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Crystal Forms of Calcium Carbonate Formed from Calcium Bicarbonate Solution Containing Heavy Metal Ions

Akira TOKUYAMA*, Yasushi KITANO** and Nobuko KANAMORI**

Summary

To study the effect of metal ions such as Cu^{2+}, Zn^{2+}, Ni^{2+}, Mn^{2+} Mg^{2+} and Pb^{2+} on the formation of the polymorphisms of calcium carbonate, calcium carbonate was precipitated from the following six solution systems :

1. $Ca(HCO_3)_2 + Me^{2+} \xrightarrow[\text{always stirred}]{36\pm2^\circ C} \text{carbonate}$
2. $Ca(HCO_3)_2 + Me^{2+} \xrightarrow[\text{sometimes stirred}]{34\pm2\ C} \text{carbonate}$
3. $Ca(HCO_3)_2 + Me^{2+} \xrightarrow[\text{sometimes stirred}]{40\pm2^\circ C} \text{carbonate}$
4. $Ca(HCO_3)_2 + Me^{2+} \xrightarrow[\text{boiling}]{97\pm2^\circ C} \text{carbonate}$
5. $Ca(HCO_3)_2 + \text{glycine} + Me^{2+} \xrightarrow[\text{always stirred}]{36\pm2^\circ C} \text{carbonate}$
6. $Ca(HCO_3)_2 + NaCl + Me^{2+} \xrightarrow[\text{boiling}]{97\pm2^\circ C} \text{carbonate}$

The presence of those heavy metal ions except Pb^{2+} in a parent solution favors the formation of aragonite. The extent of their influence on the forming of aragonite increases in the following sequence, although the influences of Zn^{2+} and Mn^{2+} in a parent solution are complex: $Cu^{2+} > Zn^{2+}, Ni^{2+} > Mn^{2+} > Mg^{2+}$. The sequence is in agreement with that of the second ionization potential value of these elements. In the solution system 1, the concentration of metal ions needed to precipitate pure aragonite is as follows: Cu^{2+} : 8×10^{-3}, Ni^{2+} : 2.2, Mg^{2+} : 22 meq/1. Lead ions over 0.2 meq/1 can not be added to the parent solution because of the small solubility of $PbCO_3$. Pure calcite was precipitated from the calcium bicarbonate solution containing lead ions.

Although metal ions such as Cu^{2+}, Ni^{2+}, Zn^{2+}, and Mg^{2+} favor aragonite formation in the solution system 4, pure aragonite was not precipitated from the solutions of the system. It is noted that pure aragonite was precipitated from solutions of the systems 1, 2, and 3. Solid solutions were precipitated more easily in the solution system 4 than in other systems at low temperatures.

In the solution system 5, aragonite was precipitated more easily from the calcium bicarbonate solution dissolving metal in both ionic form and metal-glycine complex than from the solution dissolving metal in only ionic form or in only metal-glycine complex.

In the solution system 6, metal ions inhibit vaterite formation and the extent increases in following sequence: Cu^{2+}, Zn^{2+}, $Ni^{2+} > Mn^{2+} > Mg^{2+}$. The presence of Cu^{2+}, Zn^{2+} and Mg^{2+} in a parent solution inhibits calcite formation and favors aragonite formation.

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1. Introduction

Calcium carbonate has three different crystal forms : calcite, aragonite and vaterite. In most sedimentary environments, calcites (Mg-poor calcite and Mg-rich calcite) and aragonite are dominant, but vaterite is not.

Many studies have been done on the factors which control the formation of the polymorphism of calcium carbonate[1-11),13)]. The results indicated that one of the most important factors controlling the crystal form of natural calcium carbonates is the presence of Mg^{2+} in a parent solution which favors aragonite formation and inhibits vaterite and calcite formation. However, the mechanism for the influence of Mg^{2+} has not been clarified.

$MgCO_3$ and $CuCO_3$ have only the crystal form of calcite, and $BaCO_3$ only of aragonite. The authors found the interesting facts that the presence of Mg^{2+} and Cu^{2+} in a parent solution favors aragonite formation and the presence of Ba^{2+} favors calcite formation[3,4,12)]. Then the authors have examined the effects of various heavy metal ions having various ionic radius on the crystal form of calcium carbonate formed from the parent solution, as one of the steps to clarify the mechanisms for the influence of metal ions.

2. Experimental

Carbonate was precipitated in the following six solution systems :

1. $Ca(HCO_3)_2 + Me^{2+} \xrightarrow[\text{always stirred}]{36\pm2°C}$ carbonate
2. $Ca(HCO_3)_2 + Me^{2+} \xrightarrow[\text{sometimes stirred}]{34\pm2°C}$ carbonate
3. $Ca(HCO_3)_2 + Me^{2+} \xrightarrow[\text{sometimes stirred}]{40\pm2°C}$ carbonate
4. $Ca(HCO_3)_2 + Me^{2+} \xrightarrow[\text{boiling}]{97\pm2°C}$ carbonate
5. $Ca(HCO_3)_2 + \text{glycine} + Me^{2+} \xrightarrow[\text{always stirred}]{36\pm2°C}$ carbonate
6. $Ca(HCO_3)_2 + NaCl + Me^{2+} \xrightarrow[\text{boiling}]{97\pm2°C}$ carbonate

The effects of metal ions on the crystal form of calcium carbonate at low temperature are observed in the solution systems 1, 2, and 3. Since the stirring of solution has a great influence on the crystal form of calcium carbonate precipitated from the solution, the condition of stirring was controlled in the present experimets[3,14)]. Aragonite proportions of precipitates formed from calcium bicarbonate solutions without metal ions were 0 to 20 per cent under the conditions of the systems 1,2 and 3, and 80 to 90 per cent under the condition of the system 4. Pure calcite was precipitated from the solution containing copper ions and pure aragonite from the solution containing zinc ions under the condition of the system 5[12)]. Vaterite formation is favored from the calcium bicarbonate solution containing sodium chloride at boiling[5)]. Then it is expected that the effects of metal ions on vaterite formation are seen from the experiments in the solution system 6.

Solutions and Materials

Magnesium chloride favors aragonite formation more greatly than magnesium sulfate[4]. The solubility of calcium sulfate is fairly small. Then, metal nitrates or chloride (copper nitrate, zinc nitrate, nickel nitrate, manganese nitrate, magnesium chloride, lead nitrate, and mercury nitrate) in reagent grade were used.

Calcium bicarbonate solution : A calcium carbonate suspension in distilled water was bubbled with carbon dioxide gas for three to four hours, allowed to stand for thirty minutes and filtered. The filtrate was bubbled again with carbon dioxide gas for one and half hours (calcium content : 0.4 g/1).

Procedure

Different amounts of the solution of metal nitrate or chloride and one liter of calcium bicarbonate solution were placed into one liter erlenmeyer flasks. In certain cases, sodium chloride and glycine were added to the solution as solid or solution. The flasks were stoppered with cotton, and placed in water bath at about 34°, 36°, 40° or 50°C. In some experiments, parent soutions were boiled. As carbon dioxide gas escaped from the parent solution, calcium carbonate was precipitated. pH and calcium of the solution were determined at the start and the end of the precipitation process. Eventually, the precipitates were filtered off and washed with distilled water until they became free from the parent solution. After having been dried in an air, the precipitates were used for the identification of the crystal form by the X-ray diffraction.

3. Results and Discussion

$$(1).\ Ca(HCO_3)_2 + Me^{2+} \xrightarrow[\text{always stirred}]{36\pm2°C} \text{carbonate}$$

The experimental results are shown in Fig. 1. The extent of the influences on the forming of aragonite increases in the following sequence, although the influences of Zn^{2+} and Mn^{2+} are very complex : $Cu^{2+} > Zn^{2+}$, $Ni^{2+} > Mn^{2+} > Mg^{2+}$. The minimum proportion of aragonite appeared at the concentration of 8×10^{-2} meq/1 of zinc ions in the original parent solution. The maximum proportion of aragonite appeared at the concentration of 10 meq/1 of manganese ions. The values of the second ionization potential, the solubility product of $MeCO_3$ in distilled water, ionic radius and the stability constant of the complex of element and glycine are shown in Table 1.

