# The Behavior of Various Inorganic Ions in the Separation of Calcium Carbonate from a Bicarbonate Solution*

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Calcium carbonate has three different crystal forms: calcite, aragonite and vaterite. Many studies have been made of the conditions under which calcium carbonate is formed in various forms[1-14]. No definite conclusion has yet been reached, however, as to the exactness and the significance of the results.

The factors influencing the mineralogy of carbonate sediments include: (1) the presence of certain inorganic ions, including hydrogen ions, hydroxide ions and carbon dioxide, in the mother solution; (2) the influence of organic material; (3) enzymes (carbonic anhydrase) and bacteria; (4) the mechanical conditions; (5) the temperature, and (6) the transformation of the crystal type after calcium carbonate has been formed.

Experiments on the effects of the materials in the mother solution have been few and inconclusive compared with those on the other factors. The purpose of this study is to cover one phase of this problem: the influence of various inorganic ions on the polymorphic crystallization of calcium carbonate.

In the experiments, calcium carbonate was formed from a calcium bicarbonate solution as carbon dioxide gas escaped. This reaction was used, because it is typical for the formation of calcium carbonate by inorganic processes in the hydrosphere, because it is one of the "homogeneous precipitation" reactions and reproducible precipitation is easily achieved, because no ions other than the calcium, the bicarbonate, and the carbonate ions are present in the mother solution.

## Experimental

**Materials and Solutions.**—The effects of the following alkali and alkaline earth salts (analytical grade reagents) were investigated, since most of them are expected to be found in nature: lithium chloride, sodium chloride, potassium chloride, ammonium chloride, rubidium chloride, cesium chloride, sodium nitrate, sodium sulfate, sodium

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* This study was begun at Water Research Laboratory of Nagoya University and completed at the Department of Oceanography, A & M College of Texas, College Station, Texas, U. S. A.

1) W. L. Dekeyser and L. Dugueldre, *Bull. soc. chim. Belges.*, **59**, 40 (1950).

2) J. Johnston, H. E. Merwin and E. D. Williamson, *Am. J. Sci.*, **41**, 473 (1916).

3) Y. Kitano, *J. Chem. Soc. Japan, Pure Chem. Sec.* (*Nippon Kagaku Zassi*), **76**, 581 (1955).

4) Y. Kitano, *J. Chem. Soc. Japan, Ind. Chem. Sec.* (*Kogyo Kagaku Zassi*), **59**, 1346 (1956).

5) Y. Kitano and N. Kawasaki, *J. Earth Sciences, Nagoya Univ.*, Vol. **16** No. 2, 63 (1958).

6) H. A. Lowenstam, *J. Geol.*, **62**, 284 (1954).

7) H. A. Lowenstam, *Proc. Natl. Acad. Sci. U. S.*, **40**, 39 (1954).

8) J. W. Mellor, "A Comprehensive Treatise on Inorganic and Theoretical Chemistry", Vol. 3, Longmans, Green and Co., London (1925).

9) J. W. Murray, *J. Geol.*, **62**, 481 (1954).

10) H. U. Sverdrup, M. W. Johnson and R. H. Fleming, "The Oceans", Prentice-Hall, Inc., New York (1959), p. 997.

11) N. Watabe and K. M. Wilbur, *Nature*, **188**, 4747, 334 (1960).

12) K. M. Wilbur, *Am. Assoc. Adv. Sci.*, *Washington D. C.*, 15 (1960).

13) J. L. Wray and F. Daniels, *J. Am. Chem. Soc.*, **79**, 2031 (1957).

14) E. J. Zeller and J. L. Wray, *Bull. Am. Petrol. Geol.*, **40**, 140 (1956).

bicarbonate, sodium carbonate, sodium hydroxide, magnesium chloride, calcium chloride, strontium chloride, barium chloride, magnesium sulfate, magnesium bicarbonate, strontium bicarbonate and barium bicarbonate.

For the preparation of the bicarbonate solution of alkaline earth elements, the carbonate was pulverized and suspended in distilled water, and then carbon dioxide gas was bubbled through the suspension for approximately one day at room temperature. After having been allowed to stand for 30 min., the suspension was filtered. The filtrate was aerated for another hour with carbon dioxide.

