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EXPERIMENTAL STUDY ON THE PARTITIONING OF FE AND MG BETWEEN GARNET AND OLIVINE AND ITS APPLICATIONS TO KIMBERLITES

by

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(with 15 text-figures and 6 tables)

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Abstract

The temperature dependence of the Fe-Mg partition coefficient is studied experimentally on the garnet-olivine system. The experiments are carried out in the temperature and pressure range of 1000°C – 1400°C, 25 – 30 kb, respectively. The composition of the starting materials are $(\text{Fe}_{1.7}\text{Mg}_{7.2}\text{Ca}_{1.1})$ for garnet and $(\text{Fe}_{1.2}\text{Mg}_{8.8})$ for olivine. It is shown that the temperature-pressure relation of this reaction is represented as $T = (\Delta H^{**} + P\Delta V^{**})/(\Delta S^{**} - R \ln K'^{\text{Gt-Ol}}_{\text{Fe-Mg}})$ with the thermodynamic parameters as $\Delta H^{**} = -3.06$ kcal, $\Delta S^{**} = -1.33$ cal/deg, and $\Delta V^{**} = -10.5$ cal/kb where ΔV^{**} is estimated from the unit cell volume-composition relations. The calculated temperature and pressure agree with the experimental data within an error of $\pm 50^\circ\text{C}$.

The partition coefficient of the granular lherzolites in the kimberlites from Thaba Putsoa pipe, Lesotho, varies from 2.4 – 2.8. It is shown that this variation is almost due to the effect of Cr in garnet. The effect of Cr in garnet is also demonstrated on the partitioning of the Mg-Tschermak's molecule between orthopyroxene and garnet, and the Cr-Al exchange reaction between garnet and chromite. In the present treatment, the effect of Cr in garnet is corrected by assuming a nearly isophysical condition for this granular lherzolite nodules.

The temperature and pressure of these nodules are estimated to be 975°C and 45 kb from the application of the present experiments with the combination of the garnet-orthopyroxene geobarometry.

The applications to some other granular lherzolite nodules are also presented.

Introduction

Thermal structure in the upper mantle has been estimated on the basis of the heat-flow value at the earth's surface and the heat-conduction calculations with the assumptions on the distribution of radio-active elements or heat-generating mechanisms (Clark and Ringwood, 1964, Turcotte and Oxburgh, 1970, etc.). This method, however, contains considerable uncertainties due to the assumptions employed in the calculation.

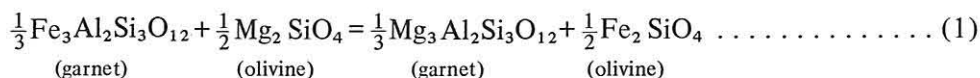
By applying the calibrated geological thermometry or barometry to the kimberlite rocks, we may obtain more direct informations on the thermal

structure of the upper mantle. Boyd (1973) proposed the inflected geotherm for South Africa district by means of the phase equilibrium analyses of the clinopyroxene-orthopyroxene and garnet-orthopyroxene systems of the ultra-basic nodules in the kimberlites. Although there are arguments on the presence and the reason of the inflection (Mercier and Carter, 1975), such abnormal temperature distribution can never be detected by the heat flow calculation method unless such abnormal heat generation is assumed in the model. As the experimentally calibrated geological thermometry or barometry, we have the phase relations of the clinopyroxene-orthopyroxene systems (Davis and Boyd, 1966, Nehru and Wyllie, 1974, Mori and Green, 1975), garnet-orthopyroxene system (Boyd and England, 1964, MacGregor, 1974, Wood, 1974), and the partitioning of Fe and Mg between garnet and clinopyroxene system (Råheim and Green, 1974) at present. It has been emphasized that the geological thermometry and barometry calibrated by the experiments on the simple systems can not be applied to the complex natural systems. In order to correct the effect of the elements excluded in the experiments, Wood and Banno (1973) proposed a correction method for the clinopyroxene-orthopyroxene and garnet-orthopyroxene systems. The experiments extended to more complex systems have also been carried out (Wood, 1974, 1976). However, in the systems where clinopyroxene is concerned, uncertainty always remains in the estimated temperature and pressure because of the complexity of the composition of clinopyroxene.

The partitioning of Fe and Mg between olivine and garnet has an advantage in this respect because of the simple chemical composition of olivine. At the same time, we may easily find out the effect of the elements in garnet on the value of the partition coefficient. Judging from the natural garnet-olivine systems, some temperature dependence of the partition coefficient is expected. For the temperature dependence of this reaction, there are only few experiments as yet. In this study, the temperature and pressure dependence of the partition coefficient is determined experimentally in the MgO-FeO-CaO-Al₂O₃-SiO₂ system and the result is applied to some kimberlite nodules.

Thermodynamic Considerations

The partitioning of Fe and Mg between olivine and garnet is expressed by the following exchange reaction:



The equilibrium equation for reaction (1) is expressed as

$$\ln K'_{\text{Fe-Mg}}^{\text{Gt-Ol}} = -(\Delta H^* + P\Delta V^*)/RT + \Delta S^*/R \quad \dots\dots\dots (2)$$

where $K'_{\text{Fe-Mg}}^{\text{Gt-Ol}} = (X_{\text{Fe}}/X_{\text{Mg}})^{\text{Gt}}/(X_{\text{Fe}}/X_{\text{Mg}})^{\text{Ol}}$. In Eq.(2), ΔH^* , ΔS^* , and ΔV^* are the apparent enthalpy, entropy and volume change of reaction (1). ΔH^* , ΔS^* , and ΔV^* are dependent on the chemical composition of the both phases.

The pyrope-rich garnet in ultrabasic rocks is represented by MgO-FeO-CaO-Al₂O₃-SiO₂ system as a first approximation. The mixing of cations in the garnet is completely represented by Fe, Mg, and Ca. Then the components are defined as follows:

$$X_{\text{Alm}} = X_{\text{Fe}}^{\text{Gt}}, \quad X_{\text{Py}} = X_{\text{Mg}}^{\text{Gt}}, \quad X_{\text{Gr}} = X_{\text{Ca}}^{\text{Gt}} \quad \dots\dots\dots (3)$$

For olivine, the following four kinds of components are formed as a result of the mixing of Fe and Mg in M1 and M2 sites.

$$X_{\text{Fo}} = X_{\text{Mg}}^{\text{M1}} \cdot X_{\text{Mg}}^{\text{M2}}, \quad X_{\text{Fa}} = X_{\text{Fe}}^{\text{M1}} \cdot X_{\text{Fe}}^{\text{M2}}, \quad X_{\text{A}} = X_{\text{Fe}}^{\text{M1}} \cdot X_{\text{Mg}}^{\text{M2}}, \quad X_{\text{B}} = X_{\text{Mg}}^{\text{M1}} \cdot X_{\text{Fe}}^{\text{M2}} \quad \dots (4)$$

By assuming the regular solution for garnet and olivine, ΔH^* , ΔS^* , and ΔV^* are represented as follows (Oka and Matsumoto 1974):

$$\begin{aligned} \Delta H^* = & \Delta H^\circ + \frac{1}{3}\alpha_{\text{Alm.Py}}(X_{\text{Alm}} - X_{\text{Py}}) - \frac{1}{2}\alpha_{\text{Fa.Fo}}(X_{\text{Fa}} - X_{\text{Fo}}) \\ & + \frac{1}{3}(\alpha_{\text{Alm.Gr}} - \alpha_{\text{Py.Gr}})X_{\text{Gr}} - \frac{1}{2}\sum_{\text{r=A,B}}(\alpha_{\text{Fa,r}} - \alpha_{\text{Fo,r}})X_{\text{r}} \quad \dots\dots\dots (5) \end{aligned}$$

$$\begin{aligned} \Delta V^* = & \Delta V^\circ + \frac{1}{3}\beta_{\text{Alm.Py}}(X_{\text{Alm}} - X_{\text{Py}}) - \frac{1}{2}\beta_{\text{Fa.Fo}}(X_{\text{Fa}} - X_{\text{Fo}}) \\ & + \frac{1}{3}(\beta_{\text{Alm.Gr}} - \beta_{\text{Py.Gr}})X_{\text{Gr}} - \frac{1}{2}\sum_{\text{r=A,B}}(\beta_{\text{Fa,r}} - \beta_{\text{Fo,r}})X_{\text{r}} \quad \dots\dots\dots (6) \end{aligned}$$

$$\Delta S^* = \Delta S^\circ$$

ΔH° , ΔS° , and ΔV° are the enthalpy, entropy and volume change of the reaction (1) for the pure substances and they can be regarded as constants in the temperature and pressure range concerned here. α_{ij} s are the non-ideal parameters and β_{ij} s are its pressure derivative, i.e. $\beta_{ij} = \partial\alpha_{ij}/\partial P$. α_{ij} and β_{ij} correspond to the excess energy and excess volume of the i-j pair formation, respectively. In Eq. (5), the effect of the excess entropy is involved in ΔH^* as a temperature dependent term of α_{ij} .

