Rb – Rubidium

Introduction

Rubidium is a member of the alkali metal group 1 of the periodic table, along with Li, Na, K and Cs. The element has an atomic number of 37, an atomic mass of 85, one oxidation state (+1) and two naturally occurring isotopes (^{85}Rb and ^{87}Rb), of which ^{85}Rb is the most abundant at 72% of the mass. Its chemical properties resemble those of other members of the alkali metal group.

Rubidium is a lithophile metallic element that does not form any minerals of its own, but is present in several common minerals in which it substitutes for potassium. Compared with K and Na, Rb is relatively rare, with a crustal abundance of just 78 mg kg^{-1} (Fyfe 1999). The Rb$^+$ ion (ionic radius 152 pm) substitutes for K$^+$ (138 pm) in mica such as muscovite and, to a lesser extent, in K-feldspar such as microcline and orthoclase, as well as rarer minerals, such as lepidolite, carnallite and pollucite, in which it replaces Cs. However, because Rb$^+$ has a larger ionic radius and, therefore, behaves incompatibly, it becomes concentrated in late stage differentiates in magmatic systems. Pervasive redistribution of Rb has been reported during deuteric and hydrothermal alteration of granite plutons (Bailey and Macdonald 1975; O'Brien *et al.* 1985). It is also associated with greisen-type Sn deposits (Pokorny 1975) and is found enriched in most ore zones of porphyry-copper deposits (Armbrust *et al.* 1977). The values quoted by Mielke (1979) are: ultramafics 0.2 mg kg^{-1}; basaltic 30 mg kg^{-1}; granitic 110–170 mg kg^{-1} and syenite 110 mg kg^{-1}. The K:Rb ratio provides an important petrogenetic index, generally decreasing with magmatic evolution (Shaw 1968). In metamorphic rocks, the distribution of Rb is largely controlled by the stability relationships of K-bearing phyllosilicate minerals (biotite and muscovite); breakdown of these minerals, coupled with the high solubility of Rb in aqueous solutions, may account for its strong depletion in medium to high pressure granulite-facies rocks (Simmons 1999a).

In sedimentary rocks, Rb is present mainly in K-feldspar, mica and clay minerals. The average Rb content of arkose and feldspathic sandstone (>60 mg kg^{-1}) is, therefore, higher than that of pure quartzite (<45 mg kg^{-1}) or dolomite (30-60 mg kg^{-1}). During weathering, ion exchange and differential adsorption mechanisms tend to concentrate Rb relative to K (Heier and Billings 1970). Many types of shale and mudstone thus have high levels of Rb (*ca.* 160 mg kg^{-1}) mainly held in clay minerals, such as illite and montmorillonite, leading to lower K:Rb ratios than those of igneous rocks. Mielke (1979) cites levels of Rb in shale, sandstone and carbonates as 140, 60 and 3 mg kg^{-1} respectively. The average value of Pb in loess is given as 85 mg kg^{-1} (McLennan and Murray 1999). Rubidium may be used as a pathfinder in geochemical prospecting for Rb-rich pegmatite intrusions. Because of its strong association with K, elevated Rb values may indicate the presence of felsic rocks, especially kaolinised intrusives.

In the surface environment, rubidium forms water-soluble compounds with common anions and radicals, such as acetate, carbonate, halide, oxide, nitrate, sulphate and sulphide (Butterman and Reese 2003). Despite the stability and solubility of Rb$^+$ and its compounds, it displays low environmental mobility, mainly due to its very strong sorption by clay minerals such as illite. Rubidium is most readily sorbed by clay minerals at high pH, so in alkaline stream environments any clay fraction of the sediment is likely to be higher in Rb than more acidic stream channels. Rubidium is also more strongly sorbed by clay minerals than is potassium, and Rb may, therefore, be enriched relative to K_2O in mudstone.

In soil, the behaviour of Rb is controlled mainly by adsorption on clay minerals and organic matter. An interesting observation is the decrease of the K:Rb in the progressive development of soil, a feature which is due to its stronger bonding in silicate minerals than K (Kabata-Pendias 2001).

