Reports

Orthopyroxene Exsolution in Augite: A Two-Step, Diffusion-Transformation Process

Abstract. *Orthopyroxene lamellae exsolved from augite on (100) are shown to grow by a two-step process involving (i) the diffusion of calcium and (magnesium, iron) to form clinohypersthene and (ii) the inversion of clinohypersthene to orthopyroxene, probably by glide twinning. If complete inversion is prevented by cooling or steep concentration gradients, the two-step process produces orthopyroxene with narrow margins of clinohypersthene. Measured elemental concentration gradients at (100) lamellar interfaces support this mechanism.*

Exsolution in minerals is usually considered to occur either by nucleation and growth or by spinodal decomposition. The latter mechanism occurs less commonly in geological systems. Exsolution in both high- and low-calcium pyroxene is common (*1*), and the compositions of the exsolved phases bear information about the thermal history of the host rock. In particular, high-calcium augite may have several generations of lamellae, including orthopyroxene (Opx) on (100) and low-calcium $P2_1/c$ pyroxene (commonly pigeonite) on or near (100) or (001). The mechanism of exsolution for such pyroxene is commonly ascribed to nucleation and growth. We provide here evidence derived from the use of a high-resolution conventional transmission electron microscope (CTEM) and an analytical electron microscope (AEM) supporting a unique two-step exsolution process for the formation of Opx in augite. The mechanism involves (i) the diffusion of calcium to form low-calcium $P2_1/c$ pyroxene lamellae and (ii) the near-isochemical transformation of the $P2_1/c$ phase to Opx.

The augites examined in this study are in granulites from Keene, New York, in the Adirondack Highlands. These rocks equilibrated under regional metamorphic conditions (pressure, 4 to 5 kbar; temperature, 700° to 800°C) (*2*). Ion-thinned specimens of augite crystals having [010] approximately normal to the section were studied with a JEOL JEM 100CX electron microscope.

Using electron diffraction, lattice imaging, and AEM, we determined three families of low-calcium lamellae: (i) $P2_1/c$ clinohypersthene (Chp) lamellae averaging 1.0 μm in width parallel within the error of observation to (001) (Fig. 1A); (ii) Chp lamellae averaging 0.1 μm in width with a new and as yet undetermined general interface index (*hkl*) (Fig. 1B); and (iii) Opx lamellae parallel within the error of observation to (100) (Fig. 1, B and C). Table 1 presents the AEM data used in the identification of these phases. Techniques for the quantitative analysis of thin foils of this type with the use of the AEM are described in (*3*).

The bulk of this report is concerned with the (100) lamellae. Although these lamellae average 1000 Å in width, some are considerably narrower. Their most significant characteristic is the presence of marginal zones of Chp approximately 100 to 200 Å wide at both lamellar interfaces between the augite and the Opx (Fig. 1C). These margins are present on all (100) lamellae and are of approximately the same width regardless of the width of the central Opx core. Furthermore, stacking faults on (100), although common in the Opx, are absent in (100) Chp. Stacking faults are commonly interpreted as an effect of inversion by glide between Opx and low-calcium clinopyroxene on (100) parallel to [001] (*4*).

Figure 2 is a composite plot of the calcium distribution across several (100)

Table 1. Results of AEM analyses of the four phases studied as elements relative to silicon, and expressed in terms of their quadrilateral components. Standard errors (in parentheses) are expressed as 95 percent confidence intervals; N.D., not detected.

