Hydrothermal Synthesis of Wurtzite and Sphalerite at T = 350°–250°C*

Shoji KOJIMA** and Hiroshi OHMOTO**

Abstract: Wurtzite and sphalerite were synthesized hydrothermally at 350°, 300° and 250°C using a temperature-gradient transporting method with sphalerite as a starting mineral. Fibrous wurtzite together with sphalerite was formed only in experiments at 300° and 250°C when a Zn-rich solution (1 m ZnCl₂ + 1 m NH₄Cl) was used as the transporting media; only sphalerite was produced in experiments using a Zn-free solvent (1 m NH₄Cl). Formation of wurtzite (vs. sphalerite) was not affected by the composition of the starting sphalerite nor by the addition of pyrrhotite and/or alabandite to the starting materials. These results agree with a thermodynamic prediction that the solubility of wurtzite is higher than that of sphalerite.

A comprehensive literature survey on the occurrence of wurtzite in hydrothermal ore deposits shows that wurtzite is not uncommon in shallow subaerial deposits and in submarine hydrothermal deposits of relatively young ages (mostly Tertiary or younger). For these deposits, drastic physicochemical changes in the ore-forming solutions, such as rapid cooling by mixing with local meteoric or sea water, have been postulated during ore mineralizations. The wurtzite crystals often exhibit fibrous or radial textures, which would be produced by the above changes. Our experimental data and the occurrence of wurtzite in ore deposits suggest that hydrothermal wurtzite is a metastable mineral that is formed by rapid crystal growth from highly supersaturated solutions.

Introduction

The stability relationships of two distinct phases of zinc sulfide minerals, sphalerite and wurtzite, is an important subject in ore mineralogy. Nevertheless, no clear explanations for their relationships in natural ores have yet been given. Some experimental studies using a dry synthetic method have suggested that wurtzite is stable only at temperatures above 1,020°C for pure ZnS (Allen and Crenshaw, 1912) and above about 850°C for Fe-rich compositions (Barton and Toumin, 1966). High concentrations of impurities, such as Mn or Cd, contribute to an extension of the wurtzite stability field to lower temperatures, ~500°C (Tauson et al., 1977; Tauson and Chernyshev, 1978; Jang, 1985). However, the compositions of wurtzite (~25 mol% MnS, 20~25 mol% CdS) used in their experimental works are far from those for most natural wurtzites. Even the temperatures around 500°C for the minimum temperature of wurtzite formation are much higher than those for wurtzite in ore deposits, mostly T ≤ 350°C (see later section). Because natural occurrence of wurtzite is limited in ore deposits formed at temperatures below 500°C, wurtzite has been considered to be a metastable phase (Barton and Toumin, 1966; Barton and Skinner, 1979; Ramdohr, 1980). Especially, Barton and Skinner (1979) have suggested that high concentrations of impurities such as Mn and Cd may enhance the metastability of wurtzite at low temperatures.

Based on the experimental results given by Allen et al. (1914), it was widely believed that the wurtzite precipitation from hydrothermal solutions was controlled by acidity and temperature of hydrothermal solution. The effect of acidity, however, has been suspected by experimental studies including Corey (1953), Kiyosu and Nakai (1971) and Scott and Barnes (1972). From hydrothermal recrystallization experiments at T = 300° to 700°C, Scott and Barnes (1972) have suggested that sphalerite and wurtzite are not polymorphs but independent phases with com-
position of \( \text{Zn}_{1-x} \text{S} \) and \( \text{ZnS}_{1-x} \), respectively. They have also suggested that the inversion between the two minerals is a univariant function of sulfur fugacity \( (f_S) \) and temperature: wurtzite is stable at lower \( f_S \), condition. However, it is not certain whether or not this theory applies to natural ores where wurtzite contains appreciable amounts of Fe, because the system studied by SCOTT and BARNES (1972) did not contain any Fe.

Based on detailed descriptions on sulfide minerals from the modern seafloor deposits on the East Pacific Rise, HAYMON and KASTNER (1981) and GRAHAM et al. (1988) have suggested that supercooling of hydrothermal fluids with high concentrations of Zn and S may cause rapid precipitation of wurtzite metastably due to a kinetic effect. For sulfide ores containing wurtzite at the Toyoha mine in Japan, a similar interpretation has been given by DOHMOTO et al. (1986).

According to the thermodynamic data summarized by HELGESON (1969), the solubility of wurtzite is higher than sphalerite at temperatures from 25° to 300°C. This recognition has led GRAHAM et al. (1988) and SAITO et al. (1989) to suggest that wurtzite may precipitate when a fluid initially saturated (or undersaturated) with respect to sphalerite is cooled rapidly to become supersaturated with respect to wurtzite (and also to sphalerite). The solubility of sphalerite estimated by HELGESON (1969) has been substantiated experimentally by BOURCIER and BARNES (1987), but that of wurtzite has not. The primary objectives of this study are therefore to experimentally verify that the solubility of wurtzite is indeed higher than that of sphalerite in a temperature range of 350° to 250°C, and that wurtzite may precipitate from solutions supersaturated with respect to both wurtzite and sphalerite. In addition, natural occurrences of wurtzite are reviewed from a literature survey to put constraints on the mechanisms of wurtzite formation and the phase relationships between wurtzite and sphalerite.

