

Introduction

Yttrium belongs to group 3 of the periodic table, which also includes Sc, La and Ac. The element has an atomic number of 39, atomic mass of 89, one oxidation state (+3) and one naturally occurring isotope (^{89}Y). Chemically, Y resembles the heavier Rare Earth Elements (REEs). The major importance of Y in geochemistry is that it has a geochemical behaviour intermediate between the smaller lanthanide elements dysprosium (Dy) and holmium (Ho) (McLennan 1999b).

Yttrium is a lithophile metallic element that forms several minerals including xenotime YPO_4 and yttrialite $(\text{Y,Th})_2\text{Si}_2\text{O}_7$, but is also present as an accessory element in biotite, feldspar, pyroxene, garnet and apatite.

The electron configuration and ionic radius of Y resemble those of the heavier REEs (Gd to Lu), with which it is associated in minerals and rocks. This is seen during magmatic processes, where the behaviour of Y is very similar to that of the heavy REEs. It is strongly partitioned into garnet, hornblende, clinopyroxene and biotite, but nevertheless shows slight enrichment in granitic (*ca.* 40 mg kg⁻¹) relative to intermediate (*ca.* 35 mg kg⁻¹) and basaltic (*ca.* 32 mg kg⁻¹) igneous rocks. Mielke (1979) gives a value of 31 mg kg⁻¹ for the crustal average of Y, which is higher than elements such as Sn and Pb. In basalt, its concentration is sensitive to the degree of partial melting (Wedepohl 1978). Disproportionately low Y concentrations may occur in calc-alkaline magmas as a result of the stabilisation of phases rich in heavy REEs in the source region and/or their fractionation from the magmas. Elevated Y and REE values are generally indicative of felsic rocks, especially intrusives, and the soil and stream sediments derived from them.

Both Y and the heavy REEs (Gd to Lu) form more stable complexes than light REEs (La to Sm), particularly with carbonate, fluoride or sulphate anions in alkaline solutions, and they are thus more prone to hydrothermal mobilisation (Kosterin 1959). However, there is little evidence of Y mobility during metamorphism (O’Nions and Pankhurst 1974, Drury 1978).

The concentration of Y in sedimentary rocks is largely determined by the abundance of heavy resistant minerals, such as zircon, xenotime and

garnet. In low-energy depositional environments, some Y may also occur in stable organic compounds and alkali carbonate complexes. Shale (*ca.* 40 mg kg⁻¹) and greywacke (*ca.* 30 mg kg⁻¹) are typically enriched in Y compared with carbonate rocks (*ca.* 4 mg kg⁻¹) and sandstone (*ca.* 15 mg kg⁻¹). There is evidence that Y is enriched in clay and shale of marine origin relative to their lacustrine counterparts (Balashov *et al.* 1964). Yttrium enrichment has been reported in laterite (Calliere *et al.* 1976) and oolitic ferro-manganese deposits (Goldberg *et al.* 1963). The average value of Y in loess is quoted as 25 mg kg⁻¹ (McLennan and Murray 1999).

Kabata-Pendias (2001) reports that Y has not been determined systematically on soil samples, therefore, little is known about its behaviour; mean Y contents for uncultivated and cultivated soil are cited as 23 mg kg⁻¹ and 15 mg kg⁻¹ respectively.

In stream sediment most of the Y is held in accessory minerals, such as garnet, apatite, sphene, monazite and zircon, all of which are resistant to weathering. The abundance of Y in river particulates is given as 28 mg kg⁻¹ (McLennan and Murray 1999). In acid environments, Y may be mobilised through the dissolution of ferromagnesian silicates, notably clinopyroxene, but subsequent dispersal is typically restricted by sorption to hydrous Fe oxides and clay minerals. In neutral and alkaline water, the formation of insoluble carbonate complexes further inhibits mobility and Y becomes prone to precipitation in much the same manner as Al (Balashov *et al.* 1964).

Yttrium displays very low mobility under all environmental conditions. In most cases, it can be treated as a trivalent REE (van Middlesworth and Wood 1998) and, like the REEs, many of its carrier minerals are resistant. Although in theory the Y^{3+} ion is soluble under acid conditions, the low solubility of the phosphate, hydroxide and carbonate species negates this (Brookins 1988). Yttrium and the REEs in stream water are often in the form of suspended particles or colloids rather than in dissolved form, and they are thought to coprecipitate with $\text{Fe}(\text{OH})_3$ (van Middlesworth and Wood 1998).

