

## Introduction

Tungsten, also known as wolfram, belongs to group 6 of the periodic table, along with Cr and Mo. The element has an atomic number of 74, an atomic mass of 184, two main oxidation states (+4 and +6), and five stable isotopes ( $^{180}\text{W}$ ,  $^{182}\text{W}$ ,  $^{183}\text{W}$ ,  $^{184}\text{W}$  and  $^{186}\text{W}$ ), of which  $^{184}\text{W}$ ,  $^{186}\text{W}$  and  $^{182}\text{W}$  are the most abundant at 30.64%, 28.426% and 26.498% respectively. Tungsten is most similar chemically to Mo, and its chemistry is amongst the most complex of the transition elements.

Tungsten is a relatively rare element, with a crustal abundance of around 1.0–1.5 mg kg<sup>-1</sup>, similar to that of its group neighbour Mo. Tungsten is a strongly lithophile element, although it is siderophile in iron meteorites, and is markedly less chalcophile than Mo. Apart from sulphides, where it occurs as the W<sup>4+</sup> cation in the rare mineral tungstenite, WS<sub>2</sub> (*cf.* molybdenite, MoS<sub>2</sub>), W has an essentially anionic geochemistry based on the tungstate WO<sub>4</sub><sup>2-</sup> ion, in which the W<sup>6+</sup> ion is present in four- or six-fold coordination. The W<sup>4+</sup> ion has a radius of 66 pm, close to that of Zr<sup>4+</sup> (72 pm) and Mo<sup>4+</sup> (65 pm). The ionic radius of W<sup>6+</sup> is 60 pm in six-fold coordination and 42 pm in four-fold coordination, compared with 59 pm and 41 pm for the equivalent Mo ions and coordination numbers. This close similarity between W and Mo is reflected in their minerals, which are often isostructural and show variable replacement and solid-solution between nominal W and Mo end members. The principal W ore minerals wolframite (Fe,Mn)WO<sub>4</sub> and scheelite CaWO<sub>4</sub> can be compared with powellite CaMoO<sub>4</sub> and wulfenite Pb(Mo,W)O<sub>4</sub>. Tungsten also occurs at trace levels (*ca.* 1 mg kg<sup>-1</sup>) in several rock-forming minerals. It is notably enriched in mica, which may commonly contain 5–50 mg kg<sup>-1</sup>, and muscovite in altered granite near W deposits may contain up to 500 mg kg<sup>-1</sup> (Wedepohl 1978). Accessory Fe-Ti oxide minerals in igneous rocks contain up to 10 mg kg<sup>-1</sup> W. In geochemical prospecting, W is used as pathfinder for its deposits and for many types of gold deposit.

Tungsten levels are generally somewhat higher in granitic rocks (1.5 mg kg<sup>-1</sup>) than in mafic (0.5–1.0 mg kg<sup>-1</sup>) and ultramafic rocks (0.1–0.8 mg kg<sup>-1</sup>). Late-stage magmatic processes tend to

concentrate W, and wolframite often occurs in pegmatite and associated quartz veins. Scheelite is more common in skarn deposits at granite-limestone contact zones. The limited data available for W in metamorphic rocks shows little evidence of mobilisation. However, it is possible that Na-rich fluids may dissolve W during metasomatism and transport it as Na<sub>2</sub>WO<sub>4</sub> at high temperatures, with subsequent concentration elsewhere. Graphitic schist and phyllite often show relatively high W levels (*ca.* 20 mg kg<sup>-1</sup>) possibly reflecting enrichment in their original black shale sedimentary source rock.

Common clastic sedimentary rocks, such as sandstone and shale usually contain W levels similar to those in igneous rocks, typically 1–2 mg kg<sup>-1</sup>. Lithochemical data for W are scarce, but limestone is generally low in W, typically <0.5 mg kg<sup>-1</sup>, while coal ashes are relatively enriched (Wedepohl 1978). Black shale may also be enriched in W. McLennan and Murray (1999) cite an average value of 1.6 mg kg<sup>-1</sup> for loess.

