Ni – Nickel

Introduction

Nickel belongs to group 10 of the periodic table, along with Pd and Pt. The element has an atomic number of 28, an atomic mass of 59, two main oxidation states (+2 and +3) and five naturally occurring isotopes (^{58}Ni, ^{60}Ni, ^{61}Ni, ^{62}Ni and ^{64}Ni), of which ^{58}Ni is the most abundant at 68.3% of the total mass.

Nickel is a siderophile metallic element with chalcophilic and lithophilic affinities and forms several minerals, including pentlandite $(Fe,Ni)_9S_8$, nickeline NiAs and ullmannite NiSbS. The Ni^{2+} ion is intermediate in size (69 pm) between Mg^{2+} and Fe^{2+} (72 and 61 pm respectively), for which it substitutes during fractionation, and it is partitioned into ferromagnesian minerals such as olivine (up to 3000 mg kg^{-1} Ni), orthopyroxene and spinel. It is, thus, strongly enriched in ultramafic and mafic lithologies relative to felsic igneous rocks. Mielke (1979) reports values for Ni in igneous rocks as: ultramafic 2000 mg kg^{-1}; basaltic 130 mg kg^{-1}; granitic 4.5-15 mg kg^{-1}, and a crustal abundance of 99 mg kg^{-1}. Nickel, like Co, is a siderophile element, but in the Earth's crust it also exhibits chalcophile and lithophile characteristics. The abundance of Ni in igneous rocks, therefore, generally correlates with those of Mg, Cr and Co. It is also present in appreciable amounts in common sulphide minerals, such as pyrite and chalcopyrite, and often correlates well with Cu in sulphide-rich rocks (Wedepohl 1978).

In sedimentary rocks, Ni is mostly held in detrital ferromagnesian silicate minerals, detrital primary Fe oxides, hydrous Fe and Mn oxides, and clay minerals. It is concentrated in shale (up to 90 mg kg^{-1}) relative to greywacke (*ca.* 40 mg kg^{-1}), quartzitic sandstone (*ca.* 20 mg kg^{-1}) and limestone (<5 mg kg^{-1}). Mielke (1979) cites levels of Ni in shale, sandstone and carbonate rocks as 68, 2 and 20 mg kg^{-1} respectively. Organic matter and coal can contain Ni concentrations in excess of 50 mg kg^{-1}. Loess contains on average 20 mg kg^{-1} Ni (McLennan and Murray 1999). Nickel is a pathfinder for magmatic nickel deposits, but its effectiveness is limited by very high background values associated with host rocks; therefore, in the search for such deposits, elevated Cu values may enable the discrimination of Ni anomalies associated with sulphide from those derived from unmineralised ultramafic rocks.

A large proportion of the Ni in stream sediment is held in detrital silicate and oxide minerals that are resistant to weathering. Limited dissolution of Ni^{2+} may occur at low pH, but its mobility is generally restricted by its tendency to be sorbed by clay minerals (Short 1961) or hydrous oxides of Fe and Mn (Ure and Berrow 1982). In soil, Ni is strongly related to Mn and Fe oxides but, especially in surface soil horizons, occurs mainly in organically bound forms (Kabata-Pendias 2001). The range of Ni values in soil vary from 0.2 to 450 mg kg^{-1} according to rock type.

Nickel is highly mobile under acidic, oxidising conditions. In natural water, Ni may exist in one of three oxidation states (+2, +3 and +4), although the free ion Ni^{2+} predominates. Chloride, NO_3^- and SO_4^{2-} compounds of Ni are very soluble in water, but $NiCO_3$ and, in particular, $Ni(OH)_2$ and $Ni_3(PO_4)_2$ are insoluble. High concentrations of PO_4^{3-} may, therefore, significantly suppress the Ni content of stream water. Colloidal $Ni(OH)_2$ is present above pH 8 and, under reducing conditions, Ni is incorporated into sulphides, such as millerite NiS, also lowering its mobility (McBride 1994). Average Ni concentrations in surface water vary from less than 1 to about 10 µg l^{-1} (Hem 1992). River particulates are reported to have an average value of 90 mg kg^{-1} (McLennan and Murray 1999). A recent study to assess the relative mobility of Cr and Ni in volcanic andosols of the Auvergne (France) has shown that their respective mobility was lower than 40 and 25% respectively and that the natural uptake of Ni by plants was very low, *i.e.*, 2 mg kg^{-1} for graminea and 0.4 mg kg^{-1} for corn (Salpeteur *et al.* 2006).

