

Fig. 7. Formation of corundum (C) and liquid (G) along grain boundaries and defects of kyanite (K) crystals at 38 kbars and 1950°C for 10 minutes. (Etched 2 minutes in 1% HF, bright field, $\times 300$.)

phase assemblages in this system was based on the direction of the reaction as determined from the runs with different starting materials. In this respect the gradient effects described in the foregoing were useful because the effect of temperature at constant pressure could be observed directly.

The tables list the phases present in the center of the cell if the sample was homogeneous except for a thin outer rim. In addition, by comparing runs made under the same pressure-temperature conditions but for different times, it was usually possible to tell which phases were disappearing. The boundary curves as shown define regions of marked changes in phase assemblages, and although some discrepancies were found, the overall reproducibility is considered to be good in view of the experimental difficulties.

In Figs. 3 through 6 the kyanite-sillimanite boundary curve determined by Clark *et al.*^{1,2} below 30,000 bars and 1500°C and their less-certain sillimanite-mullite plus quartz boundary is included for comparison. The new data have resulted in an extension of the earlier studies to higher temperatures and pressures. The interpretation of the data requires some explanation and qualification.

(2) Mullite-Sillimanite Problem

Throughout the text "sillimanite" is written with a question mark to indicate uncertainty regarding the identification in quenched runs. This means a sillimanite- or mullitelike phase which is reproducible and has a primary-phase region on the pressure-temperature plane under consideration, but because the relations with mullite and sillimanite were considered to be beyond the scope of this investigation, a more positive identification was not made.

(3) Comparison of Kyanite and Gel Results

The similarity of the kyanite decomposition curve and the curve determined by the synthesis of kyanite from a gel is seen by comparing Figs. 3 and 4. The points on the figures indicate the actual phase assemblage (usually nonequilibrium) in accordance with the tables, but the stability regions are labeled in terms of an equilibrium representing the incongruent melting of kyanite to form corundum plus glass. This trend was clear from a study of the phases present in different parts of the cell because of the temperature gradient effects

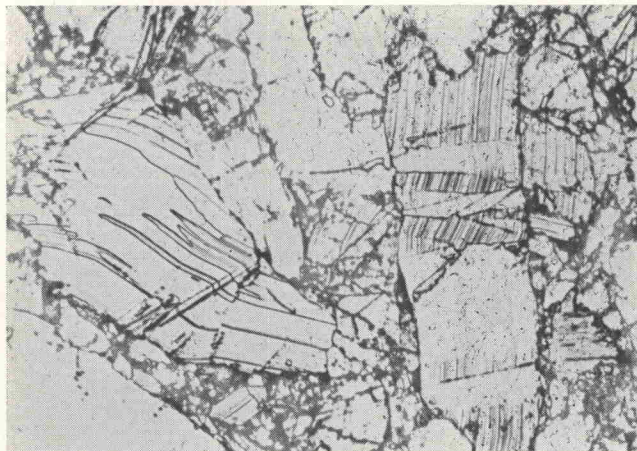


Fig. 8. Slip and kink patterns in kyanite after pressing at 28.5 kbars and 1500°C for 8 minutes. (Etched 10 minutes in H₃PO₄, bright field, $\times 390$.)

and from the amounts of phases as a function of time. A corundum plus liquid region is considered to be an equilibrium situation on the Al₂SiO₅ plane, but the exact equilibrium curve for the kyanite decomposition is uncertain.

The first evidence of kyanite decomposition was the formation of corundum plus liquid (quenched to a glass) at the grain boundaries (Fig. 7), and the decomposition was determined on the basis of the first appearance of these phases. It was important to look for this evidence in an as-polished section, as well as in etched sections, since the etchant attacked the glass preferentially, so that corundum could be almost completely removed from the surface merely by solution of its glass binder. The number and size of the corundum crystals increased with temperature at constant pressure.

By etching a kyanite sample with H₃PO₄, the complex slip and "kinking" structure which developed when kyanite was deformed could be revealed (Fig. 8). A considerable amount of crushing took place at the grain contacts, and it was the resulting fine-grained material which apparently reacted readily to form corundum plus glass. The reaction then proceeded inward from the grain boundaries, and from the etching behavior there was some evidence that the reaction proceeded faster along kink lines. The slip-kink microstructure was characteristic of deforming kyanite alone without much decomposition to other phases. If enough liquid formed so that more hydrostatic conditions prevailed in the cell, the complex structure was not seen.

Kyanite synthesized from a gel was euhedral and free from internal slip or twinning structures, but it always contained corundum as an inclusion (Fig. 9). Above 1400°C the results obtained with the gel mixture were quite straightforward. The first appearance of kyanite was easily recognized, and this was taken as evidence for being in the kyanite phase region even though not all the mixture had been converted. The idea of using both a gel (a disordered starting material) and the ordered starting material kyanite was to approach the reaction from two different directions to establish equilibrium. The evidence from the polished sections of kyanite decomposition suggests, however, that some caution in this approach is necessary in this case since the fine-grained crushed kyanite and the structure at the slip plane may represent an intermediate degree of disorder and may contribute to the metastable formation of corundum. The growth of both large and small crystals of kyanite (seemingly independent of temperature gradients) suggests that the gel may be less homogeneous than thought. Because of these complications the agreement between the kyanite and gel data is thought to be fortuitous.



