

## SUBSOLIDUS PHASE RELATIONS IN THE ARAGONITE-TYPE CARBONATES:

### I. THE SYSTEM $\text{CaCO}_3\text{-SrCO}_3\text{-BaCO}_3$

LUKE L. Y. CHANG, *Department of Geology, Miami University,  
Oxford, Ohio 45056.*

#### ABSTRACT

Subsolidus phase relations in the systems  $\text{SrCO}_3\text{-BaCO}_3$ ,  $\text{CaCO}_3\text{-SrCO}_3$ ,  $\text{CaCO}_3\text{-BaCO}_3$ , and  $\text{CaCO}_3\text{-SrCO}_3\text{-BaCO}_3$  were studied in the temperature range between 400° and 750°C and at pressures from 10 to 35 kbars using high-pressure, opposed-anvil apparatus.

A complete series of aragonite-type solid solutions exists in the system  $\text{SrCO}_3\text{-BaCO}_3$ , and variation of lattice parameters as a function of composition shows a linear relationship.

In the system  $\text{CaCO}_3\text{-SrCO}_3$ , there is a two-phase region consisting of both aragonite- and calcite-type solid solutions. Its range diminishes with increasing pressure in the temperature range studied, and no calcite-type phase was found in the system at 25 kbars. The larger strontium ion tends to stabilize the aragonite-type phase to a higher temperature at a constant pressure.

Mutual solubilities between the end members of the system  $\text{CaCO}_3\text{-BaCO}_3$  are very limited, but the binary compound, barytocalcite, is stable over a large range of compositions and can take as much as 12.5 mole percent excess  $\text{CaCO}_3$  at 660°C and 9.0 mole percent excess  $\text{BaCO}_3$  at 750°C without losing its monoclinic character.

In the ternary system, the aragonite-type solid solution forms all the way from  $\text{BaCO}_3$  through  $\text{SrCO}_3$  to  $\text{CaCO}_3$  at 15 kbars and 550°C, and is separated from the barytocalcite-type solid solution by a large two-phase region. At 10 kbars and 550°C, disordered calcite-type solid solution appears in the system and occupies the central part of the ternary system.

#### INTRODUCTION

Extensive investigations of the stability relations in the subsolidus region among calcite-type carbonates have been made in recent years, and complex phase relationships have been revealed. Binary systems of  $\text{CaCO}_3$  with aragonite-type strontianite and witherite were also studied, showing complicated behavior in the subsolidus regions of the systems. However, very little quantitative work has been done to date on the subsolidus phase relations in the systems of aragonite-type carbonates. It is evident that three major problems in carbonate mineralogy can be answered through such a study. They are: (1) the extent of solid solutions among aragonite-type carbonates, (2) the effect of the solid solution on the calcite-aragonite phase transition, and (3) the formation of multiple-carbonates and their order-disorder relations.

As the first part of a study on the subsolidus phase relations in the aragonite-type carbonates, the phase relations in the system  $\text{CaCO}_3\text{-SrCO}_3\text{-BaCO}_3$  were investigated in detail and results are reported in this paper.

## MATERIALS, APPARATUS, AND EXPERIMENTAL PROCEDURES

The starting materials were prepared from reagent grade carbonates. Binary and ternary samples of desired proportions were produced at room temperature by reacting mixed nitrates of the appropriate cations with sodium carbonate solution. The nitrate solutions were prepared by dissolving the carbonates in nitric acid, evaporating to dryness, and making a 0.1 molal solution. The precipitated carbonates were washed with distilled water to remove the remaining solutions and dried at 110°C under  $\text{CO}_2$  atmosphere for about two hours.

Mechanical mixtures of binary and ternary compositions were also made. For runs at 15 kbars,  $\text{BaCO}_3$ ,  $\text{SrCO}_3$ , and calcite-type  $\text{CaCO}_3$  were used as starting materials, while aragonite-type  $\text{CaCO}_3$  was mixed with Ba and Sr carbonates for runs at 10 kbars.

The apparatus used was the opposed-anvil, high-pressure system (Griggs and Kennedy, 1956); Goldsmith and Newton (1969) have discussed the suitability of this apparatus for research on carbonates.

Generally, a period of eight hours was used for runs above 700°C, forty-eight hours for runs in the range 500°–700°C, and ninety-six hours for runs below 500°C. Runs up to two weeks duration at each temperature range produced results similar to these in the shorter runs. A small amount of  $\text{Li}_2\text{CO}_3$  was added as a flux in some low-temperature runs, a procedure known to be effective in promoting reactions in carbonates (Goldsmith and Graf, 1957; Chang, 1965). The uncertainties in the individual runs are estimated to be  $\pm 5^\circ\text{C}$  and less than 0.5 kbars.

