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SUBSOLIDUS PHASE RELATIONS IN ARAGONITE-TYPE CARBONATES: II. THE SYSTEMS $CaCO_3$–$SrCO_3$–$PbCO_3$ AND $CaCO_3$–$BaCO_3$–$PbCO_3$

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ABSTRACT

Binary and ternary phase relations in the systems $CaCO_3$–$SrCO_3$–$PbCO_3$ and $CaCO_3$–$BaCO_3$–$PbCO_3$ were studied in the temperature range 400°–750°C and at both 10 and 15 kbars using high-pressure, opposed-anvil apparatus.

Complete series of solid solutions were observed to exist in the systems $SrCO_3$–$PbCO_3$ and $BaCO_3$–$PbCO_3$, and linear relationships between lattice parameters and composition were found in them. In the system $CaCO_3$–$PbCO_3$, there is a two-phase region of both aragonite- and calcite-type solid solutions at 10 kbars, whereas at 15 kbars, no calcite-type phase was found and an immiscibility gap of two aragonite-type phases exists in the Ca-rich portion.

In the system $CaCO_3$–$SrCO_3$–$PbCO_3$, calcite has a significant range of solid solution with saturation limits of 38 mole percent $PbCO_3$ and 6 mole percent $SrCO_3$ along the two related binaries at 550°C and 10 kbars. At 550°C and 15 kbars, besides a small region of two aragonite-type phases existing in the Ca-rich portion along the join $CaCO_3$–$PbCO_3$, the system consists of a complete series of aragonite-type solid solutions.

Subsolidus phase relations in the system $CaCO_3$–$BaCO_3$–$PbCO_3$ at 550°C and 15 kbars are quite similar to those in the system $CaCO_3$–$SrCO_3$–$BaCO_3$ at 550°C and 10 kbars, except that aragonite is the stable form of $CaCO_3$ and is present in all phase assemblages which consist of calcite in the system with $SrCO_3$.

INTRODUCTION

As the second part of a study on the subsolidus phase relations in aragonite-type carbonates, the systems $CaCO_3$–$SrCO_3$–$PbCO_3$ and $CaCO_3$–$BaCO_3$–$PbCO_3$ were investigated. $PbCO_3$ is the only carbonate under consideration containing a cation with its chemical nature close to the Group IIB cation, instead of the Group IIA, alkaline earth. In nature, lead is commonly found in aragonite substituting for calcium, although its ionic radius is approximately 20 percent larger than that of calcium. The name "tarnowitzite" has been given to plumbian aragonite from Silesian (O'Daniel, 1930) for its high lead content.

EXPERIMENTAL PROCEDURES

Experimental work was performed in the high-pressure, opposed-anvil apparatus with starting materials prepared as precipitates from reagent grade carbonates (Chang, 1965 and 1971). The apparatus and the procedures to operate it were described in detail by Griggs and Kennedy (1956) and by MacDonald (1956), while Goldsmith and Newton (1969) discussed the suitability of this apparatus for carbonate equilibrium studies.

X-ray diffraction was used for the identification of solid phases and for the measurement of lattice parameters of the solid solutions.

The attainment of equilibrium was checked by reversing experiments in the manner described elsewhere (Chang, 1971), and results are listed in Table I.

BINARY SYSTEMS

1. The Systems $SrCO_3$–$PbCO_3$ *and* $BaCO_3$–$PbCO_3$

Subsolidus phase relations in these two systems in the temperature range between 400° and 750°C and at 10 and 15 kbars are very simple, each consisting of a complete series of solid solutions of the aragonite-type structure. Lattice parameters of both series were calculated and their relationships with binary compositions are shown in Figure 1. No deviation from a linear relation was found in them.

$PbCO_3$ decomposes at temperatures much lower than those of the alkaline earth carbonates considered here. Grisafe and White (1964) found that a pressure of 0.4 kbars is necessary to maintain cerussite from decomposition at 500°C. In the pressure range of this study, no decomposition of cerussite was found.

