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Ag-Sb Minerals from the Yeonhwa 1 Mine

제 1 연화광산에서 산출되는 Ag-Sb 계의 광물

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ABSTRACT: Minerals of system Ag-Sb have been found in lead-zinc (-silver) ores from the Dongjeom and the Taebaeg ore deposits, which were formed at later stage of the Yeonhwa 1 mine mineralization. The Ag-Sb minerals are intergrown intimately with galena, pyrargyrite and alabandite. Their chemical compositions as determined by electron microprobe analyser show that they are chracterized by relatively high content of S, up to 5.89 atomic percent. Also the composition of the minerals may be separated into two: $Ag_{4.89}Sb_{1.00}$-$Ag_{7.19}Sb_{1.00}$ and $Ag_{2.96}Sb_{1.00}$-$Ag_{4.00}Sb_{1.00}$.

요약: 제 1연화광산에서 발견된 Ag-Sb계 광물은 광상의 후기 광화시기에 해당하는 동점광체와 태백광체에서 방연석, 함망간자철석, alabandite, rhodochrosite와 밀접하게 공존하고 있다. 화학성분을 보면 유황이 최고 5.89 atomic % 까지 함유되어 있으며, 성분 조성상 allargentum에 해당하는 $Ag_{4.89}Sb_{1.00}$-$Ag_{7.19}Sb_{1.00}$과 dyscrasite에 해당하는 $Ag_{2.96}Sb_{1.00}$-$Ag_{4.00}Sb_{1.00}$으로 나눌 수 있다.

INTRODUCTION

In spite of a long history of invesitigation, phase relations of the system Ag-Sb are rather complicated and has not yet been completely clarified. A phase diagram of the system Ag-Sb up to 961.5℃ (melting point of silver) was shown by Guertler (1912). The diagram given by Keighin and Honea (1969), which was drawn on the basis of the compilation by Hansen and Anderko (1958), is reproduced in Fig. 1, where the α-phase represents the (Ag, Sb) solid solution whth an isometric symmetry, the δ-phase allargentum solid solution ($Ag_{6+x}Sb$) with an hexagonal symmetry and the ε-phase represents "dyscrasite proper" solid solution ($Ag_{3+x}Sb$) with an orthorhombic symmetry. Fig. 2 is an equilibrium diagram of the Ag-rich portion of this system given by Somanchi (1966 b) slightly modified by Petruk et al. (1971). There exist some discrepancies between the two diagrams.

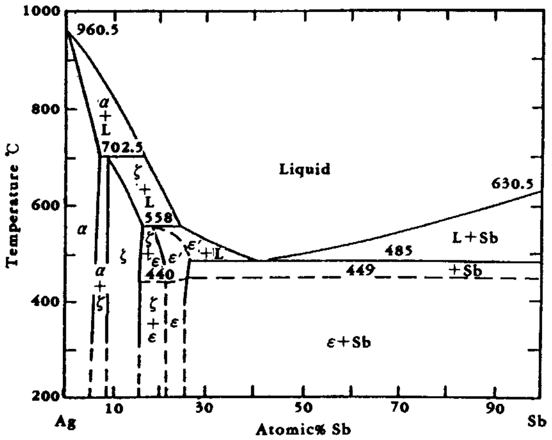

Fig. 1. Phase relations in the system Ag-Sb. (Keighin and Honea, 1969) Abbreviation; α: Ag-Sb solid solution, ζ: allargentum, ε: dyscrasite, ε': high temperature form of dyscrasite, others represents the same as shown in appendixes for mineral abbreviations.

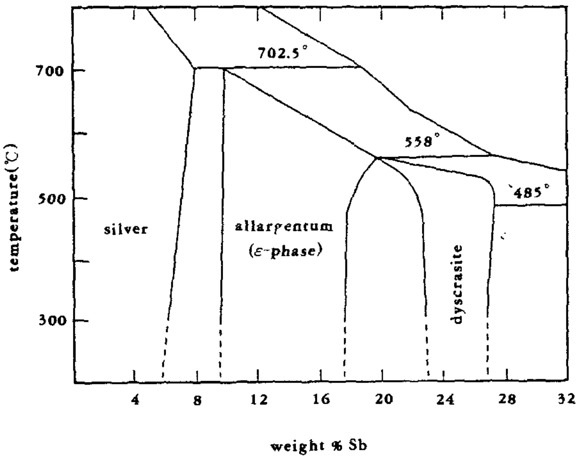

Fig. 2. Phase diagram of the Ag-rich portion in the system Ag-Sb (Somanchi, 1966b).

