A Study of the Polymorphic Formation of Calcium Carbonate in Thermal Springs with an Emphasis on the Effect of Temperature

By Yasushi KITANO

(Received July 16, 1962)

The conditions which determine the polymorphic crystallization of calcium carbonate have been discussed by many researchers[1-9]; however, many questions still remain unsolved. The temperature of the mother solution should be considered as one of the most important factors controlling the polymorphic formation. It has been reported that aragonite was formed easily from a solution at a temperature above 50°C, but this conclusion is not always reliable[3]. In the following discussion of the conditions of the polymorphic formation of calcium carbonate, the combined effect of the temperature and of the materials in the mother solution is examined. The author has attempted to show this combined effect on the formation of the various crystal forms of calcium carbonate in the thermal springs of Japan, such springs being typical areas of calcium carbonate deposition.

Crystal Forms of Calcium Carbonate Deposited in Thermal Springs of Japan.—Table I shows the chemical constituents of the thermal spring waters in Japan from which calcium carbonate deposits have been formed and the crystal forms of this calcium carbonate. Related articles have showen that the presence of sodium chloride, magnesium chloride and carbon dioxide in the mother solution greatly affects the polymorphic crystallization of calcium carbonate[10,11]. On the basis of their sodium, magnesium and chloride ion content, the spring waters are classified in two typical groups, A and B, as is shown in Table I.

Experimental and Results

When thermal waters come to the surface of the earth, they are subjected to a sudden environmental change, exposure to the air at an atmospheric pressure. Then, on the one hand, carbon dioxide gas escapes from the water to precipitate calcium carbonate, and on the other, some of the ferrous and manganous ions begin to be oxidized by the air.

Calcium carbonate is formed in thermal springs according to the following reaction: $Ca^{2+}+2HCO_3^- \rightarrow CaCO_3+CO_2+H_2O$. Therefore, the effect of temperature upon the polymorphic formation of calcium carbonate formed from a calcium bicarbonate solution has been studied in the laboratory. For the preparation of the calcium bicarbonate solution,

---

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

[6] J. W. Mellor, "A Comprehensive Treatise on Inorganic and Theoretical Chemistry", Vol. 3, Longmans, Green and Co., London (1923).

[7] J. W. Murray, *J. Geol.*, **62**, 481 (1954).

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

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

[10] Y. Kitano, This Bulletin, **35**, 1973 (1962).

[11] Y. Kitano and D. W. Hood, *J. Ocea. Soc. Japan*, **18**, 141 (1962).

