Ta – Tantalum

Introduction

Tantalum belongs to group 5 of the periodic table, along with V and Nb. The element has an atomic number of 73, an atomic mass of 181, one oxidation state (+5), and two stable isotopes (^{180}Ta and ^{181}Ta), of which ^{181}Ta is the most abundant at 99.99% of the total mass.

Tantalum is lithophile element with chalcophile affinities. Its average crustal abundance is 1.7 mg kg-1 (Fyfe 1999). Tantalum is almost exclusively found in complex oxide and hydroxide minerals, with the exception of the borate mineral behierite (Ta,Nb)[BO_4] and the only known non-oxide, tantalum carbide TaC (Wedepohl 1978). Common Ta minerals include tantalite (Fe,Mn)$(Ta,Nb)_2O_6$, formanite $YTaO_4$, and mikrolithe $(Ca,Na)_2[Ta_2O_6](O,OH,F)$. Tantalum is nearly always found in association with Nb.

The most common host minerals for Ta in igneous rock types include pyroxene, amphibole, biotite, ilmenite and sphene. Minerals such as sphene and ilmenite contain the highest concentrations of Ta (*ca.* 250–350 mg kg^{-1}), whereas pyroxene minerals contain much less, typically <7 mg kg^{-1} (Sitnin 1966). Biotite, amphibole and Ti-rich minerals are noted as the major sources of Ta in magmatic rocks. Granitic rocks may contain 5–13% biotite, which can contribute up to half the Ta content of granite (Wedepohl 1978). Granitic rock types contain on average 0.5–2.5 mg kg^{-1} Ta, whilst some alkali rocks have been reported to contain up to 33 mg kg^{-1} Ta (Borodin *et al.* 1969). Ultramafic and mafic rocks generally contain <0.5 mg kg^{-1} Ta, whilst Atkins and Smales (1960) record as little as 0.018 mg kg^{-1} Ta in dunite.

Limited data are available on the abundance of Ta in sedimentary rock types. Pachadzhanov (1963) reports average Ta concentrations of 2 mg kg^{-1} from Russian Platform shale and clay, which is similar to the average concentration found in magmatic rocks from the upper continental crust. Sedimentary rocks from humid environments have been reported to contain concentrations up to 2.4 mg kg^{-1}, whilst rocks from arid environments contain on average as little as 0.9 mg kg^{-1} Ta (Wedepohl 1978). Parekh *et al.* (1977) suggest concentrations of Ta in Upper Jurassic limestone to be as low as 0.043 mg kg^{-1} with an average of 0.22 mg kg^{-1}. The average content of Ta in river particulates is quoted as 1.25 mg kg^{-1} (McLennan and Murray 1999). In geochemical prospecting Ta may be used as pathfinder for Ta-rich pegmatite or carbonatite.

Kabata-Pendias (2001) reports that there is a paucity of information about the occurrence of Ta in soil, but give an average value for loess as 1 to 2 mg kg^{-1}. It is also believed to be less mobile than Nb during weathering, because of its lower solubility and the slight stability of organic complexes.

Data on Ta in the aquatic environment is scarce. Tantalum in natural water is most likely to be present as poorly soluble tantalic acid ($Ta_2O_5.xH_2O$) or as TaF_5. Fluoride is known to mobilise Ta, whilst most other inorganic anions form insoluble salts with Ta. The hydrated oxides will dissolve in aqueous solutions of oxalic, tartaric and citric acids. Tantalum will also form water-soluble complexes with a variety of other phenolic or carboxylic hydroxyacids, and with a number of amines (Fairbrother *et al.* 1958). Tantalum may, therefore, form complexes with organic materials, including oxalic acids and their analogues (Ciaravino *et al.* 2002), and humic and fulvic acids in natural water. Concentrations of Ta in sea water are typically <2.5 ng l^{-1}, whilst in freshwater Ta concentrations are generally <1 to 10 ng l^{-1} (Wedepohl 1974).

Tantalum is mainly used to make electrolytic capacitors and vacuum furnace parts, which account for about 60% of its use. The metal is also widely used to fabricate chemical process equipment, nuclear reactors, aircraft and missile parts, and carbide tools for metalworking equipment. Because of its biologically inert characteristics, it is also used in medical applications for plates or disks to replace cranial defects, for wire sutures and for making prosthetic devices. Tantalum has also been used in firearms manufacture and may have led to elevated concentrations of Ta around military installations (Lisa Axe 2004, pers. comm.).

