METAMORPHOSED VOLCANOGENIC ORES AT MONTAUBAN, GRENVILLE PROVINCE, QUEBEC

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ABSTRACT

The Proterozoic Montauban Pb-Zn deposit is associated with calc-silicate and cordierite gneiss units enclosed in quartzofeldspathic gneisses and amphibolites belonging to the Grenville Series. The deposit had previously been taken as a classical example of a pyrometasomatic ore. However, the ores are essentially conformable and have been deformed with the enclosing strata. Mineral parageneses in the calc-silicate and cordierite gneiss, and sphalerite compositions in pyrite – pyrrhotite – sphalerite assemblages in the ore, yield an estimate of temperature of 630-650°C and a pressure of 4.9 ± 0.4 kbar. These P-T conditions are well within the range of regional metamorphism for Grenville supracrustal rocks, suggesting that the ore-zone mineral assemblages reflect the same metamorphic grade as the enclosing gneisses. Preserved textures in the sulfides indicate metamorphic recrystallization of the ores; deformation features are attributed partly to the regional penetrative deformation and partly to late, post-orogenic movements. The massive sulfide and stringer ore at Montauban represents a volcanogenic-exhalative deposit that has been regionally metamorphosed in the almandine-amphibolite facies.

Keywords: exhalite, volcanogenic, sulfides, calc-silicate, metamorphosed ores, Grenville Series, geobarometry, geothermometry, Montauban, Quebec.

INTRODUCTION

The Montauban Pb-Zn sulfide deposit in Portneuf County, Quebec (Fig. 1), lies within a thin calc-silicate unit surrounded by a variety of gneisses in the Grenville Province of the Canadian Shield. The deposit was mined at intervals from 1915 to 1955, and in 1980 open-pit mining was started on gold mineralization adjoining and to the west of the old workings. The sulfide bodies are composed mainly of coarse-grained sphalerite, galena, pyrite, pyrrhotite and chalcopyrite, which form irregular lenses and pods. These bodies are surrounded by equally coarse-grained calc-silicate and silicate host-rocks. Diopside, tremolite, calcite and dolomite are predominant in the calc-silicate unit, and cordierite, garnet, quartz, anthophyllite and sillimanite in the gneiss.

The ores have, in the past, been classified as pyrometasomatic, related to nearby granitic to dioritic rocks (Alcock 1930, Osborne 1939, Wilson 1939), and more recently as exhalative massive sulfides (Sangster 1972, Stamatelopoulou-Seymour 1975, Stamatelopoulou-Seymour & MacLean 1977). The enclosing gneisses have volcanic (Pyke 1966, Stamatelopoulou-Seymour & MacLean 1977, MacLean et al. 1982) and sedimentary (Prabhu 1982) protoliths. According to the exhalative hypothesis, amphibolite-facies metamorphism has transformed pre-existing sulfides to the present minerals and textures. In this study we used samples of the massive ore from the old mine-workings and of adjoining stringer mineralization in the gneiss to investigate the compatibility of ore and gangue mineral-assemblages and textures with the regional metamorphic grade in the area.
ORE MINERALOGY AND TEXTURES

Both massive and stringer sulfide mineralization constitute the Montauban ore. The sulfide portion of the massive ore, enclosed in the calc-silicate rock, is composed of sphalerite, galena, pyrite, chalcopyrite, pyrrhotite and cubanite, with minor amounts of tetrahedrite, molybdenite and graphite. The sulfides in the stringer ore, comprising pyrrhotite, chalcopyrite, sphalerite and minor galena, occur in cordierite gneiss. Gold, silver and electrum have been reported by Smith (1956) and McAdam & Flanagan (1976). Gahnite, the zinc spinel, has been identified.