TABLE I. CHEMICAL CONSTITUENTS OF THERMAL SPRING WATERS AND THE CRYSTAL FORMS OF DEPOSITED CALCIUM CARBONATE

Thermal springs	Temp. °C	pH	Ions, g./l. Na$^+$	K$^+$	Ca^{2+}	Mg^{2+}	Cl$^-$	SO$_4^{2-}$	HCO$_3^-$		Vaterite %	Calcite %	Aragonite %
Futamata	35～50	6.5～6.6	1.5～2.5	0.42～0.73	0.54～0.83	0.11～0.16	3.3～5.3	0.09～0.13	1.2～1.7	A***	0	100*	0
Yunokawa	66	6.7	2.2	0.17	0.61	0.19	4.1	0.82	0.88	A	0	3～0	97～100
Yatsu	100	8.6	0.4	0.009	0.056	0.13	0.53	0.64	0.16	A	0	8	92
Masutomi	26～32	6.0～6.3	2.4～3.3	0.04～0.23	0.30	0.02	3.9～4.2	0.51～0.63	1.2～2.0	B	0	100	0
Senami	?～100	7.9	1.3	0.03	0.11	0.002	2.0	0.25	0.15	B	0	100	0**
Shirahama	64～79	7.4～7.9	1.5～3.7	0.07～0.26	0.04～1.1	0.01～0.57	1.0～4.4	0.25～0.94	2.3～4.7	A/B	0	0	100
Teshikaga	50～70	8.3～8.5	0.56～0.78	0.01～0.02	0.07～0.23	0.002～0.005	0.92～1.3	0.09～0.18	0.14～0.22	B	0	3～1	97～99
Shiobara	66		0.44	0.04	0.08	0.02	0.62	0.07	0.40	B?	0	100	0
Ikaho	40～50	5.2～6.1	0.06～0.09	0.006～0.02	0.10～0.25	0.02～0.05	0.07～0.18	0.19～0.39	0.28～0.70	B?	0	100	0
Hisayoshi	42	5.8	0.18	0.008	0.48	0.05	0.29	0.66	0.88	B?	0	100	0
Shikabe	80～100	7.0～8.1	0.7～1.2	0.04～0.09	0.07～0.10	0.008～0.013	0.73～1.6	0.40～0.48	0.23～0.46	B?	0	16～0	84～100
Mine	100	8.6	0.73	0.04	0.06	0.0007	1.1	0.16	0.080	B?	0	1～0	99～100
Atakawa	?～100	8.2～8.5	0.5～0.74	0.09～0.11	0.11～0.13	0.004～0.016	0.4～1.2	0.27～0.46	0.05～0.11	B?	0	100	0
Nigorikawa	50～90	5.9～7.3	0.4～1.4	0.04～0.14	0.1～0.16	0.04～0.05	0.5～2.3	0.007～0.04	0.8～1.4	B?	0	100～77	0～23
Fushime	100	7.2	3.8	0.32	0.63	0.012	7.3	0.11	0.06	B	0	13	87

* Aragonite was observed in some special stations (Table IV).

** Qnly one sample was of pure aragonite configuration.

*** Group A: NaCl, 5 g./l.; MgCl$_2$, 0.7 g./l.

Group B: NaCl, 5 g./l.; MgCl$_2$, 0.07 g./l.

carbon dioxide gas was bubbled into a suspension of 40 g. of calcium carbonate in 20 l. of distilled water for 48 hr. at room temperature and filtered (Whatman No. 3 filter paper) ; and then carbon dioxide gas was bubbled again into the filtrate for 2 hr. The calcium content was 300 mg. per liter. The bicarbonate solution prepared at room temperature was used throughout the present experiments. When the solution was left to stand at various temperatures, carbon dioxide gas escaped from the solution and calcium carbonate crystals appeared; even when carbon dioxide gas was passed continuously through the bicarbonate solution at high temperatures, calcium carbonate was precipitated because of the decrease in the solubilities of carbon dioxide and calcium carbonate with the increase in the temperature of the solution.

Experiment A.—Calcium carbonate was precipitated from the calcium bicarbonate solution in order to examine the effect of temperature change.

1) A 300 ml. portion of the bicarbonate solution was allowed to stand (20 min. to 3 weeks) at varying temperatures, with occasional stirring so that carbon dioxide gas escaped from the solution and calcium carbonate crystals appeared. The crystals were filtered off and washed several times with distilled water. After the crystals had been dried in an air bath and ground in an agate mortar, their crystal forms were identified by the use of an X-ray diffractometer (Fig. 1). At temperatures below 25°C, only calcite was formed. At around 30°C, both calcite and aragonite were formed, but no vaterite was. Between 40 and 60°C, all three forms were formed, but the proportion of calcite was small. At around 40°C the proportion of vaterite was large. With a rise in the temperature, the proportion of aragonite increased, and at around 60°C aragonite predominated. Between 70 and 90°C, only aragonite was formed. At the boiling point, aragonite predominated, but a small amount of vaterite was formed.

2) Calcium carbonate was formed from 300 ml. of the calcium bicarbonate solution through which carbon dioxide gas was bubbled continuously at high temperatures. The carbon dioxide content controls the pH value of the solution, and the pH value is an important factor in determining the crystal form of the resulting calcium carbonate. The experiments were conducted at various temperatures above 70°C because at lower temperatures the formation of calcium carbonate was difficult from the solution bubbled with carbon dioxide gas. When calcium carbonate was formed from the solution bubbled with carbon dioxide gas, even at a high temperature, calcite and vaterite were formed with aragonite, as is shown in Fig. 2. With a rise in the temperature, the formation of aragonite increased.

