is much lower in Scandinavia, but elsewhere the pattern is similar to that of subsoil; there is a point anomaly near the Mourne granite in northern Ireland.

Lanthanum in soil shows strong to very strong correlations (in the range 0.70 to 0.98) with the other REEs. More comments are to be found in the section on the Rare Earth Elements.

La in humus

The median La content in humus is 1.70 mg kg^{-1}, and the range varies from 0.10 to 52.5 mg kg^{-1}.

Low La values in humus (<1.10 mg kg^{-1}) occur over most of central Sweden, central Norway, north-eastern Finland, Ireland (except the north-west), western France, northern Netherlands and adjacent north-western Germany, and south-eastern Poland.

High La values in humus (>3.20 mg kg^{-1}) occur in central Britain; south-western Norway; Belgium and southern Netherlands; central-eastern Germany and the Czech Republic; and an area from the Jura in eastern France through

Switzerland into northern Italy, Slovenia and southern Austria. Note that southern Germany shows intermediate La content, and appears to be surrounded by areas with higher values, a pattern which is also observed (with modifications) for Ga, Co, Cu and Zn.

The La pattern in humus is probably geogenic, caused in part by mineral soil admixed in the humus samples, containing lanthanide-bearing phyllosilicates and/or minute grains of the phosphate monazite.

Lanthanum in humus has a good correlation with Ga (0.53) and Co (0.42), both elements exhibiting a somewhat similar geogenic distribution pattern.

La in stream water

Lanthanum values in stream water range over three orders of magnitude, from <0.002 µg l^{-1} to 16 µg l^{-1}, with a median value of 0.034 µg l^{-1}. Lanthanum data correlate most closely with all the other lanthanides. See section on REEs for a general discussion.

Lowest La values in stream water (<0.003 µg l^{-1}) are predominantly found in most of Spain, eastern and southern France, Belgium, northern and south-central Italy, western Slovenia and Croatia, most of Austria and western Hungary, Albania and Greece, north-eastern Germany and south-eastern Poland. Most of the areas of lowest values are characterised by Alpine Orogen terrains (southern Europe), whereas other areas (northern Germany and Poland) are characterised by glacial drift (Variscan and Precambrian terrains). Low La and generally low REE values in central Sweden are related to high pH values caused by Paleozoic rocks.

Highest La concentrations stream water (>1.02 µg l^{-1}) are predominantly found in southern Norway, Sweden, Finland and Denmark. The areas of highest values occur over Precambrian terrains (mostly intrusive and metamorphic rocks). Those streams are often characterised by high DOC content. Enhanced values (>0.13 µg l^{-1}) also occur in northern Fennoscandia, northern Ireland and Scotland, characterised by Caledonides, in France (Brittany and Massif Central), in north-west and south-central Spain in crystalline basement, characterised by Variscan terrains, and in northern Germany (in association with high DOC values), characterised by glacial drift.

The La distribution pattern in stream water follows well the REEs high-DOC stream water model that is chiefly climate-dominated, and the inverse of the Major-ions pattern. The stream water with high La values is acidic, of low mineralisation and high dissolved organic matter. Some rare areas which have high La in soil and/or sediment, as well as in the corresponding stream water, occur in southern and northern Norway and Sweden, and the Central Massif in France.

La in stream sediment

The median La content in stream sediment is 31.9 mg kg^{-1}, with a range from 1.3 to 553 mg kg^{-1}.

On the La stream sediment distribution map, low values (<21.5 mg kg^{-1}) are present in eastern Finland, the North European plain including Denmark, central to western Ireland, southern and eastern Spain, the western Pyrenees and adjacent Cantabrian Mountains, a small area in the central Alps, north-easternmost Italy, the Jura mountains, coastal Croatia, western and southern Greece.