Ratio to silicon	(001) Chp	(*hkl*) Chp	(100) Opx	Host augite
Magnesium	0.39 (2)	0.41 (2)	0.43 (1)	0.33 (1)
Aluminum	0.01 (0)	0.04 (0)	0.03 (0)	0.04 (0)
Calcium	0.01 (0)	0.02 (0)	0.03 (0)	0.39 (1)
Manganese	N.D.	0.00 (0)	0.00 (0)	0.00 (0)
Iron	0.50 (1)	0.49 (1)	0.49 (1)	0.22 (0)
Wollastonite	1	2	3	41
Enstatite	43	45	45	35
Ferrosilite	56	53	52	24

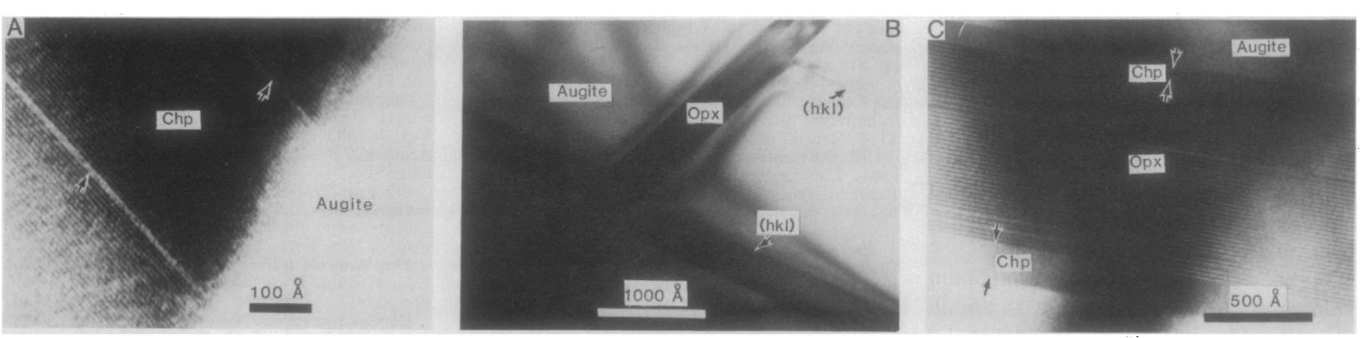

Fig. 1. (A) Lattice image of (001) clinohypersthene lamella (*Chp*) and augite host; fringes in the lamella are parallel to (100) of the Chp. Stacking faults in the Chp (arrows) terminate at ledges in the Chp-augite interface. (B) Low-magnification CTEM image of (100) orthopyroxene lamella (*Opx*) and two (*hkl*) lamellae in the augite host. One (*hkl*) lamella is seen to terminate at the Opx-augite interface, whereas the other is offset across the Opx lamella. (C) Lattice image of (100) orthopyroxene lamella (*Opx*) in the augite host, showing the characteristic marginal zones of clinohypersthene (*Chp*) (between pairs of arrows). Stacking faults are observed in the Opx.

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lamellar interfaces. The plot shows a high-calcium augite matrix and low-calcium Opx. Since the analytical technique used has a 300-Å resolution (*5*), the narrow boundary region which includes the Chp margins appears as a near-vertical concentration gradient. The most significant aspect of this plot is the high-calcium node in the augite immediately adjacent to the lamellae. We interpret this node to be due to calcium diffusion away from the lamellae as an expression of growth of the low-calcium margins into the augite matrix.

These data imply that exsolution of Opx lamellae from augite involves two separate steps after the initial nucleation event. The first step is the diffusion of calcium perpendicular to (100) and away from embryonic lamellae, presumed to have nucleated heterogeneously, and with concomitant diffusion of (magnesium and iron) to replace calcium. This initially produces Chp lamellae at least 200 to 300 Å wide. It is assumed that the calcium concentration would be highest at the margins and lowest in the center of these lamellae. The second step consists of glide-twinning inversion (polymorphic with little change in composition) to Opx by the lowest calcium clinopyroxene near the center of the lamellae. The stacking faults in the Opx are believed to represent relict planes where inversion has not occurred, because adjacent regions of Chp have inverted antiphase, and across which the stacking sequence remains locally characteristic of Chp. The strain-induced shear-transformation of Opx to clinopyroxene on (100) is well established (*6, 7*). The inversion from clinopyroxene to Opx invoked here, however, is related to the exsolution-cooling event and probably represents transformation to a less energetic state. The experimental shear-transformation of Opx to clinopyroxene has been reversed by the annealing of deformed natural materials (*6*) but required temperatures much greater (~ 1000°C) than those needed for the formation of the host augite in this study.

