THE MINERALOGY OF A SILVER-RICH AREA IN THE EDWARDS ZINC-LEAD MINE, NEW YORK

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ABSTRACT

The ore of the zinc-lead deposits of the Balmat-Edwards district in northern New York is known to be composed of very coarse-grained massive sulfides, mainly sphalerite, galena and pyrite. Typically the galena contains small amounts of silver, presumably in solid solution. Galena concentrates (60% lead) contain an average of 514 grams of silver per tonne. An unusual silver-rich zinc-lead ore pocket at the Edwards mine contains nearly 1% silver. Ore microscopy shows that this ore is characterized by abundant, relatively fine-grained chalcopyrite with anhedral pyrite inclusions. Fine-grained sphalerite, native silver, argentite, freibergite and arsenopyrite occur in association with chalcopyrite as fracture-fillings in calcite. Electronmicroprobe analyses indicate that freibergite contains up to 25.8% silver, with an average composition of $Cu_{1.87}Ag_{1.26}Sb_{0.98}As_{0.22}S_{3.25}$. The amounts of the silver minerals at the Edwards mine do not warrant recovery.

Keywords: ore microscopy, silver minerals, massive sulfide, zinc-lead ore, Edwards mine, New York.

SOMMAIRE

Le minerai des gîtes zinc-plomb du district de Balmat-Edwards, dans le Nord de l'état de New-York, se compose de sulfures massifs à grains très gros, surtout blende, galène et pyrite. Typiquement la galène accuse une faible teneur d'argent, qu'on présume s'y trouver en solution solide. Les concentrés de galène (à 60% de plomb) tiennent en moyenne 514 g d'argent à la tonne. Une poche de minerai particulièrement riche en argent en contient presque 1%. La microscopie en lumière réfléchie montre que ce minerai se caractérise par de la chalcopyrite à grain relativement fin, à inclusions de pyrite xénomorphe. Associés à la chalcopyrite, on trouve comme remplissage de fractures: blende à grain fin, argent massif, argentite (argyrose), freibergite et arsenopyrite. L'analyse à la microsonde de Castaing révèle que la freibergite tient jusqu'à 25.8% d'argent; sa composition moyenne s'écrit Cu_{1.87}Ag_{1.26}Sb_{0.98}As_{0.22}S_{3.25}. La quantité de minéraux d'argent à la mine Edwards est trop faible pour en justifier l'exploitation.

(Traduit par la Rédaction)

Mots-clés: microscopie en lumière réfléchie, minéraux d'argent, sulfures massifs, minerai de zinc et de plomb, mine Edwards, New York.

INTRODUCTION

This paper presents the results of an examination using ore microscopy and electron-microprobe analysis of silver-rich zinc-lead ores from the Edwards mine in northern New York (Fig. 1). We record for the first time the occurrence of argentite and freibergite and confirm the presence of native silver. In addition, we describe the textural development of the silver-rich ore, indicate its relationship to typical Edwards ore, and offer some speculations on its origin.

GEOLOGY OF THE EDWARDS MINE

The Edwards mine is located in the Balmat-Edwards zinc district of northern New York State, a part of the Grenville lowlands belt of the northwest Adirondack mountains. The Proterozoic rocks are metasediments of the Grenville Supergroup that consists of sixteen numbered stratigraphic units and additional unnumbered rock-units exposed in an overturned synform (Brown & Engel 1956, Lea & Dill 1968). The rocks hosting the Edwards orebodies in which the silver was found are calcitic and dolomitic marbles that constitute the "undifferentiated marbles" (Brown & Engel 1956, deLorraine 1979, de Lorraine & Dill 1982). These occur on the northeast end of the marble belt in the northwest-plunging crest of a "Z" fold on the footwall of the median gneiss. The sphalerite occurs in six separate lenticular or tabular orebodies, commonly continuous for 1675 m down plunge, that have been defined and mined over the years (Fig. 2). The silver was found in the D-4 orebody.

The typical ores at the Edwards mine contain only small amounts of silver. Galena concentrates produced from the district have contained an aver-



FIG. 1. Index map for the Edwards mine, New York.

age of 514 grams of silver per tonne of 60% lead concentrates. These small amounts of silver are believed to be present in solid solution in the galena. In contrast to the typical ore, a silver-rich pocket that is the subject of this study was found to contain about 1% silver in an area of zinc mineralization.