Anthropogenic sources of Y include REE mining and ceramic dust (Reimann and de Caritat 1998). It is widely used in household appliances, such as colour televisions, fluorescent lamps, energy-saving lamps and glasses. It is also used in the production of catalysts and to polish glass.

Yttrium is considered to be non-essential for living organisms. Its toxicity is generally regarded as low, but it is more toxic than some of

the other REE. Yttrium is mostly dangerous in the working environment, potentially causing lung embolisms with long-term exposure. Yttrium may also cause cancer, and can be a threat to the liver when it accumulates in the human body.

Table 74 compares the median concentrations of Y in the FOREGS samples and in some reference datasets.

Table 74. Median concentrations of Y in the FOREGS samples and in some reference data sets.

Yttrium (Y)	Origin – Source	Number of samples	Size fraction mm	Extraction	Median mg kg⁻¹
Crust ¹⁾	Upper continental	n.a.	n.a.	Total	21
Subsoil	FOREGS	788	<2.0	Total (ICP-MS)	23.0
Topsoil	FOREGS	845	<2.0	Total (ICP-MS)	21.0
Soil ²⁾	World	n.a.	n.a.	Total	20
Water	FOREGS	807	Filtered <0.45 µm		0.064 (µg l⁻¹)
Water ³⁾	World	n.a.	n.a.		0.7 (µg l ⁻¹)
Water ²⁾	World	n.a.	n.a.		0.04 (µg l ⁻¹)
Stream sediment	FOREGS	848	<0.15	Total (XRF)	25.7
Floodplain sediment	FOREGS	743	<2.0	Total (XRF)	20.1

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

Y in soil

The median Y content is 23 mg kg⁻¹ in subsoil and 21 mg kg⁻¹ in topsoil; the range varies from <3 to 88 mg kg⁻¹ in subsoil and up to 267 mg kg⁻¹ in topsoil. The average ratio topsoil/subsoil is 0.914.

The geochemical behaviour of Y is most similar to that of the heavy REEs (Gd, Tb, Dy, Ho, Er, Tm, Yb and Lu).

Yttrium in subsoil shows low values (<15 mg kg⁻¹) throughout most of Finland, Poland, northern Germany, Denmark and the Netherlands, northern Ireland, eastern Scotland, central Portugal and southern Spain.

High Y values in subsoil (>31 mg kg⁻¹) are located mainly in the crystalline basement of the Iberian Massif in northern Portugal and Galicia (Spain), in the Italian and northern Greece alkaline magmatic provinces (Plant *et al.* 2005), a point anomaly in Tuscany, in the Massif Central, Brittany, in residual soil on karst of Slovenia and Croatia, in southern Hungary and Austria, south-eastern Germany, the loess/palaeoplacer area of

northern France to Germany, south-western Norway, and northern Sweden (Salpeteur *et al.* 2005). Point anomalies appear in western Greece, associated with *terra rossa* soil and phosphorite mineralisation, and in northern Ireland near the Mourne granite.

In topsoil, Y is lower in Norway and Sweden, but elsewhere the pattern is similar to that of the subsoil. There is a point anomaly in the Canary Islands associated with alkali basalt.

The average ratio topsoil/subsoil is 0.914 for Y, similar to the REEs, in particular the HREEs (heavy rare earth elements).

Yttrium in subsoil has a very strong correlation (>0.8) with most of the REEs (Dy, Er, Eu, Gd, Ho, Lu, Nd, Sm, Tb, Tm, Yb), a strong correlation (>0.6) with Ce, La, Pr, Nb, Ti, Fe and In, and a good correlation (>0.4) with Mn, Co, Cu, Zn, Pb, Sc, V, Al, Ga, Zr, Hf, Rb, Tl, Ta, Te and Th. In topsoil, the same correlation pattern is present, but U and Cd also have a good correlation with Y.

Y in stream water

Yttrium values in stream water range over three orders of magnitude, from $<0.003 \mu\text{g l}^{-1}$ to $6.53 \mu\text{g l}^{-1}$ (excluding an outlier of $26.6 \mu\text{g l}^{-1}$), with a median value of $0.064 \mu\text{g l}^{-1}$. Yttrium data correlate most closely with the rare earths elements in general, and in particular with erbium.

