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The System Al_2SiO_5 at High Temperatures and Pressures

by R. C. DeVRIES

Research Laboratory, General Electric Company, Schenectady, New York

Experiments on the system Al_2SiO_5 at high temperatures and pressures with the belt apparatus indicate that kyanite melts incongruently above about 1500°C at 25,000 bars to Al_2O_3 (corundum) plus liquid. The pressure-temperature curves obtained by starting with either a 1/1 $\text{Al}_2\text{O}_3/\text{SiO}_2$ gel or with kyanite are essentially identical but differ considerably from the results with andalusite and sillimanite. The structure of the starting material has considerable influence on the kinetics of the reaction and the metastable formation of corundum in this system. An "equilibrium" curve based on the andalusite-sillimanite data is described by $P = 33.8 \times 10^{-3} T - 26.4$ (P in kbars, T in $^\circ\text{C}$).

I. Introduction

THE geological significance of pressure-temperature relations among the three forms of Al_2SiO_5 (sillimanite, andalusite, and kyanite) has stimulated several experimental investigations. The kyanite-sillimanite relations up to 1500°C and 30,000 bars have been determined by Clark.

Robertson, and Birch¹ and have been redetermined by Clark.² Kennedy³ and Griggs and Kennedy⁴ have published studies related to the same problem. The synthesis of andalusite

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At the time this work was done, the writer was mineralogist, Ceramic Studies Section, Metallurgy and Ceramics Research Department, Research Laboratory, General Electric Company. He is now associate professor, Department of Materials Engineering, Rensselaer Polytechnic Institute, Troy, N. Y.

¹ S. P. Clark, Jr., E. C. Robertson, and Francis Birch, "Experimental Determination of Kyanite-Sillimanite Equilibrium Relations at High Temperatures and Pressures," *Am. J. Sci.*, **255** [9] 628-40 (1957).

² S. P. Clark, Jr., "Redetermination of Equilibrium Relations Between Kyanite and Sillimanite," *Am. J. Sci.*, **259** [9] 641-50 (1961); *Ceram. Abstr.*, 1962, June, p. 153i.

³ G. C. Kennedy, "Pyrophyllite-Sillimanite-Mullite Equilibrium Relations to 20,000 Bars and 800°C ," *Bull. Geol. Soc. Am.*, **66**, 1584 (November 1955) (abstract).

⁴ D. T. Griggs and G. C. Kennedy, "Simple Apparatus for High Pressures and Temperatures," *Am. J. Sci.*, **254** [12] 722-35 (1956).

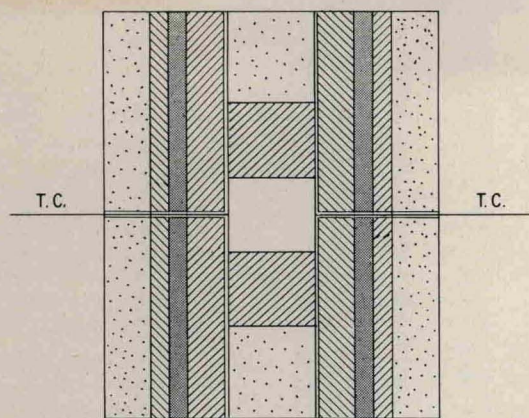


Fig. 1. High-pressure chamber. Light stippling is massive pyrophyllite (lava), crosshatched areas are alumina, and the heavy stippling is the graphite heater. Sample at the center is enclosed in Pt foil. Thermocouple wires pass through the cell in protection tubing (not shown). ($\times 50$)

by hydrothermal techniques was first reported by Roy,⁵ but later details have shown that this phase is not identical with natural andalusite.⁶ In addition, two phase diagrams based on deductions from field observations and other considerations have been published.^{7,8} As yet the phase relations of the three varieties of Al_2SiO_5 are not completely understood and more data are needed in both moderate pressure-temperature regions and higher pressure-temperature regions (e.g., above 30,000 bars and 1500°C) where the interest may be less geological and more exploratory in its emphasis.

It is the higher pressure-temperature region which was chosen for further study because of curiosity about the decomposition of kyanite at high pressures and temperatures as compared with its decomposition to mullite and quartz at 1 atm. The latter reaction is accompanied by a 21% increase in volume. By comparison, a 5% increase in volume would result from the formation of corundum and coesite from kyanite.

II. Experimental

(1) High-Pressure Equipment

An Elmes 300-ton hobbing press was adapted for experimental use.^{9,10} The belt apparatus and the basic chamber design were the same as those which have been described by several investigators.⁹⁻¹¹ The particular cell used in the present study is shown in Fig. 1. The internal resistance heater was a sleeve of graphite for most runs, although Ni or Pt heaters were used occasionally.

