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Incorporation of Sodium into Calcium Carbonate and Protodolomite

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Abstract

The incorporation of Na^+ into calcium carbonate and protodolomite was studied by precipitating carbonates from $\text{Ca}(\text{HCO}_3)_2 + \text{NaCl}$ (or NaHCO_3) + MgCl_2 solution. Relationship between sodium content of carbonate and Na^+ concentration in solution is obtained as: $\log[\text{Na}]_{\text{carbonate}} = n \log[\text{Na}^+]_{\text{solution}} + k$ (n and k are constants). The addition of NaHCO_3 and/or MgCl_2 to $\text{Ca}(\text{HCO}_3)_2$ solution increases the incorporation of Na^+ into aragonite. Incorporation of Na^+ into protodolomite precipitated from brine solution is much higher than that into Mg-poor calcite precipitated from solution having the same Na^+ concentration as that in the brine solution.

1. Introduction

The response of sodium content of carbonates to the salinity of environmental waters were studied by Rucher and Valantine¹, Harris and Pilkey², Land and Hoops³ and Fritz and Katz⁴. The low sodium content of dolomite is one of the bases for the low salinity hypothesis of dolomite formation and diagenesis. Sodium is contained preferentially in aragonite and Mg-rich calcite in reef sediments (Billings and Ragland⁵, Amiel et al.⁶). Laboratory studies on sodium coprecipitation with calcium carbonates were carried out by Kitano et al.⁷, White^{8,9} and Ishikawa and Ichikuni¹⁰. The purpose of this study is to gain information on the correlation between sodium content of carbonate and chemical composition of environmental water.

2. Procedure

Calcium carbonates were precipitated from one liter of $\text{Ca}(\text{HCO}_3)_2$ solutions containing various amount of MgCl_2 ($\text{Mg}^{2+} = 0$ to 8440 mg/l) and NaCl (or NaHCO_3) ($\text{Na}^+ = 100$ to 99300 mg/l) at 35°C (as shown in Table 1). The Ca^{2+} , Mg^{2+} , Cl^- , alkalinity, Na^+ and pH were determined every reaction time by titration, atomic absorption and using pH meter (HITACHI-F7). The precipitates formed were filtered off and washed until Cl^- could not be detected by testing with 0.02M- AgNO_3 solution. The precipitates were dried at 50°C. Sodium and magnesium contents and mineral composition of carbonates were determined by atomic absorption and X-ray diffraction, respectively.

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3. Results and Discussion

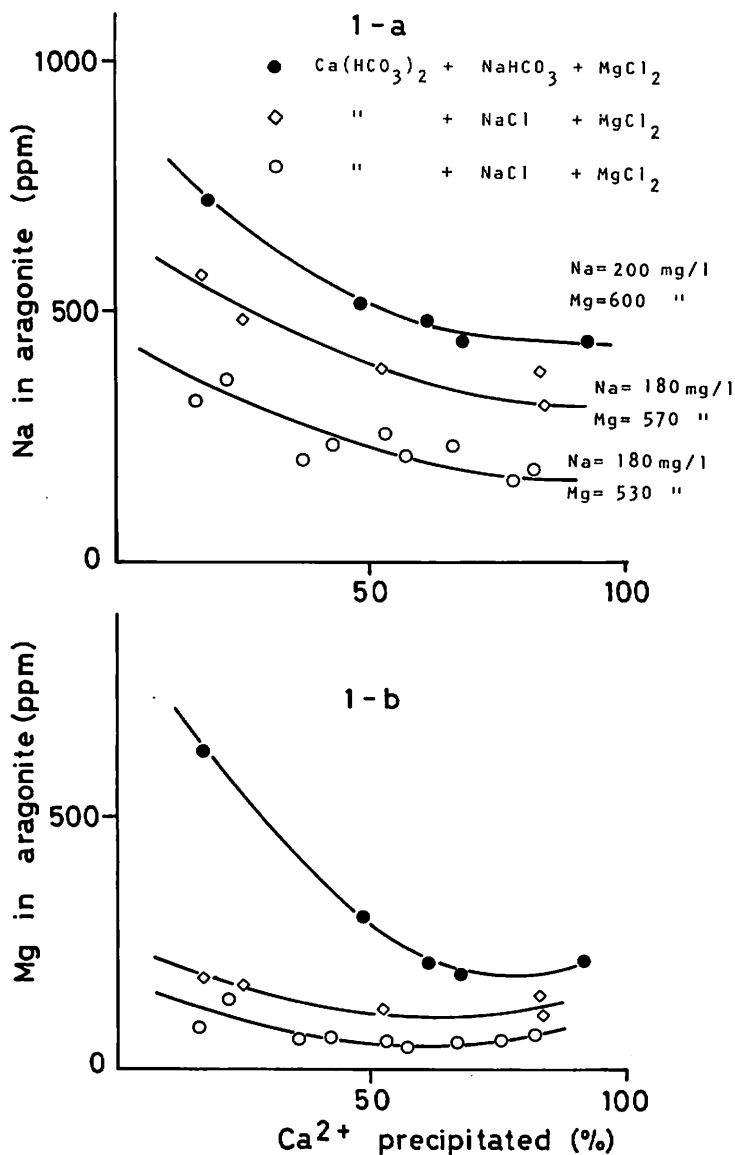
Sodium and magnesium content of aragonite