In olivine, there is no strong site-preference for Fe and Mg (Virgo and Hafner, 1972, Burns, 1970, Bancroft et al., 1967). Then Eq. (5) is simplified as (Oka, 1977)

$$\Delta H^* = \Delta H^{\circ} + \frac{1}{3}\alpha_{\text{Alm.Py}}(X_{\text{Fe}} - X_{\text{Mg}})^{\text{Gt}} - \frac{1}{2}\alpha_{\text{Fa.Fo}}(2X_{\text{Fe}} - 1)^{\text{Ol}} + \frac{1}{3}(\alpha_{\text{Alm.Gr}} - \alpha_{\text{Py.Gr}})X_{\text{Ca}}^{\text{Gt}} \dots \dots \dots (7)$$

and

$$\Delta V^* = \Delta V^{\circ} + \frac{1}{3}\beta_{\text{Alm.Py}}(X_{\text{Fe}} - X_{\text{Mg}})^{\text{Gt}} - \frac{1}{2}\beta_{\text{Fa.Fo}}(2X_{\text{Fe}} - 1)^{\text{Ol}} + \frac{1}{3}(\beta_{\text{Alm.Gr}} - \beta_{\text{Py.Gr}})X_{\text{Ca}}^{\text{Gt}} \dots \dots \dots (8)$$

where $X_{\text{Fe}}^{\text{Ol}} = (X_{\text{Fe}}^{\text{M1}} + X_{\text{Fe}}^{\text{M2}})/2$.

Table 1 Estimated values of the non-ideal parameters. Formula for garnet and olivine are defined as $\text{M}_3\text{Al}_2\text{Si}_3\text{O}_{12}$ and M_2SiO_4 , respectively.

	(kcal/gfw)	References
$\alpha_{\text{Alm. Py}}$	7.8	Oka and Matsumoto 1974
$\alpha_{\text{Alm. Gr}}$	5	see text
$\alpha_{\text{Py. Gr}}$	4	see text
$\alpha_{\text{Fa. Fo}}$	6	Obata et al. 1974
	(cal/kg)	
$\beta_{\text{Alm. Py}}$	0	Oka 1973
$\beta_{\text{Alm. Gr}}$	51.1	see text
$\beta_{\text{Py. Gr}}$	0	Ganguli and Kennedy 1974
$\beta_{\text{Fa. Fo}}$	5.88	Matsumoto 1971

The estimated value of the non-ideal parameters are listed in Table 1, in which $\alpha_{\text{Alm.Gr}}$, $\alpha_{\text{Py.Gr}}$, and $\beta_{\text{Alm.Gr}}$ are estimated as follows. According to the experiments by Ganguli and Kennedy (1974), the garnet of the pyrope-grossular series forms a complete solid solution at least above 750°C. Hariya and Nakano (1972) reported that the garnet of the almandine-grossular series also forms a complete solid solution at least above 1000°C. Referring to the equation of the critical mixing of the regular solution model, we may conclude that $1/3\alpha_{\text{Py.Gr}} \leq 4$ kcal/gfw and $1/3\alpha_{\text{Alm.Gr}} \leq 5$ kcal/gfw. The direct measurement of the enthalpy of the pyrope-grossular garnet by Newton et al. (1977) also suggests a consistent value. Here we may conclude that $1/3|\alpha_{\text{Alm.Gr}} - \alpha_{\text{Py.Gr}}| \leq 2$ kcal/gfw. According to this estimation, the variation of $X_{\text{Ca}}^{\text{Gt}}$ of 0 - 0.1 will modulate $K'_{\text{Fe-Mg}}^{\text{Gt-Ol}}$ within 1.1 at about 1000°C. Experience for natural eclogites that Ca content in garnet does not affect the Fe-Mg partition coefficient for the garnet and clinopyroxene (Mysen and Heier, 1972, Banno, 1970) support this estimation. $\beta_{\text{Alm.Py}}$ is estimated by using the unit cell volume-composition relation by Hariya and Nakano (Fig. 1).

ΔV° is determined by the formula volume of almandine (115.37 cm³), pyrope (113.24 cm³) (Oka 1973) and fayalite (46.29 cm³), and forsterite

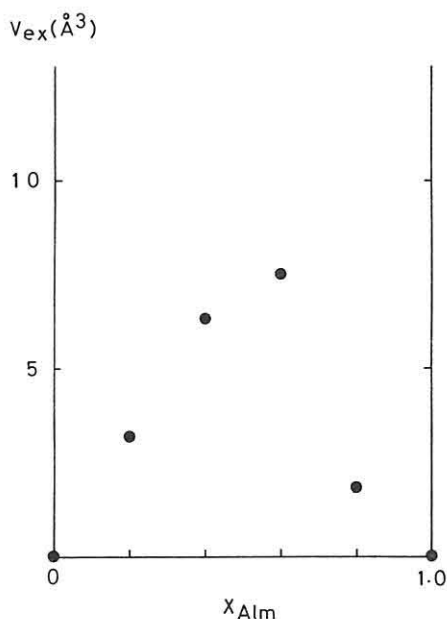


Fig. 1 The excess volume of garnet of the almandine-grossular series. The source data are from Hariya and Nakano (1972). The fitting by the parabolic curve gives $\beta_{\text{Alm.Gr}} = 51.1 \text{ cal/kb.gfw.}$

(43.68 cm^3) (Matsui and Syono 1968) as $\Delta V^\circ = -0.60 \text{ cm}^3 = -14.2 \text{ cal/kb.}$

Another problem in constructing a geological thermometry and barometry is to estimate ΔH° from experiments. For this purpose, however, it is not necessary to know ΔH° itself. The chemical composition of the garnet and olivine in kimberlite is restricted in a narrow range in respect of Fe^{2+} , Mg, and Ca. Introducing a reference composition for the garnet and olivine as $(X_{\text{Fe}}^*, X_{\text{Mg}}^*, X_{\text{Ca}}^*)^{\text{Gt}}$ and $(X_{\text{Fe}}^*, X_{\text{Mg}}^*)^{\text{Ol}}$, we can write Eqs. (7) and (8) as

$$\Delta H^* = \Delta H^{**} + \frac{1}{3}\alpha_{\text{Alm.Py}} \Delta X^{\text{Gt}} - \alpha_{\text{Fa.Fo}} \Delta X^{\text{Ol}} + \frac{1}{3}\Delta\alpha \cdot \Delta X_{\text{Ca}}^{\text{Gt}} \quad \dots\dots\dots (9)$$

$$\Delta V^* = \Delta V^{**} + \frac{1}{3}\beta_{\text{Alm.Py}} \Delta X^{\text{Gt}} - \beta_{\text{Fa.Fo}} \Delta X^{\text{Ol}} + \frac{1}{3}\Delta\beta \cdot \Delta X_{\text{Ca}}^{\text{Gt}} \quad \dots\dots\dots (10)$$

where

$$\Delta X^{\text{Gt}} = (X_{\text{Fe}} - X_{\text{Mg}})^{\text{Gt}} - (X_{\text{Fe}}^* - X_{\text{Mg}}^*)^{\text{Gt}},$$

$$\Delta X^{\text{Ol}} = X_{\text{Fe}}^{\text{Ol}} - X_{\text{Fe}}^{*\text{Ol}}$$

$$\Delta X_{\text{Ca}}^{\text{Gt}} = X_{\text{Ca}}^{\text{Gt}} - X_{\text{Ca}}^{*\text{Gt}}, \Delta\alpha_{\text{Alm.Gr}} - \alpha_{\text{Py.Gr}}, \Delta\beta = \beta_{\text{Alm.Gr}} - \beta_{\text{Py.Gr}},$$

$$\Delta H^{**} = \frac{1}{3}\alpha_{\text{Alm.Py}} (X_{\text{Fe}}^* - X_{\text{Mg}}^*)^{\text{Gt}} - \frac{1}{2}\alpha_{\text{Fa.Fo}} (2X_{\text{Fe}}^* - 1)^{\text{Ol}} \\ + \frac{1}{3}\Delta\alpha \cdot X_{\text{Ca}}^{*\text{Gt}} + \Delta H^\circ$$

$$\Delta V^{**} = \frac{1}{3}\beta_{\text{Alm.Py}} (X_{\text{Fe}}^* - X_{\text{Mg}}^*)^{\text{Gt}} - \frac{1}{2}\beta_{\text{Fa.Fo}} (2X_{\text{Fe}}^* - 1)^{\text{Ol}} \\ + \frac{1}{3}\Delta\beta \cdot X_{\text{Ca}}^{*\text{Gt}} + \Delta V^\circ$$