Anthropogenic sources of nickel include fertilisers, steel works, metal plating and coinage, fuel combustion and detergents (Reimann and de Caritat 1998). In the presence of some organic complexing agents, Ni is capable of forming neutral or negatively charged complexes, making the metal highly mobile in relation to other trace elements. Consequently, Ni concentrations may be high in stream water contaminated by sewage and leachate from waste tips.

Nickel has been shown to be essential for microorganisms and has been implicated as having an essential role in human metabolism (McGrath 1995). The World Health Organisation recommends a daily intake of 10 µg day^{-1} for humans (WHO 1996). Nickel deficiency retards growth and impairs iron uptake. Most Ni^{2+} compounds are relatively non-toxic, but some compounds are highly toxic, and extreme excesses of Ni are both toxic, causing dermatitis and gastric irritation, and carcinogenic illnesses (WHO 1996).

Table 50 compares the median concentrations of Ni in the FOREGS samples and in some reference datasets.

Table50. Median concentrations of Ni in the FOREGS samples and in some reference data sets.

Nickel (Ni)	*Origin – Source*	*Number of samples*	*Size fraction mm*	*Extraction*	*Median mg kg^{-1}*
Crust[1)]	Upper continental	n.a.	n.a.	Total	47
Subsoil	**FOREGS**	**790**	**<2.0**	**Total (ICP-MS)**	**21.8**
Subsoil	**FOREGS**	**784**	**<2.0**	***Aqua regia* (ICP-MS)**	**18.0**
Topsoil	**FOREGS**	**843**	**<2.0**	**Total (ICP-MS)**	**18.0**
Topsoil	**FOREGS**	**837**	**<2.0**	***Aqua regia* (ICP-MS)**	**14.0**
Soil[2)]	World	n.a.	n.a.	Total	20
Soil, C-horizon[3)]	Barents region	1357	<2	*Aqua regia* (ICP-AES)	12.8
Humus	**FOREGS**	**367**	**<2.0**	**Total (ICP-MS)**	**3.80**
Humus[3)]	Barents region	1357	<2	Total (HNO_3, ICP-MS)	5.92
Water	**FOREGS**	**807**	**Filtered <0.45 µm**		**1.91 (µg l^{-1})**
Water[4)]	World	n.a.	n.a.		2.5 (µg l^{-1})
Stream sediment	**FOREGS**	**852**	**<0.15**	**Total (XRF)**	**21.0**
Stream sediment	**FOREGS**	**845**	**<0.15**	***Aqua regia* (ICP-AES)**	**16.0**
Floodplain sediment	**FOREGS**	**747**	**<2.0**	**Total (XRF)**	**22.0**
Floodplain sediment	**FOREGS**	**747**	**<2.0**	***Aqua regia* (ICP-AES)**	**18.0**
Stream sediment[5)]	Canada	22 460	<0.18	Total (INAA)	22
Stream sediment[5)]	Canada	82 465	<0.18	*Aqua regia* (ICP-AES)	20

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

Ni in soil

The median total Ni content (ICP-MS analysis) is 21.8 mg kg^{-1} in subsoil and 18.0 mg kg^{-1} in topsoil, with a range from <2 to 2400 mg kg^{-1} in subsoil and up to 2690 mg kg^{-1} in topsoil. The average ratio topsoil/subsoil is 0.918.

Low Ni values in subsoil (<10.5 mg kg^{-1}) occur in southern Fennoscandia, Estonia, in the glacial drift area from the Netherlands to Poland and Lithuania, in central Portugal and central Spain, and small areas in central Hungary and central France. The relatively low Ni values in Finland are surprising given the presence of greenstone belts and Ni-deposits.

The subsoil Ni map shows a strong anomaly over most of Greece and Albania, caused by mineralised ophiolitic rocks, and sedimentary rocks derived from them. An example is the Vourinos Ni-Cr deposit in northern Greece. There are also high values of Ni (>37.4 mg kg^{-1}) over ophiolites in Liguria (Italy) and Corsica, over Slovenia and Croatia (residual soil over carbonate rocks), the Rheno-Hercynian, the Carpathians, northern Ireland (Antrim basalt), central Norway and a large area with greenstone belts in northern

Scandinavia. In Greece, the Cr and Ni anomalies are also associated with bauxite, Fe-Ni and polymetallic sulphide mineralisation. In southern Europe, some high Ni values are explained by coprecipitation with Fe-Mn oxides of supergene origin, for example, in north-west Spain.