The material to be run was placed in a tube made from 0.0005-in. foil of Pt or 80Pt20Rh. The amount of foil and the amount of sample material used in each run was kept constant. The cylindrical sample after pressing was about 1.5 mm high.

(2) Pressure Measurement

Bourdon-type gages were used to measure oil pressure in pounds per square inch on the ram. The gages were calibrated in terms of pressure in the chamber, measuring the resistance change at the Bi and Ba phase transformations at room temperature at 25,300 and 59,000 bars, respectively.* The gages were calibrated several times during the investigation. On the basis of other experience with the belt equipment, the uncertainty of the pressure measurement is considered to be ± 2000 bars. There are some qualifications which should be considered: (1) The calibration was made at room temperature only and (2) the assumption was made that the pressure was transmitted hydrostatically.

In the more usual calibration procedure with the belt a piece of calibration wire is embedded in an AgCl sleeve which is surrounded by pyrophyllite. The flow properties of AgCl presumably result in a more hydrostatic distribution of pressure. Since the actual runs are in Al_2O_3 sleeves, which on a structural basis would be expected to have more limited flow compared with AgCl, calibration runs were also made by embedding the wire in Al_2O_3 . Within the limits of error of measurement the phase transformations in Bi and Ba took place at the same pressure as in the pyrophyllite-AgCl cell.

At high temperatures the reaction within the pyrophyllite results in different crystalline phases plus liquid (or glass) so that the pressure-transmitting properties change. Some assurance of the reproducibility of the pressure measurement at high temperatures was gained by reasonably good agreement with the melting of Pt as a function of temperature.¹¹

Pressure was automatically controlled during a run by means of a Bristol pressure controller-recorder.

(3) Temperature Measurement

A power-vs.-temperature plot was first determined for each type of cell and heater by making several runs with a thermocouple in the cell shown in Fig. 1. The thermocouple was insulated from the rest of the cell by alumina thermocouple tubing. The Pt foil of the sample container completed the circuit between the two dissimilar wires so that the junction was at one side of the cell. The reproducibility of the runs with thermocouples was found to be no larger than $\pm 50^\circ C$ and in general was closer to $\pm 25^\circ C$ in the range over which more data were collected (25,000 to 40,000 bars). No correction was made for the small change in emf as a function of pressure. In the figures summarizing the data, an overall uncertainty of $\pm 75^\circ C$ for the temperature measurement is shown.

After the power-temperature curves were determined, most runs were made without thermocouples. In this way considerable time was saved without appreciable sacrifice in accuracy. The temperature was hand-controlled with a variable transformer.

(4) Other Observations Relating to Accuracy of Data

It was found in the earlier runs that rather steep temperature gradients existed lengthwise in the pressure chamber. If the final length of the sample was of the order of 3 mm, it was obvious from macroscopic examination that the ends had been

⁵ D. M. Roy, "Hydrothermal Synthesis of Andalusite," *Am. Mineralogist*, **39** [1/2] 140-43 (1954); *Ceram. Abstr.*, 1956, September, p. 201a.

⁶ Shigeo Aramaki and Rustum Roy, "Revised Phase Diagram for the System Al_2O_3 - SiO_2 ," *J. Am. Ceram. Soc.*, **45** [5] 229-42 (1962).

⁷ Akiho Miyashiro, "Stability Relations of Kyanite, Sillimanite, and Andalusite, and the Physical Conditions of Metamorphic Processes," *J. Geol. Soc. Japan*, **55**, 218-23 (1949).

⁸ J. B. Thompson, Jr., "Thermodynamic Basis for Mineral Facies Concept," *Am. J. Sci.*, **253**, 65-103 (February 1955); *Ceram. Abstr.*, 1957, October, p. 259e.

⁹ H. T. Hall, "Ultra-High-Pressure, High-Temperature Apparatus: The 'Belt,'" *Rev. Sci. Instr.*, **31** [2] 125-31 (1960).

¹⁰ H. P. Bovenkerk, F. P. Bundy, H. T. Hall, H. M. Strong, and R. H. Wentorf, Jr., "Preparation of Diamond," *Nature*, **184**, [4693] 1094-98 (1959).

¹¹ H. M. Strong and F. P. Bundy, "Fusion Curves of Four Group VIII Metals to 100,000 Atmospheres," *Phys. Rev.*, **115** [2] 278-84 (1959).

