Th – Thorium

Introduction

Thorium is a member of the actinide series of elements, along with U and the human-made elements such as Pu. The element has an atomic number of 90, an atomic mass of 232, one main oxidation state (+4) and one naturally occurring isotope (^{232}Th). Like U, it is a radioactive element and its most stable isotope, ^{232}Th, has a very long half-life of 1.4×10^{10} years.

Thorium is the most abundant of the heavy elements, *i.e.,* elements with atomic number greater than Bi (83). It has a crustal abundance of 9.6-12 mg kg^{-1}, which is more abundant than Sn and only slightly less than Pb. It is strongly lithophilic, and is more abundant in crustal rocks than in meteorites and mantle-type rocks, such as dunite. It forms several minerals including monazite (Ce,La,Nd,Th)(PO_4,SiO_4), the rarer thorite $ThSiO_4$ and thorianite ThO_2, but is more widely dispersed as an accessory element in zircon, sphene, epidote, uraninite, allanite and apatite in igneous rocks. Although Th is a transition element, possessing more than one valency state, its geochemistry is dominated by the Th^{4+} ion, which has an ionic radius of 94 pm, and shows greatest affinity to other M^{4+} elements such as U, Ce and Zr. The minerals of these elements are often isostructural, with replacement and solid-solution gradations between the end-members, *e.g.,* thorianite ThO_2, cerianite CeO_2 and uraninite UO_2; thorite $ThSiO_4$ and zircon $ZrSiO_4$; and monazite (Ce,La,Th,U)PO_4.

Thorium is generally higher in granitic than mafic igneous rocks. Since it can enter some rock-forming minerals, such as biotite, it is not as strongly concentrated in the incompatible pegmatite phase like U, although some Th-containing minerals, such as allanite do occur in pegmatite. Granite typically contains 10-40 mg kg^{-1} Th, although there is much local and provincial variation. Intermediate rocks, such as andesite have about 1–4 mg kg^{-1} Th, while gabbro usually has less than 3.5 mg kg^{-1}, and basalt less than 1 mg kg^{-1}. In metamorphic rocks, the Th content is generally immobile up to the highest grades, but anatexis will result in concentration in the mobile granitic phase. High Th values, therefore, indicate the presence of felsic rocks, especially intrusives.

Thorium in sedimentary rocks is essentially resistate in character, as its major host minerals, such as monazite and zircon, are highly resistant to both chemical and physical breakdown. Any Th released by weathering has a transient existence in solution as it is strongly sorbed by clay minerals. Thus, sandstone, arkose and graywacke may have up to 10 mg kg^{-1}, and normal shale and mudstone 10–13 mg kg^{-1}. Mielke (1979) cites levels of Th in shale, sandstone and carbonate rocks as 12, 1.7 and 1.7 mg kg^{-1} respectively. Black shale may have higher Th levels, but never as high as the U content, because of the much stronger affinity of U for organic material and the greater mobility of oxidised UO_2^{2+} in solution. Placer deposits, such as monazite sands, however, may be exceptionally rich in Th and constitute one of the major ores of Th. Limestone is normally very low in Th, since Th^{4+} cannot form a stable carbonate, unlike UO_2^{2+}; similarly, Th is almost completely absent from evaporite deposits. Marine Mn nodules are often enriched in Th (24–124 mg kg^{-1}) and Atlantic pelagic clay have been noted to contain 30 mg kg^{-1} (Wedepohl 1978). The average value for loess is quoted as 11.3 mg kg^{-1} (McLennan and Murray 1999).

Kabata-Pendias (2001) report there is very little information with respect to Th in soil. The global average for soil is given as 3.4 to 10.5 mg kg^{-1}. The mobility of Th in soil, like U, is governed by the formation of the hydrated cation Th^{4+}, which is responsible for its solubility over a wide range of soil pH. Organic acids increase the solubility of Th in soil, but its mobility may be limited due to the formation of slightly soluble precipitates (*e.g.,* phosphates, oxides) and by adsorption on clay minerals and organic matter.

