The calcite–aragonite equilibrium: effects of Sr substitution and anion orientational disorder

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Abstract

Hydrothermal experiments have been performed in the system $CaCO_3$–$SrCO_3$ from 350° to 650°C over a range of 1 to 5 kbar. The results reconcile inconsistencies in previous determinations of low-temperature phase equilibria for binary Ca–Sr carbonates, and demonstrate that the small amounts of Sr in natural metamorphic aragonite extend the field of its stability to slightly lower pressures than in the unary $CaCO_3$ system.

The phase equilibrium data also provide evidence for the existence of two structurally distinct rhombohedral carbonates at elevated pressures in the binary Ca–Sr system. Because of the exact correspondence of the present high-pressure results to previous X-ray determinations of one-atmosphere phase relations, one of these two polymorphs is identified as a calcite structure having ordered CO_3 groups, and the other as a calcite-like structure in which the CO_3 groups display rotational disordering about their triad axes. The preferential fractionation of Sr into the disordered phase favors a model for its crystal structure in which the cations occupy ninefold coordinated sites.

Experiments in the binary Ca–Sr system identify a three-phase equilibrium at which these two rhombohedral phases coexist with an orthorhombic aragonite solid solution. This three-phase equilibrium can be traced to a unary triple-point near 475°C and 10 kbar in the pure $CaCO_3$ system; aragonite, ordered calcite, and disordered calcite are all stable under these conditions.

Because the calcite–aragonite boundary is strongly curved at temperatures below the triple point but nearly linear above it, the curvature is attributed to a gradual disordering of the CO_3 groups with increasing temperature. Differential solubility of Sr in the ordered and disordered calcite phases simultaneously in equilibrium with Sr-bearing aragonite requires, however, that the transition itself be thermodynamically first-order.

Introduction and previous work

Understanding the geologic processes operating in subduction zones requires accurate determination of the conditions under which metamorphic rocks of the glaucophane schist facies have originated. The occurrence in these rocks of aragonite, the high-pressure polymorph of $CaCO_3$, offers one means of estimating their conditions of origin, provided first that the calcite–aragonite boundary can be precisely located experimentally, and second that the effects of the additional chemical components present in natural aragonite can be assessed. In the last decade, a great deal of research has been directed to these ends; a review of these studies reveals agreement on general features but also discrepancies concerning the detailed behavior of the system.

Early attempts to define the calcite–aragonite equilibrium boundary yielded inconsistent results; for a thorough review, consult Boettcher and Wyllie (1968). Later research has produced three determinations which are in much better agreement. Both Boettcher and Wyllie (1968) and Goldsmith and Newton (1969), using piston–cylinder apparatus, located the equilibrium above 400°C. Johannes and Puhan (1971) compared results obtained in gas-pressure apparatus in the temperature range 200° to 700°C with those from a variety of piston–cylinder techniques. If the piston–cylinder pressures are ad-

justed to conform to the results from the gas-pressure apparatus, all three studies agree to within an experimental error of ±500 bars. Subsequent work in the range 800° to 1100°C (Irving and Wyllie, 1973) and in the range 50° to 150°C (Crawford and Hoersch, 1972) is also consistent with these determinations, (Fig. 1), although one study (Zimmerman, 1971) placed the equilibrium from 150° to 350°C at markedly higher pressures.

Although in all these investigations the calcite–aragonite boundary was depicted with one nearly linear section below 350°C and another of steeper dP/dT slope above 500°C, the nature of the region between these linear sections is controversial. Initially, the change of slope was attributed to the transition from calcite I to calcite II, first described by Bridgman (1939). Boettcher and Wyllie (1968), who equated the high-pressure calcite I–calcite II transition of Bridgman (1939) with Boeke's (1912) high-temperature transition from β-calcite to α-calcite, showed a discontinuity in the calcite–aragonite boundary slope; they postulated, in agreement with Goldsmith and Newton (1969), a first-order calcite I–calcite II transition as its explanation. Johannes and Puhan (1971) preferred a continuously curved boundary and inferred a second-order calcite I–calcite II transition. Subsequent studies by Kondo *et al.* (1972) and Cohen and Klement (1973), however, suggested that neither the calcite I–calcite II transition nor the β-calcite–α-calcite transition can account for the change of slope of the calcite–aragoni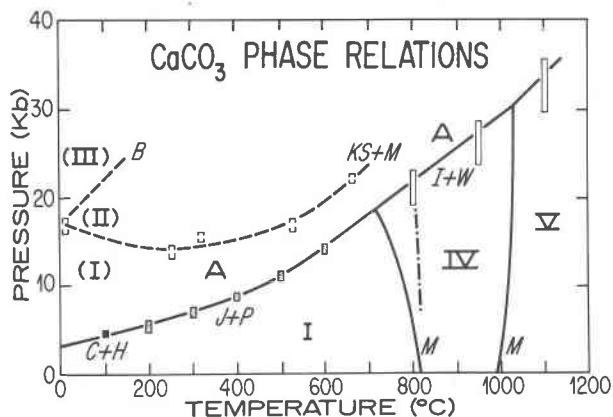te equilibrium boundary; neither transition curve intersects the boundary in the appropriate temperature range. The most recent work (Mirwald, 1976, 1979a,b) outlined stability fields at temperatures above 800°C for two additional $CaCO_3$ polymorphs, designated calcite IV and calcite V (equivalent to Boeke's β-calcite and α-calcite). Nevertheless, the changing slope of the calcite–aragonite boundary remained unexplained, and the phase transition which it seems to require remained unidentified.

