

## Mineralogy and Iron Chemistry of Garnets and Clinopyroxenes in the Skarn Deposits, the Hambaek Geosyncline Belt, Korea<sup>1)</sup>

咸白地向斜內的 스카른鑛床에서 產出되는 柎榴石과 單斜輝石의 鑛物學과 鐵化學

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**ABSTRACT:** In the southern limb of the Hambaek geosyncline belt, large-scaled skarn deposits are developed in the Cambro-Ordovician sedimentary rocks of the Chosun Supergroup. They are the Sangdong tungsten deposit, Geodo iron-copper deposit, Yeonhwa I and II lead-zinc deposits, and Ulchin zinc-lead deposit, all of which are associated with various skarn minerals. Though different occurrences and paragenesis are found in different deposits, most skarn deposits always have skarns of garnet (andradite-grossular series) and clinopyroxene (hedenbergite-diopside series). Andradite and hedenbergite are of Fe-dominant members, but show different oxidation states, that is, Fe<sup>3+</sup> for andradite and Fe<sup>2+</sup> for hedenbergite. According to iron chemistry and  $\log([Fe/Al]_{gr}/[Fe/Mg]_{cpx})$  derived from equilibrium reactions, the diopside-andradite and hedenbergite-grossular pairs suggest the oxidized state (dian type) and reduced state (hegro type), respectively.

Among skarn deposits developed in the Hambaek geosyncline, it can be classified that the Geodo and Yeonhwa I skarns are of dian type, while the Sangdong, Yeonhwa II, and Ulchin deposits are of hegro type. This classification is not applicable to all kinds of skarn deposits, but may be applicable to such deposits as are more controlled by oxygen fugacity than composition of skarn fluid.

**요약:** 강원도의 함백지향사 남익부에는 캄브로-오오도비스기의 조선계 퇴적암을 모암으로 하여 배태된 대규모의 스카른광상들이 발달하고 있다. 이들 스카른광상들은 상동W광상, 거도 Fe-Cu광상, 제 1 연화 및 제 2 연화 Pb-Zn광상, 그리고 울진 Zn-Pb광상들이 그것으로 다양한 스카른광물들을 수반하고 있다. 광상에 따라 수반광물들의 산출상태나 공생관계가 각기 다르게 나타나지만 이들 스카른광상들의 공통적인 특징으로 석류석(안드라다이트-그로슬라 계열)과 단사휘석(헤덴버자이트-투휘석 계열)이 가장 흔하게 산출되며 이들 두 광물들의 Fe단종인 안드라다이트와 헤덴버자이트는 각각 Fe<sup>3+</sup>와 Fe<sup>2+</sup>만으로 이루어진 서로 다른 이온상태를 보여준다. 또한 평형방정식으로 유도한  $\log([Fe/Al]_{gr}/[Fe/Mg]_{cpx})$ 의 값은 스카른광상을 분류하는 기준이 된다. 그 결과 석류석과 단사휘석 고용체의 Fe화학성분을 이용하여 Dian형(투휘석-안드라다이트형)과 Hegro형(헤덴버자이트-그로슬라형)으로 구분지을 수 있으며 각각 스카른생성의 산화환경과 환원환경을 지시해 주며 거도광상 및 제 1 연화광상은 Dian형으로 상동광상과 제 2 연화 및 울진광상은 Hegro형으로 분류되었다. 이러한 분류법은 모든 스카른광상에 적용되는 것은 아니나 광상생성시 광화용액의 조성보다 용액내의 산소분압이 더 큰 영향을 미치는 경우에는 좋은 분류기준으로 사용이 가능하다.

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## INTRODUCTION

In most skarn deposits, grandite garnet (grossular-andradite series) and clinopyroxene (diopside-hedenbergite series) are most abundant minerals. These two minerals show not only different spatial distribution, but also different stages in many different skarn deposits. For instance, Ca-garnet may be a predominant phase in some deposits, while clinopyroxene more predominant in other deposits. Likewise, Ca-garnet may be mainly developed during the primary stage in some deposits, while clinopyroxene during the secondary stage in other deposits. However, missing of either of two is scarcely observed in skarn deposits. Both minerals are also closely associated with other skarn minerals, such as wollastonite, calcic amphibole, epidote, calcite, and so on, as assemblages of one, several, or all of these combined in most skarn deposits.

