

Introduction

Boron is a member of group 13 elements of the periodic table, which also includes Al, Ga, In and Tl. The element has an atomic number of 5, an atomic mass of 11, one main oxidation state (+3), and two naturally occurring stable isotopes (^{10}B and ^{11}B). Boron is a lithophile element and its chemistry generally resembles that of Si more closely than those of the other group 13 elements.

During magmatic processes boron forms stable oxy-complexes such as $(\text{BO}_4)^{5-}$, which are incompatible with common silicate structures, so it tends to accumulate in late-stage igneous rocks, especially pegmatites (Ure and Berrow 1982). Tourmaline $\text{NaFe}^{2+}3\text{Al}_6(\text{BO}_3)_3\text{Si}_6\text{O}_{18}(\text{OH})_4$, which contains 2.8 to 3.6% B, and phyllosilicates, such as micas, are the principal hosts of B in igneous rocks (Wedepohl 1978). Boron concentrations are thus relatively low in basalt (0.1-6 mg kg $^{-1}$) and higher in more evolved rocks such as granite (85 mg kg $^{-1}$) (Aggarwal 1999). Elevated B values may serve to distinguish felsic intrusive rocks of distinctive composition and origin.

The highest B levels in detrital sedimentary rocks are usually in argillaceous facies and are related to the amount and type of clay mineral present (Aggarwal 1999). Extremely high values, *ca.* 9000 mg kg $^{-1}$ B, have been recorded in coal ash, showing the element's marked affinity for organic matter. Hydrated borate minerals accumulate as evaporite deposits in arid, closed-basin environments (Ure and Berrow 1982). Boron acts as an important buffering component in sea water and is incorporated into marine sediments. Marine sedimentary rocks and marine-derived drift, especially argillaceous sediments, are consequently enriched in B relative to lacustrine and fluvial sediments. McLennan and Murray (1999) quote an average value for river particulates as 70 mg kg $^{-1}$ B.

Boron is a light element and its ionic and solute species in the surface environment tend to be volatile. During chemical weathering of rocks, B is solubilised and forms several anions such as BO_2^- , $\text{B}_4\text{O}_7^{2-}$, BO_3^{3-} , H_2BO_3^- and $\text{B}(\text{OH})_4^-$. Although B is likely to be retained by clays (illite in particular, but also sesquioxides and organic

substances), its concentration in soil solutions is relatively high, ranging from 67 to 3000 mg l $^{-1}$; average B contents in soil vary from 9 to 88 mg kg $^{-1}$ (Kabata-Pendias 2001). Boron is sorbed more strongly by soil than other anions such as Cl^- and NO_3^- . It may also be entrapped in the clay lattice by substitution for Al^{3+} and/or Si^{4+} , thus forming B-silicate compounds in soil. Adsorption on Fe and Al oxides is considered to be an important mechanism governing B solubility in soil. Organic matter also affects greatly B mobility and bioaccessibility, particularly in acid soil. Adsorption of B on soil humic acid increases with increasing pH up to a maximum near pH 9. Boron adsorption by oxy- and hydroxy-bonds by surface coatings, and by incorporation into interlayer or structural positions of aluminosilicate minerals are the likely dominant mechanisms in acid and neutral soil. In arid areas, B is likely to be coprecipitated with Mg and Ca hydroxides as coatings on soil particles, and it may also occur as Na-metaborate. Adsorbed B on soil minerals is rather easily leachable, but irreversibility of B sorption has also been documented (Kabata-Pendias 2001).

Boron is liberated in volcanic gases in the form of orthoboric acid, H_3BO_3 , or as halogenides such as BF_3 ; water from volcanic areas may, therefore, contain appreciable amounts of boron. The most common B species found in natural water, however, are boric acid, $\text{B}(\text{OH})_3$, and its dissociation products such as $\text{B}(\text{OH})_4^-$. Boron is abundant in sea water (4.4 mg l $^{-1}$), but is generally low in rainwater, typically <10 $\mu\text{g l}^{-1}$. Concentrations in surface and groundwater are generally in the order of a few tenths of a mg l $^{-1}$, although much higher levels can be found in thermal springs (Hem 1992). The average abundance of B in river water is given as 10 $\mu\text{g l}^{-1}$ by Turekian (1969).

Boron compounds are used extensively as cleaning aids in detergent industry and have a wide range of industrial uses, including as buffers for pH control (Waggott 1969). Boron pentahydrate is used in very large quantities in the manufacture of insulation fibreglass and sodium perborate bleach. Boron compounds are also

extensively used in the manufacture of borosilicate glasses, and in metallurgy as a flux and in the manufacture of steel alloys. Boric acid is used widely in the textile fibreglass, in cellulose insulation as a flame retardant and as a mild antiseptic. Amorphous B is used in pyrotechnic flares to provide a green colour, and as an igniter in rockets (Aggarwal 1999). Concentrations of boron are also likely to be high in sewage.

