Abstract

Pressure estimates obtained by the application of sphalerite geobarometry to the ore from Bodenmais, Bavaria, vary within single specimens and are strongly dependent on the mineral assemblage with which sphalerite coexists. The pressure estimated for sphalerite coexisting with pyrite and pyrrhotite ranges from 2.1 to 2.9 kbar, in agreement with the pressure of metamorphism estimated by Blümel and Schreyer (1977) from the silicate mineral assemblage. Evidence, however, that sphalerite equilibrated at temperatures below the temperature of metamorphism at Bodenmais (650°–700°C) is demonstrated by (1) depletion of FeS in sphalerite at its contact with monoclinic pyrrhotite; (2) the large variation in the iron content of sphalerite with exsolved chalcopyrite over a scale of tens of micrometers within individual crystals even for sphalerite coexisting with pyrite and pyrrhotite, yielding pressure estimates between 2 and 7 kbar; (3) the low Cu content of sphalerite (0.0–0.4 wt. percent) and the low Zn content of chalcopyrite (0.08–0.16 wt. percent) in the assemblage pyrrhotite–pyrite–sphalerite–chalcopyrite. These features are indicative of equilibration at temperatures below 250°C. The sphalerite geobarometer may not yield reliable pressure estimates for ores that underwent low-temperature reactions, or for Cu-bearing zinc sulfide ores. Attempts to apply the sphalerite geobarometer, however, provide valuable insights on post-metamorphic low-temperature equilibration in these ores.

Introduction

Sphalerite is one of the refractory sulfide minerals (Barton, 1970) that tend to preserve the chemical equilibrium achieved at the time of their formation or metamorphism. The theoretical principles of sphalerite geobarometry were first proposed by Barton and Toulmin (1966). Scott (1973) and Scott and Barnes (1971) calibrated the sphalerite geobarometer experimentally. Hutcheon (1978) calculated the $P$-$T$-$X$ relations for the univariant assemblage sphalerite–pyrite–pyrrhotite and found that the calculated isobars are in agreement with the experimental data of Scott (1973).

The sphalerite geobarometer has been widely applied by various investigators (e.g., Campbell and Ethier, 1974; Grove et al., 1975; Lusk et al., 1975; Scott, 1976; Scott et al., 1977; Brown et al., 1978; Rai, 1978) to estimate pressures for metamorphosed sulfide ores.

The present investigation represents an evaluation of sphalerite geobarometry in Bodenmais ore. The ore seems most suitable for such study because the assemblage sphalerite–pyrite–pyrrhotite required for sphalerite geobarometry is well preserved in the ore, earlier studies by Schreyer et al. (1964) suggest that the equilibrium composition of sphalerite has been preserved, and independent estimates of pressure and temperature of metamorphism at Bodenmais are available from a study of the silicate mineral assemblages (Blümel and Schreyer, 1977).

Geological setting

The sulfide ores at Bodenmais, Bavaria, form an elongated mass in highly metamorphosed migmatitic cordierite-sillimanite gneisses. The ore extends over at least 750 m parallel to the strike of the gneissosity of its country rocks (Schreyer et al., 1964). The gneisses show numerous veinlets and schlieren of granitoid and pegmatoid materials, particularly in direct contacts with the ore. The regional metamorphism and its associated migmatization took place in early Hercynian times (Davis and Schreyer, 1962), and both ore and country rock now exposed at the surface seem to have endured essentially identical metamorphic conditions (Schreyer et al., 1964).

A recent study of the pelitic and psammitic
gneisses in the Lam-Bodenmais area by Blümel and Schreyer (1977) delineated two major metamorphic zones: a sillimanite-K-feldspar zone with coexisting biotite + sillimanite (+ K-feldspar + quartz) and a cordierite-K-feldspar zone with coexisting biotite + cordierite+sillimanite (+ K-feldspar + quartz). The two metamorphic zones are related to each other by the multivariant reaction:

\[
\text{biotite + sillimanite + quartz} \rightarrow \text{cordierite + K-feldspar + H}_2\text{O}
\]

The temperature and pressure of metamorphism that formed the cordierite-K-feldspar zone were estimated by Blümel and Schreyer (1977) as 650°-700°C and 2-3 kbar, assuming water pressure to be equal to total pressure.

