

## Freibergite from the Yeonhwa 1 Mine

### 제 1 연화광산에서 산출되는 프라이버자이트

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**ABSTRACT :** Freibergite is found in lead-zinc (-silver) ores from Dongjeom and Myobong are deposits, which were formed at later stage of the Yeonhwa 1 mine mineralization. This mineral is intimately intergrown with galena, pyrrhotite, pyrite, pyrrhotite, alabandite, Mn-bearing magnetite, sphalerite stannite and quartz. Its chemical composition as determined by electron microprobe in WDX shows that it is characterized by relatively high contents of silver up to about 40.5 weight percent Ag and negligible amount of zinc which in some grains is less than the detection limits of microprobe. Also some grains of the freibergite contain appreciable amount of lead up to 1.70 weight percent Pb. The chemical composition of Yeonhwa freibergite has some what peculiar features, which involve marked S-deficiency and Sb-excess compared with formula  $Me_{12}Sb_4S_{13}$ .

**요약 :** 연화 광산 동점 및 묘봉 광체에서 산출되는 프라이버자이트는 후기 광화 시기에 방연석, 피라지라이트, 황철석, 자철석, 알라만다이트, 함망간, 자철석, 섬아연석, 황석석, 석영 등과 밀접하게 공존하고 있다. 화학 조성을 보면 Ag가 최고 40.5 wt%까지 높은 함량을 보이고, Zn은 극소량 또는 microprobe의 측정 한계 이하이다. 어떤 입자들에는 Pb가 최고 1.70 wt % 함유되어 있다. 연화 프라이브자이트의 화학 조성상의 다소 고유한 특성은  $Me_{12}Sb_4S_{13}$ 을 기준으로 할 때 S가 부족하고 Sb가 많이 포함되는 점이다.

## INTRODUCTION

The name "freibergite" was first introduced into the silver-rich variety of tetrahedrite from Freiberg, Germany, containing about 18 percent of Ag by weight. The general formula of freibergite which naturally occurs tetrahedrite-tennantite (fahlore) series is  $(Cu, Ag)_6(Zn, Fe, Cd, Hg, Cu)_2(Sb, As, Bi)_4S_{13}$ . Recently, however, high-silver phase containing up to about 48 weight percent of Ag which is close to the end member composition of the silver analogue of tetrahedrite,

$Ag_6Fe_2Sb_4S_{13}$  (Patrick and Hall, 1983) has been recognized in nature (Riley, 1974; Imai and Lee, 1980).

As will be mentioned later in detail, Riley (1974) has stated that the value of about 20 weight percent of Ag (about 14 atomic percent of Ag) provides a useful division between argentian tetrahedrite and freibergite based upon his study on high-silver tetrahedrite from Mt. Isa mine; i.e., the terms, argentian tetrahedrite and freibergite are restricted to tetrahedrite-like phases containing less than, and more than 20 weight percent of

Ag respectively. Following this division, the present Yeonhwa 1 materials in question belong to "freibergite".

Hall (1972) already stated that there is no valence restriction for the silver substitution, accordingly, the composition of  $\text{Ag}_x(\text{Fe}, \text{Zn})_2\text{Sb}_2\text{S}_3$  for half unit cell is theoretically possible. The occurrence of high-silver tetrahedrite with more than 6.5 Ag atoms per formula unit is quite rare, however, Riley (1974), in his study on Ag-bearing tetrahedrite from Mt. Isa, Queensland, Australia, has found the Ag-rich variety containing up to 46 weight percent of Ag ( $=\text{Cu}_1\text{Ag}_6$ ). Subsequently, from the Janggum mine, Republic of Korea, Imai and Lee (1980) have found the Ag-rich tetrahedrite containing 47.8 weight percent of Ag which represents the highest value ever known. It has a composition  $(\text{Cu}_{0.77}\text{Ag}_{6.14})_{\Sigma 6.91}(\text{Fe}_{1.9}\text{Zn}_{0.20})_{\Sigma 2.15}\text{Sb}_2\text{S}_{12.8}$  ( $\text{Sb}=4$ ), close to the theoretical end member composition of the silver analogue of tetrahedrite  $\text{Ag}_6\text{Fe}_2\text{Sb}_2\text{S}_{13}$ , although most microprobe analyses of tetrahedrites from this mine show  $\text{Ag}<5$  atoms per half unit cell.

With respect to the site occupancy of Ag atoms in synthetic tetrahedrites, Kalbskopf (1972) already suggested that Ag substitution for Cu might start initially at the six Cu atoms in triangular planer site ( $^{\text{III}}\text{Cu}^{+}$ , Cu(2)) (Fig 1), and only when these are "full", silver would displace the four Cu atoms in tetrahedral coordination ( $^{\text{I}}\text{Cu}^{+}$ , Cu(1)).

However, Patrick and Hall (1983), on the basis of examination over three hundred microprobe analyses of Ag-bearing tetrahedrites containing Fe and Zn as the divalent elements, have revealed that most Ag-rich tetrahedrites are also Fe-rich. They also pointed out that the normal upper limit of Ag substitution in  $(\text{Zn}_2\text{Fe}_0)$  tetrahedrite is 2 atoms of Ag per half unit cell, but for Fe-rich tetrahedrites the upper limit becomes higher, to 6.5 atoms of Ag. Referring to the experimental data for the solubility of silver in Fe-rich tetrahedrite given by the increasing contents of

