

## Introduction

Selenium belongs to group 16 of the periodic table, along with O, S and Te. The element has an atomic number of 34, an atomic mass of 79, four oxidation states (-2, +2, +4 and +6) and six naturally occurring isotopes ( $^{74}\text{Se}$ ,  $^{76}\text{Se}$ ,  $^{77}\text{Se}$ ,  $^{78}\text{Se}$ ,  $^{80}\text{Se}$  and  $^{82}\text{Se}$ ), of which  $^{78}\text{Se}$  and  $^{80}\text{Se}$  account for about 73.3% of the total mass. The geochemistry of Se is similar in most respects to that of S, although Se is a much less abundant element.

Selenium is a chalcophile non-metallic element forming several rare minerals, including crookesite  $(\text{Cu,Tl,Ag})_2\text{Se}$ , berzelianite  $\text{Cu}_2\text{Se}$  and tiemannite  $\text{HgSe}$ , but is more widely present as an accessory element replacing sulphur in more common sulphide minerals, such as pyrite, chalcopyrite, pyrrhotite and sphalerite.

During volcanic activity, Se escapes with high-temperature volcanic gases and its concentrations in volcanic rocks are, therefore, generally low. The average crustal abundance of Se is 0.05–0.09  $\text{mg kg}^{-1}$ , and average concentrations in magmatic rocks rarely exceed these values. Kabata-Pendias (2001) cites values in granite of 0.01–0.05  $\text{mg kg}^{-1}$  Se. Because of similarities in the chemistry of Se and S, Se is a chalcophile element and is concentrated in sulphide ore deposits, uranium deposits in sandstone and the diagenetic pyrite of fine-grained sediments (Howard 1977). Ebens and Shacklette (1982) report levels of Se in sedimentary rocks as: limestone 0.08  $\text{mg kg}^{-1}$ , shale 0.06  $\text{mg kg}^{-1}$  and sandstone  $<0.05 \text{ mg kg}^{-1}$ . Organic-rich sediments are enriched in Se, e.g., black shale up to 675  $\text{mg kg}^{-1}$  (Adriano 1986) and phosphate rocks are reported to contain 1–300  $\text{mg kg}^{-1}$  Se (NAS-NRC 1976).

Selenium is highly mobile under oxidising, acidic, neutral and alkaline conditions, although its mobility decreases with decreasing pH (Gondi *et al.* 1992), and it is immobile under reducing conditions. The behaviour of Se in highly calcareous soil is of special concern, because Se becomes easily water soluble when soil is low in sesquioxides. Another significant observation is the adsorption of Se by clay minerals, which decreases with increasing pH values and becomes negligible above pH 8 (Kabata-Pendias 2001). The same author gives the average Se content in surface soil on a global scale as 0.33  $\text{mg kg}^{-1}$ .

Selenium's solution chemistry is principally anionic, with selenite,  $\text{SeO}_3^{2-}$ , and selenate,  $\text{SeO}_4^{2-}$ , (corresponding to sulphite and sulphate) being the main forms in aqueous solutions. Elemental Se, whilst relatively insoluble, is also stable over a wide pH range under reducing conditions (Brookins 1988). Mobile selenate entering the drainage system is reduced to selenite if the Eh drops, and at lower pH values selenite is likely to be strongly adsorbed by hydrated surfaces of ferric oxides (Howard 1977). Hamdy and Gissel-Nielsen (1977) demonstrated that clay and ferric oxide have the capacity to remove  $\text{Se}^{4+}$  from solution. Concentrations of Se in natural water rarely exceed 1  $\mu\text{g l}^{-1}$  and average concentrations may be as low as 0.1  $\mu\text{g l}^{-1}$  (Hem 1992).

In industrial areas, the burning of fossil fuels, e.g., combustion of coal in electricity generation, leads to an increase of Se in the environment from atmospheric deposition (Nriagu and Pacyna 1988). Other sources of Se include smelters, vulcanised rubber, wastewater and some phosphate fertilisers (Reimann and de Caritat 1998).

