Introduction

Cerium 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 term 'lanthanide' is also used for any of the REEs. Cerium has an atomic number of 58, an atomic mass of 140, two main oxidation states (+3 and +4) and four naturally occurring isotopes (^{136}Ce, ^{138}Ce, ^{140}Ce and ^{142}Ce), of which ^{140}Ce comprises 88.5% of the total mass.

Ce is a lithophile metallic element. It is the most abundant of all the REEs and forms several minerals including monazite $(Ce,La,Nd,Th)PO_4$ and xenotime $(Y,Ce)PO_4$, and the rarer bastnaesite $(Ce,La)CO_3(F,OH)$ and cerite $(Ce,La)_9(Mg,Fe)Si_7(O,OH,F)_{28}$. Like the other REEs, Ce is strongly electropositive, and most of its chemistry is characterised by ionic bonding. The relatively large ionic radius of Ce^{3+} (101 pm) precludes significant substitution into minerals, except where the substituted cation is also large, *e.g.,* Ca^{2+} (100 pm), Y^{3+} (90 pm) and Th^{4+} (94 pm) (Henderson 1984). Cerium differs from other REEs in that it can also occur in the Ce^{4+} oxidation state, which has a smaller solid-state ionic radius (87 pm). Accessory minerals, such as allanite, apatite, zircon and sphene are important in the enrichment of Ce in igneous rocks. Cerium minerals, such as fluocerite $(Ce,La)F_3$, loparite $(Na,Ce,Ca)TiO_3$ and monazite $Ce(PO_4)$, are primarily associated with alkalic and granitic rocks and their pegmatites, and with hydrothermal mineralisation.

The crustal average for Ce is 60 mg kg^{-1}, with granite (230 mg kg^{-1}) tending to have higher Ce contents than mafic igneous rocks (30 mg kg^{-1}) (Mason 1966, Mason and Moore 1982). Wedepohl (1978) quotes average Ce values as: basalt 16 mg kg^{-1}, intermediate rocks 60 mg kg^{-1} and granitic rocks 104 mg kg^{-1}. Abundances of Ce in sedimentary rocks reported by Wedepohl (1978) range from 67 to 91 mg kg^{-1} in shale to 33 mg kg^{-1} in sandstone and 6.5 mg kg^{-1} in limestone. However, sandstone and other sedimentary rocks containing large quantities of resistant heavy minerals, such as zircon and sphene, will have elevated Ce levels.

Elevated rare-earth element values are generally indicative of felsic rocks, especially intrusives (granite), and the weathering materials derived from them, such as soil, stream and floodplain sediment.

Cerium has very low elemental mobility, due mainly to the stability and low solubility of $CePO_4$ and CeO_2 (Brookins 1988). It is associated with the 'resistate' group of elements, which includes Zr, Hf and Th. Cerium, along with heavy REEs (Gd, Tb, Dy, Ho, Er, Tm and Yb), if released as Ce^{3+} in solution during weathering, is always absorbed onto Fe oxides (Leleyter *et al.* 1999), possibly in association with phosphate.

The abundance of Ce in soil varies from 15.8 to 97.4 mg kg^{-1}, with a quoted mean of 48.7 mg kg^{-1}. All REEs are reported to be concentrated more in alkaline than in acid soil, probably due to the easy removal of their hydroxide complexes; thus, soil developed on calcareous parent rocks show a comparative enrichment in REEs (Kabata-Pendias 2001). McLennan and Murray (1999) quote average values for river particulates and loess as 88 and 78.6 mg kg^{-1} Ce respectively.

Cerium concentrations in stream water are very low, typically <0.1 µg l^{-1} (Neal and Robson 2000).

Anthropogenic sources of cerium include glass and ceramic dust and pollution from the steel industry (Reimann and de Caritat 1998). It is also released from coal burning and nuclear energy materials processing (Kabata-Pendias 2001). Cerium oxide is an important constituent of incandescent gas mantles and is also used as a hydrocarbon catalyst in 'self cleaning' ovens. Cerium is an important catalyst in petroleum refining and is used in metallurgical applications, alloys for jet engine components and in carbon arc electrodes (McLennan 1999a).