**Procedure.**—Different amounts (0~6 g.) of the salts were placed in one liter flasks with a small amount of distilled water, and 300 ml. portions of a calcium bicarbonate solution (prepared according to the above procedure) were added to each. The flasks were left to stand at room temperature for two or three weeks, during which time carbon dioxide gas escaped from the solution and calcium carbonate crystals were separated. As the carbon dioxide gas escaped, portions of the supernatant solution were withdrawn to determine the change in the pH value and the decrease in the calcium content. The rate of calcium carbonate precipitation was estimated from these data. Eventually, the remaining precipitate of carbonate was filtered off and washed with distilled water until it was free from any trace of the mother solution. After having been dried in an air bath and ground in an agate mortar, a fraction of the crystals was used for the determination of the chemical composition, while another fraction was used for the identification of the crystal form by X-ray diffraction.

Calcium carbonate was formed at room temperature. The pH value and the calcium content in the mother solution changed during the process of calcium carbonate precipitation; therefore, it is considered that calcium carbonate precipitates were formed from solution of varying pH values and varying calcium concentrations. The author studied whether there was a difference in the polymorphic composition among the calcium carbonate crystals after different lapses of time. Under the given conditions, the difference was not significant.

## Results and Discussion

**The Effect of Alkali Chlorides.**—Table I and Fig. 1 show that alkali chlorides in the mother

TABLE I. $Ca(HCO_3)_2$-ALKALI CHLORIDE-$CO_2$-$H_2O$ SYSTEM (28±3°C)

| Composition of solutions (total volume, 300 ml.) | | | | | | | | | | Crystal form* of $CaCO_3$ formed during 14 days | |
|---|---|---|---|---|---|---|---|---|---|---|---|
| at the start | | | | on the 2nd day | | on the 5th day | | on the 14th day | | Aragonite | Calcite |
| Ca-bicarbonate solution** | Salt added | | pH | Ca | pH | Ca | pH | Ca | pH | % | |
| Ca mg. | Salt | meq. of cation | | mg. | | mg. | | mg. | | | |
| 85 | — | — | 6.7 | 40 | 7.5 | 11 | 7.9 | 7 | 7.9 | 15 | 85 |
| 85 | LiCl | 7 | 6.7 | 58 | 7.4 | 21 | 7.8 | 9 | 7.8 | 2 | 98 |
| 85 | LiCl | 24 | 6.8 | 68 | 7.6 | 26 | 7.9 | 12 | 7.9 | 0 | 100 |
| 85 | LiCl | 70 | 6.8 | 73 | 7.9 | 35 | 8.0 | 15 | 8.1 | 0 | 100 |
| 85 | NaCl | 5 | 6.7 | 60 | 7.4 | 25 | 7.8 | 9 | 7.8 | 4 | 96 |
| 85 | NaCl | 17 | 6.8 | 64 | 7.6 | 30 | 7.9 | 12 | 7.9 | 0 | 100 |
| 85 | NaCl | 50 | 6.8 | 70 | 7.9 | 36 | 8.0 | 13 | 8.1 | 0 | 100 |
| 85 | KCl | 4 | 6.7 | 61 | 7.6 | 20 | 7.8 | 10 | 7.9 | 10 | 90 |
| 85 | KCl | 14 | 6.8 | 64 | 7.8 | 24 | 7.9 | 11 | 7.9 | 1 | 99 |
| 85 | KCl | 40 | 6.8 | 70 | 7.8 | 30 | 8.0 | 13 | 8.0 | 0.5 | 99.5 |
| 85 | $NH_4Cl$ | 6 | 6.7 | 65 | 7.4 | 25 | 7.8 | 18 | 7.9 | 0 | 100 |
| 85 | $NH_4Cl$ | 19 | 6.8 | 70 | 7.5 | 35 | 7.8 | 27 | 7.9 | 0 | 100 |
| 85 | $NH_4Cl$ | 57 | 6.8 | 75 | 7.6 | 47 | 7.8 | 45 | 7.9 | 0 | 100 |
| 85 | RbCl | 3 | 6.8 | 60 | 7.4 | 20 | 7.8 | 9 | 7.8 | 11 | 89 |
| 85 | RbCl | 8 | 6.8 | 66 | 7.5 | 25 | 7.9 | 10 | 7.9 | 10 | 90 |
| 85 | CsCl | 2 | 6.7 | 57 | 7.4 | 18 | 7.8 | 9 | 7.8 | 10 | 90 |
| 85 | CsCl | 6 | 6.8 | 61 | 7.5 | 19 | 7.8 | 10 | 7.8 | 9 | 91 |
| 85 | CsCl | 18 | 6.8 | 67 | 7.8 | 22 | 7.9 | 10 | 7.9 | 9 | 91 |
| 85 | $NaNO_3$ | 4 | 6.7 | 59 | 7.5 | 21 | 7.8 | 9 | 7.8 | 11 | 89 |
| 85 | $NaNO_3$ | 12 | 6.8 | 64 | 7.6 | 25 | 7.9 | 12 | 7.9 | 10 | 90 |
| 85 | $NaNO_3$ | 40 | 6·8 | 69 | 7.8 | 30 | 7.9 | 13 | 7.9 | 7 | 93 |

* No vaterite was found.

