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Boulangerite from the Janggun Mine, Republic of Korea;

Contributions to the Knowledge of Ore-Forming Minerals in the Janggun Lead-Zinc-Silver Ores (2)*

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ABSTRACT: At the Janggun mine, boulangerite usually occurs as needles or irregularly-shaped grains, up to 500 μm in longer dimensions, closely associated with galena, minerals of a tetrahedrite-freibergite series and bournonite in the peripheries of South A and B orebodies and the zone of manganoan carbonates surrounding them. In some places, especially at the top of South B orebody, it occures as "feather ore" consisting of its fine needles or "hairs" in small drusy cavities together with fine-grained euhedral galena, pyrite, manganoan carbonates, quartz, etc.

In reflected light, it is bluish grey in colour exhibiting moderate bireflectance and is strongly anisotropic without any internal reflections. Reflectance in air is $R_{max}=43.2$, $R_{min}=35.7$ percent at wavelength of 580 nm, and VHN: 146-173 kg/mm^2 at a 50 g-load. The chemical composition on the average from 23 complete spot analyses by electron microprobe is, Pb 56.1, Sb 25.1, S 18.5, Total 99.6 (all in weight percent); the corresponding chemical formula calculated on the basis of S=11 is; $Pb_{5.16}Sb_{3.93}S_{11.0}$, which fulfils approximately the ideal formula $Pb_5Sb_4S_{11}$. The strongest reflections on the X-ray diffraction pattern are; 3.73 Å (10), 3.22 Å (5), 3.03 Å (4) and 2.82 Å (5) and the pattern is in harmonic with space group $C^5_{2h}-P2_1/a$.

From the textural evidence of the microscopic observations, the mineral is considered to have been formed at the latest stage of hydrothermal lead-zinc-silver mineralization.

INTRODUCTION

In the course of an intensive mineralogical study on liad-zinc-silver ores from the Janggun mine, Republic of Korea, an occurrence of some curious sulphides and sulphosalts has been noted by the present authors and their colleagues (e.g., Imai et al., 1978, 1979, 1982; Imai and Lee, 1980; Lee, 1981; Lee and Imai, 1986). This paper dealing with boulangerite is the second report to be issued in a series of the studies on the ore-forming metallic minerals in the Janggun complex sulphide-sulphosalt ores, following a previous paper on the Janggun stannite. Geologic setting of the mine area and outline of the ore deposits were already described in a previous paper (Imai et al., 1982; Lee et al., 1990), accordingly only a brief account for the ore deposit in relation to its mode of occurrence is given here.

An occurrence of boulangerite at Janggun was already reported by Kim (1977) and subsequently outlined by Imai and Lee (1980) and Lee (1981), however, unfortunately no detailed study on this mineral has hitherto appeared in any papers. Also, up-to-date a study on the so-called "feather ores" has still been insufficient. This paper is designed to provide some mineralogical data for the Janggun materials, together with brief discussion on the genesis.

OCCURRENCE

The lead-zinc-silver ores at Janggun are the products of hydrothermal polymetallic mineralization and consist principally of galena, sphalerite, pyrite, pyrrhotites and arsenopyrite, with lesser amounts of chalcopyrite, minerals of a tetrahedrite-freibergite series and stannite, and with but minor or trace amounts of bournonite, boulangerite, pyrargyrite, betechtinite, alabandite, cubanite, unidentified mineral (phase "X") in the $PbS-Sb_2S_3-Ag_2S$ system, etc.

Boulangerite, although minor in amount, shows widespread occurrence in the lead-zinc-silver ores, in particular it is relatively abundant in the peripheries of South A and B orebodies, the marginal manganese carbonate zone (alteration halo formed by the hydrothermal manganese-enrichment in carbonate wall ro-

