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Intracrystalline Fe^{2+}–Mg equilibria in three natural Ca-rich clinopyroxenes

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Abstract

The intracrystalline equilibria for Fe^{2+} and Mg between the $M1$ and $M2$ sites in Ca-rich clinopyroxenes have been determined at a number of temperatures. The required site-occupancy data have been obtained by complete crystal-structure refinement of single-crystal X-ray intensities constrained by the bulk chemistry determined from electron microprobe analysis. The samples used in the study were (1) a discrete clinopyroxene nodule from the Thaba Putsoa kimberlite pipe, Lesotho; (2) a clinopyroxene megacryst found in a nephelinite breccia from Kakanui, New Zealand; and (3) a clinopyroxene from a kaersutite-bearing eclogite, also from Kakanui.

The temperature corresponding to the cation distribution for the discrete nodule is 530° ± 50°C, in agreement with the results of McFadden (1973), who carried out thermal demagnetization experiments on samples of the Ventersdorp lava that was intruded by the kimberlite at the DeBeers mine. On the basis of his experimental work and heat-flow calculations, he obtained an emplacement temperature of 550°–620°C.

The megacryst from Kakanui yields a temperature of 1367° ± 120°C. Although the uncertainty is large, the lower temperature limit is consistent with crystallization temperatures inferred from garnet–clinopyroxene distribution coefficients (Akella and Boyd, 1974; Råheim and Green, 1974), in addition to the experimental study of Merrill and Wyllie (1975). The clinopyroxene from the kaersutite-bearing eclogite, which was referred to the megacryst calibration curve, gives a temperature of 710° ± 50°C, in marked contrast to the temperature of approximately 1250°C calculated from the garnet–clinopyroxene distribution coefficients. The most probable cause of the discrepancy is cooling of the eclogite in the subsolidus to 700°–800°C prior to eruption, as suggested by Merrill and Wyllie (1975).

Introduction

One of the basic problems currently facing geologists is determining the cooling histories of igneous and metamorphic rocks in order to better understand the processes that formed them. Because clinopyroxenes are found in a variety of rocks, a study was initiated to determine the distribution coefficient of Fe^{2+} and Mg between $M1$ and $M2$ as a function of temperature in (1) a discrete clinopyroxene nodule from the Thaba Putsoa kimberlite pipe, Lesotho (collected by P. H. Nixon and supplied by F. R. Boyd); (2) a clinopyroxene megacryst from the Kakanui nephelinite breccia in New Zealand (supplied by B. Mason); and (3) a clinopyroxene from an eclogite, also from Kakanui (supplied by J. Dickey). A series of annealing experiments were conducted on portions of the megacryst and discrete nodule to establish ln K_d *vs.* $1/T(°K)$ calibration curves [$K_d = (Fe^{2+}/Mg)M1/(Fe^{2+}/Mg)M2$] that could be used to determine the temperature corresponding to the untreated material. Because the parameters of the temperature calibration appear to depend strongly on the wollastonite content of the pyroxene (Hafner *et al.*, 1971; Saxena *et al.*, 1974) and because this component of the two Kakanui samples is similar, it was assumed that the calibration curve determined for the megacryst could also be used for the eclogitic pyroxene.

The individual K_d's were calculated from cation occupancies obtained by complete crystal-structure refinements. Although the technique of Mössbauer resonance spectroscopy has proved to be a rapid, useful tool for the study of intracrystalline distribu-

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tion coefficents in orthopyroxenes (*e.g.* Ghose and Hafner, 1967; Virgo and Hafner, 1969), it has been shown by Virgo (1973) and Dowty and Lindsley (1973) that it is not always possible to convert the area ratios obtained from the Mössbauer experiment into site occupancies for Fe^{2+} and Mg between $M1$ and $M2$ in clinopyroxenes, particularly when appreciable amounts of Ca are present in the structure. For this reason the alternative technique of complete crystal-structure refinements from single-crystal X-ray intensities was used to obtain site occupancies (Finger, 1969).

Methods

Annealing experiments

In order to obtain the temperature dependence of K_d for the discrete nodule and megacryst, portions of each were isothermally annealed at temperatures of 725°–927°C and 675°–927°C, respectively. The charges were held in crimped $Ag_{70}Pd_{30}$ tubes, which were placed in SiO_2 glass tubes, surrounded with iron, and evacuated to $< 100\,\mu m$ Hg. Two additional experiments were performed on the megacryst sample under conditions of 1250°C at 20 kbar and 1350°C at 30 kbar. The high-pressure runs were done in solid-media apparatus (1/2 in. diameter piston) using graphite containers to hold the crystals.

