Geochemistry of the Youngbogari deposit, Republic of Korea: An unusual mesothermal gold–silver deposit of the Youngdong area

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Mesothermal gold–quartz veins of the Youngbogari deposit in the Youngdong area, South Korea, are hosted in faulted shear zones in Precambrian gneiss of the Sobaegsan massif. The Youngbogari deposit shares many features with other metamorphic rock-hosted gold deposits in the area, including a massive single-stage nature of veins and a simple vein mineralogy. However, its ore mineralogy is unique in that (1) arsenopyrite and pyrite occur dominantly with only minor pyrrhotite and (2) electrum grains are very poor in gold content (<40 atom. % Au).

A variety of geochemical data indicate that deposition of the mesothermal gold–silver ores of the Youngbogari deposit resulted mainly from cooling of ore fluids accompanying decreasing sulfur fugacity. Fluid inclusion evidence indicates that gold deposition was not related to an early history of CO2 phase separation (at temperatures of 300° to 420°C), but rather was tied to a later history of cooling and dilution of H2O–NaCl ore fluids at temperatures of <300°C. These temperature estimates for gold deposition agree with those based on chlorite thermometry (270° to 320°C) and sulfide mineral assemblages (<290°C). Measured and/or calculated, stable isotope compositions of hydrothermal fluids (δ18O water = 5.8 to 8.0‰, δD water = –75 to –54‰) indicate an important role of rock-dominated (possibly magmatic) fluids in the mesothermal gold–silver system.

The unusual arsenopyrite–pyrite-rich nature of the Youngbogari ores and their anomalously negative δ34S values (~–2.9 to ~–5.1‰), compared to other mesothermal gold deposits of the Youngdong area, are interpreted to reflect a more oxidizing nature of the Youngbogari ore fluids, likely due to less reaction with graphite in wallrock gneiss.

INTRODUCTION

Gold–silver vein deposits in South Korea are associated intimately with major periods of Jurassic and Cretaceous granitic plutonism (Shimazaki et al., 1981, 1986). Cretaceous granites have been shown to be higher level intrusions (<2–3 km) than Jurassic granites (>5 km, Tsuue et al., 1981; Watanabe, 1981), providing an opportunity to investigate the influence of magma emplacement depth on the post-magmatic evolution of granite-related gold systems. Three major types of deposits previously documented which display a consistent relationship among depth, water-to-rock ratio (degree of meteoric water involvement), and Au/Ag ratio (So and Shelton, 1987; Shelton et al., 1988). These are: (1) mesothermal-type gold-rich deposits, (2) Korean-type (~deep epithermal) gold–silver deposits (Tsuchida, 1944; Shikazono and Shimizu, 1986), and (3) more silver-rich, epithermal-type deposits (So and Shelton, 1987; So et al., 1987a; Shelton et al., 1990; Yun et al., 1993).

Among these, mesothermal-type deposits are comparatively rare in Korea (Shelton et al., 1988; So et al., 1995, 1999; So and Yun, 1997; Yun et

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and therefore relatively little is known about their genesis and fluid characteristics. They appear to be associated genetically with Jurassic (Daebo Series) granitoids (Lee, 1981) and are characterized by high Au/Ag ratios (5:1–8:1). Geochemical studies of these deposits indicate that gold deposition occurred at temperatures of 300° to 370°C in response to CO2 separation of the fluids at depths of >4.5 km (Shelton et al., 1988; So and Yun, 1997).

Korean-type deposits are associated with Late Jurassic–Early Cretaceous (Bulgusa Series) granitoids (Lee, 1981) and are characterized by comparable Au/Ag ratios (1:5–2:1) and a general paucity of sulfide minerals (Sugaki et al., 1986). Geochemical studies of Korean-type gold–silver deposits indicate that gold deposition occurred at temperatures near 270°C in response to boiling and cooling at depths near 1.3 km (So and Shelton, 1987; So et al., 1987b).

The more silver-rich, epithermal deposits are associated genetically with Late Cretaceous–Tertiary granitoids and are characterized by lower Au/Ag ratios (1:10–1:200) and more abundant and complex sulfide mineralization. Geochemical studies of these deposits indicate that gold–silver deposition occurred at temperatures of <240°C in response to boiling and cooling at depths of <0.8 km (So and Shelton, 1987; So et al., 1987a; Shelton et al., 1990).

The Youngdong area was historically one of the important gold–silver producers in South Korea. Although accurate total production is not known, available data show that at least 1.5 tons of pure gold has been produced from twenty-five gold–silver mines (KMPC, 1986). Remaining reserves are an estimated 145,200 metric tons of ore. The Youngbogari deposit shares many features with other metamorphic rock-hosted gold deposits in the Youngdong area (Choi et al., 1988; Yun, 1991). However, its ore mineralogy is unique in that (1) arsenopyrite and pyrite occur dominantly with only minor pyrrhotite, and (2) electrum grains are very poor in gold content (<40 atom. % Au). Such mineralogical differences may reflect different physicochemical conditions (e.g., fugacities of sulfur and oxygen) during mineralization.

The main purpose of this study is to determine what conditions caused formation of the unusual Youngbogari deposit. Based on mineralogical, fluid inclusion and stable isotope studies, we decipher the fluid composition and physicochemical conditions that led to deposition of unique mesothermal ores at Youngbogari. There is special emphasis on sulfur isotope data of ore sulfurs in various types of gold–silver deposits in the Youngdong area.

**EXPERIMENTAL PROCEDURES**

For this study, about eighty samples of vein ore and wall-rocks were collected from underground ore stopes and surface outcrops of the Youngbogari deposit. Among them, representative
samples were examined in detail by microscopy in order to understand the mineralogy and paragenesis of veins and wall-rock alteration zones. X-ray diffraction analysis was also performed to identify the mineralogical characteristics in more details. The chemical compositions of electrum, arsenopyrite, sphalerite, silver-bearing sulfosalts, and chlorite were analyzed with an electron probe microanalyzer (JEOL JXA-8600 Superprobe) with energy-dispersion and wavelength-dispersion spectrometers at the Center for Mineral Resources Research (CMR), Korea University.

