

Magnetite and Scheelite-Bearing Skarns in Ulsan Mine, Korea

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ABSTRACT: The Ulsan Fe-W deposit, which can be classified as a calcareous skarn deposit, is represented by ore pipe consisting principally of magnetite and lesser amounts of scheelite with minor sulphides, sulphosalts, arsenides, sulpharsenides, etc.

At Ulsan mine, metasomatic processes of skarn growth may be divided broadly into two stages based on the paragenetic sequence of calc-silicate minerals and their chemical composition; early and late skarn stages. Early stage has started with the formation of highly calcic assemblages of wollastonite, diopsidic clinopyroxene and nearly pure grossular, which are followed by the formation of clinopyroxenes with salite to ferrosalite composition and grandite garnets with intermediate composition. Based on these calc-silicate assemblages, the temperatures of early skarn formations have been in the ranges of 550° to 450°C. The calc-silicate assemblages formed during the earlier half period of late skarn stage show the enrichment of notable iron and slight manganese, and the depletion of magnesium; clinopyroxenes are hedenbergitic, and grandite garnets are andraditic. The formation temperatures during this skarn stage are inferred to have been in the range of 430° to 470°C at low X_{CO_2} by data from fluid inclusions of late andraditic garnets. The later half period of late skarn stage is characterized by the hydrous alteration of pre-existing minerals and the formation of hydrous silicates.

The main iron-tungsten mineralization representing prominent deposition of magnetite immediately followed by minor scheelite impregnation has taken place at the middle of early skarn stage, while complex polymetallic mineralization has proceeded during and after the late skarn stage. Various metals and semimetals of Fe, Ni, Co, Cu, Zn, As, Mo, Ag, In, Sn, Sb, Te, Pb and Bi have been in various states such as native metal, sulphides, arsenides, sulphosalts, sulpharsenides and tellurides.

INTRODUCTION

The southeastern part of Korean Peninsular is well known as iron, tungsten-molybdenum and copper metallogenic provinces which contain various types of ore deposit, such as veins (Shelton et al., 1986; So et al., 1991), skarns (Choi et al., 1986; Woo, 1988) and breccia pipe (So and Shelton, 1983).

The Ulsan mine is located in Ulju Gun of Gyeongsangnam Province (latitude 35° 37'N and longitude 129° 20'E), and occupies the northern part of the Ulsan Quadrangle. The Ulsan mine, which is known as an important producer of iron, tungsten and arsenic ores in southeastern Korea, is of calcareous skarn deposit consisting mainly of magnetite with minor scheelite, sulphides and sulphosalts (Choi et al., 1985). Exploration and exploitation at the Ulsan mine have been advanced since 1964 by the Dai Han Iron Mining Development Co. Annual

production of ores in 1979 was as follows; magnetite concentrates (60 percent Fe): 100,000 metric tons, arsenopyrite concentrates: 1,200 metric tons and scheelite concentrates (74 percent WO_3): 60 metric tons.

Recently, many investigators have studied the general geology of Ulsan area and petrogeneses of Ulsan granite, carbonate rocks and serpentinite, but little is known about the skarn formation and associated iron-tungsten mineralization at Ulsan mine. The aims of the present study are to provide the intimate spatial relationship of calc-silicate mineral assemblages depending on the differences of host rocks and some physicochemical environments of skarn formation.

GENERAL GEOLOGY

The mine area is located in the southeastern border of the Gyeongsang Basin where mollase-type sediments intercalated with volcanics ranging in composition from intermediate to acidic were deposited during Cretaceous age. Also, volcano-plutonic

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complexes of granitic rocks including those of the Bulgugsa Granite Series (Cretaceous granites) and "Young granites" of Early Tertiary age crop out extensively within this sedimentary basin.

The geologic setting of Ulsan region has generally been described by Park and Yoon (1968) and Choi et al. (1980). In the mine area, crystalline limestones and ultramafic rocks consisting of partly serpentinized dunite and harzburgite, the ages of which being unknown, are exposed as a narrow "island" surrounded by the rocks of Upper Cretaceous sequence and the intruded granitic rocks (Fig. 1). These lenticular masses composed of the above two rock units has been considered to represent the basement of the Upper Cretaceous sedimentary rock. The granitic intrusive, exposed widely in the western part of the mine area, consists of hornblende-biotite granite called "Gadae-ri Granite Pluton" and the K-Ar age of biotite is 58 Ma (Lee and Ueda, 1977). Recent studies on intrusive rocks, ultramafic rock, volcanic rocks and ore deposits have been made by Lee et al. (1992), Kim et al. (1990), Choi et al. (1990), Park (1990) and Park and Park (1980).

OUTLINE OF THE ORE DEPOSITS

The iron-tungsten skarn deposit at Ulsan is represented by ore pipe consisting mainly of magnetite with minor scheelite, sulphides, sulphosalts, etc. The nearly vertical Fe-W ore pipe has been emplaced within crystalline limestones in contact with Upper Cretaceous argillaceous rocks (including pyroclastics and minor intrusives of trachyandesite) and in some places with ultramafic rocks. The skarn formations and associated iron-tungsten mineralization have proceeded along the intersections of E-W striking and steeply dipping stratigraphic boundary between crystalline limestones and Upper Cretaceous sedimentary rocks, with N-S trending high-angle fractures now occupied by post-ore younger dykes of andesite. In spite of the spatial separation from "Gadae-ri Granite Pluton", the Fe-W skarn deposit is considered to have genetic relationship to this granitic magmatism (Lee et al., 1992).

SKARN CHARACTERISTICS AND DISTRIBUTION

Skarn formations are well recognized along the contact between crystalline limestone and hornfels. The hornfels designated in the present study includes

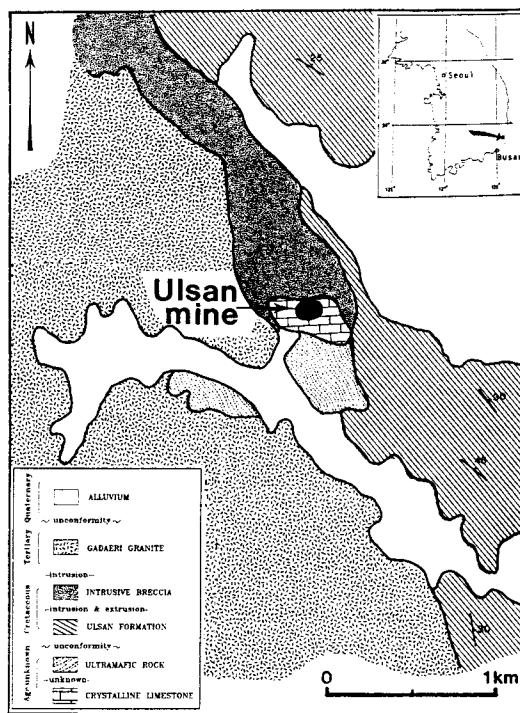


Fig. 1. Geologic map of Ulsan area modified from Park and Yoon (1968). Black area; Magnetite ore pipe.

pyroclastic rocks. Skarns are dominantly derived from crystalline limestone and hornfels, and are distinguished on the basis of subtle variations of relict texture. In detail, the spatial distribution of skarn reflects the original lithologies and the complicatedly overlapping series of veins that developed during metasomatism.

