

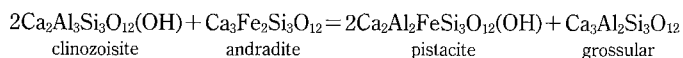
Al-Fe Partitioning between Coexisting Garnet and Epidote from Metamorphic Rocks

Hyung Shik Kim, Young Kyum Kim and Young Nam Jang*

Department of Geology, College of Science, Korea University, Seoul 136-701, Korea

*Korea Institute of Geology, Mining and Materials

ABSTRACT: The assemblage epidote and grandite garnet occurs in low-to medium-grade metabasites and calc schists of various geotectonic settings and in hydrothermally altered calcareous rocks in skarn deposits. The compositions of sixteen epidote-garnet pairs have been analysed by means of electron microprobe. Al-Fe partitioning between coexisting grandite garnet and epidote is considered and measured at the grain boundaries on the supposition that the surface equilibrium was maintained in the following exchange reaction:



Partition coefficients confirms the differences in thermal conditions between low-grade and medium-grade metamorphic rocks. K_D values ($K_D = (\text{Fe}^{+3}/\text{Al})^{\text{Ep}}/(\text{Fe}^{+3}/\text{Al})^{\text{Gr}}$, where $\text{Fe} = \text{Fe}^{+3}$) from greenschist facies rocks of the estimated metamorphic temperatures, 330~390°C, range approximately between 0.02 and 0.17. Epidote-amphibolite facies rocks and calcareous skarns of the estimated temperatures, 400~550°C, have K_D values between 0.24 and 0.37. K_D values from the rocks of the temperatures, 640~700°C, range nearly between 0.58 and 0.75. The diagrams in Figs. 2 and 3 can serve as a mineralogic thermometer for relatively shallow rocks, assuming that the pressure dependence of partition coefficients for the iron-exchange reaction in the two minerals can be neglected.

Key Words: partition coefficient, metamorphism, greenschist facies, Al, Fe, epidote, garnet, microprobe analysis, mineralogical thermometer.

INTRODUCTION

Since the middle of the 19th century, many chemical, crystallographical, thermodynamic and experimental studies of epidote, garnet and their related minerals have been completed (e.g. Fyfe, 1960; Seki, 1972; Holdaway, 1967, 1972; Strens, 1965; Liou, 1973; Kim *et al.*, 1982; Kim, 1987). P-T stabilities of epidote, zoisite and clinozoisite have been determined (Newton, 1965, 1966; Holdaway, 1967; Boettcher, 1970) and transformation of epidote to grandite + anorthite + quartz + hematite + H₂O using natural epidotes as starting material has been investigated (Nitch and Winckler, 1965; Strens, 1965; Holdaway, 1972).

Liou (1973) synthesized pure epidote from oxide mixtures, determined its maximum stability limits

and made a systematic study of the effect of temperature, fluid pressure and oxygen fugacity on the relative stability and composition of epidote. Seki (1972) deduced the low-temperature stability limit of epidote in light of natural occurrences.

Epidote and garnet are common in various low-to medium-grade metamorphic rocks and in hydrothermal assemblages from skarn deposits. They may occur together as common epidote-amphibolite facies assemblages with biotite + plagioclase + quartz (+chlorite), or they may appear separately as secondary phases. Both epidote and garnet are characterized by compositional variation within octahedral sites in basic formulae $\text{Ca}_2(\text{Al}, \text{Fe})_3\text{Si}_3\text{O}_{12}(\text{OH})$ for epidote and $\text{Ca}_3(\text{Al}, \text{Fe})_2\text{Si}_3\text{O}_{12}$ for grandite garnet. Grandite garnets show complete solid solution whereas epidote

has limited extent of solid solution. Minerals of the epidote group are rarely found with greater than 40 percent replacement of aluminum by ferric iron. The most common extreme is usually cited as approximately 33 percent of the pistacite end-member for epidote.

The assemblage epidote plus grandite garnet occurs in low- to medium-grade metabasites and calc schists of various geotectonic settings and in hydrothermally altered calcareous rocks from skarn deposits. The mineral association reasonably reflect the physico-chemical parameters of low- to medium-grade metamorphism and hydrothermal alterations. Both epidote and garnet are related to each other by complex continuous reactions; Al-epidote + Fe-grandite = Fe-epidote + Al-grandite (Kim, 1987).

Therefore, investigation of Al-Fe partitioning between coexisting garnet and epidote as a function of temperature can aid in understanding the physico-chemical conditions for their occurrences in various metamorphic environments.

