

Introduction

Vanadium is one of the lightest members of the first row transition elements, consisting of Sc, Ti, V, Cr, Mn, Fe, Co, Ni, Cu and Zn, and belongs to group 5 of the periodic table, along with Nb and Ta. The element has an atomic number of 23, an atomic mass of 51, three main oxidation states (+3, +4 and +5) and two naturally occurring isotopes (^{50}V , and ^{51}V), of which ^{51}V is the most abundant at 99.8% of the total mass.

Vanadium is a lithophile metallic element at low pressure, but may be siderophile at the elevated pressures suggested for core formation in the Earth. It is incompatible in most silicate minerals, although it may be moderately compatible in some pyroxenes (Snyder 1999). It forms several minerals including magnetite $(\text{Fe,V})_3\text{O}_4$, vanadinite $\text{Pb}_5(\text{VO}_4)_3\text{Cl}$, and carnotite $\text{K}_2(\text{UO}_2)_2(\text{VO}_4)_2 \cdot 3\text{H}_2\text{O}$. It is also present as a trace element in mica, apatite, pyroxene and amphibole. Montroseite $\text{VO}(\text{OH})$ occurs across a wide pH range under reducing conditions, exhibiting V in its lowest valency (V^{3+}), and acts as a source for a wide range of V^{3+} , V^{4+} and V^{5+} oxides and hydroxides. Sulphides of V^{4+} are found in ore deposits.

The trivalent ion V^{3+} has an ionic radius (64 pm) almost identical to that of Fe^{3+} (65 pm). Because of this, V is frequently found as a substitute for Fe in magnetite and in the ferromagnesian silicate minerals formed during primary magmatic processes (Curtis 1964). Mafic rocks are typically enriched in V relative to most intermediate and felsic rocks. Primitive magma types including calc-alkaline, alkaline and tholeiitic rocks have broadly similar V concentrations (Taylor *et al.* 1969). Mielke (1979) cites values: ultramafic 40 mg kg^{-1} , basaltic 250 mg kg^{-1} , granitic $44\text{--}88 \text{ mg kg}^{-1}$, and with an average crustal abundance of 136 mg kg^{-1} . In ultramafic rocks, the V content generally reflects the abundance of minerals, such as Fe-Ti-Cr oxides and pyroxene. Elevated V values are, therefore, indicative of mafic rocks. Although described as a trace element, V is relatively abundant even though it only rarely forms independent minerals in igneous rocks.

Vanadium is largely immobile during metamorphism (Condie 1976). The V content of sedimentary rocks reflects primarily the

abundance of detrital Fe oxides, clay minerals, hydrous oxides of Fe and Mn, and organic matter. The redox regime is important, V remaining mobile under oxidising conditions but being subject to precipitation just above the sulphate/sulphide redox threshold within a pH range of 5.0–8.0 (Brookins 1988). The average V content of quartzitic sandstone and pure carbonate sediments is low ($<15 \text{ mg kg}^{-1}$), with higher values in greywacke ($40\text{--}150 \text{ mg kg}^{-1}$), shale ($90\text{--}260 \text{ mg kg}^{-1}$), and clay (*ca.* 200 mg kg^{-1}). Coal may also contain appreciable amounts of V. The most V-rich sedimentary rock is black shale, reflecting both the affinity of the element for organic sorption sites and its relative immobility under reducing conditions. Cited average values for loess and river particulates are 73 and 170 mg kg^{-1} V respectively (McLennan and Murray 1999).

Vanadium is a highly mobile element. It displays both cationic character under acid conditions, as vanadyl VO^{2+} and VO_2^{2+} ions, and anionic character under less acid to alkaline conditions, as vanadate HVO_4^{2-} or H_2VO_4^- ions (Brookins 1988). The solubility of V is strongly controlled by its oxidation state. Its solubility is highest in oxic environments, where vanadyl cations predominate. Complexes with fluoride, sulphate and oxalate may also act to increase V solubility under oxidising conditions (Wanty and Goldhaber 1992), although the presence of U and phosphates can result in the formation of highly insoluble V^{5+} complexes. Under more reducing conditions, the relatively immobile V^{3+} state dominates.