The sulfide minerals are coarse grained. Pyrite forms subhedral to euhedral cubes, with faces in contact with gangue minerals especially planar (Figs. 2a, 3d). Grains of chalcopyrite and galena are usually anhedral, but some coarse-grained samples contain euhedral galena. Chalcopyrite and galena also mold
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Fig. 3. a. ‘Paint-brush’ exsolution lamellae of cubanite (medium grey) in chalcopyrite (light grey). Plane light, width of field 0.8 mm. b. ‘Sphalerite stars’: Skeletal forms of exsolved sphalerite at grain junctions of a chalcopyrite (light grey) – cubanite (medium grey) host. Plane light, width of field: 0.85 mm. c. Cubanite (medium grey) host, with chalcopyrite exsolution lamellae (light grey) and delicate sphalerite stars (dark grey). Plane light, width of field: 3 mm. d. Euhedral to subhedral coarse-grained pyrite (white), brittle deformed (note fine fracture-lines). The left half of the photo is occupied by a cubanite-chalcopyrite exsolution intergrowth (medium grey) enclosing partly resorbed grains of pyrite that have jagged grain-boundaries. Massive ore in calc-silicate rock, plane light, width of field: 3 mm. e. Detail of Figure 2d, clearly showing a reacted grain of pyrite embedded in chalcopyrite-cubanite (cb + cpy). Light grey mineral occupying the lower margin of the photo is chalcopyrite (cpy), and a pyrrhotite grain occupies two-thirds of the right margin (po). For discussion of metamorphic reactions in ore assemblages, see text. Plane light, width of field: 0.85 mm.

against, penetrate and vein other minerals (Figs. 2b, c). Chalcopyrite occasionally hosts ‘paint-brush’ exsolutions of cubanite (Fig. 3a), and vice versa (Fig. 3c), in assemblages containing pyrite and pyrrhotite (Figs. 3d, e). In these specimens, boundaries between pyrite and chalcopyrite–cubanite grains are ragged and clearly due to reaction (Figs. 2a, 3d, e); some remnants of pyrite porphyroblasts are isolated in a chalcopyrite–cubanite matrix (Fig. 3e). An occasional grain of chalcopyrite appears to contain exsolved pyrite along crystallographic planes (Figs. 2c, d).

Sphalerite is usually subhedral, occasionally enclosing blebs of chalcopyrite, or occurs as delicate ‘stars’ in chalcopyrite–cubanite grains (Figs. 3b, c). Sphalerite and pyrrhotite grains display spectacular alignments parallel to the regional foliation defined by mica flakes in the gneiss (Fig. 4a). Sphalerite, galena and, occasionally, other sulfides are commonly poikiloblastically enclosed in silicate grains (Fig. 4b).

Obvious deformational features include kink bands in pyrrhotite (Fig. 4c), brecciation of pyrite (Fig. 3d) and sphalerite, and bent cleavage planes in galena (Fig. 4d). Globules of round non-sulfide material coated with sulfides closely resemble the ‘kneaded’ texture of Vokes (1969).
P-T CONDITIONS IN THE ORE ZONE

Calc-silicate and silicate assemblages

Mineral assemblages in the calc-silicate and cordierite gneiss host-rocks are independently stable within wide ranges of temperature and pressure. Taken together, they define a narrow range for both these parameters.

The equilibrium assemblage diopside – tremolite – calcite – quartz of reaction (I) is common in the calc-silicate unit. Also present are the stable assemblages tremolite – calcite – quartz – dolomite (II) and dolomite – quartz – diopside (III).

\[
\begin{align*}
\text{Tremolite} + 3\text{Calcite} + 2\text{Quartz} &= 5\text{Diopside} + 3\text{CO}_2 + \text{H}_2\text{O} \quad (I) \\
5\text{Dolomite} + 8\text{Quartz} + \text{H}_2\text{O} &= \text{Tremolite} + 3\text{Calcite} + 7\text{CO}_2 \quad (II) \\
\text{Dolomite} + 2\text{Quartz} &= \text{Diopside} + 2\text{CO}_2 \quad (III)
\end{align*}
\]

The coexistence of these assemblages indicates that the reaction took place at high values of \(X(\text{CO}_2)\) close to or under the univariant P-T-X(\text{CO}_2) conditions of the assemblage tremolite – calcite – diopside – dolomite – quartz (Slaughter et al. 1975, Käse & Metz 1980, Winkler 1974, 1979). The absence of talc in the calc-silicate unit reinforces the evidence for high \(X(\text{CO}_2)\). The trace of the univariant assemblage is shown on a P-T projection in Figure 5.

