Mineralogy of Clinopyroxene from the Geodo Mine

巨道鑛山의 單斜輝石에 關한 鑛物學的 研究

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ABSTRACT: Clinopyroxene in the Geodo mine belongs to diopside-hedenbergite series. It is widely distributed throughout the mine area together with garnet and is also closely related with Fe-mineralization. Clinopyroxenes in the Geodo mine including two samples from the Sangdong and Ulchin mines are studied using polarized microscope, EPMA, XRD, and IR spectroscopy for occurrence, chemistry, structure, and crystal chemistry. Especially, variations in unit-cell parameters are examined in relation with the substitution scheme between Fe and Mg cations.

Clinopyroxenes in the Geodo mine occur in both endoskarn and exoskarn zone. It is mostly anhedral to subhedral with fine- to medium-grained in texture, but some have bigger crystals of short prismatic or columnar habits. Clinopyroxene occurs as monomineralic or is associated with mostly garnet and sometimes with Actinolite, magnetite, epidote, and chlorite. Chemical analysis reveals that the Geodo clinopyroxene is diopsidic in composition (Di: 65-96%). This fact is in good contrast with garnet chemistry showing mostly andraditic (An: 41-82%). Especially, clinopyroxene coexisting with magnetite belongs to nearly end member diopside (Di: 97-99%). Thus, diopside-andradite pair indicates that Geodo skarns were formed under the reduced environment.

X-ray diffraction analysis shows unit-cell parameters vary with increase of Fe contents: $a = 9.765-9.838\text{Å}$, $b = 8.943-9.020\text{Å}$, $c = 5.240-5.253\text{Å}$, $\beta = 105.70-104.83°$, and $V = 440.64-448.19\text{Å}^3$. It is noted from the least square regression that a, b, and V increase linearly with increase of Fe content, while β slightly decreases and c remains nearly unchanged as change in Fe content. These trends are nearly well-matched with the synthetic data. However, some difference in coefficients ascribes mainly to difference between synthetic and natural clinopyroxenes. This fact is also recognized in IR spectra which show a slight shift of several absorption bands toward lower wavenumber region with increasing Fe content.

요약 : 巨道鑛山의 單斜輝石은 透輝石 – 헤덴버가이트를 端種으로 완전한 고용체를 이루며 스카른 광물로써 석류석과 더불어 鑛山地域을 通하여 가장 흔하게 産出되며 鐵鑛化作用과도 밀접히 관련되어 있다. 상동과 울진광산에서 産出되는 단사휘석을 包含하여 거도광산의 단사휘석들에 대하여 偏光顯微鏡, 電子顯微分析, X-線 回折分析 및 赤外線分光分析 등을 실시하여 산출상태와 화학적, 구조적 및 결정화학적 특징을 研究하였으며 특히, Fe와 Mg의 치환에 따르는 單位胞의 格子常數들의 변화를 고찰하였다.

巨道鑛山의 單斜輝石은 內成 및 外成 스카른帶에서 각각 다른 共生關係를 보여주는데, 대부분이 半自形 내지 他形의 微粒 내지 中粒으로 單·鑛物로 産出되거나, 또는 주로 석류석과 일부는 陽起石, 磁鐵石, 녹염석 및 綠泥石 등과 隨伴되어 産出된다. 일부 큰 結晶은 좁은 板狀이나 柱狀의 形態를 보여 주기도 한다. 電子顯微鏡分析에 의하면, 巨道 單斜輝石은 Mg가 豊富한 透輝石(Di:65~96%)系列로써 주로 함께 隨伴되는 석류석이 Fe가 豊富한 안드라다이트(An: 41~82%) 系列인 것과 좋은 대조를 이룬다. 특히 鐵鑛石과 隨伴되는 單斜輝石은 Fe가 거의 없는 端種成分의 透輝石(Di: 97~99%) 組成을 보여 준다. 따라서 투휘석 – 안드라다이트 共生관계는 이들 광물이 각각 Fe^{2+}-poor 및 Fe^{2+}-rich 組成을 나타내며 巨道鑛山의 스카른化 作用이 還元環境 下에서 이루어졌음을 指示해 준다.

透輝石 – 헤덴버가이트 系列의 全範圍에 걸친 單斜輝石에 관한 X-線 回折分析은 單斜輝石의 單位胞 係數들은 共間群 C2/c의 對稱을 갖는 單斜晶系를 根據로 a=9.765~9.838Å, b=8.943~9.020Å, c

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=5.240~5.253Å, β =105.70~104.83Å, V=440.64~448.19Å³ 等의 範圍를 갖으며, 일정하게 변함을 보여주는데, a, b軸 및 V(체적) 값은 增加하며 c軸 값은 거의 變化가 없으며, 反對로 角β 의 크기는 減少하며 그 傾向이 헤덴버가이트 含量이 增加할수록 커진다. 이와 같은 變化는 合成 單斜輝石의 그 것들(Rutstein and Yund, 1969)과 比較할 때 거의 같은 結果를 보여주나, 增減의 기울기에 다소 差異가 있다. 또한, 單位胞 계수들의 變化現像은 赤外線分光分析에서 赤外線吸受帶의 위치가 일정하게 변하는 것으로 觀察된다.

