Introduction

Silver belongs to group 11 of the periodic table, along with Cu and Au, and is the most reactive of the precious metal elements, which include Au and Pt. The element has an atomic number of 47, an atomic mass of 108, three main oxidation states (0, +1, and +2) and two naturally occurring isotopes, ^{107}Ag and ^{109}Ag, with abundances of 51.84% and 48.16% respectively (Mango 1999).

Silver is a rather rare chalcophile metallic element that forms several minerals, including argentite Ag_2S, arsenargentite Ag_3As and native silver. It is one of the seven metals known in antiquity, along with gold, copper, iron, mercury, tin and lead. Alloys of silver and gold are widely documented (Boyle 1968, Leake *et al.* 1993). The strongly chalcophile nature of Ag means that it is widely present as a trace element in sulphide minerals such as galena, sphalerite, tetrahedrite and chalcopyrite, which contain other chalcophile elements such as Pb, Co, Ni, Sb and As (Ure and Berrow 1982). Silver is found up to levels of several per cent in galena. Silver is an important pathfinder element for most gold and silver deposits, as well as sedimentary exhalative (Sedex) or volcanic hosted massive sulphide (VHMS) mineral deposits.

Silver shows no consistent preference for felsic or mafic magmas, although Boyle (1968) reports that substitution of Na^+ by Ag^+ can lead to enrichment in alkaline rocks. Mango (1999) cites abundances in igneous rocks as: ultramafic 0.05 mg kg^{-1}; basaltic 0.10 mg kg^{-1}; granitic 0.05 mg kg^{-1}; and an average crustal abundance of 0.08 mg kg^{-1}. In sediments, Ag concentrations are typically in the range 0.05–0.12 mg kg^{-1} (Boyle 1968), with levels of enrichment during deposition generally controlled by pH and the presence of organic matter, as well as the source material. Under conditions of low acidity, Ag^+ may substitute for K^+ in clay minerals (Ure and Berrow 1982). This, coupled with preferential sorption, leads to Ag being more concentrated in clay than in silt or sand (Chao and Anderson 1974).

The surface environment geochemistry of Ag is largely controlled by pH and Eh conditions, and the concentration of halide ions, the latter being locally important in coastal areas. It is more mobile in acidic, highly oxidative environments associated with solutions of high ionic strength in which soluble complexes with anions, especially chloride, can form (Thornber 1992). Under most conditions, Ag salts are insoluble at pH values greater than 4.0. At higher pH values between 4.0 and 8.0, Ag and Pb will be adsorbed onto Fe hydroxides, in preference to Cu and Zn (Lottermoser *et al.* 1999). In the case of silver sulphide, lower oxidation potentials can assist mobility by incomplete oxidation of the sulphide, promoting the formation of thiosulphate ($S_2O_3^{2-}$) anions, which can form soluble complexes with Ag (Webster and Mann 1984). This is an important factor in the weathering of native silver associated with gold and sulphides, allowing Ag to remain mobile until entering more oxidising conditions that are likely to exist near the groundwater table (Mann 1984). The solubility of Ag^+ increases with increasing Eh; it is, therefore, dissolved from primary silver-bearing minerals by oxygenated near-surface water (Mango 1999). Subsequent transport to reduced zones below causes the deposition of Ag_2S or native silver; where chloride ions are available, cyrargirite may be deposited. The highest concentrations of Ag in soil are found overlying silver-bearing bedrock. Silver tends to occur in the surface A_o horizon, suggesting that chelated complexes of humic material are important for binding Ag (Mango 1999, Kabata-Pendias 2001). Kabata-Pendias (2001) cites a typical range for Ag in soil as 0.03 to 0.4 mg kg^{-1}.

Kharkar and others (1968) suggest an average value of 0.3 µg l^{-1} Ag in river water; Hem (1992) quotes the same value for sea water, whereas Mango (1999) gives a value of 0.4 µg l^{-1}.

Anthropogenic sources of silver, include copper, zinc, tin and lead smelters, sewage sludge and waste products from the photographic industry (Reimann and de Caritat 1998, Cooper and Thornton 1994). It is also used in making jewellery, silverware, dental products, solder and brazing alloys, electrical contacts, high capacity silver-zinc and silver-cadmium batteries, and in the production of mirrors.

Silver is biologically active, but is non-essential for all organisms. It has great potency as a microbial poison and is toxic to fish and many micro-organisms, but it is relatively harmless to higher life forms, including humans (Edwards *et al.* 1995). It occurs naturally in very low concentrations in soil, plants and animal tissues (Mertz 1987). Silver interacts metabolically with copper and selenium, preventing uptake of these elements in the human body (Mertz 1987).