Thorium has low mobility under all environmental conditions, mainly due to the high stability of the insoluble oxide ThO_2 and the strongly resistate nature of its carrier minerals such as monazite and zircon. Unlike U, Th cannot be oxidised to a stable cation equivalent to the highly mobile uranyl ion UO_2^{2+}. The soluble species $Th(SO_4)^{2+}$ may form below pH 3, and under oxidising conditions (Brookins 1988), *e.g.,* in acid mine water. Any Th released into solution will be rapidly sorbed by clay minerals and hydrolysed to the hydrous oxide $Th(OH)_4$, which will be intimately associated with the clay-mineral fraction, unless it can be mobilised by other inorganic or organic ligands (Hem 1992). Thus, Th is essentially insoluble in surface and groundwaters, and levels are extremely low at 0.01-1 µg l^{-1} (Hem 1992). Because of this, Th is a useful pathfinder element in stream sediment for locating uranium deposits associated with magmatic rocks, since almost all the Th is transported as solid mineral material with minimal loss to solution. The average Th content in river particulates is given as 14 mg kg^{-1} (McLennan and Murray 1999).

Anthropogenic sources of thorium include fertilisers, uranium mining and processing, and coal combustion (Reimann and de Caritat 1998). The amounts of Th in the environment may increase as a result of accidental releases of Th from nuclear processing plants.

Thorium has no known biological function. It is chemotoxic, radiotoxic and a carcinogen. In the environment, Th behaves similarly to the REEs, especially Ce, substituting for Ca in bones and teeth. Long-term exposure to Th increases the chances of developing lung diseases and lung, pancreas and bone cancer.

Table 67 compares the median concentrations of Th in the FOREGS samples and in some reference datasets.

Table 67. Median concentrations of Th in the FOREGS samples and in some reference data sets.

Thorium (Th)	***Origin – Source***	***Number of samples***	***Size fraction mm***	***Extraction***	***Median mg kg^{-1}***
Crust[1)]	Upper continental	n.a.	n.a.	Total	10.5
Subsoil	**FOREGS**	**790**	**<2.0**	**Total (ICP-MS)**	**7.63**
Topsoil	**FOREGS**	**843**	**<2.0**	**Total (ICP-MS)**	**7.24**
Soil[2)]	World	n.a.	n.a.	Total	9.4
Water	**FOREGS**	**807**	**Filtered <0.45 µm**		**0.009 (µg l^{-1})**
Water[3)]	World	n.a.	n.a.		<0.001 (µg l^{-1})
Stream sediment	**FOREGS**	**852**	**<0.15**	**Total (XRF)**	**10.0**
Floodplain sediment	**FOREGS**	**747**	**<2.0**	**Total (XRF)**	**8.00**
Stream sediment[4)]	Canada	26 227	<0.18	Total (INAA)	8.1

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

Th in soil

The median Th content is 8.00 mg kg^{-1} in subsoil and 7.24 mg kg^{-1} in topsoil; the range varies from <0.1 to 71.7 mg kg^{-1} in subsoil and 0.30 to 75.9 mg kg^{-1} in topsoils. The average ratio topsoil/subsoil is 0.925.

Northern Europe generally shows Th contents in subsoil below the median, with low values (<5 mg kg^{-1}) in the glacial drift area from Poland to the Netherlands, in central Finland, in northern Norway, western Ireland, and southern Spain. The southern margin of the formerly glaciated area through the Netherlands, Germany and Poland is well marked on the map, with low subsoil Th values to the north of it.

High Th values in subsoil (>11 mg kg^{-1}) appear in the crystalline basement of the Iberian Massif in Portugal and western Spain, in the alkaline magmatic province of Italy, the Massif Central in France, Slovenia, Croatia, and northern Bavaria. Elevated Th values in north-eastern Greece are related to granitic intrusions. As Th normally has a higher background in granite, gneiss and alkaline rocks, its geological distribution seems to be overprinted in northern Europe by climate- or pH-determined pedogenic processes, notably leaching. These processes are responsible for taking more Th out of the soil and transferring it to stream water, which shows relatively high values in northern Europe (see below). The Th subsoil and topsoil patterns are overall similar.

Thorium in subsoil shows a very strong correlation (>0.8) with the light REEs Ce, La and Pr, a strong correlation (>0.6) with Be, Rb, Cs, Tl, U, Nb, Ta, Ga, Sc, Nd, Sm, Gd and Tb, and a good correlation (>0.4) with Pb, Ag, Bi, Sn, Al, In, K, Y and the remaining (heavy) REEs. This pattern of correlations is similar in topsoil, but for Sn and Ag it is much weaker.

Th in stream water

Thorium values in stream water range over four orders of magnitude, from <0.002 µg l-1 to 0.37 µg l-1, with a median value of 0.009 µg l-1. Thorium data correlate most closely with the lanthanides.

