

P-T-X RELATIONS IN THE SYSTEM CaCO₃-MgCO₃ AT HIGH TEMPERATURES AND PRESSURES

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ABSTRACT. The principal subsolidus features of interest in the calcium-rich portion of the system were investigated in piston-cylinder and cold-seal apparatus in the range 400 to 800°C and 1 to 25 kb total pressure. A few reconnaissance runs were made in the piston-cylinder apparatus up to 1150°C.

The pronounced break in slope of the calcite-aragonite equilibrium near 10 kb and 500°C reported by Boettcher and Wyllie (1967) was confirmed. Attempts to detect a calcite I-II phase boundary emanating from the break in slope were made by differential thermal analysis, microscopic texture analysis of quenched charges, and measurement of MgCO₃ solubility in calcite at many temperatures and pressures. No clear-cut evidence of a transition could be found by these methods. The hypothesis of Jamieson (1957) and Boettcher and Wyllie of a stable calcite I-II transition in the P-T diagram of CaCO₃ remains unverified directly though highly probable on the basis of indirect evidence.

The effect of MgCO₃ on the location of the calcite-aragonite boundary was determined, with reversal of the univariant reactions calcite I $\rightleftharpoons$ aragonite + dolomite and calcite II $\rightleftharpoons$ aragonite + dolomite. At 700°C, the latter lies at 21.8 kb, 5.2 kb higher than in the pure CaCO₃ system. Melting was encountered at 1150°C and 12 kb in a charge of composition 20 mole percent MgCO₃.

The effect of total pressure on the solubility of MgCO₃ in the calcite structure was determined at several temperatures. The measured solubility increase with pressure was about 0.12 mole percent per kb in the range 500 to 800°C.

The present data yielded a calcite-dolomite solvus in agreement with that of Harker and Tuttle (1955) and Graf and Goldsmith (1958).

The pressure effect on the solubility of MgCO₃ in calcite was calculated by a regular solution theory, and the theory reinforces the experimental determination. The three-phase equilibria in the system CaCO₃-MgCO₃ were calculated by the regular solution theory using the measured MgCO₃ solubilities. There was satisfactory agreement between theory and experiment.

It is concluded that the calcite-dolomite solvus can be a very useful geothermometer for metamorphic calcite, especially if the depth of the metamorphism can be categorized as to shallow, intermediate, or deep.

INTRODUCTION

The phase relations in the system CaCO₃-MgCO₃ have been examined in a number of investigations (Graf and Goldsmith, 1955 and 1958; Harker and Tuttle, 1955; Goldsmith, 1959; Goldsmith and Heard, 1961). Many aspects of the system are now understood in a general way. It is desirable to determine the solubility of MgCO₃ in calcite with the greatest possible precision because of its importance as a geologic thermometer and especially to assay accurately the effect of total pressure on the MgCO₃ solubility. In addition, the calcite I-II transition, which has recently been shown to play a significant role in the pure CaCO₃ phase relations (Boettcher and Wyllie, 1967, 1968), must be investigated as to its possible effects in the CaCO₃-MgCO₃ system. Any solubility difference of MgCO₃ in calcite I and calcite II may affect the configuration of the calcite-dolomite solvus and hence the application of the geologic thermometer. Finally, the effect of MgCO₃ on the calcite-aragonite equilibrium is of interest.

In the present investigation, the effects of the variables, temperature, total pressure, and composition, have been examined in those portions of the CaCO_3 - MgCO_3 system that have the greatest petrological significance. A quantitative three-dimensional (P-T-X) view of the phase relations in the Ca-rich half of the system will be developed, and the petrologic implications will be considered.

EXPERIMENTAL METHODS

Apparatus.—Most of the present experiments were done by the “quenching” method in cold-seal vessels (Tuttle, 1949) and piston-cylinder apparatus (Boyd and England, 1960) using the 1 in.-diameter pressure vessel. Talc was used as a pressure medium in the majority of piston-cylinder runs. A graphite heater sleeve of 0.54 in.-inner diameter was immersed in the talc. Talc is useful up to above 800°C but loses water and plasticity above that temperature. A few runs at higher temperatures were made with an all-carbonate pressure medium assembly to avoid decomposition of the sample charge by water freed from the decomposition of talc as will be discussed shortly.

Encapsulation.—The sample charges were sealed in capsules welded from gold and, in a few runs, from platinum tubing. Gold is considerably less permeable to hydrogen than platinum and hence was preferable from the standpoint of carbonate decomposition problems resulting from small amounts of absorbed moisture in the talc pressure medium. The flattened welded capsules were 0.030 in. thick and $\frac{1}{8}$ in. long with the short dimension along the greatest temperature gradient. The capsules contained about two mg of sample, which was sufficient for analysis.

Temperature measurement and control.—Chromel-alumel or platinum-platinum 10 percent rhodium thermocouples were in contact with the sample capsules in the piston-cylinder arrangement. A 0.001 in. platinum foil separated the capsule and thermocouple to prevent any contamination effect by the gold on the thermocouple. Pt-Pt 10 percent Rh couples were used above 750°C . Temperatures were controlled automatically to $\pm 2^\circ\text{C}$ by a Minneapolis-Honeywell Electronik-18 controller. Run durations ranged from a few minutes to a few days. At the end of a piston-cylinder run the samples were quenched to 100°C in a few seconds by turning off the heater current. A pressure correction for the emf of the thermocouples should be considered. Pt-Pt 10 percent Rh couples, which have the larger correction, were used in a few runs at 12 kb and temperatures to 1150°C . The largest correction that would be applied, according to the estimates of Hanneman and Strong (1965), would be about 15° and would not seriously affect the interpretation of any of the runs. Chromel-alumel has a smaller correction than Pt-Pt 10 percent Rh, according to Hanneman and Strong. No correction was made for pressure on the emf of the thermocouples.

Temperatures in the cold-seal runs at 2 kb were measured with exterior chromel-alumel couples placed a small fraction of an inch from the sample. The results of cold-seal runs were consistent with those of the piston-cylinder runs.

Pressure measurement.—Pressure measurement in a solid-pressure piston-cylinder apparatus requires some discussion in each individual application at the present state of technology. Most of the present runs were made in the following manner. First the desired nominal pressure was applied to the assembly. The true pressure at this stage will be somewhat less than nominal, owing to the “in-stroke” friction which is likely to be about 7 to 10 percent of the nominal pressure. Next the temperature was raised to the desired run value. The gauge measuring the oil pressure in the master ram always responded to heating with an immediate 10 to 15 bar (1-1.5 kb nominal sample pressure) rise. The immediate thermal expansion effect and the slower subsequent gauge rise due to gradual heating of the press were held at 15 bars. The increase of pressure due to thermal expansion was considered nearly to compensate for the frictional pressure loss, and no friction correction was applied. Thus the sample pressure is subject to an uncertainty of the order of ± 500 bars in absolute magnitude, and greater accuracy in locating the absolute pressures of the reaction curves of the present study cannot be claimed. The relative uncertainty among runs that are all made the same way should be considerably less than 500 bars, however. It is on the relative differences in pressure parameters that the interpretation of this paper is mainly based. The absolute pressure location of the present determination of the pure calcite-aragonite transition at 575°C agrees precisely with the gas-media apparatus point of Clark (1957), which should be a valid determination according to our interpretation and lends considerable support to the frictional compensation assumption.

In all the runs the solid pressure on the carbonate sample was greater than the decomposition CO_2 pressure at the temperature of the run. In an effectively plastic material decomposition does not occur under such circumstances (see for example Goldsmith and others, 1962).

Starting material.—Fine-grained precipitated CaCO_3 (calcite) and well crystallized anhydrous MgCO_3 were used as starting material in most of the present runs (Goldsmith and Heard, 1961). Intimate mixtures of the compositions $\text{Ca}_{95}\text{Mg}_5$, $\text{Ca}_{90}\text{Mg}_{10}$, $\text{Ca}_{80}\text{Mg}_{20}$, and $\text{Ca}_{70}\text{Mg}_{30}$ were used to determine the effect of pressure on the calcite-dolomite solvus and the effect of MgCO_3 on the calcite-aragonite transition. In addition, most of the charges contained a small amount (about 5 percent) of Li_2CO_3 flux. This substance was highly effective in promoting reaction, as shown by large crystal growth in fluxed runs, much better-equilibrated samples with sharper X-ray powder patterns from fluxed runs in a comparison series of runs made with and without flux, and ease of reversal of the main boundaries in the presence of flux. Li_2CO_3 has a 1-atm simple eutectic melting relation with CaCO_3 at 670° with little or no solid solution (Eitel and Skalijs, 1929). In runs much above 670°C the flux must have melted and dissolved significant amounts of CaCO_3 and MgCO_3 . A simple phase rule analysis shows that magnesian calcite must have the same composition in equilibrium with dolomite whether or not a third phase capable of digesting CaCO_3 and MgCO_3 is present, as long

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 $63\frac{1}{2}$ hrs., which is long enough to achieve equilibrium in a non-fluxed run at that temperature. Both charges showed the same amount of MgCO_3 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 Li_2CO_3 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 2θ region 25° to 35° with filtered Cu radiation with a Norelco X-ray diffractometer at the rate of $\frac{1}{4}^\circ$ 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 MgCO_3 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 MgCO_3 . 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.