The attainment of equilibrium was checked by reversing experiments in the following manner: Two runs of the same composition were treated at the same  $P$ - $T$  conditions for a certain period of time depending on the temperature desired. Then one of the runs was quenched, and the other was held in the furnace but with either the temperature or the pressure lowered. After another period of time, this run was quenched. The change of phase assemblage in these two runs as a function of changing pressure or temperature was examined by X-ray diffraction. For example, two samples of composition  $\text{Ca}_{80}\text{Sr}_{20}$  were run at 550°C and 15 kbars for 48 hours. One of them was quenched and found to contain a single-phase of the aragonite-type structure. The other was held in the furnace at 550°C but the pressure was lowered to 10 kbars. After another period of ninety-eight hours, this run was quenched and was examined by X-ray diffraction. A two-phase assemblage consisting of aragonite- and calcite-type solid solutions was found. This is the same phase assemblage produced when the precipitates were treated at 550°C and 10 kbars. Thus the two-phase assemblage can be produced from the decomposition of the aragonite-type solid solution by decreasing the pressure as well as from the conversion of the precipitates by increasing the pressure at 550°C. This procedure was used because of the difficulties encountered in recovering enough sample after quenching for the second period of equilibration at different  $P$ - $T$  conditions. Pertinent data of experiments are listed in Table I.

Identification of the products was made by X-ray diffraction. Ni-filtered Cu-radiation was used throughout this work. It was found that reflection lines of both rhombohedral and orthorhombic structures in the region  $2\theta = 25^\circ\text{--}55^\circ$  were the most reliable. The (110) line of metallic tungsten (from General Electric, Lamp Metals and Components Department, Cleveland, Ohio, highly purified) at  $40.26^\circ$  ( $a = 2.1648$ , Swanson and Tatge, 1953) was used as an internal standard. Scanning was done at a rate of  $1^\circ/\text{minute}$  and a chart speed of 1 inch/degree was used. Reflection lines (022), (110), (108), and (116) of calcite-type structure and (221), (132), (113), (112), (220), and (202) of aragonite-type structure were used in the measurement of lattice parameters. For the construction of tie lines in the two-phase region, the displacements of the strongest lines of calcite-type structure (104), aragonite-type structure (111), and barytocalcite-type structure (201) were employed. Six oscilla-

TABLE 1. Pertinent data on runs related to the reversibility of reactions in the system  $\text{CaCO}_3\text{-SrCO}_3\text{-BaCO}_3$

Composition mole%			First Period of Equilibrium			Second Period of Equilibrium			Results, Phases*
$\text{CaCO}_3$	$\text{SrCO}_3$	$\text{BaCO}_3$	Pres. Kbar	Temp. °C	Time Hrs.	Pres. Kbar	Temp. °C	Time Hrs.	
50.00	50.00	-	15	550	48	-	-	-	A
50.00	50.00	-	15	550	48	10	550	168	A
80.00	20.00	-	15	550	48	-	-	-	A
80.00	20.00	-	15	550	48	10	550	98	A + C
80.00	20.00	-	10	700	24	-	-	-	A + C
80.00	20.00	-	10	700	24	15	550	212	A
90.00	10.00	-	15	550	48	-	-	-	A
90.00	10.00	-	15	550	48	10	550	102	A + C
90.00	10.00	-	10	550	48	-	-	-	A + C
90.00	10.00	-	10	550	48	15	550	96	A
95.00	5.00	-	15	550	48	-	-	-	A
95.00	5.00	-	15	550	48	10	550	98	C
45.00	10.00	45.00	15	550	48	-	-	-	B
45.00	10.00	45.00	15	550	48	10	550	96	D
30.00	40.00	30.00	15	550	48	-	-	-	B + A
30.00	40.00	30.00	15	550	48	10	550	96	D + A
30.00	40.00	30.00	10	550	48	-	-	-	D + A
30.00	40.00	30.00	10	550	48	15	550	168	B + A
70.00	26.00	4.00	15	550	48	-	-	-	B + A
70.00	26.00	4.00	15	550	48	10	550	172	D + C +
41.24	17.50	41.25	20	550	48	-	-	-	B
41.25	17.50	41.25	20	550	48	15	550	172	B + A
17.50	65.00	17.50	25	550	48	-	-	-	A
17.50	65.00	17.50	25	550	48	15	550	96	A + B
20.00	60.00	20.00	25	550	48	-	-	-	A + B
20.00	60.00	20.00	25	550	48	15	550	172	A + B

\* A: aragonite-type solid solution

B: barytocalcite-type solid solution

C: calcite-type solid solution

D: disordered calcite-type solid solution

tions were made for measurement, and the precision of the  $2\theta$  values is believed to be within  $0.01^\circ$ .

### BINARY SYSTEMS

*The System  $\text{SrCO}_3\text{-BaCO}_3$ .* Subsolidus phase relations in the system  $\text{SrCO}_3\text{-BaCO}_3$  at one atmosphere  $\text{CO}_2$  pressure have been studied (Chang, 1965). In the temperature range between  $400^\circ\text{C}$  and  $1000^\circ\text{C}$ ,  $\text{SrCO}_3$  and  $\text{BaCO}_3$  form complete series of solid solutions in both orthorhombic, aragonite-type and rhombohedral, disordered calcite-type structures, and these two series are separated from each other by a narrow two-phase region. The rhombohedral solid solution becomes stable at lower temperature toward the central part of the binary system, and there is a minimum temperature of transition at  $745^\circ\text{C}$  near the composition  $\text{Ba}_{70}\text{Sr}_{30}$ .

In the present study, the phase relations were determined at 15 kbars and in the temperature range between  $400^\circ$  and  $750^\circ\text{C}$ , which is the upper limit of the high-pressure apparatus used. The orthorhombic, aragonite-type phase is the only stable structure encountered in this range.

