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Iron, Manganese and Cadmium Contents of Sphalerites and their Genetical Implications to Hydrothermal Metallic Ore Deposits in Korea

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Abstract: Compositional variation of sphalerites from various hydrothermal metallic ore deposits in Korea were investigated in mine and local, and regional scale. The sphalerites were partially analyzed for iron, manganese, and cadmium by using an electron probe microanalyzer(EPMA).

The contents of iron and cadmium in sphalerites collected from the Weolam deposit of the No. 1 Yeonhwa mine are not variable with increase of depth, but manganese content is highly variable. Sphalerites from lead-zinc deposits which are geologically associated with hypabyssal and effusive activity are characterized by high manganese (more than 1.0 MnS mole %) and low cadmium contents (less than 0.5 CdS mole %).

Relatively manganese rich sphalerites are found in the deposits where sphalerites are enriched in iron content. Variation of cadmium content is very limited compared with that of manganese content. Sphalerites from most tungsten and some gold-silver deposits are remarkably high in cadmium content, but most of base metal and iron deposits are low in cadmium content. Cadmium content in sphalerites which occur in the metallic ore deposits genetically associated with plutonic activity shows a tendency to high variation. Available amounts of cadmium in sphalerites could be originated from the initial enrichment during the magmatic and postmagmatic processes.

INTRODUCTION

Sphalerite is the most common ore mineral of zinc occurring in hydrothermal ore deposits. In nature, it is very rare to find out the pure sphalerite(ZnS). The principal substituents for zinc in the sphalerite structure are iron, manganese and cadmium etc. in the general order of decreasing amounts. The contents of iron, manganese and cadmium in sphalerites have been studied extensively (Fleischer, 1955; Takahashi, 1963; Boyle & Jambor, 1963; Ivanov, 1964; Craig et al., 1984). Electon probe microanalysis(EPMA) has been established to be a useful technique for the determination of the above element contents in sphalerite since classical works (Williams, 1967). Recently partial analytical method by using EPMA has been applied to determine those three elements such as iron, manganese and cadmium in sphalerites(Chon et al., 1981; Chon, 1982; Shimazaki & Shimizu, 1984; Mizuta et al., 1984).

In the present paper, compositional variation of sphalerites collected from various hydrothermal metallic ore deposits in Korea was reviewed from the regional viewpoint, and some new data of sphalerite composition were presented in mine and local scale.

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SAMPLE PREPARATION AND ANALYTICAL METHOD

Brief descriptions on geology and ore deposits of the studied mines are listed in Chon (1982) and Shimazaki et al. (1984) including locality maps of the mines.

Three kinds of polished sections were prepared for the analytical work by EPMA as described in Chon et al. (1981) and Chon (1982). The first one is made from concentrates (mill products) collected from the mineral dressing plant of the mine, and the second one is composite polished sections prepared by several crushed hand specimens. The last third one is normal polished sections, and several polished sections were used to identify sphalerite grains in order to determine the compositional variation of sphalerites as many as possible.

Contents of Fe, Mn, and Cd in sphalerites were determined by a partial analysis method of EPMA. Detailed analytical procedures are found elsewhere (Chon et al., 1981; Chon, 1982; Shimazaki & Shimizu, 1984; Mizuta et al., 1984).

RESULTS AND DISCUSSION

The Fe, Mn, and Cd contents of shpalerites determined by EPMA were recalculated to FeS, MnS and CdS mole percent. The arithmetic mean, standard deviation, and range of these components were presented in Chon (1982) and Mizuta et al. (1984). Most of the compositional data of sphalerites from Pb-Zn-Cu, Fe, and W-Mo-Bi ore deposites, and those of sphalerites from Au-Ag ore deposits were compiled from Chon (1982) and Mizuta et al. (1984), respectively. Compositional variation of sphalerites in mine and local scale will be also discussed.

Weolam deposit of the No. 1 Yeonhwa mine (mine scale)

Analytical results of sphalerites taken from the Weolam deposit of the No. 1 Yeonhwa Pb-Zn mine are listed in Table 1. The Weolam deposit was major producer of lead and zinc at the No. 1 Yeonhwa mine. Eight composite polished sections were made from several crushed sulfide ore specimens which were collected from eight underground levels of the mine (from 0m level to -480m level). Abundant, common, and rare sulfide minerals occurring at each level of the Weolam orebodies are listed in Table 2. In general, pyrrhotite is abundant at the deeper levels (lower than -120m level), and pyrite and galena are abundant at the upper levels.

