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Mineralogy and Morphology of Calcium Carbonate as a Function of Magnesium Concentration in Artificial Seawater

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ABSTRACT. Magnesium ions in solution affected the mineralogy and the morphology of calcium carbonate from which they precipitated. Low magnesium calcite was precipitated from a solution of low ionic products with respect to carbonate and Mg:Ca concentration ratio of less than 3:1. Aragonite was formed in a solution of Mg:Ca concentration ratio of more than 4:1. However, the increase of carbonate concentrations in the presence of magnesium ions enhanced the formation of magnesian calcite over aragonite. The co-existence of magnesian calcite, aragonite and vaterite indicated a kinetic control precipitation. This was also shown by the increased $MgCO_3$ content of magnesian calcite with the increase of carbonate concentrations in solution.

The presence of magnesium ions in artificial seawater produced acicular rather than the equant carbonate crystals, which produced in magnesium-free artificial seawater. Furthermore, the size of the crystals decreased with the increase of magnesium ions in the test solution.

Introduction

The mineralogy and morphology of the carbonate precipitate in solution are mainly influenced by the rates of dissolution and reprecipitation, which are controlled by the nucleation and the growth of the solid phases. It has been suggested that the presence of magnesium ions in solution inhibit the precipitation of calcium carbonate (Pytkowicz 1965 and 1973), retard the nucleation of calcite during the dissolution of *aragonite* (Bischoff 1968; Bischoff and Fyfe 1968), enhance the spontaneous precipitation of aragonite over calcite at high supersaturation (Taft and Harbaugh 1964;

Pytkowicz 1973) and increase the magnesium content of calcite during overgrowth precipitation (Mucci and Morse 1984). Berner (1975 and 1978) and Thorstenson and Plummer (1977) have suggested that magnesian calcite composition are influenced by growth rates. Aragonite was found to precipitate at Mg:Ca concentration ration more than 3.83 (Kitano *et al.* 1962).

Recently, some authors correlated the mineralogy and morphology of a biogenic carbonate precipitates to chemical processes in nature. They concluded that the Mg^{2+} concentration and the rate of precipitation have significant effects upon the mineralogy and morphology of calcium carbonates (Folk 1974; Sandberg 1975; Longman 1980; Mackenzie and Pigott 1981; Given and Wilkinson 1985).

The purposes of this work were to investigate the effect of magnesium ions, in solutions of high and low supersaturation with respect to carbonate, upon the mineralogy and morphology of the precipitated calcium carbonate, and also to trace their mineralogical transformation with time when they were kept in the test solution for a period of time.

Methods

Magnesium-free artificial seawater (ASW) was prepared following the method described by Kester *et al.* (1967). Air was bubbled through the prepared ASW for two days to equilibrate with atmospheric carbon dioxide. The bubbling was stopped when the measured pH showed constant values.

The runs were made by placing 100 ml of ASW in Erlenmeyer flasks to which varying amounts of $MgCl_2$ were added from standardized 2.50 mole l^{-1} $MgCl_2$ to test their effects upon the mineralogy, and the morphology of calcium carbonate. The desired amount of Na_2CO_3 was added with stirring from a freshly prepared stock solution to increase the rate of the reaction. Analytical grade NaCl was added to replace $MgCl_2$ to maintain the ionic strength of 0.70M. This avoided, in part the effect of ionic strength on the rate of the reaction when Mg^{2+} was reduced (Bischoff 1968; Sayles and Fyfe 1973).

All solutions were at least 250% saturation with respect to calcium carbonate solid phase like warm near-surface oceanic waters without the addition of Na_2CO_3. The degree of saturation, D.S., of the test solution with respect to calcite can roughly, calculated from :

$$D.S. = (Na_2CO_3 \text{ added}) \quad \times 2.2E + 4$$

Each prepared solution corresponds roughly, to natural seawater of 35.00 salinity. The experiment was carried out in a water bath (Amico Constant Temperature bath, #4-8605) at 25.0 ± 0.4°C.

Usually, there were time ranges from the onset of the precipitation, which correspond to the interval between the addition of Na_2CO_3 and the time when cloudiness in solution occurred. The precipitates were filtered, washed with distilled water and dried after settling on the bottom of the flask, then kept for x-ray diffraction (XRD) analysis. XRD analysis were performed from 24° to 34° at 0.02°/3 sec using Cu α radiation. The mole percent $MgCO_3$ (mole % $MgCO_3$) in calcite was calculated from the empirical relationship obtained by Chave (1952).