The concentration of Rb in fresh surface water is typically 1–1.5 µg l^{-1}. Sea water contains 120 µg l^{-1} Rb, and mineral water of geothermal origin may contain Rb concentrations of 150 µg l^{-1} to a few mg l^{-1} (Hem 1992). Average levels of Rb in river particulates is reported as 100 mg kg^{-1} (McLennan and Murray 1999).

Before the 1920s, there were virtually no industrial applications for Rb but, since then, it has been used in vacuum tubes, photocells and in medical applications, for instance as an antidepressant akin to Li. Anthropogenic sources of Rb in the environment include glass dust, but generally geogenic sources are considered to be more important than anthropogenic ones (Reimann and de Caritat 1998).

Rubidium is considered to be biologically non-essential, and it is the most abundant element in the body (0.68 g in a 70 kg person) that has no known major biological role. There is, however, some evidence that Rb can substitute in microbial metabolism for K, and that it may be involved with neuro-pathway mechanisms (Mertz 1987). It is thought to be of relatively low toxicity, but it is rapidly and highly absorbed by the human body. No negative environmental effects have been reported.

Table 55 compares the median concentrations of Rb in the FOREGS samples and in some reference datasets.

Table 55. Median concentrations of Rb in the FOREGS samples and in some reference data sets.

Rubidium (Rb)	***Origin – Source***	***Number of samples***	***Size fraction mm***	***Extraction***	***Median mg kg^{-1}***
Crust[1)]	Upper continental	n.a.	n.a.	Total	84
Subsoil	**FOREGS**	**788**	**<2.0**	**Total (ICP-MS)**	**82.5**
Topsoil	**FOREGS**	**845**	**<2.0**	**Total (ICP-MS)**	**80.0**
Soil[2)]	World	n.a.	n.a.	Total	65
Humus	**FOREGS**	**367**	**<2.0**	**Total (ICP-MS)**	**4.5**
Humus[3)]	Barents region	1357	<2	Total (HNO_3, ICP-MS)	7.24
Water	**FOREGS**	**807**	**Filtered <0.45 µm**		**1.32 (µg l^{-1})**
Water[4)]	World	n.a.	n.a.		2 (µg l^{-1})
Stream sediment	**FOREGS**	**852**	**<0.15**	**Total (XRF)**	**70.0**
Floodplain sediment	**FOREGS**	**747**	**<2.0**	**Total (XRF)**	**71.0**
Stream sediment[5)]	Canada	26 227	<0.18	Total (INAA)	68

[1)]Rudnick & Gao 2004, [2)]Koljonen 1992, [3)]Salminen *et al.* 2004, [4)]Ivanov 1996, [5)]Garret 2006.

Rb in soil

The median Rb content is 83.0 mg kg^{-1} in subsoil and 80.0 mg kg^{-1} in topsoil, with a range from 5 to 378 mg kg^{-1} in subsoil and <2 to 390 mg kg^{-1} in topsoil. The average ratio topsoil/subsoil is 0.965.

In subsoil, low Rb values (<56 mg kg^{-1}) occur in northern Fennoscandia, Ireland, the glacial drift area from the Netherlands to Poland, central Hungary, Sicily, parts of Greece, and south-east Spain. The southern limit of the glacial drift covered area through Germany and Poland is well marked on the map, with low values north of it.

The subsoil distribution map shows high Rb values (>110 mg kg^{-1}) in parts of Sweden and southern Norway, in Latvia, south-west England, central Germany, an area from the French Massif Central (two-mica granite is known to be enriched in K, Rb and Cs) to Brittany, the Alps near the Austrian-Italian border, the western Iberian Peninsula, especially the felsic rocks of northern Portugal, the eastern Pyrenees, Corsica, and a few points in the Roman and Neapolitan magmatic alkaline province of Italy. These high rubidium areas are underlain by igneous felsic rocks rich in feldspar and mica, or sediments and metamorphic rocks derived from them. Contrary to K, Rb is also higher in coastal Croatia, Slovenia and southern Austria, in residual soil on karst.