Table 1. The second ionization potential[I_2 (V)], the solubility product of $MeCO_3$ in distilled water (K_{sp}), ionic radius[$R_{Me^{2+}}$(Å)] and the stability constant (β) of complex between metal ion (Me^{2+}) and glycine

Element, Me	I_2 (V)	log $K_{sp}(MeCO_3)$	$R_{Me^{2+}}$(Å)	logβ
Pb	15.02	−12.95	1.24	—
Mg	15.03	− 6.88	0.66	3.44
Mn	15.64	−11.57	0.80	5.5
Zn	17.96	− 9.15	0.71	9.3
Ni	18.15	− 6.88	0.69	11.12
Cu	20.29	− 9.61	0.72	15.38

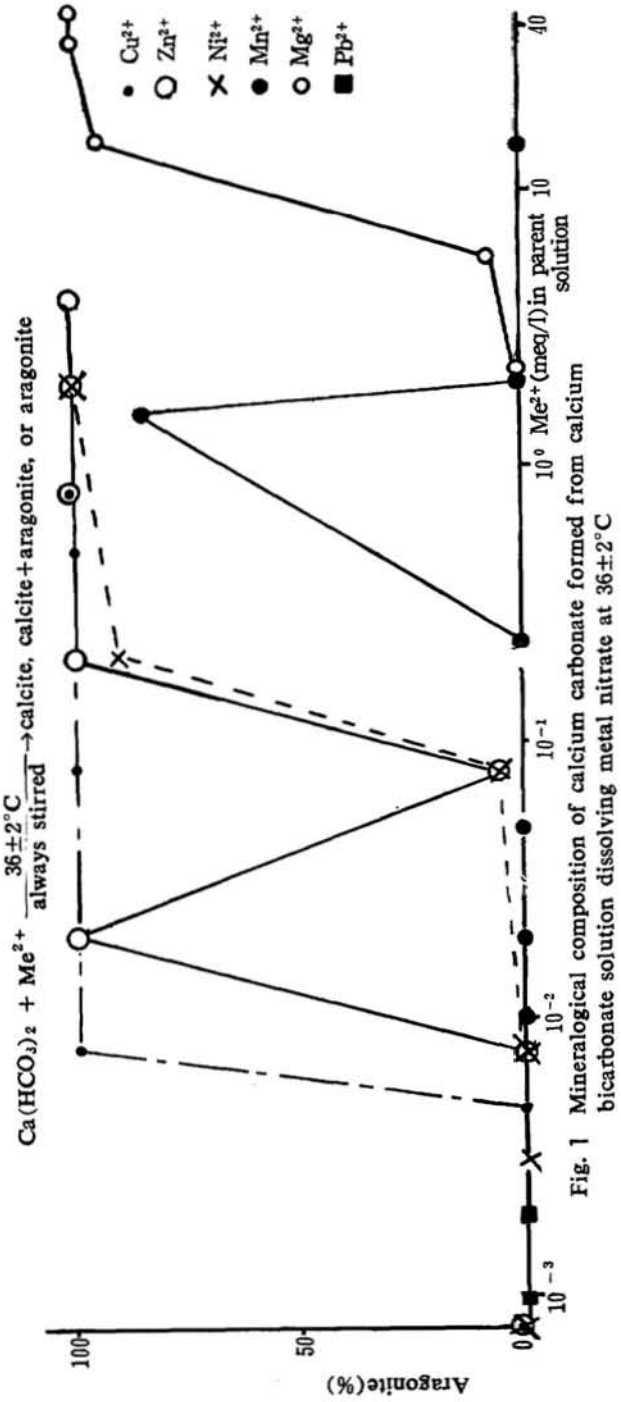

Fig. 1 Mineralogical composition of calcium carbonate formed from calcium bicarbonate solution dissolving metal nitrate at 36±2°C

It is shown from Fig. 1 and Table 1 that the sequences of the value of the second ionization potential and the stability constant of complex are in agreement with that of the extent of the effect of metal ions in a parent solution on aragonite formation. Thus, we would expect that metals dissolved as both complex and free ion are much more favorable for aragonite formation than those dissolved as either complex or free ion. However, the reasons for the appearance of the minimum aragonite content at certain concentration of zinc ions and for the appearance of the maximum aragonite content at certain concentration of manganese ions have not been clarified.

The influences of Cu^{2+} in a parent solution at about 32° and 36°C are shown in Fig. 2, which indicates that aragonite formation seems to be favored at high temperature rather than at low temperature.

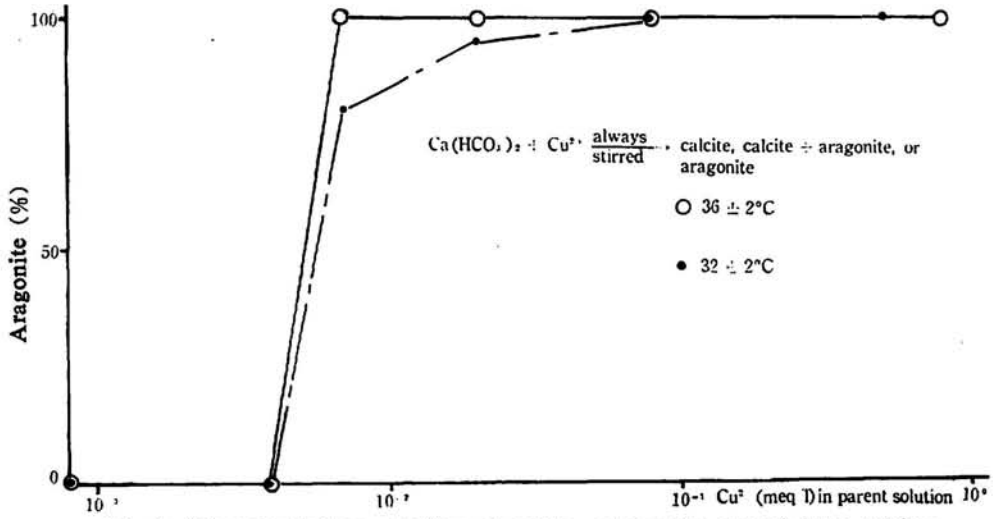

Fig. 2 Mineralogical composition of calcium carbonate formed from calcium bicarbonate solution dissolving copper nitrate at 32±2°C and 36±2°C

The rate of precipitation decreased with increasing concentration of metal ions in a parent solution[4,10,13]. And the presence of Cu^{2+} in a parent solution, which favored aragonite formation most greatly, reduced the rate of precipitation of calciun carbonate most greatly.

$$(2).\ Ca(HCO_3)_2 + Me^{2+} \xrightarrow[\text{sometimes stirred}]{40\pm2^\circ C} \text{carbonate}$$

The experimental rerults are given in Fig. 3, which indicates that the extent of the influences of metal ions in a parent solution on the forming of aragonite increases in the following sequence : $Cu^{2+} > Zn^{2+}$, $Ni^{2+} > Mg^{2+}$. The influence of Pb^{2+} was not examined in detail and clearly, because the solubility of $PbCO_3$ is very small and therefore only a very small amount of Pb^{2+} is added to the parent solution. Pb^{2+} does not seem to favor aragonite formation, though it is not very clear. A solid solution $(Ca,Mn)CO_3$ was easily formed from the calcium bicarbonate solution containing Mn^{2+} in fairly large amounts, which was identified by the X-ray diffractometer. The maximum aragonite content at certain concentration of Mn^{2+} was not observed in this solution (see Fig.3 with Fig.1). The minimum aragonite content was observed at certain concentration of Zn^{2+} under the various temperature conditions, as seen from Fig. 4.

