Mo – Molybdenum

Introduction

Molybdenum belongs to group 6 of the periodic table, which also includes Cr and W. The element has an atomic number of 42, an atomic mass of 96, five main oxidation states (+2, +3, +4, +5 and +6) and seven stable isotopes (^{92}Mo, ^{94}Mo, ^{95}Mo, ^{96}Mo, ^{97}Mo, ^{98}Mo and ^{100}Mo), of which ^{98}Mo is the most abundant at 23.78%, followed by ^{96}Mo at 16.53%, ^{92}Mo at 15.84% and ^{95}Mo at 15.72% of the total mass. Molybdenum and W are similar chemically, with a wide variety of oxidation states, and their chemistries are among the most complex of the transition elements (Cotton and Wilkinson 1972).

Molybdenum is a strongly chalcophile or siderophile metallic element forming several minerals including molybdenite MoS_2, wulfenite $PbMoO_4$ and powellite $Ca(Mo, W)O_4$, but is more widely present at trace levels in association with organic matter and sedimentary sulphide minerals, notably in black shale. It is incorporated into the common sulphides pyrite, galena and sphalerite, particularly during metamorphism. During magmatic fractionation, Mo behaves incompatibly and is only sparingly incorporated in major rock-forming silicates. It may substitute to a limited extent for Ti^{4+} and Fe^{3+} in accessory phases such as sphene and titanomagnetite, but is more readily partitioned into rare W minerals, such as scheelite and wolframite (Ure and Berrow 1982).

Molybdenum has a crustal abundance of 1.2 mg kg^{-1} (Mielke 1979). The average concentration of Mo in felsic igneous rocks is 1.5 mg kg^{-1} (Vinogradov 1962), of which some 80% may be present as minute traces in feldspar and biotite. A mean Mo value of 1 mg kg^{-1} has been reported for mafic rocks (Krauskopf 1967). It is common for Mo to accumulate in areas of discrete mineralisation during metamorphism (Wedepohl 1978). In sediments, Mo tends to follow Cu in its behaviour and is strongly complexed by organic matter. Black shale is, therefore, enriched up to 70 mg kg^{-1} Mo relative to quartzo-feldspathic and carbonate rocks, which typically have Mo values of 0.5-2 mg kg^{-1} (Ure and Berrow 1982). Molybdenum is enriched in marine ferromanganese nodules, with an average Mo content of several times the crustal average (Cronan 1976).

The behaviour of molybdenite in the surface environment is different from other metallic minerals. In acidic environments, molybdenite is either stable or Mo in solution forms stable ferrimolybdate or Mo-rich lepidocrocite. These minerals degrade to fine particles that are dispersed with the suspended load and are hardly detectable close to the site of mineralisation. In neutral to basic water, molybdenite weathers to stable detrital minerals, so that Mo anomalies are recognisable in stream sediment for many kilometres downstream from the source, illustrating the use of Mo as a pathfinder element in geochemical exploration for gold, under certain conditions, and for porphyry copper-gold mineralisation. Unlike most metals, Mo is mobile under alkaline conditions, and finds particular application in reconnaissance exploration in arid environments.

Molybdenum forms molybdate oxyanions in natural water; the dominant species are $HMoO_4^-$ between pH 2 and 5, and MoO_4^{2-} above pH 5 (Brookins 1988). Being anionic, neither Mo species are strongly adsorbed by clay particles, although they are adsorbed by Fe, Al and Mn oxyhydroxides (Kaback and Runnels 1980, Kabata-Pendias 2001); they are also readily coprecipitated by organic matter, $CaCO_3$, and several cations, such as Pb^{2+}, Cu^{2+}, Zn^{2+}, Mn^{2+} and Ca^{2+}. All these reactions are highly dependent on pH and Eh conditions and, therefore, Mo migration during weathering may be poorly predictable (Kabata-Pendias 2001). The average abundance of Mo in soil ranges from 0.013 to 17 mg kg^{-1} (Kabata-Pendias 2001).

