Introduction

Titanium is one of the lightest members of the first row transition series of elements, consisting of Sc, Ti, V, Cr, Mn, Fe, Co, Ni, Cu and Zn, and belongs to group 4 of the periodic table, along with Zr and Hf. The element has an atomic number of 22, an atomic mass of 48, three main oxidation states (+2, +3 and +4), of which +4 is the most common, and five naturally occurring isotopes (^{46}Ti, ^{47}Ti, ^{48}Ti, ^{49}Ti, and ^{50}Ti), of which ^{48}Ti is the most abundant at 74% of the total mass.

Titanium is a common lithophile metallic element that forms several minerals, including ilmenite $FeTiO_3$, rutile, brookite, anatase (all TiO_2) and sphene $CaTiSiO_5$, but it also occurs as an accessory element in pyroxene, amphibole, mica and garnet. It is a relatively abundant metal with a crustal abundance of 6320 mg kg^{-1} (Mielke 1979, Fyfe 1999).

During magmatic processes, Ti follows Fe in magmatic crystallisation. Ti^{4+} is predominantly partitioned into Fe-Ti or Fe oxides such as ilmenite and magnetite, or into one or more of the TiO_2 phases, rutile, anatase and brookite. Titanium may also substitute for Mg^{2+} or Fe^{2+} in silicate minerals, leading to enrichment of Ti in amphibole and mica. The compatibility displayed by Ti during the early stages of fractionation results in enrichment in mafic (>1% TiO_2) and ultramafic (>2% TiO_2) rocks relative to felsic igneous lithologies (*ca.* 0.2% TiO_2). Therefore, elevated Ti values are indicative of mafic and ultramafic rocks.

Titanium is relatively immobile during pro-grade metamorphism (Nicollet and Adriambololona 1980). However, it may be mobilised and enriched in amphibole during granulite-amphibolite retrogression (Beach and Tarney 1978), with rutile authigenesis occurring commonly (Ure and Berrow 1982). Titanium is not involved in normal hydrothermal sulphide mineralisation processes, but metasomatism may give rise to magnetite-rich rocks containing appreciable Ti. In sedimentary rocks, the concentration of TiO_2 is determined by the abundance of detrital oxides and silicates, such as chlorite and clay minerals, and diagenetic phases, such as anatase (Correns 1978). Consequently, the TiO_2 contents of carbonate rocks and quartzite (<0.25%) are generally lower than those of shale and greywacke (>0.5%). Mielke (1979) cites levels of Ti in shale, sandstone and carbonate rocks as 4600, 1500 and 400 mg kg^{-1} respectively. An average Ti content in loess is given as 0.41% by McLennan and Murray (1999). Note that the conversion factor for Ti to TiO_2 is 1.668.

Mielke (1979) reports that bauxite and laterite may contain up to 4% Ti. In stream sediments a large proportion of the Ti is held in minerals, such as rutile, ilmenite and sphene, all of which are relatively insoluble. The average abundance in river particulates is cited as 0.56% Ti by McLennan and Murray (1999). Some Ti may be taken into solution in stream water, through the weathering of ferromagnesian minerals and authigenic phases, such as anatase, but dispersal is generally restricted by adsorption to clays. Titanium is mobilised more readily in peats and podzols (Hutton *et al.* 1972), at low pH (<4.5) and in the presence of organic acids, which can form chelation complexes with Ti^{4+}.

Since, Ti minerals are resistant to weathering, they occur practically undecomposed in soil. Surface marsh soil may contain Fe-Mn concretions with up to 39% Ti. Under reducing conditions, Fe^{2+} ions are adsorbed on surfaces of Ti minerals and subsequent oxidation to Fe^{3+} may lead to the formation of pseudorutile (Kabata-Pendias 2001). The global average for soil has been estimated as 0.33% Ti, although it is lower for podzols and histosols (Kabata-Pendias 2001).