TABLE 2
Hydrothermal runs on CaCO_3

Notebook No.	T, °C	P, kb	Time, hr	Starting material	Result
CA 14	400	8.8	18	C + A	C increased
CA 9	400	9.3	20	C + A	A + (C)
CA 8	400	9.5	28	C + A	A + (C)
CA 7	400	9.8	28	C + A	A
CA 1	500	10.2	24	C + A	C
CA 6	500	11.2	18	C + A	C increased
CA 4	500	11.5	5	C + A	A increased
CA 3	500	12.1	7	C + A	A
CA 2	500	13.5	15	C + A	A
CA 16	600	9.4	10-1/2	Cl	Unaltered
CA 11	600	12.9	6	C + A	C
CA 12	600	13.6	5	C + A	C
CA 19	600	13.9	8-1/2	Cl	Unaltered
CA 13	600	14.1	2-1/2	C + A	C increased
CA 18	600	14.4	10	Cl	Partially altered to A
CA 17	600	15.3	9	Cl	Altered to A
CA 25	650	15.7	5-1/2	Cl	Unaltered
CA 24	650	16.1	7	Cl	Partially altered to A
CA 20	700	17.1	4	Cl	Unaltered
CA 21	700	18.0	4	Cl	Unaltered
CA 23	700	18.4	4	Cl	Partially altered to A
CA 22	700	18.9	6	Cl	Altered to A
CA 26	750	20.7	5	Cl	Partially altered to A

Abbreviations: A, aragonite; C, calcite; Cl, calcite cleavage rhomb.; (A) or (C), small amount of phase present.

H_2O = approximately 50 percent by weight.

calcite-aragonite runs in the system $\text{CaCO}_3\text{--MgCO}_3$ were made this way, and it is desirable in the analysis of phase relations with and without MgCO_3 to compare runs made with the same technique. We do not intend to give the impression that greater confidence was placed in the dry method on an absolute basis. The assumption stated in the previous section, that thermal expansion in the chamber created an increase in pressure at the sample site which closely compensated for the solid-pressure medium frictional loss, appears to be well justified. The agreement with the gas-media apparatus point of Clark at 575° is excellent. The calcite-aragonite curve at low temperatures is drawn through the 100°C determination of Crawford and Fyfe (1964).

The break in slope of the calcite-aragonite boundary at 480° and 10.0 kb confirms the observations of Boettcher and Wyllie (1968). Since their method was based on microscopic identification of calcite or aragonite crystals in equilibrium with liquids in the system $\text{CaO--H}_2\text{O--CO}_2$ or of inversion pseudomorphs of calcite after aragonite, there could be no problems of misinterpretation of quenched assemblages in their study. The same is true of the present runs made with clear calcite cleavage rhombs in water (approx 50 percent by weight). The cleavage rhomb of run CA 21, table 2 (700°C , 18.0 kb) was intact, though much

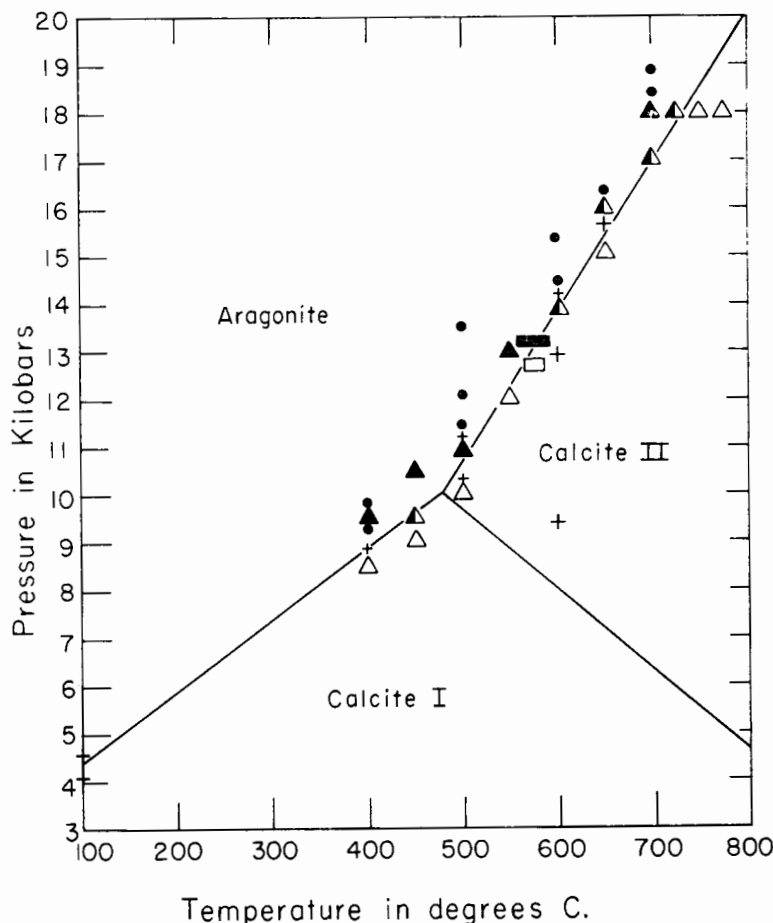


Fig. 1. P-T plot of runs made to delimit accurately the calcite-aragonite boundary in the pure CaCO_3 system. Solid triangles denote complete reaction of dry calcite to aragonite. Open triangles denote no phase reaction of dry calcite. Partially filled triangles denote partial reaction of dry calcite to aragonite. All dry runs in presence of Li_2CO_3 flux. Dots represent hydrothermal reaction of calcite to aragonite. Crosses represent no alteration of calcite in hydrothermal runs. Rectangles denote runs of Clark (1957). The horizontal lines at 100°C delimit Crawford and Fyfe's (1964) results of 4.25 ± 0.25 kb.

dissolved. The crystal of run CA 22 was opaque and of a porcelainous appearance when retrieved, and the X-ray diffraction pattern was that of aragonite. The rhomb cleavage angles of calcite are preserved pseudomorphically. The only possibility of misinterpretation of the equilibrium assemblage in a quenched charge arose in the case of the highest temperature dry CaCO_3 runs with Li_2CO_3 flux. At 700°C and higher temperatures the Li_2CO_3 melted and dissolved a substantial amount of CaCO_3 . When quenched through the aragonite field, the

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_3 - MgCO_3 system. A long run on CaCO_3 without flux at 18 kb and 750°C (MC 69, table 1) showed that the Li_2CO_3 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 $\text{I} \rightleftharpoons \text{II}$ transition discovered by Bridgman (1939) at higher pressures and lower temperatures by volumetric measurement. The calcite $\text{I} \rightleftharpoons \text{II}$ 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_3 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 $\text{I} \rightleftharpoons \text{II}$ 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_3 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 $\frac{1}{4}$ 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 $\frac{1}{4}$ in. x $\frac{1}{4}$ in. cylindrical compressed pellet of the precipitated CaCO_3 with a $\frac{1}{8}$ 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_3 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.

THE SYSTEM $\text{CaCO}_3\text{--MgCO}_3$

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 $\text{CaCO}_3\text{--MgCO}_3$, 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 $\text{CaCO}_3\text{--MgCO}_3$ 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

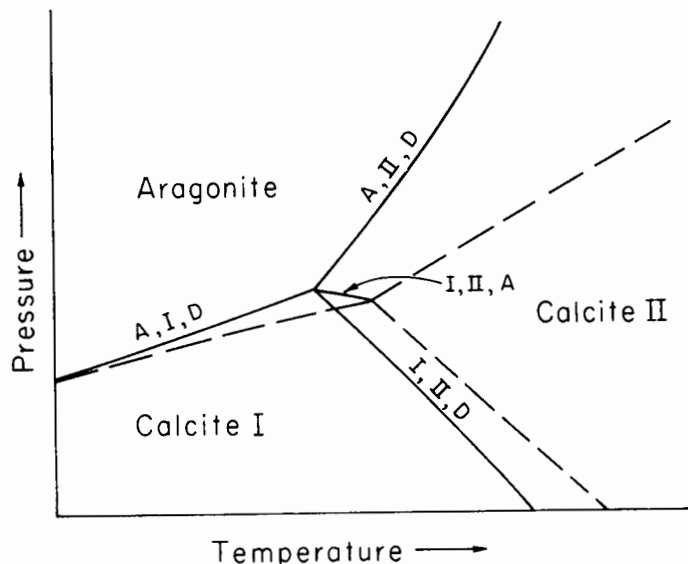


Fig. 2. Schematic P-T projection of univariant space curves in the system $\text{CaCO}_3\text{--MgCO}_3$. The curves are labelled with symbols representing the three phases in equilibrium along the curve in each case: A = aragonite, I = calcite I, II = calcite II, D = dolomite. Univariant curves for 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.

