

## Genetic Implications for Low Sulfidation Porphyry System at Ulsan Deposit, Southeastern Korea

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The Ulsan mine is located in Cretaceous volcano-sedimentary terrain at the south-eastern border of the Korean peninsula. The iron-tungsten and polymetallic mineralizations at Ulsan occur as calcic skarn and hydrothermal vein deposits near Tertiary granite stock indicating their epizonal, subvolcanic emplacement. The skarn formations display a progression from massive skarn replacement of marble to more diffuse, disseminated or veinlike replacement of earlier skarn assemblages. The Fe-W ore pipe being nearly vertical has been emplaced within marble in direct contact with the Upper Cretaceous volcanics containing thin layers of argillaceous rocks.

Development of various skarn formations and different mineralizations was a complex, multistage phenomenon, showing a silicate-oxide-sulfide sequence typical of metasomatic replacement and subsequent hydrothermal alteration. After the isochemical contact metamorphism, an early skarn stage I belonging to skarnoid is characterized by anhydrous Ca-Al-Mg skarn minerals at the granite-marble contact and barren of ore minerals. The temperature condition for the formation of early skarn minerals (diopside-wollastonite-grossular-calcite) formed near 530 to 560 °C. A main skarn stage II is characterized by the earlier development of prominent magnetite with Ca-Fe-Al-Mg skarn minerals and later deposition of Ni-Fe sulfarsenides and arsenides with calcite. Anhydrous calc-silicates representing prograde metasomatic episode evolve a trend toward the enrichment of noticeable iron and slight manganese, and magnesium depletion. The later iron-rich calc-silicates (hedenbergite+andradite) associated with magnetite during the main skarn stage (stage IIa) were formed under a temperature condition of 420 ° to 490 °C with water-rich fluids ( $X_{\text{CO}_2} < 0.2$ ) at 0.5 kbar. However, the deposition of magnetite can be interpreted to have formed from hypersaline fluids at somewhat higher temperatures above 450 °C during earlier period of stage II. On the basis of the distribution pattern of skarn formations, the magmatic water component of stage II fluids is inferred to have moved vertically through the marble before mixing with meteoric water. After the magnetite deposition of stage IIa, arsenopyrite is intergrown with loellingite+native bismuth+hexagonal pyrrhotite+bismuthinite+niccolite+rammelsbergite+gersdorffite. Fluid inclusion data suggest

that skarn calcite and iron-rich calc-silicates such as clinopyroxene and garnet formed from hotter, more saline, CO<sub>2</sub>-free fluids (Th = 370° to 550°C, 32.1 to 45.1 wt % NaCl), whereas later quartz associated with Ni-Fe sulfarsenides formed from cooler, relatively more dilute fluids (Th = 254° to 340°C, 30.1 to 35.2 wt % NaCl). The sulfur fugacity during this stage was constrained by the stability of arsenopyrite+loellingite+native bismuth, and the oxygen fugacity was close to pyrrhotite-magnetite equilibrium.

A late skarn stage III corresponding to retrograde event is characterized by minor scheelite impregnation with hydrous silicates (amphibole, biotite, epidote and chlorite). In the later period of late skarn stage, complex Cu-Zn mineralization with polymetallic characteristics has proceeded, the majority of which has been superimposed upon the previous W mineralization. Primary fluid inclusions in scheelite and quartz imply a temperature range of 156° to 425°C and salinities 1.8 to 24.4 wt % NaCl. The apparent decrease in both temperature and salinity over stage III is interpreted to be the result of mixing of originally more saline magmatic fluids with meteoric water. Stage IV represents the latest episode of hydrothermal system that forms fissure veins and has proceeded after fracturing events separated perfectly from stage III. Stage IV is characterized by Zn-Pb-Ag mineralization with siderite and quartz. Primary fluid inclusions in quartz imply a temperature range of 237° to 272°C and salinities 2.6 to 8.6 wt % NaCl. Arsenopyrite compositions of different mineral assemblages lie well inside the stability field of arsenopyrite for the temperature of its formation. Decreasing As contents of arsenopyrite indicates a gradational decrease in sulfur fugacity and temperature over all the sulfide stages. The deposition of Zn-Pb-Ag in the hydrothermal system at Ulsan was the result of rapid cooling of the ore-bearing fluids by convecting meteoric waters.

Fluid inclusion data, arsenopyrite geothermometry and stable isotope studies support a model of skarn petrogenesis for Ulsan which invokes an early high-temperature, anhydrous skarn stage formed dominantly from water-dominant, CO<sub>2</sub>-free and hypersaline fluids, followed by a later, distinctly lower temperature hydrous stage. The evolutionary trend from prograde skarn stage with Fe mineralization through retrograde skarn stage with W-Cu-Zn mineralization to vein stage with Zn-Pb-Ag mineralization suggests an influx of meteoric water to deeper levels along fractures into the waning porphyry-style hydrothermal system. These results provide the possibility of skarn deposits genetically related to low sulfidation porphyry systems.