Lowest Th values in stream water (<0.002 µg l-1) are predominantly found on Variscan terrains in south-western and north-eastern Spain and in north and south France, and on Alpine Orogen in all northern Italy, in central Austria, and in Albania and Greece.

Highest Th concentrations in stream water (>0.11 µg l-1) are predominantly found on Precambrian Shield (mostly intrusive and metamorphic rocks) in southern Norway, southern and eastern Sweden and southern Finland, and mainly on Precambrian Shield derived glacial drift in north-eastern Germany. The high Th concentration in stream water in Fennoscandia is in contrast with low values in soils and sediments, pointing to leaching of Th under the existing conditions of climate and high DOC content.

Enhanced values in stream water (>0.05 µg l^{-1}) also occur in north central Fennoscandia, and in northern Ireland and Scotland, in the Caledonides, and in France (Brittany and Massif Central), characterised by Variscan terrains. In northern Ireland, the isolated Th anomaly is associated with the Mourne granite. The enhanced point value in the Roman province is controlled by recent alkaline volcanism.

The described Th distribution on the stream water map shows clearly the similarity with the REEs and associated elements patterns in acidic, low-mineralisation and high-organic-matter stream water. The pattern is climate controlled. The association with the patterns of alkaline rocks elements is, however, largely geogenic, and appears to be responsible for high Th concentrations in Italy including Sicily and Sardinia, and in Germany.

In comparison with Th in soil and sediments, the Th patterns in stream water differ entirely. Notable exceptions are the high Th values in both stream water and solid sample media over the Massif Central in France and the Italian province of alkaline volcanism.

Th in stream sediment

The median Th content in stream sediment is 10 mg kg^{-1}, and the range varies from <1 to 253 mg kg^{-1}.

Low Th values in stream sediment (<7 mg kg^{-1}) are found in the glacial drift covered area of northern Europe extending from the Netherlands through to Poland, in southern Sweden, central Norway, parts of northern Sweden and northern and eastern Finland, western Ireland, the Po valley in northern Italy, south-eastern Spain and most of Greece. The southern margin of the ice-age glaciated area through the Netherlands, Germany and Poland is well marked on the map, with low Th stream sediment values just north of it.

High Th stream sediment areas (>13 mg kg^{-1}) include the Variscan crystalline basement in northern Portugal and Spain, and in the Massif Central in France. High values also occur in the Variscan part of Germany, the Bohemian Massif, Corsica; in the western Alps; in the Roman alkaline magmatic province, in southern Italy and Sicily, in north-eastern Greece (associated with granite and U mineralisation), northern Estonia (black shale), southern Finland, southern Norway and small areas in northern Finland and northern Norway. A point anomaly characterises the Mourne granite in northern Ireland.

Thorium in stream sediment has a very strong to strong correlation with Y and the REEs (except

Eu), a strong correlation with U (0.77), a good correlation with Ta, Nb, Tl, Sn, Eu, K, Rb and Zr, and a weak correlation with Be, Hf, W, Al, Ga and Cs.

Th in floodplain sediment

Thorium values in floodplain sediment range from <1 to 38 mg kg^{-1}, with a median of 8 mg kg^{-1}. The variation in the lower Th values is somewhat constrained by the detection limit of the XRF analytical method.

Low Th values in floodplain sediment (<5 mg kg^{-1}) occur over the glacial drift covered plain extending from north Germany and almost the whole of Poland to Lithuania and Latvia; on the crystalline rocks of the Precambrian Shield in south-eastern Finland, northernmost and central Norway; on mostly limestone and crystalline rocks in Ireland. The molasse basins in southern Germany and central Austria; in France over the fluvial deposits of the lower Garonne river; a small area in eastern Spain on clastic and carbonate rocks; in south Albania and western Greece in areas of limestone, flysch and ophiolite. The southern margin of the ice-age glaciated area through Germany and Poland is well marked on the map, with low to very Th values just north of it.

High Th values in floodplain sediment (>11 mg kg^{-1}) occur in Fennoscandia draining gneiss and granite terrains in most of central Sweden and south-western Finland, across mainly Variscan north-western and central Europe with variable lithology in Wales, south-west England; the crystalline rocks of the Iberian Massif in central to western Spain and Portugal; France (Poitou, Massif Central, Vosges, Corsica), the Bohemian Massif, most of the Czech Republic, western parts of Slovakia and Hungary, areas with granite intrusives and mineralisation, and often associated with U; Swiss-Italian border area with granitic rocks; the Roman Alkaline Province, eastern Sicily volcanics, clastic rocks in Croatia, and central Macedonia and Thrace of north-east Greece with granite, gneiss, schist and U mineralisation.