Kabata-Pendias (2001) reports that the behaviour of V in soil has received little attention. It appears that Fe oxides hold a reasonable fraction of soil V, however, the role of clay minerals as well as organic acids may be more significant than the V fraction adsorbed by Fe oxides. The highest concentrations of V in soil are reported for soil developed on mafic rocks (150 to 460 mg kg^{-1} V), while the lowest were found in peat soil (5 to 22 mg kg^{-1} V). The average V content of soil worldwide has been estimated to vary from 18 mg kg^{-1} for histosols to 115 mg kg^{-1} for rendzinas (Kabata-Pendias 2001).

Well-drained, lowland areas are likely to host the highest V concentrations in stream water and, in almost all instances, the dispersal of V will be controlled by the prevailing rates of sorption to hydrous Fe and Mn oxides, clay and organic matter (Krauskopf 1956). As a result, although V concentrations as high as 70 µg l⁻¹ have been found in some natural water, most surface and groundwater rarely exceed 10 µg l⁻¹ (Hem 1992).

Anthropogenic sources of vanadium include oil and coal combustion, steel alloy tool production and traffic pollution. Vanadium has a variety of industrial uses in metallurgy, electronics and dyeing. Although the amounts of V used are small and are insignificant in terms of any direct anthropogenic input, the combustion of coal and the waste from such processes, e.g., fly-ash, make a significant contribution to

environmental contamination.

Vanadium is biologically active and is an essential nutrient for many animals. Its precise biochemical function is still in some doubt (WHO 1996), but Frausto da Silva and Williams (1991, 1994, 2001) suggest a role in peroxidase enzymes. An intake of over 10 mg V per day can be toxic for adults, but this greatly depends on its speciation and oxidation state; the source is usually airborne anthropogenic V (WHO 1996). In severe cases, toxic levels of V causes the inhibition of certain enzymes with animals, which has several neurological effects, and can cause breathing disorders, paralyses and negative effects on the liver and kidneys.

Table 72 compares the median concentrations of V in the FOREGS samples and in some reference datasets.

Table 72. Median concentrations of V in the FOREGS samples and in some reference data sets.

<i>Vanadium (V)</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	97
Subsoil	FOREGS	790	<2.0	Total (ICP-MS)	62.8
Subsoil	FOREGS	784	<2.0	Aqua regia (ICP-MS)	33.0
Topsoil	FOREGS	843	<2.0	Total (ICP-MS)	60.4
Topsoil	FOREGS	837	<2.0	Aqua regia (ICP-MS)	33.0
Soil ²⁾	World	n.a.	n.a.	Total	90
Soil, C-horizon ³⁾	Barents region	1357	<2	Aqua regia (ICP-AES)	24.2
Water	FOREGS	807	Filtered <0.45 µm		0.46 (µg l⁻¹)
Water ⁴⁾	World	n.a.	n.a.		1 (µg l ⁻¹)
Stream sediment	FOREGS	852	<0.15	Total (XRF)	62.0
Stream sediment	FOREGS	845	<0.15	Aqua regia (ICP-AES)	29.0
Floodplain sediment	FOREGS	747	<2.0	Total (XRF)	56.0
Floodplain sediment	FOREGS	747	<2.0	Aqua regia (ICP-AES)	29.0
Stream sediment ⁵⁾	Canada	49 938	<0.18	Aqua regia (ICP-AES)	38

¹⁾Rudnick & Gao 2004, ²⁾Koljonen 1992, ³⁾Salminen *et al.* 2004, ⁴⁾Ivanov 1996, ⁵⁾Garret 2006.

V in soil

The median values for total vanadium (ICP-MS analysis) are 63.0 mg kg⁻¹ in subsoil and 60.0 mg kg⁻¹ in topsoil, with a range from 1.28 to 325 mg kg⁻¹ in subsoils and 2.71 to 537 mg kg⁻¹ in topsoils. The average ratio topsoil/subsoil is

0.953.