** A solution containing $Ca(HCO_3)_2$, $H_2CO_3$, $CO_2$ and $H_2O$ as shown in "materials and solutions" in Experimental of this report.

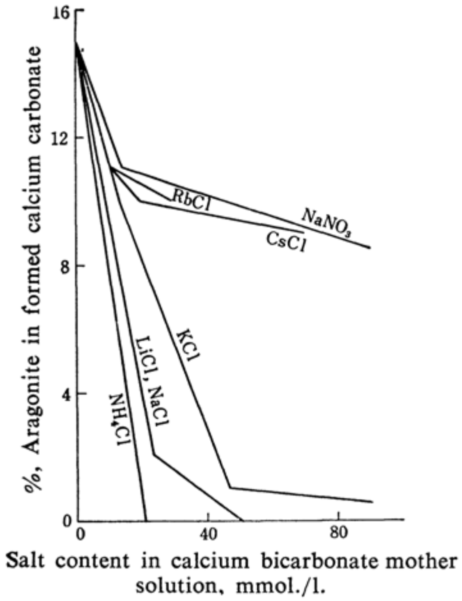

Fig. 1. Effect of alkali chloride in a mother solution on crystal type of formed calcium carbonate.

solution inhibited the formation of aragonite favored the formation of calcite. Furthermore, Table I shows that alkali chlorides had little influence on the pH value of the mother solution. The extent of the inhibition of the aragonite formation decreased in the sequence: ammonium chloride>lithium chloride, sodium chloride>potassium chloride>rubidium chloride, cesium chloride, (sodium nitrate).

Previous reports[4,8] showed that the presence of alkali chlorides favored aragonite formation. This report, covering a large number of samples in various amounts, shows, in every case, a definite decrease in the percentage of aragonite formation with an increase in the concentration of alkali chloride. The precipitate consisted only of calcium and carbonate.

**The Effect of Anions.**—Calcium carbonate was formed from the calcium bicarbonate solution containing sodium salt. The crystal form of the calcium carbonate was identified (Fig. 2), and the change in the pH value of the mother solution with time was measured (Fig. 3). The following results were obtained concerning the effect of anions on the crystallization of calcium carbonate:

*Sodium Chloride and Nitrate.*—The presence of both sodium chloride and sodium nitrate inhibited aragonite formation, although the effect of sodium chloride was stronger than that of sodium nitrate (Fig. 1).

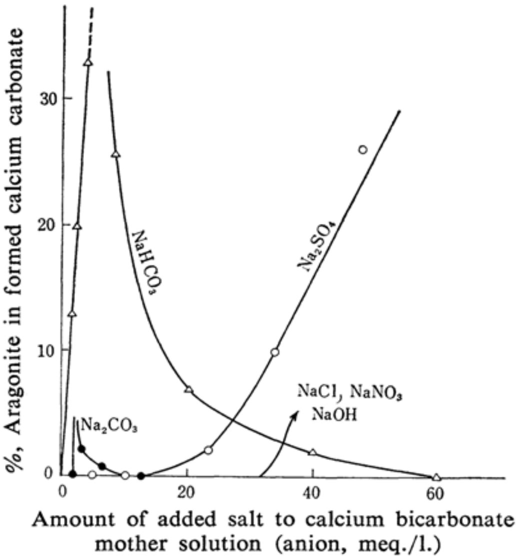

Fig. 2. Effect of sodium salts in a mother solution on crystal type of formed calcium carbonate.

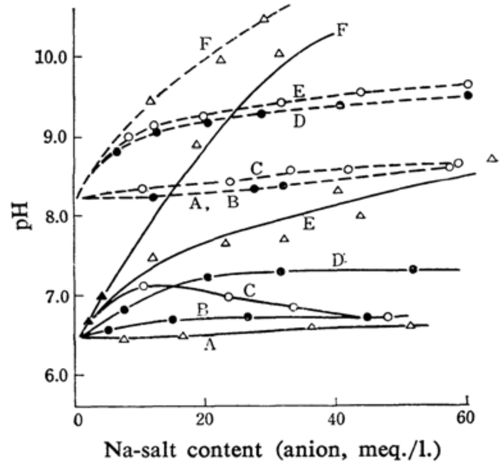

Fig. 3. pH of calcium bicarbonate solution containing sodium salt.