**Mechanisms of Wurtzite Precipitation Predicted from Thermodynamic Data**

Possible mechanisms of wurtzite precipitation from hydrothermal solutions, predicted by GRAHAM et al. (1988) and SAITO et al. (1989) based on the solubility data of sphalerite and wurtzite, are explained here in detail.

By combining the thermodynamic data reported for minerals and their pertinent ionic species, the solubility products for wurtzite and sphalerite have been computed by HELGESON (1969). While, the speciation for zinc chloride complexing has been given by BOURCIER and BARNES (1987) (see Table 1). Assuming that the dominant forms of zinc in solutions are chloride complexes, the solubilities of sphalerite and wurtzite can be evalu-
Hydrothermal synthesis of wurtzite and sphalerite at T=350°-250°C

Fig. 1 Solubility relationships of sphalerite (sp) and wurtzite (wz) for a temperature range of 350°-200°C predicted from thermodynamic data (Table 1). The conditions are: pH=4.5; m$_{ZnCl_2}$=2; and m$_{H_2S}$=10$^{-1.5}$ at 350°C, 10$^{-2.5}$ at 300°C, 10$^{-3.5}$ at 250°C and 10$^{-4.0}$ at 200°C. Also shown are (a) dissolution-precipitation process according to the Ostwald’s step rule and (b) two possible mechanisms for precipitation of wurtzite: A solution that was initially saturated with sphalerite may precipitate wurtzite either by mixing with a cooler solution or by simple closed system cooling. The amount of Zn that may precipitate during the cooling is $X_a - X_b$. See text for other symbols.

The solubilities of wurtzite and sphalerite (both with the ideal composition ZnS) are compared in a temperature range of 350° to 200°C in Fig. 1. The total molality of chloride (m$_{ZnCl_2}$) and pH are fixed at 2 and 4.5, respectively. The molalities of aqueous H$_2$S (m$_{H_2S}$; mol/kg·H$_2$O) is varied from 10$^{-1.5}$ at 350°C to 10$^{-4.0}$ at 200°C. These pH, m$_{ZnCl_2}$ and m$_{H_2S}$ values correspond to the average values for the Kuroko ore-forming fluids estimated by OHMOTO et al. (1983). The activity coefficients for the ionic species were estimated using the extended Debye-Hückel equation proposed by HELGESON (1969); the Debye-Hückel and the ion size parameters were from HELGESON et al. (1981) and TRUESDELL (1984), respectively. The activities of neutral species, such as H$_2$S (aq) and ZnCl$_2$, are assumed to be the same as that of aqueous CO$_2$ (HELGESON, 1969)

Possible mechanisms for precipitation of wurtzite and sphalerite can be discussed using the solubility curves in Fig. 1a. Consider a solution A with the composition $X_1$ at the temperature $T_1$. This solution is supersaturated with respect to both wurtzite and sphalerite. According to the Ostwald’s step rule of the empirical law of successive trans-
FORMATION (OSTWALD, 1897), wurtzite as a metastable phase is predicted to precipitate first in preference to sphalerite. Due to precipitation of wurtzite, the solution composition may change to the point B (X_wz). Sphalerite may also nucleate at any point between A and C. If the dissolution rate of wurtzite is fast, wurtzite may dissolve in solution and reprecipitate as sphalerite until the solution and sphalerite become equilibrated at the point C. However, if the wurtzite is isolated from the solution or the dissolution rate of wurtzite is slow, it may remain as a metastable phase. Furthermore, sphalerite would be formed if the solution with the composition X_{w2} is heated from T_1 to T_2.

There may be a variety of processes that cause a fluid to become supersaturated with respect to wurtzite, including rapid cooling, rapid pressure-drop, and rapid boiling. Two examples of rapid cooling, one with a closed system cooling (e.g., conductive cooling) and the other caused by mixing with a cooler and dilute solution (e.g., seawater, meteoric water) are shown in Fig. 1b. If a fluid that was saturated with sphalerite at 350°C was cooled rapidly by heat conduction, precipitation of wurtzite may first occur at lower temperatures. In such a case, the amount of supersaturation corresponding to the value of X_a-X_b may be regarded as a driving force for the growth of wurtzite. In submarine conditions, seawater mixing with an ore-forming solution may cause precipitation of wurtzite (see an arrow in Fig. 1b). According to recent studies, seawater mixing combined with heat conduction is considered a major cooling mechanism for the ore-forming fluids responsible for mineralization in modern seafloor deposits (e.g., TIVEY and DELANEY, 1986; HANNINGTON and SCOTT, 1988).

