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Precipitation of Norsethite at Room Temperature

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Abstract

Norsethite, $BaMg(CO_3)_2$, can be formed from aqueous solution by mixing a solution containing 0.06 molar barium chloride and 0.1 molar magnesium chloride with an equal amount of 0.5 molar sodium carbonate solution and allowing the precipitate to age in contact with the solution for three days or longer. Other barium and magnesium concentrations give rise to precipitates containing witherite alone, witherite plus norsethite, norsethite alone, norsethite plus hydrated magnesium carbonates, or hydrated magnesium carbonates alone. The wide range of original barium to magnesium ratios of solutions from which norsethite can be precipitated suggests that it should be a more common mineral than is presently recognized.

Introduction

The mineral norsethite, $BaMg(CO_3)_2$, although apparently rare in nature, has received a considerable amount of attention since its discovery by Mrose *et al* (1961) in the Green River Formation in Wyoming. It was first synthesized by Chang (1964) at 500°C and later by Lippmann (1967a, 1968b) at 20°C. Norsethite is structurally similar to dolomite (Lippmann, 1967b, 1968a) but, in contrast to dolomite, is easily formed at low temperatures. Hence, study of the stability relations of norsethite may aid in the understanding of the origin of dolomite and other ordered rhombohedral carbonate minerals. This paper reports the synthesis of norsethite at 20°C from aqueous solutions of widely varying barium and magnesium ratios.

Experimental Procedure

Reagent grade $BaCl_2 \cdot 2H_2O$, $MgCl_2 \cdot 6H_2O$, and Na_2CO_3 were used as starting materials. Stock solutions of 0.1 molar $BaCl_2$, 0.1 molar $MgCl_2$, and 0.1 molar $BaCl_2$ plus 0.1 molar $MgCl_2$ were prepared and used to make the various experimental solutions. The desired concentrations of barium and magnesium were obtained by mixing various amounts of these three stock solutions plus enough distilled water to bring the volume to 25 milliliters. Precipitation of the carbonate minerals was achieved by rapidly adding 25 milliliters of 0.5 molar Na_2CO_3 solution to the cation-bearing liquid while the latter was being stirred with a magnetic stirrer. After approximately two minutes of stirring, the beakers containing the precipitates and solutions were removed from the stirrer, covered, and allowed to stand at room temperature (20°C) for a period of time ranging from three days to nine months. At the end of the aging period, the liquids were separated from the precipitates and a portion of the solids smeared onto a glass slide for identification by X-ray diffraction.

Results

The results of experiments that were terminated at the end of three days and those that lasted nine months are essentially identical. Both sets gave five mineral assemblages, (1) witherite ($BaCO_3$), (2) witherite plus norsethite, (3) norsethite, (4) norsethite plus hydrated magnesium carbonates, and (5) hydrated magnesium carbonates (Fig. 1). One of the most interesting discoveries of this investigation is the very wide range of Ba/Mg ratios in the starting solutions from which norsethite can be precipitated. Although the field in which only norsethite forms is fairly limited, the assemblages norsethite plus witherite or norsethite plus hydrated magnesium carbonates were precipitated from solutions with original Ba/Mg ratios ranging from 10 down to 0.1. Norsethite by itself can easily be formed by mixing a solution containing 0.06 molar barium chloride and 0.1 molar magnesium chloride with an equal amount of 0.5 molar sodium carbonate and allowing the mixture to age a few days. It should be emphasized that the mineral assemblages shown on Figure 1 are those that precipitated from starting solutions of various concentrations. The diagram does not show the stability fields of the minerals.

