

THE SYSTEM CaCO_3 – SrCO_3 AT HIGH PRESSURES AND 500°C TO 700°C

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ABSTRACT

The system CaCO_3 – SrCO_3 has been investigated at temperatures of 560 °C and 655 °C and pressures up to 13 kb. At constant temperature, orthorhombic mix crystals of CaCO_3 and SrCO_3 are stabilized at lower pressures as the SrCO_3 content increases. For example, aragonite–strontianite of composition $(\text{Ca}_{0.9}\text{Sr}_{0.1})\text{CO}_3$ can coexist with calcite at 12.6 kb and 655 °C, whereas pure aragonite coexists with calcite at 14.2 kb and 655 °C. The amount of SrCO_3 in metamorphic aragonites (about one mole per cent) is insufficient to cause a significant lowering of the pressure of the calcite–aragonite equilibrium. Substitution of MgCO_3 in calcite coexisting with aragonite–strontianite of a certain composition raises the equilibrium pressure (at constant temperature) until a maximum value is reached, at which calcite and aragonite–strontianite coexist with dolomite.

INTRODUCTION

The occurrence of metamorphic aragonite in rocks of the glaucophane-schist facies (Coleman & Lee, 1962; McKee, 1962) has drawn attention to the significance of the calcite–aragonite transition in metamorphic petrology. Because this reaction is very pressure-sensitive, it serves as a geobarometer, particularly if the temperature can be estimated from other mineral reactions. Experimental work in the pure CaCO_3 system has shown that very high pressures are necessary to stabilize aragonite. Winkler (1965, p. 150) has estimated the temperature range of the glaucophane-schist facies, renamed by him lawsonite-glaucophane facies, as 350 °C to 450 °C. According to the experimental data of Clark (1957), the presence of aragonite indicates that pressures of approximately 9 to 11 kb must have been exceeded at these temperatures. If the pressure is lithostatic, 9 to 11 kb correspond to an overburden of about 32 to 38 km.

Many geologists think that such great depth of burial is unlikely. For example, in an interpretative cross-section through the western U.S.A., Thompson & Talwain (1964) show the depth to the bottom of the Franciscan formation as 12 km. In view of such a discrepancy, it has been suggested that the effective pressure could be increased either by a "tectonic overpressure" (Clark, 1961; Coleman & Lee, 1962) or by a "fluid overpressure" (Rutland, 1965; Winkler, 1965, p. 153). Before considering the alternative of either great depth of burial or pressure in

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excess of the lithostatic load, the possible effects of isomorphous substitutions on the calcite-aragonite equilibrium deserve some attention. Coleman & Lee (1962) report about one mole per cent SrCO_3 in metamorphic aragonites, and natural calcites may contain several per cent MgCO_3 . The substitution of MgCO_3 in calcite raises, rather than lowers, the equilibrium pressure at constant temperature. Goldsmith (Jamieson & Goldsmith, 1960) observed an increase of three kb if the calcite contained seven mole per cent MgCO_3 . On the other hand, a substitution of SrCO_3 in aragonite will lower the equilibrium pressure. However, MacDonald (1956) concluded, on the basis of thermochemical calculations, that small amounts (several mole per cent) of SrCO_3 would have no appreciable effect on the calcite-aragonite equilibrium. In order to test this, it was decided to investigate the effect of SrCO_3 experimentally. The system CaCO_3 - SrCO_3 has been studied at low pressures (one to seven bars) by Chang (1965). The present study reports experimental results at higher pressures, up to 13 kb, at 560 °C and 655 °C. Some work was also carried out in a part of the system CaCO_3 - SrCO_3 - MgCO_3 at high pressures and 660 °C to demonstrate the combined effect of SrCO_3 substitution in aragonite and MgCO_3 substitution in calcite.

EXPERIMENTAL PROCEDURE

Experiments at 7 kb and lower pressures were carried out in "cold-seal" hydrothermal bombs (Tuttle, 1949). Temperatures were measured by means of a chromel-alumel thermocouple placed in a well at the outside of the bomb. The temperature inside the bomb was obtained from calibration curves prepared by Dr. G. Hoschek by placing thermocouples inside the bomb with connections leading outside through pressure-tight seals. In this manner, readings of the inside thermocouples and of the outside one could be compared and the temperature gradient inside the bomb could be established. Thus, temperatures stated for capsules at the bottom of the bomb are certainly accurate within ± 10 °C. Only such runs were used to determine the position of the equilibrium curves. In most cases, aragonite-strontianite mix crystals were synthesized in capsules farther removed from the thermocouple. The accuracy of the temperature of such runs is only about ± 20 °C, however, a knowledge of the exact temperature is not required because these mix crystals were used only to establish a determinative curve. The pressure was read on hydraulic gauges and is estimated to be accurate within ± 2 per cent of the indicated pressure.

