

Garnet-Orthopyroxene Geothermometer and Geological Applications

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Abstract : Equilibrium relations between garnet and orthopyroxene have been investigated by reversal experiments in the range of 20-45Kb and 975-1400°C in the FeO-MgO-Al₂O₃-SiO₂(FMAS) system. A mixture of PbO with about 55 mol per cent PbF₂ was used as a flux and proved very effective. The Fe-Mg exchange reaction seems to have little or no compositional dependence at these conditions. Combination of the experimental results with the garnet mixing model of Ganguly and Saxena(1984) yields the following geothermometric expression for the common natural assemblages that can be represented essentially within the system FeO-MgO-CaO-MnO-Al₂O₃-SiO₂.

$$T^{\circ}C = (1971 + 11.91P(Kb) + 1510(X_{Ca} + X_{Mn})^{Gt}) / (\ln K_D + 0.96) - 273$$

SYMBOLS AND ABBREVIATIONS

solution

- Gt : Garnet
 Opx : Orthopyroxene
 QFM : Quartz-fayalite-magnetite buffer
 WI : Wustite-iron buffer
 WM : Wustite-magnetite buffer
 ΔC_p° : Isobaric heat capacity change of a reaction when all components are in their pure states
 ΔH_f° : Enthalpy of formation from oxides
 K(a) : Equilibrium constant of reaction(a)
 K_D : (Fe/Mg)^{Gt} / (Fe/Mg)^{Opx}
 V^o : Molar volume of an end-member component
 γ_i : Activity coefficient of the component i involving one mole of exchangeable cation
 ± σ : Plus and minus standard deviation
 r : Statistical correlation coefficient
 ΔW_i : (W_{Mgⁱ} - W_{Feⁱ}) where the Ws are 'simple mixture' interaction parameters between the specified components in garnet solid

INTRODUCTION

The Mineral pair garnet and orthopyroxene is one of the most important assemblages which make up the lower crust and upper mantle. It is found in various rock types such as garnet-peridotite nodules in kimberlite and ultrabasic rocks, charnockites and granulites, which together represent a wide range of temperature, pressure and geological environments. The garnet-orthopyroxene pair has been suggested as a good geothermometer for the formation of the above rock types because the ΔH^o value of the Fe²⁺-Mg exchange equilibrium between garnet and orthopyroxene is fairly large.

Since Ramberg and Devore(1951) published their pioneering paper which dealt with the distribution of Fe²⁺ and Mg between olivine and orthopyroxene, a great deal of interest and intensive research has been concentrated on the development of geothermometers on the basis of the compositional properties of coexisting minerals. Among these are geothermometers based on Fe-Mg exchange between garnet and

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biotite(Thompson:1976, Ferry and Spear:1978, Perchuk and Lavrenteva:1983), garnet and olivine(Kawasaki and Matsui:1977, O'Neill and Wood:1979), garnet and cordierite(Hensen and Green:1973, Thompson:1976), and garnet and clinopyroxene(Raheim and Green:1974, Oka and Matsumoto:1974, Ellis and Green:1979, Ganguly:1979, Dahl:1980, Saxena:1980).

Owing to both experimental and theoretical problems attending the calibration of mineral reactions as functions of P, T, and composition(X), most reactions which are of interest in geothermometry have been investigated repeatedly by different researchers. These problems might arise from the nature of starting samples such as synthetic glasses and natural crystalline minerals, calibration errors especially at lower temperatures, analytical errors, limited compositional range of experimental work which can not account for multi-component effects, inaccurate thermochemical data, or wrong or inadequate theoretical models. The danger of accepting data from synthesis experiments as equilibrium values, especially in systems involving garnet, has been demonstrated in a number of previous studies(e.g., Lane and Ganguly:1980, Perkins et al.,:1981).

The main objective of this study has been to obtain carefully reversed experimental data on the Fe-Mg distribution between garnet and orthopyroxene in the simple system FeO-MgO-Al₂O₃-SiO₂(FMAS). The experimental data have been combined with the available multicomponent mixing data of garnet(Ganguly and Saxena:1984) to develop a geothermometric formulation which can be applied to a wide variety of natural rocks.

PREVIOUS WORK

Dahl(1980) derived an empirical expression of $\ln K_D(\text{Fe-Mg})$ as a function of temperature(700-900°C) and composition on the basis of microprobe data for coexisting garnet and orthopyroxene of the mafic metamorphics from

the Ruby Ranges in Montana, for which pressure and temperature conditions had been estimated from other mineral equilibria.

Harley(1984) investigated the partitioning of Fe and Mg in FMAS and CaO-FeO-MgO-Al₂O₃-SiO₂(CFMAS) system, using glass and synthetic minerals, in the P-T range 5-30Kb and 850-1200°C. The reliability of this geothermometer is not clear owing to nature of starting materials and large relative errors in the experimental and natural system data.

Sen and Bhattacharya(1984) theoretically formulated from published thermochemical data. Applicability of this thermometer is seriously restricted by the fact that it was formulated for the P-T range covered by granulite facies rocks only. It is not clear how well this thermometer can be extrapolated to different P-T conditions(e.g., for mantle samples).

From the above it is evident that little work has been done so far to experimentally constrain the equilibrium compositions of coexisting garnet and orthopyroxene by determining compositional changes in crystalline starting materials, which is the most unambiguous way of determining equilibrium compositions at a given P, T, X condition.

EXPERIMENTAL METHODS

The equilibrium $K_D(\text{Fe-Mg})$ between garnet and orthopyroxene is approached from two directions, using high K_D and low K_D starting mixtures, at any given P and T, as in all classical reversal experiments which can provide the most unambiguous approach for the investigation of equilibrium compositions of coexisting minerals. In the high K_D starting mixtures, Mg-rich orthopyroxene is made to react with Fe-rich garnet, whereas in the low K_D starting mixture, Fe-rich orthopyroxene with garnet of comparable composition is used.

Apparatus, Sample Configurations and P-T Measurements

All experiments were carried out in an end-loaded Piston-Cylinder apparatus, using 1/2, 3/4 or 1 inch carbide-core pressure vessels and carbide pistons.

