

# The Experimental Determination of Activities in Disordered and Short-Range Ordered Jadeitic Pyroxenes

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**Abstract.** The activity of the jadeite ( $\text{NaAlSi}_2\text{O}_6$ ) component in synthetic pyroxenes on the binary join  $\text{NaAlSi}_2\text{O}_6 - \text{CaMgSi}_2\text{O}_6$  has been measured at  $600^\circ\text{C}$  by equilibration of pyroxene with quartz and high albite in hydrothermal experiments. The results are in good agreement with recent calorimetry (Wood et al. 1980) for pyroxenes not close to the  $\text{Jd}_{50}\text{Di}_{50}$  composition for which a considerable degree of short range ordering on the omphacite scheme is indicated by the activity measurements. For compositions close to  $\text{Jd}_{50}\text{Di}_{50}$ , the activity of the jadeite component is approximately equal to its mole fraction.

## Introduction

Pyroxenes whose compositions lie on or close to the binary join  $\text{CaMgSi}_2\text{O}_6 - \text{NaAlSi}_2\text{O}_6$  are found commonly occurring in blueschist and eclogite facies metamorphic rocks.

Petrologists have long known the barometric importance of such pyroxenes in assemblages with quartz for which the minimum pressure of equilibration is a function of the  $\text{NaAlSi}_2\text{O}_6$  activity in the pyroxene (Wood et al. 1980). In early work on omphacites from California (Essene and Fyfe 1967) it was assumed for lack of data, that the  $\text{CaMgSi}_2\text{O}_6 - \text{NaAlSi}_2\text{O}_6$  solid solution series behaved as an ideal ionic mixture. Minimum pressures of formation of eclogitic omphacites calculated on the basis of this assumption were rather low.

Experimental work involving equilibration of jadeite-diopside pyroxenes with quartz and albite at high temperatures and pressures performed by Kushiro (1969) indicated that omphacites, at least at these high temperatures ( $>1,100^\circ\text{C}$ ), approximated more nearly a simple one-site ideal mixture (Ganguly 1973). This work stood in contrast to the assertions of Bell and Davis (1969) that there existed at these temperatures a wide miscibility gap between diopside and jadeite. Calculated minimum pressures of omphacite-quartz assemblages in natural rocks, based on a simple one-site ideal solution model for these pyroxenes, are somewhat higher than for the ionic two-site model. For a pyroxene of composition  $\text{Jd}_{30}\text{Di}_{70}$  at  $600^\circ\text{C}$  the one-site model predicts minimum pressures which are about 5 kb higher than those derived from a two-site model.

To add to these uncertainties in pressure estimates for blueschists and eclogites is the existence, over a narrow range of compositions centred on the  $\text{Jd}_{50}\text{Di}_{50}$  composition in some natural pyroxenes, of cation-ordering with reduc-

tion in space group symmetry (Carpenter 1979; Clark and Papike 1968).

More recent work has shown that omphacites above  $850^\circ\text{C}$  are disordered and possess  $\text{C2/c}$  space group symmetry whereas below this transition temperature they are largely ordered on the basis of a primitive cell, probably  $\text{P2/n}$  (Fleet et al. 1978; Carpenter 1978). The thermodynamics of the high temperature  $\text{C2/c}$  pyroxenes on the  $\text{Jd-Di}$  join were shown by Wood et al. (1980) from solution calorimetry to be quite non-ideal.

At the lower temperatures applicable to many blueschists and eclogites the thermodynamic consequences of this non-ideality and symmetry reduction must be taken into account in any petrological applications.

It is the purpose of this study to *measure* the activity of the  $\text{NaAlSi}_2\text{O}_6$  component in omphacitic pyroxenes in the hope of clarifying the nature of the mixing and inversion processes in these pyroxenes. To do this, the compositions of pyroxenes co-existing with albite and quartz at  $600^\circ\text{C}$  at various pressures were determined by experimental reversals. Final compositions of omphacitic pyroxenes were approached from both the jadeite-rich and jadeite-poor directions at each run condition under hydrothermal conditions.

## Experimental Methods

### (i) Apparatus

All runs were made with the piston-cylinder apparatus using a 0.75" diameter pressure chamber and solid NaCl pressure medium. The apparatus and run technique has been described previously by Jenkins and Newton (1979) and Holland (1980), where it was shown that friction corrections for the NaCl cell are negligible for runs made in the manner described. The starting materials were sealed with excess  $\text{H}_2\text{O}$  (about 25%) in 2 mm platinum capsules placed in pairs perpendicular to the thermocouple tube axis. The thermocouple junction therefore rested in contact with and between both capsules. Runs were considered as acceptable hydrothermal experiments only when water was seen to ooze from the opened capsules.