INTRODUCTION

Clinopyroxene with the general formula $M2M1T_2O_6$ is one of the most important rock-forming minerals and occurs as a stable phase in almost every type of igneous rocks of ultrabasic to acidic in silica ranges, regional and thermal metamorphic rocks, and skarns (Deer *et al.*, 1978). When the structural formula of pyroxene is considered, it is easily found that there are two octahedral sites of M1 and M2. Each site is very suitable for a wide range of cation substitution alone or combined together. This results in large varieties of species with different physical and chemical properties and even changes in the different crystal systems as well as symmetries.

According to the pyroxene nomenclature scheme (Poldervaart and Hess, 1951; Morimoto *et al.*, 1988), clinopyroxene found in the Geodo mine belongs to the calcic pyroxenes with Ca occupation in more than two third of the M2 sites. It shows the complete solid solution series between diopside (Di, $CaMgSi_2O_6$) and hedenbergite (Hd, $CaFeSi_2O_6$). The chemical analysis reveals that the Geodo clinopyroxene shows Mg-rich diopside (Di_{65}-Di_{96}) in composition with a little or less than 3 mole% of johannsenite ($CaMnSi_2O_6$).

The structure of clinopyroxene has been known as the monoclinic system with a space group C2/c and classified as the single chain silicate of inosilicates. In spite of 'simple-looking' (actually not simple itself), chemistry of clino-pyroxene showing the simple substitution between Mg and Fe^{2+}, wide occurrences, and somewhat complicated crystal structure have driven a lot of scientists to investigate clinopyroxene in many different points of view. However, clinopyroxenes from the skarn deposits have surprisingly been received poor consideration, especially about their crystal chemistry.

As found in the granet mineralogy (Kim *et al.*, 1988: Choi, 1989), clinopyroxene is closely associated with garnet in most skarn deposits. Since these two minerals contain different Fe ionic state, that is, Fe^{3+} in andradite and Fe^{2+} in hedenbergite, the association of both minerals is surely good object to understand oxygen fuga-city, one of the controlling factors over the skarnizing environment or at least to approach the answer whether the oxygen fugacity may be the main controlling factor or not.

In this work, the authors examine occurrence, structure, and crystal chemistry of clinopyroxene in the Geodo mine. This study, especially, aims to discuss the variation of unit-cell parameters with respect to substitution scheme between Mg and Fe^{2+} in natural clinopyroxene which are compared with the variations found in synthetic ones (Rutstein and Yund, 1969).

OCCURRENCES

The clinopyroxenes in the Geodo mine belong to diopside-hedenbergite series. They occur in both endoskarn and exoskarn zones. Clinopyroxene is mostly anhedral to subhedral with fine- to medium-grained in texture, but some have more and less bigger crystals of short prismatic or columnar habits. Clinopyroxene usually occurs as monomineralic or is associated with mostly garnet and sometimes calcic amphibole, magnetite, epidote, and chlorite.

In the endoskarn zone of the Jangsan and Taebaek adits in the Myobong Formation, clino-pyroxene replaces mainly plagioclase (Fig. 1A), showing pseudomorphic texture of albite twin, and partly replaces hornblende or biotite. This clinopyroxene is gradually replaced by isotropic garnet.