$$Ca(HCO_3)_2 + Me^{2+} \xrightarrow[\text{sometimes stirred}]{40 \pm 2^\circ C} \text{aragonite, or calcite+aragonite}$$

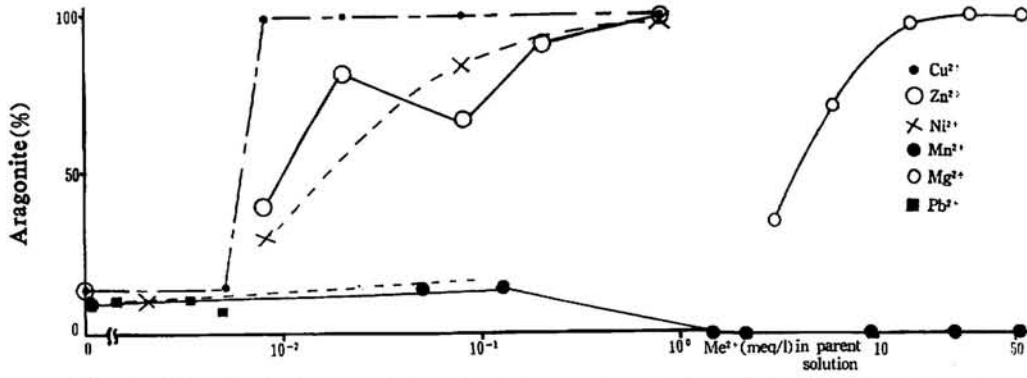

Fig. 3 Mineralogical composition of calcium carbonate formed from calcium bicarbonate solution dissolving metal nitrate at $40 \pm 2^\circ C$

$$Ca(HCO_3)_2 + Zn^{2+} \longrightarrow \text{calcite, calcite + aragonite, or aragonite}$$

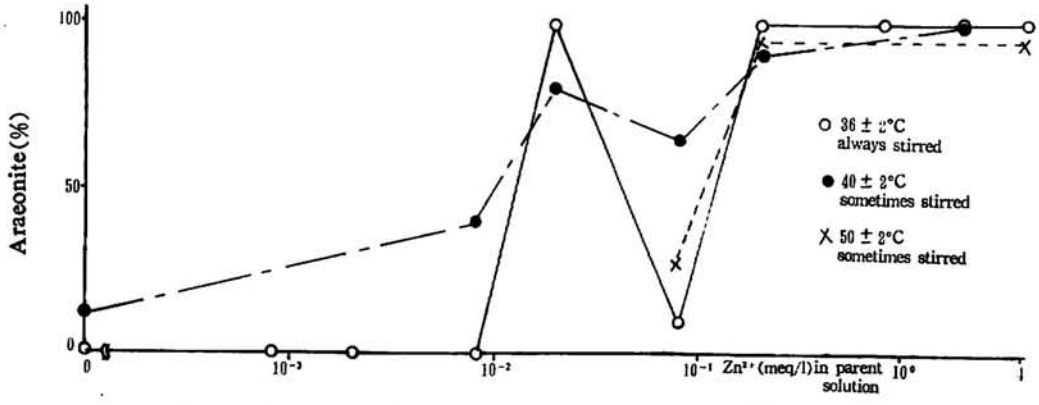

Fig. 4 Mineralogical composition of calcium carbonate formed from calcium bicarbonate solution dissolving zinc nitrate at $36 \pm 2^\circ$, $40 \pm 2^\circ$ and $50 \pm 2^\circ C$

(3). $Ca(HCO_3)_2 + Me^{2+} \xrightarrow[\text{boiling}]{97\pm2°C} \text{carbonate}$

The solution was boiled in this system. It took ten to fifteen minutes to begin to boil. The solution was boiled for about thirty minutes and precipitates were filtered off and collected. The reproducible precipitates were very difficult to be obtained especially from calcium bicarbonate solution without metal ions under the condition of boiling.

Fig. 5 shows the experimental results from which the following facts are known : Under the condition of boiling, pure aragonite was very difficult to be precipitated even from the calcium bicarbonate solutions containing Cu^{2+}, Zn^{2+} and Ni^{2+}, and the minimum aragonite content was observed at certain concentration of Cu^{2+}, Zn^{2+} and Ni^{2+} in this system. The influence of Mn^{2+} in this system is shown in Fig. 6.

(4). $Ca(HCO_3)_2 + \text{glycine} + Me^{2+} \xrightarrow[\text{always stirred}]{36\pm2°C} \text{carbonate}$

The authors examined the influence of metal ions, coexisting with organic material which forms complexes with the metal ions, on the crystal form of precipitated calcium carbonate. As the organic material, glycine was chosen. Kitano and Hood[10] reported that the presence of glycine in a parent solution favors the formation of vaterite and aragonite. To know the influence of metal ions in this system, the influence of glycine was first examined in detail.

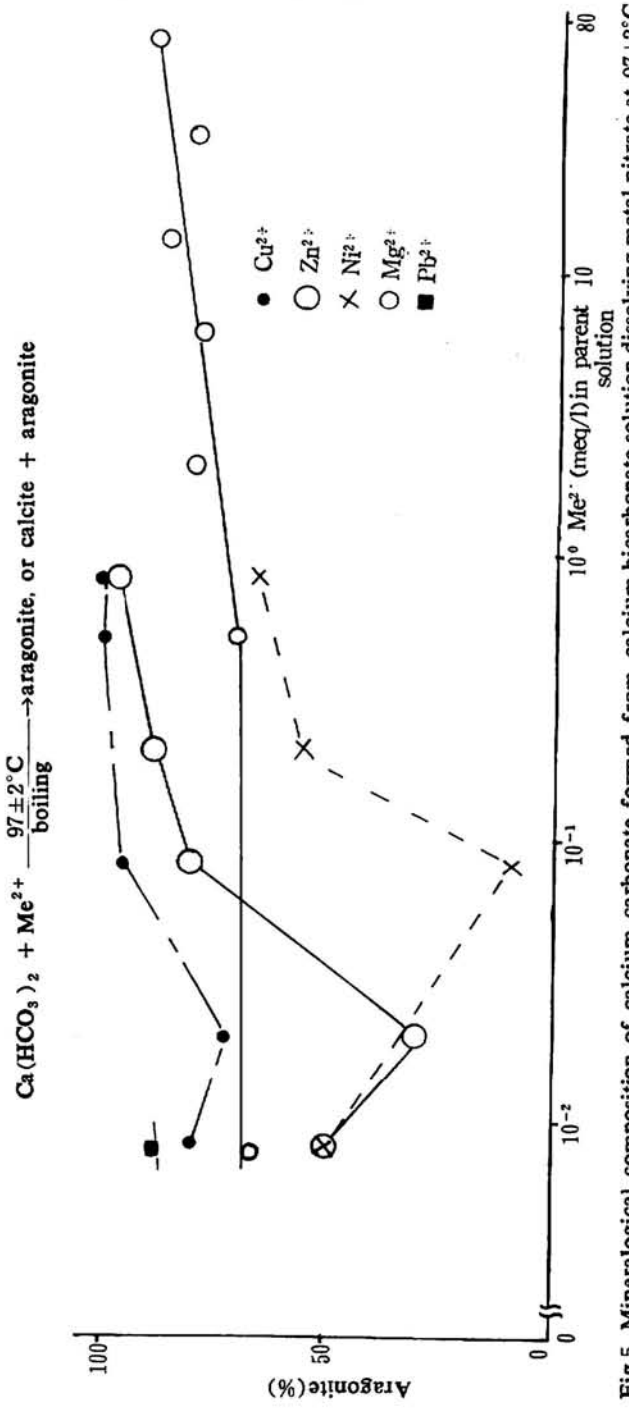

Fig.5 Mineralogical composition of calcium carbonate formed from calcium bicarbonate solution dissolving metal nitrate at 97±2°C