Titanium has very low mobility under almost all environmental conditions, mainly due to the high stability of the insoluble oxide TiO_2 under all, but the most acid conditions, *i.e.,* below pH 2 (Brookins 1988). It behaves as a refractory element during weathering, but relatively little is known about its behaviour in natural water (Skrabal 1995). Titanium only exists in a fully hydrated form, $TiO(OH)_2$, in water above pH 2, and is, therefore, transported in a colloidal state rather than as a dissolved ion. Concentrations of 'dissolved' Ti generally decrease with increasing salinity. However, higher concentrations in organic rich water (Skrabal 1995) provide further evidence of colloidal transport. Titanium may be removed from water by flocculation of colloidal material, adsorption and scavenging by precipitation of Mn and Fe oxides (Skrabal 1995).

Consequently, Ti concentrations in natural water can range up to a few tens of µg l^{-1}, but are generally as low as 1-3 µg l^{-1} (Hem 1992).

Potential anthropogenic sources of Ti in the environment include paint pigments (TiO_2 pigment accounts for the largest use of the element) and its alloys with Al, Mo, Mn and Fe, which are used extensively in aircraft, ship and missile manufacture. Cooper and Thornton (1994) report that anthropogenic anomalies in drainage are rarely recorded for Ti, which is not surprising given the general background levels for this element in the environment and its aqueous chemistry.

There is no evidence to suggest that Ti performs any necessary role in the human body (Mertz 1987). Titanium is considered to be non-toxic, because of its poor absorption and retention in living organisms (Mertz 1987). No environmental effects have been reported.

Table 68 compares the median concentrations of Ti in the FOREGS samples and in some reference datasets.

Table 68. Median concentrations of TiO_2 in the FOREGS samples and in some reference data sets.

Titanium (TiO_2)	*Origin – Source*	*Number of samples*	*Size fraction mm*	*Extraction*	*Median %*
Crust[1)]	Upper continental	n.a.	n.a.	Total	0.64
Subsoil	**FOREGS**	**788**	**<2.0**	**Total (XRF)**	**0.566**
Topsoil	**FOREGS**	**845**	**<2.0**	**Total (XRF)**	**0.572**
Soil[2)]	World	n.a.	n.a.	Total	0.7
Water *(Ti)*	**FOREGS**	**807**	**Filtered <0.45 µm**		**0.90 (µg l^{-1})**
Water *(Ti)*[3)]	World	n.a.	n.a.		3 (µg l^{-1})
Stream sediment	**FOREGS**	**852**	**<0.15**	**Total (XRF)**	**0.625**
Floodplain sediment	**FOREGS**	**749**	**<2.0**	**Total (XRF)**	**0.48**

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

TiO_2 in soil

The median TiO_2 content is 0.57% in both subsoil and topsoil, with a range varying from 0.012 to 3.14% in subsoil and 0.021 to 5.45% in topsoil. The average ratio topsoil/subsoil is 1.021.

Low TiO_2 values (<0.36%), in both topsoil and subsoil, are present over most of the Fennoscandian Shield, the north-European plains from Poland to the Netherlands, Ireland, southern Greece, southern Spain, the western calcareous Alps and several alluvial areas (Teijo, Ebro, Rhône, Danube in Hungary, Garonne and Paris Basin).

The subsoil distribution map shows high TiO_2 values (>0.78%) in several areas with outcropping Palaeozoic and crystalline basement rocks of intermediate to mafic signature, such as the north-western Iberian peninsula (including ophiolite in Galicia), Brittany, the Central Massif (Quaternary basalts), western Scotland, Wales, south-west England, the Rheno-Hercynian region and Bohemian Massif, and the Caledonian chain in Norway. Higher TiO_2 values in subsoil also occur in the younger western Pyrenees, the eastern Alpine region, and the Carpathian region of Slovakia (over Neogene andesitic rocks); the ice divide area in northern Finland shows an enrichment too. High TiO_2 contents in Slovenia and the Dinarides are typical for residual soils on karst rocks. Enrichment in Italy north of Rome is related to the Roman alkaline magmatic province, and isolated anomalies occur in southern Sicily and east of Verona in Alpine volcanic rocks (this is the richest sample both in subsoil and topsoil, with 3.14% and 4.16% TiO_2 respectively).

