

Compositional Variations of Arsenopyrite from Gold-Silver Deposits in Korea*

Seon-Gyu Choi** and In-Sik Choi***

ABSTRACT: The gold-silver mineralizations in Korea are closely related to Jurassic Daebo igneous activity (121 and 183 Ma) and Cretaceous Bulgugsa igneous activity (60 and 110 Ma). A compilation and re-evaluation of chemical data in arsenopyrite suggest that the As contents vary, reflecting different genetic environments or mineral assemblages. The gold-silver vein deposits from various mineralized area were investigated using arsenopyrite geothermometer. Arsenopyrites from the Jurassic Au-dominant deposits are distinct by high As contents (29.68~33.46 atomic %) with narrow variations, equivalent to a temperature range of 370~450°C and a sulfur fugacity of about 10^{-8} ~ 10^{-6} atm. On the contrary, arsenopyrites from the Cretaceous Au-Ag and Ag-dominant deposits show a wider range in atomic % As composition of 27.47~32.74. They may have formed at temperatures of 250~350°C and about $f_{S_2}=10^{-12}$ ~ 10^{-10} atm. The data of arsenopyrite geothermometer, electrum-sphalerite geothermometer, fluid inclusions, vein morphology and emplacement depth of igneous rocks indicate that the gold mineralizations of Group IIA occurred at temperatures between 300 and 500°C at depth of several tens km or more (about 4-5 kbar), and the gold-silver deposits of Groups III, IV and V were formed at a temperature range of about 170~370°C under the shallow environment (<1 kbar).

INTRODUCTION

Most sulfides easily undergo retrograde reactions and thus only the most refractory ones can provide reliable information on physical conditions of high temperature and high pressure. Arsenopyrite is one of the refractory sulfides and exhibits appreciable solid solution, which is a sensitive indicator to temperature or pressure. The stability of arsenopyrite in the system Fe-As-S has been determined experimentally by Clark (1960), Barton (1969), Kretschmar, Scott (1976), and Sharp *et al.* (1985). The arsenopyrite geothermometer was proposed by Kretschmar, Scott (1976), and this method is meaningful only when arsenopyrite is present in sulfur-buffered equilibrium assemblages and its minor element content does not exceed 1 wt.%. Scott (1983) constructed a phase equilibria diagram in the system Fe-Zn-As-S in which the compositions of arsenopyrite and sphalerite are determined by temperature and sulfur fugacity. Equilibrium compositions of arsenopyrite and sphalerite are usually preserved in the hydrothermal vein deposits formed by rapid cooling.

Their compositions supposedly undergo no changes during subsequent processes. Arsenopyrite has received considerable attention for estimating the formation conditions for different types of ore deposits (Lowell, Gasparini, 1982; Kay, Strong, 1983; Sundblad *et al.*, 1984; Sharp *et al.*, 1985; Bortnikov, 1993). Arsenopyrite geothermometer were employed mainly using skarn deposits and base-metal deposits by some Korean researchers (Choi *et al.*, 1986; Koh *et al.*, 1992; Park, 1990).

Many of the gold-silver vein deposits in Korea, characterized by the simple ore mineralogy such as pyrite, sphalerite, galena and arsenopyrite, formed in different geologic settings and at different times (Park *et al.*, 1986; Choi, Choi, 1995; Shimazaki, 1986). These gold-silver vein deposits are genetically associated with epithermal to hypothermal vein deposits (Shelton *et al.*, 1988; Choi, Choi, 1995). The first objective of this paper is an attempt to identify the compositional variation of arsenopyrite and to apply the arsenopyrite geothermometer to infer the formation temperature of the gold-silver deposits. Secondly, the detailed fluid inclusion, mineralogical data, the geological settings and age relations are used to discuss the varying conditions of the gold-silver mineralizations in Korea.

* The present studies were supported by the Basic Science Research Institute Program, Ministry of Education, 1997, Project No, BSRI-94-5403.

** Department of Earth and Environmental Sciences, Korea University, Seoul 136-701, Korea

*** Center for Mineral Resources Research, Korea University, Seoul 136-701, Korea

GEOLOGICAL FEATURES AND ORE DEPOSITS

The gold-silver vein deposits have wide distribution

within the Precambrian Gyeonggi metamorphic belt to the north and Cretaceous Gyeongsang sedimentary basin to the south in South Korea. Most of the gold-silver vein deposits occur along 200 km elongated Mesozoic granitic batholiths running a NE-SW Sinian direction, and tend to be limited in ten metallogenic provinces (Kim, 1971). Two main igneous activities in Korea during Mesozoic time are recognized, based on K-Ar and Rb-Sr ages: (1) Jurassic Daebo igneous activity between 183 and 121 Ma; (2) Cretaceous Bulgugsa igneous activity between 110 and 60 Ma. The Jurassic Daebo granitoids emplaced into Precambrian metamorphic rocks show wide and elongated distributions in the central part of Korea, and the Cretaceous Bulgugsa intrusions commonly cut across these rocks as small stocks and dikes in southeastern Korea (Fig. 1). The spacial distribution of the gold-silver deposits is apparently controlled by the Daebo igneous activities. However, recently radiometric age data have revealed that the precious-metal mineralizations are genetically related to both the Daebo and

Bulgugsa intrusions (Shimazaki *et al.*, 1986; Park *et al.*, 1986; So *et al.*, 1987; So, Shelton, 1987; So *et al.*, 1989).

The precious-metal vein deposits in Korea have been reported as mesothermal to hypothermal Korean-type deposits to compare these with epithermal gold-silver vein deposits in Japan (Tsuchida, 1944). These deposits were divided into Korean-type, mesothermal and epithermal deposits on the basis of the fluid inclusions and stable isotope data (Shelton *et al.*, 1988). It is known that a wide variety of geologic environments related to major tectonics, structural features and igneous activities is closely associated with genetic types for the gold-silver deposits. These precious-metal deposits can be categorized into three main groups according to their ratios of produced grades of silver and gold; Au-dominant deposits, Au-Ag deposits and Ag-dominant deposits. Although the original distinctions between the gold-silver deposits were made only by geochemical differences, these deposits are also confirmed by mineralogy. The geological and mineralogical informations on the gold-silver deposits with fineness variations in produced ore grades are listed on Table 1. Most of the gold-dominant deposits occur in metamorphic, plutonic or less commonly in sedimentary rocks. In contrast, the Au-Ag and Ag-dominant deposits are mainly hosted by the Cretaceous sedimentary and subvolcanic rocks.

