Subsolidus Phase Relations in Aragonite-type Carbonates. III. The Systems MgCO₃-CaCO₃-BaCO₃, MgCO₃-CaCO₃-SrCO₃, and MgCO₃-SrCO₃-BaCO₃

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Abstract

Subsolidus phase relations in the three ternary systems were studied at 650°C and at both 5 and 15 kbar using high-pressure, opposed-anvil apparatus. Phases found in the systems, in addition to the end members, are dolomite ($MgCa(CO_3)_2$), norsethite ($MgBa(CO_3)_2$), $MgSr(CO_3)_2$, and two forms of $CaBa(CO_3)_2$, a monoclinic barytocalcite and a rhombohedral form with disordered calcite structure.

In the system $MgCO_3$–$CaCO_3$–$BaCO_3$, both norsethite and disordered calcite have detectable ranges of solid solution at 650°C and 5 kbar, and six two-phase areas and four three-phase triangles are observed. In the system $MgCO_3$–$CaCO_3$–$SrCO_3$, a complete series of solid solution along the join $MgCa(CO_3)_2$–$MgSr(CO_3)_2$ and a significant region of calcite-type solid solution exist at 650°C and 5 kbar, whereas at 650°C and 15 kbar, aragonite is the stable form of $CaCO_3$ and forms a complete series of solid solution with $SrCO_3$. Two complete solid solution series, $SrCO_3$–$BaCO_3$ and $MgSr(CO_3)_2$–$MgBa(CO_3)_2$, were found in the system $MgCO_3$–$SrCO_3$–$BaCO_3$, and the system is represented by two large immiscibility gaps between the two solid solution series and between the dolomite series and $MgCO_3$.

Introduction

As the third part of a study on the subsolidus phase relations in aragonite-type carbonates, the systems MgCO₃–CaCO₃–BaCO₃, MgCO₃–CaCO₃–SrCO₃, and MgCO₃–SrCO₃–BaCO₃ were investigated at 650°C and two pressures, 5 and 15 kbar. Mineral phases present in the system, in addition to the well known end members, include dolomite, norsethite, barytocalcite, alstonite, and benstonite.

The temperature of 650°C was chosen because previous studies of carbonates indicated that moderate temperatures are required for mixtures involving MgCO₃ to react in a reasonable length of time (Goldsmith and Graf, 1960; Goldsmith and Newton, 1969). Because two of the systems include CaCO₃, which exhibits both calcite- and aragonite-type structures, it was decided to select pressure-temperature relationships which would offer two situations: (1) conditions under which the calcite form is stable, and (2) conditions under which the aragonite form is stable. The two pressures of 5 and 15 kbar satisfied these requirements.

Experimental Procedures

Starting materials used were Baker analyzed reagent grade CaCO₃, SrCO₃, BaCO₃, and basic magnesium carbonate. The MgCO₃ was prepared by hydrothermally treating the basic magnesium carbonate with H₂O and CO₂ in a Morey-type vessel at 200°C.

All mixtures were calculated on a molar percentage basis. The accuracy of the weighings is estimated to be ±0.05 mg, and the total weight of each mixture prepared varied from about 0.75 to 1.5 g. Mixing was made under acetone in a Spex Mixer/Mill for 15 minutes, followed by hand grinding for 45 minutes.

Experimental work was performed in the high-pressure, opposed-anvil apparatus. The apparatus and the procedures to operate it were described in detail by Griggs and Kennedy (1956) and by Mac-Donald (1956), while Goldsmith and Newton (1969) discussed the suitability of this apparatus for equilibrium studies in carbonates.

Periods of 28 hours to 132 hours, with a few

runs up to 221 hours, were used at 650°C depending on the amount of $MgCO_3$ in the the sample; the greater the amount, the longer the required run time. This apparently stems from use of crystalline $MgCO_3$ instead of a fine-grained precipitated material. A small amount of Li_2CO_3 (approximately 2 percent of the sample) was added to runs to promote the reaction. Uncertainties are estimated to be ±5°C for temperatures and within ±0.5 kbar for pressures.

