Co – Cobalt

Introduction

Cobalt is a member of the first row transition series of elements, which consists of Sc, Ti, V, Cr, Mn, Fe, Co, Ni, Cu and Zn, and belongs to group 9 of the periodic table, along with Rh and Ir. The element has an atomic number of 27, an atomic mass of 59, two main oxidation states (+2 and +3) and one naturally occurring isotope (^{59}Co).

Cobalt displays chalcophile and siderophile properties and is partitioned into a number of sulphide and sulpharsenide phases. It forms several rather rare minerals, including smaltite $(Co,Ni)As_{2-2.5}$, cobaltite (Co,Fe)AsS and linnaeite $(Co,Ni)_3S_4$, and is present as an accessory element in olivine, pyroxene, amphibole, mica, garnet and sphalerite. It may also be associated with the iron sulphides pyrite, arsenopyrite and pyrrhotite, and in oxide accessory minerals, such as magnetite (Ure and Berrow 1982). In early magmatic processes Co^{2+} substitutes for Fe^{2+} and Mg^{2+}, which are similar in charge and ionic radius, so Co is generally enriched in mafic relative to felsic igneous rocks (Wedepohl 1978). This is shown by the average abundances cited by Mielke (1979): ultramafic 150 mg kg^{-1}; basaltic 48 mg kg^{-1}; granitic 1-7 mg kg^{-1}; syenite 1 mg kg^{-1}; an average bulk continental crust abundance of 29 mg kg^{-1}, and 10 mg kg^{-1} in the upper continental crust (McLennan and Taylor 1999). Cobalt, together with Cr and Ni, is indicative of mafic rocks.

Cobalt is considered to be immobile during metamorphism (Condie 1976, Nicollet and Andriambololona 1980). Minerals such as quartz, feldspar and pure calcium carbonate generally contain very little Co (<2 mg kg^{-1}), so pure sandstone and limestone are very low in Co. In sedimentary rocks, Co tends to vary with the Fe and Mn content and is concentrated in the fine-grained fractions. Arkose and greywacke are more enriched, their Co concentrations usually reflecting the abundance of mafic minerals (Ure and Berrow 1982). Cobalt values of *ca.* 50 mg kg^{-1} are common in very fine-grained mudrocks, but mean Co concentrations in black shale are somewhat lower (Vine and Tourtelot 1970), indicating that organo-metallic complexing is not an important enrichment mechanism for Co in natural sedimentary processes. Mielke (1979) cites average values for shale, sandstone and carbonates as 19, 0.3 and 0.1 mg kg^{-1} Co respectively. McLennan and Murray (1999) quote average values for river particulates and loess as 20 and 11 mg kg^{-1} Co respectively.

Cobalt is most mobile in the surface environment under acidic and reducing conditions, where the formation of high valency phases of Fe and Mn is inhibited. It is rapidly removed from solution by co-precipitation and sorption in most oxidising, near-neutral or alkaline stream water as the dissolved Fe and Mn precipitate out as secondary oxides, hydrous Mn oxides having a particularly strong sorption affinity for cobalt. Divalent cobalt (Co^{2+}) is bioaccessible when it is organically bound (McBride 1994), and cobalt may also bind to humic and fulvic acids and inorganic colloids (Qian *et al.* 1998). Certain bacteria are known to mobilise Co already complexed as chelate compounds (Kabata-Pendias 2001). Cobalt does not form residual silicate minerals in soil. The average concentration of Co in soil is quoted as 7 mg kg^{-1} by Albrecht (1999) with a normal range from 1 to 40 mg kg^{-1} (Taylor 1964).

Uncontaminated and natural surface and groundwater contain Co concentrations between 0.04 and 0.35 µg l^{-1}; contaminated river water may have considerably higher levels, for example up 31 mg kg^{-1} near the Rhine estuary (Albrecht 1999).

