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Omphacite studies, I. The *P2/n* → *C2/c* transformation

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Abstract

Heating experiments on natural omphacite at 15 to 18 kbar, using a piston–cylinder solid-media apparatus, have established the critical temperature for the order–disorder *P2/n* ⇄ *C2/c* transition at 725 ± 20°C. The disordering reaction *P2/n* → *C2/c* is quite abrupt, and the observed transformation temperature is independent of run duration for one-day and one-week experiments. Reaction rate data give an activation energy for disordering of about 12 $\mathrm{kcal \cdot mol^{-1}}$, which suggests that cation disorder in omphacite is a cooperative process involving both *M1*-type and *M2*-type cations. It appears that the antiphase domain structure in blueschist-facies omphacite is probably a growth feature, and does not form through inversion on cooling of earlier *C2/c* omphacite. In general, the geothermometric applications of the omphacite phase relations are somewhat limited.

Introduction

Omphacite is an aluminous clinopyroxene with a composition intermediate between diopside+hedenbergite+$CaAl_2SiO_6$ and jadeite (Fig. 1). It has been reported from blueschist, amphibolite, and eclogite facies metamorphic rocks, and from eclogite inclusions in kimberlite, and hence appears to have a very wide range of temperature and pressure stability. Omphacite with composition near Ca/(Na+Ca) = 0.50 (Fig. 1), and from all parageneses except kimberlite, has a largely ordered structure with space group *P2/n* (Matsumoto and Banno, 1970, and others), or *P2* (Clark and Papike, 1966 and 1968, and others). Omphacite more Ca-rich or more Na-rich than the *P2/n* composition field has the disordered *C2/c* structure of diopside–hedenbergite and impure jadeite. The ordering in the *P2/n* structure is associated with the *M*-site cations (Fig. 2, Clark and Papike, 1968). Ordering of divalent and trivalent *M1*-type cations into *M1* and *M1(1)* positions, respectively, approaches the theoretical limit for any given composition, but ordering of monovalent and divalent *M2*-type cations is apparently limited to about (1/3Ca, 2/3Na) in *M2* and (2/3Ca,1/3Na) in *M2(1)*.

Earlier workers reported the space group of the ordered omphacite to be *P2*. However, detailed X-ray precession photographs of omphacite from Bessi, Japan and Tiburon, California (Matsumoto *et al.*, 1976) showed that the very weak reflections of the type *h0l* with $h + l \neq 2n$, which suggest this space group, are probably Renninger (simultaneous) reflections, and thus the true space group for these two specimens must be *P2/n*. Our own single-crystal studies on the Ca1059 omphacite from Venezuela (Morgan, 1970, p. 120) confirm *P2/n* symmetry for this omphacite as well. Hence, for the purposes of this paper, we will assume that the true space group of all ordered omphacite specimens is *P2/n*. It should be emphasised, though, that the structural consequences of this space-group ambiguity are rather trivial, since the structures of the two omphacites refined in *P2* (Clark and Papike, 1968; Clark *et al.*, 1969) are more-or-less equivalent to that of the Bessi omphacite refined in *P2/n* (Matsumoto *et al.*, 1975).

Transmission electron optical studies on *P2/n* omphacite from California (Champness, 1973; Phakey and Ghose, 1973) indicate the presence of antiphase domains, which Champness considered to be evidence of a temperature dependent *P2/n* ⇄ *C2/c* inversion reaction. By observing that omphacite from the kimberlite paragenesis, with a composition well within the *P2/n* composition field, has *C2/c* symmetry, Yokoyama *et al.* (1976) established that the critical temperature for the *P2/n* ⇄ *C2/c* inversion is within the stability field of natural omphacite. Furthermore, the ordering reaction (*C2/c* → *P2/n*) must be relatively sluggish compared to the high-temperature cooling rate of kimberlite.