In addition to these unresolved problems in the unary system $CaCO_3$, doubts persisted regarding the effects of large-radius cations substituting for Ca in natural aragonites. Of these substituents, Sr is the most significant, as its oxide comprises approximately 1 mole percent of typical metamorphic aragonite (Coleman and Lee, 1962). Because $SrCO_3$ below 912°C at atmospheric pressure has the aragonite structure, it is possible that the small amounts of $SrCO_3$ component in natural systems might stabilize the orthorhombic carbonate to lower pressures than in the pure $CaCO_3$ system.

To measure this effect, Froese and Winkler (1966) examined $CaCO_3$–$SrCO_3$ equilibria at 500°–700°C and 1–15 kbar. Chang (1965, 1971) also studied this system above 500°C, both at atmospheric pressure and from 10 to 25 kbar as part of the ternary system $CaCO_3$–$SrCO_3$–$BaCO_3$. The application of these experimental data in the temperature range relevant to blueschist metamorphism is, however, problematical. Despite reasonable agreement at high pressures and temperatures, extrapolations of Froese and Winkler's data lead to contradictions with Chang's data at one atmosphere, predicting a considerably more Ca-rich orthorhombic phase than is observed. For instance, Chang (1965, Fig. 5) indicated a nearly constant composition (about 53 mole percent $SrCO_3$) for orthorhombic carbonate in equilibrium with calcite at one atmosphere over the temperature range 450°–600°C; the data of Froese and Winkler (1966, Fig. 4) suggest a range of compositions (from perhaps 40 to 55 mole percent $SrCO_3$) at one atmosphere over the same temperature interval. The discrepancies become more pronounced at lower temperatures, in the experimentally uninvestigated range critical to blueschist-facies metamorphism.

Thus the detailed behavior of the calcite–aragonite equilibrium is obscured by contradictory data regarding the effect of Sr, especially at low temperatures, and by disagreement about the nature and effect of the phase transition in calcite near 500°C and 10 kbar. In this study, these problems were found amenable to hydrothermal investigation in the sys-

Fig. 1. Phase relations in the unary system $CaCO_3$. Dashed lines represent metastable equilibria. "A" = aragonite; "I" through "V" = calcite polymorphs. Data from Crawford and Hoersch, 1972 ($C+H$); Johannes and Puhan, 1971 ($J+P$); Irving and Wyllie, 1973 ($I+W$); Mirwald, 1976 (M); Kondo *et al.*, 1972 ($KS+M$); Bridgman, 1939 (B).

tem $CaCO_3$–$SrCO_3$, over the temperature range 350°–650°C and H_2O pressures of 1–5 kbar.

Experimental techniques and equilibrium criteria

All experiments were performed in standard cold-seal hydrothermal apparatus, using filler rods and external Cr–Al thermocouples. Temperature was controlled to within ±5°C and pressure uncertainties are less than 20 bars. Reactants were sealed in silver capsules with 20 weight percent of an aqueous 0.075 M Li_2CO_3 solution to catalyze reaction. (Comparison runs using pure water confirmed that the trace amounts of Li_2CO_3 did not displace the equilibria, but were somewhat effective in speeding reaction at low temperatures.)

Different techniques were required to determine the opposite boundaries of the miscibility gap. On the Sr-rich side, two types of starting materials were employed; one was a two-phase mixture of reagent $CaCO_3$ (calcite) and $SrCO_3$ (strontianite), the other was a homogeneous orthorhombic phase prepared (metastably) by precipitation from aqueous solutions at 90°C. By choosing bulk compositions lying within the miscibility gap and running charges of both types in separate capsules inside the same pressure vessel, the equilibrium compositions of the product phases were approached simultaneously from the low-Sr and high-Sr sides, thereby bracketing the curves. Run durations increased from 7 days at 650° to 61 days at 350°C. These runs were isobarically quenched by cooling to room temperature in a compressed air stream; temperatures below 100°C were typically reached in 3–4 minutes. All such runs crystallized two carbonates: a rhombohedral Ca-rich phase and an orthorhombic Sr-rich phase. Compositions of orthorhombic run products were obtained from the determinative curve of Froese and Winkler (1966, Fig. 2), based upon the 132 interplanar spacing derived from X-ray powder diffraction data and using Si metal as a standard. Multiple determinations of known compositions showed the standard errors to be approximately ±1 mole percent.

The compositions of the rhombohedral phases in these runs could not, however, be used to bracket the Ca-rich limb of the miscibility gap, owing to the difficulty of preserving a single Sr-bearing rhombohedral phase during quenching. Similar problems were noted by Froese and Winkler (1966, p. 559) and Chang (1965, p. 358). Optical examination of these runs reveals that most of the Ca-rich grains include tiny crystals with rectangular outlines, interpreted as quench crystals of strontianite. Calcite containing

these quench crystals appears as a single phase in X-ray diffraction patterns, because the strontianite comprises so small a proportion of the total, but calcite lattice parameters derived from X-ray patterns of such two-phase mixtures lead to incorrectly inferred original compositions.

Consequently, the Ca-rich limb of the miscibility gap was located by bracketing the maximum limit of Sr solubility in the rhombohedral carbonate. These experiments used a series of increasingly Sr-rich compositions at each temperature and pressure, until the rhombohedral phase became saturated with Sr and a separate orthorhombic Sr-rich phase appeared. The presence or absence of an equilibrium orthorhombic phase in the run products was determined optically, using the silver and manganese sulfate staining solution described by Deer et al. (1966, p. 500). This technique permits recognition of an orthorhombic phase present in amounts too small to be detected in X-ray powder diffraction patterns. The equilibrium was reversed in the usual manner, by obtaining at each temperature and pressure the limiting compositions for which a two-phase assemblage converts to a single phase, and vice versa. Run durations were 10 days at 650°, increasing to 68 days at 450°C. These runs were quenched by first decompressing to one atmosphere, then cooling; in consequence, quench crystals were not observed to form.