NaCl or CsCl were used as sleeves around graphite furnaces in the pressure cell (Fig. 1) in manner suggested by Boettcher et al. (1981),

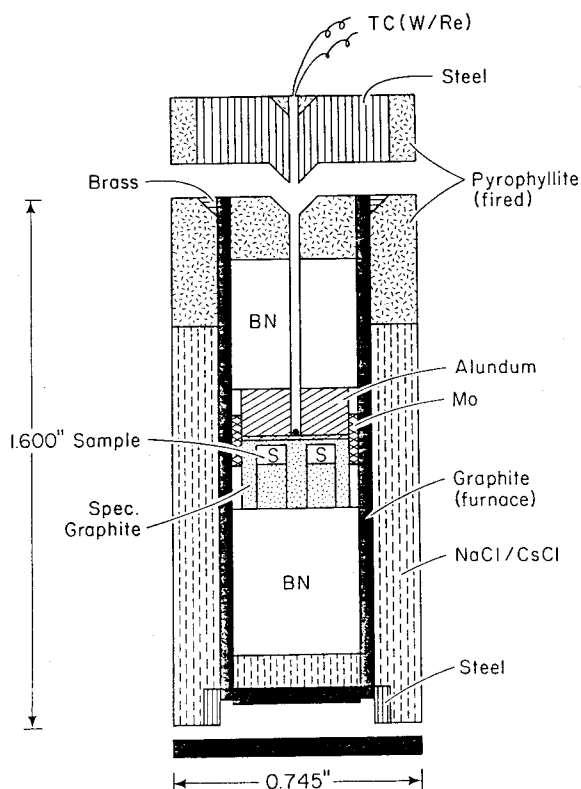


Fig. 1 Schematic illustration of the cross section of a typical pressure cell used in the experiments in Piston-Cylinder apparatus.

which greatly reduced the distortion of the furnace due to differential compression of pressure cell materials. No correction was made to the nominal pressure as salt sleeves offer very little frictional resistance to pressure (Mirwald et al., 1975). CsCl has a much lower thermal conductivity than NaCl, and thus helps reduce fracturing of the carbide cores due to thermal stress in relatively high P-T runs (Elphicks et al., 1985).

The pressure cells were wrapped with 0.002

inch thick lead foil, and the inner wall of the pressure core was coated with hydrogen free 'Molykote' (MoS_2) lubricant to reduce friction at high pressures. All pressure cells were dried in an oven at least for 12 hours at 150°C before loading inside a pressure vessel. Samples were packed inside spectrographic quality graphite disks—each hole being tightly fitted with a graphite lid.

Temperatures were measured with W3 per cent Re-W25 per cent Re thermocouples and encased in 99.99 per cent Al_2O_3 ceramic tubings. The W-Re thermocouple is known to have superior mechanical and chemical stability, compared to Chromel-alumel and Pt-Rh thermocouples. To minimize thermocouple 'poisoning' by reaction with pressure cell material, a 0.015-0.020 inch alundum (99.99 per cent Al_2O_3) disk was placed between the thermocouple junction and the top surface of the graphite container. The thermocouple junction was 0.050 inch from the sample. The thickness of the sample disk within a graphite container was within 0.12 inch. Following Elphick et al. (1985) the graphite container was surrounded by a 0.20 inch high Mo ring, which was shorted to the furnace. The central sections of the furnace and Mo ring coincided with the top surface of the sample disk. This configuration reduced the temperature difference between the thermocouple junction and the lower surface of the sample disk to within 5°C (Elphick et al., 1985). The nominal temperatures were corrected for the pressure effect on the e.m.f. of W/Re thermocouple according to the method discussed by Lane & Ganguly (1980). The corrected temperatures are $6-9^\circ\text{C}$ higher than the nominal ones. From our earlier experience with the problem of thermocouple stability in this type of pressure cell (e.g., Elphick et al., 1985), we believe that the true sample temperature for any run above 1200°C was within $\pm 10^\circ\text{C}$ of that reported for the run. The precision of temperature measurement is better at lower temperatures.

After the pressure cell is taken to the desired

nominal run pressure at room temperature, it is left overnight to allow the cell to relax. Usually the pressure would drop by about 2-3 Kb on the following day, but the pressure builds up again by the thermal expansion of the pressure cells and of the oil which drives the rams. Generally fluctuations of several hundred bars are common during a run. However, if the pressure increases too much(2 Kb), it is ad-

justed manually by releasing the oil pressure. These fluctuations are the main source of uncertainties in the nominal run pressures as shown in Table 2.

Starting Materials

Natural and synthetic garnet and orthopyroxene were used to prepare starting materials

Table 1 Microprobe analysis of starting materials.

	Orthopyroxenes					Garnet		
	Opx/1	Opx/2	Opx/3	Opx/4	Opx/5	Gt/1	Gt/2	Gt/3
FeO ⁺	9.32	46.76	31.14	-	34.86	35.37	22.74	0.04
MgO	33.81	5.09	17.80	37.77	13.55	5.34	13.01	29.80
SiO ₂	56.30	47.57	51.79	56.62	50.28	38.48	39.18	44.95
Al ₂ O ₃	0.08	0.75	0.07	6.43	0.03	21.33	23.25	25.74
CaO	0.32	0.61	-	-	0.58	0.40	1.80	0.19
MnO	0.05	0.05	-	-	1.30	0.03	0.49	-
Cr ₂ O ₃	-	0.01	-	-	-	-	-	-
TiO ₂	-	0.02	-	-	-	0.02	-	-
Na ₂ O	-	0.03	-	-	-	0.05	0.02	-
NiO	0.05	-	-	-	0.07	-	-	-
K ₂ O	-	-	-	-	-	-	-	-
Total	99.94	100.90	100.70	100.82	100.68	101.09	100.40	100.72
Fe	0.545	3.260	1.999	-	2.306	2.322	1.424	0.002
Mg	3.529	0.635	2.037	3.734	1.597	0.624	1.452	2.960
Si	3.942	3.966	3.976	3.755	3.975	3.021	2.934	2.994
Al	0.006	0.074	0.006	0.502	0.002	1.973	2.051	2.020
Ca	0.023	0.054	-	-	0.049	0.040	0.144	0.013
Mn	0.003	0.003	-	-	0.086	0.001	0.031	-
Cr	-	-	-	-	-	-	-	-
Ti	-	-	-	-	-	0.001	-	-
Na	-	0.004	-	-	-	0.007	0.003	-
Ni	0.002	-	-	-	-	-	-	-
K	-	-	-	-	-	-	-	-
Cation Total	8.050	7.996	8.018	8.091	8.015	7.989	8.039	7.989
O : 12								
Fe/Mg	0.154	5.154	0.981	0.000	1.443	3.717	0.980	0.000
Fe/Fe+Mg	0.133	0.837	0.495	0.000	0.590	0.788	0.495	0.000

Opx/1 : Sample from Telmark, Norway(UCLA Mineral Museum)

Opx/2 : Sample No. XYZ, Ramberg and Devore(1951)

Opx/3 : Synthetic sample

Opx/4 : Synthetic sample

Opx/5 : Sample No. 5, Burtler

Gt/1 : Natural sample, Schneider Co.