Subsequently to the XRD analysis, each precipitate was dissolved in HCl (0.10n) and the concentration of Mg^{2+} was determined by atomic absorption spectroscopy (AAS). To estimate the residual Mg^{2+} in calcite, it was assumed that pure aragonite had a maximum 1.5 mole % $MgCO_3$. Pure aragonite that was precipitated from the test solution was then used as standard by dissolving a known amount in HCl and determining its mole % $MgCO_3$. The weight percent (wt%) of calcite in the mixture was calculated from each sample from the following equation :

$$\text{wt\% calcite} = [(b \times 84.321/24.321) + (b \times 100.089/24.321)] \times [(100 - a)/a]$$

where a is the mole % $MgCO_3$ in calcite, calculated from XRD analysis and b is the wt% of Mg^{2+} in the total sample, determined by AAS. Therefore; the wt% of aragonite is 100 − wt% calcite.

Other precipitation runs were kept in a water bath for 35 days at a temperature of 25.0 ± 0.4°C. They were examined by XRD during the 35 days to test the transformation of their mineralogy. The XRD runs were made once each week up to about a month. In this case, the same method above was used to determine the mole % $MgCO_3$ and the wt% of calcite in each sample. Quantities of the transient vaterite and of aragonite were determined from the intensity ratio of aragonite to vaterite plus aragonite :

$$I_{(arag.)} / [\, I_{(arag.)} + I_{(vater.)} \,]$$

I is the height at 2 theta for each mineral from XRD, assuming that the height is a function of the amount of the mineral in the mixture.

Twelve samples from these homogeneous precipitates were selected for the morphological and size examination. The samples were selected from low and high ionic products of carbonates and at Mg:Ca ratios in solution from 0 to 5, to test the effect of these parameters, that is, of the Mg:Ca ratio and of the rate of growth upon the morphology of the crystals. The precipitates were examined using the Scanning Electron Microscope (SEM).

Results and Discussion

The addition of Na_2CO_3 to varying amounts of magnesium leads to the formation of carbonate minerals (Table 1). The amounts of magnesium added are shown as $(Mg^{2+}) : (Ca^{2+})$ ratios, where the Ca^{2+} concentration was 0.00993 mole l^{-1} in all cases.

X-ray diffraction results of the precipitates (Table 1) show three different calcium carbonate minerals: pure calcite (at zero Mg^{2+} ions in solution), mixture of magnesian calcite and aragonite, and pure aragonite alone. The mole % $MgCO_3$ in calcite increases with $(Mg^{2+}) : (Ca^{2+})$ concentration ratio in solution, as well as the increase of degree of saturation. Table 1 shows that high Na_2CO_3 added in the presence of

Mg^{2+} kinetically favors magnesian calcite minerals over aragonite. At lower addition of Na_2CO_3 aragonite is kinetically, favored. High Mg contents in solution favor the formation of aragonite over that of magnesian calcite. The increase of aragonite over magnesian calcite at Mg^{2+} concentration smaller than 0.03 moles l^{-1} and at lower ionic product suggests that the nuclei of high Mg contents could be formed, but because they are more soluble, they redissolved and give chance for the more stable aragonite to form.

Table 1. The effect of Mg^{2+} concentration and the degree of saturation on the mineralogy of calcium carbonate.

Ratio $(Mg^{2+}):(Ca^{2+})$	Na_2CO_3 mmolel^{-1}	Mole% $MgCO_3$	wt% (calcite).	wt% (aragonite)
0 : 1	4.80	0	100	0
	2.95	0	100	0
	1.97	0	100	0
	1.53	0	100	0
1 : 1	4.79	12.1	91	9
	2.95	7.6	59	41
	2.00	3.9	35	65
	1.50	3.9	7	93
2 : 1	4.75	12.7	61	39
	2.95	12.0	81	19
	1.95	1.7	5	95
	1.55	1.9	2	98
	1.05	0	0	100
3 : 1	4.75	11.9	60	40
	2.95	11.3	41	59
	1.95	3.8	16	84
	1.05	0	0	100
4 : 1	4.87	14.9	49	51
	2.87	12.1	4	96
	1.95	0	0	100
	1.45	0	0	100
	1.02	0	0	100
5 : 1	4.69	0	0	100
	2.89	0	0	100
	1.95	0	0	100
	1.44	0	0	100