STABILITY RELATIONS OF EPIDOTE AND GARNET SOLID SOLUTIONS

The existence of a miscibility gap between Ps 12 and Ps 22 within the epidote solid solution was suggested by Strens (1965). This gap was subsequently reported for natural epidotes from greenschist to garnet amphibolite facies metamorphic rocks (Holdaway, 1965; Hitanen, 1974; Raith, 1976). Liou, Kim and Maruyama (1983) plotted available compositions of epidote from rocks of prehnite-pumpellyite, pumpellyite-actinolite and greenschist facies; the data cover the suggested miscibility gap of Strens (1965). Bird (1981) obtained no direct experimental evidence for such a solvus within the range of temperature in which epidote occurs in nature. From the data, it is concluded that epidote solid solution is continuous at least in the range of Ps 10 to Ps 33.

Epidote was rapidly crystalized in the temperature range 600 to 700°C under various oxygen

Table 1. Compositions and abbreviations for minerals used in this paper

Mineral		Formula	
Epidote		$\text{Ca}_2\text{Al}_{3-x}\text{Fe}_x\text{Si}_3\text{O}_{12}(\text{OH})$, where $x < 1.05$	
Fe-epidote		Ps : 35 to 25	
Al-epidote		Ps : 25 to 0	
Grandite		$\text{Ca}_2(\text{Fe}, \text{Al})_2\text{Si}_3\text{O}_{12}$	
Fe-grandite		$\text{Fe}^{3+}/(\text{Fe}^{3+} + \text{Al}) : 100 \text{ to } 50$	
Al-grandite		$\text{Fe}^{3+}/(\text{Fe}^{3+} + \text{Al}) : 50 \text{ to } 0$	
Epidote	Ep	Garnet	Gr
Pistacite	Ps	Grandite	Gd
Hornblende	Hb	Andradite	And
Actinolite	Act	Calcite	Cal
Tremolite	Tr	Quartz	Qz
Prehnite	Pr	Pumpellyite	Pum
Corundum	Cor		

buffer and 5 Kb P_{fluid} . Thus it appears at higher pressure, probably at least 3 Kb.

Holdaway (1972) reported that Fe-epidote is stable only under oxidizing conditions and that epidote become more aluminous in a reducing environment. With a successive decrease in f_{O_2} epidote become progressively more aluminum-rich, coexisting garnet moves toward the grossular end-member. Winkler and Nitch (1965) worked out a univariant P-T curve for the mutual stability of quartz and epidote by using synthetic anorthite and grossular-andradite and by detecting the growth or disappearance of epidote seeds in their works. From these data, the stability limit of epidote has been determined.

Grossular was easily synthesized from gel or glass of the requisite composition at 800°C and at water-vapour pressures as low as 2,000 bars. The various experimental works on the reaction; grossular + quartz = anorthite + wollastonite are determined by many authors.

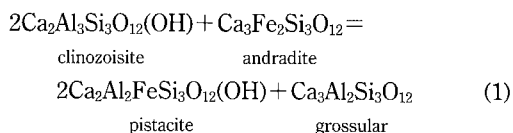
Suwa *et al.* (1976) obtained a 100% yield of andradite by appropriating heating of hydroandradite, of a glass of andradite composition and of a mixture of wollastonite and hematite, all in air at 1 atm; the andradite was prepared by dehydration of hydroandradite at 1,100~1,150°C for 10 hours. Andradite is also easily synthesized at 1,020°C and 1 atm from $\text{CaSiO}_3 + \text{Fe}_2\text{O}_3$. The low-temperature stability of andradite as a function

of temperature, X_{CO_2} and f_{O_2} at constant P_{fluid} of 2 kbar was investigated by Taylor and Liou (1978). Experimental results show that the reaction; 3 quartz + 3 calcite + 1/4 hematite + 1 1/2 magnetite + 1/8 O_2 = andradite + 3 CO_2 occurs at $550 \pm 10^\circ\text{C}$ at $X_{\text{CO}_2} = 0.22$, $596 \pm 8^\circ\text{C}$ at $X_{\text{CO}_2} = 0.5$ and $640 \pm 10^\circ\text{C}$ at $X_{\text{CO}_2} = 1.0$. The experimental studies for the following reaction; andradite + quartz = hedenbergite + wollastonite + 1/2 O_2 were reported by Liou (1974), Shoji (1977) and Helgeson *et al.* (1978), yielding results; the reaction crosses the QFM buffer curve at 600°C , 2 Kb and NNO curve at 680°C , 2 Kb.