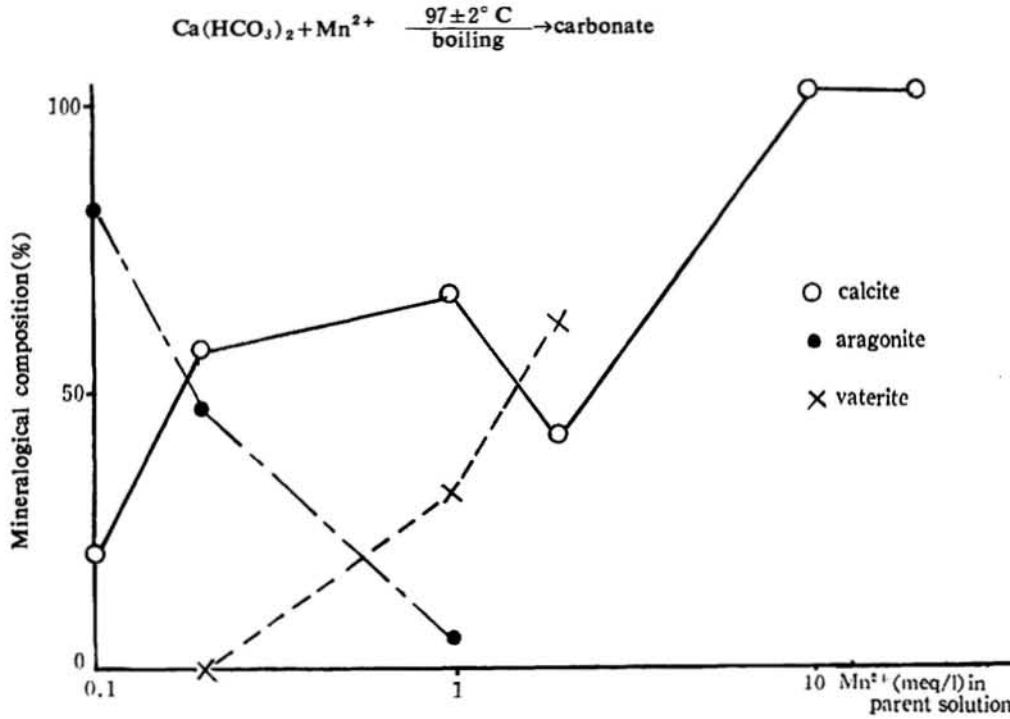

Fig. 6 Mineralogical composition of calcium carbonate formed from calcium bicarbonate solution dissolving manganese nitrate at 97 ± 2°C

(4-1) $Ca(HCO_3)_2$+glycine(0−5 g/l) $\frac{20\pm1°C}{\text{always stirred}}$ carbonate

Pure calcite was always precipitated in this solution system.

(4-2) $Ca(HCO_3)_2$+glycine(5 g/l) $\frac{30\pm2°C}{\text{always stirred}}$ carbonate

The experimental results are shown in Fig. 7, which indicates that the proportion of vaterite in carbonate precipitates increases with increasing rate of precipitation.

$$Ca(HCO_3)_2 + \text{glycine } (5\ g/\ell) \xrightarrow[\text{always stirred}]{30\pm2^\circ C} \text{calcite, or calcite + vaterite}$$

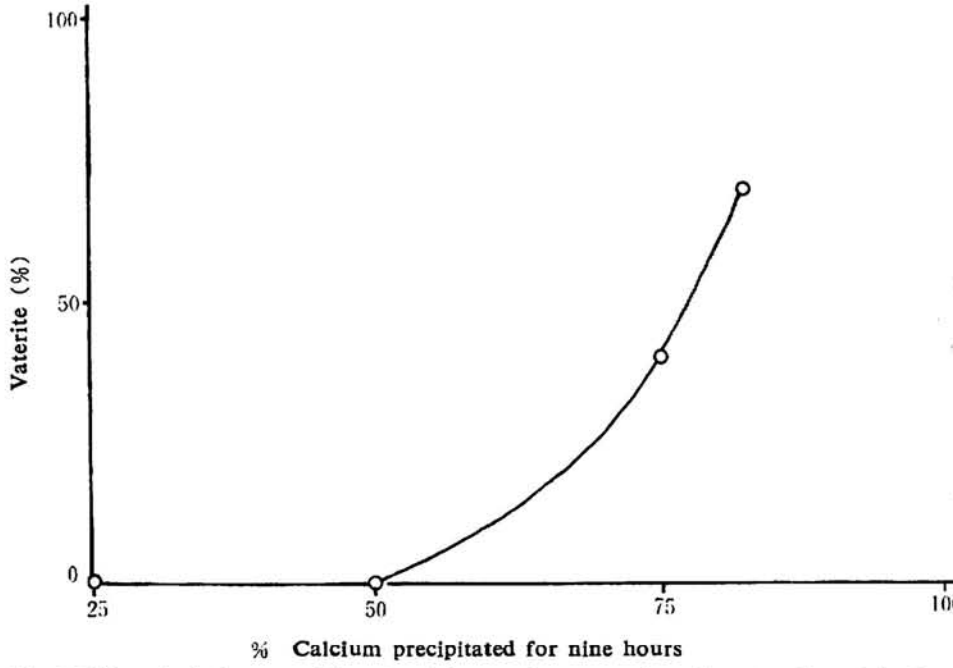

Fig. 7 Mineralogical composition of calcium carbonate against the rate of precipitation

$$\text{(4-3)} \quad Ca(HCO_3)_2 + \text{glycine}(0-10\ g/1) \xrightarrow[\text{sometimes stirred}]{33\pm1^\circ C} \text{carbonate}$$

Carbonate precipitates formed for 21 days were collected. The proportion of vaterite and aragonite in carbonate precipitates increased with increasing concentration of glycine.

$$\text{(4-4)} \quad Ca(HCO_3)_2 + \text{glycine}(0-20\ g/1) \xrightarrow[\text{sometimes stirred}]{50\pm2^\circ C} \text{carbonate}$$

Carbonate precipitates formed for 5 days were collected, and the results are shown in Fig.8. The figure indicates that the proportion of aragonite increases with increasing concentration of glycine.

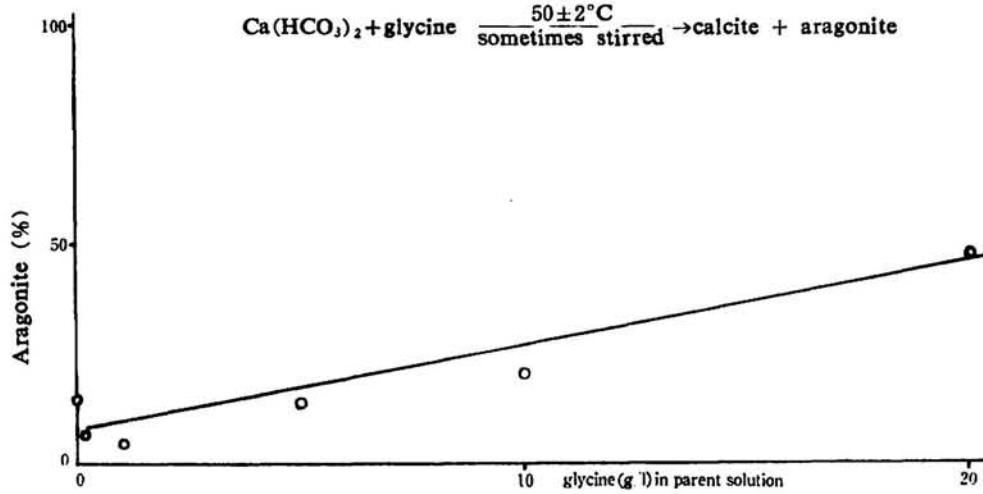

Fig. 8 Mineralogical composition of calcium carbonate formed from calcium bicarbonate solution dissolving glycine at 50±2°C

(4-5) $Ca(HCO_3)_2$+glycine(0−10 g/1) $\xrightarrow[\text{boiling}]{97\pm2°C}$ carbonate

Carbonate precipitates formed for thirty minutes were collected. The experimental results are shown in Fig. 9, which indicates that the presence of glycine in a parent solution favors the formation of vaterite and calcite and inhibits that of aragonite.