Results

Figure 2 presents those data points which bracket the equilibria on plots of pressure vs. composition, in seven isothermal sections. The results of this study are shown as circles; open symbols denote compositions lying within the miscibility gap, and filled symbols denote compositions lying in one-phase fields. Tables 1 and 2 detail experimental conditions and results for individual hydrothermal runs. Data from four other sources are also included: (1) points locating the calcite–aragonite reaction in the pure system, shown as squares, are from Johannes and Puhan (1971); (2) points indicating the pressure at which a phase transition was suspected to occur between two rhombohedral carbonates in the pure $CaCO_3$ system, shown as diamonds, are from Goldsmith and Newton (1969); (3) points defining the Sr-rich limit of the miscibility gap, shown as rectangles in Figures 2A and 2C, are from Froese and Winkler (1966)[2]; and

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[2] These data represent slightly higher temperatures than those with which they are plotted, i.e., 560°±10°C (instead of 550°C) in Fig. 2C, and 655°±10°C (instead of 650°C) in Fig. 2A.
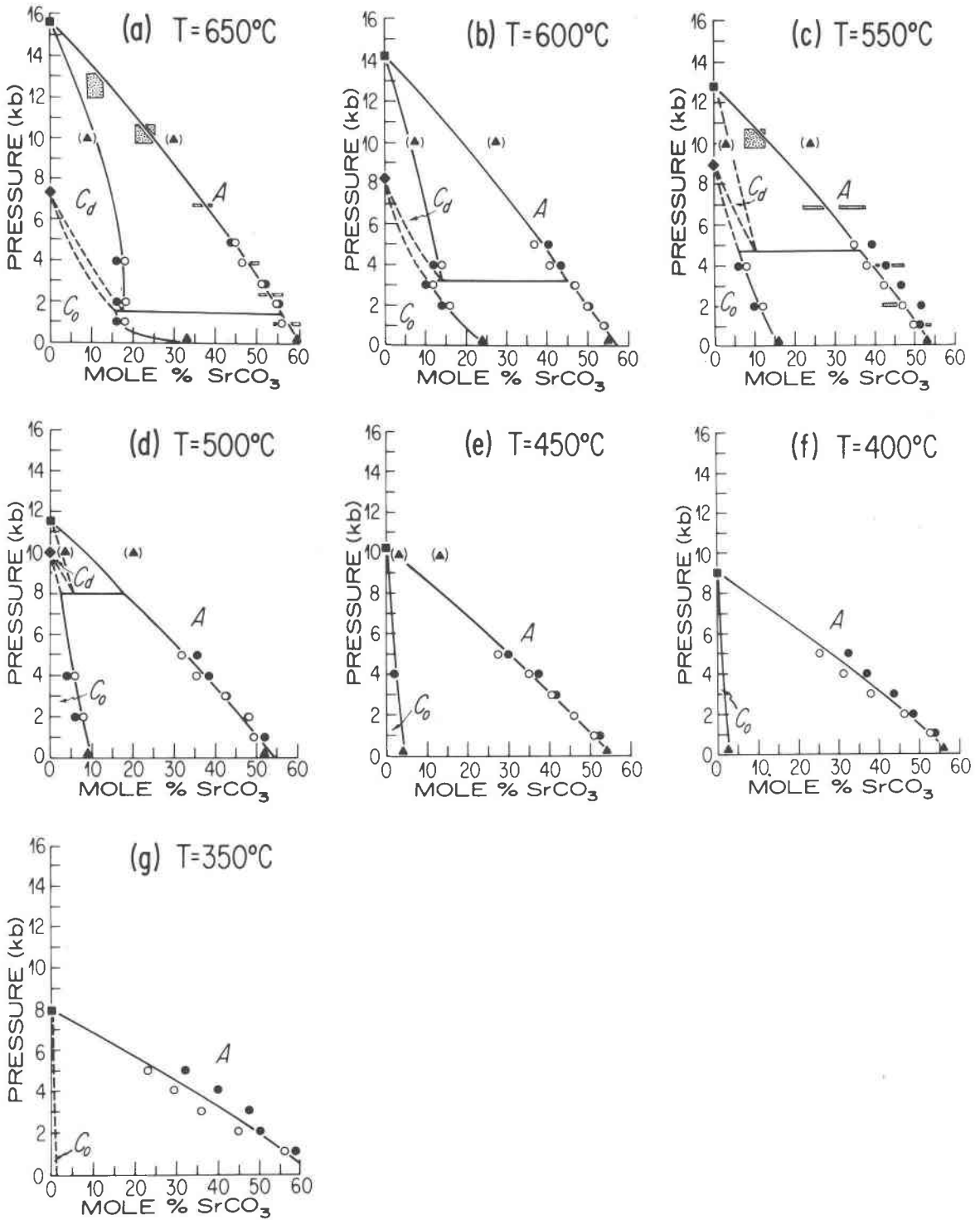
Fig. 2. Isothermal sections of the system $CaCO_3$-$SrCO_3$. "C_o" = ordered rhombohedral solid solution (ordered calcite); "C_d" = disordered rhombohedral solid solution (disordered calcite); "A" = orthorhombic solid solution (aragonite). Symbol types designate sources of data: squares, Johannes and Puhan (1971); diamonds, Goldsmith and Newton (1969); triangles, Chang (1965, 1971); circles, this study. Open circles denote compositions lying within the miscibility gap, and filled circles denote compositions lying in one-phase fields. Rectangles in Figures 2A and 2C are from Froese and Winkler (1966) and represent data obtained at slightly different temperatures (655°C±10° in Fig. 2A; 560°C±10° in Fig. 2C).

