Be – Beryllium

Introduction

Beryllium is the lightest of the group 2 elements that include Mg, Ca, Sr and Ba, although its chemistry has little in common with these more typical alkaline earth metals. The element has an atomic number of 4, an atomic mass of 9, one oxidation state (+2) and one naturally occurring isotope (^{9}Be).

Beryllium is a lithophile element and occurs in the Earth's crust at concentrations ranging from 1 to 3 mg kg^{-1} (Ryan 1999). The small size of the Be^{2+} ion (35 pm) implies that Be behaves incompatibly during early magmatic fractionation. This, and the instability of Be complexes at high temperatures, means that Be becomes concentrated in evolved granite and pegmatite (Ure and Berrow 1982). Beryllium is most highly concentrated in beryl and chrysoberyl, but the more abundant micaceous minerals, such as muscovite, are of greater importance with respect to its overall distribution in the lithosphere (Wedepohl 1978). Remobilisation of Be into secondary mica, topaz and fluorite may occur during hydrothermal processes, and as a result of metasomatism (Ure and Berrow 1982). Elevated Be values may indicate the presence of felsic intrusives.

In sedimentary rocks, Be levels are commonly intermediate between those for mafic and felsic igneous rocks, which are 1 and 5 mg kg^{-1} respectively (Reimann and de Caritat 1998). The Be concentration in sedimentary rocks generally reflects the presence of micaceous material and secondary clays. Clay minerals weathered from alkaline rocks have been reported to contain up to 100 mg kg^{-1} Be, while values of 60 mg kg^{-1} have been recorded in bauxite (Ure and Berrow 1982). The high Be content of most coal deposits (Ure and Berrow 1982), and the prevalence of inverse relationships between Be and coal ash content in numerous sedimentary lithologies (Wedepohl 1978), reflect the strong affinity of Be for organic matter. McLennan and Murray (1999) quote an average value for loess as 2 mg kg^{-1} Be.

In the surface environment, beryllium occurs mostly as the divalent cation, but complex ions such as $(BeO_2)^{2-}$, $(Be_2O_3)^{2-}$, $(BeO)^{6-}$ and $(Be_2O)^{2+}$ are also known (Kabada-Pendias 2001). Since the ionic radius of Be^{2+} is closest to Al^{3+}, it may substitute for Al in crystal lattices, and is therefore strongly bound to montmorillonitic clays (Marshall and Fairbridge 1999, Kabata-Pendias 2001). In soil, Be is present mainly in oxidic-bonded forms, and in alkaline environments forms complex anions, such as $Be(OH)CO^{3-}$ and $Be(CO_3)_2{}^{2-}$. Beryllium is highly soluble in acid forest soil (pH 3.4), suggesting a potential environmental hazard in temperate climatic regions. Generally, Be tends to be leached from topsoil and accumulates in subsoil. The concentration of Be in soil solutions varies from 0.4 µg l^{-1} to 1.0 µg l^{-1} Kabata-Pendias (2001). Average Be content in unpolluted topsoil ranges from 0.35 to 3.52 mg kg^{-1} according to Kabata-Pendias (2001), although Taylor (1964) cites a value of 6 mg kg^{-1}.

The most abundant Be minerals are highly insoluble in solutions formed during chemical weathering; thus, the Be content of surface water is very low, typically 0.5 to 17 µg l^{-1}. It is probably transported as fluoroberyllate (Me^+BeF_3 or $Me_2{}^+BeF_4$), since beryllates, chloroberyllates and carbonatoberyllates are unstable in aqueous solution at circumneutral pH. Its solubility increases with decreasing pH, however, and in areas affected by acid precipitation, surface water concentrations may reflect the Be concentrations of the underlying bedrock (Navratil *et al.* 2002). Beryllium is characterised by high ionic potential, and in surface water it is associated with finely dispersed particles, such as clay minerals, hydroxides and organic matter. It is easily removed from acidic solutions, *e.g.,* mine water, by co-precipitation with iron and manganese hydroxides and by co-precipitation with humic acids from solutions at pH 7.

According to the USEPA (1987), beryllium is released from coal combustion into the atmosphere at concentrations of up to 0.1 ng m^{-3}. Beryllium has many industrial uses that may contribute to anthropogenic pollution, *e.g.,* in brake systems of airplanes, for neutron monochromatisation, as window material for X-ray tubes, in radiation detectors, and in the electronics industry as a substrate for transistors and silicon chips, coil cores and laser tubes (Zorn *et al.* 1988).

