

SYNTHESIS OF SOME ALUMINIUM SILICATES*

By R. M. CARR† and J. B. DIXON‡

Studies in the system $\text{Al}_2\text{O}_3\text{--}4\text{SiO}_2$ under hydrothermal conditions where three different starting materials (amorphous alumina-quartz, amorphous silica-kaolinite, quartz-kaolinite) were investigated in "pinched-tube" experiments¹ were followed by a redetermination in sealed-tube experiments of the synthesis fields obtained from amorphous silica-kaolinite and quartz-kaolinite.² A synthesis diagram for the starting material amorphous alumina-quartz has now been redetermined in sealed-tube experiments.

Experimental

The pressure equipment used is similar to that already described.² Modifications to the equipment, in the form of stellite test-tube bombs each coupled to a Bourdon pressure gauge and controlled with an Ether transistrol temperature regulator, enabled more effective control to be attained in some of the experiments. Errors in temperature control were within $\pm 1\%$ at all temperatures.

Quartz and amorphous (chromatographic) alumina were mixed in the molecular proportions $\text{Al}_2\text{O}_3, 4\text{SiO}_2$ and $\text{Al}_2\text{O}_3, 8\text{SiO}_2$. Samples together with water were placed in silver capsules and sealed. Runs commenced with rapid heating periods (e.g. from room temperature to 400° in 20 min) and were terminated with air quenching. Products were examined with a Philips X-ray diffractometer using filtered Cu radiation.

Results

A comparison of synthesis field boundary temperatures for pinched-tube and sealed-tube experiments with the starting material amorphous alumina-quartz is given in Table 1.

Minor amounts of boehmite were present in many low-temperature runs, indicating sluggish reaction between this phase and quartz.

Two decomposition experiments provided confirmation of the synthesis boundaries. Synthetic corundum heated at 490° under a hydrostatic pressure of 30000 lb/in^2 was partly altered to pyrophyllite, and kaolinite was obtained from synthetic pyrophyllite at 370° .

Discussion

The general pattern of phase relationships is similar to that obtained in pinched-tube experiments. No significant change was observed in the position of

* Manuscript received June 13, 1967.

† Chemistry Department, University of Otago, Dunedin, N.Z.

‡ Mineral Technology Department, University of Otago, Dunedin, N.Z.

¹ Carr, R. M., and Fyfe, W. S., *Geochim. cosmochim. Acta*, 1960, **21**, 99.

² Carr, R. M., *Geochim. cosmochim. Acta*, 1963, **27**, 133.

the kaolinite–pyrophyllite reaction boundary, but the position of the pyrophyllite–corundum reaction shows a displacement of about 45–50° toward higher temperatures.

Since the starting material contained readily soluble alumina and sparingly soluble silica, the more richly aluminous phases, viz. kaolinite and corundum, could be expected to be favoured at the expense of pyrophyllite. This conclusion is not supported by observations on the kaolinite–pyrophyllite boundary and is in contradiction with the observed expansion of the pyrophyllite field to higher temperatures. This apparently anomalous behaviour is probably due to the high rate of solution of amorphous alumina and subsequent rapidity of supersaturation with respect to either boehmite at lower temperatures or to corundum at higher temperatures. If

TABLE 1
COMPARISON OF PINCHED-TUBE AND SEALED-TUBE EXPERIMENTS
K, kaolinite; Q, quartz; P, pyrophyllite; C, corundum

Boundary Reaction	Reaction Temperatures		Hydrostatic Pressure (lb/in ²)
	Al ₂ O ₃ –4SiO ₂ Pinched Tubes	Al ₂ O ₃ –4SiO ₂ Al ₂ O ₃ –6SiO ₂ Sealed Tubes	
K + Q ↔ P	380°	375°	15000
	390	390	30000
	405	400	45000
	420	405	60000
P ↔ Q + C	440	487	15000
	463	505	30000
	465	513	45000
	468	515	60000

boehmite is formed, reaction with quartz to produce an aluminium silicate is thermodynamically feasible. Hence boehmite, which usually appears as a third phase in a system where two solid phases only should form, is probably a metastable phase. This phase appeared both in pinched-tube and in sealed-tube experiments, and so the boehmite+quartz reaction was effectively under investigation. Provided that the rates of solution of boehmite and quartz are similar at the kaolinite–pyrophyllite boundary temperatures, no significant change in the position of that boundary should result from a change in sample enclosure.

Extension of this argument to the pyrophyllite–corundum synthesis boundary is complicated by the boehmite–corundum phase change and by lack of data on the rate of solution of boehmite, as well as uncertainty concerning the extent of the stability field of boehmite.³ Under the conditions of the current experiments it can reasonably be assumed that the maximum upper limit of the synthesis field of boehmite is coincident with the pyrophyllite field. It has been shown⁴ that the rate

³ Aramaki, S., and Roy, R., *Am. Miner.*, 1963, **48**, 1322.

⁴ Carr, R. M., and Fyfe, W. S., *Am. Miner.*, 1958, **43**, 908.

of solution of quartz in water nearly trebles over the temperature range representing the synthesis field of pyrophyllite (sealed-tube experiments) at 15000 lb/in.² If it is assumed that the change in the rate of solution of boehmite over the same temperature range is less than that of quartz (this assumption arises from the probable effect of structure differences on the relative rates of solution of quartz, boehmite, and amorphous materials), then the more highly siliceous phase, pyrophyllite, will persist at the expense of corundum.

The above results further support the conclusion that both the nature of the starting materials and the experimental method have a large influence on the nature of synthetic phases and on the extent of their synthesis fields. The apparent stability of the quartz-corundum assemblage is a consequence of the presence of amorphous alumina in the reactants. A less soluble phase containing alumina, viz. kaolinite,² reacts to give the aluminium silicate designated X-andalusite (similar to AS(H)-II).³

Acknowledgments

The writers are indebted to V. G. Tyrrell and D. H. Eteveneaux who gave invaluable technical assistance. The work was aided by support from the New Zealand University Research Fund, the Mellor Fund, and the Mineral Resources Fund.