—— pH at the start

- - - pH on the 21st day

A, NaCl B, $NaNO_3$ C, $Na_2SO_4$

D, $NaHCO_3$ E, $Na_2CO_3$ F, NaOH

*Sodium Bicarbonate and Carbonate.*—With a moderate increase in the amount of sodium bicarbonate (sodium carbonate) added to the mother bicarbonate solution, the percentage of aragonite formation increased. With a further increase in amount, however, the percentage began to decrease and reached zero (Fig. 2). The present author has previously joined to show[15] that calcium carbonate was not formed directly from a solution highly concentrated in calcium, bicarbonate or carbonate ions, but that a gelatinous, unstable compound having a

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[15] Y. Inoue, Y. Kitano and E. Yagyu, *J. Chem. Soc. Japan, Pure Chem. Sec.* (*Nippon Kagaku Zassi*), **96**, 19 (1955).

definite chemical composition was first formed. Furthermore, the present author[16-17] has reported that the unstable compound was then transformed into a calcium carbonate precipitate, and that with an increase in the concentrations of the calcium ions and the carbonate ions in the original, highly-concentrated solution, the stability of the unstable compound increased; consequently, the rate of calcium carbonate separation decreased. Therefore, one can say that the rate of calcium carbonate separation is moderate when the concentration of calcium ions or carbonate ions is either very high or very low. When calcium carbonate separation is moderate, the most stable form, calcite, is predominant. This finding helps qualitatively to explain the maximum percentage of aragonite formation for a certain value of the added carbonate salt.

*Sodium Hydroxide.*—When sodium hydroxide was added, only calcite was formed (Fig. 2). Aragonite was never formed from the solution which had been made alkaline (up to a pH value of 10) with sodium hydroxide. It has been reported by many researchers[3,4,8] that aragonite formation was favored in a solution having a pH value of more than 8. However, as can be seen from Figs. 2 and 3, aragonite was not always formed from an alkaline solution; the previous conclusion, therefore, is not always reliable.

The ease of aragonite formation does not seem always to depend upon the pH value, but upon the carbonate ion* content of the mother solution. Since the pH value and the total carbonate content changed with time in the mother solution, the estimation of the carbonate ion content in the mother solution was difficult. A more detailed study is under way on the effect of sodium bicarbonate, sodium carbonate and sodium hydroxide.

*Sodium Sulfate.*—The presence of sulfate ions favored aragonite formation.

**The Effect of Alkaline Earth Salts.**—*Magnesium Chloride, Bicarbonate and Sulfate.*—On the basis of the following facts, it can be supposed that the presence of magnesium bicarbonate or magnesium sulfate in the mother solution is more conducive to aragonite formation than is the presence of magnesium chloride. (1) Magnesium ions, bicarbonate ions and sulfate ions favored aragonite formation (Figs. 2 and 4), but chloride ions inhibited aragonite formation (Table I). (2) According to the previous conclusion[3,4], aragonite in general was formed when the rate of calcium carbonate precipitation was large, while calcite was formed when the rate was small, provided that the mechanism of calcium carbonate formation was similar. It must be noted that the rate was larger in a mother solution containing magnesium bicarbonate than in that containing magnesium chloride (Fig. 5). However, in the experiment, the presence of magnesium chloride in the mother solution was more favorable to aragonite formation than that of magnesium bicarbonate or magnesium sulfate (Fig. 4). The presence of the magnesium salts had little influence on the pH value of the solution. The result shows that the presence of magnesium ions in the mother solution seems to favor aragonite formation very strongly. Working with solutions of a low and a nearly constant ionic strength ($\mu=0.15$), Greenwald[18] concluded that following equilibria exist at 22°C:

$$\frac{M_{Ca^{2+}}\, M_{HCO_3^-}}{M_{CaHCO_3^+}} = K'_{CaHCO_3^+} = 1.6\times10^{-1}$$

$$\frac{M_{Mg^{2+}}\, M_{HCO_3^-}}{M_{MgHCO_3^+}} = K'_{MgHCO_3^+} = 1.7\times10^{-1}$$

$$\frac{M_{Ca^{2+}}\, M_{CO_3^{2-}}}{M_{CaCO_3^0}} = K'_{CaCO_3^0} = 1\times10^{-3}$$

$$\frac{M_{Mg^{2+}}\, M_{CO_3^{2-}}}{M_{MgCO_3^0}} = K'_{MgCO_3^0} = 4.3\times10^{-3}$$

and Garrels[19] concluded $K'_{MgCO_3^0}=4.0\times10^{-4}$.