Defining the reference composition of the garnet and olivine to be the mean composition of them in the kimberlite, we can regard that $\Delta X^{Gt} \cong 0$, $\Delta X^{Ol} \cong 0$, and $\Delta X_{Ca}^{Gt} \cong 0$. Referring to the value of the non-ideal parameters already estimated, it is apparent that the small perturbations of ΔX s does not affect the value of ΔH^* and ΔV^* . Then we can use ΔH^{**} instead of ΔH° and Eq. (2) is written as:

$$\ln K'_{Fe-Mg}^{Gt-Ol} = -(\Delta H^{**} + P\Delta V^{**})/RT + \Delta S^{**}/R \quad \dots\dots\dots (11)$$

The temperature dependence of K'_{Fe-Mg}^{Gt-Ol} in Eq. (11) is calibrated by the experiments on the starting materials adjusted to the reference composition.

The geological thermometry thus calibrated can be applied to the natural systems with small amount of compositional corrections. At the same time, we can reduce the errors in the corrections due to the uncertainties of the non-ideal parameters. The effect of Cr in garnet, which is not involved in the present experiments, will be discussed in later.

Experiments

Preparation of the starting materials

According to the reason described in the preceding discussion, the starting materials similar in composition to the garnet and olivine in kimberlite are selected, i.e. $(Fe_{1.7}Mg_{7.2}Ca_{1.1})$ for garnet and $(Fe_{1.2}Mg_{8.8})$ for olivine. The starting materials for garnet and olivine were prepared separately from $CaCO_3$, Al_2O_3 , SiO_2 , Fe_2O_3 , and MgO . First these mixtures were ground with guaranteed reagent ethyl alcohol in an agate mortar, and then heated individually in a CO_2-H_2 gas at $1100 - 1200^\circ C$ for several hours. CO_2/H_2 ratio was 1 - 4/3. The garnet composition and olivine were mixed in 1:1 ratio by weight.

High pressure experiments

The high pressure experiments were carried out by the piston-cylinder apparatus. The arrangement of the cell is as follows. A capsule surrounded by NaCl in order to attain hydrostatic pressure was inserted within a pyrex glass tube used as a pressure transmitting medium, which in turn was sheathed by a talc tube. The friction correction was -10% which was added to the nominal pressure. The temperature was measured by Pt-Pt87Rh13 thermocouple for runs above $1200^\circ C$ and almel-chromel thermocouple for runs below $1200^\circ C$, without the pressure correction on the e.m.f.. The fluctuation of the temperature is estimated to be within $\pm 15^\circ C$ for overnight runs. For some runs above $1200^\circ C$, 25 kb, the pressure and temperature were held at 20 kb,

1000°C for initial 1 hour to prevent the breakdown of the thermocouple.

Graphite or Pt90Rh10 tube was used as a sample capsule. They were sealed in a Pt or AgPd outer capsule with or without the buffering materials (Fig. 2). Metallic iron or iron-quartz powder was used as the buffering material. The Pt90Rh10 sample capsule was sealed in the outer capsule with iron powder to minimize the iron absorption by the capsule. 25 – 30 mg of sample was loaded in the capsule. For the runs above 1200°C, the samples were only moistened by breathings, while for the runs below 1200°C, 3 – 7 mg of distilled water was added to favor the crystal growth of the product.

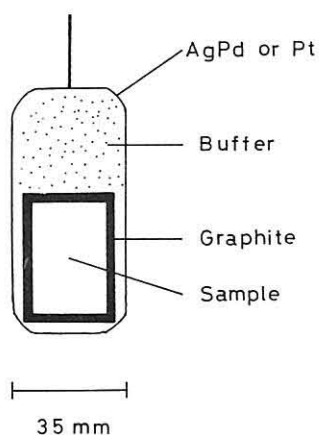


Fig. 2 The schematic representation of the graphite capsule assembly. When the buffering technique is not used, the graphite capsule is simply sealed by the Pt tube. In some cases, the graphite capsule is replaced by the Pt₉₀Rh₁₀ capsule.

Examination of the product

The run product was examined by microscope, X-ray powder diffractometer and E.P.M.A.. The homogeneity of the product can be evaluated by the examination of the shape of the peaks of the X-ray powder pattern. If a run product did not give sharp patterns, the run was discarded. E.P.M.A. analyses were carried out by JEOL JXA-50A equipment. The acceleration voltage was 15 kv, the probe current measured at the Faraday cage was 0.03 – 0.04 μ A, and the diameter of the beam spot was 1 μ m. In order to discriminate the minerals by the electron beam irradiation with sufficient resolving power, the product was crushed to get separated crystals. A kaersutite was used as the standard. The correction was carried out after the method of Bence and Albee (1968). The computer program for the correction and the numerical control of the equipment was provided by JEOL. The experimental condition is summarized in Table 2.

Table 2 Experimental conditions. * moistened by breathings.

Run No.	P(kb)	T(°C)	Duration (hour)	Capsule	Buffer	H ₂ O(wt%)
1	30	1000	77	Pt90Rh10	iron	10
2	30	1100	62	Graphite	I-Q	7
3	25	1200	50	Graphite		*
4	25	1300	22	Graphite		*
5	30	1400	8	Graphite		*

Experimental Results

Result of E.P.M.A. analyses

In Fig. 3, Fe/Mg ratio of the product is presented. If the Fe/Mg ratio scattered widely, the run was discarded. The averaged Fe/Mg ratio was calculated from the analyses, whose totals attained 98 – 102% (Table 3).

Description of the product

Run 1 Garnet, olivine and small amount of orthopyroxene were identified. The grain of the crystals were 50 – 60 μ m. The garnet and olivine were granular but the shape of the crystal was irregular. The presence of orthopyroxene may be due to the effect of the absorption of iron by the capsule. Although the Fe/Mg ratio of the garnet scattered widely, a definite convergence of the Fe/Mg was recognized at $X_{Fe}/X_{Mg} = 0.09$. This divergence may be due to the absorption of iron by the capsule. The iron-rich part may correspond to the iron rich core which was crystallized in the early stage of the run. In contrast to the garnet, the composition of the olivine converged quite well. This suggests a more rapid diffusion in olivine than in garnet. The buffer material remained unchanged.

Run 2 Garnet, orthopyroxene, and small amount of olivine were identified. The orthopyroxene may be formed as a result of the contamination of SiO₂ from the buffer material which is separated by the carbon inner capsule from the specimen. Garnet was granular, 15 – 20 μ m in size and orthopyroxene was smaller. Most of the garnet had a few inclusions less than 1 μ m in diameter. The orthopyroxene was subhedral and had no inclusions. The garnet and orthopyroxene became slightly iron-rich due to the contamination of the buffer material. Except for a few iron-poor analyses which may correspond to the core portion, Fe/Mg ratio of the garnet and orthopyroxene converged well (Fig.

3). The amount of the olivine was quite small and its Fe/Mg ratio did not give the equilibrium value of $K_{Fe-Mg}^{O^I-O^{Px}} = (Fe/Mg)^{O^I} / (Fe/Mg)^{O^{Px}}$ which is estimated to be 1.1 (Larimer, 1968, Medaris, 1969, Matsui and Nishizawa, 1974). Therefore olivine was judged to be in disequilibrium. The Al_2O_3 content of orthopyroxene is shown in Fig. 4.