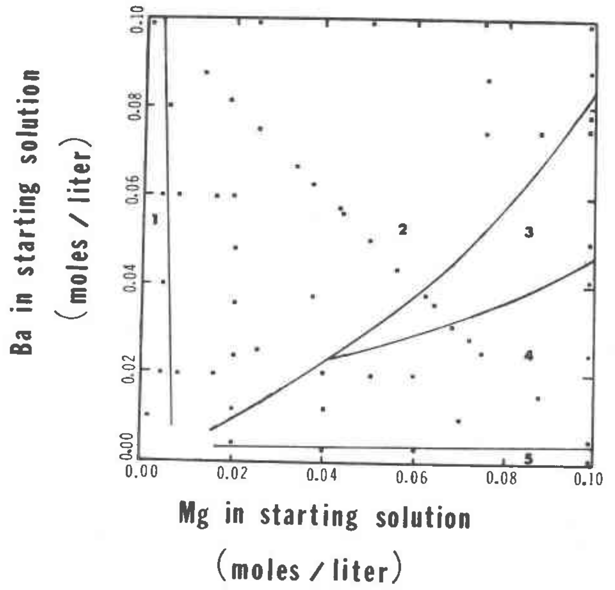

FIG. 1. Mineral assemblages precipitated as a function of various original barium and magnesium concentrations. Fields are (1) witherite, (2) witherite plus norsethite, (3) norsethite, (4) norsethite plus hydrated magnesium carbonates, and (5) hydrated magnesium carbonates.

The hydrated magnesium carbonates found during this investigation consisted of mixtures of nesquehonite ($MgCO_3 \cdot Mg(OH)_2 \cdot 4\ H_2O$), lansfordite ($MgCO_3 \cdot 5\ H_2O$), and hydromagnesite ($4MgCO_3 \cdot Mg(OH)_2 \cdot 4\ H_2O$). The relative amounts of the three minerals appeared to change randomly with time in precipitates in which they occurred, and it is uncertain which of them represents the stable phase under the conditions of the experiments. The solution compositions and temperature are not far from the nesquehonite-lansfordite-hydromagnesite triple junction on Langmuir's (1965) P_{CO_2}-T diagram, so it is not very surprising that all three phases occurred in the precipitates. Langmuir's work suggests that lansfordite easily dehydrates to nesquehonite at temperatures higher than about 10°C and both lansfordite and nesquehonite are metastable relative to hydromagnesite at relative humidities less than fifty percent. This implies dehydration after precipitation may account for part of the observed variation in amounts of the three phases.

Discussion

Norsethite can be formed from either witherite or hydrated magnesium carbonate by adding the other cation in the presence of excess carbonate and allowing the precipitate to age a few days. It will also form from a mixture of the two single-cation solids in the presence of excess carbonate. Since the results of the solutions aged three days and those aged nine months are essentially identical, time does not seem to be a major factor in determining the results. These observations taken together indicate that the presence of two minerals coexisting in a field in Figure 1 is a result of there being insufficient amounts of either barium or magnesium to convert all the solid to norsethite.

Lippmann (1967a, 1968b) synthesized norsethite by the reaction of solid barium carbonate (witherite) with dilute solutions of magnesium chloride and sodium bicarbonate according to the reaction:

$$BaCO_3 + Mg^{2+} + CO_3^{2-} = BaMg(CO_3)_2.$$

He obtained crystals of norsethite as long as 0.1 mm after times as short as two days, and his work gives insight into the problem of formation of an ordered two-cation mineral from a pre-existing single cation carbonate mineral such as the formation of dolomite from calcite. However, his work does not resolve the question of whether an ordered double-cation carbonate mineral can be precipitated directly from solutions of proper composition.

To examine whether the experiments described in this paper precipitated norsethite directly or followed some reaction similar to that described by Lippmann, samples of precipitate in the norsethite field were removed at time periods of two minutes, four minutes, twenty minutes, one hour, twenty-four hours, and three days. The precipitates extracted in one hour or less were amorphous, whereas those extracted in one and three day intervals gave well-defined norsethite X-ray patterns. Well crystallized norsethite does not form directly under the conditions of very rapid precipitation used in these experiments.

Lippmann (1973) points out that the equation for precipitation of norsethite can be written

$$Ba^{2+} + Mg^{2+} + 2CO_3^{2-} = BaMg(CO_3)_2 \qquad (1)$$

for which the equilibrium constant would have the form:

$$K = \frac{1}{(aBa^{2+})(aMg^{2+})(aCO_3^{2-})^2}.$$

If carbonate activity remains constant the activities of barium and magnesium should be inversely related to one another. On the other hand if norsethite formed by the process:

$$2BaCO_3 + Mg^{2+} = BaMg(CO_3)_2 + Ba^{2+} \qquad (2)$$

the equilibrium constant would be:

$$K = (a\mathrm{Ba}^{2+})/(a\mathrm{Mg}^{2+})$$

in which case the activities would change in direct proportion to one another.

