Hydrothermal W-Mo mineralization of the Cheongyang mine, Republic of Korea : A fluid inclusion and stable isotope study

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The Cheongyang W-Mo mine, about 120 km south of Seoul, is composed of fissure-filling quartz veins within Cretaceous granite porphyry (70.5 ± 1.6 Ma) and Precambrian banded biotite gneiss. The spatial distribution of mineralized veins exclusively within or near the granite porphyry and related acidic dykes indicates that W-Mo mineralization was associated with intrusion of the granite porphyry. The major ore minerals are wolframite, scheelite and molybdenite. Ore mineralization can be divided into three distinct stages: greisen, vein (early W-Mo, and late base-metal sulfides), and vug (carbonates).

Fluid inclusion data indicate that the hydrothermal system at Cheongyang evolved from initial high temperatures (near 400°C) to later lower temperatures (near 150°C) from fluids with salinities between 0 and 6 wt. % eq. NaCl. Deposition of W-Mo minerals occurred at temperatures between 300° and 400°C mainly as a result of pH increase due to vapor loss by fluid boiling. Later deposition of base-metal sulfides and carbonates was the result of increasing influx of cooler meteoric waters. Fluid inclusion evidence of boiling during the early W-Mo mineralization indicates pressures 100 to 260 bars. Fluid inclusion data for the Cheongyang W-Mo deposits are similar with those of W-Mo deposits in the Hwanggangri district, and are quite different with those of deposits in the Pusan-Yangsan district. This difference in temperature and compositions of hydrothermal fluids for Korean vein-type W-Mo deposits may reflect different pressure-depth conditions of W-Mo mineralization associated with late Cretaceous granitic activity in Korea.

Sulfur isotope compositions of sulfide minerals are consistent with an igneous source of sulfur with a $\delta^{34}\text{S}_{\text{SS}}$ value near 4 per mil. There is a systematic decrease in calculated $\delta^{18}\text{O}_{\text{water}}$ values with increasing paragenetic time in the Cheongyang hydrothermal system, from values of ≈ 8 per mil for greisen formation and W-Mo mineralization, to ≈ 3 per mil for base-metal sulfide mineralization, to ≈ -2 per mil for carbonate mineralization in vugs. There is a small increase in $\delta^{18}\text{O}_{\text{water}}$ values from greisen formation (6.3-6.8‰) to W-Mo mineralization (7.0-7.8‰), likely indicating boiling of ore fluids during W-Mo mineralization. The trend of overall decrease in $\delta^{18}\text{O}_{\text{water}}$ values with time is interpreted to indicate progressive meteoric water inundation of an early magmatic W-Mo hydrothermal system.

Keywords: Cheongyang mine, Korea, Tungsten-molybdenum, Quartz veins, Mineralogy, Fluid inclusions, Stable isotopes.

I. Introduction

Vein-type W-Mo deposits in Korea are located in three major districts: Hwanggangri, Pusan-Yangsan, and Cheongyang. Previous

studies have shown that vein-type W-Mo deposits in Korea display similarities in temperatures of mineralization, ore fluid salinities, pressure-depth conditions, mineralogy and paragenesis, and mineralization ages (Park and

Fig. 1. Simplified geologic map of the Republic of Korea showing location of the Cheongyang W-Mo mine.

Choi, 1974; Park *et al.*, 1981; So *et al.*, 1983a, b, 1991; Kim, 1984; Kim, 1985; Shelton *et al.*, 1986, 1987). Temperatures of tungsten deposition in most of these deposits range from 210° to 380°C, salinities vary from 2 to 14 wt. % eq. NaCl, depths of mineralization range from <1.0 to 2.5 km, and ages of mineralization are all late Cretaceous. Stable isotope studies of these deposits indicate early magmatic hydrothermal fluids during W-Mo concentration and later involvement of meteoric waters (So *et al.*, 1983a, 1991; Shelton *et al.*, 1987).

The Cheongyang W-Mo mine is located approximately 120 km south of Seoul and lies in the Precambrian Gyeonggi metamorphic belt. The mine was one of the important W-Mo producers in Korea. Tungsten grades of the mine are 0.8 to 25 wt. % WO_3 . Ore reserves are an estimated 113,000 tons of tungsten. During the mid-1940's, about 70 metric tons annually of beryl was also mined from ores containing about 3% BeO.

Previous studies have included the geology and fluid inclusions of the Cheongyang mine

(Kim, 1977; Park and Choi, 1981). However, little is known about the physicochemical conditions and evolution of ore deposition. The present study aims to document the age and nature of ore mineralization, to elucidate the origin and geochemical environments of ore-forming fluids, and to compare the data with other vein-type W-Mo deposits in Korea.

II. General geology

The Cheongyang W-Mo mine lies within the southwestern region of the Gyeonggi metamorphic belt (Fig. 1). Geology of the mine area is simple, consisting largely of Precambrian gneisses which are intruded by Cretaceous granite porphyry and related dykes (Fig. 2). Geology of the mine area has been described in detail by Kim (1977).

Precambrian metamorphic rocks in the mine area consist largely of banded biotite gneiss with minor intercalations of amphibolite. Granitic gneiss and porphyroblastic gneiss occur locally with gradational contacts with banded biotite gneiss. These metamorphic

Fig. 2. Geologic map of the Cheongyang W-Mo mine area showing locations of major orebodies.

rocks have been folded into a northeastly-striking syncline and are broken by E-W-trending fractures.

A small body of granite porphyry intrudes the banded biotite gneiss. Phenocrysts of quartz and potassium feldspars are characteristic of the granite porphyry but gradually decrease in amounts at depth. Granite porphyry has been extensively greisenized by W-Mo-bearing hydrothermal solutions. These greisenized rocks characteristically contain muscovite, beryl, wolframite and fluorite. A series of NW-trending, acidic to intermediate dykes (each <1 km long and 5-50 m thick) are widespread, especially around the mine area, as fillings of tensional open spaces in Precambrian gneiss. Some fractures within these dykes are filled by W-Mo-bearing quartz veins.

Whole-rock K-Ar dating of the granite porphyry indicates an age of 70.5 ± 1.6 Ma (Table 1). Spatial distribution of W-Mo quartz veins within or near the granite porphyry and the related dykes (Fig. 2) indi-

cates that W-Mo mineralization of the Cheongyang mine was genetically associated with late Cretaceous granitic activity.