In the Myobong and Hwajeol Formations, clinopyroxene in the early exoskarn stage occurs as monomineralic showing anhedral to subhedral and fine- to medium-grained in texture, or is associated with anisotropic garnet. In the Hwajeol Formation of the northern part of the Geodo mine, clinopyroxene occurs together with scapolite crystals in association with plagio-clase and calcic amphibole.
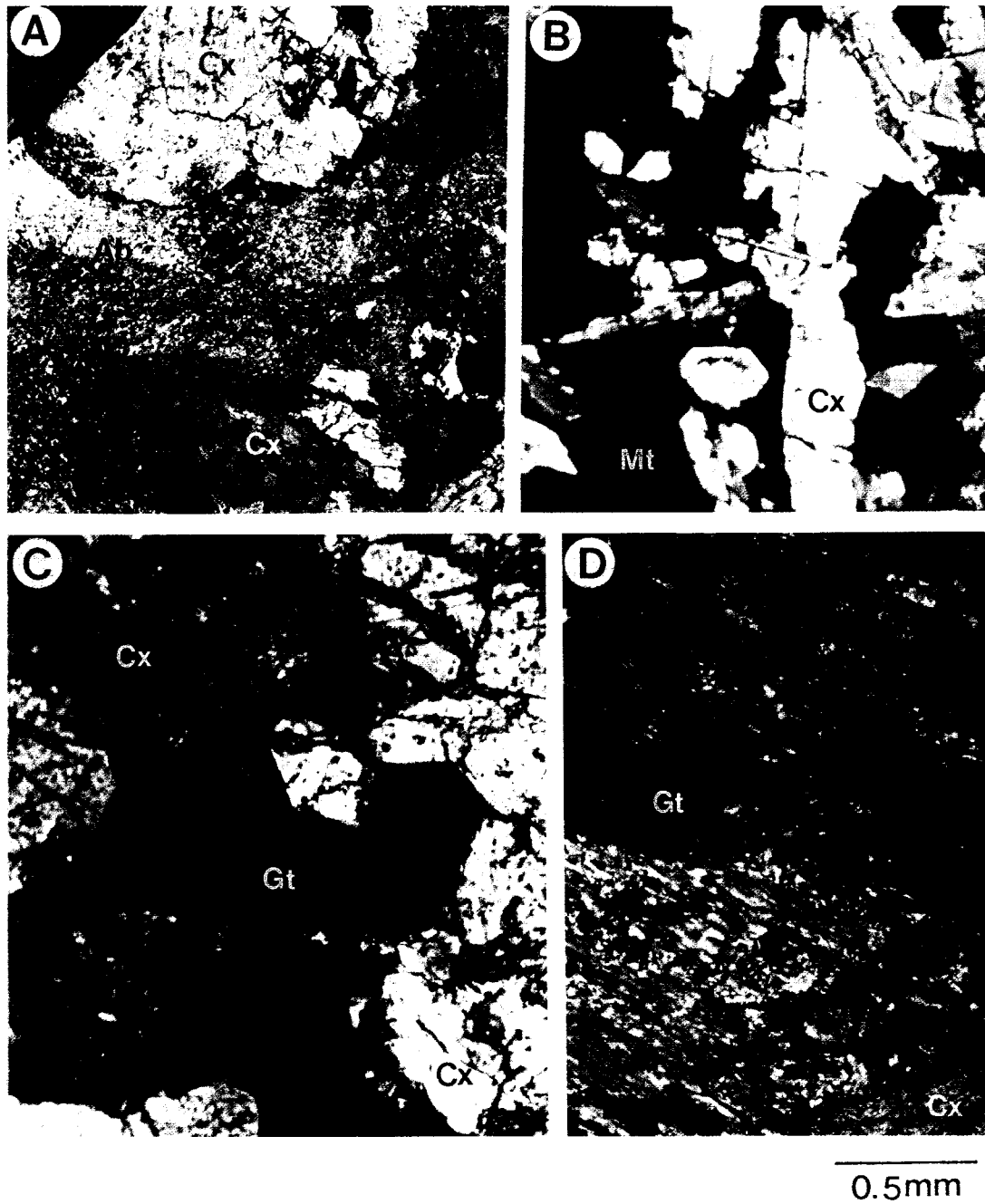
0.5mm

Fig. 1. Photomicrographs showing clinopyroxene occurrences from the Geodo mine. (All photos are the same in scale and under crossed polars.)

A: Clinopyroxene (Cx) replaces plagioclase (Ab) in the endoskarn zone. Plagioclase is nearly end member albite.

B: Clinopyroxene occurs in interstices among magnetite (Mt), showing subhedral to euhedral crystal form and diopsidic in composition.

C: Clinopyroxene replaces isotropic garnet (Gt) in the exoskarn zone of the massive skarns.

D: Hydrothermal minerals of prehnite (Pr) and illite (Il) replaces garnet and clinopyroxene in the endoskarn zone of the alteration stage.

In the late stage, clinopyroxene replaces iso-tropic garnet in barren zone (Fig. 1C) and be-comes rich in ore zone. It occurs mainly with Fe ores in the massive skarns (Fig. 1B). Clino-pyroxene of the space-filling skarns occurs as interstices among Fe ores, showing subhedral to euhedral prismatic or columnar crystals which are replaced later by chlorite along cleavages and crystal boundaries. It is. also found as veins in the early endoskarn zone. In the alteration stage, clinopyroxene in association with garnet is replaced by hydrothermal minerals of prehnite and illite (Fig. 1D).

EXPERIMENTAL

Clinopyroxne samples were collected from both the barren disposal spots near or in front of the Jangsan, Taebaek, Yugck, and 78 adits and walls of underground levels of the Jangsan and 78 adits. Because clinopyroxene in the Geodo mine shows the narrow range of chemical variation, two samples from the Sangdong (Chang, 1988) and Ulchin (Noh in pers. comm.) mines to obtain complete range of variations.

Clinopyroxene was prepared to be adquate for various methods. Polished-thin sections were prepared for the observation under the polariz-ing microscope and the electron microprobe analysis. Pure samples were powdered for the X-ray diffraction analysis and infrared absorption spectroscopy.

Chemical analysis was made by an electron probe microanalyzer JEOL-733 Superprobe with wavelength dispersive method in the Department of Geology, Yonsei University, at 15KV with beam current of $0.01\mu A$ and beam diameter of $10\mu m$. Averaged spectrum counts (10 sec. x 5 times) were compared with the natural silicate standards. Bense and Albee's method (1968) was applied for the calibration.

