Ga – Gallium

Introduction

Gallium is a member of group 13 of the periodic table, which also includes B, Al, In and Tl. The element has an atomic number of 31, an atomic mass of 70, one main oxidation state (+3) and two naturally occurring isotopes (^{69}Ga and ^{71}Ga), with abundances of 60.4 and 39.6% respectively (Schroll 1999a). The geochemical behaviour of Ga is very similar to that of its period group neighbour Al.

The Ga^{3+} ion has the same electronic configuration as Zn^{2+} but has a slightly smaller ionic radius. Consequently, Ga exhibits similar characteristics to Zn including weak chalcophile behaviour under certain hydrothermal conditions, possibly promoting Ga enrichment in sphalerite. It also acts as an accessory element replacing Al or Fe in amphibole, feldspar, mica and clay minerals. It forms a number of rare minerals including söngheite $Ga(OH)_3$ and gallite $CuGaS_2$.

Feldspar and mica are the dominant host minerals for Ga in igneous and metamorphic rocks, as they are for Al. Although the charge and ionic radius of Fe^{3+} and Ga^{3+} ions are very similar (64.5 and 62 pm respectively), there is generally no close correlation between the concentrations of Fe and Ga in geological materials, because Fe is more mobile in its reduced Fe^{2+} state. The average crustal abundance of Ga is 19 mg kg^{-1} (Fyfe 1999). Mielke (1979) cites the following values for Ga in igneous rocks: ultramafic 1.5 mg kg^{-1}; basaltic 17 mg kg^{-1}; granitic 17 mg kg^{-1}; syenite 30 mg kg^{-1}; and a crustal average of 19 mg kg^{-1}. In sedimentary environments, Ga is concentrated with Al in clay minerals during the weathering process, though some may remain in detrital feldspar. Thus, Ga concentrations are generally higher in aluminous shale, greywacke and feldspathic sandstone and lowest in pure quartzite and carbonate. This is confirmed by Mielke (1979) who quotes values of 19 mg kg^{-1}, 12 mg kg^{-1} and 4 mg kg^{-1} for Ga in shale, sandstone and carbonates respectively. For loess, McLennan and Murray (1999) give an average of 14 mg kg^{-1}. High Ga values are reported in bauxite originating from alkali rocks (*e.g.,* nepheline syenite); the carbonate-derived bauxite from central and southern Europe displays average contents around 50 mg kg^{-1} Ga (Schroll 1999a).

Gallium, like Al, is relatively immobile in the surface environment because of the low solubility of its dominant hydroxide, $Ga(OH)_3$. It is most mobile under acid conditions and is found at relatively high levels in acid mine water, formed from the weathering of sulphides (Shiller and Frilot 1996). Gallium is more likely to exist as an anion than Al (Shiller and Frilot 1996), but this only occurs at very high pH values (>9.5), which are very rarely encountered under natural conditions. Gallium concentrations in natural water are very low, typically less than 5 ng l^{-1} (Shiller and Frilot 1996). In soil the Ga content varies from 1 to 70 mg kg-1 with an average of 28 mg kg-1 (Kabata-Pendias 2001). Because of its correlation with Al, it is normally enriched in the clay fraction; it also has a relationship with Fe and Mn oxides, and soil organic matter.

Anthropogenic sources of gallium include copper, bauxite and zinc smelting, the chemical industry, coal combustion and waste incineration (Reimann and de Caritat 1998, Schroll 1999a). It is also used in the manufacture of transistors for the electronics industry, and in the manufacture of nuclear weapons.

Gallium is a non-essential element and is considered to have a low toxicity. It is found in low quantities in human tissues, but accumulation can lead to suppressed growth and reduced life span in mice (Mertz 1987). The radioactive gallium compound, gallium [^{67}Ga] citrate, can be injected into the body and used for medical scanning without harmful effects.

Table 30 compares the median concentrations of Ga in the FOREGS samples and in some reference datasets.

Ga in soil

Gallium has a median value of 13.8 mg kg^{-1} in subsoil and 13.5 mg kg^{-1} in topsoil, with a range from 0.23 to 36.6 mg kg^{-1} in subsoil, and 0.54 to 34.3 mg kg^{-1} in topsoil.

Table 30. Median concentrations of Ga in the FOREGS samples and in some reference data sets.