he topsoil TiO_2 distribution map is almost identical to that of subsoil. In Spain, however, where more topsoil samples were collected, the region from Salamanca to Extremadura appears high in topsoils, and the Pyrenees show continuous high values. A point anomaly near

Albacete in east Spain occurs on Jurassic limestone with residual or karstic Fe-Mn concentrations. Also Gran Canaria with its basaltic volcanics is high in TiO_2. Overall the TiO_2 distribution patterns show similarities with the Fe_2O_3 distribution.

Titanium in subsoil shows a very strong correlation with Fe (0.80), a strong correlation (>0.6) with Al, Ga, In, Sc, V, Co, Nb, Y and some heavy REEs, and a good correlation (>0.4) with Mn, Cu, Zn, Ta, Zr, Hf and the remaining REEs. The correlations pattern is similar for topsoil.

Ti in stream water

Titanium values in stream water range over three orders of magnitude, from <0.01 to 16.8 $\mu g\ l^{-1}$, with a median value of 0.9 $\mu g\ l^{-1}$. Titanium values tend to correlate with Ge and Pb data, especially in Fennoscandian countries and Britain.

Lowest Ti values in stream water (<0.3 $\mu g\ l^{-1}$) are found along the west and north of Fennoscandia, on rocks of the Fennoscandian Shield, on Caledonian terrains in west of Norway and in Wales, on the Variscan in western and south-eastern France, north-western and central Spain and northern Portugal, Corsica and southern Sardinia. On the Alpine Orogen, low values occur in most of the Alps and south of them in Slovenia and northern Italy, in a small area of south-central Italy, in part of the Pyrenees, in Albania and north-western Greece and on Crete.

High Ti concentrations in stream water (>2.5 $\mu g\ l^{-1}$) are found throughout southern and central Finland, in southern Sweden and small part of southern Norway on Precambrian Shield, further in Denmark, large parts of Poland and south-east Lithuania on glacial drift of Precambrian Shield origin, and in south-west Netherlands on Quaternary deposits. Enhanced Ti (>1.8 $\mu g\ l^{-1}$) also occurs in an area of central Norway, in eastern Scotland and south-eastern England on Caledonian terrains; in northern and western Poland and northern Czech Republic, in Lorraine, Brittany and north of the Massif Central in France, and in southern Spain on Variscan terrains. On the Alpine Orogen, enhanced Ti is found in the Baetics of southern Spain (mafic and ultramafic rocks of the Ronda, Ojén and Carratraca Massifs, and Fe-Cu mineralisations near Cádiz; also stream water is high in DOC here, and organic rich stream water is favourable to colloidal transport), in west central and south Italy (related to recent alkaline volcanism). A highly anomalous point in northern Croatia could be related to Tertiary clastic rocks. A point anomaly near Ciudad Real in south-central Spain is associated with Palaeozoic diabase dykes and mafic volcanic rocks.

The discussed titanium patterns in stream water are surprisingly similar to two major elemental patterns in European stream waters: the pattern of REEs in acid low-mineralisation high-DOC stream water in northern and western Europe, and the Major-ions high-mineralisation pattern in central and southern Europe. Both major patterns are primarily climate-controlled, and geology plays only a subordinate role. The high concentrations in Brittany and the Massif Central in France, the alkaline volcanic province in Italy, and easternmost Greece, appear to be geogenic. These anomalies are accompanied by high Ti contents in soil and sediments only in Brittany, and partly in Italy.

TiO_2 in stream sediment

The median TiO_2 content in stream sediment is 0.62%, with a range varying from 0.016 to 4.99%.

