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A cobaltite-framboidal pyrite association from the Kupferschiefer: possible implications for trace element behaviour during the earliest stages of diagenesis

D. J. LARGE[1], Z. SAWŁOWICZ[2] AND J. SPRATT[3]

[1] Department of Mineral Resources Engineering, University of Nottingham, Nottingham, NG7 2RD, UK
[2] Institute of Geological Sciences, Jagellonian University, ul. Oleandry 2A, 30-063 Krakow, Poland
[3] Department of Mineralogy, Natural History Museum, Cromwell Road, London, SW7 5BD, UK

ABSTRACT

Cobaltite-cemented pyrite framboids are reported from the base of the Kupferschiefer in the Lubin-Sieroszowice mining district in southern Poland. In the framboids, cobaltite occurs interstitial to the pyrite crystals. The cobaltite-cemented framboids are confined to within a few cm either side of the boundary between the Weissliegendes sandstone and the Kupferschiefer laminated organic-rich shales. Textural relations and distribution of the cobaltite is interpreted as indicating that the framboids acted as a site of preferred cobaltite precipitation and that the cobaltite precipitated in response to the changing chemical environment at the Weissliegendes/Kupferschiefer contact. It is proposed that the texture may have formed as a result of desorption of Co and/or As which had been adsorbed onto the monosulphide precursors to the framboidal pyrite. Desorption during the transition to pyrite resulted in cobaltite saturation within the framboid and subsequent precipitation. The source of the Co and As was probably oxyhydroxides which exist in the upper oxic part of the Weissliegendes.

KEYWORDS: cobaltite, pyrite, framboid, Kupferschiefer, Poland, trace elements, diagenesis.

Introduction

FRAMBOIDAL pyrite is typical of pyrite which formed, mainly in sedimentary rocks, via the monosulphide precursors mackinawite and greigite (Kalliokoski and Cathles, 1969; Love and Amstutz, 1966; Rickard, 1970; Sawłowicz, 1993*a*; Wilkin and Barnes, 1997). Bacterially precipitated FeS, the precursor of framboidal pyrite, is a highly adsorbant phase capable of reducing trace metal concentrations in solution to ppb levels (Watson and Ellwood, 1994; Watson *et al*., 1995). If bacterial FeS is present during an ore forming event, significant quantities of ore forming metals should be adsorbed onto the FeS. The reported concentrations of adsorbed metals in bacterial FeS (Watson and Ellwood, 1994) are considerably greater than the concentrations reported in framboidal pyrite (Landing and Lewis, 1991; Morse *et al*., 1987; Raiswell and Plant, 1980). It is therefore expected that during the transition of FeS to pyrite, adsorbed metals will be expelled. Metal expulsion from FeS could result in high trace metal concentrations in the vicinity of the framboid and this could influence ore mineral nucleation.

The Lower Zechstein copper deposits of SW Poland are among the largest black shale hosted copper deposits and most models of the ore genesis acknowledge that a proportion of the ore mineralization occurred during sediment deposition and/or during the earliest stages of diagenesis. Framboidal sulphides, mainly pyrite, are generally recognized as the earliest sulphides in the Kupferschiefer and are described in detail by (Kosacz and Sawłowicz, 1983; Love, 1962; Sawłowicz, 1992). This paper reports a CoAsS mineral associated with framboidal pyrite in a narrow horizon at the base of the Kupferschiefer shale and considers possible mechanisms for the formation of this texture including the desorption of Co and As from an FeS precursor.

