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Phase transitions in calcic plagioclase: A correction and further discussion

TIMOTHY L. GROVE
Department of Earth, Atmospheric and Planetary Sciences,
Massachusetts Institute of Technology, Cambridge, Massachusetts 02139
JOHN M. FERRY
Department of Earth and Planetary Sciences, Johns Hopkins University,
Baltimore, Maryland 21218
FRANK S. SPEAR
Department of Geology, Rensselaer Polytechnic Institute, Troy, New York 12181

CORRECTION AND CLARIFICATION

The subsolidus phase diagram we proposed for plagioclase feldspars (Grove et al., 1983) contains an error in the placement of the $I\bar{1} \rightarrow P\bar{1}$ transition which requires correction. X-ray diffraction heating experiments performed on anorthite at 1 atm show that the diffractions related to $P\bar{1}$ symmetry lose intensity above 230–250°C. We assumed that the persistence of these weak diffractions in experiments performed at temperatures >800°C were significant (Czank, 1973; Foit and Peacor, 1973), and we interpreted them as evidence that anorthite had not transformed completely to $I\bar{1}$ symmetry at this temperature. Adlhart et al. (1980a, 1980b) interpreted the diffuse intensity that remains above 240°C in terms of dynamically coupled vibrations of domains in the high-temperature $I\bar{1}$ phase. Ghose et al. (1983) interpreted neutron-diffraction data obtained at 280°C (~30°C above the $I\bar{1} \rightarrow P\bar{1}$ transition) with a dynamic model in which coexisting domains of $P\bar{1}$ and $I\bar{1}$ are present in the crystal. Both models are consistent with the existence of some $P\bar{1}$-like regions at temperatures >250°C. It is possible that the $I\bar{1} \rightarrow P\bar{1}$ transition requires some change in the tetrahedral site occupancy which may not be achieved on the time scale of the heating experiments. If a higher-order phase transition contains contributions both from atomic displacements and site ordering, the displacive part of the transition may occur at a temperature that varies as a function of the value of the atomic-site ordering parameter. When the site ordering approaches that of the high-temperature form, the transition proceeds at its equilibrium temperature (Landau and Lifschitz, 1958). The transition temperature measured in a crystal that retains an atomic-site distribution of the low-symmetry form could be higher or lower than the equilibrium temperature. In the case of the $I\bar{1} \rightarrow P\bar{1}$ transition in anorthite, the effect of variations in the value of the order parameter is not known, but it is likely that the temperature effect is not significant. The observed transition temperature at 1 atm, therefore, is near 250°C.

We incorrectly placed the $I\bar{1} \rightarrow P\bar{1}$ transition at 850°C. A corrected diagram (Fig. 1) shows the temperature of $I\bar{1} \rightarrow P\bar{1}$ at 250°C for anorthite and shows the position of a tricritical point and conditional spinodal associated with this transition for $P = 1$ atm.

IMPLICATIONS

Our corrected diagram shows that there could be tricritical phenomena associated with the $I\bar{1} \rightarrow P\bar{1}$ transition. Although there may be a decomposition reaction conditional on the ordering to $P\bar{1}$, it is likely that it will occur at temperatures much lower than those proposed by Grove et al. (1983), and some of the interpretations made by Grove et al. (1983) require revision. We suggested that a conditional spinodal associated with the $I\bar{1} \rightarrow P\bar{1}$ transition was responsible for the formation of Huttenlocher intergrowths (An_{66}–An_{87}). If the Huttenlocher intergrowths were associated with phase decomposition below a $I\bar{1} \rightarrow P\bar{1}$ tricritical point, they must develop at temperatures below 200°C. At such low temperatures, CaAl-NaSi interdiffusion rates are very slow (Grove et al., 1984; Yund, 1986), and estimated times required to form 100-Å lamellae exceed the age of the solar system. CaAl-NaSi interdiffusion rates are consistent with the formation of Huttenlocher