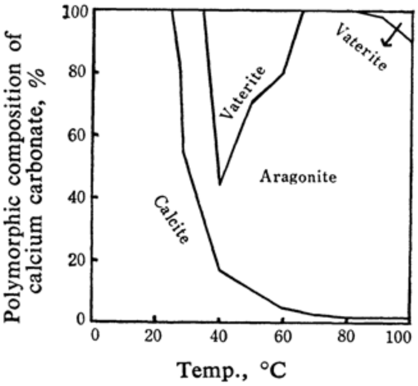

Fig. 1. Polymorphic composition of calcium carbonate formed from calcium bicarbonate solution at various temperatures.

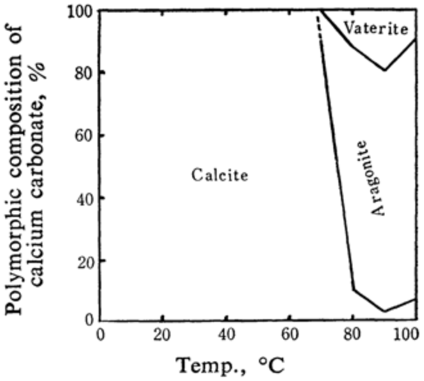

Fig. 2. Polymorphic composition of calcium carbonate formed from calcium bicarbonate solution bubbled with carbon dioxide gas at various temperatures.

Experiment B.—Calcium carbonate was precipitated from 300 ml. of the calcium bicarbonate solution containing sodium chloride and/or magnesium chloride, in order to investigate the effect of these salts on the polymorphic formation of calcium carbonate.

1) Sodium Chloride.—a) Calcium carbonate was formed as in Experiment A-1 from the calcium bicarbonate solution containing various amounts of sodium chloride (Table II). With an increase in the temperature and in the concentration of sodium chloride in the solution, the proportion of vaterite increased. At the boiling point, vaterite predominated. From Fig. 1 and Table II, it can be concluded that the presence of sodium chloride favors the formation of vaterite at a high temperature, while it favors calcite formation at a low temperature[10]. b) When calcium carbonate was formed from the solution containing sodium chloride and bubbled with carbon dioxide gas, only calcite was formed (Table II).

2) Magnesium Chloride.—a) Calcium carbonate was formed from the calcium bicarbonate solution containing various amounts of magnesium chloride according to the same procedure as in Experiment A-1 (Table III). Table III and Fig. 1 indicate that the presence of magnesium chloride in the solution favored aragonite formation and hindered vaterite formation. b) When calcium carbonate was formed from the solution containing magnesium chloride and bubbled with carbon dioxide gas continuously, only calcite was formed (Table III).

TABLE II. CRYSTAL FORMS OF CALCIUM CARBONATE FORMED FROM THE CALCIUM BICARBONATE SOLUTION CONTAINING SODIUM CHLORIDE

Mother solution		Crystal forms of $CaCO_3$		
Temp.	NaCl in calcium bicarbonate solution	Vaterite	Calcite	Aragonite
°C	g./l.	%	%	%
30	1.5	0	100	0
50	1.5	12	14	74
60	1.5	40	10	50
70	1.5	35	5	60
80	1.5	40	8	52
100	1.5	63	10	27
80	0.3	14	8	78
80	1.0	40	10	50
80	1.5	40	8	52
80	3	52	10	38
80	10	55	20	35
80	15	49	9	42
100	1.5	63	10	27
100	3	78	9	13
100	10	91	6	3
100	25	91	8	1
Solution aerated with carbon dioxide gas				
80	3	0	100	0
80	6	0	100	0
80	10	0	100	0
80	15	0	100	0