It is known that complete solid solution exists in the grandite garnet system. The linear relationship between physical properties and chemical composition was confirmed by Liou (1973). Perchuk and Aranovich (1979) also studied the thermodynamics of andradite-grossularite solid solutions from exchange-mineral equilibria with Al and Fe^{+3} aqueous chloride solutions. Their experiments demonstrate complete solid solution between andradite and grossular.

THERMODYNAMICS OF Al-Fe PARTITIONING BETWEEN GARNET AND EPIDOTE

In the present study, considerations are based on the following assumptions: the grandite garnet and epidote solid solutions have no internal diffusion within the minerals; the minerals maintained a surface equilibrium; exchange equilibrium between these minerals was maintained at the grain boundaries. The exchange equilibrium can be described as the following reaction (1);



The equilibrium constant K for the reaction (1) may be defined (Banno, 1970) as

$$K = \frac{(a_{\text{Fe}}^{\text{Ep}})^2}{(a_{\text{Al}}^{\text{Ep}})^2} \cdot \frac{(a_{\text{Al}}^{\text{Gr}})}{(a_{\text{Fe}}^{\text{Gr}})} \quad (2)$$

where a_i is the activity of component i in phase j . Taking a standard state of pure solids at the pressure and temperature of interest, then at equilibrium

$$\Delta G_{\text{P,T}}^\circ = \Delta H^\circ - T\Delta S^\circ + (P-1)\Delta V^\circ = -RT \ln K \quad (3)$$

where ΔG is the Gibb's free energy of exchange reaction (1), ΔH is the enthalpy change, ΔS is entropy change, and R is the gas constant. On the premise that grandite garnet and epidote solid solutions in the binary systems behave as ideal mixtures solutions ($a = X$), the partition coefficient for reaction (1) can be derived from the following equation:

$$K = \frac{(X_{\text{Fe}}^{\text{Ep}})}{(X_{\text{Al}}^{\text{Ep}})} \cdot \frac{(X_{\text{Al}}^{\text{Gr}})}{(X_{\text{Fe}}^{\text{Gr}})} = K_{\text{D}} = \frac{(X_{\text{Fe}}^{\text{Ep}})}{(1 - X_{\text{Fe}}^{\text{Ep}})} \cdot \frac{(1 - X_{\text{Fe}}^{\text{Gr}})}{(X_{\text{Fe}}^{\text{Gr}})} \quad (4)$$

where K_{D} is partition coefficient, $X_{\text{Fe}}^{\text{Gr}}$ is the $\text{Fe}^{+3}/(\text{Fe}^{+3} + \text{Al})$ ratio in grandite garnet, $X_{\text{Al}}^{\text{Gr}}$ is the $\text{Al}/(\text{Fe}^{+3} + \text{Al})$ ratio in the grandite garnet, $X_{\text{Al}}^{\text{Ep}}$ is the $\text{Fe}^{+3}/(\text{Fe}^{+3} + \text{Al})$ ratio in the epidote, and $X_{\text{Al}}^{\text{Ep}}$ is the $\text{Al}/(\text{Fe}^{+3} + \text{Al})$ ratio in the epidote.

The dependence of the partition coefficient on temperature is expressed by the following equation on the assumption that ΔC_{P} (heat capacity change of reaction (1) at constant pressure) is close to zero:

$$\ln \frac{K_{\text{D}1}}{K_{\text{D}2}} = \frac{\Delta H}{R} \left(\frac{1}{T_2} - \frac{1}{T_1} \right) \quad (5)$$

where $K_{\text{D}i}$ is the partition coefficient at temperature T_i . With changing temperatures, K_{D} approaches a constant values.

The pressure effect on the partition coefficient can be described by writing,

$$\ln \frac{K_{\text{D}1}}{K_{\text{D}2}} = \frac{\Delta V(P_2 - P_1)}{RT}$$

where $K_{\text{D}i}$ is the partition coefficient at pressure P_i and ΔV is the volume change of reaction (1). As ΔV is very small, about 5×10^{-3} cal/atm (0.2 cc) or less (Holdaway, 1972; Liou, 1973), pressure does not significantly affect the partition coefficient. The requisite values of $\log K (= \log K_{\text{D}})$ for reactions (1), (2) and (4) were generated from thermodynamic data taken from Bird and

Table 2. Parageneses, metamorphic facies and PT formation parameters for representative epidote-garnet rocks from Korea (Sample Nos. 1~11), foreign countries (Sample Nos. 12~15) and synthesis experiment (Sample No. 16)*