III. Ore deposits

Within the Cheongyang mine, more than 15 subparallel W-Mo-bearing hydrothermal quartz veins are developed along steeply dipping faults and related joints mainly in granite porphyry (Fig. 2). The veins can be traced along strike direction (N15°-30°W) up to 2 km and have variable thickness of 0.2 to 1.0 m. The Cheongyang mine consists of five major orebodies (Fig. 2): Main, Central, East No. 1, East No. 2, and East No. 3 orebodies.

The mineralogy of the veins consists mainly of quartz, muscovite, fluorite and calcite with W-Mo minerals and base-metal sulfides. The principal gangue mineral is coarse crystalline white quartz, comprising up to 85-90 volume % of the veins. The principal ore mineral is wolframite.

Based on crude mineralogical bands and

Table 1. K-Ar data of granite porphyry from the Cheongyang W-Mo mine area

Sample no.	K (wt. %)	Radiogenic ^{40}Ar (10^{-6}cc STP/g)	Non Rad. Ar (x)	Age (Ma $\pm 1\sigma$)
CY-2	3.64	1014	11.2	70.5 $\pm$ 1.6

occurrences of vein minerals, the following sequence of mineral precipitation is recognized: wolframite+molybdenite $\pm$ scheelite with quartz, muscovite and beryl $\rightarrow$ base-metal sulfides with quartz $\rightarrow$ fluorite+carbonates in vugs. Mineralized veins of the Cheongyang mine also show a vertical compositional zoning with depth. Wolframite and base-metal sulfides are more concentrated in upper portions of the veins, whereas molybdenite tends to be more enriched in lower vein portions. According to assay results of ores, subeconomic grades of gold and silver are often associated with base-metal-rich ores from upper vein portions.

IV. Mineralogy and paragenesis

Hydrothermal activity of the Cheongyang mine can be divided into three stages, as shown in Fig. 3, i.e., greisen, vein, and vug stages. The first stage was early quartz+muscovite greisen formation. Quartz veins with W-Mo minerals and base-metal sulfides formed in the second stage. The last stage is represented by the carbonates+fluorite deposition in vugs.

1. Greisen Stage

Intense greisenization of wall rocks is recognized in the mine area. Practically all of the orebodies are hosted and surrounded by quartz+muscovite $\pm$ beryl greisens. These greisen zones have variable thickness from 0.1 to 0.6 m, and are variable in composition according to the nature of wall-rocks.

Granite porphyry adjacent to W-Mo veins was most strongly altered to quartz+muscovite+beryl greisen in which quartz (<87 vol.

% ; determined by point counting), beryl (<58 vol. %), muscovite (<26 vol. %), and minor amounts of rutile and fluorite (<1 vol. %) are typically present, mainly as fine disseminations. Wolframite, molybdenite and pyrite are also disseminated in this inner greisen zone. The amounts of muscovite and beryl decrease from inner to outer zone in the greisen. In the contacts between W-Mo veins and banded biotite gneiss, only quartz+muscovite greisen is observed. Quartz+muscovite greisen developed in gneiss is characterized by abundant fluorite (up to 3 vol. %) and rare beryl compared with quartz+muscovite $\pm$ beryl greisen in granite porphyry.

2. Vein Stage

Vein stage is characterized by the earlier W-Mo ores+quartz mineralization and the later base-metal sulfides+quartz mineralization (Fig. 3).

Earlier W-Mo mineralization is characterized by the precipitation of molybdenite, wolframite, and scheelite accompanying quartz, muscovite, and beryl. Muscovite occurs as fine disseminations within coarse crystalline white quartz and as well-defined mineralic bands along the vein contacts with wall rocks. Beryl occurs as white to light green aggregates of hexagonal crystals (0.1 to 5.0 cm in length) which are intergrown with quartz and muscovite. Molybdenite occurs as fine disseminations and/or massive aggregates in quartz veins. Rare, prismatic or bladed bismuthinite is intergrown with or overgrows molybdenite. Wolframite, the main ore constituent, is distributed unevenly in the veins as columnar or platy crystals of 0.1-4.0 cm long and sometimes in central vein portions as segregations of large grains, often forming nests. According to Kim (1977), wolframite from the Cheongyang mine has MnO/FeO ratios ranging from about 0.80 to 0.95. Scheelite is present in the form of fine anhedral grains within quartz matrix and is

Fig. 3. Mineral paragenesis of the Cheongyang W-Mo mine. Width of lines corresponds to relative abundance. The temperature scale is based on analysis of fluid inclusion data and temperature estimation using mineral assemblages.

often associated with wolframite. Some scheelites occur along margins and fractures of quartz grains. Scheelite shows white to yellow fluorescence color under UV light, indicating the presence of minor powellite component. Pyrite and chalcopyrite are present rarely in wolframite as fine euhedral to subhedral inclusions. Pyrrhotite occurs in irregular fractures of wolframite. Pyrite usually forms aggregates intergrown with wolframite, molybdenite and sphalerite (15.3-19.2 mole % FeS; Table 2, Fig. 4). Fine arsenopyrites (29.7-31.0 atom. %

As) are often intergrown with pyrite.

Later base-metal mineralization is characterized by deposition of abundant base-metal sulfides. Sphalerite occurs mainly as polycrystalline aggregates in central vein portions and is often intergrown with chalcopyrite and pyrite. It commonly contains small blebs of pyrite, chalcopyrite and pyrrhotite. Sphalerite from the base-metal stage displays wide compositional variations from 12.6 to 17.8 mole % FeS (Table 2, Fig. 4). Stannite occurs locally as massive aggregates closely inter-