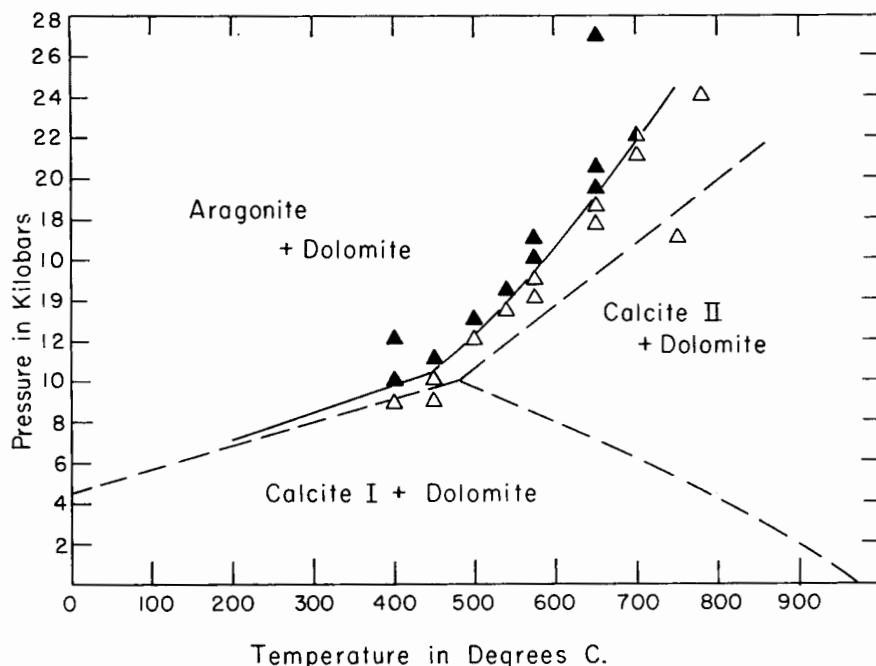


Fig. 3. P-T plot of runs made to delimit the calcite-aragonite boundary in the system $\text{CaCO}_3\text{-MgCO}_3$ with dolomite present. Solid triangles denote complete reaction to dolomite + aragonite. Open triangles denote complete reaction to magnesian calcite and dolomite. Partially filled triangle 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

carbonates but not so high as to produce aragonite in the magnesium saturated system. Alternatively, a unique polybaric solvus can be drawn in which at each point on the solvus the CO_2 pressure is just that adequate to prevent decomposition of the carbonate at all temperatures

TABLE 3
High-pressure, high-temperature runs on dry $\text{CaCO}_3\text{-MgCO}_3$ mixtures

Notebook No.	T, °C	P, kb	Time, hr	Starting material*	Resulting phases	Calcite composition, mole % MgCO_3	Remarks
MC 35	400	2.0	95-1/2	95/5 + f	C + D	Unequilibrated	Cold-seal run
MC 126	400	2.0	1008	90/10 + f	C + D	2.5	Cold-seal run
MC 33	400	9.0	39	90/10 + f	C + D	3.3	
MC 32	400	10.0	48	90/10 + f	A + D		
MC 30	400	12.0	69	90/10 + f	A + D		
MC 37	450	2.0	144	90/10 + f	C + D	3.4	Cold-seal run
MC 127	450	2.0	1008	90/10 + f	C + D	3.2	Cold-seal run
MC 45	450	9.0	45	A + D + f	C + D	4.7	Reversal run
MC 34	450	10.0	43	90/10 + f	C + D	4.5	
MC 36	450	11.0	48	90/10 + f	A + D		
MC 76	500	1.9	768	90/10 + f	C + D	4.6	Cold-seal run
MC 26	500	2.0	48	90/10 + f	C + D	4.6	
MC 25	500	12.0	42	90/10 + f	C + D	5.5	
MC 24	500	13.0	46	90/10 + f	A + D		
MC 38	540	13.5	48	90/10 + f	C + D	6.5	
MC 39	540	14.5	27	90/10 + f	A + D		
MC 77	550	1.9	768	90/10 + f	C + D	5.5	Cold-seal run
MC 19	575	3.0	42	90/10 + f	C + D	6.6	
MC 16	575	14.0	45-1/2	90/10 + f	C + D	7.7	
MC 29	575	15.0	23	90/10 + f	C + D	7.9	
MC 41	575	16.0	16-1/2	90/10 + f	A + D		
MC 20	575	17.0	30	90/10 + f	A + D		
MC 92	600	1.9	768	90/10 + f	C + D	6.9	Cold-seal run
MC 78	650	1.9	118	80/20 + f	C + D	9.0	Cold-seal run
MC 79	650	1.9	118	80/20	C + D	9.1	Cold-seal run
MC 74	650	4.0	46	80/20 + f	C + D	9.4	
MC 85	650	5.0	46	80/20 + f	C + D	9.5	
MC 84	650	6.0	10-1/2	80/20 + f	C + D	9.8	
MC 12	650	7.0	21	80/20	C + D	10.0	
MC 13	650	7.0	21	80/20 + f	C + D	9.8	
MC 86	650	8.0	45	80/20 + f	C + D	9.9	
MC 83	650	9.0	45-1/2	80/20 + f	C + D	10.0	
MC 75	650	10.0	44-1/2	80/20 + f	C + D	10.0	
MC 87	650	12.0	42-1/2	80/20 + f	C + D	10.4	
MC 88	650	14.0	3-1/4	80/20 + f	C + D	10.7	
MC 89	650	16.0	44	80/20 + f	C + D	10.9	
MC 15	650	17.0	21	80/20	C + D	10.2	
MC 95	650	17.8	43	A + D + f	C + D	10.1	Reversal run
MC 21	650	18.5	16	80/20 + f	C + D	11.0	
MC 23	650	19.5	15-2/3	80/20 + f	A + D		
MC 22	650	20.5	17	80/20 + f	A + D		
MC 14	650	27.0	22	80/20	A + D		
MC 42	700	21.0	7	80/20 + f	C + D	13.7	
MC 43	700	22.0	5-1/2	80/20 + f	C + D + A		
MC 81	720	1.9	70	85/15 + f	C + D	11.5	Cold-seal run
MC 18	750	17.0	18	80/20	C + D		
MC 47	780	1.7	17	80/20	C + D	14.6	Cold-seal run
MC 50	780	1.7	63-1/2	80/20	C + D	15.4	Cold-seal run
MC 51	780	1.7	63-1/2	80/20 + f	C + D	15.5	Cold-seal run
MC 107	780	4.0	21-1/2	70/30 + f	C + D	15.9	
MC 90	780	4.0	19-1/2	80/20 + f	C + D	16.0	
MC 94	780	4.0	21	80/20 + f	C + D	15.8	
MC 1	780	5.5	3-1/2	80/20 + f	C + D	16.5	
MC 108	780	6.0	24	70/30 + f	C + D	16.2	
MC 109	780	9.0	17-1/2	70/30 + f	C + D	16.5	
MC 96	780	12.0	20-1/4	80/20 + f	C + D	17.2	
MC 106	780	15.0	17-1/2	70/30 + f	C + D	17.7	
MC 110	780	19.0	17	70/30 + f	C + D	18.0	
MC 3	780	24.0	2-1/2	80/20 + f	C + D	18.8	
MC 58	850	2.0	4	70/30	C + D	17.6	Cold-seal unequilibrated
MC 49	900	15.0	2	70/30	C + D	24.7	All carbonate setup
MC 112	925	12.0	4	70/30 + f	C + D	26.9	All carbonate setup
MC 102	960	12.0	1	80/20	C + (D)		All carbonate setup unequilibrated
MC 103	1050	12.0	5/6	90/10	C + (D)		All carbonate setup unequilibrated
MC 104	1150	12.0	1/2	80/20	C		Melted - 2 phases present?

*95/5 = $(\text{CaCO}_3)_{0.95}(\text{MgCO}_3)_{0.05}$ etc.

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

Runs in piston-cylinder apparatus with talc pressure medium unless otherwise indicated.

along the curve. In an effectively plastic material such as the carbonates, the effect of total (applied) pressures in excess of the CO_2 pressure necessary to prevent carbonate decomposition is equivalent to increased CO_2 pressure.

A series of runs was made to determine the effect of total pressure on the solvus at different temperatures, and the data are presented in table 3. In all runs, increased pressure produced in increased solubility of MgCO_3 in calcite. At 450°C the measured effect is 1.5 mole percent per 10 kb (based on only 2 runs). At 500°C the effect is 0.9 mole percent per 10 kb, at 575° it is 1.0 mole percent per 10 kb, at 650° it is 1.2, and at 780° , 1.4. Numerous runs were made at 650° and 780° , and the results are plotted in figures 4 and 5. These runs were made not only to determine accurately the magnitude of the pressure effect but also for the purpose of attempting to detect a calcite I-calcite II transition on the basis of differential solubility of MgCO_3 in the two phases. This latter point will be reconsidered shortly. The average total pressure effect is close to an increase of 1.2 mole percent MgCO_3 per 10 kb over the temperature range considered. The effect of temperature on the composition of dolomite has been shown to be quite small (Goldsmith and Heard, 1961). The effect of pressure at constant temperature on the composition of dolomite was too small to be detected.

