Calcium Carbonate Crystal Forms Formed from Sea Water by Inorganic Processes*

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Abstract: This study was made to solve the following questions: (1) Which of the three crystal forms of calcium carbonate (calcite, aragonite and vaterite) is produced most predominantly from sea water by inorganic processes. (2) Which of the chemical constituents of sea water has the greatest influence on the polymorphic formation of calcium carbonate? The experimental results show that aragonite alone is favored in sea water media because of the strong influence of magnesium in the water on the crystal formation of calcium carbonate.

1. Introduction

This study was undertaken to determine the polymorphic form of calcium carbonate formed by inorganic precipitation in sea water. The following considerations are important and necessary for understanding the inorganic precipitation, and the results will be available for the study on diagnosis of marine calcareous sediments: (1) Which of the three crystal forms of calcium carbonate (calcite, aragonite and vaterite) is produced most predominantly from sea water by inorganic processes. (2) Which of the chemical constituents of sea water has the greatest influence on the polymorphic crystallization of calcium carbonate.

It has been reported that aragonite formation is favored when calcium carbonate is precipitated from sea water without the immediate participation of organic agencies (MONAGHAN et al., 1954; SMITH, 1940; VAUGHAN, 1924).

However, no satisfactory explanation has yet been advanced for this. The purpose of this work was to solve this problem. In the experiments, calcium carbonate was prepared from a calcium bicarbonate solution by escape of carbon dioxide gas from the solution. This reaction was used because: (1) It is one of

"homogeneous precipitation" reactions; therefore reproducible precipitates can be obtained easily. (2) The effect of elements on the crystal formation can be studied because the mother solution does not contain any ion other than calcium and carbonate ions.

Various ions were added to calcium bicarbonate solutions, and the solutions were left to stand for two or three weeks. The calcium carbonate formed was collected and the crystal form identified.

In connection with the program of this report, the following finding can be obtained from the data to be published in separate paper (KITANO, 1962 a): Ions in sea water having an influence on the polymorphic formation of calcium carbonate are Na^+ , Mg^{2+} , Ca^{2+} , Sr^{2+} , Cl^- , HCO_3^- , and SO_4^{2-} . Compounds which have a great influence on the crystal formation were chosen from salts to be expected in sea water; NaCl , NaHCO_3 , Na_2SO_4 , MgCl_2 , CaCl_2 and Sr-bicarbonate .

2. Experimental

Materials and solutions

Calcium bicarbonate solution: A calcium carbonate suspension in distilled water was bubbled with carbon dioxide gas for one day and then filtered. The filtrate was bubbled again with carbon dioxide for one hour.

Strontium bicarbonate solution: A strontium carbonate suspension was similarly treated as for the calcium bicarbonate solution.

Concentrated sea water: Sea water was

* Received July 2, 1962

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evaporated over a water bath to one-fourth of its original volume.

Materials: Analytical reagent grade NaCl, NaHCO₃, Na₂SO₄, MgCl₂·6H₂O, and CaCl₂ were used.

Procedure

All combinations of the following salts: NaCl, MgCl₂, CaCl₂, Na₂SO₄, NaHCO₃ and strontium bicarbonate were dissolved in one liter flasks with 30 ml of distilled water. Three hundred ml of the calcium bicarbonate solution were then added to each of the flasks. The amounts of the salts in solutions were such that their concentrations were equal to those in sea water.

Fifty or 100 ml of the concentrated sea water were transferred to other flasks, and 150 or 300 ml of the calcium bicarbonate solution were then added.

The flasks were left to stand at room temperature for 2 to 3 weeks so that carbon dioxide escaped from the solutions and calcium carbonate crystals separated. The crystals formed were filtered off and washed several times with distilled water until they were free of the mother solution. After being dried in an air bath and ground in an agate mortar, the crystal form of calcium carbonate was identified by the X-ray diffractometer technique.