**Experimental Method**

All hydrothermal experiments were performed by a conventional transport method using a temperature gradient in an autoclave (SCOTT, 1974). In the first series of experiments (Series I), we attempted to substantiate the formation mechanism of wurtzite shown in Fig. 1b, using only a thermal-gradient. Powdery crystals of sphalerite as starting materials were placed in the end of a closed silica glass capsule (~3.5 mm in diameter and ~9 cm in length) together with a solvent. The capsules were placed vertically in an autoclave, and heated in a vertical type of an electric furnace controlled by upper and lower heaters. The temperature gradient of approximately 10°C/cm was imposed outside the vessel. Under such a configuration, the actual temperature differences between the hotter and cooler ends were found to be approximately 10°~15°C. The thermal-gradient must be enough to generate metastabilities induced by supersaturation (SCOTT and BARNES, 1972; SCOTT, 1974). The powdery crystals were dissolved at the lower (hotter) end of the capsule, transported upward by the convecting fluid, and reprecipitated at the upper (cooler) end of the capsules. The experiments were conducted by using two modes of capsules, which are similar to those used in KOJIMA (1990); namely the mode A with a straight shape and the mode B with a necked path as a role of baffle (see Fig. 1; KOJIMA, 1990). The aqueous solution used in Series I experiments was 1 m NH_4 Cl solution with pH=4.8 at 25°C.

In the second series of experiments (Series II), attempts were made to produce wurtzite by using a solution with an excess zinc concentration. The experimental solutions were a mixture of 1 m ZnCl_2 +1 m NH_4Cl (pH=5.6 at 25°C). The starting materials and other experimental conditions were similar to Series I experiments.

The nutrient materials as powdery minerals were synthesized at 800° to 850°C by an evacuated silica glass tube method using 99.9+ percent metals and sulfur. Sphalerite solid solutions with various Fe contents (ZnS, Zn_{0.95}Fe_{0.05}S, Zn_{0.85}Fe_{0.15}S and Zn_{0.7}Fe_{0.3}S) are the main nutrient materials, and used by combining with pyrrhotite (1C, N_{FeS}=0.97), alabandite and crystalline sulfur. The experiments were carried out at temperatures between 350° and 250°C. The temperatures at the cooler end were controlled within ±3°C during the
run, and were measured directly by a chromel-alumel thermocouple inserted into the inner vessel near the top of the reaction capsule. In all runs, the confining pressure was maintained at approximately 250 kgf/cm², and monitored via a Bourdon-type pressure gauge.

After 6 to 17 days at experimental temperatures, the reaction vessel was quenched using an electric fan and the capsules were taken out from the furnace. Precipitated products in the upper (cooler) part of capsule were investigated using a transmitting microscope, a Guinier-Hagg camera and an electron microprobe analyzer. Particularly in the microscop-

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### Table 2  Summary of the conditions and results of hydrothermal experiments

<table>
<thead>
<tr>
<th>Run No.</th>
<th>T(°C)</th>
<th>Reactants¹</th>
<th>Mode</th>
<th>t²</th>
<th>pH³</th>
<th>Products</th>
<th>Morphology Textures</th>
</tr>
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<tbody>
<tr>
<td>(Series I)</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>I-1</td>
<td>350</td>
<td>sp(0)</td>
<td>A</td>
<td>9</td>
<td>6.8</td>
<td>sp</td>
<td>S</td>
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<tr>
<td>I-2</td>
<td>350</td>
<td>sp(5)</td>
<td>B</td>
<td>9</td>
<td>5.4</td>
<td>sp</td>
<td>C</td>
</tr>
<tr>
<td>I-3</td>
<td>350</td>
<td>sp(5)+po</td>
<td>B</td>
<td>9</td>
<td>6.2</td>
<td>sp&gt;py</td>
<td>C</td>
</tr>
<tr>
<td>I-4</td>
<td>350</td>
<td>sp(15)</td>
<td>B</td>
<td>10</td>
<td>5.6</td>
<td>sp</td>
<td>P*</td>
</tr>
<tr>
<td>I-5</td>
<td>350</td>
<td>sp(30)</td>
<td>B</td>
<td>10</td>
<td>5.6</td>
<td>sp</td>
<td>P*</td>
</tr>
<tr>
<td>I-6</td>
<td>300</td>
<td>sp(0)+po</td>
<td>A</td>
<td>9</td>
<td>6.2</td>
<td>sp</td>
<td>C</td>
</tr>
<tr>
<td>I-7</td>
<td>300</td>
<td>sp(5)+po</td>
<td>B</td>
<td>9</td>
<td>6.6</td>
<td>sp</td>
<td>C</td>
</tr>
<tr>
<td>I-8</td>
<td>300</td>
<td>sp(15)</td>
<td>A</td>
<td>6</td>
<td>7.0</td>
<td>sp&gt;py</td>
<td>C</td>
</tr>
<tr>
<td>I-9</td>
<td>300</td>
<td>sp(15)</td>
<td>B</td>
<td>9</td>
<td>6.6</td>
<td>sp</td>
<td>P</td>
</tr>
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<td>13</td>
<td>6.6</td>
<td>sp</td>
<td>P*</td>
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<tr>
<td>I-11</td>
<td>300</td>
<td>sp(0)+po</td>
<td>B</td>
<td>13</td>
<td>6.4</td>
<td>sp&gt;po</td>
<td>P</td>
</tr>
<tr>
<td>I-12</td>
<td>250</td>
<td>sp(5)</td>
<td>B</td>
<td>13</td>
<td>6.8</td>
<td>sp</td>
<td>S</td>
</tr>
<tr>
<td>I-13</td>
<td>250</td>
<td>sp(15)+po</td>
<td>B</td>
<td>14</td>
<td>6.0</td>
<td>sp</td>
<td>S</td>
</tr>
</tbody>
</table>

