

Introduction

Germanium is a ‘metalloid’ element and a member of group 14 of the periodic table, along with C, Si, Sn and Pb. The element has an atomic mass of 32, an atomic mass of 73, three main oxidation states (-4, +2 and +4), of which +4 is the most common in nature. It has five main natural isotopes (^{70}Ge , ^{72}Ge , ^{73}Ge , ^{74}Ge and ^{76}Ge), of which ^{74}Ge is the most abundant. Its chemical behaviour is intermediate between that of Si and Sn, although it exhibits stronger chalcophile and organophile properties than either; it also has siderophile and lithophile affinities.

Germanium is a rare element, although relatively high levels have been found in several sulphide minerals, such as the copper minerals chalcopyrite CuFeS_2 , enargite Cu_3AsS_4 , bornite Cu_5FeS_4 and tennantite $(\text{Cu,Fe})_{12}\text{As}_4\text{S}_{13}$, and others, such as low-temperature sphalerites $(\text{Zn,Fe})\text{S}$ and galena PbS . There are a few Ge minerals, including reniérite $\text{Cu}_3(\text{Fe,Ge})\text{S}_4$, briartite $\text{Cu}_2(\text{FeGe})\text{S}_4$, germanite $\text{Cu}_3(\text{Ge,Fe})\text{S}_4$ and argyrodite Ag_8GeS_6 .

The crustal abundance of Ge is estimated to be 1.5 mg kg^{-1} . This value is also typical of most igneous, metamorphic and clastic sedimentary rocks and their dominant minerals. There is relatively little difference between ultramafic, mafic, intermediate and granitic rocks, which all contain values between 0.9 and 1.5 mg kg^{-1} Ge (Mielke 1979, Schroll 1999b). Granite pegmatite, however, often shows substantially higher Ge values, typically 10 mg kg^{-1} , and some minerals, such as white mica (63 mg kg^{-1}), garnet (180 mg kg^{-1}) and especially topaz (700 mg kg^{-1}) having Ge contents up to several hundred mg kg^{-1} (Schroll 1999b).

Germanium levels in clastic sedimentary rocks are usually in the range of 1 to 2 mg kg^{-1} , similar to that of most igneous rocks. Evaporite and pure limestone, however, have very low Ge contents, typically $<0.1 \text{ mg kg}^{-1}$. Organic-rich sediments, such as black shale typically contain up to 3.3 mg kg^{-1} Ge, and coal can contain substantially higher amounts, up to several hundred mg kg^{-1} Ge. Whereas the Ge levels in black shale are

believed to be mainly authigenic, the wide range of Ge concentrations in coal seams suggests that much of the Ge is of a post-depositional diagenetic origin, and that it is predominantly bound by complexation with the humic acid component of organic matter (Wedepohl 1978). Coal ashes are often strongly enriched in Ge; the highest reported value of 0.66% Ge came from Italian lignite.

Germanium is not very mobile in the aqueous environment. A theoretical Eh-pH diagram for Ge provided by Brookins (1988) indicates that insoluble GeO_2 is stable under acid conditions, whereas soluble germanate anions can exist above pH 8. Germanium is generally present in natural water at concentrations less than 1 ng l^{-1} (Jin *et al.* 1991). In soil, Ge is partly mobilised in the form of $\text{Ge}(\text{OH})_2$, but is readily fixed as $\text{Ge}(\text{OH})_4$ by clay minerals, Fe oxides and organic matter (Kabata-Pendias 2001). Its global abundance in soil is about 1 mg kg^{-1} (Taylor 1964).

Anthropogenic sources of Ge include zinc and other base metal processing (Schroll 1999b). Coal burning is a major anthropogenic source, and fly ash, which may contain up to 250 mg kg^{-1} Ge, is one of its commercial sources (Kabata-Pendias 2001). The main industrial application of Ge is as a semiconductor, although it is also used as an alloying agent, a phosphor in fluorescent lamps, a catalyst, and in electronic materials such as X-ray and gamma detectors and high frequency integrated circuits. It is also employed in the manufacture of wide-angle camera lenses, microscope objectives, infrared spectrometers and other optical equipment, including extremely sensitive infrared detectors.