Run 3 Garnet and olivine, but no orthopyroxene, were identified. The olivine was subhedral, less than $10\mu m$ in size. The garnet was granular, and smaller than the olivine, making E.P.M.A. analyses quite difficult. In Table 3, the analyses whose totals do not attain 98% were also used as an exceptional case. Buffering technique was not employed for runs higher than $1200^\circ C$.

Run 4 Garnet, olivine and very small amount of orthopyroxene were observed. The garnet was granular and the grain size was $5 - 10\mu m$, with a few inclusions less than $1\mu m$ in diameter. The olivine was subhedral and less than $5\mu m$ in size. The composition of the garnet and olivine converged well.

Run 5 Garnet, olivine and very small amount of orthopyroxene were observed. The garnet was granular, about $10\mu m$ in size. As shown in Fig. 3, Fe/Mg ratio of the garnet and olivine converged well.

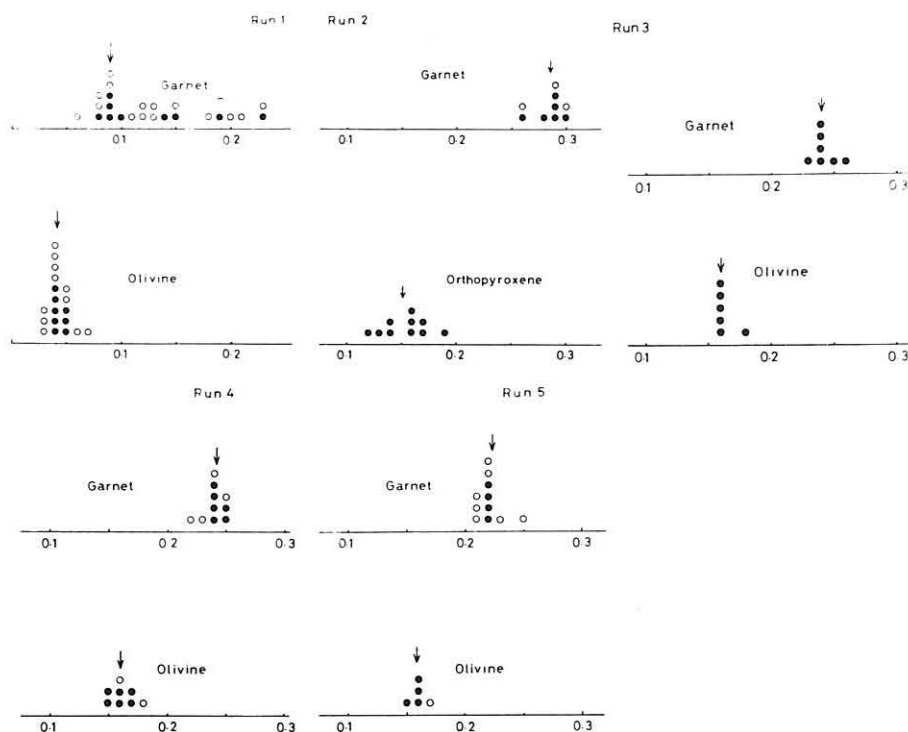


Fig. 3 Fe/Mg of the run product. The solid circle represents the analysis whose total attains 98 – 102%. The arrow indicates the estimated equilibrium position of the Fe/Mg value.

In Run 2, K'_{Fe-Mg}^{Gt-OPx} is converted to K'_{Fe-Mg}^{Gt-O1} by using the equilibrium value of K'_{Fe-Mg}^{O1-OPx} as $K'_{Fe-Mg}^{Gt-O1} = K'_{Fe-Mg}^{Gt-OPx} / K'_{Fe-Mg}^{O1-OPx}$ where $K'_{Fe-Mg}^{O1-OPx} = 1.10$ is employed (Larimer, 1968, Medaris, 1969, Matsui and Nishizawa, 1974).

Table 3 Results of E.P.M.A. analyses. The standard deviation is shown in the parenthesis.

	Garnet				Olivine			
	X _{Fe}	X _{Mg}	X _{Ca}	X _{Fe} /X _{Mg}	X _{Fe}	X _{Mg}	X _{Fe} /X _{Mg}	K'_{Fe-Mg}^{Gt-O1}
Run 1	0.0736 (0.0082)	0.813 (0.026)	0.114 (0.033)	0.903 (0.008)	0.0423 (0.0056)	0.958 (0.006)	0.0443 (0.0061)	2.04 (0.33)
Run 2	0.206 (0.007)	0.728 (0.020)	0.066 (0.021)	0.283 (0.010)	0.131* (0.014)	0.864* (0.015)	0.152* (0.018)	1.86** (0.24)
Run 3	0.172 (0.007)	0.709 (0.015)	0.120 (0.018)	0.242 (0.009)	0.140 (0.004)	0.860 (0.003)	0.159 (0.003)	1.53 (0.06)
Run 4	0.174 (0.003)	0.716 (0.008)	0.111 (0.009)	0.243 (0.005)	0.139 (0.006)	0.860 (0.005)	0.160 (0.008)	1.52 (0.08)
Run 5	0.164 (0.002)	0.733 (0.004)	0.103 (0.005)	0.224 (0.003)	0.136 (0.002)	0.861 (0.003)	0.158 (0.003)	1.42 (0.03)

Temperature dependence of K'_{Fe-Mg}^{Gt-O1}

According to Eq. (11), $\ln K'_{Fe-Mg}^{Gt-O1}$ is expected to be proportional to $1/T$ if the pressure and the composition of the both phases are similar. The experiments were carried out at 25 and 30 kb which can be regarded as similar pressure. The composition of the product deviates slightly in Runs 1 and 2. However, according to the thermodynamic considerations in the preceding chapter, the variation of K'_{Fe-Mg}^{Gt-O1} by this effect is minor. Therefore it may be most reasonable to use K'_{Fe-Mg}^{Gt-O1} , neglecting the effect of the chemical deviation of these runs.

The temperature dependence of $\ln K'_{Fe-Mg}^{Gt-O1}$ is plotted in Fig. 4 which shows a distinct correlation between $\ln K'$ and $1/T$. By combining Eq. (11) to this relationship, the thermodynamic parameters are determined as

$$\Delta H^{**} = -3.06 \text{ kcal}, \quad \Delta S^{**} = -1.33 \text{ cal/deg}$$

where ΔV^{**} is calculated to be -10.5 cal/kb at the reference composition (the composition of Run 5).

Using these thermodynamic parameters, we can construct a R-T diagram according to the following equation:

$$T = (\Delta H^{**} + P\Delta V^{**}) / (\Delta S^{**} - R \ln K'_{Fe-Mg}^{Gt-O1}) \dots \dots \dots (12)$$

The P-T diagram is plotted in Fig. 5. The observed value of K'_{Fe-Mg}^{Gt-O1} is reproduced by the calculation within the accuracy of $\pm 50^\circ \text{C}$.

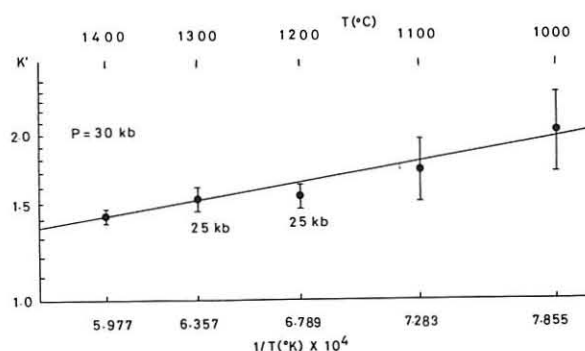


Fig. 4 $\ln K'_{\text{Fe-Mg}}^{\text{Gt-Ol}} - 1/T$ relation.

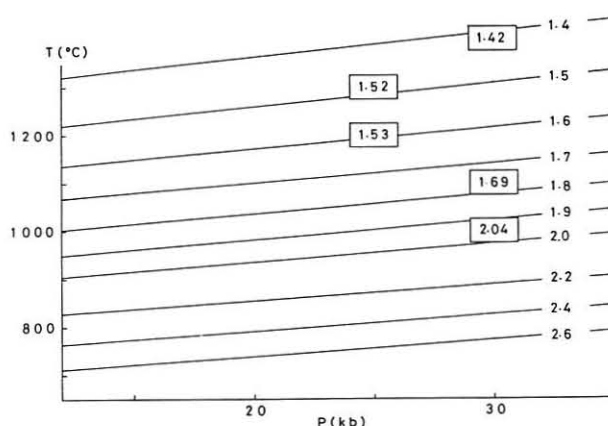


Fig. 5 P-T diagram according to Eq. (12). The parameters are the value of $K'_{\text{Fe-Mg}}^{\text{Gt-Ol}}$.

