Nb – Niobium

Introduction

Niobium, also known as columbium (Cb) in the USA, belongs to group 5 of the periodic table, along with V and Ta. It has an atomic number of 41, an atomic mass of 93, two oxidation states (+3 and +5) and one stable isotope (^{93}Nb). Although it is metallic in many respects, its chemistry in the +5 oxidation state is more typical of non-metals, as it forms numerous anionic species and very few cationic compounds.

Niobium is a lithophile metallic element. Nb^{5+} has an ionic radius of 64 pm, which is identical to that of Ta^{5+}, so these elements are usually found together in minerals. Niobium forms several rather rare, but economically important minerals, including pyrochlore $(Na,Ca)_2(Nb,Ta)_2O_6(OH,F)$, columbite-tantalite $(Fe,Mn)(Nb,Ta)_2O_6$ and stibiocolumbite $Sb(Nb,Ta)O_4$. It is more widely present at trace levels in rock-forming minerals such as biotite, rutile, sphene, cassiterite and zircon; of special geochemical significance is the ionic substitution of Nb for Zr in zircon, since this mineral is widely distributed in igneous rocks. Pollard (1989) reports that Ta and Nb mineralisation is often associated with alkali granite, characterised by high fluorine levels, and by the development of pervasive, post-magmatic alteration. Niobium also occurs in bauxite.

High Nb concentrations are found in late stage magmatic differentiates, and felsic igneous rocks generally have the highest contents. Shale and granite tend to have the highest Nb concentrations, and limestone and sandstone the lowest. Nb^{5+} also substitutes for Ti^{4+} in its compounds, and is thus found in above normal concentrations in areas with mafic rocks (Reimann *et al.* 2003). The crustal abundance of Nb is estimated to be 20 mg kg^{-1} (Wedepohl 1978, Fyfe 1999), based on averages for granitic rocks, granodiorite and diorite with 22 mg kg^{-1}; gabbro and basalt 10 mg kg^{-1}; syenite and alkalic rocks 100 mg kg^{-1}, and peridotite 1.5 mg kg^{-1}. Therefore, alkaline rock complexes, *e.g.,* syenite, nepheline syenite, alkali granite and alkaline ultramafics, have the highest Nb content of all magmatic rocks (Neiva 1999). Data on the Nb content of sedimentary rocks are scarce, although there are sufficient analyses for Wedepohl (1978) to quote a value of 17 mg kg^{-1} Nb for argillaceous rocks. Willis and Ahrens (1962) and Willis (1970) present data for Mn nodules from different oceans, giving average values in the range 32–41 mg kg^{-1} Nb. The average value for loess is given as 20 mg kg^{-1} (McLennan and Murray 1999). Data on metamorphic rocks is similarly scarce; an average of 26 mg kg^{-1} is given by Wedepohl (1978) for quartzofeldspathic rocks from the Canadian shield.

Niobium displays very low mobility under all, but the most extreme environmental conditions, due to the high stability and very low solubility of the oxide Nb_2O_5 and niobates derived from this (Brookins 1988). However, the presence of citric, tartaric and oxalic acids increase the solubility of Nb through chelation. The maximum concentration of Nb in stream water, based on solubility calculations, is likely to be about 10 µg l^{-1} (Office of Civilian Radioactive Waste Management website). In sea water and most other surface water, Nb concentrations are likely to be much lower (Sohrin *et al.* 1998).

Anthropogenic sources of niobium include nuclear fuel production, welding and steel production (Reimann and de Caritat 1998). It is also used in the manufacture of missiles, cutting tools, pipelines and super magnets.

Niobium is considered non-essential, but it is present in living organisms and can affect biological mechanisms. Little is known about its toxicity.

Table 48 compares the median concentrations of Nb in the FOREGS samples and in some reference datasets.

Nb in soil

The median Nb content is 9.76 mg kg^{-1} in subsoil and 9.68 mg kg^{-1} in topsoil; the range is from 0.24 to 133 mg kg^{-1} in subsoil and from 0.45 to 134 mg kg^{-1} in topsoil. The average ratio topsoil/subsoil is 1.008.

Low Nb values in subsoil (<6.0 mg kg^{-1}) occur in central Finland, in western Ireland, in the glacial drift area from the Netherlands to

Table 48. Median concentrations of Nb in the FOREGS samples and in some reference data sets.

