



Abstract

Stable isotope systematics of Ulsan Fe–W skarn deposit, Korea

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Abstract

From the measurements of oxygen and carbon isotope ratios ($\delta^{13}\text{C} = 1.2\text{--}4.6\text{‰}$ relative to V-PDB, and $\delta^{18}\text{O} = 13.5\text{--}22.1\text{‰}$ relative to V-SMOW) of fresh or partly altered limestones at the Ulsan skarn deposit, it is suggested that the origin of carbonate rocks is marine carbonate rather than carbonatite. Moreover, the calculated isotopic compositions ($\delta^{13}\text{C} = -7.67\text{‰}$ and $\delta^{18}\text{O} = 6.75\text{‰}$) of the hydrothermal fluid in the main Fe stage of skarn formation imply that this fluid was magmatic water derived from differentiated granitic melts. At this prograde stage, carbon and oxygen isotope data of skarn calcites show that X_{CO_2} was low (<0.1), and temperature was relatively constant (350–450 °C). Later, during the retrograde skarn and vein stages, the hydrous silicates, scheelite and polymetallic sulfides were formed from the less saline, lower-temperature ore-forming fluids. This low-temperature environment (from 340 °C down to 135 °C) related to Zn–Pb–Ag mineralization was inferred not only from the oxygen isotope ratios of siderite, but also from the fluid inclusion data of later quartz-siderite veins. This temperature drop reflects an important change in the hydrology of the hydrothermal system at this vein stage (i.e., mixing with meteoric water).

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1. Introduction

Many studies have demonstrated that stable isotopes can be used not only a powerful petrogenetic tracer, but also a paleothermometer (e.g., Taylor, 1987; Spangenberg et al., 1996; Bowman, 1998). For these reasons, stable isotope geochemistry is an essential tool for economic geologists to understand the evolution of ore-forming fluids as well as the genesis of ore deposits. Although many researchers, including the primary author, have extensively inves-

tigated the Ulsan Fe–W ore deposit (Choi and Youm, 2000), only a few stable isotope data for this skarn deposit are available so far. Therefore, stable isotope measurements of systematically sampled limestones, skarn and vein carbonates, and quartz were performed in order to (1) identify the origin of host rock carbonate, and to (2) investigate the evolutionary histories of the Ulsan skarn deposit and the natures of its ore-forming fluids.

1.1. Geology and ore deposit

The Ulsan Fe–W skarn deposit is located in the Cretaceous volcano-sedimentary terrain at the south-eastern part of Korean Peninsula. Although their ages

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are unknown, carbonate rock and serpentized ultramafic rocks are exposed as a small roof pendant, which is surrounded by the Upper Cretaceous sedimentary rocks and the intruding epizonal, subvolcanic early Tertiary granite rocks. This pendant is considered to represent the basement of the Upper Cretaceous sedimentary rocks.

The Ulsan iron–tungsten and polymetallic deposit is comprised of two distinct, but genetically related deposits. The Fe–W calcic skarn orebody is characterized as a vertical ore pipe within limestone, and this ore body consists mainly of magnetite and lesser amount of scheelite with minor base-metal sulfides, arsenides and sulfarsenides. The sequential metasomatic processes of skarn development display a progression from a center of massive fine-grained clinopyroxene skarn with magnetite and disseminated scheelite ores through minor clinopyroxene–garnet skarn or local garnet skarn to the calcite mega-crystal zone. In particular, the calcite mega-crystal zone at the outermost margin of the massive skarn or the magnetite ore body occurs along the reaction fronts by replacing the surrounding limestones. After fracturing events, a complex sulfide deposit with polymetallic characteristics was superimposed on the previous Fe–W mineralization.

Skarn and complex mineralization in the Ulsan deposit was a multistage phenomenon, producing a wide variety of minerals. After the isochemical contact metamorphism caused by the intrusion of granitic rock, the early skarn stage I, belonging to skarnoid, is characterized as anhydrous Ca–Al–Mg skarn minerals at the granite–limestone contact and the absence of ore minerals. During the main prograde skarn stage (stage II), prominent magnetite with Ca–Fe–Al–Mg skarn minerals were developed, and Ni–Fe sulfarsenides and arsenides with calcite were successively deposited later. During the late skarn stage (stage III), ore mineralization is characterized as prominent scheelite with hydrous calc-silicates. In the later period of this skarn III stage, complex Cu–Zn mineralization with polymetallic characteristic was intensively preceded, and the majority of those minerals were superimposed upon the previous W mineralization. During stage IV, Zn–Pb sulfides and Ag-bearing sulfosalts with siderite–quartz vein were developed. Stage IV represents the latest phase of hydrothermal system forming fissure veins that developed after

fracturing events, and this stage IV is separated perfectly from stage III.

