

# Topotactic replacement of augite by omphacite in a blueschist rock from north-west Turkey

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**SUMMARY.** Partial replacement of original igneous augite crystals by omphacite during blueschist metamorphism of a dolerite from the Mihalliççik area of north-west Turkey has been studied by transmission electron microscopy. The replacement occurred topotactically, apparently by ion exchange with a fluid phase, which left the basic pyroxene structure unchanged. Cation ordering in the omphacite caused a symmetry change from C-face centred to primitive with the formation of fine-scale antiphase domains. Selected-area diffraction provides evidence for  $P2$  and  $P2/c$  space groups for the ordered omphacite though the best ordered areas show a tendency towards  $P2/n$  (reflections violating the  $n$ -glide are very weak) and also contain fine, wavy, disordered precipitates approximately parallel to (100).

It is suggested that the replacement temperature was below the cation-ordering temperature and that the omphacite grew in a metastable, disordered state. Subsequent ordering occurred under irreversible conditions via a series of intermediate structures. The ordering sequence may illustrate the relationship between different ordering schemes in other blueschist pyroxenes.

THERE is often evidence of disequilibrium in rocks metamorphosed under the high-pressure, low-temperature conditions of the blueschist facies and incomplete replacement or recrystallization reactions may be observed. Jadeitic pyroxenes are amongst the commonest minerals to be found in these rocks and are potentially the most informative, but study of the mineralogical processes that operated in them during metamorphism can be made difficult by the fine scale of any relict features. This problem may be resolved by the use of transmission electron microscopy (TEM) for the examination of the finest mineral interactions and microstructures. Champness (1973) and Phakey and Ghose (1973) identified antiphase domains (APDs) by TEM in omphacites. These have been ascribed to a cation-ordering transformation since Clark and Papike (1968) had previously shown that ordering of  $\text{Na}^+$ ,  $\text{Ca}^{2+}$ ,  $\text{Mg}^{2+}$ ,  $\text{Al}^{3+}$  (with some substitution of  $\text{Fe}^{2+}$  and  $\text{Fe}^{3+}$ ) on  $M$  cation sites could occur, giving a primitive lattice as opposed to the usual C-face centred pyroxene structure.

In addition to antiphase textures, omphacites frequently contain exsolution lamellae on an electron-optical scale (Carpenter, in press) and their microstructures can be remarkably complex and variable.

The blueschist rocks of Turkey, some of which were described by Cogulu (1967), lie in the lower temperature ranges of the blueschist facies and typically contain lawsonite. They show many features of incipient metamorphism with minerals and textures belonging to earlier periods of their evolution preserved. In this paper TEM observations on a pyroxene/pyroxene replacement reaction are presented. Original igneous augite crystals in dolerite survived the metamorphic treatment but were partially replaced by omphacite. The study was undertaken to define the nature of the replacement process itself, which has also been described in blueschists from California (Essene and Fyfe, 1967) and from New Caledonia (Black, 1974), and to examine the earliest stages of cation ordering and microstructural development in omphacite. Before the scales of APDs and exsolution lamellae in blueschist pyroxenes can be used to provide thermal history information in the general manner suggested by McConnell (1975), the transformations responsible for them must be thoroughly understood. Omphacite is most unusual in that its cations do not achieve complete order (Clark and Papike, 1968). Abnormal transformation behaviour might be anticipated.

*Specimen description and methods.* The specimen investigated, no. 103484 from the Harker collection, Department of Mineralogy and Petrology, Cambridge, is a metadolerite from the Mihalliççik region of north-west Turkey. It was originally described by Cogulu (1967) who numbers it 38/62. In thin section the primary igneous texture of the rock is clearly visible. Euhedral, brownish crystals of augite, sometimes showing hourglass zoning and up to 2 mm long, sit in a finer groundmass, which was once mainly plagioclase but now consists of lawsonite + albite + chlorite + sphene. Individual

augite crystals are heavily veined by pale-green omphacite<sup>1</sup> (fig. 1a) which is replacing them.

