

liquid precipitated aragonite. This is shown by the results of runs MC 66 and MC 67, table 1. These runs were expected to be in the calcite field but showed some aragonite in the X-ray powder pattern. MC 67 showed much more aragonite than MC 66, even though it was at a higher temperature. The interpretation of a wide region of uncertainty in the calcite-aragonite boundary developing above 650°C was not consistent with the sharpness of the transition below 650°C nor with the high temperature data in the CaCO<sub>3</sub>-MgCO<sub>3</sub> system. A long run on CaCO<sub>3</sub> without flux at 18 kb and 750°C (MC 69, table 1) showed that the Li<sub>2</sub>CO<sub>3</sub> melting interpretation was correct.

The present calcite-aragonite data are in agreement with the data of Boettcher and Wyllie (1968) and confirm the phase change in calcite in the neighborhood of 500°C and 10 kb which produces a sharp deflection in the aragonite field boundary. To explain the break of slope, Boettcher and Wyllie invoked the calcite I  $\rightleftharpoons$  II transition discovered by Bridgman (1939) at higher pressures and lower temperatures by volumetric measurement. The calcite I  $\rightleftharpoons$  II transition was shown by Bridgman to have a negative dp/dt trend, the extension of which would pass very near the point 500°C and 10 kb. Jamieson (1957) had postulated a stability diagram of CaCO<sub>3</sub> similar to that of Boettcher and Wyllie on the basis of high pressure X-ray data on calcite II. The facts that (1) a projection of Bridgman's dp/dt slope for calcite I  $\rightleftharpoons$  II passes very close to the break of slope of the calcite-aragonite boundary and (2) the high temperature calcite phase is non-quenchable and therefore might be easily reversed in a compressibility experiment at 25°C lend credence to the Jamieson-Boettcher-Wyllie interpretation. It will be shown in the next section that at least two other interpretations of the CaCO<sub>3</sub> pressure-temperature diagram, involving more than three phases, might be made which explain certain other published observations to be mentioned shortly. The simplest interpretation, that of three stable phases, seems preferable at the present time and will be adopted in what follows.

Several attempts were made to locate a stable calcite I-II boundary in the pressure-temperature plane by direct means. Two different attempts were made by differential thermal analysis (DTA) in the piston-cylinder apparatus. In the first attempt, an assembly containing dry precipitated calcite mixed intimately with powdered zinc metal was used. The mixture was packed in a cylindrical iron container of about 1/4 in. height and diameter and 0.050 in. wall thickness, stoppered with a boron nitride plug. The chromel-alumel DTA thermocouple was in contact with the iron container. It was hoped that the molten zinc would provide a hydrostatic heat-conducting medium for the calcite and that the thermal arrest produced by the melting of zinc would provide a convenient check of the reliability of the DTA sensing unit. The temperature was varied by slowly turning a variable power transformer by hand. No unambiguous thermal arrests were found for the calcite I-II transition, although some diffuse indications in approximately the expected location were occasionally seen. The melting points of zinc at elevated pressures

were recorded sharply, as expected, and remained sharp on pressure cycling, which indicates that no contamination by the iron container took place. It is possible that DTA arrests on calcite I-II could be obtained with the use of continuous automatic temperature variation. The 500 to 800°C region into which the line defined by the DTA arrests encountered by Bell and England (1964) should extend was explored: there was no indication of a signal. Bell and England interpret their DTA arrests encountered between 900° and 1500°C in terms of the calcite-aragonite boundary. This interpretation is in conflict with the calcite-aragonite boundary of Boettcher and Wyllie and the present study, which extends to much higher pressures than those at which Bell and England recorded their DTA arrests.

Another set-up was made using a 1/4 in. x 1/4 in. cylindrical compressed pellet of the precipitated CaCO<sub>3</sub> with a 1/8 in.-deep axial well for the DTA thermocouple. No unambiguous DTA arrests were encountered. The absence of arrests might be due to pressure inhomogeneity over the large solid sample or sluggishness of the transition with respect to heating rates used (2 to 10°C per sec). The  $\alpha \rightleftharpoons \beta$  quartz transition can readily be detected in an inhomogeneous high pressure environment at these heating rates (Cohen and Klement, 1967).

Boeke (1912) reported abundant twinning in calcite crystals which had been heated and cooled past the thermal transition at 975°C. Several runs were made in the present study in the attempt to recognize a texture in single crystals that would indicate that a transition had taken place at high pressure. Several small untwinned cleavage rhombs were sealed with water in a platinum capsule, held at 650°C and 11.0 kb for 4 hr, and quenched. These conditions should be well within the field of calcite II according to the Jamieson suggestion. Many of the rhombs showed extremely numerous closely-spaced twin lamellae, but many rhombs were unchanged by the treatment. No positive conclusions could be drawn from this evidence, though there is a suggestion, admittedly highly subjective, that some non-reconstructive change may have affected the crystals. The quenched charges of numerous runs made both within and outside the inferred calcite II field were examined microscopically in immersion oil. Again there was a suggestion of abnormal abundance of twins in some of the runs quenched from the calcite II field. The (113) diffraction peak, absent in the high pressure X-ray powder pattern of calcite II (Jamieson, 1957), of all the charges quenched from the supposed field of calcite II was present at normal intensity.

Finally, an attempt to detect a calcite I  $\rightleftharpoons$  II transition by differential solubility of MgCO<sub>3</sub> was made. This technique, which will be described shortly, also yielded inconclusive results. The principle conclusion that must be drawn with regard to the calcite I  $\rightleftharpoons$  II transition on the basis of the present work is that the transition has little or no effect on the observed properties of calcite, even though it produces a profound change of direction of the calcite-aragonite pressure-temperature boundary curve.