Gt/2 : Natural sample No. 143895, Smithsonian Collection

Gt/3 : Synthetic pyrope

*All iron assumed to be FeO

for studying the equilibrium compositions of coexisting garnet and orthopyroxene. Natural samples with $X_{Fe} + X_{Mg} = 0.97$ were separated from various rocks and handpicked under binocular microscope. The compositions of starting materials are given in Table 1.

Pyrope

Pyrope was synthesized hydrothermally in a sealed gold capsule from a stoichiometric mixture of reagent grade MgO, SiO₂, and Al₂O₃ at 25 Kb, 1000°C for 24 hours. The X-ray diffraction pattern showed single phase pyrope.

Non-aluminous orthopyroxene

Non-aluminous orthopyroxene was synthesized from a mixture of reagent grade MgO, Fe₂O₃, and SiO₂ under dry conditions in a graphite capsule at 25 Kb, 1200°C for 48 hours. The run product consisted of grains 200 μm or larger. The average Fe/(Fe+Mg) ratio of the run product was 0.49 compared to the intended ratio of 0.6 of the starting material. Alloying of Fe with the graphite capsule (and weighing error) might have been responsible for the lower concentration of Fe in the run product. However, The X-ray diffraction pattern showed single phase orthopyroxene.

Aluminous orthopyroxene

Aluminous orthopyroxene was synthesized hydrothermally in a sealed gold capsule from a mixture of reagent grade MgO, Al₂O₃, and SiO₂ at 20 Kb, 1100°C for 48 hours. The mixture was seeded with 5 wt. per cent of synthetic aluminous enstatite (12 wt. per cent Al₂O₃) which was synthesized from an oxide mixture with 5 wt. per cent of natural pyroxene, Opx/1 (Table 1). The run product showed broad X-ray reflections implying significant inhomogeneity in the concentration of Al₂O₃. To improve homogeneity, the run product was crushed and recycled at 25 Kb, 1350°C for 48 hours in a dry graphite container. The X-ray peaks of the recycled product were sharper, and microprobe analyses of several grains yielded an average Al₂O₃ content of 6.5 wt. per cent with a range of 5-9 wt. per cent.

Flux Material

A number of workers (e.g., Gasparik: 1983, Gasparik & Newton: 1984) have successfully used PbO flux to catalyze cation exchange reactions between silicates. However, because of its relatively high melting temperature, the use of PbO as a flux material had to be essentially limited above 1200°C in high P-T experimental studies. In this work, we have used a mixture of PbO and PbF₂ as flux material. Unfortunately, there are no data on the melting behavior of this mixture under high pressure. The 1 bar binary phase diagram (Sandoni: 1914, quoted in Levin et al., 1964) shows the eutectic point for the system at about 490°C (compared to 888°C for the melting of pure PbO). The results of a trial run with two flux compositions (0.75 PbF₂ and 0.55 PbF₂) loaded separately with Gt-Opx mixtures within a graphite disk suggested 0.55 PbF₂ + 0.45 PbO to be a relatively effective flux composition at the high P-T conditions of these experiments.

The effectiveness of PbO-PbF₂ flux in promoting Fe-Mg exchange between garnet and orthopyroxene is clearly demonstrated by a run at 30 Kb, 1200°C for 2 days. A small portion of a Gt-Opx mixture was mixed with the flux and packed inside one of the sample holes of a two-hole graphite disk, the other hole containing a portion of the same mixture, but without the flux. As illustrated in Fig. 4, the products of the fluxed run showed a significantly larger shift of composition toward equilibrium.

The PbO-PbF₂ flux was found to melt substantially in the lowest temperature experiment, 750°C at 20 Kb, attempted in this work. However, we failed to get an adequate exchange reaction below 975°C. Part of the flux was usually converted to Pb by reaction with graphite capsule. As Pb has a relatively lower melting temperature (Akella et al., 1973), the reduction of PbO to Pb should promote melting of the flux. As shown in Fig. 2, the flux dissolved a substantial portion of the initial sample (40-60 per cent), and the residual material sank to the

bottom of the graphite container. Microprobe analyses of the glassy material near the top of the container showed Pb, F, Fe, Mg, Ca, Al, Si, Cs, and Cl, the last two elements being derived from the insulation CsCl sleeve around graphite furnace of the pressure cell. The substitution of Pb and F within the silicates in all run products was found to be limited to 0.1~0.3 wt. percent, which is too dilute to have any significant effect on the equilibrium compositions of coexisting garnet and orthopyroxene.

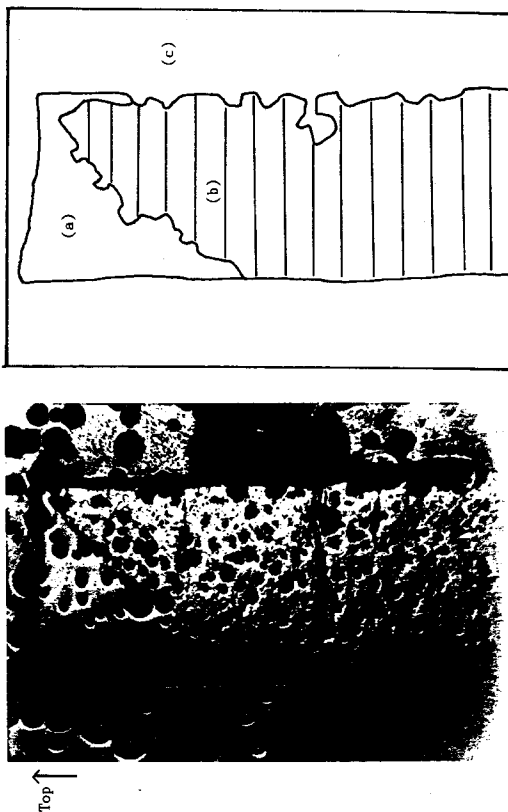


Fig. 2 Cross section of fluxed run product at 975°C, 20Kb. Top portion(a) represents glass including various constituents of starting material eg. Fe, Mg, Si, Al, pressure medium ie. Cs, Cl and flux material eg. Pb, F. Bottom portion(b) is composed of equilibrated crystals of garnet and orthopyroxene that sank through the molten flux. Surrounding the sample we have epoxy(c), which was used to mount the sample.