Experiments at pressures greater than 7 kb were carried out in a "simple squeezer" apparatus similar to the one described by Griggs &

Kennedy (1956). The pressure and temperature readings of the squeezer were calibrated by Dr. G. Hoschek. A Phillips pressure recorder was used to determine the load transmitted between the pistons. The recorder works on the principle of measuring the resistance of metal strips constrained in a box. The resistance is proportional to the distortion caused by the applied load. The pressure is estimated to be accurate within ± 5 per cent of the indicated pressure. The temperature was measured by means of a thermocouple placed at the end of one of the pistons. The temperature at the contact of the pistons, however, is somewhat higher. A correction was applied by comparing readings on two thermocouples, one placed between the pistons and one at the end of one of the pistons. The temperature is estimated to be accurate within $\pm 10^\circ\text{C}$.

Starting materials were natural calcite (sold by Merck), aragonite (from Erzberg, Austria), dolomite (from Mühlbach, Germany), and synthetic SrCO_3 (chemical reagent sold by Merck). The trace element content of these materials is given in Table 1. In the case of runs in bombs, the carbonates were sealed in gold capsules together with some water. The formation of hydroxides is of no consequence if the composition of the coexisting carbonates is independent of bulk composition. This is the case in runs used to determine the position of the equilibrium curves. Changes in bulk composition of the carbonates must be avoided in runs made to homogenize mechanical mixtures of calcite and SrCO_3 with the aim of preparing mix crystals of known composition. Because the amount of Ca(OH)_2 and Sr(OH)_2 formed due to the addition of water is very small, the change in bulk composition of the carbonates is negligible. In a few runs a small amount of oxalic acid was added. The only noticeable effect was a retardation of reaction rates at 560°C , but not at 655°C . In experiments with the simple squeezer, the sample was placed inside a nickel ring sandwiched between platinum foil. Reactions proceeded readily,

TABLE 1. TRACE ELEMENT CONTENT OF STARTING MATERIALS IN WEIGHT PER CENT

Element		Calcite (Merck)	Aragonite (Erzberg, Austria)	Dolomite (Mühlbach, Germany)	SrCO_3 (Merck)
Semi-quantitative spectrographic analysis by W. F. White, Analytical Chemistry Section, Geological Survey of Canada.	Si	0.02	nd	0.07	nd
	Al	0.02	nd	0.05	nd
	Ti	0.01	nd	0.005	nd
	Fe	0.015	nd	0.05	nd
	Mn	0.005	nd	0.05	nd
	Mg	0.02	0.005	—	0.005
nd not detected tr trace	Ca	—	—	—	tr
	Sr	nd	0.02	nd	—
	Ba	nd	0.005	nd	tr
X-ray fluorescence analysis by E. Froese	Ca	—	—	not analyzed	0.22
	Sr	<0.005	0.13	—	—