No.	Rock, parageneses	Metamorphic facies and locality	Estimated T°C ,	P kb
1	Calc schist(7-1) (Gr+Ep+cpx+Hb)	Amphibolite Dukgoo, Korea	650~700	3~4
2, 3	Calc schist(123, 130) (Ep+Gr+Hb+Act)	Epidote-amphibolite Ogcheon, Korea	500~520	2~3
4	Calcareous skarn(Y-139) (Gr+Ep+Cpx)	Yeonwha Mine, Korea	500~540	1
5, 6	Skarn deposits(2230) (Gr+Ep+Cpx)	Sangdong Mine, Korea	480~500	1
7	Calc schist(Y-230) (Ep+Gr+Tr+Cpx)	Greenschist-Amphibolite transition Yeonpyeongdo, Korea	500~550	2~3
8	Calc silicate rock(1528) (Gr+Ep+Hb+Cpx)	Amphibolite Samcheog, Korea	650~700	3~4
9	Calc schist(1282) (Ep+Gr+Chl)	Greenschist Janggun Mine, Korea	370	2
10	Basic metavolcanic rock(151) (Ep+Gr+Act+Chl),	Greenschist Chungju, Korea	380~400	2~3
11	Calcareous skarn(2321) (Gr+Ep+Tr)	Sinyemi deposits, Korea	400~540	1
12	Basic metaporphyrite(H35347A) (Gr+Chl+Ep+Act+Ab+Qz+Pum)	Greenschist, New Zealand(Coombs <i>et al.</i> , 1977)	330	2~3
13	Spilitized basalt(Bb34903) (Gr+Ep+Qz+Cal+Pr+Chl)	Greenschist, New Zealand(Coombs <i>et al.</i> , 1977)	390	2~3
14	Calcareous skarn(T-1) (Ep+Gr+Cpx+Cal)	Tyrnyaus, North Caucasus (Aranovich, 1979)	470	1
15	Skarn deposits(72070726) (Gr+Ep+Cpx)	Chichibu Mine, Japan (Kitamura, 1975)	650~700	1
16	Synthesis experiments (Ep+Gr+Cor)	(Holdaway, 1972)	640	3

*Mineral abbreviations as for Table 1.

Helgeson (1980), suggesting that $\log K (= \log K_D)$ is essentially independent of pressure. As reliable much experimental data of the grandite garnet and epidote solid solutions are lacking, only a comparison of partition coefficient with temperatures can be discussed in the present study.

MINERAL COMPOSITIONS AND PARTITION COEFFICIENTS

The samples were collected from low-to medium-grade regional metamorphosed terranes and calcareous skarn deposits in South Korea. Table 2 shows mineral paragenesis, metamorphic facies and estimated PT formation parameters of rocks containing coexisting grandite garnets and epidotes. Sample Nos. 1~11 are domestics and

Sample Nos. 12~15 from New Zealand (Coombs *et al.*, 1977), North Caucasus (Aranovich, 1979) and Japan (Kitamura, 1975). No. 16 is from synthetic experiments (Holdaway, 1972).

Calcareous skarns generally occur on contact of near-surface ($P < 1$ Kbar) granite or quartz diorite intrusions with carbonate rocks. Calc schists or calc silicate gneisses contain characteristic mineral assemblages corresponding to the greenschist, the epidote amphibolite or the amphibolite facies, respectively. We ascribed $P \approx 2\sim 3$ or 4 K bars to these parageneses. According to Coombs, metabasalts (Sample Nos. 12 and 13) in New Zealand were formed under 2~3 kilobars of pressure. However, as mentioned previously, effect of pressure is negligible in partition coefficient and need not be considered in this paper.

Table 3. Micro-probe analyses of coexisting garnets and epidotes. Sample Nos. are as for Table 2