Fig. 1. Sodium and magnesium contents of aragonite during carbonate precipitation.

Figure 1 shows Na^+ and Mg^{2+} incorporation into aragonite formed from $\text{Ca}(\text{HCO}_3)_2$ solutions containing Na^+ (180, 200 mg/l) and Mg^{2+} (530, 570, 600 mg/l). It was reported already that Na^+ in a parent solution is incorporated much more into aragonite than into calcite (Kitano et al.⁷). It is seen from Fig. 1 that the addition of NaHCO_3 and/or MgCl_2 to $\text{Ca}(\text{HCO}_3)_2$ solution increases Na^+ incorporation into aragonite. Land and Hoops³ suggested that Na^+ together with H^+ may be incorpo-

rated into carbonate mineral lattice. White⁸ discussed how Na^+ is coprecipitated as sodium carbonate with calcium carbonate, through laboratory experiments. Kitano et al.⁷ showed that Na^+ was easily coprecipitated with aragonite when the solution contained SO_4^{2-} . The concentration of sodium to coral aragonite in excess from equimolar chloride concentration was equivalent to the concentration of sulphate (Tokuyama: personal communication). So, anions such as SO_4^{2-} and CO_3^{2-} in a parent solution are considered to affect the Na^+ incorporation into aragonite.

Also, Na^+ is easily incorporated at early stage of aragonite formation (Fig. 1-a). The sodium content of aragonite decreased with increasing stage of the aragonite formation, where the $\text{Mg}^{2+}/\text{Ca}^{2+}$ concentration ratio in a parent solution increased during the aragonite formation. The high sodium content at early stage may occur kinetically. Abnormally high values of distribution coefficient of divalent cations were often observed at the early stage of carbonate formation (Kitano et al.^{11,12}).

Magnesium content of aragonite is also affected by the addition of NaHCO_3 to the parent solution, especially in the early stage of aragonite formation (Fig. 1-b). Although $\text{Mg}^{2+}/\text{Ca}^{2+}$ ratio increases during the carbonate precipitation, Mg content of aragonite decreases and becomes steady after 50% of calcium carbonate precipitation. Abnormal behavior of Mg^{2+} incorporation at early stage of precipitation should occur kinetically. Amiel et al.⁶ reported that magnesium is incorporated into both absorption site and lattice site of coral aragonite.

Sodium content of calcite

Figure 2 shows sodium content of calcite formed from $\text{Ca}(\text{HCO}_3)_2$ solutions containing NaCl . The sodium content of calcite is smaller than that of aragonite, although Na^+ in a parent solution favors calcite formation and hinders aragonite formation, as reported in previous reports (Kitano¹³, Kitano et al.^{7,14}).

