

# Solid solution and cation ordering limits in high-temperature sodic pyroxenes from the Nybø eclogite pod, Norway

M. A. CARPENTER

Dept. of Earth Sciences, University of Cambridge, Downing St., Cambridge CB2 3EQ

AND

D. C. SMITH\*

Grant Institute of Geology, Edinburgh University, West Mains Road, Edinburgh EH9 3JW, Scotland

**ABSTRACT.** A range of sodic pyroxenes ( $\text{Jd}_{78}\text{Ac}_2\text{Aug}_{20}$ – $\text{Jd}_{24}\text{Ac}_9\text{Aug}_{67}$ ) from the Nybø eclogite pod, Norway, have been examined by electron-microprobe analysis and by transmission electron microscopy. Five different microprobes give generally compatible results and new analyses completely fill the natural composition gap in jadeite-rich omphacites with ~ 3–12% acmite, confirming complete miscibility at high temperatures ( $\geq 700^\circ\text{C}$ ). Crystals with omphacite compositions around jadeite: augite = 1:1 contain antiphase domains resulting from the  $C2/c \rightarrow P2/n$  cation ordering transformation. Exsolution microstructures were not observed, from which it is concluded that there are no two-phase regions separating the  $P2/n$  and  $C2/c$  stability fields at high temperatures (~ 620–750 °C) and that cooling was too rapid for exsolution to occur in the jadeite/omphacite and omphacite/augite low-temperature solvi. Crystals whose compositions depart significantly from  $\text{Jd}:\text{Aug} = 1:1$  have weak, diffuse  $h+k = \text{odd}$  reflections in selected area electron diffraction patterns which are interpreted as being due to short-range ordering outside the true  $P2/n$  stability field. The short-range ordering and lack of exsolution are consistent with a previous suggestion that the order/disorder transformation in omphacite is second (or higher) order in character. The average antiphase domain sizes (up to ~ 3500 Å) are larger than any previously recorded in omphacites and are consistent with available petrological evidence for a long period of annealing at high temperatures before tectonic uplift and cooling.

THE subsolidus phase relations of pyroxenes in the system jadeite–acmite–augite ( $\text{Jd}-\text{Ac}-\text{Aug}$ ) have not been determined experimentally because of the prohibitively slow kinetics of reactions requiring

cation diffusion at the low temperatures ( $< 700^\circ\text{C}$ ) of principal interest. What information there is concerning this system has come mainly from observations of naturally occurring pyroxene compositions and assemblages. There are numerous, and often conflicting, reports of miscibility gaps based on the absence of crystals in particular composition ranges. Successive compilations of pyroxene analyses, however (Dobretsov, 1962; Essene and Fyfe, 1967; Coleman and Clark, 1968; Onuki and Ernst, 1969; Dobretsov *et al.*, 1971; Smith *et al.*, 1980), show progressively diminishing composition gaps and natural pyroxenes have now been found in almost the entire  $\text{Jd}-\text{Ac}-\text{Aug}$  range. A true miscibility gap between  $\text{Jd}$  and omphacite ( $\text{Om}$ ) exists at low temperatures, as shown by the observation of two-pyroxene assemblages in several specimens from the USSR (Dobretsov *et al.*, 1971) and by the presence of exsolution, on an electron optical scale, in crystals with intermediate compositions (Carpenter, 1979).

Recent transmission electron microscope (TEM) studies have provided a great deal of additional evidence for the low-temperature phase relations of this system in the form of antiphase domains (APD's) due to the  $C$ -face centred to primitive lattice transformation associated with cation ordering in omphacites (Champness, 1973; Phakey and Ghose, 1973; Carpenter, 1978*a*) and a variety of exsolution structures involving ordered and disordered components (Carpenter, 1978*a*, 1979, 1980*a*). A comparison of the observed microstructures with theoretical ordering and exsolution mechanisms has been used to predict equilibrium phase diagrams for  $\text{Jd}-\text{Aug}$  and  $\text{Jd}-\text{Ac}-\text{Aug}$  (Carpenter, 1980*a*) and these show close analogies

\* New address: Laboratoire de Minéralogie, Muséum National d'Histoire Naturelle, 61 Rue de Buffon, 75005 Paris, France.