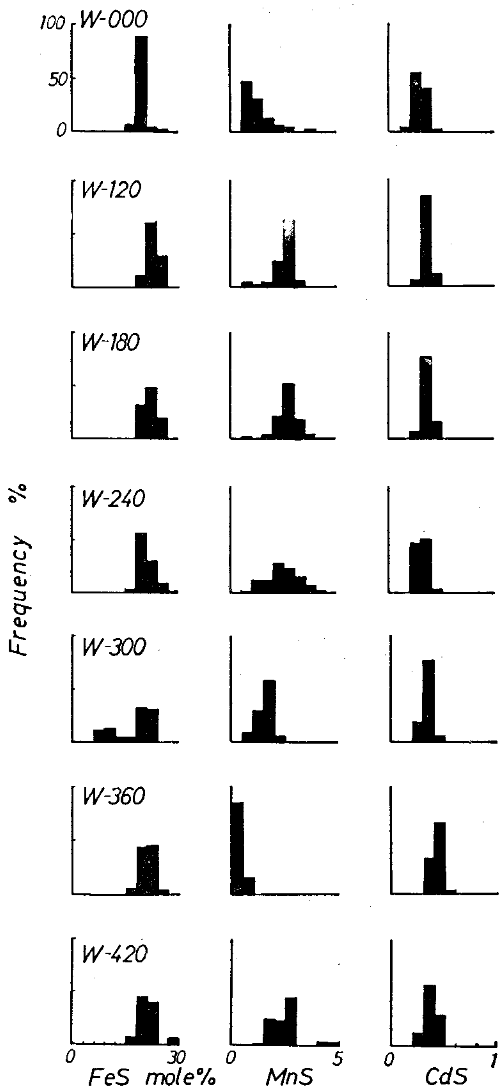

Fig. 1 Distribution of FeS, MnS and CdS contents in sphalerites from the Weolam deposit of the No. 1 Yeonhwa mine with increase of depth (W-000 and W-420 mean zero and -420 meter level, respectively).

Table 1 Contents of Fe, Mn, and Cd in sphalerites of the Weolam deposit at the No. 1 Yeonhwa mine.

Level	No. of analyzed points	FeS(mole%)			MnS(mole%)			CdS(mole%)		
		Mean	C.V.(%)	Range	Mean	C.V.(%)	Range	Mean	C.V.(%)	Range
W-000	50	19.4	6.2	16.5~24.3	1.28	49.2	0.57~3.81	0.28	21.4	0.13~0.39
W-120	55	23.0	7.1	18.9~25.9	2.54	17.7	0.91~3.07	0.35	11.4	0.28~0.44
W-180	56	22.0	9.1	18.2~26.6	2.67	19.8	0.86~3.99	0.35	11.4	0.26~0.47
W-240	60	20.9	10.3	17.2~27.7	2.42	30.5	0.94~4.07	0.31	16.1	0.21~0.45
W-300	(25) 82 (57)	(9.62) 17.2 (20.5)	(19) 30.5 (6.1)	(6.87~13.1) 6.8~23.9 (17.0~23.9)	1.54	20.1	0.89~2.38	0.33	12.1	0.27~0.44
W-360	99	21.0	8.5	16.7~24.3	0.42	21.4	0.09~0.59	0.41	9.7	0.35~0.52
W-420	85	20.8	11.5	17.3~28.0	2.45	23.6	1.49~4.58	0.36	13.8	0.27~0.48
Average	—	20.6	—	—	1.90	—	—	0.34	—	—

C.V.(=Coefficient of variation)=(Standard deviation)/(Mean)×100%

Table 2 Ore mineralogy of Weolam orebodies.

Polished section	Abundant	Common	Rare	Remark
W-000 (m)	py*	sph, gn	po	0m level
W-120	po	sph, gn	py	-120m level
W-180	po	sph, gn, py		-180m level
W-240	py	sph, po	gn	-240m level
W-300	po	sph	gn	-300m level
W-360		py, po, sph	cpy	-360m level
W-420		sph, po, py	gn	-420m level
W-480 (m)	po	py, sph		-480m level

* py(pyrite), po(pyrrhotite), sph(sphalerite), gn(galena), cpy(chalcopyrite)

The mean FeS contents of the orebodies on each level range from 19.4 to 23.0 mole%, and show normal distribution (Table 1 and Figure 1). But in case of -300m level(W-300), FeS content shows two mode of population; the first group ranges from 6.87 to 13.1 mole% with average of 9.62 mole%, and the second group from 17.0 to 23.9 mole% with average of 20.5 mole% (Figure 1). It was noticed under the microscope that sphalerites with inclusions of chalcopyrite and pyrrhotite contain high amounts of iron(the second group), while sphalerites without dots of chalcopyrite and pyrrhotite comprise low amounts of iron(the first group). In general, the FeS contents of sphalerites are not so variable with increase of depth, and the coefficient of variation is rather small (less than 12%).

MnS contents in sphalerites vary from 0.42 mole% to 2.67 mole% with average of 1.90 mole%. Sphalerites from Zn-Pb deposits, for example, No. 1 Yeonhaw, No. 2 Yeonhwa and Ulchin Pb-Zn mines of the Taebaegsan area, are characterized by high MnS and low CdS contents (Chon et al., 1981). MnS contents are very low (averaging 0.42 mole %) at the -360m(W-360) level, and CdS contents are relatively high compared with those at the other levels (Table 1). The coefficient of variation of MnS contents is very high at 0m level (49.2%).

