

Introduction

Tin is a metallic element belonging to group 14 of the periodic table, along with C, Si, Ge and Pb. The element has an atomic number of 50, an atomic mass of 119, three main oxidation states (-2, +2 and +4), of which the +4 state is by far the most common in nature, and ten naturally occurring isotopes, the largest number of all elements (^{112}Sn , ^{114}Sn to ^{120}Sn , ^{122}Sn and ^{124}Sn), of which ^{120}Sn , ^{118}Sn and ^{116}Sn are the most abundant at 32.97%, 24.01% and 14.24% respectively of its mass. Tin shows intermediate characteristics in its chemistry between that of Ge and Pb.

Like Pb, Sn is a relatively rare metal, with an average crustal abundance of 2.1 mg kg^{-1} , but it is well known as a metallic element, because of its use in household products and the relative ease of its extraction from natural sources. It is one of the seven metals known in antiquity. Tin is a siderophile metallic element forming several minerals, including cassiterite SnO_2 and the rarer stannite $\text{Cu}_2\text{FeSnS}_4$, but can also be present as an accessory element in biotite, muscovite, amphibole, sphene and rutile.

During magmatic processes, Sn^{4+} may replace Ti^{4+} and Fe^{3+} in accessory minerals such as sphene, ilmenite, rutile and magnetite. The small, highly charged Sn^{4+} ion is strongly concentrated as $(\text{SnO}_4)^{4-}$ complexes in residual melts, and thus becomes enriched in felsic relative to mafic igneous rocks. Mielke (1979) cites values for the Sn content of igneous rocks as: ultramafic 0.5 mg kg^{-1} ; basalt 1.5 mg kg^{-1} , and granite $1.5\text{--}3 \text{ mg kg}^{-1}$. Tin is generally associated with oxygen in high-temperature minerals and sulphur at lower temperatures (Mielke 1979). In later stages of magmatic differentiation, Sn will become concentrated in the remaining melt until cassiterite SnO_2 is formed, and Sn may also substitute for Cb, Ta and W. Cassiterite is often present as a disseminated accessory phase in evolved granite, and accumulates to economic levels in discrete hydrothermal veins and metasomatic deposits closely associated with highly siliceous lithologies (Ganeev *et al.* 1961, Ure and Berrow 1982). The main Sn carriers in granitic rocks are hornblende, biotite, muscovite, titanite, garnet, ilmenite and magnetite.

In sedimentary rocks, the concentration of Sn is primarily determined by the abundance of

resistate minerals such as cassiterite, sphene and magnetite. Small amounts of Sn dissolved during the weathering of mica may precipitate with Al-rich hydrolysates, thus accounting for the widespread accumulation of the metal in bauxite (Wedepohl 1978). Argillaceous and calcareous sediments typically contain Sn at levels in excess of the crustal average ($4\text{--}6 \text{ mg kg}^{-1}$), while sandstone (*ca.* 1 mg kg^{-1}) are generally depleted. In tropical soil, values of up to 60 mg kg^{-1} Sn have been recorded, with a large proportion held in clay and organic matter (Aubert and Pinta 1977). Mielke (1979) reports Sn levels of 6 mg kg^{-1} in shale, and $<1 \text{ mg kg}^{-1}$ in sandstone and carbonate rocks. The average content of Sn in loess is given as 5 mg kg^{-1} (McLennan and Murray 1999).

The mobility of Sn during weathering is highly pH dependent and, Sn^{2+} , which is a strong reducing agent, is only present in acid and reducing environments (Kabata-Pendias 2001). Soluble Sn follows the behaviour of Fe and Al and remains in the weathered residue along with hydroxides of these metals. Tin forms soluble and insoluble complexes with organic substances. The occurrence of Sn in soil has not received much study. From the available data, Kabata-Pendias (2001) report a range of values varying from 1 to 11 mg kg^{-1} Sn with an average of 1.1 mg kg^{-1} .