Table 2 and Fig. 1 show the transformation of precipitates during a 35 day period. The results showed that the formation of calcium carbonate minerals was kinetically controlled. At high supersaturation, precipitation of high-magnesian calcite was favored. Generally, it was found that the mole% $MgCO_3$ in calcite decreases with time. Vaterite was found to be less stable than magnesian calcite and aragonite, and was the transition phase between them as they increased at the expense of vaterite. The

TABLE 2. Effect of the degree of saturation and Mg^{2+} concentration upon the transformation of calcium carbonate mineralogy.

$(Mg^{2+}) : (Ca^{2+}) = 2 : 1$							
Na_2CO_3 added (mmole l^{-1})							
8.18				4.72			
Time (days)	mole% $MgCO_3$	wt% calcite	$\frac{I_{arag}}{(I_{arag} + I_{vatr})}$	Time (days)	mole% $MgCO_3$	wt% calcite	$\frac{I_{arag}}{(I_{arag} + I_{vatr})}$
1	16.4	80	0.06	1	20	78	0.04
7	14.9	66	1.05	7	10.4	50	0.31
14	13.4	65	4.00	14	9.7	64	0.46
21	13.4	65	3.6	21	8.9	62	0.44
28	11.5	66	4.0	28	8.9	56	2.29
35	11.5	68	N.V.	35	8.9	80	5.00
$(Mg^{2+}) : (Ca^{2+}) = 3 : 1$							
Na_2CO_3 added (mmolel^{-1})							
8.10				4.70			
Time (days)	mole% $MgCO_3$	wt% calcite	$\frac{I_{arag}}{(I_{arag} + I_{vatr})}$	Time (days)	mole% $MgCO_3$	wt% calcite	$\frac{I_{arag}}{(I_{arag} + I_{vatr})}$
1	23.0	20	0.06	1	00	00	N.V.
7	17.9	36	0.04	7	13.4	12	0.03
14	17.9	56	0.11	14	11.9	22	0.09
21	20.8	61	0.40	21	12.7	21	0.25
28	18.6	56	2.33	28	12.7	28	1.88
35	19.3	54	3.00	35	12.7	29	2.20

N.V. = No Vaterite.

results showed that the mineral compositions depend upon the initial supersaturation of the magnesium content and tended to approach a steady-state equilibrium. The dissolution of high magnesian calcite and the precipitation of calcite with lower $MgCO_3$ content and aragonite obviously occurred. These precipitates have stabilities which depend upon the activities of the ions in solution and the composition of the mineral itself.

The crystal forms which were precipitated at different $(Mg^{2+}) : (Ca^{2+})$ concentration ratios and different ionic products in artificial seawater were acicular (needle-like in form). The images of carbonate minerals precipitated from Mg-free artificial seawater showed equant (same diameter in all directions) in shape (Fig. 2). Some