(4) data delimiting the miscibility gap, plotted just above the composition axis and shown as triangles, are from Chang's (1965) one-atm work. The values reported by Chang (1971) at 10 kbar, shown as triangles in parentheses, are also plotted for reference. These last data were obtained in an opposed-anvil apparatus, and no details of pressure calibration were published for them. Compared to the rest of the results in Figure 2, the "10 kbar" values are clearly discrepant, especially at low temperatures. Consequently, they were not used to locate the equilibrium curves.

The boundaries of the miscibility gap are drawn to fall between the limits obtained in this study and to connect with the data from other sources on the pressure and composition axes. On the Ca-rich side, all curves are bracketed by a composition interval of two mole percent $SrCO_3$. On the Sr-rich side, the un-

Table 1. Runs bracketing Sr-rich limit of miscibility gap

T (°C)	P (kbar)	Duration (days)	Bulk composition (ml % SrCO$_3$)	Orthorhombic run products (ml % SrCO$_3$)	
				Ppt*	Mix*
650	1	7	40	56.1	55.9
650	2	7	40	54.8	56.1
650	3	7	40	51.3	52.1
650	4	7	40	46.5	46.3
650	5	7	40	44.8	44.0
600	1	7	30	54.0	54.2
600	2	7	30	50.3	50.6
600	3	7	30	47.0	46.9
600	4	7	30	40.9	43.8
600	5	7	30	37.0	40.5
550	1	7	30	49.8	51.3
550	2	7	30	47.0	51.6
550	3	7	30	42.3	46.5
550	4	7	30	38.1	43.0
550	5	7	30	34.7	39.4
500	1	14	25	49.6	52.2
500	2	14	25	48.2	47.8
500	3	14	25	42.5	42.5
500	4	14	25	35.5	38.7
500	5	14	25	31.7	35.6
450	1	34	20	50.9	52.2
450	2	34	20	46.7	46.3
450	3	34	20	40.6	41.7
450	4	34	20	35.1	37.4
450	5	34	20	27.4	30.0
400	1	39	20	52.6	53.8
400	2	39	20	46.3	48.6
400	3	39	20	37.9	43.8
400	4	39	20	31.3	37.1
400	5	39	20	25.3	32.6
350	1	61	20	56.3	58.2
350	2	61	20	45.2	50.1
350	3	61	20	36.0	47.6
350	4	61	20	29.4	40.0
350	5	61	20	23.1	32.3

*Signifies type of reactants:
Mix = mixture of reagent CaCO$_3$ (calcite) and reagent SrCO$_3$ (strontianite)
Ppt = homogeneous orthorhombic coprecipitate (aragonite solid solution)

Table 2. Runs bracketing Ca-rich limit of miscibility gap

T (°C)	P (kbar)	Duration (days)	Bulk composition (ml % SrCO$_3$)	Reactant phases*	Product phases*
650	1	10	16	C+A	C
			18	C	C+A
650	2	10	16	C+A	C
			18	C	C+A
650	4	10	16	C+A	C
			18	C	C+A
600	2	14	14	C+A	C
			16	C	C+A
600	3	14	10	C+A	C
			12	C	C+A
600	4	14	12	C+A	C
			14	C	C+A
570	4	24	10	C+A	C
			12	C	C+A
560	4	24	10	C+A	C
			12	C	C+A
550	2	24	10	C+A	C
			12	C	C+A
550	4	24	6	C+A	C
			8	C	C+A
500	2	40	6	C+A	C
			8	C	C+A
500	4	40	4	C+A	C
			6	C	C+A
450	4	68	2	C+A	C

*Abbreviations for phases:
A = aragonite solid solution
C = calcite solid solution

certainties depend upon reaction rates and run times, with allowance for error in determining compositions (±1 mole percent). At 650°C, reaction is complete and the width of the brackets is merely the range of determinative error; at lower temperatures, as the wider brackets show, the equilibrium is less tightly constrained because of sluggishness of the re-equilibration.

Also shown in Figures 2A through 2D are curves connecting the data points of Goldsmith and Newton for the calcite I–calcite II transition (now recognized as a transition to some phase other than calcite II) to isothermal invariant points along a horizontal line. This line marks a three-phase equilibrium, representing the reaction of Sr-bearing aragonite with Sr-bearing calcite to produce a second Sr-bearing rhombohedral phase. Because this second rhombohedral phase cannot be preserved on quenching, and thus cannot be confirmed in the run products, the location of these features is interpretive, based on the following rationale. The existence in the binary system of a two-phase field for rhombohedral carbonates of slightly different compositions was originally suggested by the abrupt change of slope and apparent slight offset of the Ca-rich limb of the miscibility gap shown in Figures 2A and 2B. To confirm the pres-
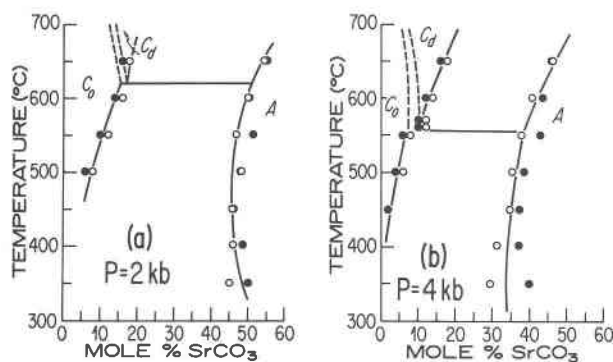
Fig. 3. Isobaric sections of the system CaCO₃–SrCO₃. Symbols and field labels as for Figure 2.

ence of such a two-phase region, additional experiments were performed at 2 and 4 kbar; the results are given in two isobaric sections in Figure 3. (Note that the boundaries of the two-phase fields are constrained to intersect for zero percent SrCO₃ at Goldsmith and Newton's transition points; these intersections, not plotted, occur near 890° for Figure 3A and 810°C for Figure 3B.) The distinct increase in solubility of SrCO₃ in the rhombohedral phase between 550° and 560°C at 4 kbar (Fig. 3B) is the primary basis for including a field for the coexistence of two rhombohedral phases in Figures 2 and 3.