1.2. Analytical procedures

Carbon, oxygen and hydrogen isotope compositions of minerals and inclusion fluids were determined. Limestones, skarn calcites and vein carbonates were systematically collected from all part of the Ulsan deposit. Thereafter, crushed carbonates were reacted with phosphoric acid at 25 °C using the classical procedure of [McCrea \(1950\)](#). Carbon and oxygen isotopic measurements were made on CO₂ gas using a Finnigan MAT 252 at CMR (Center for Mineral Resources and Research), Korea University. The acid fractionation factor, 1.01025, was applied for calcite samples, and 1.01175, obtained from [Carothers et al.'s \(1988\)](#) study, was used for siderite. The reproducibility of our isotopic analysis was 0.05‰ for carbon and 0.1‰ for oxygen. Hydrogen isotope compositions of the fluid inclusions from skarn calcite and quartz were measured at the Republic of China. Inclusion fluids were extracted by heating pure mineral separates under vacuum in a platinum crucible. A detailed description of the sampling procedure is given by [Roedder \(1984\)](#).

2. Results and discussions

Hydrothermal alternation of host rock (water/rock interaction), two fluids-mixing, and CO₂ degassing are generally considered as possible mechanisms of a skarn calcite precipitation, and the $\delta^{13}\text{C}$ and $\delta^{18}\text{O}$ covariations of each case were theoretically modeled by [Zheng \(1990\)](#) and [Zheng and Hoefs \(1993\)](#). In this paper, carbon and oxygen isotope ratios of the carbonates from all stages were examined to be applied to one of the theoretical models so that we can identify the evolution of the hydrothermal fluid as well as several important genetic parameters such as CO₂ fugacity, formation temperatures, and water/rock ratios of the Ulsan deposit.

2.1. Origin of Ulsan limestone

Over 15 analyzed limestones were divided into three distinct groups depending on the relative degree

of hydrothermal alteration, i.e. color, grain size and associated mineral. The fresh limestone is light gray in color and relatively fine-grained. Bleached limestone is white in color and was recrystallized; whereas, calc-silicate-bearing limestone is characterized by the minor amount of skarn minerals along with the characters of bleached limestones. Each group has shown a distinct isotopic signature over the $\delta^{18}\text{O}$ – $\delta^{13}\text{C}$ diagram (Fig. 1A). The fresh limestones ($\delta^{13}\text{C} = 4.1$ – 4.6 ‰, $\delta^{18}\text{O} = 22.0$ – 22.1 ‰) have shown more enriched carbon and oxygen isotopic composi-

tions relative to the bleached limestones ($\delta^{13}\text{C} = 3.4$ – 4.4 ‰, $\delta^{18}\text{O} = 16.8$ – 18.4 ‰). Likewise, bleached limestones have relatively high $\delta^{13}\text{C}$ and $\delta^{18}\text{O}$ values than the calc-silicate-bearing limestones ($\delta^{13}\text{C} = 1.2$ – 3.4 ‰, $\delta^{18}\text{O} = 13.5$ – 15.8 ‰). Therefore, this decreasing trend of carbon and oxygen isotope ratios from less to more altered limestone implies that original isotopic signatures were modified into the lower carbon and oxygen isotope ratios as limestones were repeatedly reacted with isotopically depleted hydrothermal fluids.