Garnet		1	2	3	4	5	6	7	8	9	10	11
Weight %	SiO ₂	38.41	37.53	37.15	37.09	37.25	36.58	37.58	38.45	36.54	36.58	35.45
	Al ₂ O ₃	15.18	8.47	8.35	8.41	7.38	9.69	11.64	16.78	10.78	7.18	9.41
	Fe ₂ O ₃	9.96	18.80	18.77	19.38	20.36	18.58	15.55	7.79	15.98	20.74	18.19
	MnO	2.22	1.01	0.92	0.95	0.79	1.10	0.75	0.61	0.48	0.21	0.85
	MgO	0.01	0.05	0.05	0.06	0.08	0.10	0.15	0.28	0.43	0.05	tr
	CaO	33.92	32.17	32.49	31.97	33.45	33.81	33.61	35.49	33.41	34.59	33.11
	Total	99.70	98.04	97.73	98.01	99.31	99.86	99.28	99.40	97.62	99.35	97.01
Atomic number oxygen : 12.0	Si	3.00	3.07	3.06	3.05	3.04	2.96	3.00	2.99	2.99	3.00	2.96
	Al	1.40	0.82	0.81	0.81	0.71	0.92	1.10	1.54	1.04	0.67	0.92
	Fe	0.59	1.16	1.16	1.20	1.25	1.13	0.94	0.46	0.98	1.23	1.14
	Mn	0.15	0.07	0.06	0.07	0.06	0.08	0.05	0.04	0.03	0.02	0.06
	Mg	tr	0.01	0.01	0.01	0.01	0.01	0.02	0.03	0.02	0.01	tr
	Ca	2.84	2.82	2.86	2.81	2.92	2.93	2.88	2.96	2.93	3.03	2.96
	Total	7.98	7.95	7.96	7.95	7.99	8.03	7.99	8.02	7.99	7.96	8.04
*And. mol%	29.7	58.6	58.9	59.7	63.8	56.2	46.1	23.1	48.8	64.7	56.4	
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Epidote		1	2	3	4	5	6	7	8	9	10	11
Weight %	SiO ₂	38.82	37.62	37.36	37.29	37.16	37.68	37.76	38.18	39.61	37.83	37.75
	Al ₂ O ₃	24.99	21.93	22.23	20.72	21.26	24.58	24.10	26.25	33.19	24.75	24.28
	Fe ₂ O ₃	12.02	12.96	13.65	15.60	15.46	11.98	11.72	9.28	1.41	11.90	12.25
	MnO	0.71	0.32	0.09	0.08	0.25	0.62	1.13	0.31	0.12	0.35	0.13
	MgO	n.d.	0.03	0.02	0.02	0.11	0.13	0.39	0.12	tr	0.05	tr
	CaO	22.44	22.91	23.11	22.89	23.05	23.25	23.01	3.48	24.18	23.51	23.55
	Total	98.98	95.77	96.46	96.6	97.29	98.24	98.35	7.62	98.51	98.39	97.96
Atomic number oxygen : 12.0	Si	3.03	3.06	3.03	3.04	3.00	2.98	3.00	3.01	2.99	2.99	2.99
	Al	2.30	2.11	2.12	1.99	2.03	2.29	2.25	2.44	2.96	2.30	2.27
	Fe	0.71	0.79	0.83	0.96	0.94	0.71	0.70	0.55	0.08	0.71	0.73
	Mn	0.05	0.02	0.01	0.01	0.02	0.04	0.08	0.02	0.01	0.02	0.01
	Mg	n.d.	tr	tr	tr	0.01	0.02	0.05	0.01	tr	0.01	tr
	Ca	1.88	2.00	2.01	2.00	2.00	1.97	1.96	1.98	1.96	1.99	2.00
	Total	7.97	7.98	8.00	8.00	8.00	8.01	8.04	8.01	8.00	8.02	8.00
**Ps. mol%	23.6	27.2	28.1	32.5	31.6	23.8	23.7	18.4	2.6	23.7	24.3	

tr.: below 0.1 weight percent. n.d.: not detected by EPMA.

*Calculated as octahedral Fe⁺³/(Al+Fe⁺³). **Calculated from the ratio Fe⁺³/(Al+Fe⁺³) in epidote.

The estimated temperatures of Table 2 seem quite credible for rocks of the type. In order to estimate the temperature, we have used the mineral assemblages and the garnet-biotite or calcite-dolomite geothermometers of metamorphic rocks adjacent to calc schists, calc silicate gneisses or basic metavolcanic rocks, respectively, and the sulfur isotope geothermometer or homogenization temperatures of liquid inclusions in calcareous skarn deposits (Mun, 1979; Kim and Nakai, 1980).

Chemical compositions of coexisting garnet and epidote were determined using the J.E.O.L. electron probe microanalyzer (Table 3). In general, the analysed garnet and epidote were in contact with each other. The chemical analyses were performed at the rims of the grains, close to the grain boundaries, which are the sites where the best preconditions for chemical equilibration can be expected.

