

as no solid solution takes place. A special test was made at 780° and 2 kb in the cold seal apparatus with fluxed and non-fluxed charges for 63½ hrs., which is long enough to achieve equilibrium in a non-fluxed run at that temperature. Both charges showed the same amount of MgCO₃ in the calcite, based on measurements of d-spacings. The fluxed run merely had a sharper powder pattern. The calcite-aragonite boundary was located near 700°C and 16 kb using fluxed and unfluxed charges, with identical results. It is thus quite certain that the presence of Li₂CO₃ did not chemically perturb the system but only promoted reaction.

A few runs were made hydrothermally with small clear cleavage rhombs sealed with water into platinum capsules. In these runs a large final pressure adjustment was made after the sample had come up to temperature, in order to produce "piston-in" conditions. Reaction to aragonite was easily detected by development of an opaque, milky pseudomorph of aragonite after calcite which preserved the rhomb cleavage angles.

X-ray methods.—The quenched charges were analyzed by scanning the 2 θ region 25° to 35° with filtered Cu radiation with a Norelco X-ray diffractometer at the rate of ¼° per min. The exact location of the (104) peak is diagnostic of the composition of the calcite phase (Harker and Tuttle, 1955). Debye-Scherrer X-ray films were also taken of the samples in 114.6 mm-diameter Philips cameras using filtered iron radiation. Compositions of the calcite phase were determined by measuring accurately the separation of several back-reflections. The back-reflection separations had been calibrated against composition by homogenizing a series of magnesian calcites of known composition (Goldsmith, Graf, and Heard, 1961). An accuracy of at least ± 0.2 mole percent MgCO₃ can be obtained by this method if the X-ray films are of good quality and the samples well equilibrated. Unequilibrated samples can be detected by a blurring of the back reflections. Most of the samples of the present study were well equilibrated by this criterion. Small amounts of occasional extraneous phases, such as brucite, that could not be resolved in the spectrometer scans were visible in the films.

Problem of hydrothermal decomposition.—Early in the investigation it was learned that at high temperature the charge must be carefully protected from water, even external to the capsule, to avoid decomposition of the MgCO₃. The calcite phase in runs in which water was present was anomalously low in magnesium, dolomite was absent, and brucite was present. In several runs on dry carbonate starting material in sealed platinum capsules made at temperatures above approximately 800°C and at pressures above 4 kb, the talc dehydrated, and it was observed that the charge was coated with a film of carbon, and brucite was again present. It is clear from this result that hydrogen, formed by dissociation of water from the talc surrounding the capsule, diffused through the capsule and reduced some of the carbonate. The same effect was noted to a lesser extent in runs using a gold capsule. Even at temperatures somewhat below the talc dehydration point, small amounts of

brucite would appear in some X-ray films of charges run in platinum capsules. For this reason gold capsules were used whenever possible. As an additional precaution, in runs of 780°C and higher the gold capsules were packed in powdered dolomite rather than talc to act as a water-getter. No brucite was seen in the X-ray patterns of any of these runs, and the sharpness of the back reflections further showed that no MgCO_3 was lost to produce brucite.

A few very high temperature runs were made to check on the two-phase calcite assemblages quenched from 1150°C by Goldsmith and Heard (1961). In these runs the spacers around the capsule (platinum had to be used because of contact with Pt-Pt 10 percent Rh thermocouples) were machined from a pure dolomite rock from Dover Plains, N.Y. The pressure medium external to the graphite heater shell was machined from lithographic limestone. Thus there was no source of water in the pressure chamber. These runs produced carbonate charges with no carbon or brucite present.

EXPERIMENTAL RESULTS

Pure CaCO_3 .—The experimental runs delimiting the pressure-temperature location of the calcite-aragonite transition are listed in tables 1 and 2 and plotted in figure 1. The dry fluxed CaCO_3 runs are consistent with the hydrothermal runs. In general, the hydrothermal runs indicate a transition to aragonite at pressures a few hundred bars higher than the dry fluxed CaCO_3 runs, although the two sets of piston-cylinder data overlap if each is assigned an uncertainty of ± 500 bars. The dry fluxed CaCO_3 runs were given greater weight in plotting figure 1, because the

TABLE 1
High-temperature, high-pressure runs on dry CaCO_3

| Notebook No. | T, °C | P, kb | Time, hr | Starting material | Resulting phases |
|--------------|-------|-------|----------|-------------------|------------------|
| MC 53 | 400 | 8.5 | 27 | C + f | C |
| MC 52 | 400 | 9.5 | 20 | C + f | A |
| MC 55 | 450 | 9.5 | 24 | C + f | C + (A) |
| MC 54 | 450 | 10.5 | 21 | C + f | A |
| MC 57 | 500 | 10.0 | 19 | C + f | C |
| MC 56 | 500 | 11.0 | 22 | C + f | A |
| MC 59 | 550 | 12.0 | 19 | C + f | C |
| MC 60 | 550 | 13.0 | 18-3/4 | C + f | A |
| MC 61 | 600 | 14.0 | 20-3/4 | C + f | A + (C) |
| MC 65 | 650 | 15.0 | 19-1/2 | C + f | C + (A) |
| MC 62 | 650 | 16.0 | 20 | C + f | A + (C) |
| MC 64 | 700 | 17.0 | 18-1; 2 | C + f | A + C |
| MC 63 | 700 | 18.0 | 19 | C + f | A |
| MC 68 | 725 | 18.0 | 4 | C + f | C + A |
| MC 66 | 750 | 18.0 | 3-3/4 | C + f | C + (A) |
| MC 69 | 750 | 18.0 | 18-1/2 | C | C |
| MC 67 | 775 | 18.0 | 1-3/4 | C + f | C + (A) |

Abbreviations: A, aragonite; C, calcite; f, Li_2CO_3 flux; (A) or (C), small amount of phase present.