The surface defining the Sr-rich limit of the miscibility gap is contoured in P-T projection in Figure 4, allowing comparison with other available data. Heavy lines indicate the results of the present study,
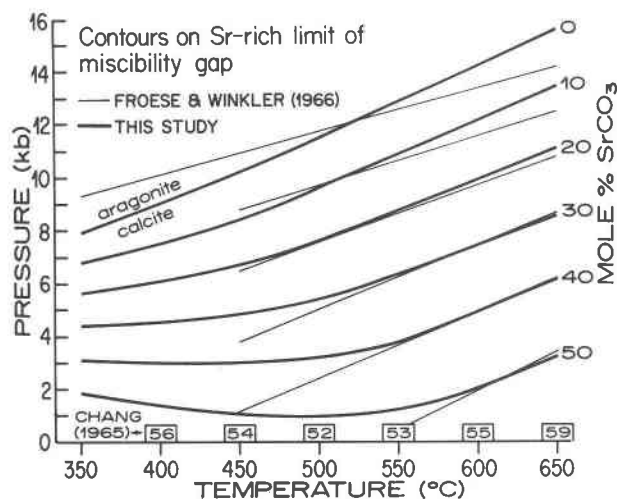

Fig. 4. Isoplethal contours on Sr-rich limit of miscibility gap. Heavy lines from this study. Light lines from Froese and Winkler (1966). Compositions in rectangles from Chang (1965). Discrepancies *at high temperatures and pressures* result from different choices of the calcite–aragonite boundary curve (see text).

constrained at the end-member calcite–aragonite boundary (the zero percent contour) by the data of Johannes and Puhan (1971). Light lines are from Figure 4 of Froese and Winkler (1966), who utilized Clark's (1957) work to locate the zero percent contour. Chang's (1965) values for the composition of orthorhombic carbonate in equilibrium with calcite at one atm appear enclosed in rectangles just above the composition axis and are expressed in mole percent SrCO₃.

Discussion

Effect of Sr on calcite–aragonite stability relations

The compatibility of Chang's (1965) determination of the Sr-rich limit of the miscibility gap with the data of the present study is apparent in Figure 4. In contrast, agreement with Froese and Winkler's (1966) results occurs only at the high temperatures at which their experiments were performed. Significant discrepancies are evident when their values are linearly extrapolated to lower temperatures. It seems, therefore, that the disagreement between Chang's data and Froese and Winkler's work is merely the result of an unwarranted linear extrapolation of the contours. With that difficulty resolved, it may be confidently asserted that, in the temperature range of blueschist metamorphism, even large amounts of SrCO₃ component have a negligible effect on the pressure at which the calcite–aragonite reaction takes place. This same conclusion was reached by Froese and Winkler; their inference is correct, despite the difference between observed and extrapolated values, because the contours in Figure 4 curve upward rather than downward with decreasing temperature.

Change in slope of the calcite–aragonite equilibrium boundary

The controversy regarding the precise location of the calcite–aragonite reaction curve between 350° and 500°C focuses upon the manner in which the calcite transition near 10 kbar and 500°C affects the equilibrium between the orthorhombic and the rhombohedral phases. The calcite–aragonite equilibrium curves published by Boettcher and Wyllie (1968) and by Goldsmith and Newton (1969) both consist of two intersecting lines with distinctly different slopes. Both teams of investigators performed experiments down to 400°C and then extended their curves through the point determined by Crawford and Fyfe (1964) at 100°C. In the absence of data between 100° and 400°C, all the points could be fitted

to a pair of straight lines whose intersection produced a discontinuity of slope, indicative of a first-order phase transition in one of the two minerals. An alternative model was invoked by Johannes and Puhan (1971) who, with gas-apparatus data extending down to 200°C, found the calcite–aragonite equilibrium boundary to be continuously curved. Because their boundary exhibits no break in slope, they inferred that the phase transition is of second order. They further noted that the uncertainties in their data are small enough to preclude fitting the data with two straight lines.

Because this portion of the calcite–aragonite boundary is quite significant petrologically, it is especially unfortunate that direct evidence for the nature of this unquenchable phase transition is difficult to obtain. Nearly all the inferences drawn so far have relied upon extrapolation either from the low-temperature high-pressure studies of Bridgman (1939), Jamieson (1957), Davis (1964), Wang (1968), and Merrill and Bassett (1975), or from the low-pressure high-temperature experiments of Boeke (1912), Smyth and Adams (1923), and Eitel (1923). As noted before, however, the transitions observed in these P–T regions do not appear to be the cause of the changing slope of the calcite–aragonite equilibrium; the data of Kondo *et al.* (1972) demonstrate this for the first group of studies,[3] and the work of Cohen and Klement (1973) and Mirwald (1976, 1979a,b) does so for the second group.