Highly anomalous Th values in floodplain sediment occur in granitic areas of northern Portugal (34 and 38 mg kg^{-1}) and northern Massif Central in France (34 mg kg^{-1}). Further anomalous Th values are found in the metallogenic provinces of south-east Sweden, the Roman alkaline magmatic province, and in the Czech Republic west of Brno on the Jihlava River draining the mineralised area of the Moravian Hills. The isolated Th point anomaly in south-west Norway is situated on the Kvina River, which drains the Knaben Mo deposit hosted in felsic gneiss. The high Th value in west Croatia is explained by accumulation in residual karstic soil.

Thorium in floodplain sediment shows a very strong correlation with Rb (0.85), strong correlations with Al_2O_3, Ga, K, Nb, Ta, Tl, Y and U, and good correlations with Be, Li, W, Zr, Cs, Fe, Ti and V. Correlations with the REEs are good to strong.

It is concluded that the distribution map of Th in floodplain sediment reflects patterns related to the geological substratum. It generally maps areas with felsic intrusives, and known U mineralised areas.

Th comparison between sample media

In general, there are broad similarities between all solid sample media; patterns in topsoil and subsoil are almost identical. In stream sediment, the average values are generally higher than in soil and in floodplain sediment. The anomalies in the Massif Central and the Czech Republic are more pronounced in floodplain and stream sediments. On the other hand, the Italian Alkaline Province has lower Th values in both floodplain and stream sediments than in soil; this is also the case for stream sediment in coastal Croatia and Slovenia and in the western parts of Austria (explained by the probable removal of fine-grained material from the residual soil and karst). In southern Norway, southern and south-western Finland and northern Estonia, stream sediment Th concentrations are higher than in the other solid sample media, possibly the result of heavy mineral concentration in stream sediment. In floodplain sediment, central eastern Sweden shows higher Th values than in soil. Also, south-western Finland has higher Th in floodplain sediment than in all other media.

A boxplot comparing Th variation in subsoil, topsoil, stream sediment and floodplain sediment is presented in Figure 47.

Patterns in stream water Th content are virtually opposite to those observed in all solid sample media. Thorium is not normally mobile except in the presence of DOC, and tends towards low concentrations in Mediterranean environments, especially in northern Italy, Greece and Albania, and higher concentrations occur in the more DOC rich environments of southern Sweden and Finland, as well as in parts of Germany and Brittany.

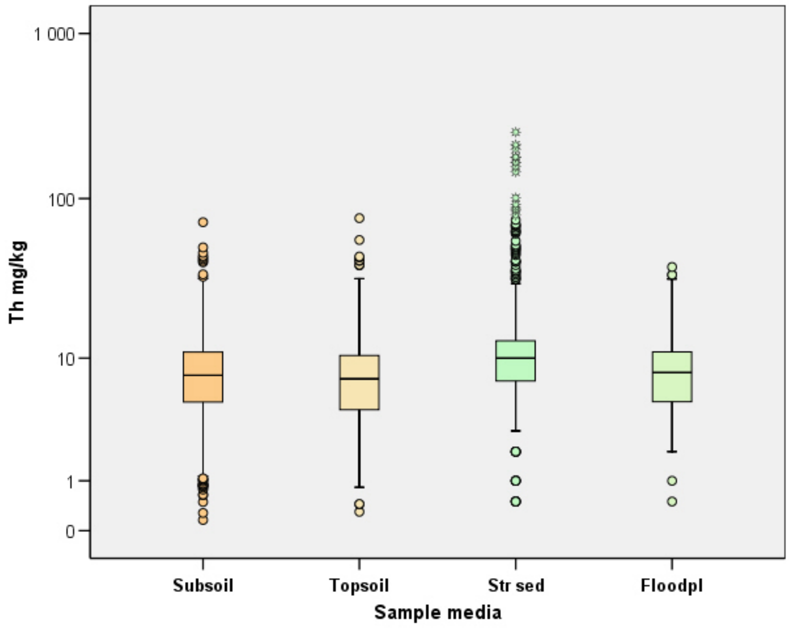

Figure 47. Boxplot comparison of Th variation in subsoil, topsoil, stream sediment and floodplain sediment.