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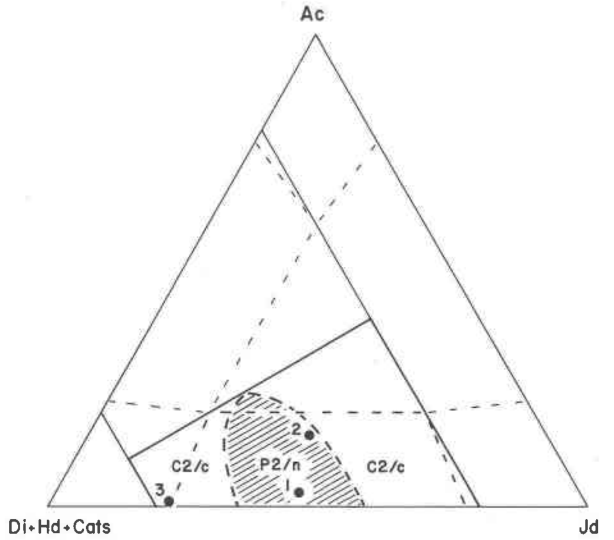

Fig. 1. Natural omphacite compositions used in present study plotted on the Di+Hd+Cats–Jd–Ac composition plane and compared to (i) the omphacite composition fields suggested by Clark and Papike (1968, full lines) and Essene and Fyfe (1967, broken lines), and (ii) stability field of *P2/n* omphacite (Clark and Papike): 1 = Ca1059; 2 = JD951; 3 = Cam958.

At the outset of the present study there was no sound basis for estimating the critical temperature for the inversion reaction, and thus outlining the temperature–composition stability field for ordered *P2/n* omphacite. As far as we are aware, no experimental work has been done on this problem, and this is not too surprising in light of the expected experimental difficulties; product analysis, in particular, is tedious and time-consuming and yet quite exacting. We appreciated that reaction rates for the ordering reaction would be prohibitively long, and thus restricted our study to heating experiments on natural omphacite under appropriate confining pressure. The present study arose from a need for some understanding of the structural states of corresponding ordered and disordered omphacite specimens in connection with a parallel study on the interpretation of omphacite Mössbauer spectra. Phase relations and order–disorder phenomena are discussed in this paper and the Mössbauer investigation of the experimental products is discussed in the following paper (Aldridge *et al.*, 1978).

Experimental

All experiments were conducted with a piston–cylinder solid-media apparatus described in detail by O'Hara *et al.* (1971). The piston-out technique with a 5 kbar overpressure was employed for all runs, resulting in an estimated error of ±1 kbar at the pressures of the experiments (O'Hara *et al.*, 1971). The furnace cell was similar to that described by Richardson *et al.* (1968), but modified by a slightly wider graphite element and a slightly thinner boron nitride sleeve in order to accommodate the large amounts of starting material required for Mössbauer spectroscopy. In each experimental run, a charge of about 0.1 g of natural omphacite, in the form of 100- to 200-mesh grains, was contained in an unsealed gold capsule about 5 mm long and 4 mm in diameter. From diopside melting calibration experiments (O'Hara *et al.*, 1971), and power–temperature calibrations of the temperature controller, the temperatures quoted are believed to be accurate to ±10°C.

Experiments were performed on three natural omphacite compositions (Table 1a, Fig. 1). Temperatures, pressures, run duration times and product analysis for each composition are listed in Table 1b.

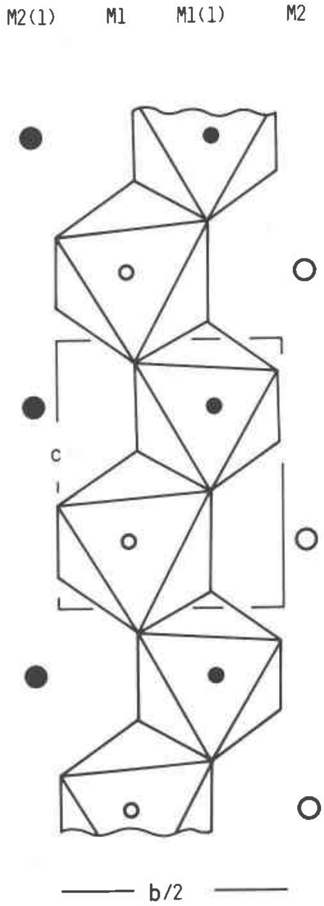

Fig. 2. Octahedral strip at $x = 1/4$ in *P2/n* omphacite showing the one-dimensional arrays of *M*-cations parallel to *c* axis: *M2(1)*–2/3Ca,1/3Na; *M1*–Mg,Fe^{2+}; *M1(1)*–Al; *M2*–1/3Ca,2/3Na.