Anthropogenic sources of cobalt include coal combustion, special steels, fertilisers and lead, iron and silver mining and processing (Reimann and de Caritat 1998), although, apart from these few cases, anthropogenic anomalies in drainage are rarely recorded. Environmental pollution problems from Co are generally less significant than those associated with some other heavy metals (Cole and Carson 1981).

Cobalt is a biologically essential element and is found in vitamin B_{12}. It can be toxic to humans at doses of 25 mg per day or more; however, problems related to deficiencies are more likely than excess dose toxicity. Cobalt has metabolic links with iron and copper, which can be depressed at high levels of cobalt intake, leading to anaemia (Mertz 1987).

Table 20 compares the median concentrations of Co in the FOREGS samples and in some reference datasets.

Table 20. Median concentrations of Co in the FOREGS samples and in some reference data sets.

Cobalt (Co)	***Origin – Source***	***Number of samples***	***Size fraction mm***	***Extraction***	***Median mg kg^{-1}***
Crust1)	Upper continental	n.a.	n.a.	Total	17.3
Subsoil	**FOREGS**	**790**	**<2.0**	**Total (ICP-MS)**	**8.97**
Subsoil	**FOREGS**	**784**	**<2.0**	***Aqua regia* (ICP-MS)**	**8.00**
Topsoil	**FOREGS**	**843**	**<2.0**	**Total (ICP-MS)**	**7.78**
Topsoil	**FOREGS**	**837**	**<2.0**	***Aqua regia* (ICP-MS)**	**7.00**
Soil2)	World	n.a.	n.a	Total	10
Soil, C-horizon3)	Barents region	1357	<2	*Aqua regia* (ICP-AES)	5.25
Humus	**FOREGS**	**367**	**<2.0**	**Total (ICP-MS)**	**0.80**
Humus3)	Barents region	1357	<2	Total (HNO_3, ICP-MS)	1.66
Water	**FOREGS**	**807**	**Filtered <0.45 µm**		**0.16 (µg l^{-1})**
Water4)	World	n.a.	n.a.		0.3 (µg l^{-1})
Stream sediment	**FOREGS**	**852**	**<0.15**	**Total (XRF)**	**8.00**
Stream sediment	**FOREGS**	**845**	**<0.15**	***Aqua regia* (ICP-AES)**	**8.00**
Floodplain sediment	**FOREGS**	**747**	**<2.0**	**Total (XRF)**	**7.00**
Floodplain sediment	**FOREGS**	**747**	**<2.0**	***Aqua regia* (ICP-AES)**	**8.00**
Stream sediment5)	Canada	26 227	<0.18	Total (INAA)	13
Stream sediment5)	Canada	82 465	<0.18	*Aqua regia* (ICP-AES)	10

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

Co in soil

The median total Co content (ICP-MS analysis) is 8.97 mg kg^{-1} in subsoil and 7.78 mg kg^{-1} in topsoil, with a range varying from <3 to 170 mg kg^{-1} in subsoils and up to 249 mg kg^{-1} in topsoils. The total Co subsoil distribution map shows many similarities to the Cr and Ni maps, and also some features similar to the MnO maps. The average ratio topsoil/subsoil is 0.918.

Low Co values in subsoil (<4.91 mg kg^{-1}) occur in parts of southern Sweden and southern Finland, in Estonia, in the glacial drift area between the Netherlands and Poland, in central Hungary, in central Portugal, and in parts of central and eastern Spain.