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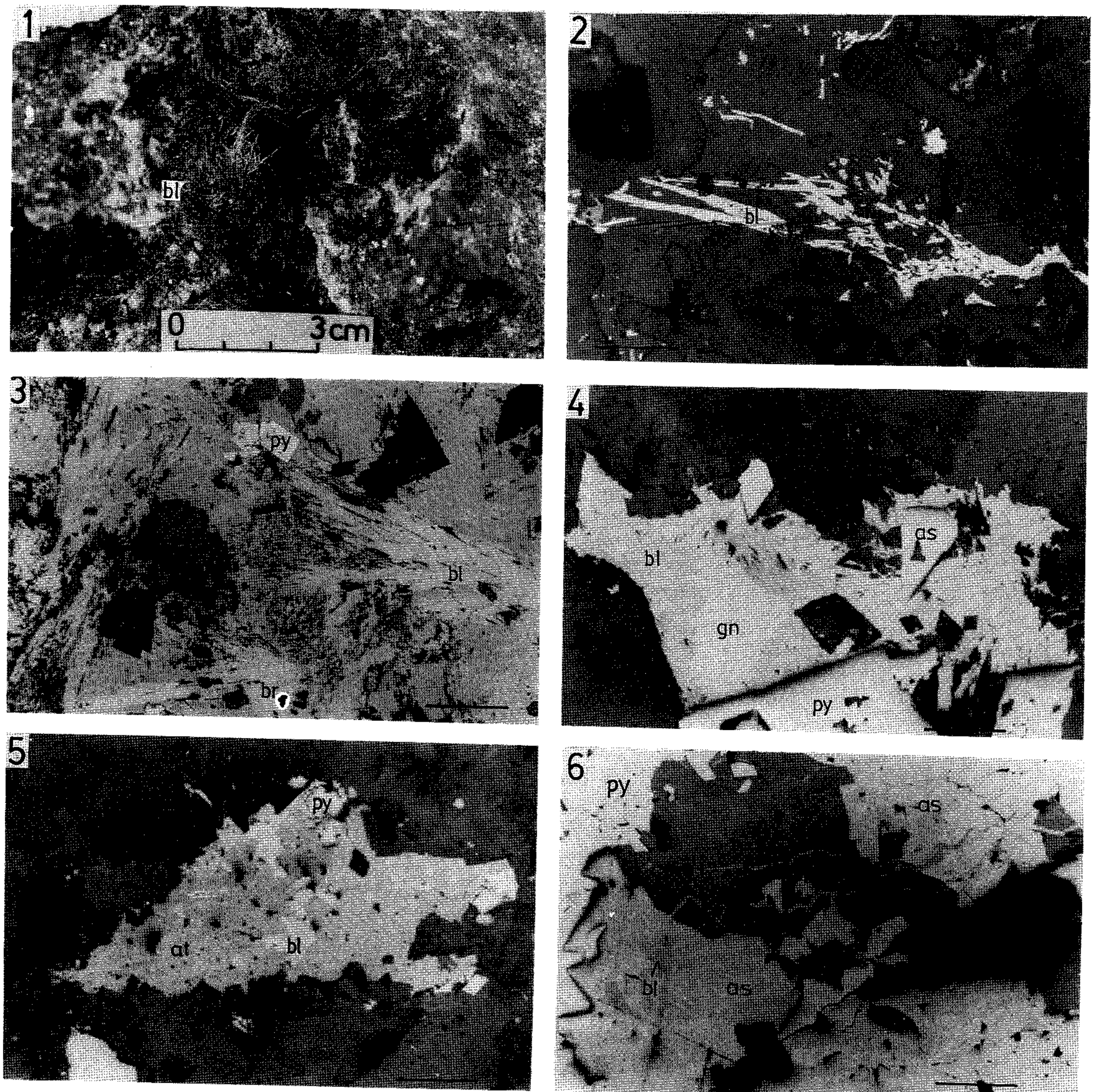

Fig. 1. Photograph of hand specimen and photomicrographs of polished sections, showning the mode of occurence of boulangerite from the Janggun mine. 1; J7705138, hand specimen, 2; J7705103, 3; J7608035A, 4; J7705195, 5; J7608035, and 6; J7705154. 2-6; polished section in reflected light. Abbreviation; as; arsenopyrite, bl; boulangerite, br; bournonite, gn; galena, py; pyrite, and sp; sphalerite. Bar scale in 2-6 indicates 100 μm in length.