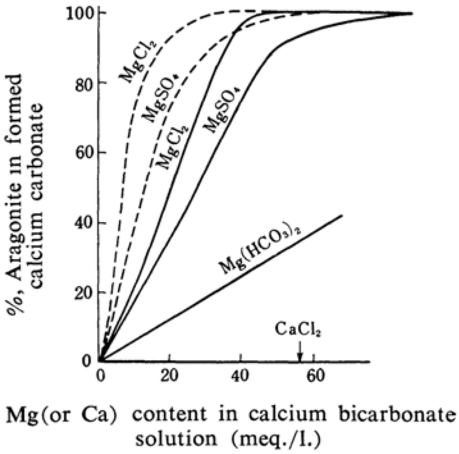

Fig. 4. Effect of calcium and magnesium salts in mother solution on crystal type of formed calcium carbonate.
—— 10±2°C
- - - 28±3°C

The concentration of magnesium ions in the mother solution was calculated by the use of

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[16] Y. Inoue, Y. Kitano and S. Koyama, ibid., **76**, 22 (1955).

[17] Y. Inoue, Y. Kitano and S. Konaka, ibid., **76**, 124 (1955).

* Carbonate ion concentration is estimated from the pH value and the total carbonate content in a solution.

[18] I. Greenwald, *J. Biol. Chem.*, **141**, 789 (1941).

[19] R. M. Gerrels, M. E. Thompson and R. Silver, *Am. J. Sci.*, **259**, 24 (1961).

TABLE II. $Ca(HCO_3)_2$-Mg SALT-$CO_2$-$H_2O$ SYSTEM (10±2°C)

| Composition of solution: at the start: Ca-bicarbonate solution: ml. | Ca mg. | Salt added: Salt | ml. | Mg mg. | on the 15th day: Ca mg. | Mg mg. | on the 50th day: Ca mg. | Mg mg. | Precipitate: Mg content (%) in precipitate: during 15 days | during 50 days | Crystal form** of $CaCO_3$ separated during 15 days: Aragonite % | Calcite |
|---|---|---|---|---|---|---|---|---|---|---|---|---|
| 250 | 106 | — | — | — | 9 | — | 7 | — | 0.00 | 0.00 | 0.0 | 100 |
| 250 | 106 | $MgCl_2$ | 50 | 48 | 18 | 48 | 11 | 48 | 0.00 | 0.00 | 33 | 67 |
| 250 | 106 | $MgCl_2$ | 150 | 145 | 29 | 145 | 20 | 145 | 0.00 | 0.00 | 78 | 22 |
| 250 | 106 | $MgCl_2$ | 250 | 242 | 42 | 247 | 31 | 247 | 0.00 | 0.00 | 99 | 1 |
| 250 | 106 | $MgCl_2$ | 400 | 394 | 53 | 397 | 40 | 399 | 0.00 | 0.00 | 100 | 0 |
| 250 | 106 | $MgSO_4$ | 50 | 60 | — | — | — | — | 0.00 | 0.00 | 28 | 72 |
| 250 | 106 | $MgSO_4$ | 150 | 100 | — | — | — | — | 0.00 | 0.00 | 37 | 63 |
| 250 | 106 | $MgSO_4$ | 250 | 200 | — | — | — | — | 0.00 | 0.00 | 63 | 37 |
| 250 | 106 | $MgSO_4$ | 400 | 400 | — | — | — | — | 0.00 | 0.00 | 92 | 8 |
| 250 | 106 | $Mg(HCO_3)_2$ | 50 | 61 | 0.0 | 61 | 0.0 | 61 | 0.00 | 0.00 | 8 | 92 |
| 250 | 106 | $Mg(HCO_3)_2$ | 150 | 184 | 0.0 | 183 | 0.0 | 185 | 0.00 | 0.00 | 21 | 79 |
| 250 | 106 | $Mg(HCO_3)_2$ | 250 | 307 | 0.0 | 308 | 0.0 | 304 | 0.00 | 0.3* | 31 | 69 |
| 250 | 106 | $Mg(HCO_3)_2$ | 400 | 491 | 0.0 | 493 | 0.0 | 485 | 0.00 | 1.2* | 43 | 57 |

* Mg is contained as $MgCO_3 \cdot 3H_2O$.