The skarns derived from crystalline limestone consist mainly of fine-grained massive clinopyroxene skarn with minor clinopyroxene-garnet skarn, garnet skarn, wollastonite skarn and diopside skarn. These skarns consist mainly of clinopyroxene, magnetite and grandite garnet with minor amphibole, epidote, wollastonite, biotite, ilvaite, scapolite and chlorite. Most magnetite ores are usually concentrated in the clinopyroxene and clinopyroxene-garnet skarns. These skarn formations are extremely heterogeneous and mineralogically complex. A rough zonation due to metasomatic alteration of crystalline limestone develops from a centre of massive clinopyroxene skarn with magnetite and disseminated scheelite ores through minor clinopyroxene-garnet skarn to a garnet skarn, calcite megacrystal zone and crystalline limestone. Also, a diopside skarn is restricted to only the limestone side in contact with ultramafic rocks

in open pit.

The zonation patterns of skarns derived from hornfels, however, are generally ambiguous and irregular. These skarns consist mainly of clinopyroxene and garnet with minor amount of amphibole, epidote, idocrase, biotite and chlorite. These skarn formations can be distinguished from those of crystalline limestone origin by the relict texture of original rock, but it is difficult to trace the boundary between fresh and altered hornfels both in the field and microscopic study.

Skarn Minerals

Skarn minerals from Ulsan mine can be divided into the prograde development of anhydrous minerals such as clinopyroxene, garnet and wollastonite and retrograde development of hydrous minerals such as amphibole, epidote, idocrase, ilvaite, scapolite and chlorite which partly replace the earlier garnet and clinopyroxene. Several generations of various skarns and vein mineral assemblages can be recognized within the skarn formations described previously.

These calc silicate minerals are divided into two principal groups on the basis of their occurrence and mineral compositions; 1) early massive stage skarns and 2) late vein skarn stage. Mineral compositions were determined on JEOL JXA-733 Superprobe electron microprobe, using the correction method of Bence and Albee (1968).

Clinopyroxene

Clinopyroxenes from Ulsan mine are the most abundant and characteristic skarn mineral in various skarns, and occur as solid solutions of diopside and hedenbergite with a maximum of 14.8 mole percent johannsenite (Table 1).

Clinopyroxene in crystalline limestone-derived skarns: The clinopyroxenes in skarns originated from crystalline limestone can be divided into the following two major groups on the basis of their occurrence. The clinopyroxenes in early skarn stage occur as fine-grained aggregates with magnetite and inclusions in anisotropic garnet, and are formed earlier than magnetite (Fig. 2), whereas the coarse-grained, euhedral clinopyroxenes in late skarn stage are contemporaneous with or later than anisotropic garnet and magnetite, and sometimes occur as fillings of vugs between anisotropic garnets (Fig. 2). There are two compositional populations; one, belonging to early skarn stage, is from diopsidic to salitic, and

another, corresponding to late skarn stage, is hedenbergitic to ferrosalitic.

Clinopyroxenes in early skarn stage show no marked compositional variation in single grain, although the composition of these clinopyroxenes slightly varied from grain to grain. There are no obvious variations from chemical composition of clinopyroxenes among garnet, clinopyroxene-garnet and clinopyroxene skarns, whereas there are clear difference for chemical composition of clinopyroxene in wollastonite and diopside skarns in marked contrast with garnet, clinopyroxene-garnet and clinopyroxene skarns. The clinopyroxenes in wollastonite skarn at the granite-limestone contact, which are in the range of 92.1 to 98.0 mole percent diopside, may have initially formed in equilibrium with relatively Mg-enriched solution of early skarn stage. The chemical compositions of clinopyroxene from the diopside skarn near ultramafic rock are nearly pure diopside and show very small range of variation. This suggests that the skarn-forming fluids affected by ultramafic rocks have metasomatically interacted to produce locally the diopside skarn which ranges from 95.1 to 98.6 mole percent diopside. However, the clinopyroxene compositions of early skarn stage vary from 1.4 to 72.1 mole percent hedenbergite with a maximum of 9.8 percent johannsenite (Fig. 3).

Clinopyroxenes of late skarn stage often display compositional zoning or complex features by alteration in single grain in contrast to early skarn stage. In some occasions, the clinopyroxenes in this stage are complexly overgrown and partly altered to different chemical compositions of clinopyroxenes which are considerably more ferroan and manganese. It thus appears that chemical compositions of clinopyroxenes seem to show a more continuous iron and manganese enrichments of metasomatic fluids with elapsing time as shown in Fig. 3. Their compositions in this stage vary from 68.7 to 84.3 mole percent hedenbergite with a maximum of 12.5 mole percent johannsenite.

Clinopyroxene in hornfels-derived skarns: Clinopyroxenes in early skarn stage are comparatively granular, fine-grained, and are intimately associated with isotropic garnet (Fig. 2). Those in late skarn stage are subhedral to euhedral, coarse-grained, and are associated with anisotropic garnet. The massive clinopyroxene-garnet skarn of early skarn stage is crosscut by discontinuous veinlets of dark brown anisotropic garnet with larger, euhedral clinopyroxene crystals (Fig. 2). These relations suggest that fractures within massive skarns during late stage were

Table 1. Representative microprobe analyses of clinopyroxenes in skarns derived from crystalline limestone and hornfels.

Specimen No.	305	105	521	112	810302	377	393	590	541
Host Rocks	Ls	Ls	Ls	Ls	Ls	Hf	Hf	Hf	Hf
Weight percent									
SiO ₂	52.84	48.29	48.10	54.75	55.38	55.73	54.10	49.57	49.28
TiO ₂	0.00	0.04	0.03	0.00	0.00	0.02	0.02	0.00	0.02
Al ₂ O ₃	0.10	0.60	0.12	0.10	0.18	0.47	0.39	0.12	0.10
FeO*	10.90	24.21	23.45	0.31	0.87	2.05	4.19	20.92	20.67
MnO	1.55	3.30	3.53	0.15	0.62	0.17	0.13	2.84	3.35
MgO	11.09	0.77	0.86	18.32	17.37	17.10	15.70	3.56	2.72
CaO	24.63	22.64	23.15	25.47	25.96	26.08	25.93	23.31	23.37
Na ₂ O	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
Total	101.11	99.85	99.23	99.10	100.36	101.61	100.47	100.32	99.52
Number of cations									
Si	1.99	1.98	1.99	2.00	2.00	2.00	1.98	1.99	2.00
Al	0.00	0.02	0.01	0.00	0.00	0.00	0.02	0.01	0.00
Sum	1.99	2.00	2.00	2.00	2.00	2.00	2.00	2.00	2.00
Ti	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
Al	0.00	0.01	0.00	0.00	0.01	0.01	0.00	0.00	0.00
Fe	0.34	0.83	0.81	0.01	0.03	0.06	0.13	0.70	0.70
Mn	0.05	0.11	0.12	0.00	0.02	0.01	0.00	0.10	0.12
Mg	0.62	0.05	0.05	0.99	0.94	0.91	0.86	0.21	0.16
Ca	0.99	1.00	1.03	0.99	1.01	1.00	1.02	1.00	1.02
Na	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
Sum	2.00	2.00	2.01	1.99	2.01	1.99	2.01	2.01	2.00
Mole percent									
di	61.3	4.8	5.3	98.6	95.4	93.2	86.6	21.0	16.8
hd	33.8	83.7	82.1	0.9	2.7	6.3	13.0	69.4	71.5
jo	4.9	11.5	12.5	0.5	1.9	0.5	0.4	9.5	11.7
Skarn Type	Massive G sk	Vein C sk	Vein CG sk	Massive Di sk	Massive Wo sk	Massive CG sk	Massive CG sk	Vein CG sk	Vein CG sk
Skarn Stage	Early	Late	Late	Early	Early	Early	Early	Late	Late

