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# PERSISTENCE OF $\mu$ -CaCO<sub>3</sub>\* IN WET CONDITIONS

by

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(with 5 Text-Figures)

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## Introduction

$\mu$ -CaCO<sub>3</sub> is thought to be the most unstable of the three modifications of calcium carbonate: calcite, aragonite, and  $\mu$ -CaCO<sub>3</sub>. It has been generally thought agreed that  $\mu$ -CaCO<sub>3</sub> formed in an aqueous solution transforms completely to a more stable modification (calcite or aragonite) if let contact with the mother liquor for several weeks (JOHNSTON and others: 1916, and GIBSON and others: 1925). Recently, however, the natural occurrence of this extremely unstable modification was reported (McCONNELL: 1960), and it is of interest to consider why such an unstable substance could have persisted under moist conditions.

The present paper reports experimental conditions in which  $\mu$ -CaCO<sub>3</sub> has existed in the presence of water for three months, which was the period of observation. There does not seem to be one-by-one correspondence between the experimental condition reported here and the natural circumstance where  $\mu$ -CaCO<sub>3</sub> was found to have occurred. Nevertheless, the present paper is expected to throw light on the reason for the persistence of  $\mu$ -CaCO<sub>3</sub>.

## Method of Experiment

Precipitates were obtained by gentle mixing of the 0.2 mol. solutions of (Ca, Sr)Cl<sub>2</sub> or (Ca, Ba)Cl<sub>2</sub> with (NH<sub>4</sub>)<sub>2</sub>CO<sub>3</sub> at the same concentration. The (Ca, Sr)Cl<sub>2</sub> solutions used were those with Ca:Sr ratios of 100:0, 90:10, 80:20, 70:30 etc., and the (Ca, Ba)Cl<sub>2</sub> solutions had Ca:Ba ratios of 95:5, 90:10, 85:15, 80:20, 75:25 and so on. NH<sub>4</sub>Cl was added beforehand to the chloride solutions to the extent of 3.5 grams per 100 cc. The speed of the reaction was kept very slow; it usually took about one hour to mix each 100 cc. of the chloride and the carbonate solutions.

The precipitates were kept in contact with the solutions for 3 days, 30 days, 60 days, and in some cases 90 days, then were washed with alcohol, and the com-

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\* Some authors synonymously call it vaterite-B or simply vaterite.

position determined quantitatively by X-ray analysis. The accuracy of the estimation of the proportion of each carbonate in a given precipitate was found to be within  $\pm 5\%$ .

### Result of Experiment

#### (1) *Precipitates from Ca-Sr solutions.*

The result of the observation after 3 day standing is shown in Fig. 1. Strontianite appears in solutions with Ca:Sr ratios from 85:15 to 0:100. In view of

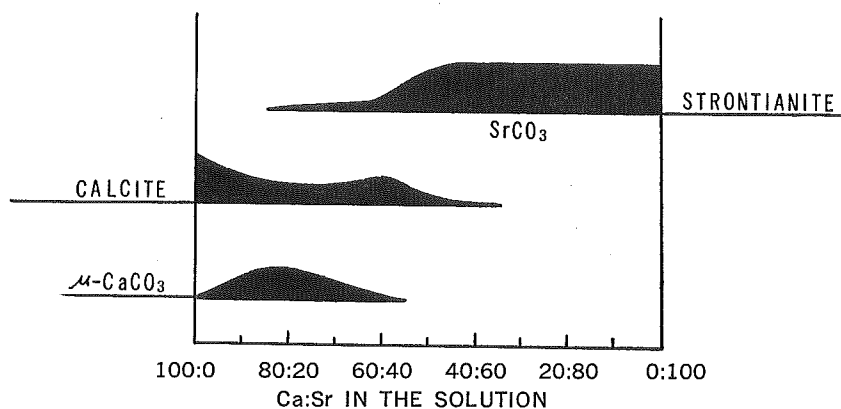


Fig. 1

Distributions of various carbonates from the Ca-Sr solutions; after 3 day standing.

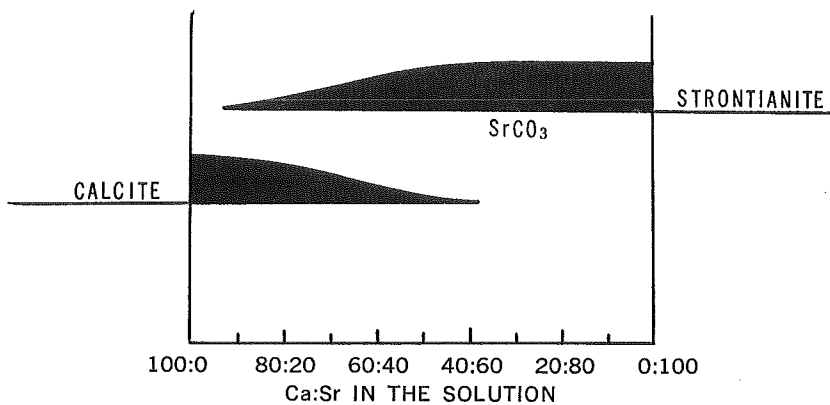


Fig. 2

Distributions of various carbonates from the Ca-Sr solutions; after 30 day standing.

marked decreases in their spacings, the strontianite formed in the solutions of larger calcium concentrations were thought to contain some appreciable amounts of calcium due to the isomorphous replacement.