** No vaterite was formed.

the dissociation constants of the complexes, $MgHCO_3^+$ and $CaHCO_3^+$, because the concentration of carbonate ions is very small compared with that of bicarbonate ions at the given pH value; even when the calculated concentration of magnesium ions was the same, aragonite formation was much more favored in the solution containing magnesium chloride than in the solution containing magnesium bicarbonate.

Figure 5 shows the rate constants* in the reaction of calcium carbonate separation from a calcium bicarbonate solution containing various amounts of salts. Magnesium and sodium were not co-precipitated with calcium carbonate (Table II). The presence of magnesium chloride (which aided aragonite formation) lowered the rate of calcium carbonate separation to a greater extent than did sodium chloride (which aided calcite formation).

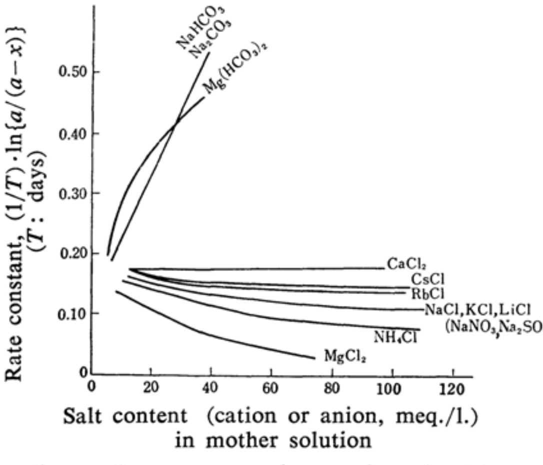

Fig. 5. Rate constant in reaction of calcium carbonate separation from calcium bicarbonate solution containing salt.

It must be said that the percentage of aragonite (unstable crystal) formation does not always increase with an increase in the rate of calcium carbonate separation and that the mechanism of the effect of ions in the mother solution upon the polymorphic crystallization is probably be different from ion group to ion group. Work is under way to investigate the mechanisms whereby magnesium chloride favors aragonite formation more than magnesium bicarbonate or magnesium sulfate and whereby magnesium chloride favors aragonite formation while sodium chloride favors calcite formation at room temperature.

*Calcium Chloride.*—Calcium chloride was added to the mother solution to accelerate calcium carbonate precipitation; its addition did not aid aragonite formation (Fig. 4).

*Strontium Chloride and Bicarbonate.*—The significant behavior of strontium ions in the

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* The decrease in the calcium content of the mother solution was measured during the process of calcium carbonate precipitation. On the basis of the measurements, the rate constant, $(1/T)\cdot\ln\{a/(a-x)\}$, of the first order reaction, and the constant, $[1/2T]\cdot[1/(a-x)^2-1/a^2]$, of the third order reaction were calculated. Judging from these calculations, the reaction seemed to be a first order reaction; therefore, in Fig. 5, the rate constants of the first order reaction are given.

separation of calcite or aragonite has been clarified previously[5]: (1) With an increase in the amount of strontium bicarbonate added to the original calcium bicarbonate solution, the percentage of aragonite formation increased to a maximum (optimum strontium content: approximately 2 mg./l.). The percentage began to decrease with a further increase in the strontium concentration (Fig. 6). When strontium chloride was added to the mother solution, aragonite formation was inhibited. (2) The strontium was always entrained in the calcium carbonate precipitate, even when the strontium concentration in the mother solution was very low.

*Barium Chloride and Bicarbonate.*—Calcium carbonate was formed from the calcium bicarbonate solution containing barium bicarbonate or barium chloride; it was also formed from the calcium bicarbonate solution containing magnesium chloride and barium bicarbonate or barium chloride (Table III and Fig. 7), judging from the fact that calcium carbonate consisting of increasing percentages of aragonite could be obtained from calcium bicarbonate solutions containing increasing amounts of magnesium chloride (Fig. 3). Table III shows the barium content in the carbonate prepared. The barium content was obtained by first adding different amounts of barium ions labeled with $^{140}$Ba to the mother bicarbonate solutions. Measured volumes of the original solution, and of the residual solution from which the calcium carbonate crystals had been collected, were dried in planchets. The radioactivities of the two samples were measured at the same time, sixteen days after the residual solution had been dried. The ratio of the distribution of barium between the precipitate and the residual solution was calculated. From this ratio, the