### (ii) Starting Materials

Starting materials included synthetic high albite, natural quartz and a variety of synthetic pyroxenes on the join  $\text{CaMgSi}_2\text{O}_6 - \text{NaAlSi}_2\text{O}_6$ .

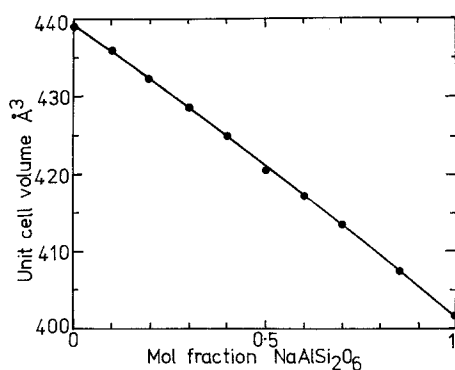


Fig. 1. Unit cell volumes of synthetic pyroxenes crystallised from glass at 30 Kb, 1,300° C

Synthetic albite was identical to that used for earlier experiments (Holland 1980), crystallised hydrothermally at 750° C, 2 kb, and characterised by  $\Delta 2\theta(\text{CuK}\alpha)$  131 – 131 of 1.90.

Synthetic pyroxenes used in this study were also calorimetrically investigated by Wood et al. (1980) and were synthesised from analysed glasses at 1,250–1,350° C and 30 kb in runs of 2–3 h. In runs at these temperatures, times of only about 1 min are required to completely convert P2/n omphacite to C2/c pyroxene (Carpenter 1981), so that the starting materials are clearly all C2/c in structure. Unit cell parameters of the synthetic pyroxenes are tabulated in Wood et al. (1980), and the quality of the cell volume data may be seen in Fig. 1.

Starting mixes were crystalline pyroxene + quartz + high albite ground together under acetone. Two mixes were used for each run – one containing a pyroxene oversaturated with jadeite component and the other a pyroxene undersaturated in jadeite component, in order to bracket the equilibrium composition of pyroxene co-existing with albite and quartz.

Experimental charges were examined optically and by powder X-ray diffraction. In addition to the starting materials (albite + pyroxene + quartz) a small amount of amphibole and paragonite mica were observed in some run products. The resulting pyroxene compositions were determined by measuring the positions of selected X-ray reflections which were calibrated from the synthetic starting-material X-ray scans. Particularly sensitive reflections are the following, whose  $2\theta$  CuK $\alpha_1$  peaks are given below:

hkl	$^{\circ} 2\theta$ CuK $\alpha_1$
311	$39.15 + 1.78 X_{\text{Jd}}$
221	$35.65 + 1.55 X_{\text{Jd}}$
150	$52.10 + 2.35 X_{\text{Jd}}$
041	$44.35 + 1.75 X_{\text{Jd}}$

where  $X_{\text{Jd}}$  is the mol fraction of the NaAlSi<sub>2</sub>O<sub>6</sub> component. The original X-ray data for the 311 peak is given in Fig. 2 to indicate the precision of the data.

Experimental charges were scanned at 1/8°  $2\theta/\text{min}$  and compositions were determined from the positions of a number of composition-sensitive reflections and the mean value taken. Either a synthetic spinel or the position of the relatively composition insensitive 002 peak in pyroxene

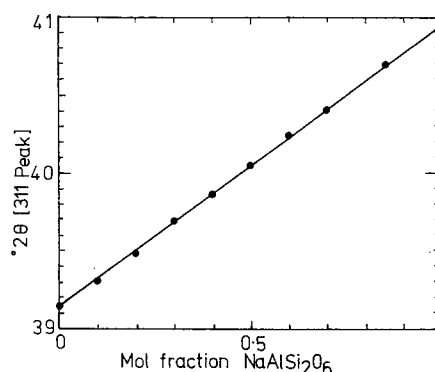


Fig. 2. Variation in the angular position of the 311 reflection in pyroxenes as a function of composition, measured in degrees  $2\theta$  for CuK $\alpha_1$  radiation

was used as an internal standard. Incomplete equilibration of pyroxene compositions was encountered in a number of runs. Some of these equilibrated in further hydrothermal runs at the same conditions, but others retained rather broad X-ray peaks which led to the larger than hoped-for errors in composition determination. Well crystallised material could be compositionally characterised to within  $\pm 1.5$  mol% NaAlSi<sub>2</sub>O<sub>6</sub> at best (see Fig. 2). The effects of ordering on the cell parameters of omphacite (Wood et al. 1980) lead to a small (<2 mol%) underestimate of jadeite content in ordered pyroxenes which is negligible in the context of other errors in this study.