Chemical determinations

The bulk chemistry of all the samples was determined on an automated electron microprobe. In addition to the untreated material, crystals from each annealing experiment were analyzed. A minimum of a dozen spot analyses were averaged to obtain a composition for each sample. Particular attention was given to determining the percentage of the total iron that is Fe^{3+}, as this component is not involved in the exchange reaction. The charge-balance or stoichiometry method of Finger (1972) was used to calculate this parameter. Because this technique is based on the difference of two quantities, the error can be large. If a precision of 1 percent is obtained for the oxide amounts, the relative uncertainty for small amounts of iron is commonly equal to 100 percent for a single analysis. This study, however, includes a large number of analyses that yield a good estimate of the precision. When these calculations are performed on the Kakanui megacryst, *e.g.*, 27 ± 10 percent of the total iron is ferric, in good agreement with the value obtained by Dickey (1968) using gravimetric techniques. This ratio was not changed by any of the annealing experiments except the two high-pressure runs on the megacryst in which the stoichiometry indicated that all the iron was ferrous. Obviously, mass-balance and charge considerations would require the formation of an additional phase or phases as the iron is reduced. There was no optical or crystallographic evidence for any extra phases; however, the small amount of iron that was converted would not require the formation of very large amounts of such phases.

The composition of the clinopyroxene in the discrete nodule is difficult to determine because the X-ray precession photographs of the ($h0l$) net indicate minor exsolution of a pigeonite phase parallel to (001) of the host. It is not possible to precisely determine the compositions of the host and exsolved phases from the cell parameters or the percentage of the exsolved phase because there are components present that lie outside the pyroxene quadrilateral, primarily 12 mole percent jadeite plus acmite. To estimate the appropriate compositions the following procedures were used: (1) the bulk composition was normalized to the components of the system wollastonite (Wo), enstatite (En), and ferrosilite (Fs); (2) the $CaSiO_3$ contents of both the host and exsolved phase were estimated from their respective β angles (Turnock *et al.*, 1973); and (3) the Fe^{2+}/Mg for each phase was taken to be equal to that of the normalized bulk composition. Mass-balance considerations for these compositions indicated approximately 10 mole percent exsolved material. This fraction of pigeonite was then subtracted from the total bulk analysis, which in turn was normalized to 4 cations to arrive at a chemical formula for the host.

X-ray data collection and refinement procedures

X-ray intensity data were obtained using an automated Picker four-circle diffractometer (Finger *et al.*, 1973) with Nb-filtered Mo$K\alpha$ radiation. Observed intensities were corrected for absorption, background, and the Lorentz and polarization effects. The secondary extinction factor of Zachariasen (1968) was calculated during the later stages of refinement. Throughout all cycles of refinement the least-squares program RFINE 2 (Finger and Prince, 1975) was used. The atomic scattering factors were those of neutral atoms given by Cromer and Mann (1968), and the anomalous scattering factors and mass absorption coefficients were those of Cromer and Liberman (1970).

For all crystals the least-squares refinement was initiated using the atomic coordinates of diopside given by Finger and Ohashi (1976). A total of approximately 700 reflections were measured for each sample, and on the average 70 were rejected because their intensity was less than 2 standard deviations of the observed intensity or because $|F_o - F_c| > 10$, the latter criterion being considered only during the final cycle of anisotropic refinement. Also, during all cycles of refinement the scale factor, atomic coordinates, temperature factors, and occupancies were refined.

Because the natural samples used in this study have complicated chemistry, certain simplifying assumptions had to be performed before the cation occupancies could be refined. For all samples, Na and Ca were assigned to *M*2 and the octahedral Al was assigned to *M*1. For the discrete nodule, Fe^{2+}, Fe^{3+}, Ti, Cr, and Mn were summed to form a ficticious species, Fe′, which was given a scattering factor equal to neutral iron. The Fe′–Mg occupancies of *M*1 and *M*2 were then refined subject to the constraint of bulk chemistry (Finger, 1969). A similar procedure was followed for the Kakanui samples; however, Ti, which has a higher concentration in these materials, was explicitly assigned to *M*1. After convergence of the structure with the average uncertainty in the refined occupancy equal to 0.004, the Fe′ occupancies were converted to Fe^{2+} values by assuming that Fe^{3+}, Cr, and Ti (necessary only for the discrete nodule) were located in *M*1 and that Mn was in *M*2.[2]