* Total iron as FeO

Abbreviations: Ls; crystalline limestone, Hf; hornfels, Massive; massive skarn, Vein; vein skarn, C sk; clinopyroxene skarn, CG sk; clinopyroxene-garnet skarn, Di sk; diopside skarn, G sk; garnet skarn, and Wo skarn; wollastonite skarn.

initially filled by coarse-grained anisotropic garnets and then later clinopyroxenes. The chemical compositions of clinopyroxenes in early skarn stage range from 5.3 to 48.6 mole percent hedenbergite with a maximum of 10.2 percent johannsenite. On the contrary, the compositions of clinopyroxenes in late skarn stage are in the range of 62.4 to 88.5 mole percent hedenbergite with a maximum of 14.8 percent johannsenite.

Clinopyroxenes of the various skarns from Ulsan mine display an increase in manganese content with an increasing iron (Fig. 3). The sequence of clinopyroxene in both skarns derived from hornfels and crystalline limestone shows that the iron and manganese rather than magnesium were mobilized

late in the skarn-forming process. A systematic relationship described previously exists between the clinopyroxene composition and the skarn stage.

Grandite Garnet

Grandite garnets from Ulsan occur as one of the abundant and characteristic calc-silicate minerals, and show the wide-ranged variation in dominant solid solutions of grossular and andradite. In addition those contain up to 4.79 weight percent MnO in vein skarn. Although the presence of almandine molecule is slightly required, charge-balance considerations indicate that iron is entirely in the trivalent state within analytical accuracy (Table 2).

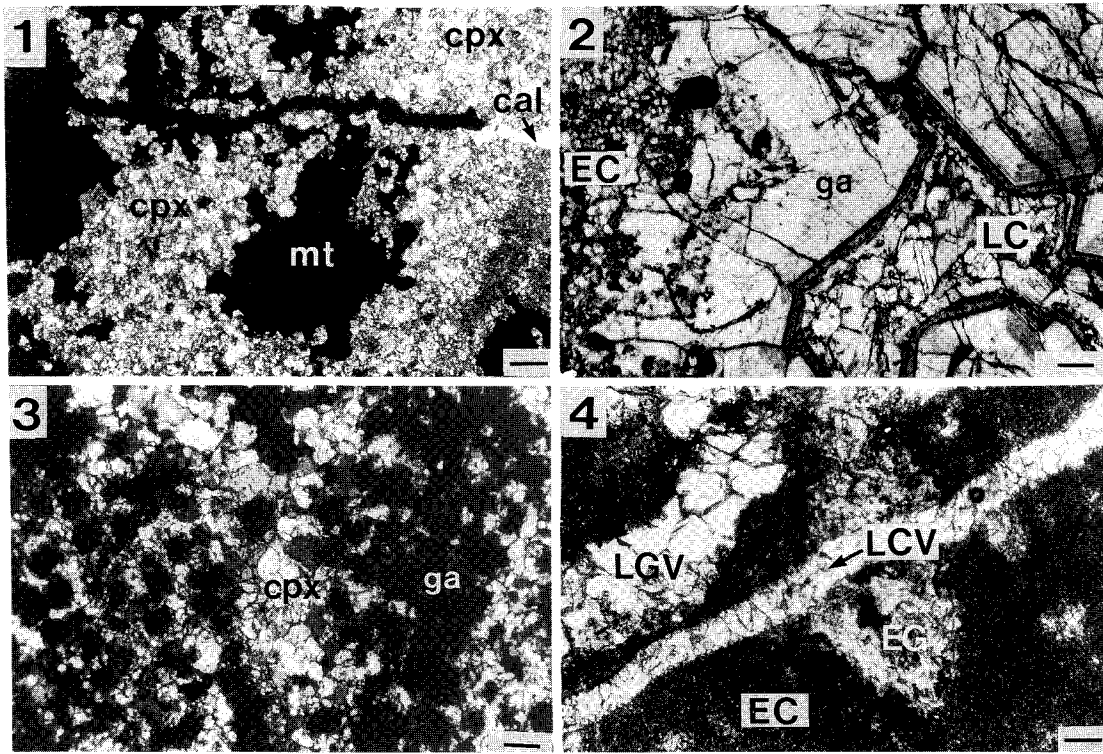


Fig. 2. Photomicrographs showing the mode of occurrence of calc-silicate minerals. 1. Magnetites (mt) with calcite (cal) occur as fillings between interstices of fine-grained aggregates of clinopyroxenes (cpx) in clinopyroxene skarn of limestone origin. 2. Zoned anisotropic garnets (ga) in garnet skarn contain small inclusion of early clinopyroxene (EC) and are filled with late clinopyroxenes (LC). 3. Clinopyroxene-garnet skarn of hornfels origin shows the fine aggregates of clinopyroxenes (cpx) and isotropic garnets (ga) crystallized during early skarn stage. 4. Clinopyroxene-garnet skarn shows the fine aggregates of early clinopyroxene (EC) and isotropic garnet (EG) crosscut by late clinopyroxene vein (LCV) and garnet vein (LGV). Bar scale indicates 0.2 mm in length.

Garnet in crystalline limestone-derived skarns: Grandite garnets can be divided into two groups. Those in early skarn stage are comparatively granular, fine-grained, isotropic to weakly anisotropic, and are associated intimately with wollastonite, diopside and idocrase. Those in late skarn stage are coarse-grained, subhedral to euhedral, strongly anisotropic, and are associated with coarse-grained clinopyroxene, amphibole, magnetite and scheelite. These garnets in garnet skarn commonly occur as polycrystalline aggregates and contain small euhedral inclusions of clinopyroxene. The grossular-rich garnets occur in wollastonite skarn particularly, whereas more andradite-rich garnets occur in garnet, clinopyroxene-garnet and clinopyroxene skarns. The spessartine-pyropite content within these grandite solid solutions increases with increasing grossular/andradite ratios (Fig. 4). Garnets in wollastonite skarn show no marked compositional variation in single

grain, and are isotropic to weakly anisotropic in optical properties. On the contrary, garnets in garnet, clinopyroxene-garnet and clinopyroxene skarns have strong anisotropy in optical properties except for end-member andradite, and show a significantly wide compositional zoning on a scale of microns within single grain.