The mean CdS contents in sphalerite range from 0.28 to 0.41 mole % with average of 0.34 mole %. Generally the range of CdS contents in sphalerite is very limited. As shown in Figure

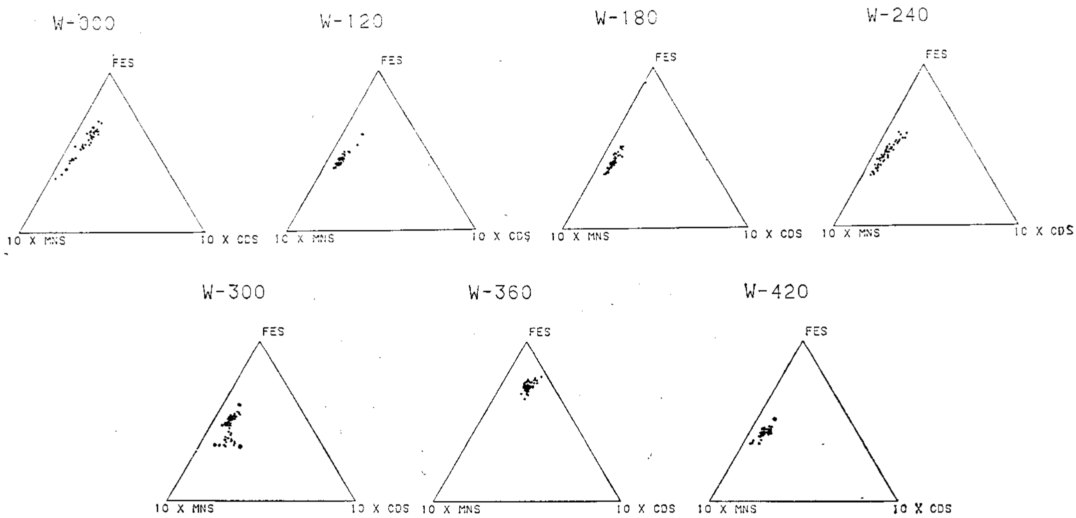

Fig. 2 Ternary relationship of FeS-MnS-CdS contents in sphalerites from the Weolam deposit of the No. 1 Yeonwha mine with increase of depth.

1, CdS contents are concentrated around 0.4 mole %.

Ternary relationship of FeS-MnS-CdS contents is shown in Figure 2. As discussed above, compositional variation of sphalerites at each level is very similar except -360m level (W-360 in Figure 2).

No. 1 Yeonhwa, No. 2 Yeonhwa, and Ulchin Pb-Zn ore deposits (local scale)

Composition of shalerites from No. 1 Yeonhwa, No. 2 Yeonhwa and Ulchin Pb-Zn ore deposits is presented in Table 3. The three mines are spatially close in the Taebaegsan area and their deposits are genetically similar.

Frequency distribution of Fe, Mn, and Cd contents in sphalerites is relatively similar (Fig. 3). In other words mean FeS contents in sphalerites range from 19.6 (No. 2 Yeonhwa) to 21.3 mole % (No. 1 Yeonhwa), and mean CdS contents in sphalerites from 0.36 (No. 2 Yeonhwa) to 0.39 mole % (No. 1 Yeonhwa). FeS and CdS contents in sphalerites from the Ulchin mine are 20.4 and 0.38 mole %, respectively (Table 3). Manganese is relatively enriched in sphalerites

Table 3 Fe, Mn, and Cd contents in sphalerite from No. 1 Yeonhwa, No. 2 Yeonhwa, and Ulchin Pb-Zn ore deposits.

Comp. \ Mine		No. 1 Yeonhwa	No. 2 Yeonhwa	Ulchin
FeS (mole %)	Mean	21.3	19.6	20.4
	C.V.	10.6	10.7	13.2
	Range	17.2~28.5	13.0~24.7	10.8~24.3
MnS (mole %)	Mean	1.39	1.79	2.07
	C.V.	48.7	37.7	66.9
	Range	0.49~3.04	0.64~3.56	0.18~6.86
CdS (mole %)	Mean	0.39	0.36	0.38
	C.V.	16.4	15.8	33.1
	Range	0.24~0.53	0.20~0.49	0.01~0.53