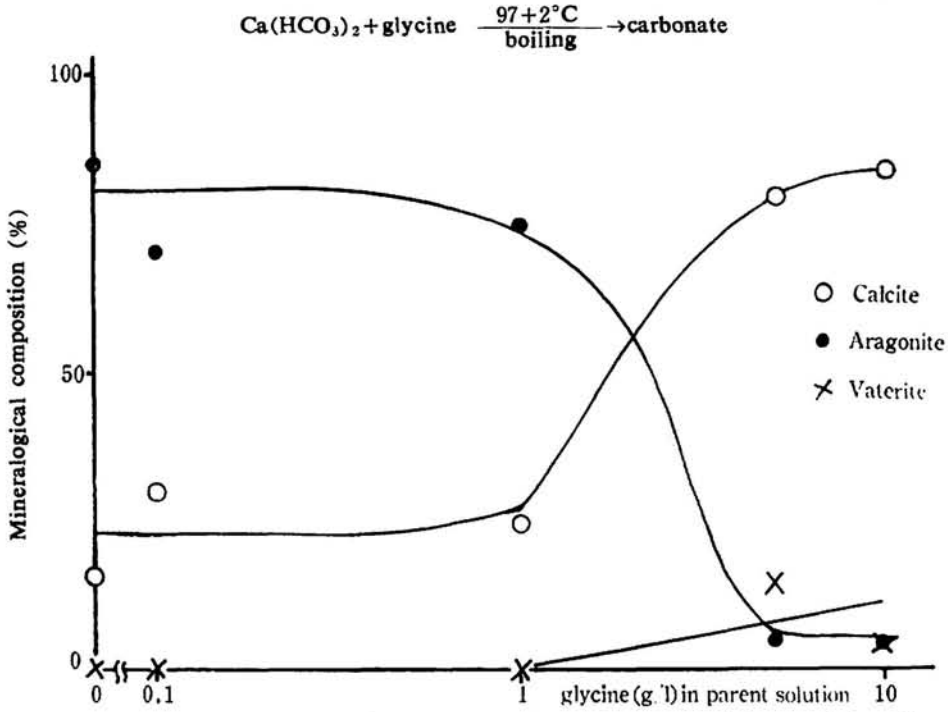

Fig. 9 Mineralogical composition of calcium carbonate formed from calcium bicarbonate solution dissolving glycine at 97±2°C

The rate of carbonate precipitation decreases with increasing concentration of glycine in the parent solutions of the systems (4-1) to (4-5).

(4-6) $Ca(HCO_3)_2$ + glycine + Zn^{2+} ⟶ carbonate

The experimental results are shown in Fig. 10, which shows a plot of the proportion of aragonite in precipitated carbonate against the concentration of zinc dissolved in the calcium bicarbonate parent solution with glycine. The value of the stability constant between zinc ions and glycine, $[Zn^{2+}][Glycine^-]^2 / [Zn\text{-}Glycine_2^0]$, is $10^{-9.4}$. Fig. 10 shows that the influence of zinc in the parent solution on the formation of aragonite increases with increasing concentration of glycine added to the parent solution up to a certain concentration, and then decreases with a further increase in the concentration of glycine. This indicates that zinc dissolved in the parent solution in both complex and free ionic forms is much more favorable for the formation of aragonite than in either complex or free ionic form alone.

$$Ca(HCO_3)_2 + Zn^{2+} + (\text{glycine}) \xrightarrow[\text{always stirred}]{36\pm2^\circ C} \text{calcite, calcite+aragonite, or aragonite}$$

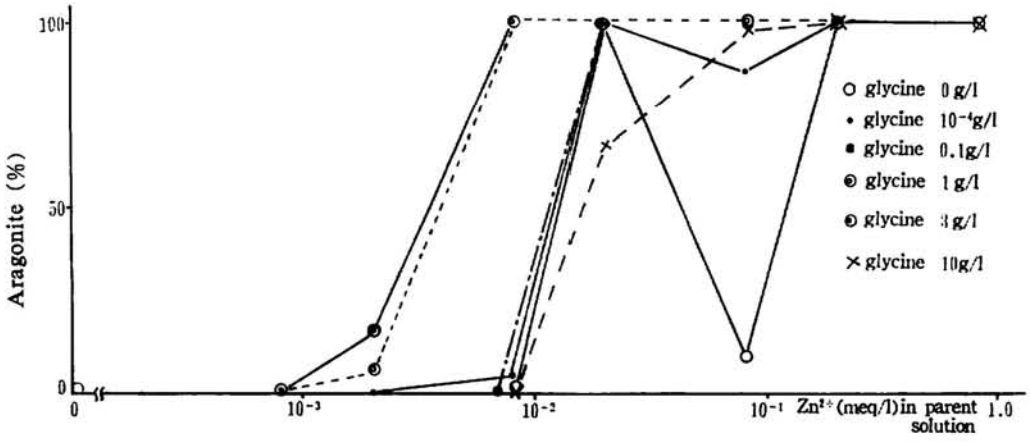

Fig. 10 Mineralogical composition of calcium carbonate formed from calcium bicarbonate solution dissolving zinc nitrate and glycine at 36±2°C

(4-7) $Ca(HCO_3)_2$ + glycine + Cu^{2+} ⟶ carbonate

The experimental results are shown in Fig. 11, from which it can be seen that the influence of Cu^{2+} in a parent solution on the favoring of aragonite formation is reduced greatly by the addition of glycine to the parent solution.

$$Ca(HCO_3)_2 + Cu^{2+} + (\text{glycine}) \xrightarrow[\text{always stirred}]{36\pm2^\circ C} \text{calcite, calcite+aragonite, or aragonite}$$

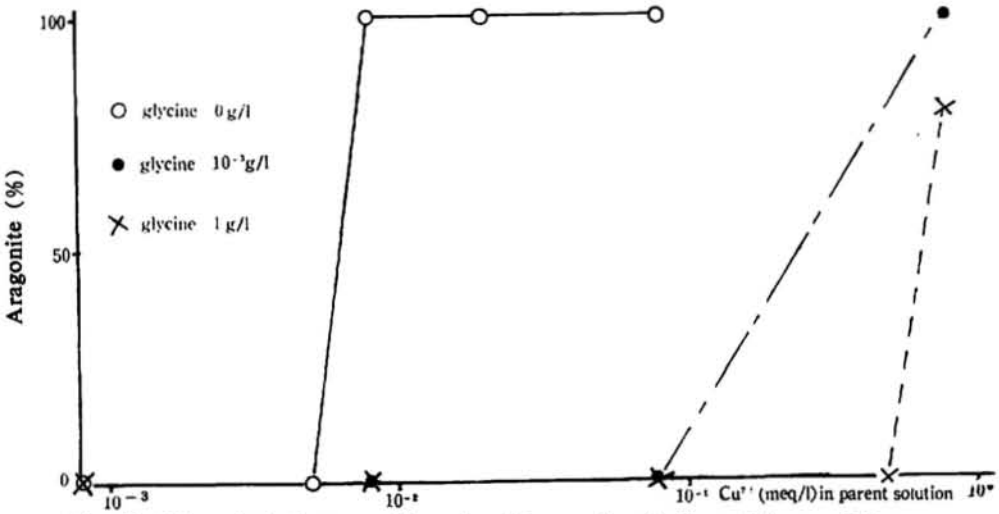

Fig. 11 Mineralogical composition of calcium carbonate formed from calcium bicarbonate solution dissolving copper nitrate and glycine at 36±2°C

(4-8) $Ca(HCO_3)_2$ + glycine + Ni^{2+} ——→carbonate

The experimental results are shown in Fig. 12, from which it is seem that the effect of Ni^{2+} in a parent solution on the favoring of aragonite formation is reduced by the addition of glycine to the parent solution.