The possibility that the albite orders significantly at 600° C in runs of a few days must be considered. In runs of about a week the albites show a small decrease in  $\Delta 2\theta$  131 – 131; however even large degrees of ordering do not affect the free energy of the jadeite-quartz-albite reaction significantly at 600° C (Newton and Smith 1967; Holland 1980) because the free energy drop due to ordering in albite is very small at these temperatures.

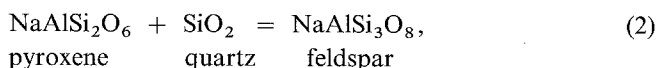
## Results

The results of hydrothermal experiments on pyroxene stability in the presence of albite + quartz are given in Table 1 and displayed in Fig. 3.

As expected, pyroxene stability increases with increasing substitution of the CaMgSi<sub>2</sub>O<sub>6</sub> component in the presence of albite and quartz at constant temperature. In the absence of any phase transformations in the minerals concerned, the decrease in stability pressure for the assemblage pyroxene + quartz should follow a simple variation with composition:

$$P - P^0 = \frac{RT}{\Delta V^0} \ln X_{\text{NaAlSi}_2\text{O}_6}^{\text{Cpx}} \gamma_{\text{NaAlSi}_2\text{O}_6}^{\text{Cpx}} \quad (1)$$

In this equation  $P$  is the pressure at equilibrium for a pyroxene of composition  $X_{\text{NaAlSi}_2\text{O}_6}^{\text{Cpx}}$ ,  $\gamma_{\text{NaAlSi}_2\text{O}_6}^{\text{Cpx}}$  is the activity coefficient for the NaAlSi<sub>2</sub>O<sub>6</sub> component,  $\Delta V^0$  and  $P^0$  are the volume change and equilibrium pressure respectively for the simple reaction

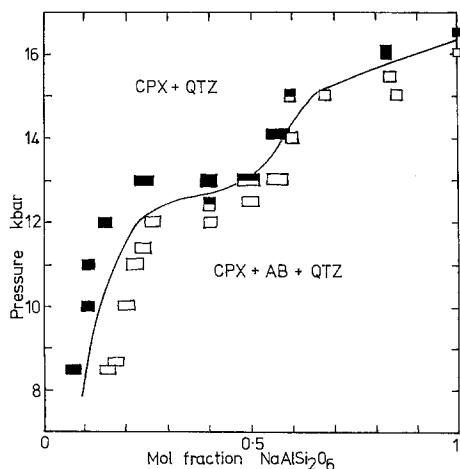


$T$  is the absolute temperature and  $R$  the universal gas constant.

**Table 1.** Experimental results. Starting and final compositions are in terms of  $X_{\text{Jd}}$ 

Pressure (kb)	Run no.	Time (hours)	Starting comp <sup>n</sup> .	Final comp <sup>n</sup> , comments
8.5	OAQ 11	94	0, 50	7.5, 14.5
10	OAQ 5	71	0, 50	11, 21
10	CP 2	45	nat (52)	20
11	OAQ 7	71	15, 50	15, 21.5
11	OAQ 13	143	0	11.5
11.5	OAQ 8	119	20, 30	20, 22
12	OAQ 10	214	0, 50	14, 24
12	OAQ 28	65	30, 40	ab grew, NR
12.5	OAQ 25	70	50	ab grew
12.5	OAQ 27	69	40	ab gone
13	OAQ 30	167	40	ab gone
13	OAQ 6	71	0, 50	15, 50
13	OAQ 12	161	0, 50	25, 50
13	OAQ 20	94	60	57 (ab grew)
14	OAQ 19	70	60	ab grew
14	OAQ 21	117	57	ab gone
15	OAQ 18	68	60	NR
15	OAQ 15	24	85	ab grew
15	OAQ 22	117	70	68 (ab grew)
16	OAQ 17	94	85	83 (ab resorbed)
16	JAQ 4	24	100	ab grew
16.5	JAQ 6	8	100	jd + qz grew
8.6	PAQ 1	89	50	17.5

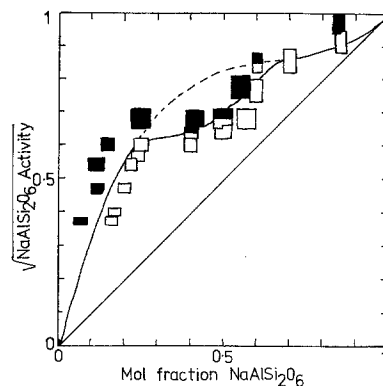
nat = natural Tauern omphacite, described in Wood et al. (1980).  
NR = No reaction