2. The System $CaCO_3$–$PbCO_3$

Subsolidus phase relations in the system at 10 kbars are shown in Figure 2. The solubility of $PbCO_3$ in $CaCO_3$ increases with increasing temperature, and lead can replace calcium extensively in the calcite-type structure. The solubility of $CaCO_3$ in cerussite, on the other hand, increases with decreasing temperature. Lattice parameters of the calcite-type solid solutions were calculated using the reflections (116) and (022). Their relationships with binary composition are shown in Figure 3. The parameter, a, increases in magnitude linearly with increasing amount of $PbCO_3$ from $CaCO_3$ toward $PbCO_3$, and an extrapolated value of a for the possible rhombohedral $PbCO_3$ is recorded at 5.13Å. For c, the relationship with composition is not a linear one, although it also increases in magnitude with increasing amount of $PbCO_3$. The deviation from linearity in c is apparently due to compression of lead ion to take the position of calcium ion in the calcite-type lattice. A similar situation was found in the system $CaCO_3$–$BaCO_3$ (Chang, 1965).

TABLE I. Pertinent Data on Runs Related to the Reversibility of Reactions in the System $CaCO_3$-$SrCO_3$-$PbCO_3$.

Composition, mole%			First Period of Equilibrium			Second Period of Equilibrium			Results, Phases*
$CaCO_3$	$SrCO_3$	$PbCO_3$	Pres. Kbar	Temp. °C	Time, Hrs.	Pres. Kbar	Temp. °C	Time, Hrs.	
50.0	-	50.0	15	550	48	-	-	-	A
50.0	-	50.0	15	550	48	10	550	142	A + C
50.0	-	50.0	10	550	48	-	-	-	A + C
50.0	-	50.0	10	550	48	15	550	156	A
60.0	-	40.0	15	550	48	-	-	-	A
60.0	-	40.0	15	550	48	10	550	148	A + C
70.0	-	30.0	15	550	48	-	-	-	A + A
70.0	-	30.0	15	550	48	10	550	138	C
70.0	-	30.0	10	550	48	-	-	-	C
70.0	-	30.0	10	550	48	15	550	142	A + A
80.0	-	20.0	15	550	48	-	-	-	A + A
80.0	-	20.0	15	550	48	10	550	145	C
60.0	10.0	30.0	10	550	48	-	-	-	A + C
60.0	10.0	30.0	10	550	48	15	550	142	A
60.0	10.0	30.0	15	550	48	-	-	-	A
60.0	10.0	30.0	15	550	48	10	550	124	A + C
75.0	5.0	20.0	10	550	48	-	-	-	C
75.0	5.0	20.0	10	550	48	15	550	124	A + A
80.0	10.0	10.0	15	550	48	-	-	-	A
80.0	10.0	10.0	15	550	48	10	550	125	A + C
80.0	10.0	10.0	10	550	48	-	-	-	A + C
80.0	10.0	10.0	10	550	48	15	550	125	A

* A: aragonite-type solid solution

C: calcite-type solid solution

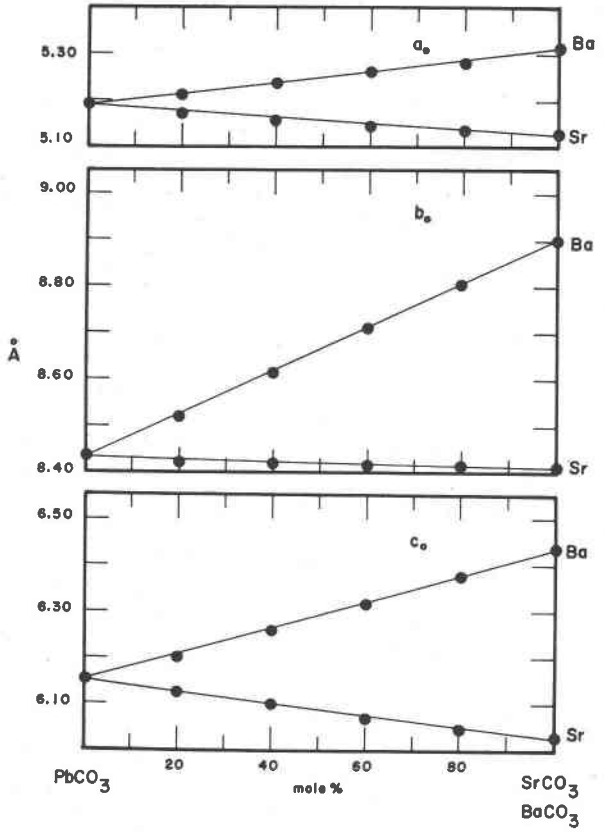

FIG. 1. Variation of lattice parameters of aragonite-type solid solutions in the systems $SrCO_3$–$PbCO_3$ and $BaCO_3$–$PbCO_3$.