The topsoil map for Ni is very similar. Gran Canaria shows a local anomaly due to basaltic volcanic rocks. The high Ni values in the central Pyrenees are associated with black shale of Ordovician, Silurian and Carboniferous age. Southern Italy is enriched in Ni in the topsoil only.

The correlation Cr-Ni is very strong, 0.89 in subsoil and 0.83 in topsoil. Nickel in both subsoil and topsoil also shows a strong correlation (>0.6) with Co, and a good correlation (>0.4) with Fe, Sc, V, Cu and Te.

The median Ni content after *aqua regia* extraction (ICP-AES analysis) is 18 mg kg^{-1} in subsoil and 14 mg kg^{-1} in topsoil, with a range from <2 to 2590 and from <2 to 2560 mg kg^{-1} respectively. This means that most of the Ni is extractable. The soil distribution maps of extractable Ni shows no major differences compared to the total Ni maps; only in northern Finland a decrease in high values may be observed.

Ni in humus

The median Ni content in humus is 3.80 mg kg^{-1}, and the range varies from <0.3 to 74.9 mg kg^{-1}.

The Ni distribution map shows that low values in humus (<2.5 mg kg^{-1}) occur over most of Sweden and central northern Norway, parts of Ireland, eastern Scotland, western France, northern Germany, Denmark and central Poland.

High Ni values in humus (>6.5 mg kg^{-1}) occur throughout most of central Europe, from northern Italy over Switzerland to Belgium and south-eastern Netherlands, central-east Germany, Czech Republic and Austria. Some high Ni values are found in south-central Norway, and an isolated anomaly occurs in northern Ireland near the Antrim basalt. High Ni values in northern Norway may be related to greenstone belts or to the smelters of the nearby Kola area in Russia. Nickel deposition is shown on moss geochemical maps in northernmost Norway and the adjacent Kola peninsula in Russia (Rühling and Steinnes 1998).

The Ni pattern is probably in large part geogenic, *i.e.,* different proportions of mineral soil admixture seem to be responsible for the variations in Ni concentration, with geological background influencing the relative content of mineral soil. The rather sharp limit between the lower-background glacial drift area (Poland to the Netherlands) and the more southern high-background area of central Europe is also observed in soil, stream and floodplain sediment.

Nickel in humus has a strong correlation (0.79) with Co, and a good correlation (0.54) with Ga.

Ni in stream water

Nickel values in stream water range over three orders of magnitude, from 0.03 to 24.6 µg l^{-1}, with a median of 1.91 µg l^{-1}. Nickel tends to correlate, broadly, with Co.

Lowest Ni values in stream water (<0.58 µg l^{-1}) are found in central and western Iberian Peninsula and in southern France and Corsica on Variscan terrains, in northern Ireland and Scotland on Caledonide terrains, in western and northern Norway on Caledonides, in central and northern Sweden on Precambrian terrains.

Enhanced Ni concentrations in stream water (>3.93 µg l^{-1}) are found in southern Spain on Alpine Orogen (Baetics) terrains, in France (Brittany) on Variscan terrains, in western Ireland, south-eastern England and northern Germany on Caledonides, in southern Germany on Variscan terrains, in south-eastern Sweden and western and eastern Finland on Precambrian terrains, in northern Germany, central and eastern Poland on Precambrian terrains, in north-western (Liguria), north-eastern (isolated high value), and southern (Apulia and Sardinia island) Italy. The high values in western Finland are related to (Litorina) clay soil, whereas the ones on eastern Finland are related to black schists and sulphide deposits. In Italy, the high values of north-western Sardinia are also related to polymetallic sulphide deposits, whereas the anomalies near Liguria are most probably related to the occurrence of ophiolitic rocks. The single high anomaly in northern Greece is most likely due to the ophiolitic lithology. Highly anomalous Ni values in eastern Poland are related to peat lands. High concentrations of Ni (as well as Fe and Mn) are in direct correlation with high organic substance (DOC) content. High Ni in stream water in southern Spain is related to ultramafic rocks of the Ronda, Ojén and Carratraca massifs and to Fe-Cu and Ni-Cr mineralisation in these massifs. A point anomaly in eastern Spain on the Mediterranean coast at Cabo de la Nao is influenced by industrial activities.