A large area with high Co values in subsoil (>14.4 mg kg^{-1}) occurs over Greece and Albania, related to mafic-ultramafic rocks, but also to bauxite and Fe-Mn mineralisation in Greece. High values (>14.4 mg kg^{-1}) also occur over Calabria-Sicily, the northern Apennines, Lazio and Corsica, north-western Spain (sedimentary rocks rich in Fe and Mn, including ferruginous sandstones and oolithic ironstones), an isolated anomaly near Salamanca (mafic intrusive), the western Pyrenees (siderite veins, with Co adsorption on Fe oxides), the Baetic zone in south Spain (Palaeozoic rocks with vein mineralisation of siderite, goethite, haematite), karst soils of Slovenia and coastal Croatia, Austria, the Poitou region in France (see Mn-Co association described above), greenstone belts in northern Scandinavia, and some scattered anomalies in Norway, Great-Britain and Germany. The highest total Co value in subsoil (an outlier with 170 mg kg^{-1}) occurs in an ophiolitic area in Liguria, Italy, in a sample poor in SiO_2 and CaO, but rich in Fe_2O_3 (12%) and MgO (18%); this sample also has the highest Cr (2137 mg kg^{-1}) and Ni (2400 mg kg^{-1}) content.

High Co values in soil are very often geogene, related to mafic or ultramafic rocks, but they can also be the result of adsorption and coprecipitation processes with Fe and/or Mn from lithologies rich in these metals or from mineralisations; these processes occur especially in Mediterranean Europe.

In the Co topsoil map, the anomalies in Scandinavia and Britain are reduced, but the Pyrenees show a more extensive high area. The Canary Islands also show a high value due to basaltic rocks.

In subsoil, Co shows a strong correlation with Ni, Cr, V, Sc, Fe, Cu, Ti and Mn, and a good correlation with Al, Ga, In, Nb, Te, Zn and most of the REEs. The same pattern applies to topsoil, with only minor variation in the correlation coefficients.

For Co determined after partial extraction with *aqua regia* (ICP-AES analysis), the median Co content is 8 mg kg^{-1} in subsoil and 7 mg kg^{-1} in topsoil, with a range from below the detection limit of 1 mg kg^{-1} to 191 mg kg^{-1} in subsoil and to 255 mg kg^{-1} in topsoil. These results indicate that most of the Co is extracted with *aqua regia*. The distribution patterns are roughly the same as for total Co content, the only exception being a much lower extractable Co content in northern Fennoscandia, both in subsoil and topsoil.

Co in humus

The median Co content in humus is 0.80 mg kg^{-1}, and the range varies from <0.1 to 19.1 mg kg^{-1}.

The Co distribution map shows low values in humus (<0.40 mg kg^{-1}) occurring over most of Sweden except the north, most of northern Scotland, south-western France, and the glacial drift covered area from the Netherlands over northern Germany, Denmark to Poland.

High Co values in humus (>2.20 mg kg^{-1}) occur throughout most of central Europe, from northern Italy over Switzerland to Belgium, central-east Germany, Czech Republic and Austria. It is to be noted that the southern half of Germany shows average Co values; this area seems to be encircled by higher values. High values are also found in south-central France. Some isolated anomalies occur in south-central Norway, western Finland, north-western Scotland and northern Ireland (the Antrim basalt).

The Co pattern in humus is probably geogenic, *i.e.,* different proportions of mineral soil admixture seem to be responsible for the variations in Co concentration, with geological background influencing the relative content of mineral soil. This is especially true for central Europe. The sharp limit near 51° latitude between the low-background glacial drift area (Poland to the Netherlands) and the more southern high-background area of central Europe is also observed in soils, stream and floodplain sediments. In Fennoscandia, where humus horizons are better developed, the pattern may reflect the actual metal content of humus; especially in Norway and Finland, local patterns dominate the picture; ultimately these are probably also related to variations in the local geological substrate.

Cobalt in humus has a strong correlation (0.79) with Ni, and a good correlation with Ga (0.57) and with La (0.42).

Co in stream water

Cobalt values in stream water range over more than two orders of magnitude, from 0.01 to 5.63 µg l^{-1} (excluding three outliers up to 15.7 µg l^{-1}), with a median value of 0.16 µg l^{-1}. Cobalt correlates broadly with Ni.