The precious-metal mineralizations formed between 138 and 71 Ma, contemporaneous with portions of the two magmatic activities. The Jurassic and early Cretaceous mineralizations are characterized by the Au-dominant type, but tend to change to the Au-Ag and Ag-dominant types at late Cretaceous. The Jurassic precious-metal deposits commonly show several characteristics: (1) the simple massive vein morphologies; (2) the relatively high fineness values in ore-concentrating parts; (3) their distinctly simple ore mineralogy. The Cretaceous precious-metal deposits are generally characterized by some features such as complex vein morphologies, low to medium fineness values in the ore concentrates, and abundance of Ag-bearing phases. Recently, an empirical classification of precious-metal vein deposits in Korea is proposed, based on the following criteria: (1) the fineness of produced grades of silver and gold, and the associated index metal in ores; (2) the morphology and alteration of veins; (3) their ore mineralogy such as iron sulfides and Ag sulfosalts; (4) their geological setting. Although the original distinction between the gold-silver vein deposits was made only by Ag/Au ratio, vein morphology and mineralogy, they are also supported by the difference in formation environment (Choi, Choi, 1995). They suggest that the vein morphology, mineral assem-

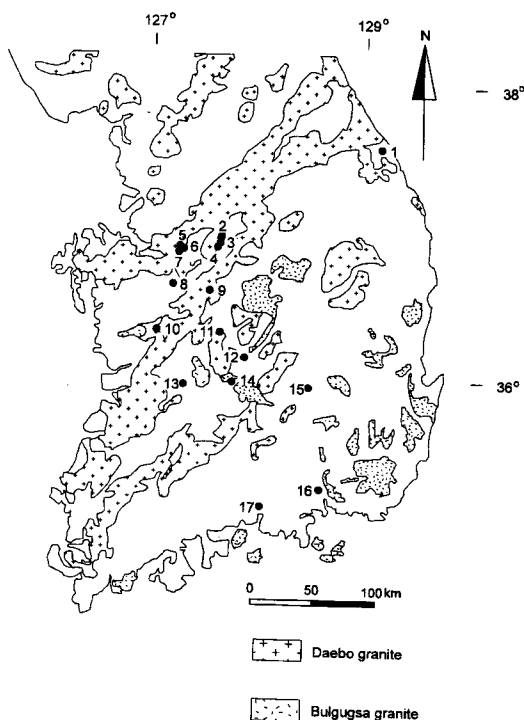


Fig. 1. Simplified map of Mesozoic granitoids showing the distribution of the studied gold-silver mines: 1; Ogkye, 2; Mugeug, 3; Geumwang, 4; Geumbong, 5; Cheonbo, 6; Ilbo, 7; Daehung, 8; Jeoneui, 9; Cheongju, 10; Namsan, 11; Manmyeong, 12; Yeongbogari, 13; Jeonjuil, 14; Yonghwa, 15; Seongju, 16; Samjeong, 17; Sangchon.

blage, geochemistry, alteration, and style of mineralization in Groups I and IIA are markedly different from those of Groups IIB, IIC, III, IV and V.

MINERALOGICAL FEATURES

The vein occurrence of the precious-metal deposits can be mainly divided into the massive vein and complex vein types on the basis of morphology and texture (Table 1). The massive vein type is characterized by simple veins that are commonly homogeneous in composition and contain interlocking networks of quartz and ore minerals within metamorphosed host rocks and plutonic-level granitoids. These veins are predominantly composed of coarse-grained quartz with lesser amounts of muscovite, K-feldspar, and relatively simple base-metal sulfides. They also have narrow selvages of sericitic and chloritic alterations. These veins, which are characterized as either buck or ribbon structure, show evidence of both brittle and ductile deformation, suggesting the conditions of deep deposit formation. The complex vein type is represented by multistage veins that have fine- to medium-granular or clear drusy quartz, and show relatively well-developed crustiform, breccia, fibre and cockade structure in hosting sedimentary and volcanic rocks. This suggests open-space fillings characteristic of high-level mineralization. These veins show relatively extensive zones (several meters) of propylitic, argillic, sericitic and silicic alterations, and mainly consist of quartz or chalcedony and carbonate

with less amounts of fluorite, clay minerals, base-metal sulfides and complex silver-bearing sulfosalt assemblages. Textural relations indicate more complex paragenetic sequence compared to the massive vein type. The distinctive vein morphologies and textures characterize each type of Korean precious-metal deposits, suggestive of different depths of emplacement (Dowling, Morrison, 1989; Vearncombe, 1993).

Pyrite, sphalerite, galena, and minor arsenopyrite, chalcocopyrite and/or Ag sulfosalts, are the common sulfide phases in the gold-silver vein deposits. In some Au-dominant deposits, the ore mineralogy of massive veins is characterized by sulfide-poor quartz veins containing minor pyrite, sphalerite and arsenopyrite with rare electrum and silver minerals. Arsenopyrite commonly occurs as coarse-grained euhedral rhombs or aggregates in association with pyrite and sphalerite, and is occasionally crosscut and filled by later veinlets of abundant galena, sphalerite and electrum. Textural relationships indicate that arsenopyrite is the earliest ore mineral, coexisted with or followed by sphalerite, pyrite and electrum.

In general, the ores of complex veins from the gold-silver and silver-dominant deposits are characterized by multistage mineralization, indicated by the significant differences in the mineralogy of these deposits. The early assemblages from these ores are dominantly pyrite, sphalerite and arsenopyrite with lesser galena, electrum and chalcocopyrite, but the later assemblages include a variety of pyrite, galena, sphalerite, chalcocopyrite, Ag sulfides, Ag sulfosalts or tel-

Table 1. Comparative geological and mineralogical characteristics for selected gold-silver vein deposits.