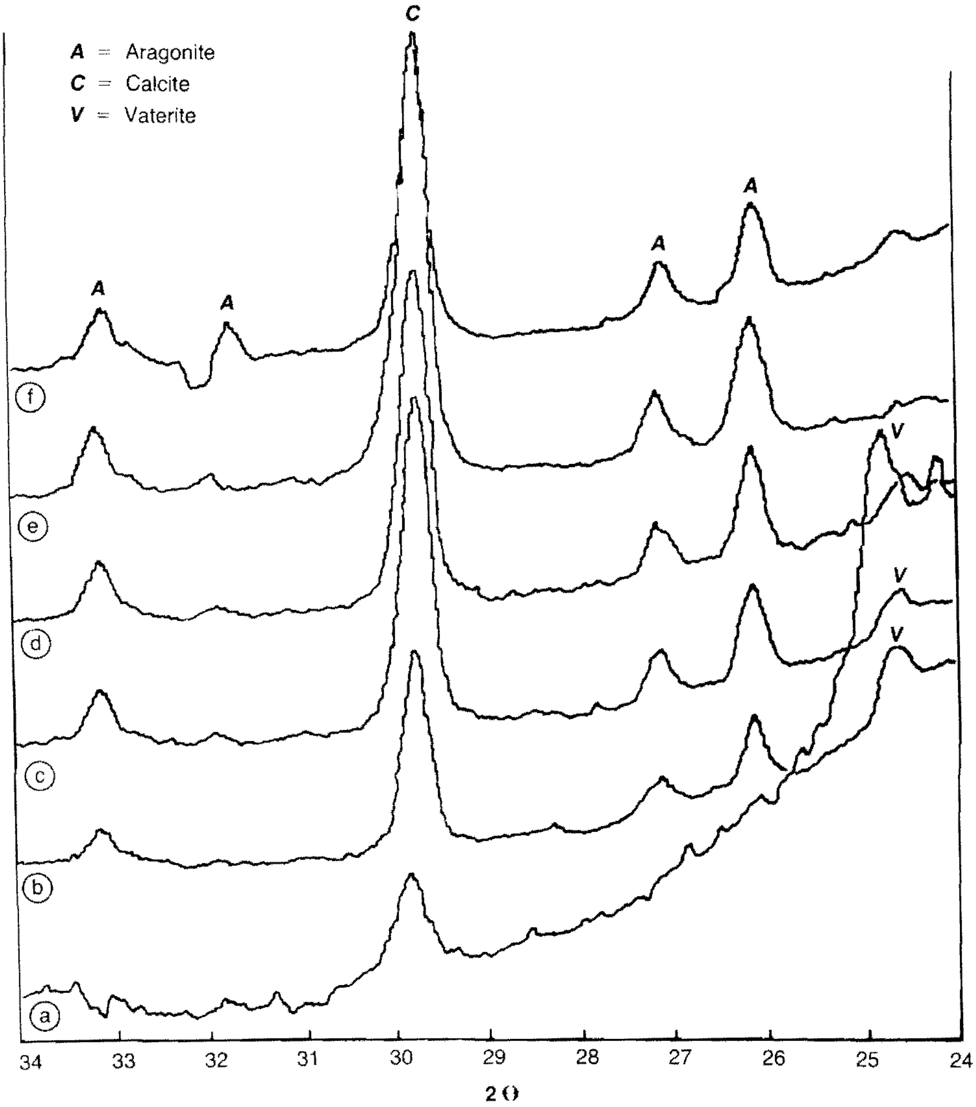

FIG. 1. XRD results for homogeneous precipitates when $(Mg^{2+}) : (Ca^{2+})$ concentration ratio is 3:1 and 4.7 mmolel^{-1} of Na_2CO_3 in artificial seawater during a period of 35 days. (a) Immediately after the massive precipitation from solution, (b) after one week in solution, (c) after two weeks in solution, (d) after three weeks in solution, (e) after four weeks in solution, and (f) after five weeks in solution.

elongated precipitates (Figs. 3 and 4) are found at $(Mg^{2+}) : (Ca^{2+})$ concentration ratio of 3 to 4.

The size of the crystals forms was found to be 10 μm or larger at zero Mg^{2+} ion in solution (Fig. 2). The size decreased with the increase of Mg^{2+} ion in the solution (1-2 μm) (Figs. 3 and 4). Aragonite crystals were the smallest ones (< 1 μm). The charac-