| (Series II) | | | | | | | |
| II-1 | 350 | sp(0)+po | B | 10 | 6.0 | sp | P* |
| II-2 | 350 | sp(5) | B | 9 | 5.4 | sp | P |
| II-3 | 350 | sp(5)+po | A | 10 | 5.4 | sp>py | P |
| II-4 | 350 | sp(15)+po | B | 9 | 5.8 | sp | C(P) |
| II-5 | 350 | sp(5)+alb+po | A | 9 | 6.0 | sp>py | P |
| II-6 | 350 | sp+alb | B | 9 | 5.6 | sp | P |
| II-7 | 300 | sp(0) | A | 12 | 5.0 | sp | S |
| II-8 | 300 | sp(0) | B | 12 | 5.4 | sp | S |
| II-9 | 300 | sp(0)+po | A | 11 | 5.6 | wz-sp>py | C |
| II-10 | 300 | sp(0)+po | B | 11 | 5.8 | wz-sp>py-po | C |
| II-11 | 300 | sp(5) | A | 12 | 5.0 | sp | P |
| II-12 | 300 | sp(5) | B | 12 | 4.8 | sp | C |
| II-13 | 300 | sp(5)+po | A | 11 | 5.6 | wz-sp>py-po-lo | C |
| II-14 | 300 | sp(5)+po | B | 11 | 5.6 | wz-sp>py | C |
| II-15 | 300 | sp(15)+po | B | 9 | 5.8 | wz-sp>py-po | C |
| II-16 | 300 | sp(15)+alb+po | A | 10 | 6.0 | wz-sp | C |
| II-17 | 300 | sp(15)+alb | A | 10 | 5.8 | wz-sp>py | C |
| II-18 | 300 | sp(0)+S | B | 12 | 0.4 | sp | C |
| II-19 | 300 | sp(5)+po+S | B | 11 | 1.6 | sp>py | C |
| II-20 | 250 | sp(0) | A | 14 | 5.4 | wz-sp | S |
| II-21 | 250 | sp(0)+po | B | 15 | 5.4 | wz-sp | C |
| II-22 | 250 | sp(5) | A | 17 | 5.4 | wz-sp | C |
| II-23 | 250 | sp(5)+po | A | 15 | 5.4 | wz-sp | S |
| II-24 | 250 | sp(5)+po | B | 14 | 5.4 | wz-sp | S |
| II-25 | 250 | sp(15) | A | 17 | 5.4 | wz-sp | C |
| II-26 | 250 | sp(15)+po | B | 14 | 5.0 | wz-sp | C |
| II-27 | 250 | sp(5)+alb+po | A | 13 | 5.6 | wz-sp | C |
| II-28 | 250 | sp(15)+alb | B | 13 | 5.6 | wz-sp | S |

1 : Values in parentheses indicate the FeS mol % of sphalerite.
2 : Run period (days). 3 : Quench pH.
Abbreviations: wz-sp, wurtzite-sphalerite aggregate; sp, sphalerite; py, pyrite; po, pyrrhotite; alb, alabandite; S, sulfur(solid); S, spherulitic (pisolithic); C, colloform; P, polyhedral; *, sector-zoned. See text for modes A and B.

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footnotes:

1 : Values in parentheses indicate the FeS mol % of sphalerite.
2 : Run period (days). 3 : Quench pH.
Abbreviations: wz-sp, wurtzite-sphalerite aggregate; sp, sphalerite; py, pyrite; po, pyrrhotite; alb, alabandite; S, sulfur(solid); S, spherulitic (pisolithic); C, colloform; P, polyhedral; *, sector-zoned. See text for modes A and B.
Fig. 2 Microscopic textures of wurtzite and sphalerite synthesized in the hydrothermal experiments. A and B, colloform wurtzite (Run No. II-21, 250°C); C, zoned wurtzite (Run No. II-9, 300°C); D, pisolitic wurtzite (Run No. II-26, 250°C); E, sector-zoned sphalerite (Run No. I-8, 300°C); F, fibrous sphalerite (Run No. I-9, 300°C). B is taken under crossed polars; the others are under plane-polarized light. The white bar is the scale of 150 μm and the black bar 300 μm.

ic analyses, both internal texture and anisotropy of the run products were carefully observed using doubly polished thin sections. For a precise identification of the products, X-ray powder diffraction analysis was carried out under the operating conditions of 30 to 35 kV and 10 to 14 mA, using the CuKα radiation monochromatized by a curved quartz crystal and reagent CaF₂ as an internal standard.