Owing to the dissolution of the sample in the flux, the choice of the optimal flux to sample ratio that would promote adequate reaction, but at the same time retain enough undissolved sample for microprobe analysis, appeared to be a tricky problem. In several runs, the entire samples were dissolved in the flux. The flux to sample ratio in the successful runs are shown in Table 2.

Analytical Method

The run products were analyzed with an automated ARL scanning electron microprobe using a 15 KV accelerating voltage and a 25mA sample current. The X-ray intensity and background for each measurement was corrected automatically by the computer program Task II(McCarthy, 1975) and the analytical data were reduced by the Bence-Albee method (Bence & Albee, 1968). Instrumental drift was handled by recalibrating at approximately 3 hour intervals. The standards used were as follows: anorthite for Al and Ca, diopside for Mg and Si, fayalite for Fe, rhodonite for Mn, albite for Na, chromite for Cr, sphene for Ti, and orthoclase for K.

Only those analyses which had total wt. per cent oxide between 99 and 101, and satisfied the theoretical stoichiometry of the mineral within 2 per cent, were considered acceptable for the determination of K_D . All iron was assumed to be in the ferrous state. (Calculations of f_{O_2} condition in the C-O₂ system in the presence of graphite suggests that for values at the run conditions were between those defined by QFM and WI buffers, and within ± 2 log units of the WM buffer. The f_{O_2} for the C-H₂O + graphite system lies between those of C-O₂ + graphite system and WI buffer.)

EXPERIMENTAL RESULTS AND THERMODYNAMIC ANALYSIS

The run data are summarized in Table 2, and the compositions of coexisting garnet and

Table 2 Summary of selected run data.

Nominal*		Time hrs	Starting mixture	Flux/sample wt. ratio	Initial		Resultst	
T°C	P, Kb				K _b	X _{Fe} ^{Gt}	X _{Fe} ^{OPx}	Final K _b
975±5	20±0.5	168	Opx/ 4, Gt/2	0.80	∞	0.44	0.26	2.17
			Opx/ 1, Gt/2	0.80	6.36	0.49	0.31	2.14
			Opx/ 1, Gt/1	0.80	2.41	0.56	0.37	2.21
			Opx/ 4, Gt/1	0.80	∞	0.58	0.38	2.24
			Opx/ 2, Gt/1	0.80	0.72	0.91	0.83	2.23
1050±5	26±1	168	Opx/ 3, Gt/3	0.80	0.00	0.36	0.21	2.12
			Opx/ 1, Gt/2	0.80	6.36	0.42	0.27	1.97
			Opx/ 1, Gt/1	0.80	2.41	0.53	0.34	2.15
			Opx/ 2, Gt/1	0.80	0.72	0.85	0.72	2.11
1100±10	25±0.5	61	Opx/ 1, Gt/1	0.10	2.41	0.55	0.37	2.06
			Opx/ 2, Gt/1	0.10	0.72	0.79	0.65	2.02
1200±5	26±1	120	Opx/ 4, Gt/2	0.10	∞	0.22	0.13	1.83
			Opx/ 1, Gt/2	0.10	6.36	0.44	0.30	1.80
			Opx/ 1, Gt/2	0.10	6.36	0.40	0.25	1.96
			Opx/ 3, Gt/3	0.10	0.00	0.34	0.22	1.89
			Opx/ 3, Gt/3	0.10	0.00	0.24	0.15	1.77
1200±10	25.5±0.5	55	Opx/ 1, Gt/2	0.05	2.41	0.64	0.47	1.98
1200±10	32.5±1.5	48	Opx/ 2, Gt/1	0.05	0.72	0.84	0.74	1.83
1300±10	37.5±0.5	24	Opx/ 1, Gt/1	0.05	2.41	0.46	0.32	1.76
1300±5	39.5±0.5	48	Opx/ 2, Gt/1	0.00	0.72	0.81	0.70	1.80
1400±5	45.5±0.5	24	Opx/ 1, Gt/1	0.00	2.41	0.55	0.43	1.60
1400±5	43.5±0.5	45	Opx/ 2, Gt/2	0.00	0.19	0.61	0.48	1.64
1400±5	43.5±0.5	45	Opx/ 5, Gt/2	0.00	0.68	0.63	0.51	1.60

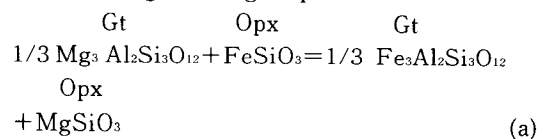
*The temperatures should be revised upward, as follows, to correct for the pressure effect on the e. m. f. of W-Rc thermocouple: 975 to 979, 1050 to 1057, 1100 to 1104, 1200 to 1206, 1300 to 1305, 1400 to 1407.

†Average of at least 20 spot analyses.

orthopyroxene at selected P-T(nominal) conditions are illustrated in Fig. 4. Fig. 3 is structure of run product illustrating the shape and size of mineral grains. Generally the grain size of orthopyroxene was small, which caused major problems during microprobe analyses and resulted in numerous analyses which were unacceptable in terms of the criteria discussed earlier. Both garnet and orthopyroxene usually displayed significant compositional inhomogeneities. Consequently, equilibrium compositions of coexisting garnet and orthopyroxene were

determined on the basis of microprobe analyses made as close to their mutual contacts as possible, but without introducing 'edge' effects (Elphick, et al.: 1985, Ganguly, et al.: 1987).

The Fe²⁺-Mg fractionation between garnet and orthopyroxene can be treated in terms of the following exchange equilibrium



Thus, at equilibrium

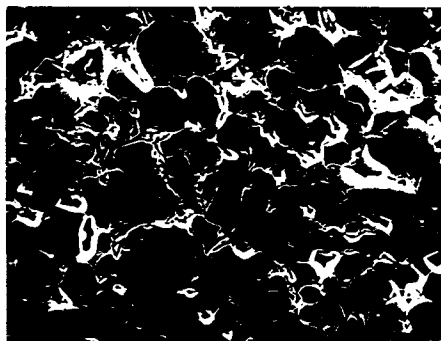


Figure 3-a



Figure 3-b

Fig. 3 Experimental run products. Horizontal bar = 20 μ m. Garnets are equant with rounded margins, and orthopyroxene grains are subhedral, elongated and prismatic. Photos were taken using the backscattered electron signal and raster scan capabilities of the microprobe.

Fig. 3-a: 1400°C, 45Kb.