The pyroxenes were analysed using an electron microprobe with a Harwell Si(Li) detector and pulse processor (Statham, 1976). Correction procedures follow Sweatman and Long (1969) and  $\text{Fe}^{2+}/\text{Fe}^{3+}$  ratios were calculated assuming six oxygens and four cations. The jadeite content of omphacite was determined using the method of Essene and Fyfe (1967). The igneous pyroxenes are titanaugites with compositions typical of alkali basalts, a representative analysis being  $\text{Ca}_{0.96}\text{Mg}_{0.69}\text{Fe}_{0.23}^{2+}\text{Al}_{0.06}\text{Ti}_{0.08}(\text{Si}_{1.74}\text{Al}_{0.26})\text{O}_6$ . Some variation in Ti content was apparent and the Fe/Mg ratio ranged between 0.21 and 0.34. Omphacite compositions could only be measured where veins were sufficiently wide (c. a few  $\mu\text{m}$ ) for overlap of the electron beam on to adjacent augite not to occur. A typical analysis is:  $(\text{Na}_{0.57}\text{Ca}_{0.43})_{\Sigma 1.00}(\text{Mg}_{0.28}\text{Al}_{0.27}\text{Fe}_{0.14}^{2+}\text{Fe}_{0.30}^{3+}\text{Ti}_{0.01}\text{Mn}_{0.01})_{\Sigma 1.01}\text{Si}_{2.00}\text{O}_6$ , i.e.  $\text{Jd}_{27}\text{Ac}_{30}\text{Aug}_{43}$ , and it has been assumed that the finer veins have a similar composition. The analyses are presented in terms of jadeite, acmite, and augite end member molecules in fig. 1b.

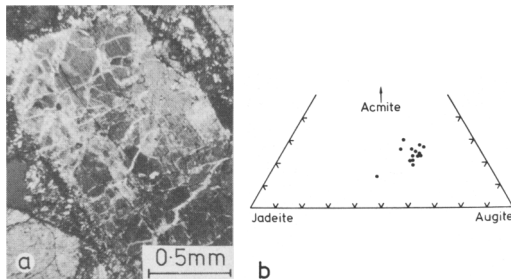


FIG. 1. (a) Optical micrograph of a single augite crystal veined by omphacite. Partially crossed polars. (b) Electron microprobe analyses of omphacite veins plotted in terms of jadeite, acmite, and augite molecules. The analyses fall in the range defined as chloromelanite by Essene and Fyfe (1967) but as omphacite by Clark and Papike (1968).

Suitably veined augite crystals were prepared for transmission electron microscopy by ion beam thinning and observations made with an AEI EM6G electron microscope operating at 100 kV.

*Electron microscopy.* On an electron-optical scale the original augite is completely homogeneous. It is

<sup>1</sup> According to the definitions of sodic pyroxenes given by Clark and Papike (1968) this pyroxene has the composition of omphacite but according to Essene and Fyfe (1967) it should be called chloromelanite.

patchily replaced and veined by rather less well crystalline material, which, from diffraction evidence, is ordered omphacite. The replacement is invariably topotactic, adjacent areas of C-face centred augite and primitive omphacite giving identically oriented diffraction patterns. There appears to be a gradation in the character of the omphacite from narrow veins (fig. 2a) through larger areas with many defects (fig. 2b) to well-crystalline areas typically containing fine-scale precipitates (fig. 2c). Dark field images using  $h+k = \text{odd}$  reflections reveal fine-scale antiphase domains whose shape and distribution also vary.

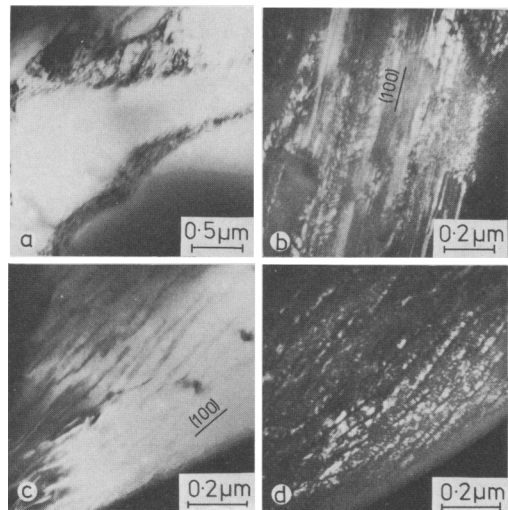


FIG. 2. Electron micrographs of omphacite replacing augite. (a) Veins of omphacite cutting homogeneous augite. Bright field. (b) Area of omphacite with many defects. Much of the contrast arises from fine-scale, irregular APDs with some APBs lined up parallel to (100). Dark field,  $g = 10\bar{1}$ . (c) Well-crystalline patch of omphacite with wavy precipitates approximately parallel to (100). Dark field,  $g = 20\bar{2}$ . (d) Same area as (c) showing fine equiaxed APDs. The precipitate is out of contrast. Dark field,  $g = 10\bar{1}$ .