Fifty-six samples of vein quartz among collected samples were prepared for fluid inclusion study. Sphalerite was not suitable for the study because of its opacity. Microthermometric data were obtained using a FLUID Inc. gas-flow heating–freezing stage calibrated with synthetic CO₂ and H₂O inclusions and various organic solvents. Before the microthermometric measurement, a relative chronology of fluid inclusions was established using the criteria of Roedder (1984). During heating experiments, heating rates were maintained near 2°C/min to avoid decrepitation of fluid inclusions. A sequential technique described by Haynes (1985) was employed during freezing experiments in order to obtain accurate temperatures of phase change in fluid inclusions. Temperatures of total homogenization (Th–tot) have standard error of ±2°C. The melting temperatures of the carbonic phase (Tm–CO₂), ice (Tm–ice) and clathrate (Tm–clath) and the homogenization temperatures of the carbonic phase (Th–CO₂) have standard errors of ±0.2°C.

We have examined the sulfur isotope compositions of 20 sulfides (pyrite, sphalerite, galena, arsenopyrite) separated by hand-picking from sulfide bands, the oxygen isotope compositions of 8 vein quartz, the carbon isotope compositions of 4 samples of CO₂ gas extracted from fluid inclusions, and the hydrogen isotope compositions of 8 samples of inclusion waters. Mineral separates used for analysis were at least 99% pure. For the preparation of vein sulfides to extract SO₂ for sulfur isotopic analysis, the conventional technique described by Grinenko (1962) was used. Oxygen isotope analysis of vein quartz was carried out with conventional fluorination techniques (Hall and Friedman, 1963). Inclusion-hosted fluids were also extracted in a line that was designed to separate H₂O, CO₂, and CH₄ from vein quartz samples for measurement of their hydrogen isotope (for water) and carbon isotope (for CO₂) ratios. The method of crushing in a vacuum was used to extract the fluids. Before the crushing of quartz samples for hydrogen isotope analysis, detailed fluid inclusion petrology of each sample was carefully examined to select the samples to minimize the percentage of obvious secondary inclusions. Careful monitoring of the CO₂/H₂O ratios in the extracted fluids also allowed us to affirm that the extracted fluids from quartz and their hydrogen isotope compositions are representative of the typical mineralizing fluids, because primary inclusions typically contain high proportions of liquid CO₂-bearing fluid inclusions. The stable isotopic compositions were analyzed with gas-isotope ratio mass spectrometers at the Institute of Mineral Deposits, Beijing, China, the Stable Isotope and Fluid Inclusion Laboratories of Missouri-Columbia, U.S.A., and the Krueger Enterprises, U.S.A. Isotope data are reported in standard δ notation relative to the CDT standard for sulfur, the PDB standard for carbon, and the V-SMOW standard for oxygen and hydrogen. The standard error of each analysis is about ±0.1‰ for S, C and O, and ±2‰ for H.

**Geochemical Setting and Ore Deposit**

**Geologic setting**

As shown in Fig. 1, the Youngdong area is located approximately 170 km SSE of Seoul between the Okchon Fold Belt (a NE-trending fold and thrust belt comprising mainly Late Precambrian to Paleozoic metasedimentary rocks) and the Sobaegsan Massif (a metamorphic terrane comprising mainly Late Archean to Early Proterozoic gneisses and schists). The basement rocks of the Sobaegsan Massif experienced amphibolite- to granulite-facies metamorphism
during the late Paleozoic to early Mesozoic collision process between the North and South China crustal blocks (Na and Kim, 1987; Ree et al., 1996; Chough et al., 2000) and were intruded by foliated or massive granites of Permian to Jurassic age (Fig. 1). Numerous hydrothermal quartz veins in the Youngdong area mostly occur in Precambrian basement rocks.

Precambrian basement rocks in the Youngbogari deposit area consist of banded biotite gneiss, granitic gneiss and small lenses of schist within the gneisses (Fig. 2). Banded biotite gneiss and granitic gneiss have a gradational contact and are locally migmatitic. A whole-rock Rb–Sr age of 1,810 ± 10 Ma was obtained for the granite gneiss by Choo and Kim (1985). Amphibolite-grade metamorphic mineral assemblages in the gneisses have been overprinted by greenschist facies assemblages, especially along mineralized fault planes. A late Jurassic granodiorite batholith intrudes these metamorphic rocks in the eastern part of the study area. So and Yun (1997) obtained a Rb–Sr age of 171 ± 10 Ma for the granodiorite, and have suggested that it was genetically related to mesothermal-type gold mineralization in the Youngdong area.

**Ore deposit**

The Youngbogari deposit comprises two major quartz veins with strike and dip directions of N20–68°E and 70–80°SE, respectively (Fig. 2). The veins extend up to 1 km along strike direction and vary in thickness from 0.6 to 1.0 m. Weak alteration of wall-rock gneiss occurs along mineralized fault planes as narrow (<0.2 m thick), pale green zones consisting of quartz, sericite, chlorite, carbonates (calcite, dolomite) and pyrite. No economic gold concentration occurs in the alteration zones. Mineralogical characteristics and chemical composition of electrum and sphalerite from Youngbogari ores have been briefly described in Choi et al. (1988). However, most data in this section were collected by this study.