With respect to the naturally occurring Ag-Sb minerals, some confusions have hitherto arised about their nomenclature; allargentum in the Cobalt-Gowganda ores, Canada, was referred to as dyscrasite by the early workers (Walker, 1921; Peacock, 1940). However, Somanachi and Clark (1966) have found that the "dyscrasite" in the Cobalt-Gowganda, Ontario corresponds to the synthetic ε-phase of the Ag-Sb system (Fig. 1). Petruk et al. (1971) showed that dyscrasite was found only in one sample of high-grade silver ores in the Deer Home mine, and that the Ag-Sb minerals in the ores display a number of unusual properties, especially some of them contain appreciable amount of mercury. The complex intergrowth textures of these Ag-Sb minerals including antimonian silvers due to exsolution were illustrated by Ramdohr (1980).

The Ag-Sb minerals have been described for the Cobalt-Gowganda ores in detail by several Canadian mineralogists, and subsequently allargentum was found in the Consol vein of the Broken Hill ore deposit, Australia (Markham et al., 1962). Recently, an occurrence of allargentums has been reported form the polymetallic deposit of Czeckoslovakia (Kvacek and Novak, 1972) and Hg-bearing allargentum from gold-silver deposit of the Okhotsk-Chukotka volcanic belt, U. S. S. R. (Nekrasova et al., 1977). In Japan, only one occurrence of dyscrasite was reported from the Kobetsuzawa mine, Hokkaido by Inshibashi (1956) and allargentum has not been ever known. The present Ag-Sb minerals from the Yeonhwa 1 mine represent the forth Korean occurrence of allargentum and dyscrasite.

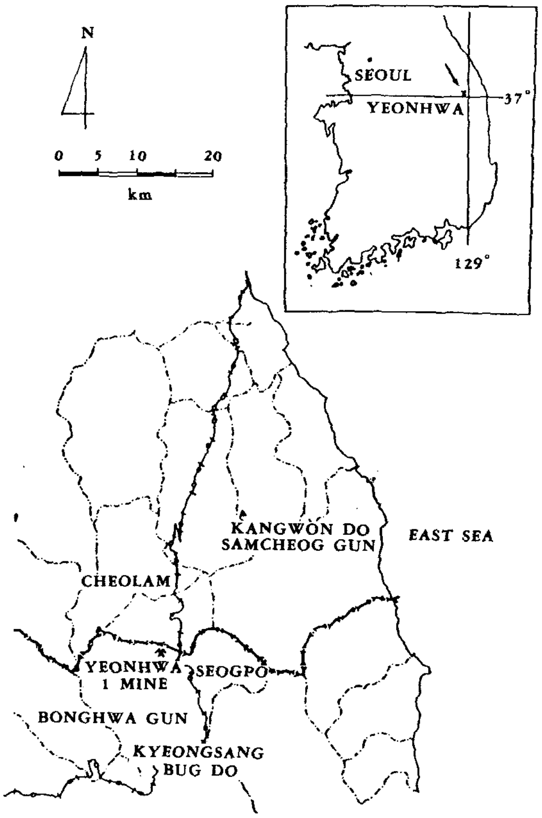

Fig. 3. Location map of the Yeonhwa 1 mine.

LOCATION AND GEOLOGIC SETTING

The Yeonhwa 1 mine is the largest producer of zinc and lead in the Republic of Korea, and is located about 5 km northwest of Seogpo Station of the Korean National Railway, approximately at latitude 37° 04'N and longitude 129° 02'E (Fig. 3). The mine area is situated in the southeastern margin of the Taebaegsan basin, where granite gneisses of precambrian age and the overlying calcareous lithofacies-dominant sedimentary succession of Cambro-Ordovician age, belonging to the Joseon Supergroup, are exposed extensively. In the northern region outside the mine area, near the axis of Hambaeg syncline, which is also called

