Cae Coch Mine

[SH 775 654]

Introduction

The Cae Coch massive pyrite deposit is of controversial origin and has been variably interpreted as an altered ooidal ironstone, an epigenetic fracture-fill, and a kuroko-type volcanogenic exhalative deposit, while the most recent examination has classed it as a syn-diagenetic inhalative body. Clearly, the deposit is of major metallogenic interest, but it is also internationally famous for the microbial ecosystem developed within the old underground workings, where acidophile autotrophic and heterotrophic bacteria form an estimated 100 m³ of gelatinous streamer-growths (Jenkins and Johnson, 1993).

Cae Coch Mine (Figure 5.37) was worked for pyrite for sulphuric acid manufacture. It was worked intermittently between 1817 and 1895, and later from 1917 to 1919, and produced 107 650 tons of ore grading in excess of 30% sulphur in that time. Further reserves of 86 000 tons have been proven (Dunham *et al.*, 1978; Ball and Bland, 1985) but the fine-grained pyrite is difficult to separate effectively from waste, which has deterred any further working.

An early account of the site was presented by Sherlock (1919), who concluded that the mineralization was of sedimentary origin and represented a pyritized ooidal iron ore-bed, with pyritization due to intrusion of a 'diabase' body beneath the bed. According to Ball and Bland (1985), an unpublished mining consultant's report had re-interpreted the orebody as being epigenetic and fault-controlled.

Ball and Bland (1985) presented the results of a detailed study into the geology, mineralogy and major- and trace-element geochemistry of the deposit. Their conclusion was that Cae Coch represented a Kuroko-style volcanogenic submarine exhalative deposit. Important evidence was described, in the form of tubular growths of pyrite, 5–10 mm in diameter, in the upper part of the ore-bed, interpreted as being fossilized 'black-smokers' or possibly 'chemical garden' growths of pyrite from a precursor gel.

The site was re-interpreted later by Sowell and Morton (1992), who investigated the deposit using a combination of isotope and elemental geochemistry. They found little or no evidence for the existing volcanogenic massive sulphide classification, suggesting instead that the sulphides had been produced by bacterial sulphate-reduction within anoxic sediments, which produced excess H_2S ; ascendant iron-rich waters then reacted with the H_2S within 5 m of the sedimentary surface to form pyrite.

Description

The Cae Coch deposit (Figure 5.38) is hosted by a package of sedimentary and volcanic rocks of Caradoc age. It is underlain by the 300 m-thick Dolgarrog Volcanic Formation, which includes pillowed basalts, basaltic tuffs and hyaloclastites; below this unit is the Crafnant Volcanic Formation, comprising acidic ash-flow tuffs. Rhyolite domes, one of which occurs close to the deposit, locally intrude the sequence. These strata correlate with the Bedded Pyroclastic and Upper Rhyolitic Tuff formations (Reedman *et al.*, 1985) of the Snowdon volcanic centre to the south-west, described at the Lliwedd Mine GCR site. The change from dominantly volcanic to sedimentary conditions is marked at the horizon at which the deposit occurs, and the pyrite body is overlain by a thick (450 m) sequence of pyritic mudstones, with only occasional thin tuffaceous bands. These mudstones, belonging to the Nod Glas Formation, are intruded by small dolerite bodies, and the entire sequence has been affected by lower-greenschist-facies regional metamorphism and Acadian deformation, which has produced a strong cleavage in the pyritic mudstones.

The pyrite deposit is up to 2.2 m in thickness, is thickest in the axial zones of folds (Ball and Bland, 1985), and extends along strike for *c*. 200 m. It consists predominantly of pyrite with minor pyrrhotite, in a gangue of minor quartz and calcite. The pyrite, which is locally framboidal, occurs in two modes, one massive and compact, and the other porous and

intergrown with the gangue minerals. The commonest ore-type is the 'rubbly ore', which tends to occur in the lower part of the deposit, and its resemblance to the Kuroko ores of Japan was commented upon by Ball and Bland (1985). Above the 'rubbly ore' the pyrite becomes more laminated, and in the upper 0.5 m of the deposit, hollow tubes of pyrite, 5–10 mm wide, and filled with radiating quartz, occur. Ball and Bland (1985), citing examples from the Carboniferous exhalative mineralization of Ireland, suggested that these tubes may be fossilized 'black smokers', sites of hydrothermal exhalation onto the seafloor. Further pyrite tubes were recorded projecting from the top of the bed into the overlying mudstones.