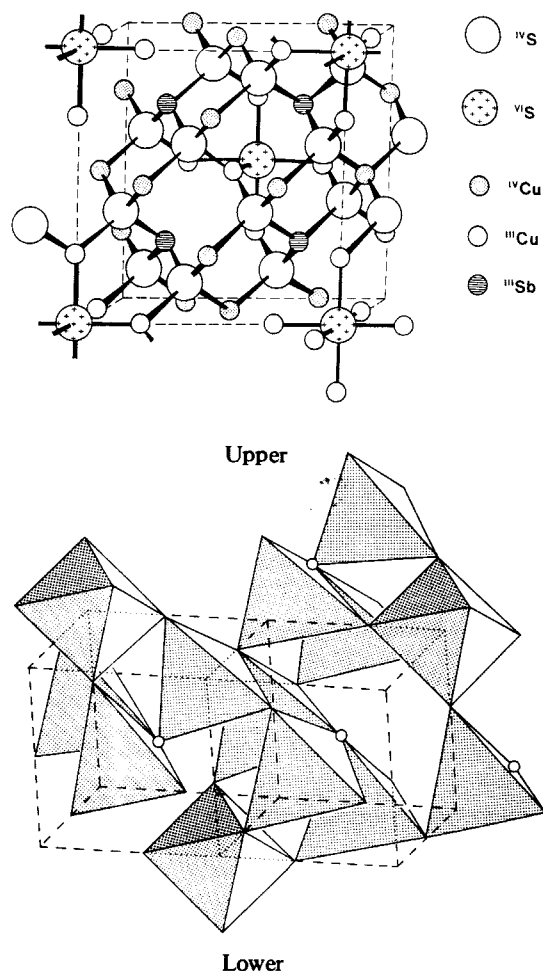


Fig. 1. Crystal structure of tetrahedrite. Upper: Diagram showing the crystal structure of half unit cell of tetrahedrite. The tetrahedral site may be occupied by Zn and Fe as well as Cu and Cd as shown (Patrick and Hall, 1983). Lower: Diagram showing the arrangement of polyhedrons formed by metal atoms coordinated about sulphur atoms in tetrahedrite, the Sb locations are represented by small circles; all other vertices of the polyhedrons represents Cu sites (Wuensch, 1964).

silver with increasing Fe contents, Patrick and Hall (1983) emphasize that the Ag substitution in tetrahedrite is strongly controlled by the Fe substitution.

The substitution of the Ag for Cu would be expected to increase the cell size of tetrahedrites, because the size of Ag atom (covalent radius : 1.53 Å for  $\text{Ag}^{+}$ ) is larger than that of Cu atom (1.35 Å for  $\text{Cu}^{+}$ ). Riley (1974), in his study on Ag-bearing tetrahedrites from Mt. Isa, has found that the cell size of tetrahedrites increases with increasing Ag contents up to  $(\text{Cu}_6\text{Ag})$  per formula unit, but with further progressive Ag substitution cell size begins to decrease. He suggests that this phenomenon is caused by the substitution of the Ag for the Cu occupying two different sites, i. e.,  $^{111}\text{Cu}$  and  $^{112}\text{Cu}$  sites, and may be related to the differences in packing and to the difference in ionic character of Ag-S and Cu-S bonds. The reflectance data for the Ag-bearing tetrahedrites from the Janggun mine given by Imai and Lee (1980), showing the relation between reflectance (R percent for  $\lambda = 500 \text{ nm}$ ) and weight percent of Ag, appear to confirm this structural change.

Lee (1980) suggests that, in case of natural Ag-bearing tetrahedrites, the Ag substitution for the Cu would begin from the four tetrahedrally coordinated Cu atoms ( $^{112}\text{Cu}$ , Cu(1)) and change to six remainders of the Cu atoms in 3-fold coordination ( $^{111}\text{Cu}$ , Cu(2)). Patrick and Hall (1983) express the same opinion in view of the expansion and subsequent contraction of cell size with increasing Ag contents recognized in the Mt. Isa as Ag-bearing tetrahedrites by Riley (1974), but they stress the belief that it also could be a feature unique in natural Fe-rich tetrahedrite.

## LOCATION AND GEOLOGIC SETTINGS

The Yeonhwa 1 mine lies about 5 Km north of Seogpo station on the Ryeongdong Line of the Korean National Railway, and the mine Province emplaces approximately at lat.  $37^{\circ} 04' \text{ N}$  and long  $129^{\circ} 02' \text{ E}$  (Fig 2).

In the mine area, the basement rocks composed of Precambrian granite gneisses—"Taebae-

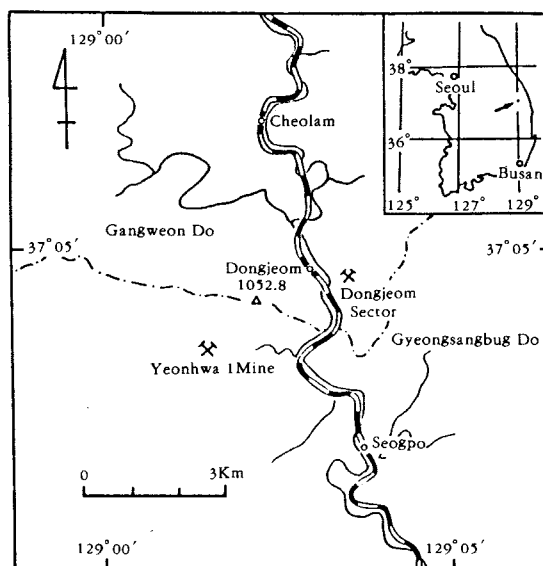


Fig. 2. Map showing the location of the Yeonhwa 1 mine district.

gsan Gneiss Complex" (Lee and Kim, 1984) and the overlying Cambro-Ordovician sedimentary rocks of the Joseon Supergroup are exposed extensively. The results of K/Ar radiometric dating on three members of the gneiss complex given by Yun and Silberman (1979) are as follows; Dongjeom gneiss:  $1,744 \pm 52 \text{ Ma}$  on muscovite, pegmatite in Dongjeom gneiss:  $1,754 \pm 53 \text{ Ma}$  for muscovite, and Hongjesa granite:  $730 \pm 22 \text{ Ma}$  on biotite. This indicates that at least two phases of precambrian intrusive and/or metamorphic events took place in the district.