The iron content was recalculated as Fe₂O₃

Table 4. Element relations and K_D of coexisting epidotes and garnet. Sample Nos. are as for Table 2

No.	X_{Fe}^{Ep}	X_{Fe}^{Gr}	$X_{Fe}^{Ep}/(1-X_{Fe}^{Ep})$	$X_{Fe}^{Gr}/(1-X_{Fe}^{Gr})$	K_D
1	0.236	0.297	0.309	0.423	0.731
2	0.272	0.586	0.374	1.416	0.264
3	0.281	0.589	0.391	1.433	0.274
4	0.325	0.597	0.482	1.481	0.325
5	0.316	0.638	0.462	1.762	0.273
6	0.238	0.562	0.312	1.283	0.243
7	0.237	0.461	0.311	0.855	0.363
8	0.184	0.231	0.226	0.300	0.751
9	0.026	0.488	0.027	0.953	0.028
10	0.237	0.647	0.311	1.833	0.170
11	0.243	0.564	0.321	1.294	0.248
12	0.026	0.493	0.027	0.972	0.027
13	0.230	0.653	0.299	1.882	0.159
14	0.240	0.530	0.316	1.128	0.280
15	0.192	0.275	0.238	0.379	0.628
16	0.160	0.270	0.190	0.370	0.514

under the reasonable assumption that all iron in the garnet and epidote is present in the ferric state. The Mn content in both minerals is usually less than 1.0 weight percent MnO except a few sample and varies in versely with the Ca content. Mg content is always negligible. Si content just satisfies the stoichiometric requirements. Table 3 shows that the $Fe^{+3}/(Fe^{+3}+Al)$ ratios in garnets and epidotes expressed as the pistacite and andradite mole percents, respectively, and the formers are always smaller than the latters.

The garnet composition can be approximately represented by the binary system andradite($Ca_3Fe_2Si_3O_{12}$)—grossular($Ca_3Al_2Si_3O_{12}$), and varies continuously from And_{65} to And_{20} . The pistacite mol. percent is always below 33. Most of ferric iron in epidote occupies the asymmetric octahedral M(3) site in the structure which means the Fe substitutes for Al, and the epidote formula can be described as $Ca[M(1)M(2)]M(3)Si_3O_{12}(OH)$. Therefore, the composition of epidote can be approximately represented by the binary system pistacite ($Ca_2Al_2FeSi_3O_{12}(OH)$)—clinozoisite($Ca_2Al_2AlSi_3O_{12}(OH)$), in the same way as garnet.

The coefficients for the Fe and Al distribution between epidote and garnet were calculated from analyses at the rims of the grains close to the grain contacts. The K_D values obtained are given in Table 4. Al-Fe partitioning can be expected

from the size of sites coordinated to oxygen in the crystals and the ionic radii of Al and Fe ions. Al-O bond lengths in the octahedral site of grossular, and M(1), M(2) and M(3) sites in epidote are 1.924, 1.906, 1.878 and 1.977 Å, respectively (Gabe *et al.*, 1973). As the Fe^{+3} ion is larger than Al^{+3} ion, it can be regarded that Fe^{+3} ion prefers the M(3) site of epidote. Partitioning has also been experimentally established by Holdaway (1972). According to his results, the partition coefficient at 640°C and 3 Kbars is 0.514 (Table 4). This value was quoted for comparison with results from natural assemblages.

DISCUSSION

The partition coefficients confirm the difference in thermal condition between low-grade and medium-grade metamorphic rocks on the basis of the assumption that garnet and epidotes are formed all together in equilibrium with accompanying metamorphic minerals such as chlorite, albite, actinolite, tremolite, hornblende or clinopyroxene. As shown in Tables 2 and 4, garnet and epidote pairs coexisting chlorite, actinolite or albite which are considered to be formed under the low grade of regional metamorphism, have smaller partition coefficient than the pairs coexisting with clinopyroxene or hornblende formed under the relatively higher thermal conditions.

Fig. 1 shows a plot of the element distribution and states the base K_D -value of 1, 0.5, 0.4 and so on. The points fall in a limited area of the diagram and $X_{Fe}^{Ep}/(1-X_{Fe}^{Ep})$ ratio in epidote is always smaller than $X_{Fe}^{Gr}/(1-X_{Fe}^{Gr})$ ratio in garnet. The partition coefficient is generally in the range 0.02 to 0.7. The pairs with relatively large partition coefficients from 0.24 to 0.36 and from 0.58 to 0.75, seem to be plotted linearly with the base gradients of 0.3 and 0.5, respectively, on the diagram.

