Bi – Bismuth

Introduction

Bismuth is a group 15 element of the period table, which also includes P, As and Sb. It has an atomic number of 83, an atomic mass of 209, two main oxidation states (+3 and +5) and one naturally occurring isotope (^{209}Bi).

Bismuth minerals are rare, the most common ones being bismuthinite Bi_2S_3 and bismite Bi_2O_3. The element has marked chalcophile properties that, though less pronounced than for As and Sb, result in its partitioning into sulphide minerals, especially galena PbS, through substitution for Pb^{2+}. Other possible host minerals for bismuth include chalcopyrite and sphalerite. Bismuth can also display lithophile tendencies, replacing calcium in apatite (Angino and Long 1969), but the mechanism of this characteristic is poorly understood due to meagre data (Lueth 1999a). During magmatic processes Bi^{3+} may substitute for Pb^{2+}, Y^{3+} and the trivalent light rare earths, all of which display similar charge and/or size. Bismuth is also found as a native metal often with traces of As, S and Te. Bismuth occurs in approximately similar levels in mafic and intermediate rocks, whether intrusive or extrusive, at a concentration of about 0.04 mg kg^{-1}. It is markedly enriched in felsic rocks: 0.9 mg kg^{-1} in rhyolite and 0.27 mg kg^{-1} in granite, although not all types of granite display consistent enrichment (Lueth 1999a).

In sedimentary rocks, the abundance of Bi is related to the presence of granitic detritus and organic matter. Bismuth shows a tendency to co-precipitate with hydrous Fe and Mn oxides, and bismite has been observed as a secondary mineral in some sediments, where it is probably derived from the oxidation of sulphide minerals (Wedepohl 1978). Shale generally displays the highest average concentrations of Bi (0.26 mg kg^{-1}) and sandstone and limestone the lowest (0.03 mg kg^{-1}) (Lueth 1999a). Bituminous materials (Brandenstein *et al.* 1960) and coal are greatly enriched in Bi (average 5 mg kg^{-1}), although the enrichment mechanism is unknown (Lueth 1999a). Goldschmidt (1970) reports a similar enrichment in ferruginous bauxite and sedimentary iron ore. Values of up to 24 mg kg^{-1} have been recorded in oceanic ferromanganese nodules (Ahrens *et al.* 1967).

Bismuth, along with As and Sb, is useful as a gold pathfinder element (Boyle 1974) as it often indicates the presence of granitic intrusive centres and discordant structures that focus lode gold mineralising systems (Plant *et al.* 1989). In France, the only economic source of Bi was the gold mine of Salsigne that produced about 1700 tons of Bi as a byproduct of the gold ore (Béziat and Bornuat 1995). Bismuth sulphide is common in late tectonic vein type Pb-Zn or perigranitic hydrothermal Sn-W vein deposits.

Bismuth has low mobility under most environmental conditions. In aqueous solutions, bismuth most commonly occurs as the trivalent cation Bi^{3+}, which is a relatively large ion (103 pm) and has the same electron configuration as Pb^{2+}. Following its release during weathering, Bi^{3+} is rapidly hydrolysed under normal surface conditions of Eh and pH and tends to form insoluble basic salts. Like As, Sb and Pb, it is also readily adsorbed by secondary Fe and Mn oxides and organic matter in soil and stream sediment. An approximate average Bi value of 0.2 mg kg^{-1} is quoted for soil by Kabata-Pendias (2001).

Sea water contains about 0.02 µg l^{-1} Bi. Bismuth concentrations in natural water are very low, typically <0.2 µg l^{-1} (Madrakian *et al.* 2003).

Anthropogenic sources of bismuth include lead, copper, gold and silver smelting, waste water and sewage sludge (Reimann and de Caritat 1998). It is used in the manufacture of pharmaceuticals and cosmetics, pearlescent pigments, ceramic glazes, permanent magnets and safety devices in fire detection and extinguishing systems, in the production of catalysers, aluminium, steel and fusible alloys, and in the electronics industry.

Bismuth is considered non-essential for organisms. It is relatively non toxic and is found in low quantities in human tissues. The normal daily intake is around 5 µg per day (Mertz 1987). It exhibits a lone pair effect and can bind to Zn^{2+} and Fe^{3+} in the human body (Feldmann *et al.* 1999). Toxic side effects can include a burning sensation and itching of the eyes and headaches (Feldmann *et al.* 1999).

Table 13 compares the median concentrations of Bi in the FOREGS samples and in some reference datasets.

Table 13. Median concentrations of Bi in the FOREGS samples and in some reference data sets.

Bi (Bismuth)	*Origin – Source*	*Number of samples*	*Size fraction mm*	*Extraction*	*Median mg kg^{-1}*
Crust[1)]	Upper continental	n.a.	n.a.	Total	0.16
Subsoil	**FOREGS**	**783**	**<2.0**	**Total (ICP-MS)**	**<0.5**
Topsoil	**FOREGS**	**840**	**<2.0**	**Total (ICP-MS)**	**<0.5**
Soil[2)]	World	n.a.	n.a	Total	0.3
Water	**FOREGS**	**808**	**Filtered <0.45 µm**		**0.002 (µg l^{-1})**
Water[2)]	World	n.a.	n.a.		0.005 (µg l^{-1})

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

Bi in soil

Most soil samples (approximately 80%) contain less than the detection limit of 0.5 mg kg^{-1} Bi. The highest value is 6.49 mg kg^{-1} Bi in subsoil and 9.57 mg kg^{-1} Bi in topsoil. The average ratio topsoil/subsoil is 1.100.