Germanium is not known to have any biological function and is generally considered to have a low toxicity. Germanium has bactericide properties and some plants, *e.g.*, green tea, are known to accumulate Ge (Reimann *et al.* 2003).

Table 32 compares the median concentrations of Ge in the FOREGS samples and in some reference datasets.

Table 32. Median concentrations of Ge in the FOREGS samples and in some reference data sets.

<i>Germanium (Ge)</i>	<i>Origin – Source</i>	<i>Number of samples</i>	<i>Size fraction</i>	<i>Extraction</i>	<i>Median mg kg⁻¹</i>
Crust ¹⁾	Upper continental	n.a.	n.a.	Total	1.4
Water	FOREGS	807	Filtered <0.45 µm		0.009 (µg l⁻¹)
Water ²⁾	World	n.a.	n.a.		0.05 (µg l ⁻¹)

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

Ge in stream water

Germanium values in stream water range over about two orders of magnitude, from <0.005 to 0.12 µg l⁻¹ (excluding two outliers of up to 0.44 µg l⁻¹), with a median value of 0.009 µg l⁻¹. About 25% of determinations are below the limit of quantification. The distribution of Ge resembles those of Hf, Pb and Ti.

Lowest Ge values in stream water (<0.005 µg l⁻¹) are found in northern Fennoscandia on Precambrian Shield and Caledonian rocks, in south-western Norway and in Wales on Caledonian terrains, and in west Estonia and part of north-east Germany on Fennoscandian glacial drift. In the Variscan part of Europe, low Ge occurs in a large part of Central Germany, in three smaller areas in north central France, including the west of the Armorican Massif, in a belt from the Alpine western Switzerland across southern France and Pyrenees to north-eastern Spain, a small area in south-east Spain and a larger one in western Spain with large parts of Portugal, and in the northern half of Sardinia. On the Alpidic Orogen, low Ge occurs in eastern and southern Hungary, south-eastern Austria and entire Slovenia and Croatia, in southern Italy and Sicily, in north-west and central as well as north-eastern part of Greece and on Crete.

Enhanced Ge values in stream water (>0.019 µg l⁻¹) are found on the Fennoscandian Shield in south-east Finland, southern Sweden (related to granite and mica schist), southernmost Norway, on the Shield derived glacial drift in the east of Estonia, Latvia and Lithuania (probably linked to an accumulative interplay between underlying sedimentary clayey Devonian rocks and peatlands), in northern, southern and eastern Poland and in Denmark. On Caledonian terrains, high Ge values are found in central and southern Scotland and northern England, explained by

coalfields and coal combustion (example: the Durham Coalfield in north-east England). Relatively high Ge concentrations are known to occur in Tertiary coal deposits in the Czech Republic; there were unsuccessful attempts to artificially extract Ge as a by-product of coal burning in the 1950s; high Ge concentrations found in north-east Czech Republic may be caused by atmospheric deposits of fly ash from burnt coal. Local seepage flow of natural mineral water into stream water is the reason for the anomalous content of Ge (0.097 µg.l⁻¹) in western Slovakia. High Ge values also occur in north-eastern Austria and in southern Sardinia. The isolated anomaly in northern Estonia is probably related to pollution from oil shale tailings. In eastern Poland, high Ge is associated with DOC in post glacial clays. In south and south-west Finland high Ge values occur where younger K-rich granite plutons outcrop and lanthanides are high on the west coast of Finland (near the city of Vaasa) where concentrations of Ge (and other trace elements) are high due to acid sulphide soil. A point anomaly in the eastern Pyrenees, Spain, is probably related to Cu and Pb-Zn mineralisation of Cape Creus. A point anomaly in central Portugal can be related to a nearby coal mine.

Germanium in the stream water map is distributed similarly to the pattern of REEs and associated elements in acid, low-mineralisation, high-DOC stream water. This pattern is exogenic, climate- and vegetation-dependent. In addition, the association of Ge with elements typical for Felsic-alkaline rocks explains its high concentration in most of central and eastern Europe. Some of the Ge patterns might be associated with the Major-ions stream water type.