

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

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.

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.

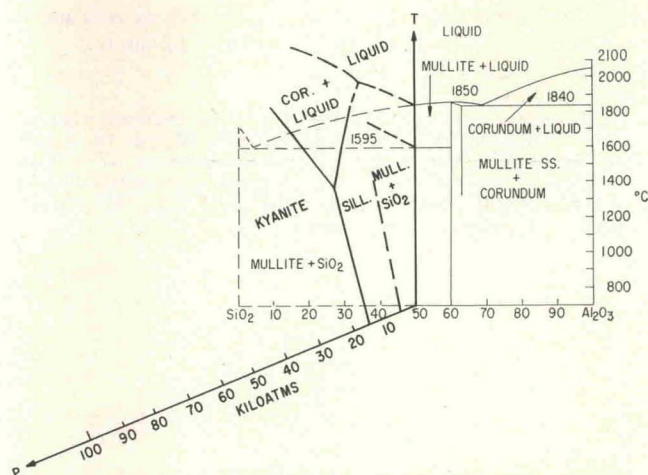


Fig. 13. Perspective drawing of the Al_2SiO_5 pressure-temperature plane showing relation of the Al_2O_3 - SiO_2 diagram at 1 bar. Kyanite decomposition boundary is that of the andalusite and sillimanite data. Data below 1500°C are from footnotes 1 and 2. The Al_2O_3 - SiO_2 diagram is from footnotes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

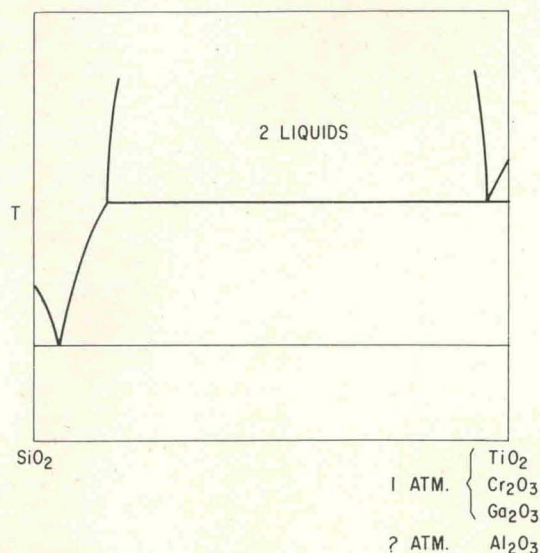


Fig. 14. Schematic representation of immiscibility characteristics of three oxides with SiO_2 at 1 bar and implied possibility for Al_2O_3 at high pressures.

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

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

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