cks) immediately surrounding the orebodies portion of "manganese breccia-pipe". The mineral almost invariably occurs as microscopic grains up to 500 μm in longer dimensions, and is closely associated with galena, minerals of a tetrahedrite-freibergite series and bournonite, and occasionally with sphalerite and arsenopyrite. In some places of the peripheries of South A and B orebodies and manganese carbonate zone, "feather ores" may occur in small drusy cavities as shown in Fig. 1-1. They consist dominantly of needles or "hairs" of boulangerite having dark iron-grey colour with small amounts of euhedral galena and pyrite together with manganoam carbonates and quartz.

Under the ore microscope, the mineral was observed to occur in the following characteristic textural relationships.

1) Isolated acicular or lath-shaped crystals and fibrous aggregates of boulangerite are disseminated within the base of rhodochrosite or manganoan dolo-

mite (magnesian kutnohorite). The individual crystals are less than 100 μm in length and extremely narrow in width, less than 30 μm (Fig. 1-2).

2) Fibrous aggregates of boulangerite is seen to replace bournonite grains, in which cube of pyrite and droplets of sphalerite are enclosed (Fig. 1-3).

3) Irregular grains of boulangerite are seen to replace galena along the contact with rhodochrosite, sphalerite and arsenopyrite, and are closely associated with bournonite. Within the grains of boulangerite, the remnants of galena with irregular outline are recoguized (Fig. 1-4).

4) Acicular or bladed crystals and irregular grains or droplets are enclosed within the comparatively large grains of minerals of a tetrahedrite-freibergite series, which are scattered through out the base of rhodochrosite, attaining to 600 μm in longer dimensions. Individual crystals of boulangerite are fine-grained, less than 50 μm across (Fig. 1-5).

5) Veinlets of boulangerite are seen to fill the irregular fractures within an intergrowth of arsenopyrite and sphalerite. The width of the veinlets is extremely narrow, less than 10 μm (Fig. 1-6).

Table 1. Dispersion of reflectance of boulangerites in air (R percent).

Wave length	(1)		(2)	
λ_0 (nm)	R_{max}	R_{min}	R_{max}	R_{min}
400	46.4	36.8		
420	45.8	37.1	42.4	40.3
440	45.6	37.2	42.0	39.4
460	45.3	37.1	41.9	39.2
480	45.2	36.7	40.4	38.5
500	44.9	37.1	39.3	37.4
520	45.0	36.9	40.1	37.9
540	44.6	36.6	40.3	38.0
560	44.2	36.8	40.2	37.8
580	43.2	35.7	39.9	37.4
600	43.0	35.8	39.6	37.1
620	41.9	35.3	39.5	36.9
640	41.1	34.5	39.1	36.6
660	40.0	33.9	38.6	36.1
680	39.5	34.0	37.9	35.5
700	39.3	33.6	37.1	35.0

(1); Boulangerite from the Janggun mine, Specimen J 7705103 and J7608035, Five grains taken at random.
(2); Boulangerite, after Picot and Johan (1982).

OPTICAL AND PHYSICAL PROPERTIES

In polarized reflected light, the Janggun boulangerite is light greyish white in colour with slightly greenish tints against the co-existing galena and exhibits moderate bireflectance in air, being enhanced in oil; i.e., colour becomes darker and bireflectance more distinct, changing in colour from bluish light grey to bluish grey. Between crossed polars, it is strongly anisotropic in air, being somewhat enhanced in oil, with a polarization colour changing from white to brownish grey as the stage is turned. No internal reflections are recognizable even with strong illumination.

Polishing or scratch hardness is higher than that of the associated bournonite and slightly higher than that of galena. Talmage hardness is probably B^+.

The reflectance measurements of the five grains taken at random were performed with Olympus MMSP-RK multi-photometric microscope. All measurements were made against WTiC standard calibrated by Carl Zeiss Jena Co., and beam spot of 7 μm in diameter was employed and the objective used had a magnification of 20X and numerical aperture of 0.40. The dispersion of reflectance in air thus obtained are listed in Table 1, together with that given by Picot and Johan (1982). The reflectance-dispersion curves show continuous but slight decrease of reflectance with increasing wavelength.

