High cadmium contents of sphalerites from major tungsten deposits in Japan

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Abstract

Cadmium contents of sphalerites are invariably higher than 0.9 wt% from both the vein-type and skarn-type major tungsten deposits at Kaneuchi, Ohtani, Takatori, Fujigatani, Kiwada, and Kuga mines. The contents are high compared with those of most natural sphalerites. Sphalerites from the quartz veins that intersect the skarns of the Fujigatani and Kiwada deposits are higher in cadmium contents than those from the skarns of the same deposits. Considering that tungsten mineralization in the Fujigatani and Kiwada deposits is closely related to the formation of quartz veins, it is likely that high cadmium contents of sphalerites have an intimate genetical relationship with tungsten mineralization in these deposits. Sphalerite from the quartz veins of the Suho ore body of the Kuga deposit is higher in cadmium content than that from the quartz veins of the Ideno-oku ore body of the same deposit. As the ore grade of tungsten in the Suho ore body seems to be higher than that in the Ideno-oku ore body, the higher cadmium content of sphalerite from the Suho ore body also supports the close relationship between cadmium content of sphalerite and tungsten mineralization.

Fluid inclusion data for the Kiwada and Kuga deposits suggest that the temperatures of the hydrothermal solutions do not significantly affect the cadmium contents of sphalerites from these deposits. It is suggested that high activity ratios of $\text{Cd}^{2+}/\text{Zn}^{2+}$ in the hydrothermal solutions are important as the cause of the enrichment of cadmium in sphalerite, and that these are characteristic for major tungsten deposits in Japan.

Introduction

Cadmium is one of the minor elements substituting for zinc in sphalerite (*e.g.*, Vaughan and Craig, 1978). Mookherjee (1958) showed that the cadmium contents of most natural sphalerites range from 0.1 to 0.5 wt%. Recently it has been shown that the cadmium contents of sphalerites from several tungsten-producing skarn deposits are higher than those from other-metal producing skarn deposits in Japan (Shimazaki and Shimizu, 1984).

Mineralization of scheelite in the major skarn-type tungsten deposits at Fujigatani, Kiwada, and Kuga in Japan is considered to be closely related to the formation of quartz veins that intersect these skarns (Kuwahara and Nakamura, 1975; Higashimoto,

1977; Nagahara, 1978; Shibue, 1986), Shibue (1987a) discussed that significant amounts of tungsten were transported in the hydrothermal solutions during the formation of quartz veins in the Fujigatani and Kuga deposits. In order to confirm the genetical relationship between tungsten mineralization and the high cadmium contents of sphalerites, it is necessary to compare the cadmium contents of sphalerites from the quartz veins with those from the skarns in these deposits. From this point of view, further compositional data are required for sphalerites from the quartz veins and the skarns of the Fujigatani, Kiwada, and Kuga deposits. The ore grade of tungsten is different among the individual ore bodies of the Kuga deposit (Higashimoto, 1977). Hence, it is also necessary to compare the cadmium contents of sphalerites from the ore bodies with different ore grade of tungsten.

A preliminary examination by Shimazaki and Shimizu (1984) indicates that cadmium contents of sphalerites from the vein-type tungsten deposits at Kaneuchi and Takatori are also high. Their results were, however, shown only as the average values of mole% of CdS. Further compositional data are required for sphalerites from the vein-type tungsten deposits including the Kaneuchi and Takatori deposits.

Partition of cadmium between sphalerite and hydrothermal solution is governed mainly by the precipitation temperature of sphalerite and the activity ratio of $\text{Cd}^{2+}/\text{Zn}^{2+}$ in the hydrothermal solution. Mookherjee (1958) argued that the cadmium contents of sphalerites are not related to their precipitation temperatures based on the following two reasons. First, cadmium contents of sphalerites were not related to the genetic types of the ore deposits, *i.e.*, contact-metasomatic, hypo-mesothermal, and epithermal types. Second, his experiments on the partition of cadmium between sphalerite and solution at 60° and 90°C showed that the temperature has a small effect on the partition coefficients. Such classification of the ore deposits is not directly related to the formation temperatures of the ore deposits, and the partition experiments were performed at low temperatures. It is still necessary, therefore, to examine the effect of the precipitation temperatures of sphalerites. The effect of temperature is discussed by fluid inclusion study in the present paper.