Cerium is considered to be biologically non-essential. Toxicological data for Ce, and the REEs in general, are relatively scarce, but the toxicity of Ce is generally considered to be low. Cerium can, however, replace Ca in the bone structure of the human body, which may cause skeletal problems. The element has also been implicated as a cause of pneumoconiosis due to inhalation of Ce-bearing dust and linked to myocardial heart disease.

Table 18 compares the median concentrations of Ce in the FOREGS samples and in some reference datasets.

Table 18. Median concentrations of Ce in the FOREGS samples and in some reference data sets.

Cerium (Ce)	*Origin – Source*	*Number of samples*	*Size fraction mm*	*Extraction*	*Median mg kg^{-1}*
Crust[1]	Upper continental	n.a.	n.a.	Total	63
Subsoil	**FOREGS**	**790**	**<2.0**	**Total (ICP-MS)**	**53.7**
Topsoil	**FOREGS**	**843**	**<2.0**	**Total (ICP-MS)**	**48.2**
Soil[2]	World	n.a.	n.a	Total	65
Water	**FOREGS**	**807**	**Filtered <0.45 µm**		**0.055 (µg l^{-1})**
Water[3]	World	n.a.	n.a.		0.79 (µg l^{-1})
Stream sediment	**FOREGS**	**848**	**<0.15**	**Total (XRF)**	**66.6**
Floodplain sediment	**FOREGS**	**743**	**<2.0**	**Total (XRF)**	**50.2**

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

Ce in soil

The median Ce content is 54.0 mg kg^{-1} in subsoil and 48.2 mg kg^{-1} in topsoil; the range is from 1.04 to 379 mg kg^{-1} in subsoil and from 2.45 to 267 mg kg^{-1} in topsoil. The average ratio topsoil/subsoil is 0.899.

In subsoil, low Ce values (<35 mg kg^{-1}) are located mainly throughout Finland, in the glacial drift covered area of northern mainland Europe (Netherlands to Poland), western Ireland, central Hungary, the Paris Basin in France, and parts of south and east Spain.

Cerium in subsoil has high values (>75 mg kg^{-1}) over Variscan granitic and metamorphic rocks in northern Portugal and north-western Spain, the Massif Central and Brittany in France; in the Italian Alkaline Province (which contains the strongest anomalies); in karst of Slovenia, Croatia and adjacent Austria; the loess/palaeoplacer area of northern France to Germany (Salpeteur *et al*. 2005); south-western Norway and northern Sweden.

In topsoil, Ce is much lower in Scandinavia, and somewhat higher in Slovakia. A much larger area in western Spain shows high values: near Almeria (south-east Spain) over clastic rocks, schist and orthogneiss; in Variscan Extremadura; in the Central and Eastern Pyrenees; and in Gran Canaria island related to alkaline basic volcanism. There is a point anomaly near the Mourne granite in northern Ireland. Elsewhere in Europe the pattern is similar to that of the subsoils.

Cerium shows strong (>0.6) to very strong (>0.8) correlations with most other REEs, both in subsoil and topsoil. Correlations are strongest with the light REEs (La, Pr, Nd, Sm) which are more similar in atomic weight and ionic radius. For additional information, the section on Rare Earth Elements (REEs) should be consulted.

Ce in stream water

Cerium values in stream water range over four orders of magnitude, from <0.002 µg l^{-1} to 10.1 µg l^{-1} (excluding an outlier of 36.5 µg l^{-1}), with a median of 0.055 µg l^{-1}. Cerium stream water data correlate most closely with the other lanthanides.

Lowest Ce values in stream water (<0.030 µg l^{-1}) are predominantly found throughout central and eastern Spain (Calcareous and clayey), south Portugal, southern and north-eastern France, Belgium, west and south Germany, south-east England predominantly on Variscan terrains, in eastern Germany and in Poland on Precambrian Shield derived glacial drift, and in most of southern Italy including Sicily and all northern Italy, western Slovenia, Croatia and Hungary, in Austria, all of Albania and Greece on the Alpidic Orogen. Low Ce values in central Sweden are related to high pH values caused by Palaeozoic rocks. A similar pattern can be noticed for Be, Cs, Dy, Er, Eu, F, Fe, Gd, Ho, La, Lu, Nd, Pd, Pr, Sm, Tb, Th, Ti, Tm, Y, Yb and Zn.