Chemical analyses of precipitated sphalerite and wurtzite were performed by the energy dispersive method using a Shimadzu-ARL, EMX-2 type electron microprobe analyzer equipped with an EDAX detecting unit.

Results and remarks
Approximately 50 runs for Series I and II experiments were carried out. Most runs produced appreciable amounts of sphalerite and/or
wurtzite (Table 2). Table 2 shows several important aspects on wurtzite formation. First, the appearance of wurtzite is limited to Series II experiments in which the ZnCl₂-bearing solution was used as a solvent, and wurtzite was not formed in Series I experiments. These results suggest that the excess zinc dissolved in hydrothermal solutions (i.e., solutions highly supersaturated with respect to sphalerite) plays an important role in nucleation and growth of wurtzite. It further suggests that the solubility of wurtzite is indeed higher than that of sphalerite. There is a distinct temperature effect for wurtzite precipitation from the experimental solutions: no wurtzite formed in the runs at 350°C, but wurtzite formed in some Series II runs at 300°C and all Series II runs at 250°C. The significance of this observation will be discussed in the next section. Table 2 also shows that both wurtzite and sphalerite were formed under nearly identical pH conditions, suggesting that the formation of wurtzite is not dependent on pH.

In Series II experiments at 300°C, wurtzite tends to form when pyrrhotite was added as a nutrient material (see Table 2). This feature may indicate that a low-sulfur fugacity \( f_S \) condition is favorable for the formation of wurtzite, as suggested by Scott and Barnes (1972). In nature, an intimate association of wurtzite and pyrrhotite is found in some base-metal and polymetallic ore deposits (e.g., Sugaki et al., 1984; Zielenberg et al., 1984; Peter and Scott, 1988; Kanbara et al., 1989). However, the fact that wurtzite was formed in the experimental runs without pyrrhotite at 250°C suggests that a low \( f_S \) is not necessarily an essential condition for wurtzite formation. Similarly, the presence or absence of alabandite in the starting materials, i.e. the presence or absence of Mn in the system, does not appear to be a determining factor in the formation of wurtzite (see Table 2). The FeS content of the starting sphalerite or the mode of the reaction capsule have no significant effect on the formation of sphalerite or wurtzite.

As is well known, there are many polytypes of wurtzite. The X-ray powder diffraction patterns of all the synthesized wurtzites show the strongest (100) reflection near \( \sim 3.309\,\text{Å} \), indicating that these wurtzites belong to the \( 2H \)-type wurtzite (Smith, 1955).

Some examples of the internal textures of the precipitated zinc sulfides are shown in Fig. 2. Most wurtzites formed at 300°C and 250°C show colloform textures with radial or fibrous structures (Fig. 2A), and distinct anisotropy under crossed polars (Fig. 2B). Usually, wurtzite appears to be intergrown closely with sphalerite. Wurtzite sometimes exhibits a growth-banded zonation from brownish core to yellowish rim (Fig. 2C), suggesting a variation of the FeS content. Wurtzite with similar color banding has been reported in wurtzite-rich ores from some modern seafloor deposits (Oudin, 1983; Koski et al., 1984). All the wurtzites formed at 250°C are submicron-sized aggregates, showing spheroidal and pisolitic textures (Fig. 2D). Such textures of wurtzite suggest the precipitation from highly supersaturated solutions (e.g., Sunagawa, 1984). Figure 3 shows a scanning electron photomicrograph of wurtzite produced at 250°C, displaying characteristic morphologies of pumpkin- and bugle-like shapes. Sphalerite crystals formed in Series I experiments show a wide variety of textures (see Figs. 2E and 2F). Polyhedral sphalerite (<1 mm) showing a sector-zoned structure, which is also found in natural ores (e.g., Barton, 1970), was frequently produced in the mode A experiments at both 350° and 300°C (Fig. 2E). In the mode B experiments, fibrous sphalerite with a growth-banded zonation was
Table 3 Compositional ranges for wurtzite and sphalerite synthesized in the hydrothermal experiments

<table>
<thead>
<tr>
<th>Mineral</th>
<th>Run No.</th>
<th>Compositional ranges (at.%)</th>
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</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td>Fe</td>
</tr>
<tr>
<td>Sphalerite</td>
<td>I-8 (5)</td>
<td>4.2 -16.0</td>
</tr>
<tr>
<td></td>
<td>I-9 (7)</td>
<td>1.9 -10.0</td>
</tr>
<tr>
<td>Wurtzite</td>
<td>II-24 (5)</td>
<td>0.8 -3.0</td>
</tr>
<tr>
<td></td>
<td>II-26 (5)</td>
<td>0.9 -3.2</td>
</tr>
<tr>
<td></td>
<td>II-9 (5)</td>
<td>1.9 -4.5</td>
</tr>
<tr>
<td></td>
<td>II-17 (9)</td>
<td>0.2 -0.7 &lt;0.1</td>
</tr>
</tbody>
</table>

Values in parentheses are numbers of analyses.

formed (Fig. 2F). Such differences in the textural features suggest that a higher degree of supersaturation with respect to sphalerite was generated in the mode B runs compared to the mode A runs.