**Fig. 3.** Experimental results displayed as a pressure-composition section at 600°C. Open boxes and filled boxes are compositions of pyroxenes partially equilibrated from  $\text{NaAlSi}_2\text{O}_6$ -oversaturated and undersaturated starting materials respectively. Half filled boxes indicate no change after the run. The position of equilibrium at  $X_{\text{NaAlSi}_2\text{O}_6} = 1$  is taken from Holland (1980)

A notable departure from the expected behaviour can be observed in Fig. 3 in the region centred on the composition  $(\text{NaAlSi}_2\text{O}_6)_{0.5}(\text{CaMgSi}_2\text{O}_6)_{0.5}$  typified by greater than predicted stability for a simple continuous solid solution. The possible causes of this behaviour are discussed later.

It is possible to transform the data given in Fig. 3 into a useful alternative form by calculating the activity of the  $\text{NaAlSi}_2\text{O}_6$  component in the pyroxene as a function of



**Fig. 4.** Activity-composition diagram derived from the data of Fig. 3. The full line corresponds to the curve in Fig. 3 and the dashed portion represents an asymmetric subregular solution model discussed in the text. The square root of the activity is plotted so that the Raoult's and Henry's law regions are displayed for a two-site disordered solution

composition for the conditions  $T = 873$  K and variable pressure. The standard state used is that of unit activity for pure  $\text{NaAlSi}_2\text{O}_6$  pyroxene with C2/c structure at the pressure and temperature of interest, as implied by equation 1. A value of  $\Delta V^0 = 1.734 \text{ J bar}^{-1}$  was used (Robie et al. 1979) to calculate values shown in Fig. 4 from Eq. 1.

The uncertainties in the calculated activities arise from possible pressure uncertainties of  $\pm 250$  bar which lead to errors of  $\pm 350$  bar for  $P - P^0$  and hence to the error in activity which is given by

$$\sigma_a^2 \approx \sigma_{\Delta P}^2 \left( \frac{\partial a}{\partial \Delta P} \right)^2$$

$$\sigma_a \approx \sigma_{\Delta P} \left| \frac{a \ln a}{\Delta P} \right|$$

where  $\Delta P$  is the pressure difference ( $P - P^0$ ), and  $a$  is the activity of jadeite calculated from Eq. (1).

These activities are certain to be affected by changes in temperature but are probably rather insensitive to variations in pressure as the molar volume plot (Fig. 1) is almost linear, implying no excess volume of mixing.

## Discussion

The most likely conclusion to be reached from inspection of Figs. 3 and 4 is that the pyroxenes are largely disordered (C2/c structure, as in the starting material) at the ends of the solid solution series, but are ordered or partly ordered in the region of the  $(\text{NaAlSi}_2\text{O}_6)_{0.5}(\text{CaMgSi}_2\text{O}_6)_{0.5}$  composition. Microstructural and experimental evidence for ordering in omphacites has been clearly documented recently (Carpenter 1978, 1981) and such ordering will lead to a reduction in the jadeite activity in the pyroxenes as has been found.

Examining, for the moment, the range of more disordered compositions away from  $\text{Jd}_{50}\text{Di}_{50}$ , it is instructive to make simple comparisons with the calorimetric work of Wood et al. (1980) who measured the heats of solution of the pyroxenes used as starting materials for this study. The simplest parameterisation of the activity data is to use a regular solution approach to estimate the magnitude of the non ideality in terms of an interaction energy,  $W_{\text{Cpx}}^{\text{Cpx}}$ ,

for the disordered solid solution. As discussed by Holland (1979), this yields a value of  $W_G^{\text{cpX}}$  of  $24 \pm 2 \text{ kJ mol}^{-1}$  for a disordered 2-site solution:

$$RT \ln \gamma_{\text{NaAlSi}_2\text{O}_6}^{\text{cpX}} = W_G^{\text{cpX}} (1 - X_{\text{NaAlSi}_2\text{O}_6}^{\text{cpX}})^2$$

and

$$a_{\text{NaAlSi}_2\text{O}_6}^{\text{cpX}} = (X_{\text{NaAlSi}_2\text{O}_6}^{\text{cpX}})^2 \gamma_{\text{NaAlSi}_2\text{O}_6}^{\text{cpX}}$$

This simple regular model does not adequately describe the activities at the  $\text{NaAlSi}_2\text{O}_6$ -rich end which appear to indicate larger degrees of non-ideality.