Table 2. Partial analyses of sphalerite from the Cheongyang W-Mo mine

Sample no.	Stage	mole percent		
		FeS	MnS	CdS
CY-22	vein (W-Mo)	19.2	0.3	1.6
		17.5	0.3	1.2
		15.7	0.3	0.2
		16.0	0.4	0.1
		18.2	0.3	1.0
CY-23	vein (W-Mo)	15.5	0.4	0.3
		17.7	0.4	1.0
		15.7	0.4	0.3
		15.3	0.3	0.3
		15.7	0.4	0.2
CY-33	vein (base-metal sulfide)	16.2	0.4	0.2
		16.4	0.3	0.4
		17.8	0.0	0.0
		13.1	0.0	0.0
		16.4	0.0	0.0
CY-41	vein (base-metal sulfide)	14.4	0.0	0.0
		14.5	0.0	0.0
		16.5	0.0	0.0
		16.7	0.0	0.0
		17.6	0.0	0.0
CY-35	vug (carbonate)	13.6	0.0	0.0
		16.3	0.0	0.0
CY-36	vug (carbonate)	12.6	0.0	0.0
		19.3	0.0	1.6
CY-40	vug (carbonate)	18.3	0.0	1.9
		20.8	0.0	2.5
		22.0	0.0	3.1
		21.3	0.0	2.9
		19.0	0.0	2.9
CY-51	vug (carbonate)	21.6	0.0	3.4
		22.7	0.0	5.2
		23.3	0.0	5.1
		23.4	0.0	2.6
		23.3	0.0	2.2
CY-51	vug (carbonate)	22.1	0.4	1.3
		21.4	0.4	1.4
		19.7	0.3	1.6

grown with sphalerite, and often contains pyrite inclusions. Galena penetrates and replaces nearly all of the early-deposited sulfides and is intimately associated with Pb-Bi sulfosalts (cosalite and galenobismutite) and native bismuth.

3. Vug Stage

Quartz, muscovite, fluorite, carbonates and minor amounts of ore minerals were deposited in vugs. Euhedral quartz (<10 cm long) is clear to smoky in color. Carbonate minerals, mainly calcite with minor siderite and rhodochrosite, occur as rhombs overgrowing prismatic quartz. Purple and pale green fluorite are commonly associated with carbonates in

vugs. Muscovite occurs mainly at the base of vugs as coarse plates and often fills microfractures of vein quartz near vugs. Wolframite in vugs overgrows quartz as small euhedral crystals. White to purple euhedral scheelites (<3 cm long) are often observed in vugs. Rare amounts of sulfides such as pyrite, chalcopyrite, pyrrhotite, sphalerite (18.3-23.4 mole % FeS; Table 2, Fig. 4) and galena, and native bismuth occur as aggregates of euhedral to subhedral crystals in vugs, which are associated with muscovite and rhodochrosite and often overgrow scheelite. Magnetite occurs as microscopic-sized inclusions within pyrite and sphalerite in vugs.

4. Comparison of Mineral Paragenesis to Other Tungsten Deposits

The overall vein mineralogy of the Cheongyang W-Mo mine changed with increasing paragenetic time from W-Mo minerals through base-metal sulfides to carbonates. Other Korean W-Mo vein deposits (e.g., Daehwa, Weolag, Sannae, Gyeongchang) commonly show similar complex sequences of W-Mo, Pb-Zn, and carbonates mineralization rather than simple quartz-wolframite-molybdenite veins (Shelton *et al.*, 1986; So *et al.*, 1983a, b, 1991). Many famous worldwide W-bearing vein deposits (e.g., Pasto Bueno, Peru; Panasqueira, Portugal; San Cristobal, Peru) have similar complex mineralization sequences (Landis and Rye, 1974; Kelly and Rye, 1979; Campbell, 1983). This complex mineralization sequences in W-bearing hydrothermal systems have been interpreted to be the results of later introduction of progressively larger volumes of cooler meteoric waters into early W-Mo-depositing magmatic hydrothermal systems (Shelton, 1984; So *et al.*, 1991).

V. Fluid inclusion studies

Fluid inclusion studies (heating and freezing experiments) were performed on 32 thin (<

1 mm), doubly polished plates of quartz, beryl, rhodochrosite, fluorite and calcite, in order to document the ranges of fluid compositions and temperatures during the hydrothermal mineralization at Cheongyang. Microthermometric data were obtained using a Fluid Inc. gas-flow-type heating-freezing stage at Korea University. Salinity data are based on freezing-point depression in the system H_2O -NaCl for H_2O -rich inclusions (Potter *et al.*, 1978) and on clathrate melting temperatures for CO_2 -bearing inclusions (Bozzo *et al.*, 1975; Collins, 1979).

Minerals examined contain numerous primary and secondary inclusions. Three types of inclusions are recognized based on their phase relations at room temperature, as follows.

Type I (liquid-rich): This type of fluid inclusions contains liquid and a water-rich vapor phase, and homogenizes to the liquid phase. The vapor bubble usually makes up 20 to 50 percent of the total inclusion volume. Type I inclusions are predominant in all minerals examined. Some type I inclusions formed traces of gas hydrates during freezing runs, indicating that minor amounts of CO_2 (≈ 0.85 molal, the level required for CO_2 clathrate formation; Hedenquist and Henley, 1985) are contained in these inclusions.

Type II (gas-rich): This type of inclusion also contains a liquid and a water-rich vapor phase whose volume (70–90 volume % of the total inclusion volume) exceeds that of the liquid phase. Type II inclusions are observed only as primary inclusions in white quartz and beryl of the vein stage and homogenize to the vapor phase upon heating.

Type III (CO_2 -bearing): This type of inclusion contains liquid CO_2 , CO_2 vapor, and an aqueous liquid at room temperature. The volumetric ratio of CO_2 (liquid+vapor)/aqueous liquid at 25°C is about 1:1. Type III inclusions occur rarely in white quartz of vein stage

Fig. 4. Variation of FeS content of sphalerite from the Cheongyang W-Mo mine.

as primary inclusions (we observed only five type III inclusions in all of the samples examined, but two homogenization temperature data were obtained due to thermal decrepitation during heating experiments). They homogenize totally to the H_2O -rich phase. Phase transition from solid CO_2 to liquid CO_2 during freezing experiments occurred at temperatures of $>-57^\circ\text{C}$, indicating a relatively pure CO_2 -rich phase in type III inclusions (Hollister and Burruss, 1976).

1. Fluid Inclusions from Vein Stage

White quartz and beryl from the vein stage contain numerous fluid inclusions ranging from 5 to $100\ \mu$ in size (typically $10\text{--}20\ \mu\text{m}$) which occur as both primary and secondary inclusions.