The relatively low solubility product of calcium molybdate suggests that water containing high Ca concentrations should not contain high concentrations of Mo. The mean concentration of Mo in river water is approximately 0.5 µg l^{-1} (Wedepohl 1978). The average content of Mo in river particulates is 3 mg kg^{-1} (McLennan and Murray 1999).

Anthropogenic contamination may occur from the use of Mo as an alloy in steel and welding rods, as an additive in lubricants and in the production of ceramics, as well as from oil refining, phosphate fertilisers and sewage sludge (Reimann and de Caritat 1998). Molybdenum is also released into the environment from the combustion of fossil fuels, the dispersion of mine waste and sewage sludge. Base metal mining is also a significant source of anthropogenic contamination.

Molybdenum is an essential element in animal and plant nutrition (Ragagopalan 1987). Both deficiencies and excesses can cause health problems, so there is considerable interest in the level of Mo and its activity in the environment. For example, 25 µg day^{-1} Mo is required by humans (WHO 1996); symptoms of Mo deficiency include coma and night blindness. Conversely, excessive Mo reduces the uptake of copper in the human body and leads to skeletal deformities (WHO 1996). In plants, Mo has a role in nitrogen fixation, but high Mo levels in vegetation can induce Cu deficiency in grazing animals.

Table 45 compares the median concentrations of Mo in the FOREGS samples and in some reference datasets.

Table 45. Median concentrations of Mo in the FOREGS samples and in some reference data sets.

Molybdenum (Mo)	*Origin – Source*	*Number of samples*	*Size fraction mm*	*Extraction*	*Median mg kg^{-1}*
Crust[1)]	Upper continental	n.a.	n.a.	Total	1.1
Subsoil	**FOREGS**	**783**	**<2.0**	**Total (ICP-MS)**	**0.52**
Topsoil	**FOREGS**	**840**	**<2.0**	**Total (ICP-MS)**	**0.62**
Soil[2)]	World	n.a.	n.a	Total	1.2
Water	**FOREGS**	**807**	**Filtered <0.45 µm**		**0.22 (µg l^{-1})**
Water[3)]	World	n.a.	n.a.		1 (µg l^{-1})
Stream sediment	**FOREGS**	**848**	**<0.15**	**Total (XRF)**	**0.63**
Floodplain sediment	**FOREGS**	**743**	**<2.0**	**Total (XRF)**	**0.62**

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

Mo in soil

The median Mo content is 0.52 mg kg^{-1} in subsoil and 0.62 mg kg^{-1} in topsoil; values range from <0.1 mg kg^{-1} to 17.2 mg kg^{-1} in subsoil and up to 21.3 mg kg^{-1} in topsoils. The average ratio topsoil/subsoil is 1.105.

Low Mo values in subsoil (<0.32 mg kg^{-1}) occur in central Finland, in the glacial drift area from the Netherlands to Poland and Lithuania, in eastern Hungary, south-western France, and small areas in Portugal, Spain and Greece with different geological substrates.

High Mo values (>0.91 mg kg^{-1}) are found in subsoil in northern Norway and north-west Sweden, most of central Ireland, southern Britain, the French Ardennes, northern Massif Central, the central Alps and northern Appenines, soil on limestone in Slovenia-Croatia (known enrichment in shaly parts of Mesozoic limestone), south-western Austria, southern Italy and Sicily. Single point anomalies occur in north-west Slovakia (Sb-Mo and Cu mineralisation), northern Portugal (W-Mo mineralisation) and the western Pyrenees (Silurian black shale). A point anomaly in Extremadura (western Spain) is associated with Mo bearing veins disseminated in leucogranite.

In topsoil, the central and eastern Alps appear more anomalous in Mo, and some other isolated anomalies are weakened. Northern Norway shows continental average values, western Scotland and the Pyrenees show enrichment, and there is a point anomaly in northern Greece, which may be related to Cu mineralisation. The average Mo ratio topsoil/subsoil is 1.105.