Lowest Co values in stream water (<0.06 µg l^{-1}) are found throughout most of Norway, central and northern Sweden, northern Finland on Precambrian Shield and partly Caledonides, and northern Scotland on Caledonide and part Laurentian terrains; as well as in southern and eastern Spain, northern Portugal; in a belt throughout southern France (Provence and Corsica) and eastern Germany on Variscan, in northern Italy and parts of Austria and Slovenia along the Alpine arc and in Albania and Greece on Alpine Orogen terrains.

Enhanced Co concentrations in stream water (>0.41 µg l^{-1}) are found on Precambrian Shield throughout southern Fennoscandia (southern Sweden and southern Finland), on Variscan of south-east England, Brittany in France, areas of southern Spain (solubilisation of Co by influence of high DOC content), an isolated point anomaly in central Spain related to Mn-Co mineralisation in small outcrops of Pliocene-Quaternary basaltic rocks), and on Alpine Orogen in southern Italy (including Sardinia and Sicily islands, Apulia and Neapolitan areas). In western Finland, the enhanced Co values are probably associated with clay-rich soil; in the east, they are possibly associated with black schist and sulphide deposits. Anomalies in Sardinia and the Neapolitan area relate to polymetallic sulphide mineralisation and alkaline volcanics respectively; the anomalies in Sicily and the Apulia regions may have anthropogenic sources. A point Co anomaly (2.36 µg l^{-1}) in south-east Poland is related to an anthropogenic source, namely the metallurgical work at Stalowa Wola. The highly anomalous Co value in eastern Slovakia (14.8 µg.l^{-1}) is related to the mining and processing of the metamorphic-hydrothermal vein mineralisation in the Spišsko-gemerské rudohorie Mountains (mainly complex siderite-sulphide ores).

Distribution of cobalt in stream water follows several models: either the patterns of high Total Dissolved Solids / Major-ions in stream water (southern Portugal and Spain, southern Italy and Sicily, north and east England, small areas in central Europe), and REEs low mineralisation DOC rich stream water (south Finland and south Sweden, Denmark, north Germany, Scotland, Ireland, and Brittany in France). The Netherlands and Sicily appear to belong to both groups. Comparison with solid sample media shows practically no correspondence in high cobalt concentrations. This indicates that high Co in stream water is primarily the result of exogenic factors, and not rock dominated. It is interesting to note that the very high Co values found in the solid media over ophiolites in Greece and Albania are not reflected in stream water, and this may be explained by the alkaline pH, which does not favour its solubility and mobility.

In north-western France two high Co values occur in areas draining Ordovician iron deposits (Sègre); this river is also contaminated with Fe, Mn,V, Zn and more exotic elements (Tl, I, Zr; but marine influence cannot be excluded for the iodine input). The Co anomalies in northern Germany, like those of Nb, Zr, Ti, Al, V, and REE, correlate with high DOC waters. They are related to environmental conditions with some anthropogenic influence. The point Co anomaly southwest of Cologne is related to anthropogenic sources (Pb-Zn mineralisations and non-ferrous metallurgical industry).

Co in stream sediment

The median total Co content (XRF analysis) in stream sediment is 8.0 mg kg^{-1}, with a range varying from < 2 to 216 mg kg^{-1}.

The Co distribution map shows low values in stream sediment (<5.0 mg kg^{-1}) throughout the north European plain including northern France, a small part of southern Sweden, the Baltic states, south-west France (Garonne alluvial plain), eastern France (Jura), in central and eastern Spain, and smaller areas in central Hungary, north-east Italy and central Austria.