* When this work was done, the pressure calibration was based on the Bi I-II and the Ba II-III transformations at 24.8 and 77.4 kbars, respectively. Since that time new values for these transitions and others have received greater acceptance (25.3 and 59, respectively; see G. C. Kennedy and P. N. LaMori, pp. 304-13 in *Progress in Very High Pressure Research* (Lake George Conference), John Wiley & Sons, Inc., New York, 1961) and the data have been replotted on the basis of the new calibration.

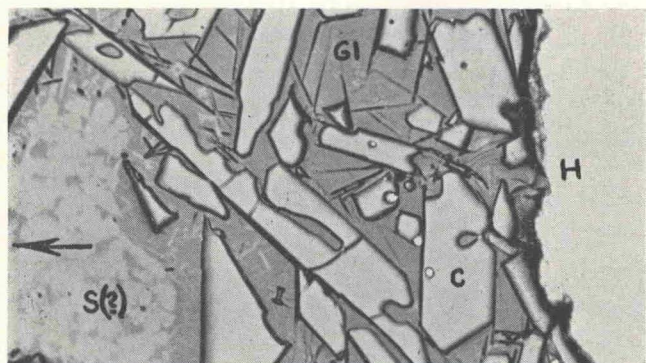


Fig. 2. Effect of temperature gradient across sample. (C) Corundum, (S) sillimanite (?), (G) glass, and (H) higher-temperature side near the heater. Arrow indicates direction to center of cell. (As polished, bright field, $\times 390$.)

considerably cooler than the center. This problem was essentially eliminated by packing so that the final height was about 1.5 mm.

The effects of a less severe gradient across the cell were sometimes seen. In Fig. 2, the part of the sample nearest the heater was hot enough to form corundum, whereas the center of the same run contained only sillimanite (?).^{*} It should be emphasized that the gradient effects were not necessarily detrimental but were very useful and were given considerable weight in interpreting the direction of the reaction at higher temperatures and constant pressure.

(5) Procedure During a Run

All the data were obtained on runs made by first raising the pressure to the desired value and then raising the temperature. The heating rate was about 400°C per minute. At the end of a run, the power to the heater was turned off and the pressure was maintained. The punches and the belt were water-cooled and the sample reached a temperature of 25° to 100°C in about 30 seconds. The pressure was then released and the sample removed.

(6) Starting Materials

The principal starting materials used for the experiments were kyanite from Minas Gerais, Brazil; sillimanite from Idaho and from Dillon, Montana; andalusite from Minas Gerais; and a synthetic $\text{Al}_2\text{O}_3\text{:SiO}_2$ gel. The chemical compositions of these materials are as follows:

Starting material	Wet chemical analysis (wt%)		Remarks
	Al_2O_3	SiO_2	
Kyanite*	62.8	37.4	Blue crystals
Sillimanite	62.8	37.4	White, fibrous, massive
Andalusite	63.4	36.4	Green single crystal
Gel	64.0	36.0	
Theoretical	62.9	37.1	

* Less than 0.2% Fe by X-ray emission analysis.

A few crystals or groups of crystals of kyanite and sillimanite were selected and washed free of external material, if present, and then broken into coarse fragments. From these, clean pieces were selected by handpicking with tweezers under a microscope at $\times 30$. These fragments were then crushed in an alumina mortar and sized by sieving; most of the experiments were with a 50 μ fraction. The homogeneity of the crushed kyanite samples was checked by observation at $\times 500$ in a 1.70 immersion liquid; the kyanite was found to be free of second phases within the resolution of this technique.

The synthetic $\text{Al}_2\text{O}_3\text{:SiO}_2$ gel was made by dissolving the proper amounts of $\text{Al}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$ and ethyl orthosilicate in ethyl alcohol and hydrolyzing to form a gel. The gel was decomposed slowly at 120°C and then heated to 500°C to form an amorphous mixture.

(7) Identification of Phases

The quenched runs were split into two parts along a plane perpendicular to the axis of the cylindrical samples. One half of the sample was crushed and used for transmitted-light observations and for X-ray analysis. The other half was polished and etched on the surface which exposed approximately the center of the sample. Normal metallographic techniques were used for polishing and etching, and a Bausch & Lomb metallograph was used for reflected-light observations. The usual etchant was a 1% HF solution, but to reveal the structural detail in kyanite it was found necessary to etch for about 10 minutes in H_3PO_4 at about 240°C. After identification by the usual optical and X-ray techniques, it was found that the reflected-light observations on polished sections provided the most useful information on what actually was taking place during the run.

None of the techniques as employed here was adequate for the differentiation of sillimanite and mullite. The more careful X-ray approach recently described¹² was not attempted. No significant difference could be seen in the X-ray powder patterns of sillimanite and mullite. This problem is considered in more detail later.