The described distribution of nickel in stream water follows chiefly the patterns of Major-ions high-TDS stream water, and Ni is present mostly as Ni^{2+}, in most of the high Ni areas. These patterns are chiefly controlled by climate and other exogenic, not geogenic factors. The exceptions, controlled by patterns of the Base metals group, are the area of high Ni concentrations in all samples from Switzerland (possibly batch contamination, the same as for Cu and Pb) and Slovenia (proved industrial pollution for a number of elements). The ophiolite masses in Albania and Greece cause a very modest nickel signature in stream water. On the other hand, Ni concentrations are quite high in stream water on entirely barren soil and sediments in north-eastern Europe.

Ni in stream sediment

The median total Ni content (XRF analysis) in stream sediment is 23 mg kg^{-1}, with a range from 1 to 1406 mg kg^{-1}.

The correlation of Cr-Ni in stream sediment is very strong (0.85), and the distribution maps are very similar.

Low Ni values in stream sediment (<12.0 mg kg^{-1}) occur over the Quaternary sediments of northern mainland Europe, over Estonia and Latvia, southern Norway and most of southern Sweden, a small area in northern Sweden, central Spain, and some smaller areas scattered over southern Europe.

The Ni stream sediment distribution map is dominated, however, by a strong anomaly throughout the ophiolite belts of Greece (one of the most important Cr-Ni mineral deposits is located at Vourinos in northern Greece) and Albania. High Ni values in stream sediment (>37.0 mg kg^{-1}) also occur in the northern Apennines of Italy and western Alps (where ophiolites are also present), northern Finland, northern Britain and northern Ireland (Antrim basalt), the Eifel in Germany, the border area between Spain and north-east Portugal (mafic rocks), the pyrite belt of southern Spain and Portugal, and some point anomalies in the central Alps.

High values of Ni in stream sediment occur over most of Britain and in eastern Ireland. This pattern is repeated with Co, Fe and Mn, suggesting likely coprecipitation with Fe and Mn. This effect occurs in the uppermost layer of the stream bed, and it is possible that this layer was not sufficiently removed prior to collection of stream sediment samples. Additional or alternative sources of Ni might be through application of sewage sludge; elevated Ni would also be expected, and has been observed at the national scale, over the coalfields of central and northern England, when compared to other sedimentary rocks.

Nickel in stream sediment shows a very strong correlation with Cr (0.80), and their distribution maps are very similar. Nickel also has a good correlation (>0.4) with Fe, V, Co and Cu.

The median Ni content in stream sediment after *aqua regia* extraction (ICP-AES analysis) is 17 mg kg^{-1}, with a range from 3 to 1201 mg kg^{-1}. These values are close to the total extraction. The distribution pattern is the same as for total Ni, except in Fennoscandia where extractable Ni levels are relatively lower.

Ni in floodplain sediment

Total Ni values in floodplain sediment, determined by XRF, vary from 2 to 1080 mg kg^{-1}, with a median of 22 mg kg^{-1}, and *aqua regia* extractable Ni concentrations range from 2 to 942 mg kg^{-1}, with a median of 18 mg kg^{-1}, indicating that almost the whole Ni is in extractable form. Therefore, geochemical patterns in floodplain sediment between total XRF and *aqua regia* extractable Ni are approximately similar.

Low total Ni values in floodplain sediment (<12 mg kg^{-1}) occur over the granitic, granodioritic and gneissic areas of southern and eastern Sweden, south-east Finland, southernmost Norway, the glacial drift covered plain extending from north Germany, Poland, Lithuania, Latvia and Estonia; the sandstone, metamorphic, and granitic rocks of north-eastern Scotland, the Garonne river basin in France; central and eastern Spain with carbonates and clastics, and parts of Sardinia and Corsica with felsic rocks.

High total Ni values in floodplain sediment (>33 mg kg^{-1}) are found over the amphibolite of central and northern Norway; the greenstone belt of northern Finland; the shale and mafic volcanics of the Scottish Midland Valley; the high total Ni values in south Wales, central-east England are possibly attributed to iron mineralisation, the Erzgebirge and Bohemian Massif to base metal mineralisation, western Italian Alps and northern Italy to mafic-ultramafic rocks; the extensive anomalous zone from the Czech Republic, Hungary, southern Austria, Slovenia and Croatia may be associated with polymetallic mineralisation; in southern Portugal with schist and mineralisation; the northern half of Italy with ophiolites, and Corsica with mafic and ultramafic rocks. Very high total Ni values (>92 mg kg^{-1}) extend over the whole of Albania and Greece, and are ascribed to ophiolite rocks and Fe-Ni and polymetallic sulphide mineralisation.