Table 1a. Composition of omphacites

Sample Abbreviation	Composition	Location	References
Ca 1059	$(Na_{0.48},Ca_{0.47})(Mg_{0.42},Fe^{2+}_{0.05},Fe^{3+}_{0.03},Ti_{0.01},Al_{0.51})(Si_{1.98},Al_{0.02})O_6$	Puerto Cabello, Venezuela	Morgan, 1967; Bancroft, Williams and Essene, 1969
JD 951	$(Na_{0.56},Ca_{0.47})(Mg_{0.42},Fe^{2+}_{0.02},Fe^{3+}_{0.15},Al_{0.39})(Si_{1.99},Al_{0.01})O_6$	Syros, Greece	Dixon, 1968
Cam 958	$(Na_{0.23},Ca_{0.75})(Mg_{0.70},Fe^{2+}_{0.04},Fe^{3+}_{0.01},Al_{0.26})(Si_{1.96},Al_{0.04})O_6$	Silverbach, Germany	Essene and Fyfe, 1967 Bancroft et al., 1969

Gold capsules were used as containers for all experiments in order to avoid Fe loss. The samples were undried and the capsules unsealed. Minute amounts of water vapor from the omphacite grain surfaces and the talc sleeve of the furnace cell were thus expected in all runs. Analysis of the Mössbauer spectra (Aldridge *et al.*, 1978) of the run products and starting materials show that in fact sufficient water vapor was present to reduce some of the iron of the omphacite samples during the course of the experiments. The oxygen fugacity conditions in the furnace are difficult to evaluate. Experiments of Eggler *et al.* (1974) using normal-size boron nitride sleeves suggest values of log fO_2 which are slightly less than the hematite-magnetite buffer but greater than the nickel–nickel oxide buffer ($-6 > \log fO_2 > -10$ at 1000°C). Merrill and Wyllie (1975) report fO_2 somewhat below the Ni–NiO buffer, and Allen *et al.* (1972) suggest fugacities very close to this buffer. If in fact boron nitride acts as a sink for hydrogen, thus explaining the higher fugacities in the experiments of Eggler *et al.* (1974), we suspect that the thin-walled boron nitride sleeves used in the furnace cells of these experiments would be instrumental in maintaining low oxygen fugacities. Therefore, it is suggested that log fO_2 is less than or equal to -8 to -10 throughout the 300–1000°C range of these experiments.

Table 1b. Experimental conditions and product analysis

Sample	T(°C)	P(Kb)	Time(hr)	Space group	$I_{10\bar{1}}$
Ca1059	Starting material			P2/n	94.9, 99.0
Ca1059-1	300	15	20	P2/n	75.6
Ca1059-2	500	15	22	P2/n	90.3
Ca1059-3	700	15	21.5	P2/n	82.1
Ca1059-4	700	15	168	P2/n	71.7, 100.0
Ca1059-5	800	15	24	*C2/c	27.2
Ca1059-6	800	15	168	*C2/c	0.0, 9.2
Ca1059-7	900	18	23.5	*C2/c	6.2, 22.8
Ca1059-8	900	18	168	C2/c	0.0
Ca1059-9	1000	18	18	C2/c	0.0
JD951	Starting material			P2/n	
JD951-1	300	15	23.5	(P2/n)**	
JD951-2	500	15	21	(P2/n)	
JD951-3	700	15	19.5	P2/n	
JD951-4	900	18	21	C2/c	
JD951-5	1000	18	21.5	(C2/c)	
Cam958	Starting material			C2/c	
Cam958-1	300	15	20	(C2/c)	
Cam958-2	500	15	20.5	(C2/c)	
Cam958-3	700	15	18	(C2/c)	
Cam958-4	900	18	24.5	(C2/c)	
Cam958-5	1000	18	22.5	C2/c	

