Introduction

The rare earth elements (REEs) are the elements from lanthanum to lutetium (atomic numbers 57–71) in the periodic table. The REEs are further subdivided on the basis of their atomic number and mass: La, Ce, Pr, Nd, Pm [N.B. promethium is unstable and not present as a natural element], Sm and Eu being described as light rare-earth elements (LREEs) and Gd, Tb, Dy, Ho, Er, Tm, Yb and Lu as heavy rare-earth elements (HREEs) (Henderson 1984). Europium is in the centre of the suite of REEs, and shows some peculiar properties. The term 'lanthanide' is also used for any member of the REEs together with yttrium. Lanthanum, cerium and yttrium are discussed in more detail in their individual sections; the remaining REEs are summarised in this section.

The REEs vary in atomic mass from 139 (La) to 175 (Lu). All REEs have one main oxidation state (+3), although Eu has a stable (+2) state and Ce a stable (+4) state. Of all the REEs, only Pm does not have a naturally occurring stable isotope. Half of the remaining REEs have three or more stable isotopes; La, Eu and Lu have two each, while the remaining four elements, ^{141}Pr, ^{159}Tb, ^{165}Ho and ^{169}Tm, are monoisotopic.

The REEs are generally dispersed as minor, non-essential elements in a wide range of rock-forming minerals. There are 70 or so minerals in which the REEs have a more defined role, normally substituting for La, Ce or Y, *e.g.,* allanite $(Ce,Ca,Y)_2(Al, Fe^{2+},Fe^{3+})_3(SiO_4)_3OH$ and yttrofluorite $(Ca,Y)F_2$. The REEs all have similar chemical and physical properties, and act as a coherent series. Their ionic radius decreases with increasing atomic number - often referred to as the 'lanthanide contraction'. All the REEs, with the exception of Eu, have a charge of REE^{3+}, although Ce^{4+} can exist in certain oxidising conditions. Europium forms Eu^{2+} and behaves differently from the other REEs as it more readily substitutes for Ca^{2+} in plagioclase.

The REEs are commonly normalised rather than being presented as absolute values, the most common method being to normalise against abundance in chondritic meteorites (Nakamura 1974). By such means, it is possible to look at the patterns in REEs relative abundance to determine features, such as high-pressure or low-pressure formation. For example, garnet tends to accommodate the HREEs more than the LREEs, as do orthopyroxene and hornblende to a lesser extent; sphene and plagioclase tend to accommodate more LREEs. A pronounced dip in the REE pattern for Eu is observed (referred to as the 'Eu anomaly') in the presence of plagioclase due to the Eu^{2+} substitution for Ca^{2+}. The anomaly may be either positive or negative, depending on whether plagioclase was removed or accumulated during a rock's formation. In general, most mafic and ultramafic rocks do not contain significant Eu anomalies. Silicic rocks tend to contain predominantly negative Eu anomalies of varying size, although positive Eu anomalies are commonly observed in K-poor granitic rocks.

Taylor and McLennan (1985) cite the upper crustal abundance of the REEs as La 30 mg kg^{-1}, Ce 64 mg kg^{-1}, Pr 7.1 mg kg^{-1}, Nd 26 mg kg^{-1}, Sm 4.5 mg kg^{-1}, Eu 0.88 mg kg^{-1}, Gd 3.8 mg kg^{-1}, Tb 0.64 mg kg^{-1}, Dy 3.5 mg kg^{-1}, Ho 0.80 mg kg^{-1}, Er 2.2 mg kg^{-1}, Tm 0.32 mg kg^{-1}, Yb 2.2 mg kg^{-1} and Lu 0.32 mg kg^{-1}.

Although there is considerable overlap in the total REE content (ΣREE from La to Lu) of igneous ultramafic and mafic rocks of the continental crust, abundances tend to decrease in the order: carbonatite (72–15,515 mg kg^{-1}) > alkalic mafic rocks (69–1453 mg kg^{-1}) = alkalic intermediate and felsic rocks (92–1750 mg kg^{-1}) > alkali basalt (130–250 mg kg^{-1}) > tholeiite (10–322 mg kg^{-1}) > komatiite (10–59 mg kg^{-1}) (Henderson 1984). There is a tendency for the concentration of LREEs in mafic and ultramafic rocks to decrease relative to the concentration of HREEs with decreasing total REE content. Intermediate and silicilic igneous rocks tend to have generally lower, but more variable REE content and LREE/HREE composition. Henderson (1984) cites ΣREE concentrations of 25-341 mg kg^{-1}, 10-499 mg kg^{-1} and 8-1977 mg kg^{-1} for andesite, diorite and granite respectively.

