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BIAXIAL CALCITE INVERTED FROM ARAGONITE

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INTRODUCTION

We have recently extended the phase relationships involving a liquid phase in the system $CaO-CO_2-H_2O$ from 4 kilobars pressure (Wyllie and Tuttle, 1960; Wyllie and Raynor, 1965) to 40 kilobars pressure (to be published). Under appropriate conditions the phase assemblage calcite +liquid+vapor undergoes a transition to aragonite+liquid+vapor. Published data indicate that the calcite-aragonite transition curve should intersect the ternary univariant solidus curve at about 580°C at a pressure between 11.5 and 13 kilobars. At temperatures above 600°C, Bell and England (1964) concluded that the aragonite which formed stably within a wide pressure interval inverted to calcite during the quench. Thus, quenching problems have apparently contributed to the conflicting reports for the position of the calcite-aragonite phase transition. Examination of the morphology of the carbonate in the quenched assemblage $CaCO_3$+liquid+vapor suggested a method for locating the calcite-aragonite transition boundary regardless of the polymorphic changes that may occur during the quench.

THE CALCITE-ARAGONITE PHASE TRANSITION

The liquid in the ternary system $CaO-CO_2-H_2O$ is a very reactive medium, and during the investigation of this system and of a variety of related systems no problems have been encountered in reaching equilibrium (Wyllie, 1966).

In runs completed at pressures well above and below the aragonite-calcite transition boundary, aragonite and calcite crystals in the assemblage $CaCO_3$+liquid+vapor were positively identified by X ray and optical properties. The morphology of the aragonite crystals in equilibrium with the ternary liquid is distinct from that of the calcite crystals, and the original shape of the equilibrium phase, calcite or aragonite, becomes frozen into the surrounding liquid during the quench and is thus preserved for microscopic examination. The shape of the carbonate crystals in the quenched assemblage $CaCO_3$+liquid+vapor was therefore used to bracket the calcite-aragonite transition boundary. For charges quenched from positions within the aragonite field close to the transition boundary, much of the primary aragonite inverted to calcite during the quench. The percentage of inversion depends upon several factors, two of these being the size of the crystals and the distance of the run from the transition boundary; large crystals of aragonite quenched without inversion under the same conditions that smaller crystals changed to calcite.

BIAXIAL CALCITE

Many of the large and small crystals with the morphology of aragonite in the quenched assemblage $CaCO_3$+liquid+vapor proved to be aragonite, but X-ray powder diffraction and refractive index measurements demonstrated that crystals with identical morphology in runs close to the transition boundary were no longer composed of aragonite, but of complexly twinned calcite. These inverted calcites are biaxial with optic axial angles ranging from near zero to an estimated 20° (axial angle for aragonite is 18°). The isogyres appear to remain just as sharp as those in a uniaxial calcite crystal, but the crystals exhibit undulose extinction. This phenomenon was noted in runs from about 400°C to 800°C at pressures between 8 and 20 kilobars. Crystals with calcite morphology in quenched assemblages of $CaCO_3$+liquid+vapor are uniaxial, confirming that the biaxial character of the inverted crystals is not caused by the effect of pressure. It therefore appears that the constraint imposed by the aragonite morphology during the quench and inversion to calcite has been sufficient to strain the calcite structure.

Although ideal calcite is uniaxial, there are many reports in the literature of calcites exhibiting small optic axial angles and irregular or incomplete extinction (*e.g.* Deer *et al.*, 1962, p. 239; Palache *et al.*, 1951, p. 150). Walker and Parsons (1925, p. 15) described calcite with axial angle up to 14° from "apatite-calcite vein-dykes" of igneous origin; they attributed the biaxial character to "molecular rearrangement which marks the inversion from α-calcite at 970°C." Gillson (1927) described biaxial calcites from crystalline limestones and schists and related this property to deformational disturbances. In a review of the available data, Paulitsch (1951) could find no satisfactory explanation for biaxial calcite. The experimental observations described in this note indicate that inversion from aragonite is one explanation.

The recognition of aragonite in metamorphic rocks provides a useful geobarometer, but conditions have to be especially favorable if the aragonite is to be preserved. (Coleman and Lee, 1962). Brown *et al.*, (1962) used optical orientation and morphological evidence to conclude that some calcite in Franciscan rocks had inverted from aragonite. Our experimental demonstration that biaxial calcite can be produced by inversion from aragonite provides an additional criterion for the former existence of aragonite, although the evidence is not definitive because biaxial calcite can be formed in other ways. Single crystal X-ray studies of natural and the synthetic (twinned) biaxial calcite crystals should yield informative crystallogrphic data.

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