Kabata-Pendias (2001) reports that there is scarcity of data concerning the occurrence of W in soil although, since the geochemical behaviour of W resembles that of Mo, some assumptions can be made. An interesting observation made by Kabata-Pendias (2001) is that the total W content in soil varies from 100 to 2000 mg kg<sup>-1</sup>, of which 50% was present in the form of primary minerals, 30% was water soluble, 15% was bound to Fe oxides and 5% was associated with organic matter. An average value for soil is given by Rose *et al.* (1979) as 1 mg kg<sup>-1</sup> W.

Although most minerals containing the tungstate oxo-anion WO<sub>4</sub><sup>2-</sup> are generally insoluble in neutral and acid waters, the WO<sub>4</sub><sup>2-</sup> (aq) ion itself is stable and soluble above about pH 3 in the absence of heavy metal M<sup>2+</sup> ions and in oxidising conditions (Brookins 1988). Scheelite and, to a much lesser extent, wolframite are soluble under alkaline conditions (pH>8); W is thus relatively mobile in alkaline water. There is some evidence of strong sorption of W by secondary Mn oxides and clays in stream sediments, so W concentrations in most surface water remain very low, typically much less than 1 µg l<sup>-1</sup>. The only significant exceptions to this are found in some hydrothermal spring water and alkaline salt lakes

in W-mineralised areas.

Tungsten is an economically important metal, being widely used in light-bulb filaments, electron and television tubes, abrasives and special alloys such as tool steels. Tungsten carbide is of great importance to the metal-working, mining and petroleum industries. Contamination from these sources is, therefore, possible in industrial and urban areas.

Evidence for a significant biological role for W

is sparse, in contrast to Mo, which is an essential trace element, although minor concentrations in some plants suggest a specialised function, perhaps substituting for Mo when this is deficient. Although there is limited ecotoxicity data available, anything higher than trace amounts of W in solution is generally considered to be toxic.

Table 73 compares the median concentrations of W in the FOREGS samples and in some reference datasets.

Table 73. Median concentrations of W in the FOREGS samples and in some reference data sets.

<b>Tungsten (W)</b>	<b>Origin – Source</b>	<b>Number of samples</b>	<b>Size fraction mm</b>	<b>Extraction</b>	<b>Median mg kg<sup>-1</sup></b>
Crust <sup>1)</sup>	Upper continental	n.a.	n.a.	Total	1.9
<b>Subsoil</b>	<b>FOREGS</b>	<b>788</b>	<b>&lt;2.0</b>	<b>Total (ICP-MS)</b>	<b>&lt;5.0</b>
<b>Topsoil</b>	<b>FOREGS</b>	<b>845</b>	<b>&lt;2.0</b>	<b>Total (ICP-MS)</b>	<b>&lt;5.0</b>
Soil <sup>2)</sup>	World	n.a.	n.a.	Total	1.5
<b>Water</b>	<b>FOREGS</b>	<b>807</b>	<b>Filtered &lt;0.45 µm</b>		<b>0.007 (µg l<sup>-1</sup>)</b>
Water <sup>3)</sup>	World	n.a.	n.a.		0.3 (µg l <sup>-1</sup> )
<b>Stream sediment</b>	<b>FOREGS</b>	<b>848</b>	<b>&lt;0.15</b>	<b>Total (XRF)</b>	<b>1.24</b>
<b>Floodplain sediment</b>	<b>FOREGS</b>	<b>743</b>	<b>&lt;2.0</b>	<b>Total (XRF)</b>	<b>1.08</b>
Stream sediment <sup>4)</sup>	Canada	65 033	<0.18	Total (INAA)	<2

<sup>1)</sup>Rudnick & Gao 2004, <sup>2)</sup>Koljonen 1992, <sup>3)</sup>Ivanov 1996, <sup>4)</sup>Garret 2006.

### W in soil

All but a few soil samples have a W content lower than the detection limit of 5 mg kg<sup>-1</sup>. In subsoil, about 25 samples have concentrations up to 16 mg kg<sup>-1</sup>. In topsoils, the maximum measured content is 14 mg kg<sup>-1</sup> W. The average ratio topsoil/subsoil is 0.987.