Ore deposit	Geologic setting	Type	Ore mineralogy	Morphology	Fineness (average)	Host rock	Age (ma) Host rock (min.)
Ilbo	Gyeonggi massif	Au-dominant	py>gl, ap, sp>el	massive	316	gneiss, schist	140 (138)
Daeheung	Gyeonggi massif	Au-dominant	py>gl, ap, sp>el, cp, agss	massive	242	pegmatite, gneiss	133-162
Yeongbogari	Yeongnam massif	Au-dominant	py>ap, sp>po, gl, cp>el, ar	massive	292	gneiss, schist	(132)
Ogkye	Taebaeksan basin	Au-dominant	py>ap, sp, gl>cp>el, agss	complex	209	limestone	
Manmyeong	Ogcheon belt	Au-dominant	py>sp, gl, ap>el	complex	532	granite	
Sangchon	Gyeongsang basin	Au-dominant	py>ap, sp>gl>el, ar	complex	362	anorthosite	Cretaceous
Namsan	Gyeonggi massif	Au-dominant	py>ap, sp, gl, cp>el	complex	281	gneiss, granite	
Jeoneui	Gyeonggi massif	Au-dominant	py>ap, sp, gl, cp>el	complex	216	gneiss, schist	(94)
Samjeong	Gyeongsang basin	Au-dominant	py>sp, gl, cp>ap, lo>el, ar	complex	334	sandstone, andesite	Cretaceous
Cheongju	Daebo granitoid	Au-Ag	py>sp, gl, po, cp>ap, el, ag, ar	complex	332	granite	(87-98)
Yonghwa	Yeongnam massif	Au, Ag	py>sp, gl, cp>ap>ag, ar, el, agss	complex	156	granite, gneiss	(96)
Mugeug	Bulgugsa granitoid	Au, Ag	py>ap>sp, gl, cp>el, ar, ag, agss	complex	181	granite	112 (98)
Geumwang	Bulgugsa granitoid	Au, Ag	py>ap>sp, gl, cp>ar, ag, el, agss	complex	145	granite	112 (98)
Geumbong	Bulgugsa granitoid	Au, Ag	py>ap>sp, gl>ar, ag, agss>el	complex	75	granite	112 (98)
Jeonjuil	Ogcheon belt	Ag-dominant	py>gl, cp, sp>ap>agss, ag, ar>el	complex	43	phyllite, schist	(71)
Seongju	Gyeongsang basin	Ag-dominant	py>sp, gl, cp>ap>ar, ag, agss>el	complex	3	shale, sandstone	(98)

Abbreviations: ag; native silver, agss; Ag sulfosalts, ap; arsenopyrite, ar; argentite or acanthite, cp; chalcocopyrite, el; electrum, gl; galena, lo; loellingite, po; pyrrotite, py; pyrite, sp; sphalerite.

lurides. The quartz and arsenopyrite in the veins tend to be interbanded, and in some specimens each band of arsenopyrite is bounded by a thin band of pyrite and/or sphalerite. The arsenopyrite of early stage is typified by fine-grained euhedral rhombs and is intimately intergrown with pyrite and sphalerite with no signs of replacement. Such textural relations may suggest an equilibrium between arsenopyrite, sphalerite and pyrite. The arsenopyrite crystallized during later stage occurs as coarse-grained euhedral crystals or aggregates along with pyrite, sphalerite, chalcopyrite and electrum. These massive aggregates are frequently fragmented, brecciated, and crosscut by veinlets of silver-rich mineral assemblages. The structural and textural relationships between gold, silver, arsenopyrite and other vein minerals indicate that arsenopyrite deposition occurred through an early to middle vein growth episode.

ARSENOPYRITE GEOTHERMOMETRY

Uniquely for arsenopyrite, sphalerite and iron sulfides assemblages deposited in equilibrium conditions, with their composition not being modified by subsequent processes, a reliable application of mineral assemblages to a geothermometer is likely possible. Changes in the composition and temperatures of the mineralizing fluids during ore deposition have been estimated using data from co-existing mineral assemblages, together with Kretschmar, Scott's (1976) arsenopyrite geothermometer. About 600 analyses of arsenopyrites were examined for this study from sixteen gold-silver vein deposits in different mineralized areas. Usually, several specimens were investigated for each deposit and several grains were analyzed in the same polished section. Emphasis was placed on selecting the arsenopyrite grains in mutual contact with iron sulfides or iron diarsenide, and on guaranteeing the homogeneity of the arsenopyrite grains. The composition of arsenopyrite was determined at Center for Mineral Resources Research (CMR), Korea University, using JEOL 8600 electron microprobe with EDS and WDS. The qualitative analysis was carried for Fe, As, S, Sb, Co and Ni. Special attentions were paid to a quantitative analysis for arsenic, and the As contents were always checked using two extrapure standards (InAs and GaAs). The average analytical error does not exceed the ± 1.0 wt.%. Kretschmar and Scott (1976) recommended using arsenopyrite grains with a total concentration of Ni+Co+Sb not exceeding one weight percent for geothermometric purposes. In general, the content of the minor elements Sb, Co and Ni was very low (< 0.2 wt.%), although the highest contents of Co (up to 1.02 wt.%) and Ni (up to 0.82

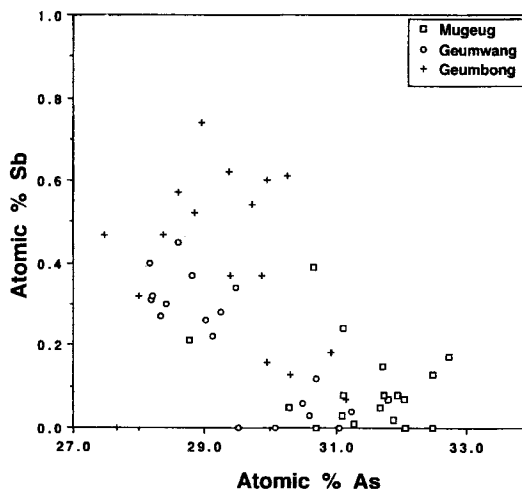


Fig. 2. Plot of As versus Sb (atomic %) for Sb-bearing arsenopyrites from Mugeug, Geumwang and Geumbong mines.

