peratures. It is interesting to note that vaterite precipitates at a lower temperature than either calcite or aragonite (Wray and Daniels, 1957).

H. Mondage-Dufy (1960) has stated that vaterite is less pure than either calcite or aragonite and has suggested that the impurity atoms are associated with crystal defects. These crystal defects would produce the microstrains shown to be present by our X-ray line broadening studies.

As thermodynamic data do not indicate any stability range relative to calcite for pure well crystallized vaterite, we may conclude that the impurities, even though they are only 0.1 percent by weight, are necessary for the formation of the complex and strained vaterite structure, rather like the role of carbon in the martensite structure. The structure is relatively unstable and any further distortion of the lattice, such as is produced by grinding, is sufficient to bring about the transformation to calcite at all temperatures.

Since the conditions in the mill, a combination of hydrostatic and shear strains, approximate to those found in the earth's crust, our results would suggest that, even if vaterite were formed, these strains would quickly bring about its transformation to calcite.

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THE PROBLEM OF QUARTZ-CORUNDUM STABILITY

R. M. Carr, *University of Otago, Dunedin, New Zealand.*

Introduction

From their results of mineral synthesis using mainly amorphous reactants of high purity in a p-T region centred at 600°C and 4 kbar, Aramaki and Roy (1963) claim the assemblage quartz-corundum may possibly be stable. Many of their experiments yielded more than the appropriate number of phases (phase rule) but other experiments indicated a direction of reaction towards quartz-corundum. The absence of this assemblage in nature was noted as the only strong argument against the tentative adoption of a stability field for quartz-corundum. In order to obtain more experimental information a synthesis study in the "quartz-corundum" *p-T* region delineated by Aramaki and Roy has been undertaken using both amorphous and crystalline reactants.

EXPERIMENTAL

Impure samples of halloysite (Te Puke, New Zealand) and kaolinite (Carr, 1963) together with a clean sample of quartz were used as crystalline reactants.

Amorphous mixes of three compositions were prepared from chromatographic alumina and silica gel by mechanical mixing.

The reactants, sealed into silver tubes, were treated hydrothermally in stellite "test-tube" bombs for periods of 7 to 14 days. Temperature and pressure control was usually better than ±1/2 percent and ±0.07 kbars respectively. Products were air-quenched and examined by X-ray diffraction.

RESULTS

The *p-T* conditions and reactants for 67 experiments are schematically shown in Figure 1, together with the "quartz-corundum" field reported by Aramaki and Roy.

Thirty-nine runs were conducted with crystalline reactants and all of the products contained mullite. The second phase was usually quartz but in three cases where failure of the sealed capsule occurred, the second phase was either corundum or ASH-II (Aramaki and Roy, 1963).

In 26 of the 28 experiments with amorphous reactants the products were quartz+corundum. Corundum only was observed in the remainder due to leaching of quartz from the split sample capsules.

DISCUSSION

Aramaki and Roy carried out only two experiments with halloysite (4.82 kbars at 600°C; 4.96 kbars at 625°C) and obtained quartz+corundum. Failure to reproduce these reactions (Te Puke halloysit decomposed to quartz+mullite) was attributed to the presence of impurities in the reactant.

The experimental results presented above indicate unequivocally that, under the conditions investigated, crystalline aluminosilicates do not form quartz+corundum. Aramaki and Roy conducted 66 of their

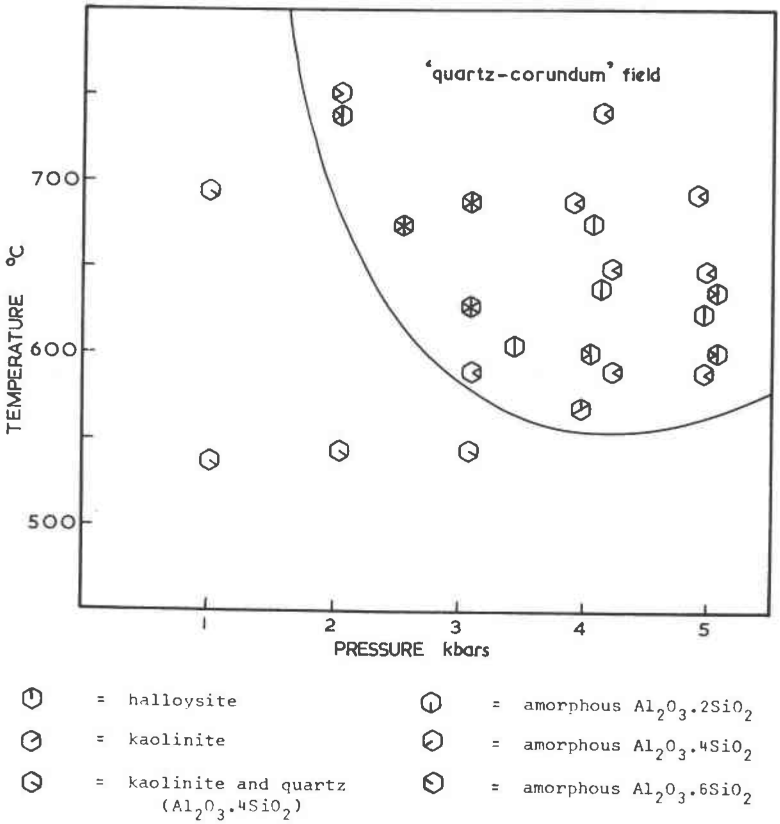

FIG. 1. Diagram showing the *p-T* conditions and the nature of the starting materials. The position of the 'quartz-corundum' field suggested by Aramaki and Roy is shown. The starting materials are identified in the legend.

76 experiments with amorphous reactants. Thirty-eight of these gave quartz+corundum while 31 yielded metastable assemblages (3 or 4 phases) and 7 gave other products. It is claimed here that these results together with those of the present investigation support the observation that amorphous reactants form quartz+corundum. The apparent stability of this assemblage under experimental conditions should not be interpreted as true thermodynamic stability in the absence of unequivocal evidence. It may be noted that the facile synthesis of quartz+corundum could be due both to structural preferences imposed by disorder and also to high purity in amorphous reactants which consist essentially of an intimate mixture of the component oxides.

Yoder and Eugster's (1955) experimental observations on the high temperature hydrothermal reactions of both muscovite and muscovite+quartz indicate indirectly the incompatibility of quartz+corundum. Using new and more reliable thermodynamic data, Weill (1966) concluded that a true stability field for quartz+corundum does not seem to be indicated. Kinetic studies on the crystallization of amorphous silica (Carr and Fyfe, 1958; Campbell and Fyfe, 1960) support the claim that the use of amorphous reactants in laboratory experiments cannot duplicate natural processes. The reactants for the mineral assemblages in rocks relative to those from laboratory reagent bottles are impure, complex and probably contain a significant proportion of crystalline material. Petrological evidence (Deer, Howie and Zussman, 1963) indicates that corundum does not normally occur in silica-rich rocks and, therefore, would not be expected to be found in association with quartz.

On the basis of petrological, chemical and both new and old experimental evidence, it is concluded that the minerals quartz and corundum appear to be incompatible with respect to the conditions obtained during the formation of naturally-occurring assemblages.

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