An asymmetric subregular solution with  $W_{\text{Gjd}}^{\text{cpX}} = 19.2 \text{ kJ mol}^{-1}$  and  $W_{\text{GDi}}^{\text{cpX}} = 29.3 \text{ kJ mol}^{-1}$  appears to agree with the data satisfactorily, and calculated activities on this basis are displayed in Fig. 4. The excess heat of mixing predicted by this model is given by

$$H_{\text{Jd-Di}}^{\text{ex}} = X_{\text{Jd}}^{\text{cpX}} X_{\text{Di}}^{\text{cpX}} (W_{\text{Gjd}}^{\text{cpX}} X_{\text{Di}}^{\text{cpX}} + W_{\text{GDi}}^{\text{cpX}} X_{\text{Jd}}^{\text{cpX}}). \quad (3)$$

The calorimetric values are slightly larger than those predicted by equation 3 (maximum  $7.5 \text{ kJ mol}^{-1}$  as opposed to a maximum of  $6.3 \text{ kJ mol}^{-1}$ ) but are asymmetric towards the jadeite end, in agreement with the calorimetry. This sense of asymmetry might be anticipated in view of the difference in cell size between jadeite (small) and diopside (large).

The possibility of some local ordering in this binary system will tend to bring down the magnitude of the positive excess enthalpies of mixing leading to smaller average interaction energies than determined by calorimetry at higher temperatures. The possibility of more intense ordering leading to a structural change to P2/n symmetry was investigated by a simple further experiment. Synthetic  $\text{Jd}_{50}\text{Di}_{50}$  pyroxene (C2/c symmetry) and a natural Tauern omphacite (Wood et al. 1980) previously heat treated at  $1,200^\circ \text{C}$  for one hour were both hydrothermally treated at  $600^\circ \text{C}$  and 15 kb for one week. The synthetic pyroxene showed only C2/c electron diffraction patterns although possibly some diffuse intensity was just visible associated with the  $h+k=\text{odd}$  ordering reflections which occur as sharp maxima in P2/n omphacite (M.A. Carpenter, pers. comm. 1982).

The natural pyroxene had sharp  $h+k=\text{odd}$  reflections indicating that it had ordered from C2/c to P2/n. Perhaps the most reasonable interpretation of these results is to suggest that the synthetic pyroxene was highly disordered at synthesis and only managed to order on a short-range (local) basis at  $600^\circ \text{C}$ , whereas the natural omphacite did not disorder to the same extent (although it did lose  $h+k$  odd reflections) in its heat treatment at  $1,200^\circ \text{C}$  and held some 'order memory', enabling it to reorder more easily in the second treatment at  $600^\circ \text{C}$ . The possibility of strong ordering effects in hydrothermal runs at  $600^\circ \text{C}$ , whether of long range or short range in character, has been demonstrated and must be considered in discussing the activity experiments of this work. If the pyroxene cannot order satisfactorily on a long range basis in the time available, it will attempt to order as best it can on a short range basis. The reduction in energy and enthalpy by this mechanism may be considerable, possibly falling not far short of that attainable by complete ordering. It is important to recognise that the order-disorder process is a cooperative or convergent mechanism which leads to the strongest effects in compositions closest to those which are capable of complete order – in this case  $\text{Jd}_{50}\text{Di}_{50}$ . These thermodynamic effects

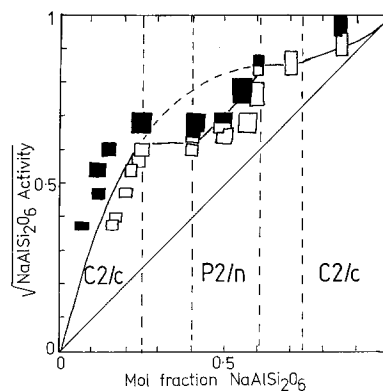


Fig. 5. The same diagram as Fig. 4, but the full curve corresponds to a situation involving a structural change to P2/n omphacite in the middle of the diagram. The horizontal portions of the  $a$ - $x$  curve represent coexisting compositions across two miscibility gaps separating P2/n omphacite from C2/c pyroxenes

of lowering the partial molar free energy of the jadeite component,  $-RT \ln a_{\text{NaAlSi}_2\text{O}_6}$ , in the middle range of the solid solution series is readily seen in Fig. 3. If long range order effects are strong, then immiscibility into ordered P2/n omphacites and disordered C2/c pyroxenes may ensue (Fig. 5).

The experimental data of Fig. 3 are not precise enough to distinguish the two possible interpretations of short range order with a continuous activity-composition curve (Fig. 4) and long range order with a discontinuous curve (Fig. 5). In nature, however, the time scales are clearly long enough in many blueschist and eclogite occurrences to initiate long range order and/or exsolution (Carpenter 1981).