Homogenization temperatures of primary fluid inclusions in white quartz from vein stage range from 180° to 398°C (type I inclusions, $180^\circ\text{--}398^\circ\text{C}$; type II inclusions, $313^\circ\text{--}390^\circ\text{C}$; type III inclusions, $324^\circ\text{--}332^\circ\text{C}$) (Fig. 5). Primary fluid inclusions in beryl homogenize at temperatures between 284° and 359°C (type II inclusions, $350^\circ\text{--}359^\circ\text{C}$) (Fig. 5).

Salinities of primary inclusions in white quartz from vein stage range from 0.7 to 6.1 wt. % eq. NaCl (type I, 0.7–6.1 wt. %; type II, 1.8–2.4 wt. %; type III, 3.8–4.3 wt. %) (Fig. 6). Primary fluid inclusions in beryl have salinities

Fig. 5. Histograms of homogenization temperatures of fluid inclusions in minerals of the Cheongyang W-Mo mine.

Abbreviations: II, vapor-rich inclusions; C, liquid CO_2 -bearing inclusions; P, primary; S, secondary.

ranging from 3.1 to 4.6 wt. % eq. NaCl (Fig. 6).

2. Fluid Inclusions from Vug Stage

Minerals examined from the vug stage are clear vug quartz, rhodochrosite, fluorite and calcite and they contain only type I inclusions. Homogenization temperature and salinity data for vug stage are shown in Figs. 5 and 6.

Homogenization temperatures of primary fluid inclusions in all examined minerals from the vug stage range from 150° to 304°C (clear vug quartz, 194°–304°C; rhodochrosite, 240°–

272°C; fluorite, 152°–248°C; calcite, 150°–237°C) (Fig. 5). There is a general decrease of homogenization temperature from clear vug quartz (up to $\approx 305^\circ\text{C}$) to calcite (down to 150°C) (Fig. 5).

Salinities of primary inclusions in minerals from the vug stage range from 0.2 to 4.7 wt. % eq. NaCl (clear vug quartz, 0.4–4.7 wt. % NaCl; rhodochrosite, 1.8–3.1 wt. %; fluorite, 1.6–3.2 wt. %; calcite, 0.2–2.4 wt. %) (Fig. 6).

3. Variations in Temperature and Composition of Hydrothermal Fluids

Variations in temperature and composition of hydrothermal fluids throughout the hydrothermal activity are recognized by fluid inclusion studies. Fluid inclusion homogenization temperature data indicate that hydrothermal fluids at Cheongyang evolved from initial high temperatures ($\approx 400^{\circ}\text{C}$) to later lower temperatures ($\approx 150^{\circ}\text{C}$).

Homogenization temperatures of primary inclusions in white quartz from the vein stage range from 180° to 400°C . Within this wide range of temperatures, analysis of peaks and clusters of data within a frequency diagram (Fig. 5) has allowed us to decipher individual events which are likely related to specific mineral assemblages (Shelton, 1983).

Homogenization temperatures of primary inclusions in white vein quartz form two main clusters (Fig. 5): a high-temperature cluster, from 300° to 400°C , possibly corresponding to early quartz+W-Mo mineralization; and a lower temperature cluster, from 300° to 180°C , corresponding to late quartz+base-metal sulfide mineralization.

The relationship between homogenization temperature and salinity for vein stage indicates a history of fluid boiling during W-Mo mineralization (Fig. 7). Prolonged and extensive boiling of vein-stage ore fluids resulted in a progressive increase in salinity from ≈ 1 wt. % eq. NaCl to ≈ 5 wt. % eq. NaCl, as vapor loss during boiling resulted in concentration of salts in residual fluids. CO_2 -bearing type III inclusions in white vein quartz may represent the trapping of an immiscible CO_2 -rich vapor formed by boiling of parent $\text{H}_2\text{O}-\text{CO}_2$ fluids.

Salinities of low-temperature ($<250^{\circ}\text{C}$), secondary inclusions in white quartz and beryl from the vein stage are about 2.5 to 5 wt. % eq. NaCl, which are comparable to those of primary inclusions (Fig. 6). Fracturing was pres-

Fig. 6. Histograms of salinities of fluid inclusions in minerals of the Cheongyang W-Mo mine. Symbols are the same as in Fig. 5.

ent throughout all of the episodes of mineralization at Cheongyang. It is therefore likely that high-salinity fluids generated by extensive fluid boiling were trapped continuously as secondary inclusions in earlier-deposited, white quartz and beryl.

Fluid inclusion data from the vug stage mineralization reflect much cooler (300° - 150°C),

Fig. 7. Homogenization temperature versus salinity diagram for fluid inclusions in minerals of vein stage of the Cheongyang W-Mo mine.

progressively more dilute (down to ≈ 0 wt. % eq. NaCl) hydrothermal fluids as a result of increasing influx of cooler, dilute meteoric waters (Figs. 5 and 6, see also "Stable Isotope Studies").

4. Pressure-Depth Consideration and Significance of Fluid Boiling

Liquid-rich (type I) and vapor-rich (type II) fluid inclusions are intimately associated in samples of white quartz and beryl from the vein stage and homogenize at similar temperatures (310° to 390°C). This indicates that hydrothermal fluids during the early W-Mo mineralization boiled extensively. No pressure corrections are therefore necessary for these high-temperature fluid inclusions because they were trapped along a liquid-vapor curve in the system H_2O -NaCl.

The data of Sourirajan and Kennedy (1962) and Haas (1971) for the system H_2O -NaCl (1-6 wt. %) indicate a range of pressures from ≈ 100 to 260 bars at the time of fluid entrapment. This range of pressures corresponds to mineralization depths near 1 km if pressure conditions changed from lithostatic toward hydrostatic regimes. The wide temperature range of

vapor-rich type II inclusions (310°-390°C) and the progressive increase of fluid salinity with decreasing temperature (Fig. 7) likely indicate that W-Mo-depositing hydrothermal fluids at Cheongyang evolved continuously near boiling conditions.

Progressive vapor loss from hydrothermal fluids due to boiling can result in chemical changes (e.g., pH, f_{O_2} , ΣH_2O , ΣCO_2 etc.) in the liquid phase (Drummond and Ohmoto, 1985). Wolframite deposition is favored by increase in pH of ore fluids by the following reaction (Polya, 1987): $FeCl^+ + HWO_4^- \rightarrow FeWO_4 + H^+ + Cl^-$. Tungsten deposition in the Cheongyang hydrothermal systems was probably a result of pH increase due to vapor loss accompanied by cooling during fluid boiling.