With the present high-pressure apparatus, it is not possible to demonstrate whether or not a rhombohedral form of $PbCO_3$ exists, for non-quenchable phases similar to those found in $BaCO_3$ and $SrCO_3$ (Lander, 1949, and Chang, 1965) seem to exist in the Pb-rich portion at temperatures above 650°C. Runs made at 650°C produced good results, from which boundary curves separating the calcite-type or the aragonite-type solid solution from the two-phase region can be drawn with confidence. Above 650°C, inconsistent data were obtained. If an extrapolation can be made on the assumption that there is no large change in slope of the solvus, the aragonite-disordered calcite phase transition in $PbCO_3$ would be expected in the temperature range around 800°C. This is far below the temperature of the similar phase transition observed in $BaCO_3$ and $SrCO_3$ (Chang, 1965, and Rapport and Pistorius, 1967). High-pressure differential thermal analysis, at the present time, seems to be an ideal tool to determine the transition temperature in cerussite, but Rapport and Pistorius (1967) did not include $PbCO_3$ in their recent study on the orthorhombic-rhombohedral phase transition in aragonite-type carbonates.

Subsolidus phase relations at 15 kbars are shown in Figure 4. A complete series of solid solutions forms above 600°C. All intermediate phases give rise to the aragonite-type structure, and the variation of lattice parameters as a function of composition shows linear relationships (Figure 5). Below 600°C, an immiscibility gap consisting of two aragonite-type phases exists (some equilibrium data are listed in Table I). The solvus is slightly asymmetrical and has a tendency

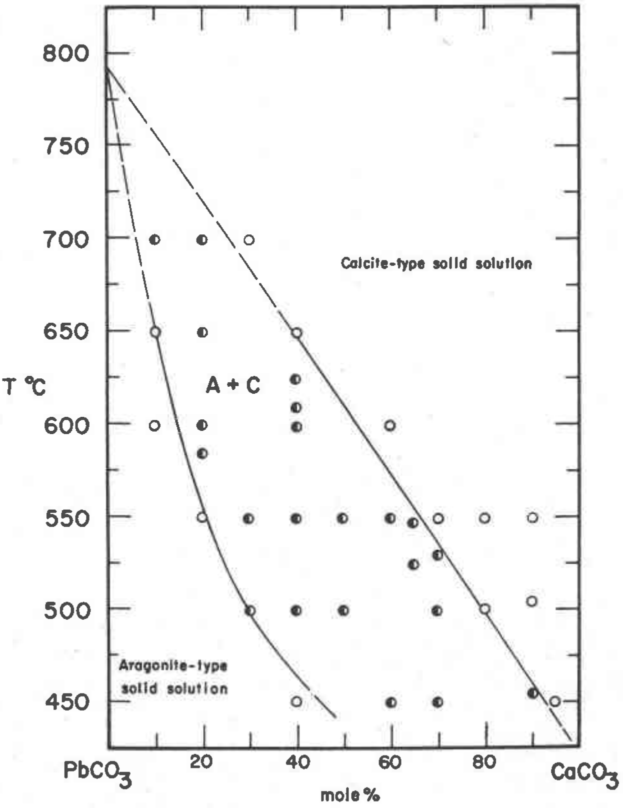

FIG. 2. Subsolidus phase relations in the system $CaCO_3$–$PhCO_3$ at 10 kbars. Some regions in this diagram are labeled with symbols representing stable phases, A: aragonite-type solution with C: calcite-type solid solution.

