SHORT COMMUNICATIONS

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Amphibole microstructures: some analogies with phase transformations in pyroxenes

THERE are many parallels between the structural relations and solid-solution behaviour of pyroxenes and amphiboles. The purpose of this short communication is to report on the microstructures (or lack of them) associated with three separate types of phase transformations in amphiboles which have analogies with specific pyroxenes. A displacive ($C2/m \rightleftharpoons P2_1/m$) transformation in cummingtonite is equivalent to the high-low ($C2/c \rightleftharpoons P2_1/c$) inversion which occurs in pigeonite. Octahedral cation ordering in omphacites might be expected to manifest itself in compositionally equivalent amphiboles but a barroisite associated with ordered omphacite from Norway retains $C2/m$ symmetry. Finally, joesmithite, a unique Pb, Be amphibole exhibits some microstructures related to Be/Si ordering on tetrahedral sites. No direct analogue pyroxene is known but there is at least the possibility of tetrahedral cation (Al/Si) ordering in calcium Tschermak's pyroxene (CaTs). The similarities and contrasts between these pyroxenes and amphiboles illuminate aspects of both mineral groups which constrain their behaviour in nature.

Ion beam thinned crystals of the three amphiboles were examined by transmission electron microscopy in an AEI EM6G microscope operating at 100 kV.

Clinoanthophyllite was first reported as exsolution lamellae in tremolite by Bown (1966). His original specimen *J* from the Wright Talc Mine, Adirondacks, was re-examined. In thin section the tremolite [$(Na_{0.29}Ca_{1.79})_{\Sigma 2.08}(Mg_{4.96}Fe_{0.02}Al_{0.07})_{\Sigma 5.05}(Si_{7.97}Al_{0.03})O_{22}(OH)_2$ = average of five electron microprobe analyses] coexists with anthophyllite and contains a homogeneous distribution of exsolution lamellae a few μm apart and less than 1 μm wide. Selected area electron diffraction patterns are consistent with $C2/m$ symmetry for the host tremolite and $P2_1/m$ for the lamellae which lie approximately parallel to $(10\bar{1})$ (fig. 1). Dark field images with reflections of the type $h+k$ = odd show the lamellae in contrast with a regular distribution of antiphase domains (APD's) (fig. 1*b*). The APD's have smooth boundaries (APB's), the traces of which have a tendency to lie approximately parallel to (100) in a^*–c^* sections. Microstructures in pigeonite lamellae intergrown with augite are

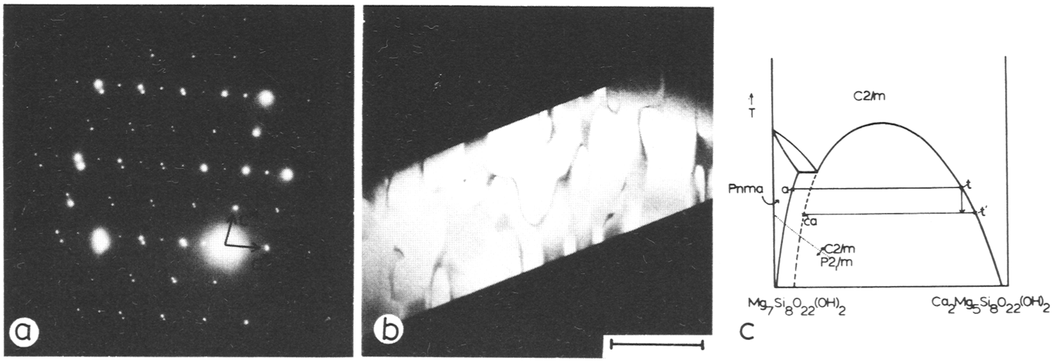

FIG. 1. Clinoanthophyllite lamellae in tremolite. (*a*) Selected area electron diffraction pattern of the host and a lamella. Reflections of the type $h+k$ = odd are absent in the pattern from the host tremolite. (*b*) Dark field image of a lamella obtained with an $h+k$ = odd reflection. The host tremolite is totally out of contrast and the clinoanthophyllite contains APD's. Scale bar = 0.25 μm. (*c*) Schematic subsolidus phase diagram for anthophyllite–tremolite based on the analogy with hypersthene–augite. (Note that liquidus relations are not shown.) Tremolite and anthophyllite crystallized together (t–a). On cooling, the tremolite exsolved clinoanthophyllite (t′–ca) with the composition of the latter controlled by the metastable limb of the $C2/m$ solvus (broken line). The lamellae then inverted ($C2/m \rightarrow P2_1/m$) on crossing the dotted line during further cooling, causing the appearance of APD's.