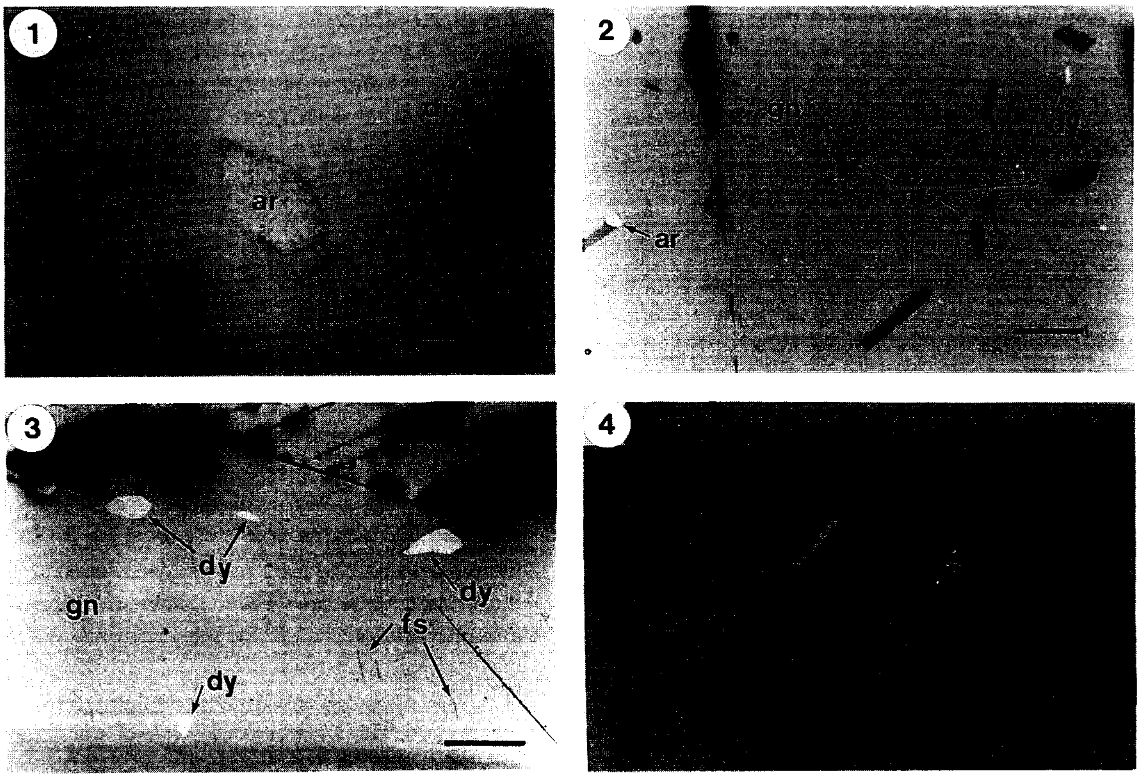

Fig. 4. Photomicrographs of the polished section (ore polar), showing the mode of occurrence of Ag-Sb minerals. Bar scale indicates 100μm in length. Abbreviation; al: alabandite, ar: allargentum, diaphorite, dy: dyscrasite, fr: freibergite, fs: freieslebenite, gn: galena, mi: miargyrite, pr: pyrargyrite.

Baegunsan syncline by some authors, developed are the sedimentary rocks of the Upper Palaeozoic that range in age from late Carboniferous to Permian belonging to the Pyeongan System.

OCCURRENCE AND OPTICAL PROPERTIES

In the Yeonhwa 1 mine, an occurrence of the Ag-Sb minerals is very rare and restricted only to two ore specimens from West orebody on the -300m adit level at the Dongjeom ore deposit and No. 1 orebody on the -600m adit level at the Taebaeg ore deposit. The ore is massive galena-rich one, and contains not only galena, but also minor amounts of Mn-bearing magnetite, alabandite, and carbonates (mostly rhodochrosite). The Ag-Sb minerals excluding native auriferous silver, which was described in other paper (Chung, 1990), involve allargentum and dyscrasite, and distinction between them under the ore microscope is quite difficult, because of their similarity in optical properties. They may be distinguished from chemical data obtained by electron microprobe. These two minerals are always randomly scattered thoughout the galena host as minute inclusions with lath-shaped, drop-like and irregular forms, together with those of freibergite, pyrargyrite, freieslebenite, etc. On some occasions, they are in direct contact with Mn-bearing magnetite and alabandite (Fig. 4). Their maximum grain size reaches 100μm across, but those with 10-20μm across are most common.

Under the ore microscope, their reflection colour is creamy yellow and they are characterized by higher reflectance, but somewhat darker than the associated native auriferous silver. Between crossed polars, they are weakly anisotropic and no internal reflections are perceptible. The polishing and scratch hardnesses are higher than those of the galena surrounding them.

In air, they gradually tarnish, but much more slowly than native auriferous silver. The result of each test with reagents having standard concentrations (Short, 1940) was all negative.