The V subsoil distribution map shows many similarities to the Fe map. Low V areas in subsoil (<36 mg kg⁻¹) are located mainly in the glacial drift covered sandy plains from Poland to the

Netherlands, and throughout much of the Baltic states, and large parts of southern Finland and Sweden.

High V values in subsoil ($>96 \text{ mg kg}^{-1}$) are present in north-western Spain (mainly associated with the ultramafic Ordenes ophiolite complex, and intermediate plutonic rocks), the western Pyrenees (black shales), Brittany, Central Massif (soils over Quaternary basalt), a north-south band in Italy from north of the Garda Lake to the Roman Alkaline Province, southern Sicily, Greece north of the Gulf of Corinth (terra rossa soil, ophiolite, bauxite and base metal mineralisation), the Dalmatian coast of Croatia, Slovenia and southern Austria (strong enrichment in karstic residual soil), eastern Slovakia (soils over volcanic rocks and Palaeogene flysch with ultramafic clasts), parts of Norway, the ice divide area of north-central Finland (which is rich in mica), the west coast of Wales and Scotland, and northern Ireland (over the Antrim basalt). High V values express crystalline rocks of intermediate to mafic or alkaline affiliation, including greenstone belts, and also karst with soil on carbonate rocks (Greece, Croatia, Slovenia). In northern Finland V-bearing iron ores are present, and magnetite has a tendency to be enriched during weathering. Vanadium in subsoil is also enhanced in southern Portugal, and the French-Belgian Ardennes. In central and eastern England, high V levels in subsoil are associated with Mesozoic sedimentary ironstone. A point V subsoil anomaly in central Spain is in igneous rocks of the Cordillera

Central.

The topsoil V map shows some differences with respect to the subsoil map. In particular, the subsoil anomaly disappears completely in the topsoil in eastern Slovakia; there is enrichment in the illuvial layer of the podzolic topsoil in northern Fennoscandia, because metals are bound to organic matter; in the Spanish Sierra Nevada, the central Pyrenees and Gran Canaria, topsoils enriched in V.

In subsoil, V shows a very strong positive correlation with Fe (0.91) and Sc (0.91), a strong correlation (>0.6) with Co, Cu, Ti, Al, Ga, In, Eu and some of the heavy REEs, and a good correlation (>0.4) with Mn, Cr, Ni, Nb, Te, Zn, Y and the remaining REEs. It has a good negative correlation with SiO_2 (-0.43). The correlations pattern is the same in topsoil.

The analysis with ICP-AES after *aqua regia* extraction yields a median V content of 33 mg kg^{-1} in both subsoil and topsoil, with ranges from 2 to 234 and from 1 to 281 mg kg^{-1} respectively. It can be concluded that only about half the vanadium was extracted with *aqua regia*. The subsoil distribution pattern shows overall similarity with total V but some areas (including Galicia in north-west Spain, Wales, Slovakia, and southern Norway) show fewer high values for extractable vanadium. On the topsoil distribution map, extractable V is much lower in north-west Spain, the western Pyrenees, south-west England and south-central Norway.

V in stream water

Vanadium values range over three orders of magnitude, from <0.05 to $19.5 \mu\text{g l}^{-1}$, with a median value of $0.460 \mu\text{g l}^{-1}$. Vanadium distribution resembles that of As, Mo, Sb, Se, U and W. Concentrations in alkaline stream water in the Mediterranean region tend to be enhanced.

Lowest V values stream water ($<0.016 \mu\text{g l}^{-1}$) are found in central and northern Sweden, almost entire Norway (Precambrian and Caledonian rocks), western Scotland, Wales and western Ireland on Caledonides, and in north-west of Iberian Peninsula on Variscan rocks. In Alpidic Europe they occur in the western Alps of south-east France and north-west Italy, in western Austria and on Crete. Typically high-relief, high rainfall areas in north-west Europe show the

lowest V values, indicating a strong topographic and climatic control factor.