very similar (e.g. Lally *et al.*, 1975) and almost certainly have an analogous origin. Prewitt *et al.* (1970) demonstrated that some cummingtonite (= iron-rich clinoanthophyllite) on heating to above *c.* 45 °C inverts to a *C2/m* structure by a rapid, reversible and presumably displacive mechanism. As in pigeonite, the inversion temperature should vary with composition and be highest for Fe-poor crystals such as in specimen J. The stable low-temperature assemblage, as indicated by coexisting crystals, is anthophyllite + tremolite so that the clinoanthophyllite lamellae must be metastable precipitates, probably favoured by growth in a monoclinic host. A displacive inversion, responsible for the formation of APD's, occurred in the exsolution lamellae during cooling and the phase relations (fig. 1*c*) are expected to be identical in form to those of hypersthene-augite, as shown, for example, by Buseck *et al.* (1980).

Omphacites in blueschists and eclogites frequently have low symmetry (*P2/n* instead of *C2/c*) due to an ordered distribution of their *M*-site cations. The ordering involves Na-rich and Ca-rich *M*2-sites and Al-rich and Mg/Fe^{2+}-rich *M*1-sites when the ratios of Na:Ca and Al:Mg/Fe^{2+} are approximately 1:1 (Clark and Papike, 1968; Clark *et al.*, 1969; Curtis *et al.*, 1975; Matsumoto *et al.*, 1975). Compositionally equivalent amphiboles might be expected to show the same tendency and a barroisite, which coexists with ordered omphacite in an eclogite from Naustdal, Sogn og Fjordane, Norway (Harker no. 101757; described by Binns, 1967), has been examined to test this possibility. Binns's analysis indicates a composition between glaucophane and hornblende and a Na:Ca ratio of approximately 1:1 for the *M*4 site: $(K_{0.03}Na_{1.06}Ca_{1.17})$ $(Mg_{2.83}Fe^{2+}{}_{1.14}Fe^{3+}{}_{0.41}Ti_{0.05}Al_{0.72})$ $(Si_{7.06}Al_{0.94}O_{22})$ $(OH,F)_2$. On an electron optical scale the amphibole crystals show no signs of exsolution or cation ordering, however, and electron diffraction patterns are consistent with *C2/m* symmetry.

The amphibole structure has a greater variety of *M* sites than the pyroxene structure and ordering could therefore be accommodated more easily, without the need for a symmetry reduction. The most likely reason for the maintenance of *C2/m* symmetry in this barroisite is that there is only one substitution ($Na \rightleftharpoons Ca$ on *M*4) with the potential for causing an ordering transformation. The *M*1 and *M*2 sites are distinct under *C2/m* symmetry so that Al and Mg could already be ordered with Al^{3+} concentrated on *M*2 and Mg^{2+} on *M*1. Furthermore the $Na \rightleftharpoons Ca$ substitution is of ions with similar radii. In omphacite the ordered structure seems to be stabilized by interactions between two sets of substituting ions ($Ca \rightleftharpoons Na$, $Al \rightleftharpoons Mg/Fe^{2+}$) and, by way of contrast, neither aegirine-jadeite ($NaAl_{0.5}Fe^{3+}{}_{0.5}Si_2O_6$), with one substitution only, nor aegirine-augite $Na_{0.5}Ca_{0.5}Fe^{3+}{}_{0.5}(Mg,Fe^{2+})_{0.5}Si_2O_6$, which has two substitutions but of similar sized ions, show signs of ordering (Clark and Papike, 1968; Carpenter, 1979). Thus an amphibole equivalent of ordered omphacite would appear to require substitutions of ions with different radii on two separate, but interacting, sets of cation sites.

The Be^{2+}/Si^{4+} ordering scheme on tetrahedral sites in joesmithite leads to a symmetry reduction from *C2/m* to *P2/a* (Moore, 1969). Moore suggested an ideal crystal chemistry of $(Ca,Pb)Ca_2(Mg,Fe^{2+},Fe^{3+})_5(Si_6Be_2O_{22})(OH)_2$. In the electron microscope the joesmithite crystals (from specimen no. 255084 of the Naturhistoriska Riksmuseet, Stockholm, locality Långban, Sweden) show no signs of exsolution but contain a substantial number of defects. Dark field images obtained with reflections of the type $h+k$ = odd show occasional and irregularly distributed APD's which are almost invariably associated with dislocations and stacking faults (fig. 2). APB's commonly end at dislocations.