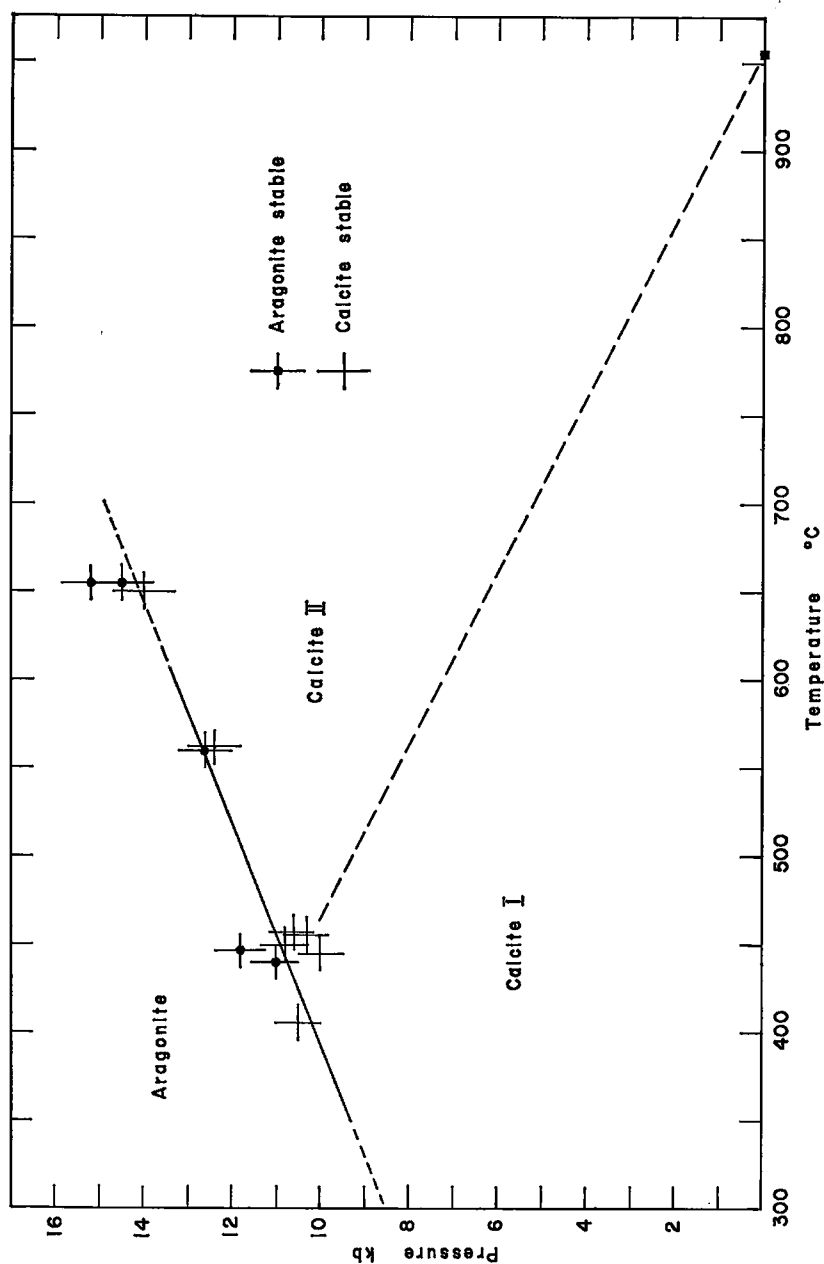


FIG. 1. The system CaCO_3 . The calcite-aragonite curve is taken from Clark (1957). Our determinations are marked by crosses. The transition temperature, at 1 bar, of calcite I to calcite II is taken from Chang (1965) and the slope of the curve is taken from Jamieson (1957).

even without the addition of water. Samples were normally quenched by lowering the temperature while maintaining the pressure (temperature quench). In a few cases, the pressure was released first (pressure quench).

THE SYSTEM CaCO_3

The system CaCO_3 has been investigated by several workers. For the temperature range of interest in this study, the best experimental data available are those of Clark (1957). The corrected values of MacDonald (1956) and the experimental results of Goldsmith (1959) agree with the transition curve established by Clark. Furthermore, the extrapolation of this curve to lower temperatures is in good agreement with the results of Jamieson (1953) and Crawford & Fyfe (1964). The curve determined by Simmons & Bell (1963) coincides with Clark's curve at 600 °C, but deviates from it considerably at lower temperatures. Clark's curve, shown in Fig. 1, is based on experiments carried out in a bomb under truly hydrostatic pressure. This allows a more accurate control of pressure than is feasible in a simple squeezer. The calcite-aragonite transition was re-determined in our squeezer as an additional check on the calibration, which proved to be satisfactory. The results are given in Table 2 and shown in Fig. 1. At the start of the experiment, the pressure was always applied first. Therefore, part of the calcite used as starting material might have been converted to aragonite while the temperature was raised. However, if the conditions of the run were within the calcite stability field, all aragonite would be quickly converted to calcite. Runs

TABLE 2. EXPERIMENTAL DATA ON THE CALCITE-ARAGONITE TRANSITION

Run	Temperature °C $\pm$ 10°	Pressure kb $\pm$ 5%	Time days	Type of quench	Starting material	Products	Stable phase
S-25	406	10.5	1	T	aragonite	aragonite + calcite	calcite
S-12	440	11.0	2	P	calcite	aragonite + calcite	aragonite
S-13	445	10.0	1	P	calcite	calcite	calcite
S-14	447	11.8	1	P	calcite	aragonite + calcite	aragonite
S-15	456	10.3	1	T	aragonite	aragonite + calcite	calcite
S-17	449	10.8	1	P	calcite	calcite	calcite
S-53	457	10.6	2	T	aragonite	aragonite + calcite	calcite
S-49	562	12.4	1	T	aragonite	aragonite + calcite	calcite
S-50	559	12.6	1	T	aragonite	aragonite	aragonite
S-42	650	14.0	2	T	aragonite	calcite	calcite
S-47	655	15.2	2	T	aragonite	aragonite	aragonite
S-51	655	14.5	1	T	aragonite	aragonite	aragonite

using calcite as starting material were quenched by lowering the pressure first; therefore, no aragonite could form during the quench. At temperatures greater than 450 °C, it was impossible to preserve aragonite by a pressure quench. Most runs were made with aragonite as starting material and quenched by lowering the temperature by means of an air blast while maintaining the pressure; therefore, no calcite could form during the quench.

On a phase diagram of the system CaCO_3 , Jamieson (1957) shows an approximate boundary between calcite I (normal calcite) and calcite II, an anion-disordered polymorph characterized by a c cell dimension of only half the length of calcite I. The transition of calcite I to calcite II is structurally minor and there is no noticeable break in the calcite-aragonite curve at the triple point calcite I—calcite II—aragonite. Calcite II cannot be quenched. In an apparatus which permits x -raying while the sample is subjected to experimental conditions, Chang (1965) has determined the transition temperature at low pressures (one to seven bars) as 955 °C. This point is shown in Fig. 1 and the slope of the curve calcite I—calcite II is taken from Jamieson (1957).

THE SYSTEM CaCO_3 — SrCO_3

The composition of aragonite-strontianite mix crystals is readily determined from a variation of their lattice parameters. Holland *et al.* (1963) give unit cell dimensions of such mix crystals. In this study, it was convenient to establish a determinative curve (Fig. 2) based on the spacing of the line (132). Mechanical mixtures of calcite and SrCO_3 were homogenized at various pressures and temperatures (Table 3). The resulting mix crystals were x -rayed with a Guinier camera using silicon as an internal standard. On the diffraction pattern, one degree 2θ is represented by 2 mm. Distances between lines were measured to 0.01 mm. Measurements of repeated runs of the same composition fell within ± 0.04 mm. For line (132), this corresponds to a variation in spacing of ± 0.0007 Å, which is equivalent to a variation in composition of ± 1.0 mole per cent SrCO_3 .