Geochemically, the deposit shows minor enrichment of other metals, with up to 450 ppm Cu, 50 ppm Ag, 100 ppm Sn, 140 ppm As and 0.1 ppm Au. Molybdenum is present in more elevated quantities (up to 7400 ppm), and molybdenite has been identified in electron microprobe studies of the ore (Ball and Bland, 1985). Cobalt and nickel values in the pyrite are low, Ni not exceeding 100 ppm, a factor of relevance in interpretation of the deposit by Bottrell and Morton (1992). Wall-rock alteration is most intense in the underlying basic volcanic rocks of the Dolgarrog Volcanic Formation and accompanying rhyolites, which are enriched in K, Ba and S and are slightly silicified (Ball and Bland, 1985). Within these rocks, veinlets and disseminations of pyrite and pyrrhotite are common, and immediately below the pyrite deposit occur a number of lenses of calcite-rich rock.

Secondary mineralization, which has locally oxidized the ore to a ferruginous clay close to the outcrop, is more important in the post-mining context. Large-scale post-mining oxidation of the pyrite has produced copious quantities of sulphate minerals, dominated by the basic hydrated iron sulphate fibroferrite, accompanied by melanterite and copiapite (Johnson *et al.,* 1979). Gypsum is widespread, as indeed it invariably is in post-mining environments wherever pyritic rocks are exposed.

It is the fact that the post-mining oxidation of pyrite is largely bacteriogenic that has brought Cae Coch to international attention (Johnson *et al.*, 1979; Jenkins and Johnson, 1993). The most significant bacteria involved in the process are autotrophic species, which obtain carbon from CO₂ and have minimal nutritional requirements. These bacteria thrive to the exclusion of others in acidic environments, and many obtain their energy from the oxidization of reduced sulphur compounds. The best-known species flourishing in such environments are *Thiobacillus ferrooxidans* and *Leptospirillum ferrooxidans*, but heterotrophic bacteria, moulds, yeasts, rotifers and protozoans are also present in what constitutes an intricate microbial ecosystem, thriving in conditions which would appear at first sight to be hostile to life.

The microbial ecosystem in Cae Coch Mine manifests itself as gelatinous, stalactite-like growths hanging from moist surfaces underground, and as 'acid-streamer' growths which inhabit the mine drainage system. These growths, which may be up to 0.5 m in thickness, are pale cream to pinkish in colour and occur in extraordinary quantities; Jenkins and Johnson (1993) have estimated that Cae Coch contains more than 100 m³ of microbial biomass. Why these growths, which are not uncommon in abandoned metal mines, are so prolific in Cae Coch Mine is not fully understood, but a major reason may lie in the almost exclusively pyritic nature of the mineralization, with relatively low contents of other metals. Interestingly, once the mine drainage exits to surface, the 'acid-streamers' disappear, a fact which Jenkins and Johnson (1993) took to infer that the bacteria may have an intolerance of light.

Interpretation

The interpretation of the Cae Coch mineral deposit has been controversial, commencing with the assertion that it was a sulphidized ooidal ironstone (Sherlock, 1919), the sulphidization being a metasomatic effect due to the underlying 'diabase'. The 'diabase' has since been remapped as a sequence of basic volcanic rocks belonging to the Dolgarrog Volcanic Formation. Although the Ordovician ooidal ironstones do contain minor pyrite (see Tyllau Mwn GCR site report, this chapter), the interpretation of Sherlock (1919) is clearly no longer valid, and neither is the other early interpretation that it is an epigenetic fracture-hosted deposit. The Cae Coch mineralization is without doubt a stratabound deposit; the problem now lies chiefly in finding the mechanism for its deposition.

Ball and Bland (1985) advocated a Kuroko-type model for the Cae Coch deposit, suggesting that the laminated ore in the upper part of the deposit represented pyrite precipitation within a brine-pool on the seafloor, with hydrothermal fluids escaping via black-smokers' represented by the pyrite tubes. The lower, rubbly ore, they suggested, had been disturbed

during debris-flow movements. In addition, they argued that alteration patterns in the basic rocks of the Dolgarrog Volcanic Formation and in the rhyolites are closely comparable to those in the Uchinotai and Uwamuki deposits in Japan, involving, particularly, an increase in overall potassium content. Ball and Bland (1985) also briefly compared Cae Coch with other Ordovician stratabound sulphide deposits, such as at the Parys Mountain GCR site, on Anglesey, and Avoca in south-east Ireland, noting the similarity of these stratabound sulphide deposits all occurring within a mudstone succession, associated with bimodal acid-basic volcanism. In conclusion, Ball and Bland (1985) suggested that the Cae Coch mineral deposit was generated from brines enriched in potassium (leached from underlying acidic volcanic rocks) and carbonates, which were discharged into an euxinic seafloor environment.