Boron is an essential element for plant growth and is often used in fertilisers, contributing to

enhanced B levels in stream water in agricultural areas. Despite its essential nature, B can be harmful to certain plants, *e.g.*, lemon and orange trees, at concentration as low as 1 mg l⁻¹ (Hem 1992, Kabata-Pendias 2001). Boron has not been shown to have any serious toxic effects in humans (WHO 1996).

Table 10 compares the median concentrations of B in the FOREGS samples and in some reference datasets.

Table 10. Median concentrations of B in the FOREGS samples and in some reference data sets.

Boron (B)	Origin – Source	Number of samples	Size fraction mm	Extraction	Median mg kg⁻¹
Crust ¹⁾	Upper continental	n.a.	n.a.	Total	17
Water	FOREGS	807	Filtered (<0.45 µm)		15.6 (µg l⁻¹)
Water ²⁾	World	n.a.			20 (µg l ⁻¹)

¹⁾Rudnick&Gao 2004, ²⁾Ivanov 1996.

B in stream water

Boron values in stream water range over four orders of magnitude, from 0.1 to 1040 µg l⁻¹ (excluding an outlier of 3030 µg l⁻¹), with a median value of 15.6 µg l⁻¹. Boron data tend to correlate to a certain extent with chloride, sulphate and strontium. Boron distribution in Europe is similar to the distribution of Major-ions in high mineralisation water, characterised by high values in central and southern Europe, and low values in north and west Fennoscandia, west Britain, Ireland and the western Iberian peninsula, and a belt including the Pyrenees and the Alps. The patterns seem to be controlled to a high degree by exogenic factors (climate, topography) and in places by geogenic factors.

Lowest B in stream water (<3.8 µg l⁻¹) are found throughout Fennoscandia on Precambrian Shield and Caledonides, western Scotland on Laurentian and Caledonian terrains, north-west Spain, across parts of the Pyrenees and the Massif Central on Variscides, and central parts of the Alps, including northern Italy on the Alpine Orogen. The low values are predominantly associated with acid igneous and metamorphic rocks, but also with mountainous areas (dilution through rainfall in high topography).

Enhanced B concentrations in stream water (>60 µg l⁻¹) are found within central and eastern

Britain on Caledonian and Variscan terrains. In the Netherlands, parts of northern Germany and Poland, and central Hungary they are mainly associated with complex inter-bedded loessic Aeolian sand, soil, till and fluvio-glacial sediment, as well as industrial influence (salt brines associated with the natural gas field of Altmark in Germany contains 110 µg l⁻¹ dissolved boron, Holdorf *et al.* 1993) and agricultural influences. High values are also observed in the Baetic mountains in southern Spain and in eastern Spain (Triassic lithologies with clay and evaporates of Keuper facies, and to a lesser extent Miocene lacustrine sediments), in southern Portugal, eastern France (Jura), Rhône-Provence area, and southernmost France and Sardinia (Variscan terrains), and in most parts of Italy, central Albania and north-western Greece, on the Alpine Orogen. The values in Italy are associated mainly with volcanics (Roman and Neapolitan Alkaline Provinces) and evaporites but, especially over the Apulia region, may also be related to the use of agricultural fertilisers. In Greece, B may be related to phosphorite and gypsum occurrences, but fertilisers are another likely source. High values in the Mediterranean climate zone are enhanced by high evaporation and resulting higher salinities in the aqueous systems.

The highly anomalous stream water B value in south-west Hungary is associated with Miocene-Pliocene volcanics and agricultural activity. Boron is often used in fertilisers in the form of borax and tetraborate (Murphy and Walsh 1972). Because of very intensive agricultural production in southern Hungary and eastern Croatia the consumption of fertilisers is relatively high there. Furthermore, the elevated content of boron could be also connected to agricultural burning (Fogg and Duce 1985) and to the use of sludge effluents in agriculture (borate and perborate in detergents) (Adriano 1986). A high boron value in northern Germany near the North Sea is associated with a maximum of alkalinity in Germany (see pH map), and points to sea water influence. The highly

anomalous boron value in Germany near the Belgian border occurs in an industrialized area, and points to industrial pollution; it is also high for Co in stream water and stream sediment and for Pb in stream sediment. The high values of boron in stream water in north-eastern and southern France are related to salt extraction, either by brining or by mechanically harvesting in small evaporitic basins. An isolated high B value located in the vicinity of Boulogne-sur-Mer in northern France is probably caused by pollution from the nearby steel industries. The other high B values in stream water delineate very well the evaporitic basin of Lorraine and Eocene in the Southern Rhone-Provence areas.

B comparison between sample media

Boron was determined only on stream water samples, so no comparison can be made between

distributions in other sample media.