Fig. 3-b: 1300°C, 35Kb.

$$K(a) = \left[\frac{X_{Fe}^{Gt}}{X_{Mg}^{Gt}} \frac{X_{Mg}^{Opx}}{X_{Fe}^{Opx}} \right] \cdot \left[\frac{\gamma_{Fe}^{Gt}}{\gamma_{Mg}^{Gt}} \frac{\gamma_{Mg}^{Opx}}{\gamma_{Fe}^{Opx}} \right] \quad (1)$$

$$= \left[\frac{(Fe/Mg)^{Gt}}{(Fe/Mg)^{Opx}} \right] \cdot \left[\frac{(\gamma_{Fe}/\gamma_{Mg})^{Gt}}{(\gamma_{Fe}/\gamma_{Mg})^{Opx}} \right]$$

where $K(a)$ is the equilibrium constant of reaction (a), and γ is the activity coefficient of the specified end-member component on a one-cation basis. We define the quantities within the first and second square brackets as K_D (distribution coefficient) and K_γ , respectively.

The data presented in Fig. 4 suggest the K_D

to be essentially independent of Fe/Mg ratio at $T > 975^\circ\text{C}$. This conclusion is corroborated by the extensive data of Kawasaki &

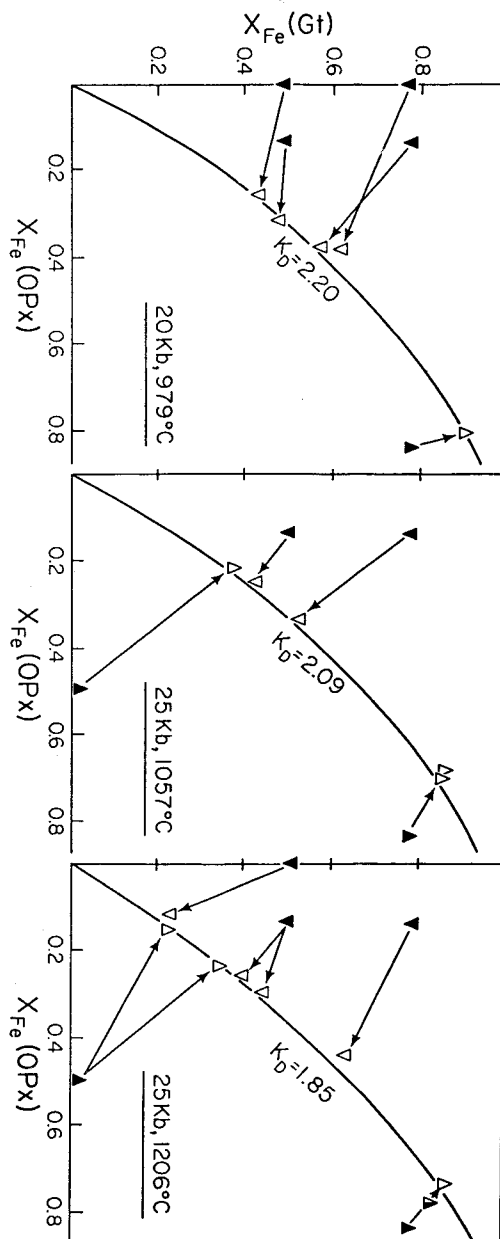


Fig. 4 Fractionation of Fe and Mg between coexisting garnet and orthopyroxene at selected P-T (nominal) conditions, $X_{Fe} = Fe/(Fe+Mg)$. See Table 2 for correction of nominal temperatures. All Fe is

assumed to be divalent. Solid triangles; starting composition; half-filled and open triangles: final compositions in dry run and in runs made with PbO-PbF₂ flux, respectively; arrows: direction of evolution of compositions. The development of two different final compositions from the same starting composition at 25 Kb, 1200°C is a consequence of different Gt/OPX ratios. All runs were in graphite capsules.

Matsui(1983, Fig.6) at 1100°C and 1300°C. The simplest explanation for this lack of compositional dependence of K_D is that Fe and Mg mix essentially ideally in both garnet and orthopyroxene at T > 975°C or that the nonideal Fe-Mg interactions in the two minerals effectively compensate for one another at T ≥ 975°C. We can, thus reduce the polybaric Fe-Mg fractionation data to an arbitrary isobaric condition

of 25 Kb as follows

$$\left(\frac{\partial \ln K_D}{\partial p}\right)_T \cong \left(\frac{\partial \ln K}{\partial p}\right)_T = \frac{-\Delta V^\circ}{RT} \quad (2.1)$$

or

$$\ln K_D(25\text{Kb}, T) = \ln K_D(P, T) - \int_p^{25\text{Kb}} \frac{\Delta V^\circ}{RT} dp \quad (2.2)$$

The last term in (2.2) is integrated by assuming ΔV° to be independent of pressure in the range of pressure (20 to 45 kb) of these experiments. The error introduced by this assumption is small compared to the uncertainty of the experimental and volumetric data.

The molar volumes for the pure end members are taken from the measurements on synthetic samples by Charlu et al. (1975), Takahashi & Kushiro (1983), and Chatillon-Colinet et

Table 3 Thermochemical data for garnet and orthopyroxene

End member	ΔH_f° (Kcal/mole)	ΔS_f° (e. u.)	C _p Coefficients (cal/mole)			V* (cm ³ /mole)	References
			a	b × 10 ³	c × 10 ⁻⁵		
Pyrope (1/3Mg ₃ Al ₂ Si ₃ O ₁₂)	-508.669 ^b	21.03 ^b	35.46	4.02	9.69 ^b	37.756 ^a	a) Takahashi & Liu (1970) b) Saxena & Erikson (1983)
Almandine (1/3Fe ₃ Al ₂ Si ₃ O ₁₂)	-423.008 ^b	22.82 ^b	32.51	11.23	6.24 (≤848°K) ^b	38.483 ^a	
Enstatite (MgSiO ₃)	-369.962 ^b	15.83 ^b	27.72	3.48	9.79 ^b	31.31 ^c	c) Charlu et al. (1975)
Ferrosilite (FeSiO ₃)	-285.494 ^a	22.60 ^b	31.78	0.0	11.58 ^b	32.99 ^d	d) Chatillon Colinet et al. (1983)

ΔH_f° , and ΔS_f° , are for formation from oxides at 1 atm., 298°K; molar volume (V*) is at 1 atm., 298°K; C_p = a + bT - c/T²

al. (1983a, b) and shown in Table 3.