Two point Ni floodplain sediment anomalies in Spain are related to lithology, *e.g.,* ophiolites of the Ordenes complex in Galicia, and near Malaga in south Spain to Cr-Ni mineralisation and mafic-ultramafic rocks (Carratraca Alora Cr-Ni deposit). The highest anomalous total Ni values occur in Greece (1080 and 555 mg kg^{-1}), and Albania (947 mg kg^{-1}).

Nickel in floodplain sediment has a strong positive correlation with Cr (0.74) and Co (0.65), and a good correlation with MgO (0.45).

The *aqua regia* extractable Ni floodplain sediment map is overall similar to the total XRF Ni map, with the exception of less pronounced high Ni patterns in Finland, Norway and France.

In conclusion, mafic and ultramafic lithologies, and ophiolite masses, together with their metamorphic equivalents (greenstone) and mineralisation, show the highest Ni concentrations in floodplain sediment. Greece and Albania appear to represent a geochemical province with respect to Ni, but also in association with Cr, Co, Mg, Cu and Mn. The distribution map of total Ni in floodplain sediment shows, therefore, the geochemical differences of the geological substratum and mineralised areas quite well, and no distinguishable influences from anthropogenic activities are recognised.

Ni comparison between sample media

Patterns in Ni distribution between all solid sample media are very similar; there is also little difference between total and leachable (*aqua regia*) Ni concentrations. Stream water Ni concentrations are much lower than in the solid sample media throughout Norway, Sweden and Scotland, possibly arising from rain water dilution. Highest Ni values occurs in solid sample media over the ophiolite belt of Greece and Albania. Unlike Cr, much lower Ni concentrations are found in associated stream water, probably as a result of co-precipitation with Fe and Mn. In the Czech Republic, Ni shows high concentrations only in humus and stream water, leading to the interpretation that they are most likely caused by armospheric deposits of fly ash from coal burning power plants. Very low Ni concentrations are found in all solid sample media throughout the Quaternary sediments of northern mainland Europe; Ni in stream water is, however, much higher over this region.

A boxplot comparing Ni variation in subsoil, topsoil, stream sediment and floodplain sediment is presented in Figure 32.

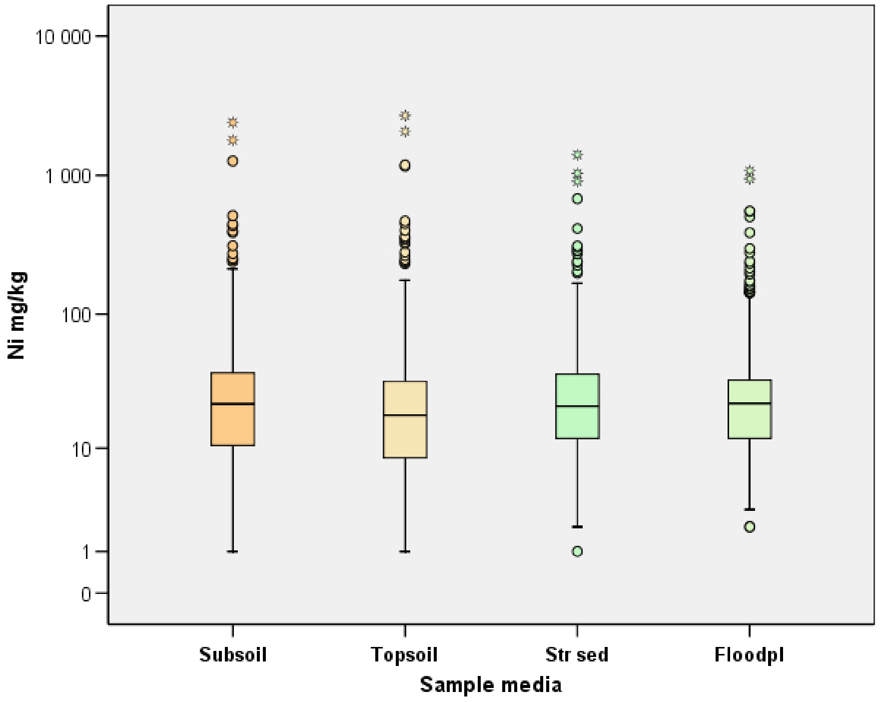

Figure 32. Boxplot comparison of Ni variation in subsoil, topsoil, stream sediment and floodplain sediment.