APDs have not been imaged within the narrow veins but in ragged areas they are highly irregular and show a tendency to have their boundaries lined up parallel to (100) (fig. 2b). The well-crystalline omphacite regions have small, equiaxed and homogeneously distributed APDs on a scale of about 100 Å (fig. 2d). The thin, wavy precipitates approximately parallel to (100) in these regions are out of contrast when imaged with  $h+k = \text{odd}$  reflections and are therefore thought to be disordered. Their cell dimensions, and hence

compositions, are, however, not very different from those of the host omphacite. In some cases exsolution is associated with coarsened APDs.

Evidence for the nature of cation ordering in the omphacite comes from (*h*0*l*) selected area diffraction patterns in which systematic absences have been observed. The fine veins are primitive with absences of the type  $l = \text{odd}$  in (*h*0*l*) indicating a *c*-glide in (010) and may have (100) stacking irregularities to account for some  $a^*$  streaking. Larger replacement areas with the fine-scale, irregular APD distribution have all reflections present. Possible space groups are  $P2/c$  and  $P2$  respectively for these. Regions with equiaxed APDs and (100) exsolution have all reflections present but those of the type  $h+l = \text{odd}$  in (*h*0*l*) are distinctly weak, indicating a tendency towards an *n*-glide in (010) and a space group of  $P2/n$ . These (*h*0*l*) sections are shown in fig. 3 and may be compared with a similar section from the augite (fig. 3*d*) which has *C*-face centering and *c*-glide absences ( $C2/c$ ).

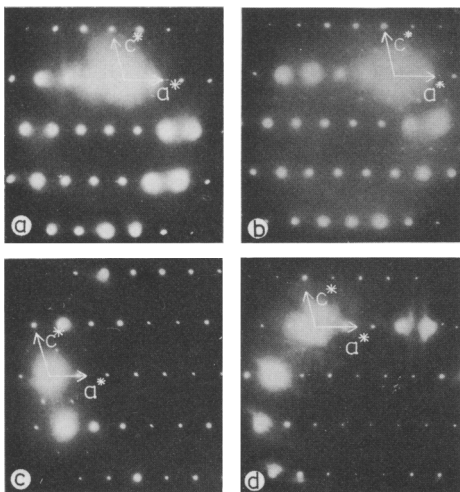


FIG. 3. Selected area electron diffraction patterns showing (*h*0*l*) sections of the reciprocal lattice. (a) From a fine omphacite vein; with absences of the type  $l = \text{odd}$  and  $a^*$  streaking indicating some (100) stacking disorder. Possible space group:  $P2/c$ . (b) From the area of fig. 2*b*; all reflections present. Possible space group:  $P2$ . (c) From an area identical to fig. 2*c*, *d*; all reflections present but those of the type  $h+l = \text{odd}$  are very weak suggesting a tendency towards  $P2/n$ . (d) From homogeneous augite; absences of the type  $h+k = \text{odd}$  and  $l = \text{odd}$ . Space group:  $C2/c$ .

**Discussion.** The mechanism for replacing augite by omphacite appears to leave the basic pyroxene structure unchanged, involving principally the

cations occupying  $M1$  and  $M2$  sites. Where the fluid phase present during metamorphism penetrated the augite crystals, ion exchange of  $\text{Na} + \text{Al} + \text{Fe}^{3+}$  for  $\text{Ca} + \text{Mg} + \text{Fe}^{2+}$  took place. Some increase in Si on tetrahedral sites, at the expense of Al, evidently also occurred. It is possible that the composition of the omphacite was dominantly controlled by the activities of ions in the fluid, which in turn may have been influenced by external factors. The presence of augite greatly assisted the formation of omphacite by alleviating the nucleation problems, which can be significant at low temperatures. Topotactic processes of this sort may be important in other low-grade metamorphic reactions.