$$Ca(HCO_3)_2 + Ni^{2+} + (\text{glycine}) \xrightarrow[\text{always stirred}]{36\pm2^\circ C} \text{calcite, calcite+aragonite, or aragonite}$$

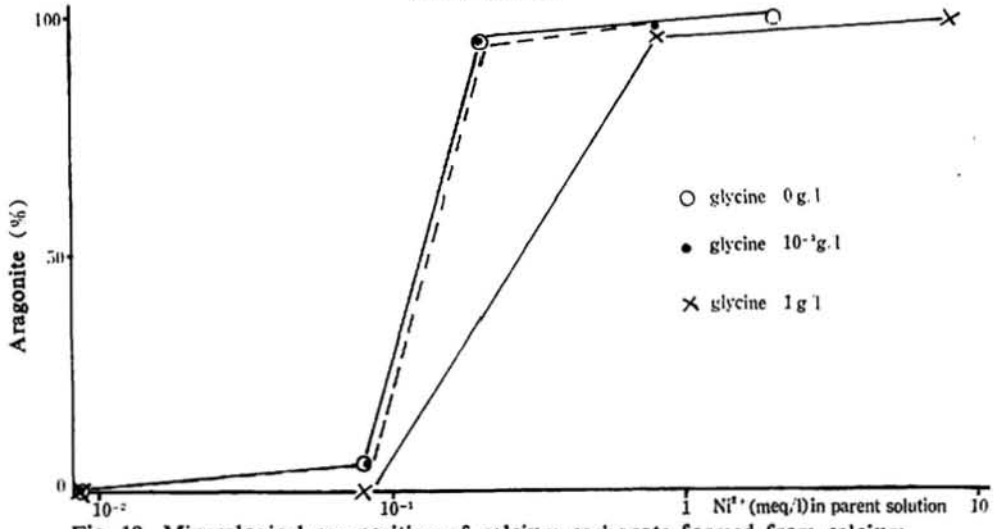

Fig. 12 Mineralogical composition of calcium carbonate formed from calcium bicarbonate solution dissolving nickel nitrate and glycine at 36±2°C

(4-9) $Ca(HCO_3)_2$+glycine+ Mn^{2+} ——→carbonate

(4-10) $Ca(HCO_3)_2$+glycine+ Mg^{2+} ——→carbonate

(4-11) $Ca(HCO_3)_2$+glycine+ Hg^{2+} ——→carbonate

The experimental results are shown in Figs. 13, 14 and 15, which indicate that glycine favors aragonite formation.

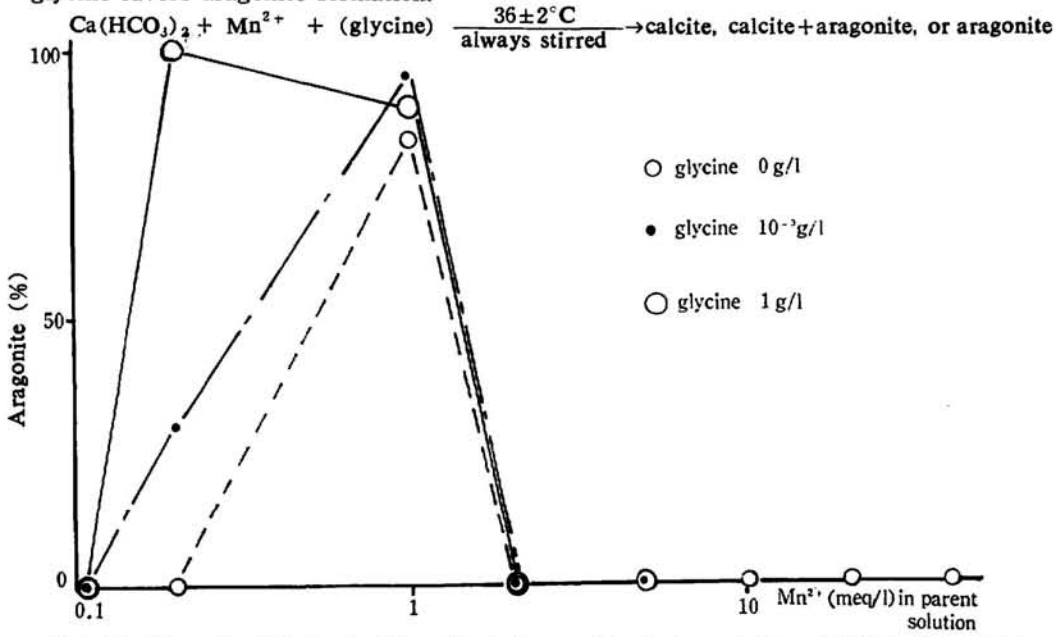

Fig. 13 Mineralogical composition of calcium carbonate formed from calcium bicarbonate solution dissolving manganese nitrate and glycine at 36±2°C

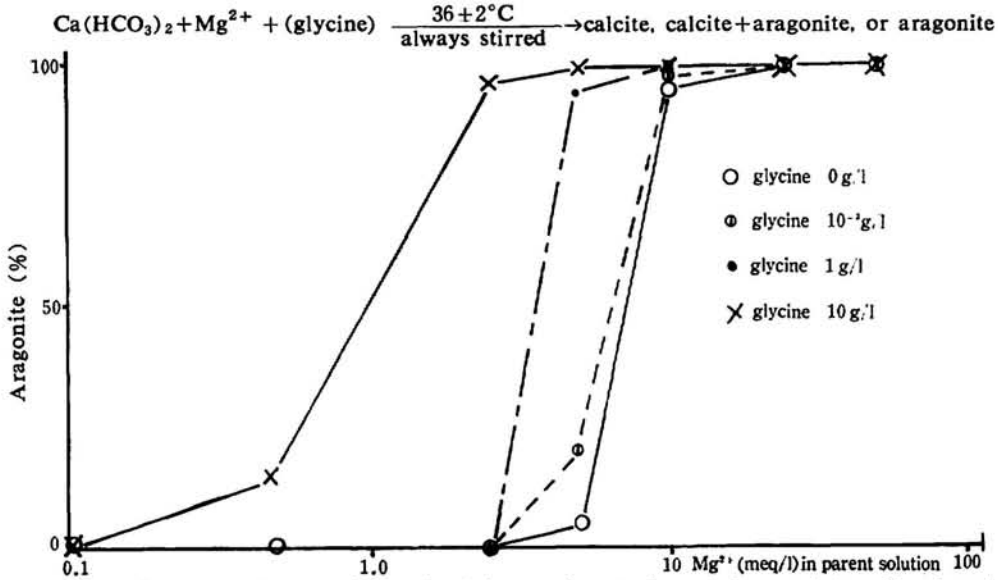

Fig. 14 Mineralogical composition of calcium carbonate formed from calcium bicarbonate solution dissolving magnesium chloride and glycine at 36±2°C

$$Ca(HCO_3)_2 + Hg^{2+} + (\text{glycine}) \xrightarrow[\text{always stirred}]{36\pm2^\circ C} \text{calcite, or calcite + aragonite}$$

