Zr – Zirconium

Introduction

Zirconium belongs to group 4 of the periodic table, which also includes Ti and Hf. The element has an atomic number of 40, an atomic mass of 91, one main oxidation state (+4) and five naturally occurring isotopes (^{90}Zr, ^{91}Zr, ^{92}Zr, ^{94}Zr and ^{96}Zr), of which ^{90}Zr is the most abundant at 51.5% of the total mass.

Zirconium is a lithophile metallic element and forms several minerals including zircon $ZrSiO_4$ and the rarer baddeleyite ZrO_2. It can substitute for Ti in ilmenite and rutile, and is also present at trace levels in clinopyroxene, amphibole, mica and garnet.

The ionic radii of Zr^{4+} and Hf^{4+} (72 and 71 pm respectively) are almost identical, resulting in very similar chemical behaviour of the two elements. During magmatic processes, the highly charged Zr^{4+} ion is incompatible with the lattice sites of most common rock-forming silicates. Limited remobilisation of Zr may occur during intense metasomatism and granite-related hydrothermal alteration (Hynes 1980). Under most other circumstances, the element appears to be immobile, with comparable levels prevailing in metamorphic rocks of all grades (Shaw 1954, Engel and Engel 1960, Tarney and Saunders 1979).

Felsic igneous rocks are generally enriched in Zr relative to mafic lithologies. Mielke (1979) reports a crustal average of 162 mg kg^{-1} Zr; ultramafic 45 mg kg^{-1}; basaltic 140 mg kg^{-1}; granitic 140–175 mg kg^{-1} and syenite 500 mg kg^{-1}. Many alkaline rocks are enriched in Zr as a result of the formation of stable Na complexes (Watson 1979). Elevated total Zr values are indicative of felsic rocks, especially intrusives.

The Zr content of sedimentary rocks is very much related to the presence of detrital heavy minerals, such as zircon and sphene. Trace quantities of authigenic zircon may also occur as adsorbed coatings on diagenetic clay minerals (Nicholls and Loring 1962). The concentration of Zr in greywacke (140–800 mg kg^{-1}) is typically higher than that in sandstone (160–220 mg kg^{-1}), shale or other mudstone (100–300 mg kg^{-1}). The abundance of Zr in limestone is generally low (20–130 mg kg^{-1}). The average content of Zr in loess is given as 375 mg kg^{-1} (McLennan and Murray 1999), and that of deep loess deposits in European Russia 470 mg kg^{-1} (Kabata-Pendias 2001).

Zirconium is considered to be only slightly mobile in soil with organic acids the main transporting agents for its migration (Kabata-Pendias 2001). The Zr content of soil is generally inherited from the parent rocks. Lower amounts tend to be found in soil developed on glacial drift (70-200; mean 140 mg kg^{-1}) and higher amounts in residual soil derived from Zr-rich parent rocks (70 to 200; mean 305 mg kg^{-1}).

Zirconium displays very low mobility under most environmental conditions, mainly due to the stability of the principal host mineral zircon and the low solubility of the hydroxide $Zr(OH)_4$. This limits the concentration of Zr in most natural water to <0.05 µg l^{-1} even in sea water. Depending on the pH, Zr^{4+}, $Zr(OH)^{3+}$, $Zr(OH)_2^{2+}$, $Zr(OH)_3^{+}$, $Zr(OH)_4$ exist in solution. At pH 7, a $Zr(OH)_2(CO_3)_2^{2-}$ complex can form, but this is unstable and decomposes with decreasing pH to form $Zr(OH)_4$. The hydro-bicarbonate ($Zr(OH)_4$-HCO_3-H_2O) complex may be the most significant Zr complex in natural water. Colloidal zirconium is also readily adsorbed by organic matter, macroplankton and siliceous material (Smith and Carson 1978).

Anthropogenic sources of zirconium include nuclear fallout and ceramic dusts. The metal and its alloys are used in the production of catalytic converters, percussion caps, furnace bricks, laboratory crucibles and surgical appliances. Zirconium is used extensively in nuclear applications since it does not readily absorb neutrons, and commercial nuclear power generation takes more than 90% of Zr metal production. Geogenic sources are, however, considered more important than anthropogenic ones (Reimann and de Caritat 1998).

Zirconium is a non-essential element, having no known biological role. Little is known about its toxicity; however, it is generally regarded as being of low risk (Mertz 1987). In general, Zr is unlikely to present a hazard to the environment, although ^{95}Zr is one of the long-lived radionuclides involved in atmospheric testing of nuclear weapons that have produced and will continue to present increased cancer risks for centuries to come.