Garnet in hornfels-derived skarns: The grandite garnets in these skarns can be clearly divided into the following two groups based on the modes of occurrence and optical properties. Grandite garnets in early skarn stage, which are associated intimately with fine-grained clinopyroxene, are optically isotropic to very weakly anisotropic, anhedral in shape. Those show a relatively homogeneous chemical composition, although the composition of single garnet in this stage varied slightly from grain to grain. Also, these garnets range from 17.6 to 89.6 mole percent grossular, and less than 1.04 weight percent

Table 2. Representative microprobe analyses of garnets in skarns derived from crystalline limestone and hornfels.

Specimen No.	702	704	714	810302	302	541	393	377	377
Host Rocks	Ls	Ls	Ls	Ls	Ls	Hf	Hf	Hf	Hf
Weight percent									
SiO ₂	37.44	37.69	37.45	40.09	34.75	37.93	36.46	36.79	37.56
TiO ₂	0.03	0.00	0.00	0.56	0.00	0.53	0.07	0.29	0.10
Al ₂ O ₃	9.85	12.33	16.21	19.01	1.89	13.34	4.84	5.56	12.12
Fe ₂ O ₃ *	18.44	15.33	10.20	4.90	29.18	13.39	25.13	22.31	15.47
MnO	1.46	2.33	2.57	0.27	0.95	0.18	1.10	0.28	2.11
MgO	0.05	0.06	0.00	0.43	0.07	0.05	0.05	0.19	0.04
CaO	33.95	32.87	32.72	36.57	32.07	34.45	33.22	34.00	32.82
Total	101.23	100.62	99.15	101.83	98.91	99.87	100.86	99.41	100.22
Number of cations on the basis of 12 oxygens									
Mn	0.10	0.16	0.17	0.02	0.07	0.01	0.08	0.02	0.14
Mg	0.01	0.01	0.00	0.05	0.01	0.01	0.01	0.02	0.01
Ca	2.89	2.78	2.76	2.94	2.92	2.90	2.91	2.99	2.79
ΣX-cations	3.00	2.95	2.93	3.01	3.00	2.92	3.00	3.03	2.94
Ti	0.00	0.00	0.00	0.03	0.00	0.03	0.00	0.02	0.01
Al	0.90	1.13	1.46	1.68	0.15	1.22	0.45	0.54	1.12
Fe ³⁺	1.10	0.91	0.61	0.28	1.87	0.79	1.55	1.38	0.92
ΣY-cations	2.00	2.04	2.07	1.99	2.02	2.05	2.01	1.94	2.05
Si	2.98	2.98	2.95	3.00	2.96	2.98	2.99	3.02	2.98
Al	0.02	0.02	0.05	0.00	0.04	0.02	0.01	0.00	0.02
ΣZ-cations	3.00	3.00	3.00	3.00	3.00	3.00	3.00	3.02	3.00
Mole percent									
pyr	0.2	0.2	0.0	1.6	0.3	0.2	0.2	0.8	0.2
sps	3.3	5.3	5.8	0.6	2.3	0.4	2.6	0.6	4.8
gr	41.4	49.8	64.8	82.3	4.7	59.1	19.8	26.4	49.5
ad	55.1	44.7	29.2	15.5	92.7	40.3	77.4	72.2	45.5
Skarn Type	Massive	Massive	Vein	Massive	Massive	Massive	Massive	Massive	Vein
	C sk	CG sk	CC	Wo sk	G sk	CG sk	CG sk	CG sk	CG sk
Skarn Stage	Late	Late	Late	Early	Late	Early	Early	Early	Late

* Total iron as Fe₂O₃

Abbreviations: Ls; crystalline limestone, Hf; hornfels, Massive; massive skarn, Vein; vein skarn, C sk; clinopyroxene skarn, CC; calcite megacrystal zone, CG sk; clinopyroxene-garnet skarn, G sk; garnet skarn, and Wo sk; wollastonite skarn.

MnO. The chemical compositions of garnets in early skarn stage of hornfels origin contain relatively more Al-rich than those in crystalline limestone. It suggests that the grossular-rich garnets of early skarn stage in hornfels were formed by local metasomatism of the dissimilar host rocks in spite of same metasomatic fluids, and were characterized by different compositional control on calc-silicate mineralogy.

Garnets of late skarn stage, which crosscut the isotropic garnet-clinopyroxene massive skarn of the early stage, show optically strong anisotropy and euhedral in shape, and significantly compositional zoning. These garnets range from 10.0 to 75.0 mole percent grossular, and contain up to 4.79 weight percent MnO. Also, the compositional variation between isotropic garnets in early skarn stage and

garnet veinlets in late skarn stage can easily be perceptible in back-scattered electron (composition) images and characteristic X-ray images (Fig. 5). That is, garnets in veinlets have clearly higher spessartine than garnets in early skarn stage. The chemical compositions of the garnets between the various skarns derived from the crystalline limestone and the vein skarns of late stage in hornfels origin have the similar trend as shown in Fig. 4.

The grandite garnet from Ulsan mine is not only characterized by two distinctly different host rocks (crystalline limestone and hornfels) but also by two skarn-forming stage (early skarn stage and late skarn stage). It indicates that a systematic relationship exists between the chemical compositions of garnets and the original rocks and/or associated silicate minerals,

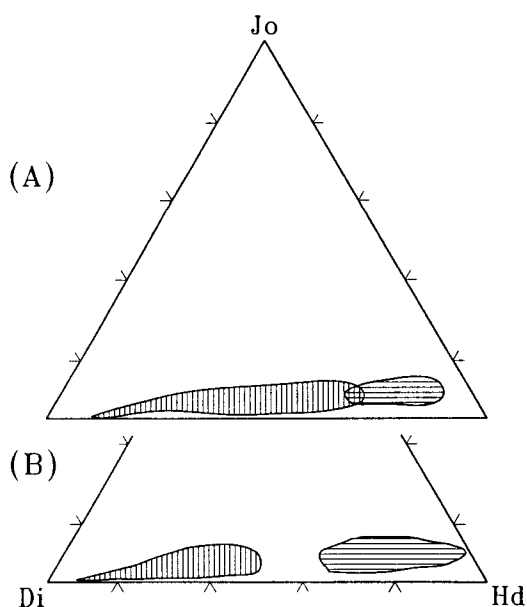


Fig. 3. Compositions of clinopyroxenes in skarns derived from crystalline limestone (A) and hornfels (B), expressed as mole proportions of johannsenite (Jo), diopside (Di) and hedenbergite (Hd). Vertical ruling area; early skarn stage. Horizontal ruling area; late skarn stage.

i.e., the skarn stage in which the garnet occurs. The variation in compositions of garnets further suggests that with elapsing time the metasomatic fluids became relatively enriched in iron and manganese as shown in clinopyroxene.

Other Skarn Minerals

Ugrandite garnet: Ugrandite garnets from Ulsan are restricted to only several localities, and occur as the extremely narrow veinlets filling the microcracks (Choi et al., 1983). Two significant features are recognized; the first is the intimate association of the ugrandite garnet with chromite, and the second is the fact that the original rocks of these skarn formations are in most cases confined to hornfels.