The most anomalous areas of high lanthanum in stream sediment are the Variscan part of the Iberian Peninsula, *i.e.,* Portugal, Galicia and the Sierra de Gredos in Old Castilia (Spain) with crystalline basement, and the Massif Central in France (Variscan granite), extending into the Poitou region and southern Brittany to the north-west. In the southern part of the Massif Central, the highest La values are associated with Nb, U, Sn and Ta, indicating hydrothermal alteration related to the late Variscan granitic phases. High La (>43.6 mg kg^{-1}) also occurs in southern Norway (including the Sovi deposit), northern coastal Norway and adjacent Sweden, parts of central and south-eastern Sweden, north-east and south-western Finland, a point anomaly in northern Estonia (phosphate deposits), Scotland and north-east England, the Bohemian Massif (including a point anomaly in a Variscan granite near the border of Austria, Czech Republic and Germany), the Roman Alkaline Province, and point anomalies in south-eastern Austria, westernmost Austria (probably Variscan granite), the Canary Islands (basalt and trachyte), and near the Mourne granite in northern Ireland.

Lanthanum in stream sediment shows very strong correlations (>0.8) with Th, Y and all the REEs except Eu and Lu. It has a strong correlation (>0.6) with Lu, Eu and U, a good correlation (>0.4) with Zr, Hf, Nb, Ta and Rb, and a weak but significant correlation (>0.3) with Al, Ga, K, Ti, Be, Cs, Tl, Sn and W.

For a comparison with the other REEs, see the section on REE.

La in floodplain sediment

Total La values in floodplain sediment, determined by ICP-MS, vary from 2.95 to 130 mg kg^{-1}, with a median of 32.5 mg kg^{-1}.

Low La values in floodplain sediment (<17.3 mg kg^{-1}) occur over the glacial drift covered plain extending from north-west Germany to Poland, Lithuania and Latvia; the schist, paragneiss, metagreywacke and granulite areas of eastern Finland; much of Ireland; the alluvial parts of the lower Garonne and Rhône rivers in France, the Ebro River basin, and La Mancha and calcareous south-eastern Spain, the molasse basin in central Austria and the calcareous Dalmatian coast in Croatia; the ophiolite, flysch and calcareous rocks of Albania and Greece.

High La values in floodplain sediment (>33.6 mg kg^{-1}) occur in mineralised areas associated with felsic intrusives, such as south-west Finland; southernmost, south-eastern, central and northern Sweden; southern and northern Norway, Wales, the crystalline Armorican Massif, Poitou and Massif Central extending to the Pyrenees in France; central and northern Portugal and adjacent parts of Spain, south-central Spain (Sierra Morena); the Roman Alkaline Province in Italy; Thuringia, Erzgebirge, Bohemian Massif, northern Bavaria, the Austrian-Czech border area, southern Austrian, eastern Slovenia and central Croatia, and eastern Hungary (sediments derived from the volcanic rocks of the Apuseni Mountains in Romania), and central Macedonia in Greece with granitic intrusions.

The highest La values in floodplain sediment occur in northern Sweden (130 mg kg^{-1}) in crystalline rocks, one near the coast in central Wales (101 mg kg^{-1}) draining Lower Palaeozoic sediments and Ordovician volcanics, and another in southern Sweden (92 mg kg^{-1}) associated with granite and granodiorite. An isolated La point anomaly (72.4 mg kg^{-1}) on the coast of north-west Spain lies over Cambrian quartzite and Ordovician sandstone, near the granodiorite stock of Boas. There is also a La point anomaly in the Canary Islands (72.5 mg kg^{-1}), associated with anomalous values in Ce, Nb and Ta, caused by alkaline basaltic volcanism (trachyte).

Lanthanum in floodplain sediment shows a strong to very strong correlation with other REEs, a strong correlation with Al_2O_3, Ga, Nb, Ta, Tl, Rb, V, Ti and Th, and a good correlation with K_2O, Fe_2O_3, Co, Be, Li, U, Zr and Hf.