X-ray powder diffraction patterns were obtained by the Ni-filtered $CuK\alpha$ (30KV/15mA) radiations using JEOL JDX-5P diffractometer. They were indexed with the data from JCPDS X-ray data file. Refinement and calculation of the unit-cell parameters were carried out by the least square method of the Appleman-Evance program called LSUCRIPC (Appleman and Evance, 1978; Benoit, 1987) which was imple-mented for the IBM PC-XT/AT computer (Garvey, 1986).

Infrared absorption spectra were obtained

with a Perkin Elmer 430 spectrometer in the Department of Geology, Kangwon National University. Approximately 2-3 mg of powdered samples was dispersed in the KBr pellets in the range of 4000-300 cm^{-1}. Spectra were obtained under the condition of scan time 6 minutes, slit program 7, and expansion 1. They were calibrat-ed at 1603 cm^{-1} with polystylene film.

RESULTS AND DISCUSSIONS

Chemical Analysis

More than 50 analyses of clinopyroxenes were obtained by an electron microprobe analyzer. The selected and averaged chemical compositions of clinopyroxenes from the Geodo mine are given in Table 1 and the whole analyzed compo-sitions of Geodo clinopyroxene are plotted on the enlarged parallelogram in the triangle diagram of (Wo)wollastonite-(En)enstatite-(Fs)ferrosilite system in Fig. 2. It is noted that several charac-teristic features are driven from Table 1 and Fig. 2.

First, clinopyroxene chemistry indicates that clinopyroxenes from the Geodo mine belong to diopside-hedenbergite series. Chemical analysis reveals that the Geodo clinopyroxenes show diopsidic in composition (Di: 65-96%) with little amounts of Mn (less than 0.4 wt% MnO).

Second, it is easily recognized from Fig. 2 that clinopyroxene compositions are scattered in the range of Wo composition between 46.5 and 52.5%. More than two thirds of clinopyro-xenes are plotted in the area above the line of Wo 50 mole%. More interesting point is that clinopyroxenes in the exoskarn zone (solid symbols in Fig. 2) are plotted above that line. On the other hand, clinopyroxenes in the endos-karn zone (open squares) are mostly below the line. These endoskarn clinopyroxenes have nearly the same Mg contents as those in the monzodio-rite (Choi, 1988) indicating the area within the broken-line in Fig. 2. This fact indicates that exoskarn clinopyroxene is of M2 site occupied mostly by Ca cations, while endoskarn clinopy-roxene contains some Na and K substituting Ca in M2 site. This depends entirely on the chemis-try of unskarned parental rock, that is, the cal-careous rock for exoskarn and the igneous rock for endoskarn. Therefore, such difference in Wo mole% strongly suggests that clinopyroxene chemistry enables us to infer the source rock
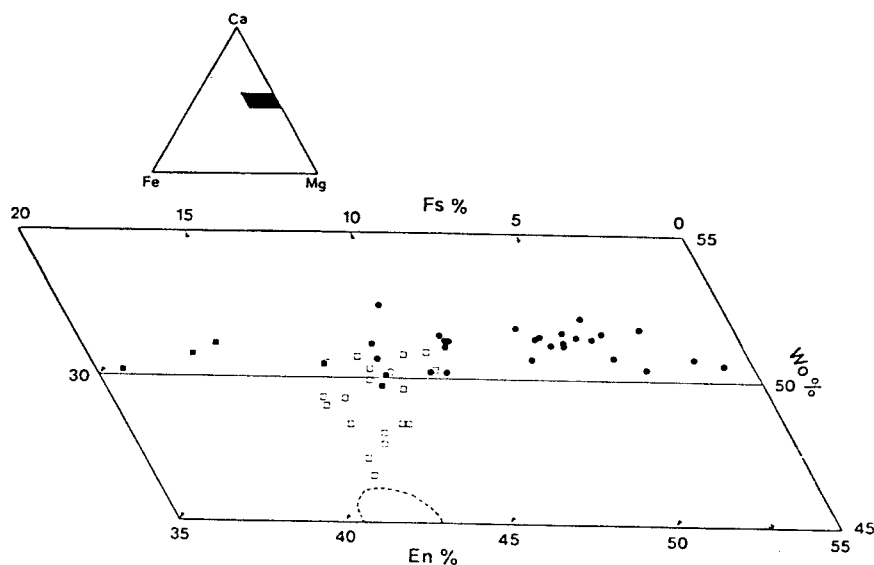
Fig. 2. The enlarged parallelogram in the triangular diagram of Wo (wollastonite)-Fs (ferrosilite)-En (enstatite) system showing clinopyroxene compositions in the Geodo mine. The area in the broken line is for clinopyroxene in the monzodiorite. (Symbols: solid circles for exoskarn, open squares for endoskarn, solid squares for exoskarn of the scapolitebearing assemblages in the Hwajeol Formation.)

before skarnization.