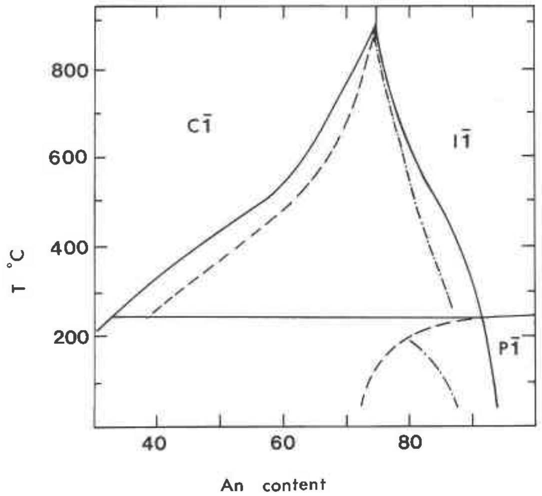

Fig. 1. A correction of the proposed temperature vs. composition diagram for the calcic portion of the system albite-anorthite at $P = 1$ atm. This diagram differs from Fig. 8 of Grove et al. (1983) in the placement of the $I\bar{1} \rightarrow P\bar{1}$ transition at ~250°C for anorthite and in the movement of the spinodal on the $I\bar{1}$ free-energy curve to more calcic compositions.

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lamellae at temperatures of about 550–650°C. Therefore, it is likely that the coexisting plagioclases that make up Huttenlocher intergrowths are not formed by decomposition within the conditional spinodal associated with the $I\bar{1} \rightarrow P\bar{1}$ transition.

There are several alternative mechanisms that could produce Huttenlocher intergrowths. (1) The intergrowths could result from unmixing related to the $C\bar{1} \rightarrow I\bar{1}$ conditional spinodal which occurs at $T \approx 500$–650°C. Because CaAl-NaSi interdiffusion is slow in this temperature range, spinodal decomposition could be incomplete, and the lamellae might never reach the compositions implied by the $C\bar{1} \rightarrow I\bar{1}$ gap. The same argument of partial decomposition could explain the occurrence of the Bøggild gap (An_{45}–An_{55}) on the other side of the $C\bar{1}$-$I\bar{1}$ two-phase region. The spinode and the metastable extension of the $C\bar{1} \rightarrow I\bar{1}$ ordering transition have been appropriately revised in Figure 1.

(2) A composition gap may arise from the development of the stable ordered periodic antiphase structure in An_{33}–An_{75} plagioclase. Decomposition of calcic plagioclase to coexisting intermediate plagioclase (An_{66}) and $I\bar{1}$ plagioclase (An_{87}) creates the Huttenlocher gap.

(3) The $I\bar{1} \rightarrow P\bar{1}$ transition may be pressure sensitive, and the $P\bar{1}$ form is stable at higher temperatures at the crustal-level pressures under which Huttenlocher lamellae develop in metamorphic rocks. The displacive characteristics of the $I\bar{1} \rightarrow P\bar{1}$ transitions are similar to those of polyhedral tilt transitions. The $I\bar{1}$ structure is a high-symmetry, less-distorted form stable at high temperature and/or low pressure and the $P\bar{1}$ structure a low-symmetry, distorted structure stable at low temperature and/or high pressure (Hazen and Finger, 1979). Increasing pressure should stabilize the low-symmetry distorted $P\bar{1}$ form to higher temperatures. Huttenlocher intergrowths could result from unmixing related to the $I\bar{1} \rightarrow P\bar{1}$ conditional spinodal stabilized to high temperatures (>500°C) by elevated pressures attained during regional metamorphism. Whether the $I\bar{1} \rightarrow P\bar{1}$ transition in anorthite is pressure dependent is unknown; even if pressure dependence were proved, it may be quite small. The pressure dependence could be measured directly at elevated pressures and temperatures, as it has been for other polyhedral tilt transitions in framework silicates, such as the high–low quartz (Cohen et al., 1974) and sanidine–microcline (Hazen, 1976) transitions. The pressure dependence could also be estimated if thermal expansion coefficients, specific heat, and elastic compliances for anorthite were well known at 1 atm near the transition temperature.

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