Selenium is a biologically active element and is essential in the diet of many organisms. Because of this, the behaviour of Se in the surface environment, particularly in soil, has been well documented (Jacobs 1989). Selenium is needed for growth and fertility in animals, while deficiency in humans leads to Keshan and Kashin-Beck diseases, affecting the heart (cardiomyopathy) and bones (tubular bone changes) respectively (Mertz 1987). Between 30 and 40  $\mu\text{g day}^{-1}$  is needed for adult humans (WHO 1996), but grains, cereal and meat usually contain enough Se to provide the necessary daily requirement. However, the optimal dietary requirement for Se lies in a narrow range. Selenium can also be toxic at higher levels, causing hair and nail loss, skin disorders, nerve damage and abdominal cramps (Mertz 1987). The seriousness of these effects depends upon the concentrations of Se in food and how often this food is eaten. Selenium poisoning may become so severe in some cases that it can even cause death.

Table 59 compares the median concentrations of Se in the FOREGS samples and in some

reference datasets.

Table 59. Median concentrations of Se in the FOREGS samples and in some reference data sets.

<i>Selenium (Se)</i>	<i>Origin – Source</i>	<i>Number of samples</i>	<i>Size fraction mm</i>	<i>Extraction</i>	<i>Median mg kg<sup>-1</sup></i>
Crust <sup>1)</sup>	Upper continental	n.a.	n.a.	Total	0.09
<b>Water</b>	<b>FOREGS</b>	<b>807</b>	<b>Filtered &lt;0.45 µm</b>		<b>0.34 (µg l<sup>-1</sup>)</b>
Water <sup>2)</sup>	World	n.a.	n.a.		0.2 (µg l <sup>-1</sup> )

<sup>1)</sup>Rudnick & Gao 2004, <sup>2)</sup>Ivanov 1996.

### Se in stream water

Selenium values in stream water range over three orders of magnitude from <0.01 to 7.63 µg l<sup>-1</sup> (excluding three outliers up to 15 µg l<sup>-1</sup>), with a median value of 0.34 µg l<sup>-1</sup>. Selenium data tend to correlate with values of As, Mo, Sb, U, and V, indicating the affinity with the ‘black shale – chalcophile/organophile’ element grouping. The Se stream water distribution map however, is also influenced by climatic effects.

Lowest Se values in stream water (<0.13 µg l<sup>-1</sup>) are found throughout Fennoscandia, in northern and central Finland, north-eastern tip of Norway and central Sweden on Precambrian Shield rocks, and in Estonia on glacial drift originating from the Shield, in areas of central and southern Norway on Caledonides terrains, in small areas in Lorraine and Massif Central of France and in north-west Spain and on Corsica in the Variscan region, and in eastern Hungary, western Austria, eastern Switzerland and part of northern Italy with western Slovenia and western Croatia, the north of Albania and central Macedonia in Greece on the Alpine Orogen.

Enhanced Se concentrations in stream water (>0.88 µg l<sup>-1</sup>) occur in northern and western Poland, north-western Germany and southern Denmark on glacial drift, and in Netherlands on Quaternary deposits. Enhanced Se values in stream water occur in western Ireland and eastern England of the Caledonian Europe, in a large area

in most of western France (the highest anomalies of which are related to Eocene continental sedimentary beds), in east and central Spain (calcareous lithologies and evaporites with gypsum), southern Spain and Portugal as well as on Sardinia (influence of mineral deposits), on Variscan terrains. High Se areas occur in the Baetic Cordillera of southern Spain, in northern, central and south-eastern Italy with western Sicily, north central Hungary, and in Thrace in north-eastern Greece, presumed to be imported pollution from mining and industrial areas in south-eastern Bulgaria, all in the region of the Alpine Orogen. Highly anomalous isolated Se values in the Ebro River basin in northern Spain are related to evaporitic sediments, but also to Se-rich stream water originating in Mesozoic and Palaeocene sandstone with Cu-U disseminations. The isolated Se anomaly in south-east Britain could be related to pollution from nearby urban areas. High Se in the Netherlands is a result of sea water intrusion in coastal sand aquifers.

The selenium pattern in stream water, as described above, is associated with the Major-ions type stream water in alkaline conditions, in which the element is present mainly as the selenate ion SeO<sub>4</sub><sup>2-</sup> similar to sulphate; and also to the Sea-influence elements type, near the western coasts of Europe and in evaporitic deposits.

### Se comparison between sample media

The analytical data for Se in stream and floodplain sediments have not been reported,

because the analytical data did not pass the quality control checks. No data are available for soil.