The origin of the sulfide ores at Bodenmais is still controversial; a summary of the various hypotheses was given by Schreyer et al. (1964). A contact metamorphic origin was proposed by Hegemann and Maucher (1933). Fischer (1938) suggested that the ore formed by preferential mobilization from the gneisses during regional metamorphism. Schröcke (1955) concluded, on the basis of petrological and structural studies, that the ore formed earlier than the regional metamorphic episode. Schreyer et al. (1964) objected to a contact metamorphic origin because of the lack of discordant late granite in contact or even in the vicinity of the ore. They noted, however, that the mineral assemblages show similarities to those of certain metamorphic ore deposits in the Fennoscandian shield that are generally known as Mg-rich skarn deposits.

**Methods of study**

The ore specimens were studied in both reflected and transmitted light. Electron microprobe analyses of sulfides were performed using an automated MAC-500 electron microprobe. Synthetic sphalerite, pyrrhotite of different compositions, and pure Cd, Mn, and Cu were used as standards. Data reduction was performed with the computer program Magic IV (Colby, 1971). For distinction between monoclinic and hexagonal pyrrhotite, both etching and X-ray diffraction were used.

**Mineralogy**

The samples were collected from a massive sulfide-rich ore from Barbarastollen, Silberberg, Bodenmais. The ore is composed mainly of sphalerite, pyrite, pyrrhotite, and chalcopyrite. Sphalerite occurs as large crystals that may reach 1 cm. Where coexisting with pyrite and pyrrhotite, the three-phase assemblage forms interlocking crystal aggregates in mutual contact. In many instances, sphalerite coexists with either pyrrhotite (Fig. 1a) or pyrite. The iron sulfides occasionally display intergrowths of sphalerite and anhedral inclusions of galena. Chalcopyrite is abundant in some specimens as large discrete crystals that may enclose small crystals of sphalerite. Chalcopyrite exsolutions in sphalerite are rare. Optical examination of pyrrhotite in reflected light reveals no intergrowths. However, on etching with 50 percent HI by the technique of Schwarzc and Harris (1970), monoclinic pyrrhotite was found to coexist with hexagonal pyrrhotite in many specimens. In addition to its oc-

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**Fig. 1.** (a) Large crystal of sphalerite in mutual contact with pyrrhotite. Bar = 1 mm; reflected light; oil immersion. (b) Pyrrhotite in contact with sphalerite, pyrite, and silicates etched with 50% HI. Note rims of unetched monoclinic pyrrhotite at contact with sphalerite, pyrite, and silicate and formation of monoclinic pyrrhotite along cracks. Bar = 1 mm; reflected light.
currence as discrete grains, monoclinic pyrrhotite is commonly observed as rims on hexagonal pyrrhotite, as thin veinlets along cracks, and as irregular domains within hexagonal pyrrhotite crystals (Fig. 1b). The rims of monoclinic pyrrhotite are well developed, particularly in pyrrhotite that coexists with sphalerite and pyrite as well as in pyrrhotite in contact with silicate minerals. In individual sphalerite crystals, rims in contact with monoclinic pyrrhotite are more translucent and show internal reflections that are lighter in color relative to the cores, due to variation in the iron content of sphalerite from rim to core. Pyrrhotite occasionally shows alteration to aggregates of pyrite, marcasite, or both. Magnetite is a rare mineral in some specimens, where it occurs in association with silicate minerals or pyrrhotite, but not with sphalerite. In all sulfide-rich specimens, the ore forms a matrix enclosing large granoblastic crystals of silicate minerals such as cordierite, K-feldspar, plagioclase, quartz, and biotite. Offshoots of pyrrhotite or pyrite are occasionally observed transecting the silicate minerals or following the cleavage planes in biotite.