Variation of lattice parameters as a function of composition shows a linear relationship. This confirms the previous findings (Chang, 1965).

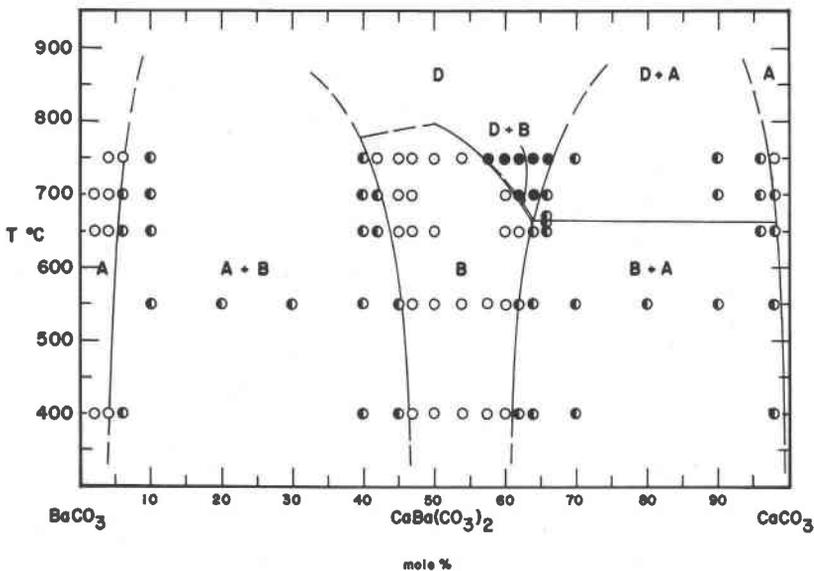


FIG. 1. Subsolidus phase relations in the system  $\text{CaCO}_3\text{-BaCO}_3$  at 25 kbars. The regions in this and following diagrams are labelled with symbols representing stable phases, A: aragonite-type solid solution, B: barytocalcite-type solid solution, C: calcite-type solid solution, and D: disordered calcite-type solid solution.

*The System CaCO<sub>3</sub>-BaCO<sub>3</sub>.* Subsolidus phase relations at 25 kbars are shown in Figure 1. The most characteristic feature, compared with phase relations in the system at low pressure (100 lb/in<sup>2</sup> CO<sub>2</sub> pressure) (Chang, 1965), is the greatly enlarged stability region of barytocalcite, a monoclinic CaBa(CO<sub>3</sub>)<sub>2</sub> (Alm, 1960). It is stable for the entire temperature range of this investigation and can take as much as 12.5 mole percent excess CaCO<sub>3</sub> at 660°C and 9.0 mole percent excess BaCO<sub>3</sub> at 750°C into its solid solution without losing its monoclinic character. In a similar fashion as in the system at relatively low pressure (Chang, 1965), there is no apparent two-phase region existing in the monoclinic-rhombohedral phase transition. The change of intensity of ordering reflections of barytocalcite can be detected only at the transition temperature. This monoclinic barytocalcite-rhombohedral, disordered-calcite phase change was also found in the unmixing region of the Ca-rich part of the system. Runs at 650°C from compositions in this part gave equilibrium assemblages consisting of orthorhombic aragonite and monoclinic barytocalcite, whereas those made at 660°C produced orthorhombic aragonite and rhombohedral disordered calcite.

The rhombohedral phase was not found in the range between BaCO<sub>3</sub> and CaBa(CO<sub>3</sub>)<sub>2</sub>. Barytocalcite is in equilibrium with witherite over the entire temperature range of this investigation.

*The System CaCO<sub>3</sub>-SrCO<sub>3</sub>.* Subsolidus phase relations in the system at one atmosphere CO<sub>2</sub> pressure have also been studied (Chang, 1965). A complete series of solid solutions forms above 912°C, which is the temperature of the orthorhombic-rhombohedral phase transition in SrCO<sub>3</sub>. The solubility of CaCO<sub>3</sub> in the aragonite-type strontianite decreases with increasing temperature.

Froese and Winkler (1967) studied a part of this system under pressures up to 20 kbars and in the temperature range between 500°C and 700°C. They established the boundary curve separating the orthorhombic solid solution from the two-phase region of orthorhombic and rhombohedral phases. Froese and Winkler stated that they could not determine the boundary curve between the rhombohedral form and the two-phase region because of quenching difficulties.

In the present study, subsolidus phase relations in the system were investigated at three pressures and in the temperature range between 400° and 750°C. At 25 kbars, the system shows a very simple phase relationship, consisting of a complete series of solid solutions of the orthorhombic, aragonite-type structure. There is no omission or addition of X-ray diffraction lines throughout the entire series. The variation of lat-