Ugrandite garnets in transmitted light are emerald green in colour and optically anisotropic. No regular zonation has been recognized at all. These garnets display a relative wide range of solid solution between uvarovite and grossular with up to 30 mole percent andradite. Their compositions range from 1.9 to 16.5 weight percent Cr_2O_3 .

Wollastonite: Wollastonites, which are rare mineral among skarn minerals, are white in colour and have glassy lustre. Wollastonites occur as monomineralic

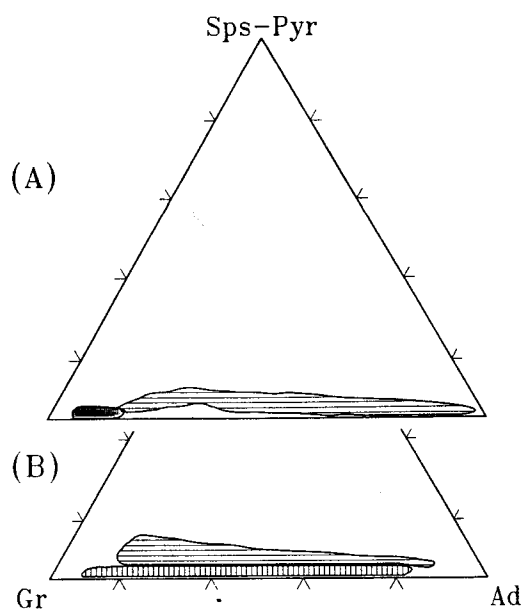


Fig. 4. Compositions of grandite garnets in skarn originated from crystalline limestone (A) and hornfels (B), expressed as mole proportions of spessartine+pyrope (Sps-Pyr), grossular (Gr) and andradite (Ad). Dark area; early skarn stage at the granite-limestone contact. Vertical ruling area; early skarn stage. Horizontal ruling area; late skarn stage.

aggregates of fibrous or long-prismatic crystals in the crystalline limestone-granite contact. Those are associated with diopside, idocrase and grossular. Small patches of fine-grained wollastonites are sometimes recognized within crystalline limestone. These wollastonites are never associated with magnetite, scheelite and sulphide minerals. The chemical composition of wollastonites is nearly pure.

Amphibole: Amphiboles are not abundant in various skarns, but locally present. Amphiboles occur generally as: (1) rims on partial replacement of ferrosalitic to hedenbergitic clinopyroxene, (2) fine-grained aggregates intergrown with clinozoisite, biotite, chlorite and quartz and (3) fibrous (acicular) inclusions in quartz and calcite. Amphiboles occur as dominantly solid solutions of actinolite and tremolite. Their compositions show a wide variation of $\text{Mg}^{2+}/(\text{Mg}^{2+} + \text{Fe}^{2+})$, varying from 0.14 to 0.47.

Epidote: Epidotes are not common mineral in the study area, however, those are relatively abundant in skarns of hornfels origin than in those of crystalline limestone origin. Epidotes occur as: (1) as mainly discontinuous veinlets crosscutting both early skarn and late garnet vein, (2) partial replacement

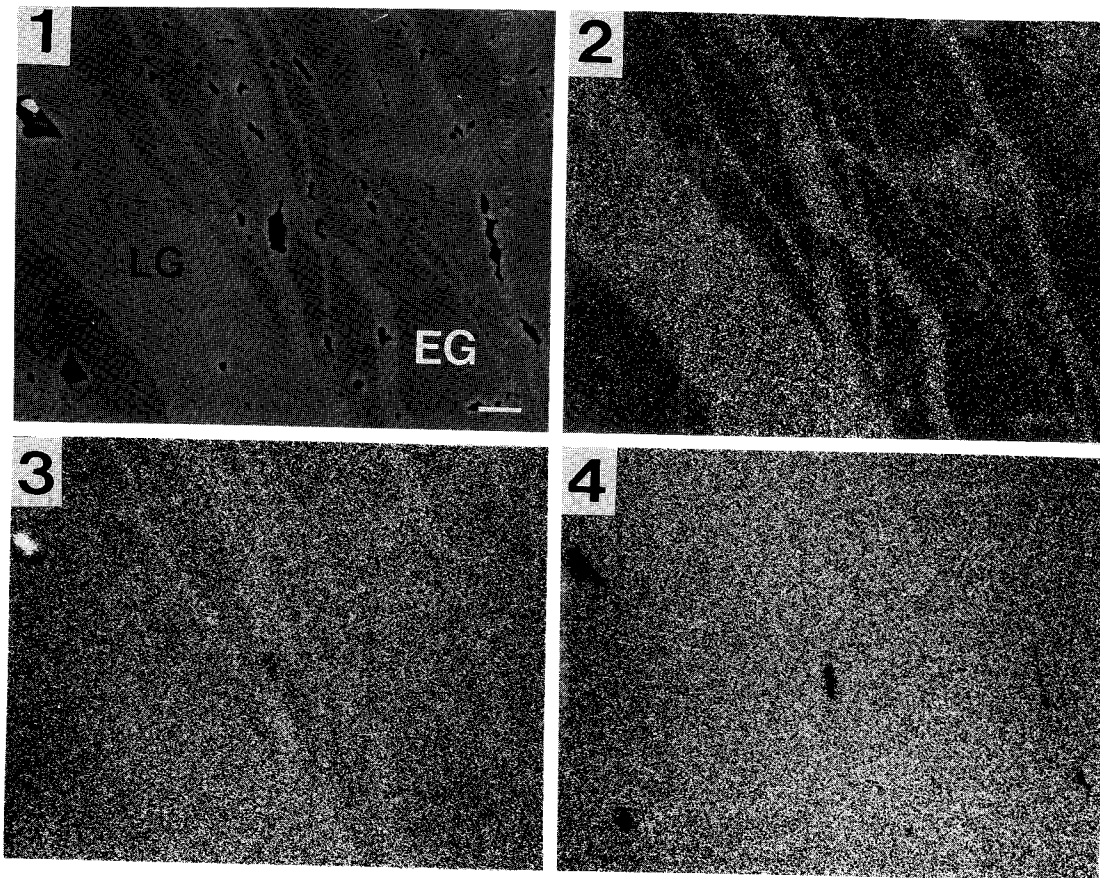


Fig. 5. Back-scattered electron (composition) image and corresponding X-ray images, showing the textural relationships between Al-rich garnet (EG) of early skarn stage, and Fe- and Mn-rich garnet (LG) of late skarn stage. 1. Back-scattered electron image. 2-4. Characteristic X-ray images in the area of 1. 2. Mn K_{α} . 3. Fe K_{α} . 4. Al K_{α} . Bar scale indicates 0.01 mm in length.

of garnet and (3) as fine-grained aggregates intimately associated with amphibole, chlorite, and quartz. Those belong to a solid solution of clinozoisite and pistacite, and show a significant variation in $Fe^{3+}/(Fe^{3+} + Al)$ mole fractions in the M3 site of epidote. The compositions of epidote range from 0.32 to 0.95 $Fe^{3+}/(Fe^{3+} + Al)$ mole fractions.