**Mineral chemistry**

The average mole percent FeS in sphalerite coexisting with both pyrrhotite and pyrite varies from one sample to another, but lies within a narrow range of 15.8–16.5 (Table 1; Fig. 2). Within individual samples, the FeS content of sphalerite associated with pyrrhotite and pyrite varies from grain to grain and within individual grains as well. However, sphalerite in individual samples is essentially homogeneous (standard deviations in mole percent FeS are between 0.39 and 0.53). Sphalerite crystals in the immediate vicinity of monoclinic pyrrhotite showed a lower iron content at the rims relative to the cores (12–13 mole percent FeS at the rims vs. 15.5–16.5 mole percent FeS at the cores). This observation is true whether the sphalerite occurs in association with pyrrhotite alone or with pyrrhotite and pyrite.

Sphalerite in contact with either pyrite or pyrrhotite shows a slightly lower FeS content than sphalerite coexisting with both iron sulfides. The mole percent FeS in sphalerite coexisting with pyrite ranges between 15.5 and 16.0, whereas that in sphalerite coexisting with pyrrhotite ranges between 15.4 and 16.3.

Sphalerite with exsolved chalcopyrite shows a wide range in FeS content. A large crystal of sphalerite displaying exsolutions of chalcopyrite and showing mutual contacts with pyrrhotite and pyrite was analyzed. Fifteen analyses performed on this crystal show that it is inhomogeneous, having a mole percent FeS in the range 12.0 to 17.2, with an average of 14.6. This heterogeneity is real and cannot be attributed to sampling some of the chalcopyrite exsolutions during the analyses, because the concentration of copper in the fifteen sphalerite analyses is low, ranging between 0.03 and 0.38 wt. percent. Another

<table>
<thead>
<tr>
<th>Sample No.</th>
<th>Assemblage**</th>
<th>Mole % FeS in sphalerite</th>
<th>P, kbar**</th>
<th>P, kbar†</th>
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<tbody>
<tr>
<td>68919</td>
<td>sp, py, mpo, hpo</td>
<td>15.35–17.2 15.5–15.98</td>
<td>16.31 (0.48)++</td>
<td>2.3 1.7</td>
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<tr>
<td>69919</td>
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<td>2.1 1.4</td>
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<tr>
<td>Bo1</td>
<td>sp, py, mpo, hpo</td>
<td>14.92–16.67 14.97–13.95</td>
<td>15.80 (0.53) 15.44 (0.36)</td>
<td>2.9 2.1 3.5 2.7</td>
</tr>
<tr>
<td>Bo2</td>
<td>sp, mpo, (hpo)</td>
<td>9.63–14.41</td>
<td>13.49 (1.22)</td>
<td>6.1 5.6</td>
</tr>
<tr>
<td>Bo7</td>
<td>sp, cp</td>
<td>15.72–16.93 15.72–16.53</td>
<td>16.55 (0.39) 16.2 (0.36)</td>
<td>2.2 2.4 2.2 1.8</td>
</tr>
<tr>
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<td>4.8 4.0 2.4 1.8</td>
</tr>
<tr>
<td>Bo11</td>
<td>sp, mpo, (hpo)</td>
<td>14.93–16.26</td>
<td>15.35 (0.35)</td>
<td>3.5 2.8</td>
</tr>
</tbody>
</table>

**Abbreviations:** sp, sphalerite; py, pyrite; hpo, hexagonal pyrrhotite; mpo, monoclinic pyrrhotite; parentheses indicate minor amounts.

**Pressure estimates from the experimentally determined isobars of Scott (1973, 1976).**

**Pressure estimates from the calculated isobars of Hutcheon (1978).**

**Standard deviations.**
A large sphalerite crystal, totally surrounded by chalcopyrite and containing chalcopyrite exsolutions, was also analyzed. Pyrrhotite is present a few millimeters from the sphalerite–chalcopyrite assemblage, in direct contact with chalcopyrite but not with sphalerite. The mole percent FeS in the sphalerite crystal ranges between 9.63 and 14.4, with an average of 13.49 for 14 analyses. The Cu content of the analyzed sphalerite is in the range 0.09 to 9.32 wt. percent.