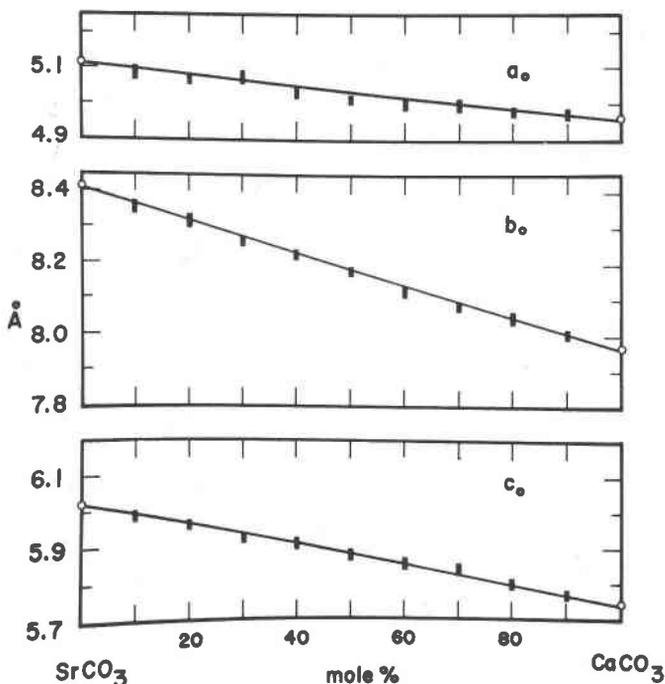


FIG. 2. Variation of lattice parameters of aragonite-type solid solution in the system  $\text{CaCO}_3\text{-SrCO}_3$ .

tice parameters as a function of composition shows linear relationships (Fig. 2).

At 15 kbars, the system does not change much in its phase relations, except in the Ca-rich side at relatively high temperatures. As shown in Figure 3, calcite is present, coexisting with aragonite-type solid solutions in a very limited region.

The effect of SrCO<sub>3</sub> component on the phase change between rhombohedral, calcite-type and orthorhombic, aragonite-type phases is better illustrated at 10 kbars (Fig. 4). The range of the orthorhombic solid solution decreases with increasing temperature from a complete series below 420°C to a limited series between Sr<sub>100</sub> and Ca<sub>65</sub>Sr<sub>35</sub> at 750°C, while the solubility of SrCO<sub>3</sub> in calcite increases up to nearly 15 mole percent at 750°C. The two-phase region is bounded by two smooth curves without any apparent inflection in their slopes. Calcite II is a non-quenchable phase (Bridgman, 1939), it can not be present in quenched sample. There is, therefore, no indication of a phase change in the rhombohedral solid

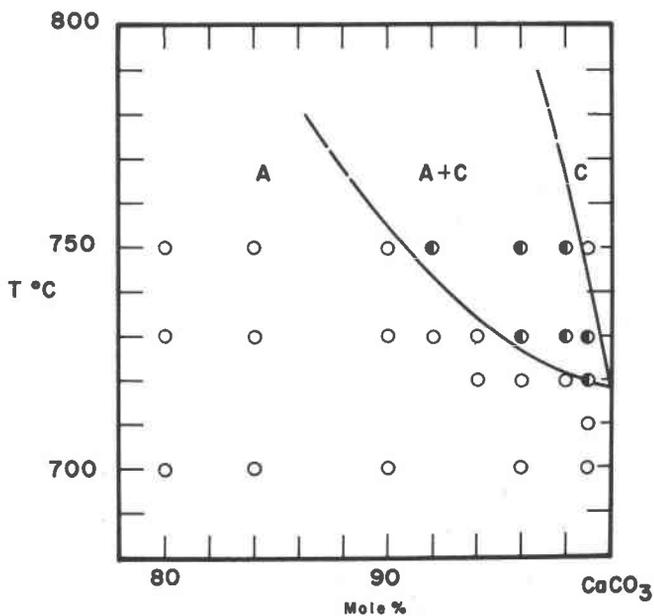


FIG. 3. Subsolidus phase relations in the system  $\text{CaCO}_3$ - $\text{SrCO}_3$  at 15 kbars.

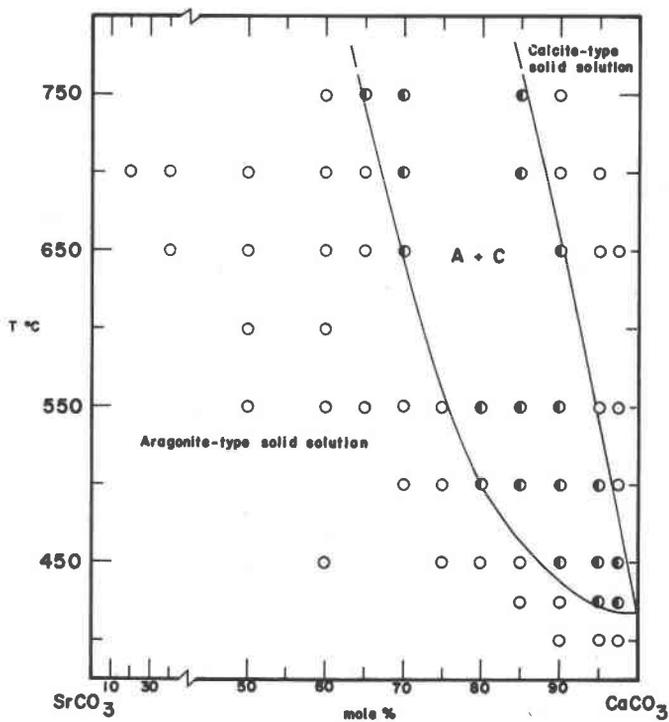


FIG. 4. Subsolidus phase relations in the system  $\text{CaCO}_3$ - $\text{SrCO}_3$  at 10 kbars.

solution. This is not in conflict with previously established results (Jamieson, 1957; Boettcher and Wyllie, 1967; Goldsmith and Newton, 1969) that show the calcite I-calcite II transition near  $500^\circ\text{C}$  and 10 kbars. High-temperature X-ray diffraction (Chang, 1965) shows that even though the calcite I-calcite II transition can be determined in the system  $\text{CaCO}_3\text{-SrCO}_3$  at one atmosphere  $\text{CO}_2$  pressure, no break in slope was detected.