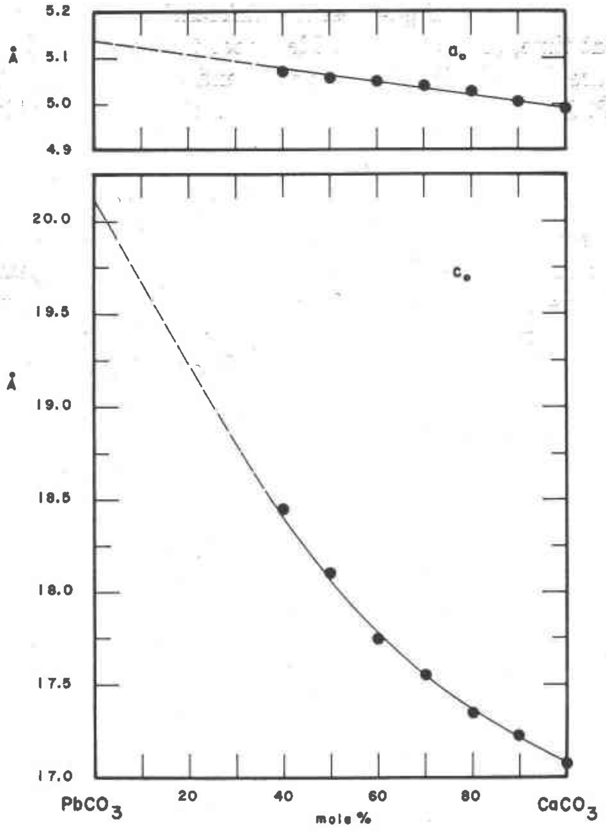

FIG. 3. Variation of lattice parameters of calcite-type solid solutions in the system $CaCO_3$–$PbCO_3$.

to approach the equimolar composition at lower temperatures. No experimental runs were made above 650°C. It is expected from what has been established in the system $CaCO_3$–$SrCO_3$ (Chang, 1971) that calcite would be present in the system above 718°C, the aragonite-calcite transition temperature in $CaCO_3$ at 15 kbars, and it would co-exist with aragonite-type solid solution in a small two-phase region in the Ca-rich side.

Subsolidus phase relations in the system between 10 and 15 kbars are schematically shown in Figure 6. In the temperature range studied, the two-phase regions of both aragonite + aragonite and aragonite + calcite shift toward the Ca-rich side with pressure increasing from 10 to 15 kbars. At a pressure in the neighborhood of 13 kbars, a complete series of aragonite-type solid solutions forms in the system, which separates the two-phase region of aragonite + aragonite from that of aragonite + calcite.

Ternary Systems

1. *The System $CaCO_3$–$SrCO_3$–$PbCO_3$*

Subsolidus phase relations in the system at 550°C and 10 kbars are shown in Figure 7. Calcite is present in the ternary system as the stable form of $CaCO_3$, and has a significant range of solid solutions with saturation limits of 38 mole percent $PbCO_3$ and 6 mole percent $SrCO_3$ along the two related binaries. It is interesting to note such difference in the extents of solid solutions when the size difference between calcium and lead is larger than that between calcium and strontium. This must be attributed to the polarizing ability of lead, which is more pronounced in comparison with that of alkaline earths. The

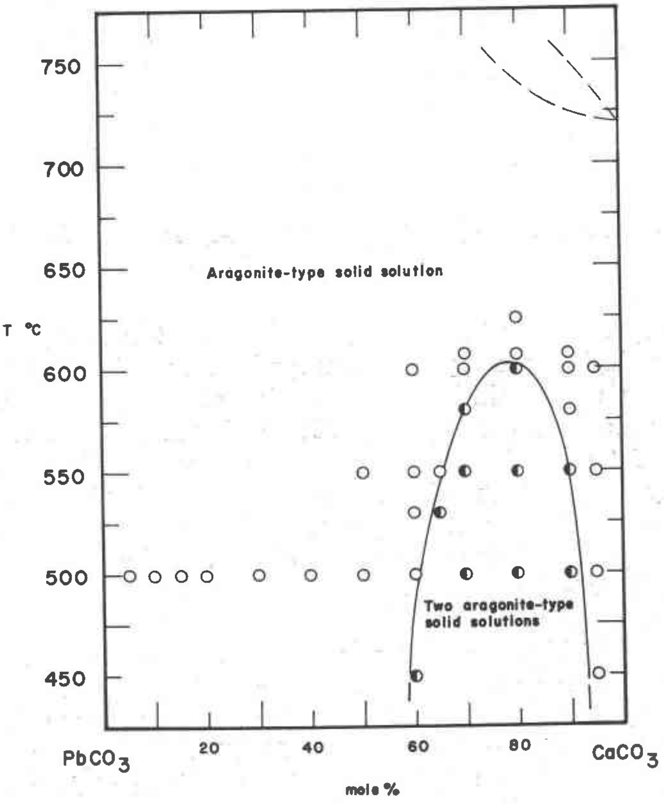

Fig. 4. Subsolidus phase relations in the system $CaCO_3$–$PbCO_3$ at 15 kbars.