TABLE 1. Chemical and crystallographic data for the discrete nodule

Cations per 6 oxygen atoms	Bulk material	Host chemistry
Na	0.105*	0.118†
Mg	1.109	1.059
Al	0.107	0.119
Si	1.975	1.973
K	0.000	
Ca	0.522	0.553
Ti	0.009	
Cr	0.008	
Mn	0.004	
Fe^{2+}	0.138	
Fe^{3+}	0.022	0.025
Fe′‡		0.153
Ni	0.000	
Cell dimension§		
a, Å		9.699(5)
b, Å		8.871(2)
c, Å		5.251(3)
β		107.03(3)
V, $Å^3$		431.9(3)
Calculated density, g/cm^3	3.34	
Size of crystal, mm	0.04 × 0.11 × 0.30	
Linear absorption coefficient, cm^{-1}, for MoKα	20.00	

*Original analysis without Fe^{3+} correction given by Nixon and Boyd (1973) as sample No. 1600 E4.

†Chemistry determined by subtraction of 10 mole percent $Ca_{0.240}Mg_{1.560}Fe_{0.200}Si_2O_6$ from bulk chemistry.

‡Fe′ = ΣFe^{2+} + Mn + Ti + Cr.

§Cell parameters determined from four-circle diffractometer.

TABLE 2. Equilibrium distribution coefficients as a function of temperature for the discrete clinopyroxene nodule from the Thaba Putsoa Pipe, Lesotho

T, °C	Time, hr	K_d
625	739.0	0.082 ± 0.011
675	158.5	0.108 ± 0.019
675*	168.0	0.108 ± 0.019
802	141.5	0.123 ± 0.014
927	42.0	0.175 ± 0.022

*Initially disordered at 927°C.

Results

Discrete nodule

The bulk chemical analysis of Nixon and Boyd (1973), the host composition corrected for the exsolved pigeonite, and crystallographic data for the untreated material from the discrete nodule are presented in Table 1. The results of the annealing experiments are summarized in Table 2. One of the points at 675°C was initially disordered at 927°C and therefore represents a reversal. The uncertainty in K_d was determined from a propagation of errors calculation based on the occupancy constraint equations. The weighted least-squares fit to these data was obtained and is shown in Figure 1. The temperature corresponding to the K_d of the untreated material (0.068 ± 0.013) is 530° ± 50°C.

Kakanui samples

Chemical as well as crystallographic data for the untreated megacryst and eclogitic clinopyroxenes are given in Table 3. Because no exsolution was detected by either X-ray precession photography or transmission electron microscopy, the bulk compositions of these pyroxenes did not have to be corrected. The K_d's obtained for the annealing experiments made with the megacryst are presented in Table 4. The two data points at 927°C are a measure of the precision of the method, since two completely different sets of

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[2] The details of the crystal-structure refinements are available from the authors on request.

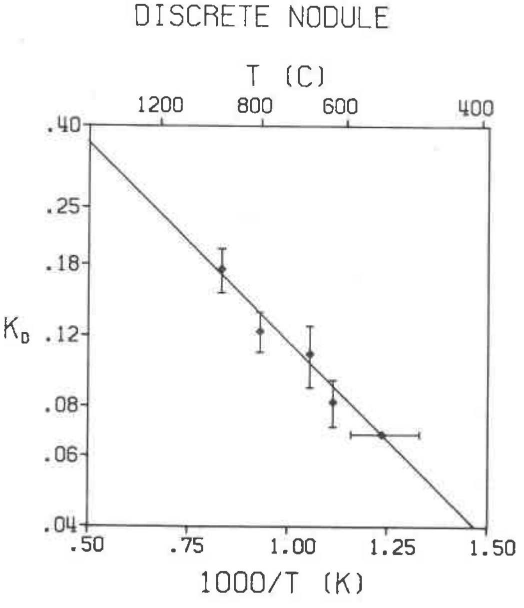

FIG. 1. Ln K_d *vs.* $1/T$°K × 1000 for the discrete clinopyroxene nodule from the Thaba Putsoa kimberlite pipe, Lesotho. Error bars represent 1σ.

data were obtained for two crystals from the same run. The pair of runs at 802°C represents a reversal, the material for the disordering experiment being initially ordered at 675°C. A weighted least-squares fit to all the data is shown in Figure 2 and results in equilibration temperatures of 1367° ± 120°C for the megacryst (K_d = 0.289 ± 0.042) and 710° ± 50°C for the eclogitic sample (K_d = 0.077 ± 0.021).