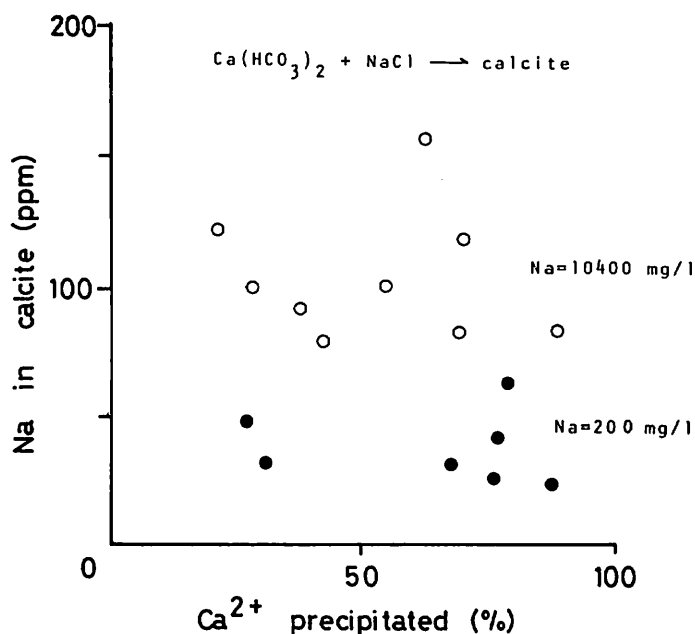


Fig. 2. Sodium content of calcite during carbonate precipitation.

Sodium content of protodolomite

In order to get information on the relationship between sodium content of protodolomite and salinity of environmental water, the sodium content of synthesized protodolomite from evaporatic brine water was measured. The brine water[A] was prepared by evaporating sea water several times by salinity and it was equilibrated to calcium carbonate through CO₂ gas bubbling. Protodolomite was precipitated from this solution by adding Na₂CO₃ solution drop by drop. Details of the procedure are described in a previous report (Oomori et al.¹⁵). The results are shown in Table 1. For the purpose of comparison, calcite and aragonite were also precipitated from artificial brine solutions[B] containing NaCl (Na⁺: 50 to 100 g/l) and MgCl₂(Mg²⁺: 0, 5 and 10 g/l). The sodium content of

Table 1. Analytical results on synthesized carbonates from brine waters such as, A; (evap. sea water + Ca(HCO₃)₂ + Na₂CO₃ → carbonate) and B; (Ca(HCO₃)₂ (Ca²⁺, 350 mg/l) + MgCl₂ + NaCl → carbonate).

Run No.	parent solution				precipitates		
	Mg ²⁺ (g/l)	Na ⁺ (g/l)	Cl ⁻ (g/l)	Na ₂ CO ₃ (mM/l)	Mg/Ca (mole ratio)	Na (mg/kg)	mineral composition
A-2	10.2	79.0*	140*	5	0.03	4250	aragonite
A-3	10.2	"	"	10	0.04	6100	"
A-6	10.2	"	"	25	0.44	3800	arag. + protodolomite
A-8	10.3	"	"	34	1.01	5150	protodolomite
A-10	10.1	"	"	42	1.14	6450	"
A-12	10.1	"	"	51	1.62	4750	arag. + protodol. + huntite
A-13	10.1	"	"	55	2.31	4800	huntite
B-1	0	50.5	73		9 × 10 ⁻⁵	360	calcite
B-2	0	99.0	140		6 × 10 ⁻⁵	510	"
B-3	4.4	51.0	87		1.9 × 10 ⁻³	2900	aragonite
B-4	8.4	52.5	99		2.4 × 10 ⁻³	2350	"
B-5	4.2	94.5	145		1.3 × 10 ⁻³	2800	"
B-6	8.1	99.0	165		9.0 × 10 ⁻³	2800	"

* ; Only one sample was analyzed.

protodolomite precipitated from brine water is much higher than that of Mg-poor calcite precipitated from artificial brine waters having the same Na⁺ concentration. Enhanced incorporation of Na⁺ into protodolomite may be caused by the alteration of the lattice due to the introduction of magnesium. In the White's study, the effect of MgCO₃ in calcite type carbonates on the incorporation of Na⁺ is large at high Na⁺ concentration. Sodium content of aragonite precipitated from evaporated sea water[A] is relatively high compared to that of aragonite precipitated from artificial brine solution [B]. This is explained by the preference of sodium in aragonite lattice and the enhanced incorporation of Na⁺ by the presence of SO₄²⁻ in solution. Kitano et al.¹¹ suggested that a part of sodium was incorporated with sulphate and another significant part of sodium with carbonate into aragonite. Sodium content of huntite (CaMg₃(CO₃)₄) is also high compared to that of Mg-poor calcite. Huntite has the same lattice structure as that of aragonite (orthorhombic). But, limited data on the sodium

content of huntite preclude discussion on this in detail.