Table 77 compares the median concentrations of Zr in the FOREGS samples and in some reference datasets.

Table 77. Median concentrations of Zr in the FOREGS samples and in some reference data sets.

Zirconium (Zr)	***Origin – Source***	***Number of samples***	***Size fraction mm***	***Extraction***	***Median mg kg^{-1}***
Crust[1)]	Upper continental	n.a.	n.a.	Total	193
Subsoil	**FOREGS**	**787**	**<2.0**	**Total (ICP-MS)**	**222**
Topsoil	**FOREGS**	**845**	**<2.0**	**Total (ICP-MS)**	**231**
Soil[2)]	World	n.a.	n.a.	Total	230
Water	**FOREGS**	**807**	**Filtered <0.45 µm**		**0.053 (µg l^{-1})**
Water[3)]	World	n.a.	n.a.		2.6 (µg l^{-1})
Stream sediment	**FOREGS**	**852**	**<0.15**	**Total (XRF)**	**391**
Floodplain sediment	**FOREGS**	**747**	**<2.0**	**Total (XRF)**	**215**

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

Zr in soil

The median Zr content is 220 mg kg^{-1} in subsoil and 230 mg kg^{-1} in topsoil, with a range from 10 to 1020 mg kg^{-1} in subsoil and 5 to 1060 mg kg^{-1} in topsoil The average ratio topsoil/subsoil is 1.088.

Low Zr values in subsoil (<160 mg kg^{-1}) are present in central Finland, southern France, southern Spain, central Portugal, most of Greece, northern Alpine Italy and adjacent Switzerland, and small areas in south-west Poland and in the eastern Paris Basin in France.

The subsoil zirconium map shows high values (>300 mg kg^{-1}) occurring mainly in south-western Norway and Sweden, in north-central Sweden and in Scotland, all related to crystalline rocks, where zircon is normally abundant. A large zone from southern England, north-western France into central Germany is related to Quaternary loess deposits rich in weathering-resistant heavy minerals, and to palaeofluviatile deposits (palaeoplacers) and palaeoshorelines of the Ypresian sea (Lower Eocene) (Salpeteur *et al.* 2005). Further, Zr subsoil anomalies occur in the Bohemian Massif, Hungary, Slovenia and most of Croatia (in residual soil on karstified carbonate rocks and on predominantly clastic Tertiary sediments), and the Italian alkaline province. In Spain, point Zr subsoil anomalies occur in eastern Extremadura, Asturias and Galicia. Isolated anomalies appear in south-east Poland, possibly also related to Quaternary loess.

The topsoil Zr map is very similar, but elevated values are also present in Lithuania and Estonia. This may be due to leaching of other soil components, especially Ca and clay particles, causing relative enrichment of the weathering resistant zircon. In addition, formerly imported phosphate fertilisers from the Kola peninsula were rich in zircon and thus contribute to higher topsoil Zr values in the agricultural soil of Lithuania. An isolated Zr anomaly appears in topsoil in the eastern Pyrenees.

Zirconium has a very strong correlation with Hf, 0.97 in subsoil and 0.96 in topsoil, which is explained by the substitution of Hf in all Zr minerals. Zirconium has a weak to good correlation (>0.4 in subsoil, >0.3 in topsoil) with the REEs, Nb, Ta, and Ti. This relationship points to the association of the resistant ubiquitous heavy minerals zircon, monazite, columbo-tantalite and rutile-anatase-brookite-leucoxene, which are concentrated together in a range of geological materials.

It is noted that the ratio topsoil/subsoil for Zr and Hf is slightly higher than 1 (1.088 and 1.080 respectively), which means that topsoil is more enriched in resistant minerals; to a lesser degree this also happens with SiO_2 and TiO_2 (Table 4), representing the resistant minerals quartz and the rutile group.

Zr in stream water

Zirconium values in stream water range over three orders of magnitude, from <0.002 µg l^{-1} to 2.41 µg l^{-1}, with a median value of 0.053 µg l^{-1}. Zirconium data correlate relatively well with Nb.

Lowest Zr values in stream water (<0.003 µg l^{-1}) are predominantly found in Caledonian western Norway and western Scotland, in Variscan terrains of northern Portugal, across northern Spain to southern France (including Corsica), to Alpidic terrains of northern Italy and Switzerland, and throughout most of Greece.