Table 3 summarizes the ranges of Fe and Mn contents of the wurtzite and the sphalerite shown in Fig. 2. The wurtzite crystals formed in Series II experiments show a limited range of Fe content, from 0.2 to 4.5 at.%, regardless of the presence or absence of pyrrhotite in the nutrient. The Mn contents of wurtzite formed in the presence of alabandite are extremely low (>0.1 at.%), suggesting that the concentrations of impurities such as Mn do not play an important role in the wurtzite formation. In contrast to the wurtzite, the sphalerite exhibits a wider range of Fe content from 1.9 to 16.0 at.%. The sphalerite shown in Fig. 2E contains ~5.0 at.% Fe in the Fe-poor sector, ~8.0 at.% Fe in the Fe-rich sector, and ~16.0 at.% Fe in an extremely Fe-rich sector. The fibrous sphalerite in Fig. 2F shows a marked compositional heterogeneity: its central part is Fe-rich (~10.0 at.% Fe) and the periphery is Fe-poor (~1.9 at.% Fe). In the literature (e.g., PANKRATZ and KING, 1965; SCOTT and BARNES, 1972), nonstoichiometries of zinc sulfide minerals have been discussed: sphalerite is zinc-deficient and wurtzite is sulfur-deficient. However, such deviations in the Zn/S stoichiometry were not observed within a range of 0.5 at.% (see Table 3).

Discussion

Degree of supersaturation

As stated in the previous section, excess zinc in the experimental solutions appears to have played the most important role in the formation of wurtzite. In crystal growth theory, the degree of supersaturation (saturation index) has often been related to the stability of mineral and the variation of crystal morphology (e.g., SUNAGAWA, 1984). The degree of supersaturation with respect to wurtzite is defined as the ratio of the activity product of pertinent aqueous species in a solution to the equilibrium constant for the following reactions involving wurtzite (wz):

\[ \text{ZnS(wz)} + 2\text{H}^+ + n\text{Cl}^- = \text{ZnCl}_{2-n}^+ + \text{H}_2\text{S(aq)} \]

Therefore, saturation index can be evaluated quantitatively by estimating pH and activities of \( \text{ZnCl}_{2-n}^+ \) and \( \text{H}_2\text{S(aq)} \). In the calculations, it was assumed that \( \text{NH}_4\text{Cl} \) is completely dissociated into \( \text{NH}_4^+ \) and \( \text{Cl}^- \). Judging from the quench pH values in Table 2 and stability of \( \text{NH}_4^+ \), the pH range was estimated as 5.0±0.5 at the experimental temperatures. As mentioned earlier, the temperatures of the hot ends were regarded as ~360°C for the 350°C runs, ~310°C for the 300°C runs, and ~265°C for the 250°C runs. All the equilibrium constants at these temperatures were interpolated or extrapolated using a least-squares method. For the experimental solutions of Series I, saturation index corresponds to the ratio of activity products of \( \text{ZnCl}_{2-n}^+ \) and \( \text{H}_2\text{S(aq)} \) at the temperatures of sphalerite dissolution (360°C, 310°C, and 265°C) to those of wurtzite at precipitation temperatures (350°C, 300°C, and 250°C). For the experimental solutions of Series II, dissolved zinc contents \( (m_{\text{ZnCl}_{2-n}}) \) at the temperatures of sphalerite dissolution were firstly calculated using the speciation for the zinc chloride complexes given by BOURCIER and BARNES (1987) and the following charge and mass balance equations:

\[ m_{\text{Cl}^-} + m_{Zn\text{Cl}_{2-n}} + 2m_{Zn\text{Cl}_{2+}} = m_{\text{NH}_4^+} + m_{Zn\text{Cl}^+} \]

\[ m_{\text{Cl}^-} + m_{Zn\text{Cl}_{2+}} + 2m_{Zn\text{Cl}_{2+}} + 3m_{Zn\text{Cl}_{3+}} + 4m_{Zn\text{Cl}_{4-}} = 3 \]

Next, \( a_{\text{H}_2\text{S(aq)}} \) in the solutions at pH = 5 was inferred from the \( m_{Zn\text{Cl}_{2-n}} \) and equilibrium con-
The calculated saturation indices (SI) of experimental solutions with respect to wurtzite. See text for detailed explanations.

Fig. 4. The calculated saturation indices (SI) of experimental solutions with respect to wurtzite. See text for detailed explanations.