The assemblage cordierite – almandine – sillimanite – quartz in the adjoining cordierite gneiss may also be used to outline P-T conditions. The presence of sillimanite alone indicates a minimum temperature of 600°C (Fig. 5). The reaction for garnet low in Mn and Ca

\[
\text{Cordierite} = \text{Almandine} + \text{Sillimanite} + \text{Quartz} \quad (IV)
\]

is relatively insensitive to temperature, at least from 600° to 800°C (Currie 1971, Weisbrod 1973, Mueller & Saxena 1977), but the Fe/Mg ratio in cordierite changes significantly with pressure and water con-

Fig. 4. a. Chalcopyrite and pyrrhotite foliated parallel to the regional foliation defined by the biotite flakes. Disseminated ore in cordierite gneiss, plane light, width of field: 3 mm. b. Poikiloblastic enclosure of sphalerite ore in tremolite metacrysts. Massive ore in calc-silicate rock, plane light, width of field: 3 mm. c. Kink bands developed in pyrrhotite. Massive ore in calc-silicate rock, plane light, width of field: 3 mm. d. Curved cleavage traces in galena. Pb-Zn ore in calc-silicate rock, plane light, width of field: 3 mm.
tent (Weisbrod 1973, Mueller & Saxena 1977, Martignole & Sisi 1981). Equilibrium conditions for the reaction have been worked out for various FeO/(MgO + FeO) ratios of bulk-rock compositions (Currie 1971, Winkler 1979). Our value of 0.55 for this ratio for the cordierite gneiss, which contains 0.2 wt. % MnO, is plotted on the P-T diagram in Figure 5. The intersection of this reaction zone with the univariant reaction in the calc-silicate rock yields a range of metamorphic temperatures of 630–650°C and pressures of 5.5–6.5 kbar for the Montauban ore zone.

Sulfide assemblages

Pressure of equilibration can be estimated for sulfide ores using the sphalerite geobarometer (Scott & Barnes 1971), but reliable high-temperature sulfide geothermometers are not readily available owing to the ease with which most sulfides react and revert to lower-temperature forms. The only direct evidence from the sulfides that the Montauban ores were at high temperatures is found in the relics of chalcopyrite–cubanite exsolved grains (formerly intermediate solid-solution iss) associated with pyrite and pyrite–pyrrhotite. Above 550°C, chalcopyrite is completely converted to iss (MacLean et al. 1972), but chalcopyrite–iss assemblages can exist to below 300°C (Sugaki et al. 1975).

The vertical attitude of the sphalerite–pyrite–hexagonal pyrrhotite solvus in relation to the temperature axis precludes its use as a geothermometer between 265° and 600°C at 1 bar pressure (Boorman 1967), but the change in the amount of FeS in sphalerite with increasing pressure along this solvus makes it a useful geobarometer (Scott & Barnes 1971, Scott 1973, Lusk & Ford 1978, Hutchinson & Scott 1981). This assumes that sphalerite is a refractory mineral that does not re-equilibrate during cooling and decompression. For pressures up to at least 10 kbar, the composition of sphalerite is independent of temperature from 265°C to a range of temperatures from 550° to 750°C, depending on pressure (Hutchinson & Scott 1981). Minor amounts of other elements in sphalerite generally do not affect its function as a geobarometer, but an appreciable amount of copper is dissolved in sphalerite when it is in equilibrium with chalcopyrite or iss, and this causes a deflection of the solvus to higher FeS contents (see Fig. 7).