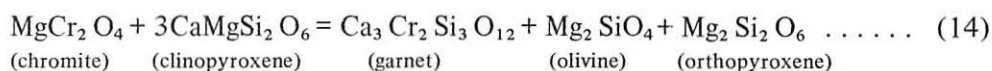
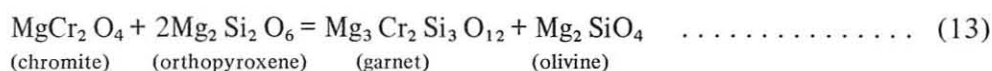
Petrological Applications

In order to estimate the physical condition of the formation of natural rocks by using the experiments on the simple systems, we must correct the effect of the components excluded in the experimental system. For the present system, the elements which we must correct are Cr and Fe^{3+} in garnet. According to Nixon and Boyd (1973), the garnet in the granular lherzolite nodule is rich in Cr, while the garnet in the sheared lherzolite nodule is estimated to be rich in Fe^{3+} as well as Cr.

Applications to the granular lherzolite of Lesotho

In Fig. 6, $K'_{\text{Fe-Mg}}^{\text{Gt-Ol}}$ of the granular lherzolite in the kimberlite from Thaba Putsoa pipe, Lesotho described by Nixon and Boyd (1973) is plotted. For some of the granular lherzolites, chromite coexists with garnet. The value of $K'_{\text{Fe-Mg}}^{\text{Gt-Ol}}$

varies from 2.4 to 2.8 according to the Cr content in the garnet. This suggests the variation of the equilibrium condition or the effect of Cr in garnet at an isophysical condition. The Cr content of the garnet may be buffered by the following reactions:



However, chromite and garnet changes their compositions according to the Cr and Ca content of the system (Fig. 7) so that the Cr content of the garnet does not always indicate the physical condition. Although these specimens were collected from a common kimberlite pipe, this does not necessarily give the confidence that the isophysical equilibrium was maintained. In order to discuss this problem another kind of reaction is examined.

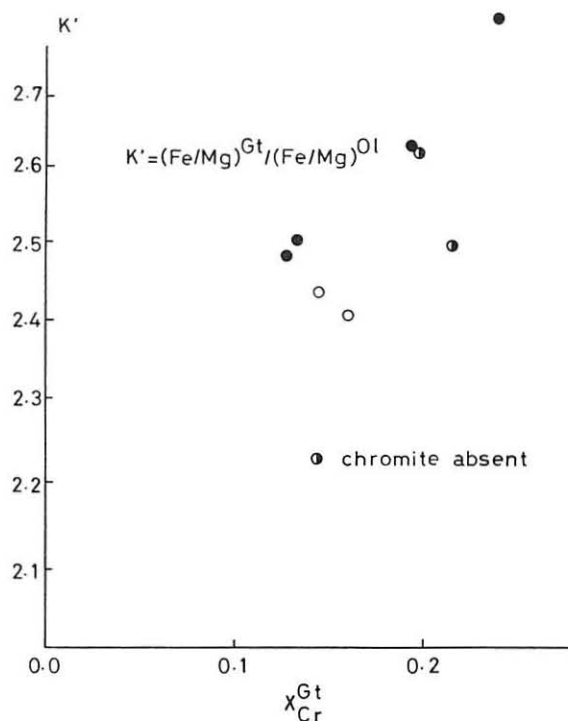
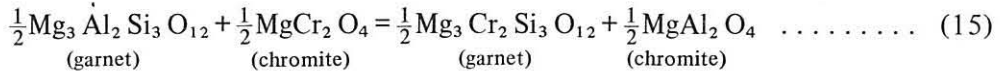


Fig. 6 The $K'_{\text{Fe-Mg}}^{\text{Gt-Ol}} - X_{\text{Cr}}^{\text{Gt}}$ relation of the granular lherzolite nodules of Thaba Putsoa pipe of Lesotho, where $X_{\text{Cr}}^{\text{Gt}} + X_{\text{Al}}^{\text{Gt}} = 1$. The solid circle represents the data whose garnet satisfies the structural formula as $\text{Al} + \text{Cr} \geq 1.98$ while for two open circles, $\text{Al} + \text{Cr} = 1.96$ and 1.93 , respectively. An almost linear relation is recognized except for three points.

Partitioning of Cr and Al between garnet and chromite

It is possible to discuss the exchange reaction of Cr and Al between chromite and garnet as follows.



The partition coefficient is defined as:

$$K_{\text{Al-Cr}}^{\text{Gt-Chr}} = (X_{\text{Al}}/X_{\text{Cr}})^{\text{Gt}} / (X_{\text{Al}}/X_{\text{Cr}})^{\text{Chr}} \quad \dots\dots\dots (16)$$

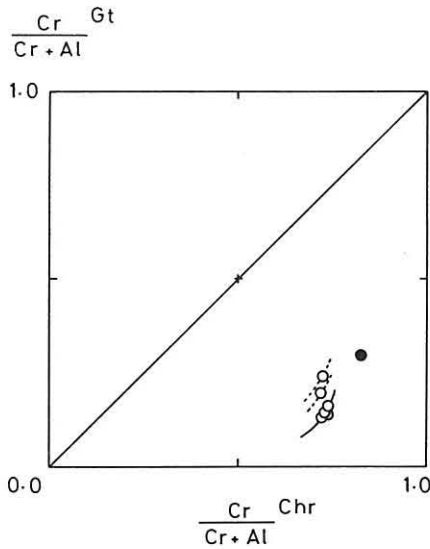


Fig. 7 The relation of the composition of the coexisting garnet and chromite. The open circle represents the granular lherzolite of Lesotho and the solid circle represents the granular harzburgite of the Premier mine (RVD 183). The solid line represents the group whose garnet contains constant amount of Ca as $X_{\text{Ca}}^{\text{Gt}} = 0.15$. For this group, a continuous relation is recognized between the Cr content of the garnet and chromite. The dashed lines are the estimated relation with different Ca content in the garnet. For the lower line, $X_{\text{Ca}}^{\text{Gt}} = 0.19$ and for the upper line, $X_{\text{Ca}}^{\text{Gt}} = 0.21$.

In Fig. 8, the correlation of $K_{\text{Fe-Mg}}^{\text{Gt-Ol}}$ and $K_{\text{Al-Cr}}^{\text{Gt-Chr}}$ is represented. Since the partition coefficients approach to near unity as the temperature increases, there must be a positive correlation between $K_{\text{Fe-Mg}}^{\text{Gt-Ol}}$ and $K_{\text{Al-Cr}}^{\text{Gt-Chr}}$ if the scattering of the both kinds of partition coefficients are due to the variation of the equilibrium temperatures. Thus from the negative relationship in Fig. 8, the temperature variations are eliminated from the cause of the scattering of the

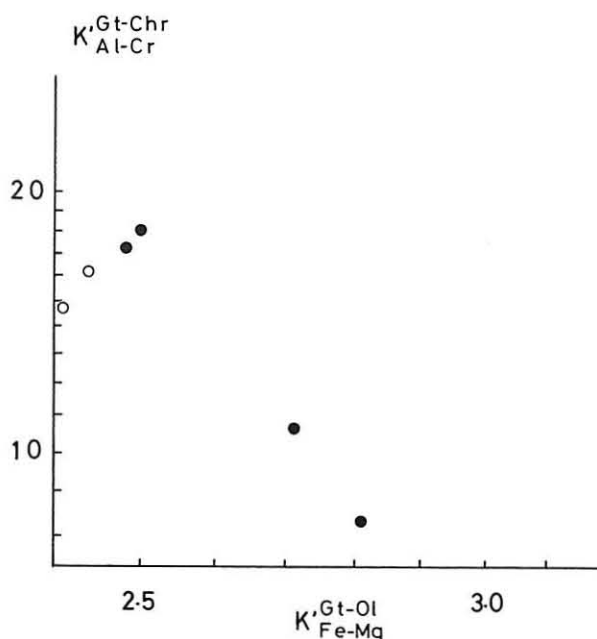


Fig. 8 The correlation of K'_{Al-Cr}^{Gt-Chr} and K'_{Fe-Mg}^{Gt-Ol} . The symbols are the same as in Fig. 6. A negative correlation is recognized except for two points which are also abnormal in Fig. 6.