Geological setting and sample localities

The Kupferschiefer ore deposits are stratabound deposits considered to contain both syngenetic and epigenetic ores. In the Lubin-Sieroszowice mining district the ore-bearing horizon occurs at the base of the Permian Zechstein Formation, where Cu-Pb-Zn ores are hosted in the Weissliegendes, Kupferschiefer and the Zechstein Limestone. The regional setting of the Lubin Copper Mining district is north of the Fore-Sudetic Block, in the Fore-Sudetic Monocline. Details of the regional geological setting of the Fore-Sudetic copper deposits have been summarized by Oberc and Serkies (1968), Oszczepalski (1986, 1989) and Speczik (1993). The Rotliegendes deposits (up to 200 m thick) are overlain by the Weissliegendes sandstones. The origin of the Weisliegendes was described by Jerzykiewicz *et al.* (1976), and by Nemec and Porebski (1981). They are of complex origin. The lower portion, which is 0–30 m thick, represents coastal dunes, and is generally similar to the underlying sandstones except in colour which is white-grey. The upper part (0–18 m thick) is interpreted as having originated from the erosional/depositional activity of waves. The topmost 0.1 m of the Weissliegendes is often fossiliferous and shows evidence of bioturbation. Directly overlying the Weissliegendes is the Kupferschiefer bed. It is 0.05–0.6 m thick and typically can be split into two distinct units; a lower mud unit characterized by silt, illite and organic-rich laminae; and an upper unit characterized by thin organic and illite laminae, and a high proportion of authigenic carbonate. The upper part of the mineralized horizon is typically located in the lower part of the overlying Werra dolomites and limestones.

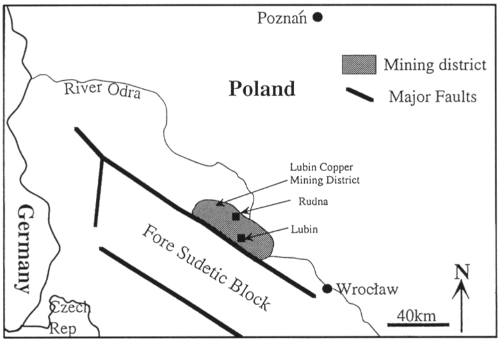

FIG. 1. A map indicating the location of the Rudna Mine in the Lubin Copper Mining district of southern Poland.

The samples, collected primarily for organic geochemical analysis, come from five vertical traverses in the Rudna Mine (Fig. 1). The traverses cover the stratigraphic range from the Weissliegendes 1 m below the base of the Kupferschiefer, to the dolomite 2 m above the base of the Kupferschiefer. The sample traverses were selected to provide typical sections through the mineralized Kupferschiefer and adjacent units. A stratigraphic section typical of the traverses, with details of the distribution of common sulphide minerals is presented in Fig. 2.

One of the most striking features of the ore mineralogy in the Kupferschiefer is its vertical zonation (Mayer and Piestrzynski, 1985). Copper

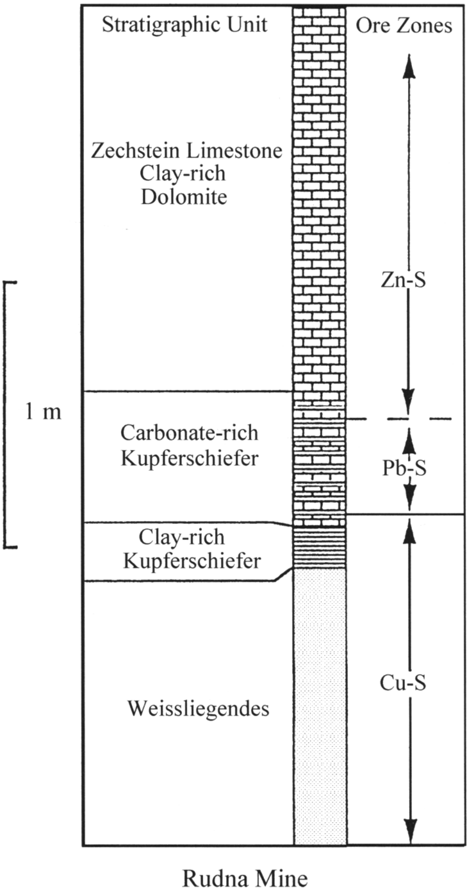

FIG. 2. The typical stratigraphy and major ore zones in the area from which samples were collected.