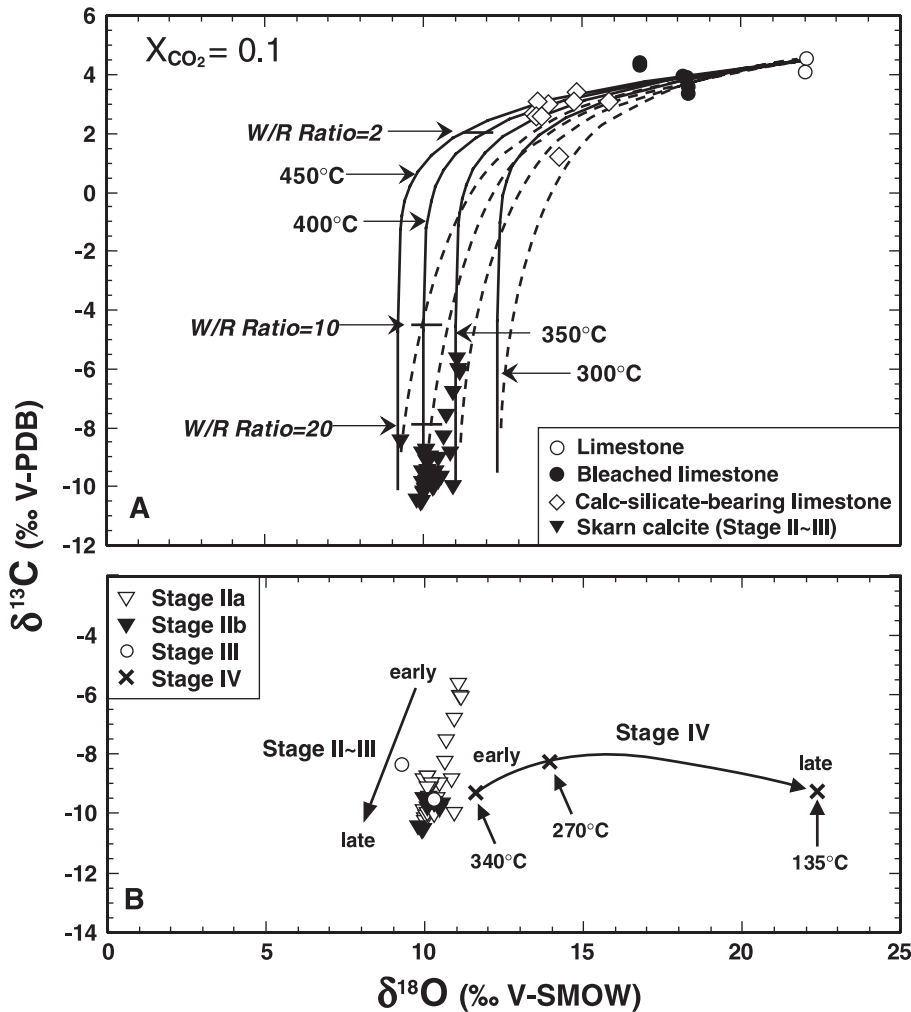


Fig. 1. A $\delta^{13}\text{C}$ – $\delta^{18}\text{O}$ diagram for the Ulsan carbonates. (A) Theoretical variations of carbon and oxygen isotope ratios for skarn calcites in an open (solid line) and closed (dashed line) system at various fluid/rock ratios ($X_{\text{CO}_2} = 0.1$) are shown. (B) Temperature drop from stage III to stage IV is obvious. Formation temperatures of siderite from stage IV are also calculated.

Because “fresh” limestones are likely to preserve the isotopic signatures of their origin, the measured carbon isotope composition ($\delta^{13}\text{C}=4.1\text{--}4.6\text{‰}$) of “fresh” limestones suggests that the host rock of the Ulsan deposit is marine carbonate rather than igneous carbonatite, which generally has a negative carbon isotopic signature (Hoef, 1997).

2.2. Origin of hydrothermal fluid

The isotopic compositions of the hydrothermal fluid, from which skarn and vein calcite were precipitated, can be calculated if (1) a fractionation factor at a given temperature, (2) isotopic compositions of calcite, (3) the homogenization temperature of calcite precipitated from the fluid are known. Oxygen isotope fractionation factors between calcite and water at high temperatures were adopted from O’Neil et al. (1969). For carbon, isotope fractionation factors between CO_2 and calcite were taken from Bottinga (1968), and it is assumed that there is no isotopic fractionation between CO_2 (g) and H_2CO_3 . $\delta^{13}\text{C}=-10\text{‰}$ and $\delta^{18}\text{O}=10\text{‰}$ were selected as representative isotope compositions of skarn calcites (stage II) of the Ulsan deposit (Fig. 1), and the homogenization temperature of skarn calcites at this stage, 400 °C , was taken from fluid inclusion data by Choi and Youm (2000). Consequently, with all the information given, $\delta^{13}\text{C}$ (-7.67‰ relative to V-PDB) and $\delta^{18}\text{O}$ values (6.75‰ relative to V-SMOW) were calculated for the stable isotope compositions of the skarn-forming fluid.