Linear least squared fit of the reduced isobaric $\ln K_D$ data versus 1/T yields the following relation (r = 0.96)

$$\ln K_D(25\text{Kb}) = \frac{2269(\pm 142)}{T(\text{K})} - 0.96 \quad (3.1)$$

or, using (2.2),

$$\ln K_D = \frac{1971(\pm 166) + 11.9 P(\text{Kb})}{T(\text{K})} - 0.96 \quad (3.2)$$

where the uncertainties represent one σ value. All 23 K_D values, obtainable from table 2, have been used for the regression. The expression (3.2) yields a value of ΔH_a° of -3916(±282) cal. at 1 bar, 975-1400°C.

Fig. 5 shows a conventional plot of $\ln K_D$ vs. 1/T according to the regressed expression (3.1), along with the experimental data. We performed an additional experiment at 20Kb, 750°C with PbO-PbF₂ for one week to constrain the low temperature exchange equilibrium. However, it

failed to yield any significant reaction between garnet and orthopyroxene even though the flux was molten in the charge.

Fig. 6 shows a comparison of our results on the temperature dependence of $\ln K_D$ with the experimental results of Kawasaki and Matsui(1983) and Harley(1984) in the FMAS

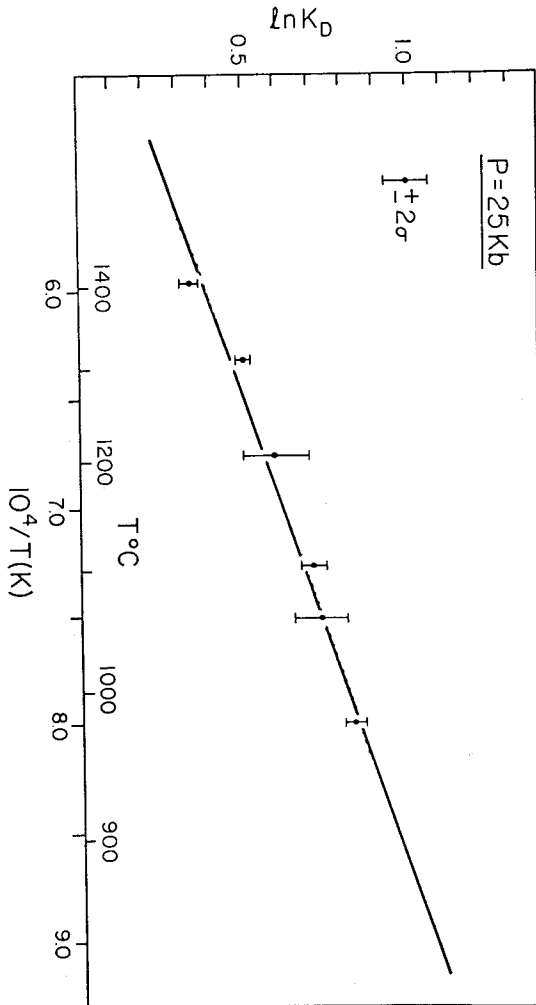


Fig. 5 $\ln K_D$ versus reciprocal temperature. The data with vertical bars represent mean with 2σ uncertainty of the reversed experimental determinations in the FMAS system. All data are normalized to 25 Kbar. The solid line represent least squared fits to all (23) experimental data according to the assumptions of $\Delta C_p = 0$

system, and the theoretical deductions of Sen and Bhattacharya(1984). All data are normalized to 25Kb. The various experimental results agree within the limits of their uncertainties. However, the best fit to Harley's data lies about 70–85°C lower than that to our data.

Harley(1984) performed some of his experiments in Fe–capsules, and noted substantial iron addition to the charge from the encapsulating material. He revised the $\ln K_D$ values upward by 0.15–0.20 units on the basis of the observation that the run “in graphite capsules with mixes not susceptible to Fe–addition” yielded $\ln K_D$ values greater by the above magnitude compared to those made in Fe capsule. The K_D values obtained through these arbitrary adjustments may not be very precise. Further, the data shown in Fig. 4 and those of Kawasaki and Matsui(1983: Fig.4) do not suggest any significant dependence of K_D on Fe/Mg ratio at the temperatures of Harley's experiments.

In Sen and Bhattacharya's(1984) formulation, K_D depends on Fe/Mg ratio. In view of the experimental data, discussed above, suggesting lack of any significant effect on Fe/Mg ratio on K_D at $T \geq 975^\circ\text{C}$, we have ignored the Fe–Mg nonideality term in their formulation to compare it with the experimental data. Dependence of K_D on Fe/Mg ratio can not be ruled out at lower temperatures, but correction for this effect has to await further experimental Fe–Mg fractionation and/or mixing property data at lower temperatures.

DEVELOPMENT OF GARNET– ORTHOPYROXENE GEOTHERMOMETER

The application of the Fe–Mg fractionation data to the geothermometry of natural assemblages obviously requires correction for the effects of additional components which can substitute significantly in garnet and orthopyroxene solid solutions. The major substitutional cations in natural assemblages are Ca, Mn, and Cr^{+3} . The last one is relatively unimportant in crustal assemblages, but may have significant effect in mantle xenoliths (Wood and Nicholls,