wt.%) on arsenopyrite were found in the Namchang deposits (Kaneda, 1986). Thus, the presence of these element should not significantly affect the result on the arsenopyrite geothermometer. But, the Sb contents of the arsenopyrite in some specimens from the Mugeug, Geumwang and Geumbong deposits exceed one weight percent (up to 1.7 wt.%) and are also the least in As concentrations of all analyses. There appears to be a slight but consistent relation between antimony and arsenic in Sb-bearing arsenopyrite (Fig. 2). However, analyses more than 0.5 wt. % Sb were excluded for the arsenopyrite geothermometer.

According to the experimental data of Kretschmar, Scott (1976), synthetic arsenopyrites are deficient in Fe due to stoichiometric composition. But the variations in Fe content of arsenopyrite from the Au-Ag deposits of concern are not significant and fall within 33.3 ± 0.5 atomic %, as displayed in a triangular Fe-As-S diagram (Fig. 3). The arsenopyrite compositions from the gold-silver deposits vary approximately between the limits $\text{FeAs}_{0.83}\text{S}_{1.17}$ and $\text{FeAs}_{1.09}\text{S}_{0.91}$. The range and average of As contents in arsenopyrite from individual deposits are shown in Fig. 4. Arsenopyrites in the Au-Ag deposits have wide ranges of As contents and are associated with pyrite or loellingite which have same compositional ranges with those studied by Sharp *et al.* (1985). The most common mineral assemblage of arsenopyrite-pyrite in all available gold-silver deposits in Korea are characterized by S-rich and As-deficient composition. The As contents of the arsenopyrite in association with pyrite exhibit wide variation from 27.47 to 33.46 atomic %. This value is in excellent agreement with equilibrium maximum value of 33.33

Table 2. The As contents of arsenopyrite from gold-silver vein deposits.

Ore deposit	Atomic % As				Associated iron sulfides	Reference
	Average	S.D.*	Range	N**		
Yeongbogari	32.19	0.43	31.42~33.43	61	py	
Daeheung	31.02	0.98	29.68~33.46	54	py, po	
Ilbo	30.95	0.46	30.22~31.74	22	py, po	
Cheonbo	32.17			1	py	Kaneda <i>et al.</i> (1984)
Namchang	30.95	0.72	29.80~32.13	7	py	Kaneda <i>et al.</i> (1984)
Jeoneui	30.59	0.69	28.99~31.97	44	py	
Manmyeong	29.72	0.60	28.56~30.72	21	py	
Namsan	29.91	0.55	29.04~31.31	32	py	
Sangchon	30.75	0.70	29.02~31.80	43	py	Choi <i>et al.</i> (1994)
Ogkye	31.18	0.80	29.41~32.86	59	py	Choi <i>et al.</i> (1997)
Samjeong						Choi <i>et al.</i> (1994)
early stage	34.77	0.72	33.28~36.49	40	lo	
late stage	31.84	0.63	30.83~32.72	12	py	
Cheongju	30.35	0.72	29.12~31.57	20	py, po	
Yonghwa	29.68	0.41	29.09~30.32	6	py	Youn, Park (1991)
Mugeug	30.93	1.11	28.53~32.74	46	py	
Geumwang	29.72	1.06	28.16~31.24	36	py	
Geumbong	29.26	1.05	27.47~31.16	31	py	
Jeonjuil	30.20	0.83	28.65~31.42	47	py	
Seongju	30.32	0.55	29.15~31.63	24	py	Choi <i>et al.</i> (1994)

* Standard deviation.

** Number of spot analyses by electron microprobe.

terized by the relatively high As contents in arsenopyrites with narrow ranges. They formed at temperatures of 370–450°C with a sulfur fugacity of 10^{-8} – 10^{-6} atm. The Au-Ag deposits (Groups III and IV) and Ag-dominant deposits (Group V) usually show a wide range in composition from 27.47 to 32.74 atomic % As. Interpretation of the arsenopyrite suggests that the early to middle mineralization formed at temperatures between 250 and 350°C with a sulfur fugacity of about 10^{-12} – 10^{-10} atm. In the Samjeong (Group IIC), early arsenopyrite coexisting with loellingite are interpreted as being deposited at temperature range of 430 to 540°C. Cooling might cause the deposition of later arsenopyrite and pyrite with a lower arsenic content at $410 \pm 50^\circ\text{C}$. A compilation and re-evaluation of chemical analyses of arsenopyrite suggests that the As contents are variable for different genetic environments.

DISCUSSION AND SUMMARY

Two episodes of the gold-silver mineralizations in Korea are recognized by recent radiometric age data: a) Jurassic gold mineralization (132–162 Ma) associated with the Daebo granitoids and b) Cretaceous gold-silver mineralizations (71–98 Ma) closely related to the Bulgugsa igneous activities (Park *et al.*, 1986; So, Shelton, 1987; Shimazaki *et al.*, 1986; So *et al.*, 1989;

Youn, Park, 1991). These precious-metal vein deposits evolved under different conditions of hydrothermal activities at each times. In most of gold-silver deposits, only Yeongbogari, Daeheung, Ilbo and Cheonbo deposits (Group IIA) are strongly linked to Jurassic Daebo igneous activity, whereas the rest of the gold-silver deposits are associated with Cretaceous Bulgugsa igneous activity.