Fig. 9. Kyanite formed from gel at 41.5 kbars and 1450°C for 35 minutes. The inclusions are corundum. The matrix is composed of corundum, kyanite, and glass. (As polished, bright field, $\times 500$.)

The formation of sillimanite (?) plus corundum plus glass from kyanite is shown in Fig. 10. Corundum appeared to have formed early in the decomposition and was then enclosed by the other phases as they nucleated and grew.

(4) Comparison of Sillimanite and Andalusite Results

The results with sillimanite defined quite sharply a boundary between a kyanite field (drawn on the basis of the first appearance of this phase) and a corundum plus glass region. On the basis of the trend of the reaction in the hotter parts of the cell, i.e., corundum crystals growing (not disappearing) at higher temperatures, it is concluded that corundum plus liquid is an equilibrium assemblage. The crenulated borders

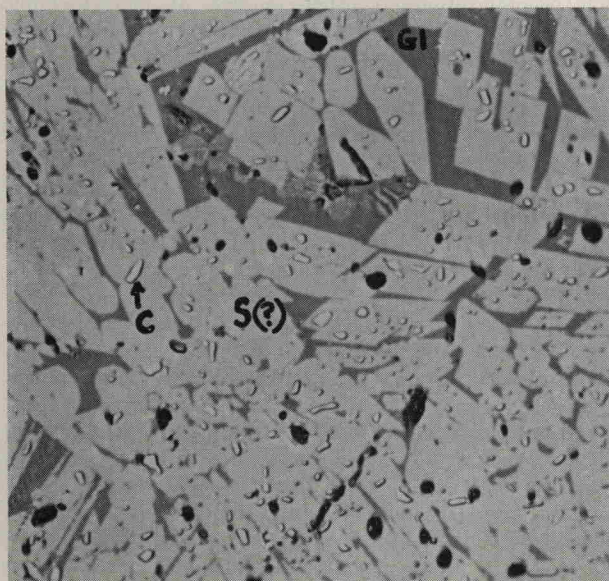


Fig. 10. Sillimanite (?) with included corundum in glass at 28.5 kbars and 1850°C for 4 minutes. (As polished, bright field, $\times 500$.)

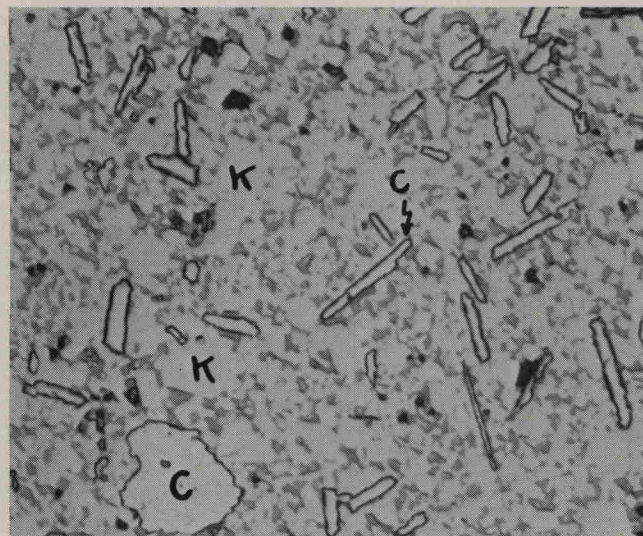


Fig. 11. Kyanite with corundum plus glass from sillimanite at 54 kbars and 1850°C for 3 minutes. Crenulated borders of the corundum needles and plates indicate that corundum is dissolving. (As polished, bright field, $\times 500$.)

of corundum crystals in a kyanite-glass matrix in the cooler portion of the cell were considered to be good evidence for the incomplete solution of corundum (Fig. 11); or, in other words, corundum was disappearing in the lower-temperature region.

For the andalusite runs the kyanite stability region was easily delineated from a region where sillimanite (?) was a persistent phase along with corundum and glass. The trend of the reaction to corundum and liquid was obvious, however, in the outer rim of the runs. The kyanite decomposition boundary was nearly the same for both sillimanite and andalusite as starting materials but differed considerably from the results for the kyanite and the gel. With both sillimanite and andalusite, kyanite was formed in a pressure-temperature region which would be unstable for this phase on the basis of the results for the kyanite and the gel. Further discussion of the anomaly is given later.

When kyanite was formed from sillimanite and andalusite, a microstructure with grain boundaries typical of a dense sintered compact was found (effectively a high-density, hot-pressed kyanite body) and the internal grain structure as revealed by etching was simpler and looked more like growth twinning than the slip-kink structure, suggesting little or no shearing. The rate of conversion to kyanite was very high and the amount converted was also high compared with runs with the gel mixture.

IV. Discussion

It was shown in the foregoing that by using the three forms of Al_2SiO_5 and $Al_2O_3:SiO_2$ gel as starting materials, corundum was a persistent phase in most of the runs. Clark *et al.*^{1,2} described the same problem (plus the formation of quartz) in their runs and concluded that both corundum and quartz were metastable in their experiments. In the present work the observation of the solution of corundum crystals provides experimental confirmation for that conclusion for corundum in the stability region shown for kyanite in Fig. 6.

On the basis of the sillimanite and andalusite data, the pressure-temperature curves obtained from the gel mixture and from kyanite are judged to represent the metastable formation of corundum. The sharp and relatively complete conversion of andalusite and sillimanite to kyanite, the stability of this kyanite until the temperature was increased, and the growth of corundum crystals with time at the higher temperatures lead to the interpretation that an equilibrium region