SKARN EVOLUTION

The history of metasomatic skarn growth from Ulsan may be divided broadly into the following two events on the basis of paragenetic sequence of calc-silicates assemblages and their chemical composition; early skarn stage (massive type) and late skarn stage (vein type).

The early skarn stage, related to the massive skarns, formed extensive areas of fine-grained cli-

nopyroxene and/or minor or trace amounts of wollastonite and isotropic garnet in crystalline limestone, and fine-grained clinopyroxene and subordinate isotropic garnet in hornfels (including volcanics). Significant compositional zoning of individual clinopyroxene and garnet in this stage was not observed. Early skarn stage of prograde skarn growth has started with the formation of wollastonite, grossular-rich garnet and diopsidic clinopyroxene assemblages, which is essentially barren of ore minerals. Mineralogic sequence and its composition of this stage are followed by the formation of fine-grained clinopyroxene with salite to ferrosalite composition and/or isotropic grandite garnets with intermediate composition. It is considered, however, that the main iron-tungsten mineralization representing prominent deposition of magnetite immediately followed by minor scheelite impregnation has

taken place at the end of this early skarn stage.

The metasomatic reactions of late skarn stage formed narrow areas of coarsened-grained clinopyroxene and anisotropic zoned garnet and/or subordinate amphibole, chlorite, epidote, and biotite in crystalline limestone, and recognized limited areas or veinlet of coarse-grained anisotropic zoned garnet and clinopyroxene and subordinate amphibole, idocrase, epidote and chlorite in hornfels.

Several generations of coarse-grained brown garnet and/or epidote vein are crosscutting massive skarns of early garnet and clinopyroxene. Significant compositional zoning of garnet grain and replacement of individual clinopyroxene were well observed in this stage. The earlier half period of late skarn stage, representing prograde skarn growth, shows a trend towards the enrichment of notable iron and slight manganese, and magnesium-depletion in the calc-silicate assemblages; coarse-grained clinopyroxenes have hedenbergitic composition containing considerable amounts in johannsenite molecule, and anisotropic zoned grandite garnets have very wide ranged composition with slightly high spessartine. On the other hand, the later half period of this late skarn stage is retrograde, in which the hydrous alteration of the pre-existing skarn minerals and the formation of hydrous silicates and sulphides are prevailed.

The amount of amphibole formed by retrograde alteration of clinopyroxene is not large, and appears to be partly associated with sulphides and sulphosalts rather than magnetite and scheelite. In this stage of skarn growth, complex polymetallic mineralization has proceeded; various kinds of metals such as Fe, Co, Ni, Cu, Zn, Ag, Mo, In, Sn, Sb, Te, Pb and Bi have been fixed as arsenides, sulpharsenides, sulphides, sulphosalts and tellurides, although these ore minerals are minor in amounts (Choi and Imai, 1985).

IRON-TUNGSTEN MINERALIZATION

Magnetites, which occur as the most common metallic mineral in the Ulsan mine, make up a pipe-shaped orebody within crystalline limestone bordering the hornfels. Most magnetites are generally observed in the various skarns originated from the crystalline limestone, whereas the skarns originated from hornfels contain only trace amounts of magnetite with anisotropic garnet occurring as veins.

Among the skarns from crystalline limestone, magnetites tend to be concentrated in the clinopyroxene skarn rather than in the garnet and cli-

nopyroxene-garnet skarns. Also, magnetites are not found at the wollastonite skarn but are rarely observed at the diopside skarn. Magnetites in clinopyroxene skarn generally occur as fine- to medium-grained anhedral aggregates replacing calcite, and fill up the interstices between fine-grained clinopyroxene aggregates. Although most magnetites, constituting especially massive ore bodies, are associated with clinopyroxene skarn, they occur locally as disseminated grains within clinopyroxene-garnet and garnet skarns. In the clinopyroxene-garnet skarn, magnetites are interstitial to fine- to medium-grained clinopyroxenes and partially replace anisotropic garnet. This suggests that magnetite is formed later than clinopyroxene and garnet. But, magnetites in the garnet skarn show different texture from that in clinopyroxene skarn and clinopyroxene-garnet skarn, suggesting that magnetites in the garnet skarn are possibly contemporaneous with anisotropic garnets.

In the skarn originated from hornfels, magnetite is not observed in fine-grained clinopyroxene-isotropic garnet massive skarn belonging to early skarn stage. In some cases, it occurs as vein associated with anisotropic garnet and calcite cutting the early skarn formations. However, magnetites tend to concentrate predominant in skarns of crystalline limestone origin rather than in those of hornfels origin. Most magnetites, which correspond generally to the main stage, may be formed from the middle to late periods of the early skarn stage. Those are intergrown intimately with the fine-grained clinopyroxene and anisotropic garnet.

Magnetite is rarely observed in the Cu-Zn ores from the Ulsan mine, although it is relatively small in amount. Magnetite, which is intergrown intimately with chalcopyrite, arsenopyrite, ilvaite, loellingite, occurs as aggregates between chalcopyrite and arsenopyrite, suggesting that it is replacing them. This is substantiated by very fine-grained and abundant inclusions of very fine-grained chalcopyrite within magnetite.

Scheelites occur in minor amounts, but are one of the important commercial metallic minerals. Scheelites are mostly distributed within magnetite ore pipe, and are particularly concentrated in the northern part of magnetite ore body. Scheelites are most abundant as disseminations within the magnetite ore body and various skarns originated from crystalline limestone. Scheelites are generally present as fine-grained to medium-grained masses replacing the calcite, which is interstitial to clinopyroxene and

magnetite grains. Occasionally large scheelite crystals are crosscut by fine-grained magnetite. Although the greater part of magnetite predates scheelite, some does not. Field and microscopic evidences generally indicate that scheelite mineralization is slightly later than the magnetite mineralization in the previously described metasomatic process, and is followed by the formation of amphibole, biotite, epidote and chlorite.

The Ulsan scheelite shows two distinctly different behaviours in fluorescent colour, which are pale blue and yellow or pale yellow. The pale blue scheelite is generally more abundant than the yellow one, and the former often surrounds latter. The two types of scheelites in the Ulsan mine are nearly pure CaWO_4 . It indicates that the fluorescent colours of scheelite probably arise from molybdenum and one or more of the trace elements.

PHYSICO-CHEMICAL ENVIRONMENTS OF SKARN FORMATION

Many investigators have noted that the small number of phases formed at any one time in skarn formations makes it difficult to determine the intensive variables of skarn-forming environments. Anhydrous assemblages formed in the early skarn stage consist of simple phases. The variations in the bulk chemical composition of the host rocks may reflect obviously the different mineral assemblages and the chemical compositions of the skarn minerals produced during this skarn stage. These suggest that variations in mineralogy during the skarn stage are mainly due to continuously progressive changes in the composition of fluids caused by their reaction with the rocks as they migrated through the system. Complex calc-silicate mineral assemblages were formed later during the hydrous destruction of the earlier formed anhydrous assemblages. The high variance of the assemblages is clearly attributed to the activity of components controlled externally.