minerals occur in the sequence (from bottom to top) — chalcocite, bornite, chalcopyrite. In the lowermost chalcocite zone, which extends from the white sandstone into the basal 0.2 m of the Kupferschiefer, chalcocite is the main ore mineral with lesser amounts of bornite and other Cu-S minerals. Moving upward, bornite becomes the dominant copper sulphide and then chalcopyrite. At the same time the total amount of copper sulphide decreases. Superimposed on this pattern of copper minerals is a zoned distribution of galena and sphalerite. A zone in which galena is the dominant mineral overlaps with the bornite zone and the top of the chalcocite zone. The base of the galena zone is sharp and, in our samples, corresponds closely with the boundary between the lower clastic mud unit and the upper carbonate dominated mud unit (Large *et al.*, 1995). The galena zone grades upwards into a zone, in which sphalerite is the dominant sulphide with minor amounts of galena and chalcopyrite. The sphalerite zone continues into the dolomite overlying the Kupferschiefer, but its upper boundary, estimated to be 2 m above the top of the Kupferschiefer (Mayer and Piestrzynski, 1985), did not occur within our sample traverses. Framboidal pyrite was observed in all the ore zones.

Analytical procedures

Selected polished blocks and polished thin-sections were carbon coated and examined by backscattered electron microscopy (Jeol 6400, equipped with Link eXL energy dispersive X-ray analytical system). Energy-dispersive X-ray analysis on the scanning electron microscope was employed to determine the composition of each mineral. Cobalt, Ni, As, Cu, Fe, S, Ag, Si, and Ca were analysed using an accelerating voltage of 15 kV, a beam current of 1.5 nA and a beam diameter of 1 mm at a working distance of 39 mm. Silicon was analysed to detect contamination from silicate mineral inclusions and Ca to detect contamination from carbonate inclusions. Copper and S were measured using a natural covellite standard; Fe, As, Co, Ni and Ag using element standards; and Ca and Si using wollastonite. Approximate errors (wt.%) are: Co, Ni, As, Cu 0.55%; S 0.11%; Ag 0.15%; Fe 0.13%; Si 0.32%; and Ca 0.47%.

Wavelength-dispersive analysis using a Cameca SX-50 microprobe was used to produce element maps of cobaltite framboids. The elemental maps were produced at 2000 × magnification by beam scanning with a spatial resolution of 256 × 256 points, the conditions used were 15 kV accelerating voltage, with a beam current of 100 nA and a counting time of 200 mS per point. An attempt was made to analyse for PGE and Au quantitatively. However, none of these elements was detected at concentrations above the detection limits of 300–600 ppm.

Textural observations

Pyrite framboids were observed in all the stratigraphic units sampled. Within 1 cm on either side of the boundary between the Kupferschiefer and the Weissliegendes, pyrite framboids are numerous, and many of the framboids are cemented by cobaltite. The cobaltite-cemented framboids are enclosed by later generations of pyrite, dolomite, bornite and various Cu-sulphides (chalcocite, djurleite, anilite).

The pyrite framboids are generally 10–30 µm in diameter. A variety of framboid structures were observed. Some framboids have a rosette-like appearance with radial pyrite crystals enclosing a rounded core of equidimensional pyrite crystals, so-called sunflower framboids (Kosacz and Sawłowicz, 1983), others are composed only of equidimensional pyrite (Fig. 3) and others are quite irregular. Cobaltite is anhedral and occurs filling the submicron interstitial gaps between the

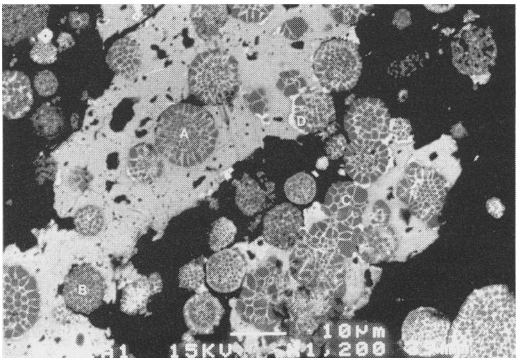

FIG. 3. Backscattered electron image of the cobaltite-cemented framboids enclosed in a bornite cement. A variety of textures are present including: (A) 'sunflower framboids'; (B) framboids containing equidimensional pyrite crystals; (C) framboids with an irregular internal structure, and (D) framboids with thin cobaltite rims.

pyrite crystals (Fig. 4). In most framboids the cobaltite is confined within the boundaries of the framboid and in only a few framboids did the cobaltite extend beyond the margins of the framboid to form a thin cobaltite rim <5 μm thick (Fig. 3). In some framboids the pyrite crystals are anhedral and of variable size: cobaltite appearing to be replaced by the pyrite, particularly in the centre of some framboids. An extreme example of this are textures similar to 'atoll textures' (England and Ostwald, 1993; Sawłowicz, 1993*a*) in which the core of a framboid has been completely replaced by cobaltite (Fig. 5). In other framboids the cobaltite appears to be only an interstitial cement.