POCKET OF SILVER-RICH ZINC ORE

A small silver-rich pocket of disseminated zinc ore was discovered in the Edwards mine in 1970. The pocket was about 0.9 m by 0.9 m on the vertical mine face (Figs. 3A, B) and may have extended as much as 1.2 m to 1.5 m in a direction perpendicular to the mine face. The pod occurred in the 1900 level, D-4 orebody, on the third mining sublevel, and at an elevation of 311 m below sea level. The sampled area is nearly devoid of lead and contains significant amount of copper in the form of "gash veins" of chalcopyrite. These features, together with thin coatings of native silver on fractures and the unusual abundance of chalcopyrite, distinguish the pod from typical zinc ore.

Only three other occurrences of silver have been reported in the Balmat-Edwards district (all unpublished). In 1939, small flakes of native silver were found in the D-7 orebody (located 39 metres structurally above the D-4 orebody), 1700 level, grizzly sublevel, at an elevation of 272 m below sea level. The flakes appeared to have come from a fracture surface and are associated with pyrite and traces of pyrrhotite and galena.

Flakes of native silver (0.2 to 0.8 cm) were found in 1953 associated with traces of pyrite and chal-



FIG. 2. Generalized geological section for the Edwards mine (modified from Lea & Dill 1968).





FIG. 3. Underground photograph of the silver-rich pocket. A. Nearly vertical veinlets of native silver flakes in place in a photograph entirely within the limits of the silver-rich pocket. B. Sketch of photograph showing the locations of flakes of native silver.

copyrite. Very small disseminated specks of silver were also seen in a quartz-diopside rock. They were found in the D-7 orebody, 2100 level, at an elevation of 419 m below sea level.

ORE MICROSCOPY OF THE SILVER-RICH SAMPLES AT THE EDWARDS MINE

The ore minerals were identified by ore microscopy, including quantitative measurements of reflectance and Vickers indentation hardness. The mineral identifications were confirmed by means of scanning-electron microscopy and energy-dispersion spectrographic analysis. The composition of freibergite was determined with an ARL EMX-SM electron microprobe operated at a 15 kV accelerating potential with 145 nA sample current. One-micrometre spots were analyzed for 400,000 counts of beam current. Backgrounds were measured on both sides of the peak for all samples and standards. Five points were analyzed at the peak position and three points at each background position. Compositions were calculated from X-ray counts using EMPADR VII, the ZAF (matrix) correction program of Rucklidge & Gasparrini (1969). Standards used were Silver Mine (Missouri) chalcopyrite for copper, Homestake (South Dakota) arsenopyrite for arsenic, Cobalt (Ontario) argentite for silver and sulfur, and metals in the A.R.L. standard mount for antimony.

The ore minerals in the silver-rich ores, in order of abundance, include: sphalerite, chalcopyrite, galena, pyrite, native silver, freibergite, argentite and arsenopyrite. The three silver minerals are present principally in veinlets that traverse fractured gangue minerals, mostly silicates.

Chalcopyrite

Chalcopyrite is the most abundant mineral

associated with the silver-bearing mineral phases. It occurs in veins that are 30 to $1000 \ \mu m$ wide. These veins are much wider than those containing galena, native silver, and the other minerals present. The chalcopyrite veins are discontinuous and traverse fractured gangue minerals, especially silicates. The chalcopyrite veins contain ubiquitous pyrite grains.

Pyrite

Pyrite occurs as highly fractured crystals that appear to exhibit all degrees of replacement by chalcopyrite. Some pyrite crystals have only thin veinlets of chalcopyrite. Most commonly, pyrite remains as irregularly shaped grains distributed throughout the chalcopyrite veins (Fig. 4A). Most of the thicker chalcopyrite veins originally consisted of pyrite that subsequently was brecciated and partly replaced by chalcopyrite.

Sphalerite

Sphalerite is the most abundant phase in the silverrich pockets but may not always be associated with the silver minerals. It occurs largely as grains 25 to 40 μ m across and as veintlets that traverse fractured silicates (Fig. 4B). Sphalerite typically occurs at the margins of the chalcopyrite-pyrite veins (Fig. 4C), but locally it is included within the chalcopyrite (Fig. 4D). Some sphalerite grains are veined and partly replaced by chalcopyrite.