In figure 6, data from this investigation are plotted as the unique polybaric solvus. The calcite at each temperature on this solvus contains the smallest amount of MgCO_3 in solid solution possible in equilibrium with dolomite. All the runs plotted in figure 6 were corrected for the observed pressure effect. Because of the relatively small effect of total

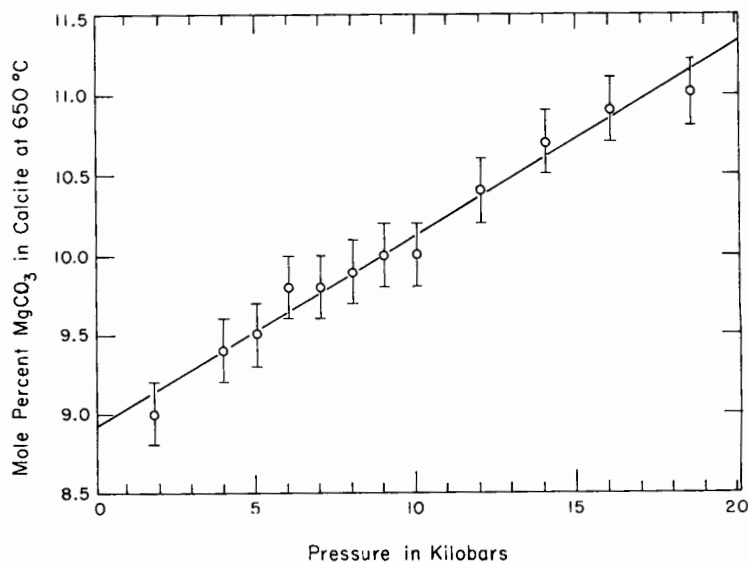


Fig. 4. The effect of total pressure on the solubility of MgCO_3 in calcite at 650°C .

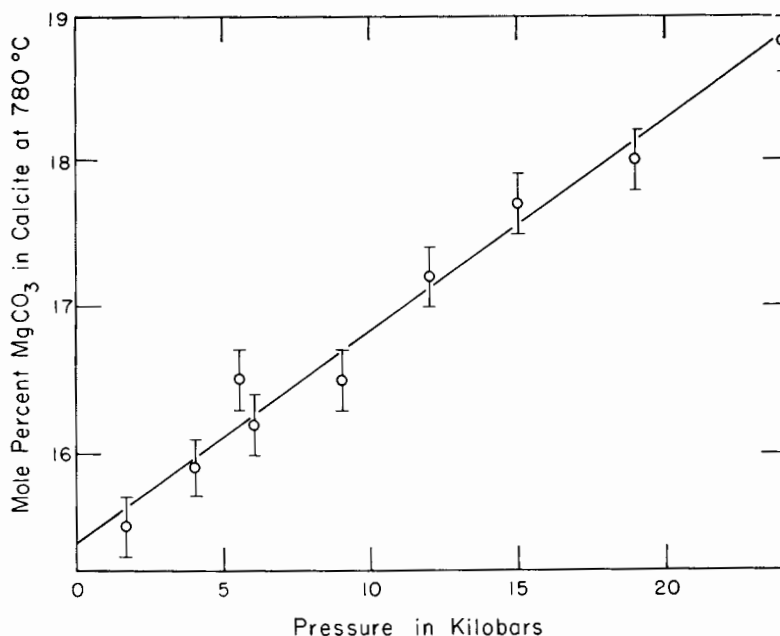


Fig. 5. The effect of total pressure on the solubility of MgCO_3 in calcite at 780°C .

pressure on the position of the solvus, and because of the relatively low CO_2 pressures necessary to maintain the carbonates as such at moderate to low temperatures, the polybaric solvus does not differ greatly in configuration from, say, a 1 or 2 kb isobaric solvus.

The calcite I-calcite II transition.—If a significant difference in the solubility of MgCO_3 in calcite I and calcite II existed, the isothermal pressure versus composition curves of figure 4 and 5 would show a discontinuity at the pressure at which calcite II becomes stable. Further, a change in slope at the discontinuity would indicate a differential pressure coefficient of solubility. Neither possibility is clearly revealed in the data, although the pressure range covered was adequate to cross the inversion boundary at any conceivable location. The curves were drawn through the data as straight lines, although the 1.4 mole percent per 10 kb slope at 780° might possibly contain in it a small increase in solubility as calcite II becomes stable. If so, the differential solubility of MgCO_3 in calcite I and II must certainly be less than 0.5 mole percent and probably less than 0.3 mole percent. It has not been proven that the calcite $\text{I} \rightleftharpoons \text{II}$ transition is a first-order phase change. The possibility thus remains that the transition is smeared over a finite range of temperature and of pressure. The possibility also exists that if the transition is a higher order phase change, the introduction of MgCO_3 in solid solution could smear the transition even further. One can not discount the possibility that the lack of a clearly observable transition using the above method is due to a somewhat smeared or higher order transformation.

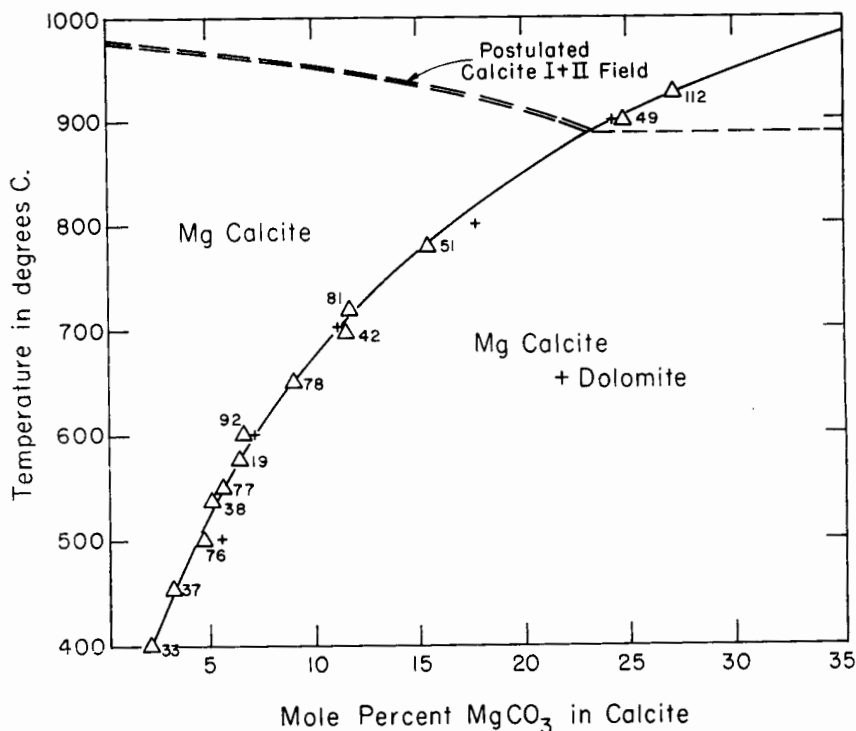


Fig. 6. Unique polybaric calcite-dolomite solvus. Triangles denote runs made in this study, and numbers are from table 3. Crosses are data of Harker and Tuttle (1955). The dashed lines represent the narrow (postulated) two-phase field of calcite I and calcite II and the estimated temperature of the calcite I-II inversion at the solvus. All runs along the solvus are corrected to the minimum pressure necessary to prevent decomposition of the carbonates. See text for discussion of pressure variation along solvus.

A substantial differential solubility between calcite I and II may also show an effect on the calcite-dolomite solvus. Goldsmith and Heard (1961, see fig. 8A) discussed the possibility that a first order calcite I $\rightleftharpoons$ II transition in a temperature-composition projection would intersect the solvus in the range 500° to 900°C. This would be the case if calcite II took more MgCO_3 in solid solution than calcite I, and a discontinuity and a change of slope would be the result. If the transition is of higher order, the two-phase field emanating from the transition in pure CaCO_3 would not be present, but a perturbation in the solvus might be seen. If on the other hand, calcite II took less MgCO_3 in solid solution than calcite I and the transformation was of the first order, a two-phase field extending to higher temperatures (see Goldsmith and Heard, 1961, fig. 8C) would be present and would either intersect the solvus at a temperature above 975°C or miss it altogether. No clear evidence of any of these possibilities was encountered.

Goldsmith and Heard (1961) observed that two calcite phases were produced in several runs at 1150°C on compositions of $\text{Ca}_{90}\text{Mg}_{10}$ and

$\text{Ca}_{80}\text{Mg}_{20}$. The possibility of quenching through a two-phase field with the preservation of two phases was considered. A few runs were made in the present study in an effort to locate a two-phase field (see runs MC 102 at 960°C , MC 103 at 1050°C , and MC 104 at 1150° in table 3). The lower temperature runs produced a single magnesian calcite, but the run at 1150°C produced a sample that gave an X-ray diffraction pattern of a rather non-homogeneous magnesian calcite, indicating either a range of compositions or an ill-defined multiphase assemblage. This sample was visibly different from all the other runs in the system, with a texture strongly indicative of having crystallized from a melt. There seems little doubt that this sample as well as the 1150° runs of Goldsmith and Heard had melted. The subsequent rapid crystallization in a two-component system could account for the inhomogeneous or two-phase result, and one would expect somewhat different compositional results as a function of cooling rate. We have not been able to observe the existence of a two-calcite field in quenching experiments.

It will be shown in the next section that the calcite $\text{I} \rightleftharpoons \text{II}$ equilibrium in the pressure-temperature projection of the MgCO_3 -saturated system must nearly coincide with the pure calcite $\text{I} \rightleftharpoons \text{II}$ transition because of the low differential solubility of MgCO_3 in the two phases. The approximate location of a two-calcite phase field may be sketched in the temperature-composition projection on this basis. The elevated pressures necessary to prevent carbonate decomposition in the higher temperature range will produce a lowering of the temperature of the calcite $\text{I} \rightleftharpoons \text{II}$ equilibrium according to our favored interpretation, assuming a first-order transition. The solvus would be intersected slightly below 900° , and the schematic relation is shown in figure 6.