A comparison between the results of Froese and Winkler (1967) and the current study is shown in Figure 5. In general, phase relations established at  $650^\circ\text{C}$  agree better than those at  $560^\circ\text{C}$ . There is no problem in this study in quenching single rhombohedral, calcite-type phases from Ca-rich samples. Thus, the phase boundary between rhombohedral, calcite-type solid solution and the two-phase region is well defined.

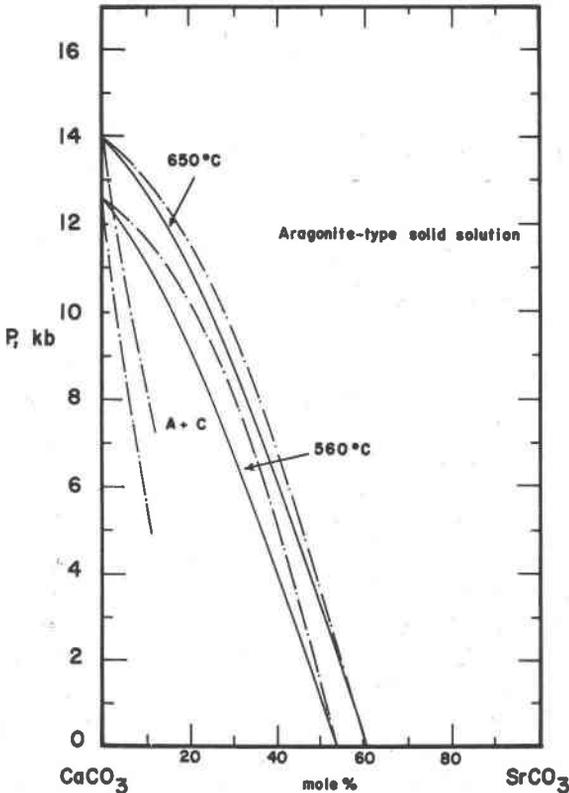


FIG. 5. A comparison of results of Froese and Winkler (1967) and the present study for the system  $\text{CaCO}_3\text{-SrCO}_3$ . Solid lines denote results of Froese and Winkler, and bar-and-dot lines denote those obtained in the present study.

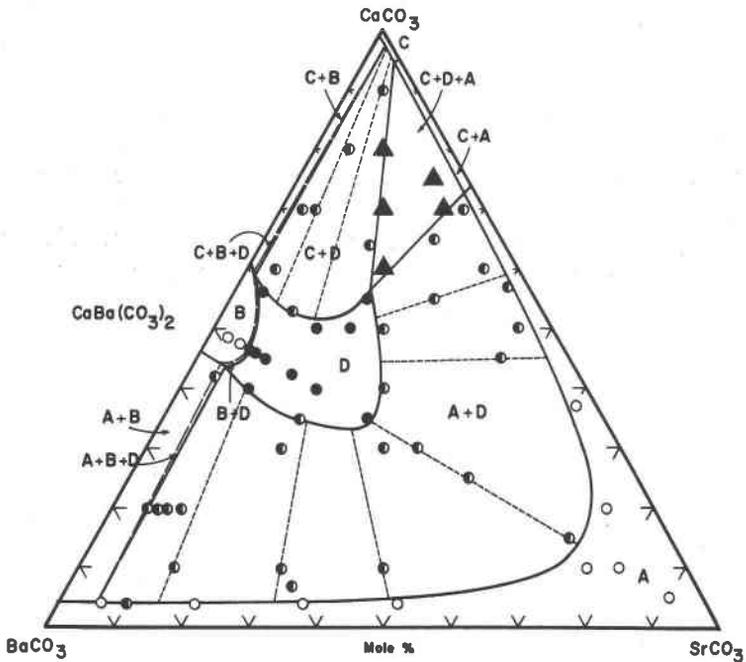


FIG. 6. Subsolidus phase relations in the system  $\text{CaCO}_3\text{-SrCO}_3\text{-BaCO}_3$  at  $550^\circ\text{C}$  and 10 kbars. Possible phase assemblages,  $\text{B}+\text{D}$ ,  $\text{A}+\text{B}+\text{D}$ , and  $\text{C}+\text{B}+\text{D}$ , are also shown in the diagram. Tie lines are represented by dashed lines.

#### TERNARY SYSTEM

At  $550^\circ\text{C}$  and 10 kbars. Subsolidus phase relations are shown in Figure 6. Two single-phase regions were found experimentally in the system. The orthorhombic, aragonite-type phase is the extension of the solid solution along binaries into the ternary system. Within this solid solution, the solubility of barium in the Ca-rich part has the least range with less than 3 mole percent, the solubility of  $\text{CaCO}_3$  in the Ba-rich part is limited to 5 mole percent, and  $\text{SrCO}_3$  can take approximately 30 mole percent of combined Ca and Ba carbonates. The rhombohedral, disordered calcite-type phase is stable in the central part of the system and transforms to the monoclinic barytocalcite when the Sr-content is less than 5 mole percent. The rhombohedral-monoclinic transition in the ternary system is similar to that in the binary system, that is, no detectable two-phase coexisting assemblage is involved in this transition.

