In – Indium

Introduction

Indium is a metallic element belonging to group 13 of the periodic table, along with B, Al, Ga and Tl. It has an atomic number of 49, an atomic mass of 115, one main oxidation state (+3) and two naturally occurring isotopes (^{113}In and ^{115}In), of which ^{115}In forms 96% of the total mass.

Indium displays distinct chalcophilic behaviour (Goldschmidt 1970), forming solid solutions in zinc and sulphide minerals such as chalcopyrite $CuFeS_2$ and sphalerite ZnS (up to 1.1%) (Wedepohl 1978), with a preference for tin minerals, especially cassiterite SnO_2 (up to 1%), hydrocassiterite (2%), kylindrite $6PbS.6SnS_2.Sb_2S_3$ (1%), teallite $PbS.SnS_2$ (0.3%) and stannite Cu_2FeSnS_4 (0.3%). Minerals in which indium is an essential element are very rare – indeed only three have been observed: dzahlindite $In(OH)_3$, indite $FeIn_2S_4$ and roquésite $CuInS_2$ (Genkin and Muraveva 1964). Indium is equally rare in common rock forming minerals, occurring as either inclusions in the mineral or occupying lattice sites in the mineral crystal.

Concentrations of indium in rock-forming minerals are commonly in the low mg kg^{-1} range, except in sulphide minerals, such as cassiterite (Wedepohl 1978). In general, the occurrence of In in sulphide ores depends on the presence of Sn in the particular ore province (Schroll 1999c). Felsic igneous rocks tend to have higher indium contents (up to 2 mg kg^{-1}), when compared to more mafic rock types (up to 0.22 mg kg^{-1}), although the overall variation in concentration is negligible. Granite tends to have the highest indium concentrations, especially those associated with metal mineralisation. No significant concentrations of In have been observed in the very high temperature ultramafic Cu-Ni sulphide associations (Schroll 1999c). Vinogradov (1962) reports average In concentrations in sedimentary rocks of around 0.05 mg kg^{-1}. In general, clay tends to contain around 0.07 mg kg^{-1} In, whilst shale contains concentrations closer to Vinogradov's average of 0.05 mg kg^{-1} (Wedepohl 1978) and the value of 0.06 mg kg^{-1} reported by Schroll (1999c). Voland (1969) reports indium concentrations as low as 0.009 mg kg^{-1} in limestone.

During weathering, indium oxidises to In^{3+} following Fe^{3+}, Mn^{4+} and, partly, Al^{3+}, and usually precipitates under conditions forming hydrous Fe oxide (Kabata-Pendias 2001). In soil, indium appears to be associated with organic matter and, therefore, its concentration is increased in the surface soil horizon; it is also found in some Fe oxides as a result of their sorption capacity (Kabata-Pendias 2001).

Indium forms a number of complex ions, mainly with halide, when OH$^-$ concentrations are low and hydrolysis is incomplete. In neutral aqueous solutions, indium forms a number of insoluble compounds, such as $In(OH)_3$, In_2S_2, $In(CO_3)_3$ and $InPO_4$. Indium in acid solutions may form several ionic species, *e.g.,* InCl^{2+} and In(OH)$^{2+}$, which are precipitated in the pH range of 5 to 9 (Kabata-Pendias 2001). Several organic anions, *e.g.,* oxalate, are also capable of complexing indium. Compounds of trivalent indium are the most stable and only the trivalent ion is stable in aqueous solution. Compounds of lower oxidation states undergo oxidation in the presence of water to form In^{3+} and elemental indium. There are very few data on indium concentrations in natural water; in sea water the solubility appears to be controlled by $In(OH)_3$ in equilibrium with $In(OH)_4^-$. In river water, indium is likely to occur in ultra-trace amounts, mainly in the form of small colloidal particles, which are efficiently removed in estuaries and coastal water by salt-induced flocculation and settling (Regina Krachler 2004, pers. comm.).

Anthropogenic sources of In include Pb and Zn processing, coal and oil industries, and sewage sludge (Schroll 1999c, Kabata-Pendias 2001). Indium is not widely used in industry, although it is used to coat high-speed bearings, in solar cells, mirrors, regulators in nuclear power, photo cells and transistors, as well as in medical research concerned with blood and lungs. Relatively small amounts are used in dental items and in electronic semiconductors.