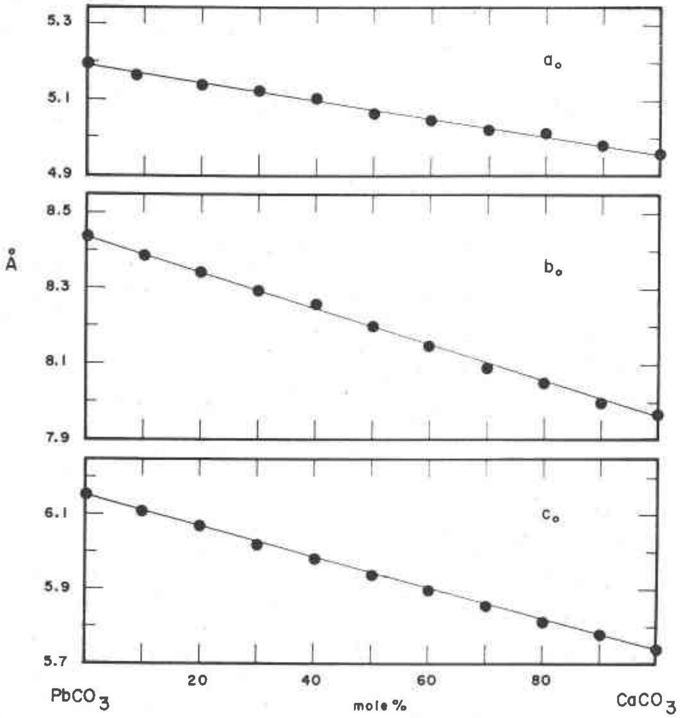

FIG. 5. Variation of lattice parameters of aragonite-type solid solutions in the system $CaCO_3$–$PbCO_3$.

calcite-type solid solution is separated in the ternary system from another single-phase region, the aragonite-type solid solution, by a two-phase region, which is the extension of the immiscibility gaps existing along binaries $CaCO_3$–$SrCO_3$ and $CaCO_3$–$PbCO_3$.

Several tie lines in the two-phase region are also shown in Figure 7. They were constructed from measurements of spacings of both calcite-type reflection (104) and aragonite-type reflection (111) of co-existing phases in the two-phase region and the single phases in the related one-phase regions.

Subsolidus phase relations in the system $CaCO_3$–$SrCO_3$–$PbCO_3$ at 550°C and 15 kbars are shown in Figure 8. No calcite-type phase is stable under these *p-t* conditions. The immiscibility gap existing along the binary system $CaCO_3$–$PbCO_3$ extends into the ternary system, but is eliminated with increasing amount of $SrCO_3$. All samples with more than 10 mole percent $SrCO_3$ produced single phase of the aragonite-type structure.

The change of phase configuration with pressure can be realized without difficulties. As pressure increases from 10 to 15 kbars, the single-phase region of the calcite-type structure as well as the two-phase region decrease in range and more toward Ca-rich corner. Above 12 kbars, where aragonite becomes the stable form of $CaCO_3$ at 550°C, the calcite-type phases are completely out of the ternary field. The two-phase region consists, instead of calcite + aragonite, of only aragonite-type phases, differing in composition.

Variation of spacings of reflections (111) and (221) was calculated as a function of composition. Linear relationships were observed in both cases. Several lines of equal $d_{(221)}$-spacing are shown in Figure 8.