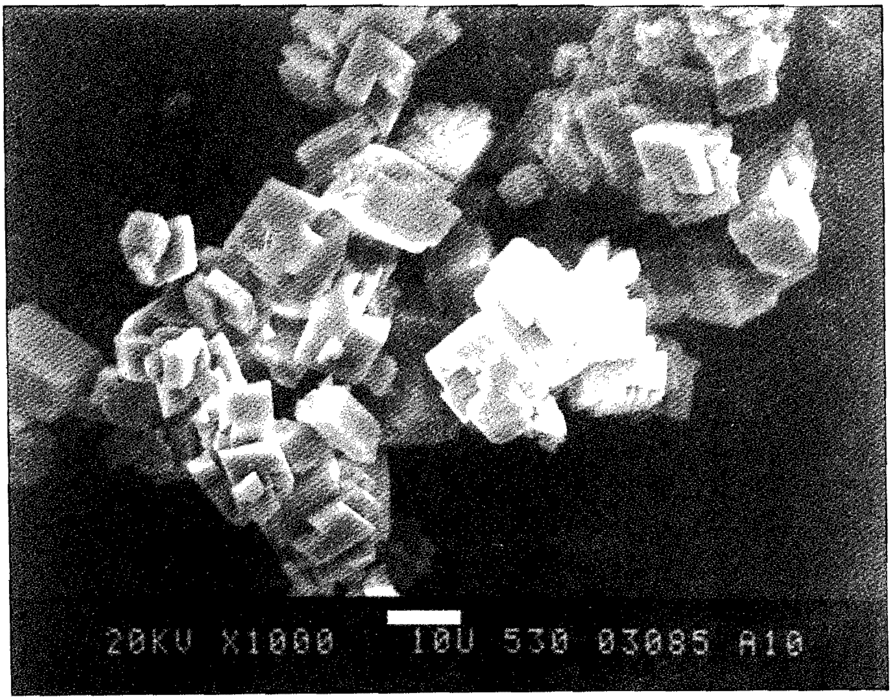

FIG. 2. SEM images of equant pure calcite precipitated from artificial seawater at addition of 1.48 mmolel^{-1} Na_2CO_3.

teristics of the surface of the crystals also appeared to be affected by the rate of the reaction and the $(Mg^{2+}) : (Ca^{2+})$ concentration ratio. In the presence of magnesium ions in solution, the crystals appeared in the forms of bundles of fibrous or needle-like aggregates.

Furthermore, the experimental results showed that the presence of Mg^{2+} in solution was one of the parameters that controlled the morphology of calcium carbonate. At zero magnesium concentration in solution the crystal morphology was equant (Fig. 2) both at high and low concentration of carbonates and, thus, at fast and low reaction. Therefore, one would expect that the reaction rate of precipitation was not the main control in determining the morphological feature of calcium carbonate crystals but rather the presence of different ions in the solutions, especially the magnesium ions.

Conclusion

The mineralogy of inorganic homogeneous precipitation is a results of the Mg^{2+} ion concentration and rate of the reaction at constant T and P conditions. Pure calcite is favored in Mg-free solution; low-magnesian calcite is favored at Mg:Ca ratio <