The sequence of Cambro-Ordovician sediments in Duwibong (platform) belonging to Joseon Supergroup have been divided into the following seven formations in ascending order (Kobayashi, 1953); the Jangsan Quartzite and Myobong Slate-Yangdeok Series; the Dongjeom Quartzite, Dumugol Shale and Maggol Limestone-Great Limestone Series. The boundary of Cambrian and Ordovician has been defined at the base of the Dongjeom Quartzite for convenience, though the biostratigraphic boundary lied at the upper horizon of the Hwajeol Formation (Koba-

yashi, 1953). Stocks of dykes of lamprophyre (K/Ar age:  $213 \pm 4$  Ma on muscovite; Yun and Silberman, 1979) have intruded into the above basement rocks and the sedimentary rocks of the Yangdeok Series. Dykes of quartz-monzonite porphyry and diabase of unknown age also crop out in some places.

Structurally, the Yeonhwa 1 mine area occupies the eastern segment of the southern limb of Hambaeg syncline (called Baegunsan syncline by some authors), whose axis trending approximately EW~NW and plunging westwards. The structure of strata on the surface in the mine area is fairly steep; they strike NE and dip between  $40^\circ$  and  $60^\circ$  NW in general, whilst in the underground mine they dip more gentle, from  $25^\circ$  to  $30^\circ$  NW. In some places, the strata was overturned due to local disturbance of faultings. Minor foldings and warpings are developed locally. The dominant faults in the mine area include (1) steep reverse faults of EW strike with dips of about  $60^\circ$  in north of the mine workings, that places the Pungchon Limestones over the Hwajeol Formation, (2) steep reverse faults trending NS~N $30^\circ$ E, and (3) steep reverse faults striking N $20^\circ$ ~ $30^\circ$ W with dips of  $45^\circ$ ~ $85^\circ$ W-SW.

## OCCURRENCE

An occurrence of freibergite in zinc-lead (-silver) ores from the Yeonhwa 1 mine is rather rare and seems to be restricted to galena-rich ores formed in later stage. Accordingly, among numerous ore specimens, freibergite has been recognized in only two specimens; (1) galena-rich massive ore taken from the West ore body on the -300 m adit level in Dongjeom sector (No. YH82-101), and (2) galena-and rhodochrosite-rich banded ore taken from vein type deposit, which cuts clearly the massive skarn ores of the Myobong deposit on -360 m adit level (No. YH84-301). These two ore specimens are respectively called "Dongjeom ore" and "Myobong ore" for

convenience in this paper.

On the basis of the mode of occurrence and optical properties, freibergite now under investigation may be divided into three species; i. e., freibergites I, II and III. Among them, freibergites I and II are contained in "Dongjeom ore", where as freibergite III in "Myobong ore".

The freibergite I is usually contained in galena and closely associated with pyrargyrite, pyrite, pyrrotite, alabandite and Mn-bearing magnetite. It is anhedral in shape, and on some occasions shows spindle-like shape, with a grain size up to  $200 \mu\text{m}$  across, but grains  $20\sim 50 \mu\text{m}$  across most common.

On the other hand, the freibergite II is always enclosed in galena as "silver carrier". In some parts of the polished section, it occurs as small platy bodies oriented parallel to (100) of galena. The plate attains to  $100 \mu\text{m}$  in maximum length, but length  $50\sim 60 \mu\text{m}$  of it is most common. In other parts of the polished section, it occurs as minute inclusions with rounded shape in galena, ranging from  $20$  to  $30 \mu\text{m}$  across. The textural relationship not same above suggests the exsolution (Fig 3(3) and (4)).

The freibergite III also occurs as a member of polymineralic particles in galena and is closely associated with sphalerite, stannite and gangue minerals (mainly quartz). It is anhedral in shape and its grain size is commonly about  $10 \mu\text{m}$  across.

## OPTICAL PROPERTIES

Under the ore microscope, some contrast may be recognized in optical properties among freibergites I, II and III. The freibergite I is white-greenish grey in colour and no bireflectance is recognizable. Between crossed polars, it is optically isotropic and no internal reflections are observed.

On the other hand, the freibergite II is white-brownish grey in colour and no bireflectance is