In addition, Ca-garnets whose end members are andradite ( $\text{Ca}_3\text{Fe}_2\text{Si}_3\text{O}_{12}$ ) and grossular ( $\text{Ca}_3\text{Al}_2\text{Si}_3\text{O}_{12}$ ) ideally contain trivalent cations in octahedral site, whereas clinopyroxene whose end members are hedenbergite ( $\text{CaFeSi}_2\text{O}_6$ ) and diopside ( $\text{CaMgSi}_2\text{O}_6$ ) contains divalent cations in octahedral site. Each of the Fe-dominant members has ideally  $\text{Fe}^{3+}$  for andradite and  $\text{Fe}^{2+}$  for hedenbergite in its octahedral site. Although skarns cannot be uniquely characterized by their garnet and clinopyroxene compositions by themselves, the association of garnet and clinopyroxene or compositional characters of both minerals in a certain skarn deposit yield a relatively unique features which can serve as an aid in classification and defining the environments of skarn formation.

Several important skarn deposits are developed in the southern limb of the Hambaek geosynclinal basin, where the huge Cambro-Ordovician carbonate sedimentary rocks are deposited. These skarn deposits are the Sangdong tungsten deposit, Geodo iron deposit, Yeonhwa I and II lead-zinc deposits, and Ulchin zinc-lead deposit listing from west to east. Using Ca-garnet and clinopyroxene from the above four deposits, the authors attempted not only to compare their

chemical compositions with one another, but to figure out the characteristic features with respect to their environments of skarn formation. From this study, it could be possible to classify skarn deposits into two different types.

## OXIDATION STATE OF IRON IN GARNET AND CLINOPYROXENE

General chemistry of garnets and pyroxenes are summarized in Table 1, which shows the ideal chemistry of grandite (grossular-andradite series) and clinopyroxene (diopside-hedenbergite series). Garnet and clinopyroxene have their Fe end members, that is, andradite and hedenbergite whose octahedral cations are composed of all ideally ferric ( $\text{Fe}^{3+}$ ) and ferrous ( $\text{Fe}^{2+}$ ), respectively. A simple question comes at this point, that is, "Are they really composed of single state such as  $\text{Fe}^{3+}$  alone or  $\text{Fe}^{2+}$  alone in the natural system?" If the answer is "yes", it is simple to derive the significance of grandite and clinopyroxene chemistry and easy to conclude that either of two represent unique ionic state, that is, grandite as oxidized state ( $\text{Fe}^{3+}$ ) and clinopyroxene as reduced one ( $\text{Fe}^{2+}$ ). On the other hand, if the answer is negative, the next question follows as "What amounts of the other ionic state, such as  $\text{Fe}^{2+}$  in grandite and  $\text{Fe}^{3+}$  in clinopyroxene, exists in either of two?" In order to know the oxidation state and/or  $\text{Fe}^{2+}/\text{Fe}^{3+}$  ratios, and to determine site occupancies of Fe cation in different structural sites, the Mössbauer spectral analysis has recently been applied (Burns, 1972; Bancroft, 1973; Marfunin, 1979; 1979; Kim *et al.*, 1988)

### Garnet

As mentioned already, grandite is characterized by single ionic state of  $\text{Fe}^{3+}$  occupying the octahedral Y-site in andradite-grossular series. Although the Y-site is relatively small enough to admit the trivalent cations such as  $\text{Fe}^{3+}$ , Al, Ti, and Cr, divalent cations such as  $\text{Fe}^{2+}$  may possibly occupy either Y-site or dodecahedral X-site, or even both sites. Among natural garnets, the

**Table 1.** Chemistry and nomenclature of garnets and pyroxenes.

Garnets*	Pyroxenes**
$X_3Y_2Z_3O_{12}$ X=Ca, Mg, Fe <sup>2+</sup> , Mn Y=Fe <sup>3+</sup> , Al, Cr, Ti Z=Si, Al	$XYZ_2O_6$ X=Mg, Fe <sup>2+</sup> , Mn, Li, Ca, Na Y=Al, Fe <sup>3+</sup> , Ti, Mg, Fe <sup>2+</sup> , Mn Z=Si, Al
<u>Pyralspite:</u> Pyrope Mg <sub>3</sub> Al <sub>2</sub> (SiO <sub>4</sub> ) <sub>3</sub> Almandine Fe <sub>3</sub> Al <sub>2</sub> (SiO <sub>4</sub> ) <sub>3</sub> Spessartine Mn <sub>3</sub> Al <sub>2</sub> (SiO <sub>4</sub> ) <sub>3</sub>	<u>Magnesium-Iron Pyroxenes:</u> Enstatite Mg <sub>2</sub> Si <sub>2</sub> O <sub>6</sub> Ferrosilite Fe <sub>2</sub> Si <sub>2</sub> O <sub>6</sub>
<u>Ugrandite:</u> Uvarovite Ca <sub>3</sub> Cr <sub>2</sub> (SiO <sub>4</sub> ) <sub>3</sub> Grossular Ca <sub>3</sub> Al <sub>2</sub> (SiO <sub>4</sub> ) <sub>3</sub> Andradite Ca <sub>3</sub> Fe <sub>2</sub> (SiO <sub>4</sub> ) <sub>3</sub>	<u>Calcium Pyroxenes:</u> Diopside CaMgSi <sub>2</sub> O <sub>6</sub> Hedenbergite CaFeSi <sub>2</sub> O <sub>6</sub> Johannsenite CaMnSi <sub>2</sub> O <sub>6</sub>
	<u>Calcium-Sodium Pyroxenes:</u> Omphacite, Aegirine-augite
	<u>Sodium Pyroxene:</u> Jadeite, Acmite, Ureyite
	<u>Lithium Pyroxenes:</u> Spodumene
<u>Ca-garnets (grandite)</u> Andradite-Grossular series Ca <sub>3</sub> (Fe <sup>3+</sup> , Al) <sub>2</sub> Si <sub>3</sub> O <sub>12</sub>	<u>Clinopyroxenes (cpx)</u> Hedenbergite-Diopside series Ca(Fe <sup>2+</sup> , Mg)Si <sub>2</sub> O <sub>6</sub>