5. Comparison of Fluid Inclusion Data with Other Korean W-Mo Vein Deposits

Several Korean hydrothermal vein-type tungsten-molybdenum deposits (e.g., Daehwa, Weolag, Sannae, Gyeongchang, Susan etc.) have been the subjects of detailed fluid inclusion studies (Park and Choi, 1974; Park *et al.*, 1981; Kim, 1985; Shelton *et al.*, 1986, 1987; So *et al.*, 1983a, b, 1991). Vein-type W-Mo deposits in

Table 3. Comparison of selected features of Korean hydrothermal vein-type W-Mo deposits

Mine district	Mine	Geology	Ore occurrence ¹⁾	Alteration	Mineralization age (Ma)	CO ₂ -bearing inclusions ²⁾
Cheongyang	Cheongyang	Granite porphyry (70.5 Ma) in gneiss	Quartz veins with wf+mo+sch; abundant sulfides, Pb-Bi sulfosalts	Greisen, chloritic	70.5 ± 1.6	rare
Hwanggangri	Daehwa	Granite (87.6 Ma) in gneiss	Quartz veins with wf+mo+sch; minor sulfides	Greisen, chloritic	87.6 ± 1.6(?)	minor (<10 mole % CO ₂)
	Weolag	Granite (87-90 Ma) in limestones	Quartz veins with wf+sch+mo; abundant base-metal sulfides	Greisen	Late Cretaceous	minor (<3 mole % CO ₂)
	Susan	Granite (83-94 Ma) in limestones	Quartz veins with mo+wf+sch; minor sulfides	Greisen	83	variable, (3-100 mole % CO ₂)
Pusan-Yangsan	Gyeongchang	Granite (83.7 Ma) in volcanosedimentary rocks	Quartz veins with mo+wf+sch; abundant sulfides, Ag-Pb-Bi-Sb sulfosalts	Sericitic, propylitic	82.4 ± 1.4	absent
	Sannae	Quartz monzonite (75.5 Ma) in volcanic rocks	Quartz veins with mo+wf+sch; minor sulfides	Potassic, sericitic	65 ± 3	absent

Mine	Fluid inclusions		Estimated pressure (bars)	Estimated depths (m)	Fluid evolution	Reference
	Th (°C) ³⁾	Salinity (wt. % NaCl)				
Cheongyang	150 to 400 (>300)	0 to 6	100 to 260	~1,000	Boiling and later meteoric water mixing	This study
Daehwa	160 to 395 (>250)	0 to 8	100 to 350	1,250 to 3,000	Meteoric water mixing after fluid boiling (CO ₂ effervescence)	So et al. (1983b) Shelton et al. (1987) Park and Choi (1974) Kim (1985)
Weolag	155 to 395 (>250)	4 to 11	~180	<1,000 to 2,300	Meteoric water mixing after fluid boiling (CO ₂ effervescence ?)	So et al. (1983a)
Susan	105 to 385 (>200)	0 to 10	~220	800 to 2,500	CO ₂ effervescence and later meteoric water mixing	So and Yun (in prep) Park et al. (1981)
Gyeongchang	190 to 550 (>300)	1 to 33	300 to 500	1,200 to 2,000	Meteoric water mixing after liquid condensation from magmatic vapor	So et al. (1991)
Sannae	180 to 555 (>300)	5 to 25	100 to 300	~1,250	Meteoric water mixing after fluid boiling	Shelton et al. (1986)

1) W-Mo minerals (mo = molybdenite, sch = scheelite, wf = wolframite) are arranged in orders of decreasing abundance

2) Data in parentheses are estimated CO₂ contents of liquid CO₂-bearing inclusions

3) Data in parentheses are estimated temperatures of W-Mo deposition

South Korea occur in three major mining districts: Hwanggangri, Pusan-Yangsan, and Cheongyang. Table 3 summarizes some features of Korean vein-type W-Mo deposits, including the results of fluid inclusion studies.

These deposits display similarities in geologic setting, mineralogy and paragenesis, alteration assemblages and mineralization age.

All of the vein-type W-Mo mineralization in Korea are of late Cretaceous age (65-88 Ma),

Fig. 8. Temperature versus atomic % As (in arsenopyrite) diagram, showing temperature conditions (hatched area) pertinent to pyrite-sphalerite-arsenopyrite assemblages (black dots) in early W-Mo mineralization of the Cheongyang W-Mo mine (after Hutchison and Scott, 1981; Scott, 1983). Numbered dashes indicate compositional isopleths of sphalerite (mole % FeS) in equilibrium with pyrite. Abbreviations: As, arsenic; Asp, arsenopyrite; L, arsenic-sulfur liquid; lö, löellingite; Po, pyrrhotite; Py, pyrite.

and are associated intimately with Cretaceous Bulgugsa granites, not with Jurassic Daebog granites. Cretaceous granites in Korea were solidified at shallower portions (<2-3 km) than Jurassic granites (>5 km, Tsusue *et al.*, 1981; Watanabe, 1981). Therefore, it is likely that the deposition of tungsten and molybdenum occurred as a result of lower pressures and depths of hydrothermal systems associated with shallow Cretaceous granitic activity (Ishihara *et al.*, 1981). However, fluid inclusion data from these Korean W-Mo vein deposits are variable, as follows.

W-Mo vein deposits in the Hwanggangri mine district (e.g., Daehwa, Weolag, Susan) are characterized by the common occurrence of liquid CO₂-bearing fluid inclusions (Table 3). The peculiar occurrence of CO₂-bearing inclusions seems not to have been tied genetically to

Fig. 9. Log a_{S_2} versus temperature diagram showing depositional conditions for W-Mo mineralization of the Cheongyang W-Mo mine (dotted area) (after Kretshmar and Scott, 1976). Numbered lines indicate compositional isopleths of arsenopyrite (atom. % As).