Ore mineralization occurs in massive quartz veins whose ore mineralogy is relatively simple, consisting mainly of iron sulfides (dominantly arsenopyrite and pyrite) and base-metal sulfides (sphalerite and galena). The veins contain variable amounts of sulfides (generally <10 vol %, but locally up to 50 vol % of the vein) in massive gray to milky quartz and locally show crude sulfide bands in the following sequence, from vein margins to center: arsenopyrite + pyrite + sphalerite; sphalerite + chalcopyrite + pyrite ± pyrrhotite; sphalerite + galena + pyrite + Au–Ag minerals (electrum, argentite, pyrargyrite). Mineralogy and paragenesis of veins are summarized in Fig. 3.

Arsenopyrite (31.4–33.4 atom. % As) is the most abundant sulfide mineral (>40 vol % of ore
minerals in veins) and occurs mainly as large, euhedral to subhedral aggregates (up to 5 mm in size) in marginal to intermediate portions of the veins. Along vein margins, arsenopyrite and pyrite form a crude band. Pyrite in association with arsenopyrite rarely contains tiny grains of pyrrhotite. Pyrrhotite also occurs as a rare sulfide intergrown with or included in sphalerite. Arsenopyrite is commonly fractured and healed by later quartz, sulfides (mainly galena and sphalerite) and electrum grains (Fig. 4A). Sphalerite ($X_{\text{FeS}} = 0.04–0.18$) is also abundant and occurs typically as anhedral grains intergrown with pyrite, chalcopyrite, galena and tetrahedrite. Late sphalerite ($X_{\text{FeS}} = 0.04–0.10$) occurs in microscopic veinlets cutting arsenopyrite and pyrite, and is associated with late quartz, chlorite, galena, electrum and argentite (Figs. 4B and C). Gold in the Youngbogari ores occurs as silver-rich electrum (60.3–87.6 atom. % Ag) which is intergrown with galena that fills fractures in arsenopyrite. Due to the intimate association of electrum grains within arsenopyrite fractures, the Youngbogari ores have been undervalued in spite of high gold grades (up to 30 g/ton Au), because refining of arsenopyrite-rich ores has been avoided due to environmental problem.
many common features: (1) occurrence within Precambrian gneiss; (2) massive and single-stage quartz veins; (3) simple vein mineralogy. However, some characteristics of the Youngbogari ores are unique: (1) arsenopyrite is the most abundant sulfide mineral (other deposits do not contain significant arsenopyrite); (2) pyrrhotite is rare among the iron sulfides (pyrrhotite is the most abundant sulfide in other deposits); (3) the electrum has very high silver contents (up to 87.6 atom. % Ag), whereas electrum from other deposits are gold-rich (mostly >70 atom. % Au).

DEPOSITIONAL CONDITIONS OF ORE MINERALIZATION

Chlorite thermometry

Cathelineau (1988) suggested that the Al(IV) content of chlorite can be used to estimate the temperature of geothermal fluids. The suggested equation is $T (°C) = 322Al(IV) – 62$ for chlorites converted to the formula $8Si + Al(IV)$, and can be used to reconstruct temperatures within the error of $±10°C$. Following the correction of increase in Al(IV) content with $Fe/(Fe + Mg)$, the compositions of chlorites ($N = 18$) in association with galena, sphalerite, electrum and argentite (Fig. 4C) in late periods of hydrothermal mineralization were used to estimate the temperatures of hydrothermal fluids. Calculated temperatures of formation range from $270°$ to $320°$ C. These temperatures likely reflect the depositional conditions of gold and silver.

Temperature and fugacity of sulfur conditions based on sulfide mineral assemblages

Temperatures and fugacities of sulfur of the ore-forming fluids can be estimated based on the available ore mineral assemblages and their compositions. In marginal portions of veins, arsenopyrite (31.4–33.4 atom. % As) coexists with pyrite as a crude bimineralic band. This assemblage indicates temperature and fugacity of sulfur conditions of approximately $>380°C$ and $>10^{-8}$ bars, respectively (Fig. 5; Kretschmar and Scott, 1976). Electrum grains (Ag content = 60.3–87.6

Fig. 4. Reflected light photomicrographs showing the occurrence of electrum and chlorite. A and B: Electrum grains (el) intergrown with late quartz (qz), galena (gn) and iron-poor (5–9 mole % FeS) sphalerite (sp), which fill fractures in arsenopyrite (apy). C: Chlorite (chl) intergrown with late quartz, sphalerite and galena. Scale bars are 0.1 mm.
atom. %) are associated with chlorite, galena, late iron-poor sphalerite ($X_{FeS} = 0.04–0.10$) and argentite, which fill fractures in arsenopyrite. This late assemblage indicates a fugacity of sulfur of about $<10^{-10}$ bars at temperatures of $<290°C$ (Fig. 5; Barton and Toulmin, 1964; Barton and Skinner, 1979). These data indicate that the ore fluids evolved progressively toward lower temperatures and sulfur fugacities with time.

** Fluid Inclusions **

*Occurrence and compositional types of fluid inclusions*

Vein quartz is typically inclusion-rich, due to repeated fracturing and healing events both during and after quartz deposition. The size of fluid inclusions ranges from $<3$ to $30 \mu m$. Two main types of fluid inclusions were identified based on their phase relations at $20°C$ and their behavior on cooling to $-15°C$: liquid-rich, aqueous inclusions and liquid CO$_2$-bearing inclusions.

Liquid-rich, aqueous inclusions consist of an aqueous liquid and vapor. The vapor bubble comprises $10$ to $45$ vol.%. These inclusions homogenize to liquid phase upon heating. Upon cooling, CO$_2$-clathrate formed in some aqueous inclusions. These clathrate-forming inclusions appear to be primary, as they do not show obvious fracture control, and are classified herein as type “a” aqueous inclusions. Most aqueous inclusions are relatively small (mostly $<10 \mu m$) and irregular in shape, and occur along fractures cutting across individual quartz grains. These inclusions do not nucleate clathrate on cooling and are classified as type “b” aqueous inclusions.