X-ray powder diffraction was used in phase identification. Since all phases involved are well crystallized, any phase of more than 2 mole percent in the quenched assemblage can be easily detected. Measurement of lattice parameters, construction of tie lines, and checking of attainment of equilibrium were made in the manner described previously (Chang, 1971). Results from runs made to show

the reversibility of reaction in the systems are listed in Table 1.

The System $MgCO_3$–$CaCO_3$–$BaCO_3$

Subsolidus phase relations in the systems $MgCO_3$–$CaCO_3$ (Goldsmith and Heard, 1961; Goldsmith and Newton, 1969) and $CaCO_3$–$BaCO_3$ (Chang, 1965, 1971) have been well established, whereas the only reported work on the system $MgCO_3$–$BaCO_3$ has centered around the synthesis of norsethite, the 1:1 compound $MgBa(CO_3)_2$ (Chang, 1964; Lippman, 1967). No studies on the ternary phase relations in the system are known.

In the present study, subsolidus phase relations in the system $MgCO_3$–$BaCO_3$ were found to be very simple. Three phases, witherite, norsethite, and magnesite, are stable, and there is no solid solubility among them. According to Mrose *et al* (1961),

TABLE 1. Pertinent Data on Runs Related to the Reversibility of Reactions in the Systems $MgCO_3$–$CaCO_3$–$BaCo_3$ and $MgCO_8$–$CaCO_3$–$SrCO_3$

Composition mole%			First Period of Equilibrium			Second Period of Equilibrium			Products, Phases*
			Pres. kbar	Temp. °C	Time, Hrs.	Pres. kbar	Temp. °C	Time, Hrs.	
$MgCO_3$	$CaCO_3$	$BaCO_3$							
40.0	50.0	10.0	15	650	84	–	–	–	Do + N ss + C ss
40.0	50.0	10.0	15	650	84	5	650	160	Do + N ss + C ss
40.0	50.0	10.0	5	650	84	–	–	–	Do + N ss + C ss
40.0	50.0	10.0	5	650	84	15	650	160	Do + N ss + C ss
20.0	50.0	30.0	15	650	64	–	–	–	A + N ss + B ss
20.0	50.0	30.0	15	650	64	5	650	96	C ss + N ss + Cd ss
20.0	50.0	30.0	5	650	64	–	–	–	C ss + N ss + Cd ss
20.0	50.0	30.0	5	650	64	15	650	96	A + N ss + B ss
10.0	80.0	10.0	15	650	48	–	–	–	A + N ss
10.0	80.0	10.0	15	650	48	5	650	64	C ss + N ss + Cd ss
10.0	80.0	10.0	5	650	48	–	–	–	C ss + N ss + Cd ss
10.0	80.0	10.0	5	650	48	15	650	64	A + N ss
10.0	40.0	50.0	15	650	48	–	–	–	N ss + B ss
10.0	40.0	50.0	15	650	48	5	650	64	N ss + Cd ss
10.0	40.0	50.0	5	650	48	–	–	–	N ss + Cd ss
10.0	40.0	50.0	5	650	48	15	650	64	N ss + B ss
$MgCO_3$	$CaCO_3$	$SrCO_3$							
5.0	92.0	3.0	15	650	32	–	–	–	A ss + C ss
5.0	92.0	3.0	15	650	32	5	650	68	C ss
5.0	92.0	3.0	5	650	32	–	–	–	C ss
5.0	92.0	3.0	5	650	32	15	650	68	A ss + C ss
5.0	85.0	10.0	15	650	32	–	–	–	A ss + C ss + Do ss
5.0	85.0	10.0	15	650	32	5	650	68	C ss
5.0	85.0	10.0	5	650	32	–	–	–	C ss
5.0	85.0	10.0	5	650	32	15	650	68	A ss + C ss + Do ss
5.0	80.0	15.0	15	650	32	–	–	–	A ss + C ss + Do ss
5.0	80.0	15.0	15	650	32	5	650	68	C ss
5.0	80.0	15.0	5	650	32	–	–	–	C ss
5.0	80.0	15.0	5	650	32	15	650	68	A ss + C ss + Do ss
20.0	50.0	30.0	15	650	96	–	–	–	A ss + Do ss
20.0	50.0	30.0	15	650	96	5	650	124	A ss + C ss + Do ss
20.0	50.0	30.0	5	650	96	–	–	–	A ss + C ss + Do ss
20.0	50.0	30.0	5	650	96	15	650	124	A ss + Do ss
20.0	20.0	60.0	15	650	96	–	–	–	A ss + Do ss
20.0	20.0	60.0	15	650	96	5	650	124	A ss + Do ss
20.0	20.0	60.0	5	650	96	–	–	–	A ss + Do ss
20.0	20.0	60.0	5	650	96	15	650	124	A ss + Do ss