The X-ray diffractometer patterns were obtained with nickel-filtered copper radiation at 2° 2 θ per minute and a chart speed of 0.4 in. per minute. As is often the case with crystals with a good cleavage, special precaution must be taken to avoid preferred orientation during the preparation of a slide of kyanite for an X-ray diffractometer pattern. Pertinent peaks showing intensity variations as a function of preferred orientation are found at 46°, 46.7°, 67.7°, and 69.7° 2 θ (Cu $K\alpha$). A slide with preferred orientation made by the settling of kyanite grains out of a liquid shows high-intensity peaks at 46° and 69.7° 2 θ and low-intensity peaks at 46.7° and 67.7°.

A more random orientation obtained by sprinkling kyanite grains onto a grease smear on a slide, or as found in the usual synthetic kyanite pattern in which grains are small and held in a more random arrangement by other phases, shows complete reversal of these intensities. Similar intensity reversals for natural and synthetic kyanite for the peaks between 45° and 47° 2 θ (Cu $K\alpha$) are seen in the patterns given by Clark *et al.*¹

III. Experimental Results

(1) General

The results of experiments in terms of each of the different starting materials are given in Tables I through IV[†] and shown graphically in Figs. 3 through 6.

An inspection of the data shows that most of the runs were of short duration (of the order of 2 to 45 minutes) and most of the results probably represent nonequilibrium conditions. The interpretation of what constitutes equilibrium

* The question mark after "sillimanite" throughout this paper indicates that the identification of this phase was doubtful, as discussed later.

¹² S. O. Agrell and J. V. Smith, "Cell Dimensions, Solid Solution, Polymorphism, and Identification of Mullite and Sillimanite," *J. Am. Ceram. Soc.*, **43** [2] 69-76 (1960).

[†] Tables I through IV have been deposited as Document No. 7865 with the ADI Auxiliary Publications Project, Photoduplication Service, Library of Congress, Washington 25, D. C. A copy may be secured by citing the document number and by remitting \$1.25 for photoprints or \$1.25 for 35-mm microfilm. Advance payment is required. Make checks or money orders payable to: Chief, Photoduplication Service, Library of Congress.

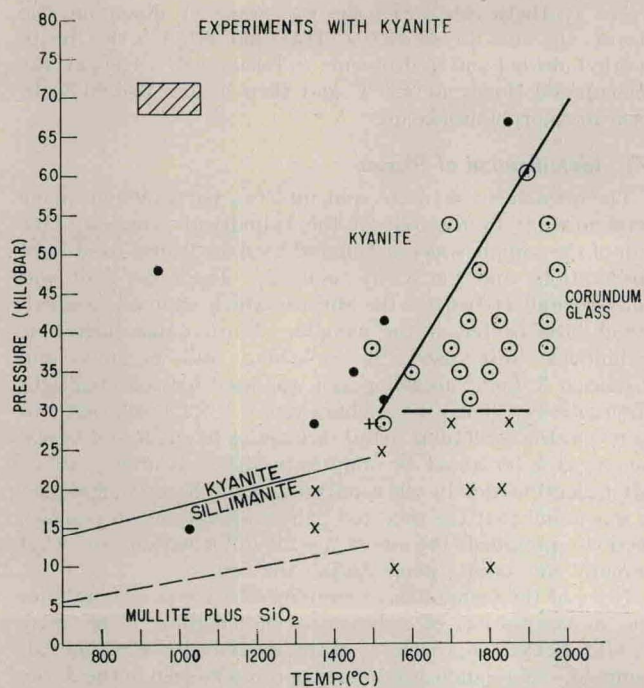


Fig. 3. Kyanite decomposition curve. Data for this figure are given in Table I. Primary-phase regions are labeled in this figure and in Figs. 4, 5, and 6 on the basis of an equilibrium assemblage as interpreted from the data. Symbols indicate actual nonequilibrium assemblages identified in the quenched runs as listed in the tables. Lighter lines are the results from footnotes 1 and 2. Rectangle defines uncertainty of pressure and temperature measurement associated with each point. ● = kyanite; ○ = kyanite, corundum, glass; × = sillimanite (?), corundum, glass; + = sillimanite (?), glass, kyanite.