In stream sediment, most detrital Sn is held in resistant oxide phases, such as cassiterite, which release Sn very slowly during weathering. Weathering of most natural and anthropogenic Sn carriers is intensified under acid, reducing conditions, although SnS_2 is insoluble under reducing conditions (Brookins 1988). Any Sn^{2+} released oxidises rapidly and is subsequently bound to secondary oxides of Fe or Al as $\text{Sn}(\text{OH})_4$ or $\text{Sn}(\text{OH})_3\text{O}^-$. The human-made organo-tin pesticide tributyltin readily adsorbs onto suspended particulate material (De Mora and Phillips 1997). In areas where Sn mineralisation is absent, Sn is an excellent indicator of contamination. Contaminated samples are often indicated by the presence of high levels of other metals such as Pb, Zn and As, which are not associated with Sn mineralisation. Concentrations of Sn in United Kingdom river water are typically

less than 0.5 $\mu\text{g l}^{-1}$ (Neal and Robson 2000). Reimann and de Caritat (1998) claim average concentrations in stream water to be less than 0.01 $\mu\text{g l}^{-1}$.

Anthropogenic sources of tin include coal and wood combustion, waste incineration and sewage sludge (Reimann and de Caritat 1998). Other anthropogenic Sn sources include alloys such as solder (Sn-Pb), agricultural pesticides and wood preservatives in which organo-Sn compounds have been used.

Tin is believed to be an essential trace element in some organisms, potentially including humans, although its function has not been determined. Many Sn compounds are toxic to lower

organisms. Organo-tin compounds, which are persistent and not easily biodegradable, are of particular concern, for example in the well documented cases of shell abnormalities in shellfish and imposed in gastropods caused by tributyltin in anti-fouling paints for ships (De Mora and Phillips 1997). Toxic levels of inorganic Sn can cause growth depression and anaemia in humans, and also interferes with the metabolism of Zn, Cu and Ca (WHO 1996). Fortunately, Sn is poorly absorbed by the human body.

Table 62 compares the median concentrations of Sn in the FOREGS samples and in some reference datasets.

Table 62. Median concentrations of Sn in the FOREGS samples and in some reference data sets.

<i>Tin (Sn)</i>	<i>Origin – Source</i>	<i>Number of samples</i>	<i>Size fraction mm</i>	<i>Extraction</i>	<i>Median mg kg⁻¹</i>
Crust ¹⁾	Upper continental	n.a.	n.a.	Total	2.1
Subsoil	FOREGS	788	<2.0	Total (ICP-MS)	3.00
Topsoil	FOREGS	845	<2.0	Total (ICP-MS)	3.00
Soil ²⁾	World	n.a.	n.a.	Total	4
Stream sediment	FOREGS	852	<0.15	Total (XRF)	2.25
Floodplain sediment	FOREGS	747	<2.0	Total (XRF)	2.00
Stream sediment ³⁾	Canada	47 216	<0.18	Total (INAA)	1

¹⁾Rudnick & Gao 2004, ²⁾Koljonen 1992, ³⁾Garret 2006.

Sn in soil

The median Sn content in both subsoil and topsoil is 3 mg kg⁻¹, and slightly less than half the values are below the detection limit of 2 mg kg⁻¹. The maximum value in both subsoil and topsoil is 106 mg kg⁻¹ Sn. The average ratio topsoil/subsoil is 1.134.

Low Sn values in subsoil (<2 mg kg⁻¹) occur in Ireland, northern Britain, large parts of Fennoscandia, the Baltic states, Poland, northern Germany, part of northern France and adjacent Belgium, central Hungary, the Dalmatian coast of Croatia, Albania, northern and southern Greece, and south-east Spain.

In subsoil, Sn shows high values (>5 mg kg⁻¹) in south-west England, southern Brittany, the Massif Central, the Erzgebirge, the Black Forest, western Austria, the Central Iberian Zone of

northern Portugal and western Spain (granitic basement, and some W-Sn mineralisation), one point anomaly in north-east Greece (with the highest Sn value near to the Simvolos granite). In most cases enrichment can be traced back to known ore deposits or tin-bearing districts. The distribution map for W shows some resemblance, but on closer inspection the point anomalies of W seldom coincide with the highest Sn values.