Bottrell and Morton (1992), in contrast, adopted a different approach to investigating the Cae Coch mineralization, concentrating upon sulphur isotope ratios and Co/Ni ratios in pyrite. Most of the orebody pyrite samples gave δ^{34} S ratios in the -20% to -24% range, with occasional samples giving heavier signatures. These values are much lighter than would normally be expected had the deposit been of volcanogenic origin (they are in fact much lighter than 'sedimentary' pyrite values from the host rocks) and were interpreted by Bottrell and Morton (1992) as being the signature of bacterial sulphate reduction. For such light δ^{34} S ratios, either the site of deposition had to be open to permit re-supply of seawater sulphate, or the bacterial reduction involved sulphate derived from both seawater and from the underlying, and still warm, volcanic succession. The latter alternative, involving fluids leaching the volcanic succession, could also have supplied the requisite iron to the system.

The ratio of Co:Ni in the pyrite was found to be < 0.5, a value typical for sedimentary pyrite (Braila *et al.*, 1979), but not characteristic of volcanogenic deposits, where values of 5 to 50 would be expected. Taking all the available data into account, Bottrell and Morton (1992) proposed a new genetic model for the Cae Coch deposit, in which bacterial sulphate reduction within anoxic muds generated H_2S and Fe, which combined as early framboidal pyrite. In time, H_2S production exceeded Fe availability; so that the sediment porewaters were H_2S -rich. Iron, in solutions generated from porewaters in the underlying Dolgarrog Volcanic Formation, interacted with the H_2S when the solutions were expelled upwards into the still unlithified, H_2S -rich muds, producing the ore pyrite. This process, operating over a prolonged timescale, resulted in the eventual pyritization of the mud, preserving sedimentary structures in its upper part. Eventual isolation of the system from further sulphate availability resulted in an end to the bacterial reduction: at this time any sulphate migrating up into the deposit from the underlying igneous rocks would have combined with iron to form pyrite with a much heavier isotopic composition ($\delta^{34}S = > 0\%$).

Such an inhalative replacement model is clearly supported by the data of Bottrell and Morton (1992), and the textures described by Ball and Bland (1985), namely laminated ore and pyrite tubes, could represent pyritized original sedimentary structures. It is possible that the pyritized tubes are mineralized burrows. The leaching and upward migration of fluids from the underlying bimodal volcanic succession could also have supplied molybdenum to the system, together with the other low-level metal concentrations. In this model, the formation of an ore deposit has depended largely on two factors: firstly the sedimentary environment, namely a euxinic seafloor but with a continuing supply of seawater; and secondly the nature of the underlying succession, being a still warm acid/basic volcanic sequence capable of driving a hydrothermal leaching/migration system.

The extraordinary post-mining acidophilic bacterial community developed underground is the subject of ongoing research. The decomposition of pyrite through microbiological activity is a phenomenon which has many implications in biotechnology, in particular the treatment of pyritic ores containing fine-grained gold and other metals. Bio-leaching technology is now being used in many parts of the world as an agent in ore beneficiation. Conversely, the bacterial oxidation of pyrite is responsible for major environmental problems due to acid mine drainage.

Conclusions

The Cae Coch Mine massive stratabound pyrite deposit is of controversial origin. The most recent model for the genesis of the Cae Coch deposit involves the large-scale bacterial reduction of sulphate to sulphide, in the presence of an iron-rich flux leached from the underlying volcanic rocks, while the post-mining, large-scale bacterial oxidation of sulphide to sulphate, resulting in an acidic iron-rich mine drainage, constitutes the second principal point of scientific interest at

References



(Figure 5.37) Map of the Cae Coch Mine GCR site. After Ball and Bland (1985).



(Figure 5.38) Photograph of the Cae Coch Mine GCR site, showing the top open-pit. (Photo: T Colman.)