Forty-five measurements were made of sphalerite compositions on grains from samples containing pyrite–pyrrhotite–sphalerite, pyrite–pyrrhotite–sphalerite–chalcopyrite–cubanite, marcasite–pyrrhotite–sphalerite and pyrite–sphalerite. Where possible, the pyrite, pyrrhotite and sphalerite grains analyzed are taken in contact, and the sphalerite grains selected are free of obvious exsolved lamellae of pyrrhotite and chalcopyrite. Marcasite replaced pyrrhotite grains and is considered to have formed during retrograde metamorphism; hence the high-temperature assemblage for these samples was pyrrhotite–sphalerite.

The sphalerite compositions are plotted on a frequency versus mole % FeS diagram in Figure 6, where they are distinguished by mineral assemblages. Sphalerite compositions in the assemblage pyrite–pyrrhotite–sphalerite form a cluster at 14.62 (standard deviation: ± 0.46) mole % FeS, which yields a pressure of 4.9 ± 0.4 kbar for temperatures to 650°C (Hutchinson & Scott 1981). This is the most reliable estimate of pressure from sphalerite: its FeS content is buffered by pyrite and pyrrhotite, its grains in this assemblages are unaffected by copper contamination, and the pyrite–pyrrhotite–sphalerite solvus isobar is only slightly deflected at 650°C (Fig. 7).

Sphalerite in the assemblage pyrite–pyrrhotite–chalcopyrite–cubanite–sphalerite contains 16.26 ± 0.45 mole % FeS. Although it does not now contain copper, the shift to higher FeS contents is similar to that encountered by Hutchinson & Scott (1981) for copper-bearing sphalerite in the system Cu–Fe–Zn–S. However, the change in FeS content is greater than expected in the 630–650°C range. This could be due to re-equilibration of sphalerite at lower tem-

![Fig. 5. P–T diagram adapted from Winkler (1979) and Currie (1971), showing the reaction relations for cordierite (cord) and almandine (alm) for FeO/(MgO + FeO) bulk ratio of 0.55 for the cordierite gneiss. The univariant line for the assemblage tremolite–calcite–quartz–diopside–dolomite (tr–calc–qz–dl–dol) is from Slaughter et al. (1975), Käse & Metz (1979) and Winkler (1979); the intersection of this line with the cord + alm field (dotted) yields an estimate of 630–650°C and 5.5–6.5 kbar. Phase relations for siliimanite (sili), kyanite (ky) and andalusite (and) are also shown.](image)
Mole % FeS in Sphalerite

Fig. 6. Histogram of the frequency of sphalerite compositions in the Montauban ore, distinguished by mineral assemblages.

DISCUSSION

P–T conditions

The pressure estimate from the sphalerite geobarometer using the pyrite–pyrrhotite–sphalerite assemblage in the Montauban ore is about 1 kbar lower than that determined from mineral assemblages in the calc-silicate and cordierite gneiss. Textures indicating retrograde (decompression) equilibration are not apparent. If retrograde equilibration was attained at high temperature, sphalerite would have absorbed pyrrhotite and become iron-rich, particularly at sphalerite–pyrrhotite contacts. Partly absorbed grains of pyrrhotite would probably have recrystallized, but the lack of compositional zoning in sphalerite at these contacts, such as occurs at some sphalerite–pyrite contacts, is evidence against this reaction having occurred.

At a similar sulfide deposit in Grenville rocks at
Balmat, New York, metamorphic temperature and pressure were estimated to be $625^\circ \pm 25^\circ$C using the calcite – dolomite and sulfur isotope geothermometers, and 5.5 to 6.5 kbar using chalcopyrite-free sphalerite grains for the sphalerite geobarometer (Brown et al. 1978, Hutchinson & Scott 1981). These are in good general agreement with our results of 630–650°C and 5.5–6.5 kbar from the wallrock assemblages, but are higher than our pressure estimate from sphalerite of 4.9 ± 0.4 kbar. The lack of evidence of re-equilibration of sphalerite in the pyrite – pyrrhotite – sphalerite assemblage at Balmat, which is more iron-deficient and thus more likely to re-equilibrate than that at Montauban, reinforces our contention that the pressure determination based on sphalerite in the Montauban ore is reliable. The compositions of sphalerite at Balmat associated with chalcopyrite are, like ours, erratic and yield pressure estimates lower than sphalerite associated only with pyrite and pyrrhotite.

