A Petrochemical Study of Granite and Fe-W Mineralization in the Ulsan Skarn Deposit

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1. Abstract

The Ulsan Fe-W deposit is located within the Cretaceous Gyeongsang volcano-sedimentary basin at the southeastern edge of the Korean peninsula. Distinct hydrothermal events resulted in calcic skarn and vein deposits in recrystallized limestone near a Tertiary epizonal granite stock. The Ulsan deposit presents a unique opportunity to document geochemically the complex evolution of a skarn-vein system that is related genetically to a low sulfidation system. The various skarn-forming events and ore minerals developed as a result of silicate-oxide-sulfide metasomatism. It is interpreted to have resulted from an evolutionary trend from hypersaline magmatic fluids during prograde skarn formation associated with Fe-As(-Ni) mineralization to low-salinity and low-temperature fluids during retrograde skarn formation associated with W-Cu-Zn mineralization. As the influence of magmatic-derived fluids waned, surficial fluids descended to deeper levels along fractures, resulting in siderite-quartz deposition associated with Zn-Pb-Ag mineralization.

2. Geological setting and Ore deposit

At the Ulsan mine, recrystallized limestone and partly serpentinized ultramafic rocks (dunite and harzburgite) are exposed as a small roof pendant within the Upper Cretaceous sequence and intruding granitic rocks. Although the ages of both the ultramafic rock and recrystallized limestone are unknown, they are considered to represent the basement of the Cretaceous volcano-sedimentary piles. Early Tertiary granite, which display the characteristics of epizonal, subvolcanic emplacement, intruded the center of a dome structure located in the western part of the mine area. It consists of the Gadae-Ri granite and albitite of the latest product, hornblende-biotite granite whose biotite yields a K-Ar age of 58 and 62.9±1.9 Ma. In spite of the spatial separation (<100 m) between the mineralized zones and the Gadae-Ri granite stock, the ore deposit is related genetically to this pluton. Although albitite locally formed calcic-sodic skarn, the calcic Fe-W skarn deposit at Ulsan occurs as a nearly vertical ore pipe within recrystallized limestone at direct contact with the Upper Cretaceous volcanics containing thin layers of pelitic sediments. Its ore mineralogy consists mainly of magnetite and lesser amounts of scheelite with minor sulfides, arsenides, sulfosalts and sulfarsenides.

주요어: Ulsan, skarn, calcic, albitite

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3. Skarn evolution and Ore mineralization

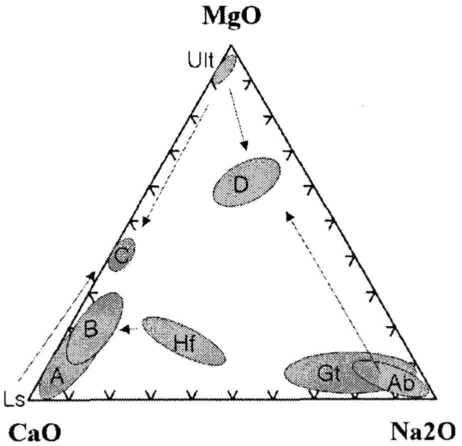

Fig. 1. Variation of skarns is represented in MgO-CaO-Na2O diagram from whole rock data

The skarn development and ore mineralization in the Ulsan deposits are the results of complex, multistage geochemical phenomena. Skarn formation and mineralization due to intrusion of the Gadae-Ri granite and serpentinized ultramafic rock took place in four distinct stages determined through an evolution of cross-cutting features, replacement textures, relationships among mineral and mineral assemblages. Calcic(-magnesian) skarn is related to limestone, hornfels and ultramafic rock, whereas calcic-sodic skarn is influenced by albitite. The whole rock chemical data reflect gross difference in the chemistry of host rock and skarn-forming fluids during the formation of skarn(Fig. 1). The compositions of clinopyroxenes and grandite garnets from calcic skarns near the ore pipe is shown in Fig. 2.

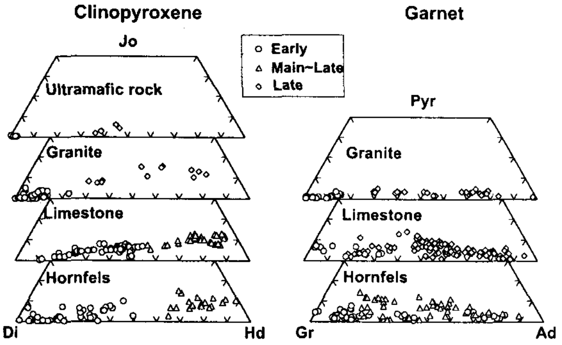

Fig. 2. Compositions of clinopyroxenes and garnets in skarns, expressed as mole proportions of johannsenite(Jo), diopside(Di), hedenbergite(He), grossular(Gr), andradite(Ad), and pyralspite(Pyr)