Carbonic, liquid CO$_2$-bearing inclusions contain liquid CO$_2$, vapor CO$_2$ and aqueous liquid. Based on the relative abundances of CO$_2$ and H$_2$O, they are classified into two subtypes: type “a” carbonic (H$_2$O $>$ CO$_2$) and type “b” carbonic (H$_2$O $<$ CO$_2$). The volume proportions of CO$_2$ (liquid + vapor) are about 10 to 35% for type “a” carbonic inclusions and 55 to 90% for type “b”. The

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*Fig. 5. Sulfur fugacity versus temperature diagram showing the depositional conditions of ore mineral assemblages in the Youngbogari ores. Hatched area indicates deposition of arsenopyrite $+$ pyrite $+$ pyrrhotite (early; pre-gold); shaded area, deposition of electrum $+$ iron-poor (4–10 mole % FeS) sphalerite $+$ argentite (late; gold-depositing). The sources of stability curves are: isopleths (atom. fraction of Ag; $N_{Ag}$) of electrum from Barton and Toulmin (1964); isopleths (mole % FeS) of sphalerite from Barton and Skinner (1979); and isopleths (atom. % As; numbers 31, 32 and 33) of arsenopyrite from Kretchmar and Scott (1976).*
entire range of CO₂ volume is typically observed within a single grain. Carbonic inclusions appear mostly to be primary in origin, as they occur as regular-shaped and isolated inclusions with no obvious fracture control. Upon heating, most carbonic inclusions decrepitated prior to homogenization. Therefore, we could obtain only a small number of Th–tot data. When the thermal decrepitation occurred slightly before anticipated homogenization, the decrepitation temperature was used as a minimum estimate of the real homogenization temperature.

Microthermometric data

Microthermometric data of 301 fluid inclusions (260 primary and pseudosecondary, and 41 secondary) in vein quartz were obtained by freezing and heating experiments. The salinity data reported for 131 fluid inclusions are based on freezing point depression in the system H₂O–NaCl (Bodnar, 1993) for aqueous inclusions and on clathrate melting temperatures (Bozzo et al., 1975; Diamond, 1992) for liquid CO₂-bearing inclusions.

Aqueous inclusions The first ice melting of liquid-rich, aqueous inclusions was recognized at temperatures near −21°C, indicating the dominance of NaCl among dissolved salts (Crawford, 1981). Final melting of ice (Tm–ice) occurred at temperatures between −6.1°C and −1.6°C. If we neglect the effect of a small amount of clathrate formation by which ice melting temperatures can be depressed (Collins, 1979; Hedenquist and Henley, 1985), the Tm–ice values correspond to salinities of 9.3 to 2.7 wt. % eq. NaCl (Fig. 6). Aqueous inclusions homogenized to the liquid phase at temperatures of 232°C to 418°C (Fig. 7). Tm–clath data of type “a” aqueous inclusions were very difficult to obtain because of their small size, but fall in the range of 5.9°C to 8.6°C (corresponding to salinities of 2.8 to 7.6 wt. % eq. NaCl, within the range estimated from Tm–ice data).

The salinity and homogenization temperature data obtained for obvious secondary aqueous inclusions (type “b”) fall in the range 1.2 to 10.4 wt. % eq. NaCl (corresponding to Tm–ice values of −0.7°C to −6.9°C) and 163°C to 228°C, respectively (Figs. 6 and 7).

Carbonic inclusions Melting temperatures of the CO₂-bearing phase (Tm–CO₂) in type “a” carbonic inclusions range between −60.4°C and −56.6°C (Fig. 8A), indicating the presence of small amounts of CH₄ in the carbonic phase (Burruss, 1981). Homogenization of the CO₂-rich portion (Th–CO₂) in type “a” carbonic inclusions to the liquid CO₂ phase occurred at temperatures of 19.2°C to 29.6°C (Fig. 8B). Within a single quartz grain,
Th–CO₂ values range widely, indicating that the density of the CO₂-rich phase was highly variable during the fluids' entrapment. Tm–clath values of type “a” carbonic inclusions range from 7.1° to 11.0°C (Fig. 8C). Tm–clath values above 10°C indicate the presence of CH₄ (Hollister and Burruss, 1976; Burruss, 1981; Diamond, 1992). If we neglect the presence of CH₄ clathrate, which acts to raise the clathrate melting temperature, the Tm–clath values correspond to salinities of less than 5.6 wt. % eq. NaCl. The Th–tot values of these inclusions (to the aqueous phase) range from 257° to 367°C (Fig. 7).

Type “b” carbonic inclusions have Tm–CO₂ and Th–CO₂ (to the liquid) values of –61.4° to –56.4°C and 18.3° to 28.4°C, respectively (Figs. 8A and B). Tm–clath values of these inclusions range from 8.0° to 9.7°C (Fig. 8C), corresponding to salinities of 0.6 to 3.9 wt. % eq. NaCl if we neglect the presence of CH₄ clathrate. A total of 88 Th-tot (to the CO₂-rich phase) values obtained for type “b” carbonic inclusions range from 253° to 353°C, similar to the range for type “a” carbonic inclusions (Fig. 7).

Fluid immiscibility and mineral precipitation

As described earlier, hydrothermal fluids trapped as apparent primary inclusions in vein quartz are composed of three types: (1) a low to moderate-salinity (<9.3 wt. % eq. NaCl) aqueous fluid with the ability to form CO₂-clathrate; (2) an H₂O-rich, H₂O–CO₂ fluid with low salinity (<5.6 wt. % eq. NaCl); (3) a CO₂-rich, H₂O–CO₂ fluid with low salinity (<3.9 wt. % eq. NaCl).