* largely transformed to C2/c
** ( ) indicates assumed symmetry

The pressures of the experiments were selected to meet two criteria. The first is that they be geologically realistic of those required to form omphacite in the lower continental crust and uppermost mantle. The second was the need to prevent the omphacite samples from reacting to their low-pressure breakdown products through the reactions:

$$2NaAlSi_2O_6 \rightleftarrows NaAlSi_3O_8 + NaAlSiO_4 \qquad (1)$$

which has been determined experimentally (Robertson *et al.*, 1957), and:

$$\text{omphacite(1)} \rightleftarrows \text{plagioclase} + \text{nepheline} + \text{omphacite(2)} \qquad (2)$$

which has also been explored experimentally on a composition similar to Ca1059 and JD951 (Bell and Kalb, 1969).

Optical examination confirmed that omphacite was the single product in all the experimental charges; no breakdown products were observed. Space-group assignment of the product of all of the runs with Ca1059 and of selected runs with JD951 and Cam958 was made by single-crystal X-ray diffraction precession analysis. The original omphacite grains were extensively crushed, and fragments suitable for single-crystal study were quite small. We realized at an early stage that, for the high-temperature runs in particular, the apparent degree of order varied from one run product to another. This phenomenon was particularly evident in the variation in the intensity of $10\bar{1}$, the strongest reflection characteristic of the *P2/n* structure within the $h0l$ reciprocal lattice plane. Thus, for the products of runs with Ca1059, the intensity of $10\bar{1}$ Mo$K\alpha$ Friedel pairs was measured using a Joyce-Loebl densitometer and normalized relative to the intensity of the adjacent $20\bar{2}$ Mo$K\beta$ Friedel pairs (Table 1b). These data were obtained from a set of zero-level, b-axis precession films (unfiltered Mo radiation, 35 kV, 20 mA, no layer-line screen, $\mu = 15°$). The scatter for duplicate determinations is generally well outside the experimental error and is considered to represent a real grain-to-grain structural heterogeneity. On the basis of qualitative comparison of precession films, the relative intensities of $10\bar{1}$ reflections for respective 700 and 900°C run products of JD951 and Ca1059 are very similar.

An attempt was made to develop an X-ray powder diffraction technique for examination of the run products. However, whilst low-angle diffraction lines of the ordered structure were resolved on Jagodzinski and Debye-Scherrer films, the degree of resolution was very much inferior to that of the single-crystal technique. Hence, our success with powder diffraction analysis was little better than that of Clark and Papike (1968).

Discussion

The results of the heating experiments (Table 1b; Fig. 3) indicate that the critical temperature for the $P2/n \rightleftarrows C2/c$ transition in omphacite is between 700 and 800°C. Whilst the transformation is much more abrupt than we had anticipated, there is nevertheless an appreciable reaction rate effect, in that the disordering reaction is much more complete at any given temperature after one week than after one day. Although the reaction rate data contained in Figures 3 and 4 do not allow a quantitative extrapolation, they do suggest that the actual transition temperature is closer to 700 than 800°C. In fact 725 ± 20°C would seem to be a reasonably conservative value. Since the intensity data for the one-day and one-week experiments at 700°C are similar, we consider this to be the *stable* inversion temperature rather than the temperature required to activate the transformation. The transformation temperature is fairly independent of composition within the compositional range investigated (the results with JD951 are similar to those with Ca1059) and thus the maximum transformation temperature, which is the critical temperature for the system, is also about 725 ± 20°C. The present temperature is higher than the estimate of Yokoyama *et al.* (1976, 300 to 400°C) and lower than that suggested in the phase diagram of Champness (1973).

