

MINERALOGICAL NOTES

Speculation on an Order-Disorder Transformation in Omphacite

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Abstract

Antiphase domains, detected by electron microscopy, indicate that a primitive (ordered) omphacite from Jenner, California, crystallized in the (disordered) C space-group and later underwent a transition to the P space group. Evidence that the ordering occurred by a first-order mechanism is given, and a possible phase diagram for the jadeite-diopside system is proposed which contains a narrow two-phase field separating the ordered and disordered regions.

Recently Clark and co-workers (1968, 1969) reported that omphacites within a composition region enclosed roughly by $Jd_{64}Di_{36}$, $Jd_{35}Di_{65}$ and $Jd_{25}Di_{50}Ac_{25}$ (where Jd = jadeite, $NaAlSi_2O_6$; Di = diopside, $CaMgSi_2O_6$; Ac = acmite, $NaFe^{3+}Si_2O_6$) have different space group symmetry from their component end-members, all of which have space group $C2/c$. Crystal structure refinements of omphacites from California and Venezuela showed that they have a largely ordered cation distribution, leading to a $P2$ space group.¹ The structure is similar to that of diopside except that the four $M1$ octahedra which are symmetrically equivalent in diopside are unrelated by symmetry in $P2$ omphacite. Similarly the four eight-fold coordinated $M2$ cation sites of diopside become four distinct sites in the $P2$ structure.

Clark and Papike (1968) suggested that the main reason for the formation of omphacites with space group $P2$ is the large size difference between Al^{3+} and Mg^{2+} , resulting in a high degree of order in the $M1$ octahedral chains. Clark, Appleman, and Papike (1969) pointed out that the "ideal" $P2$ omphacite may be considered as a clinopyroxene in which the octahedrally coordinated cations are one-half Mg and one-half Al and the $M2$ cations are one-half Ca and one-half Na , i.e. $Ca_{0.5}Na_{0.5}Mg_{0.5}Al_{0.5}Si_2O_6$. The requirement that the small, highly charged Al^{3+} cations are as far from each other as possible leads

to alternating Al and Mg cations in the $M1$ chains. In the $M2$ sites, however, the maximum degree of order to be expected is $\frac{1}{3}$ Na and $\frac{2}{3}$ Ca or $\frac{2}{3}$ Na and $\frac{1}{3}$ Ca . The Californian and Venezuelan omphacites were found to possess a degree of order approaching this maximum.

During an electron microscopic investigation of the microstructure of an omphacite² with composition approximately $Jd_{31}Di_{52}Ac_{17}$ in an eclogite from Jenner, California,³ antiphase domains were found which formed a "foam" structure approximately 0.2μ in diameter (Fig. 1a). The domain boundaries are visible whenever a reflection for which $(h + k) \neq 2n$ is operating; thus the displacement vector across the boundaries is $\frac{1}{2}[a \pm b]$.

The presence of the domains suggests that the omphacite crystallized with the disordered $C2/c$ structure and later adopted the ordered, primitive structure. The anti-phase domain boundaries developed because, in the change of space group from C -face centered to primitive which accompanied the cation ordering, one lattice point was lost per unit cell. As a result there were two possible "registers" for the origin of the primitive cell. If two adjacent regions adopted different registers, an antiphase boundary with a displacement vector $\frac{1}{2}[a \pm b]$ formed between them. Geometrically, the situation is analogous to the $C2/c \rightarrow P2/c$ transition in pigeon-

¹ More recently Matsumoto and Banno (1970) reported finding an omphacite to have space group $P2/n$. A pyroxene with this space group would have two types of $M1$ and $M2$ sites rather than the four in a $P2$ structure.

² Electron diffraction shows that the omphacite has a primitive lattice, but no distinction could be made between space groups $P2$ and $P2/n$ due to the double diffraction effects which always occur with this technique.

³ A petrographic description and discussion of the paragenesis of this rock has been given by Crawford (1965).

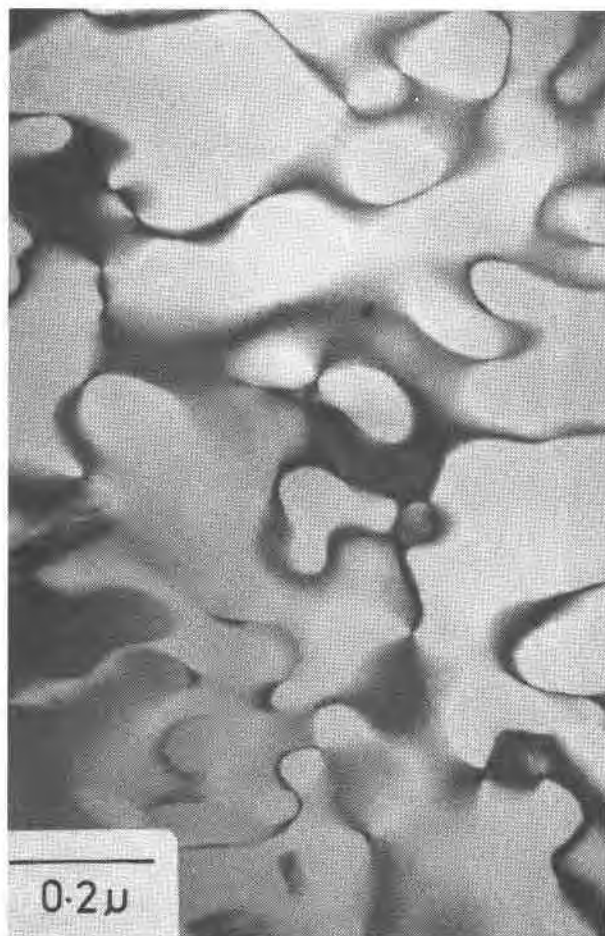


FIG. 1a. Electron micrograph (100 kV) of anti-phase boundaries in Jenner omphacite. Operating reflection 101. Specimen prepared by ion-thinning.

ite (Morimoto and Tokonami, 1969), although in this case the transformation is primarily a displacive one not involving significant cation ordering (Smyth and Burnham, 1972).