The pressure discrepancy between the two methods used at Montauban may be due to uncertainties in the P–T conditions of equilibration of the calc-silicate (Käse & Metz 1980) and cordierite gneiss (Currie 1971, Weisbrod 1973, Martignole & Sisi 1981) assemblages. Besides Fe/Mg changes, the cordi¬rite – garnet geobarometer is sensitive to P(H$_2$O), for which we have no data. P–T determinations made by Martignole & Nantel (1982) in cordi¬rite–garnet-bearing gneisses bordering the northeast side of the St Didace Complex, about 50 km southwest of Montauban, range from 4.1–5.0 kbar and 597–690°C at a site farthest from the complex and closest to Montauban, in close agreement with our estimate of 4.9 ± 0.4 kbar from the sphalerite geobarometer.

**Metamorphic textures**

The deformational characteristics of the Montauban deposit and its enclosing rocks were recognized and described by previous investigators (Osborne 1939, Wilson 1939, O’Neil & Osborne 1939, Smith 1950), but they did not consider the possibility of a premetamorphic existence for the deposit. The properties of sulfides that render them susceptible to changes during metamorphism and deformation result in features that make them appear to have an epigenetic origin. For example, rimming, veining and penetration of silicates by galena and chalcopyrite may suggest an epigenetic origin for the ores, or they may simply signify that these sulfides were mobile during metamorphism and structural deformation. The relative ease with which sulfide minerals respond to differential stress is, in decreasing order: galena, chalcopyrite, pyrrhotite, sphalerite, pyrite (Gill 1969, 1970, Salmon et al. 1974, Roscoe 1975, Atkinson 1975).

No relict primary textures have been observed in the Montauban sulfides. But as the thermal peak of an orogeny usually postdates the deforma¬tional peak and, given the ease with which sulfides tend to anneal, metamorphic temperatures in the range of 630 to 650°C would probably have obliterated all traces of primary textures, as well as most of the traces of the penetrative regional deformation. Late post metamorphic movements in the calc-silicate rocks could explain the deformation textures, such as kinking in the pyrrhotite, bent cleavage in galena, brecciation of pyrite and sphalerite, and kneaded sulfides. However, the penetrative deformational overprint has been preserved in the mineralized cordierite gneiss, where spectacular ‘stringing out’ of sphalerite and pyrrhotite is observed parallel to the regional foliation defined by the mica flakes.

The thermal effects of metamorphism on the ores result in textural as well as mineralogical modifications; the coarseness of the ores can be attributed to granoblastic growth of grains due to high regional metamorphic temperatures. Poikiloblastic enclosure of sulfide grains by silicate metacrysts attests to the metamorphic origin of these sulfides. High metamorphic temperatures promoted diffusion of chalcopyrite into sphalerite and vice versa, at least where these minerals were in contact. Chalcopyrite globules in some sphalerite grains, and sphalerite ‘stars’ in chalcopyrite, indicate exsolution due to decrease in temperature following metamorphism. Chalcopyrite – cubanite exsolutions and isolated remnants of pyrite porphyroblasts in chalcopyrite – cubanite grains are similarly formed during retrograde thermal conditions. Pyrrhotite may or may not have been present in the original ore, but in any case some was probably formed during the thermal metamorphic event owing to the breakdown of pyrite in a system that was partly open to sulfur:

$$\text{FeS}_2 = \text{FeS} + \text{S}.$$  \hspace{1cm} (V)

This produced the assemblage pyrite – pyrrhotite – chalcopyrite that would be stable to 550°C (Fig. 8a). Above 550°C the assemblage would be pyrite – pyrrhotite – iss (Fig. 8b) (MacLean et al. 1972, Cabri 1973). If the bulk composition remained within the iss – pyrite field, a small amount of extra pyrite would have been generated at this time (Fig. 8b).