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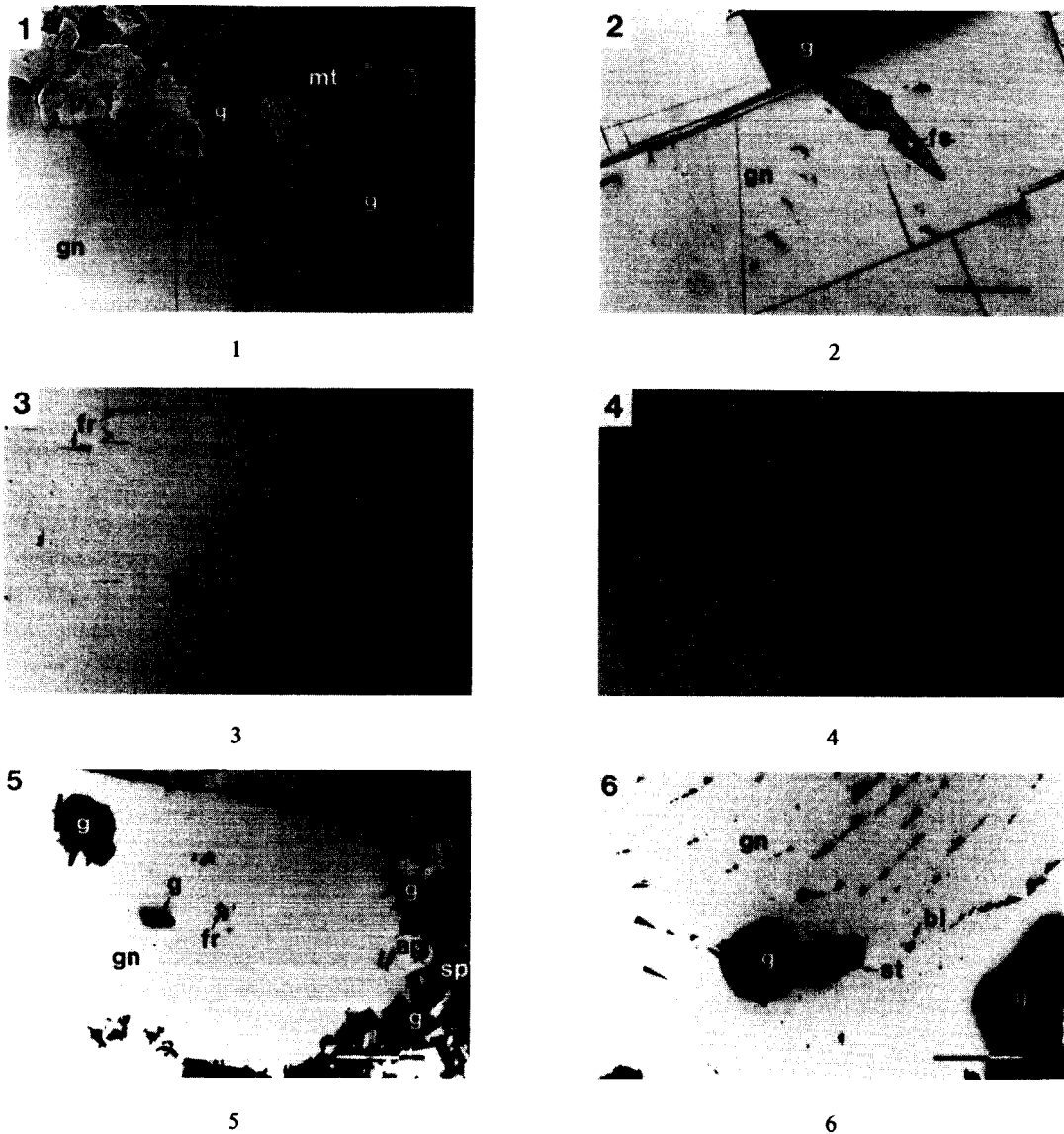


Fig. 3. Photomicrographs of the polished sections (one polar), showing the mode of occurrence of freibergite. Bar scale indicates 100 mm in length. Abbreviations; ap: angenopyrite, bl: boulangelite, fs: freislebenite, fr: freibergite, gn: galena, mt: magnetite, po: pyrrhotite, py: pyrite, sp: sphalerite, st: stannite, g: gangue mineral. 1~4: Specimen No. YH82-101, 5~6: Specimen No. YH84-301.

also recognizable. Between crossed polars, no internal reflection is discernible, but it is anisotropic with colour effects changing in colour from bright brownish grey with greenish tints to dark brownish grey when the stage is turned.

The freibergite III has the optical properties

similar to those of freibergite I, i. e., it is optically isotropic.

### CHEMICAL COMPOSITION

Chemical analyses, both qualitative and quan-

titative, were performed with electron microprobe operated in a wavelength dispersion X-ray spectrometer (WDX). In this study, the microprobe with three-channel detecting system and a 40° X-ray take-off angle was used.

Qualitative microprobe analyses by spectrometer-scans indicate the presence of Cu, Ag, Fe, Zn, Sb and S, and on some occasions Pb and other elements such as As, Hg, Cd and Bi are below the detectable limits of microprobe in spite of the careful peak searches.

In quantitative microprobe analyses, accelerating voltage of 20 kV, specimen current of 20 nA on MgO and spot size of 2~3  $\mu\text{m}$  were employed. The analyzing crystal and characteristic X-ray are as follows; LiF for FeK $\alpha$ , CuK $\alpha$  and ZnK $\alpha$  radiations and PET for SbL $\alpha$ , PbM $\alpha$  and SK $\alpha$  radiations.

As microprobe standards, the following materials were utilized; natural chalcopyrite of known composition for Cu and Fe, pure metal and synthetic Ag<sub>3</sub>SbS<sub>3</sub> for Ag, synthetic ZnS for Zn, natural galena of known composition for Pb and natural stibnite of known composition for Sb and S.

The chemical compositions as expressed by atomic percent and numbers calculated as total atoms=29, and those as Sb=4 are tabulated in Table 1. Also, the composition (atomic percent) is plotted into enlarged parallelogram in the triangle diagram of Me-Sb-S, where Me=Cu+Ag+Fe+Zn+Pb. From these tables it may be seen that the present materials are characterized by relatively high contents of silver up to about 40.5 weight percent of Ag and negligible amount of zinc and in some grains it is less than the detection limits of microprobe. This is consistent with the statement by Patrick and Hall (1983) that "the solubility of silver in freibergites is strongly controlled by Fe substitution". These tables and figures also show that the chemical composition of the present materials has somewhat peculiar features, which involve marked S-deficiency and

Sb-excess from the composition Me<sub>2</sub>SbS<sub>3</sub>. Also, some grains of this mineral contain appreciable amount of lead up to 1.70 weight percent of Pb. However, Bishop et al. (1977) found tennantite at Sark's Hope mine, Channel Islands with up to 4.64 weight percent of Pb. This incorporation of lead into tetrahedrite-tennantite cannot be easily explained, because it exists in other sulphosalts in poorly-defined sites of large coordination number (usually 6-fold coordination) and variable bond length (Patrick and Hall, 1983).