In subsoil, Mo shows a weak but significant positive correlation (>0.3) with Ga, In, Nb, Fe, V, As, Te and Y. In topsoil, only V and Te have a weak positive correlation with Mn.

Mo in stream water

Molybdenum values in stream water range over three orders of magnitude, from <0.01 to 10.1 µg l^{-1} (excluding an outlier of 16 µg l^{-1}), with a median value of 0.22 µg l^{-1}. Molybdenum distribution is similar to those of As, Sb, Se, U, V and W.

Lowest Mo values in stream water (<0.05 µg l^{-1}) are found in west central, southern and east central Finland, in western Sweden and eastern and north-easternmost Norway on Precambrian shield rocks, in large parts of Norway, in western Scotland (partly on Laurentian rocks), Wales and in northern Ireland on the Caledonides. In the Variscan part of Europe, low Mo occurs in south-central Germany, northern and south-central France, north-western Spain and northern Portugal. In the Alpidic region of Europe no low Mo values occur.

Enhanced Mo values in stream water (>0.82 µg l^{-1}) occur in Estonia, Latvia, Lithuania (leached from underlying Devonian sulphur-rich calcareous deposits and mobilised in alkaline conditions), north-west Poland and north-east Germany on Precambrian Shield derived glacial drift cover, and in the Netherlands and bordering parts of Belgium and Germany on Quaternary deposits. Isolated high Mo values in Finnish Lapland have no clear explanation, though in the contiguous Kola Peninsula is registered a Mo anomaly which extends from Finnish Lapland to Northern Russia, related to alkaline magmatism (Salminen *et al.* 2003). In the Caledonides region, high Mo values are found in a small area of north-western Norway, and in central (related to coal combustion) and south-eastern England. Anomalously high Mo in west Scotland is caused by Mo mineralisation in granite. The isolated anomaly in northern Estonia is probably related to glacial till. In Variscan Europe, only a few enhanced Mo values, explained by the presence of base metal deposits, are found in east-central France, eastern and south-western Spain (leucogranite with Sn-W-Bi mineralisation and Mo-bearing veins) and in the northern half of Sardinia. High Mo is found in Alpine parts of northern Italy, east Switzerland and western Austria, and in Slovakia and most of Hungary, in the Baetic range of southern Spain (vein-type mineralisation of Cu-As, Pb-Zn and Fe-Cu ores), in central and southern Italy with Sicily (associated with sulphide mineralisation and gypsum and sulphur evaporites), in south Albania and entire northern Greece (associated with mineralisation and hydrothermal activity). In northern and southern mainland Italy, the anomalous values are associated with inter-bedded euxinic-anoxic rocks (marlstone and cherty limestone) in calcareous dolomitic sequences; in Sardinia, high Mo is associated with polymetallic sulphide deposits. In northern Spain high and anomalous Mo values are associated with Lower Palaeozoic black shale; along the Catalonian coast also from W-Mo mineralisation associated with granite. In north-east France, some high Mo values in stream water are correlated with SO_4^{2-} and high EC and may be explained by a dissolution of pyritic layers in the upstream Triassic grey marl. A point Mo anomaly west of Hannover could be related to anthropogenic sources (mining and processing of sedimentary iron-ores).

The described Mo distribution in European stream waters clearly reveals its affinity with the Major-ions pattern and also with the Felsic-alkaline group of elements. The first mentioned association is mostly exogenic, dependent upon climate, topography *etc.*, and the second is geogenic, *e.g.,* in Italy and Greece. Under conditions prevailing in stream water, molybdenum is present as the molybdate anion. High Mo concentrations in stream water only rarely correspond to high contents in soil and sediments, but they do in southern Spain, Italy, Greece and England.

Mo in stream sediment

The median Mo content in stream sediment is 0.60 mg kg^{-1}, and values range from 0.12 to 117 mg kg^{-1}.