Discussion and conclusions

Discrete nodule

From the bulk composition of this clinopyroxene, Nixon and Boyd (1973) estimated an equilibration temperature of approximately 1375°C; the presence of exsolved pigeonite, however, indicates a later event at a much lower temperatue or slow cooling until diffusion effectively ceased. On the basis of this observation the crystals should be relatively ordered, and the temperature of 530° ± 50°C obtained from the data in Figure 1 is consistent with this expectation. In order to understand the geological significance of this temperature the result was compared with the data of McFadden (1973). He performed a paleomagnetic study on samples from the DeBeers diamond mine in order to obtain an emplacement temperature for the kimberlite. Both kimberlite and the surrounding Ventersdorp lava were samples from deep underground in the DeBeers mine. The degree of magnetic updating of the lava at the contact was used to obtain the maximum intrusion temperature of the kimberlite by defining a mathematical model of the kimberlite pipe and the heat flow within it. Using the appropriate boundary conditions on the system, a range of 550°–620°C was suggested for the intrusion temperature of the kimberlite. This result compares favorably with that obtained from the present study (530° ± 50°C) and indicates that whereas emplacement of kimberlite may be extremely rapid, the associated temperature is low. It is worth noting that a similar observation has been made by Brookins and Meyer (1974), who have suggested that the final emplacement temperature of kimberlite in Riley County, Kansas, was of the order of 200°C.

Kakanui samples

The temperature of 1367° ± 120°C obtained for the megacryst indicates that it was brought from depth at a very rapid rate, and the high degree of disorder

TABLE 3. Chemical and crystallographic data for the Kakanui clinopyroxenes

	Megacryst*	Eclogite
	Cations per 6 Oxygen Atoms	
Na	0.093	0.198
Mg	0.885	0.677
Al	0.350	0.316
Si	1.822	1.854
Ca	0.634	0.594
Ti	0.023	0.024
Cr	0.004	0.004
Mn	0.005	0.007
Fe^{2+}	0.134	0.213
Fe^{3+}	0.048	0.114
	Cell Dimensions†	
a, Å	9.684(2)	9.683(3)
b, Å	8.840(3)	8.846(3)
c, Å	5.266(1)	5.264(1)
β	106.89(3)	106.83(2)
V, Å^3	431.3(2)	431.6(2)
	Calculated Density, g/cm^3	
	3.35	3.39
	Size of Crystal, mm	
	0.070 × 0.140 × 0.210	0.042 × 0.019 × 0.168
	Linear Absorption Coefficient, cm^{-1}, for MoKα	
	21.9	25.6

*Data are representative and were taken from the untreated sample.
†Cell dimensions were obtained from four-circle diffractometer.

indicated by the relatively large K_d is preserved. As a basis for independent comparison, a temperature of crystallization was determined by assuming that both garnet and augite megacrysts were in equilibrium, and the intercrystalline distribution coefficient for Fe and Mg between the two phases was calculated. The garnet analysis used in this calculation was taken from sample OU20308 of Dickey (1968). The two calibration methods used to estimate the temperature are taken from Råheim and Green (1974) and Akella and Boyd (1974). Whereas the former authors derive an expression for temperature in terms of not only K_D [where $K_D = (FeO/MgO)_{Gar}/(FeO/MgO)_{Cpx}$] but also pressure, Akella and Boyd (1974) assumed no pressure dependence on K_D [where $K_D = (Fe^{2+}/Mg)_{Gar}/(Fe^{+2}/Mg)_{Cpx}$] over the range 31–44 kbar.

The result obtained using the data of Akella and Boyd (1974) yields a temperature of 1274°C. In a separate study using kaersutite and kaersutite-bearing eclogite from Kakanui, Merrill and Wyllie (1975) suggested that the megacrysts of garnet and clinopyroxene were precipitated at 1200°–1300°C at a depth of 75–85 km (22–24 kbar). Finally, if it is assumed that the pressure estimate of Merrill and Wyllie (1975) (approximately 25 kbar) is correct, the calculated temperature using the equation of Råheim and Green (1974) is 1210°C. Thus, within the respective uncertainties, the results from both inter- and intracrystalline equilibrium studies and calculations using the megacrysts from Kakanui agree.