CHEMICAL COMPOSITION

Chemical analyses, both qualitative and quantitative, were performed with electron microprobe operated in a wavelength dispersion mode (WDX). In this study, the JEOL JXA-733 Superprobe with three-channel detecting system and a 40° X-ray take-off angle was used. Qualitative microprobe analyses detected the elements of Ag, Sb and S alone. In spite of the careful peak searches, Hg and As were below the detection limits of microprobe. The instrumental settings of the JXA-733 for X-ray intensity measurement in quantitative microanalysis were as follows; X-ray excitation potential: V_o=20kV, absorption current: i_{ab}=20nA on MgO, spot size of electron beam on the specimen surface: =1−2μm, method of X-ray intensity measurements: fixed-time counting mode, preset of period of integral time: 10 sec. Each analysis represents the mean value of five to seven spot analyses. Analyzing crystals and characteristic X-rays used; PET for AgLα-, SbLα- and SKα-radiations. As for reference standards, the following materials were used; native silver for Ag, natural stivenite of known composition for Sb, and natural chalcopyrite of known composition for S, respectively. After the correction for dead time and background, matrix effects corrections were made with reference to atomic number, absorption and fluorescence (ZAF corrections) and calculation was performed by BASIC computer program "ZAFSU", originally written by Yui and Shoji (1976), with high-speed digital computer system.

Table 1. Selected electron-microprobe analyses of Ag-Sb minerals

point	Gr.	Weight percent				Atomic percent		
		Ag	Sb	S	Total	Ag	Sb	S
1	A	84.33	13.93	0.87	99.13	84.67	12.39	2.93
2	B	84.57	13.89	1.03	99.49	84.28	12.21	3.45
3	C	83.62	13.61	0.99	98.22	84.46	12.18	3.36
4	D	84.49	13.41	0.91	98.81	84.97	11.95	3.08
5	E	84.04	13.20	0.90	98.14	85.09	11.84	3.07
6	F	85.15	13.96	0.93	100.04	84.60	12.29	3.11
7	G	83.00	14.12	0.97	98.09	84.03	12.67	3.30
8	H	81.90	17.56	1.32	100.78	80.37	15.27	4.36
9	I	78.76	18.17	1.54	98.47	78.73	16.09	5.18
10	J	83.09	17.34	0.67	101.10	82.51	15.25	2.24
11	K	81.41	17.83	1.62	100.86	79.30	15.39	5.31
12	L	81.05	17.93	0.62	99.60	81.85	16.04	2.11
13	M	80.20	17.60	1.35	99.15	79.93	15.54	4.53
14	N	81.31	18.42	1.18	100.91	80.03	16.06	3.91
15	O	81.87	18.16	1.40	101.43	79.74	15.67	4.59
16	P	85.36	15.29	1.84	102.49	81.22	12.89	5.89
17	Q	84.24	13.72	0.82	98.75	85.86	11.95	2.17
18	R	83.77	13.91	0.93	98.61	85.71	12.08	2.19
19	S	84.25	13.46	0.89	98.60	85.86	11.95	2.17
20	T	83.64	13.62	0.92	98.18	85.71	12.08	2.19
21	U	84.26	13.39	0.94	98.59	85.86	11.95	2.17
22	V	71.69	27.34	1.08	100.11	72.02	24.33	3.65
23	W	75.07	23.62	0.19	98.88	77.68	21.66	0.66
24	X	76.42	21.95	—	98.57	79.71	20.29	—
25	Y	76.48	21.60	—	98.08	79.99	20.01	—