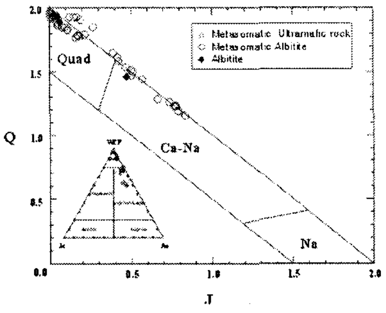

Fig. 3. Composition of clinopyroxenes from albitite, metasomatic albitite, metasomatic ultramafic rock

Also, the composition of clinopyroxenes from calcic-sodic skarn derived from albitite, metasomatic albitite, and metasomatic serpentinite is represented in Fig. 3.

During stage I, skarnoid formation began with a highly calcic assemblage represented by diopsidic clinopyroxene + wollastonite + grossular-rich garnet + vesuvianite at the granite-marble contact. This stage did not involve ore minerals.

During stage II, prograde metasomatic skarn formation can be further divided into two substages (IIa and IIb) depending on whether the predominant ore mineral is magnetite or arsenopyrite. Skarn minerals formed at high temperature during the main prograde event (substage IIa) are characterized by fine-grained anhydrous calc-silicates, magnetite and skarn calcite. Clinopyroxene is, however, the volumetrically most important mineral formed during this stage. The early fine-grained phases were followed by formation of medium-grained clinopyroxenes with 9.6-49.9 mole % hedenbergite and grandite garnets with intermediate compositions (9.7-87.9 mole % andradite). The main Fe mineralizing event, which played an important role in the development of massive magnetite bodies in the ore pipe, took place in the middle period of this skarn stage. During latest stage IIa, vein skarns that crosscut earlier skarn minerals, consist of coarse-grained clinopyroxene and garnet that become progressively more iron-enriched and magnesium-depleted. At the beginning of substage IIb, minor amounts of niccolite, rammelsbergite, löllingite, gersdorffite, arsenopyrite, and native bismuth were deposited with calcite and minor quartz. The Fe-As(-Ni) association is present mainly as massive and disseminated ores with skarn minerals, magnetite and calcite within the magnetite ore pipe and the surrounding calcite zone.

During stage III (retrograde skarn stage), hydrous alteration of pre-existing skarn minerals occurred, such as the alteration of clinopyroxene to calcic amphibole, with chlorite, ilvaite, epidote, calcite and quartz. Scheelite overgrew and replaced magnetite and calc-silicates within the ore pipe during substage IIIa. Copper-zinc and polymetallic mineralization overprinted previous tungsten mineralization during substage IIIb. Substage IIIb is also represented by the crystallization of chalcopyrite, sphalerite, hexagonal pyrrhotite, pyrite, arsenopyrite, cubanite, bornite, chalcocite and bismuthian tennantite, with minor or trace amounts of bismuth, bismuthinite, roquesite, tetrahedrite, cobaltite, wittchenite, miharaite, hessite, mawsonite and aikinite, although these ore minerals are present in minor or trace amounts. Substages IIIa and IIIb are successive, and must be regarded as a single mineralization event.

Stage IV represents the formation of fissure-controlled veins that clearly cut the Fe-W ore pipe and surrounding skarns. This stage represents the latest phase of hydrothermal ZnPb-Ag mineralization superimposed on the skarn alteration described previously. The Zn-Pb-Ag association occurs in veins of siderite-quartz-chlorite gangue with galena, sphalerite, pyrite, arsenopyrite, monoclinic pyrrhotite, and minor amounts of chalcopyrite, molybdenite, Ag-bearing tetrahedrite, pyrargyrite, polybasite, gudmundite and marcasite. It is volumetrically insignificant and is uneconomical.

4. Model of mineralization

The evolutionary trend from hypersaline magmatic fluids associated with Fe mineralization to low-salinity, lower temperature ore-forming fluids related to W-Cu-Zn and Zn-Pb-Ag mineralizations suggests an influx of meteoric water to deeper levels along fractures into the waning hydrothermal system. The relationship between homogenization temperature and salinity suggests a complex history of simple cooling, dilution and local CO2 effervescence. Based on the arsenopyrite geothermometry and the fluid inclusion data, it can thus be considered that the beginning of the Fe mineralization was deposited at about > 460℃ and > 45 equiv. wt.% NaCl. Considered to have genetic relation to the felsic magmatism of the Gadae-Ri granite pluton, the nature of Fe-W and polymetallic mineralizations at the Ulsan deposit may be regarded as having been formed at high temperature and shallow depth (0.5 kbar). These results suggest that the Ulsan skarn deposit may be due to its proximal position to the magma source which is genetically related to a low sufidation porphyry system.