Indium has no known biological role, although in small doses it may stimulate the metabolism. There is some unconfirmed evidence suggesting that indium has a low level of toxicity. In the welding and semiconductor industries, where indium exposure is relatively high, there have been no reports of any toxic side effects. However, because insufficient data are available on the effect of In on human health, it should be regarded as potentially toxic.

Table 38 compares the median concentrations of In in the FOREGS samples and in some reference datasets.

Table 38. Median concentrations of In in the FOREGS samples and in some reference data sets.

Indium (In)	*Origin – Source*	*Number of samples*	*Size fraction mm*	*Extraction*	*Median mg kg^{-1}*
Crust[1)]	Upper continental	n.a.	n.a.	Total	0.056
Subsoil	**FOREGS**	**783**	**<2.0**	**Total (ICP-MS)**	**0.05**
Topsoil	**FOREGS**	**840**	**<2.0**	**Total (ICP-MS)**	**0.05**
Soil[2)]	World	n.a.	n.a.	Total	0.07
Water	**FOREGS**	**807**	**Filtered <0.45 µm**		**<0.002 (µg l^{-1})**

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

Indium in soil

The median In content is 0.05 mg kg^{-1} in both subsoils and topsoils, with a range varying from <0.01 to 0.25 mg kg^{-1} in subsoils and up to 0.41 mg kg^{-1} in topsoils. The average ratio topsoil/subsoil is 0.982.

Low In values in subsoil (<0.03 mg kg^{-1}) occur in most of Finland, Estonia, in the glacial drift area from the Netherlands to Poland, in central Hungary, and calcareous southern Spain.

Indium shows high values in subsoil (>0.07 mg kg^{-1}) in northern Portugal (possibly associated with Sn mineralisation, very frequent in northern Portugal) and north-western Spain (granitic basement of the Cordillera Central), the Pyrenees (mineralised intrusions of the Cinco Villas district), the Central Massif and Brittany, Cornwall, Wales, an area in northern Italy extending until the Roman Alkalilne Province, western Austria, Slovenia and coastal Croatia, and scattered point anomalies in Greece (including Lavrion), and the alkaline igneous province of central Macedonia, the Erzgebirge (Czech-German border) and Norway.

The topsoil In distribution map shows higher values in France and a more extended anomaly in the western Iberian Peninsula (including the Pedroches granitic batholith and Linares-La Carolina granites in south-central Spain), and additional point anomalies in northern Germany, the English Lake District and the Canary Islands. Indium in Italy is generally lower in topsoil than in subsoil. The remaining patterns of the topsoil map are very similar to those on the subsoil map. Indium enrichment in some topsoil may be related to fly ash from coal power plants and also from smelting of tin ores, but also to soil forming processes.

In subsoil, indium shows a very strong correlation with Ga (0.81), a strong correlation (>0.6) with Al, Fe, Sc, V, Ti, Nb, Ta, Rb, Zn, Y and the REEs, and a good correlation (>0.4) with Mn, K, Be, Co, Pb, Th, As, Bi, Cs, Cu, Te and Tl. This pattern is consistent with the presence of indium as a trace element in phyllosilicates where most In^{3+} substitutes for Al^{3+}. It is thus enriched in shale and crystalline rocks. The pattern of correlations is very similar in topsoils, with additionally a good correlation between In and U.

In in stream water

Indium values in stream water range from <0.002 to 0.015 µg l^{-1}, with a median value below the detection limit of 0.002 µg l^{-1}. More than 90% of the data are less than the analytical limit of quantification, so only the highly anomalous values are clearly resolved, and proper interpretation of the results is impossible.

A few isolated enhanced indium values in stream water occur in the Netherlands and in northern Germany on glaciofluvial terrains, in central and eastern Germany, and in Sicily (Italy).

In comparison between sample media

The analytical data for indium in stream and floodplain sediments have not been reported, because the analytical data did not pass the quality control checks. There is generally good agreement between patterns in topsoil and subsoil. Indium concentrations in stream water are generally less than the analytical limit of detection.