# Geochemistry of Cu–Pb–Zn–Ag Deposits from the Euiseong Mineralized Area

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ABSTRACT : The Cu–Pb–Zn–Ag hydrothermal vein type deposits which comprise the Dongil and Dongcheogogsan mines occur within the Cretaceous sedimentary rocks in the Euiseong Basin of the southern Korean peninsula. The ore mineralization is contained within three stage(I,II and III) quartz and calcite veins. Ore minerals occur as dominant chalcopyrite, galena, sphalerite, tetrahedrite and Pb, Ag, Sb and Bi–bearing sulfosalts. Stage I ore minerals were deposited between 400° and 200 ℃ from the fluid with moderate salinities(7.0 to 4.5 eq. wt. % NaCl). Evidence of boiling suggests pressure of less than 150 bars during stage I mineralization. This pressure corresponds to maximum depths of 650 m and 1700 m, respectively, assuming lithostatic and hydrostatic loads. The data on mineralogy, temperature and salinity, together with information on the solubility of Cu complex, suggest that Cu deposition is a result of boiling coupled with declining temperature from 350°to 250℃ or declining log $a_{O_2}$(from −29.8 to −35.9 atm.)and increasing in pH. Pb, Ag, Sb and Bi–bearing sulfosalts were deposited by cooling and dilution at temperature of less than 250℃ from the ore fluid with less than −35.9 atm. of log $a_{O_2}$.

## INTRODUCTION

The Cu–Pb–Zn–Ag–bearing hydrothermal vein–type deposits occur within Cretaceous volcanic and sedimentary rocks in the Gyeongsang Basin of the southern Korean peninsula. Cu–bearing deposits occuring dominantly in three mineralized areas(Haman–Gunbuk, Goseong and Euiseong areas) are associated with Cretaceous granites (Sillitoe, 1980, Jin et al., 1981, Sato et al., 1981, Shimazaki et al., 1981, and So et al., 1985).

It is known that Korean Cu–bearing hydrothermal ore deposits display similarities in temperature, ore fluid salinities, pressure condition, mineralogy and age of mineralization. Park et al.(1985) indicate that fluid inclusion data of Cu–mineralization in the Haman–Gunbuk area reveal nearly the same ranges as those of the Goseong mining area. The features of Korean Cu–bearing deposits are very similar to those of the Casapalca mine, Peru and Providencia mine, Mexico, except for their high ore–fluid salinities. Fluid inclusion and stable isotope studies suggest that ore deposition in the Goseong Cu–Pb–Zn–Ag mineralization area was likely a result of boiling and influx of meteoric water in hydrothermal system(So et al., 1985). The different paragenetic mineral assemblages of Cu–bearing veins in these mineralization areas indicate that the evolution of hydrothermal fluids varies with time and space in relation to granitic stock.

The regional geological mapping of the studied area was carried out by Chang et al.(1976 and 1980). No investigators have studied the physical and chemical conditions of ore deposition of copper mines in the Euiseong mineralized area. There are two Cu–Pb–Zn–Ag mines(Dongil and Dongcheogogsan)near the Geumseongsan volcanic caldera in the Euiseong mineralization area. The average ore grades of the Dongcheogogsan mine are 0.27 to 9.51 wt.% Cu, 1.42 to 27.9 wt.% Pb, 0.3 to 7.38 wt.% Zn, 58 to 816 ppm Ag and < 5.1 ppm Au, those of the Dongil mine, 1.46 to 5.9 wt.% Cu, 0.3 to 11.5 wt.% Zn, 2.5 to 16.0 wt. % Pb, 120 to 320 ppm Ag and < 16.4 ppm Au.

The aim of the present study is to determine the nature of ore mineralization in the Euiseong Cu–Pb–Zn–Ag mineralized area and to study physical and chemical conditions of ore deposition.

## GEOLOGY

The Lower to Middle Cretaceous non–volcanic sedimentary rocks(Hayang Group) of the Gyeongsang Supergroup occur regionally in the Euiseong Cu–Pb–Zn–Ag mineralization area. They are unconformably overlain by the Upper Cretaceous intrusive–extrusive volcanic

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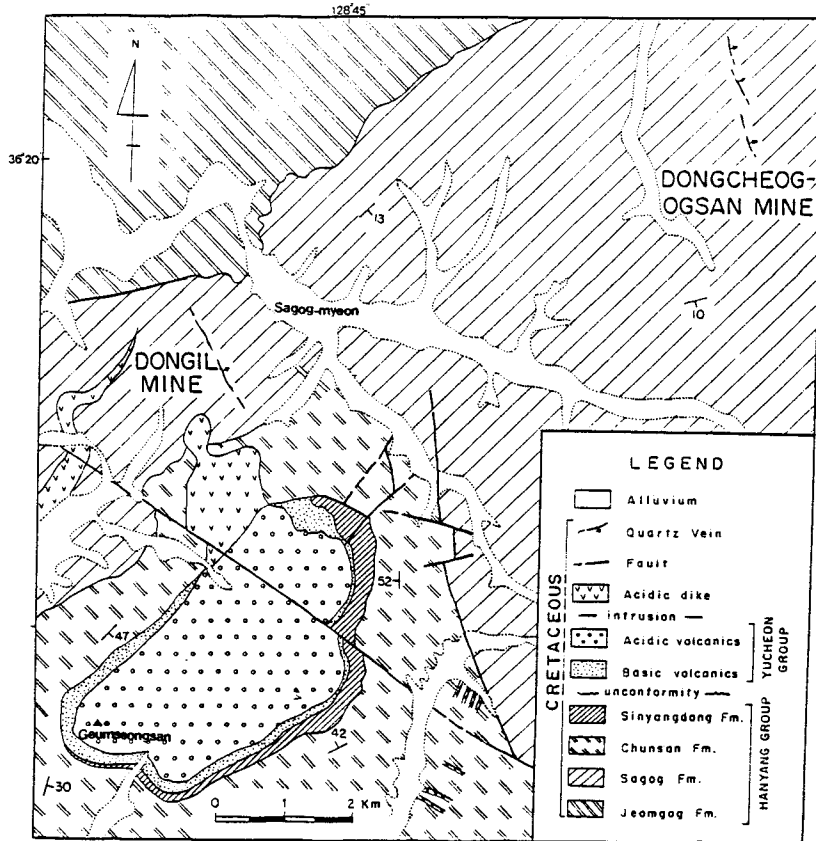   *** Dept. of Earth Sci. Education, Korea National University of Education, Chungbuk, 363–791, Korea.

Fig. 1. Geologic map of the Cu–Pb–Zn–Ag mining area.

pile(Yuchon Group), and intruded by Late Cretaceous Bulgugsa granitic rocks out of the mine area.

Two studied mines(Dongil and Dongcheogogsan) exist in the northeastern parts of the Geumseongsan caldera. Geology of the studied mine area consists of, in ascending order, Jeomgog, Sagog, Chunsan and Sinyangdong Formations of the Middle to Upper Hayang Group, and the Geumseongsan volcanic complex(Fig.1).

The Jeomgog Formation occurring in the northern parts of the mine area consists of grayish sandstone and dark grayish to greenish shale interlayered with thin mudstone. Subangular sandstone and shale pebbles are poorly sorted and vary in size from 2 to 10 cm in middle parts of the formation. The Sagog Formation occurs in most parts of the mine area and regionally overlies the Jeomgog Formation. It comprises reddish sandstone interlayered with reddish shale and dark grayish sandy shale. The Chunsan Formation is composed of a rhyodasitic crystal tuff ranging from 2 to 3 m in thickness, grayish and reddish shale to sandstone. The rhyodasitic crystal bearing rock fragments (less than 3 cm in size) are interbedded with thin

alloclastic tuffaceous sandstone layers. The Sinyangdong Formation, the uppermost unit of Hayang Group, occurs around the Geumseongsan caldera as thin bed (less than 140m in thickness). This formation is made up dominant grayish to black laminated shale interlayered with sandstone beds.