In conclusion, the spatial distribution of La in floodplain sediment, and its relationships with other elements, show that the geochemical variation is due to the bedrock geology, and no distinguishable influences from anthropogenic activities are recognised.

La comparison between sample media

In general, there are broad similarities between all solid sample media. Topsoil is relatively low in La compared to subsoil in parts of Sweden, Lithuania and northern Spain, but trends between topsoil and subsoil are otherwise virtually identical. In Lithuania, La depletion in topsoils results from the general depletion of clay particles, which carry most of the REEs (Gregorauskiene and Kadunas 2000, 2006). Coastal Croatia and Slovenia and western parts of Austria are low in La in stream sediments compared to other solid sample media (removal of fine-grained material from the residual soil and karst). In stream and floodplain sediments, higher La concentrations are observed in southern and northern Norway and south-western Finland compared to soils. In stream sediments, northern Estonia is enriched in La compared to other solid sample media, possibly related to the phosphorite lower-Palaeozoic sediments. Central and northern Britain show high La in stream sediments only. In parts of Sweden and Wales, floodplain sediment is enriched in La compared to other solid sample media, because floodplain is richer in the clay fraction where La is most likely adsorbed. In the alkaline volcanic province of Italy, and parts of western Greece, La is low in sediments compared to soil. A boxplot comparing La variation in subsoil, topsoil, stream sediment and floodplain sediment is presented in Figure 24.

The distribution pattern of La in humus roughly resembles that of subsoil, although the concentrations are significantly lower.

The distribution of La in stream water is complex, but generally forms opposite patterns to those observed in solid sample media, except in Brittany, the Central Massif of France and the Variscan western part of the Iberian Peninsula. Lanthanum solubility is strongly controlled by acid pH and the presence of DOC, and highest concentrations are found throughout Fennoscandia.

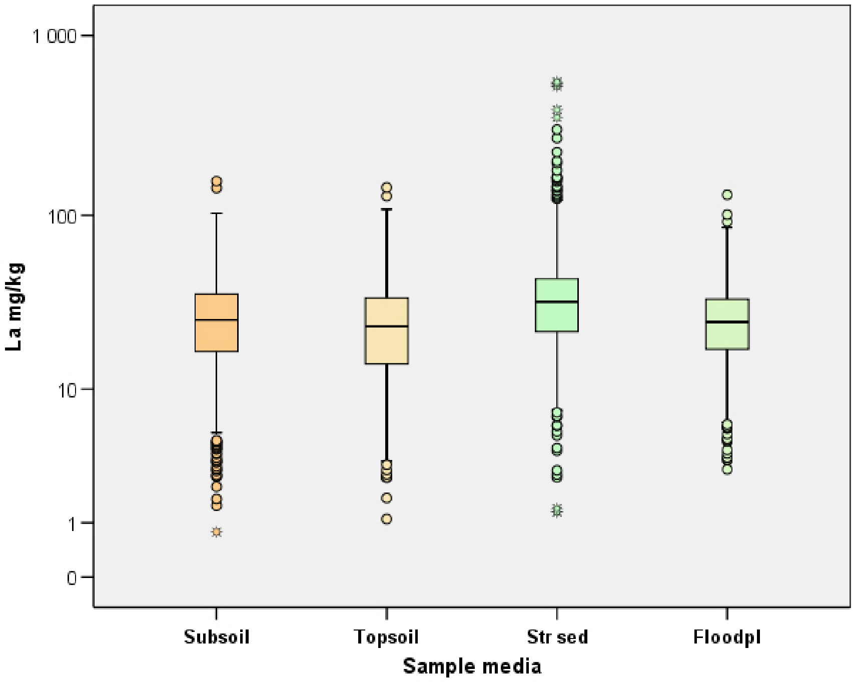

Figure 24. Boxplot comparison of La variation in subsoil, topsoil, stream sediment and floodplain sediment.