K_D values from greenschist facies rocks (Sample Nos. 9, 10, 12 and 13) of the estimated metamorphic temperatures, 330~390°C, range approximately between 0.02 and 0.17. K_D values from epidote-amphibolite facies rocks and calcareous

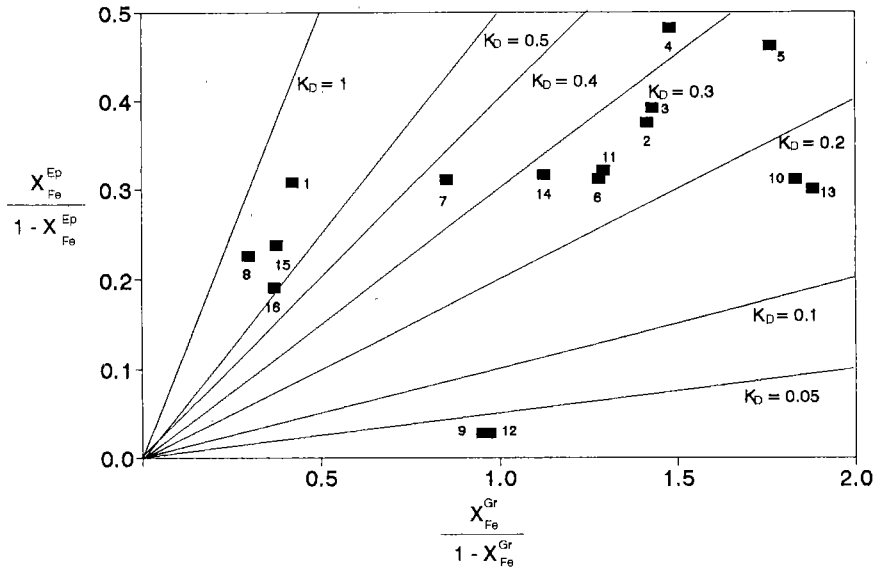


Fig. 1. Distribution of Fe and Al between coexisting garnet and epidote from metamorphic rocks, calcareous skarns and experimental run products. Nos are as for Table 2.

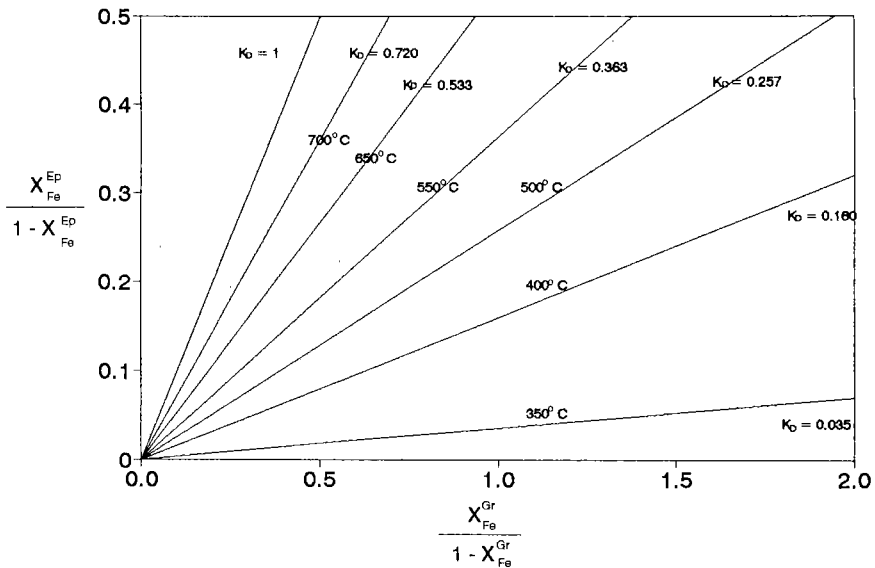


Fig. 2. Relationship between partition coefficient (K_D) and temperature.

skarns (Sample Nos. 2~7, 11 and 14) of the estimated temperatures, 400~550°C, range approximately between 0.24 and 0.37. K_D values from amphibolite facies rocks, calcareous skarns and experimental run products (Sample Nos. 1, 8, 15 and 16) of the temperatures, 640~700°C, range

nearly between 0.58 and 0.75. Therefore, K_D values can be used to differentiate between rocks of low and high metamorphic grade.