with the carbonate systems  $\text{CaCO}_3\text{-MgCO}_3$  and  $\text{CaCO}_3\text{-MnCO}_3\text{-MgCO}_3$  (Goldsmith and Graf, 1960; Goldsmith and Heard, 1961; Navrotsky and Loucks, 1977). The postulated subsolidus phase relations are compatible with petrological data from blueschist rocks to the extent that: (a) the Jd-Om miscibility gap narrows with increasing solution of Ac (Dobretsov *et al.*, 1971; Carpenter, 1979); (b) there also appears to be a miscibility gap between Om and Aug (Brown, 1973; Bondi *et al.*, 1978; Brown *et al.*, 1978; Carpenter, 1980b); (c) no two-phase field has been detected between ordered Om and C2/c Ac-rich pyroxenes; this boundary is interpretable as a line marking a second (or higher) order ordering transformation; (d) the composition range of ordered Om initially widens with increasing solution of acmite before diminishing (Carpenter, 1979). The most stable ordered structure probably has  $P2/n$  symmetry (Matsumoto *et al.*, 1975; Curtis *et al.*, 1975; Rossi *et al.*, 1977, 1978, 1980) rather than  $P2$  as was suggested earlier by Clark and Papike (1968) and Clark *et al.* (1969), though during topotactic replacement reactions  $P2/c$  and  $P2$  may occur metastably (Carpenter and Okay, 1978).

Compositional data for sodic pyroxenes which crystallized at temperatures higher than those of blueschist-facies metamorphism are available in the literature, but in general the crystals have not been characterized with regard to cation ordering and/or submicroscopic exsolution. It is the purpose of the present paper to redress this deficiency and present ordering/composition relations for a suite of high-temperature sodic pyroxenes from the Nybø eclogite pod, Norway, obtained using electron microprobe (EMP) and TEM analysis. Several clinopyroxene crystals from the Nybø eclogite have already been investigated by X-ray structural refinement methods. Smith *et al.* (1980) found that a crystal whose composition falls within the Jd-Om low-temperature immiscibility range has space group  $C2/c$  and is homogeneous within the experimental limits of resolution of X-ray diffraction and EMP analysis. Omphacites with Jd:Aug  $\approx 1:1$  have  $P2/n$  symmetry and ordered cations (Rossi *et al.*, 1977, 1978, 1980). Preliminary EMP analyses (Lappin and Smith, 1978) suggested that the pyroxenes have a remarkably wide range of compositions between impure Jd and Aug. The present study indicates that their microstructures and transformation behaviour are compatible with the ideal phase relations postulated by Carpenter (1980a) and Smith *et al.* (1980), and with the metamorphic history of the Nybø eclogite proposed by Lappin and Smith (1978).

*Specimen description.* The Nybø eclogite pod (Smith *et al.*, 1980) is one of a series of ortho-

pyroxene-eclogites (Lappin and Smith, 1978) and also of a series of carbonate-eclogites (Lappin and Smith, in prep.) which occur as tectonic pods enclosed within amphibolite-facies gneisses of the Basal Gneiss Region of south-west Norway. The origin of eclogites within gneiss in this region has often been attributed to *in-situ* metamorphism of basaltic rocks during a prograde subduction-related geological event with a peak temperature of  $\sim 800^\circ\text{C}$  (see review by Bryhni *et al.*, 1977). None of the *in-situ* advocates has, however, examined the Nybø pod. In the case of this eclogite pod, and many others in the nearby Selje and Vartdalsfjorden districts, the *in-situ* origin has been rejected in favour of an origin by tectonic introduction of foreign slices equilibrated initially at mantle depths (Lappin, 1966, 1977; Smith, 1978, 1980a, b, and in prep.; Lappin and Smith, 1978, and in prep.).

In hand specimen the Nybø eclogites show marked compositional layering with garnet-rich, -poor, or -free bands a few millimetres wide. The pyroxenes described in this paper come from clinopyroxenite (C413), simple garnet + clinopyroxene eclogite (C410), and orthopyroxene-eclogite (C414). They are extremely clear and their pale-green colour deepens with decreasing Jd content. Incipient amphibolitization, manifested by fine-grained to cryptocrystalline symplectites of plagioclase with secondary clinopyroxene and/or clinoamphibole penetrates some grains and grain boundaries. Further field and petrographic data are given by Lappin and Smith (1978) and Smith *et al.* (1980).

Two thin sections were made from opposite faces across a sawcut through each of several small hand specimens. One section was prepared for TEM and the other for EMP analysis. Of critical importance is the relationship between chemical composition and microstructure, so great care was taken to match up crystals from one section with their immediate neighbours in the second. In several cases the TEM mounts that were examined in the electron microscope were themselves analysed, either before or after the TEM observations were made.