The Vickers hardness number (VHN) was measured with an Akashi MVK-C microhardness tester, and it was found that the VHN ranged from 146 to 172 kg/mm^2 at a 50 g-load, which was approximately identical with that of 116~182 kg/mm^2 at a 50 g-load given by Uytenbogaardt and Burke (1971).

Etch reactions with reagents having standard concentrations (Short, 1940); HNO_3, stains slightly brownish, tarnishes washed off; HCl, stains slightly brownish, some areas unaffected, tarnishes wash off; aqua regia, quickly stains brown; KCN, KOH, $HgCl_2$, H_2O_2: all negative.

CHEMICAL ANALYSIS

The chemical analysis, both qualitative and quantitative for the Janggun materials were carried out using a JEOL JXA-50A electron microprobe with 35° X-ray take-off angle and two-channel detecting system. Qualitative spot analysis by spectrometer scans and careful peak searches indicated that the detected elements were Pb, Sb, Sn, Zn and S, and other elements such as Fe, As and Cl were below the detective limits of microprobe. Line or scanning profiles by spectral lines of PbMα, SbLα, and SKα obtained by electron microprobe traverses indicated that, there was no significant compositional heterogeneity within

Table 2. Selected microprobe analyses of boulangerites.

	Weight percent									
	(1)	(2)	(3)	(4)	(5)	(6)	(7)	(8)	(9)	(10)
Pb	55.7	55.2	56.0	56.7	55.4	56.1	55.8	56.1	58.2	55.24
Sb	25.0	25.2	25.0	24.9	25.6	25.1	24.8	25.1	25.2	26.96
Sn	–	–	–	–	–	0.1	–	–		
Cu	0.1	–	–	–	–	–	0.1	–		
S	18.8	18.0	18.5	18.5	18.8	18.4	18.5	18.5	19.8	18.80
Total	99.6	98.4	99.5	101.1	99.8	99.7	99.1	99.6	103.2	100.00
	Atomic proportion as S=11.0									
	(1)	(2)	(3)	(4)	(5)	(6)	(7)	(8)	(9)	(10)
Pb	5.04	5.22	5.15	5.22	5.02	5.19	5.13	5.16	4.96	5
Sb	3.85	4.06	3.91	3.90	3.94	3.95	3.88	3.93	3.69	4
Sn	0.00					0.02				
Cu	0.03						0.03			

(1)-(7); Boulangerites from the Janggun mine, (8); Average value from 23 complete analyses. (9); Boulangerite from the Uwamuki deposit, Kosaka mine, After Matsukuma et al., 1974. (10); Ideal composition, $Pb_5Sb_4S_{11}$. (1); Specimen J7608034, gn-br-py-sp-bl*, (2); J7608035, br-py-sp-bl*, (3); J7705103*, td-br-bl*, (4); J7705138, boulangerite in rhodochrosite, (5); J7705138, td-br-bl*, (6); J 7705195, gn-as-bl*, and (7); J7705103, "X"-gn-bl*.
–; less than the detective limit of microprobe.
*Mineral assemblage. Abbreviation, as=arsenopyrite, bl =boulangerite, br=bournonite, gn=galena, py=pyrite, sp=sphalerite, td=mineral of tetrahedrite-freibergite series, and "X"=undetermined mineral of the system PbS-Sb_2S_3-Ag_2S.

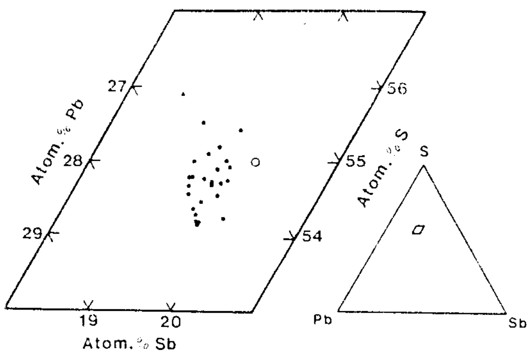

Fig. 2. Enlarged parallerogram in the triangle diagram of the system Pb-Sb-S, in which electron microprobe analyses of the Janggun boulangerite are plotted (dot). Open circle: $Pb_5Sb_4S_{11}$.