Fig. 2 illustrates the relationship between K_D values and temperatures on the diagram representing the base thermal gradients at intervals

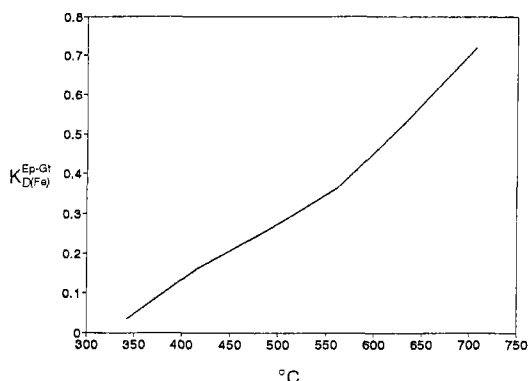


Fig. 3. Plot of partition coefficient (K_D) against the estimated temperature. Effect of pressure is not considered. The selection of the values is based on Tables 2 and 4 and Fig. 2.

of one hundred or fifty degree centigrades. Effect of pressure is not considered, as discussed in the previous sections. The area of compositions with high $\text{Fe}_2\text{O}_3/\text{Al}_2\text{O}_3$ ratio of epidote, that is $X_{\text{Fe}}^{\text{Ep}}/(1 - X_{\text{Fe}}^{\text{Ep}}) > 0.5$, does not appear to be stable in the metamorphic rocks and the experimental run products. However, the composition ratio for equilibrium epidote and garnet are very important. Temperature gives a pronounced effect on the distribution of Al and Fe between epidote and garnet. With increasing temperature, Fe^{+3} becomes redistributed from garnet into epidote, whereas aluminium becomes redistributed from epidote into garnet. This fact is coincident with the general principle of phase correspondence (Perchuk and Aranovich, 1979): as the temperature increase the more electropositive aluminum metal redistribute from the hydrous epidote into the anhydrous garnet mineral, from monoclinic epidote into cubic garnet structure.

As shown in Fig. 3, it may be possible to present approximately linear relationship between partition coefficients and temperatures. The selection of the values in Fig. 3 is based on Fig. 2 and Tables 2 and 4. Figs. 2 and 3 show that the variation in K_D should be more pronounced at higher temperatures than at lower temperatures because the effects of substitution change depending on temperatures. As said previously, if we neglect the pressure dependence of partition

coefficients for the ion-exchange reaction in the two minerals, the diagrams can serve as a mineralogic thermometer for estimation of the approximate temperature of low-to medium-grade metabasites and calc schists of various geotectonic settings and hydrothermally altered calcareous rocks from skarn deposits, which contain coexisting garnet and epidote. But we need more experimental studies about stability relations of epidote and garnet for completion of the applicability of this thermometer.

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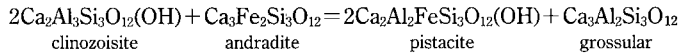
(책임편집 : 권성택)

변성암류내에 공존하는 석류석과 녹염석의 Al-Fe 분배에 관한 연구

金亨植 · 金英謙 · 張永南*

高麗大學校 理科學科 地質學科, *韓國資源研究所

요 약: 그란다이트 석류석과 녹염석 광물군은 저 내지 중급 변성작용을 받은 염기성암이나 갈크편암 또는 스카른 광상에서 열수 변질작용을 받은 석회질 암석에서 주로 나타난다. 16개의 표본 중에 함유된 석류석과 녹염석이 전자현미분석에 의해 그 화학성분이 분석되었다. 다음의 화학반응식:



에서 표면평형이 유지되었다고 전제하고 공존하는 석류석과 녹염석 사이의 Al-Fe 분배 계수가 측정되었다. 분배계수에 의해 저 내지 중급 변성암류 사이의 온도 차이를 확인할 수 있다. 추정 변성온도가 약 330~390°C 에 해당하는 녹색 편암상의 변성암류는 0.02 내지 0.17 사이의 K_D 값을 가지고, 추정 변성온도가 약 400~550°C 의 녹염석-엠펜블라이트상에 속하는 변성암과 석회질 스카른 암석은 약 0.24 내지 0.37 사이의 K_D 값을 가진다. 또 추정온도가 약 640 내지 700°C 사이의 변성암류는 약 0.58 내지 0.75 사이의 K_D 값을 가진다. 압력은 상기와 같은 이온 교환 반응에 있어 K_D 값에 거의 영향을 미치지 않는다는 전제하에 그림 3과 4는 비교적 낮은 압력조건에서 생성된 변성암류에 대해 광물학적 지질온도계 역할을 할 수 있다.

핵심어: 분배계수, 변성작용, 녹색편암상, Al, Fe, 녹염석, 석류석, 전자현미분석, 광물학적 지질온도계