* Abbreviations: A = aragonite; B = barytocalcite; C = calcite; Cd = disordered calcite; Do = dolomite; N = norsethite; ss = solid solution.
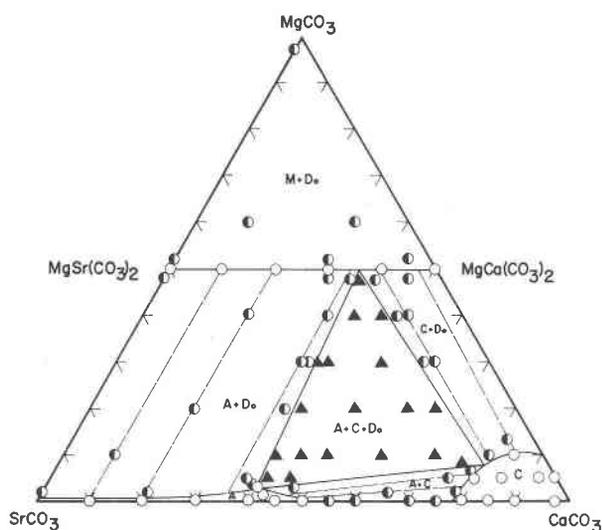
norsethite closely remembles calcite and dolomite in crystal structure with a possible space group of *R*32. X-ray powder diffraction data of norsethite produced in this study correspond well with those reported in literature (Mrose *et al,* 1961; Chang, 1964; Sundius and Blix, 1965).

Phase relations in the ternary system at 650°C and 5 kbar are shown in Figure 1. Norsethite has an extensive range of solid solution and forms equilibrium assemblage with every phase presented in the ternary system. A maximum amount of 22 mole percent $CaCO_3$ enters the norsethite solid solution along the join $CaCO_3$–$MgBa(CO_3)_2$, a case of substitution of Ba + Mg by Ca. On the other hand, no solid solution was detected between $MgCa(CO_3)_2$ and $MgBa(CO_3)_2$.

Barytocalcite, the 1:1 compound $CaBa(CO_3)_2$, is not a stable phase in the system $CaCO_3$–$BaCO_3$ at 650°C and 5 kbar. Instead, the disordered calcite-type $(Ca,Ba)CO_3$ solid solution forms between compositions of $Ca_{42.5}Ba_{57.5}$ and $Ca_{62.5}Ba_{37.5}$ along the binary join $CaCO_3$–$BaCO_3$ and extends into the ternary system, taking a maximum of 9 mole percent $MgCO_3$ in solid solution. This disordered phase can be differentiated from the calcite-type phase by the absence of a (113) peak and by the differences in position of other peaks in the X-ray diffraction patterns. The absence of this (113) peak, as described previously (Chang, 1965), is due to the random arrangement of CO_3 groups in the structure, and the difference in position of other peaks is due to different chemical composition.