The four sets of analyses form distinct populations with small standard deviations, and the average compositions of arsenopyrite are 31.53 ± 0.92 , 30.60 ± 0.87 , 30.14 ± 1.22 and 30.24 ± 0.75 atomic % As, respectively (Fig. 6). Arsenopyrites from the Jurassic Au-dominant deposits corresponding to Group IIA are recognized by its high As contents (29.68–33.46 atomic %) with narrow variations. Temperatures of 370 to 450°C by arsenopyrite geothermometer are determined for these deposits. Arsenopyrites from the Cretaceous Au-Ag deposits (Groups III and IV) and Ag-dominant deposits (Group V) show a wide range in composition from 27.47 to 32.74 atomic % As, corresponding to temperatures of 280 to 370°C. The Cretaceous deposits hold multistage complex veins with several generations of arsenopyrites reflected by a slight but consistent zonation of compositions with relatively As-rich cores and S-rich rims. This suggests that ore fluids rapidly change in composition in response to varying P-T-X parameters in the epither-

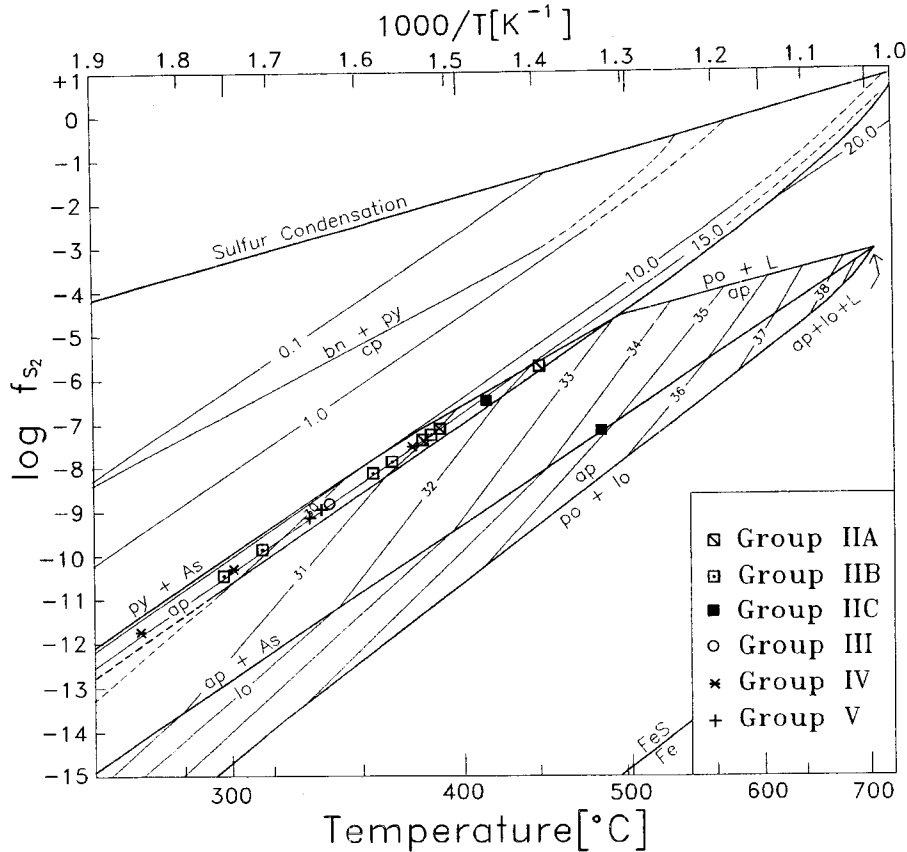


Fig. 5. Temperature- f_{S_2} diagram of the stability field of arsenopyrite from Kretschmar, Scott (1976). Numbers refer to arsenopyrite composition in atomic % As. The average compositions of arsenopyrite from the gold-silver deposits are also shown. See Table 1 for mineral abbreviations.

mal environment. Most of the Au-Ag and Ag-dominant deposits may be resulted from several mineralization stages accompanied by a individual pulse of mineralization after a silver mineralization stage, followed by a gold or base-metal pulse. These characteristics suggest that different physicochemical conditions play an important role in transport and deposition of Au and Ag in ore-forming hydrothermal systems (Table 3).

Combination of sphalerite solid solution equilibria with arsenopyrite compositions in the presence of pyrite provides unique values of both f_{S_2} and temperature. Scott (1983) suggested that the sphalerite in equilibrium with arsenopyrite and pyrite should contain at least 10 mole % FeS at 1 kbar. The sphalerite from the Au-dominant deposits should contain about 10 or more mole % FeS. These data indicate that the mineral assemblages were in chemical equilibrium during crystallization. The coexisting arsenopyrite and sphalerite compositions give an estimated temperature range of

310 to 460°C. Temperature ranges estimated by arsenopyrite-sphalerite geothermometer and arsenopyrite geothermometer are consistent each other. Despite the correspondance in the constraints on temperatures, the sphalerites coexisting with arsenopyrite and pyrite from most of the Au-Ag and Ag-dominant deposits vary from 1.8 to 9.8 mole % FeS. These sphalerites may have not attained equilibrium with arsenopyrite or have precipitated metastably under wide range in physicochemical conditions. Therefore, the arsenopyrite-sphalerite geothermometer may not be considered as a reliable geothermometer because of the lack of the petrologic equilibrium.

The precious-metal vein deposits in Korea evolved under the varying pressure conditions of hydrothermal activities at each times. For instance, it was reported that the pressures at which the Daebo granites emplaced range from 3.4 to 7.8 kb and the Bulgugsa intrusions emplaced at less than 2.8 kb (Cho, Kwon, 1994), based on the amphibole geobarometer of Sch-