Many of the sphalerite grains contain tiny blebs of chalcopyrite, 0.5 to 5 μ m across (Figs. 4C,D). Although they are uniformly distributed throughout most sphalerite grains, in some grains the blebs are restricted to what apparently were iron-rich bands in the host sphalerite. This feature, along with the apparent elongate shape of some blebs, suggests that the intergrowth is a "chalcopyrite disease" texture



FIG. 4. A. Pyrite (white) brecciated and largely replaced by chalcopyrite (light grey). B. Sphalerite (white) veinlets traversing grains of brecciated, brittle calc-silicates (medium grey) in calcitic marble. C. Sphalerite (grey) grain with small chalcopyrite (white) inclusions; grain occurs at the edge of chalcopyrite (white) vein in gangue (black). D. Sphalerite (SI) grains within a chalcopyrite (Cp) vein. The sphalerite contains small inclusions of chalcopyrite, freibergite (Fr) and argentite (Ar), which locally replace sphalerite, and replacement remnants of pyrite (Py) are present in the chalcopyrite. Scale bars: 100 μm in A, 500 μm in B, 50 μm in C, 100 μm in D. Reflected light, oil immersion.

(Barton 1978) that has developed by chalcopyrite replacement of sphalerite rather than by exsolution.

Sphalerite commonly occurs as small, irregularly shaped grains in freibergite (Fig. 4D). Sphalerite veins are partially replaced by chalcopyrite, freibergite and argentite (Fig. 5A).

Freibergite

Freibergite is an abundant phase in the silver-rich samples. Electron-microprobe analyses of the freibergite indicate that it is very silver-rich, and contains as much as 25.8% silver. Its average composition is Cu_{1.87}Ag_{1.26}Sb_{0.98}As_{0.22}S_{3.25}. The formula was calculated from analytical data for five spots on each of two grains (Table 1).

Freibergite occurs as grains 100 to 400 μ m across, typically in association with sphalerite adjacent to or within the chalcopyrite veins (Fig. 5B). The areibergite replaces sphalerite (Fig. 5A). Freibergite commonly replaces chalcopyrite (Figs. 5B,C), but

locally the freibergite grains appear to be partially replaced by chalcopyrite. Freibergite also occurs in close association with veinlets of native silver. The two minerals are in intimate intergrowth and appear to have been coprecipitated (Fig. 5D). Freibergite may also occur as occasional grains in galena veins.

Argentite

Argentite is closely associated with freibergite. It occurs as irregularly shaped grains, $3-25 \,\mu\text{m}$ across, disseminated throughout most areas of freibergite (Figs. 5C, 6A, B). Argentite and freibergite replace sphalerite with which they are commonly associated (Figs. 4D, 5A). Argentite locally appears to be replaced by chalcopyrite, and remnant grains of argentite occur within chalcopyrite.

Argentite occurs with galena in some veins. Where the veins are largely argentite, galena is present as irregularly shaped central areas surrounded by argentite.



FIG. 5. A. Sphalerite (SI) partially replaced by chalcopyrite (Cp), argentite (medium grey), and pyrite (Py). B. Pyrite (Py) partially replaced by chalcopyrite (Cp), which in turn is partially replaced by freibergite (Fr) and arsenopyrite (Ap). C. Pyrite (Py) and chalcopyrite (Cp) partially replaced by freibergite (Fr), argentite (dark grey), and arsenopyrite (white grains disseminated in freibergite). D. Freibergite (light grey) and native silver (white) veinlet traversing gangue (black). Scale bars: 50 μm in A, 40 μm in B, 50 μm in C, 50 μm in D. Reflected light, oil immersion.

Arsenopyrite

Arsenopyrite occurs as tiny, $5-10 \mu m$, subhedral to euhedral crystals that are sparsely disseminated throughout most areas of freibergite, argentite, and some areas of galena (Figs. 5C, 6A, B). The arsenopyrite crystals appear to have developed in association with those three minerals or to have preferentially replaced them. Many of the arsenopyrite crystals have small, $2-3 \mu m$, inclusions of freibergite, argentite and native silver. The small crystals of arsenopyrite are either absent from adjacent areas of the chalcopyrite and sphalerite veins, or only locally replace these minerals. Larger, $250-450 \,\mu\text{m}$ crystals of arsenopyrite are present rarely as euhedral crystals with small amounts of associated chalcopyrite, sphalerite, native silver, galena, and freibergite as inclusions and marginal grains (Fig. 6C).