A large two-phase region consisting of orthorhombic, aragonite-type and rhombohedral, disordered calcite-type solid solutions extends throughout much of the diagram, whereas a smaller field in which calcite

and disordered calcite coexist is restricted to the Ca-rich part. Several tie lines in the two-phase regions are shown in Figure 6. They were constructed by comparing  $d$ -spacings of both calcite-type reflection (104) and aragonite-type reflection (111) of coexisting phases in the two-phase regions with the  $d$ -spacings of the single phases in the related solid solution series. There are three minor two-phase regions, between calcite- and barytocalcite-type solid solutions, aragonite- and barytocalcite-type solid solutions, and, calcite- and aragonite-type solid solutions.

A three-phase region was detected experimentally in the system, and is defined by a calcite with small amount of  $\text{SrCO}_3$ , an aragonite-type phase with a composition close to  $\text{Ca}_{72}\text{Sr}_{26}\text{Ba}_2$ , and a disordered calcite-type phase with a composition of  $\text{Ca}_{56}\text{Sr}_{20}\text{Ba}_{24}$ .

*At 550°C and 15 kbars.* Figure 7 represents the phase relations at 550°C and 15 kbars. Under these conditions, aragonite is the stable form of  $\text{CaCO}_3$ , and the interrupted series of aragonite-type solid solutions along the join  $\text{CaCO}_3\text{-SrCO}_3$  at 10 kbars becomes a continuous one, which gives a complete series from  $\text{BaCO}_3$  through  $\text{SrCO}_3$  to  $\text{CaCO}_3$ . This aragonite-

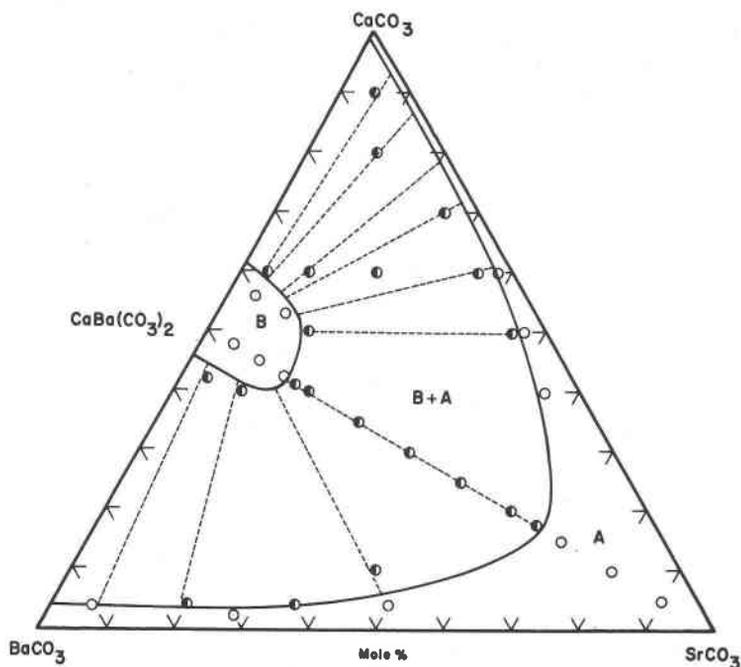


FIG. 7. Subsidiary phase relations in the system  $\text{CaCO}_3\text{-SrCO}_3\text{-BaCO}_3$  at 550°C and 15 kbars.

type solid solution is separated from another single-phase area in the system, monoclinic barytocalcite, by a huge two-phase region, which almost takes the entire ternary field. The solubility of strontium in barytocalcite increases with increasing pressure, an amount of 16 mole percent under these conditions as compared with 5 mole percent at 10 kbars and 550°C.

Tie lines in the two-phase region are also plotted in Figure 7.

*AT 550°C and Pressures Between 10 and 15 kbars.* A few runs between 10 and 15 kbars were made along joins  $\text{Ca}_{50}\text{Ba}_{50}\text{-Ca}_{80}\text{Sr}_{20}$ ,  $\text{Ca}_{50}\text{Ba}_{50}\text{-Ca}_{50}\text{Sr}_{50}$ , and  $\text{Ca}_{50}\text{Ba}_{50}\text{-Sr}_{100}$  to illustrate the change of field configuration in the ternary system.

With pressure increasing from 10 to 15 kbars, the three-phase region decreases in range as a result of the diminishing unmixing gap along the binary system  $\text{CaCO}_3\text{-SrCO}_3$ , and it moves toward the Ca-apex. The three-phase region disappears when aragonite becomes the stable phase of  $\text{CaCO}_3$  above 12 kbars at 550°C. In the central part, the single-phase region of disordered calcite-type solid solution, in like fashion, diminishes in range with increasing pressure. In Figure 8, probable phase relations, as deduced from the equilibria established at 10 and 15 kbars and experimental data obtained at 13 kbars, are shown.