On cooling, after the peak of thermal metamorphism, the sequence of reactions would be reversed. The presence of cubanite in a few samples shows that equilibrium was not attained. Figures 3a and 3b show grains of exsolved cubanite – chalcopyrite associated with pyrite and, sometimes, pyrrhotite (Fig. 3c). Intermediate solid-solution apparently did not fully react with pyrite at this time, probably owing to the inertness of pyrite in retrograde reactions. Instead, it exsolved chalcopyrite, and the remaining iss approached cubanite in composition (MacLean et al.
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Assumed phase-relations in the Cu-Fe-S system at 550°C. The composition of the Montauban ore is shown by the star. Chalcopyrite solid solution cps is stable to about 550° when pyrite + pyrrhotite are present (Maclean et al., 1972). The black dots represent analyzed cubanite compositions. b. Phase relations are after Cabri (1973). The disappearance of chalcopyrite as a phase leaves the bulk composition of the Montauban ore in the intermediate solid-solution (iss) - pyrite field. Pyrite is consumed in this reaction. The positions of CuFeS₂ (chalcopyrite) and CuFe₂S₃ (cubanite) are shown for reference.

1972, Sugaki et al. 1975). In other samples, corroded porphyroblasts of pyrite in chalcopyrite and chalcopyrite-cubanite grains are evidence that this reaction is reversible and that some pyrite has been resorbed. Thin lamellar grains of pyrite that appear to have been produced by exsolution in chalcopyrite (Figs. 2c, d) likely formed by local retrograde sulfurization of iss (cubanite) lamellae in chalcopyrite by the reaction:

\[ \text{CuFe}_2\text{S}_3 + \text{S} = \text{CuFeS}_2 + \text{FeS}_2. \]  

Similar retrograde reactions caused partial replacement of pyrrhotite by marcasite in pyrrhotite - sphalerite assemblages, and a decrease in iron in small grains of sphalerite in pyrite - sphalerite assemblages.

The presence of gahnite ZnAl₂O₄ in the Montauban ores implies that zinc was already present and that the zinc spinel formed under high-grade regional metamorphism. Its association with sphalerite in the ore indicates that it formed by the reaction (Spry & Scott 1982):

\[ 2(\text{Zn,Fe})\text{S} + 2\text{Al}_2\text{O}_3 + \text{O}_2 = 2(\text{Zn,Fe})\text{Al}_2\text{O}_4 + \text{S}_2 \]  

Gahnite has been reported from other deposits in strongly metamorphosed terranes such as Broken Hill (Australia), Franklin (New Jersey), Bleikvassli (Norway), Falun (Sweden) and Geco and Willroy (Ontario) (Richards 1966, Vokes 1969, Suffel et al. 1971).

CONCLUSIONS

The Montauban sulfide deposit, associated with calc-silicate and cordierite gneiss units, is enclosed in quartzofeldspathic gneisses and amphibolites belonging to the Grenville Series. Mineral parageneses in the calc-silicate and cordierite gneiss, combined with geobarometry based on sphalerite in the ore, yield an estimate of metamorphic temperature of 630–650°C and a pressure of 4.9 ± 0.4 kbar, which is well within the framework of regional metamorphism in that section of the Grenville Province.

The Montauban deposit is essentially conformable and has been deformed and metamorphosed with its enclosing rocks. The coarseness of the ores and other structures and textures can be attributed to regional high-grade metamorphism and secondary metamorphic remobilization. Stamatelopoulou-Selmenour & MacLean (1977) considered the Montauban deposit to be an exhalative massive sulfide that constituted part of the initial volcanic-sedimentary sequence. In this interpretation, the ore in the calc-silicate represents the massive deposit, and that in the copper-bearing cordierite gneiss, the underlying Mg-rich alteration zone.

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