In all analyzed samples, sphalerite contains minor amounts of MnS and CdS in solid solution. The largest MnS content of sphalerite is 1.8 mole percent, whereas the CdS content does not exceed 0.3 mole percent. Representative microprobe analyses of sphalerite are given in Table 2.

The pyrrhotite composition ranges between 46.9 and 48.0 atom percent Fe. In specimens where monoclinic pyrrhotite is abundant, the range for pyrrhotite composition reported above can be observed in a single polished section. Representative microprobe analyses of pyrrhotite are given in Table 3.

**Sphalerite geobarometry**

The mole percent FeS in sphalerite coexisting with pyrite and pyrrhotite was used to estimate the pressures from the experimentally determined isobars of Scott (1973, 1976) and from the calculated isobars of Hutcheon (1978) (Table 1). Pressures were also estimated for sphalerite coexisting with either pyrrhotite or pyrite alone and for sphalerite in chalcopyrite-bearing assemblages.

The temperature of metamorphism at Bodenmais was estimated by Blümel and Schreyer (1977) to be in the range 650°–700°C. The temperature estimate was based on the observation that the first products of anatexitis at Bodenmais are found in the higher-
grade part of the sillimanite–K-feldspar zone, in which the assemblage muscovite–quartz is unstable. Therefore, the cordierite-producing reaction biotite + sillimanite + quartz → biotite + cordierite + K-feldspar + H₂O must lie below the intersection at 656°C and 3.6 kbar of the curve for the reaction muscovite + quartz → K-feldspar + Al₂SiO₅ + H₂O and the melting curve of granite. The metamorphic gradient must lie slightly above the point of intersection at 610°C and 2.25 kbar of the muscovite + quartz → K-feldspar + Al₂SiO₅ + H₂O reaction curve and the andalusite ⇌ sillimanite equilibrium. An upper temperature limit of 700°C was inferred from the reaction phlogopite + sillimanite + quartz → Mg-cordierite + K-feldspar + H₂O, which occurs at 5 kbar and 700°C but is expected to shift to lower pressures in iron-bearing rocks. A metamorphic temperature of 650°C was selected for sphalerite geobarometry. Although a change in temperature of 50°C may not always be crucial when considering silicate mineral equilibria, it is very significant in the case of the sphalerite geobarometer because there is a large change in the slope of the experimentally determined isobars in the temperature range 650°–700°C. If the upper temperature limit of 700°C is taken as the temperature of metamorphism, sphalerite compositions in the assemblage sphalerite–pyrrhotite–pyrite will fall outside the field for this ternary assemblage and plot in the pyrrhotite–sphalerite field. The pressure at 700°C will be ≈1.4 kbar lower than that estimated at 650°C.

The pressures estimated from the data of Scott (1973, 1976) for sphalerite coexisting with pyrite and pyrrhotite are in the range 2.1–2.9 kbar, in agreement with the 2–3 kbar pressure of metamorphism determined by Blümel and Schreyer (1977) from the silicate mineral assemblages. The maximum pressure estimated for sphalerite coexisting with pyrite is 3.4 kbar, whereas the minimum determined for sphalerite coexisting with pyrrhotite is 2.4 kbar.

The average mole percent FeS of sphalerite associated with chalcopyrite and pyrrhotite but not in direct contact with the latter yields a pressure of 6.1 kbar. The wide range in mole percent FeS for such sphalerite, however, corresponds to a pressure range of 5 to ~10 kbar. Similarly, the pressures determined for chalcopyrite-bearing sphalerite that coexists with pyrite and pyrrhotite range between 2 and 7.1 kbar, with an average of 4.7 kbar.

Pressures estimated from the calculated isobars of Hutcheon (1978) are somewhat lower than those estimated from the experimental data of Scott (1973, 1976); however, the two pressure estimates are in reasonable agreement.

### Discussion

The application of sphalerite geobarometry to the ores from Bodenmais shows that the pressure estimates vary in single specimens and are dependent on the mineral assemblage with which sphalerite coexists, particularly the presence of exsolved chalcopyrite in sphalerite and its association with monoclinc pyrrhotite. Two observations suggest that the equilibrium composition of sphalerite attained during metamorphism was not preserved during the post-metamorphic history of the Bodenmais ore: (1) the depletion of sphalerite in FeS where it coexists with monoclinc pyrrhotite; (2) the large variation in the iron content of sphalerite in chalcopyrite-bearing assemblages, even within individual crystals.