Molybdenum shows low values in stream sediment (<0.410 mg kg^{-1}) in central Finland, Poland, Hungary, Pannonian Croatia, central Germany, Normandy and Aquitaine in France, a large area of north-central Spain, central Portugal, and most of Greece.

High Mo values in stream sediment (>1.02

mg kg^{-1}) occur throughout most of Sweden, in northern Finland, northern, southern Norway (known molybdenite deposits related to Precambrian granite), and Scotland (vein-type hydrothermal sulphides associated with Caledonian granite), England, Wales, Ireland (point anomaly near the Mourne granite), part of southern Italy, Sicily, and the central-southern Alps in Italy (including a point anomaly for Zn, Sn, Cd, Cu and Mo related to the Triassic tuffitic andesitic sandstone of Arenarie di Val Sabbia Formation); the Spanish side of the central Pyrenees (anomalous for Pb, Mo and Zn, related to W-As-Au skarn in the contact between granodioritic stocks and Devonian limestone), Sicily, southern Sardinia, Crete and a point anomaly in northern Greece (associated with Mo mineralisation, and also anomalous for W). Most of the patterns can be explained by mineralisation. High values in Britain are associated with black shale in the upper Ordovician of Wales, and the lower Carboniferous of central England; on the island of Crete they are related to marly limestone.

Highly anomalous values in stream sediment, up to 117 mg kg^{-1}, are found in northern and central Sweden. In central Sweden, they are related to Mo- and U-rich granites; also in western Sweden Palaeozoic shale is rich in Mo. In northern Sweden Mo anomalies are associated with sulphides and granite.

Molybdenum in stream sediment has no significant correlations >0.3 with other elements.

Mo in floodplain sediment

The total Mo distribution in floodplain sediment, determined by ICP-MS, varies from <0.05 to 190 mg kg^{-1}, with a median of 0.62 mg kg^{-1}.

Low Mo values in floodplain sediment (<0.4 mg kg^{-1}) occur over the glacial drift covered north-west Germany, and most of Poland; the crystalline rocks and Old Red Sandstone of north-east Scotland, the lower Garonne alluvial plain in France, much of central Spain with calcareous, clastic and crystalline rocks, southernmost Italy with calcareous, clastic and volcanic rocks, Pannonian Croatia with mostly clastic rocks, southern Albania and much of central Greece with calcareous and clastic rocks, flysch and ophiolites.

High Mo values in floodplain sediment (>1.01 mg kg^{-1}) are found in the mineralised areas of south-western and northern Finland, northern Sweden (*e.g.,* Viscaria Cu, Attik Cu-Au, Munka Mo), the amphibolite-phyllite-granite belt of central Norway and Sweden with Cu mineral deposits, the mineralised south-eastern part of Sweden, and southern Norway (*e.g.,* Knaben Mo, Central Telemark Cu-Mo-Pb-F); the mineralised areas of southern Pennines, Wales, Mendips and south-west England, and in south-east Ireland (Namurian shale rich in Mo); the upper reaches of Saône River draining the granitic terrain and mineralisation of the Vosges (*e.g.,* Chateau-Lambert Cu-Mo); the Italian-Swiss Alps (*e.g.,* Pb-Zn-Ag deposits of Gorno, Oneta, Oltre il Colle, Novazza, Valvedello); the mineralised areas of central Italy and Sicily; Erzgebirge (*e.g.,* Cinovec Sn-W, Altenberg Sn) to the Bohemian Massif, and the Slovakian Ore Mountains. The high Mo values in the Croatian Dalmatian are in flysch sediments, which are not related to mineralisation. Similarly, on the island of Crete they are associated with marly limestone.