*Electron-microprobe data.* Nybø clinopyroxenes have now been analysed with five different probes (by force of circumstance rather than choice), using an energy-dispersive system (EDS), a wavelength-dispersive system (WDS), or both. Technical descriptions for published data from the Aberdeen WDS and Edinburgh EDS probes are provided by Lappin and Smith (1978) and Smith *et al.* (1980), respectively. For the new data, the Edinburgh WDS probe technique is similar to that at Aberdeen, whilst the Cambridge EDS probe has a Harwell Si(Li) detector and pulse processor

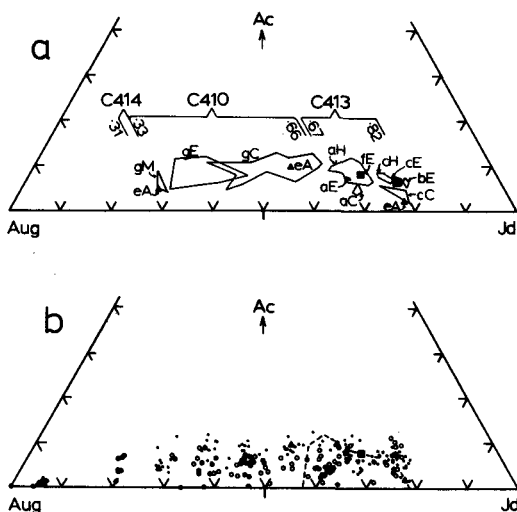


FIG. 1. (a) Comparison of primary clinopyroxene analyses (specimens C410, C413, C414) obtained with different probes. Small letters identify fragments of the same original hand specimen (e.g. C413a, C413c). Large letters indicate which probe was used: A = Aberdeen (WDS), C = Cambridge (EDS), E = Edinburgh (EDS for C410g and C413f, WDS for C413a, b, c), H = Harvard (WDS), M = M.I.T. (WDS). Triangles: mean analyses from Lappin and Smith (1978); encircled triangle: mean C413eA with 0.70 wt% Na<sub>2</sub>O added arbitrarily to correct for suspected error in Na determination; square: mean analysis C413fE from Smith *et al.* (1980). Numbers indicate X<sub>Na</sub> range for each specimen. (b) Compilation of all available analyses of clinopyroxenes from the Nybø eclogite pod. Filled circles: 100 individual analyses from (a). Square and triangles from (a) with additional mean analyses from specimen C411 (Lappin and Smith, 1978, and in prep.). Open circles: 97 individual analyses from a number of new specimens (Edinburgh, EDS; Rossi *et al.*, 1980 and in prep.; Smith, in prep.). Dashed line: previous natural composition gap from Smith *et al.* (1980). Fe<sup>2+</sup>, Fe<sup>3+</sup> calculated from Fe<sup>3+</sup> = Na-Al, Fe<sup>2+</sup> = ΣFe - Fe<sup>3+</sup>; Jd, Ac, Aug proportions recalculated to 100% from Jd = Al, Ac = Fe<sup>3+</sup>, Aug = Ca (Carpenter, 1979).

$$X_{\text{Na}} = \frac{\text{Na}}{\text{Na} + \text{Ca}}, X_{\text{Fe}^{3+}} = \frac{\text{Fe}^{3+}}{\text{Fe}^{3+} + \text{Al}} \text{ Smith } et al. (1980).$$

(Statham, 1976) follows the correction procedures of Sweatman and Long (1969), and is similar to the Edinburgh EDS probe. The Harvard WDS and Massachusetts Institute of Technology WDS probes use the correction procedures of Bence and Albee (1968). A selection of analyses is given in Table I and the complete data set of over 100 new analyses is plotted in fig. 1.\*

The calculation method for obtaining Fe<sup>2+</sup>/

\* A complete listing of the analyses plotted in fig. 1 may be obtained from one of the authors (D. C. S.).

Fe<sup>3+</sup> ratios (fig. 1 legend) yields oxide totals in the range 98.3–101.2 wt%. Calculating cation proportions to Si = 2.00 (Carpenter, 1979) yields cation totals in the range 3.95–4.08, and oxygen totals in the range 5.95–6.08 (except for analysis C413eA, see below). The majority of the totals are within ± ½% (relative) of perfect stoichiometry. For estimation of the Jd, Ac, Aug molecular proportions (fig. 1 legend), Ca-tschermak, enstatite, and ferrosilite molecules were ignored since they generally form less than 3% of the total.