The relative positions of the two activity curves in Fig. 4 may be used as a measure of the free energy of ordering at  $600^\circ \text{C}$ . For a rough approximation, the solid solution is assumed symmetrical so that at the  $\text{Jd}_{50}\text{Di}_{50}$  composition

$$\begin{aligned} \Delta G_{\text{ord}} &\approx RT \ln a_{\text{NaAlSi}_2\text{O}_6}^{\text{P2/n}} - RT \ln a_{\text{NaAlSi}_2\text{O}_6}^{\text{C2/c}} \\ &\approx -1,900 \pm 800 \text{ J mol}^{-1} \end{aligned}$$

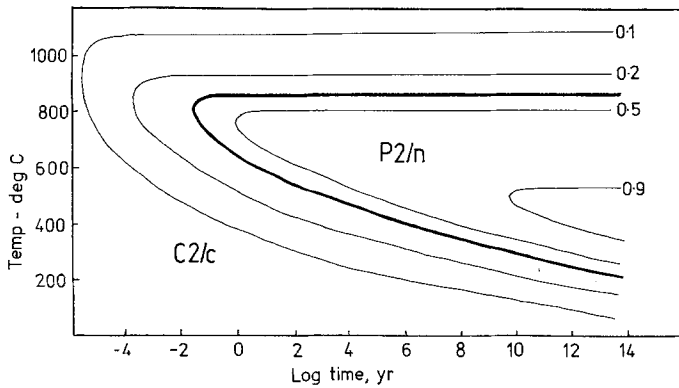
This value may be compared with that calculated using the disordering temperature for omphacite (Carpenter 1981)  $T_c = 1,138 \pm 20 \text{ K}$  and the calorimetric enthalpy of ordering (Wood et al. 1980)  $\Delta H_{\text{ord}} = -7,530 \pm 1,000 \text{ J mol}^{-1}$ .

$$\begin{aligned} \Delta G_{\text{ord}} &\approx \Delta H_{\text{ord}} [1 - T/T_c] \\ &= -1,750 \pm 1,000 \text{ J mol}^{-1}. \end{aligned}$$

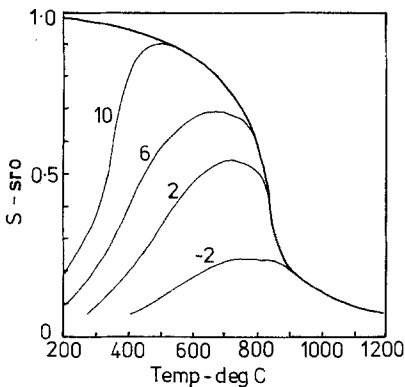
The favourable comparison in ordering free energy so derived reinforces the suggestion that the pyroxenes in these experiments have undergone a degree of short range ordering energetically similar to the effect of long range ordering.

#### Kinetics of Short-Range Ordering

If long-range order is kinetically impeded, the temperature-time characteristics of short-range ordering will have an important bearing on the problem of pyroxene behaviour at low temperatures. The kinetics of disordering omphacites have recently been studied by Carpenter (1981) who suggests a TTT plot for the possible ordering to a P2/n omphacite as in Fig. 6. The critical temperature,  $860^\circ \text{C}$  was determined by Carpenter's rate study at higher temperatures. On Fig. 6 have been drawn contours for a short range order



**Fig. 6.** Temperature-time-transformation (TTT) diagram for ordering of C2/c omphacite ( $Jd_{50}Di_{50}$ ) contoured schematically for degree of short range order ( $\sigma=0$ , disordered and  $\sigma=1$ , ordered). The bold curve is Carpenter's (1981) best estimate for the onset of long range order leading to the P2/n structural change



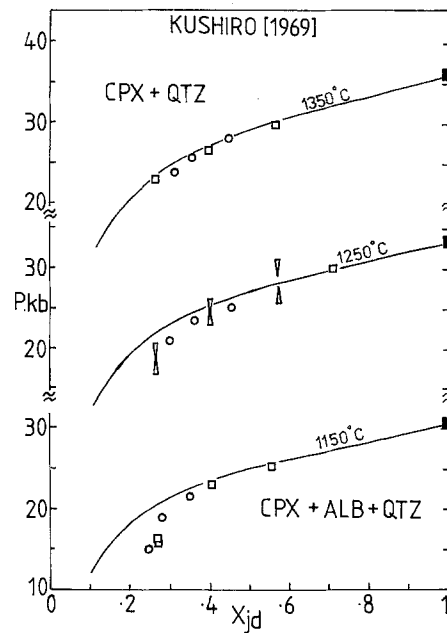
**Fig. 7.** Short range order parameter as a function of temperature. Bold curve is for the equilibrium state and light curves are for various times given as log  $t$  in years; these curves are schematic only

parameter ( $\sigma=0$  for complete disorder,  $\sigma=1$  for complete order) based on the probability of occurrence of unlike nearest neighbours on the M1 site in pyroxene. These curves have no experimental basis and are schematic for the purpose of illustration only. A considerable degree of short range order is indicated for both higher temperatures and lower run times than the field of P2/n ordered omphacites.