Relationship between sodium content of carbonate precipitates and Na⁺ concentration in parent solution.

In order to examine the possibility for the use of sodium content of carbonates as salinity indicator, relations between sodium content of carbonate precipitates and Na⁺ concentration in parent solution were studied. Carbonate precipitates were obtained from Ca(HCO₃)₂ + NaCl + MgCl₂ by stirring until 70% or more of dissolved Ca²⁺ was precipitated as carbonates. The initial and the final Ca²⁺ concentration were around 400 m/l and 100 mg/l in solution, respectively. The results were presented in Fig. 3. The Freundlich type relationship was used for the presentation of these results. It

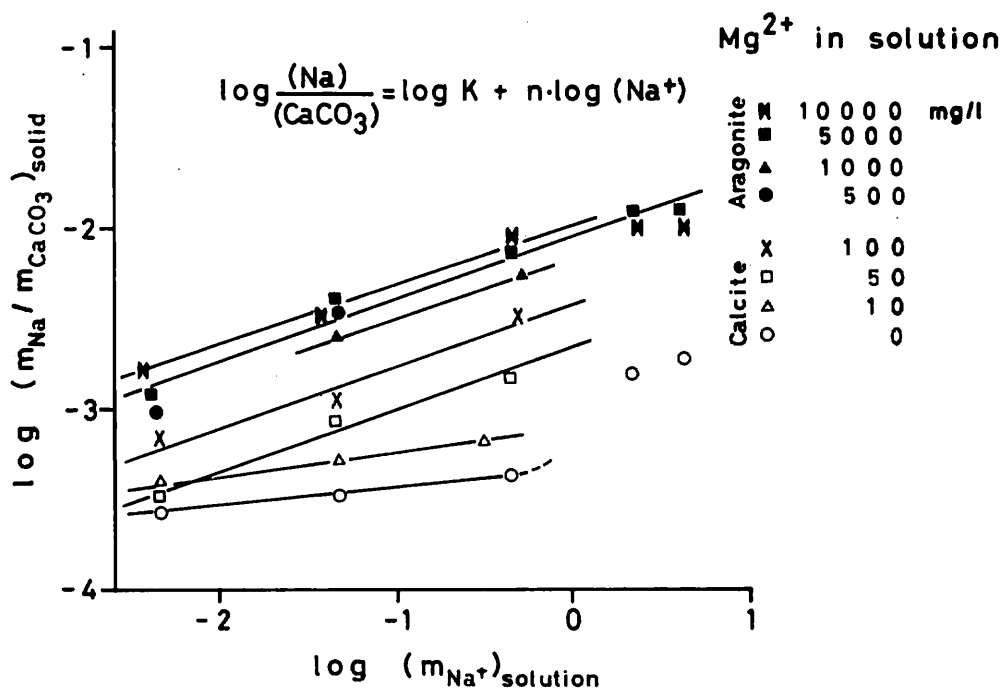


Fig. 3 Plots of sodium content of carbonate vs. Na⁺ concentration in solution in Ca(HCO₃)₂ + MgCl₂ + NaCl → calcite or aragonite system.

gives suitable relationship between sodium content of carbonate and Na⁺ in solution for salinity indicator. It is apparent that Na⁺ and Mg²⁺ in a parent solution considerably affect the sodium content of calcite and aragonite formed. Na⁺ is readily coprecipitated with aragonite. The effect of Mg²⁺ on the sodium content of aragonite was small, compared to that of calcite.

The enhanced effect of Mg²⁺ on the Na⁺ incorporation into calcite was observed when the solution contained more than 50 mg/l of Mg²⁺ in a parent solution. The formation of solid solution between MgCO₃ and CaCO₃ (calcite) decreases the thermodynamical stability of carbonates. Ishikawa and Ichikuni¹⁰ suggested that the sodium is incorporated in inter-lattice site. White⁹ showed that incorporation of sodium in calcite was increased in the range from 0 to 6 mole percent MgCO₃, but it was decreased over this MgCO₃ range.

As the consequent of the present study, it is considered that sodium content of carbonates is useful for discussing the chemical composition of waters associated with carbonate precipitation and/or its diagenetic recrystallization.

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