C.V. (=Coefficient of variation) = (Standard deviation) / (Mean) × 100%

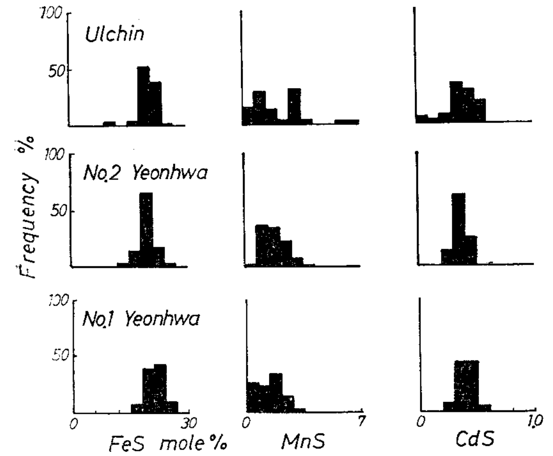

Fig. 3 Frequency distribution of FeS, MnS and CdS mole % in sphalerites from the No. 1 and the No. 2 Yeonhwa and the Ulchin mines.

(up to 6.86 MnS mole %) from the Ulchin ore deposits. Mean MnS contents in sphalerites from the above three ore deposits range from 1.39 to 2.07 mole %. Variation of MnS in sphalerites from the Ulchin ores is very high (coefficient of variation, 67%). Scatter diagrams of Fe-Mn, Mn-Cd and Cd-Fe are shown in Figure 4, and ternary relationship of Fe-Mn-Cd concents in sphalerites in Figure 5. High Fe and Mn, and low Cd contents in sphalerites are characteristic in these ore deposits. In particular, distribution of FeS and CdS contents in sphalerites is concentrated around 20 and 0.4 mole %, respectively, but MnS contents are relatively variable.

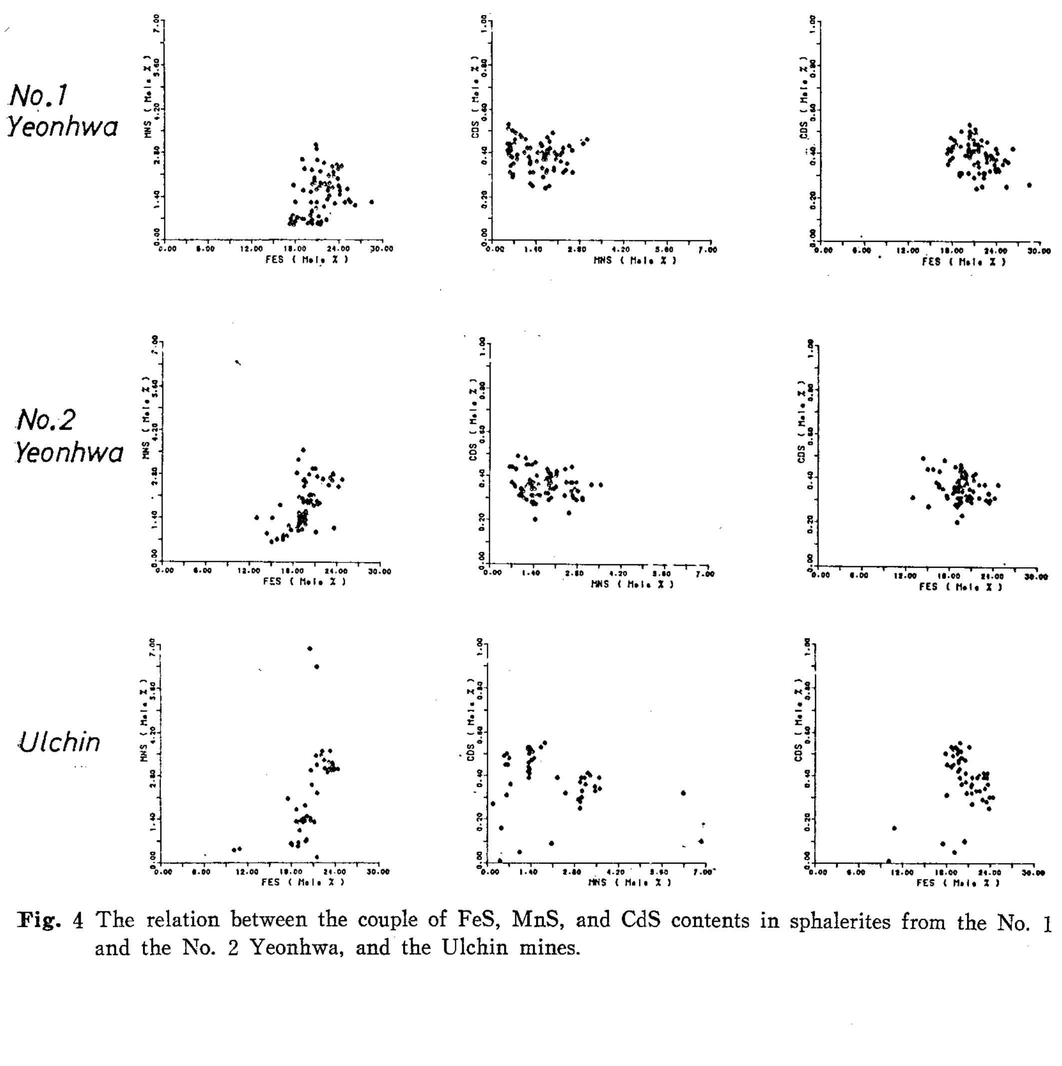

Fig. 4 The relation between the couple of FeS, MnS, and CdS contents in sphalerites from the No. 1 and the No. 2 Yeonhwa, and the Ulchin mines.