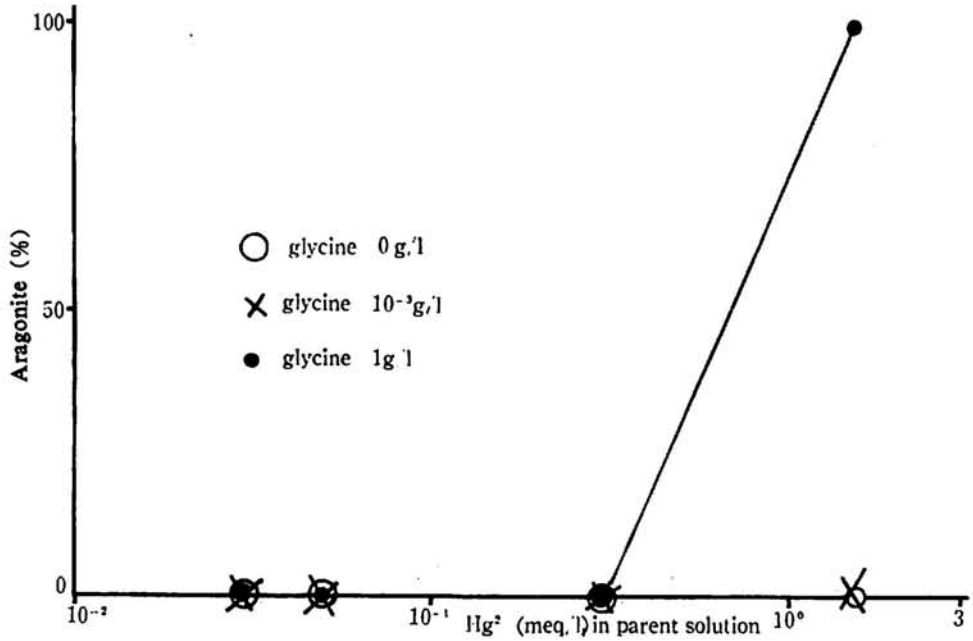

Fig. 15 Mineralogical composition of calcium carbonate formed from calcium bicarbonate solution dissolving mercuric nitrate and glycine at 36±2°C

(4-12) $Ca(HCO_3)_2$ + glycine (10^{-3} , 1 g/1) + Pb^{2+} ——→carbonate

Pure calcite was precipitated in this system.

(5). $Ca(HCO_3)_2$ + NaCI(20 g/1) + Me^{2+} $\xrightarrow[\text{boiling}]{97\pm2^\circ C}$ carbonate

The experimental results reported by Kitano[5] indicated that vaterite is very easily precipitated by boiling the calcium bicarbonate solution containing sodium chloride and the presence of Mg^{2+} in a parent solution inhibits vaterite formation (Figs. 16 and 17). The effects of metal ions, smaller than calcium in ionic radius, are chiefly examined on vaterite formation, by the identification of the crystal form of carbonates formed by boiling the calcium bicarbonate solutions containing sodium chloride (20 g/1) and the metal ions.

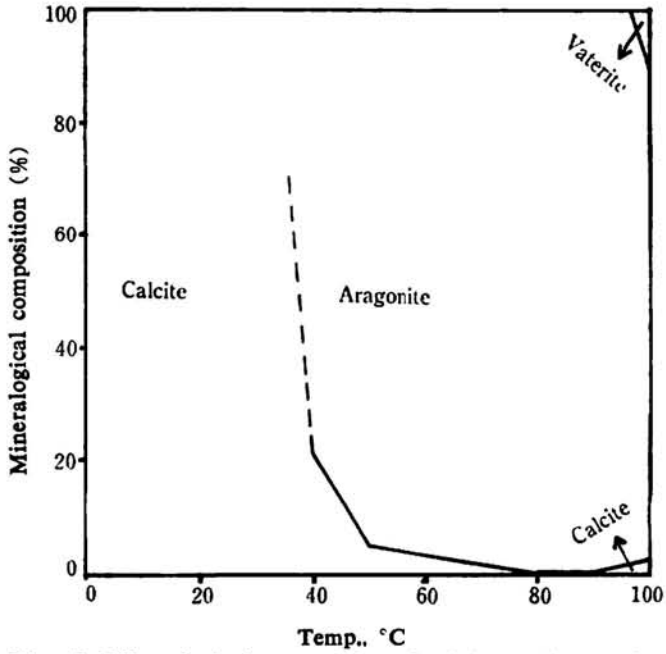

Fig. 16 Mineralogical composition of calcium carbonate formed from calcium bicarbonate solution dissolving sodium chloride (5g/ℓ)and magnesium chloride (0.7g/l). (After Kitano, 1962b)

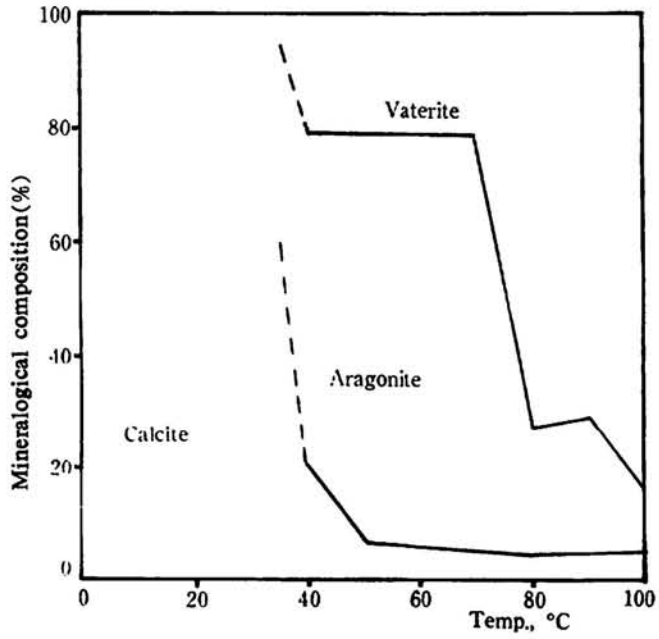

Fig. 17 Mineralogical composition of calcium carbonate formed from calcium bicarbonate solution dissolving sodium chloride (5g/ℓ) and magnesium chloride (0.07g/ℓ). (After Kitano, 1962b)

(5-1) $Ca(HCO_3)_2 + NaCl + Cu^{2+} \longrightarrow$ carbonate

(5-2) $Ca(HCO_3)_2 + NaCl + Zn^{2+} \longrightarrow$ carbonate

(5-3) $Ca(HCO_3)_2 + NaCl + Mg^{2+} \longrightarrow$ carbonate

The experimental results are shown in Figs. 18, 19 and 20, which indicate that the presence of Cu^{2+}, Zn^{2+} and Mg^{2+} in a parent solution favors aragonite formation, and inhibits calcite and vaterite formation (see Figs. 16 and 17, too). The influences of Cu^{2+} and Zn^{2+} on the inhibition of calcite and vaterite formation are greater than that of Mg^{2+}.

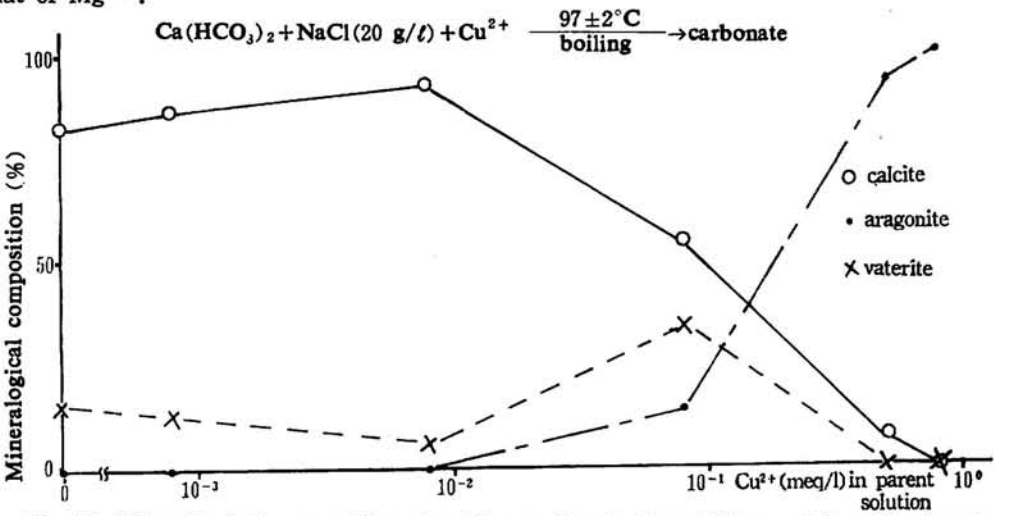

Fig. 18 Mineralogical composition of calcium carbonate formed from calcium bicarbonate dissolving copper nitrate and sodium chloride at 97±2°C