Table 3. X-ray powder diffraction data for boulangerite.

(1)		(2)		hkl
I/I_o	$d(\text{Å})_{meas}$	I/I_o	$d(\text{Å})^*_{meas}$	
0.5	6.80	0.5	6.74	310
1	6.08	1	6.13	320
0.5	5.18	0.5	5.20	410,240
0.5	4.84	0.5	4.86	420
		0.5	4.61	150
1	4.40	1	4.36	430
1	3.99			520
2	3.92			350,060
1	3.86	2	3.89	160
10	3.73	10	3.71	112,530
2	3.44	1	3.43	540
2	3.32	3	3.32	170
5	3.22	5	3.21	630,232
4	3.03	4	3.02	242,640
5	2.823	8	2.815	730,342
1	2.784			062,$\bar{2}$62
3	2.692	3	2.691	740
1	2.582	1	2.578	820,480
1	2.513	0.5	2.515	830
			2.435	390
1	2.370			622,$\bar{8}$22
2	2.336	5	2.337	490,910
1	2.307	0.5	2.303	182,$\bar{3}$82
		0.5	2.226	
1	2.145	4	2.145	
		1	1.967	
1	1.918	1	1.920	
2	1.862	7	1.861	
		0.5	1.829	
1	1.759	6	1.757	

(1) Boulangerite, feather ore from the Janggun mine, Specimen J7705138.
(2) Boulangerite from Sullivan mine, British Columbia, Canada (Robinson, 1948).
*In original table by Robinson, *d*-spacings were fiven in kX unit, and in this table kX unit is converted into unit, using nonvertion factor=1.00202 kX.

single grains.

Analyzing conditions employed throughout this study were as follows; accelerating potential: 20 kV, specimen current: 10～30 nA on MgO, analyzing crystals and spectral lines used: LiF for ZnKα and CuKα, and PET for PbMα, SbLα and SKα. Microprobe standards used: natural galena for Pb, natural stibnite for Sb and S, and synthetic SnS and ZnS for Sn and Zn, respectively, and natural chalcopyrite for Cu. Above natural sulphides are of known composition.

The ZAF correction for matrix effects was applied to the values at first approximation using the computer programs written by Yui and Shoji (1969). Selected microprobe analyses and the average of 23 analyses are given in Table 2, together with that of boulangerite in Kuroko from the Uwamuki ore deposit of the Kosaka mine given by Matsukuma et al. (1974)

and the ideal composition of boulangerite. Each analysis represents the average of three sets or more of spot analyses within single grains. The average of 23 analyses is, Pb 56.1, Sb 25.1, S 18.5, Total 99.6 (all in weight percent) and the corresponding chemical formula calculated on the basis of S=11 is, $Pb_{5.16}Sb_{3.93}S_{11.0}$. Also, the results of 23 complete analyses are plotted into the enlarged parallerogram in the triagle diagram of the system Pb-Sb-S in Fig. 2. As can be seen in the figure, they show a narrow spread.

X-RAY POWDER DIFFRACTION

The feather aggregates of boulangerite in a small drusy cavity (Specimen J7705138-Fig. 1-1) were extracted by a steel needle and the purification of sample was made by the careful selection as being free from impurities as possible under the binocular microscope.

X-ray powder-diffraction patterns of the sample thus prepared were recorded with a Rigaku diffractometer "Geigerflex" (2026) using Mn-filtered FeKα-radiation (λ=1.9373Å). The X-ray powder-diffraction data for the present material are listed in Table 3, together with those on boulangerite from the Sullivan mine, British Columbia, Canada given by Robinson (1948). A few reflections with weak intensity are omitted, since they are identified as deriving from galena. There are good agreement between the two and the data are in harmony with the space group $C_{2h}^{5}-p2_{1/a}$.