TABLE III. CRYSTAL FORMS OF CALCIUM CARBONATE FORMED FROM THE CALCIUM BICARBONATE SOLUTION CONTAINING MAGNESIUM CHLORIDE

Mother solution		Crystal forms of $CaCO_3$		
Temp.	$MgCl_2$ in calcium bicarbonate solution	Vaterite	Calcite	Aragonite
°C	g./l.	%	%	%
10	0.6	0	88	12
10	1.8	0	40	60
10	3∼4.5	0	0	100
30	0.5	0	30	70
30	0.8	0	23	77
30	1.5	0	0	100
50	0.15	0	7	93
50	4.5	0	0	100
60	0.15	0	5	95
60	4.5	0	0	100
70	0.15	0	5	95
70	4.5	0	0	100
80	0.15	0	0	100
80	4.5	0	0	100*
100	0.15	0	0	100*
100	4.5	0	0	100*
Solution aerated with carbon dioxide gas				
70	3	0	100	0
80	3	0	100	0

* A small amount of magnesium carbonate was precipitated with calcium carbonate. (The details are; Y. Kitano, K. Park and D. W. Hood, "Pure Aragonite Synthesis," *J. Geophys. Research,* in press).

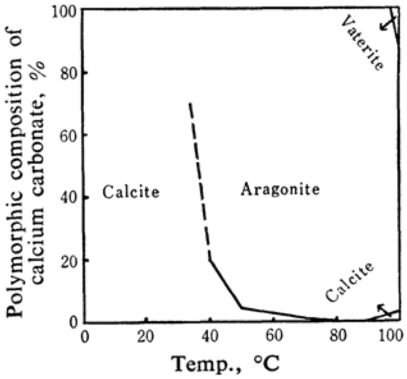

Fig. 3. Polymorphic composition of calcium carbonate formed from calcium bicarbonate solution containing sodium chloride (5 g./l.) and magnesium chloride (0.7 g./l.).

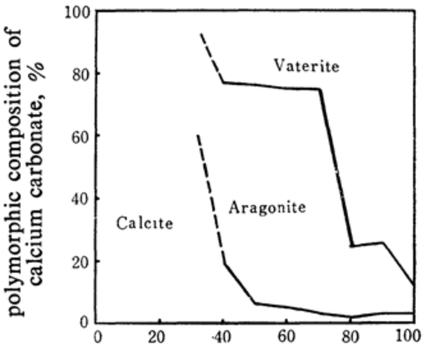

Fig. 4. Polymorphic composition of calcium carbonate formed from calcium bicarbonate solution containing sodium chloride (5 g./l.) and magnesium chloride (0.07 g./l.).

3) *Sodium Chloride and Magnesium Chloride.*— A) When calcium carbonate was formed from the calcium bicarbonate solution containing both sodium chloride (5 g./l.) and magnesium chloride (0.7 g./l.) (group A in Table I), vaterite was not formed at a lower temperature than the boiling point (Fig. 3). At a temperature above 50°C, aragonite predominated. This indicates that the magnesium chloride in the solution had a greater effect than the sodium chloride, so that the composition of the crystal forms was dependent upon the magnesium chloride content (Fig. 3, Tables II and III). When calcium carbonate was formed from the calcium bicarbonate solution containing both sodium chloride (5 g./l.) and magnesium chloride (0.07 g./l.) (group B in Table I), vaterite was always

TABLE IV. CRYSTAL FORMS OF CALCIUM CARBONATE IN FUTAMATA THERMAL SPRINGS

Station No.	Distance from orifice to station, m.	Water		Crystal forms of $CaCO_3$		
		Temp. °C	pH	Vaterite %	Calcite %	Aragonite %
1	0	42	6.6	0	100	0
2	15	38	7.0	0	95~90	5~10
3	40	27	7.3	0	80~35	20~65

formed (Fig. 4). At a temperature above 50°C the proportion of calcite was very small, at below 70°C aragonite predominated, and at above 70°C vaterite predominated and its proportion increased with a rise in the temperature. Apparently the magnesium chloride content in the solution was too small to affect the polymorphic formation of calcium carbonate, so that the composition of the crystal forms of calcium carbonate was dependent upon the sodium chloride content (Fig. 4, Tables II and III).
b) When calcium carbonate was formed from the calcium bicarbonate solution containing sodium chloride and magnesium chloride and bubbled with carbon dioxide gas continuously during the formation of the calcium carbonate, only calcite was formed, even at a high temperature.