Third, clinopyroxenes in association with Fe ores (#WT2-2 and #30T0 in Table 1) show more Mg-rich in composition than those found in the early stage skarns. Especially, some clinopyroxenes (#30T0) belong to nearly end member diopside with little amounts of Fe (Fs: 0.9-3.3 %). As clinopyroxene was formed during Fe mineralization, Fe-rich fluid was supposed to result in formation of Fe-rich clinopyroxene. However, Fe-poor or nearly Fe-free clinopyroxenes were associated with Fe ore in the Geodo mine. This fact indicates that Fe contents in clinopyroxenes are not always controlled by the Fe chemical potential in fluid. This is also supported by garnet chemistry (Choi, 1989). As shown in Fig. 3, garnets in the Geodo mine are andraditic in composition (An: 40.5-81.6%). Nearly almost all of garnets have over 50% of andradite content. As already mentioned, garnets are closely associated with clinopyroxene in the Geodo mine, where the association of both minerals makes it possible to understand main factor to control skarnizing environment. Therefore, coexisting pair of diopside and andradite strongly indicates that Geodo skarns were formed under the reduced environment, because diopside and andradite are Fe^{2+}-poor and Fe^{3+}-

rich in composition, respectively. It can be concluded that skarnization in the Geodo mine was controlled by oxygen fugacity more severely than by Fe chemical potential in fluid.

X-ray Powder Diffraction Analysis

The X-ray powder diffraction patterns for the clinopyroxene are illustrated in Fig. 4. Since clinopyroxene chemistry in the Geodo mine shows narrow range of compositions, two clinopyroxenes from the Ulchin mine (#ULPG) (Noh in pers. comm.) and the Sangdong mine (#516) (Chang, 1988) were included in this study to examine the whole range variation of compositions. Refined X-ray data and calculated unit-cell parameters are given in Table 2.

As shown in Fig. 4 and Table 2, characteristic reflections of the clinopyroxenes are 3.24-3.27Å (220), 2.993-2.998Å (221), 2.957-2.962Å (310), 2.894-2.899Å (311), and 2.568-2.580Å (131). The other major peaks of clinopyroxenes show a slight shift toward the lower two theta angle region with increasing Fe contents. It is noted that the peak (110) disappears in the clinopyroxene with less than 50 mole% hedenbergite. Other missing peaks in Table 2 are too small to be discriminated from the background.

Table 1. Chemical Analyses of clinopyroxenes by EPMA.

Sample #	WT2-2 (13)	30T0 (3)	K4028 (8)	J2A (2)	SPC2 (7)	K4215 (3)	K4206 (15)	S5115 (6)
SiO_2	53.33	54.72	50.51	51.91	52.13	52.01	52.60	52.79
TiO_2	0.01	0.19	0.51	0.21	0.10	0.03	0.12	0.18
Al_2O_3	0.65	1.12	3.86	2.33	0.66	3.69	1.48	0.52
FeO*	3.92	0.95	5.53	1.44	10.49	2.63	6.87	8.20
MnO	0.24	0.13	0.18	0.11	0.32	0.12	0.22	0.22
MgO	15.65	17.49	14.08	16.40	11.20	15.80	14.25	14.09
CaO	26.33	25.95	25.01	26.30	24.74	25.53	24.50	23.64
Na_2O	0.04	–	0.10	0.01	0.40	0.06	0.26	0.38
K_2O	0.02	–	0.01	–	0.01	0.02	0.01	0.04
Total	100.19	100.55	99.79	98.71	100.05	99.89	100.31	100.06

Numbers of ions on the basis of 6 O

	WT2-2 (13)	30T0 (3)	K4028 (8)	J2A (2)	SPC2 (7)	K4215 (3)	K4206 (15)	S5115 (6)
Si	1.964 } 1.99	1.972 } 2.00	1.879 } 2.00	1.920 } 2.00	1.977 } 2.00	1.904 } 2.00	1.952 } 2.00	1.973 } 2.00
Al^{IV}	0.028	0.028	0.121	0.080	0.023	0.096	0.048	0.026
Al^{VI}	–	0.020	0.048	0.022	0.006	0.063	0.017	–
Ti	tr.	0.005	0.014	0.066	0.003	0.001	0.003	0.005
Fe^{2+}	0.121 } 0.99	0.029 } 1.00	0.172 } 1.02	0.045 } 1.04	0.333 } 0.99	0.080 } 1.01	0.213 } 1.03	0.256 } 1.05
Mn	0.007	0.004	0.006	0.003	0.010	0.004	0.007	0.007
Mg	0.859	0.939	0.781	0.904	0.633	0.863	0.789	0.785
Ca	1.039 } 1.04	1.002 } 1.00	0.997 } 1.01	1.043 } 1.04	1.005 } 1.04	1.002 } 1.01	0.975 } 0.99	0.947 } 0.98
Na	0.003	–	0.007	0.001	0.020	0.004	0.019	0.027
K	0.001	–	0.001	–	tr.	0.001	tr.	0.002
Wo(%)	51.3	50.8	51.0	52.3	50.7	51.4	49.1	47.5
En(%)	42.4	47.6	39.9	45.3	32.0	44.3	39.8	39.3
Fs(%)	6.3	1.7	9.1	2.4	17.3	4.3	11.1	13.2