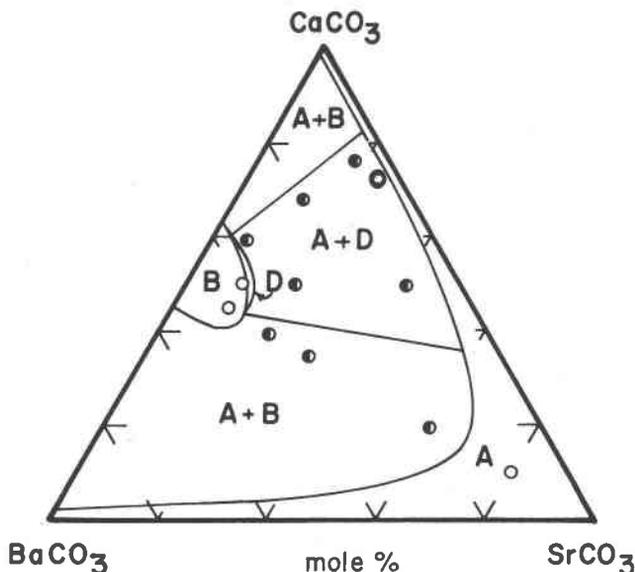


FIG. 8 Schematic representation of phase relations in the system  $\text{CaCO}_3\text{-SrCO}_3\text{-BaCO}_3$  at 550°C and 13 kbars. Results of a few experimental runs are also shown in the diagram.

TABLE 2 . High-pressure runs along the join  $\text{CaBa}(\text{CO}_3)_2\text{-SrCO}_3$ 

Composition, mole%			Temp., °C	Pressure, Kbars	Time, Hrs.	Results, Phases*
$\text{CaCO}_3$	$\text{SrCO}_3$	$\text{BaCO}_3$				
45.00	10.00	45.00	550	18	48	B
43.75	12.50	43.75	550	18	48	B
42.50	15.00	42.50	550	18	48	B
41.25	17.50	41.25	550	18	48	B + A
40.00	20.00	40.00	550	18	48	B + A
43.75	12.50	43.75	550	25	48	B
42.50	15.00	42.50	550	25	48	B
41.25	17.50	41.25	550	25	48	B
40.00	20.00	40.00	550	25	48	B + A
42.50	15.00	42.50	550	30	40	B
41.25	17.50	41.25	550	30	40	B
40.00	20.00	40.00	550	30	40	B
38.75	22.50	38.75	550	30	40	B + A
37.50	25.00	37.50	550	30	40	B + A
40.00	20.00	20.00	550	35	24	B
38.75	22.50	38.75	550	35	24	B
37.50	25.00	37.50	550	35	24	B + A
20.00	60.00	20.00	550	18	48	B + A
18.75	62.50	18.75	550	18	48	B + A
17.50	65.00	17.50	550	18	48	B + A
16.25	67.50	16.25	550	18	48	A
15.00	70.00	15.00	550	18	48	A
20.00	60.00	20.00	550	25	48	B + A
18.75	62.50	18.75	550	25	48	B + A
17.50	65.00	17.50	550	25	48	A
16.25	67.50	16.25	550	25	48	A
15.00	70.00	15.00	550	25	48	A
21.25	57.50	21.25	550	30	40	B + A
20.00	60.00	20.00	550	30	40	A
18.75	62.50	18.75	550	30	40	A
17.50	65.00	17.50	550	30	40	A
21.25	57.50	21.25	550	35	24	A
20.00	60.00	20.00	550	35	24	A

\* A: aragonite-type solid solution

B: barytocalcite-type solid solution

*At 550°C and pressures higher than 15 kbars.* At pressures higher than 15 kbars, the system does not change much in its configuration although the single-phase regions of both barytocalcite- and aragonite-type solid solutions are enlarged. At 35 kbars, 24 mole percent  $\text{SrCO}_3$  in barytocalcite and 44 mole percent  $\text{CaBa}(\text{CO}_3)_2$  in strontianite were found. The increase in mutual solid solubilities between barytocalcite and strontianite with pressure (Table 2) indicates that a complete series of solid solutions between them is possible at higher pressures (above 35 kbars). To form such a series there must be a phase transition between barytocalcite and strontianite. If such a change could occur in barytocalcite, this would mean that at some pressures barytocalcite would transform to an orthorhombic, aragonite-type structure, and thus produce alstonite (Chang, 1965). Unfortunately, experimental proof of this proposal can not be obtained with the high-pressure apparatus presently employed.

#### SUMMARY AND CONCLUSION

Three binary systems and one ternary system have been studied. Among them, a complete series of solid solutions was found in the system  $\text{SrCO}_3\text{-BaCO}_3$ , while large and limited ranges of solid solutions exist in the systems  $\text{CaCO}_3\text{-SrCO}_3$  and  $\text{CaCO}_3\text{-BaCO}_3$ , respectively. In the system  $\text{CaCO}_3\text{-SrCO}_3\text{-BaCO}_3$ , the aragonite-type solid solution forms from  $\text{BaCO}_3$  through  $\text{SrCO}_3$  to  $\text{CaCO}_3$  at 15 kbars and 550°C, whereas the disordered calcite-type solid solution appears in the central part at 10 kbars and 550°C.