The maximum degree of order obtainable for given run times is shown schematically in Fig. 7, on which the equilibrium values at infinite run times are given by the bold line.

The hypothesis put forward here is that the run times of this study at  $600^\circ\text{C}$  are probably insufficient to promote long-range ordering to the P2/n structure but are adequate for ensuring a considerable degree of short-range order. It is important to note that the position of the P2/n field boundary with respect to temperature itself is highly uncertain, not having been experimentally verified, and may conceivably require shifting to shorter times.

The curves of Figs. 6 and 7 are drawn up for the omphacite composition only ( $Jd_{50}Di_{50}$ ) and are applicable to the case where the only free energy reduction possible is that of some ordering from a disordered to a partly ordered situation. In the experiments of this study large changes in composition commonly occurred, often from a jadeite-



**Fig. 8.** Pressure-composition sections for equilibration of pyroxene with albite and quartz at high temperatures. Open circles and squares – unreversed data of Kushiro (1969), wedges – reversed data of Kushiro (1969), filled squares – extrapolated data from Holland (1980). The curves are calculated from a simple regular solution model discussed in the text. The asymmetric model described in the text produces a result barely distinguishable from the one illustrated. Kushiro's data have been corrected by a 7% reduction in pressure to be consistent with recent work on the albite to jadeite + quartz reaction (Holland 1980)

poor starting material to a composition near the middle of the solid solution series. The additional driving force provided by the loss in mixing free energy as the pyroxenes changed composition, and the possibility of a solution-precipitation mechanism for this process, may have enabled a greater degree of order to have been achieved.

#### Geological Application

The practical application of mixing and ordering behaviour in sodic pyroxenes lies in the barometric significance of the jadeite substitution in blueschist or eclogite facies pyroxenes. The probable nucleation and growth of many omphacite pyroxenes initially in the disordered state (Carpenter 1978) suggests that it is instructive to consider the stability of disordered sodic pyroxenes in the presence of albite and quartz. Before examining the details, the simple regular solution approach is first checked against independent experimental work in this system performed at very much higher temperatures by Kushiro (1969) in Fig. 8. The predictions based on this study at  $600^\circ\text{C}$ , together with the simple model interaction parameter of  $W=24\text{ kJ mol}^{-1}$  are seen to be in quite excellent agreement with Kushiro's experiments except for rather diopsidic compositions. It is in this diopside-rich region that pyroxenes coexisting with quartz are suspected of non-stoichiometry (Wood 1978) and hence show enhanced entropic stability. At face value it would seem that  $W$  is independent of temperature, implying no excess entropy of mixing. The two-parameter solution model discussed earlier predicts virtually identical results in the range  $X_{jd}=0.1$  to 0.5.

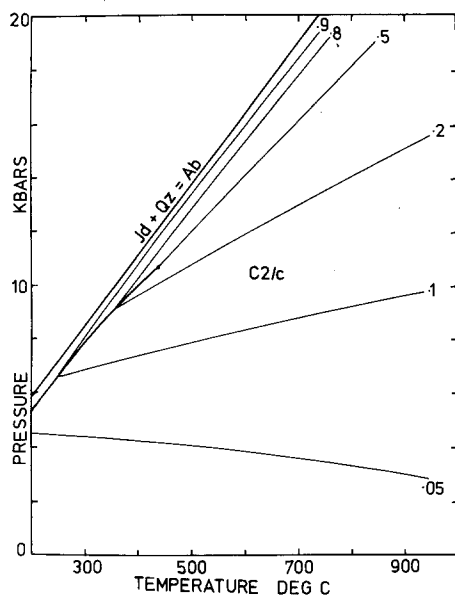
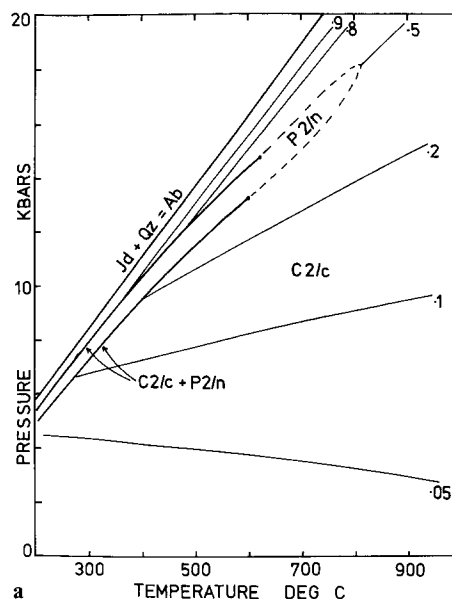