There are some minor differences between the subsoil and topsoil Sn distribution maps. A slight enrichment occurs in topsoil, as indicated by the average ratio topsoil/subsoil of 1.134.

In subsoil, Sn shows a good correlation (>0.4) with Ta, Be, Th, Cs, Bi, Tl, Rb and Y, and a weak correlation (>0.3) with Ce, Nb, Ga, In, U, As and Zn. This pattern is very similar in topsoil. The

association with Be, Bi, As, Ta, Nb, Cs and Rb points to the leucogranitic/ greisen association,

typical for tin mineralisation.

Sn in stream sediment

The median Sn content in stream sediment is 2.10 mg kg^{-1} , with a range varying from <1 to 188 mg kg^{-1} . About 22% of the values are below the detection limit.

The Sn stream sediment distribution map shows low areas ($<1 \text{ mg kg}^{-1}$) throughout most of Finland, central and northern Norway, the Baltic states, the northern European lowlands in Poland, Denmark, Netherlands and north-western Germany, central Austria, eastern Hungary and parts of Greece.

High Sn values in stream sediment ($>4.0 \text{ mg kg}^{-1}$) occur mainly in southern England (with anomalous values in Cornwall), a large area in France over the Massif Central and extending into Brittany, the Vosges Mountains, the northern Bohemian Massif, southern Norway, the Central Iberian Zone of northern Portugal (where W-Sn

mineralisations are known) and western Spain (granitic basement with mineralisation), Corsica and the alkaline magmatic province in Italy. In most cases, the high Sn values can be traced back to known ore deposits or tin-bearing districts. A point anomaly appears over the Mourne granite in northern Ireland, and in Attica, Greece, where it may either indicate unknown mineralisation or contamination by industrial activities.

Tin in stream sediment has a good positive correlation (>0.4) with Ta, W, Y, Rb, U and Th, and a weak correlation (>0.3) with Cd, Tl, Cs and most REEs. This is caused by the leucogranitic/greisen association characterising tin mineralisation or enrichment, possibly enhanced in stream sediments by the gravity concentration of heavy minerals such as cassiterite, tantalite, wolframite, xenotime and monazite.

Sn in floodplain sediment

Total Sn values in floodplain sediment vary from <1.0 to 649 mg kg^{-1} , with a median of 2.0 mg kg^{-1} ; it is noted that about 25% of the XRF determinations are below the detection limit of 1 mg kg^{-1} . Therefore, the variation in the lower Sn values is constrained by the detection limit of the analytical method.

Low Sn values in floodplain sediment ($<1.00 \text{ mg kg}^{-1}$) occur in the north of Europe over most of Finland and Sweden on the Precambrian crystalline rocks; parts of Norway, and north Scotland on predominantly Caledonide metamorphic rocks; most of Ireland on limestone, clastics and crystalline rocks; glacial drift covered north-west Germany, and over the glacial drift covered plain extending from Poland to the Baltic countries; in southern Europe, low Sn values are found in small areas in southern Spain on clastic and calcareous rocks, southern Italy with Tertiary sediments, and the calcareous Dalmatian coast of Croatia, and central Greece on clastic, carbonate and ophiolitic rocks.

High values Sn in floodplain sediment ($>4.00 \text{ mg kg}^{-1}$) occur in the Variscan areas of south-west England (Camborne-Redruth Sn-W), northern

Portugal (can be associated to the drainage of the W-Sn Panasqueira mine) and adjacent part of Spain associated with the Extremadura and Pedroches granite batholiths; Galicia in north-west Spain (Santa Comba Sn-W, Fontao Sn-W-Mo, San Finx W-Sn-Mo) and adjacent areas of Zamora and Salamanca with Sn-W mineralisations; the Bilbao anomalous zone draining calcareous rocks and shale is ascribed to industrial contamination; in France along the Pyrenees, and over the Massif Central to Brittany, associated with granite and mineralisation (e.g., Abbaretz Sn, Echassieres Li-Sn-Be-Ta); near the German-Czech border (Altenberg Sn-Ag, Cinovec Sn-W deposits in the Erzgebirge); and northern Sardinia (granite).