\* nomenclature after Winchell (1933)

\*\* nomenclature after Deer *et al.*, (1978)

pyralspite group showing the complete solid solution series clearly have the Fe<sup>2+</sup> cations in X-site (Table 1). However, compositional gap exists between the pyralspite and ugrandite group (Meagher, 1980). This fact suggests that only a single substitution occurs within either of X- or Y-sites alone in natural common garnets. The substitution in grandites, therefore, occurs in Y-site alone. This is strongly supported by the Mössbauer spectral study (Choi, 1989).

The Mössbauer spectroscopy of grandite shows clearly the distribution of Fe<sup>3+</sup> and/or Fe<sup>2+</sup> in crystallographic sites. Mössbauer spectra and calculated parameters are obtained from grandites ranging from 18 to 98% Ad (Choi, 1989). It is recognized that all grandites exhibit substitution in Y-site only. Although Fe<sup>2+</sup> cations in the pyralspite group generally occupy X-site, small amounts of Fe<sup>2+</sup> in grossular occupy X-site. Moreover, one grossular containing small amounts of Fe (18% Ad) have Fe<sup>2+</sup>, whereas the other three andradites have no evidence for Fe<sup>2+</sup>.

This may suggest that grossular formed in the relatively reduced environment. From these several facts, it can be concluded that Fe cations in grandite consists mostly of Fe<sup>3+</sup> cations and only small amounts of Fe<sup>2+</sup> cations are present in grossular. Therefore grandite can be represented as a mineral of the oxidized ionic state.

### Clinopyroxene

Site populations of Fe cations in clinopyroxene are somewhat complicated, compared to those of grandite. As shown in Table 1, general substitution scheme exhibits the presence of both Fe<sup>2+</sup> and Fe<sup>3+</sup> in two octahedral sites of X and Y. These X- and Y-site, as crystal chemical terms, are referred to M2 and M1 sites, respectively. M2 site is represented as relatively bigger size, while M1 as smaller one. Since M1 and M2 sites of orthopyroxenes are similar in size (mean M1-O=2.11Å)(Table 2), both positions are occupied by Mg and Fe<sup>2+</sup> cations at a certain proportion. On

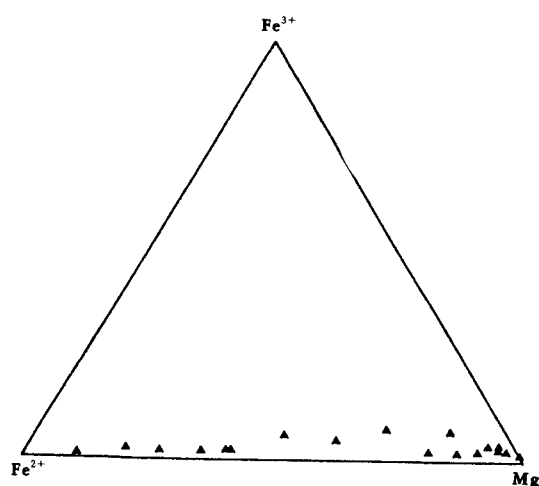
**Table 2.** Mean metal-oxygen distance(Å) of pyroxenes.