Gallium (Ga)	*Origin – Source*	*Number of samples*	*Size fraction mm*	*Extraction*	*Median mg kg^{-1}*
Crust[1)]	Upper continental	n.a.	n.a.	Total	17.5
Subsoil	**FOREGS**	**790**	**<2.0**	**Total (ICP-MS)**	**13.8**
Topsoil	**FOREGS**	**843**	**<2.0**	**Total (ICP-MS)**	**13.5**
Soil[2)]	World	n.a.	n.a	Total	17
Humus	**FOREGS**	**367**	**<2.0**	**Total (ICP-MS)**	**0.90**
Water	**FOREGS**	**807**	**Filtered <0.45 µm**		**0.011 (µg l^{-1})**
Water[3)]	World	n.a.	n.a.		0.1 (µg l^{-1})
Stream sediment	**FOREGS**	**852**	**<0.15**	**Total (XRF)**	**12.0**
Floodplain sediment	**FOREGS**	**747**	**<2.0**	**Total (XRF)**	**11.0**

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

The correlation coefficient between Al_2O_3 and Ga is 0.966 for subsoil, and 0.956 for topsoil, and their geographical distribution is almost identical. This is reflected in the similarity of the geochemical maps. Gallium is especially abundant in clay minerals and feldspars, like Al.

The Ga subsoil distribution map shows low values (<9.0 mg kg^{-1}) throughout the sandy plains extending from the Netherlands over northern Germany and Denmark to Poland and Lithuania, as expected, because of the glacial sand and loess cover. Low values are also found in a small part of metasedimentary rocks in central Scandinavia, throughout most of western Ireland, in south-east England, over the Paris Basin of France, and in southern and eastern Spain with mainly calcareous lithology.

High Ga values in subsoil (>18.0 mg kg^{-1}) occur mainly in the western Iberian Peninsula, where crystalline and shale-rich Palaeozoic rocks provide a substrate rich in feldspar and phyllosilicate minerals (mica and clay). A similar lithology, with high Ga values, extends from the Central Massif to Brittany in France, on the island of Corsica, in south-west England, Wales, south-western Norway, northern Fennoscandia, the eastern Alps, and the Carpathians of Slovakia (crystalline and shale-rich Palaeozoic rocks together with Palaeogene to Neogene clayey sediments). In Slovenia, Croatia, and parts of western and northern Greece, Ga enrichment occurs in soil on carbonate rocks of karst areas, after CaO has been leached from soil. In north-eastern Greece Ga enrichment results from weathering of granite and granodiorite intrusions, gneiss, and shale. In western Italy (Lazio and Tuscany) the high Ga concentrations are explained by the presence of alkaline volcanic rocks with high alumina content.

The Ga topsoil distribution map is very similar. Notable differences are a relative depletion in eastern Slovakia (smaller amount of clay minerals) and a high Ga content in the eastern Pyrenees (Palaeozoic shale) and the Sierra Nevada (micaschist and orthogneiss) in southern Spain. On Gran Canaria, the Ga anomaly is related to mafic and intermediate volcanic rocks.

In subsoil, Ga shows a very strong correlation with Al (0.96) and In (0.81), a strong correlation (>0.6) with Nb, Ta, Fe, Sc, V, Ti, Th, K, Rb and the REEs, and a good correlation (>0.4) with Be, Co, Pb, Bi, U, Cu, Cs, Tl, Ba, Zn and Y. In topsoil, the pattern of linear correlation coefficients is very similar, but correlations are somewhat weaker with In and the REEs, and there is also a good positive correlation with Na and a good negative correlation with SiO_2 (-0.44).

Ga in humus

The median Ga content in humus is 0.90 mg kg^{-1}, and the range varies from <0.1 to 6.80 mg kg^{-1}.

The humus Ga geochemical map shows low values (<0.6 mg kg^{-1}) distributed in an arc linking central and northern Norway with northern and western Finland (with a suspect border effect at the Swedish border, possibly caused by different sampling procedures), most of Ireland, eastern Scotland, western France and parts of northern Germany and central Poland.

High Ga values in humus (>1.60 mg kg^{-1}) are located in a patchwork of seemingly unrelated areas: western Scotland; central Britain; the Ardenne-Eifel in and around southern Belgium; the border area of France, Switzerland and Germany near the Jura and Black Forest mountains; north-eastern Italy; central-eastern Germany and adjacent Czech Republic; an area in west-central Norway, and a small area in south-eastern Sweden. An isolated anomaly occurs near the Antrim basalt of northern Ireland.

Gallium in humus has good correlations with Co (0.57), Ni (0.54), La (0.53) and Rb (0.47).

As Ga replaces Al in phyllosilicates (mica, clay minerals), it can be used to roughly estimate the mineral content of the humus samples.

In central Europe, the Ga distribution pattern in humus, showing average values in the Danube River basin of southern Germany is surrounded by mostly mountainous (shaly) areas with higher metal content, and shows strong similarities with the distribution patterns of Ni, Co, La and Rb, elements that are well correlated with Ga. There is also some similarity to the distribution in soil, suggesting a geogenic character in their distribution in central Europe. Humus samples seem to be very heterogeneous, containing varying amounts of mineral matter. Admixed mineral soil determines the variation in metal content in two ways: a higher proportion of admixed mineral soil increases the metal concentration, and so does a higher proportion of phyllosilicates within the mineral soil itself.