The small size of the areas of cobaltite cement makes analysis difficult. The best analyses were obtained from thin cobaltite rims. Analyses from these areas gave good stoichiometry and compositions (atom.%) of appoximately 32% S, 33% As, 27% Co, 4.0–5.0% Ni and 2% Cu. It is difficult to establish whether or not the Co-As-S mineral in the core of the framboids has the same composition as the Co-As-S mineral at the rim is difficult to establish and analysis only confirms its Co-Ni-As-S composition. Pyrite in the framboids could reasonably be expected to be enriched in Co and As but this is also difficult to establish due to the scale of analysis.

X-ray maps of cobaltite-cemented framboids enclosed in a later generation of pyrite cement confirm the enrichment of Co, As and Ni in the framboids and indicate that concentrations of Cu and Ag are elevated at the edges of the framboids (Fig. 6). This was observed only where the framboids were enclosed in pyrite and bore no relation to the presence or absence of thin cobaltite rims. Where the framboids were enclosed in later generations of Cu or Cu-Fe sulphides no enrichment in Ag or Cu could be detected and if present would be masked by the high concentrations of Ag and Cu present in the enclosing sulphides.

Discussion

Based on the above observations, two questions arise. Why should the cobaltite be associated with framboidal pyrite, the earliest authigenic sulphide? Why should cobaltite-cemented framboids be localized to within a few cm of the boundary between the Weissliegendes and the Kupferschiefer?

The textural evidence indicates that the framboidal pyrite was a preferred site of cobaltite precipitation. This could either reflect a period of general cobaltite saturation in a mineralizing fluid or localized cobaltite saturation in the vicinity of the framboid. If the texture resulted from a period of general cobaltite saturation, selective nucleation on pyrite could be reasonably expected as the mineral structures of cobaltite and pyrite are closely related. A problem with this interpretation is that if the mineralizing fluid was saturated with respect to cobaltite it is difficult to explain why the cobaltite occurs predominantly within the framboids and only rarely as a rim. Support for a general phase of Co enrichment could be considered to come from the presence of minute cobaltite-gersdorffite inclusions in lenses of Cu

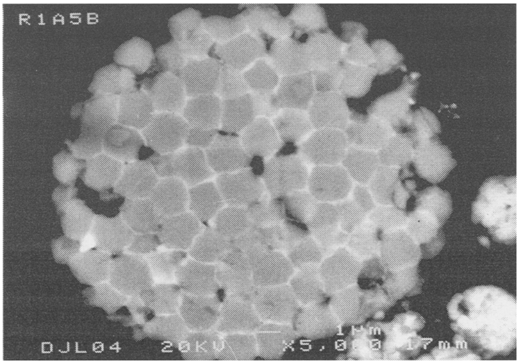

FIG. 4. Backscattered electron microscope image of a framboid containing equidimensional pyrite crystals with interstitial cobaltite.

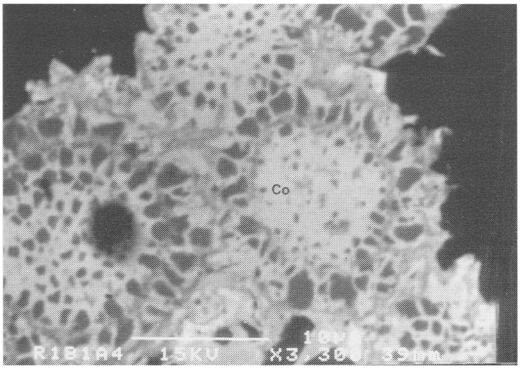

FIG. 5. Possible 'atoll textures' in which the cores of pyrite framboids appear to have been replaced by cobaltite (Co).