Demonstration of equilibrium.—The unequivocal interpretation of the phase relations depends on a clear-cut demonstration of the attainment of equilibrium. Carbonates are in general more reactive than silicates, and solid solution equilibrium can be achieved in runs of hours' or days' duration at temperatures in the range 500 to 800°C . Some feeling for the time necessary to equilibrate $\text{CaCO}_3\text{--MgCO}_3$ solid solutions at 780°C in an unfluxed run is provided in the present study. A 2 kb cold seal run on unfluxed $\text{Ca}_{80}\text{Mg}_{20}$ mix at 780°C for 17 hr yielded a value of 14.6 mole percent MgCO_3 in the calcite. An unfluxed run at the same conditions for 63.5 hr yielded 15.4 mole percent. A fluxed run of the same duration yielded the same result. Fluxed runs in the piston-cylinder device at higher pressures for 1 day each were highly consistent with the longer cold-seal vessel runs. Hence there is a strong presumption of chemical equilibrium in the 780° runs. Similarly, Harker and Tuttle (1955) found that 8 hr at 800°C was not sufficient to give a final solid solution value but that 48 hr was long enough. The presence of Li_2CO_3 greatly shortens the time required. Some of the runs showed that equilibrium is attained in 3 hr or less at 780° in the presence of Li_2CO_3 .

The calcite-aragonite and solvus curves were verified at 450°C , near the low end of the temperature span of the present investigation. A fluxed

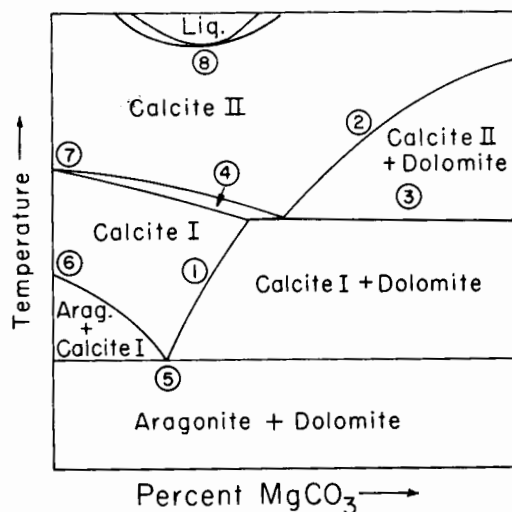


Fig. 7. Schematic isobaric section of the system $\text{CaCO}_3\text{--MgCO}_3$. See text for explanation of numbered curves and points.

run with a pure aragonite from Herrungrund, Hungary, and the Dover Plains, N.Y. dolomite made only 1 kb below the Mg-saturated calcite-aragonite boundary (run MC 45, table 3) reacted completely to yield a magnesian calcite at the identical composition deduced from the solvus runs. It is considered that this run demonstrates the equilibrium nature of the calcite-aragonite boundary deduced in the present study and indicates a high degree of confidence in the equilibrium nature of the solvus deduced. A similar reversal was made at 650°C with equally gratifying results (Run MC 95, table 3).

Summary of phase relations.—Figure 7 is a schematic isobaric phase diagram in the system $\text{CaCO}_3\text{--MgCO}_3$. Curves 1 and 2 are the solvus, above and below the calcite I $\rightleftharpoons$ II transformation, which is at the temperature of curve 3 at the pressure of this diagram. The field labeled 4 is the postulated two-phase field of calcite I and calcite II (see fig. 6), terminating at point 7, which is the value for the transition in pure CaCO_3 . Point 5 is an invariant point and represents the intersection of the isobaric plane with the calcite I-aragonite-dolomite curve. The solvus is terminated at point 5 at this particular pressure by the formation of aragonite. Point 6 represents the temperature of the calcite-aragonite transformation in pure CaCO_3 , or in other words, the equivalent of point 5 in the absence of MgCO_3 . No field of solid solution of MgCO_3 in aragonite is indicated. The curves above point 8 represent a possible configuration for the melting relations suggested by the run at 1150°C . Inasmuch as pure CaCO_3 melts at about 1300°C at 10 kb, it is apparent that MgCO_3 lowers the melting temperatures, and assuming no decomposition, the melting loop is of the general form indicated.

Figure 8 is a true representation of the system at 1, 9, and 20 kb. The three isobaric sections are shown on the one diagram so that the relative

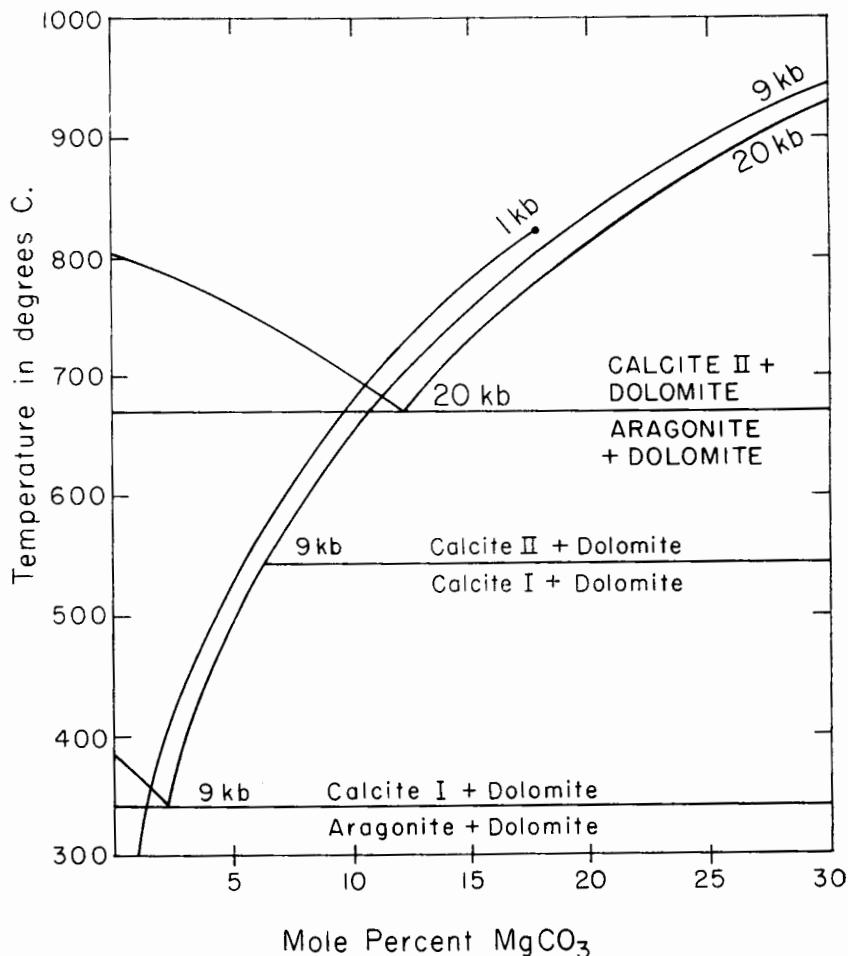


Fig. 8. Isobaric curves in the Ca-rich portion of the system $\text{CaCO}_3\text{--MgCO}_3$. 1 kb, 9 kb, and 20 kb solvuses are shown. One kb solvus terminates by decomposition at the dot at approximately 820°. See text and figure 7 for explanation of the curves. A thin two-calcite phase field (area 4 in fig. 7) is omitted for the sake of clarity.

positions of the phase boundaries can be seen. The calcite I-II two-phase field (area 4 in fig. 7) has been deleted for simplification inasmuch as it cannot be located precisely and has no observable effect on the solvus. The suggested melting relations have also been omitted. The configuration of the aragonite-calcite field boundary (the line between points 5 and 6 in fig. 7) was not directly determined, but its position is fixed by the location of points 5 and 6, which are well located. At rather low pressures, the upper portion of the solvus is terminated by decomposition of the carbonates (see 1 kb solvus), and the locus of all such points determines the unique polybaric solvus of figure 6.

Comparison of piston-cylinder apparatus with simple squeezer.—Many runs were made in this system with an externally heated opposed anvil device (simple squeezer) as early as 1956 by one of the present authors. Much criticism has been written of the squeezer (Kitahara and Kennedy, 1964, for example), and many of the phase diagrams based on squeezer runs, especially in silicate systems, have required revision. However, considerable studies using the squeezer for systems appear to have produced valid results (MacDonald, 1956; Goldsmith and Graf, 1960). It is of interest, therefore, to compare the present piston-cylinder determination of the phase relations with the earlier squeezer work as evidence regarding the effectiveness of the squeezer as a tool for petrologic research, at least in carbonate systems. The pure CaCO_3 calcite-aragonite curve based on simple-squeezer runs rises in pressure to about 20 kb at 800°C and is essentially coincident with the present piston-cylinder determination. The calcite-aragonite curve based on simple-squeezer runs for the CaCO_3 – MgCO_3 system is everywhere with 1 kb of the piston-cylinder determination. This curve also shows the break of slope, although at the time the experiments were made, this effect was attributed to the increasing MgCO_3 concentration in calcite with increasing temperature. Finally, considerable number of squeezer experiments made at much higher pressures to determine an effect of pressure at constant temperature on the calcite-dolomite solvus are in agreement with the piston-cylinder determination. These data constitute strong evidence that the squeezer can produce quantitatively correct results in carbonate systems. The probable reasons for better success with carbonates compared to silicates in squeezers are greater rate of reaction among carbonates and higher plasticity at elevated temperatures, which gives more uniform pressure distribution under the flat pistons.