Tantalum is considered to be a non-essential element, although almost nothing is known about its abundance in living organisms, and little is known of the environmental impacts of Ta. Its poor solubility and mobility imply that toxicological effects are probably insignificant, at least at current environmental concentrations.

Table 64 compares the median concentrations of Ta in the FOREGS samples and in some reference datasets.

Table 64. Median concentrations of Ta in the FOREGS samples and in some reference data sets.

Tantalum (Ta)	*Origin – Source*	*Number of samples*	*Size fraction mm*	*Extraction*	*Median mg kg⁻¹*
Crust[1)]	Upper continental	n.a.	n.a.	Total	0.9
Subsoil	**FOREGS**	**790**	**<2.0**	**Total (ICP-MS)**	**0.69**
Topsoil	**FOREGS**	**843**	**<2.0**	**Total (ICP-MS)**	**0.68**
Soil[2)]	World	n.a.	n.a.	Total	1.1
Water	**FOREGS**	**807**	**Filtered <0.45 µm**		**<0.002 (µg l⁻¹)**
Stream sediment	**FOREGS**	**848**	**<0.15**	**Total (XRF)**	**1.01**
Floodplain sediment	**FOREGS**	**743**	**<2.0**	**Total (XRF)**	**0.83**
Stream sediment[3)]	Canada	26 227	<0.18	Total (INAA)	0.9

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

Ta in soil

The median Ta content is 0.69 mg kg^{-1} in subsoil and 0.68 mg kg^{-1} in topsoil, and the range varies from <0.05 to 7.18 mg kg^{-1} in subsoils and up to 6.78 mg kg^{-1} in topsoils. The average ratio topsoil/subsoil is 0.999.

Niobium and tantalum are closely associated in phyllosilicate and oxide minerals, among them are columbo-tantalite and pyrochlore, but they are also present as traces in other oxides. As expected, their correlation coefficient is very high: 0.87 in subsoil, and 0.89 in topsoil. Anomalies of Ta-Nb can be subdivided into those related to primary crystalline massifs (see Be), and those related to alluvial deposits (see Zr).

Low Ta values in subsoil (<0.46 mg kg^{-1}) occur in central Finland, in the glacial drift area from the Netherlands to Lithuania, in western Ireland, and in south-eastern Spain.

In subsoil, Ta shows high values (>0.94 mg kg^{-1}) in the Massif Central in France, in northern Portugal and Galicia in north-west Spain, and reflects the major leucogranitic bodies and related greisen cupola mineralisation (enriched in Be, Li, Nb, W, Sn, Ta, etc). Other anomalies occur in the loess/palaeoplacer area from northern France to central Germany (Salpeteur *et al*. 2005), in the alkaline magmatic province of Italy, and in a large area including north-eastern Italy, Slovenia, Croatia and adjacent areas of Austria and Hungary. It is also enriched in northern Sweden, and a few isolated points in southern Norway, clay-rich old residual soil near Rovaniemi (Finland), Mourne granite (northern Ireland), Glasgow (Scotland), and the Canary Islands. Elevated Ta values in Greece are found in *terra rossa* soil (Epirus, Kefallinia), felsic rocks (central Macedonia) and near to bauxite mineralisation (central and western Greece).

There is little difference between the topsoil and subsoil Ta distribution maps, and the average ratio topsoil/subsoil is 0.999.

Tantalum in soil shows a very strong positive correlation with Nb (0.85), a strong correlation (>0.6) with Be, Th, Rb, Al, Ga, In, and some light REEs, and a good correlation (>0.4) with Pb, U, K, Sn, Cs, Tl, Fe, V, As, Bi, Ti, Hf, Y and the remaining REEs.

Ta in stream water

Tantalum values in stream water range from <0.002 µg l^{-1} to 0.014 µg l^{-1} (excluding two outliers up to 0.12 µg l^{-1}), with about 80% of the data below the analytical limit of quantification. This naturally makes a realistic and definitive interpretation of the distribution patterns very difficult.

Low Ta values in stream water (<0.002 µg l^{-1}) are distributed almost all over Europe, with the exception of restricted areas of higher values, due to the poor data resolution.