In general, three types of hydrothermal fluids (i.e., magmatic, meteoric and seawater) are recognized with respect to the genesis of hydrothermal mineralization, and each fluid is known to have a distinctive stable isotope signature. According to Zheng and Hoefs (1993), magmatic water has $\delta^{18}\text{O}$ values in the range of $6\text{--}15\text{‰}$, and its $\delta^{13}\text{C}$ values is similar to that of normal mantle (from -9‰ to -4‰). Considering that (1) the calculated isotopic compositions ($\delta^{18}\text{O}=6.75\text{‰}$, $\delta^{13}\text{C}=-7.67\text{‰}$) of the skarn-forming fluid fall exactly within the field of magmatic water, and (2) high temperature ($350\text{--}450\text{ °C}$) and high salinity (>30 equiv. wt.% NaCl) are also observed from the fluid inclusions at the main skarn stage (Choi and Youm, 2000), it is evident that the hydrothermal fluid involved at the main prograde skarn stage

(stage II) was a magmatic or deep-seated crustal fluid.

Oxygen isotope ratios of the skarn-forming fluid were calculated based upon the known calcite–water fractionation factors at a given temperature and the measured $\delta^{18}\text{O}$ values and the fluid inclusion data of skarn calcites. For hydrogen isotope compositions, isotopic ratios of fluid inclusions were directly measured. These stable isotope data ($\delta^{18}\text{O}_{\text{H}_2\text{O}}=6.9\text{‰}$ to 8.1‰ , $\delta\text{D}_{\text{H}_2\text{O}}=-42$ to -78‰) in Fig. 2 indicate that magmatic water was involved in the Fe–W mineralization and mixed magmatic–meteoric water was responsible for the subsequent Zn–Pb mineralization (inclusions of quartz from stage IV: $\delta^{18}\text{O}_{\text{H}_2\text{O}}=3.1\text{‰}$, $\delta\text{D}_{\text{H}_2\text{O}}=-68\text{‰}$).

2.3. Mechanism of calcite precipitation

In case of hydrothermal calcites at stages II and III, stable isotope analyses revealed that a secondary alteration with a progressive increasing water/rock ratio in an open system is the best explanation for the genesis of Ulsan skarn calcites. Theoretical models for open and close systems suggested by Zheng

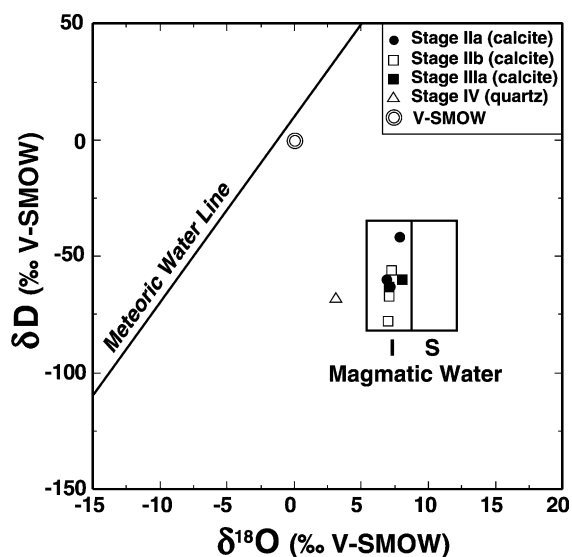


Fig. 2. A $\delta\text{D}-\delta^{18}\text{O}$ diagram showing the isotopic compositions of fluid inclusions from stages II to IV at the Ulsan mine. Meteoric water line and magmatic water (both I-type(I) and S-type(S)) box are presented.

and Hoefs (1993) are employed in order to examine the stable isotope data (Fig. 1A).

As can be observed in Fig. 1A, during the prograde and retrograde skarn stages, the skarn calcites ($\delta^{13}\text{C} = -10.5\text{‰}$ to -5.6‰ , $\delta^{18}\text{O} = 9.3\text{‰}$ to 11.1‰) became much depleted in ^{13}C and ^{18}O with respect to the host limestone because calcites were repeatedly reacted with the isotopically light magmatic water. As the magmatic water was infiltrated through the structurally weakened fractures and reacted with the host-limestone, crystal calcites began to be crystallized. The earliest calcite of stage IIa, precipitated within the Fe-ore pipe, occurs mainly as the fillings of interstice among magnetite, clinopyroxene, or anisotropic garnet grains, and as the infillings of vein skarns. Stage IIb calcite usually occurs in the reaction front (calcite mega-crystal zone), which is disseminated with arsenopyrite. The calcite mega-crystal zone refers to the outmost area of the ore pipe where the large crystal calcites were found. This outmost calcite zone is believed to have been generated as skarn front zone as CO_2 gas could be degassed from the hydrothermal solution. Stage IIIa calcite is associated with hydrous calc-silicate mineral and characterized by the overprinting of the former calcites.