A comparison of the composition ranges obtained using the different probes (fig. 1a) shows that they are in reasonable agreement. The principal variation is in the Ac content, as is shown most clearly for the subfragments a–f of C413. Any errors in Na and Al determinations combine in the error of Fe<sup>3+</sup> because of the method used for calculating Fe<sup>2+</sup>/Fe<sup>3+</sup> ratios. The Cambridge EDS gives relatively high Al and low Na values for C413, while the Aberdeen WDS Na content is apparently slightly low (arbitrarily adding 0.70 wt% Na<sub>2</sub>O to C413eA makes Fe<sup>3+</sup> similar to the other analyses and brings the cation and oxygen totals very close to perfect stoichiometry). These irregularities are perhaps due to electron-beam damage effects (Autefage, 1980) and it is probable that the real Ac content of the Nybø pyroxenes varies much less than is shown in fig. 1.

In both C410 and C413 pyroxenes there is a continuous variation in Jd:Aug ratio normal to the garnet/pyroxene layering. The total ranges are Jd<sub>27</sub>Ac<sub>11</sub>Aug<sub>62</sub> to Jd<sub>56</sub>Ac<sub>11</sub>Aug<sub>33</sub> for C410 and Jd<sub>58</sub>Ac<sub>9</sub>Aug<sub>33</sub> to Jd<sub>78</sub>Ac<sub>2</sub>Aug<sub>20</sub> for C413, each in a distance of ~ 3–5 cm. Individual crystals are chemically homogeneous within the limits of precision except in a zone of C413 approximately 2–3 mm wide where the over-all composition gradient seems to be sufficiently steep to be detectable within single crystals. Pyroxenes with Jd contents in excess of 50% occur in regions of the eclogite which are free of garnet. Garnet is the only additional phase where the Jd content of the pyroxene is 30–50% and orthopyroxene coexists with clinopyroxenes whose Jd contents are less than 30%. The compositions of crystals used for TEM examination are plotted in fig. 2.

**TEM observations.** TEM observations were made on ion-beam thinned specimens using an AEI EM6G or Philips 300 electron microscope operating at 100 kV. The microstructures of these pyroxenes are remarkably simple, involving only the presence or absence of antiphase domains (apart from deformation textures which were ignored). Three principal observations were made:

1. No signs of exsolution were found in any of the 20 TEM mounts examined.

TABLE I. A representative selection of clinopyroxene analyses

	C414gM	C410gC	C410gC	C410gC	C410gC	C413aC	C413hH	C413cH	C413cC
SiO <sub>2</sub>	55.64	55.21	55.62	56.21	56.56	57.46	57.58	57.07	57.55
TiO <sub>2</sub>	n.a.	n.d.	n.d.	0.20	0.23	n.d.	n.a.	n.a.	n.d.
Al <sub>2</sub> O <sub>3</sub>	6.06	7.59	9.60	12.01	13.29	15.36	15.70	17.23	17.59
Fe <sub>2</sub> O <sub>3</sub>	1.89	3.67	3.38	3.68	3.94	1.16	2.28	2.59	1.76
FeO	2.95	2.23	2.15	1.49	1.42	2.68	1.89	1.66	2.30
MgO	12.37	10.22	8.79	6.78	6.27	5.39	5.14	3.63	3.67
CaO	16.83	14.11	12.66	10.50	8.75	7.59	7.45	5.41	5.19
Na <sub>2</sub> O	4.42	6.04	7.15	8.73	9.61	9.79	10.43	11.48	11.38
Total	100.16	99.07	99.35	99.60	100.07	99.43	100.47	99.07	99.44
<i>Cations per 2 Si</i>									
Si <sup>4+</sup>	2.00	2.00	2.00	2.00	2.00	2.00	2.00	2.00	2.00
Ti <sup>4+</sup>	—	—	—	0.01	0.01	—	—	—	—
Al <sup>3+</sup>	0.26	0.32	0.41	0.50	0.55	0.63	0.64	0.71	0.72
Fe <sup>3+</sup>	0.05	0.10	0.09	0.10	0.11	0.03	0.06	0.07	0.05
Fe <sup>2+</sup>	0.09	0.07	0.07	0.04	0.04	0.08	0.06	0.05	0.07
Mg <sup>2+</sup>	0.66	0.55	0.47	0.36	0.33	0.28	0.27	0.19	0.19
Ca <sup>2+</sup>	0.65	0.55	0.49	0.40	0.33	0.28	0.28	0.20	0.19
Na <sup>+</sup>	0.31	0.42	0.50	0.60	0.66	0.66	0.70	0.78	0.77
ΣM	4.02	4.01	4.03	4.01	4.03	3.96	4.01	4.00	3.99
Jd	27	33	41	50	56	67	66	72	75
Ac	5	10	9	10	11	3	6	7	5
Aug	68	57	50	40	33	30	28	21	20

n.d. = not detected, n.a. = not analysed. Fe<sup>2+</sup>/Fe<sup>3+</sup>, Jd, Ac, Aug proportions calculated as in fig. 1.