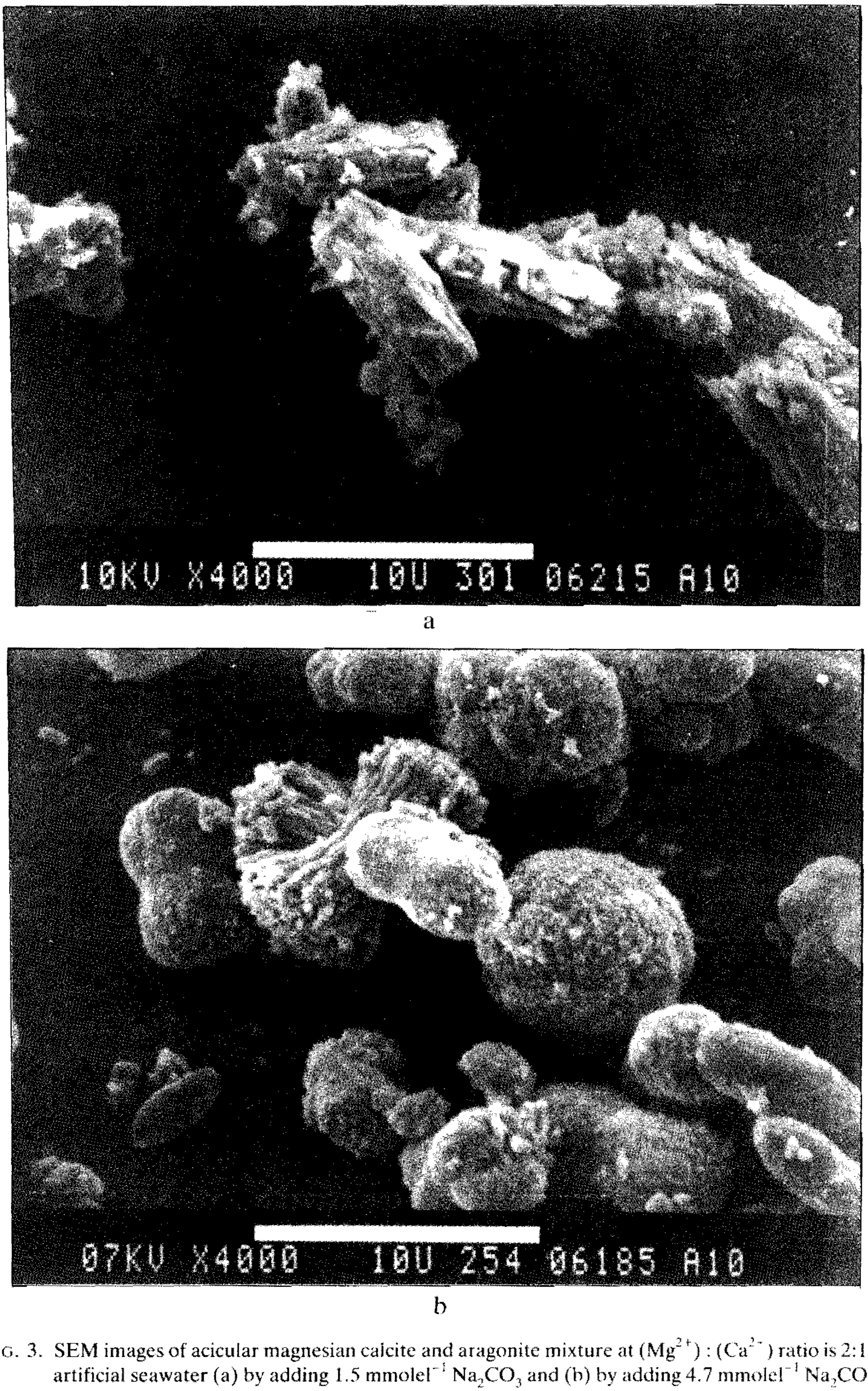

FIG. 3. SEM images of acicular magnesian calcite and aragonite mixture at (Mg^{2+}) : (Ca^{2+}) ratio is 2:1 in artificial seawater (a) by adding 1.5 mmolel^{-1} Na_2CO_3 and (b) by adding 4.7 mmolel^{-1} Na_2CO_3.