Occurrences of sphalerites

Locality map of the studied deposits is shown in Fig. 1. Locations of the analyzed sphalerites, and the associated minerals are listed in Table 1. Major vein minerals from the Kaneuchi, Ohtani, and Takatori deposits were summarized in Shibue (1986). Vein minerals from the Fujigatani, Kiwada, and Kuga deposits are quartz, muscovite, scheelite, chlorite, calcite, chalcopryite, pyrrhotite, and sphalerite.

Skarn sphalerites from the Fujigatani and Kiwada deposits distribute scatterly in the skarns and show anhedral forms as well as the other skarn sulfides. Sphalerites

FIG. 1. Locality map of the vein-type tungsten deposits at Kaneuchi, Ohtani and Takatori, and the skarn-type tungsten deposits at Fujigatani, Kiwada and Kuga.

TABLE 1. Locations of the analyzed sphalerites, and the coexisting minerals with the analyzed sphalerites.

Location	Coexisting minerals
<i>Kaneuchi deposit</i> [*] -180 m level of the western veins -240 m level of the central veins -300 m level of the eastern veins	quartz-pyrite-chalcopyrite, pyrrhotite (sometimes), arsenopyrite (sometimes)
<i>Ohtani deposit</i> ^{**} 200 m level, No. 4 veins	quartz-pyrrhotite-chalcopyrite, pyrite (sometimes)
<i>Takatori deposit</i> ^{***} -4 level, No. 7 veins	quartz-galena-chalcopyrite-pyrite, pyrrhotite (sometimes)
<i>Fujigatani deposit</i> Clinopyroxene skarn (Akemidani No. 5 ore body) Quartz veins (Akemidani No. 1 ore body)	chalcopyrite-pyrrhotite, pyrite (sometimes) quartz-chalcopyrite-pyrrhotite
<i>Kiwada deposit</i> Garnet-clinopyroxene skarn (No. 10 ore body) ^{****} Quartz veins (No. 11 ore body) ^{****}	chalcopyrite-pyrite, quartz (sometimes) quartz-chalcopyrite-pyrrhotite
<i>Kuga deposit</i> Quartz veins (Suho ore body) ^{****} Quartz veins (Ideno-oku ore body) ^{****}	quartz-chalcopyrite-pyrrhotite quartz-chalcopyrite-pyrrhotite

*: 0 m level = 150 m above the sea level.

**: 200 m level = The sea level.

***: -4 level = 60 m above the sea level.

****: Samples are used for fluid inclusion study.

often replace skarn silicates (Fig. 2). Skarn sphalerite is associated with quartz in some samples from garnet-clinopyroxene skarn of the Kiwada deposit. Scheelites in the skarns of the Fujigatani and Kiwada deposits also replace skarn silicates.

Analytical method of sphalerite

Chemical analyses of sphalerites were performed with electron probe

FIG. 2. Photomicrographs of sphalerites. (1) Clinopyroxene skarn of the Akemidani No. 5 ore body of the Fujigatani deposits. (2) Garnet-clinopyroxene skarn of No. 10 ore body of the Kiwada deposit. The abbreviations are as follows: Sph, sphalerite; Cpx, clinopyroxene; Sch, scheelite; Gar, garnet; Qtz, quartz. White bars show 0.4 mm.

microanalyzers Model JXA-733A and JXA-5A at an accelerating voltage of 25 kV and a sample current of 20 nA. The standards used are natural chalcopyrite of known compositions for Fe and Cu, synthetic MnS for Mn, synthetic CdS for Cd, and synthetic ZnS for Zn and S. Quantitative corrections of X-ray intensity data are performed by the method of Sweatman and Long (1969). Four specimens from each deposits, at least, were provided for the six-element analyses. These analyses revealed that copper contents of sphalerites are always less than 1.0 wt%, and that the metal/sulfur ratios are close to unity. Thus, three elements, iron, manganese, and cadmium were measured for most of the examined sphalerites. These partial analyses were also intended to examine the relationships between cadmium and iron contents, and between cadmium and manganese contents of sphalerites. Quantitative corrections

of the intensity data were performed according to the method of Chon *et al.* (1981). Deviations of the results by the partial analyses from those by the six-element analyses were within $\pm 10\%$.