The TiO_2 distribution map shows low values in stream sediment (<0.45%) over southern Sweden, eastern Finland, the Baltic states, the North European Plain from Poland to the Netherlands, central Ireland, eastern France, the western Alps, central and southern Italy, eastern Spain, Slovenia and coastal Croatia, and parts of Greece.

High TiO_2 values in stream sediment (>0.82%) are located mainly in areas with outcropping Palaeozoic and crystalline basement rocks of intermediate to mafic signature, such as the western Iberian Peninsula (Palaeozoic and Proterozoic terrains), the Canary Islands (basalts), the Massif Central (also basalt) and Brittany in France, Cornwall, Wales, northern England, Scotland and northern Ireland, Norway

(Caledonides, with Ti deposit at Tellnes in south-west Norway), northern Fennoscandia, the Bohemian Massif, the western Alps, and a region from south-east Austria to northern Croatia. In addition, some point anomalies are scattered over the continent. The highest TiO_2 anomaly in stream sediment occurs in southern Brittany (4.99% TiO_2), it is also high in iron (14.43% Fe_2O_3) and can be traced to former iron mining of Ordovician sedimentary ores. The second highest TiO_2 value is east of Verona in young volcanic rocks (3.15% TiO_2 and 14.49% Fe_2O_3). The point TiO_2 anomaly in central Macedonia in Greece is related to amphibolite.

The TiO_2 stream sediment distribution shows similarities with that of Fe_2O_3 in northern Europe, but much less in the Mediterranean area. TiO_2 in stream sediment has a strong correlation (>0.6) with Fe_2O_3, V, Nb and Eu, and a good correlation (>0.4) with Al_2O_3, Ga, Ta, Co, Y and most of the REE. TiO_2 has a good negative correlation with CaO (-0.42).

TiO_2 in floodplain sediment

Titanium oxide values in floodplain sediment vary from 0.05 to 2.15%, with a median of 0.48%.

Low TiO_2 values in floodplain sediment (<0.31%) occur over the glacial drift covered plain extending from north Germany to Poland, Lithuania and Latvia. Other areas with low TiO_2 values are the metasedimentary, granitic and gneissic basement rocks of central Sweden; the glacial drift covered carbonate rocks of Ireland; the alluvial plain of the lower Garonne and Rhône rivers in France, the clastic and carbonate rocks of the Meseta Central and eastern Spain, and the molasse basin in Austria.

High TiO_2 values in floodplain sediment (>0.67%) are found in areas with mafic and ultramafic crystalline rocks and sometimes with Ti mineralisation, as in most of Norway (*e.g.,* the mineralised area around Tellnes Ti-Fe-Ni) and adjacent parts of Sweden, central and northern Sweden (*e.g.,* Ruoutevare and Akkavara V-Ti-Fe), and northern Finland (amphibolite, mica schist), southern Finland (metagraywacke, schist, phyllite), north-east Scotland (Aberdeen gabbro), western Scotland (mafic alkaline volcanics), Wales (shale, slate, schist, Ordovician volcanics), the Armorican Massif in Brittany (island arc lavas, shale), Massif Central in France (basaltic volcanics), Portugal and western Spain (variety of igneous rocks), Italian-Swiss Alps (mafic rocks), central Macedonia and Thrace in Greece (amphibolite and ophiolite).

There is an almost continuous zone with high TiO_2 values in floodplain sediment extending from the Austrian Alps into Slovenia, Croatia, Slovakia and ending at the Bohemian Massif and Erzgebirge mineralised areas. In the karst region of Slovenia and Croatia, the high TiO_2 values in floodplain sediment may be explained by accumulation in residual karstic soil, and its subsequent erosion and deposition on the floodplains.