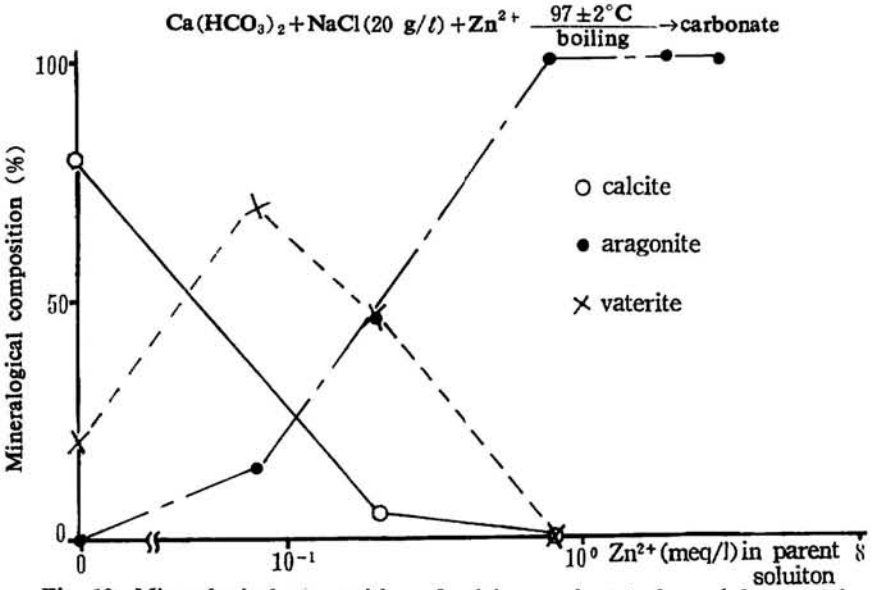

Fig. 19 Mineralogical composition of calcium carbonate formed from calcium bicarbonate solution dissolving zinc nitrate and sodium chloride at 97±2°C

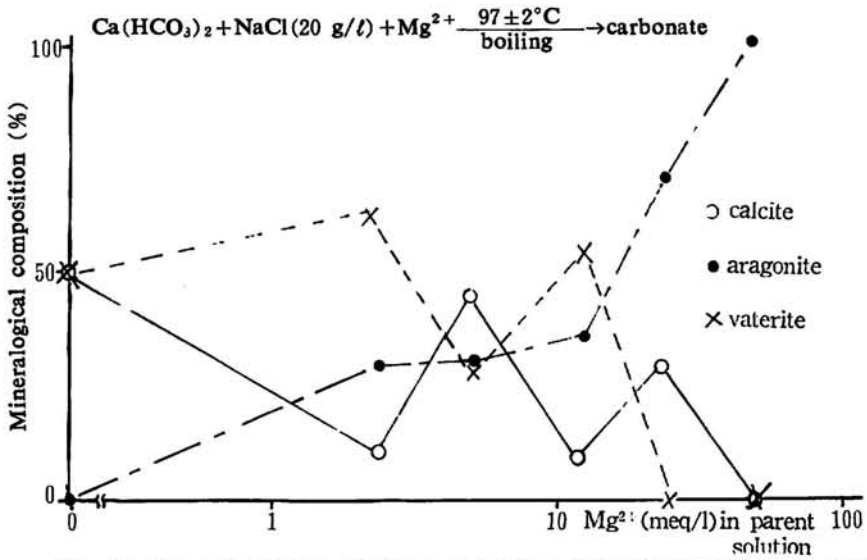

Fig. 20 Mineralogical composition of calcium carbonate formed from calcium bicarbonate solution dissolving magnesium chloride and sodium chloride at 97±2°C

(5-4) $Ca(HCO_3)_2 + NaCl + Ni^{2+}$ ——→carbonate

The experimental results are shown in Fig. 21, which indicates that the presence of Ni^{2+} seems to inhibit vaterite formation and to favor aragonite formation.

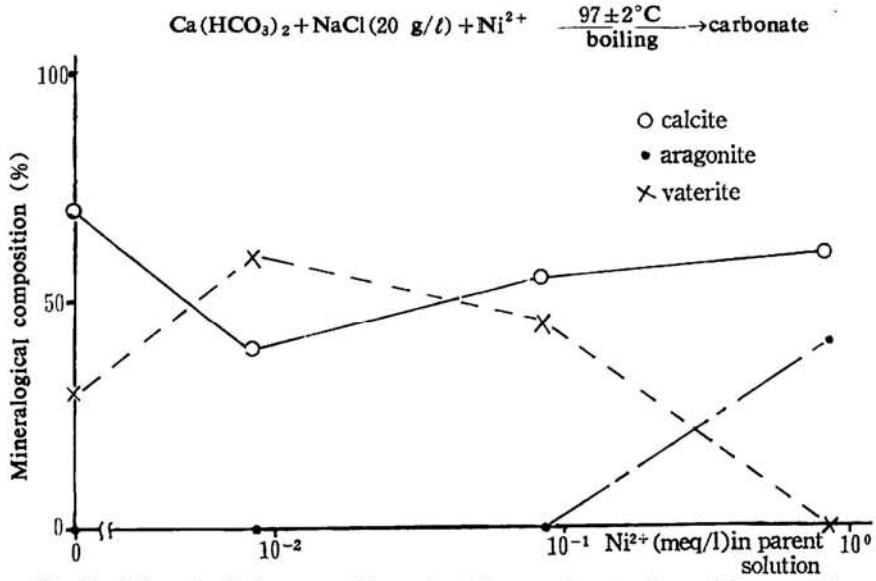

Fig. 21 Mineralogical composition of calcium carbonate formed from calcium bicarbonate solution dissolving nickel nitrate and sodium chloride at 97±2°C

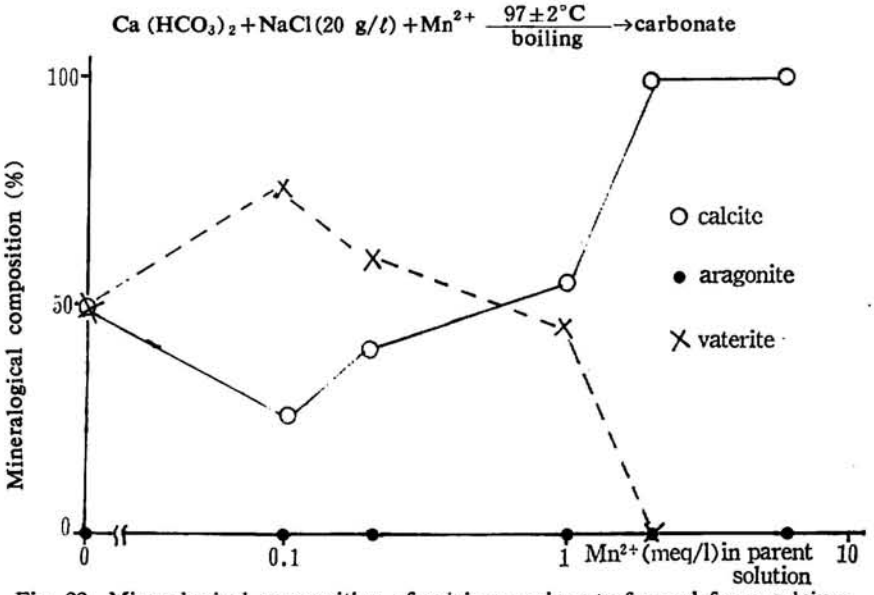

Fig. 22 Mineralogical composition of calcium carbonate formed from calcium bicarbonate solution dissolving manganese nitrate and sodium chloride at 97±2°C

(5-5) $Ca(HCO_3)_2$ + NaCl + Mn^{2+} ——→carbonate

The experimental results are shown in Fig. 22, which indicates that the presence of Mn^{2+} inhibits vaterite formation.

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