The composition of aragonite-strontianite mix crystals coexisting with calcite was determined at 560 °C and 655 °C and various pressures. Two runs were carried out at 510 °C and 1.96 kb. Results are given in Table 4 and shown in Fig. 3. At 655 °C equilibrium is readily attained; the nature of the starting material and the duration of the experiment have no effect on the composition of aragonite-strontianite. The composition can be reproduced in repeated runs within ± 2.5 mole per cent SrCO_3 . On the other hand, at 560 °C equilibrium is attained with much

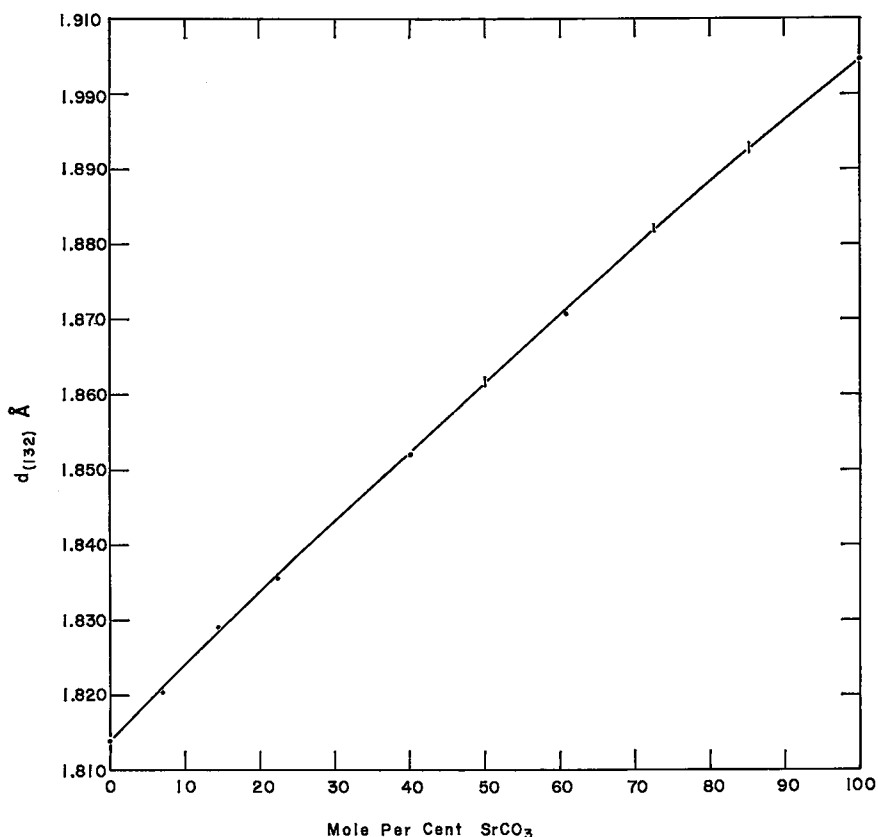


FIG. 2. Determinative curve for aragonite-strontianite mix crystals, based on the spacing of line (132).

greater difficulty. The number of runs carried out at 3.92 kb is sufficient to show a dependence of the composition on the duration of the experiment. In this case, values based on runs of longer duration have been accepted, because they represent a closer approach to equilibrium. The addition of oxalic acid apparently retards reaction rates and, in a given time, equilibrium is not as closely approached as in runs with only water added. Furthermore, at 560 °C and 510 °C the nature of the starting material has a marked effect. Mixtures of calcite and SrCO_3 produce mix crystals of higher SrCO_3 content than mixtures of aragonite and SrCO_3 . For this reason, the values obtained at 560 °C from different starting materials are plotted with different symbols in Fig. 3. A curve drawn through the available data indicates that values obtained from mixtures of aragonite and SrCO_3 represent a closer approach to equi-

TABLE 3. VALUES OF $d(132)$ OF ARAGONITE-STRONTIANITE MIX CRYSTALS

Composition mole per cent SrCO_3	Run	Temperature $^{\circ}\text{C} \pm 20^{\circ}$	Pressure kb $\pm 2\%$ ($\pm 5\%$ if over 7 kb)	Time days	$d(132)$ Å
0.0	S-39	655	14.0	2	1.8139
0.0	S-40	655	14.5	2	1.8139
0.0	S-41	660	15.2	1	1.8139
0.0	S-52	550	12.8	2	1.8141
7.0	S-38	665	14.4	7	1.8204
14.4	S-31	530	13.0	6	1.8291
22.4	S-48	615	12.8	12	1.8356
40.1	7-1-3	615	6.86	33	1.8521
50.1	19-22-4	625	3.92	21	1.8620
50.1	19-22-6	555	3.92	21	1.8620
50.1	19-24-4	620	3.92	28	1.8610
50.1	19-24-6	555	3.92	28	1.8624
60.8	19-2-2	565	3.92	7	1.8709
60.8	10-18-3	635	3.92	7	1.8705
60.8	19-20-3	635	3.92	28	1.8709
60.8	39-4-3	600	0.98	14	1.8709
72.5	19-2-1	565	3.92	7	1.8816
72.5	19-10-4	445	3.92	11	1.8824
72.5	19-14-3	530	0.98	7	1.8824
72.5	19-16-5	540	0.98	5	1.8827
72.5	19-18-4	635	3.92	7	1.8819
85.3	19-2-3	535	3.92	7	1.8928
85.3	19-10-3	445	3.92	11	1.8930
85.3	19-14-4	530	0.98	7	1.8935
85.3	19-15-4	530	0.98	8	1.8922
85.3	19-16-6	540	0.98	5	1.8930
85.3	19-18-5	565	3.92	7	1.8926
85.3	39-2-5	540	0.98	21	1.8934
85.3	22-13-6	530	0.98	22	1.8935
85.3	19-15-6	470	0.98	8	1.8934
100.0	22-13-8	450	0.98	22	1.9046
100.0	23-8-6	540	3.92	14	1.9049
100.0	30-3-3	520	3.92	39	1.9048
100.0	39-6-5	535	0.98	21	1.9046