Fig 4 shows that the composition of the freibergites I and II is plotted into the two separated areas near Cu<sub>12</sub>SbS<sub>12</sub> (Me<sub>12</sub>SbS<sub>12</sub>) composition, whereas that of the freibergite III into elongated area ranging from Cu<sub>12</sub>SbS<sub>13</sub> (Me<sub>12</sub>SbS<sub>13</sub>) to Cu<sub>12</sub>SbS<sub>12</sub>. The composition of the Janggum freibergites and argentine tetrahedrites is plotted in the area around Cu<sub>12</sub>SbS<sub>13</sub> (Me<sub>12</sub>SbS<sub>13</sub>), and S-deficiency and Sb-excess are not recognizable, accordingly two sets of chemical formulae calculated on the basis of a Sb=4.00 and total atoms=29 per half unit cell are approximately identical. In case of the Yeonhwa 1 freibergite, however, marked differences may be recognized between them as shown Table 1.

In Fig 5, the variation of Cu-Ag contents versus Zn-Fe substitution in tetrahedral sites of freibergites from the Yeonhwa 1 mine is compared with that of the Janggum freibergite and argentine tetrahedrite. This indicates that Ag contents of the present materials lie in the blank interval in the Janggum materials, and that, although Ag>4 in the present materials, the freibergite III is characterized by relatively lower contents of iron.

## SUMMARY AND DISCUSSION

Throughout the present study, it has been shown that minerals of the tetrahedrite-freibergite series have complex mineralogical features and involve many mineralogical, in particular

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Table 1. Selected electron-microprobe analyses of freibergite.

No.	Weight percent								Atomic number on the basis of total=29								Atomic number on the basis of Sb=4					
	Cu	Ag	Fe	Zn	Pb	Sb	S	Total	Cu	Ag	Fe	Zn	Pb	Sb	S	Cu	Ag	Fe	Zn	Pb	S	
1	12.04	36.16	5.31	—	—	25.65	19.26	98.42	3.84	6.76	1.93	—	—	4.27	12.17	3.60	6.36	1.81	—	—	11.41	
2	12.01	36.44	5.30	—	—	25.94	19.37	99.06	3.81	6.81	1.91	—	—	4.29	12.18	3.55	6.34	1.78	—	—	11.34	
3	12.45	36.45	5.05	—	—	25.82	19.11	98.88	3.97	6.84	1.83	—	—	4.29	12.07	3.70	6.37	1.71	—	—	11.24	
4	12.27	36.42	5.12	—	—	25.74	19.57	99.12	3.88	6.78	1.84	—	—	4.25	12.26	3.65	6.39	1.73	—	—	11.55	
5	12.55	36.14	5.04	—	—	26.12	19.52	99.37	3.96	6.72	1.81	—	—	4.30	12.21	3.68	6.25	1.68	—	—	11.35	
6	12.43	34.80	5.72	—	—	26.00	19.23	98.18	3.96	6.51	2.07	—	—	4.32	12.13	3.66	6.04	1.92	—	—	11.23	
7	12.68	35.69	5.40	—	—	25.77	19.38	98.92	4.01	6.65	1.94	—	—	4.25	12.15	3.77	6.25	1.83	—	—	11.42	
8	12.44	35.91	5.37	—	—	25.90	19.60	99.22	3.92	6.66	1.92	—	—	4.26	12.24	3.68	6.26	1.81	—	—	11.50	
9	12.52	36.03	5.41	—	—	25.65	18.96	98.57	4.00	6.77	1.96	—	—	4.27	11.99	3.74	6.34	1.84	—	—	11.23	
10	10.84	37.40	5.00	0.83	—	26.51	19.64	100.22	3.41	6.93	1.79	0.25	—	4.36	12.25	3.13	6.37	1.64	0.23	—	11.25	
11	11.84	36.43	4.55	1.11	—	26.38	18.79	99.10	3.79	6.87	1.66	0.35	—	4.41	11.93	3.44	6.23	1.50	0.31	—	10.82	
12	11.31	36.99	4.83	0.94	—	26.38	19.03	99.48	3.60	6.94	1.75	0.29	—	4.39	12.02	3.29	6.33	1.60	0.27	—	10.96	
13	10.47	39.11	4.34	0.47	—	25.99	19.49	99.87	3.33	7.33	1.57	0.15	—	4.32	12.30	3.09	6.79	1.46	0.13	—	11.39	
14	10.51	40.42	3.96	0.34	—	26.36	19.32	100.91	3.34	7.57	1.43	0.11	—	4.37	12.18	3.06	6.92	1.31	0.10	—	11.13	
15	10.56	40.58	3.85	0.44	—	25.93	19.22	100.58	3.37	7.63	1.40	0.14	—	4.32	12.15	3.12	7.07	1.29	0.13	—	11.26	
16	12.91	36.63	4.95	—	—	27.32	19.95	101.76	3.99	6.66	1.74	—	—	4.40	12.21	3.62	6.05	1.58	—	—	11.09	
17	13.20	35.16	5.17	—	—	27.03	19.52	100.08	4.13	6.49	1.84	—	—	4.42	12.12	3.74	5.87	1.67	—	—	10.97	
18	13.48	35.63	5.23	—	—	26.43	19.99	100.76	4.17	6.49	1.84	—	—	4.26	12.25	3.91	6.09	1.73	—	—	11.49	
19	12.43	36.60	5.16	—	—	27.54	19.79	101.52	3.86	6.69	1.82	—	—	4.46	12.17	3.46	6.00	1.63	—	—	10.92	
20	12.72	36.19	5.41	—	—	27.08	19.58	100.98	3.96	6.64	1.92	—	—	4.40	12.08	3.60	6.03	1.74	—	—	10.98	
21	13.07	34.61	5.56	—	—	26.88	19.62	99.74	4.09	6.38	1.98	—	—	4.39	12.17	3.73	5.81	1.80	—	—	11.09	
22	13.13	34.83	5.31	—	—	26.37	19.42	99.06	4.14	6.47	1.91	—	—	4.34	12.14	3.82	5.96	1.76	—	—	11.19	
23	12.63	36.36	5.40	—	—	27.05	19.44	100.88	3.94	6.69	1.92	—	—	4.41	12.04	3.58	6.07	1.74	—	—	10.92	
24	12.34	35.59	5.07	—	—	26.78	19.35	99.13	3.91	6.65	1.83	—	—	4.43	12.17	3.53	6.00	1.65	—	—	10.98	
25	12.72	35.73	5.10	—	—	27.05	20.01	100.61	3.95	6.54	1.80	—	—	4.39	12.32	3.60	5.96	1.64	—	—	11.24	
26	12.14	36.27	4.89	—	—	26.11	19.26	98.67	3.87	6.82	1.78	—	—	4.35	12.18	3.56	6.27	1.63	—	—	11.21	
27	12.75	35.74	5.37	—	—	26.87	20.01	100.74	3.95	6.52	1.89	—	—	4.39	12.29	3.64	6.01	1.74	—	—	11.31	
28	13.60	34.73	5.28	—	—	26.93	19.51	100.05	4.25	6.39	1.88	—	—	4.33	12.09	3.87	5.82	1.71	—	—	11.40	
29	12.61	34.96	5.67	—	—	26.28	19.43	98.95	3.98	6.50	2.04	—	—	4.61	12.16	3.68	6.01	1.88	—	—	11.23	
30*	12.27	36.07	5.50	—	—	27.82	18.65	100.31	3.90	6.75	1.99	—	—	4.55	11.75	3.38	5.85	1.72	—	—	10.18	
31*	12.00	35.59	5.07	—	—	26.87	18.49	98.04	3.89	6.80	1.87	—	—	4.57	11.89	3.42	5.98	1.64	—	—	10.45	
32*	11.93	36.58	5.37	—	—	27.57	18.84	100.29	3.79	6.84	1.94	—	—	4.50	11.86	3.32	5.99	1.70	—	—	10.38	
33*	11.88	36.26	5.29	—	—	27.19	19.14	99.76	3.77	6.78	1.91	—	—	4.54	12.04	3.35	6.02	1.70	—	—	10.69	
34*	12.51	35.79	5.60	—	—	27.43	18.76	100.09	3.97	6.68	2.02	—	—	4.59	11.79	3.49	5.89	1.78	—	—	10.39	
35*	11.87	34.73	5.48	—	—	27.28	18.73	98.09	3.83	6.60	2.01	—	—	3.88	11.97	3.33	5.75	1.75	—	—	10.43	
36*	12.54	35.96	5.36	0.39	1.69	23.63	19.72	99.29	3.95	6.67	1.92	0.19	0.16	3.91	12.30	4.07	6.87	1.98	0.12	0.17	12.68	
37	12.66	36.18	5.48	0.39	0.78	23.80	19.70	98.99	3.98	6.70	1.96	0.12	0.08	3.90	12.27	4.08	6.86	2.01	0.12	0.08	12.57	
38	12.44	35.81	5.38	0.39	0.80	23.66	19.71	98.19	3.93	6.67	1.94	0.12	0.08	4.03	12.36	4.03	6.83	1.98	0.12	0.08	12.65	
39	12.66	35.44	5.15	0.33	1.19	24.54	19.88	99.19	3.98	6.56	1.84	0.10	0.11	4.02	12.38	3.95	6.52	1.83	0.10	0.11	12.31	