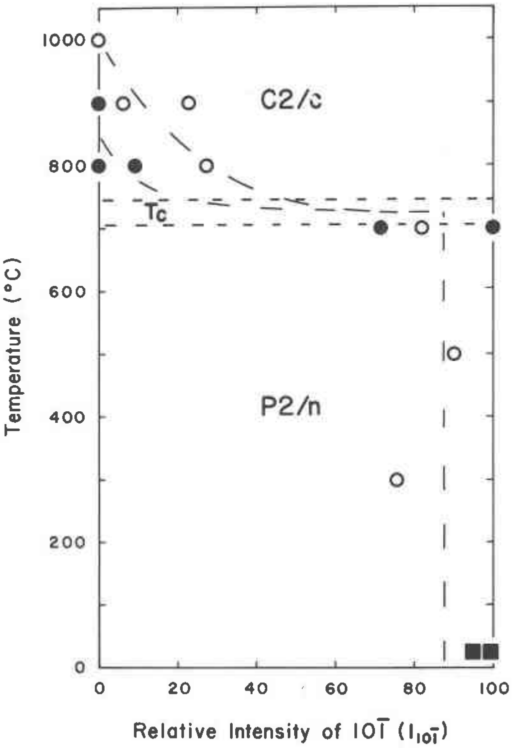

Fig. 3. Variation of $I_{10\bar{1}}$ with temperature for heated samples of Ca1059: stability fields for $P2/n$ and $C2/c$ omphacite and suggested critical temperature (T_c) are indicated: full squares, unheated samples; open circles, samples heated for one day; full circles, samples heated for one week.

A value for the activation energy (E) for the disordering reaction may be calculated using the Arrhenius equation $ln\ k = ln\ C - ER/T$, with an appropriate expression for the rate constant (k). Because the reaction is intragranular, regardless of whether it is partially continuous or wholly discontinuous in character, it will tend to behave similarly to a homogeneous reaction. Thus, after Christian (1975), the rate constant may be equated to the fraction transformed (V) in time (t) through an expression of the type $k = -ln\ (1 - V)/t^n$. With $n = 1$, that is, assuming the reaction is a first-order one as homogeneous reactions appear to be (Christian), $E \simeq 18$ kcal mol^{-1} for the temperature range 800 to 900°C. This calculation is made with the assumption that the intensity of the $10\bar{1}$ reflection ($I_{10\bar{1}}$) is proportional to the volume of the $P2/n$ phase present, and uses mean $I_{10\bar{1}}$ data for the untransformed and partially transformed products. However, the expression for the rate constant (k) with $n = 1$ does not provide a satisfactory fit to our experimental data (Fig. 4). With $n = 0.5$, $E \simeq 12$ kcal·mol^{-1} and the agreement between the observed and calculated rate data is much better (Fig. 4).

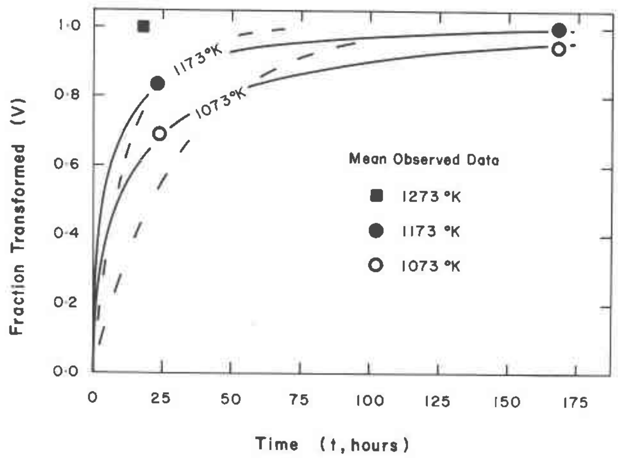

Fig. 4. Reaction-rate data for $P2/n \rightarrow C2/c$ transformation: open circles, observed data, 1073°K; closed circles, 1173°K; closed squares, 1273°K; solid lines, calculated for $n = 0.5$, where n is exponent in $k = -ln(1 - V)/t^n$ (see text); broken lines, calculated for $n = 1$.

Whilst we prefer the latter value, we recognize that the agreement with the experimental data may be quite fortuitous, in view of the paucity of these data. Furthermore, the value for the activation energy is predicated on the other assumption we have made; for example, Chipman and Warren (1950) show that long-range order in simple AB compounds is proportional to $I^{1/2}$, and using this assumption, $E \simeq 8$ kcal mol^{-1} with $n = 0.37$.