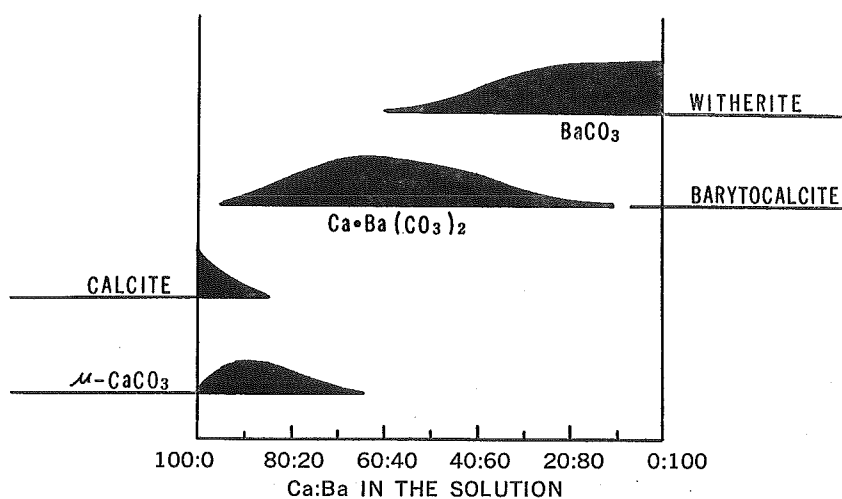
No aragonite was found in any precipitates from the Ca-Sr solutions. This fact is contrary to the observations of most earlier researchers. It is possible, however, that in some cases in earlier work calcium-bearing strontianite might have been identified as aragonite. Calcite was found in the solutions of the Ca:Sr ratios from 100:0 to 35:65, and  $\mu$ -CaCO<sub>3</sub> from 100:0 to 55:45. In this case also both minerals showed indications of the isomorphous replacement of some calcium by strontium, as shown in Fig. 5.

Observation on the precipitates after 30 day standing showed that all  $\mu$ -CaCO<sub>3</sub> crystals had disappeared. There were no appreciable changes found in the amounts of calcite and strontianite (Fig. 2).

(2) *Precipitates from Ca-Ba solutions.*

Precipitates after 3 day standing were witherite at the Ca:Ba ratios from 60:40 to 0:100, barytocalcite from 95:5 to 10:90, and calcite and  $\mu$ -CaCO<sub>3</sub> from 100:0 to 85:15 and 65:35 respectively, as illustrated in Fig. 3.

The result of 30 day standing was as shown in Fig. 4. The range of witherite was reduced to a higher barium concentration region, and that of barytocalcite extended more or less to either sides. An interesting fact is that  $\mu$ -CaCO<sub>3</sub> in the solutions of the Ca:Ba ratios from 100:0 to 85:15, the range where  $\mu$ -CaCO<sub>3</sub> had coexisted with calcite in the earlier stage, has disappeared, while that in the solutions



**Fig. 3**

Distributions of various carbonates from the Ca-Ba solutions; after 3 day standing.

of higher barium concentrations (from 85:15 to 65:35) has remained unchanged.

No further changes in the proportion of each precipitate were found after further 30 days' standing. The  $\mu$ - $\text{CaCO}_3$  in the solution of the Ca:Ba ratio 80:20 was arbitrarily chosen for a still further 30 days' standing, the total being 90 days. It was found to have persisted during the total period.

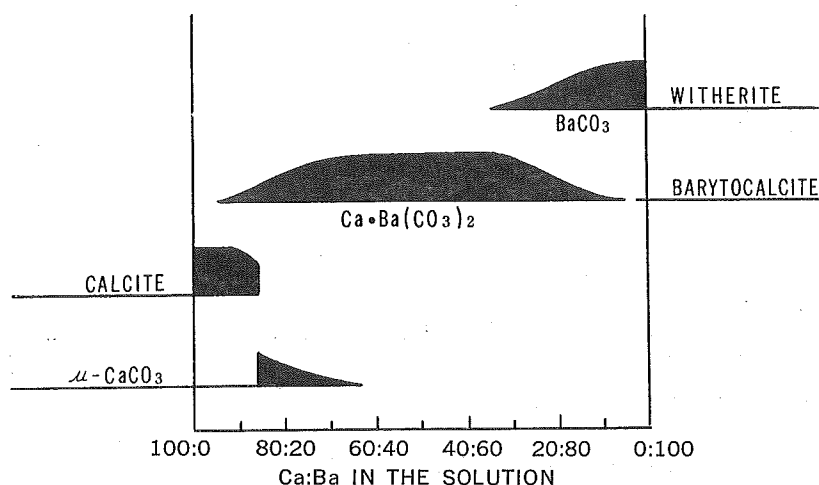


Fig. 4

Distributions of various carbonates from the Ca-Ba solutions; after 30 day standing.

