

Stable Isotope and Fluid Inclusion Studies of Iron-Tungsten Mineralization at Ulsan Skarn Deposit, Southeastern Korea.

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Four general stages of paragenetic development at Ulsan are an early skarn stage characterized by barren and anhydrous Ca-Al-Mg skarn minerals at the granite-marble contact; a main skarn stage II characterized by the development of magnetite, Ni-Fe arsenides and sulpharsenides, and Ca-Fe-Al-Mg skarn minerals with calcite ; a late skarn stage III characterized by scheelite, Cu-Zn sulfides, sulfosalts and tellurides with hydrous silicates; a stage IV characterized by Zn-Pb-Ag sulfides and sulfosalts with siderite and quartz vein. Stage IV represents the latest phase of hydrothermal system that forms fissure veins and has proceeded after fracturing events separated perfectly from stage III.

The ore and gangue minerals developed during the skarn or vein stages are closely related to the infiltration of two quite different types of fluids. During the main skarn stage, the skarn-forming fluids are characterized by high salinity (45.1-30.1 equiv. wt % NaCl) and high temperature (up to 559°C), which could be originated by direct exsolution of an immiscible high-saline brine from a crystallizing granitic magma. The presence of type I inclusion in garnet indicates a mixing with meteoric water locally during later period of stage IIa. Evidence for boiling during this stage has not been observed. These high-salinity and high-temperature fluid, , underwent simple cooling (relatively constant salinity with decreasing temperature) causing anhydrous calcic skarns and Fe and Ni-Fe mineralizations. During late skarn stage(stage III), skarn-forming fluids for retrograde skarn alteration and tungsten mineralizations were comprised of moderate salinity liquids (22.9-2.7 equiv. wt % NaCl) trapped at temperatures ranging from 425° to 156°C. Fluid inclusions of quartz in vein stage (stage IV) have low homogenization temperature (<272°C) and low salinity (<8.6 equiv. wt % NaCl). The linear relationships between temperatures and salinities for the retrograde skarn-forming and vein-forming fluids indicate fluid-mixing.

Fluid inclusion studies suggest that the metasomatic alteration and vein systems evolved from an early magmatic-dominated stage to a late meteoric- dominated stage.

Following the Fe mineralization from a magmatic hydrothermal system during stage II, the progressive cooling and dilution of the mineralizing system due to mixing with influx of groundwater results in deposition of scheelite and Cu-Zn sulfides during stage III, and Zn-Pb-sulphides during stage IV. This is interpreted to reflect the intensity of interaction between magmatic hydrothermal solutions from melts emplaced at high crustal levels and circulating meteoric waters through fractures. The relation between homogenization temperatures and salinities suggests a complex fluid evolution of local immiscibility, mixing and CO₂ effervescence.

Carbon and oxygen isotope analyses of the host rock marbles and skarn calcites at Ulsan were carried out for the better understanding of Fe-W mineralizations. Based upon our carbon and oxygen isotope data, 1) Ulsan marbles ($\delta^{13}\text{C} = +1.2$ to 4.6% relative to PDB and $\delta^{18}\text{O} = +13.5$ to 22.1% relative to SMOW) are considered as marine originated carbonates rather than carbonatite because of their positive carbon isotope values. 2) A secondary alteration with a progressively increasing water/rock ratio in an open system was taken as the best explanation of the isotopic covariations of Ulsan carbonates. 3) With the homogenization temperature ($=400^\circ\text{C}$) of calcite during stage II, the isotopic composition of the hydrothermal fluid, which induced the Fe mineralization and the formation of anhydrous calcic skarn, is calculated ($\delta^{18}\text{O} = 6.75\%$, $\delta^{13}\text{C} = -7.67\%$), and this value implies the fluid is a magmatic or deep-seated crustal fluid. 4) The X_{CO_2} value of the skarn-forming fluid is estimated by using the isotopic signatures of both calcites and marbles. This estimated value ($X_{\text{CO}_2} = 0.1$) is also well supported by the absence of a CO₂-rich phase in the fluid inclusions. Southern and northern sides of Fe orebody seem to have the same X_{CO_2} value that implies both sides of the mine had undergone the same geological events during the skarn formations.