Niobium (Nb)	*Origin – Source*	*Number of samples*	*Size fraction mm*	*Extraction*	*Median mg kg⁻¹*
Crust[1]	Upper continental	n.a.	n.a.	Total	12
Subsoil	**FOREGS**	**790**	**<2.0**	**Total (ICP-MS)**	**9.76**
Topsoil	**FOREGS**	**843**	**<2.0**	**Total (ICP-MS)**	**9.68**
Soil[2]	World	n.a.	n.a.	Total	12
Water	**FOREGS**	**807**	**Filtered <0.45 µm**		**0.004 (µg l⁻¹)**
Water[3]	World	n.a.	n.a.		0.001 (µg l⁻¹)
Stream sediment	**FOREGS**	**852**	**<0.15**	**Total (XRF)**	**13.0**
Floodplain sediment	**FOREGS**	**749**	**<2.0**	**Total (XRF)**	**10.0**

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

Lithuania, in calcareous areas of southern and eastern Spain, and in small alluvial areas in coastal Portugal, the Paris basin and central Hungary.

In subsoil, Nb shows high values (>13 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.*). In Galicia it has been shown that Nb anomalies are related to episyenites developed in shear bands within granitic rocks. High values also occur in central Germany, 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 high in northern Sweden, and a few isolated points in southern Norway, near Rovaniemi (Finland), Mourne granite (northern Ireland), and Glasgow (Scotland). High Nb values in Greece are found in *terra rossa* soil (Epirus, Kefallinia), felsic rocks (central Macedonia) and near to bauxite and phosphorite mineralisation (central and western Greece).

There is little difference between the topsoil and subsoil Nb distribution maps. However, the Pyrenees show a continuous Nb anomaly in topsoil, and in southern Italy, Nb anomalies are stronger, related to peralkaline volcanics.

Niobium and Ta are closely associated in phyllosilicate and oxide minerals, such as columbo-tantalite and pyrochlore, but they are also present as traces in other oxides. As expected, their correlation is very strong: 0.85 in subsoil, and 0.83 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).

In subsoil, Nb also shows a strong correlation (>0.6) with Th, Y, the REEs, Al, Ga, In, Ti and Rb, and a good correlation (>0.4) with Be, U, Fe, V, Sc, Mn, Co, Zr, Hf, K, Ba, Cs, Tl, Pb, Ag and Zn. Correlations are very similar in topsoil.

Nb in stream water

Niobium values in stream water range over only two orders of magnitude, from <0.002 µg l^{-1} to 0.096 µg l^{-1} (excluding an outlier of 0.34 µg l^{-1}), with a median value of 0.004 µg l^{-1}. Analysis is not adequate, since about 25% values are below the analytical quantification limit.

Lowest Nb values in stream water (<0.002 µg l^{-1}) in stream water are predominantly found in most of Spain and northern Portugal, in western, southern and north-eastern France and southern Sardinia (Variscan and Alpine Orogen terrains), in all Switzerland and most of Austria and Slovenia, western Croatia, in all northern Italy, most of Greece, eastern Hungary and southern Poland, all characterised by Alpine Orogen terrains. The low values in south-western and northern Norway, throughout northern Sweden and Finland, are characterised by Caledonides and Precambrian terrains, and in western Scotland and central England in the Caledonides, may show a dilution effect by heavy rainfall. There appears to be no reliable correlation with the geology at these low (near-detection) levels.

Highest Nb concentrations in stream water (>0.03 μg l^{-1}) are found in the glacial drift of Denmark, southern Sweden and Finland, characterised by Precambrian terrains, and in central and southern Italy, controlled by recent alkaline volcanism and related hydrothermalism of the Roman Neapolitan and Vulture geochemical provinces. Enhanced Nb values (>0.015 μg l^{-1}) also occur in southern Sweden and Finland and northern Poland (Precambrian terrains), and over the Massif Central of France (Variscan terrains). In northern Poland, as well as in the Baltic Countries and southern Fennoscandia, high concentrations are correlated with DOC, which shows a regional relationship with peat land, and is responsible for increasing the mobility of certain ions in a humid climate and alkaline conditions; the geochemical mobility of Nb is thus similar to that of Ba, Mo, Ni, Sr, Zn and even Zr (Kabata-Pendias2001, Perel'man 1977, 1989, Ivanov 1996). Complexation by chelation with organic acids in peaty waters may be responsible for the mobilisation of small amounts of Nb in these areas. The Nb anomalies in northwestern Germany, like those of Zr, Ti, Al, V and the REE, correlate with high DOC values. They are mainly related to environmental conditions. Highly anomalous values in eastern France are in streams affected by salt exploitation.