Gr.: Grain number

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

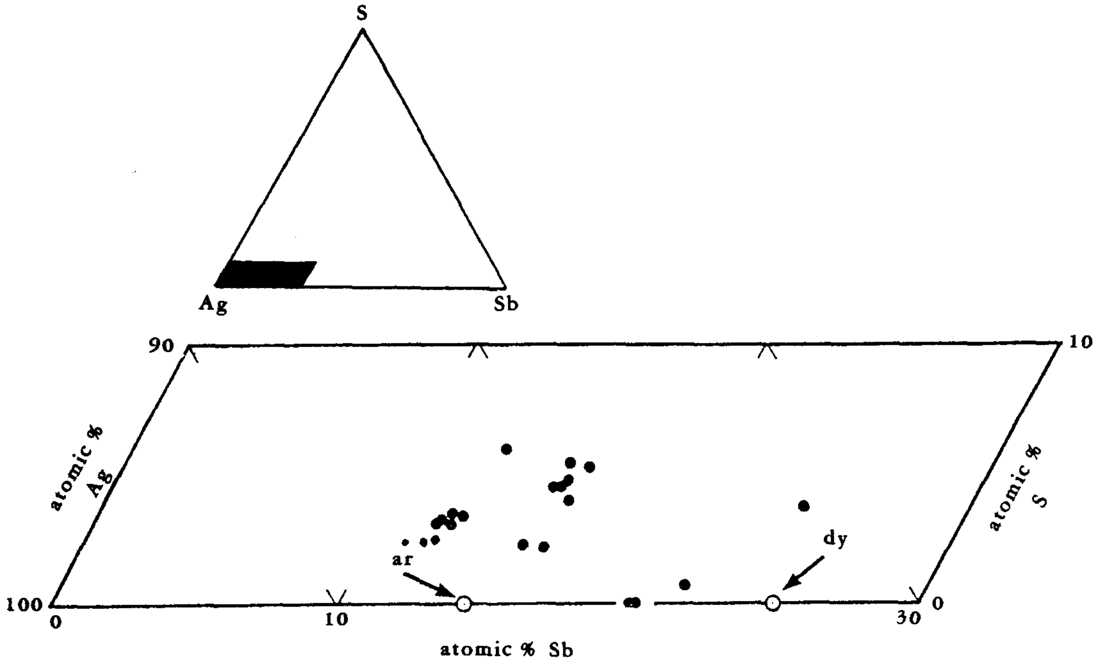

Fig. 5. Enlarged parallelogram in the triangle digram of the system Ag-Sb-S, showing the composition of minerals from the Yeonhwa 1 mine.
Abbreviation; ar: allargentum, dy: dyscrasite.

The selected microprobe analyses of the present materials thus performed are listed in Table 1, together with the corresponding atomic proportion as Sb= 1.00. Also, the results are plotted into the enlarged parallelogram in Ag-rich portion of the Ag-Sb-S triangle diagram (Fig. 5).

From these table and figures, it may be seen that, the composition of the minerals tends to be plotted in two distinct fields. One is represented by the compositional range from $Ag_{4.89}Sb_{1.00}$ to $Ag_{7.19}Sb_{1.00}$ corresponding the composition of allargentum solid solution ($Ag_{6+x}Sb$), the other is by that from $Ag_{2.16}Sb_{1.00}$ to $Ag_{4.00}Sb_{1.00}$ corresponding to dyscrasite solid solution ($Ag_{3+x}Sb$).

SUMMARY AND DISCUSSION

In the previously reported allargentums and dyscrasites, no sulphur has been detected, though some of them contain minor amounts of mercury. On the contrary, the present materials contain sulphur, although trace in amounts, and mercury is less than the detection limits of microprobe as mentioned before. However, our knowledge on the phase relations of the system Ag-Sb-Hg-S at present is too scanty to explain the above phenomena. This remains future problems to be solved.

With reference to the Cobalt-Gowganda ores, Petruk et al. (1971) stated that the allargentum has a very narrow compositional range, suggesting its formation under conditions, where all-argentum has a narrow stability field. They noticed that, in the Ag-Sb equilibrium diagram given by Somanchi (1966 a), allargentum shows a wide solid solution field at elevated temperatures at least higher than 300℃. They suggested that allargentum might have a narrow solid solution field at lower temperatures, and that, in the Cobalt-Gowganda ores, this field was reached during cooling, In case of the Yeonhwa 1 all-argentum, however, it has a wide compositional range as noted before, and this is compatible with the equilibrium diagram given by Somanchi (1966 b).

However, the Yeonhwa 1 materials show particular occurrence, which did not appear in the

Ag-Sb minerals previously recognized; i.e., their occurrence as inclusions within the galena host, suggesting an exsolution from galena upon cooling. Also, the Yeonhwa 1 allargentum does not show complex intergrowth with antimonian silver, which was commonly observed in the Cobalt-Gowganda ores. The Yeonhwa 1 ores containing the Ag-Sb minerals now in question represents the product in late stage, but the formation temperature is considered to be not so low, probably about 300℃. These facts appear to indicate that the conditions where the present Ag-Sb minerals were formed were somewhat different from that of other localities; i.e., somewhat higher temperature conditions; especially low concentration of silver in the Yeonhwa 1 ores as compared with other ores (e.g., Cobalt-Gowganda ores) may be an important factor.

In the present study, X-ray diffraction studies have not been carried out, because of the fine particles of the Ag-Sb minerals. However, recent microdiffraction technique has been greatly improved by the development of microdiffractometer with PSPC (position sensitive proportional counter). Further investigation for phase identification by X-ray microdiffractometer is thus needed.

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