The entire range of CO₂ concentration is observed within single quartz grains. Total homogenization temperatures of type “a” and “b” carbonic inclusions are similar (253° to 367°C, with the peak at 280°–320°C in their distribution, Fig. 7). These observations likely indicate CO₂ phase separation of hydrothermal fluids during deposition of vein quartz. The wide range of total homogenization temperatures (232° to 418°C) is thought to reflect several episodes of CO₂ phase separation during vein formation, as indicated by textural evidence of repeated fracturing and filling of the veins.

The relationship between Th–total values and salinities of fluid inclusions (Fig. 9) may also record a history of CO₂ separation over a temperature range of approximately 250° to 370°C. Within this temperature range, data for aqueous and carbonic inclusions are quite variable, but show recognizable systematic trends: (1) liquid CO₂-bearing inclusions generally have lower salinities than aqueous inclusions; (2) more CO₂-rich, type “b” carbonic inclusions have lower salinities than type “a” carbonic inclusions; (3) above temperature of...
300°C, aqueous inclusions tend to display a trend of increasing salinity with decreasing temperature. All of these trends can be interpreted to indicate CO₂ phase separation, because phase separation of a relatively low-salinity, H₂O–CO₂ fluid produces both a high-salinity H₂O-rich fluid and a low-salinity CO₂-rich fluid, owing to the fractionation of nearly all of the salt into the H₂O-rich liquid phase (Bowers and Helgeson, 1983). If this interpretation is true, secondary aqueous inclusions with low homogenization temperatures (<200°C) and high salinities (>9 wt. % eq. NaCl; Fig. 9) may represent the continued trapping of remnant fluids evolved through CO₂ separation.

Precipitation of most sulfides occurring intergrown with vein quartz may have resulted from this early history of CO₂ separation, which would have resulted in increase in pH of the aqueous fluid and the escape of H₂S to vapor phase. The two processes could effectively result in precipitation of sulfides (e.g., Bowers, 1986). The separated CO₂ could have reacted with adjacent wall rocks, forming carbonates in alteration zones.

**Gold–silver deposition**

As described earlier, electrum and other silver-bearing minerals (argentite, argentian tetrahedrite and pyrargyrite) occur along fractures cutting earlier sulfides and quartz. This indicates that gold and silver mineralization occurred late in the history of vein formation. We consider that gold deposition was related temporally to the fluids trapped as lower temperature, pseudosecondary and/or secondary inclusions in vein quartz. Thus, gold deposition at Youngbogari likely occurred from aqueous fluids with lower Th–total values (<300°C), not from higher temperature carbonic fluids.

It is important to recognize the fact that lower temperature (<300°C) aqueous inclusions tend to show a trend of decreasing salinity with decreasing temperature (Fig. 9). This trend likely records

### Table 1. Sulfur isotope data of sulfide minerals from gold–quartz veins of the Youngbogari deposit

<table>
<thead>
<tr>
<th>Sample No.</th>
<th>Mineral</th>
<th>δ³⁴S (‰)</th>
<th>Δ and Temp.¹</th>
<th>T (°C)²</th>
<th>δ³⁴S_H₂S (‰)³</th>
<th>Remarks</th>
</tr>
</thead>
<tbody>
<tr>
<td>YB-2-1</td>
<td>Sphalerite</td>
<td>-2.6</td>
<td>sp–gn 2.3 (287 ± 45°C)</td>
<td>285</td>
<td>-2.9</td>
<td>middle; sp + gn band</td>
</tr>
<tr>
<td>YB-2-2</td>
<td>Galena</td>
<td>-4.9</td>
<td></td>
<td>285</td>
<td>-2.9</td>
<td>middle; sp + gn band</td>
</tr>
<tr>
<td>YB-2-3</td>
<td>Arsenopyrite</td>
<td>-3.4</td>
<td></td>
<td>380</td>
<td></td>
<td>early; apy + py band</td>
</tr>
<tr>
<td>YB-5</td>
<td>Galena</td>
<td>-6.6</td>
<td></td>
<td>270</td>
<td>-4.5</td>
<td>late; gn-rich band</td>
</tr>
<tr>
<td>YB-5-1</td>
<td>Arsenopyrite</td>
<td>-2.5</td>
<td></td>
<td>370</td>
<td></td>
<td>early; apy + py band</td>
</tr>
<tr>
<td>YB-5-2</td>
<td>Pyrite</td>
<td>-3.6</td>
<td></td>
<td>370</td>
<td>-4.6</td>
<td>early; apy + py band</td>
</tr>
<tr>
<td>YB-6-1</td>
<td>Sphalerite</td>
<td>-4.1</td>
<td>sp–gn 2.3 (287 ± 45°C)</td>
<td>285</td>
<td>-4.4</td>
<td>middle; sp + gn band</td>
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<tr>
<td>YB-6-2</td>
<td>Arsenopyrite</td>
<td>-6.4</td>
<td></td>
<td>285</td>
<td>-4.4</td>
<td>middle; sp + gn band</td>
</tr>
<tr>
<td>YB-15-1</td>
<td>Sphalerite</td>
<td>-4.4</td>
<td>sp–gn 2.0 (328 ± 50°C)</td>
<td>320</td>
<td>-4.7</td>
<td>middle; sp + gn band</td>
</tr>
<tr>
<td>YB-15-2</td>
<td>Galena</td>
<td>-6.4</td>
<td></td>
<td>320</td>
<td>-4.6</td>
<td>middle; sp + gn band</td>
</tr>
<tr>
<td>YB-16</td>
<td>Arsenopyrite</td>
<td>-2.4</td>
<td></td>
<td>370</td>
<td></td>
<td>early; apy + py band</td>
</tr>
<tr>
<td>YB-20-1</td>
<td>Sphalerite</td>
<td>-4.8</td>
<td></td>
<td>360</td>
<td>-5.0</td>
<td>early; apy + sp band</td>
</tr>
<tr>
<td>YB-20-2</td>
<td>Arsenopyrite</td>
<td>-2.7</td>
<td></td>
<td>370</td>
<td></td>
<td>early; apy + py + sp band</td>
</tr>
<tr>
<td>YB-21-1</td>
<td>Sphalerite</td>
<td>-2.8</td>
<td>sp–gn 2.4 (276 ± 42°C)</td>
<td>275</td>
<td>-3.1</td>
<td>late; sp + gn + py band</td>
</tr>
<tr>
<td>YB-21-2</td>
<td>Galena</td>
<td>-5.2</td>
<td></td>
<td>275</td>
<td>-3.1</td>
<td>late; sp + gn + py band</td>
</tr>
<tr>
<td>YB-21-3</td>
<td>Pyrite</td>
<td>-2.8</td>
<td></td>
<td>290</td>
<td>-4.1</td>
<td>late; sp + gn + py band</td>
</tr>
<tr>
<td>YB-25</td>
<td>Chalcopyrite</td>
<td>-4.4</td>
<td></td>
<td>310</td>
<td>-4.3</td>
<td>middle; sp + cp band</td>
</tr>
<tr>
<td>YB-26</td>
<td>Galena</td>
<td>-5.4</td>
<td></td>
<td>280</td>
<td>-3.1</td>
<td>late; gn-rich band</td>
</tr>
<tr>
<td>YB-27-1</td>
<td>Sphalerite</td>
<td>-5.4</td>
<td></td>
<td>310</td>
<td>-5.1</td>
<td>middle; sp + gn band</td>
</tr>
<tr>
<td>YB-27-2</td>
<td>Galena</td>
<td>-5.9</td>
<td></td>
<td>310</td>
<td>-4.0</td>
<td>middle; sp + gn band</td>
</tr>
</tbody>
</table>