Growth of the lamellae occurs by further diffusion of calcium normal to (100), and thus the process is related to exsolution by simple nucleation and growth. As the leading edges of the low-calcium margins advance into the augite matrix, there occurs the inversion of the trailing edges, which are poorer in calcium than the leading edges. By this process, the margins maintain approximately constant width and the widest lamellae appear to consist entirely of Opx. If lamellar growth continued for an indefinite period, this process would generate optically detectable Opx lamellae with Chp margins remaining suboptical.

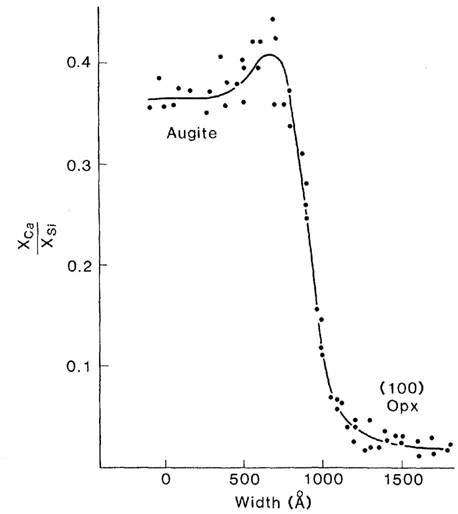

Fig. 2. Concentration profile for calcium relative to silicon across the (100) lamellar interface.

Similar low-calcium Chp margins adjacent to Opx lamellae in augite have been observed in another study but were not interpreted (*8*). The small size of the Chp margins makes them difficult to detect, even with CTEM. This difficulty must in part account for the small number of reported occurrences. However, if the process described above occurs at high temperatures (for example, ≳ 1000°C), high rates of diffusion and inversion could result in Chp margins of negligible thickness. In the limit, the two-step process would approach a single step. For these reasons, we suggest that two-step Opx exsolution in augite may be universal.

Petrologic data (*2*) imply that the Opx exsolution event in these rocks occurred during the waning stages of retrograde metamorphism and continued to the lowest temperature at which activation energies for the process could be exceeded. We envision the diffusion-transformation process to have extended over a wide temperature range, with the textures preserved because of a lack of subsequent annealing. The separate energy barrier for nucleation of the initial Chp in augite and the activation energies for lamellar growth by diffusion and subsequent glide transformation to Opx may be significantly less than that for a one-stage exsolution process. This relation may explain why the process apparently continued to relatively low temperatures, where it was preserved.

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Are Ions Involved in the Gating of Calcium Channels?

Abstract. *The rates of activation and deactivation of the currents carried by calcium, strontium, or barium ions through the voltage-sensitive calcium channel of* Paramecium *are different. The differences cannot be attributed to complications due to internal ion concentration, calcium channel inactivation, potassium current activation, surface charge effects, or incomplete space clamping. The findings indicate participation of the divalent cations in the voltage-driven calcium channel gating process.*

Gating, the opening or closing of a voltage-sensitive ion channel, has been viewed as a multistep process corresponding to changes in the conformation or aggregation of the channel molecules. Movements of charges or dipoles correlated with gating by sudden changes in voltage have been measured (*1*). The kinetics of gating must be a reflection of the energy profile traversed by the charges or dipoles. For a given channel, the gating mechanism has been considered to be governed only by the transmembrane voltage and not to be dependent on ions. While the kinetics of inactivation (the fall of current during a voltage step) has been found to be affected by ions in certain calcium, potassium, and sodium channels (*2–4*), the kinetics of activation (the rise of current upon

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