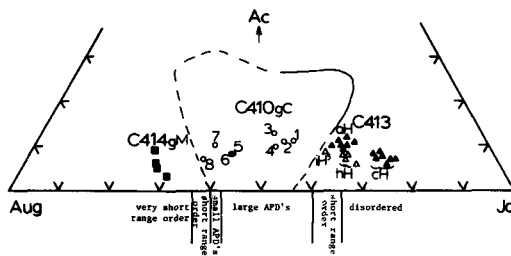


FIG. 2. Individual analyses of primary pyroxenes examined by TEM. Squares: C414; triangles: C413; circles: C410. Open symbols represent analyses of TEM mounts; crystals 1–8 of C410 were remounted for probe analysis after and crystals C413i, h before TEM study. Solid symbols represent analyses of crystals near to those examined by TEM. C413c, C413h have space group *C2/c*. C414g, C413a, C413i, and C410g crystal 8 have diffuse  $h+k = \text{odd}$  reflections and space group *P2/n*. Crystals 1–6 of C410g have 1000–3500 Å APD's, crystal 7 has 100–200 Å APD's, *P2/n*. Continuous and broken lines represent composition limits of cation ordering under blueschist facies conditions (from Carpenter, 1979). Approximate composition ranges of interpreted structural states are indicated schematically; the actual variation with composition is probably continuous.

2. Systematic absences in selected area diffraction patterns were compatible with the space group *P2/n* for C410g, C413a, C413i, and C414g, and *C2/c* for C413c and C413h. Crystals from C414g and C413a, crystal C413i (Jd<sub>58</sub>Ac<sub>9</sub>Aug<sub>33</sub>) and crystal 8 of C410g (Jd<sub>35</sub>Ac<sub>7</sub>Aug<sub>58</sub>) had extremely weak and diffuse  $h+k = \text{odd}$  reflections. In C414g these diffuse reflections were only just detectable in grossly overexposed diffraction patterns. The diffuse reflections were far too weak to be used for dark-field imaging.

3. In the omphacite crystals 1–6 of C410g, APD's were imaged in dark field using  $h+k = \text{odd}$  reflections. Individual domains were invariably equiaxed with smoothly curving boundaries. The average domain diameter was measured from dark-field micrographs of different areas of each single crystal examined; each area had an average domain size in the range 1000–3500 Å. Differences in average domain size within individual crystals were not associated with compositional variations since the crystals were shown to be chemically homogeneous on the microprobe, nor was there any systematic correlation of APD size with Jd:Aug

ratio. Crystal 7 of C410g ( $\text{Jd}_{36}\text{Ac}_{10}\text{Aug}_{54}$ ), however, had APD's on a scale of only 100–200 Å.

The relationship between composition and microstructure is illustrated in fig. 2.

*Discussion.* Estimation of the equilibration pressures and temperatures of certain eclogite pods in the Basal Gneiss Region of western Norway is attempted by Lappin and Smith (1978, in prep.). Two early equilibration periods (regime A,  $P \sim 30\text{--}40$  kb,  $T \sim 1200\text{--}1370$  °C, regime B,  $P \sim 30\text{--}45$  kb,  $T \sim 700\text{--}850$  °C) were followed by the predominant recrystallization event (regime C) at  $P \sim 15\text{--}28$  kb,  $T \sim 700\text{--}850$  °C which formed hydrous-eclogite-facies assemblages (Smith, 1971, 1976, 1980a). Subsequent partial amphibolitization, estimated at  $P \sim 5\text{--}13$  kb,  $T \sim 650\text{--}720$  °C (regime D) is thought to have occurred during and after tectonic emplacement of the eclogite into the country-rock gneiss.

The preserved clinopyroxene crystals probably grew within the temperature range 700–850 °C. Their wide composition range, from augite to impure Jd ( $\text{Jd}_{78}\text{Ac}_2\text{Aug}_{20}$ ), indicates that complete solid solution (with  $\sim 3\text{--}12\%$  Ac) is possible at such temperatures. The compositional gap recorded by Smith *et al.* (1980) represents incomplete sampling rather than limited miscibility, as, almost certainly, do the remaining gaps apparent in fig. 1b.