The Nb distribution pattern in stream water follows generally the REEs patterns model that is chiefly climate dominated, but also the "Alkaline rocks elements", and the inverse "Major- ions" pattern. Stream water high in Nb is acidic, of low mineralisation and high soluble organic matter, and the major soluble species are organic complexes. The rare high Nb areas in soil and/or sediment with a high Nb signature in corresponding stream water occurs only in the south of Sweden and Finland, in the Central Massif in France, and in alkaline volcanic areas of Italy; in the latter two cases, they are related to alkaline magmatism.

Nb in stream sediment

The median Nb content in stream sediment is 13 mg kg^{-1}, and the range is from <1 to 281 mg kg^{-1}.

The Nb distribution map shows low stream sediment values (<10 mg kg^{-1}) mainly in eastern Finland, central Sweden, the glacial drift covered northern European plain from Poland to the Netherlands, the Baltic states, central Ireland, the Jura and south-eastern France, most of Greece, northern and central Italy, north-easternmost Italy and adjacent part of Austria, Dalmatian Croatia, southern and eastern Spain.

High Nb values in stream sediment (>16 mg kg^{-1}) are found mainly in the French Massif Central (often associated with Be-Sn enriched granite), the north-west Iberian Peninsula (granitic and metamorphic rocks of the Iberian Massif), the Canary Islands, the Roman Alkaline Province, Corsica, an area from south-east Austria to Pannonian Croatia and western Hungary, western Bohemia and adjacent areas of Germany, Scotland, Cornwall, southern and central Norway, the granitic Kiruna area of northern Sweden and south-western coastal Sweden. Point anomalies are found in Estonia (phosphorite mineralisation), northern Ireland (Mourne granite), northern Germany, northern Hungary, in Campania (volcanics), near Verona in Italy, and in western Crete over Neogene sediments with Fe mineralisation.

Niobium in stream sediment shows a strong correlation with Ti (0.77), Ta (0.72), and with some heavy REEs (Dy, Ho, Er, Tm, Yb). It has a good correlation (>0.4) with Th, U, Zr, Rb, Al, Ga, Fe, V, Y and all the remaining REEs. Niobium has a good negative correlation with CaO (-0.41). Concentration of heavy minerals in detrital sediments is probably responsible for some point anomalies in which Nb-Ta (columbite), Zr (zircon), REEs (monazite) and Ti (rutile) are associated.

Nb in floodplain sediment

Niobium values in floodplain sediment vary from <1 to 125 mg kg^{-1}, with a median of 10 mg kg^{-1}.

A notable feature of the Nb distribution in floodplain sediment are the low values (<7 mg kg^{-1}) over the glacial drift covered plain extending from north Germany and Poland to the Baltic countries. Other areas with low Nb values are the metamorphic basement rocks of northern Norway and eastern Finland; most of calcareous Ireland and carbonate rocks of north-east England, the karst Dalmatian coast of Croatia, parts of Albania and Greece with ophiolite, limestone and flysch; the carbonate and clastic rocks of the Meseta Central and eastern Spain, the alluvial plains of the lower Garonne and the Rhône river basins in France; the molasse basin of southern Germany and central Austria.

High Nb values in floodplain sediment (>13 mg kg^{-1}) occur in south-west Finland (crystalline rocks), southern, eastern, central-eastern and northern Sweden (felsic crystalline rocks), northern-central-southern Norway, western Scotland, Wales (felsic volcanics), in south-east England, Cornwall (granitic area with an anomalous value of 42 mg kg^{-1}), the southern Armorican Massif with felsic rocks in France, a small area in north-east France and adjacent Belgium with sediments rich in heavy minerals, and the Massif Central (associated with Be-Sn enriched granite). Further, high Nb values occur over central and northern Portugal and adjacent western Spain (granitic and metamorphic rocks of the Iberian Massif), the Harz Mountains, Erzgebirge (with two anomalous values of 43 and 29 mg kg^{-1}) and Bohemian Massif, which are all apparently associated with granitic intrusions and mineralisation. Similarly, the large area with high Nb values extending from the Austrian-Italian Alps, into Slovenia, Croatia, Hungary to south-west Slovakia and the Moravian Heights in the Czech Republic; in this area there is a striking similarity with the Ti pattern, suggesting that the origin is not related to granite.