The lack of an equiaxed APD texture of the sort which is typically the result of an ordering transformation suggests that the crystals grew with substantially ordered cations. The APB's are most probably mistakes incorporated during crystal growth under the hydrothermal conditions of the Långban ore body or were generated by the passage of partial dislocations during deformation. The final textures are the product of interactions between APB's and other defects which are reminiscent of those found in omphacite by van Roermund and Boland (1981) and which were attributed in part to dislocations of the type $\frac{1}{2}\langle 110 \rangle$ (which is also the antiphase vector). It is interesting to note that Moore (1969) suggested a coupled relationship between the *A*′ site cations, Pb^{2+}/Ca^{2+}, and the Be-bearing tetrahedra. The *A*′ cations are displaced towards the Be tetrahedra to help make up the local charge deficiency associated with replacing Si^{4+} by Be^{2+}. This suggestion contributes to the recurring theme of charge balancing in the analysis of ordered pyroxenes and amphiboles. In this case it seems unlikely that disordered crystals would be stable relative to an assemblage of different phases and the free energy drive for ordering is probably large.

In contrast to joesmithite, the closest pyroxene analogue with the potential for tetrahedral cation ordering, CaTs, has substantially, if not totally disordered cations in synthetic specimens in spite of an Al^{IV}:Si ratio of 1:1 (Okamura *et al.*, 1974). In view of the coupled cation ordering behaviour of omphacite and joesmithite, involving cations

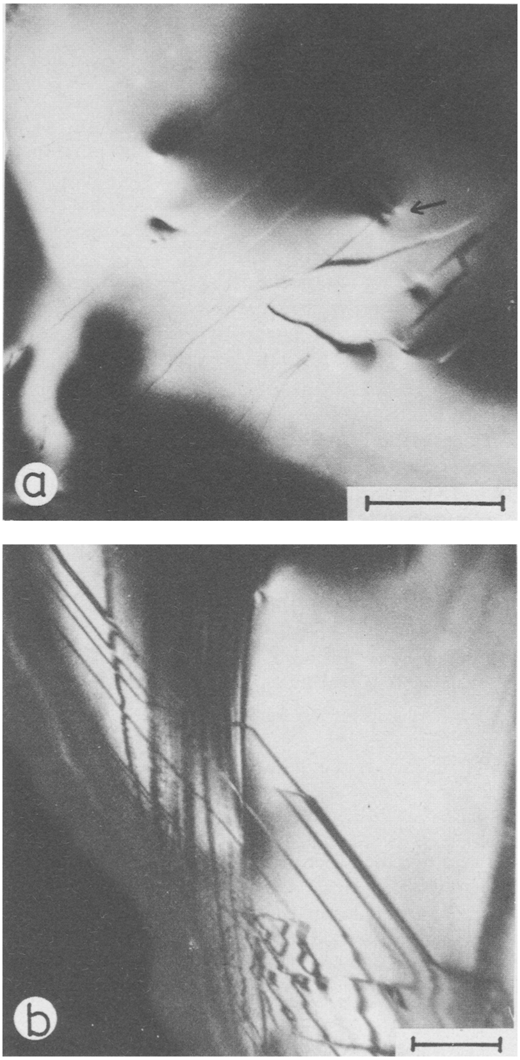

FIG. 2. Dark field images of joesmithite obtained with $h+k$ = odd reflections showing irregularly distributed APB's. (*a*) Wavy APB's interacting with linear stacking faults and ending at dislocations (e.g. arrowed). (*b*) Straight APB's with wavy segments interacting with other defects. These APB's are considered to have originated as mistakes incorporated during crystal growth or by the migration of partial dislocations. Scale bar = 0.25 μm.

with different charges, and the absence of ordering in barroisite, this failure of CaTs to order could perhaps be ascribed to charge balancing problems. $M1$ and $M2$ sites in CaTs are totally filled by Al and Ca respectively so that there is no secondary ordering scheme which might interact with, and stabilize, an ordered distribution of tetrahedral Al and Si.

These observations on three amphiboles re-emphasize the value of comparing amphibole and pyroxene transformation behaviour. The high-low displacive transformations appear to be exactly analogous, even in the resulting microstructures. Among the requirements for an ordering transformation of differently charged octahedral or tetrahedral ions are, not only that they should have significantly different ionic radii, but also that there should be a second set of ordered cations (omphacite) or a displacement effect (joesmithite) which assists in the attainment of local charge balancing.

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