The Geumseongsan Volcanic Complex, Caldera filling-unit, consists of basic and acidic lava flows and pyroclastic rocks interlayered with volcanic lacustrine sediments. The basic volcanic rocks(about 300 m in thickness) occur as basalt and basalt flows. A basal tuff breccia underlain by basic volcanic rocks occurs locally as thin bed (less than 10 m in thickness) and contains rounded to angular fragments(less than 25 cm in diameter) of shale and volcanic rocks.

The acidic volcanic rocks(less than 100m in thickness) made up top of the volcanic complex overlie unconformably the lower basic volcanic rock. They comprise rhyolitic lapilli tuff, rhyolitic lava flows and vitrophyre. Breccias(usually, 10 cm in diamter) of volcanic and sedimentary rocks are dominant in the basal parts of rhyolitic lapilli tuff beds. The tuff beds(dipping 30 to 50)inclined to the central part of the caldera.

Pinkish rhyolite intrudes along ring faults in sedimentary rocks around caldera. Park(1985) gave the detail classification of Geumseongsan volcanic complex based on composition, rock types, and welding degree, and represented the evolution history of caldera.

## ORE DEPOSITS

Cu–Pb–Zn–Ag mineralization occurs in hydrothermal quartz veins in the Euiseong mineralization area. Economic quantities of Cu–bearing minerals in the studied mine area were deposited along regional fracture systems caused by Geumseongsan caldera collapse. Regional fracture systems controlled the localization of acidic dikes and ore veins. The quartz veins that fill fracture system are narrow (0.01 to 1.0 m) and rarely exceed 1.0 m in width. Numerous thinner veins occur parallel to the principal veins through with abundant spilits. The veins strike NW and dip 70°–85°NE. The ore deposits in the Dongil mine area occur as three types (narrow stockworks, disseminations and vein) along the fractures in margin of the caldera. The ore deposits of the Dongcheogogsan mine show an only vein type along the NW fracture system.

Cu–bearing hydrothermal veins are tabular, coarse grained, massive and locally vuggy. Brecciated fragments (less than 10 cm long) of the wall–rock are often contained in the veins. Contacts between veins and wall–rock are commonly sharp and rarely slickensided. Ore minerals (dominantly base metal sulfide and sulfosalts) are concentrated mainly at margins of the veins. Often ore veins display sulfide banding in mineral sequence from margins to centers : pyrite–arsenopyrite : sphalerite–galena–chalcopyrite : Pb, Ag, Bi and Sb–bearing sulfosalts.

In the Dongcheogogsan mine area, there are 4 main mineable quartz veins (Oggyedong, North Jugdong, South Jugdong and Silupdong Veins). The Oggyedong vein, striking N25°W and dipping 80°–85°NE, can be traced about 150m along strike and varies in thickness from 0.05 to 0.4 m. The vein is occupied in the upper parts of the small ore shoots by relatively large concentration of galena and sphalerite than other portions of the vein. Aggregates of coarse grained galena and sphalerite from often a thin mineralic bands in the hanging–wall side of the vein and commonly are disseminated through the vein. The ore grades of the Oggyedong vein are 0.27 to 0.45 wt.% Cu, 17.85 to 27.93 wt. % Pb, 0.88 to 7.38 wt. % Zn, 175 to 815 ppm Ag and < 5.1 ppm Au.

The North Jugdong vein, striking N25°W and dipping 75°–80°NE, runs over 100m and vary in thickness from 0.4 to 0.5m. The vein shows

slightly bands of Cu–sulfide minerals. Galena aggregates (5 cm long) are locally concentrated within the vein. The vein shows relatively higher Cu grade than other veins. The ore–grades of the vein are 5.92 to 9.51 wt. % Cu, 5.25 to 25.83 wt. % Pb, 0.32 wt. % Zn, 552–816 ppm Ag and<3.1 ppm Au. The South Jugdong vein, striking N50°W and dipping 75°NE, extends over 250m along strike and has a maximum thickness of less than 0.4 m.

The Silupdong vein, striking N35°to 40°W and dipping 75°NE, can be traced for 80 m along strike and varies from 0.2 to 0.25 m in thickness. The veins are mineralogically similar to other veins in Dongcheogogsan mine, but do not show mineral banding, and contains the lowest concentrations of ore minerals except for Cu–bearing minerals. The ore grades are 2.82 to 3.77 wt. % Cu, 1.42 to 5.26 wt. % Pb,<0.2 wt. % Zn and 58 to 102 ppm Ag.

The Dongil mine consists of only one main minable quartz vein (less than 3 m in thickness) filled in fault breccia zone with a thickness of 20 m. Several thinner veins occur parallel to the main vein. The main vein extended over vertical distances of 50 m. The vertically plunged tabular ore body contains relatively a large concentration of ore minerals. The ore grades are 1.46 to 5.88 wt.% Cu, 2.48 to 16.0 wt.% Pb, 0.28 to 11.48 wt.% Zn, 120 to 305 ppm Ag and 0.1 to 16.4 ppm Au.

## HYDROTHERMAL ALTERATION

Three types of hydrothermal alteration, based on major mineral assemblages, can be discerned. Each alteration type grades into a next type without sharp boundary. Away from the vein margin, the alteration changes from advanced argillic, through sericitic, to argillic alterations. Advanced argillic alteration makes up mainly kaolinite, dickite and rare sericite. Sericite, kaolinite, quartz and pyrite occur together in the groundmass of strong sericitic alteration. Weak argillic alteration consists of kaolinite, chlorite, calcite and feldspar. Relict plagioclase grains exist in argillic alteration zone.