TABLE III. $Ca(HCO_3)_2$-$MgCl_2$-Ba SALT-$CO_2$-$H_2O$ SYSTEM (12±3°C)

| Composition of solutions | | | | | | | Precipitate formed duaring 15 days | | | |
|---|---|---|---|---|---|---|---|---|---|---|
| at the start | | | | | | on the 15th day | Crystal form | | | Fractionation factor |
| Ca-bicarbonate solution | | $MgCl_2$ | Ba salt | | | Ca, mg. | Vaterite % | Aragonite % | Calcite % | ((Ba/Ca) in ppt.)/((Ba/Ca) in soln.) |
| ml. | Ca mg. | m. M | Salt | ml. | Ba mg. | | | | | |
| 300 | 75 | 0 | 0 | 0 | 0 | 14 | 0 | 0 | 100 | — |
| 300 | 75 | 0 | $BaCl_2$ | 0.05 | 0.05 | 18 | 0 | 0 | 100 | 0.40 |
| 300 | 75 | 0 | $BaCl_2$ | 0.1 | 0.1 | 19 | 0 | 0 | 100 | 0.40 |
| 300 | 75 | 0 | $BaCl_2$ | 0.3 | 0.3 | 20 | 0 | 0 | 100 | 0.41 |
| 300 | 75 | 0 | $BaCl_2$ | 0.7 | 0.7 | 21 | 0 | 0 | 100 | 0.36 |
| 300 | 75 | 0 | $BaCl_2$ | 2 | 2 | 21 | 0 | 0 | 100 | 0.33 |
| 300 | 75 | 0 | $BaCl_2$ | 10 | 10 | 26 | 0 | 0 | 100 | 0.33 |
| 300 | 75 | 0 | $BaCl_2$ | 50 | 50 | — | 94 | 0 | 6 | — |
| 300 | 75 | 0 | $BaCl_2$ | 75 | 75 | — | 100 | 0 | 0 | — |
| 300 | 75 | 0 | $BaCl_2$ | 100 | 100 | — | 100 | 0 | 0 | — |
| 300 | 75 | 0 | $Ba(HCO_3)_2$ | 0.05 | 0.04 | 20 | 0 | 0 | 100 | 0.35 |
| 300 | 75 | 0 | $Ba(HCO_3)_2$ | 0.1 | 0.07 | 20 | 0 | 0 | 100 | 0.33 |
| 300 | 75 | 0 | $Ba(HCO_3)_2$ | 0.3 | 0.2 | 20 | 0 | 0 | 100 | 0.34 |
| 300 | 15 | 0 | $Ba(HCO_3)_2$ | 0.7 | 0.5 | 21 | 0 | 0 | 100 | 0.34 |
| 300 | 75 | 0 | $Ba(HCO_3)_2$ | 2 | 1.5 | 22 | 0 | 0 | 100 | 0.31 |
| 300 | 75 | 0 | $Ba(HCO_3)_2$ | 10 | 6 | 23 | 0 | 0 | 100 | 0.32 |
| 300 | 75 | 0 | $Ba(HCO_3)_2$ | 50 | 28 | — | 0 | 0 | 100 | — |
| 300 | 75 | 0 | $Ba(HCO_3)_2$ | 75 | 42 | — | 46 | 0 | 54 | — |
| 300 | 75 | 0 | $Ba(HCO_3)_2$ | 100 | 60 | — | 96 | 0 | 4 | — |
| 300 | 75 | 1.5 | 0 | 0 | 0 | 20 | 0 | 30 | 70 | — |
| 300 | 75 | 4 | 0 | 0 | 0 | 26 | 0 | 70 | 30 | — |
| 300 | 75 | 5 | 0 | 0 | 0 | 37 | 0 | 95 | 5 | — |
| 300 | 75 | 1.5 | $BaCl_2$ | 5 | 5 | 24 | 0 | 0 | 100 | 0.41 |
| 300 | 75 | 4 | $BaCl_2$ | 5 | 5 | 29 | 0 | 0 | 100 | 0.49 |
| 300 | 75 | 5 | $BaCl_2$ | 5 | 5 | 37 | 0 | 0 | 100 | 0.67 |
| 300 | 75 | 1.5 | $Ba(HCO_3)_2$ | 5 | 3 | 20 | 0 | 0 | 100 | 0.35 |
| 300 | 75 | 4 | $Ba(HCO_3)_2$ | 5 | 3 | 27 | 0 | 0 | 100 | 0.48 |
| 300 | 75 | 5 | $Ba(HCO_3)_2$ | 5 | 3 | 35 | 0 | 0 | 100 | 0.63 |

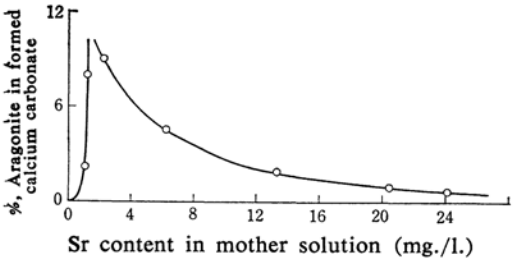

Fig. 6. Effect of strontium ions on the crystal type of formed calcium carbonate.