Lowest Y values stream water ($<0.002 \mu\text{g l}^{-1}$) are predominantly found in most of eastern Spain, western, south-eastern and north-eastern France, southern Italy (including Sicily and southern Sardinia) and most of northern Italy, in western Slovenia, Croatia and western Austria, north-eastern Germany and throughout Albania and Greece. Most of the areas of lowest Y values in stream water are characterised by Variscan and Alpine Orogen terrains (southern Europe), whereas other areas (mainly northern Germany) are represented by glacial drift. Low Y and low REE stream water values in central Sweden are related to high pH values caused by Palaeozoic rocks.

Highest Y concentrations stream water ($>0.95 \mu\text{g l}^{-1}$) are predominantly found in northern Denmark, southernmost Norway and in southern Sweden and Finland. The

areas of highest values are characterised by Precambrian terrains (mostly acid intrusive and metamorphic rocks). Enhanced stream water Y values ($>0.34 \mu\text{g l}^{-1}$) also occur throughout central and southern Norway, in central and northern Sweden and Finland, eastern and northern Ireland, northern Scotland, characterised by Scandinavian and Irish-Scottish Caledonides, and in France (Brittany and Massif Central) on Variscan terrains (intrusive and volcanic rocks). In Northern Ireland, the anomalously high Y stream water values are associated with the Mourne granite. Highly anomalous Y values in northern Germany are associated with high DOC values.

The Y stream water distribution discussed above follows most closely the REE and related elements pattern in acid, low mineralisation, high DOC stream water that is clearly climate-dependent. Yttrium in river water occurs predominantly in organic complexes. A geogenic explanation appears to be possible for yttrium stream water anomalies in Spain, Ireland, Brittany and Massif Central, and of weaker intensity in Italy. In most of these areas, higher Y is found also in sediments and/or soil.

Y in stream sediment

The median Y content in stream sediment is 25.7 mg kg^{-1} , and the range varies from 1.3 to 426 mg kg^{-1} .

The Y stream sediment distribution map is similar to the distribution of the heavy REEs. Low Y values in stream sediment ($<18.1 \text{ mg kg}^{-1}$) are present in most of eastern Finland, the northern European plain including Denmark, western Ireland, eastern Spain, the western Alps, northern Apennines and north-easternmost Italy, coastal Croatia, western and southern Greece.

The two areas with the highest anomalous Y values in stream sediment (up to 62.9 mg kg^{-1}) are the Variscan part of the Iberian Peninsula, *i.e.*, Portugal, Galicia and the Sierra de Gredos in Old Castilia (Spain), and the Massif Central in France (Variscan granite), extending into the Poitou region to the north-west. High Y in stream sediment ($>33.6 \text{ mg kg}^{-1}$) also occurs in southern Norway (including the Sovi deposit), northern Norway, northern, southern and eastern Sweden, a

point anomaly in northern Estonia (phosphate deposits), eastern Scotland, the Bohemian Massif (including a point anomaly in Variscan granite near the border of Austria, Czech Republic and Germany, and a point anomaly near the U deposit of Dolny Rozinka in the central Czech Republic), the Roman Alkaline Province, south-eastern Austria, and near the Mourne granite in northern Ireland.

Yttrium in stream sediment has very strong correlations (>0.8) with Th and the REEs (except Eu), a strong correlation (>0.6) with Eu and U, and a good correlation (>0.4) with Nb, Ta, Ti, Zr, Hf, Sn and Ga. The main Y-bearing minerals are xenotime (yttrium phosphate) and monazite (also the main carrier of REEs, Th and U). These behave as heavy minerals in sediments and are concentrated together with other heavy minerals such as zircon, rutile, columbo-tantalite and cassiterite, thus explaining the pattern of correlations.

Y in floodplain sediment

The Y distribution in floodplain sediment varies from 2-130 mg kg⁻¹, with a median of 20.1 mg kg⁻¹.

Low Y values in floodplain sediment (<14.7 mg kg⁻¹) occur over most of eastern Finland and north-eastern Norway on the crystalline rocks of the Fennoscandian Shield, north Ireland on Caledonide terrains, over the glacial drift covered plain from north Germany to most of Poland and Latvia, in parts of eastern and north-eastern Spain on calcareous and clastic rocks, the lower alluvial sediments of the Garonne river in France, the molasse basin of southern Germany and Austria, and Calabria in southern Italy.