It is expected that crystalline leucogranitic and alkaline areas are more likely to be enriched in tungsten. The distribution maps of W show the scattered distribution of the few points above the detection limit. In subsoil, they occur in the eastern Alps of southern Austria, the Lazio-Campania region in Italy, the Massif Central, south-west England, and some further isolated

points, which should be investigated in relation to the local geology. The topsoil W map shows some additional isolated anomalous points in the western Iberian Peninsula, and a point near the Mourne Mountain granite in northern Ireland.

Although more than 95% of the soil samples are below the detection limit, correlations still express common enrichment in particular geological environments. In subsoil, W has a weak correlation with Be (0.36), and a very weak correlation (0.2 to 0.3) with Be, Bi, Sn, Ta, Th, Rb, Tl and Cs. In topsoil, a similar pattern applies. This points to a common enrichment in greisen and leucogranitic environments.

### W in stream water

Tungsten values in stream water range over three orders of magnitude, from <0.002 to 3.47

µg l<sup>-1</sup> with a median value of 0.007 µg l<sup>-1</sup>. About one quarter of the data are below the

determination limit. Tungsten data tend to be broadly correlated with Mo, Sb and V values.

Lowest W values in stream water ( $<0.002 \mu\text{g l}^{-1}$ ) are found in northernmost Finland and Norway on Precambrian Shield terrain, in south-west Norway on Caledonides and partly on Precambrian Shield rocks, in north Scotland (partly on Laurentian rocks), central and western Scotland, north-western England, Wales and most of Ireland on Caledonian terrains, and in Cornwall on Variscan rocks. The low stream water W area of Estonia is on glacial drift. In Variscan terrains, low W values in stream water occur in central Germany, and in a long belt extending from Belgium across France to the coastal area of the Bay of Biscay and into northern Spain, including also a part of Alpidic Pyrenees, and north-central Spain; smaller areas occur in Portugal and south (Alpidic Baetic range) and south-east Spain. A low stream water W area stretches from southern France to the western Alps and Torino in Italy. In the Alpidic Orogen, low W values in stream water are found in central Austria, central Croatia, in central and east Sicily, and in most of peninsular Greece.

High tungsten values in stream water ( $>0.025 \mu\text{g l}^{-1}$ ) occur in central and southern Sweden and western Finland on Precambrian Shield, in north-west Germany on glacial drift, and in Netherlands and part of Belgium on Quaternary sediments. Enhanced W in stream water is found on Variscan terrains in Czech Republic and some in bordering Poland and Germany; in southern England, in southern Portugal, Corsica and Sardinia; in Lorraine, partly Massif Central and south-western France extending across Alpidic east Pyrenees to Spain (W skarn mineralisation in eastern Pyrenees, and granite with scheelite veins in the Catalan Coastal Range). High W stream water values in the Cordillera Central in central Spain

are associated with W-Sn intragranitic veins and the W-Sn-Zn-Cu mineralisation of Otero de Herreros; to the south, an anomaly is related to the Los Pedroches batholith and its W-Sn mineralisation; a point anomaly in Galicia lies in the granitic W-Sn district of Silleda-Beariz-Marcofán. The high W level in the eastern Erzgebirge is related to geogenic sources. But an isolated point anomaly in south-eastern Germany is due to anthropogenic sources (pollution impact).

On the Alpidic Orogen, high W stream water values occur in south-east Poland, Slovakia, most of Hungary and eastern Austria, in Switzerland and north Italy (Oligocene intrusives), central and partly southern (related to recent volcanic activity) Italy, in Albania and northern Greece. The isolated stream water W anomaly in central Britain is probably related to coal mining and steel production in the Yorkshire coalfield. Highly anomalous stream water W values in northern Greece are related to felsic rocks and mineralisation.