The divalent Be^{2+} ion is toxic to both humans and animals; micromolar concentrations of Be^{2+} are known to inhibit certain enzymes. Virtually all Be compounds exhibit significant pulmonary toxicity, the most common form of exposure being through inhaled dusts and vapours (ATSDR 2006). Beryllium itself is not biotransformed, but inhaled Be is absorbed slowly and localises, due to transformation of soluble Be to insoluble compounds, in the lungs, bone, liver and kidneys (Stiefel *et al.* 1980, Zorn *et al.* 1988). Epidemiological studies have also suggested that Be and its compounds may be carcinogenic (Berg and Burbank 1972). The monitoring of Be in the environment is important, because of its possible harmful effects on aquatic biota and root systems of plants.

Table 12 compares the median concentrations of Be in the FOREGS samples and in some reference datasets.

Table 12. Median concentrations of Be in the FOREGS samples and in some reference data sets.

Beryllium (Be)	*Origin – Source*	*Number of samples*	*Size fraction mm*	*Extraction*	*Median mg kg^{-1}*
Crust[1)]	Upper continental	n.a.	n.a.	Total	2.1
Subsoil	**FOREGS**	**790**	**<2.0**	**Total (ICP-MS)**	**<2.0**
Topsoil	**FOREGS**	**843**	**<2.0**	**Total (ICP-MS)**	**<2.0**
Soil[2)]	World	n.a.	n.a	Total	3
Water	**FOREGS**	**807**	**Filtered <0.45 µm**		**0.009 (µg l^{-1})**
Water[3)]	World	n.a.	n.a.		0.1 (µg l^{-1})
Stream sediment	**FOREGS**	**848**	**<0.15**	**Total (XRF)**	**1.44**
Floodplain sediment	**FOREGS**	**743**	**<2.0**	**Total (XRF)**	**1.20**

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

Be in soil

More than half the soil samples have a Be content below the detection limit of 2 mg kg^{-1} (ICP-MS analysis). The maximum Be content is 17.7 mg kg^{-1} in subsoil, and 18.4 mg kg^{-1} in topsoil. The average ratio topsoil/subsoil is 0.904.

As expected, the Be distribution in soil shows large areas with values below the detection limit. For subsoil, these include most of Greece, Albania, Sicily, eastern (calcareous) Spain, the western Alps and northern Appenines, the sandy plains of France, through Benelux, Germany, Denmark, Poland, the Baltic States, eastern Austria, Hungary, most of Great-Britain, Ireland, and large parts of Scandinavia seemingly unrelated to the geological substrate of felsic and intermediate crystalline rocks.

The most prominent anomalous Be areas in subsoil (>5 mg kg^{-1}) are the Massif Central in France (where younger leucogranite is typically enriched in Be, Li, Sn, Nb, B and As), the Roman and Neapolitan magmatic provinces in Italy, northern Portugal, western and northern Spain (especially over leucogranite and evolved granitic facies in the central range of the Iberian Massif). Granitic and alkaline intrusive rocks are responsible for these anomalies. There is a point anomaly near the Mourne granite in Northern Ireland. In south-east Finland rapakivi granite with Be minerals are found. A point anomaly in northern Finland can be linked to the high clay content of the old weathered residual subsoil.

In topsoil, the distribution pattern is very similar to that of the subsoil, but the values in Britain and Scandinavia are generally more depressed, and below the detection limit. The average ratio of topsoil/subsoil is 0.904 for Be, indicating a slight depletion in topsoil.

Beryllium in subsoil has a strong correlation (>0.6) with Rb, Tl, Ta and Th, and a good correlation (>0.4) with Cs, Bi, Pb, Ag, Sn, U, K, Al, Ga, In and the lighter REEs (Ce, La, Pr, Nd, Sm, Gd, Tb). With minor variations this is also the pattern of correlations in topsoil; the correlation with Ag is only 0.26 in topsoil.

Be in stream water

Beryllium values in stream water range over two orders of magnitude, from <0.005 to 0.65 µg l^{-1} (excluding an outlier of 2.72 µg l^{-1}), with a median value of 0.009 µg l^{-1}. About 30% of the values are below the limit of quantification of <0.005 µg l^{-1}. The continental pattern of the Be distribution is similar to that of the REEs and associated elements, with the imprint of climatic zonality. In southern Fennoscandia, high Be concentrations are related to acid pH and high DOC content. With respect to patterns observed in solid sample media, Be in stream water shows both similarities and differences, indicating predominance of either a lithology- or rainfall-dominated origin of the element in stream water.