The point Sn floodplain sediment anomaly in the Vesdre basin of Belgium is attributed to pollution by metallurgical activities. Further, large areas with high Sn values in France, central Britain and Germany, not associated with mineralisation, are suspected to be caused by agricultural pollution (possible use of organo-Sn pesticides, which should however be investigated). The high Sn value in floodplain

sediment near Glasgow in Scotland may be related to volcanic rocks of the Midland Valley, but is more likely to be of industrial origin.

Several outliers of Sn in floodplain sediment are present in two Variscan areas that were close together before the opening of the Bay of Biscay: south-west England with the Dartmoor granite (649 mg kg⁻¹) and Saint Austell granite (118 mg kg⁻¹), and northern Portugal with three highly anomalous points (260, 238 and 181 mg kg⁻¹), all related to mineralisation.

Tin in floodplain sediment shows a good correlation with As, Ta, Rb and W, and a weak correlation with Be, Li, Tl, Nb, Cs, Th and U.

In conclusion, high Sn values in floodplain sediment are related to granite intrusives hosting mineralisation. However, there are high Sn values in France, central Britain and Germany, which are not directly associated with mineralised granite, and are suspected to be caused by agricultural pollution, and others by industrial processes (*e.g.*, Bilbao in Spain and Vesdre basin in Belgium).

Sn comparison between sample media

Patterns in Sn distribution between all solid sample media are broadly similar, although there are some significant differences. Compared to soil, stream sediment is higher in Sn in southern Norway, Britain, central Italy, Corsica, Albania and in the border area between Poland and the Czech Republic. Floodplain sediment (and to a lesser extent stream sediment) is enhanced throughout France, and in a belt extending from central Germany to the Czech Republic influenced by the mineralisation and historical mining of the

Erzgebirge. There is a depletion in sediment Sn concentration in the coastal area of Croatia compared to soil concentrations. A boxplot comparing Sn variation in subsoil, topsoil, stream sediment and floodplain sediment is presented in Figure 44.

Stream water data have been rejected on the grounds that a significant number of samples were contaminated during sampling and subsequent storage prior to analysis.

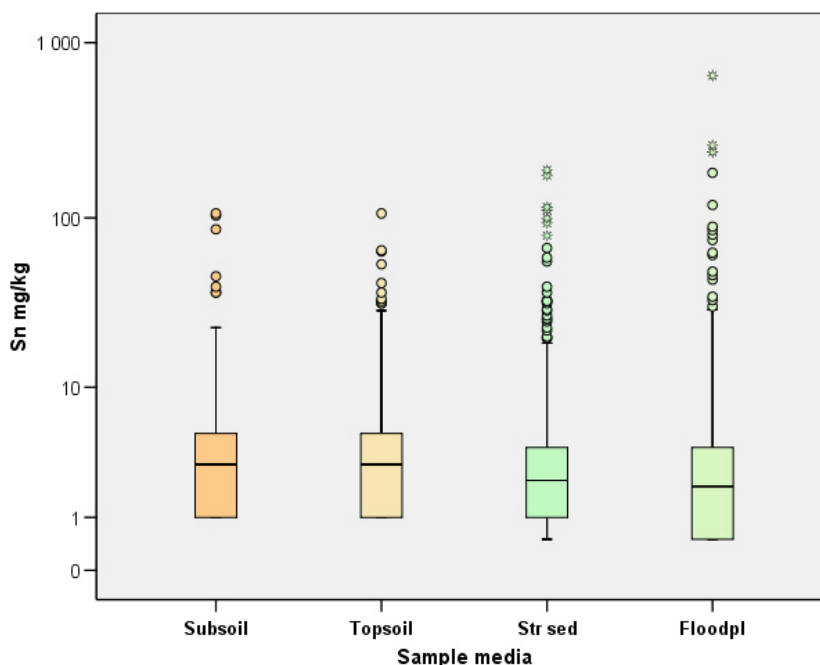


Figure 44. Boxplot comparison of Sn variation in subsoil, topsoil, stream sediment and floodplain sediment.