Abbreviations: As, arsenic; Asp, arsenopyrite; L, liquid; lö, löellingite; Po, pyrrhotite; Py, pyrite.

specific host rock petrology (namely, the association of carbonate-rich wall rocks) because carbonate-rich rocks are absent in the Daehwa mine area. If depth (pressure) were one of the controlling factors for the occurrence of CO₂-bearing inclusions, then mineralization depths for the W-Mo vein deposits in the Hwanggangri district might have been deeper than those for the deposits in the Cheongyang and Pusan-Yangsan mine district. Estimated depths of W-Mo mineralization at the Hwanggangri district range from 800 to 3,000 m. Previous fluid inclusion studies also suggest that W-Mo deposition in the Hwanggangri district was likely a combined result of fluid boiling (and CO₂ effervescence) and later meteoric water mixing.

W-Mo vein deposits in the Pusan-Yangsan mine district (e.g., Gyeongchang, Sannae) are characterized by higher temperatures (up to 550°C, which is close to the solvus temperature of granitic melts) and salinities (up to 25-33 wt. % eq. NaCl) of ore-forming fluids (Table 3). Liquid CO₂-bearing fluid inclusions are absent.

Table 4. Sulfur isotope data of sulfide minerals from the Cheongyang W-Mo mine

Vein	Level-stage	Mineralization phase	Sample no.	Mineral	$\delta^{34}\text{S}$ (‰)	T (°C) ¹⁾	$\delta^{34}\text{S}_{\text{H}_2\text{S}}$ (‰) ²⁾
East No.2	+2-greisen	greisen	2E-S1	molybdenite	4.7	370	3.6
		greisen	2E-S2	pyrite	4.3	370	3.3
	+2-vein	base-metal sulfides	2E-S3	pyrite	4.9	300	3.7
Central	-3-greisen	greisen	3C-S1	pyrite	4.9	380	4.0
	-3-vein	W-Mo	3C-S2	pyrite	4.6	330	3.5
		W-Mo	3C-S3	pyrite	4.5	350	3.5
Main	-1-vein	base-metal sulfides	3C-S4	pyrite	5.0	300	3.8
		base-metal sulfides	1M-S1	pyrite	4.5	280	3.2
		base-metal sulfides	1M-S2	chalcopyrite	4.2	280	4.4
	-1-vug	vug(carbonate)	1M-S3	pyrite	4.8	250	3.3
	-2-greisen	greisen	2M-S1	pyrite	5.0	380	4.1
	-2-vein	W-Mo	2M-S2	molybdenite	4.4	350	3.2
	-3-vein	base-metal sulfides	3M-S1	pyrite	5.1	280	3.8
		base-metal sulfides	3M-S2	chalcopyrite	4.5	280	4.7
	-3-vug	vug(carbonate)	3M-S3	pyrite	4.9	250	3.4
	-4-greisen	greisen	4M-S1	pyrite	4.7	370	3.7
	-4-vein	W-Mo	4M-S2	molybdenite	4.5	350	3.3
		base-metal sulfides	4M-S3	pyrite	5.9	270	4.5

1) Based on fluid inclusion temperatures and paragenetic constraints

2) Calculated using the sulfur isotope fractionation equations in Ohmoto and Rye (1979)

with more extensive CO_2 loss from hydrothermal fluids due to fluid boiling at shallower depths. More complexity of vein mineralogy, including the occurrence of Pb-Bi sulfosalts, may also reflect shallower depths of W-Mo mineralization at Cheongyang compared to deposits in the Hwanggangri district. Therefore, fluid inclusion characteristics of Korean hydrothermal W-Mo vein deposits may be a useful guide to the influence of depth of emplacement on postmagmatic evolution of granite-related W-Mo systems and may help to delineate metallogenic provinces of W and Mo in Korea.

VI. Redox and sulfur chemistry of mineralization

The physicochemical constraints of mineral deposition at Cheongyang can be estimated by ore and gangue mineral assemblages in relation to time and space, combined with

chemical compositions of ore minerals and fluid inclusion data.

1. Vein-Stage Mineralization

(1) *Early W-Mo Mineralization*: Wollframite and molybdenite in early vein mineralization are associated with minor amounts of pyrite, arsenopyrite (29.7–31.0 atom. % As), and sphalerite (15.3–19.2 mole % FeS). Formation temperatures for the W-Mo mineralization can be estimated using the compositions of coexisting sphalerite and arsenopyrite (black dots in Fig. 8). Estimated temperatures for W-Mo mineralization range from $\approx 300^\circ$ to 380°C (hatched area in Fig. 8), which are in good agreement with W-Mo deposition temperatures (300° – 400°C) estimated from fluid inclusion homogenization temperatures. Based on these temperatures, the sulfidation state for W-Mo mineralizing fluids can be constrained by mineral stability in the system Fe-As-S (Kretschmar and Scott, 1976). The stability of pyrite +

Table 5. Carbon, oxygen, and hydrogen isotope data for various minerals and inclusion fluids, Cheongyang W-Mo mine

Vein	Level-stage	Sample no.	Mineral	Mineralization phase	$\delta^{13}\text{C}$ (‰)	$\delta^{18}\text{O}$ (‰)	δD (‰)	T (°C) ¹⁾	$\delta^{18}\text{O}_{\text{water}}$ (‰) ²⁾	$\delta\text{D}_{\text{water}}$ (‰)
East No. 2	+2-greisen	2E-1	mus	greisen		8.7	-98	370	6.8	-64 ³⁾
	+2-vein	2E-2	qtz	W-Mo		12.9	-	350	7.6	-69
	+2-vein	2E-3	qtz	base-metal sulfides		10.6	-	300	3.7	-67
Central	-3-vein	3C-1	wf	W-Mo		5.6	-	320	7.0	-
		3C-2	qtz	W-Mo		13.6	-	330	7.8	-69
	-3-vug	3C-3	qtz	vug(carbonate)		7.5	-	250	-1.4	-67
Main	-1-vug	1M-1	rd	vug(carbonate)		7.2	-	260	0.3	-
	-2-greisen	2M-1	qtz	greisen		11.1	-	380	6.6	-71
	-2-vein	2M-2	qtz	W-Mo		13.1	-	350	7.8	-
		2M-3	mus	W-Mo		9.9	-108	340	7.5	-68 ³⁾
	-2-vein	2M-4	qtz	base-metal sulfides		10.3	-	280	2.7	-64
	-2-vug	2M-5	qtz	vug(carbonate)		8.9	-	260	0.5	-69
		2M-6	rd	vug(carbonate)	-7.0	8.2	-	265	1.5	-
	-3-greisen	3M-1	qtz	greisen		10.6	-	390	6.3	-70
	-3-vein	3M-2	wf	W-Mo		5.5	-	330	7.2	-
	-3-vug	3M-3	cc	vug(carbonate)	-5.5	10.8	-	220	2.3	-

1) Based on fluid inclusion temperatures and paragenetic constraints

2) Calculated using the following oxygen isotope fractionation equations: quartz-water, Matsuhashi et al. (1979); calcite (and rhodochrosite)-water, O'Neil et al. (1969); muscovite-water, Friedman and O'Neil (1977); and wolframite-water, Landis and Rye (1974).