It is essential to state how the squeezer runs were performed. A 0.005 in.-thick stainless steel containing ring was used which had an internal diameter slightly less than the $\frac{1}{4}$ in. diameter piston faces. The powdered sample was placed within the ring, and the assembly was brought to a pressure of 15 to 20 kb or higher to consolidate the sample and the gasket. The gauge pressure was then bled off to the desired nominal value. The sample was brought up to temperature, and gauge-pressure was kept constant by continual bleeding during the period of thermal expansion. It is of interest to note that the transition pressures of several metals, notably barium and cesium, determined by Bridgman (1952) at 25° in an opposed anvil device on decrease of pressure are in much better agreement with the presently-accepted values (Kennedy and LaMori, 1962) than the transition pressures found by Bridgman on the increasing-pressure cycle, which are erroneously high. It is thus possible that pressures in the opposed-anvil device can be homogeneous and rather accurately computed on the basis of geometry alone if the sample is relatively plastic and has first been pressed to elevated pressures, and the pressure released to the desired value before heating.

THERMODYNAMIC DISCUSSION

The relatively large amount of thermo-chemical data available for the system $\text{CaCO}_3\text{--MgCO}_3$ makes possible several detailed calculations of the phase relations encountered at high temperature and pressure. The most useful data are the standard enthalpies of formation and entropies of calcite, magnesite, and dolomite (Robie, ms) and the molar volumes of magnesian calcites, which may be calculated from the unit-cell constants determined by Goldsmith and Graf (1958) and Goldsmith, Graf, and Heard (1961). These data, in conjunction with the measured solubility of MgCO_3 in calcite as a function of temperature, allow theoretical calculation of the pressure-temperature locations of the three-phase curves of figure 2 and the effect of pressure on the calcite-dolomite solvus curve.

CaCO₃ system.—The measured slopes of the univariant curves meeting at the triple-point calcite I–calcite II–aragonite (A) determine the volume change per mole of the I → II transition. The relation for the volume change is, assuming a first-order transition:

$$\Delta V_{\text{I} \rightarrow \text{II}} = \frac{-\Delta V_{\text{A} \rightarrow \text{I}} \left(\frac{dp}{dt}_{\text{A} \rightleftharpoons \text{I}} - \frac{dp}{dt}_{\text{A} \rightleftharpoons \text{II}} \right)}{\frac{dp}{dt}_{\text{I} \rightleftharpoons \text{II}} - \frac{dp}{dt}_{\text{A} \rightleftharpoons \text{II}}}$$

If the transition takes place over a finite temperature and pressure interval, such as would be the case for certain kinds of higher-order transitions, the $\Delta V_{\text{I} \rightarrow \text{II}}$ would still be calculated by the above expression using the slopes measured on opposite ends of a ΔT interval sufficient to enclose the transition. The values of the slopes presented in the preceding section and the $\Delta V_{\text{A} \rightarrow \text{I}}$ of $2.78 \text{ cm}^3/\text{mole}$, neglecting any differential compression to 10 kb and differential thermal expansion to 480°C , yield a $\Delta V_{\text{I} \rightarrow \text{II}}$ of $-1.01 \text{ cm}^3/\text{mole}$. This value is nearly ten times as large as that measured by Bridgman (1939) by the method of piston-displacement at 25°C and might also seem surprisingly large in view of the inability to detect clearly the $\text{I} \rightleftharpoons \text{II}$ transition by various means in the present study. The I-II transition has a marked effect on the course of the calcite-aragonite boundary, however, and the abrupt change of direction argues persuasively for a first order transition of significant volume change or for a higher order transition of significant net volume change which is complete over a rather small temperature and pressure interval. It is not probable that a few hundred degrees temperature increase could increase $\Delta V_{\text{I} \rightleftharpoons \text{II}}$ by a factor of nearly 10. The strong indication of the present work is that the ΔV measured by Bridgman was erroneously small because of sluggishness of the transition at the low temperatures at which he worked. Bridgman reported an anomalously high apparent compressibility of calcite II, which would be due to a sluggish transition if the present surmise is correct.

If $\Delta S_{\text{I} \rightarrow \text{II}}$ is calculated from the Clausius Clapeyron equation the result is $\Delta S = 0.349 \text{ cal/}^\circ\text{C mole}$. This value provides some support for the Jamieson-Boettcher-Wyllie hypothesis of correlating Bridgman's calcite I-II transition with the thermal arrest at 975°C in the 1-atm heating and cooling curves of Boeke (1912). Jamieson estimated a ΔS of 0.273 to $0.409 \text{ cal/}^\circ\text{C mole}$ for the thermal transition based on the duration of Boeke's signal and the heat capacity of calcite. This relatively large heat effect is not consistent with the small volume change and small dp/dt slope given by Bridgman but is in close agreement with the $\Delta S_{\text{I} \rightarrow \text{II}}$ of $0.349 \text{ cal/}^\circ\text{C mole}$ predicted from the measured slopes at the triple-point. The simplest hypothesis, that of the identity of Bridgman's and Boeke's transitions, therefore seems preferable in spite of failure to detect the location of the transition in the pressure-temperature plane by means other than a break in slope of the calcite-aragonite curve.

The $\Delta S_{\text{I} \rightarrow \text{II}}$ value of 0.349 is smaller than the value of $\sim 1.4 \text{ cal/}^\circ\text{C mole}$ which is the configurational entropy increase due to disordering the planar CO_3^{2-} groups of the calcite structure (Boettcher and Wyllie, 1968). There may also be an entropy decrease attendant on the decrease in volume which could amount to as much as $1 \text{ cal/}^\circ\text{C mole per cc}$ (Fyfe, Turner, and Verhoogen, 1958, p. 30), so that the hypothesis of an order-disorder transition cannot be ruled out on this basis. The percentage entropy and volume changes of the calcite $\text{I} \rightleftharpoons \text{II}$ transition are quite similar to those at the high-low quartz transition. There is only a slight change in the X-ray powder pattern, assuming that Jamieson's high pressure X-ray data are applicable, as in the α to β quartz case, which is also a non-quenchable transition. A slight bond-angle change in calcite analogous to that in quartz might be a reasonable structural explanation.

If the correlation of Bridgman's calcite I-II transition with the thermal effect of Boeke is made, as the present data seems to favor, neither the DTA arrests encountered by Bell and England (1964) nor the shear-wave velocity anomaly found by Dandekar (ms) at 3 to 4 kb and 25°C in single calcite crystals are elucidated. Alternative CaCO_3 pressure-temperature diagrams may be brought forth that explain one or both of these effects by reversible phase changes and that are not wholly ruled out by the present data.

Figure 9A shows the diagram that would result if the observations of Bell and England are due to a first-order phase change which makes a virtual (metastable) triple point with the calcite I-II line inside the field of aragonite. A metastable prolongation of this postulated phase change might be made to explain the observed ultrasonic effects near 3 to 4 kb. The postulated new transition would require a rather small volume change; otherwise it would have been observed in earlier volumetric studies. Bridgman's I-II transition would have to have a substantial volume change under this hypothesis as well, because the "I-X" transition must have a large ΔV in order to deflect the calcite-aragonite curve as it

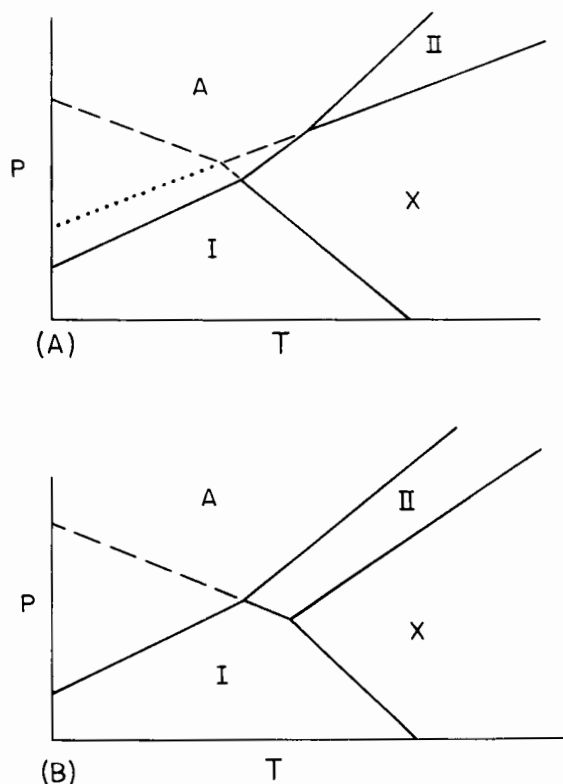


Fig. 9. Possible alternative CaCO_3 stability diagrams. Figure 9A shows possible relations if a hypothetical phase "X" makes a metastable triple point with aragonite and calcite II in the field of aragonite. Metastable portions are indicated by dotted and broken lines. Figure 9B shows possible relations if a hypothetical phase "X" has a stable invariant relation with respect to calcite I and calcite II.

does, and the $\Delta_{\text{I-II}}$ must be the sum of $\Delta V_{\text{I-X}}$ and $\Delta V_{\text{X-II}}$. This hypothesis would also eliminate the need for curvature in the calcite I-II curve. A deflection of the calcite-aragonite curve by the II-X transition as it crosses it might be too small to be easily observed.