Lowest Be values in stream water (<0.005 µg l^{-1}) are found throughout Spain, eastern France, Switzerland, northern Italy, central and eastern Austria and western Slovenia, southern Italy (including the islands), Albania and all Greece, in Hungary, Slovakia and eastern Croatia, in western Ireland, eastern England and Scotland, and, in a belt from northern France to the Netherlands, north-eastern Germany, and in Lithuania and Latvia, in western Norway and northern Fennoscandia.

High Be concentrations in stream water (>0.04 µg l^{-1}) are found in Brittany and central areas of France on Variscan terrains (connected with Late Hercynian peraluminous leucogranite intrusives), in north-eastern Scotland on Scottish Caledonides terrains, in different areas of Germany (at the border with eastern France, along the border with the Czech Republic, central and northern areas) on Variscan terrains, in southern Fennoscandian countries and Denmark on Precambrian terrains, and in central western Italy on alkaline volcanic terrains (Roman-Tuscan province). In Finland, Be concentrations are generally higher in the south and south-west (Proterozoic area) compared to the Archean basement. Beryllium levels tend to be elevated in areas where younger Be-rich granite occurs and concentrations of lanthanides are high. On the west coast of Finland (near the city of Vaasa) concentrations of Be (and other trace elements) are high due to acid sulphide soil. Higher Be values in southern Sweden probably derive from younger granites. In Northern Ireland, the anomalously high Be data are associated with the Mourne granite and thick drift peat cover giving rise to acid waters resulting in the release of trace metals into solution. All the remaining parts of Europe show concentration values in the range between 0.005 and 0.04 µg l^{-1}.

Two isolated stream water Be anomalies in northern Germany are characterised by low pH and high DOC, Al, and high REEs in stream water, but low Be values in solid samples. A high Be value in Germany close to the French border in water and stream sediment, with low pH, may be influenced by granitic rocks of the Black Forest. Also in Germany, an isolated anomaly west of the Czech border in stream water and stream sediment, with low pH, may be associated with granitic rocks of the Bohemian Massif. High Be values in stream water and stream sediment in the Erzgebirge (German-Czech border) are heavily influenced by lignite mining and power plants using lignite; the sample near the German-Czech-Polish triangle lies just west of a Polish power plant, and is also high for bismuth in stream water.

Be in stream sediment

The median Be content in stream sediment is 1.42 mg kg^{-1}, with a range between <0.02 and 18.7 mg kg^{-1}.

The Be distribution map shows low stream sediment values (<0.78 mg kg^{-1}) prevailing over northern and south-central Finland, Estonia, Latvia, Poland, northern Germany, Denmark, the Netherlands, northern France, the western Alps and the Rhône valley in France, southern Spain, north-eastern Italy, eastern Croatia, and Albania.

High Be values in stream sediment (> 2.48 mg kg^{-1}) occur throughout northern Portugal and neighbouring Spain (granite, leucogranite, alkaline rocks of the Iberian Massif), the northern part of the Massif Central in France (leucogranite), the eastern Pyrenees (granodioritic rocks), the Roman and Neapolitan volcanic provinces in central and southern Italy, the Bohemian Massif and Slovakia, Lithuania (adsorbed by calcareous clay minerals, in particular Ca-type montmorillonite), northern Norway and adjacent Sweden and parts of central and southern Sweden, and a point anomaly near the Mourne granite in northern Ireland. Felsic and alkaline bedrock accounts for most of the high values. Point anomalies occur in France and Germany. On the northern margin of the Massif Central (Marche and Morvan areas) in France, high Be values in stream sediments are inherited from the basal Triassic sandstone enriched in heavy minerals.

Beryllium in stream sediment has a strong positive correlation with Rb (0.70), a good correlation (>0.4) with Li, Ta, Tl, Al, Ga, K, Cs and U, and a weak correlation (between 0.3 and 0.4) with Y, Ce, La, Nb and Th.

Be in floodplain sediment

The Be distribution in floodplain sediment varies from <0.02 to 47.5 mg kg^{-1}, with a median of 1.2 mg kg^{-1}.

Low Be values in floodplain sediment (<0.69 mg kg^{-1}) occur in the glacial drift covered area extending from north Germany to Poland and the Baltic states. Further low Be values are found in eastern Finland, central Sweden, south-east England, parts of the Paris, Garonne and Rhône river basins in France, and eastern Spain (alluvial fan of the Ebro delta, coastal plain of Valencia and La Mancha region).