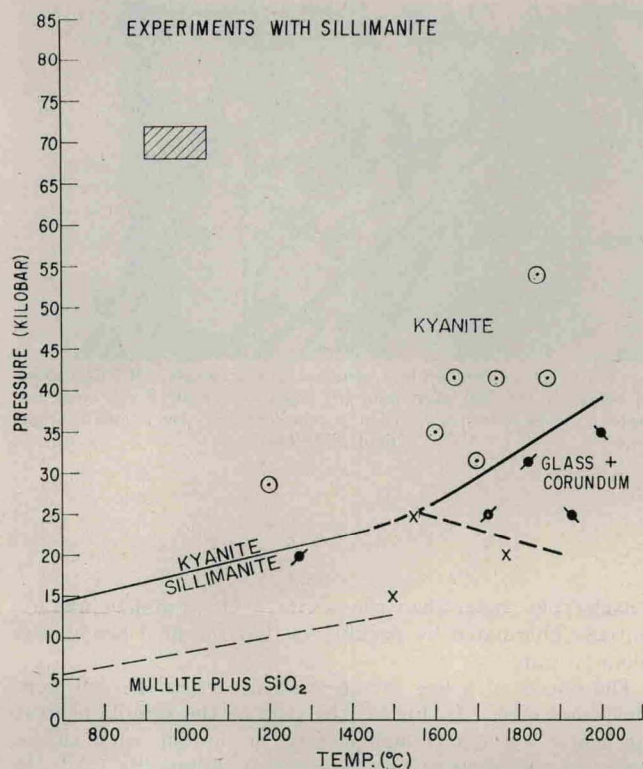


Fig. 5. Formation of kyanite from sillimanite. Data for this figure are given in Table III. ○ = kyanite, corundum, glass; ● = corundum, glass; × = sillimanite (?), corundum, glass; ● = glass, corundum, quartz.

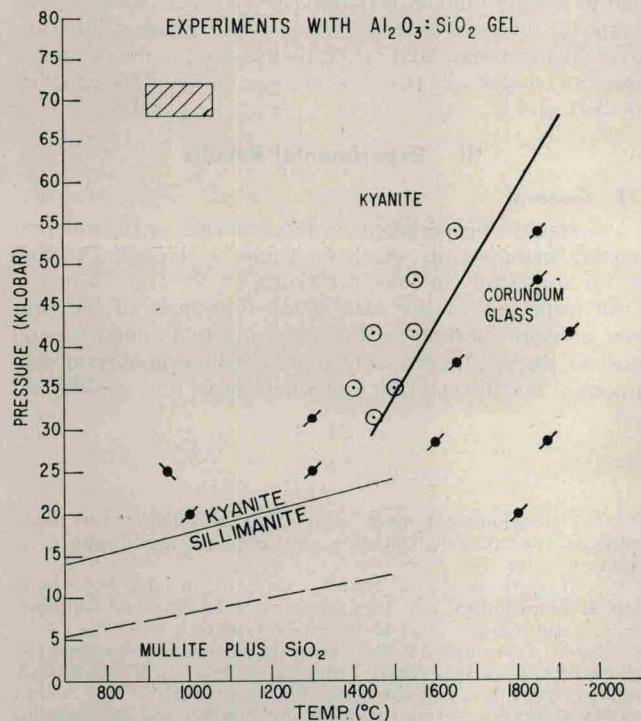


Fig. 4. Formation of kyanite from $Al_2O_3:SiO_2$ gel. Data for this figure are given in Table II. ○ = kyanite, corundum, glass; ● = corundum, glass; ● = corundum, quartz.

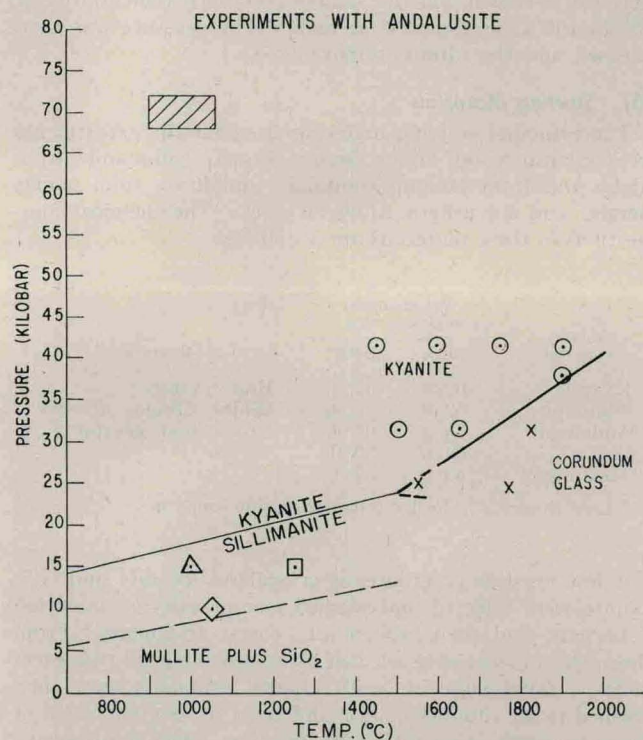


Fig. 6. Formation of kyanite from andalusite. Data for this figure are given in Table IV. ○ = kyanite, corundum, glass; × = sillimanite (?), corundum, glass; ◇ = andalusite; □ = sillimanite (?), corundum, quartz; △ = andalusite, corundum, quartz.