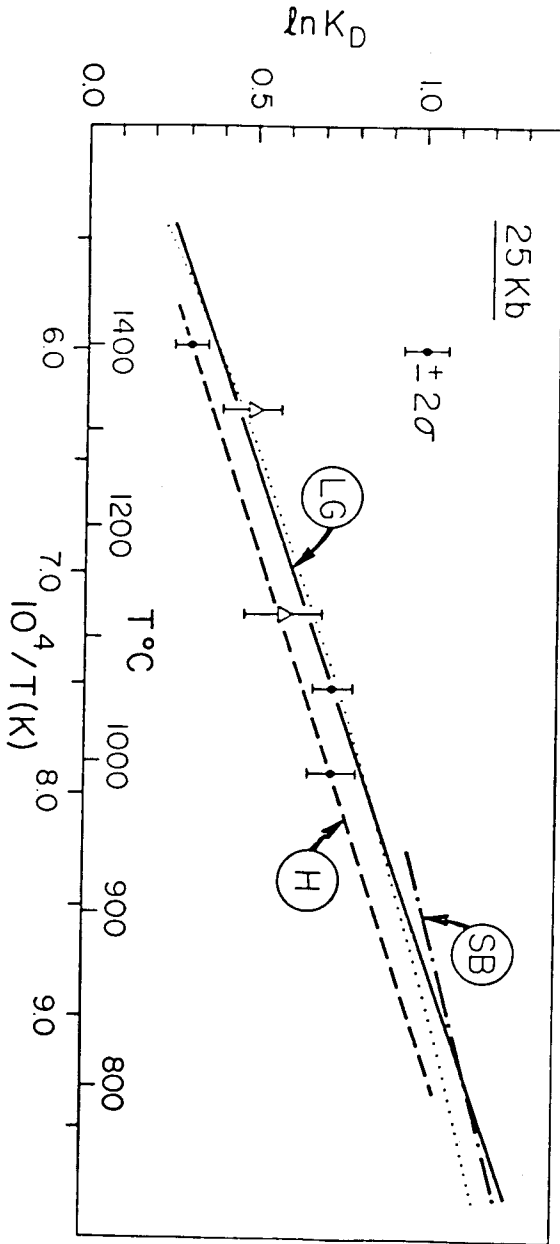


Fig. 6 Comparison of the $\ln K_D$ vs $1/T$ relation determined in this work (LG: solid line) with the experimental determinations of Kawasaki and Matsui (1983), shown by triangles, and Harley (1983), and the theoretical calibration of Sen & Bhattacharya (1984), neglecting their Fe-Mg nonideality term.

1978).

Mn and Ca substitute highly preferentially in garnet relative to coexisting orthopyroxene (e.g. Dahl, 1980). Consequently, the effect of possible nonideal interactions of Mn and Ca in orthopyroxene of K_D is usually expected to be negligible compared to those in garnet, especially in the range of compositions of common natural assemblages. Following the multi-component simple mixture model of Ganguly and Kennedy (1974) for the quaternary garnet solid solution $(\text{Fe, Mg, Ca, Mn})_3\text{Al}_2\text{Si}_3\text{O}_{12}$,

$$RT \ln(\gamma_{\text{Fe}}/\gamma_{\text{Mg}})^{\text{Gt}} = W_{\text{FeMg}}^{\text{Gt}}(X_{\text{Mg}} - X_{\text{Fe}})^{\text{Gt}} + (W_{\text{FeCa}} - W_{\text{MgCa}})^{\text{Gt}} X_{\text{Ca}}^{\text{Gt}} + (W_{\text{FeMn}} - W_{\text{MgMn}})^{\text{Gt}} X_{\text{Mn}}^{\text{Gt}} \quad (4)$$

where W_{ij} indicates a 'simple mixture' interaction parameter between i and j components, as defined by Guggenheim (1967). In eqn. 4, $W_{\text{FeMg}}^{\text{Gt}}$ becomes zero since Fe and Mg in both garnet and orthopyroxene are assumed to mix ideally at $T \geq 975^\circ\text{C}$. Thus, K_γ in reaction (a) can be expressed as follows

$$RT \ln K_\gamma = -\Delta W_{\text{Ca}}^{\text{Gt}} \cdot X_{\text{Ca}}^{\text{Gt}} - \Delta W_{\text{Mn}}^{\text{Gt}} \cdot X_{\text{Mn}}^{\text{Gt}} \quad (5)$$

where $\Delta W_{\text{Ca}}^{\text{Gt}}$ and $\Delta W_{\text{Mn}}^{\text{Gt}}$ indicate $(W_{\text{MgCa}} - W_{\text{FeCa}})^{\text{Gt}}$ and $(W_{\text{MgMn}} - W_{\text{FeMn}})^{\text{Gt}}$ respectively and according to Ganguly and Saxena (1984), $\Delta W_{\text{Ca}} = \Delta W_{\text{Mn}} = 3000(\pm 500)$ calories per mole of cation for $X_{\text{Ca}}^{\text{Gt}} \geq 0.30$ and $X_{\text{Mn}}^{\text{Gt}} \geq 0.30$. Using relation of $\ln K_D = \ln K - \ln K_\gamma$ in eqn. 1, we can recast (3.2) and (5) into the following geothermometric expression

$$T = \frac{1971 + 11.91P + 1510(X_{\text{Ca}} + X_{\text{Mn}})^{\text{Gt}}}{\ln K_D + 0.96} \quad (6)$$

where T is in K and P is in Kb.

The assumption of the independence of K_D on Fe/Mg ratios, which has been used to develop the geothermometric expression above, is well justified by our experimental data and those of Kawasaki and Matsui (1983) for $T \geq 975^\circ\text{C}$ (that is for most assemblages in mantle derived xenoliths), but may not be valid at sig-

nificantly lower temperature. Thus, the application of the geothermometer to granulite facies assemblages should be made caution.

We do not, as yet, have adequate mixing property data to correct for the effect of Cr^{+3} . However, substitution of Cr^{+3} in garnet would still affect K_D (see Wood & Nicholls, 1978). Thus, the above geothermometric expression may not yield reliable temperature for Cr^{+3} rich compositions.

APPLICATION TO NATURAL SYSTEMS

In common with virtually any other geothermometer (or geobarometer) based on the composition of the coexisting minerals, the major uncertainties in the application of the above thermometer to natural assemblages are due to those in the mixing property terms and determination of equilibrium compositions by microprobe analyses. It can be shown that a given percentage uncertainty in K_D translates into approximately half of that in the temperature estimate. (This problem is even worse with cation exchange geothermometers such as garnet-biotite which have flatter $\ln K_D$ vs. $1/T$ slopes.) Thus, considering the various factors, we believe that the uncertainties in the mixing property and analytical data will contribute an uncertainty of around 30–50°C to the temperature estimate of most natural assemblages, at least above 1000°C, if the equilibrium mineral compositions were determined carefully.

The application of (6) to 33 garnet-lherzolite xenoliths from Lesotho, South Africa, yield temperatures that are systematically higher, on the average by 78°C compared to the 'mean of 5 preferred methods' (Wells, 1977; Ellis & Green, 1979; O'Neill & Wood, 1979; Mori & Green (2 methods), 1978), and by 58°C compared to the 'mean of 10 preferred methods' (Wood & Banno, 1973; Raheim & Green, 1974; Mysen, 1976; Ganguly, 1979; Saxena, 1979; and the above 5 preferred methods) of Carswell & Gibb (1980). The temperature of these garnet-lherzolite nodules fall in the range of 950–

1500°C. There is, however, no objective reason for preferring the 'preferred methods' of Carswell & Gibb (1980) to the expression (6), especially since it is based on carefully reversed experiments. The 'preferred methods' of Carswell & Gibb lack these qualities.