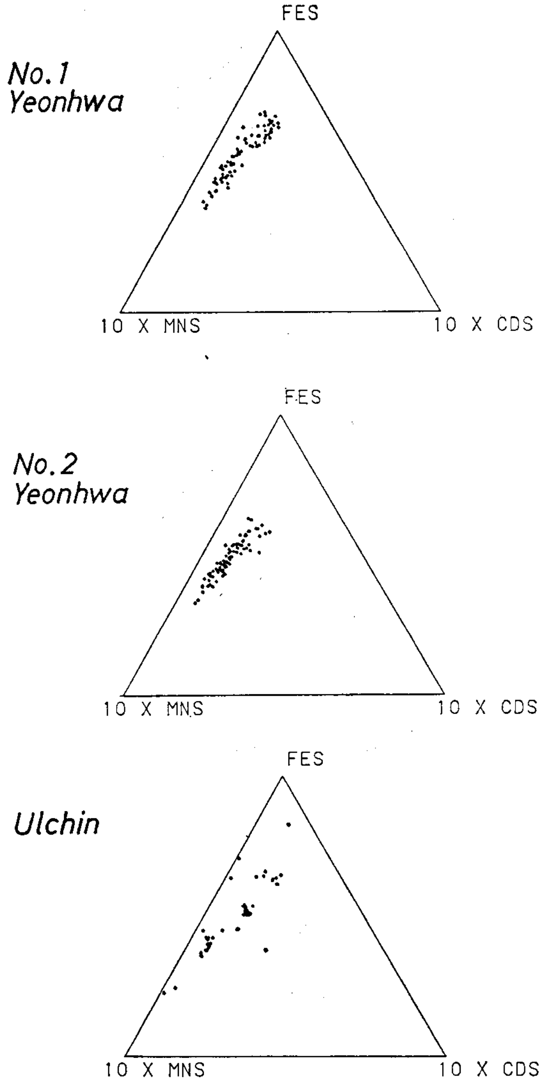

Fig. 5 Ternary relationship of FeS, MnS and CdS contents in sphalerites from the No. 1 and the No. 2 Yeonhwa and the Ulchin mines.

Compositional variation of sphalerites (regional scale)

A total of 42 metallic mines comprising W-(Mo-Bi), Cu-(Pb-Zn), Zn-Pb-(Cu), Fe, Ag and Au mines were concerned in regional scale to determine the variation of Fe, Mn and Cd contents in sphalerites.

Interrelation of mean FeS and MnS contents in sphalerites is plotted in Figure 6. In general, the FeS contents seem to be proportional to the

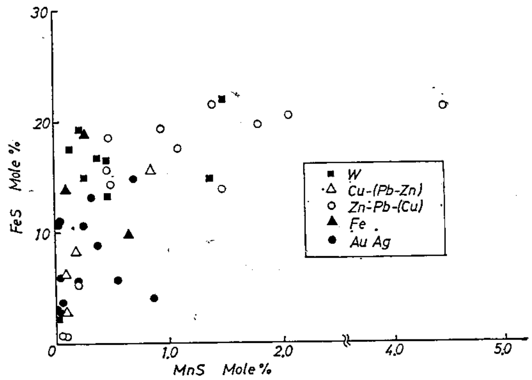

Fig. 6 The relation between mean MnS and FeS contents in sphalerites collected from 42 various metallic ore deposits.

MnS contents. The relationship between mean CdS and MnS contents is shown in Figure 7. Dotted line in Figure 7 means the average value of CdS mole % in sphalerites (up to 0.5 mole %) from hydrothermal metallic ore deposits (Mookherjee, 1962; Shimazaki & Shimizu, 1980). Most of Cu-(Pb-Zn), Zn-Pb-(Cu), and Fe deposits are characterized by low CdS contents in sphalerites (less than 0.5 mole %). Most of tungsten deposits and some gold deposits (Samgwang, Gubong, and Gyeolseong Au mine) have high CdS contents in sphalerite (more than 0.5 mole %). Tungsten deposits include Daewha, Sangdong, Susan, Weolak, Ilgwang, and Garisan mines. The MnS contents in sphalerites show two modes of distribution: one is relatievly high MnS (more than 1.0 MnS mole %) and the other is low MnS (less than 1.0 mole %). It is noteworthy that sphalerites from Zn-Pb-(Cu) deposits contain variable amounts of manganese ranging from 0.05 mole % (Sambo mine) to 4.53 mole % (Janggun mine). Compared with other mines, MnS contents in sphalerites from Janggun, Ulchin, Sinyemi, No. 1 Yeonhwa, No. 2 Yeonhwa and Younggug Zn-Pb mines have high range more than 1.0 mole %. Such results correspond to the abundance of manganese minerals in orebodies or skarns of these deposits.