The total REE abundance in sedimentary rocks tends to be lower than in igneous rocks. In general, REE content decreases with clay mineral and rock fragment content and increasing quartz content. The ratio of LREEs to HREEs also tends

to decrease in the same order. Wedepohl (1978) cites typical ranges of ΣREE in shale, greywacke, sandstone and limestone as 116–360 mg kg^{-1}, 100-190 mg kg^{-1}, 40-270 mg kg^{-1} and 18-55 mg kg^{-1} respectively.

Taylor and McLennan (1985) give the values of REEs in average shale as La 38.2 mg kg^{-1}, Ce 79.6 mg kg^{-1}, Pr 8.83 mg kg^{-1}, Nd 33.9 mg kg^{-1}, Sm 5.55 mg kg^{-1}, Eu 1.08 mg kg^{-1}, Gd 4.66 mg kg^{-1}, Tb 0.774 mg kg^{-1}, Dy 4.68 mg kg^{-1}, Ho 0.991 mg kg^{-1}, Er 2.85 mg kg^{-1}, Tm 0.405 mg kg^{-1}, Yb 2.82 mg kg^{-1} and Lu 0.433 mg kg^{-1}.

The relative rates of light and heavy REE mobilisation are subject to considerable contention (Burkov and Podporina 1967), but there is evidence that the latter may be preferentially leached on account of the greater stability of the fluoride and carbonate complexes with which they are generally associated (Balashov and Khitrov 1967).

Elevated REE values are generally indicative of felsic rocks, especially intrusives, and the soil and stream sediment derived from them.

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).

The behaviour of the REEs in river water has been studied quite extensively in the last two decades. In general, whilst there is often an inverse correlation between the REE concentrations and water pH, a more important control on REE abundance is the amount of particulate and colloidal-sized material commonly carrying the major load of the REEs. These colloidal and particulate fractions tend to be enriched in the light REEs and/or the middle REEs (Åström and Corin 2003). In contrast, the heavy REEs form more stable complexes than light REEs, particularly with carbonate, fluoride, hydroxide or sulphate anions in alkaline solutions, and they are thus more prone to hydrothermal mobilisation (Kosterin 1959, Åström and Corin 2003).

Complexation results in only a small fraction of each REE in circumneutral waters being present in the form of free hydrated REE ions (M^{3+}). For alkaline water with CO_2 partial pressures greater than or equal to that of the atmosphere, REE complexation is generally dominated by the carbonate complexes MCO_3^+ and $M(CO_3)_2^-$ (Luo and Byrne 2004). Tang and Johannesson (2003) applied a speciation model to world average river water, which predicted that organic matter complexes are the dominant form of dissolved REEs in bulk river water draining the continents. The model suggests that organic matter complexes would dominate La, Eu and Lu speciation within the pH ranges of 5.4–7.9, 4.8–7.3 and 4.9–6.9, respectively. For acidic water, the model predicts that the free metal ion and sulphate complexes dominate. Surface water concentrations for all the REEs are typically <1 μg l^{-1} (Neal and Robson 2000).

Anthropogenic sources of the REEs include mining and processing of alkaline rocks, petrol-producing industries and disposal of household electrical equipment. A wide range of the REEs are used in household appliances, such as colour televisions, fluorescent lamps, energy-saving lamps and glasses. Some are also used in the carbon arcs employed by the motion picture industry for studio lighting and projection, in the production of catalysers and to polish glass. Misch metal, used in making cigarette lighters, contains about 5% Pr. Promethium is used as a portable X-ray source. Europium-activated yttrium vanadate is in commercial use as the red phosphor in colour television tubes. Gadolinium is used in specialised magnetic applications. Natural sources of the REEs are, however, considered to be much more important than anthropogenic ones (Reimann and de Caritat 1998).

The REEs are considered to be biologically inactive and non-essential. Toxicological data for the REEs are relatively scarce, but their toxicity is generally considered to be moderate to low. REEs inhaled as dusts probably cause pneumoconiosis, and ingested REEs can accumulate in the skeleton, teeth, liver and lungs.