Subsolidus phase relations at 650°C and 15 kbar are shown in Figure 2, based on the few runs illustrated in the diagram. They are similar to those shown in Figure 1 except that both barytocalcite and aragonite become stable phases representing $CaBa(CO_3)_2$ and $CaCO_3$, respectively, in the system. The presence of the calcite-type phase in the binary system $MgCO_3$–$CaCO_3$ (Goldsmith and Heard, 1961; Goldsmith and Newton, 1969) was observed in the present study. It requires the existence of a three-phase region of aragonite, a calcite-type solid solution, and a dolomite-type solid solution in the system.

The System $MgCO_3$–$CaCO_3$–$SrCO_3$

Phase relations in the system have been studied in part by Froese and Winkler (1966) and Froese (1967). The former determined the composition of aragonite-strontianite solid solutions coexisting with

FIG. 1. Subsolidus phase relations in the system $MgCO_3$–$CaCO_3$–$BaCO_3$ at 650°C and 5 kbar. A = aragonite; C = calcite; Cd = disordered calcite; Do = dolomite; M = magnesite; N = norsethite; W = witherite.

calcite and dolomite at 660°C and in the pressure range 1–10 kbar, whereas the latter synthesized the 1:1 compound, $MgSr(CO_3)_2$ and presented a phase diagram of the ternary system at 660°C and 3.9 kbar. The diagram shows there are no solid solutions between $MgCO_3$, $SrCO_3$, and $MgSr(CO_3)_2$, and an

FIG. 2. Subsolidus phase relations in the system $MgCO_3$–$CaCO_3$–$BaCO_3$ at 650°C and 15 kbar. A = aragonite; B = barytocalcite; C = calcite solid solution; Do = dolomite; M = magnesite; N = norsethite; W = witherite.

FIG. 3. Subsolidus phase relations in the system $MgCO_3$–$CaCO_3$–$SrCO_3$ at 650°C and 5 kbar. The tie lines in this and following diagrams are represented by dashed lines. A = aragonite-type solid solution; C = calcite solid solution; Do = dolomite-type solid solution; M = magnesite.

immiscibility gap exists between $MgSr(CO_3)_2$ and $MgCa(CO_3)_2$. Froese refers to the possible difficulty of quenching Ca-rich $Mg(Ca,Sr)(CO_3)_2$ solid solutions. However, an apparent solubility gap could also be produced by incomplete reaction.
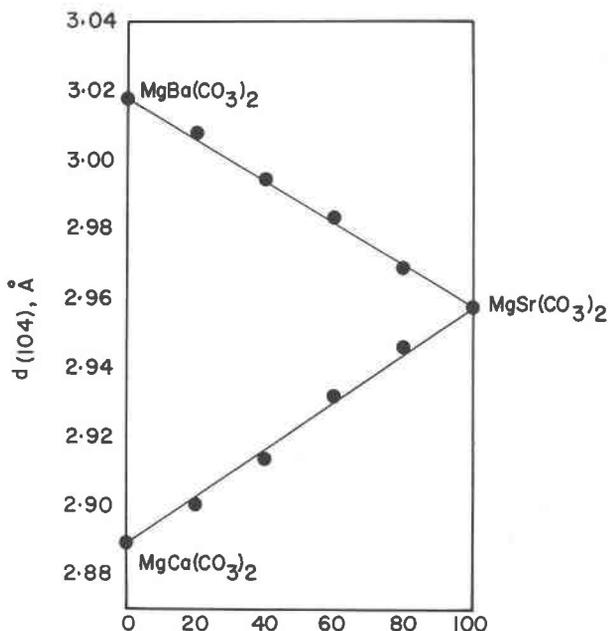
FIG. 4. Variation of $d_{(104)}$ along the joins, $MgCa(CO_3)_2$–$MgSr(CO_3)_2$ and $MgSr(CO_3)_2$–$MgBa(CO_3)_2$.