The structural heterogeneity in the untransformed and partially-transformed experimental products most probably reflects a compositional heterogeneity. Since the X-ray scattering factors of Mg^{2+} and Al^{3+} are very similar and the $P2/n$ structure is not greatly distorted relative to the equivalent $C2/c$ structure, the 'visibility' of ordered Mg-rich omphacite is largely associated with the partial order of the $M2$-type cations. Hence, grain-to-grain variation in Na_2O and CaO, as documented by Yokoyama *et al.* (1976), would result in corresponding variations in $I_{10\bar{1}}$. A second possible factor contributing to the structural heterogeneity may be variation in degree of order. This is not likely to be associated with the heat treatment, since the phase transition is quite abrupt. It could be inherited from the unheated material, but we have no data with which to evaluate this possibility. Whilst the reflections characteristic of the $P2/n$ structure ($10\bar{1}$, and so on) show variation in intensity, they remain sharp and non-diffuse. Thus, it does not seem likely that the grain-to-grain structural heterogeneity reflects a variation in size and shape of the antiphase domains.

A schematic temperature-composition (T–X) stability field for $P2/n$ omphacite is illustrated in Figure 5. This is a synthesis of (i) the present data on the thermal stability of the $P2/n$ structure, (ii) the marked compositional dependence of the Ca-rich side of the T–X surface (Yokoyama *et al.*, 1976), and (iii) the compositional field of Clark and Papike (1968). Yokoyama *et al.* actually found the Ca-rich-composition limit for amphibolite omphacite to be at about Ca/(Na+Ca) $\simeq$ 0.435. We have placed it at Ca/(Na+Ca) = 0.40 to include the most Ca-rich $P2$ composition of Clark and Papike. The latter composition is for a blueschist-facies omphacite, presumably annealed to a lower temperature than the amphibolite omphacite, and the Ca-rich limb of the $P2/n$ stability field may be inclined less steeply than we have indicated. However, the present indications are that the two-phase ($P2/n$ + $C2/c$) region surrounding the $P2/n$ stability field is very narrow, and this tends to support the present representation.

The geothermometric applications of the omphacite phase relations are somewhat limited. Clearly,

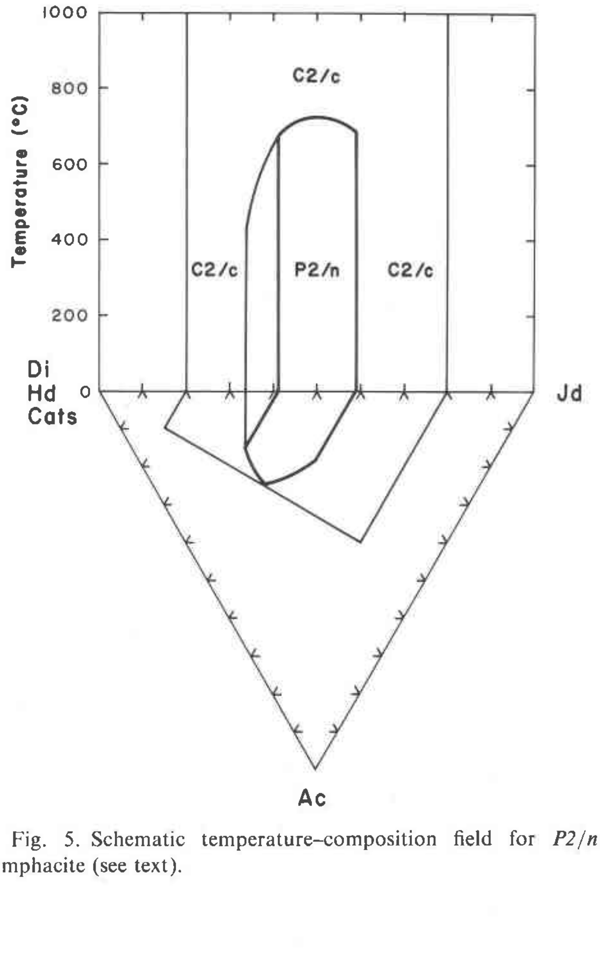

Fig. 5. Schematic temperature–composition field for $P2/n$ omphacite (see text).