Fluid inclusion technique

Samples provided for fluid inclusion study are listed in Table 1. The examined quartz in veins is associated with sphalerite and/or chalcopyrite. Some examined quartz in the skarn of the Kiwada deposit is associated with skarn sphalerite. Fluid inclusions in sphalerites could not be observed by microscope owing to the opacity.

Doubly polished plates, approximately 0.1 mm thick, were prepared from the samples. Heating and cooling measurements are made on a Chaixmeca apparatus (Poty *et al.*, 1976). The heating stage was calibrated relative to the melting temperatures of pure substances and Merck standards. The obtained homogenization temperatures are accurate within $\pm 5^{\circ}\text{C}$ between 150° and 400°C . Repeated measurements of homogenization temperatures showed a reproducibility within $\pm 2^{\circ}\text{C}$. The cooling stage was calibrated relative to the melting temperatures of ice in the NaCl solutions of known concentrations. Repeated measurements of melting temperatures of ice showed a reproducibility within $\pm 0.5^{\circ}\text{C}$ between 0° to -23°C . The uncertainty of determination is correspondingly within ± 1 NaCl eq. wt%.

Results and Discussion

Chemical compositions of sphalerites

Representative analyses of sphalerites, and the averages and standard deviations of mole% of FeS, MnS, and CdS are listed in Table 2. Cadmium contents of sphalerites from the studied deposits range from 0.91 to 5.41 wt%. Sphalerites from major tungsten deposits in Japan, including the vein-type deposits, are high in cadmium contents, compared with the reported values for most natural sphalerites (*e.g.*, Mookherjee, 1958). Vaughan and Craig (1978) stated that the maximum concentration of cadmium in natural sphalerites known so far is about 4.4 wt%. Present analysis on sphalerite from the Fujigatani deposit shows higher concentration of cadmium than the stated value by them.

The average values of CdS mole% of sphalerites in each specimen are plotted against those of FeS and/or MnS (Fig. 3). The variation of cadmium contents of sphalerites from each deposit is smaller than that of iron, and is independent of the variations of iron and manganese contents.

Cadmium contents of sphalerites from the quartz veins of the Fujigatani and Kiwada deposits are higher than those from the skarns of the individual deposits by

TABLE 2a. Representative analyses of sphalerites from major tungsten deposits in Japan.

	1	2	3	4	5	6	7	8	9
Zn	55.05	52.94	56.86	50.63	49.84	53.92	50.41	50.77	53.84
Fe	10.61	10.52	8.22	13.05	10.95	11.24	10.78	12.04	11.66
Mn	0.02	0.33	0.20	0.15	0.08	1.38	0.08	1.46	1.15
Cd	2.84	2.50	1.13	1.79	5.41	1.50	3.92	1.58	0.99
Cu	0.54	0.50	0.05	0.46	0.52	0.05	0.78	0.17	0.03
S	31.91	32.78	32.73	32.98	32.59	32.17	32.91	34.08	32.35
Total	100.97	99.57	99.18	99.06	99.39	100.28	98.89	100.10	100.02
atom%									
Zn	40.9	39.4	42.4	37.6	37.5	39.9	37.8	37.0	39.8
Fe	9.2	9.2	7.2	11.4	9.7	9.8	9.5	10.3	10.1
Mn	0.0	0.3	0.2	0.2	0.1	1.2	0.1	1.3	1.0
Cd	1.2	1.1	0.5	0.8	2.4	0.7	1.7	0.7	0.5
Cu	0.4	0.4	0.0	0.4	0.4	0.1	0.6	0.1	0.0
S	48.3	49.7	49.8	49.9	50.0	48.5	50.4	50.7	48.7

