



Fig. 12. Detail of the P-T region adjacent to the invariant points in the  $\text{CaCO}_3$  and  $\text{CaCO}_3\text{-MgCO}_3$  systems. The upper set of curves is for the  $\text{MgCO}_3$ -saturated system. The lower set of curves is for pure  $\text{CaCO}_3$ . P is the pressure of the calcite I-calcite II-dolomite-aragonite invariant point.  $P^I$  is the pressure of the pure  $\text{CaCO}_3$  calcite I-aragonite curve at the temperature of the invariant point in the  $\text{MgCO}_3\text{-CaCO}_3$  system.  $P^{II}$  is the pressure of the metastable extension of the pure calcite II-aragonite curve at the same temperature.

and  $P^{II}$  are shown at  $450^\circ\text{C}$ , the invariant-point temperature in the binary ( $\text{MgCO}_3$  saturated) system. It is to be noted that  $P^{II}$  lies on the metastable extension of the pure calcite II-aragonite curve at a temperature  $30^\circ$  below the invariant-point temperature of the pure  $\text{CaCO}_3$  system. Simultaneous solution of the regular solution equations together with the relation  $\sum \Delta V = 0$  around the  $\text{CaCO}_3$  invariant point leads to:

$$\begin{aligned} \Delta V_{I \rightarrow II} &= \Delta V_{A \rightarrow I} \left[ \frac{P^{II} - P^I}{P - P^I} \right] \\ &= 2.78 \left( \frac{9.1 - 9.6}{10.4 - 9.6} \right) = -1.07 \text{ cc/mole} \end{aligned}$$

The excellent agreement of this  $\Delta V$  with the value of  $-1.01$  cc/mole deduced from the slopes of the univariant equilibria in the pure  $\text{CaCO}_3$  system lends considerable confidence to the seemingly somewhat opposed notions that the calcite I-II transition has a relatively large  $\Delta V$  even though the change in  $\text{MgCO}_3$  solubility is small.

It is easily shown by an analysis similar to the preceding ones that the increase of pressure at a given temperature of the calcite I-calcite II-dolomite curve over the pure calcite I-calcite II curve is given by:

$$P - P^{\circ} = \frac{RT \ln \left( \frac{1 - X_m^{\text{II}}}{1 - X_m^{\text{I}}} \right) + \Omega (X_{\text{mc}}^{\text{II}} - X_{\text{mc}}^{\text{I}})^2}{V^{\text{I}} - V^{\text{II}}}$$

A calculation at 720° may be made using  $X_{\text{mc}}^{\text{I}} = 0.115$  and  $X_{\text{mc}}^{\text{II}} = 0.120$ . The difference  $X_{\text{mc}}^{\text{II}} - X_{\text{mc}}^{\text{I}} = 0.005$  is the upper limit that the present measurements allow.  $P - P^{\circ}$  is 330 bars by this calculation, which is within the experimental error of pressure measurement. Thus the calcite I-calcite II-dolomite pressure-temperature curve is essentially coincident with the calcite I-II pressure-temperature curve in the pure  $\text{CaCO}_3$  system.

#### PETROLOGIC INTERPRETATION

The calcite-dolomite solvus has already been used as a geological thermometer in a number of petrologic studies, one of the latest being an interesting paper by Carpenter (1967) on the Crestmore, California, metamorphic marbles. Carpenter presents evidence for temperatures as high as 760°C, based on the total amount of  $\text{MgCO}_3$ , some contained in dolomite exsolution lamellae, that he deduces to have been in solid solution in the calcite. This study, as well as all previous studies, has been limited in a sense by lack of precise knowledge of the effect of total pressure on the solvus. The effect had been assumed to be small, and this had been substantiated in the work with the simple squeezer, and the present study clarifies the situation over a significant range of pressures and temperatures. The pressure coefficient of solubility is close to 0.12 mole percent  $\text{MgCO}_3$  per kb over the temperature and pressure range of interest. A total pressure range of 0 to 10 kb is the maximum that can be expected in the genesis of crustal rocks. A pressure uncertainty of 10 kb would be equivalent to a temperature uncertainty of approximately 40°C at 500°C, and of 25° at 800°C. It is desirable, therefore, that some independent criteria be applied for at least a qualitative estimate of depth of burial during crystallization or metamorphism. If this is done at least to the extent of being able to categorize the depth of burial as shallow, moderate, or deep, it seems unlikely that a temperature error due to the pressure effect would exceed 15°C. It would appear that analytical errors and uncertainty as to the amount of dolomite actually exsolved as opposed to "primary" dolomite could lead to a temperature uncertainty larger than that introduced by an unknown pressure.

If the presence of  $\text{MgCO}_3$  were to lower significantly the temperature and pressure for the stability of calcite II, it would be a consequence of a higher solubility of  $\text{MgCO}_3$  in calcite II than in calcite I. This could introduce a complication in the application of the geologic thermometer, for it is conceivable that the larger amount of  $\text{MgCO}_3$  could be metastably quenched in the calcite I formed by inversion or that during inver-