Subsolidus phase relations in the system $MgCO_3$–$CaCO_3$–$SrCO_3$ determined in the present study at 650°C and 5 kbar are shown in Figure 3. A complete solid solution series forms along the dolomite join with little deviation from the 1:1 cation ratio, and interplanar spacing d_{104} shows a linear relationship with composition (Fig. 4). As a result of this complete series only one three-phase region exists in the system, and it is defined by an aragonite-type solid solution with a composition of $Mg_3Ca_{40}Sr_{57}$, a dolomite-type solid solution near $Mg_{50}Ca_{36}Sr_{14}$, and a calcite-type solid solution of $Mg_8Ca_{80}Sr_{12}$.

The calcite-type solid solution has a range from a maximum of 22 mole percent $SrCO_3$ in the binary system $CaCO_3$–$SrCO_3$ to a maximum of 10 mole percent $MgCO_3$ in the binary system $MgCO_3$–$CaCO_3$. The aragonite-type solid solution in the binary system $CaCO_3$–$SrCO_3$ was found to extend into the ternary system with a maximum of 3 mole percent $MgCO_3$ near the composition of $Ca_{40}Sr_{60}$.

Subsolidus phase relations in the system at 650°C and 15 kbar are shown in Figure 5. Aragonite is the stable form of $CaCO_3$ under these conditions, and there is a complete series of solid solution with $SrCO_3$. No effect of changing pressure was found on the solid solution along the join $MgCa(CO_3)_2$–$MgSr(CO_3)_2$, but the three-phase region is greatly reduced in size, as is the region of the calcite-type solid solution which is now confined near $Mg_{10}Ca_{90}$. At 650°C and 15 kbar, the three-phase region is defined by an aragonite-type phase with a composition of $Ca_{83}Sr_{17}$, a calcite-type solid solution with a composition of $Mg_9Ca_{90}Sr_1$, and a dolomite-type solid solution with a composition of $Mg_{50}Ca_{44}Sr_6$.

In the Mg-poor half of the system, a large two-phase region of dolomite-type and aragonite-type solid solution exists. The dolomite-type phases tend to be Sr-poor as compared with their co-existing aragonite-type phases.

The System $MgCO_3$–$SrCO_3$–$BaCO_3$

Subsolidus phase relations in the system at 650°C and 5 kbar are shown in Figure 6. Two complete series of solid solutions exist along the joins $SrCO_3$–$BaCO_3$ and $MgSr(CO_3)_2$–$MgBa(CO_3)_2$, and the system is represented by two large immiscibility gaps between the two solid solution series and between the dolomite series and $MgCO_3$. In the Mg-poor half of the system, tie lines in the two-phase region show that the dolomite-type phases, $Mg(Sr,Ba)(CO_3)_2$, tend to be Sr-poor as compared with their

coexisting aragonite-type phase, $(Sr,Ba)CO_3$. This combined with the observation that the dolomite-type phases of composition $Mg(Ca,Sr)(CO_3)_2$ tend to be Sr-poor as compared with their coexisting aragonite-type phases of composition $(Ca,Sr)CO_3$ clearly illustrates that the strontium atom has an affinity for the aragonite-structure over the dolomite structure.

The phase relations at 650°C and 5 kbar are expected to be similar at higher pressures, because no phase transition is anticipated in any of the phases involved.

The Dolomite Plane

Subsolidus phase relations in this plane at 650°C and 5 kbar (Fig. 7) reflect the difference in ionic size between calcium, strontium, and barium. The immiscibility gap along the join $MgBa(CO_3)_2$–$MgCa(CO_3)_2$ extends into the ternary plane and represents a large two-phase region of two dolomite-type solid solutions; one Ba-rich, the other Ca-rich. With increasing Sr-content, the immiscibility gap decreases in range and a complete series of solid solution forms when the Sr-content is greater than 70 mole percent. The tie lines in this two-phase region are essentially parallel to the base line of the join $MgCa(CO_3)_2$–$MgBa(CO_3)_2$. For both joins, $MgSr(CO_3)_2$–$MgBa(CO_3)_2$ and $MgSr(CO_3)_2$–$MgCa(CO_3)_2$, d_{104} varies linearly with composition (Fig. 4).