Highest Zr concentrations in stream water (>0.49 µg l^{-1}) are found in Denmark, southern Sweden and Finland, eastern Poland and in northern Germany. Enhanced values (>0.24 µg l^{-1}) also occur in eastern Scotland, in southern and northern Sweden, in southern Finland, Brittany area of France, in Estonia, Latvia and Lithuania, northern Poland and in central and southern Italy. In Poland (and in the other Baltic Sea countries and in southern Fennoscandia) high concentrations of Zr in stream water are in direct correlation with DOC (organic substance), which shows regional relationships with peat lands. The same relationships exist as well with Hf and Nb. Isolated enhanced stream water Zr values occur in central southern and northern Germany and in France (Brittany). The high enhanced stream water Zr values occurring in Italy (from northern to southern areas) are certainly controlled by recent alkaline volcanism of the Roman and Neapolitan geochemical provinces and Vulture volcano (Plant *et al*. 2005). The Zr anomalies in northern Germany, like those of Nb, Ti, Al, V and Zn, correlate with high DOC values; they thus depend on environmental conditions.

Patterns in stream water Zr data are different from distributions in the solid sample media, especially throughout northern Europe. Distributions are close to the REEs pattern, controlled strongly by DOC, since Zr is highly insoluble, unless complexed with organic matter. The highest Zr concentrations are, therefore, associated with the organic rich environments of most of southern and central Fennoscandia, the Baltic states, Brittany and Ireland. The pattern of Zr distribution in stream water in most of the Mediterranean area is close to the Alkaline elements group, and is similar to the solid sample media.

Zr in stream sediment

The median Zr content in stream sediment is 392 mg kg^{-1}, with a range from 1 to 4865 mg kg^{-1}. These figures are much higher than for soil, pointing to a heavy mineral concentration mechanism of detrital zircon in active streams sediment.

The Zr distribution map of stream sediment shows that low values (<259 mg kg^{-1}) are present in eastern and southern Finland, Wales, south-eastern Spain, most of northern and central Italy, central Austria, coastal Croatia, and most of Greece including Crete.

High Zr values in stream sediment (>616 mg kg^{-1}) are located mainly in the Massif Central of France, central Spain (granitic and lower Palaeozoic clastic sediments), southern France (including the Aquitaine Basin) and the eastern Pyrenees, eastern Scotland (Caledonian granite), south-western Norway, south-western and a small area of northern Sweden, Denmark, a zone from north-east Germany to central Poland (fluvio-glacial detrital zircon), Estonia and adjacent Latvia. A point anomaly in northern Portugal is over granitic rocks.

Zirconium has a very strong correlation with Hf (0.84), a good correlation (>0.4) with Y, the REEs (except Eu), Si, Nb and Th, a weak correlation (>0.3) with U and Ta, and a weak negative correlation with Ca (-0.35).

Zr in floodplain sediment

Total Zr contents in floodplain sediment vary from 17 to 695 mg kg^{-1}, with a median of 220 mg kg^{-1}. This median is lower than for stream sediment, pointing to the generally finer grain size of floodplain sediment, with heavy minerals being diluted in a mass of clay, silt and fine sand.

Low Zr values in floodplain sediment (<150 mg kg^{-1}) occur in north-eastern Germany and western Poland on glacial drift, and western Ireland largely on Palaeozoic limestone. Low Zr values occur over clastics of the Ebro River basin and the variable lithology of the Pyrenees, and south-east Spain over calcareous rocks; in France, the unconsolidated deposits of the Gironde area, the Rhône-Saône River basin and western Alps with limestone; the Jura Mountains limestone in Switzerland, the molasse sediments of southern Germany and central-north Austria; over most of Italy and Sardinia on carbonates, ophiolite and clastic rocks; on the unconsolidated deposits of central Hungary, limestone and flysch beds of Dalmatian part of Croatia; a belt extending from Albania to the western part of Greece with carbonates, ophiolite and clastic rocks.

High Zr values in floodplain sediment (>280 mg kg^{-1}) occur on the Fennoscandian Shield in large parts of north, east-central and south-western Sweden on predominantly gneiss and granite, and in the Kongsberg-Telemark sector of southern Norway (possibly associated with alkaline igneous rocks); on glacial drift of western Latvia and in Lithuania; most of Scotland over largely older Palaeozoic metamorphic rocks, and in northern (younger Palaeozoic clastics) as well as southern England, and in south-west England associated with Permian granite intrusions; elsewhere on Mesozoic and Tertiary clastics. High Zr values in floodplain sediment are found on a variety of lithologies from the Armorican Massif (metamorphic and igneous rocks) across the Paris Basin (carbonate and clastic Mesozoic and Tertiary rocks containing palaeo-placer deposits of heavy minerals), Ardennes in Belgium and in central Germany (Quaternary loess deposits) to the Erzgebirge and the Bohemian Massif (crystalline rocks and Mesozoic cover). Areas with high Zr values in floodplain sediment occur also in west-central (Guadiana River basin on continental clastics) and north-western Spain (on Tertiary clastic rocks); over Tertiary clastic rocks in the northern part of Massif Central (alkaline volcanics), and upper section of the Garonne River basin in France; over Tertiary clastics in eastern Slovakia and eastern Hungary (derived from the mineralisation of Apuseni Mountains in Romania) and Croatia on Tertiary clastics.