Highest Ce values in stream water (>1.85 µg l^{-1}) are predominantly found in southern and central Norway, in southern Sweden and Finland characterised by Precambrian Sveconorwegian and Svecofennian terrains (mostly intrusive and metamorphic rocks). Enhanced values (between 0.21 and 1.85 µg l^{-1}) also occur across central Fennoscandia, northern Ireland and Scotland, over the Fennoscandian and Irish-Scottish Caledonides, and in Denmark and northern Germany (in association with high DOC values), characterised by Precambrian Shield derived glacial drift, in France (Brittany and Massif Central), and small areas in Variscan north-west Spain and central-southern Spain (Valle de Alcudia-Pedroches batholith and Linares granites). There are no high values in terrains of the Alpine Orogen. The relatively enhanced values occurring in central and southern areas of Italy are certainly controlled by recent alkaline volcanism of the Roman and Neapolitan geochemical provinces and Vulture volcano.

The Ce distribution in stream water closely follows the distribution pattern of REEs and their numerous asscociates in high-organic-carbon acid low-mineralisation stream water that is to a large degree controlled by exogenic factors: climate, especially rainfall, vegetation and topography. Organic matter complexes are the dominant form in stream water. In alkaline stream water, carbonate complexes are important. Geogenic supplies to high Ce concentrations in stream water are rare, occurring in the Armorican and Central Massifs in France, and a few small areas in Spain and in Italy, as deduced from a comparison with the Ce patterns for the solid sample materials.

Ce in stream sediment

The median Ce content in stream sediment is 65.1 mg kg^{-1}, with a range from 2.2 to 1080 mg kg^{-1}.

The cerium distribution map shows low values in stream sediment (<43.5 mg kg^{-1}) over most of eastern Finland, the northern European plain including Denmark, western Ireland, southern and eastern Spain, the western Alps and northern Appenines, north-easternmost Italy, the Jura Mountains, Slovenia, coastal Croatia, and western and southern Greece.

High Ce contents in stream sediment (>90.8 mg kg^{-1}) are well represented in Variscan Spain and Portugal, where they outline the granitic basement of the Iberian Massif; the highest Ce anomalies are found over the granitic-metamorphic rocks of the eastern Cordillera Central, which is in agreement with data from the Spanish geochemical mapping in this area: Ce contents of up to 1500 mg kg^{-1} were found in stream sediments; moderate values fit with metamorphic areas of the Iberian Massif in a similar way as they do in the French Massif Central. Here the area with high values extends into the Poitou region and southern Brittany. In the southern part of the Massif Central, the highest Ce values are associated with Nd, U, Sn and Ta, indicating hydrothermal alteration related to the late Variscan granitic phases.

High Ce values in stream sediment also occur 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 Variscan granite near the border of Austria, Czech Republic and northern Bavaria), the Roman Alkaline Province, and point anomalies in south-eastern Austria, westernmost Austria (probably Variscan granite), the Canary Islands, and near the Mourne granite in northern Ireland.

Cerium in stream sediment has a very strong correlation (>0.8) with Y, with the other REE except Lu and Eu, and with Th (0.90); a strong correlation (>0.6) with Lu, Eu and U, and a good correlation (>0.4) with Nb, Ta, Ti, Zr, Hf and Rb. In part, this points to the association of the heavy minerals columbo-tantalite, monazite, zircon and rutile, which are often enriched together in sediments.

For a comparison with the other rare earth elements, refer to the section on REEs.

Ce in floodplain sediment

The Ce distribution in floodplain sediment, determined by ICP-MS, varies from 1.9 to 231 mg kg^{-1}, with a median 50.2 mg kg^{-1}.

Low Ce values in floodplain sediment (<34.6 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; most 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 southern calcareous Dalmatian coast in Croatia; the ophiolite, flysch and calcareous rocks of Albania and Greece.

High Ce values in floodplain sediment (>68.2 mg kg^{-1}) occur overall in areas with felsic intrusives and mineralisation, as in south-west Finland, southernmost, south-eastern, central and northern Sweden; southern, central 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); central Swiss-Italian Alps; the Roman Alkaline Province in Italy; Harz Mountains, 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 and mineralisation of the Apuseni Mountains in Romania).