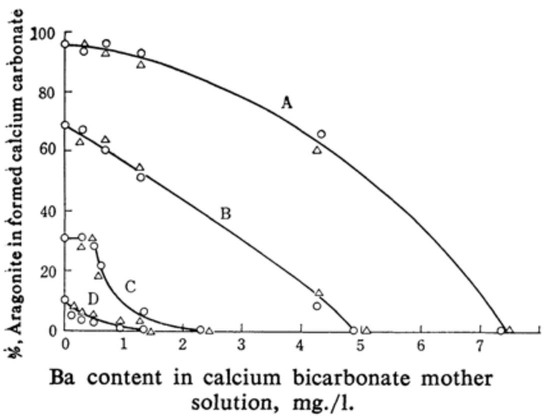

Fig. 7. Effect of barium ions in mother solution on crystal type of formed calcium carbonate (36±3°C).

○ $BaCl_2$ △ $Ba(HCO_3)_2$
A $MgCl_2$ 12 mmol./l.
B $MgCl_2$ 4.5 mmol./l.
C $MgCl_2$ 2.5 mmol./l.
D $MgCl_2$ none

original and the residual calcium content and the original barium content in the solution, the barium content of the precipitated carbonate was calculated.

The behavior of barium ions in the separation of calcium carbonate from a bicarbonate solution has been clarified. (1) Contrary to previous findings[4,9,14] that the presence of a small number of barium ions in the mother solution favored aragonite formation, the presence of barium ions favored calcite formation (Table III, and Fig. 7). (2) The presence of a large amount of barium ions favored vaterite formation[2] (Table III). (3) Even at a low concentration in the mother solution, barium was always entrapped in the precipitates (Table III). The behavior of barium ions did not follow the law of solubility. (4) With an increase in the barium concentration of the mother solution, the amount of barium entrapped in the calcium carbonate increased and the specific peak for calcite configuration became diffuse when measured with an X-ray diffractometer. Therefore, it can be expected that barium is present in calcium carbonate as a form of $(Ca, Ba)CO_3$. As can be seen from Table III, the amount of entrapped barium in calcium carbonate increased with an increase in the magnesium chloride concentration of the mother solution. The presence of the barium salts had little influence on the pH value of the solution.

## Summary

The author has shown the effect of various inorganic ions on the polymorphic crystallization of calcium carbonate from a bicarbonate solution. No definite conclusion regarding the mechanism to give calcite, aragonite or vaterite can yet be made, but these data help to give a pattern of the influence of inorganic ionic species and the concentration of the mother solution on the polymorphic crystallization of calcium carbonate.

(1) Alkali chlorides in the mother solution inhibited aragonite formation and favored calcite formation. The extent of the inhibition of the aragonite formation decreases in the sequence: ammonium chloride>lithium chloride, sodium chloride>potassium chloride >rubidium chloride, >cesium chloride (sodium nitrate).

(2) (a) Sodium chloride and sodium nitrate in the mother solution inhibited aragonite formation, sodium chloride more strongly than sodium nitrate. (b) With a moderate increase in the amount of sodium bicarbonate (sodium carbonate) added to the mother solution, the percentage of aragonite formation increased to a maximum. With a further increase in the amount, however, the percentage began to decrease and reached zero. (c) When sodium hydroxide was added to the mother solution, only calcite was formed. Aragonite was never formed from the solution which had made alkaline with sodium hydroxide. (d) The presence of sulfate ions favored aragonite formation.

(3) (a) Magnesium ions in the mother solution favored aragonite formation very strongly. The presence of magnesium chloride in the mother solution was more favorable to aragonite formation than that of magnesium bicarbonate or magnesium sulfate. Magnesium was not co-precipitated with calcium carbonate. (b) The presence of calcium chloride in the mother solution had no effect on the crystallization. (c) With an increase in the strontium concentration in the original solution, the percentage of aragonite formation increased to a maximum (optimum strontium content: approximately 2 mg./l.). The percentage began to decrease with a further increase in strontium

concentration. The strontium was always entrained in calcium carbonate precipitates, even when the strontium concentration was very low. (d) The presence of a small number of barium ions in the mother solution favored calcite formation. The presence of a large number of barium ions favored vaterite formation. Even at a low concentration in the mother solution, barium was always entrapped in the precipitates.

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