In the karstic soil of Slovenia and Croatia, the high Nb values in floodplain sediment may be explained by their association with TiO_2, which tends to be concentrated in the residual soil, and its subsequent erosion and deposition on the floodplains. High Nb values are also found in the central Swiss-Italian Alps (felsic intrusives and mineralisation), the Roman Alkaline Province, and Corsica (felsic intrusives and mineralisation).

The Nb point floodplain sediment anomaly in northern Italy is associated with the Colli Euganei alkaline volcanic rocks. The high value in western Crete is over Mesozoic and Neogene sediments (phyllite, limestone) with nearby Fe mineralisation (limonite, haematite, pyrolusite, alunite). An outlier of 125 mg kg^{-1} Nb occurs on Gran Canaria in the Canary Islands (draining basaltic and trachytic alkaline volcanic rocks, rich in Nb).

Niobium in floodplain sediment has a very strong correlation with Ti_2O (0.86), a strong correlation (>0.6) with Ta, Al_2O_3, Ga, Fe, V, Rb, Th, Y and most REE, and a good correlation (>0.4) with K_2O, Co, Li, Be, U, Tl, Zr and the remaining REEs - Ho, Tm, Yb and Lu.

It is concluded that the Nb spatial distribution in floodplain sediment is related to bedrock geology, but also to clay-rich soil with high Al_2O_3 contents.

Nb - comparison between sample media

Patterns in Nb distribution between all solid sample media are generally similar. The main differences are the higher Nb observed in soil in the alkaline volcanic provinces of Italy compared to all other solid sample media. Niobium is also lower in stream sediments along coastal Croatia and Slovenia (possibly removal of fine-grained material from the residual soil). In floodplain sediments throughout south-west Finland, Nb data are higher than in all other solid sample media.

A boxplot comparing Nb variation in subsoil, topsoil, stream sediment and floodplain sediment is presented in Figure 31.

Patterns in stream water Nb data are generally opposite to distributions observed in solid sample media, except in the volcanic provinces of Italy (in which Nb is high in all sample media) and in Greece (where all data are generally low). In northern Europe, distributions are controlled strongly by DOC, since Nb is generally highly insoluble unless complexed with organic substances. Highest concentrations are, therefore, associated with the organic rich environments of most of southern and central Fennoscandia, as well as throughout Lithuania, Latvia and northern Poland. In southern Europe, low Nb in stream water is influenced more by pH, since Nb is insoluble under alkaline conditions.

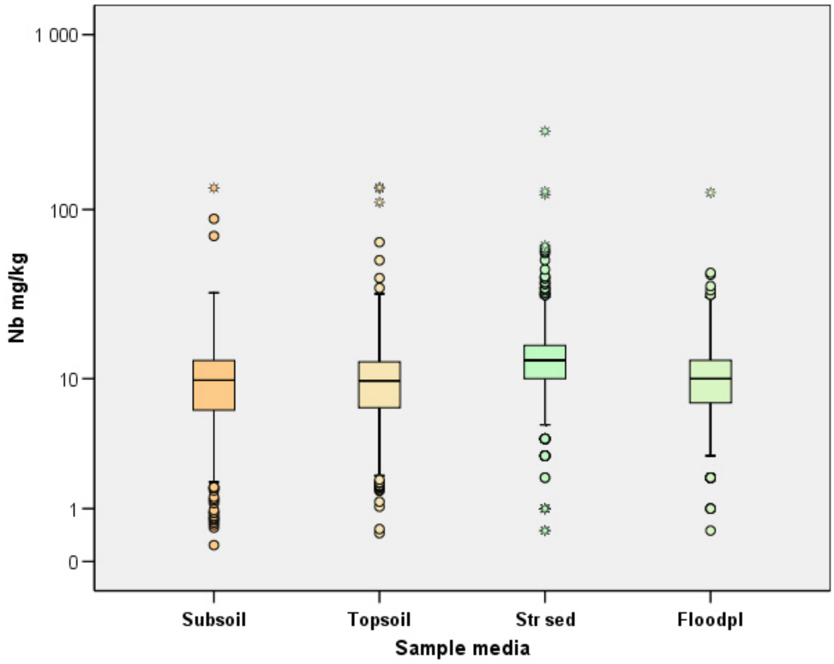

Figure 31. Boxplot comparison of Nb variation in subsoil, topsoil, stream sediment and floodplain sediment.