Highly anomalous TiO_2 values in floodplain sediment occur in Gran Canaria (2.15%) and Midland Valley of Scotland (2.01%), both associated with alkaline basaltic rocks, and the Erzgebirge in the Czech Republic (1.68%). A point TiO_2 anomaly in floodplain sediment on the south-east coast of Spain near Almeria (1.12%) is related to gneiss and amphibolite lithologies, and volcanic rocks of Cabo de Gata-Rodalquilar. The point TiO_2 anomaly in northern Italy (1.39%) is probably related to the Colli Euganei alkaline volcanics near Verona.

Titanium oxide in floodplain sediment shows a very strong positive correlation with Nb (0.86) and V (0.82), a strong correlation with Fe_2O_3, Co, Al_2O_3, Ga and Y, and a good correlation with K, Rb, Mn, Be, Ta, Zr and Th. The REEs have a good to strong correlation with TiO_2.

It is concluded that the TiO_2 spatial distribution in floodplain sediment is related to bedrock geology and mineralisation, especially mafic and ultramafic lithology, but also to clay-rich soil with high Al_2O_3 contents.

Ti comparison between sample media

Titanium distribution patterns between all solid sample media are broadly similar, although lower Ti is present in stream sediment throughout the coastal region of Croatia and Slovenia (possibly explained by the removal of fine-grained material from residual soil and karst). Titanium in parts of the western Iberian Peninsula is higher in sediments than in soil. Stream sediment values in Norway tend to be higher than those of floodplain sediment and soil. Floodplain sediment data in parts of Finland tend to be higher than those of stream sediment and soil.

A boxplot comparing TiO_2 variation in subsoil, topsoil, stream sediment and floodplain sediment is presented in Figure 48.

Stream water Ti values show almost exactly the opposite patterns to those observed in solid sample media, with highest concentrations found throughout central and southern Finland, southern Sweden and parts of Poland, and are associated with low TDS and high DOC environments, under which Ti is most stable in solution. In Finland, the Ti is also associated with anomalously high F, with which Ti forms complexes. Lowest Ti concentrations are found throughout most of western and northern Fennoscandia, the northern Iberian Peninsula and parts of the Mediterranean.

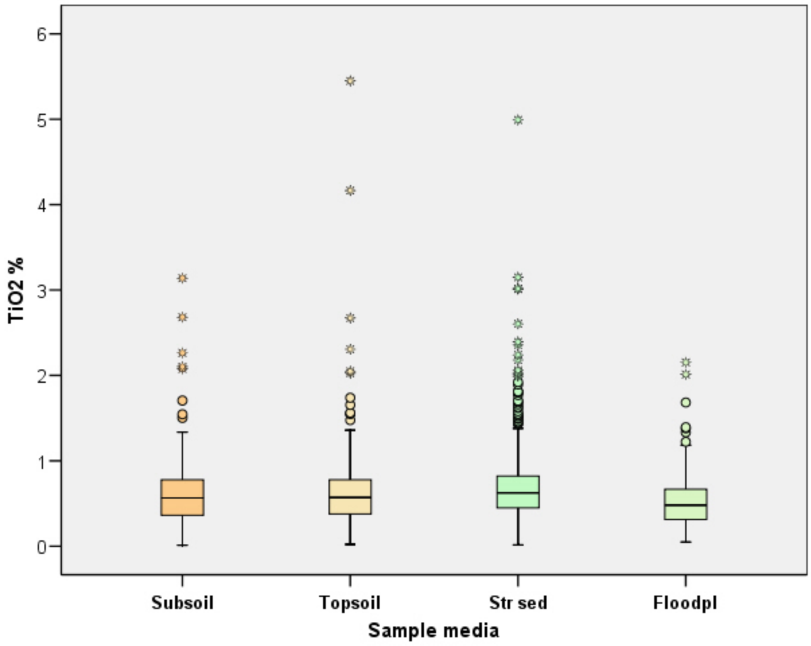

Figure 48. Boxplot comparison of TiO_2 variation in subsoil, topsoil, stream sediment and floodplain sediment.