3) Calculated using the hydrogen isotope fractionation equation of SuzuoKi and Epstein (1976).

Abbreviations: cc = calcite, mus = muscovite, qtz = quartz, rd = rhodochrosite, wf = wolframite

arsenopyrite + sphalerite assemblage in the W-Mo stage indicates the log f_{S_2} (atm) values of ≈ -10.3 to -7.0 , as shown in Figure 9.

The probable f_{O_2} conditions for the W-Mo mineralization can be drawn on the log f_{S_2} versus log f_{O_2} diagram (Fig. 10). The diagram has been constructed for 300°C (the lower end of estimated temperatures for W-Mo mineralization) where pyrrhotite is stable along with pyrite and wolframite. Assuming a log f_{CO_2} value of 0.6 atm (based on the general absence of liquid CO_2 -bearing inclusions), the minimum log f_{O_2} value for W-Mo mineralization is defined by the C- CO_2 curve because graphite is absent. The estimated log f_{O_2} (atm) values range from ≈ -35.5 to -32.0 (Fig. 10).

(2) *Late Base-Metal Sulfide Mineralization*: During periods of base-metal sulfide mineralization, pyrrhotite was precipitated as an important Fe-S mineral. Fluid inclusion data indicate that deposition of base-metal sulfides occurred at temperatures below 300°C. The probable range of log f_{S_2} (atm) values for

the base-metal sulfide mineralization can be estimated to be ≈ -11.0 to -13.5 by the pyrite-pyrrhotite reaction curve (Fig. 9).

2. Vug-Stage Mineralization

Pyrite, pyrrhotite, magnetite and sphalerite (18.3-23.4 mole % FeS) were deposited in vugs, together with native bismuth, carbonates and fluorite. Pyrrhotite and sphalerite were deposited only during early periods of vug-stage mineralization. The early assemblage pyrrhotite-sphalerite-magnetite-bismuth can be used to estimate fugacities of sulfur and oxygen during vug-stage mineralization. Estimated temperature and fugacity of sulfur (log f_{S_2}) for vug-stage (carbonate) mineralization are about $<250^\circ\text{C}$ and <-14 atm, respectively (Fig. 9). Figure 9 also shows a general decrease in log f_{S_2} (atm) values with increasing paragenetic time from ≈ -7 (for W-Mo mineralization) to <-16 (for carbonate mineralization). Assuming a temperature of 200°C for carbonate mineralization in vugs, a log f_{S_2} versus log f_{O_2} diagram was constructed (Fig. 11). The assem-

Fig. 12. Variation of calculated oxygen isotope composition of waters in equilibrium with various minerals from the Cheongyang W-Mo mine.

blage pyrite (-pyrrhotite)-magnetite indicates log f_{O_2} values near -44 atm (Fig. 11).

VII. Stable isotope studies

In order to elucidate the origin and evolution of hydrothermal fluids and their constituents in the Cheongyang W-Mo deposits, we measured sulfur isotope compositions of 18 sulfides, carbon isotope compositions of 3 carbonates (calcite, rhodochrosite), oxygen isotope compositions of 9 quartz, 3 carbonates, 2 muscovites and 2 wolframites, and hydrogen isotope compositions of 2 muscovites and 8 fluid inclusion waters extracted from quartz. Gas extraction techniques for the mass spectrometer analysis were taken from McCrea (1950) for carbonates, Grinenko (1962) for sulfides, Hall and Friedman (1963) and Roedder *et al.* (1963) for fluid inclusions, and Rye and Sawkins (1974) for silicates, respectively. Isotopic data are reported in standard δ notation relative to the CDT standard for sulfur, the PDB standard for carbon, and the Vienna

SMOW standard for oxygen and hydrogen. The standard errors of each analysis are about ± 0.1 per mil for sulfur, carbon, and oxygen, and ± 2 per mil for hydrogen (Tables 4 and 5).

1. Sulfur Isotope Study

Sulfur isotope compositions of hand-picked sulfide minerals (13 pyrites, 3 molybdenites, 2 chalcopyrites) are shown in Table 4. The sulfides have nearly uniform $\delta^{34}S$ values ranging from 4.2 to 5.9 per mil. There is no spatial variation in the $\delta^{34}S$ values of sulfide minerals from the ore veins within the deposits.

Assuming depositional temperatures of 350° to 400°C for sulfides from greisen stage, 300° to 350°C for sulfides from early W-Mo mineralization in veins, 270° to 300°C for sulfides from late base-metal sulfide mineralization in veins, and 220° to 270°C for sulfides from vug (carbonate) stage, based on paragenetically constrained temperature estimates (using fluid inclusion homogenization temperatures), the ranges of possible $\delta^{34}S_{H_2S}$ values of the hydrothermal fluid were calculated (using the compiled data of Ohmoto and Rye, 1979) (Table 4): greisen-stage sulfides, 3.3 to 4.1 per mil; early W-Mo-stage sulfides, 3.2 to 3.5 per mil; late base-metal-stage sulfides, 3.2 to 4.7 per mil; and vug-stage sulfides, 3.3 to 3.4 per mil. There is no recognizable temporal variations of the calculated $\delta^{34}S_{H_2S}$ values of hydrothermal fluids.