In contrast to these interpretations based on extrapolations, Goldsmith and Newton (1969) tried to obtain direct evidence of the nature of this transition at pressures and temperatures near the change in slope of the calcite–aragonite boundary. They utilized differential thermal analysis, sought twinning in single crystals cycled through the transition, and attempted to demonstrate differential solubility of $MgCO_3$ in the two phases—all methods intended to detect a discontinuity in some physical property at the transition. Although their findings were sugges-

tive of a first-order phase transition, no technique produced an unequivocal result.

The present study presents observations at high temperatures and pressures which should help to explain the change in slope of the calcite–aragonite boundary. I suggest that the phase change which alters the slope of the boundary is correlative with the order–disorder transition observed in binary Ca–Sr carbonates by Chang (1965), a transformation distinct from both the calcite I–II and the calcite IV–V (β–α) transitions. Chang noted the gradual disappearance of 113-type reflections in X-ray diffraction patterns taken at high temperature at atmospheric pressure. The 113 reflection is the strongest of a class of reflections whose presence implies orientational ordering of the CO_3 groups in a rhombohedral carbonate structure; their absence results in a halving of the c-translation distance and a change of space group from $R\bar{3}c$ to $R\bar{3}m$. The disordering under discussion here refers to the angular orientation of the trigonal planar CO_3 groups about their three-fold axes. In the ordered structure of calcite I, the CO_3 groups of successive layers have opposite orientations, while the observed symmetry of the high-temperature forms requires the orientation of successive CO_3 groups to be, at least on the average, the same. As pointed out by Megaw (1973), this may be reasonably accomplished by one of two means: either the CO_3 groups retain their two possible calcite I orientations but with a random sequence of alternations, or the CO_3 groups may be rotated (either plus or minus 30°) to a new orientation halfway between the two possible orientations of calcite I. In either case, the orientational disorder makes an additional contribution to the molar entropy of the crystal, making the disordered polymorph the higher entropy form.

Chang's (1965) experiments at atmospheric pressure show that the intensity of the 113 reflection for a composition of 44 mole percent $SrCO_3$ diminishes to zero at 705°C, thus marking the completion of the order–disorder transition and producing an equilibrium among three carbonate polymorphs. Similarly, the phase diagrams in Figures 2 and 3 of my study locate a phase change between two rhombohedral carbonates; they likewise depict three phases simultaneously stable in the binary system, but at elevated pressures. The isobaric sections of Figure 3, which are based on phase equilibrium data, are topologically identical to the one-atm phase diagram of Chang (1965, Fig. 5), which is based on the loss of those X-ray peaks which imply rotational ordering of the CO_3 groups in the carbonate structure. Because

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[3] It would seem prudent, however, to regard these results (based on ultrasonic velocity measurements) as tentative, because of the likelihood that partial inversion of calcite to aragonite occurs in experiments run at these relatively high temperatures. The kinetics data of Davis and Adams (1965) show appreciable conversion in only a few minutes near 450°C and 8 kbar, and reaction rates will increase exponentially with temperature. Additionally, single samples were cycled through multiple runs, prolonging the exposure to high temperature. In the absence of characterizations of the phase(s) present at the end of each run, this conclusion should perhaps be accepted with reservation.

of this precise equivalence, the two fields for rhombohedral carbonate in this investigation have been identified as ordered and disordered calcite.

The $P-T$ conditions for the binary three-phase equilibrium observed in this study connect smoothly with Chang's conditions for the coexistence of three phases (705°C at one bar) and the triple-point region of the calcite–aragonite curve (500°C at 10 kbar), also strongly suggesting that the transitions are equivalent. To see this more graphically, the set of points at which the transition occurs in the binary system may be projected onto the pressure–temperature plane, producing a line with negative slope which intersects the contours of the Sr-rich limit of the miscibility gap. Such a projection is made in Figure 5. Significantly, the points of intersection divide each of the contours into a highly curved portion at lower temperatures and a nearly linear portion at higher temperatures. The slope of each contour is the ratio of the entropy change to the volume change for the reaction of the two-phase assemblage to a single orthorhombic phase, for the composition appropriate to each contour: $dP/dT = \Delta S/\Delta V$. Thus where aragonite solid solution is in equilibrium with the ordered calcite solid solution, $\Delta S/\Delta V$ is gradually increasing with temperature; above the calcite transition temperature, where aragonite solid solution is in equilibrium with the disordered rhombohedral phase, $\Delta S/\Delta V$ is nearly constant.

Thus the curvature of the contours in the binary system and, by extension, the much less apparent curvature of the calcite–aragonite boundary in the unary system, may be regarded as evidence of a gradual orientational disordering taking place in the rhombohedral carbonates. This requires that much of the disordering occur in the unary system over an interval, rather than taking place entirely at the transition point. In support of this viewpoint, Raman spectroscopy of calcite by Salje and Viswanathan (1976) identified an ionic rotational mode correlated to the coupling of oppositely oriented CO_3 groups, which weakens and eventually disappears at high temperatures. Their calculated calcite–aragonite equilibrium based upon the premise of anion disorder reproduces, with excellent agreement, the curvature of the boundary determined by Johannes and Puhan (1971).