In Fig. 1B, three types of skarn calcites, based on their stage of occurrence, are presented on a $\delta^{18}\text{O}$ – $\delta^{13}\text{C}$ diagram. Stage IIa calcites show a wide range of carbon isotopic compositions ($\delta^{13}\text{C} = -6.0\text{‰}$ to -9.5‰) compared to stages IIb and III calcites. As the amount of magmatic water increased and skarn evolved further, crystal calcites formed earlier (stage IIa) might be recrystallized or replaced by new (stages IIb and III) crystal calcites; therefore, the isotopic compositions of the previous (stage IIa) crystal calcites might be erased or homogenized. This recrystallization and replacement events also explain why there are no data available for water/rock ratio between 2 and 10 in Fig. 1A. Skarn calcites having been repeatedly dissolved and recrystallized with the reaction of isotopically light magmatic water, their initial isotopic signatures might have been removed; therefore, only finally homogenized isotopic signatures could be remained. The magmatic water would have assimilated later calcites at the fluid-dominant (water/rock ratio > 20) environments during stage III.

Contrasting the abrupt change of the carbon isotope compositions as water/rock ratio increases, the oxygen

isotope compositions of the skarn calcites did not change much because most of the skarn calcites were believed to be formed in a relatively narrow range of temperature. Fig. 1A shows that most skarn calcites have $\delta^{18}\text{O}$ values around 10‰ implying that (1) there were only small temperature variations (350 – 450 °C) when the skarn calcites were precipitated (stages II and III) and (2) oxygen isotope signatures were also somehow homogenized as the skarn calcites were repeatedly recrystallized. This temperature range also well supported by the homogenization temperatures of the primary calcite (338 – 464 °C).

The CO_2 mole fraction (X_{CO_2}) was also estimated from the carbon and oxygen isotopic covariations as shown in Fig. 1A. As a result, the graph generated by using X_{CO_2} value of 0.1 was selected as the best fit of the Ulsan limestone and the skarn calcites, and this low CO_2 mole fraction is well consistent with the fluid inclusion study (Choi and Youm, 2000) showing no CO_2 phase in the fluid inclusions.

2.4. Genesis of siderite

Siderite (FeCO_3) at the Ulsan deposit occurred at a relatively later vein stage (stage IV). Therefore, the formation temperature of siderite might have been lower than that of crystal calcite (stages II and III) as the main skarn stage ended and meteoric water was introduced into the ore pipe through the fractures from the surface. According to the fluid inclusion study (Choi and Youm, 2000), not only the homogenization temperature was decreased from 350 to 230 °C , but salinity was also drastically lowered in stage IV. This decrease in salinity was explained as the effect of introducing a secondary fluid, possibly meteoric water, to the vertical ore pipe through the fractures from the surface. Therefore, this new event might have triggered the precipitation of siderite.

As can be seen in Fig. 1B, siderite samples show relatively high oxygen isotopic compositions (11.6 – 22.3‰) compared to the stages II and III skarn calcites, but the same range (-9.3‰ to -8.3‰) with respect to carbon isotopes. If this range of oxygen isotope ratio is used to estimate the formation temperatures of siderite, siderites were crystallized approximately from 340 to 135 °C . This highest calculated precipitation temperature (340 °C) of siderite is also well consistent with the homogenized

temperatures (234–352 °C) of quartz from the early stage IV from Choi and Youm (2000).

3. Conclusions

Stable isotope systematics of the Ulsan Fe–W skarn deposit were examined from the measurements of stable isotope ratios of carefully selected host limestones, skarn calcites, and fluid inclusions. Based upon the carbon isotope compositions of fresh unaltered host limestones, it is suggested that the Ulsan host rock limestone has a marine origin. In addition, magmatic origin of the fluids and the evolutionary history (i.e., low CO₂ fugacity and relatively constant temperature range) of the Ulsan mine at the main Fe skarn stage were also unveiled from the carbon and oxygen isotope covariations of skarn calcites from stage II. Directly measured hydrogen isotope compositions of fluid inclusions from stages II to III also support the magmatic origin of the hydrothermal fluid involved in stage II. At the later vein stage, meteoric water was introduced from the surface of the ore pipe through the structurally weak fractures, and the hydrous silicates and Zn–Pb sulfides were precipitated. Oxygen isotope compositions of siderite from this stage support this temperature changes (from 340 °C down to 135 °C) at this stage IV.

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