## MINERALIZATION AND PARAGENESIS

Mineralization in the Dongil and Dongcheogogsan mines is represented by several textural varieties (massive, brecciated and banded) which are occasionally mixed. The common characteristics of open space filling, such as crustification, are rarely present. However, small vugs commonly occur, in which milky to clear euhedral quartz occur often in association with calcite. The textural rela-
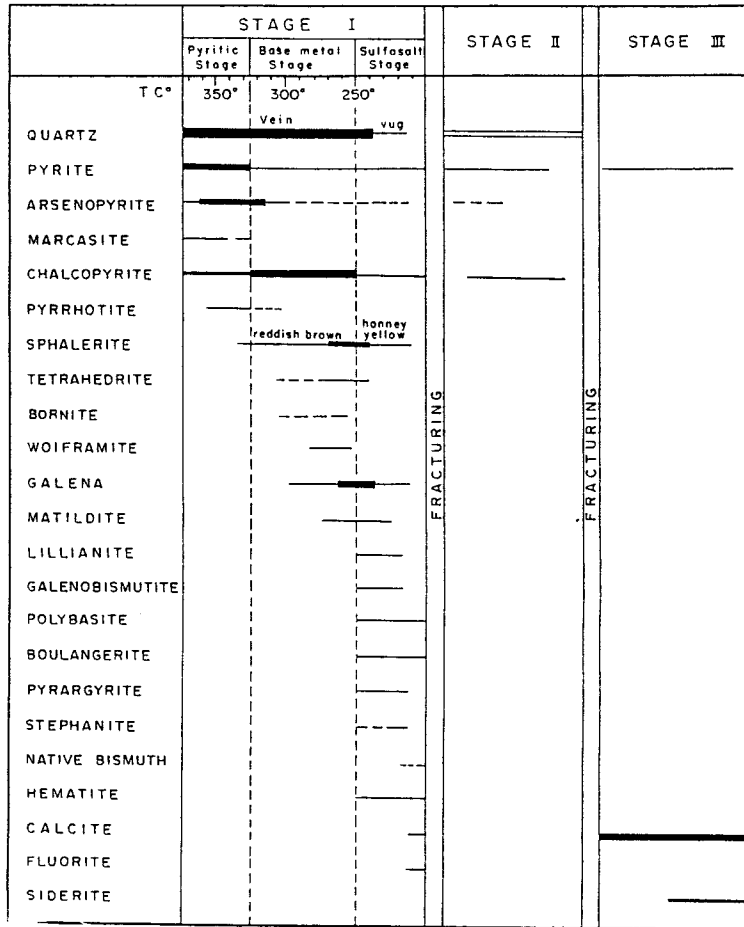
| | STAGE I | | | STAGE II | STAGE III |
|---|---|---|---|---|---|
| | Pyritic Stage | Base metal Stage | Sulfosalt Stage | | |
| T C° | 350° | 300°  250° | | | |
| | | Vein          vug | | | |
| QUARTZ | | | | | |
| PYRITE | | | | | |
| ARSENOPYRITE | | | | | |
| MARCASITE | | | | | |
| CHALCOPYRITE | | | | | |
| PYRRHOTITE | | | | | |
| SPHALERITE | | reddish brown   honney yellow | | | |
| TETRAHEDRITE | | | | | |
| BORNITE | | | | | |
| WOIFRAMITE | | | | | |
| GALENA | | | | | |
| MATILDITE | | | | | |
| LILLIANITE | | | | | |
| GALENOBISMUTITE | | | | | |
| POLYBASITE | | | | | |
| BOULANGERITE | | | | | |
| PYRARGYRITE | | | | | |
| STEPHANITE | | | | | |
| NATIVE BISMUTH | | | | | |
| HEMATITE | | | | | |
| CALCITE | | | | | |
| FLUORITE | | | | | |
| SIDERITE | | | | | |

(between STAGE I and STAGE II, and between STAGE II and STAGE III, vertical text reads "FRACTURING")

Fig. 2. Generalized paragenetic sequence of vein minerals in the Cu–Pb–Zn–Ag Dongil and Dongcheogogsan mines. Width of lines corresponds to relative abundance.

tionships in field and handspecimens indicate that the veins were formed in three mineralization stages separated by fracturing and brecciation events.

During stage I, quartz with economic concentration of Cu, base metal sulfides and rare Pb–Bi, Pb–Sb and Ag–Sb–sulfosalts were deposited. In stage II, barren milky quartz with minor amounts of sulfides were introduced into the fracture system. Stage III is marked by carbonates. The main vein of the Dongcheogogsan mine and the Oggyedong vein of Dongil mine contain mineralization of all three stages. Mineralization and paragenesis of the studied mines are summarized in Fig. 2.

Stage I Vein Mineralization

Stage I veins are economically the most signi-

ficant and display a paragenetic sequences in which three mineral assemblages are present in relation to time and space: a pyritic, a base metal sulfide and a sulfosalt mineralizations.

Pyritic Mineralization: This mineralization is represented by mostly early quartz with a large amounts of pyrite, arsenopyrite, and minor amounts of chalcopyrite, marcasite, pyrrhotite and sphalerite.

Pyrite occurs as dominant subhedral to euhedral cubic grains and rarely massive bands, ranging from a few millimeters to 10 mm in thickness at the edges of the veins. It is intimately intergrown with arsenopyrite. Fine euhedral grains commonly disseminated in the wall–rocks do not contain inclusions of other ore minerals, but pyrite in the vein often includes small irregular and rounded grains of pyrrhotite and chalcopyrite. Often pyrrhotite grains exsolved

with chalcopyrite are included by coarse – grained pyrite.

Arsenopyrite is commonly observed as euhedral to subhedral grains with characteristic rhombic shaped in wall–rocks and pyrite matrix. Some arsenopyrites are in the forms of polycrystalline aggregates near the margin of the vein. Electron microprobe analyses of representative arsenopyrite are shown in Table 1. The compositions of arsenopyrites lie close to the line representing the stoichiometric composition and do not show compositional zoning. Marcasite often is associated with early pyrite. Minor amounts of chalcopyrite are interstitial to a granular aggregates of pyrite and arsenopyrite. Sphalerite occurs as iron–poor and iron–rich varieties which range in from dark reddish brown to honney yellow in the mines. Sphalerites in stage I vein show a wide compositional variation ranging from 0.19 to 20.7 FeS mole % as shown in Table 2. Dark reddish brown sphalerites of the pyritic mineralization display little compositional variations; 18.1 to 20.7 FeS mole % in the Dongil mine and 16.4 to 17.9 FeS mole % in the Dongcheogogsan mine. The analyzed sphalerite grains do not show compositional zoning.

Base Metal Sulfide Mineralization: This mineralization is characterized by variable portions of chalcopyrite, sphalerite, galena with microscopic tetrahedrite, bornite and wolframite.

Pyrite and arsenopyrite occur as fine grained disseminates. Irregular corroded margins are commonly observed on pyrite by galena advancing along irregular cracks. Some of highly brecciated pyrite fragments are cemented by galena and chalcopyrite. Coarse–grained rhombic arsenopyrite occurred with pyrite is commonly fractured and rehealed later by quartz.

Chalcopyrite, the most dominant copper mineral in the mine, is present as mainly masses with no regular outline and as fine–grained disseminates. It also occurs as anhedral grains intergrown with other sulfides. Chalcopyrite is associated with pyrite in the early pyritic assemblage, with galena–sphalerite in the base metal sulfide assemblage and with Pb–Bi, Pb–Sb and Ag–Sb–bearing sulfosalts in the late sulfosalt mineralization, indicating that chalcopyrite was deposited over a long period.

Reddish brown to honney yellow sphalerite occurs as commonly polycrystalline aggregates associated with chalcopyrite and galena in the intermediate zone of the veins. Their FeS contents in two mines are between 2.17 and 3.35 mole %. Highly brecciated sphalerite is cemented and replaced by galena and tetrahedrite. Most of sphalerite contains oriented rows of chalcopyrite blebs. The marginal portions of some sphalerite in contact with chalcopyrite include many chalcopyrite blebs.

Tetrahedrite, containing less than 1.0 wt. % Ag, is commonly associated with chalcopyrite replacing sphalerite (Fig. 3A). Tetrahedrite grains are often coprecipitated with Pb–Bi sulfosalts within galena matrix and are interstitial to euhederal quartz crystals. Bornite occurring as massive grains is often exsolved with galena and is included as a tiny grains with chalcopyrite blebs in the pyrite.

Laths and irregular grains of wolframite are observed in several polished sections only from the Dongil mine. It is closely associated with sphalerite (Fig. 3B). Some laths of wolframite are disseminated within the vein quartz.

Coarse–grained galena occurs as anhedral polycrystalline aggregates and often as massive bands intergrown with sphalerite and chalcopyrite. It is commonly interstitial to other sulfides.

Sulfosalt Mineralization: This mineralization is represented by Pb–Bi, Pb–Sb and Ag–Sb–sulfosalts, native bismuth, hematite and minor amounts of base metal sulfides. Sulfide minerals are mainly honney yellow sphalerite, galena and

Table 1. Compositions(Atomic %) of stage I arsenopyrites analyzed by E.P.M.A. from the Dongil and Dongcheogogsan mines.

| Mine | stage | Fe | As | S |
|---|---|---|---|---|
| Dongil | pyritic | 33.0158 | 32.49 | 34.4942 |
| | pyritic | 32.8262 | 32.4124 | 34.7614 |
| | pyritic | 33.3275 | 32.6814 | 33.9912 |
| Dong-cheogogsan | pyritic | 32.1729 | 32.4824 | 35.3447 |
| | pyritic | 33.0224 | 32.0573 | 34.9203 |

Table. 2. Compositions(mole%) of stage I sphalerites analyzed by E.P.M.A. from the Dongil and Dongcheogosan mines.