The topsoil Rb map is very similar to that of the subsoil. The eastern Pyrenees show a more extensive anomalous area (granitic rocks and schist), but this is a sampling bias because fewer subsoil samples were collected. Southern Italy has a higher Rb content in topsoils, which may be related to secondary mobility and subsequent adsorption on clay minerals in a dry climate. Still in topsoil, Rb levels are lower in Latvia and south-eastern Sweden, probably due to increased mobility (leaching), but without subsequent adsorption on clay. The ratio topsoil/subsoil is 0.96 for Rb, with northern Europe being relatively more depleted in topsoil.

Rubidium substitutes for potassium in silicate minerals, and shows very similar distributions in soils, except for lower Rb values over Fennoscandia. The correlation K-Rb is very strong, 0.83 in subsoil and 0.82 in topsoil. In subsoil, there is also a strong correlation (>0.6) with Be, Al, Ga, In, Nb, Ta, Th, U, Cs, Tl and most of the REEs, and a good correlation (>0.4) with Ba, Sn, Pb, Bi, Ag, Y and the remaining REEs. The pattern is similar in topsoil, but correlation of Rb is stronger with Tl (0.82)

Rb in humus

The median Rb content in humus is 4.50 mg kg^{-1}, and the range varies from 0.20 to 41.7 mg kg^{-1}.

The Rb distribution map shows that low Rb in humus (<2.40 mg kg^{-1}) is present in the glacial drift covered area of northern mainland Europe (Netherlands to Poland), Slovakia, south-central Germany, most of Britain, Ireland, western France and parts of eastern France.

High Rb values in humus (>7.50 mg kg^{-1}) are found in most of northern and central Sweden; south-central Finland; west-central Norway; the Czech Republic; northern Italy and adjacent parts of Austria and Switzerland, extending into the French Jura and the Black Forest in Germany; and the Central Massif in France.

The Rb distribution pattern in humus shows some similarity with the corresponding soil maps, and is probably of mainly geogenic origin, reflecting geological substrates with high K-content (and hence high Rb-content). Some exceptions occur, *e.g.,* Brittany in France has high Rb in soil, but is low in humus. The opposite is true in south-eastern Finland. In the western Czech Republic, high Rb in humus may be the result of coal burning with subsequent atmospheric deposition.

Rubidium in humus has a good correlation with Ga (0.47), and a weak correlation with Co (0.37) and Ni (0.34). These are also elements with a strong geogenic component in humus.

Rb in stream water

Rubidium values in stream water range over three orders of magnitude, from <0.1 to 112 µg l^{-1}, with a median value of 1.32 µg l^{-1}. Rubidium data tend to correlate most closely with K, but with marked differences in southern Spain and southern Finland.

Lowest Rb values stream water (<0.5 µg l^{-1}) are found throughout northern and western parts of Fennoscandia, western Scotland and Wales, most of Spain, southern France, northern Italy, central Austria, southern Germany, Albania and most of Greece. The low values are associated with a range of lithologies, foremost among them is limestone in Mediterranean and mountainous areas.

Enhanced Rb concentrations stream water (>3.35 µg l^{-1}) are found in central and southern Britain, Belgium, the Netherlands, the northern tip of Germany and Denmark, Brittany, north-west Spain, central and eastern France, parts of east Germany, western Poland, Slovakia and northern Hungary. In Italy, similarly to K, the highest Rb values are associated with alkaline volcanics and accompanying hydrothermalism in the Roman and Neapolitan magmatic provinces and Sardinia and southern Sicily. However, the anomaly over the Apulia area in south-eastern Italy is associated with agricultural influences. In general, high Rb data are associated with a variety of geogenic sources but, especially in the area that extends across south-east Britain, across northern mainland Europe and towards Hungary, are also strongly associated with agricultural input from potassium-rich fertilisers. This is also true for an isolated Rb anomaly in south-west Hungary. A point anomaly in southern Spain can be explained by Triassic shale and evaporite, also containing much K.