	M1 cation	mean M1-O	M2 cation	mean M2-O	Reference
<b>Orthopyroxene</b>					
enstatite	Mg	2.076	Mg	2.149	Hawthorne & Ito (1977)
forrosilite	Fe <sup>2+</sup>	2.135	Fe <sup>2+</sup>	2.228	Sueno <i>et al.</i> (1976)
<b>Clinopyroxene</b>					
diopside	Mg	2.077	Ca	2.498	Clark <i>et al.</i> (1969)
hedenbergite	Fe <sup>2+</sup>	2.130	Ca	2.511	Cameron <i>et al.</i> (1973)

the other hand, clinopyroxenes show relatively confined substitution scheme of Mg and Fe<sup>2+</sup> mostly found in M1 sites, while M2 site is occupied by bigger cation of Ca without or little Na. Because the gap between the sizes of two positions is much significant (mean M1-O=2.10Å; mean M2-O=2.51Å) (Table 2), the smaller cations of Fe<sup>2+</sup> and Mg are more preferable to M1 and the bigger Ca to M2. The residual site of M2 is filled with smaller Fe<sup>2+</sup> and Mg, while the residual M1 with Mn, Fe<sup>3+</sup>, Al or Ti. This fact is supported by Mössbauer spectral study (Bancroft and Williams, 1971) of which clinopyroxene exhibits all single doublet of Fe<sup>2+</sup>, assigned to M1 position. Only one spectrum from most Fe-rich specimen shows an additional small doublet, assigned to M2 position also occupied by Fe<sup>2+</sup>.

As shown in Table 1, clinopyroxene contains ideally Fe<sup>2+</sup> as a single ionic occupying M1 site. According to Mössbauer study (Bancroft and Williams, 1971), there is no direct evidence for the presence of Fe<sup>3+</sup> cations in diopside-hedenbergite series. In spite of this fact, small amounts of Fe<sup>3+</sup> may exist in the natural clinopyroxene. The problems are what amounts of Fe<sup>3+</sup> exist in clinopyroxene and whether Fe<sup>3+</sup>/Fe<sup>2+</sup> ratios may be or not related with the compositional variations in clinopyroxene. Since the separate analyses of Fe<sup>2+</sup> and Fe<sup>3+</sup> are possible by wet analyses, the recent instrumental methods are not valid any more. Fortunately, a lot of clinopyroxene analyses obtained by wet method become available to the authors. Deer *et al.* (1978) collected numerous clinopyroxene data from all over the world. Using their data, selected skarn-origin clinopyroxenes are plotted in Figs. 1 and 2. As shown in Fig. 1, triangular diagram shows that most clinopyroxenes

contain relatively small amounts of Fe<sup>3+</sup> and Mg-rich clinopyroxene (diopside) contains more Fe<sup>3+</sup> cations than Fe-rich clinopyroxene (hedenberite). This fact is even clear in Fig. 2 that the ratios of Fe<sup>3+</sup>/total Fe drastically increase as the Mg contents in clinopyroxene increase. This diagram indicates that Fe-rich clinopyroxenes contain almost all of Fe<sup>2+</sup>, while Fe-poor clinopyroxenes contain relatively significant amounts of Fe<sup>3+</sup>. This may suggest that the latter formed at the relatively oxidized environment. It is concluded from the above several facts that the ionic state of Fe exists as Fe<sup>2+</sup> in most clinopyroxenes and small Fe<sup>3+</sup> can be present at the Fe-poor ones. Therefore, clinopyroxene can be represented as the mineral of the reduced ionic state.

**Fig. 1.** Triangular diagram of Fe<sup>3+</sup>-Fe<sup>2+</sup>-Mg components showing compositions of hedenbergite-diopside series.

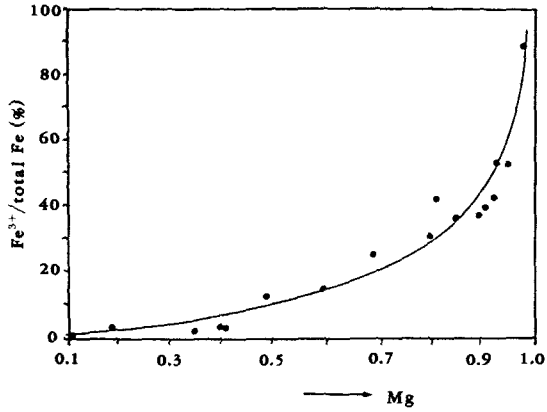


Fig. 2. The variation diagram showing the ratios of  $\text{Fe}^{3+}/\text{total Fe}$  in hedenbergite–diopside series.

### CHEMICAL RELATIONSHIP BETWEEN GARNET AND CLINOPYROXENE

Chemical compositions of garnets and clinopyroxenes obtained from the Sangdong tungsten deposit (some are from Moon, 1983 and Chang, 1988), Geodo iron-copper deposit, Yeonhwa I, II, and Ulchin lead-zinc deposits (some are from Yun, 1978) are plotted in Fig 3A to C, respectively.