Abbreviations: apy = arsenopyrite, cp = chalcopyrite, gn = galena, py = pyrite, sp = sphalerite.

¹Sulfur isotope fractionation between two minerals, and the calculated isotope temperature in parenthesis (Ohmoto and Rye, 1979).

²Based on the average fluid inclusion and/or sulfur isotope temperatures and paragenetic constraints.

³Using the sulfur isotope fractionation equation in Ohmoto and Rye (1979).
the simple cooling and dilution of hydrothermal fluids. The temperatures (<300°C) suggested for gold deposition agree with temperature estimates based on chlorite thermometry (270°C to 320°C) and sulfide mineral assemblages (<290°C). Therefore, we consider that gold deposition at Youngbogari was not directly related to the early history of CO₂ separation (at temperatures of >300°C), but rather was tied to a late history of cooling and dilution of ore fluids. As discussed earlier, decreasing sulfur activity accompanying sulfide precipitation also may have acted to precipitate gold.

### Stable Isotopes

#### Sulfur isotope study

The sulfur isotope compositions of twenty samples of vein sulfides are summarized in Table 1. Within the range of δ³⁴S values (−6.6 to −2.4‰), the δ³⁴S values generally increase in the order of galena < sphalerite < pyrite (~arsenopyrite). This order agrees with the theoretical ³⁴S enrichment order (Ohmoto and Rye, 1979), likely indicating the approach toward isotopic equilibrium between sulfide minerals and hydrothermal fluids.

Four sphalerite–galena pairs with textures indicating possible coprecipitation were obtained from middle sulfide bands and were analyzed to determine equilibrium isotope temperatures (Table 1). The sphalerite–galena pairs yield calculated temperatures of 276 ± 42°C to 328 ± 50°C (Ohmoto and Rye, 1979). These sulfur isotope temperatures are in fair agreement with temperature estimates from homogenization temperatures of fluid inclusions in adjacent quartz. Assuming appropriate depositional temperatures of >350°C, 280°C to 350°C, and <280°C for early, middle, and late sulfides, respectively, based on fluid inclusion data, sulfur isotope temperatures, thermodynamic considerations of chlorite and sulfide mineral assemblages, and paragenetic constraint, the δ³⁴S values of H₂S in hydrothermal fluids were determined (Table 1). Calculated δ³⁴S_H₂S values fall in the range of −5.1 to −2.0‰ (Ohmoto and Rye, 1979).

#### Carbon, oxygen, and hydrogen isotope studies

The carbon, oxygen, and hydrogen isotope data are summarized in Table 2. The δ¹³C values of CO₂ in inclusion fluids extracted from quartz range from −10.4 to −7.4‰, suggesting a well-mixed crustal or igneous carbon source (Field and Fifarek, 1986; Chivas et al., 1987). The δ¹⁸O values of vein quartz have a narrow range from 11.7 to 13.8‰. Based on average total homogenization temperatures of primary fluid inclusions in each sample and/or on sulfur isotope temperatures, δ¹⁸O values of water in equilibrium with quartz were calculated using the fractionation equation of Matsuhisa et al. (1979). The calculated δ¹⁸O_H₂O

<table>
<thead>
<tr>
<th>Sample No.</th>
<th>δ¹³C_CO₂ (‰)</th>
<th>δ¹⁸O_water (‰)</th>
<th>T (°C)¹</th>
<th>δ¹⁸O_water (‰)²</th>
</tr>
</thead>
<tbody>
<tr>
<td>YB-1</td>
<td>12.1</td>
<td>−67</td>
<td>330</td>
<td>6.2</td>
</tr>
<tr>
<td>YB-2</td>
<td>13.6</td>
<td>−71</td>
<td>285</td>
<td>6.2</td>
</tr>
<tr>
<td>YB-5</td>
<td>12.8</td>
<td>−71</td>
<td>370</td>
<td>8.0</td>
</tr>
<tr>
<td>YB-6</td>
<td>13.8</td>
<td>−72</td>
<td>300</td>
<td>6.9</td>
</tr>
<tr>
<td>YB-9</td>
<td>12.6</td>
<td>−75</td>
<td>320</td>
<td>6.4</td>
</tr>
<tr>
<td>YB-10</td>
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<td>−54</td>
<td>330</td>
<td>5.8</td>
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<tr>
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<td>−61</td>
<td>320</td>
<td>6.9</td>
</tr>
<tr>
<td>YB-20</td>
<td>11.8</td>
<td>−67</td>
<td>360</td>
<td>6.8</td>
</tr>
</tbody>
</table>

qₑ = quartz.