High V concentrations stream water ($>1.25 \mu\text{g l}^{-1}$) occur in central and south-west Finland and southernmost Sweden on Svecofennian rocks, in Denmark, north-west Germany on glacial deposits and in the Netherlands on Quaternary. In southern and western coast of Finland, the stream catchments are dominated by V-bearing clay soil, and some V occurrences are known in the central parts of the country with anomalies in stream sediment. In Variscan Europe, enhanced V occurs in the south-eastern tip of England, in Lorraine and in an area from Paris to Brittany in France, in the Iberian Pyrite Belt of southern Portugal and Spain. In the Alpidic part of Europe, high V in

stream water occurs in eastern Czech Republic (partly Variscan), eastern Austria, south-western Slovakia and across Hungary to eastern Croatia, in the latter two mostly on Quaternary deposits of Pannonian basin. In Italy, moderately high V stream water values in the Po River valley, and widely distributed in central and southern Italy are in part associated with alkaline volcanism, in western Sicily, and eastern and north-eastern Greece bordering the Aegean Sea (Plant *et al.* 2005). Isolated high V values in central and the extreme south-east of England may be associated with ironstone and the Weald district respectively. High V point anomalies in Greece are related to ophiolite, amphibolite, Fe-Ni and base metal mineralisation. Anomalous stream water V contents in south-central Slovakia are caused by Tertiary volcanic rocks of predominantly andesitic composition. An isolated stream water V anomalous point in Hungary has no apparent explanation.

In Spain and Portugal, vanadium shows a

distribution opposite to the one in solid sample media; it is controlled by pH, Eh and climate, with the highest values found in alkaline stream water with much dissolved organic carbon (DOC).

The discussed patterns of V in stream water of Europe are distributed according to two major models, the Major-ions and the REEs distribution patterns. Both of them are mainly exogenic, in response to the climatic N-S zonation of the continent, and to rainfall and infiltration in connection with topography. The much stronger Major-ions pattern explains most of the V distribution in southern and central Europe, and the REEs pattern anomalies in Finland, Sweden, Denmark and adjacent Germany. Geogenic features include high V concentrations in stream water in the Italian and Greek alkaline volcanic provinces (Plant *et al.* 2005). The anomalies appear also in the solid sample media of these regions. In other areas the concordance of stream water and solid media patterns is very rare.

V in stream sediment

Total vanadium in stream sediment has a median value of 62.0 mg kg⁻¹ (XRF analysis), with a range from < 2 to 407 mg kg⁻¹.

The V stream sediment distribution map shows low V areas (<37 mg kg⁻¹) located mainly in the sandy plains from Poland to the Netherlands, throughout much of the Baltic states, south-central Sweden, western Ireland, eastern France and most parts of central southern and eastern Spain.

High V values in stream sediment (>89 mg kg⁻¹) are located mainly in southern Finland, northern Fennoscandia (iron ores), central Norway (Caledonian layered mafic intrusions such as Sulitjelma), and the Caledonides of Norway generally. The North-Atlantic Tertiary volcanic province shows high V stream sediment values in western Scotland (central complexes of Skye, Mull, Rhum and Ardnamurchan) and in northern Ireland (Antrim plateau basalt). Most of Britain shows high V values, which may be caused by coprecipitation with iron in stream sediment. In central and southern Europe, in contrast, V anomalies are scarce and are limited to southern Portugal and adjacent Spain (Palaeozoic flysch sediments and Ossa Morena metamorphic zone), north-western Spain (ultramafic rocks of the Ordenes ophiolite complex), the Central Pyrenees,

the Bohemian Massif, an area in the highest western Alps (ophiolites near Mont Blanc and Matterhorn), the Roman Alkaline Province in Italy, a point anomaly at Roccamonfina in Campania, and north-eastern and central Greece (ophiolite, lignite, Fe-Ni, Cr, phosphorite and base-metal mineralisation). In addition, scattered V stream sediment point anomalies throughout Europe could be caused by local geological substrate or by coprecipitation conditions in stream sediment, and should be investigated locally.