brum than those from mixtures of calcite and SrCO_3 . Probably the same is true at 510°C . Fig. 3 also contains some data from Chang (1965) and Clark (1957). The curve giving the composition of aragonite-strontianite shows no inflection at a point where calcite I might be expected to change to calcite II. This is in agreement with results of Chang (1965), who determined the composition of coexisting aragonite-strontianite and calcite at low pressures (one to seven bars) and various temperatures.

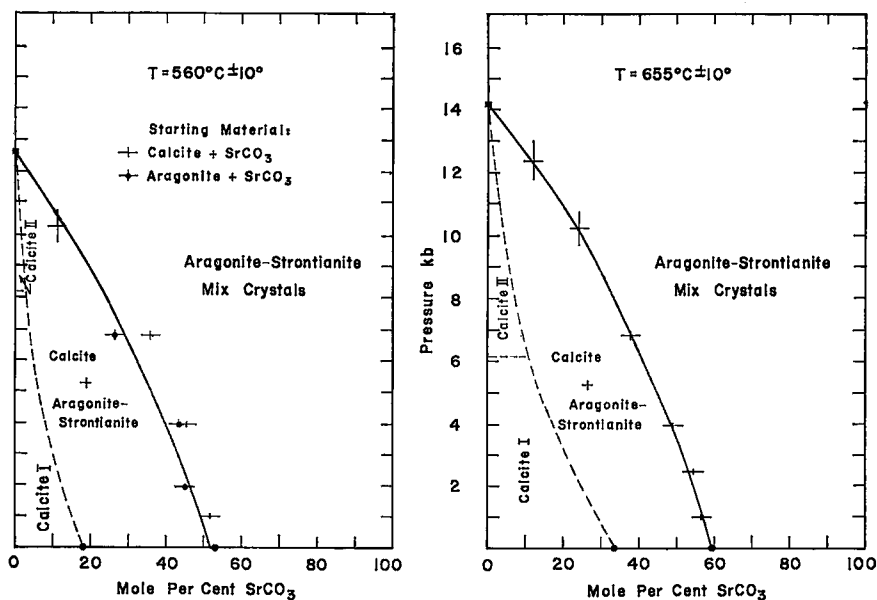


FIG. 3. The system $\text{CaCO}_3\text{--SrCO}_3$ at 560 °C and 655 °C. Points marked by squares are taken from Clark (1957) and points marked by dots are taken from Chang (1965).

The information of Fig. 3 can be shown on a pressure-temperature diagram (Fig. 4) with contours giving the composition of aragonite-strontianite mix crystals coexisting with calcite. It may be noted that the run at 510 °C and 1.96 kb, using aragonite and SrCO_3 as starting materials, gives a composition which is compatible with the contours shown in Fig. 4.

The composition of calcite coexisting with aragonite-strontianite could not be determined by the available experimental techniques because of quenching difficulties. In some runs, a doubling of the calcite lines was observed, one set of lines corresponding to a normal calcite diffraction pattern and the other set of lines indicating an expanded cell of Sr-bearing calcite. This doubling of the lines was particularly evident if a pressure quench was used. But in no case was it possible to obtain a single set of lines corresponding to Sr-bearing calcite.

A PART OF THE SYSTEM $\text{CaCO}_3\text{--SrCO}_3\text{--MgCO}_3$

A substitution of MgCO_3 in calcite stabilizes calcite to higher pressures (Jamieson & Goldsmith, 1960). The maximum effect is reached when