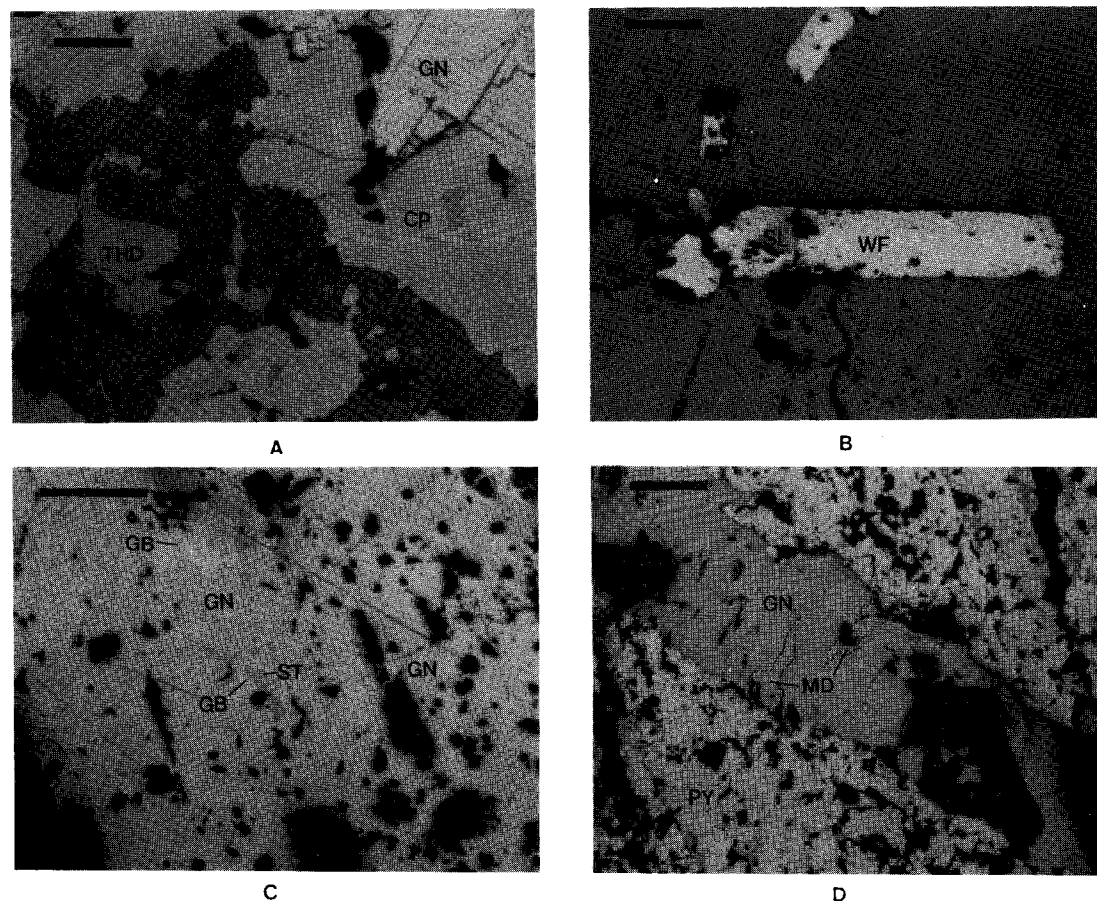| Mine | stage | FeS | CdS | MnS |
|---|---|---|---|---|
| Dongil | pyritic | 20.77 | 0.27 | 0.01 |
| | pyritic | 20.57 | 0.27 | 0.16 |
| | pyritic | 18.12 | 0.19 | 0.49 |
| | pyritic | 19.23 | 0.16 | 0.31 |
| | base metal | 2.26 | 0.33 | 0.26 |
| | base metal | 2.17 | 0.36 | 0.42 |
| Dong-cheogogsan | pyritic | 17.92 | 0.92 | 0.23 |
| | pyritic | 16.42 | 1.16 | – |
| | base metal | 2.26 | 0.16 | – |
| | base metal | 3.35 | 0.15 | 0.02 |
| | sulfosalt | 0.19 | 0.48 | 0.01 |
| | sulfosalt | 0.23 | 0.02 | – |
| | sulfosalt | 0.24 | 0.94 | – |

Fig. 3. Photomicrographs of stage I ore minerals of the Dongil and Dongcheogogsan mines. scale bars=0.1 mm.(A) Galena (GN) replacing chalcopyrite (CP) intergrown with tertrahedrite (THD). (B)Wolframite (WF)including sphalerite (SI) grain. (C) Galena intergrown with stephanite(ST) and galenobismutite(GB). (D) Galena veinlet exsolving with matildite(MD) penetrates polycrystallined pyrite.

pyrite. The honney yellow vug sphalerite contains lower FeS mole % (<0.24 mole % FeS) than earlier reddish brown sphalerite as shown in Table 2.

Sulfosalt minerals occur as irregular grains in aggregation with other sulfides and are interstitial to euhedral quartz crystals near vugs. They were coprecipitated with calcite and fluorite in vugs. Some sulfosalts fill along microcracks of quartz in the central portions of the veins. Pb–Bi–sulfosalts occurring as matildite, lillianite and galenobismutite are found intimately intergrown with galena (Fig. 3 C and D). Irregular grains of matildite are commonly exsolved with galena penetrating aggregates of pyrite and arsenopyrite along fractures. Lillianite occurring as rounded or irregular grains exsolved with stephanite are often observed in the late galena.

Galenobismutite replaces the galena along rims, leaving unreplaced residual islands of galena.

Ag–Sb–sulfosalt minerals occur as mainly polybasite, rare pyrargyrite and stephanite. Polybasite and pyrargyrite occur as irregular and subhedral grains in aggregates with galena and are commonly interstitial to quartz crystal boundaries.

Native bismuth in rounded blebs is rarely exsolved with the late galena precipitated in microfractures of quartz near vugs. Boulangerite, Pb–Sb–sulfosalt, is interstitial to late quartz grains and often overgrows on quartz euhedral in vugs. It replaces galena along rims.

Hematite occurs as euhedral micaceous crystal and laths. It is disseminated in quartz in the central portions of the veins and is precipitated with honney yellow sphalerite and pyrite. White

calcite and violet fluorite are the latest gangue minerals in the stage I mineralization. Most of massive calcite and fluorite overgrows on the vug quartz. Their fine euhedral crystals are rarely observed in small vugs.

## Stage II Vein Mineralization

Stage II veins with a maximum thickness of 10 cm contain breccia of earlier materials and occur near the hanging–wall and foot–wall sides of the stage I veins. This stage is composed of white quartz and minor amounts of pyrite, arsenopyrite and chalcopyrite. Quartz displaying often comb structure is the most important gangue minerals and has a massive appearance. It contains many elongated cavities with clear quartz prism, and often chalcedonic quartz rhythmically overgrowing around orbs of earlier materials.

Pyrite and arsenopyrite are disseminated through the vein as fine euhedral to subhedral grains. Chalcopyrite occurs as fine massive grains in the intermediate to central portions of the vein.

## Stage III Vein Mineralization

This mineralization is the final stage of hydrothermal mineralization. The lastest phase of tectonic activity occurred after mineralization of the stage II veins. Later movement in the vein is indicated by the presence of several narrow later carbonate veinlets within the massive quartz vein. This stage is composed of dominant massive white calcite and siderite. Siderite often occurs in the central portions of the calcite vein. Pyrite grains are often disseminated in the vein and some euhedral pyrite overgrows on vug quartz crystals.