A further important feature of the present data is the evidence for a discontinuity in the disordering when the transition point is actually reached. The data in Figure 3 display an abrupt increase in the solubility of $SrCO_3$ in the rhombohedral phase between 550° and 560°C at 4 kbar. In view of the smooth curves evident above and below this small temperature interval, the offset is taken to represent the order–disorder transition. If the transition were of second order, no offset in the curve would occur; only its slope would be discontinuous. The observed effect can be reconciled only with a first-order phase transition. Evidence for the same phenomenon near 630°C at 2 kbar (Fig. 3) is equivocal; the data are permissive of a small offset of the curve, but do not require it. Chang (1965, p. 357) described attempts to locate a two-phase region at 775° and 825°C and one atm, using a high-temperature X-ray diffractometer. Employing compositions spaced at intervals of 2 mole percent $SrCO_3$, he found no evidence for the coexistence of two rhombohedral forms. This is not surprising, considering that the two-phase field spans a compositional range of only about 4 mole percent at 4 kbar (Fig. 3B), decreasing to a range of 2 mole percent or less at 2 kbar (Fig. 3A).

The observed fractionation of Sr preferentially into the disordered phase serves to constrain possible models for its crystal structure. For $NaNO_3$, which is isomorphous with calcite, Megaw (1973) discussed the disordering models introduced above. She favors the second model, involving 30° rotations of the anionic groups, for the high-temperature structure because it produces more nearly optimal interatomic distances, and because it agrees with extant thermal expansion and X-ray diffuse scattering data. She also pointed out that in the first model the randomized calcite I orientations led to coordination of the Na ion (or Ca ion in $CaCO_3$) by 12 equidistant "half-ox-
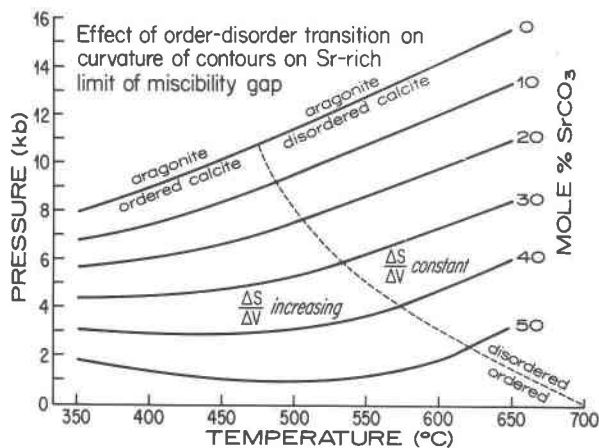

Fig. 5. Projection of order–disorder transition boundary onto pressure–temperature plane. The intersections with the contours of the Sr-rich side of the miscibility gap mark the change from increasing slopes to constant slopes of the contours.

ygens," of which only six could represent actually present neighbors of one cation. The second model, involving rotation of the NO_3 groups (or CO_3 groups in $CaCO_3$) to new halfway positions, resulted in each cation being surrounded by eighteen "half-oxygens" or nine true neighbors. In an isothermal section such as Figure 2, it is evident that despite its higher entropy the disordered phase is denser than the ordered phase. Furthermore, Sr is a larger cation than Ca and is preferentially fractionated into the disordered structure. Both observations tend to support the second structural model, in which the cations are more highly coordinated, and which is therefore more likely to be the denser structure.

One alternative possibility, namely that the transition which inflects the calcite–aragonite equilibrium curve involves Bridgman's calcite II, has also been investigated experimentally. Merrill and Bassett's (1975) structure determination of calcite II demonstrates that, despite a smaller cell volume, calcite II has a greater average Ca–O bond length than calcite I. In consequence, calcite II is expected to accommodate substitution of the larger Sr ion for Ca more readily than calcite I. This is compatible with the observed distribution of Sr between the two rhombohedral phases seen in Figures 3A and 3B. Thus the calcite II structure is a potential candidate for the disordered calcite phase encountered in the present study, the results of Kondo *et al.* (1972) notwithstanding. However, if calcite II were actually the phase involved, then the disordered rhombohedral phases of Chang (1965) would be expected to have the calcite II structure, in view of the apparent correspondence between the $CaCO_3$ triple point and the binary three-phase equilibrium.

Given the subtlety of the features distinguishing the calcite II structure from a disordered rhombohedral structure, it is conceivable that these details of the X-ray diffraction pattern might previously have been overlooked in binary Ca–Sr carbonates, as they were in the first two X-ray characterizations of calcite II. To explore this possibility, high-temperature X-ray powder diffraction patterns of binary Ca–Sr carbonates were obtained using a Norelco diffractometer with a platinum strip heater. These experiments were designed to observe, if possible, the presence of diffraction maxima corresponding to the 011, 221, 214, and 104 peaks reported as new reflections for calcite II by Merrill and Bassett (1975). Under a CO_2 atmosphere, metastable orthorhombic coprecipitates were observed to undergo transition at temperatures consistent with Chang's (1965, Fig. 5) phase diagram.

Diffraction patterns were obtained for the composition $Ca_{56}Sr_{44}$ at 750° and 800°C, and for the compositions $Ca_{80}Sr_{20}$ and $Ca_{20}Sr_{80}$ at 900°C. In addition, a rhombohedral starting material of composition $Ca_{56}Sr_{44}$ (synthesized at 925°C in CO_2 and quenched in water) was examined at 800°C. None of the experiments showed any increase of intensity above background in the vicinity of the peaks noted in the calcite II diffraction pattern, although even low-intensity peaks of the disordered rhombohedral structure were easily detected. The implication, despite the strong similarity in the behavior of the 113-type peaks reported by Jamieson (1957) and Davis (1964) for calcite II and by Chang (1965) for disordered binary carbonates, is that the two phases are in fact distinct entities. This result lends credence to the finding of Kondo *et al.* (1972) that calcite II is nowhere stable with respect to aragonite.