Evidence for the compositional extent of ordered omphacites and for their cation-ordering behaviour is provided by the additional ( $h+k = \text{odd}$ ) diffraction maxima in selected area diffraction patterns and the nature of the APD's which can be imaged with them. Fleet *et al.* (1978) obtained a possible value for the equilibrium-ordering temperature ( $T_{\text{ord}}$ ) of an omphacite with 3% Ac of  $725 \pm 20$  °C by following the disordering reaction experimentally.  $T_{\text{ord}}$  is likely to be almost independent of pressure because the volume change associated with ordering is small (Carpenter, unpublished data). As noted by Smith *et al.* (1980) the temperature uncertainties are clearly too great to distinguish between crystallization above and below  $T_{\text{ord}}$ . The presence of APD's, however, strongly suggests that the omphacites experienced a C-face centred to primitive lattice transformation. If, as proposed by Fleet *et al.* (1978), the APD's were features incorporated during crystal growth it is unlikely that they would adopt the equiaxed, smooth boundary configuration which they display in many omphacites and which is so typically the result of phase transformations in other materials. Thus, the ordered crystals probably grew with  $C2/c$  symmetry. There is a uniformity in the range of average APD sizes in crystals 1–6 of C410g suggesting that ordering and APD growth started at about the same time and temperature over this composition range, regard-

less of any variations in  $T_{\text{ord}}$ . This is at least consistent with metastable crystallization below  $T_{\text{ord}}$  for these crystals, followed at an early stage by cation ordering and APD formation.

The composition limit for primitive ordered omphacite in blueschist pyroxenes (Carpenter, 1979) falls approximately between the Nybö crystals with APD's and those with weak and diffuse  $h+k = \text{odd}$  reflections. Since diffuseness of superlattice reflections is normally due to diffraction from ordered crystals in which the cation ordering is only on a limited scale (i.e.  $\leq 50$  Å), this boundary appears to mark a change over from long-range order to short-range order. Alternative explanations of the diffuse  $h+k = \text{odd}$  reflections, such as small APD's or small ordered domains in a disordered matrix, do not differ realistically from short-range order when the domains are only a few unit cells, or less, in size. There actually appears to be a gradation from well-ordered omphacite with large APD's (C410g crystals 1–6) through crystals with small APD's (C410g crystal 7), to the crystals with short-range order (C410g crystal 8, C413a, C413i, C414g), and finally to  $C2/c$  pyroxenes (C413c, C413h). This is compatible with the suggestion that the ordering transformation ( $C2/c \rightarrow P2/n$ ) is second, or higher, order in character (Carpenter, 1980a) and should be represented as a single line on the equilibrium phase diagram at high temperatures. No sign of the narrow two-phase field separating  $C2/c$  from  $P2/n$  pyroxenes, as shown in the tentative phase diagrams of Champness (1973) and Yokoyama *et al.* (1976), was found.

Short-range ordering correlations (giving rise to diffuse diffraction maxima) are commonly observed in materials held just outside their stability field of long-range order (e.g. see Chen and Cohen, 1979). They may be regarded as an anticipation, with changing temperature or composition, of the fully ordered structure. Aldridge *et al.* (1978) concluded from Mössbauer data that significant local correlations of cation site occupancies remain in experimentally disordered ( $C2/c$ ) omphacites. There therefore appears to be a tendency for Mg to prefer Al neighbours and Na to prefer Ca, even when the average symmetry is  $C2/c$ , and this could be effective even in crystals whose compositions deviate substantially from  $\text{Jd}:\text{Aug} = 1:1$ , outside the true  $P2/n$  stability field. The effect is illustrated by substituting composition for temperature in a typical plot of degree of order against temperature for a second-order transformation (fig. 3).

Equilibration of the pyroxenes at  $\sim 700$  °C could have led to the observed microstructures and diffraction patterns, but it is necessary also to

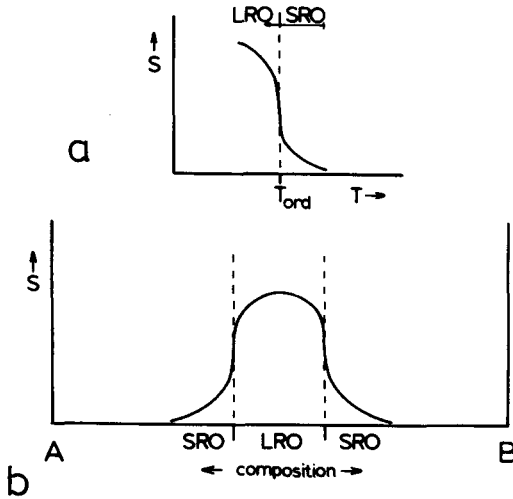


FIG. 3. Variation in equilibrium degree of order ( $s$ ) with temperature (a) and composition (b) for an ordered structure (AB) intermediate between disordered end members (A and B), in which the ordering transformation is second order in character. (a) Above the equilibrium ordering temperature ( $T_{ord}$ ) short range ordering (SRO) can give diffuse intensity at superlattice positions in diffraction patterns. Diagram is for composition = AB. Long-range order (LRO) occurs below  $T_{ord}$ . (b) Outside the composition field of LRO for AB, SRO may be detected. Dashed lines mark the stability limits of LRO. Diagram drawn for a  $T < T_{ord}$ .