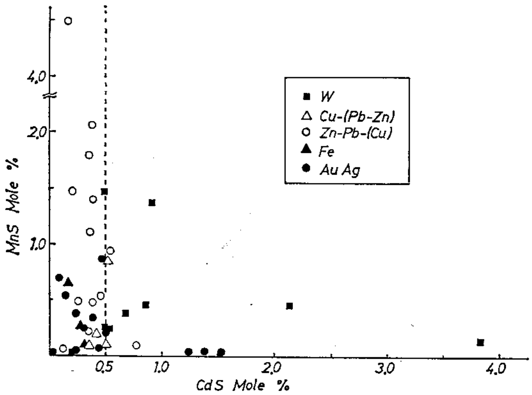

Fig. 7 The relation between mean CdS and MnS contents in sphalerites collected from 42 various metallic ore deposits. Dotted line means the average value of CdS mole % in sphalerites(~0.5 mole %) suggested by Mookherjee (1962), and Shimazaki and Shimizu(1980).

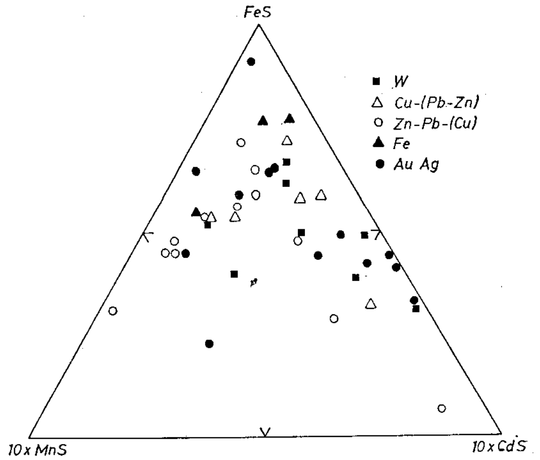

Fig. 8 Ternary relationship of FeS, MnS, and CdS contents in sphalerites from 42 various metallic ore deposits.

All of Cu, Fe, Au, Ag, and W deposits are characteristic in low MnS contents except two W deposits such as Susan and Cheongyang mines.

Ternary relationship of FeS-MnS-CdS contents in sphalerites is plotted in Figure 8. As discussed above, sphalerites from Cu-(Pb-Zn), Zn-Pb-(Cu), and Fe deposits are relatively depleted in cadmium, whereas sphalerites from W and some Au mines are enriched in Cd. MnS contents are relatively variable in sphalerites from base metal deposits.

Considering the related igneous rocks of the studied ore deposits, low Mn contents in sphalerites seem to be associated with plutonic igneous activity, and low Cd contents tend to be associated with hypabyssal to effusive activity (Figure 9). But Cd contents in sphalerites from the studied ore deposits which are geologically associated with plutonic activity are highly variable.

Source of cadmium in sphalerites

Cadmium contents in sphalerites occurring in W ore deposits are exceptionally high, ranging up to 3.83 mole % CdS in the Daewha mine.

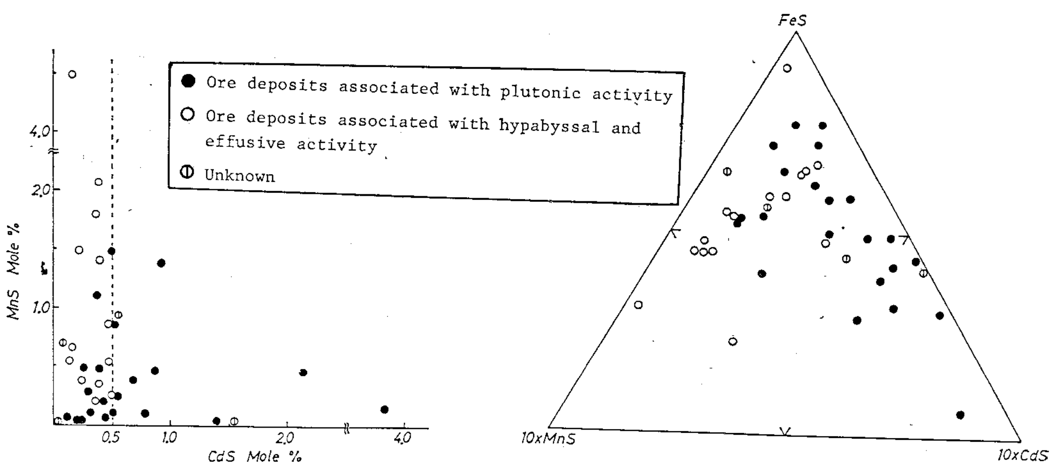

Fig. 9 The relationship of CdS-MnS, and FeS-MnS-CdS contents in sphalerites with reference to the related igneous rocks of the studied 42 ore deposits.