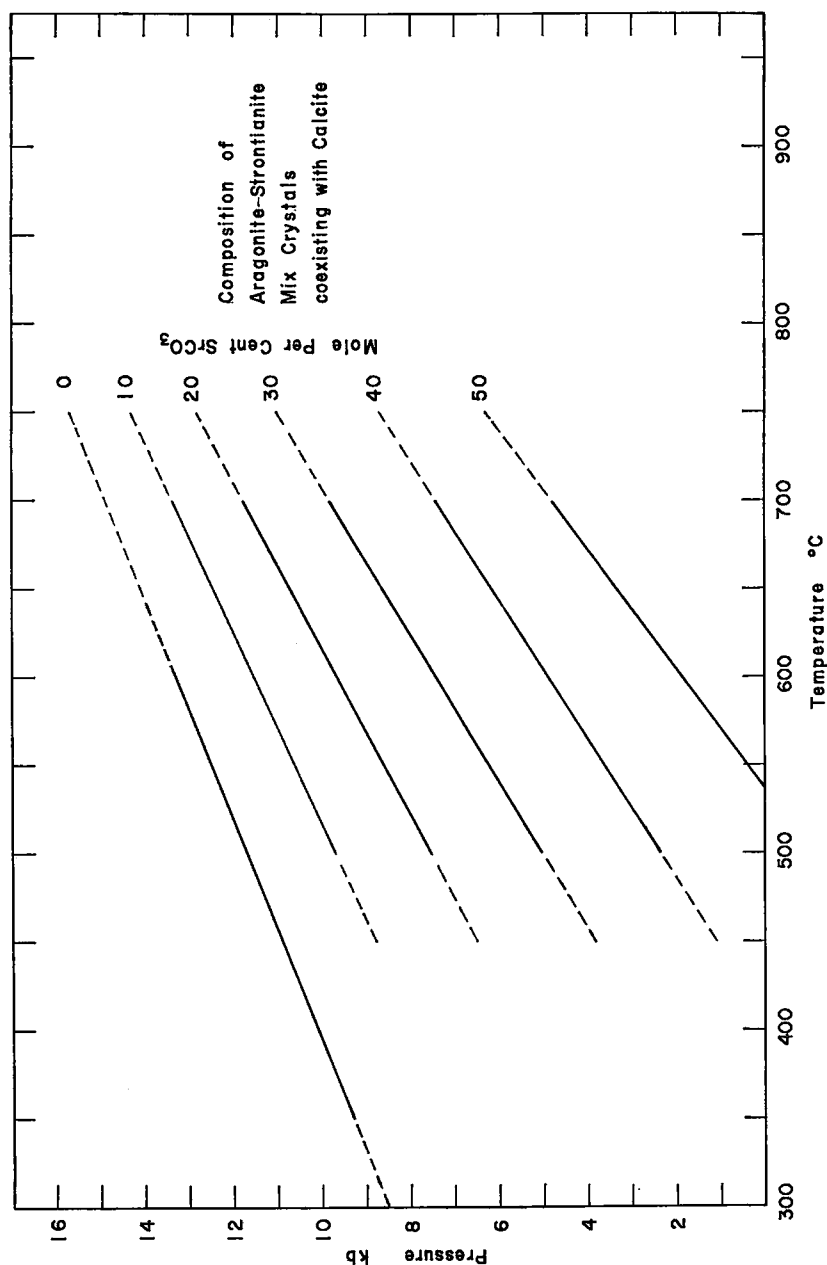
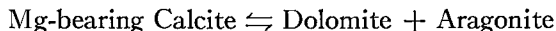


FIG. 4. The system $\text{CaCO}_3\text{-SrCO}_3$ represented on a pressure-temperature diagram by contours giving the composition of aragonite-strontianite mix crystals coexisting with calcite. The transition curve for pure CaCO_3 is taken from Clark (1957).

dolomite coexists with calcite and aragonite. According to J. R. Goldsmith (personal communication), the equilibrium pressure for the reaction



is about 20.0 kb at 660 °C. A substitution of SrCO_3 in aragonite will lower this pressure. The system CaCO_3 – SrCO_3 – MgCO_3 can be represented, at constant temperature, by a triangular prism with pressure as the vertical axis. Two sides of the prism, MgCO_3 – CaCO_3 and CaCO_3 – SrCO_3 , are shown in Fig. 5 for a temperature of 660 °C. The composition of Sr-free calcite, coexisting with dolomite at 660 °C and 2 kb is 9 mole per cent MgCO_3 and the solubility is increased by about one mole per cent MgCO_3 per 5 kb (Goldsmith & Heard, 1961). Within the prism, the assemblage calcite + dolomite + aragonite-strontianite is represented by a volume, which terminates at 20.0 kb and 660 °C in a line (calcite + dolomite + aragonite) on the MgCO_3 – CaCO_3 side. Above 20.0 kb no calcite of any composition is stable. According to Goldsmith (1959), aragonite takes no significant amount of MgCO_3 into solid solution, even when coexisting with dolomite. In order to determine whether strontianite dissolves any MgCO_3 , the assemblage strontianite + $\text{SrMg}(\text{CO}_3)_2$ was synthesized. It was found that the strontianite had a diffraction pattern characteristic of pure SrCO_3 . Because aragonite-strontianite incorporates only trace amounts of MgCO_3 , the composition of aragonite-strontianite coexisting with calcite and dolomite, at constant temperature, can be conveniently shown on the CaCO_3 – SrCO_3 side of the prism. Also, for the same reason, the determinative curve of Fig. 2 can be used. The composition of aragonite-strontianite coexisting with calcite and dolomite has been determined at 660 °C and various pressures. Pertinent data are listed in Table 5 and plotted in Fig. 5. The curve defined by these compositions must terminate at 20.0 kb. In this diagram, the composition of aragonite-strontianite coexisting with Mg-free calcite can be compared with that of aragonite-strontianite coexisting with Mg-saturated calcite (dolomite present). The appreciable effect of small amounts of MgCO_3 in raising the equilibrium pressure is well illustrated. It should be pointed out that the CaCO_3 – SrCO_3 side of the prism is not complete. The composition of aragonite-strontianite coexisting with dolomite and $(\text{Sr}, \text{Ca})\text{Mg}(\text{CO}_3)_2$ is not shown.