## Discussion

For  $\mu$ - $\text{CaCO}_3$  to be able to last in a system (solution), the system must be such that it allows the nucleation of only  $\mu$ - $\text{CaCO}_3$ . If a system contains stable modifications (calcite and aragonite) together with  $\mu$ - $\text{CaCO}_3$ , the higher solubility of  $\mu$ - $\text{CaCO}_3$  inevitably leads to the transformation through dissolution of  $\mu$ - $\text{CaCO}_3$  to calcite or aragonite, and finally the disappearance of  $\mu$ - $\text{CaCO}_3$ . In view of its low density (2.54),  $\mu$ - $\text{CaCO}_3$  is thought to have a structure more open than that of calcite or aragonite, the density of which is 2.71 and 2.93 respectively. Therefore,  $\mu$ - $\text{CaCO}_3$  may not so much be affected by contamination with large cations like barium as calcite and aragonite should be. This is the reason why  $\mu$ - $\text{CaCO}_3$  can nucleate in solutions of a high barium content in preference to calcite and aragonite.

To keep the system free from any macro-size seeds of calcite or aragonite is another essential factor for the long lasting of  $\mu$ - $\text{CaCO}_3$ . Even if a solution allows  $\mu$ - $\text{CaCO}_3$  to nucleate but not calcite and aragonite, this merely means that the nucleus of  $\mu$ -form is more stable than that of calcite and aragonite, and not neces-

sarily means that the macro-crystal of  $\mu\text{-CaCO}_3$  is also more stable than calcite- and aragonite-macrocrystal. In fact, if discussed as to the crystals of macro-size, calcite and aragonite are always more stable than  $\mu\text{-CaCO}_3$  in any solutions under moderate temperature and pressure conditions. Therefore, any macro-seeds of calcite or aragonite pre-existed in or added later to the system can always remain stable with a lower solubility than that of  $\mu\text{-CaCO}_3$ , leading again to a sooner or later disappearance of  $\mu\text{-CaCO}_3$ . In this regard, a solution of the Ca:Ba ratio between 85:15 and 65:35 might be used for a suitable medium for the artificial growth of calcite single crystal.

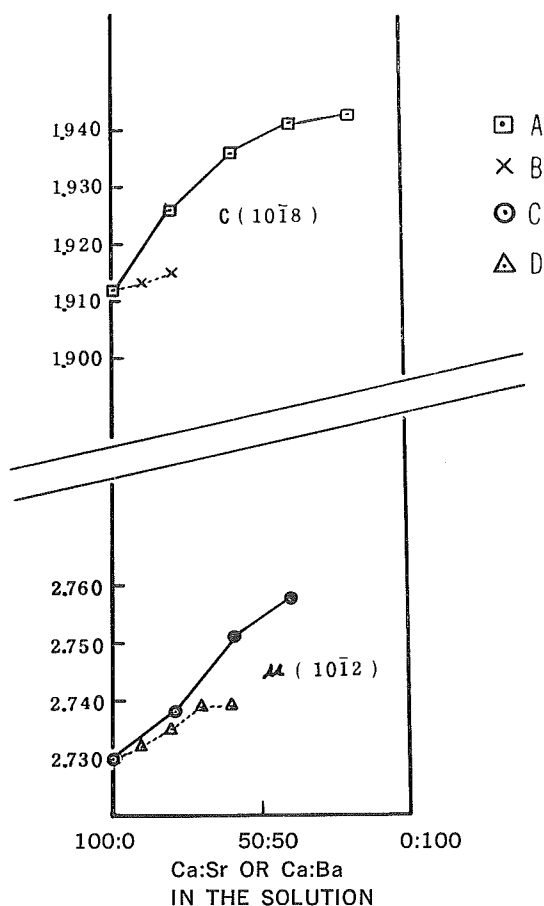


Fig. 5

Changes of some spacings of various carbonates with varying Ca:Sr or Ca:Ba ratios of solution. A; strontium-bearing calcite, B; barium-bearing calcite, C; Strontium-bearing  $\mu\text{-CaCO}_3$ , D; barium-bearing  $\mu\text{-CaCO}_3$ .

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