partition coefficients. Explanation by the variation of the pressure is also unrealistic because it requires about 30 kb of pressure variation to account for the variation of K'_{Fe-Mg}^{Gt-Ol} of 2.5 – 2.8 while it requires less than 10 kb of pressure variation for $K'_{En.MgTs}^{Gt-OPx}$, which will be defined in the later section. If the garnet and chromite are equilibrated at an isophysical condition, the variation of K'_{Al-Cr}^{Gt-Chr} must be explained by a reasonable solution model. The natural garnet is complex and the substitution of Al and Cr makes the treatment of the multicomponent regular solution model (Oka and Matsumoto, 1974) quite difficult. Instead of using the complex solution model with numerous non-ideal parameters, let us employ the binary simple solution approximation (Thompson, 1967) for garnet and chromite to simplify the discussion. The garnet and chromite are approximated by $Mg_3Al_2Si_3O_{12}$ – $Mg_3Cr_2Si_3O_{12}$ and $MgAl_2O_4$ – $MgCr_2O_4$ systems, respectively. The equilibrium equation for reaction (15) is represented as

$$\ln K'_{Al-Cr}^{Gt-Chr} = -\Delta G^*_{(15)}/RT + \alpha_{Al-Cr}^{Chr}/RT \cdot (2X_{Cr}^{Chr} - 1) - \alpha_{Al-Cr}^{Gt}/RT \cdot (2X_{Cr}^{Gt} - 1) \quad (17)$$

where $\Delta G^*_{(15)}$ is the free energy change of Eq. (15) and $\alpha^*_{\text{Al-Cr}}^{\text{Chr}}$, and $\alpha^*_{\text{Al-Cr}}^{\text{Gt}}$ are the apparent non-ideal parameters. Since the real garnet and chromite are multicomponent systems, the thermodynamic parameters are functions of the composition of each phase. Fortunately, the composition of the garnet and

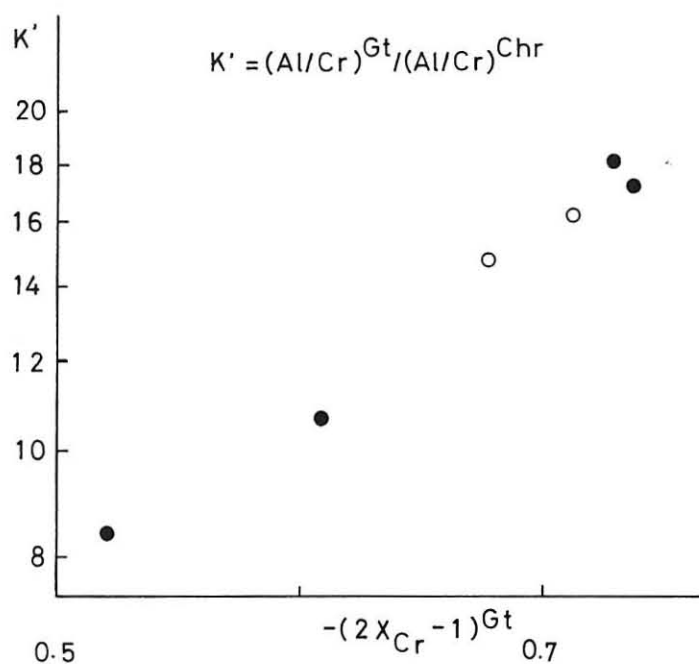


Fig. 9 The plot of $K'_{\text{Al-Cr}}^{\text{Gt-Chr}}$ according to Eq. (17), where $X_{\text{Cr}}^{\text{Gt}}$ is regarded as constant. The open and solid circles correspond to the symbols in Fig. 6.

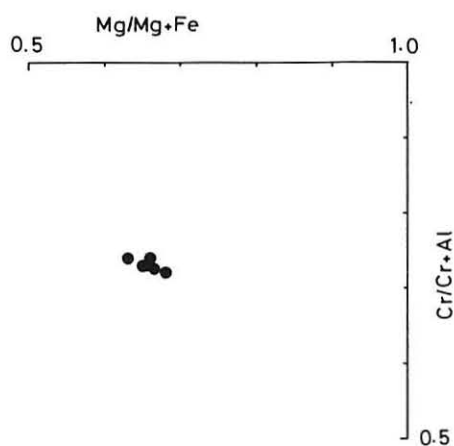


Fig. 10 The chemical composition of the chromites in the granular lherzolites.

The internal partition coefficient for clinopyroxene is assumed as $K_i = (\text{Fe/Mg})^{\text{M}2\text{-CPx}} / (\text{Fe/Mg})^{\text{M}1\text{-CPx}} = 7$. $K'_{(18)}$ for the granular lherzolite is listed in Table 4. With the variation of the physical condition, $K'_{(18)}$ and the $\text{Ca}/(\text{Ca}+\text{Na})^{\text{CPx}}$ value of the clinopyroxene are expected to increase (or decrease)

Sample No.	$K'_{(18)}$	$\text{Ca}/(\text{Ca}+\text{Na})^{\text{CPx}}$
1595	0.579	0.908
1567	0.826	0.900
1592	1.05	0.867
1570	0.503	0.918
1573	0.409	0.888
1569	0.335	0.888
1568	2.12	0.844
1572	3.32	0.820
1591	0.226	0.921
E3	1.77	0.877
1611	1.85	0.827
1610	2.22	0.834
1566	0.931	0.838
1596	1.50	0.810
1597	1.30	0.802
1582	4.98	0.814

Table 4

The value of $K'_{(18)}$ and $\text{Ca}/(\text{Ca}+\text{Na})$ of clinopyroxene for the lherzolite nodules of Lesotho.

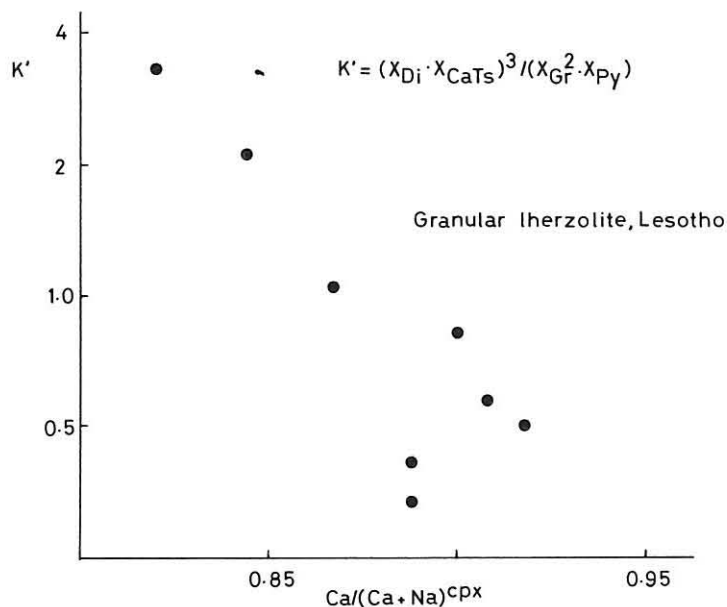


Fig. 12 $K'_{(18)}$ – $\text{Ca}/(\text{Ca}+\text{Na})^{\text{CPx}}$ relation of the granular lherzolite of Lesotho.

together if the Ca content of the system is constant. However, the clear negative correlation in Fig. 12 suggests the variation of the Ca content of the system. Therefore it is concluded that the variation of the $\text{Ca}/(\text{Ca}+\text{Na})$ value in Fig. 12 reflects the chemistry of the rock and does not correspond to the temperature and pressure. This also means that the variation of the $\text{Ca}/(\text{Ca}+\text{Mg})$ value according to the relation in Fig. 11 does not indicate the variation of the temperature and pressure. From the clear convergence to the relationship in Fig. 11, we may conclude that the temperature, and perhaps pressure were almost constant for this group of specimens. It is also concluded that the variation of $K'_{(18)}$ in Fig. 12 is due to the effect of Na of the clinopyroxene at an isophysical condition. In Fig. 13, the $K'_{(18)}-\text{Ca}/(\text{Ca}+\text{Na})^{\text{Cpx}}$ relation is represented for the sheared lherzolite of Lesotho. For this group, a clear positive correlation, which suggests the variation of the physical condition, is recognized.