Figure 9B is a diagram that would result if there is a "II-X" transition that makes a stable invariant point with the I-II transition. The observations of Bell and England could be explained by this hypothesis, but the observation of Dandekar could not. Again the I-II transition would have to have a large ΔV and need not have much curvature.

It is conceivable that both calcite II and a "calcite X" might have a calcite I-like X-ray diffraction powder pattern with the (113) line missing, whether or not an anion-rotation phenomenon is responsible for the line deletion. Thus a diagram involving three calcite phases is not eliminated as a possibility by the present data. The scientists' prejudice for the simplest workable hypothesis may lend favor to the relatively straightforward calcite I-II interpretation as shown in figure 1.

Binary system.—Many of the features of the pressure-temperature diagram of the system $\text{CaCO}_3\text{--MgCO}_3$ can be investigated by using the theory of regular solutions. Following Robie (1957), CaCO_3 (cc)- MgCO_3 (mc) solutions in the calcite structure are treated as regular solutions, so that:

$$\begin{aligned}\mu_{\text{cc}} &= \mu_{\text{cc}}^{\circ} + RT \ln (1-X_{\text{mc}}) + \Omega X_{\text{mc}}^2 \\ \mu_{\text{mc}} &= \mu_{\text{mc}}^{\circ} + RT \ln X_{\text{mc}} + \Omega (1-X_{\text{mc}})^2\end{aligned}$$

where μ denotes the partial molal Gibbs energy of the components, R is the gas constant per mole, T is the absolute temperature, X is the mole fraction of a component, Ω is the "inter-change energy" per mole (Guggenheim, 1952), and a superscript zero refers to the pure component.

The equilibrium relation of the solvus is given by:

$$\mu_{\text{cc}}^{\text{c}} + \mu_{\text{mc}}^{\text{c}} - \mu^{\text{D}} = 0$$

Here the superscript C represents calcite, and D represents dolomite. Inserting the regular solution equations gives:

$$0 = \Delta\mu^{\circ} + RT \ln X_{\text{mc}} (1-X_{\text{mc}}) + \Omega [X_{\text{mc}}^2 + (1-X_{\text{mc}})^2]$$

The standard Gibbs energy change for the pure substances, $\Delta\mu^{\circ}$, is evaluated by:

$$\Delta\mu^{\circ} = \Delta H_{298}^{\circ} - T\Delta S_{298}^{\circ}$$

where ΔH_{298}° is the standard enthalpy change, and ΔS_{298}° is the corresponding entropy increment. The latter equation assumes that ΔS° is constant over the temperature interval 298°K- T , an assumption that is necessary because of the lack of high-temperature heat content data for magnesite and dolomite. This assumption is likely to be valid with a high degree of accuracy in the temperature range of interest, as evidenced by the fact that the heat capacity of dolomite in the range 70 to 300°K is equal to the sum of the heat capacities of calcite and magnesite to within 0.2 percent (Robie, ms, p. 73). Hence,

$$\Omega = \frac{-\Delta H_{298}^{\circ} + T\Delta S_{298}^{\circ} - RT \ln X_{\text{mc}}(1-X_{\text{mc}})}{2X_{\text{mc}}^2 - 2X_{\text{mc}} + 1}$$

The values of $\Delta H_{298}^{\circ} = 3150$ cal/mole and $\Delta S_{298}^{\circ} = 0.81$ cal/°C-mole used by Robie are adopted. Table 4 shows the values of Ω that are calculated at several temperatures when the best solvus data of the present work, reduced to a 1-atm basis by applying the measured pressure correction, are used. The Ω values fall within a fairly narrow spread, which is some justification for the use of the regular solution theory.

The effect of total pressure on the MgCO_3 solubility can be calculated as follows. The total variation at constant temperature of the Gibbs energy change of the solvus reaction, $\Delta\mu = \mu_{\text{cc}}^{\text{c}} + \mu_{\text{mc}}^{\text{c}} - \mu^{\text{D}}$,

TABLE 4

Calculated interchange energy for regular solution
calcite-dolomite solvus

T, °K	X _{mc} (1 atm) mole. fraction	 cal/mole
673	0.022	2650
723	0.032	2615
773	0.043	2605
823	0.055	2630
873	0.069	2680
923	0.089	2630
973	0.111	2605
993	0.117	2705
1053	0.152	2690
1173	0.245	2740

must remain zero under arbitrary differential changes in pressure and composition of the calcite phase:

$$d(\Delta\mu) = 0 = \left(\frac{\partial\Delta\mu}{\partial p}\right)_{T, X_{mc}} dp + \left(\frac{\partial\Delta\mu}{\partial X_{mc}}\right)_{P, T} dX_{mc}$$

$$\therefore \left(\frac{\partial X_{mc}}{\partial P}\right)_T = - \frac{\left(\frac{\partial\Delta\mu}{\partial P}\right)_{T, X_{mc}}}{\left(\frac{\partial\Delta\mu}{\partial X_{mc}}\right)_{T, P}}$$

The numerator may be evaluated as:

$$\left(\frac{\partial\Delta\mu}{\partial P}\right)_{T, X_{em}} = V_{cc}^c + V_{cm}^c - V^D$$

where V indicates partial molal volume, and V is volume per mole. If the denominator is evaluated by differentiating the regular solution expressions, the pressure effect becomes:

$$\left(\frac{\partial X_{mc}}{\partial P}\right)_T = \frac{V_{cc}^c + V_{mc}^c - V^D}{(2X_{mc}-1) \left[\frac{RT}{X_{mc}(1-X_{mc})} - 2\Omega \right]}$$

In order to evaluate the partial molal volumes, a plot of volume per mole of calcite solid solution versus mole fraction of MgCO_3 in solid solution was made using the unit cell data of Goldsmith, Graf, and Heard (1961). Table 5 gives the molar volumes of the solid solutions and dolomite. The partial molal volumes are the intercepts on the calcite and magnesite axes of the tangents to the molar volume curve. Very careful plotting on large sheets of millimeter paper and careful straight-edge measurements were necessary in order to get acceptable values be-

TABLE 5
Molar volumes of magnesian calcite and dolomite

Composition, mole % MgCO_3	a_o , Å	c_o , Å	V , cm^3	Source*
Calcite	4.9900	17.062	36.931	1
(Johnson-Matthey Spec-Pure CaCO_3)				
4.94	4.9691	16.952	36.386	1
9.89	4.9440	16.851	35.805	1
10.0	4.9483	16.870	35.908	2 (avg)
19.78	4.9022	16.637	34.755	1
20.0	4.9122	16.699	35.027	2 (avg)
30.0	4.8760	16.514	34.131	2
40.0	4.8419	16.283	33.184	2 (avg)
42.5	4.8328	16.235	32.962	2
45.0	4.8244	16.167	32.710	2 (avg)
47.5	4.8152	16.111	32.472	2
50	4.8050	16.061	32.234	2
Magnesite, synthetic	4.6331	15.015	28.018	1
Dolomite, ordered, Gabbs, Nev.	4.8064	23.102	32.139	2
Dolomite, disordered, Gabbs, Nev.	4.8031	16.037	32.161	2
Dolomite, ordered, Serra das Eguas, Brazil	4.8065	16.004	32.140	2
Dolomite, disordered, Serra das Eguas, Brazil	4.8017	16.037	32.142	2

*Source 1 is Goldsmith and Graf (1958); source 2 is Goldsmith, Graf, and Heard (1961).

cause of the slight departure from Vegard's Law. Two separate plots were made, and the tangent-intercepts averaged.

Figure 10 shows the averaged partial molal values of MgCO_3 and CaCO_3 in solid solution in the composition range 0 to 30 mole percent MgCO_3 . It should be remembered that the data are taken from samples at room temperature and at 1 atm pressure. The correction of the values to the elevated temperature and pressure of the desired calculation was necessarily ignored. The present solubility data, reduced to 1-atm values, were used in the pressure-effect calculation. The computed increases of solubility due to pressure are 0.52 mole percent/10 kb at 520°, 0.82 mole percent/10 kb at 650°, and 0.82 mole percent/10 kb at 780°. These values may be compared with the measured values of approximately 0.9 mole percent/10 kb at 500°C, of 1.2 mole percent/10 kb at 650°, and of 1.4 mole percent/10 kb at 780°. The agreement is close enough to indicate that the regular solution theory provides a nearly quantitative estimate of the pressure effect on the solvus. The discrepancies could be due to the several obvious sources of error, such as ignoring the pressure and temperature effects on the molar volume curve, the difficulty of obtaining accurate tangents to it by graphical means, or not taking into account any slight increase of solubility of MgCO_3 at the calcite I-II