High Be values in floodplain sediment (>1.9 mg kg^{-1}) are found in the mineralised granitic areas of south Finland, south and south-east Sweden and south Norway; Wales, most of England, and southern Scotland; the crystalline Armorican Massif in north-west France (Echassieres Li-Sn-Be-Ta), central France (derived from rivers draining the granitic northern Massif Central); an extensive zone in the Iberian Peninsula over Al-rich rocks of central and north Portugal, into Galicia (Renouta and Santa Comba deposits), Asturias (Reocin deposit), Cantabria and western Pyrenees in Spain; the Swiss, Italian and Austrian Alps, north Hungary, the Slovak Ore Mountains, Bohemian Massif to the Erzgebirge; also in northern Sardinia (calc-alkaline and shoshonitic volcanics), and central-west Italy (Roman Alkaline Province); central Macedonia and Thrace in Greece with granite and gneiss lithologies and mineralisation. Rather high is also the value on the basalt of the Canary islands.

Three outliers of Be occur in the granitic areas of northern Portugal (47.5 mg kg^{-1}) and Galicia (21.8 and 15.3 mg kg^{-1}) in Spain.

The high Be values in floodplain sediment samples N37E08F1 (9.94 mg kg^{-1}) and N36E10F5 (8.63 mg kg^{-1}) in Poland are probably analytical mistakes. The content of Be in these samples analysed with the ICP-AES *aqua regia* method was <0.5 mg kg^{-1}.

Beryllium in floodplain sediment shows a strong correlation (>0.6) with Li and Rb, a good correlation (>0.4) with K, Ti, Ga, Nb, U, Al_2O_3 and Th, and a weak, but significant, correlation (>0.3) with Ta, Fe, V, Co, Cs and Sn. The REEs have a good to weak correlation with Be.

In conclusion, the Be distribution in floodplain sediment in floodplain sediment is mainly of geogenic origin, and is associated with mineralised granitic rocks. It does, however, map Be concentrations in materials derived mining activities.

Be comparison between sample media

Patterns in Be distribution between all solid sample media are generally similar, although it is difficult to compare at lower concentrations since the detection limit for soil data is not as good as that for stream and floodplain sediments. There are, however, some noticeable differences. Stream sediment Be data in Lithuania are higher than in all other solid sample media, which is due to a different sampling strategy, with finer grain-size than in other countries. Wales and south-west Britain and north-eastern Greece have higher Be in floodplain sediments compared to all other solid sample media. Beryllium in the Italian alkaline magmatic province is comparatively low in floodplain sediments. A boxplot comparing Be variation in subsoil, topsoil, stream sediment and floodplain sediment is presented in Figure 5.

The distribution of Be in stream water is complex and bears both similarities and differences to trends observed in solid sample media. In southern Sweden and Finland, high Be concentrations are related to the occurrence of young granite and to acid pH and high DOC content.

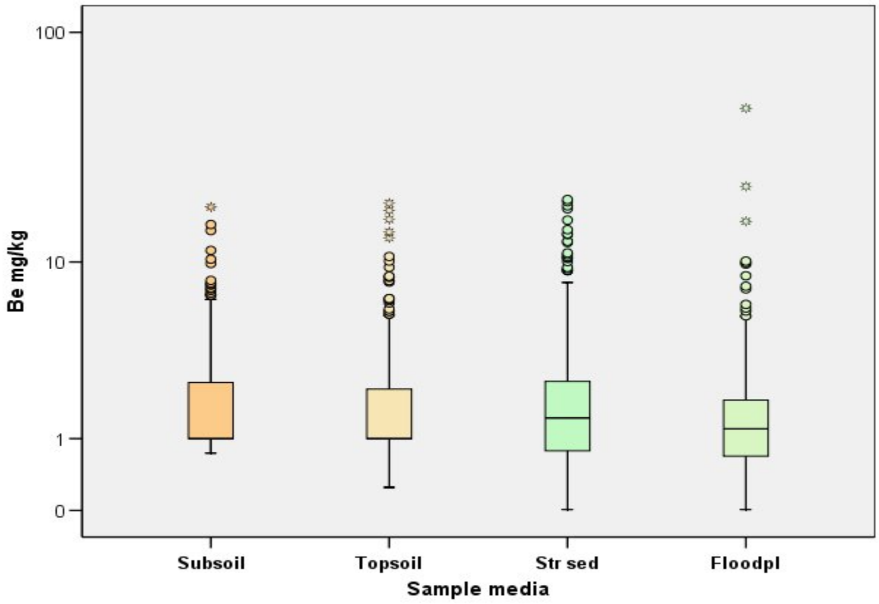

Figure 5. Boxplot comparison of Be variation in subsoil, topsoil, stream sediment and floodplain sediment.