consider possible changes in ordering during cooling. The cooling rate of the Nybø eclogite must have been too rapid for diffusion on a scale sufficient to give phase separation in the low-temperature Jd–Om miscibility gap. Cation ordering, however, could have continued down to low temperatures since it requires only exchange of cations between adjacent sites even though it may be metastable with respect to exsolution. Some of the crystals outside the  $P2/n$  field at high temperatures would have moved into it during cooling and reached a degree of order dependent on the kinetics of the ordering reaction. The further the composition away from Jd:Aug = 1:1, the lower the temperature at which ordering starts and hence the slower the rate of ordering and the smaller the degree of order achieved. Any early gradation from  $P2/n$  to  $C2/c$  cation distributions would be enhanced in the final, observed crystals.

An equilibrium phase diagram which may be used to adequately describe the transformation behaviour of the Nybø pyroxenes is shown in fig. 4. It has been modified only minimally from the diagram proposed by Carpenter (1980a) to explain ordering and exsolution reactions in blueschist

pyroxenes and is compatible with the widening of the  $P2/n$  field with increasing temperature discussed by Smith *et al.* (1980). At high temperatures there is a complete solid solution between Jd and Aug with  $C2/c$  symmetry. At lower temperatures (between  $\sim 600$  and  $\sim 700$  °C) the  $P2/n$  field appears but without any two-phase bounding regions. The broad  $C2/c + P2/n$  solvi exist only below  $\sim 600$  °C.

While the Nybø pyroxenes help to further constrain these stability relations, they clearly illustrate the problems associated with trying to map out a precise equilibrium phase diagram using observations on natural samples. Firstly, it must be pointed out that evidence for the nature of order/disorder transformations in most minerals is necessarily circumstantial since, for kinetic reasons, the definitive experiments or thermochemical measurements cannot at present be performed. Evidence for a second- or higher-order transformation is essentially negative, i.e. first-order properties are not observed. Proof of a first-order process would be provided by one or more of the following criteria:

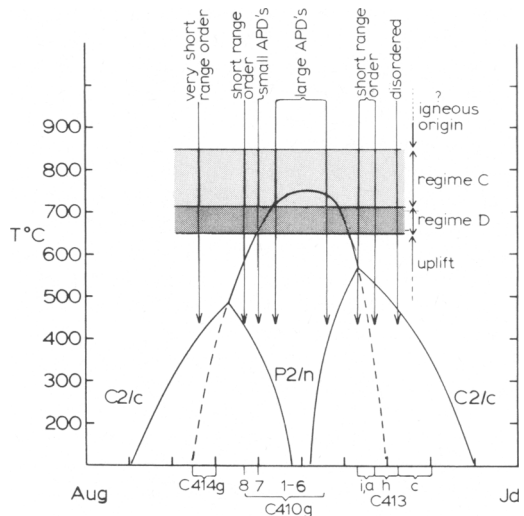


FIG. 4. Schematic pseudobinary phase diagram for jadeite-augite (with 3–12% acmite). The topology is identical to that shown by Carpenter (1980a); the temperatures of the phase boundaries must be considered as only approximate estimates. The  $C2/c \rightarrow P2/n$  transformation is shown as second (or higher) order with no miscibility gaps at high temperatures. Broken lines represent metastable extensions of the long-range ordering limits into the low-temperature two-phase fields. The light-stippled region represents the dominant eclogite facies recrystallization conditions (regime C) of the Nybø pyroxenes, while the dark-stippled region represents the amphibolitization conditions (regime D). Arrows indicate cooling paths for a selection of compositions.