The described W distribution in stream water resembles several pattern types: the basic Major-ions distribution that is essentially climate controlled, and three patterns that contain elements, characteristic for alkaline and felsic rocks. The Major-ions pattern appears to be responsible for high concentrations in central Europe. The Felsic and Alkaline associations explain elemental patterns for areas in Spain and Portugal, in southern France, north Italy and Switzerland, Corsica, Sardinia and north Greece; especially the Alkaline rocks pattern may be responsible for W anomalies in Fennoscandia, for alkaline volcanism in Italy, northern Greece and Albania (Plant *et al.* 2005). It appears that most of these stream water W anomalies are geogenic in origin.

### W in stream sediment

The median W content in stream sediment is  $1.24 \text{ mg kg}^{-1}$ , with a range between  $<0.05$  and  $81.5 \text{ mg kg}^{-1}$ .

The W distribution map shows areas with low stream water values ( $<0.72 \text{ mg kg}^{-1}$ ) throughout all of Finland, central and south-western Sweden, northern Norway, the northern European plain from eastern Germany through northern Poland,

the Baltic states, central Ireland, central Greece, and the eastern Iberian Peninsula.

Anomalously high W values in stream water ( $>5.78 \text{ mg kg}^{-1}$ ) are located mainly in crystalline areas in northern Portugal and adjacent north-west Spain (vein mineralisation of Sn and W), in France from the Massif Central to Brittany, in south-western England (vein mineralisation in

Dartmoor granite). High W values in stream water ( $>1.97 \text{ mg kg}^{-1}$ ) also occur in the central Alps, southern Germany and the Bohemian Massif, Slovakia, south-eastern Austria and Pannonian Croatia, the Roman Alkaline Province, Corsica, southern Italy, Albania, and isolated anomalies in central Norway, Scotland near Glasgow, England (Yorkshire coalfield) and

northern Greece (possibly associated with Mo mineralisation).

Tungsten in stream water has a good correlation with Sn (0.50), and a weak correlation ( $>0.3$ ) with Rb, U, Th, Ta, As, Y and the REEs (except Eu), pointing to a geological pattern of enrichment in leucogranitic rocks.

### W in floodplain sediment

The total W distribution in floodplain sediment, determined by ICP-MS, varies from  $<0.05$  to  $123 \text{ mg kg}^{-1}$ , with a median of  $1.08 \text{ mg kg}^{-1}$ .

Low W values in floodplain sediment ( $<0.65 \text{ mg kg}^{-1}$ ) occur over most of Finland, northernmost and southern Sweden on the Fennoscandian Shield, northernmost and western Norway, Scotland on mainly crystalline rocks, and most of Ireland on calcareous, clastic and crystalline rocks; the glacial drift covered plain from north-west Germany to most of Poland, Lithuania and western Latvia; southern, central, eastern and northern Spain on largely clastic and carbonate rocks, and the molasse basin of Austria.

High W values in floodplain sediment ( $>1.81 \text{ mg kg}^{-1}$ ) occur almost exclusively on the Variscan areas of Europe, over igneous, metamorphic and clastic rocks, and known mineralised areas as in south-west England, the western Iberian peninsula (northern half of Portugal and west central and north-west Spain), Massif Central in France extending towards the south (Montagne Noire area); on Corsica and Sardinia felsic rocks; from the Harz Mountains to the Bohemian Massif. High W values in floodplain sediment are also found with less intensity in some Alpine areas, such as northern Italy and adjacent part of Switzerland, and are especially high in the Roman Alkaline Province, Slovakia and adjacent parts of Hungary (Carpathians), and in Croatia and Slovenia; central Macedonia in north Greece, where they are related to granite and mineralisation. Elevated W values are found in the mineralised areas of Bergen and Sulitjelma in

Norway.