Although vanadium is generally a lithophile element in the primary (igneous) environment (except in magnetite and some Fe-silicates), it occurs with the siderophile element iron in the secondary environment, adsorbed or in coprecipitation with Fe-oxides/hydroxides. The distribution of V on the stream sediment map is very similar to that of Fe. The correlation coefficient Fe-V is 0.87 (very strong) in stream sediment. Vanadium also shows a strong correlation (>0.6) with Al, Ga, Ti and Co, and a good correlation (>0.4) with Eu, Ni, Cu, Zn and Nb.

The analysis of stream sediment samples by ICP-AES after *aqua regia* extraction yields a

median extractable V content of 29 mg kg⁻¹, and a range from 4 to 306 mg kg⁻¹. This indicates that about 70% of the total V is extracted on average. The *aqua regia* extractable V stream sediment

distribution pattern is the same everywhere except in the Pyrenees (black shale) and northern Portugal-Spain (mafic/ultramafic rocks) where the extractable V is lower.

V in floodplain sediment

Total V values in floodplain sediment, determined by XRF, vary from <2 to 266 mg kg⁻¹, with a median of 56 mg kg⁻¹, and the *aqua regia* extractable from 3 to 140 mg kg⁻¹ V, with a median of 29 mg kg⁻¹. The *aqua regia* leach extracts on average 52% of the total V. The general distribution across the continent is roughly similar, but varies in detail.

Low total V values in floodplain sediment (<34 mg kg⁻¹) occur over the glacial drift covered plain from Elbe river in Germany across the whole of Poland and Lithuania to western Latvia; in central and eastern Spain on mostly Mesozoic and Tertiary rocks (clastics and carbonates); on carbonate and clastic rocks of Aquitaine and Rhône basins in France; on loose molasse basin deposits of central-north Austria. Low total V values in floodplain sediment also occur in south-east Finland, south Sweden and southernmost Norway on largely granitic rocks of the Fennoscandian Shield, and over metamorphic and granitic rocks and Old Red Sandstone in the northern half of Scotland.

High total V values in floodplain sediment (>81 mg kg⁻¹) occur in the Precambrian Shield rocks of Fennoscandia on old marine clay areas of southern, central and northern Finland (e.g., Koitelainen Cr-V-PGE); in northern Sweden (e.g., Kirunavaara-Norrbotten mineralised area), central and southern Sweden (also near Taberg V-Ti-Fe deposit); in greenstone belts of central and northern Norway, and in the Caledonides part, in north and south-central Norway, partly over gabbroic areas; the Midland Valley of Scotland (mafic volcanics, 200 mg kg⁻¹), Wales (mafic volcanics) and south-east England (possibly industrial pollution). In Variscan Europe, high V values in floodplain sediment are found over rocks of the Iberian Portuguese-Spanish Pyrite Belt extending into the Córdoba-Pedroches Zn-Pb district with Carboniferous black shale; and the north-west part of Spain and adjacent Portugal (mafic and ultramafic rocks of the Ordenes

complex, and intermediate plutonic rocks); in France, the Armorican Massif, part of Massif Central (basaltic volcanics in Auvergne), the western Pyrenees, and the Jura Mountains the mineralised Erzgebirge and Bohemian Massif; in the Alpine realm, high V values are found in southern and eastern parts of Austria, most of Slovakia, Hungary and Croatia, northern Corsica, north-western Italy and the upper Po River basin and the Roman alkaline magmatic province; Albania and northern Greece with ophiolite, lignite, Fe-Ni, Cr, base-metal and phosphorite mineralisation. A very high V value in floodplain sediment occurs on the basalt of Canary Islands (181 mg kg⁻¹).

The highest floodplain sediment V value is found in the mineralised Oslo Rift (266 mg kg⁻¹). High V values that occur in England on the Blackwater River to the north-east of London may be due to industrial pollution, and in Germany on the Weser river (224 mg kg⁻¹) to the north of Bremen to coal and oil combustion. The high floodplain sediment V value in western Croatia is explained by enrichment in karstic soil.