Ga in stream water

Gallium values in stream water range over two orders of magnitude, from <0.002 µg l^{-1} to 0.16 µg l^{-1}, with a median value of 0.011 µg l^{-1}. Gallium data correlate, to a certain extent, with caesium and aluminium. In Fennoscandia the distribution of Ga in stream water is similar to that of Zn.

Lowest Ga values in stream water (<0.006 µg l^{-1}) are found in central Portugal and in south-eastern and north-eastern Spain, in north-eastern France (Variscan terrains), in north-western and north-eastern Italy, western Slovenia and western Croatia (Alpine Orogen terrains), in central and north-eastern Germany (Variscan terrain and glacial drift), in south-western and in northern Norway (Fennoscandian Caledonides), in northern Sweden and Finland (Precambrian Shield), in southern Albania and central Greece (Alpine Orogen terrains).

Highest Ga concentrations in stream water (>0.022 µg l^{-1}) are found in central Spain (in acidic water over igneous rocks, including the Pedroches and Linares granites, and Tertiary continental sediments derived from them), in Massif Central and part of Brittany (Variscan terrains), in Denmark (glacial drift), in southern Sweden and Finland (Precambrian Shield), in central and southern Italy. The latter (from central to southern Italy) are controlled by recent alkaline volcanism of the Roman and Neapolitan geochemical provinces and Vulture volcano (Plant *et al.* 2005). In south and south-west Finland the high Ga values occur where younger K-rich granite outcrops and lanthanides are high; also on the west coast of Finland (near the city of Vasa) concentrations of Ga (and other trace elements) are high due to acid sulphide soil. Isolated enhanced values occur as well in Scotland and in northern Germany. In France, one river draining the Variscan basement of northern Brittany shows an association of Ga with Zn, Fe, Co, Mn, I, V, Tl, Hf and Zr. This association may characterise a spectrum of elements enriched in surface water after dissolution of a Fe-Mn oxides precursor. However, some Ga, like Tl, may also be inherited from Zn sulphide oxidation from various lithologies or old vein mining.

The Ga distribution in stream water is similar to the pattern of REEs and associated elements in acid, low-mineralisation, high-DOC stream water. This pattern is exogenic, caused by climate and vegetation. Gallium in association with Base metals may explain the high Ga stream water in Czechia and Slovakia, and the association with Felsic-alkaline rocks explains high Ga concentrations in Spain, the Italian alkaline volcanic provinces and northern Greece with alkaline volcanics (Plant *et al.* 2005). Gallium patterns in stream water differ much from those in soils and sediments, but some correspondence occurs in Fennoscandia, and more of it in Spain, France, Corsica, the Italian alkaline volcanic province, northern Greece and the Slovak Ore Mountains.

Ga in stream sediment

The median Ga content in stream sediments is 12 mg kg^{-1}, with a range from <1 to 36.0 mg kg^{-1}. The correlation coefficient between Al_2O_3 and Ga is 0.920, and their geographical distribution is nearly identical.

The sandy plains extending from the Netherlands over northern Germany and Denmark, to Poland and the Baltic states, have low Ga values in stream sediment (<7.0 mg kg^{-1}), because of the clay-deficient fluvial and glacial sand and loess cover. Low Ga is also found in western Ireland, parts of central and western France and throughout all but eastern Spain .

The Ga map shows high values in stream sediment (>16.0 mg kg^{-1}) in the western Iberian Peninsula, where crystalline and shale- or gneiss-rich Palaeozoic rocks provide a source area for feldspar and phyllosilicate minerals (mica and clay). The same general lithology causes high values in the Pyrenees, the Central Massif (Cévennes area) and Brittany (Vendée) in France, Corsica, south-west England, Wales and northern England, western Scotland, southern and western Norway, southern Finland, eastern Bavaria and the Czech Republic, eastern Slovakia, the central Alps and northern Greece. In the Canary Islands and in north-east Sicily, high Ga is related to weathering of basaltic rocks. Further, high Ga values occur in parts of Italy. In the Roman Alkaline Province and northern Greece, high Ga values are related to alkaline igneous rocks (Plant *et al*. 2005).

Gallium in stream sediment shows a very strong correlation with Al (0.93), a strong correlation with K, Rb, Fe and V, and a good correlation (>0.4) with Be, Li, Na, Ba, Ti, Ta, Nb, Tl, Co, Eu, Y, Dy and U. It has a good negative correlation with CaO (-0.41).

Ga in floodplain sediment

The Ga distribution in floodplain sediment shows a marked variability ranging from <1.0 to 52 mg kg^1, with a median of 11 mg kg^{-1}.