High Co values in stream sediment (>14.0 mg kg^{-1}) occur over Britain and Ireland (possible coprecipitation with Mn and Fe), Greece and Albania (ophiolite association with Cr and Ni enrichment and Fe-Mn mineralisation), southern Portugal and adjacent Spain (western Iberian Pyrite Belt, with widespread Mn of volcano-sedimentary origin), south-eastern Brittany in France, the Bohemian Massif, north-western Italy, the Roman Alkaline Province, northern Finland, northern Norway and adjacent northern Sweden, parts of southern Sweden and southernmost Finland, and south-western Norway. Point anomalies occur in northern Eifel in Germany, in the Po River valley near Verona in Italy, and in the central Alps (De Vos *et al.* 2005). Point anomalies in north-east Ireland and north-west Scotland are related to basaltic rocks (see Cr and Ni). The main explanation for high Co values in stream sediment seems to be coprecipitation and adsorption on Fe and Mn oxides. A geogenic explanation prevails in Fennoscandia and Greece/Albania, with mafic or ultramafic substrates.

Cobalt in stream sediment has a strong correlation (> 0.6) with Fe and V, a good correlation (>0.4) with Mn, Ti, Ni, Cu, Zn, Al and Ga, and a weak correlation (0.3 to 0.4) with Eu and Cr.

For Co determined on stream sediment after partial extraction with *aqua regia* (ICP-AES), the median content is also 8.0 mg kg^{-1}, with a range from <1 to 245 mg kg^{-1}. This indicates that most of the Co in stream sediment is extracted with *aqua regia*. The distribution pattern is the same for total and *aqua regia* extractable Co, except for Fennoscandia, where extractable Co levels are relatively lower than total content with XRF analysis.

Co in floodplain sediment

Total Co XRF values in floodplain sediment vary from <2.0 to 63 mg kg^{-1}, with a median of 7 mg kg^{-1}. *Aqua regia* extractable Co concentrations range from <1 to 55 mg kg^{-1}, with a median of 8 mg kg^{-1}, suggesting that overall most of the Co is extracted by *aqua regia*. Therefore, geochemical patterns of total XRF and *aqua regia* extractable Co are approximately similar.

Low total Co values in floodplain sediment (<4.0 mg kg^{-1}) occur over the granitic, granodioritic and gneissic areas of the Scandinavian countries, southern Sweden, south-east Finland, and southernmost Norway, the glacial drift covered plain extending from north Germany to Poland, and the Baltic countries; the crystalline and clastic rocks of north-east Scotland; the alluvial sediments of lower Garonne in France; central and eastern Spain with clastic and calcareous rocks.

High total Co values in floodplain sediment (>12 mg kg^{-1}) are found over the amphibolite of central and northern Norway; the greenstone belt of northern Finland; the mineralised areas of south-west Finland and the Stockholm hinterland in Sweden; the shale, alkaline mafic volcanics in the Scottish Midland Valley; high total Co values occurring in Wales, the Midlands and south-west England are attributed to base metal and iron mineralisation. High total Co values occur in France over the crystalline Armorican Massif and Corsica with mafic and ultramafic rocks, in north-west Spain (mafic-ultramafic Ordenes complex in Galicia), south-west Portugal, the upper Po River basin in north-west Italy, the Roman Alkaline Province, and the extensive anomalous zone from the Czech Republic, Slovakia, western Hungary, southern Austria, Slovenia and Croatia; another extensive zone with high total Co values extends from Albania to Greece and is attributed to both ophiolite rocks and mineralisation (other elements with high values are Mg, Cr and Ni); a high Co value on Gran Canaria in the Canary Islands is explained by basaltic rocks. Cobalt is often enriched in the secondary environment (stream and floodplain sediments) by coprecipitation with iron and/or manganese; this occurs over Palaeozoic rocks in the Ardenne-Rhenish Massif of Belgium and adjacent Germany, and the Bohemian Massif.

The highest Co values in floodplain sediment occur in Euboea in Greece (63 mg kg^{-1}), and Albania (51 mg kg^{-1}), and are associated with mafic rocks and magnesite mineralisation, and ophiolitic rocks and copper mineralisation respectively.

The *aqua regia* extractable Co in floodplain sediment is lower in central Norway and north-east Finland in comparison to the total XRF Co, and it is comparatively higher in south-west England and southern Hungary.