Low Bi values in subsoil (<0.50 mg kg^{-1}) occur over most of northern and central Europe, Greece and eastern Spain.

On the subsoil Bi distribution map, northern Portugal, the Massif Central and the Italian alkaline province show the highest values (>1.03 mg kg^{-1}). These areas are characterised by granitic or alkaline rocks, and are also enriched in U, Th and Be. Other high values (>0.58 mg kg^{-1}) occur in northern Spain, south-west England, the Erzgebirge, Brittany, south-central Switzerland, south-central Austria, karstic Slovenia and Dalmatian Croatia, and two points in Greece related to sulphide mineralisation, one of them being Lavrion in Attica. In Finland, Bi anomalies are associated with hydrothermal Au mineralisations. Isolated high values in Spain are mostly associated with mineralisation (*e.g.,* Pb-Ag-Bi in the Demanda Range, Pb in Extremadura).

The topsoil Bi distribution map is very similar to that of the subsoil, with additional anomalies in eastern Slovakia (mineralisation in the Spišsko-gemerské Rudohorie Mountains ore district), north-east Greece (associated with gold and sulphide mineralisation) and central Sweden. The high Bi area in the Pyrenees extends eastwards, and is related to a Pb-Zn district (west) and W-As-Au skarn mineralisation (east).

The highest value observed in a subsoil (6.49 mg kg^{-1}) occurs in southern France just north of Mende (near a former fluorite mine). The second highest Bi value is in Lavrion (Greece), in the ancient Pb-Ag mining district, which is anomalous in Pb, Zn, Ag, As, Sb, Bi, Cd, Hg, I, Ni, Cr, Mg, Ca, Co, Fe, V and Sc. The highest value in topsoil (9.59 mg kg^{-1}) occurs in Spain, in the Sierra Morena south of Almadén, in an area with vein-type Pb mineralisation and Hg deposits; it is also anomalous in Hg. Nearby, another high Bi value is associated with Bi (Espiel) and Pb veins hosted by granitic rocks.

Because so many soil samples are below the detection limit for Bi, correlations are only indicative of certain tendencies. In subsoil, Bi shows a good correlation with Al, Ga, In, Tl, Be, Ta, Rb, Cs, Sn, U, Th and La, and a weak correlation (between 0.3 and 0.4) with Pb, Ag, As, Te, Nb, K, Pr, Nd, Sm and Tb. Hg, W, Tl, Ga and Al. In topsoil, Bi has a good correlation with Be, Sn, Cs, Rb, Ta, Tl and U, and a weak correlation with Pb, W, Th, Ga and In.

Bi in stream water

Bismuth values in stream water range over two orders of magnitude, from <0.002 to 0.16 µg l^{-1}, with a median value of 0.002 µg l^{-1}. Almost 50% of data for stream water Bi concentrations are less than the analytical limit of detection; the following discussion is, therefore, only tentative. The bismuth distribution pattern in Europe resembles that of the REEs. High Bi occurs in acid stream water with low mineralisation and high organic content in the Baltic parts of Fennoscandia. Patterns in Germany, the Netherlands, Spain and Slovenia are attributed to pollution. In France and southern Italy, the patterns are attributed to alkaline volcanism.

Lowest Bi values in stream water (less than or equal to the analytical limit of quantification of 0.002 µg l^{-1}, and constituting over 30% of all determinations) are found throughout most of Europe, covering all types of terrains.

Highest Bi values in stream water (>0.006 µg l^{-1}) occur throughout Finland and southern Sweden and, to a lesser extent, in parts of Poland; they are generally associated with high DOC in stream water. Southern Italy, including Sicily, is also enhanced in Bi in stream water, possibly related to alkaline volcanic hydrothermal activity. Point anomaly Bi values are found in southern Spain (one in the Pb district of the Sierra Morena, the southernmost one in a stream draining Permo-Triassic clastic rocks and ultramafic rocks), in central France (Massif Central) on Variscan terrains, in southern Finland on Precambrian terrains, in eastern Germany, and in Sardinia. Elevated Bi values in southern Sweden are probably related to Palaeozoic rocks. The highly anomalous Bi data in Slovenia most likely result from contamination during sampling and handling of samples. In Finland, the high values could be linked to the abundance of peat deposits or mires (dissolved humus can be a carrier of Bi in these cases), whereas on coastal areas, colloidal clay particles can bind Bi. The high Bi values in both Sardinia and Calabria regions in Italy are clearly related to the presence of polymetallic mineralisation in surrounding areas.

There are five highly anomalous Bi values in stream water in Germany: east of Hamburg, it points to possible influence by a huge copper smelter (bismuth is often found in sulphide minerals); two high Bi values in north-eastern Germany seem to show anthropogenic influence in the Berlin area; one sample in the German-Czech-Polish triangle, also high in Be in stream water, lies just west of a lignite-burning power plant in Poland; one sample is in a mineralized area in Thuringia. The only contrasted Bi value in France (0.260 µg l^{-1}) is correlated with Fe, Pb, Cu, As, Cd, Sb, Tl, W and clearly indicates an upstream contribution from the past mining district of Pontgibaud and its related smelting factory.

Bi comparison between sample media

The analytical data for Bi in stream and floodplain sediments have not been reported because they did not pass the quality control checks.

Patterns in Bi distribution between topsoil and subsoil are generally similar. The main areas of enhanced Bi concentration in stream water, throughout Finland and southern Sweden, are not observed in soil data.