¹Based on the average fluid inclusion and/or sulfur isotope temperatures and paragenetic constraints.

²Calculated water-isotope composition based on quartz–water oxygen isotope fractionation equation in Matsuhisa et al. (1979).
values range from 5.8 to 8.0‰ (Table 2). The δD values of inclusion waters range from −54 to −75‰, and with the exception of sample YB-10, the range is −61 to −75‰. The δ18O and δD values (Table 2) significantly overlap the “magmatic water” box of Taylor (1979). These isotope values of the Youngbogari ore fluids could represent magmatic fluids, or fluids from meteoric or metamorphic sources that equilibrated isotopically with nearby Jurassic granodiorite at high temperatures and low water : rock ratios. A similar fluid source was suggested for other mesothermal-type gold deposits in the Youngdong area (So and Yun, 1997; So et al., 1995, 1999).

**COMPARISON OF SULFUR ISOTOPE DATA**

The δ34S values for Youngbogari ores (−6.6 to −2.4‰) are the lowest among those reported from Korean metallic ore deposits (e.g., Shelton et al., 1990; So and Shelton, 1987; So et al., 1987a, 1999; Ishihara et al., 2000). Sulfide minerals from Korean metallic ore deposits predominantly have δ34S values in the range of 3 to 7‰ (>80% of measured samples). This may indicate that igneous sulfur was predominant in hydrothermal systems formed in the Korean Peninsula.

**Typical mesothermal and epithermal ores in the Youngdong area**

Various types of gold–silver deposits occur together in the Youngdong area, therefore providing a unique opportunity to examine sulfur isotope systematics in relation to depth and fluid chemistry. Figure 10 shows frequency diagrams of δ34S values (N = 109) obtained from hydrothermal gold–silver deposits in the Youngdong area. Deposit types represented are: (1) the unusual Youngbogari gold–silver deposit; (2) gold-rich, mesothermal-type deposits (e.g., Samhwanghak, Samdong, Heungdeok, Daewon, and Ilsaeeng deposits), which are more typical of the Youngdong area (So et al., 1995, 1999; So and Yun, 1997); (3) epithermal-type gold–silver deposits (e.g., Wolyu, Keumryeong, Namkwang, and Taesung deposits; Yun et al., 1993; So et al., 1994a, b).

Mesothermal-type gold deposits occur in graphite-bearing, Precambrian gneisses and formed at high-temperatures (up to 480°C) and relatively high pressures (up to 2 kbar), from CO2 (±CH4)-rich fluids that were genetically related to Jurassic “Daebo” granitoids (around 166 Ma; So and Yun, 1997). These deposits are commonly simple in ore mineralogy and contain large amounts of pyrrhotite, suggesting relatively low fO2 conditions of ore fluids. Based on fluid chemistry, So and Yun (1997) suggested that the mesothermal auriferous fluids were evolved under reducing conditions that were defined by both graphite–fluid interactions and the QFM buffer.
By contrast, epithermal-type deposits are hosted in diverse rock types (Precambrian gneiss, Cretaceous volcanic and sedimentary rocks), and commonly show a multi-stage, complex silver-rich ore mineralogy containing various As-Sb-Ge-bearing silver sulfosalts. Epithermal-type gold–silver deposits formed with CO2-poor fluids at shallow depths (<600 m from lower temperature (generally 200° to 300°C)). The ore fluids were evolved meteoric waters whose circulation resulted from intrusion of late Cretaceous granitic rocks such as quartz porphyry (around 80 Ma; Yun et al., 1993; So et al., 1994a). Both the predominance of pyrite (without pyrrhotite) and the occurrence of hematite indicate more oxidizing conditions for epithermal fluids than for mesothermal fluids.

Careful examination of the data in Fig. 10 shows that the δ34S values of sulfide minerals from each deposit generally follow the theoretical order of 34S enrichment (galena < chalcopyrite < sphalerite < pyrrhotite < pyrite; Ohmoto and Rye, 1979), suggesting general attainment of isotopic equilibrium between sulfide minerals and hydrothermal fluids. Compared to the δ34S values from epithermal-type gold–silver deposits (~0 to 8‰, but mostly between 4 and 7‰) in the Youngdong area, those of mesothermal-type gold deposits are clearly lower and fall mostly in the range of –4 to 2‰ (Fig. 10). Except for one pyrite sample from an alteration zone (~5‰), sulfide minerals from the Samdong deposit tend to have δ34S values below 0‰. It is noteworthy that the mesothermal Samdong ores contain only small amounts of pyrrhotite, whereas ores from the mesothermal Samhwanghak, Heungdeok, Daewon, and Ilsaeang deposits are characteristically pyrrhotite-rich.

The pyrrhotite-rich nature of the ores from the Samhwanghak, Heungdeok, Daewon, and Ilsaeang deposits indicates the predominance of reduced species (H2S and HS−) among the dissolved sulfur species in their hydrothermal fluids (Ohmoto and Rye, 1979). Therefore, the δ34S values (0 ± 2‰; So and Yun, 1997; So et al., 1999) calculated for those deposits may be taken as an approximation of the sulfur isotopic composition of the entire hydrothermal fluids (δ34S). This δ34S value (0 ± 2‰) obtained from pyrrhotite-rich, mesothermal-type deposits is considered to reflect the derivation of sulfur from Jurassic granitic rocks. It should be noted that the δ34S values obtained from Jurassic mesothermal-type deposits are lower (by about 4‰) than those obtained from late Cretaceous epithermal-type deposits (around 4‰; Yun et al., 1993; So et al., 1994a,b).