2. The System $CaCO_3$–$BaCO_3$–$PbCO_3$

Subsolidus phase relations in the system at 550°C and 15 kbars are shown in Figure 9. There are two single-phase regions, one of them

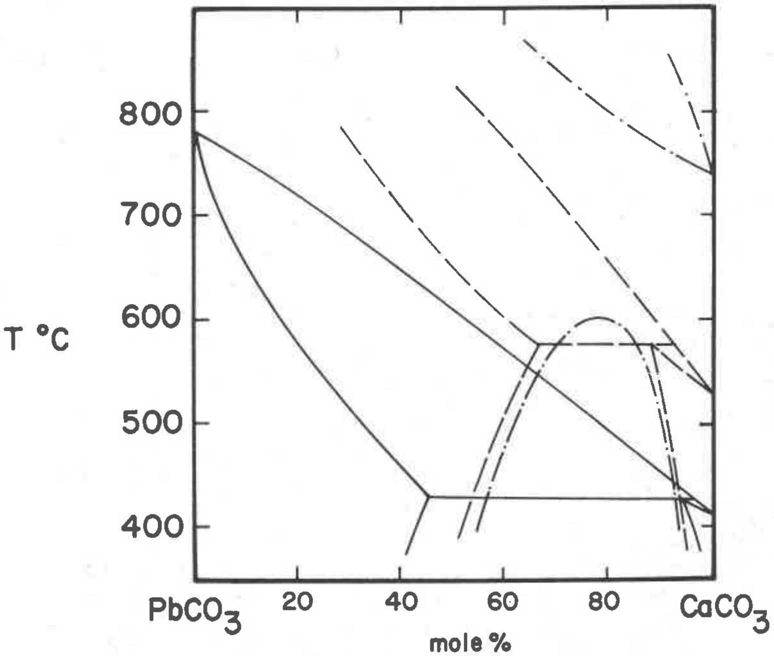

FIG. 6. Schematic representation of phase relations in the system $CaCO_3$–$PbCO_3$ between 10 and 15 kbars. Solid lines, bar-and-dot lines, and dashed lines represent, respectively, phase relations at 10 kbars, 15 kbars, and a pressure between them.

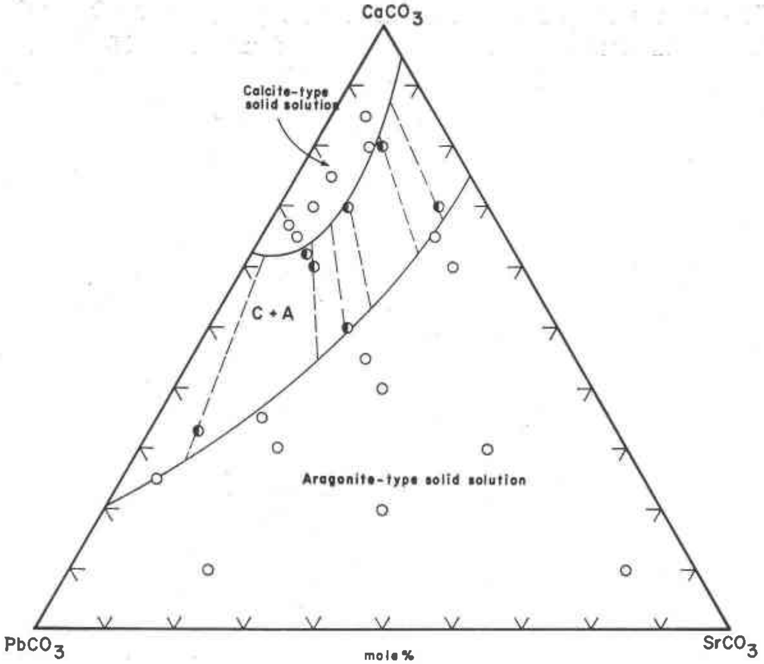

FIG. 7. Subsolidus phase relations in the system $CaCO_3$–$SrCO_3$–$PbCO_3$ at 550°C and 10 kbars. Some regions in this diagram are labeled with symbols representing stable phases A: aragonite-type solid solution and C: calcite-type solid solution.

is an aragonite-type solid solution extending into the ternary system from the binaries, and the other is a disordered, calcite-type solid solution, stable only in the central portion of the system. The rhombohedral-monoclinic phase transition was also observed in the system. Again, there is no two-phase assemblage consisting of monoclinic barytocalcite and rhombohedral, disordered calcite involved in this phase transition. Barytocalcite can take some $PbCO_3$ into its monoclinic solid solution, for 8 mole percent $PbCO_3$ was found to be soluble in barytocalcite at 550°C and 15 kbars, as compared with 16 mole percent $SrCO_3$ under the similar p-T conditions.