1: -240 m level of the eastern vein of the Kaneuchi deposit, 2: 200 m level of No. 4 vein of the Ohtani deposit, 3: -4 level of No. 7 vein of the Takatori deposit, 4: Clinopyroxene skarn of the Akemidani No. 5 ore body of the Fujigatani deposit, 5: Quartz vein of the Akemidani No. 1 ore body of the Fujigatani deposit, 6: Garnet-clinopyroxene skarn of No. 10 ore body of the Kiwada deposit, 7: Quartz vein of No. 11 ore body of the Kiwada deposit, 8: Quartz vein of the Suho ore body of the Kuga deposit, 9: Quartz vein of the Ideno-oku ore body of the Kuga deposit.

TABLE 2b. FeS, MnS, and CdS moist of sphalerites.

	1*	2*	3*	4*	5*	6*	7*	8*	9*
n**	400	64	324	10	8	71	10	227	81
FeS***	17.49	17.74	14.54	18.90	19.52	18.29	19.39	20.37	19.22
S.D.****	0.77	0.46	0.98	0.69	0.29	0.52	0.71	0.52	0.54
MnS***	0.20	0.38	0.61	0.38	0.23	1.78	0.17	1.93	1.81
S.D.****	0.07	0.06	0.16	0.05	0.06	0.17	0.04	0.13	0.19
CdS***	2.55	2.19	0.95	1.54	4.20	1.10	3.42	1.62	0.88
S.D.****	0.16	0.15	0.08	0.11	0.26	0.14	0.20	0.13	0.12

*: Numbers denote the same localities as in TABLE 2a.

** : Numbers of analyzed grains.

***: Average values.

****: Standard deviations.

about 2.7 and 2.3 CdS mole% (Table 2b), respectively. The quartz veins are considered to be related with tungsten mineralization in these deposits. Thus, it is likely that cadmium contents are high in sphalerites related with tungsten mineralization. Cadmium content of sphalerite from the Suho ore body of the Kuga deposit is higher than that from the Ideno-oku ore body of the same deposit. The ore grade of tungsten in the Suho ore body is considered to be higher than that in the Ideno-oku ore body from the discussions by Higashimoto (1977) and Matsueda *et al.* (1981). Present result also agrees well with the statement given above.

FIG. 3. The relations between CdS mole% and FeS mole% (A) and CdS mole% and MnS mole% (B). Symbols are common to (A) and (B).

Fluid inclusion data on the Kiwada and Kuga deposits

Primary fluid inclusions in quartz from the Kiwada and Kuga deposits are liquid-rich two-phase ones (Fig. 4). Frequency diagrams on homogenization temperature data and salinity data for the Kiwada deposit are shown in Figs. 5 and 6, respectively. Homogenization temperatures of primary fluid inclusions in quartz from No. 10 ore body and vein quartz from No. 11 ore body of the Kiwada deposit range

FIG. 4. Photomicrographs of fluid inclusions. (1) Quartz replacing garnet from the garnet-clinopyroxene skarn of No. 10 ore body of the Kiwada deposit. (2) Vein quartz from No. 11 ore body of the Kiwada deposit. (3) Vein quartz from the Suho ore body of the Kuga deposit. (4) Vein quartz from the Ideno-oku ore body of the Kuga deposit. White bars show 0.05 mm.

from 299° to 181° and from 298° to 210°C , respectively. Salinities of inclusions from No. 10 and No. 11 ore bodies range from 12 to 4 and from 12 to 2 NaCl eq. wt%, respectively. Homogenization temperatures of primary fluid inclusions in vein quartz from the Suho and Ideno-oku ore bodies of the Kuga deposit range from 373° to 196° and from 372° to 197°C , respectively (Fig. 7). Salinities of the inclusions from the both ore bodies range from 12 to 2 NaCl eq. wt% (Fig. 8). Shibue (1987b, 1988) summarized the previous fluid inclusion data for tungsten deposits in Japan. Homogenization temperature data for the Kaneuchi, Ohtani, and Takatori deposits were shown to be from 337° to 151°C , from 375° to 164°C , and from 350° to 150°C , respectively. Salinity data for these vein-type deposits were shown to be less than 10 NaCl eq. wt%. Thus, present data agree well with the previous data for the vein-type deposits.