CONCLUSIONS

A content of 6 mole per cent SrCO_3 in aragonite is necessary to lower the pressure of the calcite-aragonite equilibrium by 1 kb, in the temperature range of 500 °C to 700 °C. It is probably safe to extrapolate this value

TABLE 4. COMPOSITION OF ARAGONITE-STRONTIANITE COEXISTING WITH CALCITE

Starting material	Run	Temperature °C $\pm 10^\circ$	Pressure kb $\pm 2\%$ ($\pm 5\%$ if over 7 kb)	Time days	$d(132) \text{ \AA}$	Composition mole % SrCO ₃	Averaged value of composition $\pm 2.5\%$
calcite + SrCO ₃	22-10-1	510	1.96	48	1.8627	51.5	51.5
aragonite + SrCO ₃	22-10-2	510	1.96	48	1.8551	43.0	43.0
calcite + SrCO ₃	19-14-1	564	0.98	7	1.8622	50.5	51.5
calcite + SrCO ₃	19-14-2	564	0.98	7	1.8622	50.5	
calcite + SrCO ₃	19-15-1	564	0.98	8	1.8635	52.0	
calcite + SrCO ₃	19-15-2	564	0.98	8	1.8643	53.0	
aragonite + SrCO ₃	29-2-2	551	1.96	38	1.8572	45.0	45.0
aragonite + SrCO ₃	30-3-2	555	3.92	39	1.8540	42.0	43.5
aragonite + SrCO ₃	2-2-2	560	3.92	27	1.8570	45.0	
calcite + SrCO ₃	30-3-1	555	3.92	39	1.8585	46.5	45.5
calcite + SrCO ₃	2-2-1	560	3.92	27	1.8563	44.5	
calcite + SrCO ₃	19-3-1	567	3.92	7	1.8590	47.0	
calcite + SrCO ₃	19-3-2	567	3.92	7	1.8595	47.5	
calcite + SrCO ₃	19-4-1	567	3.92	7	1.8599	48.5	49.0
calcite + SrCO ₃	19-4-2	567	3.92	7	1.8608	49.0	
calcite + SrCO ₃ *	23-2-1	553	3.92	27	1.8620	50.5	
aragonite + SrCO ₃ *	23-2-2	553	3.92	27	1.8599	48.5	
aragonite + SrCO ₃	7-2-1	560	6.86	26	1.8400	26.5	26.5
calcite + SrCO ₃	7-2-2	560	6.86	26	1.8486	36.0	36.0
calcite + SrCO ₃	S-22	567	10.2	9	1.8248	11.0	11.0
aragonite + SrCO ₃	39-4-2	656	0.98	14	1.8653	54.0	56.5
aragonite + SrCO ₃	39-7-2	653	0.98	28	1.8669	56.0	
calcite + SrCO ₃	39-4-1	656	0.98	14	1.8658	55.0	
calcite + SrCO ₃	39-7-1	653	0.98	28	1.8673	56.5	
calcite + SrCO ₃ †	39-5-1	656	0.98	7	1.8696	59.0	
calcite + SrCO ₃ †	39-5-2	656	0.98	7	1.8680	57.0	

calcite + SrCO_3^*	39-9-2	656	2.45	7	1.8656	54.5	54.5
aragonite + SrCO_3	19-22-1	659	3.92	21	1.8625	51.0	49.0
aragonite + SrCO_3	19-24-2	657	3.92	28	1.8587	47.0	
calcite + SrCO_3	19-22-2	659	3.92	21	1.8629	51.5	
calcite + SrCO_3	19-24-1	657	3.92	28	1.8592	47.5	
calcite + SrCO_3	22-14-1	650	3.92	39	1.8604	48.5	
calcite + SrCO_3	30-2-1	657	3.92	21	1.8604	48.5	
calcite + SrCO_3^*	23-3-2	652	3.92	27	1.8622	50.5	
calcite + $\text{SrCO}_3^\dagger$	23-8-1	657	3.92	14	1.8592	47.5	
calcite + SrCO_3	7-1-1	655	6.86	33	1.8507	38.0	38.0
calcite + SrCO_3	S-33	667	10.2	11	1.8377	24.0	24.0
calcite + SrCO_3	S-37	653	12.4	12	1.8258	12.0	12.0

TABLE 5. COMPOSITION OF ARAGONITE-STRONTIANITE COEXISTING WITH CALCITE AND DOLOMITE

Starting material	Run	Temperature $^{\circ}\text{C} \pm 10^{\circ}$	Pressure kb $\pm 2\%$ ($\pm 5\%$ if over 7 kb)	Time days	$d(132) \text{ \AA}$	Composition mole % SrCO_3	Averaged value of composition $\pm 2.5\%$
calcite + dolomite + SrCO_3^*	23-3-1	653	0.98	31	1.8721	62.0	62.0
calcite + dolomite + SrCO_3^*	39-9-1	656	2.45	7	1.8699	59.5	59.5
calcite + dolomite + SrCO_3	19-19-1	668	3.92	14	1.8674	56.5	56.0
calcite + dolomite + $\text{SrCO}_3^\dagger$	19-21-1	666	3.92	10	1.8672	56.0	
calcite + dolomite + SrCO_3	19-23-1	658	3.92	21	1.8678	57.0	
calcite + dolomite + SrCO_3	19-23-2	658	3.92	21	1.8656	54.5	
calcite + dolomite + SrCO_3	7-1-2	655	6.86	33	1.8602	48.5	48.5
calcite + dolomite + SrCO_3	S-35	667	10.0	11	1.8505	38.0	38.0

*Oxalic acid added.