An order-disorder transition can occur by a first or second order mechanism, but the latter is thought to be very rare, especially in the case of the ordering of different atomic species (Christian, 1965). Evidence that the transition in omphacite is predominantly a first-order one involving a nucleation and growth mechanism (and hence a two-phase region on the phase diagram) is provided by electron micrographs (such as Figure 1b) which show domains which are larger than the average and have apparently nucleated on defects such as individual dislocations and subgrain boundaries.

A possible phase diagram for the diopside-jadeite

binary which is consistent with the observations described in this paper is shown in Figure 2. It contains a narrow two-phase field separating the single-phase ordered and disordered regions. The diagram is also in agreement with recent chemical analyses of omphacites (Iwasaki, 1963; Essene and Fyfe, 1967; Seki and Onuki, 1967) which suggest nearly complete solid solution in sodic pyroxenes. If the two-phase region is narrow, as it is in most metal systems (Hansen, 1958), the two phases will be very similar in composition and lattice parameters and may thus be difficult to distinguish using X-rays. In addition, if the antiphase structure of the Jenner omphacite is an indication of the spatial distribution of the two phases, it will not be possible to detect them optically or by electron probe analysis.

The temperature of formation of the Jenner eclogite is generally thought to be not more than 300°C,

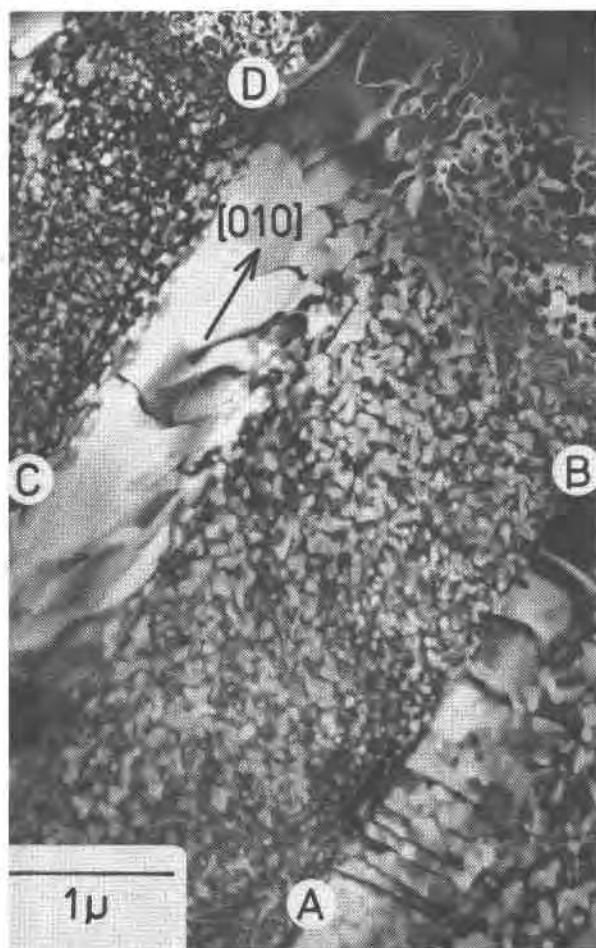


FIG. 1b. Larger antiphase domains have nucleated on long, straight dislocations AB and CD. Operating reflection 101.

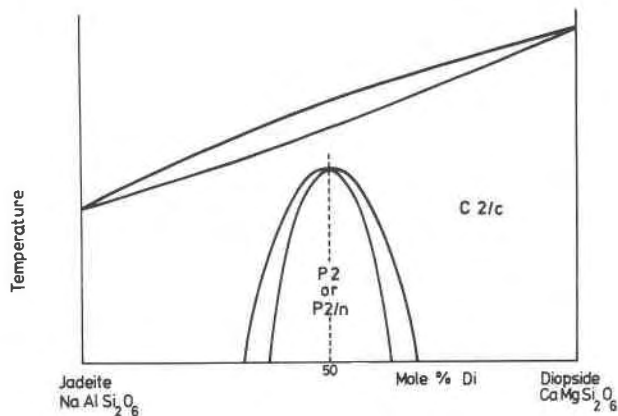


FIG. 2. Possible phase diagrams for the jadeite-diopside binary. It has been assumed that the point of equal composition occurs at the "ideal" composition of 50 mole percent. The extent of the ordered region is taken from Clark and Papike (1968) and the form of the liquidus and solidus from Bell and Davis (1969).

a temperature below which it might be thought unlikely for an ordering reaction to occur on the phase diagram. It is therefore possible that the Jenner omphacite formed metastably (at high supersaturation) as a disordered phase in the stability field of the ordered phase, a phenomenon which is common in feldspars synthesized in the laboratory.

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