There has been some debate as to what the true space group for ordered omphacite is. Clark and Papike (1968) and Clark *et al.* (1969) reported  $P2$  but Matsumoto *et al.* (1975) ascribed reflections violating the *n*-glide to multiple diffraction and suggested  $P2/n$ . The latter is supported by Curtis *et al.* (1975) though both are theoretically possible, as is  $P2/c$  (Brown, 1972). Cation-ordering schemes can be devised to account for all three space groups but over a limited composition range only one should operate and the coexistence of two in this case implies disequilibrium.

The presence of antiphase domains, which resulted from a  $C \rightarrow P$  lattice transformation, shows that the omphacite was initially disordered or ordered only on some short range basis. Most of the ordering took place after the replacement had occurred. This is possible even at replacement temperatures that are less than the equilibrium-ordering temperature ( $T_{\text{ord}}$ ) if cation exchange with the fluid was rapid relative to cation ordering within the solid. The narrow veins in the augite represent the earliest stages of the replacement process that are preserved and they are apparently ordered with a  $P2/c$  space group. Where replacement was more extensive, and thus presumably more time had passed since the first omphacite formed, ordering gave a  $P2$  space group. These areas, however, still have a large number of defects and have a highly irregular and very fine-scale APD texture. The best-ordered regions of omphacite have regular, coarser APDs and tend towards  $P2/n$ . They also contain fine, disordered precipitates.

These observations can be most readily explained if the replacement reaction occurred at  $T < T_{\text{ord}}$  and ordering then proceeded irreversibly via metastable intermediate structures, for, at the low temperatures prevailing, the ordering scheme that could develop most rapidly would be used in preference to the energetically most stable one. It is suggested that the first ordering scheme achieved in the disordered parent had  $P2/c$  symmetry. This

gave way to a  $P2$  scheme and finally progressed towards  $P2/n$  as ordering continued. This may be a slightly oversimplified view as the finest veins have not been proved to be identical in composition to the large omphacite patches. Sequential behaviour should be anticipated, however, since the cations available for ordering on the  $M$  sites ( $\text{Na}^+$ ,  $\text{Ca}^{2+}$ ,  $\text{Al}^{3+}$ ,  $\text{Mg}^{2+}$ ,  $\text{Fe}^{2+}$ ,  $\text{Fe}^{3+}$ ) can diffuse, and hence order, at different rates. Because of the low temperatures, the driving force to order would be large, but the rate slow and compromise metastable schemes dominated by the faster moving cations could develop. With time, more stable schemes controlled by the more slowly diffusing ions such as  $\text{Al}^{3+}$  could be used.  $P2/c$  symmetry can be obtained by stacking alternating monolayers of augite and jadeite parallel to (100) and the APBs<sup>1</sup> lined up on (100) in the  $P2$  areas (fig. 2b) may represent an inheritance from such an earlier layered structure.

The (100) disordered precipitates are not very different in composition from the ordered host omphacite. They probably formed as the omphacite attempted to improve its ordering and rejected excess material that could not be incorporated into the ordering scheme. Ordering preceded exsolution because it required smaller-scale diffusion of ions and therefore was a faster process.

The upper temperature limits for blueschist metamorphism in Turkey must be less than about 350 °C, as shown by the stable occurrence of lawsonite (Nitsch, 1972). At such low temperatures any transformations requiring diffusion would be slow, making metastable behaviour highly probable. There is no evidence to suggest that the omphacite anywhere achieved a stable equilibrium state. Indeed, it is unlikely to have done so if each stage of ordering was determined by the fastest available reaction pathway and not by the largest possible drop in free energy. The over-all behaviour is an example of metastable transformations proceeding under irreversible conditions and obeying the Ostwald step rule (Eitel, 1954). On the basis of their microstructures, similar kinetically controlled behaviour has been inferred for omphacites from the blueschist rocks of Syros, Greece (Carpenter, in press). In these pyroxenes evidence for the

<sup>1</sup> i.e. antiphase boundaries.

three primitive space groups was also found but the relationships between them were not clear. The ion exchange process appears to influence the initial choice of ordering scheme in that systematic absences appropriate for  $P2/c$  symmetry have only been found in areas where omphacite replaced augite. A successive relationship between ordering under  $P2$  and  $P2/n$ , however, could be more general.

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