†Pressure quench.

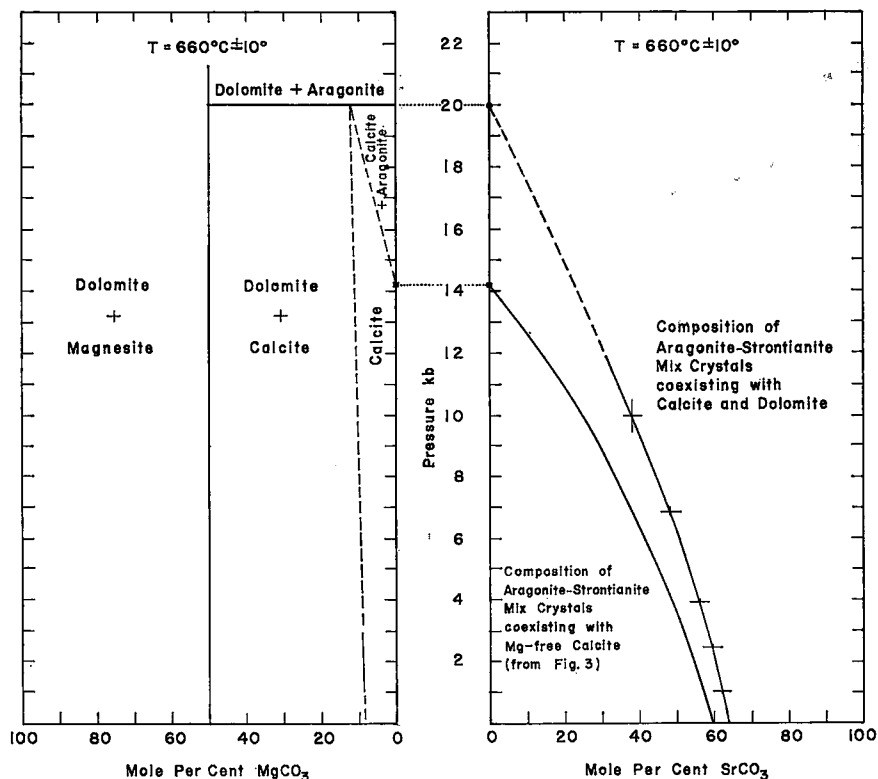


FIG. 5. A part of the system CaCO_3 - SrCO_3 - MgCO_3 at 660°C . Two sides of a prism, with composition as base and pressure as vertical axis, are shown. The point marked by a square is taken from Clark (1957) and the one marked by a dot from Goldsmith (personal communication). The composition of calcite coexisting with dolomite is shown according to data from Goldsmith and Heard (1961).

to the temperature range of the lawsonite-glaucophane facies (350°C to 450°C) because lines of constant composition of aragonite-strontianite coexisting with calcite are nearly parallel to the transition curve of pure CaCO_3 , particularly if the SrCO_3 content is small (see Fig. 4). In contrast, a content of 7 mole per cent MgCO_3 in calcite raises the equilibrium pressure about 3 kb (Jamieson & Goldsmith, 1960). Natural metamorphic aragonites contain only about one mole per cent SrCO_3 (Coleman & Lee, 1962). The lowering of the pressure of the calcite-aragonite equilibrium due to such small amount is insignificant. The presence of aragonite, when formed in the temperature range of 350°C to 450°C , indicates pressures of 9 to 11 kb. Either the effective pressure during metamorphism is increased by phenomena other than weight of overburden,

such as "tectonic" or "fluid overpressure", or a very great depth of burial must be postulated. It is interesting to note that Ernst (1965) suggests an accumulation of 30 km of Franciscan rocks in the deepest portion of the trench, although such a great depth of geosynclines is not generally accepted.

For a given composition of aragonite-strontianite, coexisting with calcite, the presence of MgCO_3 in calcite raises the pressure of the calcite-aragonite equilibrium (at constant temperature) until a maximum value is reached, at which pressure aragonite-strontianite coexists with calcite and dolomite. This effect is particularly pronounced if aragonite contains small amounts of SrCO_3 only, which is the geologically interesting case. If the original calcite, which was converted to aragonite, had contained appreciable amounts of MgCO_3 , the assemblages Mg-bearing calcite + aragonite and dolomite + aragonite would be expected to occur in nature. Because such assemblages have not been reported, it may be concluded that the original calcite contained little MgCO_3 ; therefore, the pressures indicated by the calcite-aragonite transition for pure CaCO_3 need not be corrected to higher values in petrological considerations.

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