## FLUID INCLUSION STUDY

Fluid inclusion studies were carried out on 85 samples from the Dongil and Dongcheogogsan mines. Doubly polished plates were prepared from a vein materials including quartz, sphalerite, fluorite and calcite. During measurement, temperature determinations were made on 724 inclusions and salinity on 54 inclusions. Microthermometric measurements were made using USGS gas–flow heating freezing system. Replicate measurements of homogenization temperatures showed a reproducibility within $\pm 3.0°C$ at temperature near $350°C$. Replicate measurements of melting temperature of $H_2O$–and $CO_2$–rich fluid inclusions showed a reproducibility within $\pm 0.2°C$. The salinity data are based on freezing point depression in the system

$H_2O$–NaCl (Potter et al., 1978).

Minerals studied in most of the plates contained numerous primary and secondary inclusions. Two types of inclusions are recognized on the basis of their phase relations at room temperature according to the terminology of Nash (1976).

Type I(liquid–rich) : This type of fluid inclusion contains a liquid and a vapor phase. The bubble usually makes up 20 to 40 % of the total volume of the inclusions and homogenized to the liquid phase. This type inclusion, occurring as primary and secondary fluid inclusions, was the most abundant and was present in all mineral plates examined. No daughter minerals were observed in these inclusions. They are generally less than 30 $\mu$m (up to 80 $\mu$m in fluorite) in diameter. $LCO_2$ ($< 0.05$ mole %) is not observed during the freezing test.

Type II(gas–rich) : This type of inclusion also contains a liquid and a vapor phase, but the volume of vapor exceeds that of the liquid phase. Fluid inclusions contain more than 60% vapor by volume, and homogenized to vapor phase.

### Inclusion in Stage I Quartz Veins

Stage I minerals examined for fluid inclusions study were quartz, sphalerite, fluorite and calcite. Stage I quartz contains predominantly type I inclusions and rarely type II inclusions. Clear vug quartz contains only type I fluid inclusion usually occurring as regular faceted cavity. The cavity size of the inclusions is less than 25 $\mu$m. Stage I honney yellow sphalerite contains mainly secondary and rarely primary type I inclusions. The cavity size of inclusions range from less than 10 $\mu$m. Many inclusions were not suitable to measurement of heating and freezing temperatures, because they were too small in cavity size.

Homogenization temperatures of fluid inclusions for all minerals in the stage I quartz veins from the Dongil and Dongcheogogsan mines range from 185°to 388°C and from 195°to 379°C, respectively. Type II inclusions occurred only in quartz are homogenized at temperature of 270° to 343°C in the Dongil mine and 295° to 312°C in the Dongcheogogsan mine (Fig. 4).

Homogenization temperature of primary inclusions in the stage I quartz from the Dongil and Dongcheogogsan mines ranges from 205° to 388°C and 210° to 379°C, respectively. The homogenization temperature of primary inclusions in reddish brown to honney yellow sphalerite is in a narrow range of 250° to 285°C (the Dongil mine) and 205° to 258°C (the Dongcheogogsan mine). Fluid inclusions of honney yellow vug sphalerite from two mines homoge-
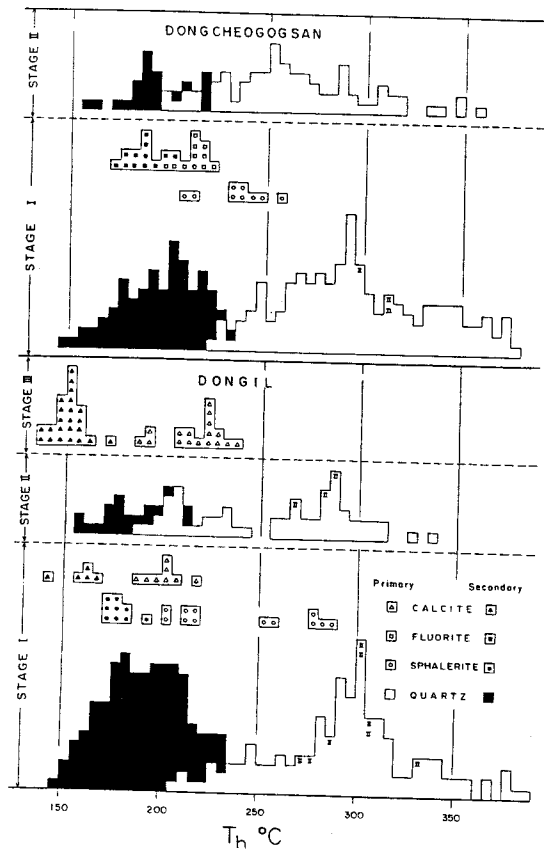
Fig. 4. Histograms of homogenization temperatures of fluid inclusions in vein minerals of the Dongil and Dongcheogogsan mines. II = vapor – rich inclusions, primary = primary fluid inclusions, secondary = secondary fluid inclusions.

quartz. The inclusion vary in cavity size from 5 to 20 $\mu$m. The limited data obtained were gathered from tiny veinlets overgrowing and cutting stage I gray quartz. The only inclusions present were liquid–rich. The homogenization temperatures of primary fluid inclusion in white quartz from the Dongil and Dongcheogogsan mines range from 186° to 337℃ and 136° to 357℃, respectively (Fig. 4). The obtained salinity of primary type I fluid inclusions in white quartz from the Dongil and Dongcheogogsan mines range from 3.5 to 6.5 and 3.4 to 6.4 equivalent wt. % NaCl, respectively(Fig. 5).
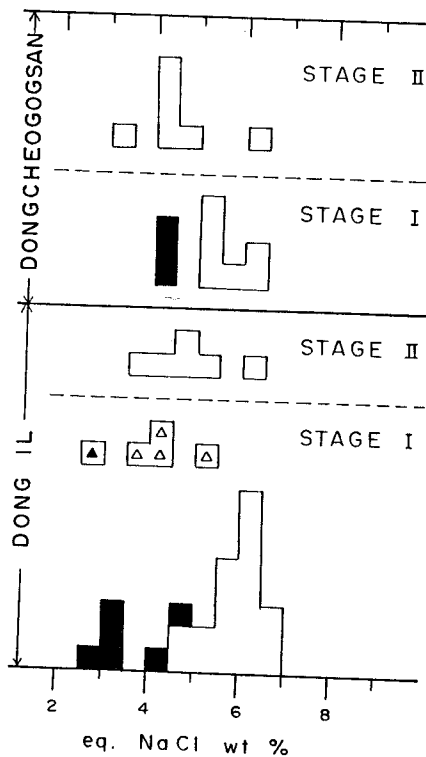


Fig. 5. Histograms of salinities of fluid inclusions in vein minerals of the Dongil and Dongcheogogsan mines. Symbols are same in Fig. 4.

nized at temperatures of 200° to 218℃. The homogenization temperatures of primary type I inclusions in calcite (the Dongil mine) and fluorite (the Dongcheogogsan mine) range from 185° to 219℃ and 195° to 221℃, respectively.

Measured salinities of the primary type I inclusions of stage I minerals are between 3.6 and 6.9 equivalent wt. % NaCl. Salinities of primary type I fluid inclusions in quartz from the Dongil and Dongcheogogsan mines ranges from 4.5 to 6.9 and 5.0 to 6.1 equivalent wt. % NaCl, respectively. The primary type I fluid inclusion of calcite(the Dongil mine) has a salinity ranging from 3.6 to 5.0 equivalent wt. % NaCl(Fig. 5).