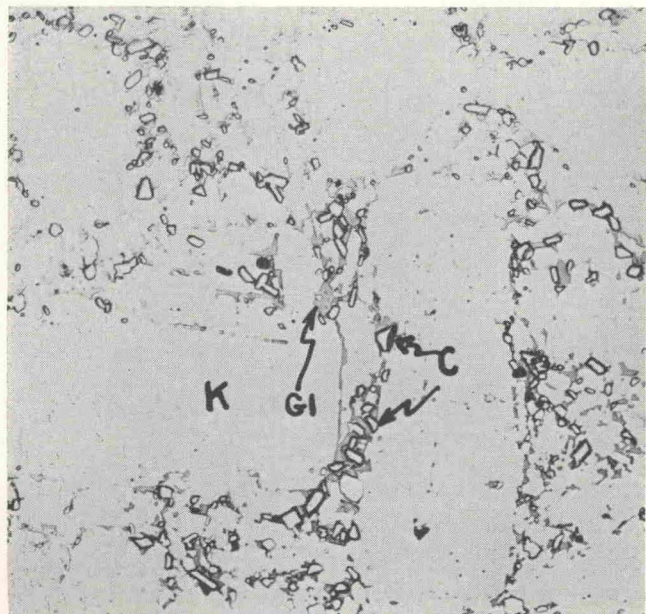


Fig. 7. Formation of corundum (C) and liquid (Gl) along grain boundaries and defects of kyanite (K) crystals at 38 kbars and 1950°C for 10 minutes. (Etched 2 minutes in 1% HF, bright field, $\times 300$.)

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

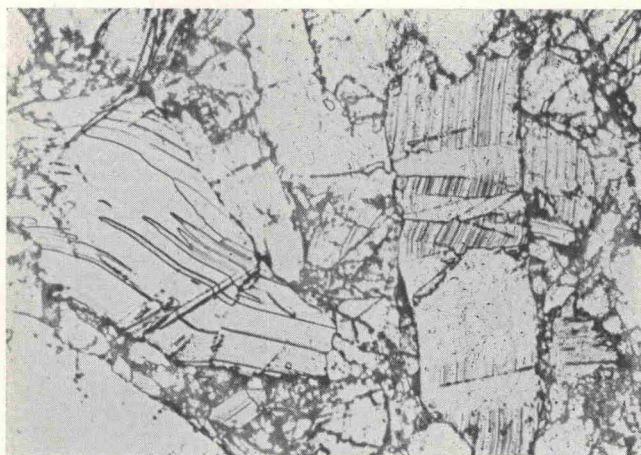


Fig. 8. Slip and kink patterns in kyanite after pressing at 28.5 kbars and 1500°C for 8 minutes. (Etched 10 minutes in H₃PO₄, bright field, $\times 390$.)

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

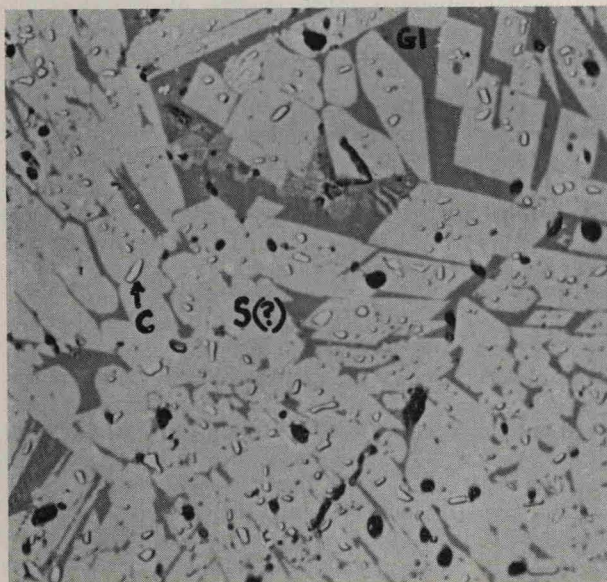


Fig. 10. Sillimanite (?) with included corundum in glass at 28.5 kbars and 1850°C for 4 minutes. (As polished, bright field, $\times 500$.)