REEs 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 topsoil. The median Ce content is 53.7 mg kg^{-1} in subsoil and 48.2 mg kg^{-1} in topsoil, with a range from 1.04 to 379 mg kg^{-1} in subsoil and 2.45 to 267 mg kg^{-1} in topsoil. The other lanthanides (Table 1) have median values varying from 22.4 mg kg^{-1} for Nd to 0.31 mg kg^{-1} for Lu, decreasing with atomic number, but with somewhat higher abundance for even atomic numbers (Table available in electronic format on website). The average ratios topsoil/subsoil vary between 0.884 (Eu) and 0.947 (Lu) - see the discussion below.

All REEs in soil are strongly correlated among themselves, with all correlation coefficients higher than 0.7. The highest correlation coefficients are 0.995 for Nd-Pr (subsoil), and 0.991 for Ho-Er (topsoil). These pairwise neighbouring elements constitute the correlation nucleus for the two groups of REEs: the ceric LREEs - La, Ce, Pr, Nd, Sm and Eu; and the yttric HREEs - Gd, Tb, Dy, Ho, Er, Tm, Yb, Lu, and also Y (yttrium), which although not a lanthanide element, is generally known to show a geochemical behaviour similar to the HREEs.

The geochemical distribution patterns of most of the REEs in soil are, of course, very similar. However, it can be expected that Ce and Yb show two extremes in the natural occurrence of the REEs. Refer to the discussion of the Ce and Y soil distribution maps.

With only minor variations La, Pr, Nd, Sm and Eu in soil follow the Ce pattern, whereas Gd, Tb, Dy, Ho, Er, Tm and Lu follow the Yb pattern. Europeum patterns in soil are somewhat intermediate, since they follow the Yb pattern in Portugal, north-west Spain and Greece. There is no soil Eu anomaly near Mourne in northern Ireland. In France, REEs anomalies in subsoil underline better the loessic unit (with Zr), whereas in the topsoil, they reflect better the Variscan lithologies.

The ratios topsoil/subsoil show a general leaching of the REEs content in clay during pedogenesis (with topsoil more leached than subsoil), and this effect is stronger for the ceric LREEs subset, *i.e.,* the ratio is 0.905 for La, 0.899 for Ce, 0.897 for Pr, 0.896 for Nd, 0.888 for Sm, and 0.884 for Eu. For the HREEs subset the ratio varies between 0.897 (Gd) and 0.947 (Lu), gradually increasing with atomic number. It is remarkable that for such a large dataset, even this ratio obeys the systematic pattern expected of REEs behaviour, with figures following the sequence of atomic number in each subset (Table 4), decreasing for the LREEs towards Eu, but increasing for the HREEs away from Eu. Europeum is the element most affected by pedogenic processes. Probably in relation to this phenomenon, Eu has stronger correlations than the other REE with Fe, V, Sc, Ti, Mn, Al, Ga, Cu, *etc.*, especially in topsoil.

REEs in stream water

The REEs distribution is so dominant in one of the characteristic patterns of elemental distributions in European stream water that it is called the REEs distribution pattern. Many additional elements are associated with it, such as the lithophile elements Al, Be, (Cs), Fe, Hf, Mn, Nb(Ta), Rb, Th, Ti, (V), Zr, the siderophile elements Fe, Co and the chalcophile elements Bi, Cd, Ga, Ge, Mo, Pb, Tl, Zn. The stream water with high REEs is characterised by very low mineralisation, high acidity (low pH value) and high concentration of dissolved organic matter. Their origin and distribution are to a large degree controlled by exogenic factors: cold climate, especially high rainfall, nordic vegetation and mostly low topography. Their main distribution domain is Fennoscandia, Denmark, Scotland and north Ireland. Free cations are very subordinate, organic matter complexes are the dominant molecular species in stream water. In Alkaline stream water carbonate complexes are important. Geogenic supplies to high Ce concentrations in stream water are rare: two large regions of partly alkaline igneous and metamorphic rocks, the Armorican and Central Massifs in France, and a few small areas of only lightly enhanced values in Spain; and areas of young alkaline volcanism in Italy and, depending upon the element, elsewhere in Europe. Distribution patterns vary insignificantly from element to element. No

systematic difference between the LREEs and HREEs can be noticed.

A somewhat different pattern in stream water may be observed only for europium, the only REE that can exist in both +2 and +3 valence state. High Eu concentrations are situated only in the south of Fennoscandia, and higher concentrations appear also in eastern Ireland, south Spain and south Sardinia, south France, but not in the Central Massif, south Germany or the Sudetes in the Czech Republic. The distribution of Eu in stream water is complex, and it generally forms opposite trends to those observed in solid sample media, which is an additional indication of exogenic and not geogenic origin of stream water anomalies. Exceptions to the above observations are mentioned in the appropriate sections.