Compositional distribution of both minerals in the Sangdong tungsten deposit (Fig. 3A) indicates that clinopyroxenes from the Main ore bed are rich in Fe (more than 60% Hd) and some clinopyroxenes from the Hangingwall ore bed are rich in Mg (diopside). Grandite from the Main ore bed are rich in Al (more than 50% Gr). In the Sangdong deposit, tungsten ores are generally enriched in the Main ore bed (Moon, 1983; Chang, 1988). Therefore, it can be said that chemical compositions of coexisting grossular and hedenbergite in the Main ore bed strongly implies that the Sangdong deposit is of “reduced” skarn type.

Contrary to the Sangdong deposit, the compositional distribution of garnets and clinopyroxenes in the Geodo deposit (Fig. 3B) shows that garnets have the Fe in the range from 50 to 80% except few analyses (less than 50% Ad) from scapolite-bearing assemblage and that clinopyroxenes are poor in Fe (more than 70% Di). According to earlier study (Choi, 1989), clinopyroxenes in close

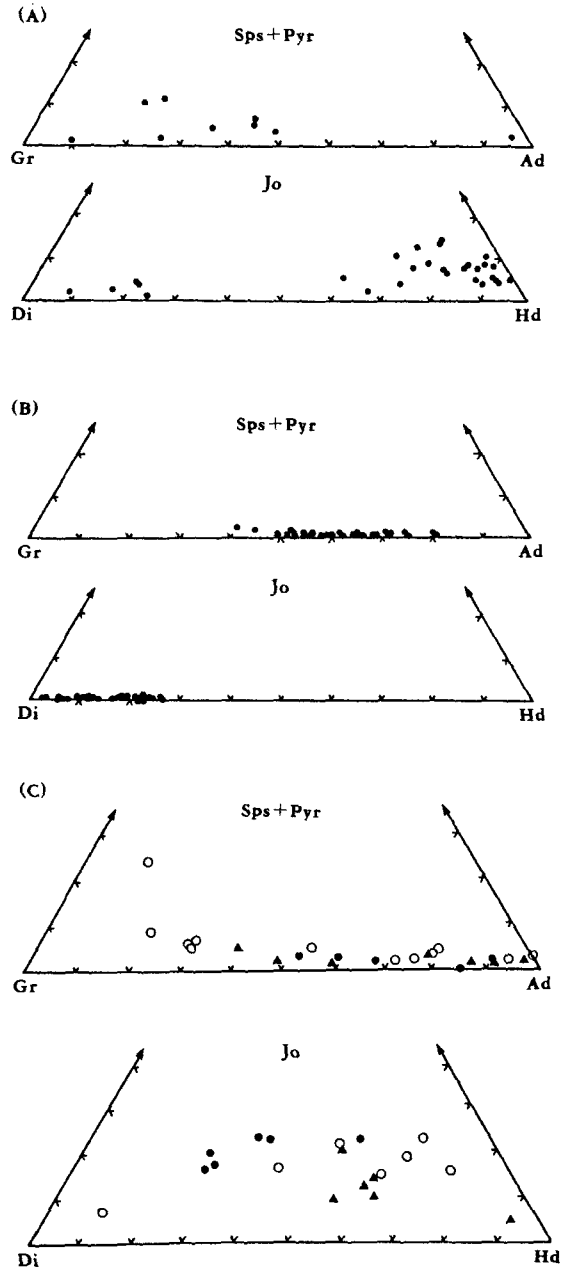


Fig. 3. Compositional distribution of garnet and clinopyroxene plotted on the triangular diagrams of grossular (Gr), andradite (Ad), and spessartine-pyropite (Sps+Pyr) and of diopside (Di), hedenbergite (Hd), and johansenite (Jo) components. A: Sangdong tungsten deposit, B: Geodo iron-copper deposit, C: Yeonhwa I (solid circles), Yeonhwa II (open circles), and Ulchin (triangles) lead-zinc deposits.

association with Fe ores consist of nearly end member diopside. It can, therefore, be said that chemical compositions of the coexisting andradite and diopside strongly imply that the Geodo iron deposit is of "oxidized" skarn type.

In the Yeonhwa I, II, and Ulchin lead-zinc deposits, minerals are characterized by the irregular and wide range of compositional distribution and relatively high Mn contents in clinopyroxenes (up to 27% Jo) (Fig. 3C). In the Yeonhwa I deposit (solid circles in Fig. 3C) garnets are plotted in Fe-rich field and clinopyroxenes in Mg-rich field. In the Yeonhwa II and Ulchin deposits (open circles and triangles, respectively in Fig. 3C) both minerals show broad-range scattering. However, a careful observation may lead us to recognition that garnets are relatively more concentrated in the Al-rich range and clinopyroxenes in Fe-rich range. Though these deposits do not clearly exhibit the preference to either of grossular-hedenbergite or andradite-diopside pair, it may be said that Yeonhwa I deposit is close to the type of andradite-grossular type indicative of the oxidized environment, whereas Yeonhwa II and Ulchin deposits close to that of the grossular-hedenbergite type indicative of reduced environment.