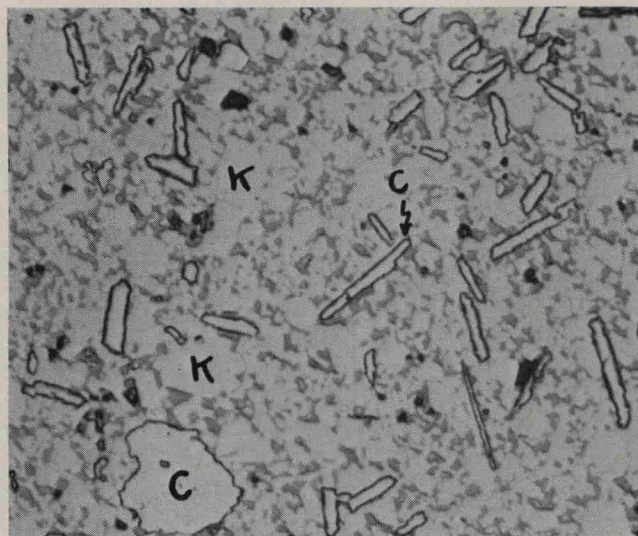


Fig. 11. Kyanite with corundum plus glass from sillimanite at 54 kbars and 1850°C for 3 minutes. Crenulated borders of the corundum needles and plates indicate that corundum is dissolving. (As polished, bright field, $\times 500$.)

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

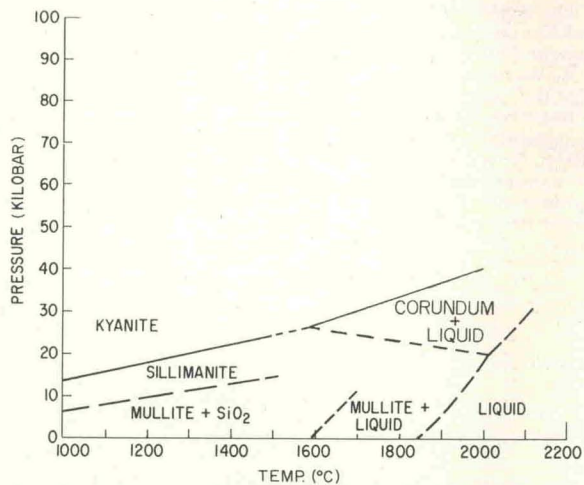


Fig. 12. "Equilibrium" diagram deduced from the data. Kyanite-sillimanite and sillimanite-mullite plus SiO_2 boundary from footnotes 1 and 2.

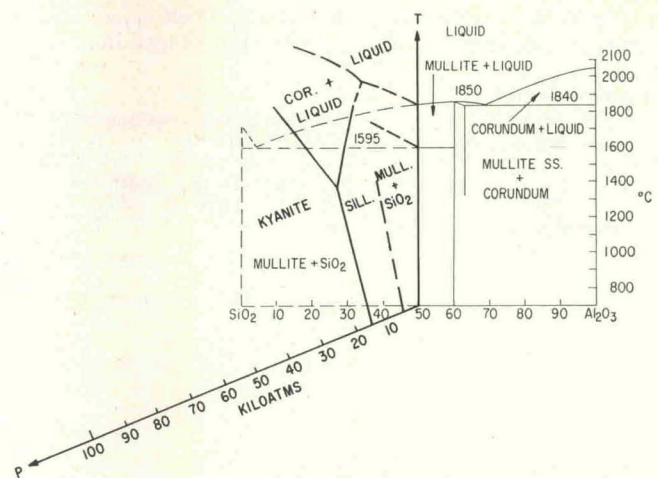


Fig. 13. Perspective drawing of the Al_2SiO_5 pressure-temperature plane showing relation of the Al_2O_3 - SiO_2 diagram at 1 bar. Kyanite decomposition boundary is that of the andalusite and sillimanite data. Data below 1500°C are from footnotes 1 and 2. The Al_2O_3 - SiO_2 diagram is from footnotes 6 and 13.

of corundum plus liquid exists and that the andalusite-sillimanite data are probably the better representations of the reaction. The rapidity and completeness of the formation of kyanite from andalusite and sillimanite as compared with the other starting materials emphasize the structural control imposed by the starting material.

An "equilibrium" diagram deduced from the andalusite-sillimanite data is shown separately in Fig. 12 and in relation to the latest version of the system Al_2O_3 - SiO_2 ,¹³ at 1 atm in Fig. 13. The interpretation of the new data resulted in pressure-temperature curves for the incongruent decomposition of kyanite and the sillimanitelike phase at high temperatures and pressures; the intersection of three boundary curves between the regions of kyanite, a sillimanitelike phase, and corundum plus liquid is shown near 1500°C and 25,000 bars.