CONCLUDING REMARKS

Boulangerite ($Pb_5Sb_4S_{11}$) belonging to the Pb-Sb-S system lies on the pseudo-binary PbS-Sb_2S_3 join, along which at least 19 distinct natural and synthetic lead sulphantimonide have been reported in literatures (e.g., Craig et al., 1973; Garvin, 1973; Hoda et al., 1975), and it is close to semseyite ($Pb_9Sb_8S_{21}$) in composition. Also, Robinson (1948) already showed that the X-ray powder-diffraction patterns of falkmanite ($Pb_{12}Sb_8S_{24}$) and yenerite ($Pb_{11}Sb_8S_{23}$) were distinguishable from that of boulangerite. Summarizing the mineralogical data given so far, however, it may be concluded that the present Janggun matertial is identical with boulangerite in all mineralogical properties.

It has already been pointed out that boulangerite, jamesonite and other lead sulphantimonides synthesized in aqueous solutions of chlorines at temperature of 300~400℃ or in liquids of chlorides at 300℃, contain appreciable amount of chlorine and the natural occurrence of chlorine-bearing sulphosalts has already been reported (Breskovska et al., 1978; Moëlo, 1978). In spite of the careful examination, however, chlorine was not detected from the present material by electron microprobe as mentioned before, and also qualitative analysis by means of X-ray fluorescence spectroscopy did not give any indications of presence chlorine.

The mode of occurrence of the boulangerite and the textural relationships observed in the sulphide-sulphosalt assemblages as noted previously indicate that, the mineral represents the latest product in the course of hydrothermal polymetallic-mineralization.

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REFERENCES

Breskovska, V. V., Mozgova, N. N., Bortnikov, H. S. and Tsepin A. J. (1978) Chlorine-containing sulphosalts from the Madjarovo polymetallic deposit in Bulgaria. XIth General Meeting, IMA, Abstr. v. 1, p. 136-137 (Novosibirsk, U.S.S.R.).

Craig, J. R., Chang, L. L. Y. and Lees, W. R. (1973) Investigation in the Pb-Sb-S system. Canad. Miner., v. 12, p. 199-206.

Garvin, P. L. (1973) Phase relations in the Pb-Sb-S system. Neues Jahrb. Miner. Abh., v. 118, p. 235-267.

Hoda, S. N. and Chang, L. L. Y. (1975) Phase relations in the systems PbS-Ag_2S-Sb_2S_3 and PbS-Ag_2S-Bi_2S_3. Amer. Miner., v. 60, p. 621-633.

Imai, N. and Lee, H. K. and Sakai, T. (1978) Boulangerite from the Janggun mine, Republic of Korea-Studies on the ore-forming minerals in the Janggun lead-zinc ores (2) (abstr. in Japanese). Coll. Abstr. Annual Meet. Miner. Soc. Japan, A-65, p. 80.

Imai, N., Lee, H. K. and Iino, R. (1979) Stannite from the Janggun mine, Republic of Korea-Studies on the ore-forming minerals in the Janggun lead-zinc ores (4) (abstr. in Japanese). Mining Geol., v. 29, p. 62.

Imai, N. and Lee, H. K. (1980) Complex sulphide and sulphosalt ores from the Janggun mine, Republic of Korea. In Complex Sulphide Ores. Proc. Internat'l. Conf. for Complex Sulphide Ores, Rome, Oct. 5-8, 1980, p. 248-259.

Imai, N., Lee, H. K. and Sakai, T. (1982) Bournonite from the Janggun mine, Republic of Korea-Contributions to the knowledge of ore-forming minerals in the Janggun lead-zinc-silver ores (1). Jour. Japan. Assoc. Miner. petrolog. Econ. Geol., v. 77, p. 310-321.

Kim, S. J. (1977) Mineralogical study of zinc ores and mill products from the Janggun mine (with emphasis on the cause of low-grade concentrate and the scheme of raising its grade). Jour. Korean Inst. Mining Geol., v. 8, p. 117-124.

Lee, H. K. (1981) Studies on the complex sulphide-suphosalt ores from the Janggun mine, Republic of Korea (in Japanese with English abstr.). Doctoral thesis submitted to the Graduate School of Sci. Eng'ng., Waseda Univ., p. 1-328.