Discussion

Calcium carbonate formed in the laboratory from the calcium bicarbonate solution bubbled with carbon dioxide gas continuously during the formation of calcium carbonate is comparable to calcium carbonate deposited in the original orifice of thermal spring waters where carbon dioxide gas gushes forth, while calcium carbonate formed from the solution without aeration of carbon dioxide gas is comparable to calcium carbonate deposited with the escape of carbon dioxide gas from spring waters during the flow.

The following facts were observed in thermal springs:

1) When the temperature of thermal spring waters was very high, aragonite was usually formed (Table I). Futamata spring waters were made to flow through an open wooden conduit from the orifice to a bath[12,13]. As carbon dioxide gas escaped from the waters, calcium carbonate was deposited. The crystals of calcium carbonate formed at various locations in the flow were sampled and their crystal forms were identified (Table IV). The data indicate that calcite was formed readily at the original location of thermal springs despite a high temperature, where carbon dioxide gas was supplied to the water. Aragonite was formed at a location where carbon dioxide gas was not supplied, despite a low temperature. These observations were supported by the experimental results in the laboratory (Fig. 2, Tables II and III, Experiment B-3-b). The content of carbon dioxide controls the pH value of the solution. The solution bubbled with carbon dioxide gas is acid. It can be said that even at a high temperature calcite was formed from the solution containing carbon dioxide, sodium chloride and/or magnesium chloride, in other words, from an acid solution. This appears to be attributable to the facts that the solubility of calcium carbonate is very large in the acidic solution containing carbon dioxide, sodium chloride and/or magnesium chloride[14] and that the rate of the calcium carbonate formation is very small, because calcite (a stable crystal) is formed easily when the rate of calcium carbonate formation is very small. It can also be said that, even at a low temperature, aragonite is formed from the basic solution which does not contain a large amount of carbon dioxide.

2) Calcite was formed from Futamata spring waters running still, while aragonite was formed when the same waters struck a rock so strongly that carbon dioxide gas escaped rapidly; calcium carbonate was also formed rapidly. In the laboratory, calcite was formed from Futamata water which was kept still so that carbon dioxide gas could gradually escape from the water with a slow separation of calcium carbonate crystals, at 30 and 35°C; a mixture of calcite and aragonite was formed from the same Futamata water which was repeatedly stirred, whereby the escape of the carbon dioxide gas and calcium carbonate formation were accelerated, at the same temperatures, 30 and 35°C. The result makes it possible to conclude that, in waters with the same chemical constituents, pH value, and temperature, with an increase in the rate of carbon dioxide gas escape from the waters and in the rate of calcium carbonate formation, the proportion of aragonite (an unstable crystal) increases and that of calcite (a stable crystal) decreases.

3) Vaterite has not been found in thermal

---

[12] Y. Uzumasa and Y. Kitano, *J. Chem. Soc. Japan, Pure Chem. Sec.* (*Nippon Kagaku Zassi*), 73, 901 (1951).

[13] Y. Uzumasa and Y. Kitano, ibid., 73, 720 (1952).