Two two-phase regions and a three-phase region are the other major phase assemblages in the system. Both the two phase regions consist of aragonite- and disordered, calcite-type solid solutions, and the three-phase region is defined by an aragonite-type $CaCO_3$ with a small amount of $PbCO_3$, an aragonite-type solid solution with a composition close to 68 mole percent $CaCO_3$, 2 mole percent $BaCO_3$ and 30 mole percent $PbCO_3$, and a disordered, calcite-type solid solution with a composition of 63 mole percent $CaCO_3$, 18 mole percent $BaCO_3$ and 19 mole percent $PbCO_3$.

In comparison, subsolidus phase relations in this system at 550°C and 15 kbars are quite similar to those found in the system $CaCO_3$–$SrCO_3$–$BaCO_3$ at 550°C and 10 kbars (Chang, 1971), except that aragonite is the stable form of $CaCO_3$ at 15 kbars and 550°C in the system with $PbCO_3$, and is present in all phase assemblages, where calcite is present in the system with $SrCO_3$. It is also noted that $PbCO_3$ is more effective than $SrCO_3$ in producing disordered, calcite-type phases in the systems with Ca- and Ba-carbonates.

SUMMARY AND CONCLUSION

Three binary and two ternary systems have been studied. Among them, complete series of solid solutions were found in the systems $SrCO_3$–$PbCO_3$ and $BaCO_3$–$PbCO_3$, while extensive ranges of solid solutions exist in the system $CaCO_3$–$PbCO_3$ and $CaCO_3$–$SrCO_3$–$PbCO_3$.

The effect of solid solution on the calcite-aragonite transition is clearly shown in the system $CaCO_3$–$PbCO_3$. The large cation of lead

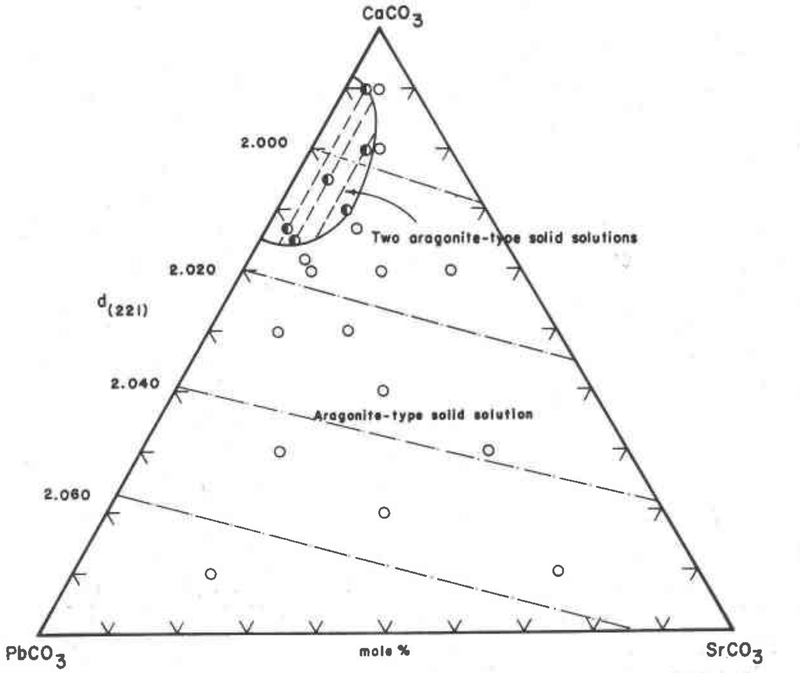

FIG. 8. Subsolidus phase relations in the system $CaCO_3$–$SrCO_3$–$PbCO_3$ at 550°C and 15 kbars.