REEs in stream sediment

The median La content is 31.9 mg kg^{-1}, with a range from 1.3 to 553 mg kg^{-1}. The median Ce content is 65.1 mg kg^{-1}; with a range from 2.2 to 1080 mg kg^{-1}. The other lanthanides (Table 1) have median values ranging from 27.6 mg kg^{-1} for Nd to 0.38 mg kg^{-1} for Lu, decreasing with atomic number, but with 5 to 6 times higher abundance for even atomic numbers with respect to uneven neighbours (Table available in electronic format on website).

Since the light REEs (La, Ce, Pr, Nd and Sm) in stream sediment follow the Ce pattern with minor variations, these will be grouped here. Low LREEs values in stream sediment are present in 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, coastal Croatia, western and southern Greece.

The two most anomalous areas with high concentrations of light REEs in stream sediment 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 and southern Brittany to the north-west. In the southern part of the Massif Central, the highest values in stream sediment are associated with U, Sn and Ta, indicating hydrothermal alteration related to the late Variscan granitic phases. Part of the LREEs anomaly in this area may delineate the Permo-Triassic basal sandstone enriched in yellow and grey monazite from the Variscan granite and phosphatic layers in the Cambrian basement. High LREE 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 Germany), the Roman alkaline magmatic province, and point anomalies in south-eastern Austria, westernmost Austria (probably Variscan granite), the Canary Islands, and near the Mourne granite in northern Ireland.

Since the heavy REEs (Gd, Tb, Dy, Ho, Er, Tm, Yb and Lu) in stream sediment follow the same pattern with minor variations, they will be described together here. Low HREEs values in stream sediment are present in most of eastern Finland, the northern European plain, western Ireland, eastern Spain, the western Alps and northern Apennines to north-easternmost Italy, the Jura Mountains, a small area in central-eastern Italy, coastal Croatia, western and southern Greece.

High concentrations of the heavy REEs in stream sediment are found mainly in the Variscan part of the Iberian Peninsula, *i.e.,* Portugal and the Sierra de Gredos in Old Castilia (Spain), and the Massif Central in France (Variscan granite), extending into the Poitou region and southern Brittany to the north-west. High HREEs values in stream sediment also occur in all of Norway, most of Sweden, north-east Estonia (phosphate deposits), eastern Scotland, the Bohemian Massif (including a point anomaly near the U deposit of Dolny Rozinka in the central Czech Republic), Pannonian Croatia, eastern Slovakia, south-eastern Austria, westernmost Austria and eastern Switzerland, northern France, north-westernmost Galicia, Albania, the Canary Islands, and near the Mourne granite in northern Ireland.

In comparison with the LREEs, the patterns of HREEs and yttrium in stream sediment show that

Norway is slightly more anomalous, Britain and Portugal slightly less anomalous, and the anomaly of Bavaria-Bohemia is more extended into the central Alps. The other features are the same.

All Rare Earth Elements (REEs) in stream sediment are very strongly correlated among themselves and with yttrium, and most correlation coefficients are higher than 0.8. The only exception is Eu, which has correlations in the order of 0.6 to 0.7 with the other REEs. The REEs in stream sediment show a strong (>0.6) to very strong (>0.8) correlation with thorium, generally a strong correlation with uranium, and a good (>0.4) correlation with Zr, Hf, Ti, Nb and Ta. This points to the association of heavy minerals in stream sediment (monazite, xenotime, zircon, rutile and columbo-tantalite).

REEs in floodplain sediment

The distribution of REEs in floodplain sediment has been discussed in their individual sections, and below only some general features will be described. The statistical distribution of REEs elements in floodplain sediment shows the following characteristics with respect to the median and range of values (*in brackets*) (it is noted that figures were rounded where possible):-