During cooling of an assemblage of sphalerite, hexagonal pyrrhotite, and pyrite, monoclinc pyrrhotite forms at a temperature of 254°C. The formation of monoclinc pyrrhotite implies an increase of f(S₂). Because a(FeS) is inversely proportional to f(S₂), the iron content of sphalerite equilibrating with monoclinc pyrrhotite is expected to be lower than that of sphalerite in equilibrium with hexagonal pyrrhotite.

### Table 2. Representative electron microprobe analyses of sphalerite

<table>
<thead>
<tr>
<th>Element</th>
<th>1ª</th>
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<th>5++</th>
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<tbody>
<tr>
<td>Mn</td>
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<td>0.89</td>
<td>0.41</td>
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<td>Fe</td>
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</tr>
<tr>
<td>Cu</td>
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<td>0.01</td>
<td>0.05</td>
<td>0.16</td>
<td>0.32</td>
</tr>
<tr>
<td>Zn</td>
<td>55.96</td>
<td>55.72</td>
<td>56.13</td>
<td>57.16</td>
<td>60.34</td>
</tr>
<tr>
<td>Cd</td>
<td>0.24</td>
<td>0.38</td>
<td>0.26</td>
<td>0.47</td>
<td>0.31</td>
</tr>
<tr>
<td>S</td>
<td>33.93</td>
<td>34.27</td>
<td>34.30</td>
<td>33.96</td>
<td>34.04</td>
</tr>
<tr>
<td></td>
<td>100.27</td>
<td>100.20</td>
<td>100.83</td>
<td>99.81</td>
<td>100.84</td>
</tr>
</tbody>
</table>

ªSphalerite coexisting with pyrrhotite and pyrite.  
ªªSphalerite coexisting with pyrrhotite.  
++Sphalerite with chalcopyrite exsolution.
as has been demonstrated experimentally (Scott and Kissin, 1973) and observed in other ores (e.g., Grove et al., 1975; Ethier et al., 1976).

The large variation in FeS content of sphalerite-containing chalcopyrite exsolutions at Bodenmais was recently observed in other ores, e.g., in Balmat-Edwards ore, New York (Brown et al., 1978), and at Ducktown, Tennessee (Barton, personal communication, 1978). The addition of Cu to the system Zn–Fe–S is likely to affect sphalerite geobarometry because the solubility of FeS and CuS in sphalerite is dependent on the Fe:Cu ratio, temperature, and f(S₂) (Wiggins and Craig, 1975). Hutchison and Scott (1978), however, found experimentally that Cu does not affect the geobarometer over its temperature-independent range and attributed the inhomogeneity in the FeS content of sphalerite to extensive exsolution of chalcopyrite. They interpreted the anomalous FeS content of chalcopyrite-bearing sphalerite as an indication of high temperature, former pyrrhotite–sphalerite equilibria, or disequilibrium assemblages (Hutchison and Scott, 1978). At Bodenmais, chalcopyrite-bearing sphalerite in mutual contacts with pyrrhotite and pyrite is compositionally inhomogeneous—a feature that cannot be attributed to exsolution of chalcopyrite alone (Hutchison and Scott, 1978). The exsolved phase in sphalerite from Bodenmais is always chalcopyrite, and no other Fe–Cu sulfides were observed in this ore. At the temperature of metamorphism at Bodenmais, chalcopyrite would be represented by a more-iron-rich intermediate solid solution (Iₚ) (Barton, 1973; Cabri, 1973). Hutchison and Scott noted that in the temperature range 600°–350°C and at 5 kbar sphalerite in equilibrium with pyrrhotite, pyrite, and Iₚ contains 0.0–0.4 wt. percent Cu in solid solution. The Iₚ is unstable below 350°C, and chalcopyrite containing about 0.4 wt. percent Zn coexists with sphalerite, pyrrhotite, and pyrite. In the assemblage chalcopyrite–sphalerite–pyrrhotite–pyrite at Bodenmais, sphalerite contains 0.03–0.4 wt. percent Cu, while the coexisting chalcopyrite contains 0.08–0.16 wt. percent Zn in solid solution. The presence of chalcopyrite as the only exsolved Cu–Fe sulfide, its low Zn content, and the low Cu content of sphalerite suggest that the assemblage chalcopyrite–pyrrhotite–pyrite–sphalerite at Bodenmais equilibrated to temperatures below 350°C. In this assemblage the pyrrhotite that occurs as veinlets in sphalerite or at the immediate contact with sphalerite crystals is monoclinic. The presence of monoclinic pyrrhotite extends the limits of low-temperature equilibration of this assemblage to below 250°C. It also suggests that reaction with the monoclinic pyrrhotite is at least partly responsible for the inhomogeneity observed in these sphalerites.