* Total Fe as FeO

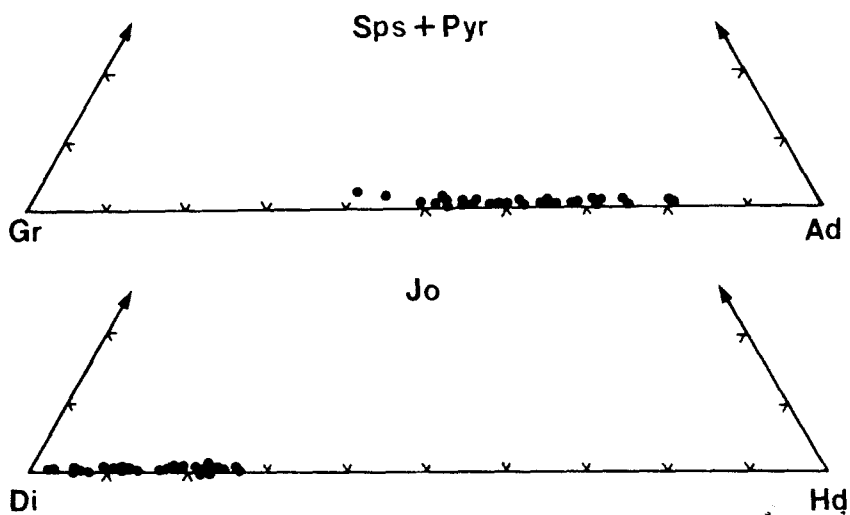Number in parenthesis indicates total counts for average.

Fig. 3. Compositional distribution of garnet and clinopyroxene in the Geodo mine plotted on the triangular diagrams of grossular (Gr), andradite (Ad), and spessartine + pyrope (Spc+Pry), and of diopside (Di), hedenbergite (Hd), and johannsenite (Jo).
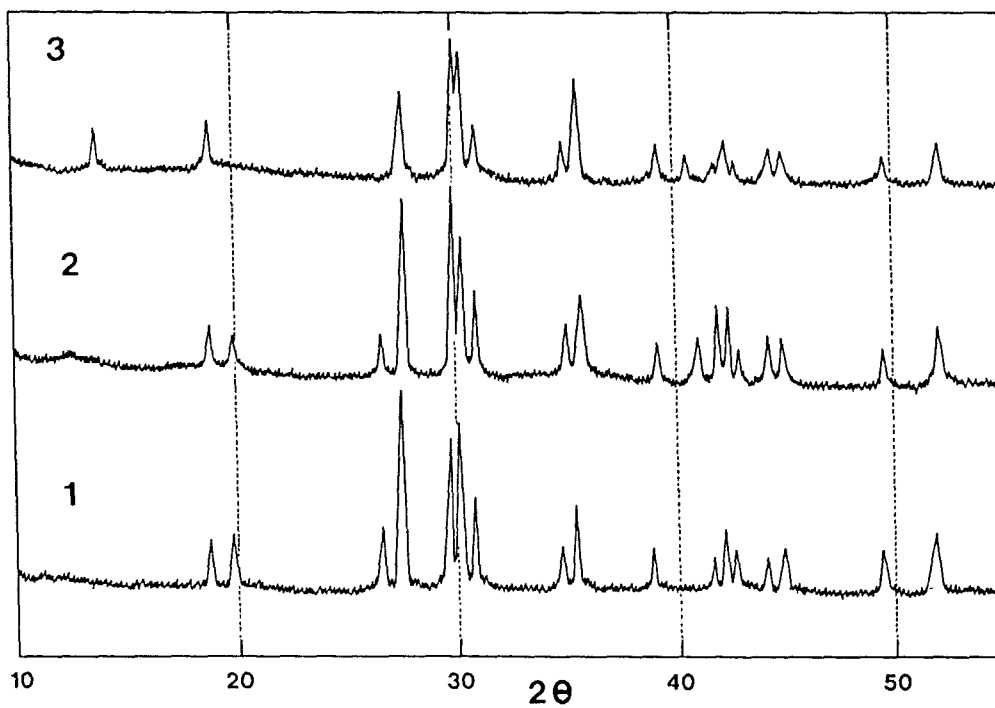

Fig. 4. The X-ray powder diffraction patterns of clinopyroxenes from Geodo mine. (Sample numbers are the same as explained in Table 2)

Table 2. X-ray powder diffraction data of clinopyroxenes from Geodo mine.