## EQUILIBRIUM OF GARNETS AND CLINOPYROXENES

As mentioned already, both garnet and clinopyroxene show their characteristic features in terms of ionic state of iron. The association pairs of grossular-hedenbergite and andradite-hedenbergite can be referred to as reduced skarns and oxidized skarns, respectively. If these two minerals are formed under equilibrium in a certain skarn deposits, the association pairs can be used for environmental characterization of skarn deposits. In other words, such a close association makes it possible to answer the question such as "What kind of factor may play the more important role in the formation of a certain skarn deposit?" In order to understand this, some equilibrium reactions in which both garnet and clinopyroxene participate should be considered and

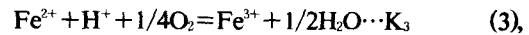
the result can be applied to characterize the skarn deposits.

## Equilibrium Reactions

According to Sasaki and Shoji (1981), the equilibrium reaction of substitution between ferric and Al ions in between garnet (gd) and skarn-fluid (herein called simply to fluid) and another reaction of substitution between ferrous and Mg ions in between clinopyroxene (cpx) and fluid are, respectively, given as



and oxidation reaction of ferrous to ferric ions in the fluid is



where  $K_1$ ,  $K_2$ , and  $K_3$  indicate equilibrium constants of equation (1), (2) and (3), respectively. If the fluid is assumed as an ideal solution, three equations above can be deduced as

$$\begin{aligned} & \log\left(\frac{[\text{Fe}/\text{Al}]_{\text{rd}}}{[\text{Fe}/\text{Mg}]_{\text{cpx}}}\right) \\ &= \log[\text{Fe}/\text{Al}]_{\text{rd}} - \log[\text{Fe}/\text{Mg}]_{\text{cpx}} \\ &= \{\log K_1 - \log K_2 + \log K_3 - 1/2 \log f_{\text{H}_2\text{O}} + \\ & \quad \log[\text{H}^+]_{\text{aq}}\} - \log[\text{Al}^{3+}/\text{Mg}^{2+}]_{\text{aq}} + 1/4 \log f_{\text{O}_2} \quad (4), \end{aligned}$$

where  $[\text{Fe}/\text{Al}]_{\text{rd}}$  and  $[\text{Fe}/\text{Mg}]_{\text{cpx}}$  indicate concentration ratio of ferric cation and aluminum in garnet and of ferrous cation and magnesium in clinopyroxene, respectively and  $f_{\text{H}_2\text{O}}$ ,  $[\text{H}^+]_{\text{aq}}$ ,  $[\text{Al}^{3+}/\text{Mg}^{2+}]_{\text{aq}}$ , and  $f_{\text{O}_2}$  are water fugacity, pH, concentration ratio of aluminum and magnesium ions, and oxygen fugacity, respectively, all in fluid. The left-handed side of equation (4),  $\log\left(\frac{[\text{Fe}/\text{Al}]_{\text{rd}}}{[\text{Fe}/\text{Mg}]_{\text{cpx}}}\right)$ , indicates the relative iron concentration ratio between garnet and clinopyroxene. Thus, iron becomes enriched relatively in garnet, if the ratio is big and contrarily, iron relatively in clinopyroxene, if the ratio is small.

From the equation (4), it can be considered that skarns are generally formed under the given temperature and pressure which are regarded as constant, so equilibrium constants  $K_1$ ,  $K_2$ , and  $K_3$  remain constant in such conditions. In addition,

the effect of pH is assumed to be small enough to be ignored and it is known that main constituent of skarn-forming fluid is water (Shoji, 1978). Therefore, several factors in braces of equation (4) can be considered as constants with certain given values. In such case, the value of  $\log ([\text{Fe}/\text{Al}]_{\text{rd}}/[\text{Fe}/\text{Mg}]_{\text{cpx}})$  wholly depends on two factors of concentration ratio of aluminum and magnesium ions in fluid and oxygen fugacity. In other words, the relationship of oxidation state between garnet and clinopyroxene is the function of both Al/Mg ratio (actually, change in relative ratio of Al/Mg in fluid corresponds to change in relative  $\text{Fe}^{3+}/\text{Fe}^{2+}$  ratio or Fe contents in fluid) and oxygen fugacity in skarn-forming fluids. As far as co-existing garnet and clinopyroxene are considered, either of two factors or both may play more important role in skarn formation.