The rubidium distribution in stream water in Europe follows three pattern types: the REE high-DOC acidic stream water type, the Major-ions high-mineralisation stream water, and the Felsic-rocks stream water type. For the first type, in Sweden and Norway, higher Rb in stream water seems to reflect patterns in soil and sediment, but not in Denmark, north Germany, Netherlands and Scotland. Rubidium related to Major-ions high-TDS stream water and to Felsic-rock stream water is high in north Germany and the Netherlands, south-east Britain, Slovakia, Hungary and Sicily; in none of these areas Rb is abundant in solid sample media. However, high Rb in stream water in the Italian volcanic province, Sardinia, Armorican and Central Massifs of France, north-west tip of Spain, Black Forest and Erzgebirge in Germany, Czechia, Slovakia, and part of Hungary, appear to be geogenic, generated by high Rb concentrations in soil, sediments, and presumingly rocks.

Rb in stream sediment

Rubidium has a median value in stream sediment of 70 mg kg^{-1}, and range from 2 to 339 mg kg^{-1}.

Rubidium shows low stream sediment values (<47 mg kg^{-1}) in northern Finland, central Norway, western calcareous Ireland, the northern European plain, north-western, south-western and eastern France, northern Italy, central Austria and central Hungary, southernmost Spain, and the Greek island of Crete.

High Rb values in stream sediment (>97 mg kg^{-1}) are found mainly in areas with granitic and alkaline bedrock, over the western Iberian Peninsula, especially northern Portugal and Galicia, the Massif Central in France, the eastern Pyrenees, the Roman Alkaline Province and southern Italy, Corsica and Sardinia (Variscan granite), south-west England (Variscan granite in Devonshire), and in a point anomaly in northern Ireland over the Tertiary Mourne granite. The Bohemian Massif, the central Alps, Lorraine and Black Forest, parts of central Sweden, and southern Finland (clay-rich Holocene marine sediments) are also high in Rb.

The overall Rb pattern in stream sediment is similar to that of K_2O, except over the Baltic Shield where Rb is generally much lower. The correlation Rb-K is very strong (0.86). Rubidium in stream sediment also shows a strong correlation (>0.6) with Be, Cs, Tl, Al and Ga, and a good correlation (>0.4) with Li, Ba, Ta, Nb, Sn, Th, U, Ce and La.

Rb in floodplain sediment

Total Rb values in floodplain sediment vary from 7 to 536 mg kg^{-1}, with a median of 71 mg kg^{-1}.

Low Rb values in floodplain sediment (<46 mg kg^{-1}) occur over the glacial drift covered region extending from north Germany to Poland; the amphibolite belt of central Norway, and the greenstone belt of the Finnmark region; the northern half of Ireland with schist, gneiss and basalt; north-east England with mainly limestone; and southern Scotland with mainly limestone, shale, quartzite and basalt; the lower alluvial basins of Garonne and Rhône rivers in France; parts of calcareous southern and eastern Spain; the molasse basin of central Austria; the karst limestone and flysch of the Dalmatian coast in Croatia; the ophiolite and calcareous rocks of Albania and Greece.

High Rb values in floodplain sediment (>97 mg kg^{-1}) occur over the granite, granodiorite and gneiss terrains of south Norway, Sweden and south Finland; south-west England granite; the Poitou in France; the felsic intrusive areas of central and northern Portugal, Galicia and central Iberian Meseta in Spain; the easternmost Pyrenees, Massif Central in France, Vosges and Black Forest, Harz Mountains, Erzgebirge, Bohemian Massif (durbachite melasyenite occurrence in south-east Bohemia), central Swiss Alps, the bordered area of Austria-Czech Republic-Slovakia-Hungary, and the eastern Pannonian Basin in south-eastern Hungary with derived felsic volcanic material from the Apuseni Mountains in Romania; the alkaline volcanic and granitic rocks of Sardinia and Corsica, the Roman Alkaline Province, alkaline granitic rocks in

Calabria and eastern Sicily (Na-alkaline volcanics), and the granite-granodiorite-gneiss of central Macedonia and Thrace in north-east Greece.