## Inclusion in Stage II Quartz Veins

The stage II mineral examined was only white

## Inclusion in stage III Carbonate Vein

Massive white calcite from the stage III mineralization of the Dongil mine contains primary and secondary type I inclusion. Cavity size of inclusions is generally less than 40 $\mu$m and bubbles occupy 30% of the inclusion volume. Homogenization temperature of the primary type I fluid inclusions in white calcite ranges from 185° to 236℃ (Fig.4).
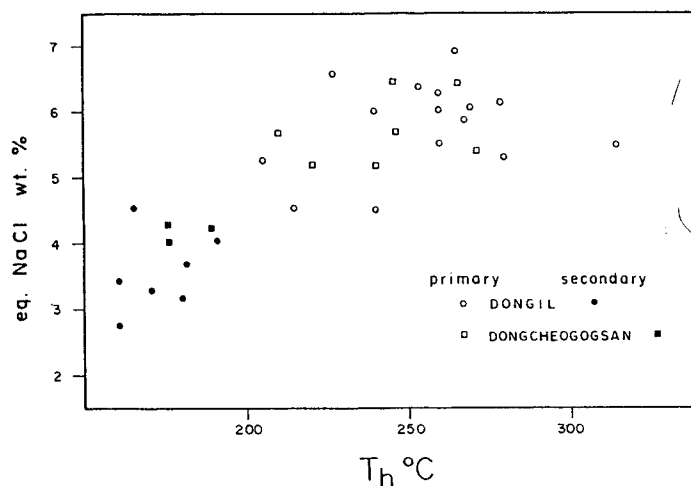
**Fig. 6.** Homogenization temperature versus salinity diagram for fluid inclusion in stage I vein minerals from the Dongil and Dongcheogogsan mines.

## Variations in Temperatures and Compositions of Ore Fluids

During the mineralization episodes, variation in temperatures and compositions of Cu–Pb––Zn–Ag–bearing hydrothermal fluids are recorded by fluid inclusions. Fluid inclusion data indicate that the stage I and II evolved from initial high temperature($\approx$380℃) to later lower temperature($\approx$200℃). The homogenization temperature and salinity of primary inclusions in stage I vein minerals decrease systematically with time and space(Figs. 4 and 5).

The relationship between homogenization temperature and salinity in the stage I suggests a complex history of boiling, cooling and dilution(Fig. 6). Boiling of fluids which deposited early quartz in the mines resulted in an increase in salinity (up to 6. 9 wt. % equiv. NaCl) at temperatures near 270℃. The salinity increase reflects concentration of salts in the residual liquid as vapor was lost during boiling. During late quartz vein in the mines, cooling and dilution of ore fluids (from 270℃ and 6.9 wt. % to 200℃ and 4.5wt. % equiv. NaCl) resulted in a linear relationship between temperature and salinity. Homogenization temperature and salinity decrease indicated that hydrothermal ore fluid was cooled and diluted by increasing influx of meteoric water during mineralization.

### Pressure Consideration

Liquid–rich type I and vapor–rich type II fluid inclusions are intimately associated in the same samples of stage I quartz and they tend to homogenize at similar temperatures. It indicates that the fluids of stage I boiled at temperature ranges of near 330° to 270℃(Figs. 4 and 5). Therefore no pressure corrections are necessary for these inclusions because they were trapped along two–phase boundary curve of the system $H_2O$–NaCl.

The data of Sourirajan and Kennedy(1962) and Haas (1974) for the system $H_2O$–NaCl, combined with the temperature and salinity data for stage I fluids, suggest a maximum pressure of less than 150 bars at fluid entrapment. This pressure corresponds to maximum depth of about 650 to 1700 m, assuming lithostatic and hydrostatic loads.

## CHEMICAL ENVIRONMENT OF ORE DEPOSITS

To investigate the environmental conditions of main ore mineralization in the stage I veins from the Dongil and Dongcheogogsan mines, compositions of arsenopyrite and sphalerite were analyzed by EPMA. The data on these minerals are shown in Tables 1 and 2.

### $a_{S_2}$ and $a_{O_2}$ Conditions of Stage I Mineralization

Sulfide assemblages document decreasing sulfidation lateral away from the margin of the stage I vein. The sulfidation limit for pyritic, base metal sulfide and sulfosalt mineralizations of the stage I veins is provided by fluid inclusion data and compositions of the arsenopyrite and sphalerite in equilibrium with pyrite, pyrrhotite and hematite, respectively(Fig. 7).

Pyritic Mineralization : The presence of dominant pyrite and arsenopyrite and absence of tet-
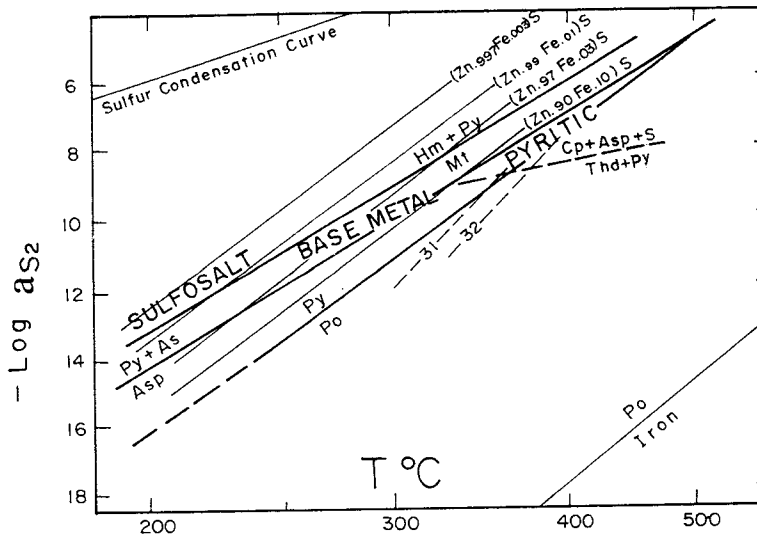
Fig. 7. T – log $a_{S_2}$ diagram showing the possible range(dotted area) by mineral assemblages observed in stage I mine – ralization from the studied mines. Abreviations : Asp = arsenopyrite, Cp = chalcopyrite, Hm = hematite, Mt = magnetite, Po = pyrrhotite, py = pyrite, Pyritic = pyritic mineralization, Base Metal = base metal mineralization, Sulfosalt = sulfosalt mineralization, – : isopleths(FeS Mole%) of sphalerite, – : isopleths(Atomic %)of arsenopyrite.

rahedrite in the early mineralization of stage I restricts the $a_{S_2}$ to a narrow range. The upper limit of $a_{S_2}$ can be set by pyrite–arsenopyrite reaction curve (Kretschmar and Scott, 1976), because the pyrite–native arsenic are not occurred. The lower limit of $a_{S_2}$ may be set by As contents of arsenopyrite and pyrite– pyrrhotite (Barton and Toulmin, 1966) and chalcopyrite–tetrahedrite (Barton and Skinner, 1979) reaction curves. The obtained formation temperature and log $a_{S_2}$ range may be near 330°to 430°C and –9 to –6 atm., respectively.