No.	Weight percent								Atomic number on the basis of total=29								Atomic number on the basis of Sb=4					
	Cu	Ag	Fe	Zn	Pb	Sb	S	Total	Cu	Ag	Fe	Zn	Pb	Sb	S	Cu	Ag	Fe	Zn	Pb	S	
40	12.74	35.28	5.34	0.33	1.19	24.66	20.03	99.57	3.98	6.49	1.90	0.10	0.11	4.02	12.40	3.96	6.46	1.89	0.10	0.11	12.34	
41	12.89	35.39	5.42	0.33	1.19	24.71	19.90	99.83	4.02	6.51	1.92	0.10	0.11	4.03	12.31	4.00	6.47	1.91	0.10	0.11	12	
42	12.76	35.24	5.22	0.33	1.19	24.41	19.91	99.06	4.01	6.51	1.87	0.10	0.12	4.00	12.39	4.01	6.52	1.86	0.10	0.11	12	
43	12.75	35.38	5.34	0.33	1.19	24.48	19.81	99.28	4.00	6.54	1.91	0.10	0.12	4.01	12.32	3.99	6.52	1.90	0.10	0.11	12	
44	12.67	35.69	5.16	0.33	1.19	24.20	19.75	98.99	3.99	6.23	1.85	0.10	0.11	3.98	12.34	4.01	6.66	1.86	0.10	0.12	12	
45	12.74	35.81	4.91	0.33	1.19	23.98	19.80	98.76	4.02	6.66	1.76	0.10	0.12	3.95	12.39	4.07	6.74	1.79	0.10	0.12	12	
46**	12.77	33.18	4.43	1.61	1.53	26.60	21.67	101.79	3.85	5.89	1.52	0.47	0.14	4.18	12.94	3.68	5.63	1.45	0.45	0.14	12	
47**	14.52	31.61	4.45	1.61	0.11	27.02	21.70	101.02	4.34	5.57	1.52	0.47	0.01	4.22	12.87	4.12	5.28	1.44	0.44	0.01	12	
48**	13.22	33.57	4.05	2.39	—	26.75	19.11	99.09	4.18	6.25	1.46	0.73	—	4.41	11.97	3.79	5.67	1.32	0.67	—	10	
49**	12.14	34.76	5.11	1.08	—	26.40	20.22	99.71	3.77	6.36	1.81	0.33	—	4.28	12.45	3.52	5.94	1.69	0.30	—	11	
50**	12.15	34.80	5.11	1.08	—	26.43	20.22	99.79	3.77	6.37	1.81	0.33	—	4.28	12.45	3.52	5.94	1.69	0.30	—	11	
51**	12.08	34.06	5.48	1.14	—	26.83	20.66	100.25	3.71	6.16	1.91	0.34	—	4.30	12.57	3.45	5.73	1.78	0.32	—	11	
52**	18.78	24.47	4.26	1.35	—	28.31	21.53	98.70	5.63	4.32	1.45	0.39	—	4.43	12.78	5.08	3.90	1.31	0.36	—	11	
53**	18.65	24.43	4.61	1.49	—	27.90	21.62	98.70	5.57	4.30	1.57	0.43	—	4.35	12.76	5.12	3.95	1.44	0.40	—	11	

Po.: point number, Gr.: Grain number.