		1			2		3		4	
a (A)		9.765			9.776		9.812		9.838	
b (A)		8.943			8.947		9.009		9.020	
c (A)		5.240			5.251		5.253		5.252	
β (A)		105.70			105.63		105.16		104.83	
V (A³)		440.64			442.36		445.62		448.19	

h k l		d_{cal}	d_{obs}	I/I_o	d_{cal}	d_{obs}	d_{cal}	d_{obs}	d_{cal}	d_{obs}
1 1 0							6.48	6.48	6.54	6.54
2 2 0		4.70	4.71	15	4.71	4.72	4.71	4.70	4.76	4.75
0 2 0		4.47	4.48	8	4.47	4.46			4.51	4.51
1 1 1		3.66	3.67	5						
2 2 0		3.24	3.24	85	3.24	3.23	3.24	3.24	3.27	3.27
2 2 $\bar{1}$		2.993	2.993	100	2.994	2.998	2.995	2.992	2.998	2.995
3 1 0		2.957	2.954	75	2.962	2.959	2.962	2.961		
3 1 $\bar{1}$		2.894	2.898	40	2.897	2.894	2.899	2.896	2.899	2.898
1 3 $\bar{1}$		2.568	2.571	20	2.569	2.571	2.569	2.570	2.580	2.579
2 2 1									2.549	2.549
0 0 2		2.522	2.525	45	2.528	2.525	2.533	2.534		
2 0 $\bar{2}$		2.526	2.525	45	2.528	2.525	2.535	2.534		
4 0 0		2.350	2.353	3						
3 1 1		2.307	2.312	4	2.312	2.311	2.313	2.311		
1 1 2		2.215	2.212	4			2.223	2.226		
3 3 0		2.160	2.161	25	2.162	2.161	2.161	2.158	2.181	2.181
3 3 $\bar{1}$		2.135	2.133	25	2.136	2.132	2.136	2.140	2.145	2.146
4 2 $\bar{1}$		2.110	2.110	7	2.111	2.113	2.112	2.116	2.119	2.120
0 4 1		2.044	2.045	5	2.046	2.049	2.044	2.044		
2 4 0		2.019	2.021	3	2.020	2.019	2.019	2.018		
5 1 0		1.840	1.843	5	1.843	1.843	1.843	1.843		
1 5 0		1.757	1.755	18	1.759	1.759	1.766	1.766	1.773	1.773
4 4 0									1.636	1.637
2 2 $\bar{3}$		1.621	1.621	15	1.624	1.624	1.627	1.626		

* Sample explanation;
1: #S5115, salite (Hd: 15%), endoskarn in the Jangsan adit.
2: #YG5, salite (Hd: 30%) in the Yugok adit.
3: #ULGP, green ferrosalite (Hd: 65%) in the Ulchin mine, data from Kim et al. (1988).
4: #516, hedenbergite (Hd: 90%) in the Sangdong mine, data from Chang, S.W. (1988).

Thus they are not missed, but omitted.

A complete series of hedenbergite-diopside does not seem to change in symmetry nor space group with change of composition. Indexing of clinopyroxene is, therefore, based on the monoclinic symmetry with a space group C2/c for the complete series. The ranges of unit-cell parameters are a = 9.765-9.838Å, b = 8.943-9.020Å, c = 5.240-5.253Å, β = 105.70-104.83°, and V = 440.64-448.19Å^3 with change of Fe contents (Hd: 15-90%).

To examine the variations in unit-cell parameters with respect to substitution scheme between Fe and Mg in octahedral sites, the least square regressions were done for each unit-cell parameters. Linear regression calculation was performed for all parameters except β for which exponential function was loaded in regression. The result is illustrated in Fig. 5 and least square equations are given in Table 3. As shown in Fig. 5, it is noted that a, b, and V increase linearly with increase of hedenbergite (Hd) mole contents. Thus one of these equations can easily

determine chemical compositions of clinopyroxene using X-ray diffraction pattern of unknown composition without doing chemical analysis. On the other hand, β slightly decreases and c remains nearly unchanged as the change in Hd mole contents. These trends are well-matched with the results usiing synthetic complete series of hedenbergite-diopside (Rutstein and Yund,
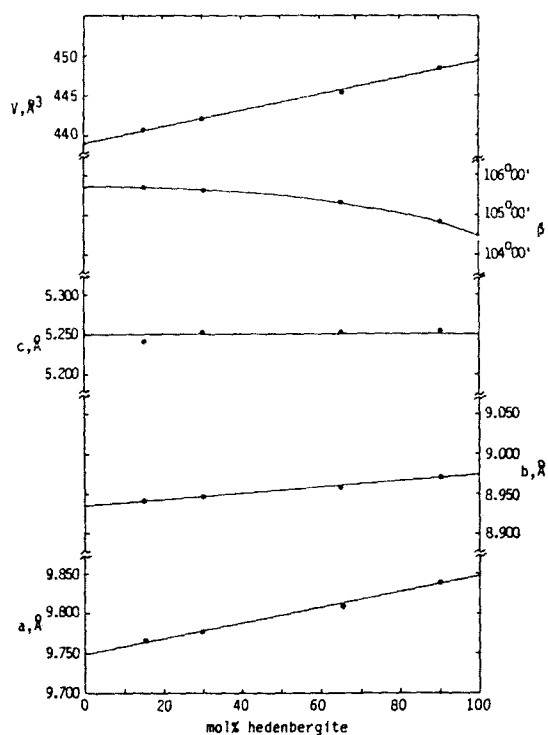

Fig. 5. The variation diagram of unit cell parameters a, b, c, β, and cell volume (V) against Hd mole % for clinopyroxenes from Geodo mine.