The homogenization temperature data for quartz, which replaces garnet and is associated with sphalerite from No. 10 ore body (sample is shown in Fig. 2), are similar to those for vein quartz from No. 11 ore body. Homogenization temperature and salinity data for quartz from No. 10 ore body agree well with those for vein quartz

FIG. 5. Homogenization temperature data for the Kiwada deposit.

from No. 11 ore body.

Frequency diagrams on homogenization temperature data for the Suho and Ideno-oku ore bodies display the peaks at 290 $^{\circ}$ and 260 $^{\circ}\text{C}$, respectively (Fig. 7). Salinity data for the Suho and Ideno-oku ore bodies show the peaks at 7 and 6 NaCl eq. wt%, respectively (Fig. 8). The difference in the precipitation temperature is within a few tens of degrees*.

Sphalerite in the skarn of Fujigatani deposit can be assumed to be precipitated at the similar temperature to skarn scheelite from the same deposit because both sphalerite and scheelite replace skarn silicates. Shibue (1987a) discussed that vein scheelite precipitated at the similar temperature to skarn scheelite from the Fujigatani deposit. These indicate that vein sphalerite was also precipitated at similar temperature to skarn sphalerite.

FIG. 6. Salinity data for the Kiwada deposit.

*: When homogenization temperature and salinity data are 290 $^{\circ}\text{C}$ and 7 NaCl eq. wt%, and 260 $^{\circ}\text{C}$ and 6 NaCl eq. wt%, the corrected temperatures at 1 kb pressure (Shibue, 1988) are 379 $^{\circ}$ and 347 $^{\circ}\text{C}$, respectively (Potter and Brown, 1977). These temperatures agree well with the estimated precipitation temperatures, 412 $^{\circ}$ to 351 $^{\circ}\text{C}$, for sphalerite-galena pair from their sulfur isotopic compositions (Sato, 1980).

FIG. 7. Homogenization temperature data for the Kuga deposit.

FIG. 8. Salinity data for the Kuga deposit.

Present inclusion data as well as those by Shibue (1987a) suggest that the temperatures of the hydrothermal solutions do not significantly affect the cadmium contents of sphalerites. The enrichment of cadmium in sphalerites can, then, be ascribed to the high activity ratio of $\text{Cd}^{2+}/\text{Zn}^{2+}$ in the hydrothermal solution. High cadmium contents of sphalerites should have an intimate genetical relationship with tungsten mineralization in Japan.

Conclusion

Sphalerites from the vein-type tungsten deposits at Kaneuchi, Ohtani, and Takatori as well as those from the skarn-type tungsten deposits at Fujigatani, Kiwada, and Kuga contain more than 0.9 wt% of cadmium, which are high in cadmium contents compared with most natural sphalerites (*e.g.*, Mookherjee, 1968). Cadmium contents of sphalerites from each deposit are independent of iron and manganese contents.

Not only does the present study reinforce the previous finding by Shimazaki and Shimizu (1984) and complete the compositional data for sphalerites from the vein-type tungsten deposits, but also the present study shows the variations of cadmium contents of sphalerites within the individual deposits at Fujigatani, Kiwada, and Kuga mines. Higher cadmium contents of sphalerites are shown to be related with more intense mineralization of tungsten in the Fujigatani, Kiwada, and Kuga deposits.

Fluid inclusion data for these deposits, including the data for the Fujigatani deposit (Shibue, 1987a), show that the temperatures of the hydrothermal solutions do

not significantly affect the cadmium contents of sphalerites. It is suggested that high cadmium contents of sphalerites have an intimate genetical relationship with tungsten mineralization in Japan.

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