The highly anomalous Mo value in floodplain sediment (190 mg kg^{-1}) occurring in southern Norway is possibly related to the Knaben Mo deposit mining activities, and the one in northern Sweden (53.2 mg kg^{-1}) is in the Skellefte mineralised belt. The point Mo value (6.6 mg kg^{-1}) in central Sweden, and the one in northern Finland (6.0 mg kg^{-1}) are also related to mineralisation. Other point Mo anomalies are: (a) north-west Ireland (5.19 mg kg^{-1}) is due to the Namurian shale with naturally high levels of Mo, U and V (the sample site is misplotted and is actually at Tullinloughan area, Co. Leitrim); (b) Galicia in Spain (3.6 mg kg^{-1}) may be related to Sn-W mineralisation (*e.g.,* Fontao Sn-W-Mo); (c) southern Portugal (4.36 mg kg^{-1}), and (d) southern Spain in the Sierra Morena (4.48 mg kg^{-1}) is related to the Linares mineralised area.

Molybdenum in floodplain sediment shows a weak linear correlation coefficient (>0.3) with Mn, Fe, V, Ga and U.

In conclusion, the distribution of Mo in floodplain sediment is related mainly to the geological substratum and mineralised areas, and particularly to areas with felsic rocks and shale, and base metal mineralisation.

Mo comparison between sample media

Patterns in the distribution of Mo in topsoil and subsoil are very similar, with the exception of northern Norway, in which Mo is depleted in topsoil compared to subsoil. In stream sediments, enhanced Mo is found throughout Britain and Ireland; in floodplain sediments, enhancement is restricted to the southern parts of these islands. In sediments, Mo is generally low in comparison to soil throughout the Iberian Peninsula except for the south-western most point of Portugal. Southern Norway is very high in Mo in floodplain and stream sediments compared to soil (mineralised areas). In southern Finland, floodplain sediment is enriched in Mo compared to other solid sample media. The central and eastern Alps and Slovenia have much lower Mo in floodplain and stream sediments compared to soil.

A boxplot comparing Mo variation in subsoil, topsoil, stream sediment and floodplain sediment is presented in Figure 29.

The behaviour of Mo in stream water is complex, but trends in stream water Mo tend to oppose those observed in the solid sample media. Molybdenum is more mobile under alkaline than acid conditions, and high concentrations are found around parts of the Mediterranean, including the volcanic provinces of Italy and northern Greece. Concentrations of Mo are very low in acid stream water throughout Fennoscandia, Scotland and northern Ireland, Brittany, the Massif Central and northern Iberian Peninsula.

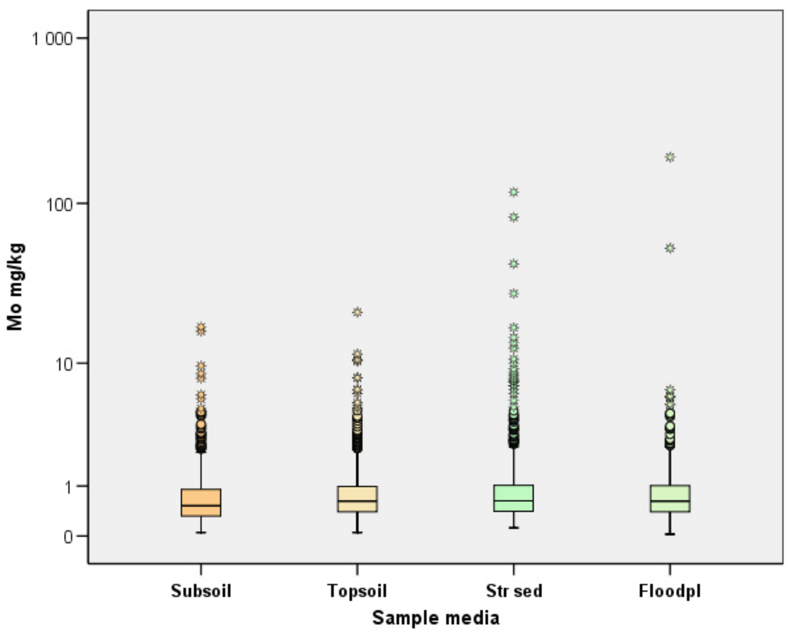

Figure 29. Boxplot comparison of Mo variation in subsoil, topsoil, stream sediment and floodplain sediment.