The formation of ordered compounds under high pressures was found in the systems  $\text{CaCO}_3\text{-BaCO}_3$  and  $\text{CaCO}_3\text{-SrCO}_3\text{-BaCO}_3$ , and it is very unlikely in the other systems considering the small differences in ionic size between the divalent cations involved. In general, increasing similarity of ionic size increases the range of solid solution, and decreases the tendency to form an ordered phase.

The effect of solid solution on the calcite-aragonite transition is clearly shown in the system  $\text{CaCO}_3\text{-SrCO}_3$ . The larger strontium ion tends to stabilize the aragonite-type phase to a higher temperature at a constant pressure. Application of this experimental conclusion to metamorphic petrology is hindered by the fact that the amount needed for any significant effect on the equilibrium is far above that found in natural aragonite. In the system  $\text{CaCO}_3\text{-SrCO}_3$ , more than 5 mole percent  $\text{SrCO}_3$  is necessary in order to reduce the equilibrium pressure of the calcite-aragonite transition by 1 kbar.

The lack of natural carbonates of an intermediate composition in the system  $\text{SrCO}_3\text{-BaCO}_3$  has been noted (Deer, Howie, and Zussman, 1964; Sidorenko, 1947; Ermilova and Sendervora, 1959; and Harden, 1964).

This field evidence indicates that the complete series of solid solutions in the system  $\text{SrCO}_3\text{-BaCO}_3$  would have a lower limit of stability.

The naturally occurring mineral, alstonite, has not been successfully synthesized, so its stability relations in the system  $\text{CaCO}_3\text{-BaCO}_3$  or  $\text{CaCO}_3\text{-SrCO}_3\text{-BaCO}_3$  can not be defined. High-pressure data obtained indicate the existence of a possible phase in the system  $\text{CaCO}_3\text{-SrCO}_3\text{-BaCO}_3$  having composition and crystal structure similar to that of alstonite, but no direct proof has been obtained.

## ACKNOWLEDGEMENTS

The author is indebted to Professors J. R. Goldsmith, D. L. Graf, and W. F. Bradley for reviewing the manuscript. This work was supported by the National Science Foundation Grant GA-1366.

## REFERENCES

- ALM, K. F. (1960) The crystal structure of barytocalcite. *Arkiv Mineral. Geol.* **2**, 399-410.
- BOETTCHE, A. L., AND P. J. WYLLIE (1967) Revision of the calcite-aragonite transition, with location of a triple point between calcite I, calcite II, and aragonite. *Nature* **213**, 792-793.
- BRIDGMAN, P. W. (1939) The high pressure behavior of miscellaneous materials. *Amer. J. Sci.* **237**, 7-18.
- CHANG, L. L. Y. (1965) Subsolidus phase relations in the systems  $\text{BaCO}_3\text{-SrCO}_3$ ,  $\text{SrCO}_3\text{-CaCO}_3$ , and  $\text{BaCO}_3\text{-CaCO}_3$ . *J. Geol.* **73**, 346-368.
- DEER, W. A., R. A. HOWIE, AND J. ZUSSMAN (1963) *Rock Forming Minerals, Vol. 5, Carbonates*. Longmans Green, London, p. 51-57.
- ERMILOVA, L. P., AND V. M. SENDEROVA (1959) On the strontianite from the western Davoabiasky deposits in central Kazakhstan. *Mat. Geol. Rud. Mestorozhden. Petrograf. Mineral. Geokhimiya Akad. Nauk SSSR*, 294-300. [*Mineral. Abstr.* **15**, 208 (1961)].
- FROESE, E., AND H. G. F. WINKLER (1967) The system  $\text{CaCO}_3\text{-SrCO}_3$  at high pressures and 500° to 701°C. *Can. Mineral.* **8**, 551-556.
- GOLDSMITH, J. R., AND D. L. GRAF (1957) The system  $\text{CaO-MnO-CO}_2$ : solid solution and decomposition relations. *Geochim. Cosmochim. Acta* **11**, 310-334.
- GOLDSMITH, J. R., AND R. C. NEWTON (1969) P-T-X relations in the system  $\text{CaCO}_3\text{-MgCO}_3$  at high temperatures and pressures. *Amer. J. Sci.* Schairer Vol., 160-190.
- GRIGGS, D. T., AND G. C. KENNEDY (1956) A simple apparatus for high pressures and temperatures. *Amer. J. Sci.* **254**, 727-735.
- HARDEN, H. (1964) Geochemische Untersuchungen zur Genese der Strontianite-lagerstätten des Munsterlandes. *Beitr. Mineral. Petrogr.* **10**, 198-215.
- JAMIESON, J. C. (1957) Introductory studies of high pressure polymorphism to 24000 bars by X-ray diffraction with some comments on calcite II. *J. Geol.* **65**, 334-343.
- SIDORENKO, A. V. (1947) The genesis of witherite of the western Kopet-Dag, Turkey. *Dokl. Acad. Sci. USSR* **55**, 149-151.
- SWANSON, H. E., AND E. TATGE (1953) Standard X-ray diffraction powder pattern. *Nat. Bur. Stand. (U.S.), Circ.* **539-I**, p. 28.

Manuscript received, August 7, 1970; accepted for publication, April 26, 1971.