In experiments in which the cation concentration in the starting solution is 0.1 molar and the anion concentration 0.2 molar, the barium and magnesium are almost entirely precipitated out and hence carbonate activity in the remaining solution can be considered to be nearly constant. Some solutions of these cation and anion concentrations were aged nine months, analyzed, and the ratios of barium to magnesium in the solutions calculated (Table 1).

Analyses were made by atomic absorption spectrophotometry. The detection limit for barium was approximately 0.05 ppm and little reliance should be placed on the two measurements near this value. Even with these limitations, the concentrations of barium and magnesium (and presumably the activities because both elements are present in low concentrations) appear to show an inverse relation to one another and the barium-to-magnesium ratios decrease as the original solutions change from barium-rich to magnesium-rich. These results are interpreted as supporting Lippmann's equation for the precipitation of norsethite (Eq. 1 above), even though norsethite does not appear to precipitate directly from concentrated solutions of the required ions.

Another possible interpretation of the data in Table 1 is that there are two groups of barium to magnesium ratios, one with a value of about 0.3 and another with a value of about 0.003. These convert to molecular ratios of about 0.05 and 0.0005 respectively, which would be the approximate values of equilibrium constants for solutions in equilibrium with witherite and norsethite and solutions coexisting with norsethite plus hydrated magnesium carbonates.

The effect of changing the ratio of cation- to carbonate-concentration was not fully explored in this investigation. Since the amount of sodium carbonate was kept constant in each precipitation experiment (whereas the cation concentration varied), the ratio of cations to carbonate also varied. The variation in the ratio was, however, only from 0.02 to 0.40, *i.e.*, carbonate always greatly exceeded cations. Using a solution with initial barium and magnesium concentrations of 0.06 and 0.10 molar, which should have yielded pure norsethite under ordinary experimental conditions, the addition of a single milliliter of the sodium carbonate solution produced only witherite.

TABLE 1. Barium and Magnesium Remaining in Solution After Precipitation of Carbonate Phases

Original Ba:Mg Ratio*	Solid Phases Identified**	Barium in Solution (ppm)	Magnesium in Solution (ppm)	Final Ba:Mg Ratio (wt.)
10:0	W	1.9 ± 0.2	0.0 ± 0.00	
8:2	W,N	0.43 ± 0.10	1.0 ± 0.05	0.43
6:4	N,W	0.35 ± 0.07	2.0 ± 0.1	0.18
4:6	N	0.25 ± 0.06	62 ± 2	0.004
2:8***	N,H	0.05 ± 0.06	26 ± 1	0.002
0:10	H	0.08 ± 0.06	85 ± 2	0.001

**Molecular ratio*
***W=witherite, N=norsethite, H=hydrated magnesium carbonates*
****Sample evaporated somewhat during experiment.*

Thus the possibility exists that there may be an upper limit of the cation to carbonate ratio in which norsethite is stable. A similar observation was made in Lippmann's (1967a, 1968b, 1973) work, where no alteration of witherite to norsethite occurred with magnesium chloride solutions unless sodium bicarbonate was added as well.

Judging from the wide range of barium-to-magnesium ratios in the original solutions from which norsethite was synthesized, it would seem that norsethite should be a more common mineral than is presently known. Steyn and Watson (1967) have pointed out the difficulty of identifying norsethite in the field. Since magnesium is a very common element whereas barium is relatively rare, it appears possible that a solution that contained enough barium to form witherite might have also contained enough magnesium and carbonate to form norsethite as well. Thus a promising place to search for norsethite should be in an area where witherite is known to occur. One such place is the Minerva Mine of the Southern Illinois fluorspar district, where norsethite has not yet been found. However, benstonite ($\mathrm{MgBa_6Ca_6(CO_3)_{13}}$ or $\mathrm{(Ca, Mg)_7Ba_6(CO_3)_{13}}$) has recently been discovered in the Minerva Mine (White and Jarosewich, 1970). The apparent absence of norsethite may be due to the formation of benstonite in its place because of the presence of calcium. The relationship of benstonite to norsethite merits further investigation.

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