The maximum $a_{O_2}$ condition of pyrite–pyrrhotite stability is at the pyrite–pyrrhotite–magnetite triple point.
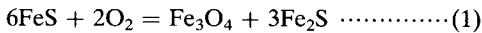
$$6FeS + 2O_2 = Fe_3O_4 + 3Fe_2S \quad \cdots\cdots\cdots\cdots(1)$$
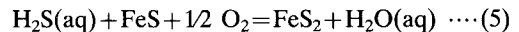$$\log a_{O_2}(max.) = -1/2 \log K \quad \cdots\cdots\cdots\cdots(2)$$

Because the $a_{H_2}$ is unlikely to exceed that of water in hydrothermal ore fluid, minimum $a_{O_2}$ condition for pyrite–pyrrhotite coexistance can be obtained from
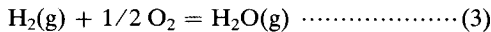
$$H_2(g) + 1/2 O_2 = H_2O(g) \quad \cdots\cdots\cdots\cdots\cdots(3)$$
$$a_{H_2} = a_{H_2O}, \log a_{O_2}(min.) = -2 \log K \cdots(4)$$

Assuming a possible temperature of coexisti –ng pyritepyrrhotite is near $350° \pm 20°C$, the maximum and minimum $a_{O_2}$ can be obtained from equations (2) and (4). The obtained log $a_{O_2}$ values range near –29.8 to –32.0 atm.. By expressing the maximum and minimum $a_{O_2}$ con-

ditions that ore fluid are equilibrium with pyrite and pyrrhotite, log $m \Sigma H_2S$ (Where $H_2S$ is predominant, $m \Sigma H_2S = m \Sigma S$) may be calculated from following equations :

$$H_2S(aq) + FeS + 1/2 O_2 = FeS_2 + H_2O(aq) \quad \cdots(5)$$
$$\log m \Sigma S = -(1/2 \log a_{O_2} + \log K + \log \gamma H_2S) \quad \cdots\cdots\cdots\cdots\cdots\cdots\cdots\cdots\cdots\cdots\cdots\cdots(6)$$

$\gamma H_2S$ is the activity coefficient of $H_2S$. From equation(6), the calculated log $m \Sigma S$ is –1.8 to –0.5.

**Base Metal Sulfide Mineralization** : The sulfidation of base metal mineralization was estimated from phase relations in Fe–Zn–S system(Scott and Barnes, 1971). By decreasing temperature below 300°C, FeS content of sphalerite gradually decrease from 16–20 to 2.2–3.4 FeS mole %.

During the base metal sulfide mineralization, chalcopyrite and tetrahedrite were equilibrium with pyrite and pyrrhotite. The formation temperature and $a_{S_2}$ ranges of base metal sulfide mineralization may be defined by pyrite–pyrrhotite and pyrite–hematite reaction curves, and isopleths of sphalerite in Fig. 7. The formation temperature of base metal sulfide mineralization is near 250°to 330°C which is corresponded to log $a_{S_2}$ value of –12 to –9 atm.. This formation temperature range well corresponds to fluid inclusion data showing that honney yellow sphalerite associated with large amount of chalcopyrite were deposited near 250°to 280°C.

Assuming that pyrite and hematite were cop-recipitated near 250℃ based on fluid inclusion data of sphalerite coprecipitated with hematite, the $a_{O_2}$ value can be calculated from following equation :

$$2FeS_2 + 3/2O_2(g) = Fe_2O_3 + 2S_2 \cdots\cdots (7)$$
$$\log a_{O_2} = -2/3(2 \log a_{S_2} - \log K) \cdots\cdots (8)$$

The obtained maximum log $a_{O_2}$ value of late mineralization(at 250℃) of base metal sulfide mineralization is between –34.2 and –35.9 atm.. Therefore, log $a_{O_2}$ of base metal sulfide mineralization are between –32 and–35.9 atm..

Sulfosalt Mineralization : Homogenization temperature of honney yellow vug sphalerite, fluorite and calcite, in equilibrium with pyrite and hematite, indicates the formation tempera-ture of sulfosalt minerals. These data indicate that the deposition of Pb, Ag, Sb and Bi–bear-ing sulfosalts occurred at temperature of less than 250℃. The estimated log $a_{S_2}$ and log $a_{O_2}$ values at temperature of less than 250℃ are less than –12 atm. and –35.9 atm., respectively.

## Copper Transport and Deposition

The chalcopyrite–pyrite and chalcopyrite–pyr-ite–bornite coexisiting stably from 230 ± 568℃ (Barton and Skinner, 1967) are character-istic in many Cu–bearing hydrothermal deposits. Available data on Cu–sulfide solubility were summarized by Romberger and Barnes (1970), Sinclair(1972), Vakotic(1961) and Crerar(1974). Crerar and Barnes(1976)have measured solubil-ity of copper in pure water and weakly acid NaCl solutions.

Fig. 8 shows the $a_{O_2}$–pH diagram and the sta-bility areas of the ore fluid from the Dongil and Dongcheogogsan mines is hatched for reference. From Fig. 8, the concentration exceeding $10^3$ ppm of Cu can be dissolved and transported by weakly acid NaCl solutions at temperature of 350℃ and above. Medium 1000 and 10 ppm Cu contours transact hatched area at 350° and 250℃, respectively. Cooling such solution to 250℃ precipitated roughly 90 % of dissolved Cu. It suggests that the Cu–bearing minerals tend to precipitate between 350℃ and 250℃ in a nice compatibility to mineral paragenesis and fluid inclusion data. In contrast, the cuprous bisulfide contours fall to the basic side of hatch-ed area, and solubilities in the areas of ore fluid are negligible at both temperatures.

Cathles (1973) indicates that temperature gra-dients are an likely reason for ore precipitation, but boiling seem more reasonable from inves-tigation on the influence convective circulation. Taylor(1974) has shown isotopically that deposi-tions take place at the interface between hyd-
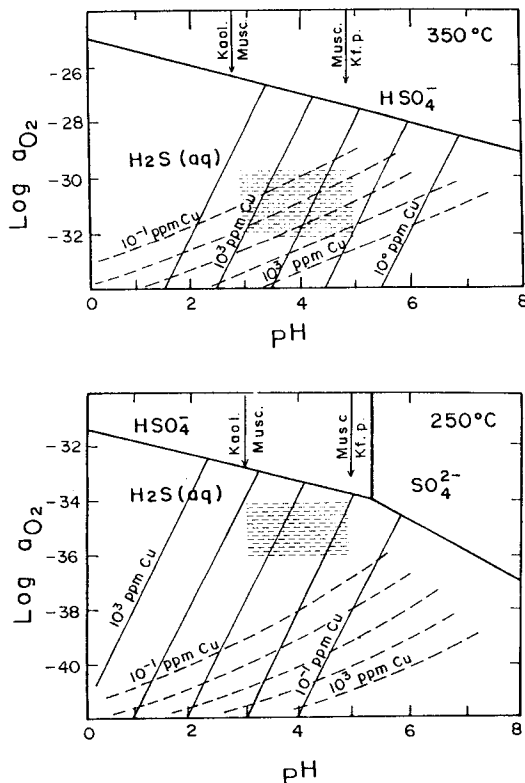


Fig. 8. Solubility of the chalcopyrite+pyrite+bo-rnite assemblage in hydrothermal NaCl and NaHS –H₂O solutions. Cl activity = 0.1. (A) and(B)so-lid contours show the concentration of CuCl com-plex at 250℃ and 350℃, respectively. Dashed conturs represent the concentration of [Cu + Cu(HS)₂(H₂S)⁻]. Hatched area is a stability field of ore fluid from the Dongil and Dongcheogogsan mines.

rothermal and meteoric water. Crerar and Barnes(1976) implied that ore deposition is caused by decreasing temperature, but wall–rock alteration causing an increase in pH is the local cause for precipitation.

Cu solubility data from Fig. 8, combined with fluid inclusion and wall–rock alteration studies, we interpret Cu deposition of the ore fluids in the Dongil and Dongcheogogsan mines to be a results of boiling coupled with declining temper-atures or $a_{O_2}$ with fluid mixing and increasing in pH.