Table 7 compares the median concentrations of Ag in the FOREGS samples and in some reference datasets.

Table 7. Median concentrations of Ag in the FOREGS samples and in some reference data sets.

Silver (Ag)	Origin – Source	Number of samples	Size fraction mm	Extraction	Median mg kg^{-1}
Crust[1]	Upper continental	n.a.	n.a.	Total	0.53
Subsoil	**FOREGS**	**783**	**<2.0**	**Total (ICP-MS)**	**0.25**
Topsoil	**FOREGS**	**840**	**<2.0**	**Total (ICP-MS)**	**0.27**
Soil[2]	World	n.a.	n.a	Total	0.70

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

Ag in soil

The median Ag content is 0.25 mg kg^{-1} in subsoil and 0.27 mg kg^{-1} in topsoil with a range from 0.02 to 2.07 mg kg^{-1} in subsoil and 0.01 to 3.15 mg kg^{-1} in topsoil. The average ratio topsoil/subsoil is 1.053.

In subsoils, low Ag values (<0.15 mg kg^{-1}) occur in parts of the Caledonides of Norway, part of Denmark, and in most of the glacial drift covered North European plain (Netherlands, northern Germany and Poland) where the relative coarse grain size of glacial drift Quaternary sediments precludes the presence of sufficient clay minerals (see Al and Si maps) which usually contain most of the Ag. The southern border of the former glacial extension is sharp on the map, as for many elements.

Low Ag also prevails in mostly calcareous areas, such as parts of Hungary, Austria, northern Croatia and southern Germany, the French-Swiss border area, Corsica, Umbria in Italy, most of Greece, and south-eastern, north-eastern and central-north Spain. The pattern is the same for the topsoils, except for a larger area of low Ag values (<0.17 mg kg^{-1}) in eastern Spain and the northern Apennines in Italy.

In subsoil, high silver values (>0.36 mg kg^{-1}) occur in northern Finland, southern Finland, eastern Sweden, the northern Baltic states, Brittany, the Massif Central, a region from the Harz in Germany to all of the northern Czech Republic and south-west Poland (a region known for its former silver mines, *e.g.,* Joachimsthal in the Erzgebirge), the Variscan area of the Iberian Peninsula, south-western Italy including the Roman and Neapolitan alkaline magmatic provinces (Washington 1906), Attica (Lavrion) in Greece, southern Croatia (Dalmatia), and a few scattered points in Scotland (Glasgow), Switzerland and northern Italy (De Vos *et al.* 2005).

The topsoil Ag distribution map is roughly similar to that of subsoil, but the Bohemian Massif shows higher Ag content, as do other Variscan areas of west-central Europe. Silver values in topsoil of Baltic countries are on average 1.3 times higher than in subsoil and are anthropogenic in origin (airborne and agrogenic silver fixed by soil organic matter).

The most obvious cause of Ag enrichment is mineralisation, often in well-known Pb-Zn-Ag and U mining districts (south-west and north-west Massif Central, Lavrion in Greece, the Harz Mountains and Erzgebirge in Germany/Czech Republic, although the latter one is very faint). In south-central Spain, the high Ag values are related to Pb-Ag-Zn vein mineralisation in the large mining district of Valle de Alcudia in the Sierra Morena. In north-west Spain, relation with mineralisation is not probable, but the association Ag-Nb-Ti could be associated with subparallel

regional shear zones and the presence of episyenite in granitic rocks. Still in Spain, some Pb-Ag mining districts show no medium or high Ag values (Baetic Range, Cartagena, Iberian Pyritic Belt) (De Vos *et al*. 2005).

In subsoil, Ag shows a good positive correlation (>0.4) with Th, Be, Tl, Ba, Rb, K, Al, Nb, Ce, La, Nd, Pr and Sm, and a weak correlation (>0.3) with Cs, Pb, Bi, Zr, Hf, Y, Ti, U, Ta, Ga and the remaining heavy REEs.

In topsoil, Ag shows a good correlation with Nb and Tl, and a weak correlation with Rb, Ba, Zr, Hf, Al, Ga, K, U, Th, Ta, and most of the REEs.

Ag comparison between sample media

The analytical data for Ag in stream and floodplain sediments have not been reported because they did not pass the quality control checks. The analytical data for Ag in stream water have also been rejected as there are clear country boundary effects related to sampling contamination. Patterns in Ag distribution between topsoil and subsoil are generally similar.