#### Importance of Iron Chemistry in Skarn Deposits

The relationship between oxidation states of garnet and clinopyroxene is illustrated in the diagram of  $\log [\text{Fe}/\text{Al}]_{\text{rd}}-\log [\text{Fe}/\text{Mg}]_{\text{cpx}}$  plot as shown in Fig. 4 which is based on the equation (4). In Fig. 4, the dotted line indicates that the value of the left-handed side  $\log ([\text{Fe}/\text{Al}]_{\text{rd}}/[\text{Fe}/\text{Mg}]_{\text{cpx}})$  of equation (4) is equal. This diagram exhibits that the trend with positive slope indicates iron enrichment of both coexisting garnet and clinopyroxene (e.g., Ad content in garnet increases as Hd content increases.). In this case, the skarn formation is controlled by the chemical compositions of fluid (e.g.,  $\log [\text{Al}^{3+}/\text{Mg}^{2+}]$ ) rather than oxygen fugacity which is considered more or less as constant. On the contrary, the negative trend indicates that Fe content of one mineral increases, while that of the other decreases. The negative trend, therefore, can support the fact that skarns are controlled more severely by oxygen fugacity.

Coexisting garnet and clinopyroxene from four skarn deposits are plotted in this diagram (Fig. 4). Compositional distribution in Fig 4 has two characteristic features. First, chemical compositions of coexisting both minerals in the Sangdong deposit (open circles) are characterized by low values of  $\log [\text{Fe}/\text{Al}]_{\text{rd}}$  (-0.6 to 0) and the

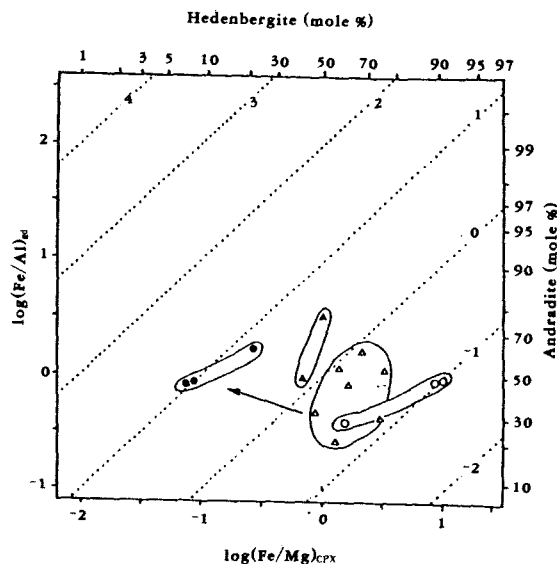


Fig. 4. A  $\log [\text{Fe}/\text{Al}]_{\text{rd}}$  vs.  $\log [\text{Fe}/\text{Mg}]_{\text{cpx}}$  plot of coexisting grandites (gd) and clinopyroxenes (cpx). Dotted line indicates that the value of  $\log ([\text{Fe}/\text{Al}]_{\text{rd}}/[\text{Fe}/\text{Mg}]_{\text{cpx}})$  is equal. Arrow represents the general trend with a negative slope, indicating significant effect of oxygen fugacity on the skarn deposits in the Hambaek geosyncline belt. (open circles: Sangdong, solid circles: Geodo, solid triangles: Yeonhwa I, and open triangles: Yeonhwa II and Ulchin)

highest values of  $\log [\text{Fe}/\text{Mg}]_{\text{cpx}}$  (0.2 to 1.0), indicating reduced state. Those in the Geodo deposit (solid circles), on the other hand, shows relatively high  $\log [\text{Fe}/\text{Al}]_{\text{rd}}$  (0 to 0.3) and the lowest  $\log [\text{Fe}/\text{Mg}]_{\text{cpx}}$  (-1.2 to 0.5), indicating oxidized state. In the Yeonhwa I (solid triangles), values of  $\log [\text{Fe}/\text{Al}]_{\text{rd}}$  are high (0 to 0.6) and those of  $\log [\text{Fe}/\text{Mg}]_{\text{cpx}}$  are slightly low (a little less than 0), implying somewhat oxidized state. The values of  $\log [\text{Fe}/\text{Al}]_{\text{rd}}$  and  $\log [\text{Fe}/\text{Mg}]_{\text{cpx}}$  in the Yeonhwa II and Ulchin deposits (open triangles) are in the range from -0.9 to 0.2 from -0.1 to 0.5, respectively, seemed to be close to reduced state. The compositional distribution for four skarn deposits shows the trend with negative slope (arrow shown in Fig. 4) from the Sangdong, through Yeonhwa II and Ulchin, Yeonhwa I, to Geodo deposits, suggesting the gradual change of skarn environment from the reduced to oxidized state. Therefore, skarn deposits developed along the southern limb

of the Hambaek geosyncline belt might have been formed under the control of the oxygen fugacity increased from the Sangdong to Ulchin deposits eastward.