Highly anomalous Zr values in floodplain sediment occur in central Spain (695 mg kg^{-1}) and in north-western Spain (586 mg kg^{-1}), and a point anomaly on the Guadalquivir River (530 mg kg^{-1}), all on Tertiary clastics. A point Zr anomaly occurs on Corsica associated with Variscan granite. The point Zr anomaly in floodplain sediment on the Canary Islands is associated with alkaline basalt.

Zirconium in floodplain sediment shows a strong positive correlation with Hf, a good correlation with TiO_2, Y, Ce, La, Nb and Th, and a good negative correlation with CaO (-0.49).

In conclusion, the patterns of high Zr values in floodplain sediment map areas with gneiss, granite and alkaline igneous rocks, and also the zone of palaeo-placer deposits in northern Europe (Salpeteur *et al.* 2005).

Zr comparison between sample media

Patterns in Zr distribution between topsoil and subsoil are very similar, but there are significant differences between the distribution patterns in soil and sediments. Stream sediment is generally higher in Zr, because zircon is concentrated in the heavy mineral fraction in active stream sediments. Stream sediment is relatively higher in Zr in an area extending from Denmark over north and eastern Germany to southern Poland compared to floodplain sediment and soil; the same pattern is observed over the Central Massif and in Estonia. However, Zr is relatively low in stream sediment in an area extending from northern France to central Germany, as well as the alkaline province of Italy, and in Croatia and Slovenia. Floodplain sediment Zr tends to lower values in south-west Norway compared to all other solid sample media.

A boxplot comparing Zr variation in subsoil, topsoil, stream sediment and floodplain sediment is presented in Figure 55.

Patterns in stream water Zr data are different from distributions in the solid sample media, especially throughout northern Europe. Distributions are controlled strongly by DOC, since Zr is highly insoluble unless complexed with organic materials. Highest concentrations are, therefore, associated with the organic rich environments of most of southern and central Fennoscandia and Ireland. Patterns in Zr distribution throughout most of the Mediterranean area is similar in stream water and solid sample media.

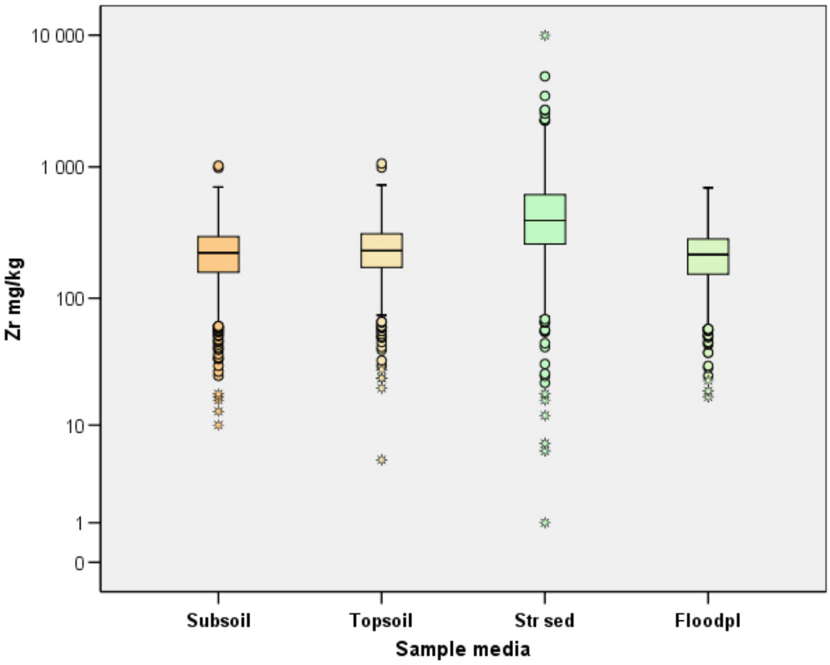

Figure 55. Boxplot comparison of Zr variation in subsoil, topsoil, stream sediment and floodplain sediment.