- LREEs: $La_{(57)}$ 24.9 (*3-130*) mg kg^{-1}, $Ce_{(58)}$ 50.2 (*2-231*) mg kg^{-1}, $Pr_{(59)}$ 5.50 (*0.5-28*) mg kg^{-1}, $Nd_{(60)}$ 21.3 (*2-117*) mg kg^{-1}, $Sm_{(62)}$ 4.25 (*0.4-24*) mg kg^{-1};
- $Eu_{(63)}$ 0.87 (*0.1-4*) mg kg^{-1};
- HREEs: $Gd_{(64)}$ 3.92 (*0.2-23*) mg kg^{-1}, $Tb_{(65)}$ 0.60 (*0.02-3*) mg kg^{-1}, $Dy_{(66)}$ 3.45 (*0.2-20*) mg kg^{-1}, $Ho_{(67)}$ 0.68 (*0.5-4.5*) mg kg^{-1}, $Er_{(68)}$ 1.96 (*0.1-12*) mg kg^{-1}, $Tm_{(69)}$ 0.29 (*0.02-1.9*) mg kg^{-1}, $Yb_{(70)}$ 1.80 (*0.1-13*) mg kg^{-1}, $Lu_{(71)}$ 0.27 (*0.02-2.2*) mg kg^{-1}.

This arrangement of REEs, according to their atomic number (subscript), shows that in floodplain sediment, like in soil and stream sediment, there is a decrease in their abundance from La to Lu, with generally higher abundances for even compared to odd atomic number elements, verifying in fact the Oddo-Harkins (odd-even) effect (Fairbridge 1972, Marshall and Fairbridge 1999). Overall, the LREEs (La to Sm) are more abundant than the HREEs (Gd to Lu), with the break in the level of values becoming evident at Eu.

In general, the geochemical distribution patterns of the REEs in floodplain sediment are approximately similar, with minor variation between the LREEs and HREEs, but significant from the geological point of view. The whole of Norway, parts of Sweden and Estonia (phosphorite mineralisation) are comparatively more anomalous in the HREEs and Eu, in terms of the percentile grouping of values, than the LREEs. Especially in Norway, the HREEs and Eu patterns crosscut established lithological units ranging from felsic to mafic-ultramafic rocks, with the exception of the metamorphic sedimentary rocks of Proterozoic age in part of northern Norway. Other differences between the HREEs and LREEs are that the HREEs show a slightly more intensive and extensive anomaly in the lower part of the Seine River basin in France (an association with heavy minerals, see Zr map), whereas the LREEs are more anomalous almost over all Portugal and adjacent parts of north-western Spain, and in Brittany, France, where there is a relationship with felsic intrusives and mineralisation.

REEs comparison between sample media

Light Rare Earth Elements (LREEs) comparison between sample media

In general, there are broad similarities between all solid sample media. Topsoil is relatively low in LREEs 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 LREEs in stream sediment compared to other solid sample media (possibly removal of fine-grained material from the residual soils and karst). In stream and floodplain sediments, higher LREEs

concentrations are observed in southern and northern Norway and south-western Finland compared to soil. In stream sediment, northern Estonia shows two point anomalies of LREEs absent in other solid sample media, possibly related to the phosphorite lower-Palaeozoic sediments. Central and northern Britain show high LREEs in stream sediment only. In parts of Sweden and Wales, floodplain sediment is enriched in LREEs compared to other solid sample media. In the alkaline volcanic province of Italy, and parts of western Greece, LREEs are low in sediments compared to soil.

The spatial distribution of LREEs in stream water is complex, but generally shows 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. LREEs solubility is strongly controlled by acid pH and the presence of DOC and, therefore, the highest concentrations are observed throughout Fennoscandia.

Heavy Rare Earth Elements (HREEs) comparison between sample media

In general, there are broad similarities between all solid sample media. Topsoil is relatively low in HREEs compared to subsoil in parts of Norway and Sweden, and richer in the alkaline province of Italy and central and south-western Spain, but patterns between topsoil and subsoil are otherwise virtually identical. Coastal Croatia and Slovenia and central parts of Austria are low in HREEs in stream sediment compared to other solid sample media (removal of fine-grained material from the residual soils and karst). In stream and floodplain sediments, higher HREEs concentrations are observed throughout Norway, most of Sweden and Estonia compared to soil. In stream sediment, northern Estonia shows two point anomalies of HREEs, possibly related to the phosphorite lower-Palaeozoic sediments, and the whole of Estonia is anomalous in floodplain sediment. Scotland shows high HREEs in stream sediment only, and Wales is enhanced in floodplain sediment. In stream sediment, the Central Massif of France and central Spain, are enhanced in HREEs compared to all other solid sample media. In the alkaline volcanic province of Italy, and parts of western Greece, HREEs are low in sediments compared to soil.

The distribution of HREEs in stream water generally forms opposite patterns to those observed in solid sample media, although many data are below the limit of detection, so comparison is difficult. HREEs solubility is strongly controlled by acid pH and the presence of DOC, and highest concentrations are observed throughout southern Fennoscandia.