Second, the compositional variation in each deposit shows positive trend. The fact indicates that skarns are also controlled by the chemical composition of fluid.

Based on the above two facts, it can be concluded that a certain skarn deposit is developed under the influence of given oxygen fugacity determining the oxidation state (e. g., the value of  $\log ([\text{Fe}/\text{Al}]_{\text{gr}}/[\text{Fe}/\text{Mg}]_{\text{cpx}})$  becomes nearly fixed in this state) as well as the compositions of fluid.

## DISCUSSION

In the skarn deposits, the chemical compositions of coexisting garnet and clinopyroxene makes it possible to group the skarn minerals into two paragenetic types; 1) diopside-andradite type and 2) hedenbergite-grossular type. These two types occur as different oxidation states. For the convenience's sake, the coexisting pair of diopside-andradite is abbreviated to "dian" and the of hedenbergite-grossular to "hegro". The dian type represents the oxidized state and the hegro the reduced state. The detailed comparison between the dian and hegro types are summarized in Table 3.

As shown in Table 3, the skarn deposits such as Geodo and Yeonhwa I belong to the dian type. In the United State, the Yerington Cu-Fe deposit in Nevada (Harris and Einaudi, 1982)

shows good correlation to the Geodo Fe-Cu deposit. Skarn formation in Yerington is divided into two stages. Early skarnoid stage is characterized by massive fine-grained grandite garnet and subordinate clinopyroxene. Late metasomatic stage is characterized by extensive formation of clinopyroxene and coarse-grained garnet skarns. Iron contents are high in garnet (most 60-90% Ad) and very low in clinopyroxene (0-30% Hd) in the early stage, which can be classified as a typical dian type. Iron contents somewhat vary in the late stage due to intense formation of alteration zone. However, irons in clinopyroxene decrease from 45% to 0% toward intrusive body, whereas those in garnet remain constant in the range of 45-75%. This fact may suggest that it be the dian type, too. As a whole, Yerington skarns were formed under oxidized environment. Cananea skarn deposit in Mexico (Meinert, 1982) shows iron chemistry of garnet (47-100% Ad) and clinopyroxene (3-42% Hd), suggesting the dian type.

On the other hand, skarn deposits such as Sangdong, Yeonhwa II and Ulchin have characteristic iron chemistry suggesting the hegro type. In general, tungsten skarn deposits are known as reduced type as in the Sangdong deposit. Mactung W deposit (Yukon-N. W. T.) in Canada is of typical hegro type, showing Fe-poor garnet (2-20% Ad) and Fe-rich pyroxene (44-91% Hd) (Dick and Hodgson, 1982). Pine Creek W deposit in California is another example of hegro type (Newberry, 1982).

In this study, the authors tried to classify the

Table 3. Comparison of paragenetic type of grandite and cpx.

	Dian type	Hegro type
Grandite	andradite	grossular
Clinopyroxene	diopside	hedenbergite
Composition in grandite	Fe <sup>3+</sup> rich/Al poor	Al rich/Fe <sup>3+</sup> poor
cpx	Mg rich/Fe <sup>2+</sup> poor	Fe <sup>2+</sup> rich/Mg poor
Environment	oxidized	reduced
Skarn deposits	Geodo, Yeonhwa I Cananea in Mexico Yerington in Nevada	Sangdong, Yeonhwa II and Ulchin, Mactung in Canada Pine Creek in California

Cananea, Mexico (Meinert, 1982); Yerington, Nevada (Harris and Einaudi, 1982); Mactung, Canada (Dick and Hodgson, 1982); Pine Creek, California (Newberry, 1982)



skarn deposits into dian and hegro types using skarn dominant minerals of grandite garnet and clinopyroxene, leading to appropriate outcome. However, this is not applied to all skarn deposits. For instance, the Shasta magnetite deposit in northern Vancouver, Canada (Haug, 1976) has both iron-rich garnet (68-100% An) and clinopyroxene (79-96% Hd) and the Strawberry tungsten deposit in California (Nockleberg, 1981) has no typical trend (An: 31-64%; Hd: 29-80%). As a conclusion, it can be said that this classification is not applicable to all kinds of skarn deposits, but may be applicable to such deposits as are more controlled by oxygen fugacity than composition of skarn-forming fluids.

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