To determine the general environment of skarn formation and metallic mineralization (including arsenides, sulphides, sulphosalts and tellurides) it is necessary to consider the effects of variable oxygen and sulphur fugacities in addition to temperature, pressure and X_{CO_2} . The thickness of the Ulsan formation which overlies crystalline limestone at Ulsan is about 2,500 m, estimated by Choi et al. (1980). This is equivalent to about 700 bars for maximum lithostatic pressure. Therefore, the author concluded that a pressure of 0.5 kb for skarn

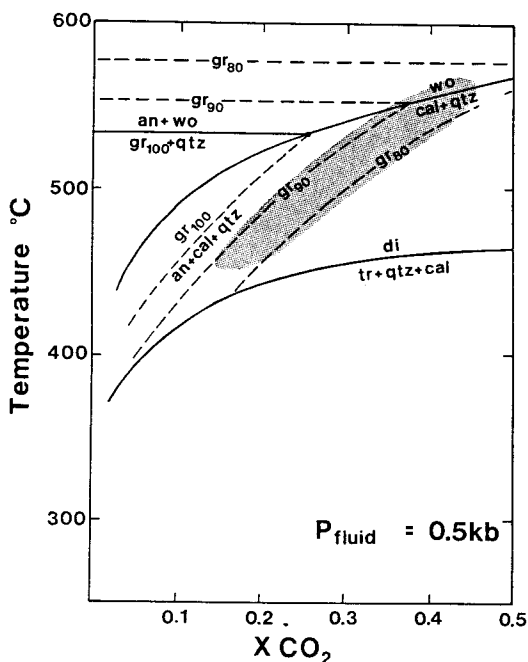


Fig. 6. T- X_{CO_2} diagram showing the general environment for early skarn stage at the granite-limestone contact (ruled area). Calc-silicate equilibria based on the experimental work of Gordon and Greenwood (1971), Greenwood (1967), Slaughter et al. (1975), and Newton (1966). This diagram is after Meinert (1982). Mineral abbreviations: an; anorthite, cal; calcite, di; diopside, gr; grossular, qtz; quartz, tr; tremolite, and wo; wollastonite.

formation and iron-tungsten mineralization from Ulsan is reasonable on the basis of the stratigraphic evidence and erosion. Fig. 6 is a T- X_{CO_2} section at 0.5 kb showing the equilibria applicable to the skarn assemblages. This diagram shows only the equilibria relevant to skarn parageneses; the T- X_{CO_2} relation for this system is given by Gordon and Greenwood (1971). The presence of wollastonite in the early skarn stage is observed at crystalline limestone-granite front, suggesting that the reaction $\text{CaCO}_3 + \text{SiO}_2 = \text{CaSiO}_3 + \text{CO}_2$ has proceeded. The zonal distribution from granite toward crystalline limestone is: granite → grossular-rich garnet skarn → wollastonite skarn with discontinuous diopside band → limestone. The formation of wollastonite at the contact between limestone and granite is due to the diffusion of Si into the marble ahead of the other components such as Mg, Al and Fe in the skarn-forming fluid. An upper temperature and lower X_{CO_2} limit for the early skarn stage can be generally estimated by the presence of wollastonite and the absence of anorthite

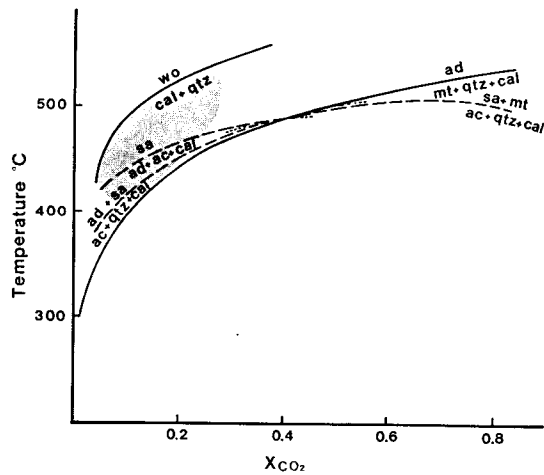
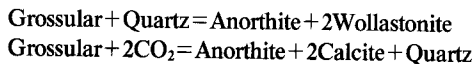


Fig. 7. T- X_{CO_2} diagram for some reactions in the system Ca-Fe-Mg-Si-C-O-H at the pressure of 0.5 kb showing the general environment for massive skarn (ruled area) of clinopyroxene, granodite garnet and magnetite assemblages. Wollastonite reaction from Greenwood (1967) and andradite reaction from Taylor and Liou (1978) at f_{O_2} values on the Hm-Mt buffer. This diagram is after Harris and Einaudi (1982). Mineral abbreviations: ac; actinolite, ad; andradite, cal; calcite, di; diopside, gr; grossular, mt; magnetite, qtz; quartz, sa; salite, tr; tremolite, and wo; wollastonite.

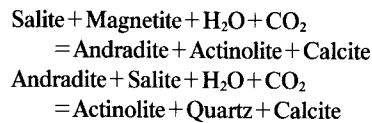
in the skarn front near granite. As previously described, diopsidic clinopyroxene, which is intimately associated with wollastonite, may be crystallized simultaneously with it. This indicates that the first-formed clinopyroxenes associated with wollastonite are Mg-rich ones. The absence of tremolite and the common occurrence of diopside in the early skarn stage can establish a general lower temperature limit and upper X_{CO_2} limit for the metasomatic processes. Also, the isotropic garnet which is found within or closer to the wollastonite skarn is nearly pure grossular. These data suggest that the initially-formed garnets in the calc-silicate skarn formation are from Newton (1966), and Gordon and Greenwood (1971) for the reactions



The shifts of 10 mole percent andradite increments for the invariant point intersection of reactions $gr + qtz = an + wo$ and $gr + CO_2 = an + qtz + cc$ are shown in Fig. 6. The use of the specific granodite component ranging from 90 to 80 mole percent grossular in the early skarn stage at the contact between granite and limestone results in a restricted environment of

formation bounded by the wollastonite, diopside and grossular-rich granodite assemblages. The resulting T- X_{CO_2} environment in the early skarn stage near granite is shown in Fig. 6.

Main prograde metasomatic process in early skarn stage, which have started with the formation of wollastonites, grossular-rich garnets and diopsidic clinopyroxenes, are followed by the formation of clinopyroxenes with salite to ferrosalite composition, magnetites and andradite-rich garnet. The absence of wollastonite and the common occurrence of clinopyroxene, magnetite and anisotropic garnet in clinopyroxene skarn, clinopyroxene-garnet skarn and garnet skarn generally determines an upper temperature and lower X_{CO_2} limit for the skarn formation of this stage. The absence of actinolite in the early skarn stage can establish a general lower temperature limit and upper X_{CO_2} limit for the metasomatic processes.



The resulting T- X_{CO_2} environment of salite, magnetite and andradite-rich garnet in early skarn stage is shown in Fig. 6. The evidence for range of temperatures from calc silicate mineral assemblages is supported by data from fluid inclusions of anisotropic garnets ($>430^\circ\text{C}$) and geothermometer of arsenopyrites ($>420^\circ\text{C}$) in late skarn stage (Choi et al., 1986).