Similar phase relations are observed in a few runs made at 650°C and 15 kbar. A run of composition 15:15:70 mole percent of $MgCa(CO_3)_2$:$MgBa$ $(CO_3)_2$:$MgSr(CO_3)_2$ produces a single phase instead of the two-dolomite assemblage observed at 5 kbar. This suggests that the effect of Sr-content on the formation of solid solution in the plane is greater at higher pressures.

Geological Consideration

This investigation has revealed the possibility of extensive solid solubility of strontium in both norsethite and dolomite. At pressures of 5 and 15 kbar and a temperature of 650°C, the solid solution is complete from norsethite through $MgSr(CO_3)_2$ to dolomite. Experimental results also indicate that strontium is more likely to be found in an aragonite structure than in a dolomite structure. This may explain, at least in part, why $MgSr(CO_3)_2$ has not yet been found in nature.

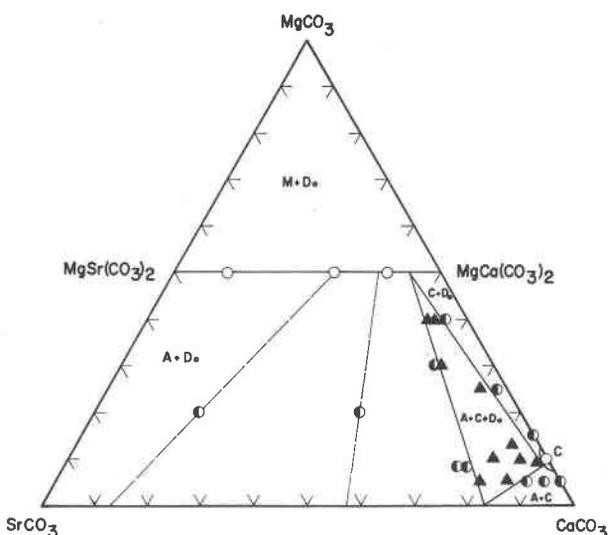A number of occurrences of norsethite have been reported since the first report by Mrose *et al* (1961).

Fig. 5. Subsolidus phase relations in the system $MgCO_3$–$CaCO_3$–$SrCO_3$ at 650°C and 15 kbar. A = aragonite-type solid solution; C = calcite solid solution; Do = dolomite-type solid solution; M = magnesite.

Norsethite at the Rosh Pinah deposit (Steyn and Watson, 1967) occurs in dolomite gangue as irregularly shaped veins and as masses several feet across. It is also associated throughout with calcite in more or less equal quantities. A similar assemblage was found at Langban, Sweden (Sundius and Blix, 1965), and chemical analyses of the three co-exist-
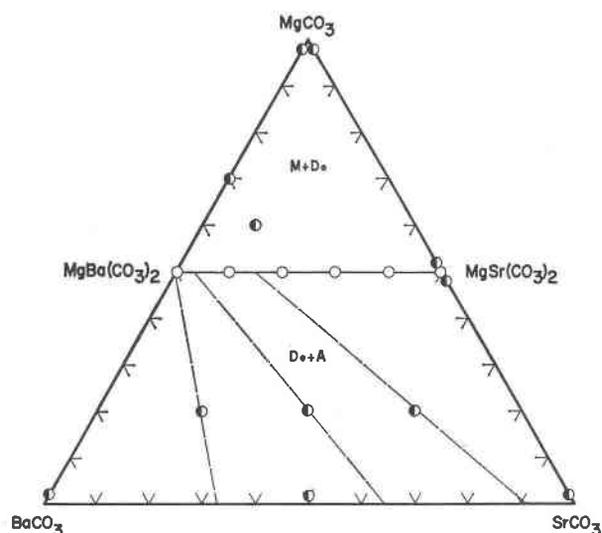