Native silver

Native silver occurs as abundant thin veinlets,

TABLE 1	1.	CHEMICAL.	COMPOSITION	0F	FREIBERGITE	FROM	THE	EDWARDS	MINE,	Ν.	۱.
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Grain	Cu	Ag	Sb	As	<u>s</u>	total	formula
1	23.0	25.9	21.8	3.5	19.9	94.1	Cu _{1,90} Ag _{1,26} Sb _{0,94} As _{0,24} S _{3,25}
2	22.3	25.7	23.4	2.8	19.9	94.1	Cu _{1.84} Ag ₁₂₅ Sb _{1.01} As _{0.19} S ₃₂₅
	Avera	ge of	the tw	10 CO	$Cu_{1,87}Ag_{1,25}Sb_{0,98}As_{0,22}S_{3,25}$		

Determined by electron-microprobe analysis (composition in wt.%).

1–1.5 cm wide, that traverse gangue minerals. Most veinlets consist entirely of native silver (Fig. 6D), but some contain native silver and freibergite (Fig. 5D). Locally, native silver veinlets traverse the chalcopyrite-pyrite veinlets. Irregularly shaped grains of native silver occur locally in the wallrock adjacent to chalcopyrite and pyrite veins.

Galena

Galena occurs as abundant thin veinlets, about 10 to 100 μ m wide, that traverse fractured minerals locally in the silver pod. The galena veinlets are best developed in fractured silicate crystals. Galena veinlets adjacent to the larger chalcopyrite veinlets are partially replaced by chalcopyrite. Galena also occurs



FIG. 6. A. Abundant argentite (medium grey) intergrown with freibergite (light grey) and arsenopyrite (white) (gangue is black). B. Arsenopyrite (white) associated with freibergite (light grey) and argentite (medium grey). C. Large arsenopyrite (light grey) crystal with inclusions of sphalerite (dark grey) and galena (white) and enclosed in calcite (black). D. Native silver (white) veinlet traversing calcite (dark grey). Scale bars: 40 μm in A, 50 μm in B, 100 μm in C, 500 μm in D. Reflected light, oil immersion.

in small amounts in those areas where the dominant minerals are freibergite, argentite and arsenopyrite. Chalcopyrite tends to replace galena in preference to argentite, and argentite in preference to freibergite.

SUMMARY AND CONCLUSIONS

This study has identified the presence of eight ore minerals in silver-rich samples from a single pocket in the D-4 orebody in the Edwards mine. Three of the ore minerals contain silver. Two of the three silver minerals, freibergite and argentite, had not been known to occur in the Edwards mine. These two minerals and native silver were previously unreported in the literature on the Balmat-Edwards district.

Arsenopyrite is typically associated with the freibergite, argentite, and native silver mineralization. Its presence and constant association with the silver mineralization indicate that the source of the silver was also arsenic-rich. Sphalerite, galena and, to a lesser extent, chalcopyrite are common minerals in the Balmat-Edwards ores. Abundant chalcopyrite and minor galena in the silver-rich samples indicate that this occurrence is unique in the context of the normal Balmat-Edwards ores.

The veining and replacement relationships described may have resulted during high-grade metamorphism and deformation, during which the more brittle minerals, such as pyrite, were brecciated, whereas the more ductile minerals, such as chalcopyrite, flowed into the fractures formed in the brittle phases. The general restriction of the ore minerals to fractures developed in brittle gangue silicates appears to support this concept. On the other hand, the abundant replacement relationships shown by the ore minerals in the silver-rich samples may indicate that a hydrothermal event has been superimposed upon the event responsible for the metamorphic textures of the ore.

This study has shown the importance of ore microscopy in recognizing valuable silver mineralization in a base-metal deposit. The recognition of precious-metal minerals in base-metal ores is especially important during times, such as the present, when the prices for the latter metals are depressed. The added value from the precious metals can be an important factor in determining whether a base-metal prospect is mineable or can provide a significant added by-product revenue from a mine that is already in production. Unfortunately, no other silver-rich pockets have been discovered.

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