The majority of highly anomalous W values in floodplain sediment ( $>4.63 \text{ mg kg}^{-1}$ ) are related to W-enriched rocks, mostly of Palaeozoic age, and to numerous known mineralised and mining areas. The three highly anomalous floodplain sediment W values in Portugal of 123 and  $84.2 \text{ mg kg}^{-1}$  can be related to mineralisation and  $42.3 \text{ mg kg}^{-1}$  is possibly downstream from Panasqueira Sn-W deposit. The floodplain sediment point anomaly ( $104 \text{ mg kg}^{-1}$ ) in Galicia of north-west Spain is related to Sn-W mineralisation (*e.g.*, Santa Comba Sn-W, San Finx, Fontao). Point W anomalies in floodplain sediment also occur in south-west England (*e.g.*, Saint Austell granite Sn-W, Camborne-Redruth Sn-W), the Central Massif of France (*e.g.*, Puy les Vignes W, Montredon W, Aumessas W, Les Montmins W), and the Erzgebirge (*e.g.*, Cinovec Sn-W). In Slovakia, a point W anomaly in floodplain sediment corresponds to the Banska Stiavnica ore district. The highly anomalous W value in floodplain sediment near Coventry in the English Midlands ( $82.2 \text{ mg kg}^{-1}$ ) is probably related to industrial pollution, but it may also be related to coal mining.

Tungsten in floodplain sediment shows a good positive correlation ( $>0.4$ ) with As, Sn, Ta, Tl, Rb and Th, and a weak correlation ( $>0.3$ ) with K, Ga, Nb, Cs, U, Ce, La, Pr, Nd, Sm.

In conclusion, the distribution of W in floodplain sediment maps mainly areas with felsic igneous and metamorphic rocks, which are often accompanied by mineralisation. Some high W values appear to be related to industrial pollution.

### W comparison between sample media

Patterns in W distribution between stream and floodplain sediments are very similar. Although it is difficult to compare with soil data, since the detection limit for soil by XRFS is not as good as that for sediments by ICP-MS, the point anomalies in soil correspond to high W areas in the sediment data. A boxplot comparing W variation in subsoil, topsoil, stream sediment and floodplain sediment is presented in Figure 52.

There are some similarities between stream water and sediment distributions, *for example*, high W values throughout the alkaline volcanic provinces of Italy, over the Pannonian Basin and in Albania and northern Greece. However, there are also many differences and opposite behaviour in W distributions between stream water and sediment data, particularly over most of the Iberian Peninsula, most of western and northern mainland Europe, and most parts of Fennoscandia.

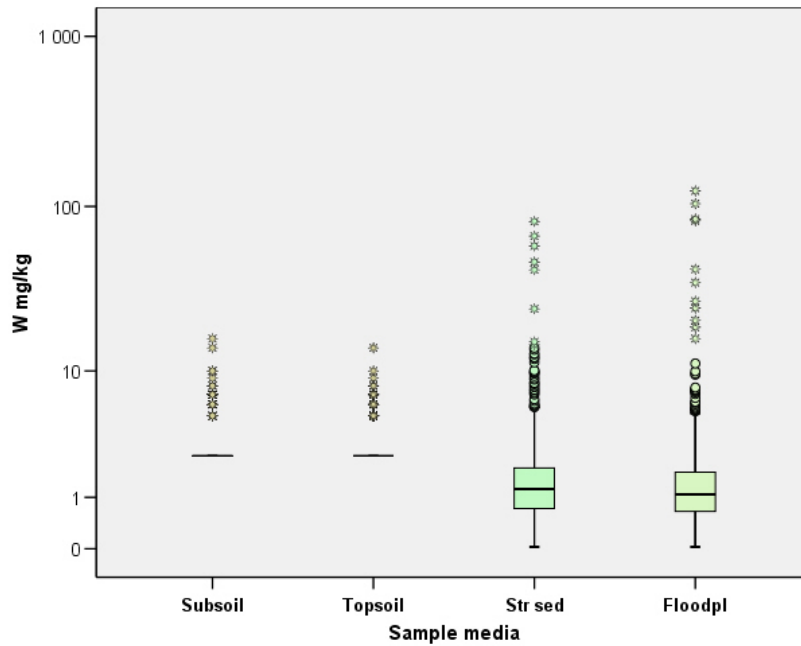


Figure 52. Boxplot comparison of W variation in subsoil, topsoil, stream sediment and floodplain sediment.