Enrichment of cadmium in sphalerites in tungsten ore deposits has been suggested as one of impressive characteristics (Chon et al., 1981; Chon, 1982; Mizuta et al., 1984). Similar compositional variation of sphalerite was also recognized in sphalerites from some tungsten skarns in Japan (Shimazaki & Shimizu, 1980, 1984). Vlasov (1966) also has pointed out that high cadmium contents are characteristic of sphalerites from some Soviet Central Asian tungsten and tungsten-tin skarn deposits, although he wondered if this fact is a general feature of tungsten mineralization. Cadmium contents in sphalerites from the Chojlla W-Sn and Enramada W mines in northern Bolivia are exceptionally high ranging up to 2.09 and 1.17 mole % CdS, respectively (Harwood, 1983, personal communication).

The reason of the cadmium enrichment is not yet clearly solved physicochemically, but Shibue et al. (1984) discussed the relationship between the Cd contents in sphalerite and Cl concentration in hydrothermal solution. Boyle & Jambor (1963) already recognized the the Cd content of the sphalerites in the Pb-Zn-Ag lodes of the Keno Hill area, Yukon, Canada, varies over a narrow range (0.71−1.16 Cd%), and suggested that neither the presence of major elements nor temperature has affected the incorporation of cadmium, and that the availability of the element in the solutions or the diffusion currents is the main consideration in the uptake of Cd during crystallization of Keno Hill sphalerites.

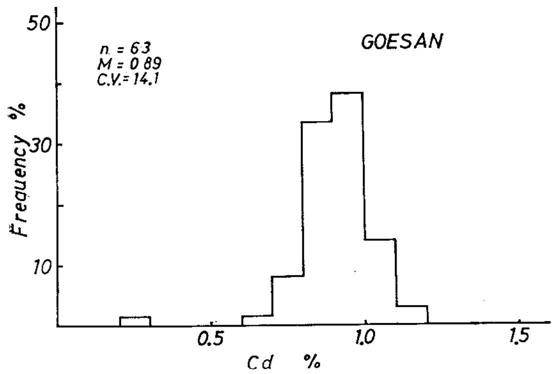

Fig. 10 Frequency distribution of cadmium content in sphalerites from the Goesan quartz veins with wall rocks of coal shale. n: number of analyzed points, M: mean value of analyzed data, C.V.: coefficient of variation (%).

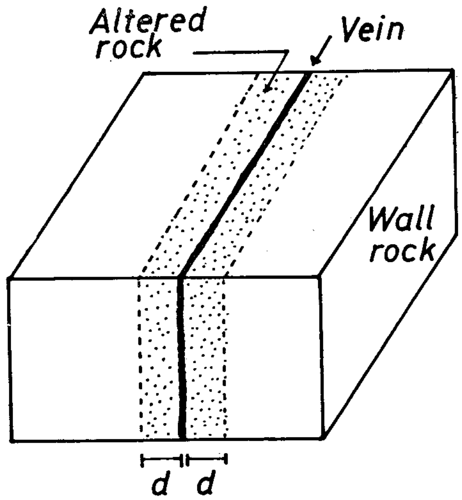

Fig. 11 Brief model of vein-type ore deposit surrounded by alteration halo in wall rocks. d means the lateral width of the leached part of the wall rock.

Probability of host rocks as a source of cadmium in sphalerite is not feasible because abundance of cadmium in most of rocks in the earth's crust is only 0.1 to 0.2ppm Cd. But Boyle (1969) proposed a possibility that the cadmium in sphalerite from the Keno Hill area, Yukon, diffused from the country rocks, particularly the graphitic sediments. Sphalerites in coals from the Illinois basin are generally cadmium rich, ranging up to 2.18% Cd (Hatch et al., 1976). It is interesting to note that the sphalerites collected from the Goesan low-grade uranium-bearing coal shale (or black shale) are enriched in Cd contents, ranging up to 1.15% Cd (Figure 10). The sphalerites coexisting with pyrite and pyrrhotite occur in quartz veins with host rocks of coal shale.