Table 3. Least square equations for unit-cell parameters.

a (Å) = 9.7484 ± 0.0020 + 0.0987 x

b (Å) = 8.9219 ± 0.0080 + 0.1157 x

c (Å) = 5.2424 ± 0.0020 + 0.0132 x

V (Å^3) = 439.24 ± 0.08 + 9.922 x

V* (Å^3) = 439.68 ± 0.15 + (11.10 ± 0.28) x

β (°) = 105.933 exp (-0.0114 x) ± 0.050

x indicates hedenbergite mole fraction.
* equation from Rutstein and Yund, 1969

Table 4. Comparison of cell parameters for diopside and hedenbergite from the Geodo mine.

	a(Å)	b(Å)	c(Å)	β	Reference
Diopside					
Synthetic	9.752	8.926	5.248	105°50′	Rutstein & Und, 1969
	9.748	8.924	5.251	105°47′	Nolan & Edgar, 1963
Natural	9.754	8.916	5.249	105°49′	Viswanathan, 1966
	9.748	8.922	5.242	105°93′	This study
Hedenbergite					
Synthetic	9.851	9.021	5.252	104°44′	Rutstein & Yund, 1969
Natural	9.821	9.036	5.249	104°38′	Viswanathan, 1966
	9.847	9.038	5.255	104°73′	This study

1969). Compared to synthetic results, equation for cell volume (V) in Table 4 indicates that some modification is found in new equation. This ascribes mainly to the differences between synthetic and natural clinopyroxenes. Therefore, the modified equations are more practical than old ones in applying in natural samples. Using modified equations, cell parameters for end-member diopside and hedenbergite are obtained and compared with ealier data in Table 5.

Infrared Absorption Spectroscopy

The infrared absorption spectra of clinopyroxenes and their wavenumbers are shown in Fig. 6 and Table 5, respectively.

The infrared absorption bands of clinopyroxene are characterized by four strong bands in the range between 1200 and $800 cm^{-1}$, assigned to Si-O stretching vibrations in the symmetry of the $(Si_2 O_6)_n$ chain. Among them, the former two bands with higher wavenumbers are due to bridging oxygens (S_3 and S_{11}) and the others to non-bridging oxygens (S_4 and S_{16}) which strongly repluse each other (Omori, 1971). It is not cleary observed how the other structural sites are affected by Fe substitution for Mg in octahedral M2 site, possibly due to structural complexity It is, however, noted in Table 5 that above four absorption bands show a slight shift toward lower wavenumber region with increasing Fe contents.
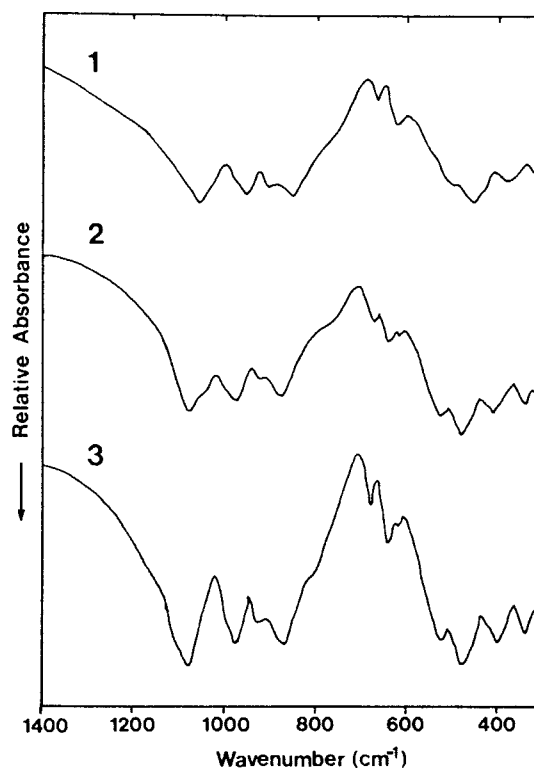

Fig. 6. The infrared absorption spectra of clinopyroxenes from Geodo mine (Sample numbers are the same as explained in Table 2.)

The other absorption bands in the range of 670-600 cm^{-1} are assigned to O-Si-O bending (S_3), 530-450 cm^{-1} to O-Mg-O bending in the M1 site of the octahedral symmetry, and 420-380 cm^{-1} to O-Ca-O bending vibrations in the M2 site of the same symmetry.

Table 5. Infrared absorption spectral data of clinopyroxenes from Geodo mine.

1	2	3	4
1080	1076	1065	1058
999	970	961	955
928	920	914	898
870	865	855	850
680	677	673	657
645	640	627	610
518	520	510	514
480	475	460	455
402	410	395	398
340	340	330	340
			312

Sample numbers are the same as indicated in Table 2.

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