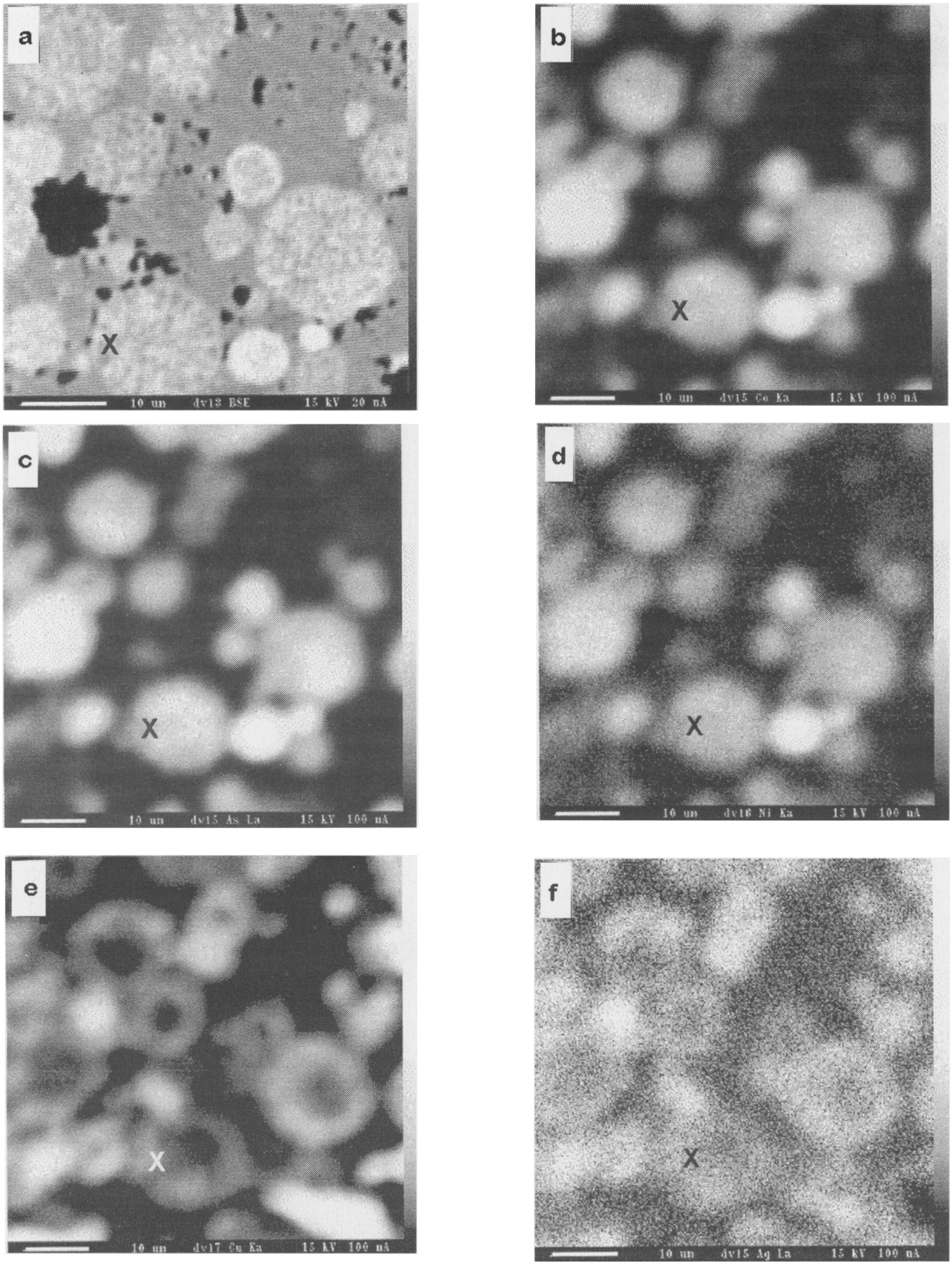

FIG. 6. (*a*) A backscattered electron image of cobaltite-cemented pyrite framboids enclosed in a pyrite cement and X-ray maps illustrating the relative concentrations of (*b*) Co, (*c*) As, (*d*) Ni, (*e*) Cu, and (*f*) Ag. Images (*e*) and (*f*) illustrate that Cu and Ag are enriched around the rims of the framboids. In images *b–f* the grey scale represents the relative concentration of each element, the darker the shade the lower the concentration. Note the backscattered electron map has a linear grey scale and the element maps have a logarithmic grey scale. A 10 μm scale bar is located in the bottom left hand corner of each image and point X is positioned at the left hand side of the same framboid in each image.

and Cu-Fe sulphides that are sometimes observed in the lower part of the Kupferschiefer bed.