The results of the calculations, showing the changes in the saturation indices of the experimental solutions with respect to wurtzite, are illustrated in Fig. 4. It shows that hydrothermal fluids in Series I experiments are highly undersaturated with respect to wurtzite, and that those in Series II experiments are apparently supersaturated with respect to wurtzite at 300° and 250°C, but slightly undersaturated at 350°C. These features are in excellent agreement with the observation that wurtzite formed in some Series II experiments of 300° and 250°C.

In the systems containing liquid sulfur at 300°C, only sphalerite (+pyrite) was formed (see Table 2). The hydrolysis reaction of sulfur is the likely cause for an extremely low pH (0.4 – 1.6), as seen in the following reaction:

\[ 4S^+ + 4H_2O = 3H_2S + HSO_4^- + H^+ \]

As inferred from the dissolution reactions in Table 1, pH is the most effective parameter controlling the solubilities of wurtzite and sphalerite. The above experimental condition created a situation where the solubilities of sphalerite (and wurtzite) are much higher than in other experimental solutions. It is therefore considered that supersaturation with respect to wurtzite was not produced in Series II experimental solutions with liquid sulfur. However, Kiyosu and Nakai (1971) have succeeded in hydrothermal synthesis of wurtzite in a similar system ZnCl_2–S–Na_2CO_3–H_2O. Generally, the addition of dissolved carbonate (Na_2CO_3) causes an increase of fluid pH (and also a decrease of f_Ca) at the starting conditions, so that supersaturation with respect to wurtzite may have been produced in their study.

A similar effect of excess zinc in the formation of wurtzite has been previously observed in some experiments under dry conditions. In synthetic experiments by a vapor depositing method, Shalimova and Morozova (1965) have demonstrated that the addition of ZnCl_2 to ZnS leads to a high abundance of wurtzite in the deposited film at temperatures between 600° and 400°C. This phenomenon is very similar to our experimental results in the respect that the excess zinc is likely to cause the formation of wurtzite.

Natural occurrence of wurtzite

In order to obtain information on conditions favorable for formation of wurtzite, a literature survey on natural occurrence of wurtzite was carried out. Major ore deposit types and mining districts where wurtzite was reported are summarized in Table 4. The deposits in the table, including low-temperature deposits such as the Mississippi Valley-type and the Alpine-type, are all regarded as hydrothermal deposits formed under shallow-subaerial or submarine conditions. In particular, wurtzite appears to occur frequently in base-metal (polymetallic) ore deposits of relatively young geologic ages; most abundantly in those formed during Neogene Tertiary or Quaternary ages (see Table 4).

The transformation of wurtzite to sphalerite without solution/dissolution reactions is a kinetic process, and probably a function of temperature, pressure and time. Some old deposits (e.g., Mississippi Valley-type) may...
Table 4 Reported occurrences of wurtzite in ore deposits

(A) Vein-type deposits* (<39)

1. Pb-Zn-(Ag)
   Japan: Odorni(1), Hosokura(1); USA: Last Chance(2), Hornsilver(2), Era(3),
   Tintic(4), Thomaston Dam(5); Canada: Fairview(6); Bolivia: Berenguela(7),
   Pucacayo(8); CSSR: Pribram(9); Romania: Oas-Baia Mare(10); Bulgaria: Mad-
   zarevo(11)

2. Mn-Pb-Zn
   Japan: Inakuraishi(12), Jyokoku(13); USA: Morey(14); Peru: Uchucchacua(15)

3. Au-(Ag,Cu)
   Japan: Teine(16), Tomiymasu(17), Ohmori(18); Taiwan: Chinkawan(19); USA:
   Goldfield(20)

4. Pb-Zn-Cu-Ag-(Sb)
   Japan: Toyoha(21); USA: Butte(22), Horn Silver(23); Mexico: Topia(24); 
   Peru: Huania(25); Bolivia: San Jose(8), Humuni(8), Moneerrat(8), Siglo
   XX(26), Antequera(8), Poope(8), Potosi(27), Cargunicello(7), Chocaya-
   Animas(28), Tatki(28); Hungary: Gyongyosorzosi(29); Italy: Acesca(30)

(B) Stratiform deposits (<20)

5. Kuroko-type
   Japan: Chage(31), Okoppe(32), Aomori(33), Abeshiro(34), Yunosawa(35),
   Hanaka(16), Hanawa(33); Fiji: Nakuduama(36)

6. Mississippi Valley (Alpine)-type
   USA: Wisconsin(37), Joplin(38); Canada: Nanisivik(39); Poland: Silesia(7),
   FRG: Auchen(40), Wieilo(40), Baden(40); Belgium: Moesnet(40); Italy: 
   Ra1i(41); Austria: Bleiberg-Kreuth(42); Australia: Narlurala(43)

7. Sandstone-associated Cu
   USA: White Pine(44)

(C) Modern seafloor deposits* (<16)

8. Explorer Ridge(45); Endeavour Segment(46); Axial Seamount(47); Southern
   Juan de Fuca(48); Quaymas Basin(49); East Pacific Rise 11°N(50), 13°N(50),
   21°S(51), 18°S(52); Snakepit(53); Izena(54); Iheyasa(55); North Fiji(56);
   Atlantis II Deep(57), Kebrit Deep(58)

< >: total number of deposits. * : deposits of Tertiary or Quaternary ages.