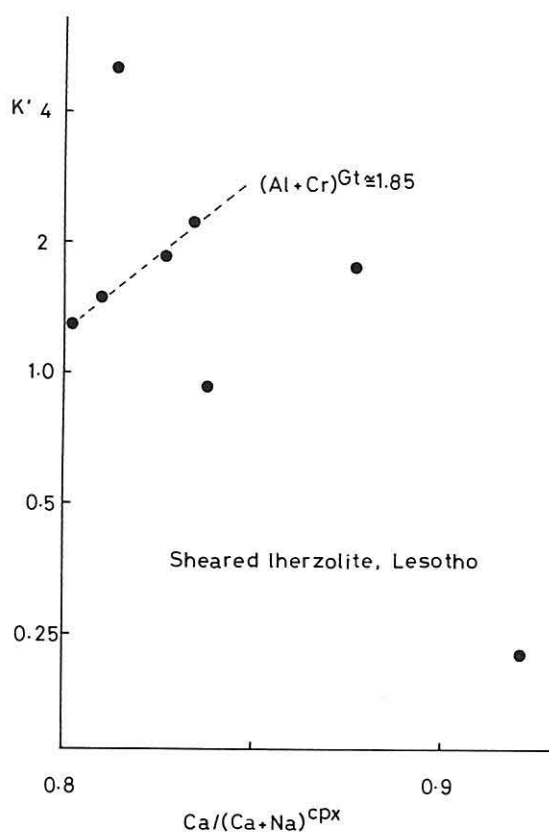


Fig. 13 $K'_{(18)} - \text{Ca}/(\text{Ca}+\text{Na})^{\text{Cpx}}$ relation of the sheared lherzolite of Lesotho.

Although there may be slight variation of the physical condition, in the following discussions it is assumed that this group of samples had equilibrated at an isophysical condition.

Effect of Cr in garnet on K'_{Fe-Mg}^{Gt-O1}

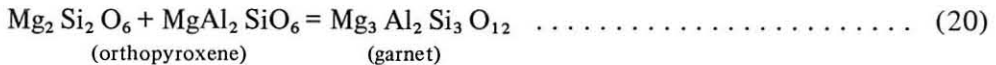
Since the specimens in Figs. 6 and 9 correspond to each other, it is concluded that the variation of K'_{Fe-Mg}^{Gt-O1} is due to the effect of Cr in garnet. In Fig. 6, a distinct linearity is recognized except for three points. By extrapolating the linear relation to $X_{Cr}^{Gt} = 0$, we obtain $K'_{Fe-Mg}^{Gt-O1} = 2.13$ for this group of samples. The correction is carried out according to the following empirical equation

$$\ln K'_{Fe-Mg}^{Gt-O1} = \ln K'_{Fe-Mg}^{Gt-O1} + (A/RT)X_{Cr}^{Gt} \quad \dots\dots\dots (19)$$

where K'_{Fe-Mg}^{Gt-O1} is the corrected value.

Estimation of the temperature and pressure

In order to estimate the temperature and pressure of rocks, another kind of reaction is needed in addition to Eq. (1). Since the reaction (1) is sensitive to temperature, it is desirable that the other reaction is sensitive to pressure. The pressure sensitive reaction available at present is the partitioning of Al and Mg between garnet and orthopyroxene:



The equilibrium equation correspond to Eq. (20) is as follows

$$RT \ln K'_{En.MgTs}^{Gt-OPx} = -(\Delta G_{(20)}^{\circ} + \Delta G_{(20)}^{ex}) \quad \dots\dots\dots (21)$$

where

$$K'_{En.MgTs}^{Gt-OPx} = (X_{Mg}^{M1} \cdot (X_{Mg}^{M2})^2 \cdot X_{Al}^{M1})^{OPx} / (X_{Mg}^3 \cdot X_{Al}^2)^{Gt}$$

According to Wood and Banno (1973), $\Delta G_{(20)}^{\circ}$ and $\Delta G_{(20)}^{ex}$ are given as follows.

$$\Delta G_{(20)}^{\circ} (\text{cal}) = 4207 - 2.67 T - 186 P \quad \dots\dots\dots (22)$$

$$\Delta G_{(20)}^{ex} (\text{cal}) = 180 X_{Al}^{M1} (1 - X_{Al}^{M1}) P \quad \dots\dots\dots (23)$$

The value of $K'_{\text{En.MgTs}}^{\text{Gt-OPx}}$ at 1000°C is listed in Table 5, where the site occupancy of Mg^{M1} and Mg^{M2} is reduced from the experiments by Saxena and Ghose (1971). The tetrahedral site of orthopyroxene is assumed to be occupied by Si and Al. The site occupancy of Fe and Mg in M1 and M2 sites is almost insensitive to the assumption on the temperature in such Mg-rich composition. There is also a correlation between the value of $K'_{\text{En.MgTs}}^{\text{Gt-OPx}}$ and $X_{\text{Cr}}^{\text{Gt}}$ (Fig. 14).

Table 5 Partition coefficients of the granular lherzolite from Thaba Putsoa pipe, Lesotho.

No	$K'_{\text{Fe-Mg}}^{\text{Gt-O1}}$	$K'_{\text{En.MgTs}}^{\text{Gt-OPx}}$	$(\text{Ca}/\text{Ca}+\text{Mg})^{\text{CPx}}$	$X_{\text{Gr}}^{\text{Gt}}$	$X_{\text{Al}}^{\text{M1-OPx}}$	
1959	2.63	0.0521	48.0	0.195	0.014	
1567	2.48	0.0393	47.6	0.132	0.014	
1592	2.50	0.0384	47.5	0.134	0.014	
1570	2.43	0.0383	47.3	0.144	0.013	
1573	2.81	0.0574	47.2	0.240	0.012	
1569	2.49	0.0516	46.9	0.215	0.013	chromite absent
1568	2.63	0.0526	46.8	0.197	0.015	chromite absent
1572	2.40	0.0411	46.6	0.160	0.014	

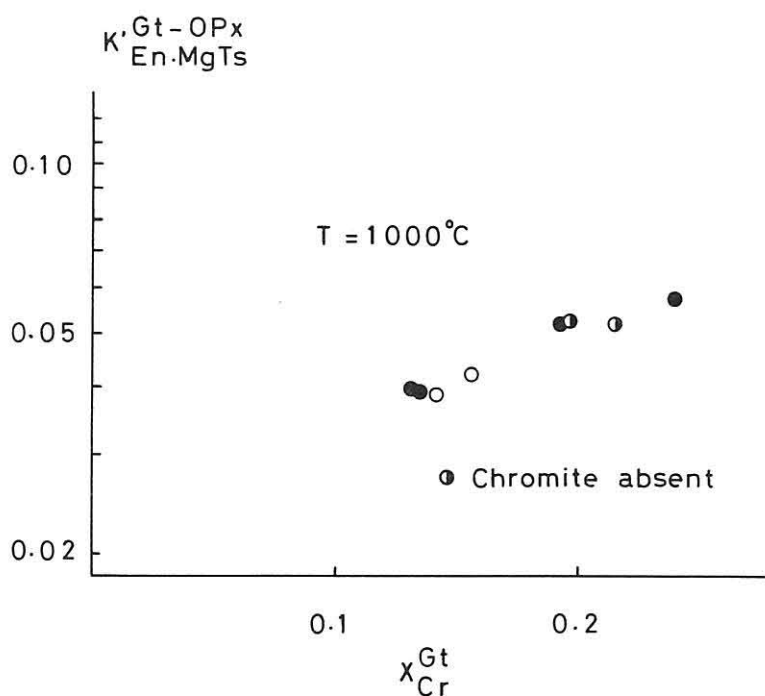


Fig. 14 The $K'_{\text{En.MgTs}}^{\text{Gt-OPx}}$ — $X_{\text{Cr}}^{\text{Gt}}$ relation of the granular lherzolite. The symbols are the same as in Fig. 6. There is also a nearly linear relation between $\ln K'$ and $X_{\text{Cr}}^{\text{Gt}}$.