(1) Possibility of Immiscibility

Directly related to the high pressure-temperature decomposition of kyanite and the appearance of corundum is the possibility of finding a two-liquid region under such conditions in the system Al_2O_3 - SiO_2 .

Such a region might exist if the increasing stability of AlO_6 groups found at high pressures in crystalline materials also existed in the liquid state for a silicate at high pressure. The systems Cr_2O_3 - SiO_2 , TiO_2 - SiO_2 , and Ga_2O_3 - SiO_2 all show extensive liquid immiscibility at high temperatures at 1 atm, as shown schematically in Fig. 14. In the first two of these systems a very stable sixfold coordination exists at 1 atm, and assuming stabilization of the sixfold coordination of Al^{3+} in the presence of Si^{4+} at high pressures the phenomenon of immiscibility might be expected. Although it was not observed, it should be pointed out that the large extension of the corundum plus liquid region with increasing pressure is not incompatible with the increasing stability of the sixfold coordination. On the basis of the index of refraction of the glasses in equilibrium with corundum in conjunction with the composition-index of refraction data,⁶ the liquid composition for several runs was found to be about 75% SiO_2 . The constancy of this composition for a variety of runs suggests a rather steep liquidus surface for the corundum plus liquid phase region. This also is compatible with a tendency toward dissociation in this system.

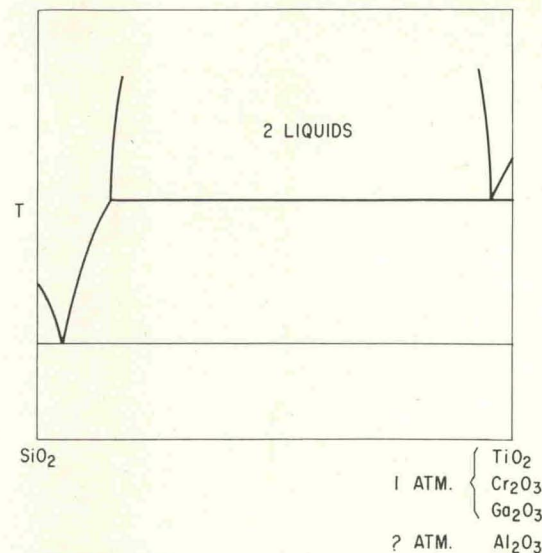


Fig. 14. Schematic representation of immiscibility characteristics of three oxides with SiO_2 at 1 bar and implied possibility for Al_2O_3 at high pressures.

V. Summary and Conclusions

From this investigation the following conclusions can be made:

(1) Above 1500°C and 25,000 bars kyanite decomposed incongruently to corundum plus liquid. From observations of the direction of the reaction from four different starting materials, corundum plus liquid is considered to be an equilibrium assemblage on the 1/1 Al_2O_3 / SiO_2 plane, but the exact equilibrium curve is somewhat uncertain.

(2) The widespread formation of corundum, particularly in runs with gel and with kyanite, was interpreted as being due to metastability which is related at least in part to the structure of the starting materials.

(3) There was no evidence for two-liquid separation on the 1/1 plane at high temperatures and pressures, although the metastable formation of corundum and the large extent of the corundum plus liquid region is not inconsistent with immiscibility.

(4) The use of polished and etched sections was very helpful in interpreting the direction of reactions, the deviations

¹³ Shigeo Aramaki and Rustum Roy, "Revised Equilibrium Diagram for the System Al_2O_3 - SiO_2 ," *Nature*, **184** [4686] 631-32 (1959); *Ceram. Abstr.*, 1960, July, p. 178f.

from ideal experimental conditions in the belt apparatus, and in noting differences in the microstructure of kyanite.

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Correction to the paper: "High Pressure Synthesis of PbCrO_3 " by
R. C. DeVries and W. L. Roth, J. Am. Cer. Soc., 51(2), 72-75
(1968)

The next to last sentence of the abstract is incorrect because octahedrally coordinated Cr^{4+} is well known in CrO_2 and recently has been found in SrCrO_3 [B.L. Chamberland, Solid State Communications, 5(8), 663-666 (1967)]. It was our intent to refer to mixed oxides containing octahedrally coordinated Cr^{4+} , a correct statement at the time our companion paper, Crystal and Magnetic Structure of PbCrO_3 , J. Appl. Phys., 38(3), 951-52 (1967), was written.

R. C. DeVries
W. L. Roth