the presence of the disordered $C2/c$ structure [at Ca/(Na+Ca) $\simeq$ 0.5] indicates a high temperature of formation and cooling rates appreciably greater than those associated with regionally metamorphosed terrains. The $P2/n$ structure indicates prolonged annealing below 700°C. At the present time, we do not attach any significance to the correspondence of the upper stability limit of the $P2/n$ structure and the highest temperature of equilibration of host eclogite rocks with $P2/n$ omphacite, as reported by Yokoyama *et al.* Essene and Fyfe (1967) and Coleman and Clark (1968) have shown most convincingly that many, if not all, Californian omphacite pyroxenes have actually crystallized under blueschist facies conditions (200 to 300°C, 6 to 9 kbar, Coleman and Clark, 1968). Our study places this temperature range well below the $P2/n \rightleftarrows C2/c$ inversion temperature and clearly argues against the formation of the antiphase domain structure through inversion, on cooling, of earlier $C2/c$ omphacite. Champness (1973) has suggested that the preexisting $C2/c$ phase crystallized metastably within the $P2/n$ stability field. However, it is more probable that the antiphase domain structure is not related to a structural inversion, but is simply a growth feature. Further study of this problem seems called for. In particular, it has not been established if antiphase domain structure is a ubiquitous feature of all $P2/n$ omphacites.

Although the $P2/n$ structure of omphacite has two non-equivalent $M2$-type positions (and the $P2$ structure has four), Clark *et al.* (1969) have argued that the observed degree of order, approximately (1/3Ca, 2/3Na) in $M2$ and (2/3Ca,1/3Na) in $M2(1)$, is the maximum degree of order to be expected. However, as Figure 2 illustrates, the maximum degree of order in *ideal* omphacite is in fact (0Ca,1Na) and (1Ca,0Na), respectively. Apparently, charge (or valence) balancing is not the sole criterion regulating the ordering process. The difference in effective ionic radius between Al^{3+}(0.53A), and Mg^{2+}(0.72) and Fe^{2+}(0.77, data from Shannon and Prewitt, 1969) is appreciable. Thus both cation charge difference and ionic radius difference must contribute to the virtually complete ordering of (Mg,Fe^{2+}) and Al. However, the difference in ionic radius between Ca^{2+} (1.00) and Na^{+}(1.02) is slight, and the tendency of these two cations to order is correspondingly diminished.

The activation energy for the disordering reaction ($P2/n \rightarrow C2/c$) is largely a measure of the energy required to initiate cation diffusion in ordered omphacite. Cation mobility is related to metal–oxygen bond strength, and should increase in the sequence $Na < Ca < (Mg,Fe^{2+}) < Al(C.N. = 6) < Al(C.N. = 4) < Si$. Thus, $E \simeq 20$ kcal mol^{-1} at 500 to 1000°C for Mg/Fe^{2+} disorder in orthopyroxene (Virgo and Hafner, 1969) but increases markedly to $\simeq 74$ kcal mol^{-1} at 920 to 1080°C for Si/Al disorder in Amelia albite (McKie and McConnell, 1963). Compared to these data the present value for omphacite ($E \simeq 12$ kcal mol^{-1}) cannot be associated solely with Mg/Al disordering. Possibly, cation disorder in omphacite is a cooperative process which is facilitated by the greater mobility of the $M2$-type cations.

We have no data to suggest any significant continuous component to the disordering reaction. The $P2/n \leftrightarrows C2/c$ transformation is quite abrupt and any tendency for $I_{10\bar{1}}$ to vary systematically with temperature would be obscured by the reaction-rate effect and structural heterogeneity. The long-range order/disorder process in omphacite appears to be quite different to that in classical AB alloy phases, for which, with continued heating, a well-defined continuous reaction event precedes the phase discontinuity at T_c. Furthermore, in omphacite the short-range order (next-nearest neighbor cation environment) appears to be maintained in the disordered phase (Aldridge *et al.*, 1978).

Acknowledgments

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