3. Discussion of Results

The results obtained are shown in Tables 1-3, and from them the following can be seen: (1) According to Tables 1 and 2, the magnesium in the mother solution had the greatest influence on the polymorphic formation of cal-

cium carbonate among all other chemical constituents in the media. Aragonite formation alone was favored because of the magnesium in the mother solution, in which the concentration of magnesium was equal to that in sea water (Mg²⁺: 1.2 g/liter). Work is under way to investigate the mechanism for the strong effect of magnesium (KITANO, 1962 a). (2) The inorganic precipitation of the aragonite form of CaCO₃ is most probable in sea water (Table 3), since sea water contains magnesium (1.2 g/liter). In dilute sea water, a significant percentage of calcite was found with aragonite (Table 3); this is due to decrease in magnesium content in solution and to more favorable conditions for calcite precipitation (Fig. 1). (3) Vaterite was not formed under the conditions of the experiments. This is explained by the result presented in another publication (KITANO, 1962 b); vaterite formation increased with increase in the temperature and the concentration of NaCl in the mother solution, but MgCl₂ greatly inhibited vaterite formation. Vaterite was never formed in water at a temperature of less than 40°C when the water contained 23 g of NaCl and 5 g of MgCl₂ in one liter, because of the high concentration of magnesium.

It must also be noted that calcium carbonate precipitates were formed from solutions having pH values between 7 and 8.8* and various Ca:Mg ratios**. Therefore, it can be expected aragonite alone is formed by inorganic processes throughout the entire body*** of sea water.

* CaCO₃ separated from bicarbonate solution as CO₂ escaped from the solution; therefore the pH of solution changed during the process of the CaCO₃ separation.

** Calcium was precipitated as CaCO₃ but magnesium was not coprecipitated with the carbonate (Tables 1 and 2) (KITANO, 1962 a). *,** It took 2 to 3 weeks to prepare CaCO₃ crystals in the experiments. The author studied whether there was difference in the polymorphic composition among the CaCO₃ crystals produced during different periods. Under the conditions of the present experiments, the difference was not significant.

*** The experiment was not done at temperature of lower than 10±2°C (Fig. 1). Even at temperature of lower than 10°C aragonite alone will be produced in sea water media because of the high magnesium concentration.

According to JAMIESON's report (JAMIESON, 1953), calcite is a stable modification at a low pressure; therefore, aragonite formation is expected in sea water under a high hydrostatic pressure. In the actual ocean, CaCO₃ is not formed under the high hydrostatic pressure (HINDMAN, 1943; PARK, 1961).

Table 1. $\text{Ca}(\text{HCO}_3)_2\text{-MgCl}_2\text{-NaCl-Na}_2\text{SO}_4\text{-CaCl}_2\text{-Sr}(\text{HCO}_3)_2\text{-CO}_2\text{-H}_2\text{O}$ System.
($15 \pm 2^\circ\text{C}$)

Ca-bicarbonate solution Ca mg	Initial composition of solutions (total volume 330 ml; pH 6.5)					On the 20th day pH	Crystal form of CaCO ₃ formed during a 20 day period			Mg content in CaCO ₃ formed during a 20 day period Mg %
	MgCl ₂	NaCl	Na ₂ SO ₄	CaCl ₂	Sr-bicarbonate** solution Sr mg		vaterite	aragonite	calcite	
	g	g	g	g	g		%	%	%	
90	0	0	0	0	0	7.7	0	0	100	—
"	1.64	0	0	0	0	8.5	0	100	0	0.0
"	0	7.82	0	0	0	8.5	0	0	100	—
"	0	0	1.31	0	0	8.5	0	0	100	—
"	0	0	0	0.37	0	8.2	0	0	100	—
"	0	0	0	0	3	7.7	0	0	100	—
"	1.64	7.82	0	0	0	8.5	0	100	0	0.0
"	1.64	0	1.31	0	0	8.5	0	100	0	0.0
"	1.64	0	0	0.37	0	8.4	0	99	1	0.0
"	1.64	0	0	0	3	8.5	0	100	0	0.0
"	0	7.82	1.31	0	0	8.5	0	0	100	—
"	0	7.82	0	0.37	0	8.5	0	0	100	—
"	0	7.82	0	0	3	8.5	0	0	100	—
"	0	0	1.31	0.37	0	8.1	0	0	100	—
"	0	0	1.31	0	3	8.1	0	0	100	—
"	0	0	0	0.37	3	8.0	0	0	100	—
"	1.64	7.82	1.31	0	0	8.4	0	100	0	0.0
"	1.64	7.82	0	0.37	0	8.5	0	100	0	0.0
"	1.64	7.82	0	0	3	8.5	0	100	0	0.0
"	1.64	0	1.31	0.37	0	8.5	0	100	0	0.0
"	1.64	0	0	0.37	3	8.4	0	99	1	0.0
"	1.64	0	1.31	0	3	8.5	0	100	0	0.0
"	0	7.82	1.31	0.37	0	8.5	0	0	100	—
"	0	7.82	1.31	0	3	8.5	0	0	100	—
"	0	7.82	0	0.37	3	8.5	0	0	100	—
"	0	0	1.31	0.37	3	8.5	0	0	100	—
"	1.64	7.82	1.31	0.37	0	8.5	0	100	0	0.0
"	1.64	7.82	1.31	0	3	8.5	0	100	0	0.0
"	1.64	7.82	0	0.37	3	8.5	0	100	0	0.0
"	1.64	0	1.31	0.37	3	8.4	0	100	0	0.0
"	0	7.82	1.31	0.37	3	8.5	0	0	100	—
"	1.64	7.82	1.31	0.37	3	8.5	0	100	0	0.0