Fig. 6. Subsolidus phase relations in the system $MgCO_3$–$SrCO_3$–$BaCO_3$ at 650°C and 5 kbar. A = aragonite-type solid solution; Do = dolomite-type solid solution; M = magnesite.
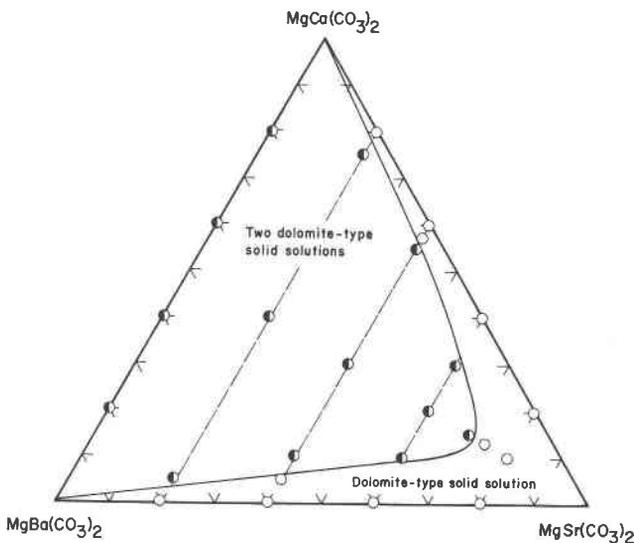
FIG. 7. Subsolidus phase relations in the dolomite plane $MgCa(CO_3)_2$–$MgSr(CO_3)_2$–$MgBa(CO_3)_2$ at 650°C and 5 kbar.

cent $MgCO_3$ plane of the four-component system $MgCO_3$–$CaCO_3$–$SrCO_3$–$BaCO_3$. At 650°C and 5 kbar (Fig. 1) compositions close to that of benstonite produce phases of the disordered calcite-type structure. A comparison of X-ray powder diffraction data of benstonite with those of phases produced from compositions which are close to that of benstonite is shown in Table 2. The match of spacings is close enough to suggest that benstonite may be a low-temperature ordered equivalent of the disordered phases at 650°C and 5 kbar. Benstonite has been reported in deposits with barytocalcite and norsethite (Steyn and Watson, 1967) and with dolomite and norsethite (Sundius, 1963).

Acknowledgments

ing minerals are given. Except for the high percentage of $MnCO_3$ (in mole percent, 4.7 in norsethite, 7.03 in dolomite, and 6.5 in calcite), these minerals fit the three-phase assemblage predicted by the phase relations shown in Figure 1. Temperature and pressure conditions for this deposit were estimated by Sundius (1965) to be 500°–600°C and about 10 kbar.

Norsethite in association with strontianite and other minerals was reported by Kapustin (1965) in carbonatite veins in pyroxenite. Analysis shows that norsethite contains 1.4 mole percent $SrCO_3$, indicating solid solution in nature.

Benstonite, according to Lippman (1962), has a crystal structure derived from that of calcite by the ordering of cations within the cation plane, and a composition close to $Mg_6Ca_{47}Sr_6Ba_{41}$. This composition should occur as a phase on the 6 mole per-

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TABLE 2. X-ray Powder Diffraction Data for Benstonite and Disordered Calcite with Compositions to That of Benstonite

Benstonite[1]		Benstonite[2]		Disordered calcite[3]			
$Mg_6Sr_6Ca_{47}Ba_{41}$		$Mg_{18}Mn_3Ca_{33}Pb_2Ba_{44}$		$Mg_6Ca_{47}Ba_{47}$		$Ca_{47.5}Sr_5Ba_{47.5}$	
d, A	I/I₀	d, A	I/I₀	d, A	I/I₀	d, A	I/I₀
3.92	38	3.89	60	3.97	40	3.98	50
3.08	95	3.07	100	3.13	100	3.15	100
2.536	28	2.52	70	2.55	60	2.56	50
2.127	23	2.11	60	2.145	40	2.149	40

1. Benstonite from Arkansas, Lippmann (1967)
2. Benstonite from Langban, Sundius (1963)
3. Disordered calcite obtained at 650°C and 5 kbars

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