Fig. 9. Isopleths of  $\text{NaAlSi}_2\text{O}_6$  in disordered pyroxenes coexisting with albite and quartz, calculated using the simple model discussed in the text. A miscibility gap below  $450^\circ\text{C}$  is inferred

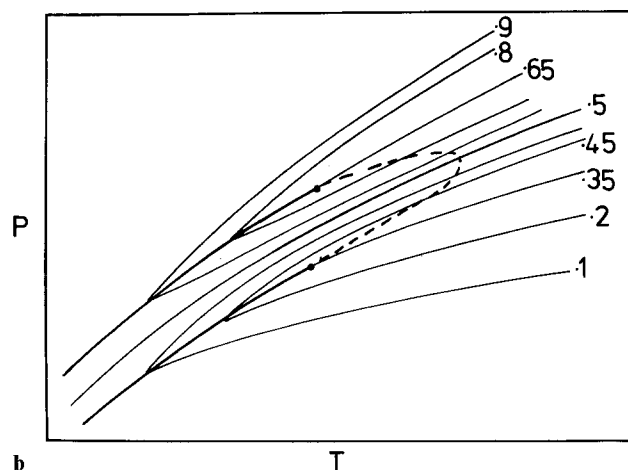
The consequences of the large interaction energy term are that the stability of sodic pyroxenes with albite + quartz is reduced somewhat relative to ideal disordered solutions and that an immiscibility region is predicted at low temperatures ( $<450^\circ\text{C}$ ). The isopleths for jadeite content in such assemblages predicted by the simple model are shown in Fig. 9, which also displays the coexisting miscibility-gap pyroxene compositions. The kinetics of the unmixing process are such that exsolution by this mechanism into jadeite and diopside solid solutions is unlikely. Unmixing has been shown to occur in blueschist and eclogite facies pyroxenes by Carpenter (1979); however it invariably involves the twin process of ordering and exsolution into coexisting P2/n and C2/c partners. The effects on the pyroxene-albite-quartz relations of ordering and exsolution are demonstrated in Fig. 10a which is based on the jadeite-diopside phase relations of Carpenter. In contrast with Fig. 9, it can be seen that there are now two miscibility gaps separating a field of ordered pyroxene which extends to higher temperatures than the critical temperatures of the miscibility gaps. Figure 10b displays in a schematic fashion the details which might be expected in the ordered field.

The geological significance of these features lies in the decompression portion of the  $P-T$  time path undergone by blueschists and eclogites which almost invariably passes through this ordering region on the  $P-T$  plane. If quartz, a silica-bearing fluid, or even Si diffusing in the grain boundary networks is present, the pyroxenes will show tendencies to react and produce feldspar. The common occurrence of symplectite alteration of omphacite to diopside + albite could be interpreted in such terms. It can also be seen that pyroxenes other than those very poor in  $\text{NaAlSi}_2\text{O}_6$  component that coexist with quartz and albite are restricted to pressures that are close to the jadeite + quartz breakdown curve.

The message for barometry is clear. The use of the ideal-solution model with a disordered entropy of mixing will grossly underestimate the pressures of pyroxene equilibra-



a



b

Fig. 10a. The same as Fig. 9, but with ordering to P2/n allowed for omphacites near to  $\text{Jd}_{50}\text{Di}_{50}$ . Note the two miscibility gaps below  $T \approx 600^\circ\text{C}$  and a disordering critical temperature at  $T > 800^\circ\text{C}$ ; b Schematic display of isopleths from a drawn to show qualitative relations in the ordered region. Coexisting compositions on miscibility gaps may be read from the intersecting isopleths

tion. For pyroxenes which lie outside the cation proportion limits for P2/n omphacite ordering, the disordered solution model with large interaction energy may be a realistic one. For pyroxenes which are thought to have grown ordered, barometric estimates may be approximated by setting the activity of the jadeite component equal to its mole fraction.

It is a curious feature that even in the disordered pyroxenes, the overall combined effect of using a two-site entropy of mixing with a large positive interaction energy is to simulate the simple ideal situation  $a=x$ .

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