Highest Ta concentrations in stream water (>0.006 µg l^{-1}) are found in central Sweden (probably related to Nb-bearing granite and pegmatite, but alum shale can contribute to higher Ta values in soil and stream water), in western Finland, in north-eastern England, in southern Portugal, and in all Albania. Enhanced values (between 0.003 and 0.006 µg l^{-1}) also occur in western Finland, southern Lithuania, along the border between Germany and Poland, northern Ireland, western Portugal and southern Italy. In Finland fluoride and humic acids enhance mobility of Ta. Still in Finland, Ta concentrations are high in the Proterozoic areas and low in the Archean basement; Ta-bearing pegmatite is documented from south and south-west Finland. The relatively high Ta in north-east England is associated with both heavy industrial industries in the surrounding areas, and could also be related to the underlying Durham Coalfield. Isolated enhanced values occur in central Sweden, western Slovakia, northern Germany, in France (Brittany and Lorraine) and in central-southern Italy. The latter values in Italy are certainly controlled by recent alkaline volcanism of the Roman and Neapolitan geochemical provinces and related hydrothermalism in groundwaters. The isolated Ta anomaly in south-eastern Germany is attributed to anthropogenic pollution.

The distribution pattern of high Ta in stream water follows generally the REEs acid, low-mineralisation, high-DOC stream water pattern type that is chiefly climate-dominated, and the Alkaline-rock-elements pattern which is geogenic. The major soluble species in the former water type are organic complexes. Some correspondence of aqueous anomalies with those in solid sample materials occurs over alkaline rocks of the Central Massif in France, over volcanic areas in Italy, and the Erzgebirge in Germany. The source for very high concentrations in Albania is either in Neogene volcanism or Triassic-Jurassic rifting volcanism.

Ta in stream sediment

The median Ta content in stream sediment is 1.01 mg kg^{-1}, and the range varies from 0.05 to 58.4 mg kg^{-1}.

Low Ta areas in stream sediment (<0.71 mg kg^{-1}) include much of eastern Finland, the northern European plain from Poland to the Netherlands, the Baltic states, central Ireland, eastern France, most of Greece, small parts of northern and central Italy, Catalonia and most of the Baetic cordillera in Spain.

On the Ta distribution map, the strongest stream sediment anomaly can be observed in northern Portugal and adjacent areas of Spain, reflecting the geological background with leucogranitic bodies and related greisen mineralisation (enriched in Be, Li, Nb, W, Sn, Ta, etc), and the lower Palaeozoic sediments of the Sierra Morena in southern Spain. Other areas with high Ta in stream sediment (>1.42 mg kg^{-1}) are the Massif Central and southern Brittany in France, the Canary Islands (alkaline volcanism rich in Ta and Nb, low in Y), Corsica, the Pannonian part of Croatia, south-eastern Austria, Albania (possibly related to Mesozoic rifting volcanism), the border area between Czech Republic and Germany, eastern France (Vosges), western Scotland, and parts of southern and central Norway and northern Sweden. Point anomalies are present in northern Estonia, near Oslo (alkaline granite in the Oslo graben), near the Mourne granite in northern Ireland, and in western Austria. A point anomaly near the French-Belgian border may be related to pollution by a former smelting operation.

Tantalum in stream sediment shows a strong correlation (>0.6) with Nb, Tl, Lu, Yb and Tm, and a good correlation with Be, Al, Ga, K, Rb, Cs, Ti, Sn, Th, U, Y and the remaining REEs.

Ta in floodplain sediment

Tantalum values determined by ICP-MS on floodplain sediment vary from 0.1 to 38.1 mg kg^{-1}, with a median of 0.83 mg kg^{-1}, but the range is from 0.1 to 5 mg kg^{-1} if two outliers above 10 mg kg^{-1} are excluded.

A notable feature of the Ta distribution in floodplain sediment is its low content (<0.52 mg kg^{-1}) over the glacial drift covered plain extending from north Germany and Poland to western Latvia. Other areas with low Ta values in floodplain sediment are the metamorphic basement rocks in eastern Finland; most of Ireland, the Tertiary basins of Duero and Ebro Rivers, and the La Mancha and the Pyrenees in Spain, the molasse basin of Austria, and parts of Albania and Greece with carbonate and ophiolite rocks.