Unfortunately, the attempt to calculate a corresponding temperature for the intercrystalline equilibrium between garnet and clinopyroxene in the kaersutite-bearing eclogite gave inconsistent results. If the garnet analysis given by Dickey (1968) for sample OU19865 is used, both the calculations of Akella and Boyd (1974) and those of Råheim and Green (1974) result in a temperature of approximately 1250°C. This result is at variance with the work of Merrill and Wyllie (1975), who determined the upper stability limit for kaersutite to be roughly 1150°C. It is possible that, if the uncertainties in the various methods are taken into account, the presence of kaersutite may not be inconsistent. Also the reaction of clinopyroxene with melt to form the amphibole may have modified the intercrystalline distribution coefficients to a value not representative of the temperature at which the reaction took place; however, both these suggestions need further verification.

TABLE 4. Equilibrium distribution coefficients as a function of temperature for the clinopyroxene megacryst from Kakanui, New Zealand

T, °C	Time, hr	K_d
1350*	3.75	0.250 ± 0.024
1250†	7.0	0.253 ± 0.024
927	152.25	0.162 ± 0.022
927	152.25	0.139 ± 0.022
802	89.25	0.096 ± 0.015
802‡	96.0	0.123 ± 0.020
675	302.5	0.066 ± 0.013

*30 kbar, graphite container.
†20 kbar, graphite container.
‡Disordered from 675°C.

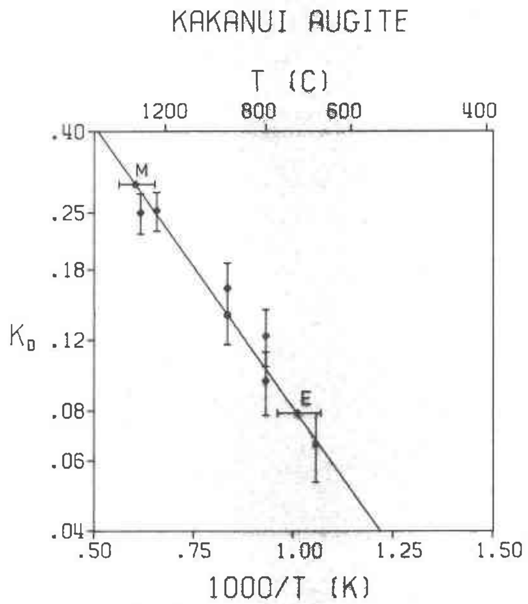

FIG. 2. Ln K_d *vs.* $1/T$°K × 1000 for the clinopyroxene samples from Kakanui, New Zealand, Solid diamonds are the results of annealing experiments at 20 kbar and 1350° and 1250°C, respectively; open diamonds represent runs performed in evacuated SiO_2 glass tubes. The diamonds labeled *M* and *E* are the data for the untreated megacryst and eclogite clinopyroxenes, respectively. Error bars represent 1σ.

In any event, the intracrystalline equilibrium clearly represents a different temperature than the intercrystalline relationship. Merrill and Wyllie (1975) suggested that the kaersutite-bearing eclogite at Kakanui reequilibrated in the subsolidus to 700°–800°C and 20–30 kbar prior to eruption. The latter explanation seems probable, because the present study has shown that the time required for complete reequilibration in this temperature range is a few hundred hours; this hypothesis is therefore consistent with the cation ordering.

Summary

This investigation has shown that intracrystalline equilibria in clinopyroxenes are very sensitive over a relatively large temperature range and thus can provide insight into the thermal history of these minerals. The agreement between the data obtained in this study and those from other sources for the same materials is encouraging. Also, the ease with which complete crystal-structure refinements (and K_d's) can now be obtained through utilization of the automated X-ray diffractometer suggests that additional systematic studies on clinopyroxenes must be made. These studies should include determining not only the equilibrium K_d's in synthetic samples as a function of temperature and composition but also the kinetics of ordering and disordering. Whereas the former type of data yield information on activity-composition relationships in clinopyroxenes, the latter experiments are necessary for the interpretation of the thermal history of natural clinopyroxenes.

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