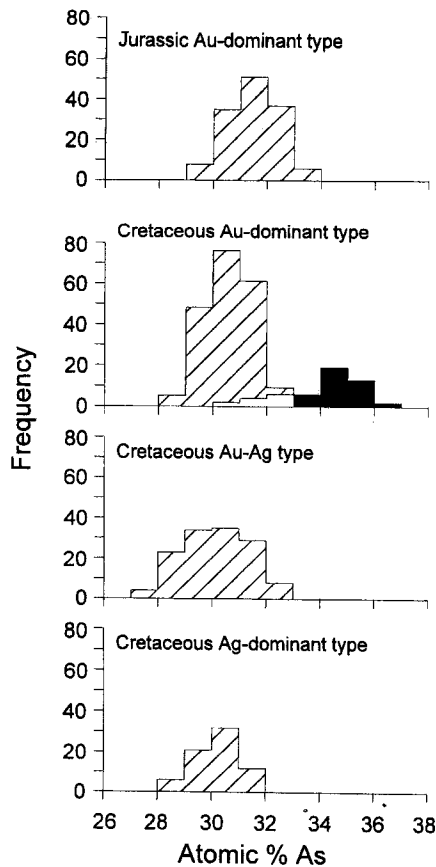


Fig. 6. Histogram of the frequency of arsenopyrite compositions (atomic % As) distinguished by four types in the gold-silver deposits. Black area=arsenopyrite coexisting with loellingite from Samjeong mine; white area=arsenopyrite coexisting with pyrite from Samjeong mine.

midt (1992). The temperatures of mineral formation estimated by the average composition of arsenopyrite are compared with the values obtained from the homogenization of fluid inclusions (Table 3). The homogenization temperatures of fluid inclusions should be taken as the minimum temperatures of mineral formation, and the determination of true formation temperatures requires the corrections for salinity of solutions and pressure. An application of the phase diagram from Kretschmar, Scott (1976) to the average As compositions for most of the Cretaceous Au-Ag and Ag-dominant deposits yields slightly higher temperatures than the peak temperatures of fluid inclusions. The discrepancy between two methods reaches about 50 to 70°C. The differences in temperature are not significant and lie within the limits of certainty, as the effect of pressure on fluid inclusions

for these deposits can be applied under low-pressure conditions (<1 kbar). On the other hand, the temperatures of mineral formation in the Jurassic Au-dominant deposits (Yeongbogari, Daeheung and Ilbo deposits) estimated by the composition of arsenopyrite are much higher (more than 120°C) than the homogenization temperatures of fluid inclusion in associated minerals. Apparently such a disagreement prompts to the correction for the formation pressure and salinity of solutions. Oh, Choi (1993) reported that the formation pressure for the Jurassic Au-dominant deposit was estimated about 4-7 kbar by combining the calculated isochores and sulfur isotope data. As these deposits formed at high pressures, the effect of pressure on the homogenization temperatures of fluid inclusions is very large and cannot be ignored for the study of high-pressure hydrothermal deposits. These results seem to be consistent with the intrusion depth of surrounding igneous bodies (>3.4 kb). These arguments give significant differences in temperatures estimated by fluid inclusions method. The homogenization temperatures of the fluid inclusions after correction for pressure and salinity may vary from about 100 to 150°C. Therefore, the Jurassic Au-dominant mineralizations belonging to Group IIA is clearly hypothermal in nature. The arsenopyrite geothermometry appears to be a useful method for estimating formation temperature of hydrothermal deposits with careful study of equilibrium ore texture.

The data of arsenopyrite geothermometer, electrum-sphalerite geothermometer and fluid inclusion indicate that the gold mineralizations corresponding to Groups IIA and IIB occurred at temperatures between 250 and 500°C, whereas the gold-silver deposits of Groups III, IV and V formed at a temperature range of about 170-350°C. Accordingly, the Au-dominant mineralization (129-158 Ma) in Korea, proceeded at the depth of several tens km or more during of the emplacement the Daebo intrusions. The Au-dominant mineralization occurred at relatively deep level during the early stage of the Bulgugsa igneous activity (94-108 Ma). Furthermore, the depth of ore formation progressively changed to shallow environment with time resulting in Au-Ag (73-109 Ma) and Ag-dominant mineralization (79-98 Ma). These gold-silver deposits can be divided into four types with respect to different genetic environment: Group IIA (hypothermal type), Group IIB (hypothermal-mesothermal type), Group IIC (xenothermal type), and Groups III, IV and V (epithermal type).

ACKNOWLEDGEMENT

Financial research grant for this study was provided by the Center for Mineral Resources Research spon-

Table 3. Comparison of temperatures estimated by arsenopyrite geothermometry with electrum geothermometry and homogenization temperature of fluid inclusions from gold-silver vein deposits.

Ore deposit	Arsenopyrite geothermometry			Electrum geothermometry			Homogenization temperature of fluid inclusions			Reference
	Range (°C)	Peak (°C)	Stage	Range (°C)	Peak (°C)	Stage	Range (°C)	Peak (°C)	Stage	
Yeongbogari	410~490	450	E-M	270~310	300	M-L	246~372	320	E-L	So <i>et al.</i> (1989)
Dacheung	300~490	390	M	210~370	290	L	175~360	250	E-L	So, Shelton (1987)
Ilbo	320~420	370	M	280~390	310	L	211~344	300	E-L	So, Shelton (1987)
Cheonbo		450	E-M				192~407	330	E-L	So, Shelton (1987)
Jeoneui	270~430	340	E-M	230~270	250	M	180~367	280	E-L	So <i>et al.</i> (1987)
Manmyeong	<250~350	300	E-M	240~300	270	M	206~285	250	E-L	Choi <i>et al.</i> (1988)
Namsan	280~400	310	E-M	200~250	220	M				
Sangchon	270~410	350	E-M	220~250	240	M				
Ogkye	290~470	400	E-M	240~340	300	M	227~436	360	E-L	Choi <i>et al.</i> (1997)
Samjeong	350~500	430	E-L	250~400	300	M-L				
Cheongju	280~400	330	E-M	250~350	300	M	130~280	260	E-L	Lee, Choi (1988)
Yonghwa	270~320	300	E-M	200~260	240	M	194~312	230	E-L	Youn, Park (1991)
Mugeug	<250~450	370	E-M	150~320	260	M-L	196~368	250	E-L	Kim <i>et al.</i> (1990)
Geumwang	<250~400	300	E-M	170~310	240	M-L	171~341	240	E-L	Sugaki <i>et al.</i> (1986)
Geumbong	<250~400	280	E-M	210~240	230	M				
Jeonjuil	<250~410	320	E-M	240~300	260	M	170~360	265	E-L	So <i>et al.</i> (1987)
Seongju	280~390	330	E-M	200~270	240	M	210~318	270	E-L	So <i>et al.</i> (1989)

Abbreviations: E; early stage of vein mineralizations, M; middle stage of vein mineralizations and L; late stage of vein mineralizations.

sored by the Korea Science and Engineering Foundation which is greatly acknowledged. Authors also thank Prof. H.K. Lee and Dr. J.M. Lee for improving the quality of our manuscript. This work was done during first author's sabbatical year in Canada.