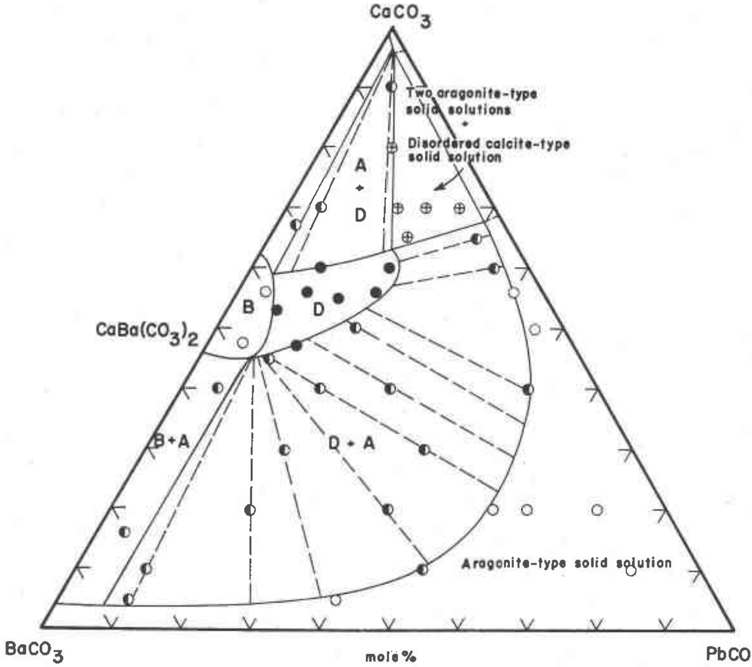

FIG. 9. Subsolidus phase relations in the system $CaCO_3$–$BaCO_3$–$PbCO_3$ at 550°C and 15 kbars. Some regions in this diagram are labeled with symbols representing stable phases, A: aragonite-type solid solution, C: calcite-type solid solution, B: barytocalcite-type solid solution, and D: disordered, calcite-type solid solution.

tends to stabilize the aragonite-type phase, in the same fashion as the strontium cation does, to a higher temperature at a given pressure.

Phase relations in the systems $CaCO_3$–$BaCO_3$–$PbCO_3$ and $CaCO_3$–$SrCO_3$–$BaCO_3$ have some similar features, and a comparison between them shows several interesting points which illustrate the difference in crystal chemistry between lead and alkaline earths. At 15 kbars and low temperatures, the size difference, larger between lead and calcium and smaller between strontium and calcium, must play an important role in shaping phase relations in the respective system. Thus, a two-phase region consisting of two aragonite-type solid solutions exists below 600°C in the system $CaCO_3$–$PbCO_3$, while a complete series of solid solutions forms in the system $CaCO_3$–$SrCO_3$. But at 10 kbars and moderate temperatures, the polarizing ability of lead becomes more pronounced so it is this crystal-chemical property that is the predominant factor in defining the pattern of phase relations. This is shown by the formation of an extensive range of calcite-type solid solution in the system $CaCO_3$–$PbCO_3$ in the temperature range where solubility of $SrCO_3$ in calcite is quite limited. And this ability of lead to replace calcium in the calcite-type structure with greater ease is further shown by the phase relations in the ternary system with $CaCO_3$ and $BaCO_3$. $PbCO_3$ was found to be more effective in producing disordered, calcite-type solid solution than $SrCO_3$.

The occurrence of natural carbonate of an intermediate composition in the systems $SrCO_3$–$PbCO_3$ and $BaCO_3$–$PbCO_3$, has not been reported. Experimental results established here indicate that the complete series of solid solutions should at least extend to the temperature range around 400°C. Although no equilibrium data are available to rule out any miscibility gaps existing at lower temperatures, it seems unlikely because the ionic sizes of divalent cations involved in the systems $BaCO_3$–$PbCO_3$ and $SrCO_3$–$PbCO_3$ are quite similar. Geological occurrences show the close association of witherite and strontianite with galena, so explanation of lack of intermediate carbonate in the systems $SrCO_3$–$PbCO_3$ and $BaCO_3$–$PbCO_3$ on the basis of cation deficiency in nature cannot be applied. It is most likely that the difference in chemical nature between alkaline earths and lead plays an important role in their selection of anion or anion group for compound formation under geological conditions. Generally speaking, lead prefers S or SO_4 to give rise to sulfide or sulfate, while barium and strontium form carbonates. Thus, cerussite is, in most cases, a secondary mineral resulting from oxidation of sulfide or sulfate of lead, whereas witherite and strontianite are generally primary minerals in hydrothermal veins.

Experimental data suggest that there may be a phase transition, similar to the orthorhombic-rhombohedral phase change in $BaCO_3$ and $SrCO_3$, in $PbCO_3$. The transition temperature, as extrapolated, would be around 800°C at 10 kbars.

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