* Solution containing $\text{Ca}(\text{HCO}_3)_2$, H_2CO_3 , CO_2 and H_2O , as shown in "Experimental".** Solution containing $\text{Sr}(\text{HCO}_3)_2$, H_2CO_3 , CO_2 and H_2O , as shown in "Experimental".

Table 2. $\text{Ca}(\text{HCO}_3)_2$ - MgCl_2 - NaCl - Na_2SO_4 - CaCl_2 - NaHCO_3 - CO_2 - H_2O System.
($29 \pm 2^\circ\text{C}$)

Ca-bicarbonate solution Ca mg	Initial composition of solutions (total volume 330 ml; pH 6.5)					On the 14th day pH	Crystal form of CaCO ₃ formed during a 14 day period			Mg content in CaCO ₃ formed during a 14 day period Mg %
	MgCl ₂	NaCl	Na ₂ SO ₄	CaCl ₂	NaHCO ₃		Vaterite	Aragonite	Calcite	
	g	g	g	g	g		%	%	%	
90	0	0	0	0	0	8.2	0	10	90	—
"	1.64	0	0	0	0.064	8.6	0	100	0	0.0
"	1.64	7.82	0	0	0.064	8.6	0	100	0	0.0
"	1.64	0	1.31	0	0.064	8.6	0	100	0	0.0
"	1.64	0	0	0.37	0.064	8.0	0	100	0	0.0
"	1.64	7.82	1.31	0	0.064	8.6	0	100	0	0.0
"	1.64	7.82	0	0.37	0.064	8.1	0	100	0	0.0
"	1.64	0	1.31	0.37	0.064	8.1	0	100	0	0.0
"	1.64	7.82	1.31	0.37	0.064	8.2	0	100	0	0.0
"	0	7.82	0	0	0.064	8.5	0	10	90	—
"	0	0	1.31	0	0.064	8.5	0	20	80	—
"	0	0	0	0.37	0.064	7.9	0	10	90	—
"	0	7.82	1.31	0	0.064	8.5	0	10	90	—
"	0	7.82	0	0.37	0.064	8.1	0	10	90	—
"	0	0	1.31	0.37	0.064	8.0	0	20	80	—
"	0	7.82	1.31	0.37	0.064	8.0	0	20	80	—

Table 3. $\text{Ca}(\text{CO}_3)_2$ - CO_2 - H_2O -Concentrated Sea Water System.
($15 \pm 2^\circ\text{C}$)

Initial composition of solutions			Crystal form of CaCO ₃ formed during a 20 day period			Concentration of salt in solution
Ca-bicarbonate solution		Concentrated sea water	Vaterite %	Aragonite %	Calcite %	Concentration of salt in sea water
ml	Ca mg	ml				
150	40	100	0	99	1	1.6
300	80	100	0	99	1	1
300	80	50	0	93	7	0.55
300	80	0	0	0	100	0

Fig. 1. Effect of MgCl_2 in mother solution on crystal form of CaCO_3 .

4. Conclusion

When calcium carbonate is precipitated from sea water by inorganic processes, aragonite formation alone is favored because of the strong influence of the magnesium in the water on the polymorphic crystallization of calcium carbonate.

Acknowledgements

The authors express their thanks to Miss Lila M. JEFFERY and Dr. Brian W. LOGAN in A & M College of Texas for their critical

reading of the manuscript.

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