REFERENCE

- Barton, P.B., Jr. and Skinner, B.J. (1979) Sulfide mineral stabilities. In: *Geochemistry of Hydrothermal Ore Deposits* (H.L. Barnes, ed.), Wiley-Interscience. New York. p. 278-403.
- Barton, P.B., Jr. and Toulmin, P., III. (1964) The electrum-tarnish method for the determination of the fugacity of sulfur in laboratory sulfide systems. *Geochim. Cosmochim. Acta*, v. 28, p. 619-640.
- Barton, P.B., Jr (1969) Thermochemical study of the system Fe-As-S. *Geochim. Cosmochim. Acta*, v. 33, p. 841-857.
- Bortnikov, N.S. (1993) On the validity of arsenopyrite and arsenopyrite-sphalerite geothermometers. *Geol. Ore deposits*, v. 35, p. 159-172.
- Boyle, R.W. (1979) The Geochemistry of Gold and its Deposit. *Geol. Surv. Can. Bull.*, v. 280, 584p.
- Cho, D.L. and Kwon, S.T. (1994) Hornblende geobarometry of the Mesozoic granitoids in south Korea and the evolution of crustal thickness. *J. Geol. Soc. Korea*, v. 30, p. 41-61.
- Choi, S.G., Park, N.Y. and Park, S.W. (1986) Gold-silver mineralization of Taechang-Boryeon and Geumwang mines in northeastern Chungcheong Provinces. *J. Korean Inst. Mining Geol.*, v. 19, Special issue, p. 193-206.
- Choi, S.G., Chi, S.J. and Park, S.W. (1988) Gold-silver mineralization of the Au-Ag deposits at Yeongdong district, Chungcheongbuk-Do. *J. Korean Inst. Mining Geol.*, v. 21, p. 367-380.
- Choi, S.G. and Choi, S.H. (1995) Contrasting styles of gold and silver mineralization in the central and southeastern Korea. *Econ. Environ. Geol.*, v. 28, p. 587-597.
- Choi, S.G., Choi, S.H. and Lee, H. K. (1997) Mineralogy and geochemistry of the Ogkye gold deposits, Gangwondo Province. *Econ. Environ. Geol.*, v. 30, p. 15-23.
- Choi, S.G., Chung, J.I. and Imai, N. (1986) Compositional variation of arsenopyrites in arsenic and polymetallic ores from the Ulsan mine, Republic of Korea, and their application to a geothermometer. *J. Korean Inst. Mining Geol.*, v. 19, p. 199-218.
- Choi, S.G. and Wee, S.M. (1992) The genetic characteristics of gold and/or silver vein deposits related to chemical composition of electrum in Central Korea. *J. Geol. Soc. Korea*, v. 28, p. 196-217.
- Choi, S.G., Park, M.E. and Choi, S.H. (1994) Chemical variations of electrum from gold and/or silver deposits in the Southeast Korea. *Econ. Environ. Geol.*, v. 27, p. 325-333.
- Clark, L.A. (1960) The Fe-As-S system: Phase relations and applications. *Econ. Geol.*, v. 55, p. 1345-1381, 1631-1652.
- Cole, D.R. and Drummond, S.E. (1986) The effect of transport and boiling on Ag/Au ratios in hydrothermal solutions: a preliminary assessment and implications for the formation of epithermal precious-metal ore deposits. *J. Geochem. Explor.*, v. 25, p. 45-80.
- Dowling, K. and Morrison, G. (1989) Application of quartz textures to the classification of gold deposits using north Queensland examples. *Econ. Geol. Monograph* v. 6, p. 342-355.