The highest Ce anomalies in floodplain sediment occur near the coast in central Wales (231 mg kg^{-1}, not shown on map) draining Lower Palaeozoic sediments and Ordovician volcanics, one point in southern (192 mg kg^{-1}) and another in northern Sweden (190 mg kg^{-1}) over crystalline rocks. Cerium is high in north-west Spain in southern Galicia over granitic and metamorphic rocks; in western Asturias-León, anomalous values are related to Lower Cambrian quartzite and feldspathic sandstone, Ordovician sandstone and several small granitic stocks intruding throughout that zone: these include the isolated Ce point anomaly (149 mg kg^{-1}) on the coast of north-west Spain. A point anomaly (for Ce, Nb, Ta) is found on Gran Canaria island, caused by alkaline volcanic lithologies (basalt, trachyte) rich in REEs, Nb and Ta, outcropping in the catchment basin.

Cerium in floodplain sediment shows a 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.

It can be concluded that the distribution map of Ce in floodplain sediment shows the geochemical differences of the bedrock geology and mineralisation, and no distinguishable influences from anthropogenic activities are recognised.

Ce comparison between sample media

In general, there are broad similarities between all solid sample media. Topsoil is relatively low in Ce compared to subsoil in parts of Norway, Sweden and Lithuania, but patterns between topsoil and subsoil are otherwise virtually identical. Coastal Croatia and Slovenia and western parts of Austria are low in Ce in stream sediment compared to other solid sample media, which is possibly explained by the removal of fine-grained material from the residual soil and karst. In stream and floodplain sediments, higher Ce concentrations are observed in southern and northern Norway and south-western Finland compared to soils. In stream sediment, northern Estonia shows two point anomalies of Ce absent in other solid sample media, possibly related to the phosphorite lower-Palaeozoic sediments. Central and northern Britain show high Ce in stream sediment only. In parts of Sweden and Wales, floodplain sediment is enriched in Ce compared to other solid sample media. In the alkaline volcanic province of Italy and parts of western Greece, Ce is low in sediments compared to soil.

A boxplot comparing Ce variation in subsoil, topsoil, stream sediment and floodplain sediment is presented in Figure 12.

The distribution of Ce in stream water is complex, but generally forms opposite patterns to those observed in solid sample media, except in Brittany and the Central Massif of France and the Variscan western part of the Iberian Peninsula.

Cerium solubility is strongly controlled by acid pH and the presence of DOC and, therefore, the highest concentrations are observed throughout Fennoscandia.

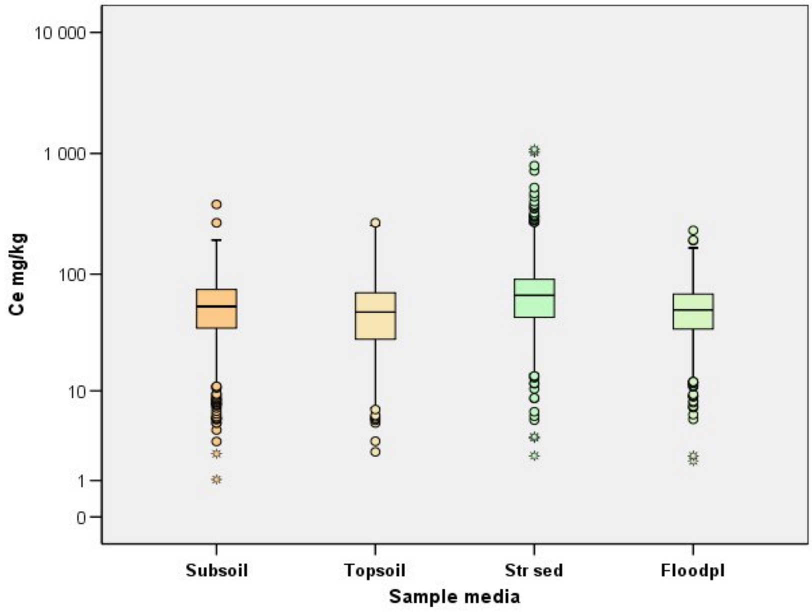

Figure 12. Boxplot comparison of Ce variation in subsoil, topsoil, stream sediment and floodplain sediment.