Alternatively the framboids may have acted as sites where the concentrations of Co and/or As were elevated to allow local saturation with respect to cobaltite only in the framboid. This would require pyrite or its sulphide precursors to preferentially adsorb Co and/or As from solution. In anoxic marine environments Co is associated with Fe-sulphides, and based on chemical equilibrium considerations, it is thought that the Co is most likely adsorbed by the Fe-sulphides rather than co-precipitated as a discrete Co-S phase (Jacobs and Emerson, 1985; Landing and Lewis, 1991). In anoxic sediments As is also concentrated with Fe-sulphides with which it is thought to co-precipitate (Soma *et al.*, 1994) and has been shown to occur in enhanced concentrations in pyrite framboids (Graham and Robertson, 1995; Ostwald and England, 1979). Recent work has shown that bacterial iron monosulphides, the precursor to framboidal pyrite, are amongst the most absorbent substances known. In a series of experiments Watson *et al.* (1995) demonstrated that nearly all heavy and transition metals tested were preferentially adsorbed onto the sulphide and the most strongly adsorbed element was Co. The maximum adsorbed concentrations of Co reported by Watson *et al.* (1995) were 414 mg per g of FeS with a residual concentration of Co in solution of 60 ppb. It would therefore appear that bacterial iron monosulpides can preferentially adsorb Co from relatively low concentration solutions. It has also been shown that high concentrations of As can be adsorbed onto bacterial iron monosulphide from solutions containing a mixture of heavy metals (Watson and Ellwood, 1994).

During the transition from monosulphide to pyrite, which typically takes place in several stages (Wilkin and Barnes, 1997), desorption of adsorbed metals would be expected as the structure becomes more ordered and surface area is reduced. Such a process has been proposed by others. Korolev (1958), showed experimentally that 70–96% of Mo was coprecipitated from solutions by iron sulphides and that coarsely-crystalline pyrites had only minor amounts of Mo due to its loss during the ageing process. He also suggested that a similar mechanism could be important for Ni and Co. Dill and Kemper (1990) suggested that substitution of the cube for the octahedron in Fe-bisulphide aggregates led to a continuous removal of As and Ni from the pyrite. Metals desorbed during this transformation to pyrite could attain locally high concentrations in the framboid. High concentrations of Co and/or As desorbed in this manner could potentially result in cobaltite being precipitated within the framboid. The temporary nature of this adsorptive process and the desorptive expulsion of trace metals during the monosulphide-to-pyrite transition has previously been proposed (Morse and Arakaki, 1993). Precipitation of cobaltite under these conditions would depend on its solubility, the rates of Co and As desorption, availability of S and the rate of diffusion of chemical species to and from the microenvironment of the framboid. The enrichment of copper and silver at the margins of the framboids could be due to a similar mechanism as neither Cu nor Ag fit comfortably in the pyrite crystal lattice.

The cobaltite-cemented framboids typically contain ~10% cobaltite. To produce 10% cobaltite cement would require that the precursors to the pyrite adsorb approximately 68 mg Co and 86 mg As per g of FeS. The capacity of iron monosulphide to adsorb Co (Watson *et al.*, 1995) is therefore more than sufficient to account for the cobalt in the cobaltite cement.