[14] Y. Seidell, "Solubilities of Inorganic and Metal Organic Compounds", Van Nostrand, New York (1940), pp. 273-275.

springs. On the basis of the laboratory results, possible explanations for this are: a) The spring waters contain a rather large amount of magnesium chloride (Tables II and III, Fig. 3), or calcium carbonate is formed near the orifice where carbon dioxide gas is supplied (Fig. 2, Tables II and III, Experiment B-3-b). b) When vaterite is formed, it changes to calcite or aragonite because of its high instability in a solution. It seems probable, however, that vaterite can be found in thermal springs when calcium carbonate is formed at a high temperature from the waters of group B in Table I (NaCl 5 g./l., MgCl$_2$ 0.07 g./l.), at a location where carbon dioxide gas is not supplied to the waters (Fig. 4).

4) The mechanical and physical conditions and the minor elements in the waters have an influence on the polymorphic formation of calcium carbonate in thermal springs. Aragonite was found in precipitates which were floating on the surface of the waters, but it was not found in precipitates deposited on the wall or on the bottom in the same waters[3]. In addition, strontium ions[7,10,15] and barium ions[10] are minor elements affecting the polymorphic formation. The presence of strontium ions favored aragonite formation and that of barium ions favored calcite formation, but the effects of these factors are less significant than those of carbon dioxide (pH), sodium ions, magnesium ions, and chloride ions and the temperature of the mother solution.

Summary

1) When calcium carbonate was formed in the laboratory from the calcium bicarbonate solution through which carbon dioxide gas had not been bubbled during the process of the calcium carbonate formation: a) Only calcite was formed at a temperature below 25°C; aragonite was formed above 25°C, and vaterite was formed above 40°C. Between 40 and 60°C a large amount of vaterite was formed. With a rise in the temperature of the mother solution, the proportion of calcite decreased. b) Vaterite was easily formed from the calcium bicarbonate solution containing sodium chloride at a high temperature. With an increase in the temperature and in sodium chloride concentration, the proportion of vaterite increased. c) With an increase in both temperature and magnesium chloride concentration, the proportion of aragonite increased but that of calcite decreased. The presence of magnesium chloride in the mother solution hindered the formation of vaterite.

2) When calcium carbonate was formed in the laboratory from the calcium bicarbonate solution containing sodium chloride (or magnesium chloride) and bubbled with carbon dioxide gas continuously during the calcium carbonate formation, only calcite was formed despite a high temperature.

3) When calcium carbonate was deposited in thermal spring waters of a high temperature, aragonite was formed. However, from the waters into which carbon dioxide gas was supplied, in other words, from the acidic solution, calcite was formed despite a high temperature, and aragonite was formed from the waters to which carbon dioxide was not supplied, in other words, from the basic waters, despite a low temperature.

4) Up to the present time, vaterite has not been found in the deposits of thermal springs because: a) Calcium carbonate deposits of thermal springs were either formed at a location where carbon dioxide gas was supplied to the mother waters or where the concentration of magnesium ions in the waters was rather high, or b) even if vaterite had been formed, it would have changed to calcite or aragonite very quickly because of its low stability in solution.

5) In spring waters with the same chemical constituents, pH value, and temperature, the proportion of aragonite increased and that of calcite decreased with an increase in the rate of carbon dioxide gas escape from the waters and in the rate of calcium carbonate formation.

6) Aragonite was readily found in calcium carbonate precipitates formed floating on the surface of thermal spring waters, but it was not likely to be found in the precipitates deposited on the wall or bottom in the same waters.

The polymorphic formation of calcium carbonate formed in thermal springs depends mainly on the temperature, the concentrations of sodium ions, magnesium ions and carbon dioxide (pH) in the waters, and on the rate of calcium carbonate formation when calcium carbonate is formed from a similar water.

The author wishes to express his deep appreciation to Professor Ken Sugawara of Nagoya University and to Professor Donald W. Hood and Mr. Edward R. Ibert of Texas A & M College for their encouragement throughout this work.

Water Research Laboratory
Faculty of Science
Nagoya University
Chikusa-ku, Nagoya

---

15) Y. Kitano and N. Kawasaki, *J. Earth Sciences, Nagoya Univ.*, **6**, 63 (1958).