Cobalt in floodplain sediment shows a very strong correlation with Fe_2O_3 (0.84), a strong correlation with Ni, Ga, V and TiO_2, and a good correlation with Cr, Cu, Nb, MgO, MnO, Li, Al_2O_3 and some of the REE.

In conclusion, the Co distribution in floodplain sediment reflects the bedrock mafic and ultramafic lithology, and also mineralised areas. Anthropogenic influences, if any, are masked by the stronger natural distribution of Co. A similar distribution is displayed by other elements that are associated with mafic and ultramafic rocks, *i.e.*, Cr, Co, Ni, Mg, Cu and Mn.

Co comparison between sample media

Patterns in Co distribution between all solid sample media are very similar. The main differences are in Ireland and throughout Britain, where very high Co is observed in stream sediments but much lower concentrations in floodplain sediment and soil. This effect is also observed in Mn data. Stream sediment Co data are relatively low in Croatia and Slovenia compared to other solid sample media (possible removal of fine-grained material from the residual soil). In western Hungary, floodplain sediment is richer in Co with respect to soil and stream sediment (presence of loess). High levels of Co in northernmost Fennoscandia are observed in all solid sample media apart from stream sediment. There is generally good agreement between trends in total and leachable (*aqua regia*) Co concentrations in soil and sediments with the exception of the extreme northern part of Fennoscandia, where Co associated with magnetite is lower in the leachable fraction.

A boxplot comparing Co variation in subsoil, topsoil, stream sediment and floodplain sediment is presented in Figure 13.

Stream water Co data show almost exactly the opposite patterns to those observed in the solid sample media, with highest concentrations found in western central Finland, southern Sweden and Denmark, and lowest concentrations throughout most of western and northern Fennoscandia and parts of the Mediterranean. The Co concentration in humus is generally very low and of geogenic origin.

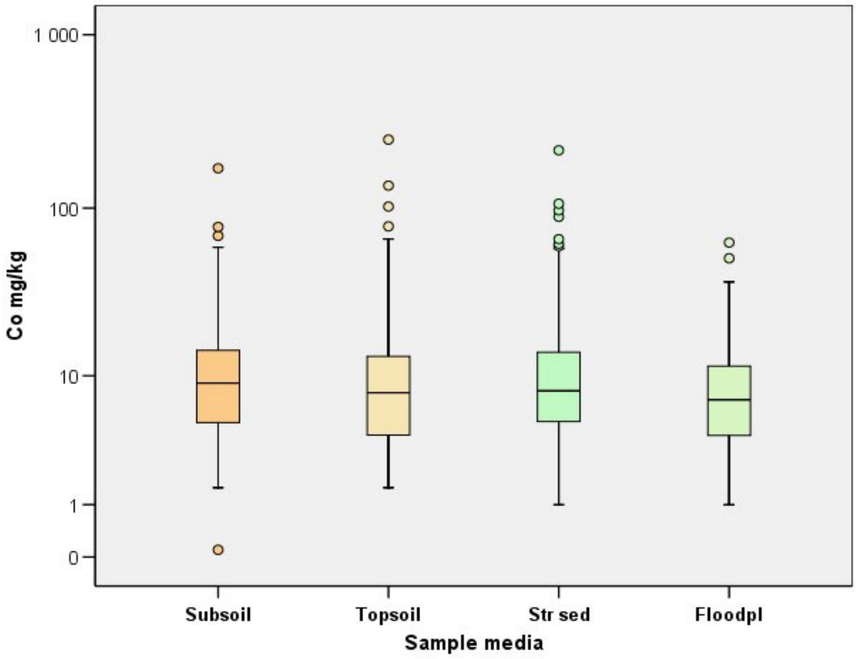

Figure 13. Boxplot comparison of Co variation in subsoils, topsoils, stream sediments and floodplain sediments.