Overlap of the ranges of calculated $\delta^{34}S_{H_2S}$ values suggests that a fluid with a $\delta^{34}S_{H_2S}$ value near 4 per mil was responsible for mineralization at Cheongyang. The small variation of $\delta^{34}S_{H_2S}$ values over a temperature range of 400° to 220°C, and the assemblages of pyrite (-pyrrhotite)-magnetite in veins and of muscovite (-K-feldspar)-quartz in alteration zones indicate that sulfur in the fluid was dominantly H_2S (Ohmoto, 1972). Therefore, the $\delta^{34}S_{H_2S}$ value near 4 per mil may be taken as an approxima-

Fig. 13. Hydrogen versus oxygen isotope diagram showing temporal variation of stable isotope compositions of the Cheongyang hydrothermal fluids. Meteoric water line is from Craig (1961); magmatic and metamorphic water boxes are from Taylor (1974). Range of isotopic compositions of modern Korean groundwaters(*) is from Kim and Nakai (1988).

tion of the sulfur isotope composition of the entire hydrothermal fluids. This $\delta^{34}\text{S}_{\text{ss}}$ value near 4 per mil indicates that the primary source of sulfur in the Cheongyang hydrothermal fluids was an igneous source (Ohmoto and Rye, 1979), likely the host granite porphyry.

2. Carbon, Oxygen, and Hydrogen Isotope Study

The $\delta^{13}\text{C}$, $\delta^{18}\text{O}$ and δD values for various minerals and inclusion fluids are summarized in Table 5.

Carbonate minerals (2 rhodochrosites and 1 calcite) for the vug(carbonate)-stage have $\delta^{13}\text{C}$ values of -7.0 to -5.5 per mil. The $\delta^{18}\text{O}$ values of the carbonate minerals are 7.2 to 10.8 per mil. Using the calcite-water oxygen isotope fractionation equation of O'Neil *et al.* (1969), coupled with temperature estimates based on fluid inclusion and paragenetic constraints, the range of $\delta^{18}\text{O}$ values of waters in equilibrium with the carbonates is 0.3 to 2.3 per mil (for this calculation, the oxygen isotope fractionation

between rhodochrosite and water was assumed to be approximate that between calcite and water) (Table 5).

The $\delta^{18}\text{O}$ values of quartz, muscovite and wolframite are (Table 5): quartz, 7.5 to 13.6 per mil [greisen-stage quartz, 10.6-11.1 per mil; W-Mo-stage quartz, 12.9-13.6 per mil; base-metal-stage quartz, 10.3-10.6 per mil; vug(carbonate)-stage quartz, 7.5-8.9 per mil]; muscovite, 8.7 to 9.9 per mil; and wolframite, 5.5 to 5.6 per mil. Using the appropriate oxygen isotope fractionation equations, coupled with the estimated temperatures based on paragenetic constraints and fluid inclusion data, the oxygen isotope compositions of waters in the hydrothermal fluids are calculated as follows (Table 5): greisen stage, 6.3 to 6.8 per mil; early W-Mo mineralization in the vein stage, 7.0 to 7.8 per mil; late base-metal sulfide mineralization in the vein stage, 2.7 to 3.7 per mil; quartz deposition in the vug stage, -1.4 to 0.5 per mil.

The δD values of 2 muscovites are -98 and -108 per mil (Table 5). Assuming depositional temperatures based on fluid inclusions in associated quartz, the calculated δD values of waters in equilibrium with muscovite are -64 and -68 per mil (using the hydrogen isotope fractionation equation of Suzuoki and Epstein, 1976).

Inclusion waters extracted from 8 quartz samples were analyzed for hydrogen isotope compositions (Table 5). The δD values of inclusion waters from quartz have a narrow range from -71 to -64 per mil.

3. Interpretation of Oxygen and Hydrogen Isotope Results

The $\delta^{18}O_{\text{water}}$ values of hydrothermal fluids decrease systematically with increasing paragenetic time, from ≈ 8 per mil for greisen stage and W-Mo mineralization, to ≈ 3 per mil for base-metal sulfides mineralization, to ≈ -2 per mil for vug(carbonate)-stage deposition (Fig. 12). This decrease of $\delta^{18}O_{\text{water}}$ values with time indicates a progressive increase of meteoric water interaction in the Cheongyang hydrothermal system.

There is a slight increase of $\delta^{18}O_{\text{water}}$ values from the greisen stage ($\delta^{18}O_{\text{water}} = 6.3$ to 6.8 per mil) to the early W-Mo mineralization in vein stage ($\delta^{18}O_{\text{water}} = 7.0$ to 7.8 per mil) (Table 5, Fig. 12). This small positive change in $\delta^{18}O_{\text{water}}$ values may coincide with fluid boiling documented in fluid inclusion studies [vapor-rich type II inclusions ($T_h C = 310^\circ - 390^\circ C$) were observed exclusively in white quartz and beryl from vein stage]. Boiling of ore fluids during W-Mo mineralization could result in preferential loss of ^{16}O -enriched vapor, resulting in higher $\delta^{18}O_{\text{water}}$ values for the residual mineralizing fluid (Friedman and O'Neil, 1977).

Figure 13 shows the distribution of measured and calculated hydrothermal water compositions from the Cheongyang mine on a δD vs. $\delta^{18}O$ diagram. The data from the greisen

to W-Mo mineralization stages fall within the calculated range of primary magmatic waters in equilibrium with normal igneous rocks (Taylor, 1974) and may therefore represent magmatic water or water from any source whose isotopic composition was controlled by isotopic exchange with a large volume of granitoids at near magmatic temperatures.

Quartz from the base-metal sulfide stage yielded isotopic values for fluids which fall significantly outside the range of magmatic waters toward more negative $\delta^{18}O$ values (Fig. 13). This could represent mixing of magmatic or highly exchanged meteoric water with less exchanged meteoric water, or exchange of meteoric water with granitic rocks at elevated temperatures and low water/rock ratios. Data from the vug (carbonate) stage (Fig. 13) are consistent with mixing of highly exchanged meteoric water with unexchanged meteoric water or exchange of meteoric water with granitic rocks at elevated temperatures and high water/rock ratios. Using either a mixing or exchange model, the isotopic compositions of fluids in the Cheongyang hydrothermal system show a progressive shift from magmatic hydrothermal dominance in the W-Mo stage toward meteoric hydrothermal dominance in the base-metal sulfide and vug (carbonate) stages.

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