Some evidence that the cobaltite may have formed during the transition from iron monosulphide to pyrite comes from atoll textures in which some framboid cores appear to have been replaced by cobaltite. Sawłowicz (1993*a*) suggested that the conversion of monosulphide to pyrite occurs from the rim of the framboid inwards and that atoll textures result from the replacement of iron monosulphide or greigite cores by copper sulphides after the formation of an outer rim of pyrite crystals. This reasoning could also be applied to explain the formation of similar atoll textures in the cobaltite framboids. Similarly, the occurrence of cobaltite-gersdorffite minerals as inclusions in copper sulphides could also be interpreted as resulting from the replacement of iron monosulphides and consequent precipitation of the adsorbed Co as cobaltite. The difference between the cobaltite textures and those observed by Sawłowicz is that the copper sulphides in the pyrite atoll textures are often continuous with extensive areas of copper sulphide cement enclosing the atoll. By comparison, in the cobaltite-cemented framboids, cobaltite is confined almost exclusively to the framboid. England and Ostwald (1993) propose that atoll textures may form by the recrystallization of pyrite in the presence of a chalcopyrite gel and a similar mechanism may be responsible for the cobaltite-gersdorffite inclusions in bornite. It is, however, questionable whether the direct replacement of pyrite by Cu sulphides is reasonable at the low temperatures under which the ores formed (Rickard and Cowper, 1994).

The location of the cobaltite-cemented framboids is consistent with reported high concentrations of Co, Ni and As from the boundary between the Kupferschiefer and the Weissliegendes. In the Fore-Sudetic Cu deposits the average concentration of Co is 50–80 ppm, locally up to 1.7% Co. The main carriers of Co are siegenite, cobaltite-gersdorffite, rammelsbergite-safflorite, and substitutions in pyrite and Cu-Fe-S minerals. In pyrite, Co generally prevails over Ni (Kucha, 1990). Highest concentrations occur at the bottom part of organic-rich black shale, and also in the uppermost part of the Weissliegendes sandstone (Banas *et al.*, 1996; Wojciechowska and Serkies, 1968). Arsenic shows a similar vertical distribution (Salamon *et al.*, 1993). The bulk geochemical ratio of Co to Ni is ~1 but significant lateral variations occur between the mines (Salamon, 1993). One of the main reasons for this could be that Ni shows a high affinity to the organic matter (Sawłowicz, 1985).

The restricted occurrence of this texture close to the base of the Kupferschiefer may indicate that Co and/or As were removed from solution in response to the sharp change in chemical environment encountered at this boundary. The most likely source of the As and Co are Mn and Fe oxyhydroxides, which are common in desert environments. Cobalt, in particular is one of the metals more easily leached from oxyhydroxides in redbeds (Rose and Bianchi-Mosquera, 1993). During the marine transgression that reworked the upper part of the Weissliegendes, Co and As were taken into solution from reduced oxyhydroxides. The first formed iron sulphides in the Kupferschiefer scavenged these metals, and this resulted in the localization of the cobaltite-cemented pyrite framboids at the base of the Kupferschiefer.

It is also possible that monosulphides could play a role in concentrating other metals during early diagenesis. In particular Watson and Ellwood (1994) demonstrated that bacterially precipitated FeS can adsorb Au and a variety of PGE and this could aid the accumulation of these elements in appropriate ore-forming environments. Alternatively, precious metal precipitation could also result from the semiconductivity in the cobaltite-framboidal pyrite texture. Substitution of either Ni or Co for Fe in pyrite results in n-type conductivity (Shuey, 1975) and the substitution of As for S results in p-type conductivity (Moeller and Kersten, 1994). This can result in conductivity-controlled gold precipitation (Moeller and Kersten, 1994) and it is possible that the complex association of a pyrite with cobaltite may create a specific type of conductivity which could result in precious metal adsorption and precipitation. Retention of adsorbed metals could also result in framboids acting as potential pathfinders to synsedimentary and early diagenetic ore deposits.

Conclusion

Cobaltite-cemented framboidal pyrite raises a number of questions regarding the association of trace metals with framboidal pyrite. In particular, the texture may be evidence of adsorption-desorption processes and their influence in establishing local cobaltite saturation. If the FeS precursors of framboidal pyrite have acted as a sink for Co and As this may have implications for the potential of framboids to concentrate economically important metals like the PGE. The relationship between Fe, Cu and Co mineralization in the Kupferschiefer may also give clues to the genesis of other deposits. In particular, textures reported from the Kupferschiefer may represent precursors to the cobaltite atoll textures reported from the Raipas Mine, Norway (Vokes and Strand, 1982). Similarly, some pyrite euhedra from the Zambian Copperbelt contain rounded Co-rich cores (Bowen and Gunatilaka, 1977) which could have resulted from recrystallization of a framboidal pyrite precursor.

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