Lee, H. K. and N. Imai (1986) Stannite from the Janggun mine, Republic of Korea - Contributions to the knowledge of ore-forming minerals in the Janggun lead-zinc-silver (3) (in Korean with English abstr.). Jour. Korean Inst. Mining Geol., 19, Spec. Iss., p. 121-130.

Lee, H .K.,Imai, N. and Ko, S. J. (1990) Genesis of the lead-zinc-silver and iron deposits of the Janggun mine, as related to their structural features - Structural control and wall rock alteration of ore - formation-. Jour. Korean Inst. Mining Geol., v. 23, p.161-181.

Matsukuma, T., Niitsuma, H., Yui, S. and Wada, F. (1974) Rare minerals from Kuroko ores of the Uwamuki deposits of the Kosaka mine, Akita Prefecture. In Geology of Kuroko Deposits (Eds.: S. Ishihara et al.), Mining Geol. Spec. Issue, v. 6, p. 349-361.

Moëlo, Y. (1978) Minor constituents of acicular lead sulphantimonides: Their part in conditions of formation of these sulphosalts. XIth General Meeting, IMA, Abstr. v. 1, p. 138-139 (Novosibirsk, U.S.S.R.).

Picot, P. and Johan, Z. (1982) In atlas of ore minerals, v. 178, p. 99-100, Elsevier Press, Amsterdam.

Robinson, S. C. (1948) The identity of falkmanite and yenerite with boulangerite. Amer. Miner., v. 33, p. 716-723.

Short, M. N. (1940) Microscopic determination of the ore minerals. U.S. Geol. Surv. Bull., v. 914, p. 99.

Yui, S. and Shoji, T. (1976) Computer programs used in the ZAF correction (in Japanese). Jour. Miner. Soc. Japan, 12, Spec. Issue, p. 70-81.

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한국 · 장군광산산 보울란저라이트에 대하여; 장군 연 · 아연 · 은 구성광물의 지식에 대한 기여 (2)

이현구 · 이마이 나오야

요 약: 장군광산산 보울란저라이트는 침상이나 불규칙한 형태로 방연석,차골석,함은 사면동석과 밀접하게 공생하여 남광상에서 산출되며, 특히 남광상 A광체와 B광체 주변의 능망간석대에 그 산출이 뚜렷하다. 어떤 장소, 특히 남광상 B광체 상부에는 방연석, 황철석, 유비철석, 함망간 방해석, 석영 등과 공생하여 작은 정동중에 "머리털"이나 "깃털"모양의 보울란저라이트 집합체를 형성하기도 한다. 이광물의 반사색은 녹회색을 띠고, 반사다색성은 차골석보다 강하고 이방성이 명료하다. 반사율은 공기중에서 파장이 560 nm일 때 $R_{max.}=42.3\%$, $R_{min.}=35.7\%$이고, 비커스경도 (VHN)는 50 g의 하중에서 146~173 kg/mm^{2}이다. 표준시약 (Short, 1941)에 의한 반응에서는 HNO3에서는 즉시 흑색으로 변하지만, 그외의 시약과는 거의 반응하지 않는다. 8개 시료 23개 입자에 대하여 EPMA로 분석한 결과 $Pb_{56.1}Sb_{25.1}S_{18.5}$, Total 99.6 wt.%이고, S=11로해 계산된 화학식은 $Pb_{5.16}Sb_{3.94}S_{11}$로서 거의 보울란저라이트의 이상적인 화학식 $Pb_5Sb_4S_{11}$을 만족하고 있다. X-선 회절분석에 의해 얻어진 X-선 회절패턴에 나타나는 주요한 회절선은 3.73 Å (10), 3.22 Å (5), 3.03 Å (4), 2.82 Å (5)로서 공간군 $C^5_{2h}-P2_{1/a}$과 잘 일치한다.

이상의 장군광산산 보울란저라이트는 그 산출상태와 광물의 공생관계로부터 열수성 연-아연-은광화작용의 최후기에 생성된 광물로 판단된다.