High Ta values in floodplain sediment (>1.19 mg kg^{-1}) occur on felsic and alkaline igneous and on sediments derived from them. Such values are found in parts of Fennoscandia, central and eastern Sweden, and central and northern Norway, on mostly felsic crystalline rocks. High Ta contents are encountered on mostly felsic crystalline rocks of western Iberian Peninsula, in the Central Massif of France, on Corsica, over carbonate and clastic rocks of the lower Paris Basin (heavy mineral concentrates in Tertiary clastics) and on the Lorraine plateau of France; in a belt of mostly clastic and partly crystalline rocks from Belgium across Germany to the Erzgebirge and western part of the crystalline Bohemian Massif; over crystalline and sedimentary rocks of the Swiss-Italian Alps, north central Apenninic Italy and the Roman Alkaline Province, volcanic north part of Sardinia, Corsica (granite and schist), the loose sediments of southern Hungary and Croatia, and on carbonate rocks of Croatia and Slovenia, where Ta appears to be enriched in karstic soil.

The floodplain sediment sample with the highest anomalous Ta value of 38.1 mg kg^{-1} is in Portugal, possibly related to the Borralha W deposit, and the second highest in Cornwall, associated with the St. Austell granite. Anomalous Ta contents were also found on young basalt of Gran Canaria in the Canary islands.

An isolated high Ta value in floodplain sediment appears on the Lule River in the Norbotten province of north Sweden, which may be related to granitic rocks and mineralisation. It is worth noting that no Ta and Nb signatures are recorded by the floodplain sediment sample on the Kemi River draining the large Sokli P-Nb deposit in carbonatite in north-east Finland.

Tantalum in floodplain sediment shows a strong positive correlation with Nb, Tl, Rb, Th and most of the REEs, a good correlation with Al_2O_3, Ga, K, Ti, V, Hf, Sn, Cs, W, U and Y, and a weak correlation with Fe, Be, Li, As, Zr and Cs.

In conclusion, high Ta values in floodplain sediment are mainly due to felsic crystalline and alkaline igneous rocks and mineralisation.

Ta comparison between sample media

Patterns in Ta distribution between all solid sample media are generally similar. The main differences are the higher Ta observed in soil in the alkaline volcanic provinces of Italy, and the higher values in stream sediment in Albania compared to all other solid sample media. Tantalum is also lower in stream sediments along coastal Croatia and Slovenia (possibly explained by the removal of fine-grained material from residual soil).

A boxplot comparing Ta variation in subsoil, topsoil, stream sediment and floodplain sediment is presented in Figure 46.

Tantalum in stream water tends to be less than the detection limit throughout most of Europe, although areas of higher concentration tend not to correlate with high Ta values in solid sample media, except in the alkaline volcanic province of Italy and in Albania (Ta is known to be enriched in volcanic rocks). Distributions are partially controlled by DOC, since Ta is normally highly insoluble unless complexed with organic materials. High concentrations are, therefore, associated with the organic rich environments of parts of southern and central Fennoscandia. Other Ta highs are probably explained by local anthropogenic influences.

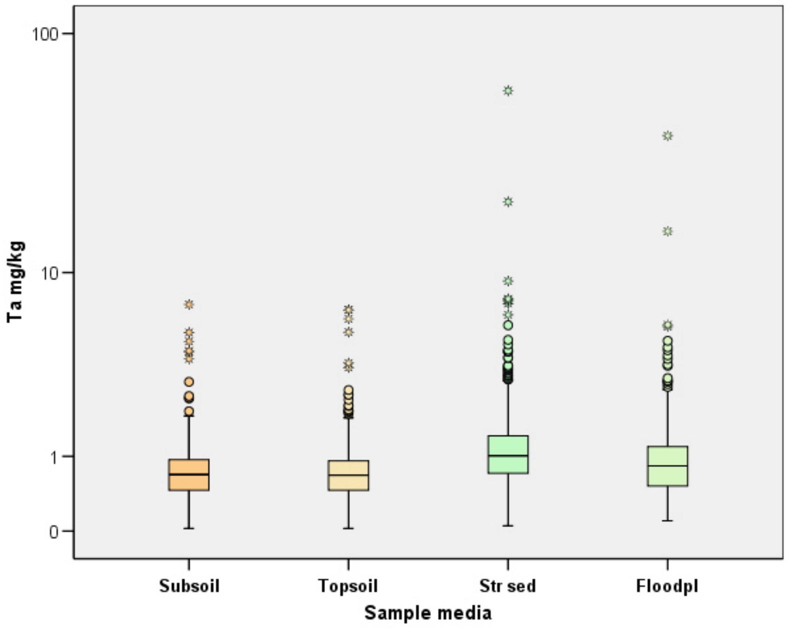

Figure 46. Boxplot comparison of Ta variation in subsoil, topsoil, stream sediment and floodplain sediment.