Low Ga values in floodplain sediment (<7.0 mg kg^1) are found over the glacial drift region extending from Germany to Poland and the Baltic states; the calcareous area of central Ireland, the lower Garonne and Rhône alluvial basins in France; the calcareous and clastic region of eastern Spain and the Baetic Cordillera; the molasse basin of southern Germany and central Austria, and the calcareous and flysch areas of coastal Croatia.

High Ga values in floodplain sediment (>15 mg kg^1) occur in the Scandinavian countries (granite and gneiss of the Fennoscandian Shield and Caledonides), Wales (schist, shale, felsic volcanics) and south-west England (granite), the Armorican Massif in Brittany (felsic rocks), the Massif Central and the Pyrenees in France (mostly felsic crystalline rocks); the north-western Iberian Peninsula (crystalline and shale-rich Palaeozoic rocks, and younger sediments derived from them); Corsica (alkaline volcanics), Italian-Swiss Alps (granite); a belt beginning from the Bohemian Massif in the Czech Republic to the border areas of Austria with Slovakia, Hungary and Croatia (in part residual soil in karst); north-eastern Greece (Rhodope and Serbomacedonian Massifs with gneiss, schist and granite). High Ga is also found in the basalt of Gran Canaria (Canary Islands).

The highest Ga value in floodplain sediment, an outlier with 52 mg kg^{-1}, and occurs in Cornwall (Hercynian granite), south-west England; it is also an outlier for Al_2O_3.

Gallium in floodplain sediment shows a very strong correlation with Al (0.9), a strong correlation with K, Rb, Th, Y, Nb, Ti, Fe, Co and V, and a good correlation with Li, Be, Na, Ba, U, Ta, Tl; the REEs show a good to strong correlation (0.54 to 0.73).

It is concluded that the Ga spatial distribution in floodplain sediment is related to bedrock geology, but also to clay-rich soil with high Al_2O_3 contents.

Ga comparison between sample media

Patterns in Ga distribution between all solid sample media are broadly similar, although lower Ga is present in stream sediment throughout the coastal region of Croatia and Slovenia and in the western parts of Austria (removal of fine-grained material from the residual soil and karst). In the southern tip of Finland and in parts of Britain, higher Ga is observed in stream sediments than other solid sample media. A boxplot comparing Ga variation in subsoil, topsoil, stream sediment and floodplain sediment is presented in Figure 19.

The Ga distribution in humus shows some similarities to patterns in subsoil, indicating geogenic mineral origin, although there are some differences in the distribution patterns. There appear to be some analytical or sampling problems with the humus data for Ga over Sweden.

Patterns in stream water Ga data are markedly different from distributions in the solid sample media and are controlled strongly by pH and DOC, with highest concentrations in acid environments over most of southern Finland, Sweden and Denmark.

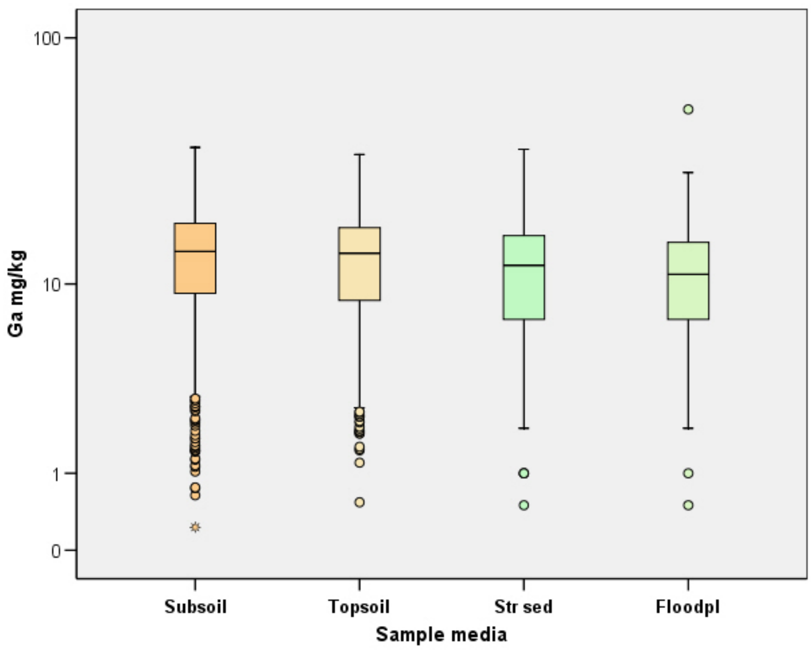

Figure 19. Boxplot comparison of Ga variation in subsoil, topsoil, stream sediment and floodplain sediment.