The highest value in floodplain sediment, with 536 mg kg^{-1} Rb, occurs in Cornwall, south-west England (St. Austell granite); this sample is an outlier for Ga and Ta and it is anomalous for Al, Li, Cs, Nb, Sn, W and Tl; it may be the result of pollution related to Sn mining in alkaline-granitic rocks. Another point anomaly of 351 mg kg^{-1} Rb in floodplain sediments occurs in south-west England and is related to the Dartmoor granite.

Rubidium in floodplain sediment shows a very strong correlation with K_2O (0.89) and with Th (0.85), a strong correlation with Al_2O_3, Ga, Tl, Nb, Ta, Be, U, Ce, La, and a good correlation with Ti, Li, Cs, W, Sn, Y and the remaining REEs.

It is concluded that the distribution map of Rb in floodplain sediment reflects the geochemical differences of the lithology quite well, since it is related to the potassium distribution. It also maps areas related to mining pollution.

Rb comparison between sample media

Patterns in Rb distribution between all solid sample media are very similar, although data in floodplain sediment tends to be lower over the eastern Pyrenees compared to the other solid sample media. Rubidium is also lower in stream sediment throughout Croatia, Slovenia, southern Austria (possibly removal of fine-grained material from the residual soils) and southern Norway compared to other solid media. A boxplot comparing Rb variation in subsoil, topsoil, stream sediment and floodplain sediment is presented in Figure 36.

The distribution of Rb in humus reflects mineral content, and patterns are similar to those observed in solid sample media in most of Fennoscandia, the Baltic states and throughout the Quaternary area of northern mainland Europe. South of this area, no correspondence is visible between the distributions in humus and the solid sample media, probably because the humus samples are very heterogeneous and contain varying amounts of mineral matter.

Stream water Rb data show similar trends to solid sample media in some areas, and totally different trends in other areas. Throughout south-eastern England and an area extending from

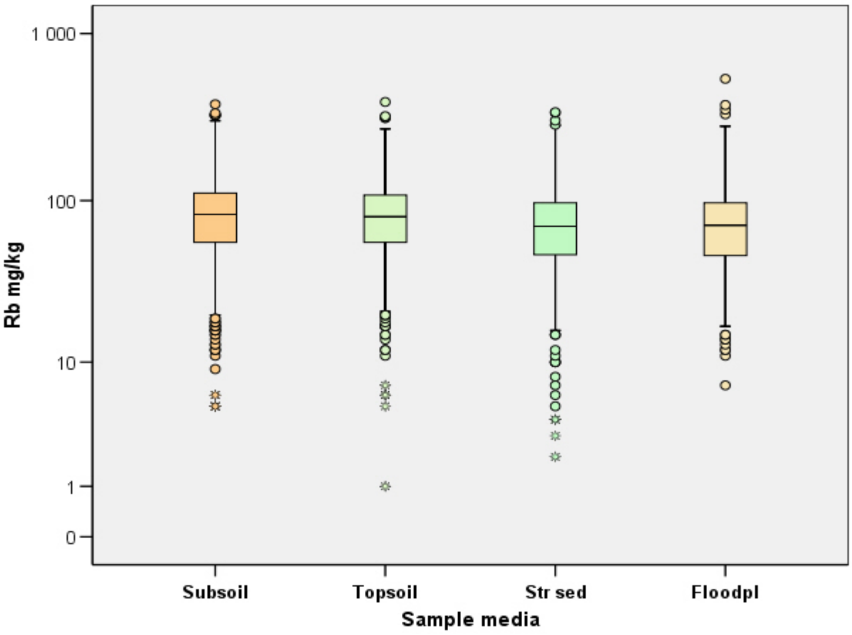

Figure 36. Boxplot comparison of Rb variation in subsoil, topsoil, stream sediment and floodplain sediment.

Belgium through Denmark and, to a lesser extent, the Quaternary area of northern mainland Europe, stream water Rb is relatively higher than in solid sample media. Stream water Rb is however, relatively lower than solid sample media throughout most of the northern central and western Iberian Peninsula, throughout the Alpine region, Slovenia, Croatia, Albania and Greece. Rubidium distributions throughout Fennoscandia, the Baltic states, Brittany and Central Massif areas of France, parts of central Italy (connected to alkaline hydrothermal volcanic activity) are similar in all sample media.