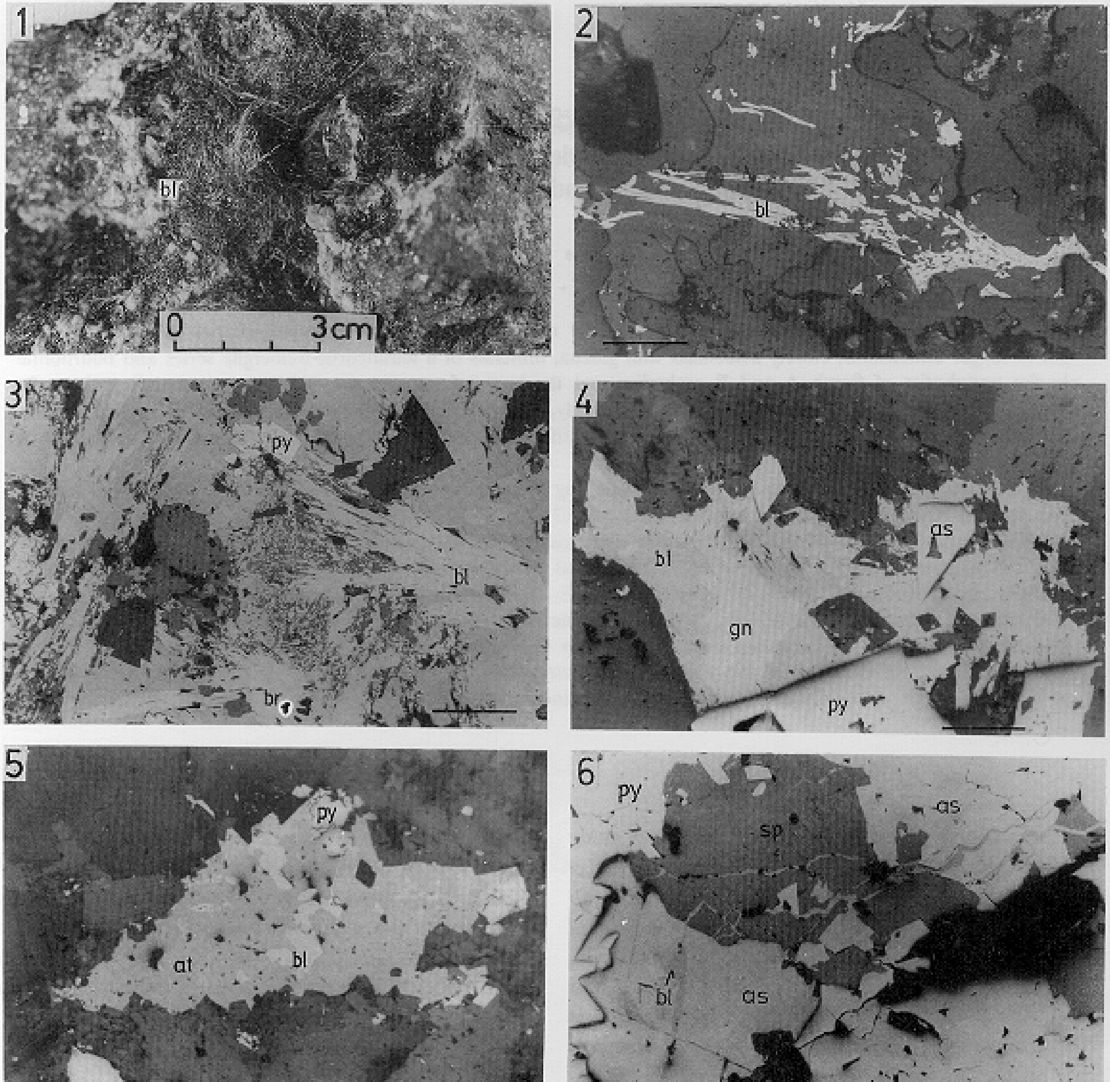

Fig. 1. Photograph of hand specimen and photomicrographs of polished sections, showning the mode of occurence of