In Fig. 7 are plotted the data for the Cretaceous (0.1 b.y.) Lesotho geotherm to study the thermal evolution of the upper mantle. The pressures for these data are based on the Al_2O_3 content of orthopyroxene. This study yields a paleogeotherm for these areas which is very similar to that of Lane & Ganguly (1980). Earlier, Boyd (1973) had also constructed a paleogeotherm for the same area using X_{Ca} and Al_2O_3 content in enstatite to estimate tempera-

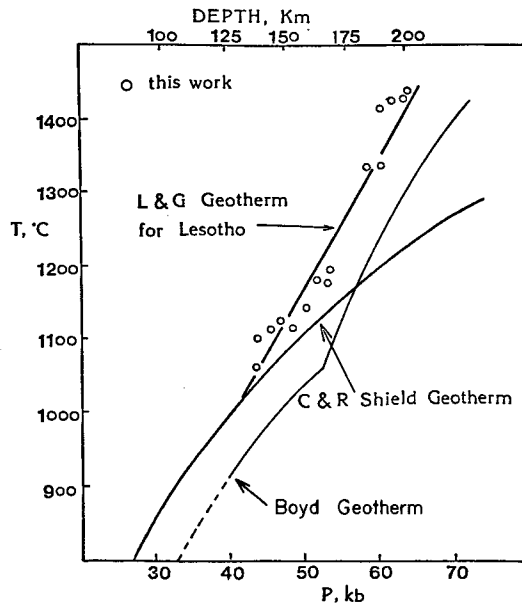


Fig. 7 Lesotho mantle geotherm estimated from this model. Pressure is based on the raw Al_2O_3 content of orthopyroxene (Lane and Ganguly, 1980). Open circles represent garnet-lherzolite nodules in kimberlite pipes. Shield geotherm is a conduction model derived by Clark & Ringwood (1964). The kinked geotherm of Boyd (1973) shows that the solid segments indicate granular (low-P-T segment) and sheared nodules.

ture and pressure without correction for the possible effects of other components and pressure. According to his result, nodules with a 'sheared' texture had equilibrated at higher P-T conditions than those with 'granular' texture. Thus, Boyd (1973) suggested that the granular nodules probably define a primitive steady state geotherm, whereas the sheared nodules reflect an unsteady state at greater depth. However, this model has been criticized by Mercier & Carter (1975) and Howells & O'Hara (1978) due to an artifact of the method of calculation of the P-T relations. Although the results of this study and Lane & Ganguly (1980) do not agree with that of Boyd (1973), it seems that the nodule geotherm is evidently divergent from the Clark & Ringwood shield geotherm.

The above geothermometric formulation has also been applied to granulite facies assemblages described in the literature (Weaver et al., 1978; Glassley & Sorensen, 1978; Wells, 1978; Dahl, 1980; and Janardhan et al., 1982). The

estimated temperatures versus the original estimates are illustrated in Fig. 8 and showed good agreement to within $\pm 50^\circ\text{C}$. The original estimates are based on geological constraints or other geothermometers.

These illustrative applications to natural systems make it clear that this model can contribute positively to studies on thermal evolution of a wide variety of rocks ranging from mantle nodules through ultramafic rocks to granulites by allowing precise estimation of temperatures encountered by these rocks.

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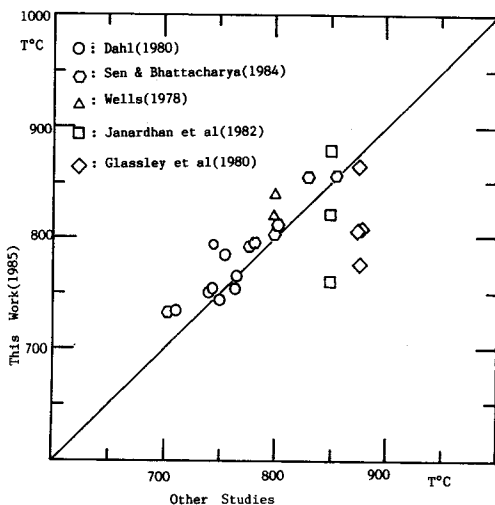


Fig. 8 Comparison of the temperatures of granulite facies assemblages determined from this model with those in the earlier studies.

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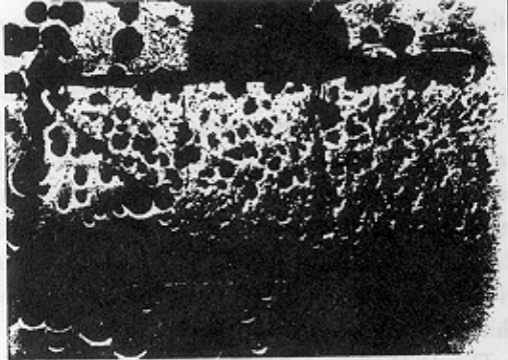
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석류석-사방휘석 지질온도계와 지질학적 응용

李 漢 永

요 약 : 석류석과 사방휘석의 평형관계를 20-45kb, 975-1400°C, FMAS시스템에서 상호역반응 실험을 통해서 연구하였으며 반응 촉매제로써 사용한 PbO와 0.55 PbF₂의 혼합물은 매우 효과적이었다. Fe-Mg의 교환반응은 이 실험 온도, 압력범위 내에서는 조성성분의 영향을 받지 않는다. 실험결과와 석류석의 혼합 모델을 사용한 석류석-사방휘석의 지질온도계는 다음과 같다.

$$T^{\circ}\text{C} = (1971 + 11.91P(\text{Kb}) + 1510(X_{\text{Ca}} + X_{\text{Mg}})^{\text{Cl}} / (\ln K_D + 0.96) - 273$$



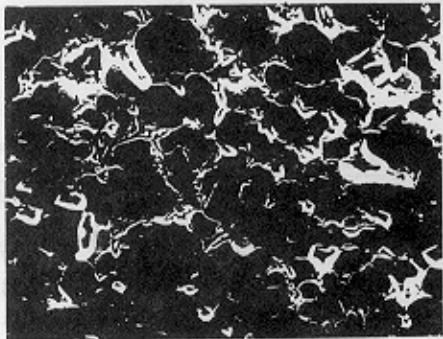


Figure 3-a

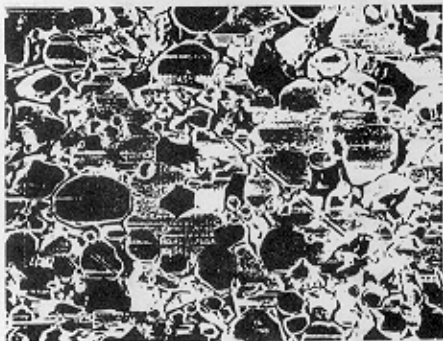


Figure 3-b