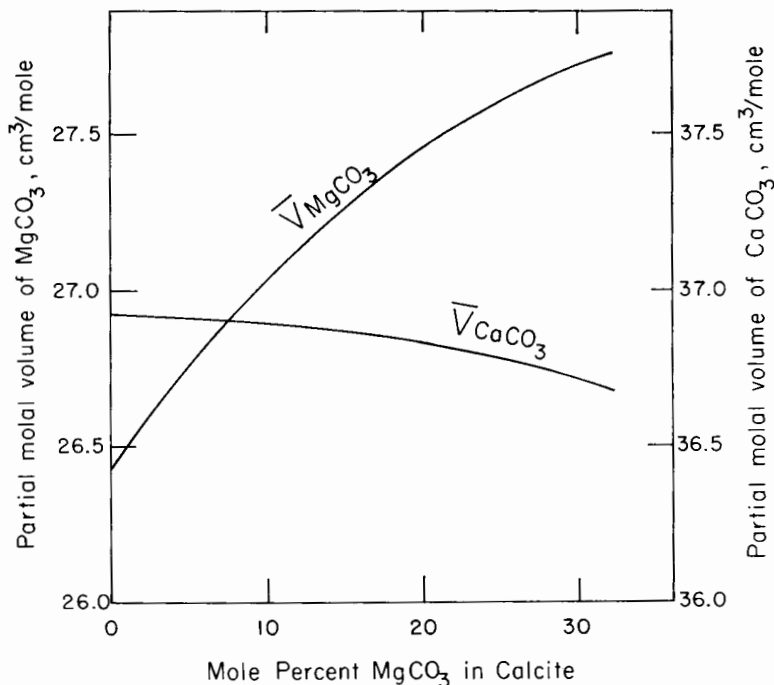


Fig. 10. Partial molal volumes of CaCO_3 and MgCO_3 in calcite as functions of composition, as obtained from quenched solid solutions at 1 atm and room temperature.

transition. The present data fail to establish clearly a discontinuity in the solubility versus pressure curves but place an upper limit of 0.3 to 0.5 mole percent on an increase of MgCO_3 solubility going into the calcite II structure. This number is itself quite useful in determining the location of the calcite I–calcite II–dolomite line in the pressure-temperature projection, as will be seen shortly.

Theoretical curves for the calcite I–dolomite–aragonite and calcite II–dolomite–aragonite pressure-temperature projections can be constructed from the regular solution theory starting with the diagram for pure CaCO_3 . By setting the chemical potential of CaCO_3 in magnesian calcite equal to the chemical potential of aragonite, one finds the increase in pressure necessary to produce the calcite–aragonite transition when MgCO_3 is saturated in the calcite structure so that dolomite is present:

$$P - P^I = \frac{1}{\Delta V_{A \rightarrow I}} \left[-RT \ln (1 - X_{mc}^I) - \Omega X_{mc}^{I^2} \right]$$

$$P - P^{II} = \frac{1}{\Delta V_{A \rightarrow II}} \left[-RT \ln (1 - X_{mc}^{II}) - \Omega X_{mc}^{II^2} \right]$$

where P^I is the equilibrium transition pressure from pure calcite I to

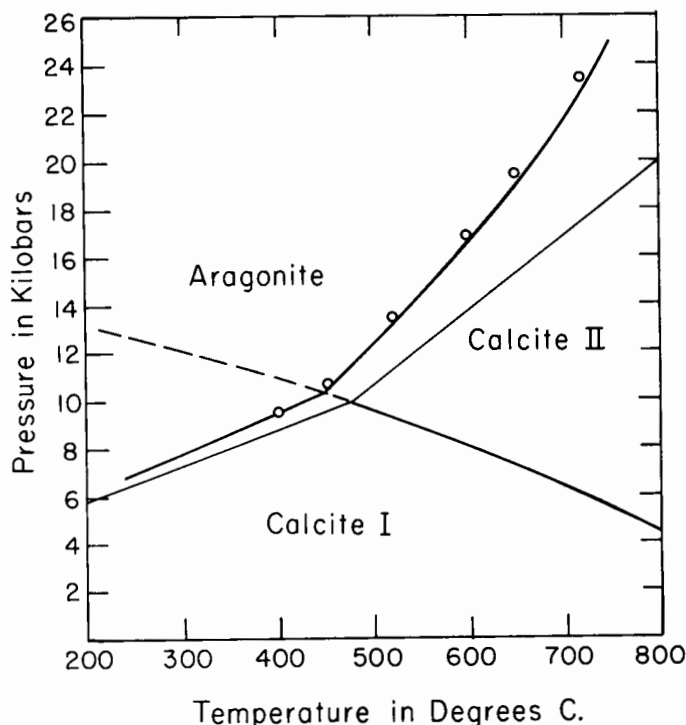


Fig. 11. Computed points on the calcite-aragonite-dolomite curve, compared with the experimentally determined curve. Phase boundaries for pure CaCO_3 are shown. The metastable portion of the calcite I-calcite II curve is dashed.

aragonite at a given temperature and P^{II} is the corresponding pressure for pure calcite II. The fundamental finding that there is a negligible solubility difference of MgCO_3 in calcite I and calcite II is now applied. A corollary of this is that the Ω values for calcite I and calcite II are very nearly the same. The X_{mc} values are given an appropriate incremental increase in Mg-content due to the pressure increase from the 1-atm values to the pressure of the pure CaCO_3 calcite-aragonite curve. Figure 11 shows the calculated points compared with the least-square fit to the data: The agreement is surprisingly good. The calculated points lie a few hundred bars above the experimental curve, but the discrepancy is within the combined error limits. A change of ΔV of the calcite-aragonite transition with temperature and pressure or a change of Ω with temperature and pressure might also be responsible for the slight discrepancy.

An independent estimate of $\Delta V_{\text{I} \rightarrow \text{II}}$ in pure CaCO_3 can be made from the two preceding equations by comparing the dispositions of the univariant curves around the triple points in the pure CaCO_3 and the MgCO_3 saturated system. The experimental determinations of the univariant curves are shown enlarged in the region of the univariant points in the pressure-temperature diagram in figure 12. The pressures P , P' ,

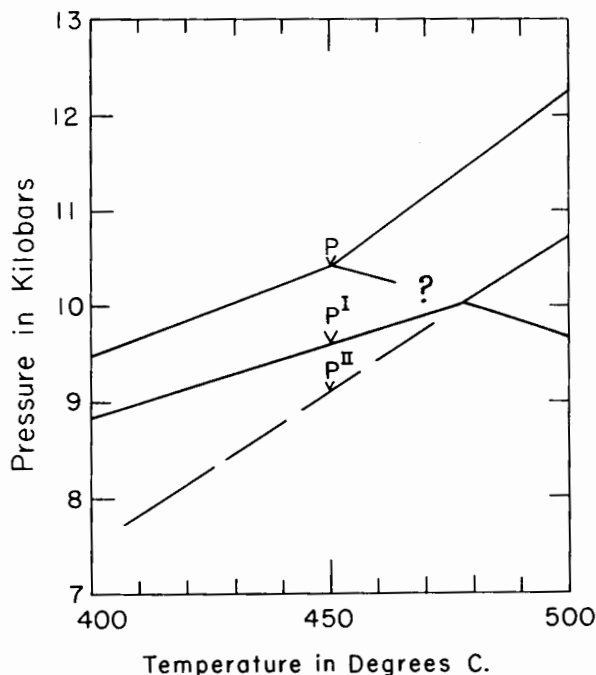


Fig. 12. Detail of the P-T region adjacent to the invariant points in the CaCO_3 and $\text{CaCO}_3\text{--MgCO}_3$ systems. The upper set of curves is for the MgCO_3 -saturated system. The lower set of curves is for pure CaCO_3 . P is the pressure of the calcite I-calcite II-dolomite-aragonite invariant point. P^I is the pressure of the pure 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°C , the invariant-point temperature in the binary (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° below the invariant-point temperature of the pure CaCO_3 system. Simultaneous solution of the regular solution equations together with the relation $\sum \Delta V = 0$ around the 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 ΔV with the value of -1.01 cc/mole deduced from the slopes of the univariant equilibria in the pure CaCO_3 system lends considerable confidence to the seemingly somewhat opposed notions that the calcite I-II transition has a relatively large ΔV even though the change in 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:

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

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 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 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 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 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 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 MgCO_3 could be metastably quenched in the calcite I formed by inversion or that during inver-

sion a Mg-poor calcite I could be exsolved. In either case, there would be a resulting confusion as to the original composition of the primary phase. The present data indicate that such an effect is not of real concern, because the differential solubility is so slight that the geologic thermometry would not be affected. It is a consequence of the small solubility differential that the field of calcite II remains at high temperatures and pressures and that calcite II as a primary phase is probably not often encountered in ordinary metamorphic conditions. For example, if the temperature of the Crestmore, California, carbonates as interpreted by Carpenter (1967) is correct, calcite II would have been the primary phase if the pressure exceeded approximately 5 kb. This represents a depth of burial in excess of 15 km, which, although perhaps not impossible, is unlikely.

The presence of MgCO_3 increases the field of stability of calcite with respect to aragonite. The effect is rather small at temperatures up to approximately 450°C , but at higher temperatures the difference between the transition curves for pure CaCO_3 and for the MgCO_3 -saturated system becomes large. It is unlikely, however, that aragonite is produced in nature in the higher grades of metamorphism, as the necessary pressures are unrealistically high. The presence of MgCO_3 in the system makes it all the more unlikely that aragonite would be formed under equilibrium conditions. Metamorphic aragonite is known from several low-grade metamorphic terranes (Coleman and Lee, 1962). These rocks probably never reached temperatures higher than about 250°C , at which point the pure calcite-aragonite and MgCO_3 -saturated calcite-aragonite curves are separated by but a few hundred bars. Therefore, the presence of MgCO_3 in rocks probably has little effect on a geobarometer based on the equilibrium calcite-aragonite transition.

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