Point No. 1-18: Specimen No. YH82-101-(5). Point No. 18-29: Specimen No. YH82-201-(1).

Point No. 29-35: Specimen No. YH82-201-(7). Point No. 36-45: Specimen No. YH82-101-(1).

Point No. 46-51: Specimen No. YH84-301-(1). Point No. 52-53: Specimen No. YH84-301-(2).

—: Its content represents less than the detection limits of microprobe.

\* represents freibergite II. \*\* represents freibergite III. No asterisk represents freibergite I.

# represents freibergite of analyses by using an electron microprobe with energy dispersion X-ray spectrometer (EDS) and others are analyses using an electron microprobe with wavelength dispersion X-ray spectrometer (WDX).

crystal-chemical problems.

Even though we take the precision of our electron microprobe analyses for sulphosalts, which involve some difficulties at the present analytical level into consideration, the S-deficiency and Sb-excess in the Yeonhwa I freibergites could be now evident. Especially, some grains exhibit the S contents lower than the composition  $Me_3Sb_3S_{12}$  as shown in Fig 4. One possible explanation to this is the sulphur-antimony substitution in the octahedral sites ( $^VI S, S(2)$ ) in the manner  $1.5 S^{2-} \rightarrow Sb^{3+} + 0.5 \square$ , because  $Sb^{3+}$  cannot occupy the tetrahedral sites ( $^IV S, S(1)$ ). However, this explanation seems not to satisfy the scheme of tetrahedrite structure. Further examination in this respect is necessary.

In spite of the differences in the mode of occurrences and the optical properties recognized between freibergite I and II, no marked contrasts in chemical composition between them

were recognized as mentioned before. However, in comparison of chemical composition in the freibergite I and II of "Dongjeom ore" with that in freibergite III of "Myobong ore", there are some differences between two groups. Namely, the former is characterized by high contents of iron adhering to  $(Fe_2Zn_0)$  and higher contents of silver,  $(Ag_6Cu_4) \sim (Ag_7Cu_3)$ . On the other hand, the latter is characterized by lower contents of iron, with a range of  $(Fe_{1.1}Zn_{0.9}) \sim (Fe_{1.5}Zn_{0.5})$  and relatively lower contents of silver,  $(Ag_{4.2}Cu_{5.0}) \sim (Ag_{6.2}Cu_{3.0})$  as shown in Fig 5.

The cause of the differences in chemical composition recognized between the above two groups is not still clarified. However, it seems important to notice that the mineral assemblage of "Dongjeom ore" and that of "Myobong ore" show somewhat marked differences, although these two ore specimens are considered to have been



Freibergite from the Yeonhwa 1 Mine

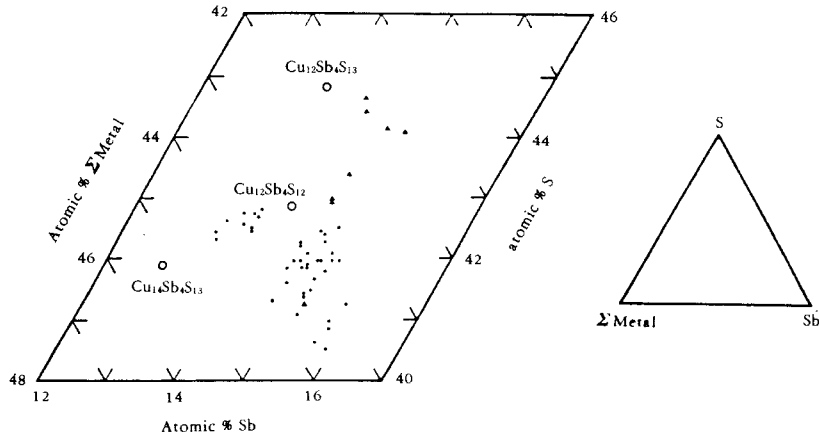


Fig. 4. The enlarged parallelogram in the triangle of the ternary system metal-Sb-S, showing the composition of freibergite. Full small circles represent the compositions of freibergite-1 and 2 from the Yeonhwa 1 mine. Full triangles represent the composition of freibergite-3 from the Yeonhwa 1 mine. Metal represents (Cu+Ag+Fe+Zn+Pb).