Vanadium in floodplain sediment has a very strong positive correlation with Fe₂O₃ and Ti₂O, a strong correlation with Al₂O₃, Ga, Co, Nb, Ce, La, Eu, Sm, Gd and Y, and a good correlation with Li, Ta, Cu, Th and the remaining REE.

The *aqua regia* V floodplain sediment distribution map is similar to the total XRF map, but with a more pronounced anomaly in southern England, southern Italy and Sicily, southern and northern Finland, and north-east France. On the other hand the area with high V values is less conspicuous in central Norway, in Austria, Hungary and Slovenia, southern Portugal and in Brittany in France.

It is concluded that the V 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 Al₂O₃ contents.

V comparison between sample media

Patterns in V distribution between all solid sample media are broadly similar, although stream sediment concentrations are higher than in other sample media throughout most of Britain and Ireland and in southern Norway (Fe and Mn oxide precipitation induced by low pH, high rainfall conditions). These patterns are similar to those seen for Fe, but weaker. Lower V is present in stream sediment throughout Croatia, Slovenia and southern Austria (possibly explained by the removal of fine-grained material from the residual soils). Vanadium values in subsoil in north-western Spain are higher than in other solid sample media. Vanadium is higher in stream sediment in southern Portugal compared to other solid sample media. Lower V values are observed in floodplain sediment throughout the Pyrenees compared to the other solid sample media.

Patterns between total and leachable (*aqua regia*) V concentrations are broadly similar, except in north-eastern Portugal and over the Pyrenees, where leachable V data are lower than total data in all sample media (no explanation).

A boxplot comparing V variation in subsoil, topsoil, stream sediment and floodplain sediment is presented in Figure 51.

Stream water V data show similar patterns to those observed in solid sample media throughout most of southern and eastern Europe, but opposite patterns occur throughout Fennoscandia (relatively immobile V^{3+} associated with reducing conditions), the Quaternary sediments of northern mainland Europe and most of the Iberian Peninsula (in the south, higher concentrations associated with oxic conditions).

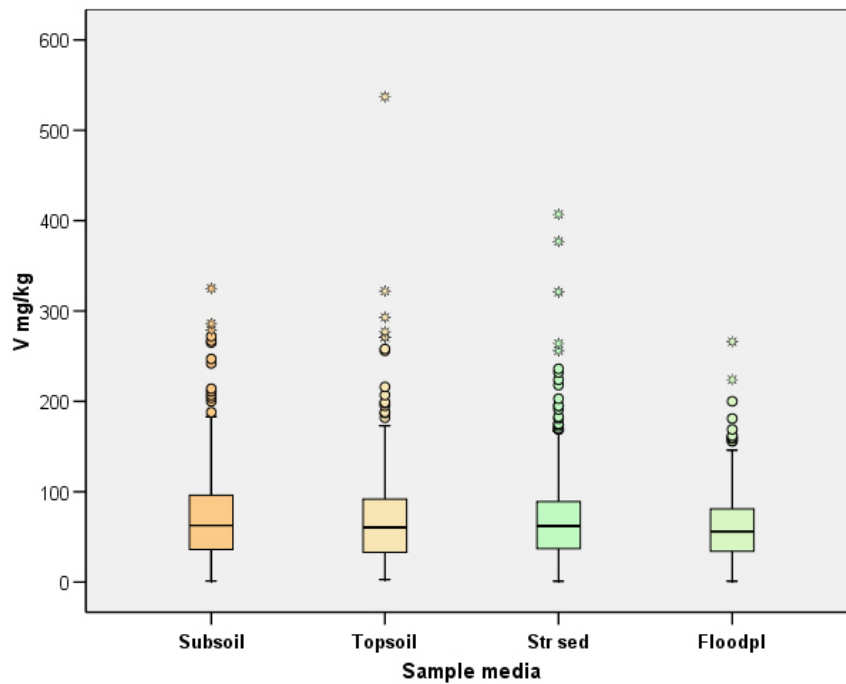


Figure 51. Boxplot comparison of V variation in subsoil, topsoil, stream sediment and floodplain sediment.