The iron content of sphalerite coexisting with either pyrrhotite or pyrite is essentially similar to or slightly lower than that of sphalerite in the univariant assemblage sphalerite–pyrite–pyrrhotite. Under equilibrium conditions sphalerite in equilibrium with pyrrhotite alone or pyrite alone should have higher or lower iron contents, respectively, than sphalerite in equilibrium with both minerals. Scott (1976) observed that in many metamorphic terrains the equilibrium composition of sphalerite coexisting with iron-sulfide assemblages varies over a few meters or even a few centimeters. He concluded that in the absence of a fluid phase, the equilibrium domains of iron and sulfur are very small relative to the size of the ore body, and therefore several local equilibria are established in which the composition of sphalerite is buffered by the iron sulfide that occurs in its immediate vicinity. At Bodenmais, migmatization and the presence of hydrous phases strongly suggest that the P(H₂O) was high during metamorphism. It is therefore possible that sulfur was mobile in the presence of a fluid phase and that the f(S₂) varied within narrow ranges during the metamorphism of Silberberg ore; these factors would account for the similarity in composition of sphalerite coexisting with pyrite or pyrrhotite or both.

A different interpretation, however, was given by Barton and Skinner (1979) for the slightly lower iron content observed in sphalerite coexisting with pyrrhotite relative to sphalerite associated with pyrite and pyrrhotite in ores that underwent slow cooling, such as the Sullivan ore, British Columbia (Ethier et al., 1976), and the Sulitjelma ore, Norway (Rai, 1978). Barton and Skinner interpreted this observation as an indication of metastability, which they attributed to the reluctance of pyrite to nucleate at low temperatures even under conditions of pyrite supersaturation. They suggested that the low FeS content of sphalerite in equilibrium with pyrrhotite relative to that in the three-phase assemblage pyrite–pyrrhotite–sphalerite can be explained by assuming that the composition of sphalerite can still be adjusted by reaction with pyrrhotite under conditions in which pyrite can no longer nucleate, although it may continue to grow on previously existing nuclei. Under such conditions the assemblage pyrite–pyrrhotite–sphalerite remains close to the equilibrium condition on cooling, whereas a pyrite-free assemblage undergoes
reaction, yielding a metastable assemblage of monoclinic pyrrhotite and FeS-depleted sphalerite (and possibly marcasite). In Bodenmais ore, monoclinic pyrrhotite commonly occurs in association with both hexagonal pyrrhotite and pyrite, and this association suggests that it is a metastable phase. The common occurrence of monoclinic pyrrhotite at the interface between hexagonal pyrrhotite and sphalerite and the depletion of sphalerite in the immediate vicinity of monoclinic pyrrhotite suggest that the reaction postulated by Barton and Skinner (1979) between hexagonal pyrrhotite and sphalerite apparently took place but did not proceed to completion.

In conclusion, the application of sphalerite geobarometry may not be a reliable method for estimating pressure in ores that underwent low-temperature reactions, or in Cu-bearing zinc sulfide areas. However, attempts to apply sphalerite geobarometry provide valuable insights on the post-metamorphic low-temperature equilibration in these ores.

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