Finally, the relationship between the order–disorder transition examined here and the calcite I–calcite IV transition of Mirwald (1976, 1979a,b) deserves attention. Although the location of the order–disorder transition in the binary system seems well-determined, its P–T path in the unary $CaCO_3$ system can only be guessed at. The location of the transition identified by Goldsmith and Newton (1969) is adopted here, but because of ambiguities in that determination, the boundary may depart significantly from that trajectory (the diamonds in Figs. 2A through 2D) as it moves away from the triple-point region. It must, however, have a negative dP/dT slope, and the recent discovery of a possible phase change in $CaCO_3$ at 725°C and 40 bars (Mirwald, 1979b) provides a tempting candidate for the low-pressure location of the order–disorder transition. Mirwald, however, interpreted his data as indicating the onset of disordering near 725° at 40 bars, with completion near 800°C. In his view, the transition of calcite I to calcite IV is an order–disorder transition which intersects the calcite–aragonite boundary near 800°C, not near its change of slope. Possibly more than one disordered structure is involved; thus the calcite I–IV phase change and the order–disorder transition of this study may intersect in a triple point at elevated pressures. But experimental confirmation of such speculation will be extremely difficult to obtain, owing to the subtlety of the distinctions among the phases. For the present, it must suffice to say that the variety of possible disorder mechanisms (*e.g.,* Megaw, 1973; Strømme., 1975) allows for a great complexity of polymorphic transitions at high temperatures; even this comparatively simple unary sys-
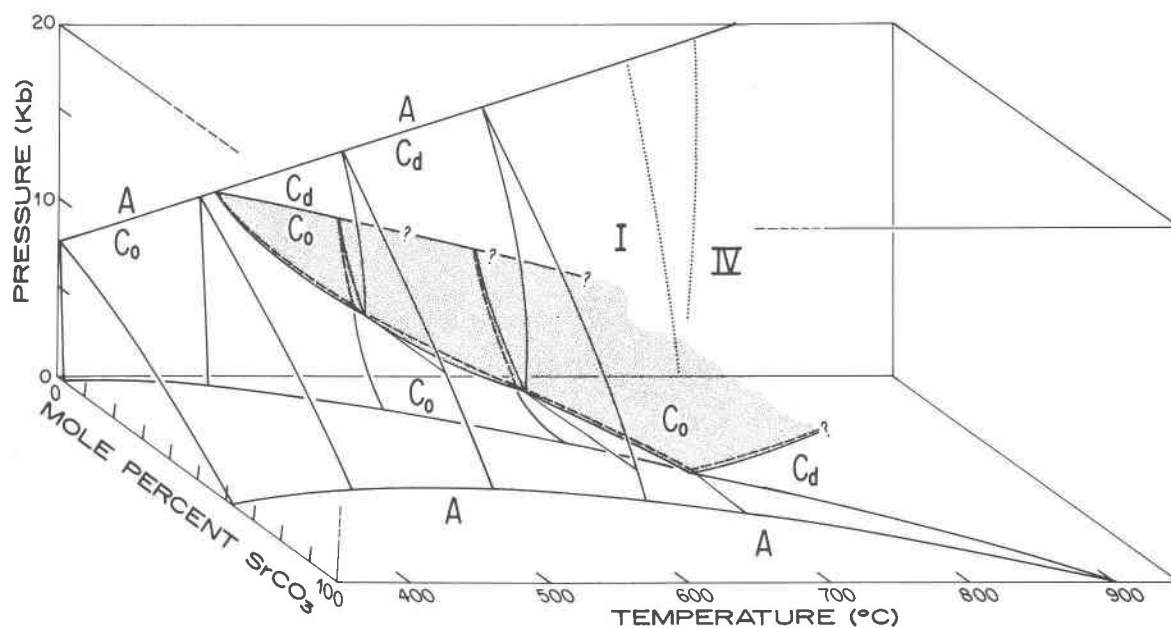
Fig. 6. *P–T–X* diagram of phase relations in the system CaCO₃–SrCO₃. Surfaces bounding the two-phase field for ordered and disordered calcite are indicated by shading. Data on rear face from Johannes and Puhan (1971), Mirwald (1976), and after Goldsmith and Newton (1969); data on bottom face after Chang (1965). Field labels as for Figs. 1 and 2.

tem of fundamental geologic significance cannot be regarded as fully determined.

Summary

Phase relations in the binary system CaCO₃–SrCO₃ are summarized in Figure 6, a rectangular diagram with axes of pressure, temperature, and mole percent SrCO₃. The bottom face of the prism presents Chang's (1965) one-atmosphere data, modified to show a two-phase field for the coexistence of ordered and disordered rhombohedral carbonate. The width of that field is slightly exaggerated for clarity. The rear face displays the calcite–aragonite reaction determined in gas-pressure apparatus by Johannes and Puhan (1971), the order–disorder transition consistent with Goldsmith and Newton (1969), and the stability field of calcite IV after Mirwald (1976). The curved lines in the interior of the prism reproduce Figures 2A, 2C, 2E, and 2G. The two shaded surfaces are those which enclose the two-phase field for rhombohedral carbonates.

The data of this study demonstrate that the small amounts of Sr found in natural aragonites are nearly inconsequential with regard to pressure estimates of origin for metamorphic rocks of the glaucophane-schist facies. The results further imply that the change of slope of the calcite–aragonite equilibrium boundary between 350° and 500°C is due to anion
orientational disordering in calcite, premonitory to a first-order phase transition. This in turn suggests that the calcite–aragonite reaction is best represented by the continuously curved boundary of Johannes and Puhan (1971), modified to show a small discontinuity in slope in the vicinity of the triple point inferred by Boettcher and Wyllie (1968) and Goldsmith and Newton (1969).

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