THE SYSTEM $CaCO_3$–$MgCO_3$

The calcite-aragonite relations.—The presence of $MgCO_3$ further complicates the phase relations by introducing dolomite in equilibrium with calcite (magnesian) and aragonite. The three univariant curves in the $CaCO_3$ system (fig. 1) are replaced by four curves in the system $CaCO_3$–$MgCO_3$, each curve being defined by the coexistence of three of the four phases: calcite I, calcite II, aragonite, and dolomite. Figure 2 is a schematic projection from composition-space onto the P-T plane of the system. The aragonite field boundary lies at higher pressures than in the pure $CaCO_3$ system by virtue of the fact that $MgCO_3$ in solid solution in the calcite relative to aragonite raises the pressure of the transition.

The data for the magnesian calcite-dolomite-aragonite equilibrium relations are presented in table 3 and plotted in figure 3. The curves for the pure $CaCO_3$ system are also shown for comparison. The sharp break in slope of the calcite-aragonite boundary is also evident in the $MgCO_3$–saturated system.

The data proved to be clearly defined. Most of the reactions went to completion, with runs showing reaction in opposite directions over a 1-kb band as the calcite-aragonite boundary was crossed. The invariant point at which aragonite, calcite I, calcite II, and dolomite coexist in the $CaCO_3$–$MgCO_3$ system is at 450°C and 10.4 kb, according to our interpretation. At 450°C the Mg-saturated transition lies less than 1 kb above

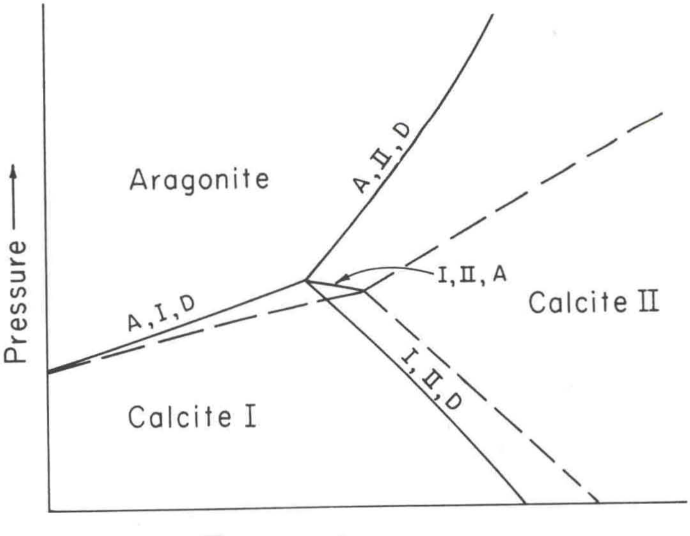

Fig. 2. Schematic P-T projection of univariant space curves in the system $CaCO_3$–$MgCO_3$. The curves are labelled with symbols representing the three phases in equilibrium along the curve in each case: A = aragonite, I = calcite I. II = calcite II, D = dolomite. Univariant curves for pure $CaCO_3$ are shown as dashed lines. The curves as drawn are consistent with the assumption that calcite II takes more $MgCO_3$ in solid solution than does calcite I at a given temperature.

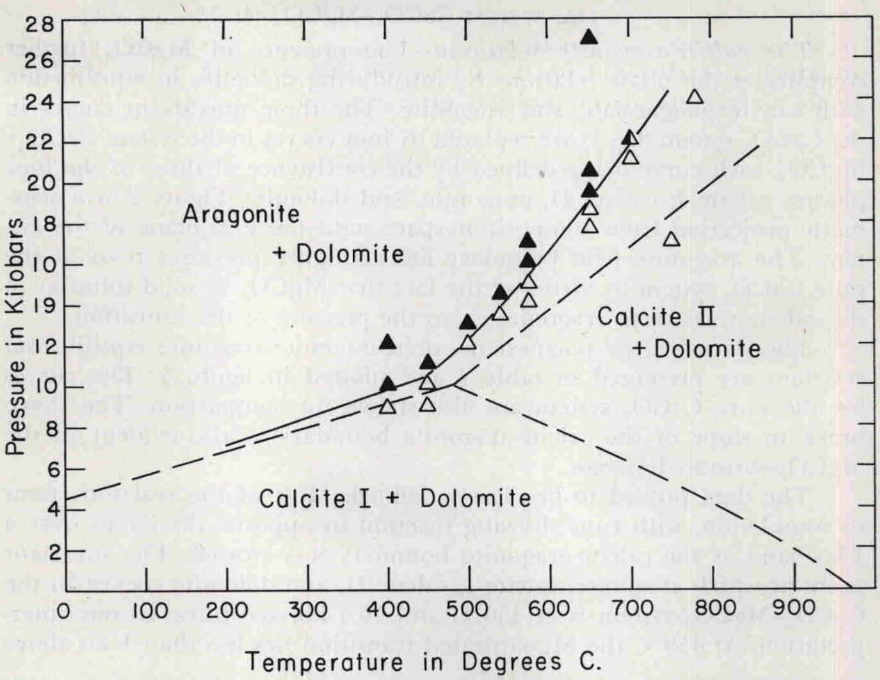

Fig. 3. P-T plot of runs made to delimit the calcite-aragonite boundary in the system $CaCO_3$–$MgCO_3$ with dolomite present. Solid triangles denote complete reaction to dolomite + aragonite. Open triangles denote complete reaction to magnesian calcite and dolomite. Partially filled triangle denotes reaction to calcite, aragonite, and dolomite. Phase boundaries for pure $CaCO_3$ are shown as dashed lines.

the pure $CaCO_3$ transition and at 700°C the separation of the two curves is slightly more than 5 kb. At very low temperatures the magnesium saturated calcite I-dolomite-aragonite curve must become essentially coincident with the pure $CaCO_3$ calcite I-aragonite curve because of the small $MgCO_3$ solubility at low temperatures. At increasingly elevated temperatures the magnesian calcite II-dolomite-aragonite curve deviates increasingly from the pure $CaCO_3$ calcite II-aragonite curve due to higher solubility of $MgCO_3$ in calcite. The aragonite that forms in the Mg-saturated system shows no evidence of $MgCO_3$ in solid solution at the most elevated temperatures of the investigation. The X-ray diffraction pattern of the aragonite had the same spacings and intensities as that of aragonite formed from pure $CaCO_3$.

The calcite-dolomite solvus and the effect of pressure.—The solvus curve in the Ca-rich half of the system has been at least in part determined in several investigations, but some additional runs were made as a further check on the accuracy of its location. The solubility of $MgCO_3$ in calcite is strongly temperature dependent, but in addition, there is a pressure effect on the solubility. Thus, the solvus must be defined in terms of total pressure as well as temperature. An isobaric solvus can be drawn at any pressure high enough to prevent decomposition of the