Our sulfur isotope data from the Youngdong area’s hydrothermal deposits (Fig. 10) indicate isotopically distinct sulfur reservoirs for the hydrothermal systems that formed Jurassic mesothermal and late Cretaceous epithermal deposits. We speculate that the Jurassic granitic hydrothermal system incorporated 32S-enriched sulfur (possibly, sedimentary sulfur in basement rocks) during magma generation (Sasaki and Ishihara, 1979; Ishihara et al., 1996). Jurassic granitoids in South Korea generally belong to the ilmenite-series, whereas Cretaceous granitoids belong mostly to the magnetite-series. Similarly, ilmenite-series granitoids and associated ore sulfides in Japan typically have more negative δ34S values (average ~5‰), than magnetite-series granitoids and their related sulfide ores (Sasaki and Ishihara, 1979).

**Low δ34S values in the Youngbogari ores**

The δ34S values for the Youngbogari ores are remarkably negative (Fig. 10). Although we could not obtain a reliable age for the Youngbogari deposit because of the absence of appropriate minerals for absolute age dating, the geologic setting and oxygen–hydrogen isotope data suggest a mesothermal origin for the Youngbogari deposit, likely associated with nearby Jurassic granitic rocks. If that is true, the difference in δ34S values between the Youngbogari deposit and other mesothermal deposits of the area (Samhwanghak, Heungdeok, Daewon, and Ilsaeang) can be caused by either of the following mechanisms: (1) the presence of at least two distinct reservoirs (both igneous, with δ34S values of ~5‰ and 0 ± 2‰) for Jurassic mesothermal-type, gold–silver deposits in the Youngdong area; (2) different degrees of the mixing (assimilation) of 32S-enriched sulfur...
(possibly sulfur in Precambrian pelitic basement rocks) during the generation and/or subsequent ascent of magma (cf., Sasaki and Ishihara, 1979); and/or (3) different degrees of the oxidation of an H$_2$S-rich, magmatically derived sulfur source ($\delta^{34}$S = 0 ± 2‰) during ascent to mineralization sites (cf., Ishihara et al., 1996). We consider that the first and second mechanisms cannot be successfully applied to the Youngdong area, because the geologic setting (especially the host rock petrology) is the same for all of the mesothermal-type deposits in the Youngdong area. Therefore, we prefer the third mechanism.

If we pay attention to the observed differences in ore mineralogy (especially, iron-bearing ore minerals) in the mesothermal-type deposits, as described earlier, ores from the Samhwanghak, Heungdeok, Daewon, and Ilsang deposits are predominantly pyrrhotite-rich with rare amounts of pyrite, whereas ores from the Samdong and Youngbogari deposits are characteristically pyrrhotite-poor. Though the Samdong and Youngbogari ores are both rich in pyrite, the Youngbogari ores also contain large amounts of arsenopyrite and base-metal sulfides. Such mineralogical differences among the mesothermal-type deposits reflect differences in oxygen fugacity of hydrothermal fluids: the pyrrhotite-rich deposits formed from relatively lower $f_{O_2}$ fluids which were evolved near the QFM buffer condition (So and Yun, 1997) than pyrite-rich deposits, and the Youngbogari deposit formed from comparably higher $f_{O_2}$ fluids. The different $f_{O_2}$ conditions were possibly the results of varying degrees of reduction of the ascending magmatic fluids by the reaction with graphite in wallrock gneiss (So and Yun, 1997). According to So and Yun (1997), fluid inclusions in quartz from pyrrhotite-rich, mesothermal-type deposits in the Youngdong area contain variable, but high concentrations of CH$_4$ (6 to 48 mole %, average ~15 mole %). By contrast, fluid inclusions from the pyrite-rich Samdong deposit are lower in CH$_4$ content (up to 20 mole %, but mostly <10 mole %; So et al., 1995). Similarly, microthermometric data for fluid inclusions from the Youngbogari deposit also indicate low concentrations of CH$_4$ in fluid. The difference in CH$_4$ concentrations in inclusion fluids may be taken as an estimation of the extent of both graphite–fluid interaction and resultant reduction of hydrothermal fluids during mineralization. Nevertheless, we conclude that pyrrhotite-rich deposits formed from higher temperature (up to 480°C) and more reducing fluids than did pyrite-rich deposits.

We speculate that the Youngbogari deposit possibly formed from the most oxidized fluids. Higher oxygen fugacity of ascending hydrothermal fluids would have formed sulfate from reduced sulfur species (H$_2$S and HS$^-$). Sulfate preferentially incorporates $^{34}$S, resulting in lower $\delta^{34}$S values of H$_2$S (Ohmoto, 1986) and the observed lower values of precipitated sulfides in the Youngbogari deposit.

**SUMMARY**

A variety of types of geochemical data indicate that deposition of mesothermal, gold–silver ores of the Youngbogari deposit resulted mainly from cooling of ore fluids accompanying decreasing sulfur fugacity. Fluid inclusion evidence indicates that gold deposition was not related to an early history of CO$_2$ separation (at temperatures of >300°C), but rather was tied to a later history of cooling and dilution of H$_2$O–NaCl ore fluids at temperatures of <300°C. These temperature estimates for gold deposition agree with those based on chlorite thermometry (270° to 320°C) and sulfide mineral assemblages (<290°C). The unusual arsenopyrite–pyrite-rich nature of the Youngbogari ores and their anomalously negative $\delta^{34}$S values, compared to other mesothermal gold deposits of the Youngdong area, are interpreted to reflect more oxidizing nature of the Youngbogari ore fluids, likely due to less reaction with graphite in wallrock gneiss.

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