- Gallagher, D. (1963) Mineral resources of Korea. Issued by Mining Barch, Industry and Mining Div. USOM/Korea. In cooperation with Geol. Surv. Republic of Korea. 3 (A and B). 124p. and 118p.
- Kaneda, H., Shimazaki, H. and Lee, M.S. (1986) Mineralogy and geochemistry of the Au-Ag ore deposits of the South Korean Peninsula. *Mineral. Deposita*, v. 21, p. 234-243.
- Kay, A. and Strong, D.F. (1983) Geologic and fluid controls on As-Sb-Au mineralization in the Moretous Harbour area, Newfoundland. *Econ. Geol.*, v. 78, p. 1590-1604.
- Kim, O.J. (1971) Metallogenic epochs and provinces of south Korea. *J. Geol. Soc. Korea*, v. 7, p. 37-59.
- Koh, Y.K., Choi, S.G., So, C.S., Choi, S.H. and Uchida, E. (1992) Application of arsenopyrite geothermometry and sphalerite geobarometry to the Taebaek Pb-Zn (-Ag) deposit at Yeonhwa I Mine, Republic of Korea. *Mineral. Deposita*, v. 27, p. 58-65.
- Kretschmar, V. and Scott, S.D. (1976) Phase relations involving arsenopyrite in the system Fe-As-S and their application. *Can. Min.*, v. 14, p. 364-386.
- Lowell, G.R. and Gasparini, C. (1982) Composition of arsenopyrites from topaz greisen veins in southeastern Missouri. *Mineral. Deposita*, v. 17, p. 229-238.
- Oh, C.W. and Choi, S.H. (1993) The application of computer program for determination of fluid properties and P-T condition from microthermometric data on fluid inclusions. *J. Korean Inst. Mining Geol.* v. 26, p. 21-27.
- Park, N.Y., Choi, S.G. and Park, S.W. (1986) Ore genesis of gold-silver hydrothermal deposits in Chungcheong province, Republic of Korea. In: *A Study on Geology and Metallic Mineral Deposits. KR-86-10*, Korea Institute of Energy and Resources, p. 387-436.
- Park, M.E. (1990) Mineralization and paragenesis of the cobalt-bearing sulfide and arsenide minerals in Gyeongsan area. *Jour. Geol. Soc. Korea*, v. 26, p. 18-31.
- Scott, S.D. and Barnes, H.L. (1971) Sphalerite geothermometry and geobarometry. *Econ. Geol.*, v. 66, p. 653-669.
- Scott, S.D. (1973) Experimental calibration of the sphalerite geobarometer. *Econ. Geol.*, v. 68, p. 466-474.
- Scott, S.D. (1983) Chemical behaviour of sphalerite and arsenopyrite in hydrothermal and metamorphic environments. *Mineralogical magazine*, v. 47, p. 427-435.
- Schmidt, M.W. (1992) Amphibole composition in tonalite as a function of pressure: experimental calibration of the Al-in-hornblende barometer. *Cont. Min. Petrol.*, v. 110, p. 304-310.
- Sharp, Z.D., Essene, E.J. and Kelly, W.C. (1985) A re-examination of the arsenopyrite geothermometer: Pressure considerations and applications to natural assemblage. *Can. Min.*, v. 23, p. 517-534.
- Shelton, K.L., So, C.S. and Chang, J.S. (1988) Gold-rich mesothermal vein deposits of the Republic of Korea: Geochemical studies of the Jungwon gold area. *Econ. Geol.*, v. 83, p. 1221-1237.
- Shimazaki, H., Lee, M.S., Tsusue A. and Kaneda, H. (1986) Three epochs of gold mineralization in south Korea. *Mining Geol.* v. 36, p. 265-272.
- So, C.S. and Shelton, K.L. (1987) Stable isotope and fluid inclusion studies of gold-silver bearing hydrothermal vein deposits, Cheonan-Cheongyang-Nonsan mining district, Republic of Korea: Cheonan area. *Econ. Geol.*, v. 82, p. 987-1000.
- So, C.S., Chi, S.J. and Shelton, K.L. (1987a) Stable isotope and fluid inclusion studies of gold-silver-bearing vein deposits, Cheonan-Cheongyang-Nonsan mining district, Republic of Korea; Nonsan area. *Neues Jb. Min. Abh.*, v. 158, p. 47-65.
- So, C.S., Chi, S.J. and Shelton, K.L. (1987b) The Jeonui gold-silver mine, Republic of Korea: A geochemical study. *Mining Geol.*, v. 37, p. 313-322.
- So, C.S., Choi, S.H., Chi, S.J., Choi, S.G. and Shelton, K.L. (1989) Geochemical studies on Au-Ag hydrothermal vein deposits, Republic of Korea: Geryeong-Waegwan mineralized area. *J. Korean Inst. Mining Geol.*, v. 22, p. 221-235.
- So, C.S., Yun, S.T., Choi, S.H. and Shelton, K.L. (1989) Geochemical studies of hydrothermal gold-silver deposits, Republic of Korea: Youngdong mining district. *Mining Geol.*, v. 39, p. 9-19.
- Sugaki, A., Kim, O.J. and Kim, W.J. (1986) Gold and silver ores from Geumwang mine in South Korea and their mineralization. *Mining Geol.*, v. 36, p. 555-572.
- Sundblad, K., Zachrisson, E., Smeds S.A., Berglund S. and Alinder C. (1984) Sphalerite geobarometry and arsenopyrite geothermometry applied to metamorphosed sulfide ore in Swedish caledonides. *Econ. Geol.*, v. 79, p. 1660-1668.
- Tsuchida, T. (1944) *Ore Deposits in Korea*. Kasumigaseki Book Co. Tokyo. 329p (In Japanese).
- Vearncombe, J.R. (1993) Quartz vein morphology and implications for formation depth and classification of Archean gold-vein deposits. *Ore Geol. Rev.*, v. 8, p. 407-424.
- Youn, S.T. and Park, H.J. (1991) Gold and silver mineralization in the Yonghwa mine. *Jour. Korean Inst. Mining Geol.*, v. 24, p. 109-129.

한국 금은광산에서 산출되는 유비철석의 조성변화

최선규 · 최인식

요 약 : 한국의 금은광화작용은 쥐라기 대보화성활동 (121~183 Ma) 및 백악기 불국사화성활동 (60~110 Ma) 과 밀접한 연관성을 보이며, 이러한 열수광맥형 금은 광산에서 산출된 유비철석은 광물공생관계 또는 생성환경에 따라 현저한 조성 변화를 나타내고 있다. 쥐라기 금광단일형 광산에서 산출된 유비철석은 비교적 높은 As함량 (29.68~33.46 atomic %)으로 균질한 조성을 나타내며, 유비철석 지질온도계에 적용하면, 생성온도 및 유황분압은 370~450°C와 10^{-8} ~ 10^{-6} 이다. 또한 백악기 금은혼합형 광산과 은광단일형 광산의 유비철석은 쥐라기 광산에 비하여 상대적으로 심한 조성변화 (27.47~32.74 atomic %)를 보이며, 250~350°C 및 10^{-12} ~ 10^{-10} 의 환경 조건하에서 정출된 것으로 추정된다. 한편, 금은광맥의 산출상태, 유비철석 지질온도계, 에렉트럼-섬아연석 지질온도계, 유체 포유물 연구자료 및 화성암의 정체심도 등을 종합적으로 비교검토했던 결과, 쥐라기 금광화작용 (Group IIA)은 심부조건 (약 4~5 kbar)에서 300~500°C의 정출환경에서 진행되었지만, 백악기 금은광화작용 (Groups III, IV, V)은 1 kbar 미만의 천부조건하에서 170~370°C의 온도조건하에서 형성된 것으로 사료된다.