(References)

(1) Imai (1941, 1978), (2) Anderson (1947), (3) Upleby (1917), (4) Morris (1968),
(5) Myer (1962), (6) Thompson(1950), (7) Randolph(1980), (8) Ahfeld and Schneider-
Scherbina (1964), (9) Fleet (1977), (10) Ivanovic and Borcescu (1982), (11) Bogdanov
Russell et al.(1990), (16) Sakurai(1973), (17) Watanabe (1941a), (18) Watanabe
(1941b), (19) Huang (1955, 1965), (20) Tolman and Ambrose (1937), (21) Haraguchi
al.(1985), Fukahori and Sakogaichi (1990), (26) Smith et al.(1957), (27) Sugaki et
and Sakurai(1947), (32) Hemmi(1941), (33) Urabe (1974), (34) Takahashi and Nambu
(1951), (35) Watanabe and Nakano (1936), (36) Frenzel and Oettmann (1967), (37)
Behre et al.(1937), (38) Evans and McKnight(1959), (39) Olson(1984), (40) Roederer
(1968), (41) Lindgren (1928), (42) Schulz (1968), (43) Playford (1975), (44) Brown
Hannington and Scott (1988), (48) Kosaki et al.(1984), Paradis et al.(1988), (49)
preserve wurtzite if they were not buried to greater depths and/or subjected to higher temperatures. Even in young deposits, some primarily precipitated wurtzites have changed to the stable cubic phase (sphalerite) over a geologic period. In fact, pseudomorphic texture suggesting the transformation of primary wurtzite to sphalerite has been observed frequently in zinc-rich ores from both ancient (Tertiary age) and modern deposits (e.g., Behre et al., 1937; Imai, 1941, 1978; Paradis et al., 1988). This instability of wurtzite explains why wurtzite is found only in relatively young deposits.

Natural wurtzite occurs commonly as radial or fibrous aggregate forms, and exhibits heterogeneous compositions. As it is stated in the earlier section, such features probably indicate that the wurtzite precipitated from solutions of very high degrees of supersaturation (e.g., Sunagawa, 1984). Because the supercooling of fluid caused by rapid mixing of hydrothermal fluid with cold seawater should cause a high degree of supersaturation with respect to sphalerite and wurtzite, radial and fibrous minerals such as wurtzite are likely to form in submarine-type deposits. A similar process of supercooling has been postulated for some shallow subaerial deposits, such as the Bolivian-type polymetallic ore deposits (Grant et al., 1980), where meteoric water appears to have mixed with hotter hypersaline fluid during ore mineralizations. All of the above features suggest that wurtzite is a metastable phase precipitated from solutions that attained supersaturation with respect to wurtzite due to drastic changes in the physicochemical parameters. This suggestion is compatible with the results obtained for our experimental study.

Conclusions

Wurtzite was produced at 300° and 250°C in the hydrothermal transporting experiments using a zinc-rich solution and synthetic sphalerite crystals as starting materials. Our experimental results suggest that the solubility of wurtzite is higher than that of sphalerite, and that wurtzite precipitation is favored by the rapid cooling of highly supersaturated fluids. Precipitation of wurtzite from highly supersaturated conditions explains why wurtzite formed usually exhibits radial and fibrous textures.

In nature, the occurrence of fibrous wurtzite appears to be limited to geologically recent deposits formed under either shallow-subaerial or submarine conditions. This phenomenon may lead to an interpretation that wurtzite from hydrothermal ore deposits is a metastable product formed by drastic physicochemical changes in the fluids.

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MINING GEOLOGY:


350°～250℃におけるウルツ鉱および隕亜鉛鉱の熱水合成

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要旨：出発物質に隕亜鉛鉱を用い、温度勾配熱水法により350°, 300°および250℃でウルツ鉱ならびに隕亜鉛鉱の熱水合成が試みられた。亜鉛を含む溶液（1m ZnCl₂ + 1m NH₄Cl）が熱水媒体として用いられた場合、300°および250℃の実験においてのみ繊維状ウルツ鉱が隕亜鉛鉱とともに生成されたが、亜鉛を溶存しない溶液（1m NH₄Cl）を用いた実験では隕亜鉛鉱のみが生じた。また、ウルツ鉱の生成は出発物質あるいは隕亜鉛鉱の組成や過剰亜鉛、過剰マンガンの添加により変化させた。これらの結果はウルツ鉱の溶解度が亜鉛鉛鉱のそれに比べて高いと判断する熱力学的予測と一致する。

熱水性鉱床におけるウルツ鉱の産出に関する包括的な文献調査により、ウルツ鉱は相対的に若い年代である。