The extrapolated value at $X_{Cr}^{Gt} = 0$ is 0.023.

By combining reactions (1) and (20), we obtain the equilibrated pressure and temperature of the granular lherzolite as 45 kb, 975°C.

The Cr correction on $K'_{En.MgTs}^{Gt-OPx}$ may be written as

$$RT \ln K'_{En.MgTs}^{Gt-OPx} = RT \ln K'_{En.MgTs}^{Gt-OPx} + (B/RT) X_{Cr}^{Gt} \dots \dots \dots (24)$$

where $K'_{En.MgTs}^{Gt-OPx}$ is the corrected value. Since $T = 975^\circ\text{C}$, A in Eq. (19) and B in Eq. (24) are determined as $A = -2.75$ kcal, $B = -10.5$ kcal, respectively. Without these corrections, we have the value of P and T as $P = 20 - 30$ kb, $T = 700 - 800^\circ\text{C}$, both of which are abnormally low for kimberlites. This again, support the hypothesis of the isophysical equilibrium for this group of samples.

Boyd (1973) estimated the temperature and pressure of this group of samples by means of the garnet-orthopyroxene and clinopyroxene-orthopyroxene equilibria. Although the present result is surprisingly consistent with the estimation by Boyd, this consistency may not be meaningful because of the difference in the method of P - T calculation.

According to the clinopyroxene-orthopyroxene geothermometry calibrated by Mori and Green (1975, 1976), a slight low temperature is obtained for this group of samples. However, if we correct the effect of Na in clinopyroxene by means of the relation in Fig. 11, we obtain remarkable low temperature from the phase diagram by Mori and Green.

Comparison with the garnet-clinopyroxene geothermometry

The partition coefficient of Fe and Mg between garnet and clinopyroxene ($K'_{Fe-Mg}^{Gt-CPx} = (X_{Fe}/X_{Mg})^{Gt}/(X_{Fe}/X_{Mg})^{CPx}$) for the granular lherzolite of Thaba Putsoa pipe varies from 2.6 – 4.1. However, no definite correlation appears between K'_{Fe-Mg}^{Gt-CPx} and X_{Cr}^{Gt} . According to the experiments on the P - T dependence of K'_{Fe-Mg}^{Gt-CPx} by Råheim and Green (1974), the temperature is obtained as 1000 – 1200°C at 40 kb, higher than that obtained by other methods. From the preceding discussions, these specimens were estimated to be equilibrated at an isophysical condition. This discrepancy may suggest the presence of a small amount of ferric iron in the clinopyroxene.

Applications to the Granular Lherzolites and Harzburgites

In Fig. 15 and Table 6, the estimated temperatures and pressures of the several granular lherzolites and harzburgites of kimberlite are represented. In this calculation, the specimen whose garnet satisfies the structural formula as $Al+Cr \geq 1.95$ were selected except for RVD 181 ($Al+Cr = 1.93$). The age of the kimberlite from the Udachnaya pipe, Yakutia is late Paleozoic and the age of

the Lesotho kimberlite is late Cretaceous. On the contrary, the kimberlite from the Premier mine, South Africa is Precambrian, older than 1115 my (Allsopp et

Table 6 Estimated temperatures and pressures of the garnet lherzolite and garnet harzburgites in kimberlites. UV 198/75 – M607 are from Boyd et al. (1976) and RVD 183 – 155 are from Dachin and Boyd (1976).

P(kb)	T(°C)	$K'_{\text{Fe-Mg}}^{\text{Gt-O1}}$	$K'_{\text{Fe-Mg}}^{\text{Gt-O1}}$	$K'_{\text{En.MgTs}}^{\text{Gt-OPx}}$	$K'_{\text{En.MgTs}}^{\text{Gt-OPx}}$	Sample No.	Locality
37	847	2.86	2.41	0.0513	0.0266	UV 198/75	Udachnaya, Yakutia
38	857	2.75	2.39	0.0454	0.0264	UV 71/75	Udachnaya, Yakutia
40	879	2.78	2.34	0.0462	0.0239	UV 244/75	Udachnaya, Yakutia
49	908	2.56	2.35	0.0181	0.0131	M 511	unknown, Yakutia
43	893	2.46	2.33	0.0231	0.0188	M 607	unknown, Yakutia
88	1459	2.06	1.63	0.0243	0.0100	RVD 183	Premier mine, South Africa
61	1230	2.09	1.77	0.0355	0.0187	RVD 181	Premier mine, South Africa
47	1050	2.11	1.98	0.0335	0.0261	RVD 155	Premier mine, South Africa

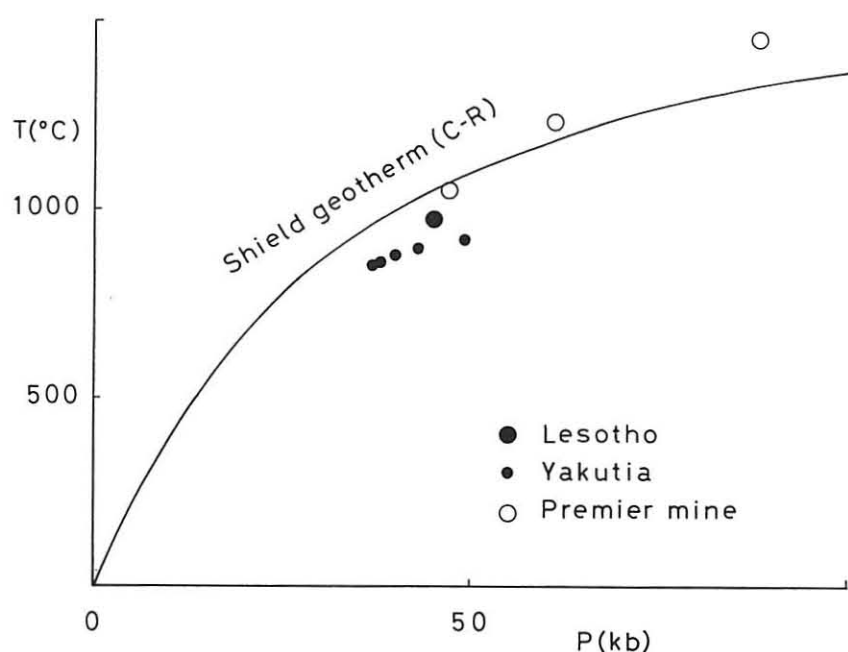


Fig. 15 The estimated temperatures and pressures of some granular lherzolites and granular harzburgites of the kimberlites of several districts. The shield geotherm is the estimation by Clark and Ringwood (1964).

al., 1967). Thus it is estimated that the thermal structure of the upper mantle is different as regards to the region and the age. For this problem, however, further study is needed.

Applications to the Eclogites of Mt. Higasiakaisi

Mori and Banno (1973) described the eclogite of Mt. Higasiakaisi, south-western Japan, where two garnet-olivine pairs are included. The garnet is free from Cr and Fe^{3+} and slightly iron-rich as compared to the garnet in the kimberlites. $K'_{\text{Fe-Mg}}^{\text{Gt-Ol}}$ is calculated for these pairs to be 3.12 and 2.79, respectively. Assuming $P = 6 - 10$ kb, we obtain $T = 597 - 608^\circ\text{C}$ and $654 - 667^\circ\text{C}$, respectively. Although the reason of this difference between the two specimens is not clear, the former value is quite consistent with the estimation by Mori and Banno. It may be concluded that the garnet-olivine geothermometry calibrated in the present experiments does not indicate unrealistic value in the low temperature region.

Remained Problems

It is demonstrated that the partitioning of Fe and Mg between garnet and olivine is a useful geothermometry. However, in order to confirm the present results, it is necessary to carry out the reversal runs, which is now under investigation.

The effect of Ca in garnet on the partition coefficients is also interesting. However, the correlation between Ca and Cr in garnet in the lherzolite nodules makes the separation of the effect of Ca and Cr very difficult. From the thermodynamic estimation, the effect of Ca in garnet on the partition coefficients is expected to be insignificant. However, it might be possible to classify the relations in Figs. 6 and 9 according to the Ca content of the garnet. Unfortunately, the extent of the variation of the Ca content in the garnet independent of the Cr variation in the garnet is not sufficient to make a definite conclusion on this problem at present.

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