DISCUSSIONS AND SUMMARY

The morphology, mineral assemblage and mineral chemistry of iron-tungsten skarn deposits of the Ulsan mine suggest the following generalized models for the skarn formation and ore mineralizations.

Petrological evidences of the "Gadae-Ri Pluton", which is characterized by the porphyritic, micrographic and granophyric textures, suggest that this pluton is formed under the hypabyssal, shallow-seated, rapid cooling condition. The formations of skarns and orebody have been primarily controlled by the geological structure and chemical nature of the host rocks. The skarn-forming and ore-forming fluids, heated by and at least in part supplied by "Gadae-Ri Pluton", were structurally channeled into crystalline limestone and hornfels, although the ore pipe and the associated skarn zones are spatially separated from "Gadae-ri Granite Pluton". They

tended to migrate and proceed along the intersection of E-W trending and steeply dipping stratigraphic boundary between limestones and hornfelses, and the N-S trending high-angle fractures now occupied by the post-ore andesitic dykes. Also, it is possible that the hornfelses have partly a damming effect on upward-migrating metasomatic fluids. Therefore, the ore deposits are considered to have been genetically related to granitic magmatism of this felsic pluton. Based on the stratigraphic thickness and erosion, the total pressure during metasomatic process is 0.5 kb.

The metasomatic process of skarn growth in the time-evolutional trend can be divided broadly into the two stages in terms of the paragenetic sequence of calc-silicates and their chemical composition; the early skarn stage and late skarn stage.

The early skarn stage representing the prograde skarn growth has started with the formation of highly calcic assemblages of wollastonite-diopside clinopyroxene-grossular recognized at the frontal margin of skarns in crystalline limestone, which is followed by the formation of clinopyroxenes with salite to ferrosalite composition and grandite garnets with intermediate composition, and is essentially barren of ore minerals throughout the earlier period. Clinopyroxene in the skarn near the ultramafic rocks shows a marked increase in magnesium. This suggests that the diopside skarn is related to the drastic change (magnesium enrichment) in the bulk composition of the metasomatic fluids, during they are channeled into the ultramafic rocks. It is shown, however, that the main iron-tungsten mineralization involving the prominent deposition of magnetite immediately followed by minor scheelite impregnation has taken place at the later period of this early skarn stage.

The first half period of late skarn stage shows a trend towards the enrichment of notable iron and slight manganese and the depletion of magnesium; clinopyroxenes have hedenbergitic composition containing considerable amounts in johannsenite molecule. Although the garnets in this stage also have andraditic composition with considerable amounts in spessartine molecule, fine compositional zoning in the single crystal of garnet would indicate that the relative activity of Al and Fe were not buffered to constant value during the crystallization of garnet, but the bulk composition of metasomatic fluid fluctuated irregularly due to additions from magmatic fluids and local precipitation reactions in the skarn. Based on the homogenization temperature of fluid inclusions in the anisotropic zoned garnet, which is

later than magnetite, these garnets may have crystallized above 430°C, and probably less than $X_{\text{CO}_2} = 0.1$. The minimum temperature of prograde skarn growth in the late skarn stage is probably more than 430°C. Throughout the late skarn stage of skarn growth, complex polymetallic mineralization has proceeded; various kinds of metals such as Fe, Co, Ni, Cu, Zn, Ag, Mo, In, Sn, Sb, Te and Bi have been fixed as sulphides, arsenides, sulpharsenides, sulphosalts and tellurides, although these ore minerals are minor in amounts. The arsenopyrite in this stage, coexisting with loellingite, native bismuth and/or bismuthinite is arsenian (As-excess, S-deficient). Utilizing the T- f_{S_2} diagram of Kreschmar and Scott (1976), a range of the arsenopyrite crystallization temperature from 420 to 480°C and sulphur activity from -7.0 to -8.0 is indicated for this stage (Choi et al., 1986). This temperature is somewhat higher than the maximum value of the homogenization temperature of fluid inclusions in anisotropic zoned garnet. On the other hand, the later half periods of the late skarn stage is retrograde, in which the hydrous alteration of the pre-existing skarn minerals and formation of hydrous silicates, carbonate and quartz are prevailed. That is, clinopyroxene and garnet are replaced by amphibole, epidote, idocrase, calcite and quartz.

The evolution of ore-forming fluids has started with the formation of magnetite during the early skarn stage, and has been immediately followed by the minor scheelite impregnation during the end of this early skarn stage. The late skarn stage has started with the formation of Ni-Fe-Co or Fe arsenides and sulpharsenides, and is followed by the formation of polymetallic mineralization consisting mainly of Cu-Zn or Cu ores. Throughout the hydrothermal mineralization, Pb-Zn ores are produced.

The Ulsan ore deposit is considered to have genetical relation to the felsic magmatism of the "Gadae-ri Granite Pluton", and also they are regarded as having been formed at high-temperature and shallow depth with a steep geothermal gradient-xenothermal conditions.

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울산 광산의 철-텅스텐 스킨화작용

崔善奎 · 今井直哉

요 약: 경상분지 남동부에 위치한 울산광산은 석회암을 교대한 전형적인 calcareous skarn 광상으로 Fe·W 광화작용 이외에도 Cu, Pb, Zn, As, Bi, Ni, Co, Cr, Ag, Sn, In, Te, Sb 등이 수반되는 다금속광화작용의 특성을 보여주고 있다. 본 광산은 직립에 가까운 파이프상 광체로 산출되며, 자철석과 함께 북측의 혼펠스와의 경계부근에 회중석이 부분적으로 광염되어 있다.

본 광산의 스킨대는 석회암 및 혼펠스를 교대한 피상 스킨과 양자를 각기 절단하는 맥상 스킨으로 구분된다. 피상 스킨은 석회암 기원의 스킨이 주체를 이루며, 이러한 스킨대는 규회석 스킨, 석류석 스킨, 단사회석-석류석 스킨, 단사회석 스킨으로 분류되며, 부분적으로 스킨대 주변부를 따라 기정질 방해석대가 존재하고 있다. 스킨 진화과정은 초기스킨 및 후기스킨의 두 시기로 분류되며, 초기스킨은 prograde한 스킨 생성시기로 초기에는 규회석, Mg-rich 단사회석, Al-rich garnet가 주로 정출되며 광석광물은 거의 불모한 시기이나, 초기스킨의 말기로 진행됨에 따라 자철석과 회중석이 정출된다. 그리고, 후기스킨의 전반기까지는 Fe-rich 단사회석, Fe-rich garnet와 함께 자철석·회중석이 연속적으로 정출되었으나, 후기스킨의 중기부터는 Ni, Co, As, Cu, Zn, Fe, Bi 등의 황화광물이 정출되는 다금속광화작용의 특징을 보인다. 또한, 최후기 열수작용시기에는 섬아연석과 방연석 등의 Base-metal 황화광물이 주로 정출되는 연·아연 광화작용의 양상을 나타낸다. 이러한 각 광화시기별 스킨 광물과 광석광물의 변화양상은 고온의 열수용액이 천부로 유출되는 과정에서 광화용액의 온도가 급격히 떨어진 결과 (telescope)에 기인된 것으로 사료된다.