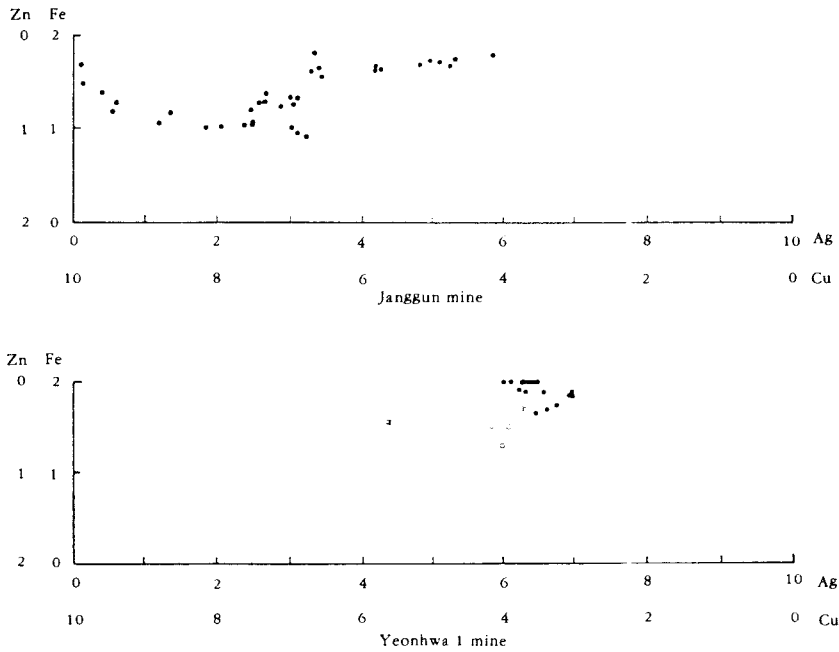


Fig. 5. Variation diagram showing the relation of Cu-Ag contents versus Fe-Zn contents in argentian tetrahedrite and freibergite. Numerical values are atoms per half unit cell represented by the general formula  $(\text{Cu}, \text{Ag})_{10}(\text{Zn}, \text{Fe})_2\text{Sb}_4\text{S}_{13}$ . In case of Yeonhwa 1 mine, full circle depicts freibergite (I and II) of "Dongjeom ores" and open circle freibergite (III) of "Myobong ores".

formed by hydrothermal mineralization during late stage, separated perfectly from the earlier mineralization during early stage associated with skarn formation. Namely, the mineral assemblage

of the former is galena+sphalerite+Mn-bearing magnetite+pyrite+pyrrhotite+alabandite+Ag-bearing sulphatimonides+freibergite, whereas that of the latter is sphalerite+galena+pyrite+

stannite + pyrrhotite + chalcopyrite + boulangerite + freibergite (+ rhodochrosite). Also, it must be remembered here that "Dongjeom ore" represents the massive ore formed by metasomatic process, while "Myobong ore" the banded ore formed by fissure filling. These facts suggest that some differences might exist in physicochemical condition of the formation between them.

In the Janggun polymetallic ores, argentian tetrahedrite and freibergite are the main silver-carrier (Imai and Lee, 1980; Lee, 1980), but in case of the Yeonhwa 1 ores, freibergite is minor silver-bearer. Contribution of freibergite to silver contents in galena of "Dongjeom ore" is greater than that of "Myobong ore", in which exsolved freibergite from galena never exist.

Thus, it become clear that the Yeonhwa 1 freibergites embrace important mineralogical as well as ore genetical problems, but the present study is still unsatisfactory to understand these features. Further investigation must be continued.

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## REFERENCES

- Bishop, A. C., Criddle, A. J. and Clark, A. M. (1977) : Plumbian tennantite from Sark, Channel Islands. *Miner. Mag* 41, 59-63.
- Hall, A. J. (1972) : Substitution of Cu by Zn, Fe and Ag in synthetic tetrahedrite,  $Cu_{12}Sb_3S_{13}$ . *Buss. Soc. Fr. Miner. Crist.* 95, 583-594.
- Imai, N. and Lee, H. K. (1980) : Complex sulphide-sulposalt ores from Janggun mine, Republic of Korea. In "Complex sulphide ores" (Proc. Inter. Conf. for Complex Sulphide Ores), Rome, 248-259.
- Kalbskopf, R. (1972) : Strukturverfeinerung des Freibergits. *Tschermaks Miner. Petr. Mitt.* 18, 147-155.
- Karup-Møller, S. (1974) : Mineralogy of two copper-antimony-sulfide-oxide occurrence from the Ilimanssag intrusion in south Greenland. *N. Jb. Miner. Ab.* 122, 291-313.
- Lee, H. K. (1980) : Ore deposit and ore mineralogy of complex sulphide-sulphosalt ores from the Janggun mine, Republic of Korea. Unpub. Ph. D. Thesis submitted to the Graduate Sch. Sci. Eng, Waseda Univ., 341.
- Machatschiki, F. (1928) : Formel und kristallstruktur des tetrahedrites. *Norsk. Geol. Tid.* 10, 23.
- Makovicky, E. and Skinner, B. J. (1979) : Studies of the sulfosalts of copper VII. crystal structure of the exsolution products  $Cu_{12}Sb_3S_{13}$  and  $Cu_{13}Sb_3S_{13}$  of unsubstituted synthetic tetrahedrite. *Canad. miner.* 17, 619-634.
- Mozgova, N. N. (1982) : A New scheme for divalent metal isomorphism in fahlore. *Dokl. AN. SSSR*, 205, 712-728 (in Russian).
- Patrick, R. A. D. and Hall, A. J. (1983) : Silver substitution into synthetic zinc, cadmium and iron tetrahedrites. *Miner. Mag*, 47, 441-451.
- Pauling, L. and Neuman, E. W. (1934) : The crystal structure of binnite  $(Cu, Fe)_{12}As_3S_{13}$ , and the chemical composition and structure of minerals of the tetrahedrite group. *Z. Krist.* 88, 54-62.
- Riley, J. F. (1974) : The tetrahedrite-freibergite series with reference to the Mount Isa Pb-Zn-Ag orebody. *Miner. Deposita*, 9, 117-124.
- Springer, G. (1969) : Electronprobe analyses of tetrahedrites. *N. Jb. Miner. Mh.* 1, 24-33.
- Wuensch, B. J. (1964) : The crystal structure of tetrahedrite,  $Cu_{12}Sb_3S_{13}$ . *Z. Krist.* 119, 437-453.
- Wuensch, B. J., Takeuchi, Y. and Nowacki, W. (1966) : Refinement of the crystal structure of binnite,  $Cu_{12}As_3S_{13}$ . *Z. Krist.* 123, 1-20.