High Y values in floodplain sediment (>26.9 mg kg⁻¹) occur mainly in areas with Nb and REE mineralisation as in many parts of Norway (Söve Nb-REE-Th, Fen REE), including the Oslo graben, patchwise across Sweden, and in south-western Finland on the crystalline Fennoscandian Shield terrains, in western Ireland and Wales (Coed Y Brenin porphyry Cu); in France in the Poitou, Massif Central towards the Pyrenees associated with felsic rocks and mineralisation; Corsica with granite and mineralisation, and the Roman Alkaline Province. The belt of high Y values in floodplain sediment extending from Belgium over to the Harz Mountains may be related to heavy minerals in the loess deposits; the

high Y values are related to felsic igneous rocks occurring in the Erzgebirge in Germany, Bohemian Massif and southern Moravia in the Czech Republic to eastern and southern Austria, western Hungary, Slovenia, and in karstic soil in western Croatia. High Y values in floodplain sediment also occur in eastern Hungary, their source being the calc-alkaline intrusive and volcanic rocks of the Apuseni Mountains in Romania, and over the mineralised granitic rocks of central Macedonia in northern Greece.

Outlying and highly anomalous Y values in floodplain sediment occur in the Skellefte mineralised area in northern Sweden (130 mg kg⁻¹), in southern Sweden (56.4 mg kg⁻¹), the Poitou region in France (56.1 mg kg⁻¹), and in Northumberland in north-east England (49.1 mg kg⁻¹), which may be related to phosphorite deposits.

Yttrium in floodplain sediment shows a strong to very strong positive correlation with the REEs, a strong correlation with Al₂O₃, Ga, Ti₂O, Fe, V, Nb and Th, and a good correlation with K₂O, Rb, Co, Tl, Zr, Hf, Be, Li, Ta, and U.

It can be concluded that the distribution map of Y in floodplain sediment shows the geochemical differences of the bedrock geology and mineralisation, especially its association with felsic crystalline rocks.

Y comparison between sample media

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

Ireland, floodplain sediment is enriched in Y compared to other solid sample media. In the alkaline volcanic province of Italy and parts of western Greece, Y is low in sediments compared to soil. In central Spain, Y is anomalously higher in stream sediment than in soil, whereas floodplain sediment does not show this feature. The Czech Republic and adjacent area of Germany is enriched in Y in stream sediment compared to soil; parts of this anomaly are also visible in the floodplain sediment extending to northern Germany.

A boxplot comparing Y variation in subsoil, topsoil, stream sediment and floodplain sediment is in Figure 53.

The distribution of Y 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. Yttrium solubility is strongly controlled by acid

pH and the presence of DOC, and highest concentrations are observed throughout Fennoscandia.

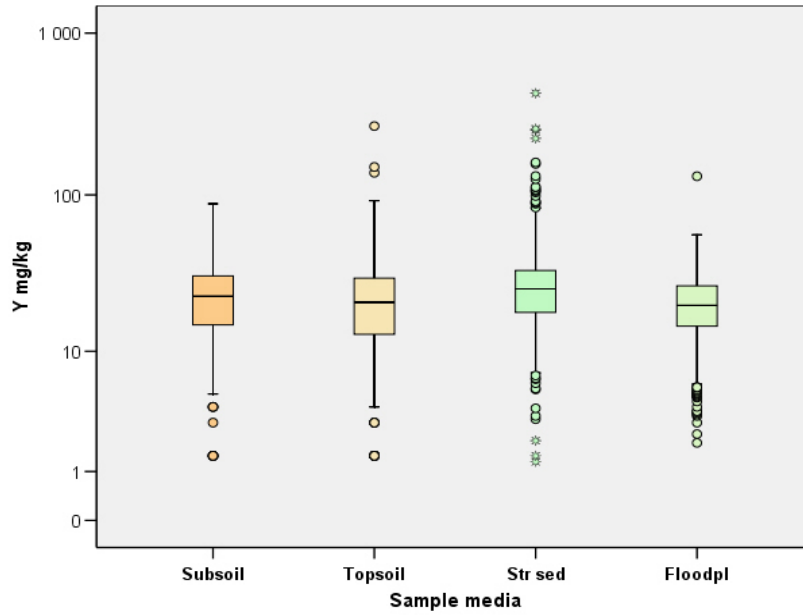


Figure 53. Boxplot comparison of Y variation in subsoil, topsoil, stream sediment and floodplain sediment.