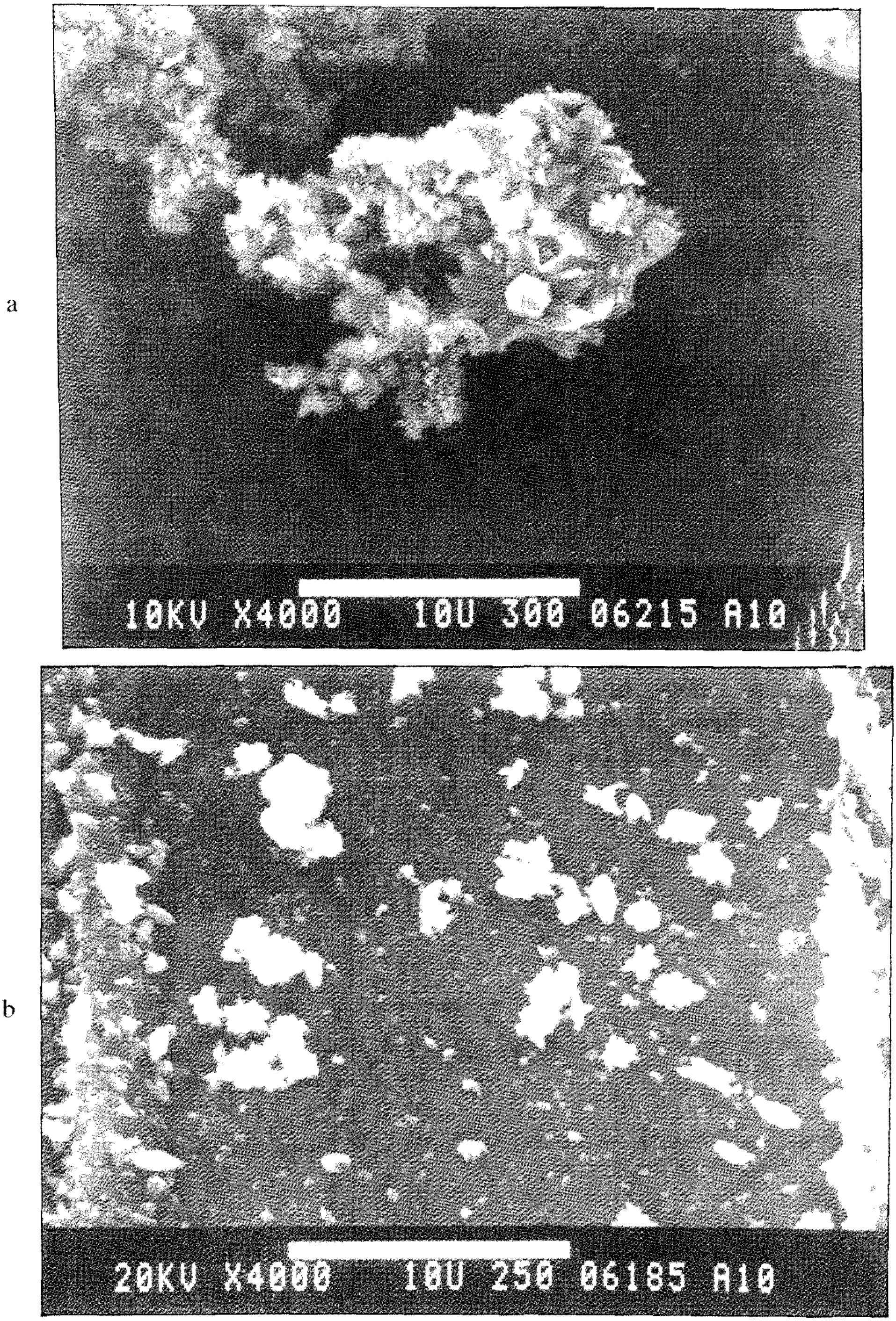

FIG. 4. SEM images of acicular aragonite at (Mg^{2+}) : (Ca^{2+}) ratio of 5:1 in artificial seawater (a) by adding 1.44 mmolel^{-1} Na_2CO_3 and (b) by adding 4.64 mmolel^{-1} Na_2CO_3.

2 and low degree of saturation, pure aragonite is favored at Mg:Ca > 4, high magnesian calcite is favored at higher rates of reaction. This different mineralogy may affects the equilibrium condition of calcium carbonate, especially, those of the surface coatings. These surface coatings of the minerals are known to be the interface where they are in contact with seawater (Mucci, *et al.* 1985).

The morphology of calcium carbonate is also influenced by the concentration of magnesium ions in the solution, and the rate of the reaction. The morphology of calcium carbonate, its size and surface edges and corners will have different activities in solution (Chave and Schmalz 1966; and Pytkowicz 1969), so both mineralogy and morphology may control the interaction of carbonate crystals with surrounding solution.

Acknowledgement

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تأثير عنصر الماغنسيوم على ترسبات معدن كربونات الكالسيوم في مياه البحر : دراسة معملية

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المستخلص . في هذا البحث المعملي وجد أن عنصر الماغنسيوم الذائب في محلول ماء البحر يؤدي إلى تغيرات معدنية ومورفولوجية لكربونات الكالسيوم المترسبة من هذا المحلول على النحو التالي :

١ – معدن الكالسيت الماغنسيومي المنخفض والذي يحتوى على نسبة قليلة من كربونات الماغنسيوم يترسب من المحلول الذي يحتوى على نسبة تركيز عنصري الماغنسيوم : الكالسيوم أقل من ٣ : ١ ، ويكون تركيز الكربونات الذائبة قليلة (أي بدرجة تشبع منخفضة) .

٢ – معدن الأراجونيت يترسب من المحلول الذي يحتوى على نسبة الماغنسيوم : الكالسيوم أكثر من ٤ : ١ .

٣ – معدن الكالسيت الماغنسيومي العالي مع معدن الأراجونيت وذلك عندما يكون المحلول ذو درجة تشبع عالية بالكربونات الذائبة حيث يساعد ذلك على تفاعل عنصر الماغنسيوم مع الكربونات الذائبة ليصبح جزءًا من مركب معدن الكالسيت .

إن تزامن ترسب معادن ثلاثة الكالسيت ، الأراجونيت والفيترات يدل على ترسيب ذات طابع كاينتيكي (حركي) ، وهذا واضح من زيادة كمية كربونات الماغنسيوم عند زيادة تركيز الكربونات في المحلول .

كما دلت الدراسة على أن وجود عنصر الماغنسيوم في المحلول يعمل على بناء بلورات معدنية من كربونات الكالسيوم ذات أشكال طولية ، في حين أن البلورات المعدنية المتكونة في عدم وجود ذلك العنصر في المحلول تظهر بأبعاد متساوية . إضافة إلى ذلك فقد لوحظ أن حجم البلورة المتكونة تتضائل وتتناقص في الحجم مع ازدياد تركيز عنصر الماغنسيوم في المحلول