## SUMMARY

1. The ore minerals of the Dongil and Dong-cheogogsan Cu–Pb–Zn–Ag mines are con-tained within three stages(I,II and III) of quartz and calcite veins by fracturing and

Table 3. Selected Equilibrium Constants

| Reaction | log K | | | | |
|---|---|---|---|---|---|
| | 200℃ | 250℃ | 300℃ | 350℃ | Ref |
| $2FeS + S_2(g) = 2FeS_2$ | 16.56 | 13.46 | 10.91 | 8.76 | c |
| $3FeS_2 + 2O_2(g) = Fe_3O_4 + 3S_2(g)$ | 38.11 | 35.81 | 35.93 | 32.36 | a |
| $3FeS + 3/2O_2(g) = Fe_3O_4 + 3/2S_2(g)$ | 63.56 | 56.91 | 51.39 | 46.74 | a |
| $2FeS_2 + 3/2O_2(g) = Fe_3O_4 + 2S_2(g)$ | 31.72 | 29.35 | 28.19 | 25.60 | a |
| $H_2O(g) = H_2(g) + 1/2O_2(g)$ | −24.5 | −21.9 | −19.8 | −18.0 | a |
| $3KAISi_3O_8 + 2H^+ = KAl_3Si_3O_{10}(OH)_2$ $+ 6SiO_2 + 2K^+$ | | 9.8 | 8.4 | 7.8 | b |
| $2KAl_3Si_3O_{10}(OH) + 2H^+ + 3H_2O(l)$ $= 3Al_2Si_2O_5(OH)_4 + 2K^+$ | 7.04 | 6.20 | 5.44 | 4.9 | a |

a. Helgeson(1969)Values at 350℃ extrapolated.
b. Extrapolated from Shade(1974)and data at 300℃ by Usdowski and Barnes(1972).
c. Schneeberg(1972). See also Schneeberg(1973)and Barton and Skinner(1967).

brecciation events.

2. Fluid inclusion data indicate that ore minerals were deposited between 400° and 200℃ from fluids with moderate salinities(7.0 to 4.5 eq. wt. % NaCl). Evidence of boiling indicates pressure of 150 bars, corresponding to depth of 650m and 1700m assuming lithostatic and hydrostatic loads.

3. Sulfide assemblages document decreasing sulfidation (from −6 to <−12 of log $a_{S_2}$) lateral away from early to late mineralization of stage I vein.

4. The data on mineralogy, temperature, salinity together with information on the stability of Cu complex suggest that copper deposition is a result of boiling coupled with declining temperature(from 350°to 250℃) or log $a_{O_2}$(from−29.8 to−35.9 atm.) and increasing in pH. Pb, Ag, Sb, and Bi–bearing sulfosalts were deposited by cooling and dilution at temperature of less than 250℃ (log $a_{O_2} =$ <−35.9 atm.)

## ACKNOWLEDGEMENT

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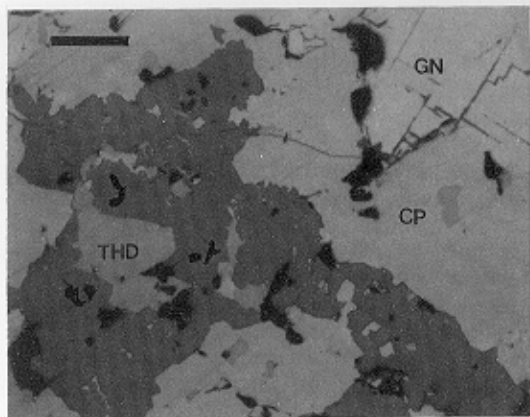# 의성 광화대 동–연–아연–은 광상의 지화학적 연구

池世定 · 都城宰 · 崔善奎 · 李哉昊

## 요 약

경북 의성 퇴적분지내에는 수개조의 함 Cu·Pb·Zn·Ag 열수석영맥이 주향 N 20°–40°W, 경사 70°–80°NE의 단층면을 따라 충진되어 있으며, 맥폭은 1.0m 이하이고, 약 200m 이상 연장되어 있다. 광화작용은 구조운동에 수반되어 3회(I, II, III기)에 걸쳐 진행되었다.
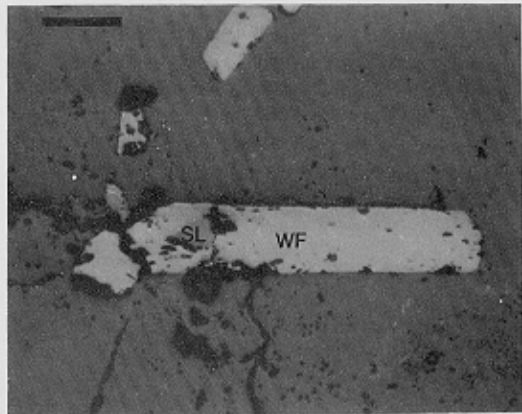
주 광화시기인 제 I 광화시기에는 주로 황동석, 유비철석, 황철석, 방연석, 섬아연석과 미량의 사면동석 및 함Pb, Ag, Sb, Bi 유염 광물 등이 산출된다. 유체 포유물 연구에 의하면, 제 I 광화작용시 銅을 위시한 광석 광물은 7.5–4. 5wt.% 염상당농도를 갖는 광화유체로부터 초기 400℃에서 후기 200℃에 걸쳐 침전되었고, 350℃ 부근에서 광화유체의 비등 현상이 있었음을 확인하였다. $H_2O$–NaCl 임계곡선에 의해 구한 광화유체의 최대 압력은 150bar이고, 이는 1.7km
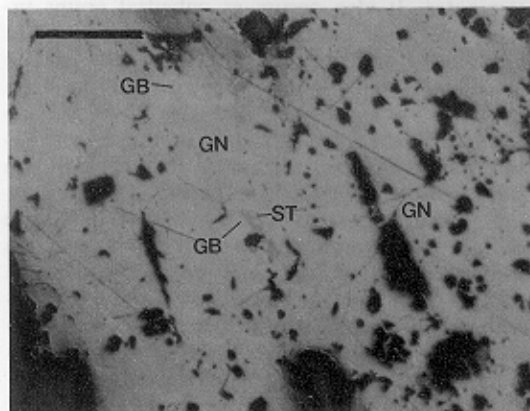
의 심도에 해당된다.

    Cu의 침전은 전 유황種의 농도가 $10^{-0.5} - 10^{-1.8}$M인 광화유체가 약 350℃에서 250℃로 감소되면서 비등작용과 함께 천수유입에 의한 냉각 작용에 의하여, 광화유체 내의 유황, 산소의 분압이 각각 $10^{-8}$, $10^{-30}$atm. 에서 $10^{-12}$, $10^{-36}$atm. 으로 감소되고, 한편 pH가 증가되어, Cu complex 이온의 농도가 $10^3$에서 10ppm으로 감소되면서  주로 황동석으로 침전되었다. 함 Pb, Ag, Sb, Bi 유염광물은 250℃ 이하에서 유황과 산소분압이 각각 $10^{-12}$, $10^{-36}$atm. 이하인 광화유체에서 계속되는 천수유입으로 인한 냉각작용과 희석작용에 의해 침전되었다.
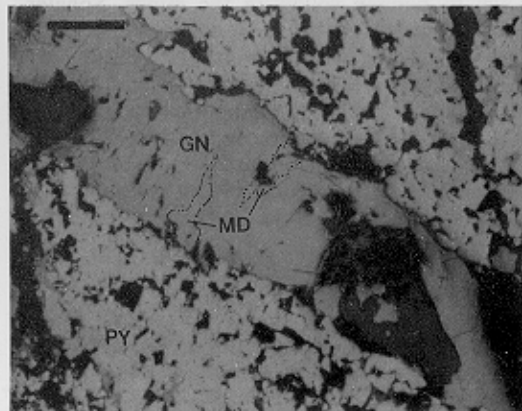
A

B

C

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