Abundance of cadmium in shale is only 0.2~0.3 ppm, but in bituminous shale cadmium is enriched up to 500ppm (Wakita & Schmitt, 1970). If a quartz vein of 1 m thickness introduced in the coal shale contains 0.5% sphalerite, and the extension of the vein is 100m with dipping extension of 50m (refer to Figure 11), then

(total volume of the vein) $= 100m \times 1m \times 50m$

$= 5,000m^3$

if specific gravity of the vein is 2.7, then

(total weight of the vein) $= 5,000 \times 2.7$

$= 13,500$ M/T

ZnS grade is 0.5% and Cd content in ZnS is 1.2%,

(total weight of Cd) $= 13,500 \times 0.005 \times 0.012$

$= 0.81$ M/T

if the cadmium were diffused from the country rocks (coal shale),

0.81 M/T $= 500/1,000,000 \times 2.7 \times$ (rock volume)

therefore,

(rock volume) $= 600m^3$

$2d \times 100m \times 50m = 600$

$d = 0.06m$

$= 6cm$

where, d is the lateral width of the leached part of black shale.

As shown in the above example, leaching possibility of cadmium from black shale seems to be highly possible, because the leached lateral part of the host rock is only 6 cm (in general, the width of alteration halo around hydrothermal veins ranges up to several tens of meters). But in case of granites as host rock, abundance of Cd is only 0.1ppm (Rose et al., 1979) and the calculated d is 300m. In case of limestone host rocks, the calculated d is 857m (mean Cd content in limestone is 0.035ppm). Therefore, it is nearly impossible to consider the source of cadmium as granite or limestone wall rocks. In this case, available amounts of cadmium could be originated from the initial enrichment during the magmatic and postmagmatic processes.

SUMMARY AND CONCLUSION

Compositional variation of sphalerites were investigated in mine and local, and regional scale. Iron, manganese and cadmium contents in sphalerites were determined by partial analytical method of EPMA. The number of analyzed points of sphalerites collected from various hydrothermal metallic ore deposits are generally several tens on each representative polished section in order to compare the distribution of iron, manganese and cadmium contents in sphalerites.

Iron and cadmium contents in sphalerites from the Weolam deposit of the No. 1 Yeonhwa mine are not variable with increase of depth. Their contents are concentrated around 20 FeS and 0.4 CdS mole %, respectively. Manganese content is highly variable with depth.

Variation of sphalerite composition is very similar especially in the No. 1 Yeonhwa, the No. 2 Yeonhwa, and the Ulchin Pb-Zn deposits which formed in spatially close and genetically similar environment. Sphalerites from Zn-Pb-(Cu) deposits geologically associated with hypabyssal and effusive activity are characterized by high manganese (more than 1.0 MnS mole%) and low cadmium contents (less than 0.5 CdS mole %).

From the regional viewpoint, relatively manganese rich sphalerites are found in the deposits where sphalerites are enriched in iron content. Variation of cadmium content is very narrow compared with that of manganese content in each deposit. Sphalerites from most tungsten and some gold-silver deposits are remarkably high in cadmium content, but most of base metal and iron deposits are low in cadmium content. Cadmium content in sphalerites which occur in the metallic ore deposits genetically associated with plutonic activity shows a tendency to high variation.

Available amounts of cadmium in sphalerites could be originated from the initial enrichment during the magmatic and postmagmatic processes. Probability of host rocks as a source of cadmium in sphalerite is not feasible except for the leaching possibility of cadmium from coal shale.

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國內產 閃亞鉛石의 Fe, Mn, Cd含量變化와 熱水金屬鑛床 成因과의 關聯性

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要約：國內의 여러 熱水金屬鑛床에서 採取한 閃亞鉛石의 組成 變化를 鑛山 및 局地的 單位, 그리고 廣域的 單位로 調査하였다. 閃亞鉛石의 Fe, Mn, Cd 含量은 electron probe microanalyzer(EPMA)에 의한 部分分析 方法으로 測定하였다.

第一蓮花鑛山의 月岩鑛床에서 深度別(0m에서 −420m level까지)로 採取한 閃亞鉛石의 경우 Fe, Cd 含量은 深度에 따라 큰 變化가 없는 反面 Mn 含量 變化는 현저하였다. 半深成岩 및 噴出岩의 活動과 成因的으로 關聯된 Zn-Pb 鑛床의 경우 閃亞鉛石은 그 Mn 含量이 높고(MnS 1.0 mole% 以上) Cd 含量이 낮은(CdS 0.5 mole% 以下) 特徵을 보인다.

比較的 Mn含量이 높은 閃亞鉛石은 Fe含量도 높다. 一般的으로 各 鑛床別로 보면 Mn에 比해 Cd 含量 變化는 一定하다. 大部分의 W鑛床과 一部 Au-Ag鑛床에서 產出된 閃亞鉛石의 경우 Cd含量이 현저하게 높으나, 大部分의 base metal 鑛床 및 Fe鑛床에서는 Cd含量이 낮다. 成因的으로 深成岩의 活動과 關聯된 金屬鑛床에서 產出되는 閃亞鉛石의 Cd 含量 變化는 다양한 경향을 나타낸다. 閃亞鉛石中의 Cd 根源은 magma性 乃至는 後 magma性 過程中 原來부터 存在하던 有用 含量에 起因된다고 判斷된다.