(a) violation of the group-theoretical requirements for a second-order transformation (Landau and Lifshitz, 1958; de Fontaine, 1975); (b) observation of the equilibrium coexistence of ordered and disordered phases with the same composition; (c) the presence of a finite miscibility gap between the ordered and disordered phase fields attributable solely to the order/disorder reaction; (d) the observation of microstructures which can unambiguously be interpreted as arising from homogeneous nucleation.\* That none of these criteria apply to the high-temperature pyroxenes described here is necessary but not sufficient to 'prove' a second- or higher-order character for the cation ordering. Secondly, if there is short-range ordering above the equilibrium order/disorder temperature of a mineral, the composition range of its ordered structure may be hard to define. A different result will be obtained according to the sensitivity of the technique used to detect the appearance of superlattice reflections. Electron diffraction may in general allow the detection of weaker reflections than X-ray diffraction and will therefore indicate wider limits of cation ordering. The true boundary should actually be taken as the composition or temperature at which long-range ordering (i.e. in this case resolvable APD's) first appears. Thirdly, in natural rocks equilibration occurs over a range of temperatures and not at a precise, or accurately identifiable, temperature. For the Nybø pyroxenes there is some uncertainty in relating the cation ordering to temperature as well as to composition. The same applies to blueschist omphacites for which it has been possible only to assess the sequences of solid-state transformations and not their precise dependence on temperature or composition (Carpenter, 1978a). Finally, there is evidence to suggest that metastable processes can control the structural evolution of sodic pyroxenes in metamorphic rocks (Carpenter, 1978a; Carpenter and Okay, 1978). Metastable crystallization of pyroxenes within the miscibility gaps cannot at present be ruled out, especially since the degree of cation ordering in growing omphacite crystals can influence their composition and may vary with crystal growth conditions (Carpenter, 1980b). Even in those samples which have been carefully characterized by TEM, there are problems in discriminating between equilibrium and metastable behaviour. Pressure variations may further blur the phase boundaries (Smith *et al.*, 1980) for although they

\* Heterogeneous nucleation of an ordered structure at defects in a disordered host (as described in omphacite by Champness, 1973) may be possible in a second-order reaction, particularly when the ordering proceeds under metastable conditions at a temperature well below the equilibrium ordering temperature.

probably do not affect the equilibrium ordering temperatures, they may modify the extent of equilibrium solid solution.

The size of APD's in ordered omphacites appears to reflect their thermal history (Carpenter, 1978b); during a long- and/or high-temperature-history domain coarsening should lead to a large final average size, while APD's in low-temperature, short-history omphacites would be relatively small. The Nybø omphacites have larger APD's (up to  $\sim 3500$  Å) than any previously reported (Champness, 1973, describes 2000 Å APD's in specimens from a California eclogite while the blueschist omphacites from Syros have domains on a scale of  $\sim 200$ –500 Å, Carpenter, 1978a). The absence of exsolution shows that the total time spent from  $\sim 500$  °C to the temperature at which diffusion effectively stops must have been less than experienced by the Syros pyroxenes which developed exsolution lamellae on a scale of  $\leq 500$  Å. A long period of annealing at high temperatures followed by relatively rapid cooling would be an appropriate thermal history to yield the observed microstructures. This is compatible with the history of the eclogite inferred from petrological evidence: slow 'mantle-carriage' and recrystallization (Lappin and Smith, 1978) while temperatures remained at  $\sim 700$ –850 °C, followed by 'deep-level obduction' (Lappin and Smith, 1978) into amphibolite gneisses at 650–720 °C allowing amphibolitization reactions to proceed, predominantly at the edges of the eclogite pods, and ending with uplift during two-continent collision (Lappin, 1977; Lappin and Smith, 1978; Smith, 1978, 1980b). The enveloping amphibolite-facies gneisses show no significant evidence for low-temperature ( $< 500$  °C) retrograde mineral reactions.

In conclusion, although the Nybø pyroxenes cannot be used to draw out a precise phase diagram, several generalizations can be made. The observed compositions and microstructures are consistent with the  $P2/n$  omphacite field, above  $\sim 600$  °C, being bounded by a single line to represent a second- or higher-order transformation, in agreement with the ideal behaviour postulated by Carpenter (1980a). Long-range ordering, with APD development, at high temperatures occurs in a composition range which is comparable to that found for blueschist pyroxenes. Miscibility gaps between Jd and Om and between Om and Aug appear to effectively operate only in blueschist facies environments. The strictly geothermometric applications for pyroxenes in the system Jd-Ac-Aug may be limited (Fleet *et al.*, 1978) but omphacite microstructures have significant potential for establishing, or confirming, relative time scales for metamorphic histories.

*Acknowledgements.* M. A. C. acknowledges a Research Studentship held at the Department of Mineralogy and Petrology, Cambridge University, and a Research Fellowship, both from the Natural Environment Research Council of Great Britain, and support from an NSF grant EAR76-22689 to Professor C. W. Burnham. D. C. S. acknowledges a Research Fellowship funded by NERC grant GR3/3002 to Professor M. J. O'Hara. We thank Professor J. B. Vander Sande for the use of the TEM facilities in the Department of Materials Science and Engineering, Massachusetts Institute of Technology, and Professor C. W. Burnham for critical comments on the manuscript.

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[Manuscript received 21 May 1980;  
revised 8 August 1980]