# Kinetics of Calcite Overgrowth as a Function of Magnesium Concentrations and Supersaturation in Artificial Seawater

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ABSTRACT. The effects of different magnesium: calcium concentration and the degree of saturation in artificial seawater (ASW) upon the kinetics of carbonate solid overgrowth have been investigated. It is shown that the mechanism of calcite overgrowth is a surface-controlled (interface) reaction in the presence or absence of  $Mg^{2+}$  in ASW. The reaction is a second order in Mg-free ASW and a third order in the presence of magnesium ion in the tested solution. The rates of the overgrowth reaction decrease with the increased  $Mg^{2+}$  concentration in ASW. The decrease of reaction confirm the involvement of magnesium ions in overgrowth by magnesian calcite. The reaction order, in presence of  $Mg^{2+}$  tend to approach a second order at high degree of supersaturation and large surface area of calcite.

# Introduction

Precipitation and dissolution reactions of carbonate minerals are the processes that control their composition and behaviour. The unique characteristics of carbonates, such as retention of supersaturation, metastability of solid phases and slow transformation of one phase to another, are indications of the special importance of kinetics during the processes of precipitation and dissolution. So, thermodynamics and kinetics are equally important to fully understand the chemical behaviour of carbonate minerals in natural water. While geochemists have made a fairly good progress in developing and applying thermodynamic principles to carbonate system, the kinetics of the reactions remains poorly defined (Lasaga 1981; Morse 1983; Reddy 1983). The

major methods that have been applied to describe reactions rates include theoretical and experimental laboratory studies of calcite dissolution and precipitation (for example, Sjoberg 1976; Plummer *et al.*, 1978; Reddy *et al.*, 1981), but the laboratory rate laws are still to be tested in field situations (Plummer and Back 1980).

Most of the investigations of reaction kinetics have been focused on calcite and aragonite in simple or mixed electrolyte and in seawater solutions, because they are the most common carbonate minerals in sediments and soils (for example, Reddy and Nancollas 1971; Nancollas and Reddy 1971; Plummer *et al.*, 1979; Morse and Berner 1979). However, the majority of studies have been focused on the dissolution kinetics in the ocean, because of the interest of dissolution processes of calcite and aragonite during particle settling from the surface to the bottom of the water column. Still the precipitation is also important because there are overgrowth processes that occur in the water column on foreign surfaces and most commonly in sediments.

The first major study of calcite precipitation in simple solutions was done by Nancollas and Reddy (1971) and Reddy and Nancollas (1971). The precipitation rate was interpreted as a second order surface controlled process expressed by :

$$\frac{\delta \Gamma_{Ca^{2+}}}{\delta T} = -k_n A [(Ca^{2+})(CO_3^{2-}) - \frac{K_{sp}}{f_{(2)}^2}]$$

Where  $T_{Ca^{2}+}$  is the total concentration, T is the time,  $k_n$  is the rate constant, A is the surface area,  $f_{(2)}^2$  is the divalent ion activity coefficient and  $K_{sp}$  is the solubility product of calcium carbonate. They found that precipitation rate was independent of stirring rate. It was also suggested that the Plummer *et al.* (1978) model could be used for calcite precipitation (Plummer *et al.*, 1979). The observation of the degree of saturation on the rate of the reaction suggested that the standard empirical equation could not be used (Reddy *et al.*, 1981; House 1981). House (1981) tested the equation of Davies and Jones (1955), Nancollas and Reddy (1971) and the spiral growth mechanism model, he concluded none of them was adequate. The rates of calcite precipitation measured in the field were compared with the rates predicted from laboratory derived studies (Plummer *et al.*, 1978) and the agreement in the rates was within a factor of 3 (Herman and Lorah 1988).

Inskeep and Bloom (1985) tested, almost all the rate equations for calcite precipitation and concluded that, the rate equations which were described by Plummer *et al.* (1978) and Nancollas and Reddy (1971) were more successful. They also concluded that, the best successful model which described calcite participation at high pH (*e.g.* pH > 8) is the Nancollas and Reddy's model (1971).

The purpose of this work was to conduct a laboratory investigation of calcite precipitation rates at different  $(Mg^{2+})$ :  $(Ca^{2+})$  concentration ratios in artificial seawater in order to test the effect of magnesium concentration on the reaction rates, and on the total order of the reaction. The equation of the reaction rate, developed by Nancollas and Reddy (1971), will be used, with slight modification to represent the calcite overgrowth.

# **Experimental Procedure**

# Experiment

 $(Mg^{2+})$ ,  $(Sr^{2+})$  and  $(H_3 BO_4)$ -free artificial seawater (ASW) was prepared following the procedure of Kester *et al.* (1967). The ASW, which has ionic strength of 0.526 M was equilibrated with laboratory pCO<sub>2</sub> for about two days by bubbling air through the solution. The bubbling was stopped when the measured pH was stable. The concentration of  $(Ca^{2+})$  in this solution was 9.754 mmole kg<sup>1-</sup> ASW. Various amounts of magnesium were added from prestandardized stock solution, by Mohr titration (Blaedel and Meloche 1957), to prepare  $(Mg^{2+})$ :  $(Ca^{2+})$  of 1, 2, and 5. Different amounts of predried reagent grade NaCl were added to these prepared solutions to maintain the ionic strength of 0.718 M. Each solution was kept in a closed bottle and its pH was measured every 24 hours, it only changed by  $\pm$  0.005 pH unit. It was noticed that the pHs of the solutions were decreased with increasing magnesium concentrations.

A reaction cell (volume  $103.76 \pm 0.27$  ml) was constructed from a glass beaker fitted with a water jacket for the determination of the reaction rates of overgrowth on different surface areas of calcite in ASW of different (Mg<sup>2+</sup>) : (Ca<sup>2+</sup>) concentrations ratios and constant ionic strength of 0.718 M at 25°C. The cell involved a combination electrode (Radiometer GK2401C), a stop cock for flushing excess solutions, a ground syringe piston for displacement of the excess solution and a stirring bar. The closed system reaction cell is shown in Fig. 1.

The seeds used in this experiment were reagent grade artificial calcite (J.T. Baker). The artificial calcite was washed with double deionized distilled water (DDW), three times, filtered and dried at 110-130°C for about four hours, before being exposed to ASW. The x-ray diffraction showed that they were pure calcite ( $2\theta = 29.4^{\circ}$ ). The specific surface area of calcite seeds was estimated from its density and the seed mean volume, which was determined by SEM images. It was estimated that the specific area was 0.589 m<sup>3</sup> · g<sup>-1</sup>.

The combination electrode was calibrated with NBS buffer, 185f (pH = 4.006 at 25°C) and 186-I-C (pH = 7.415 at 25°C). The slope of the electrode was determined following the instruction in the PHM64 Research pH meter Operating Instruction. Usually, the slope was 99.00  $\pm 0.21\%$ .

Before each experiment, the initial total alkalinity of each test solution was measured using the Gran titration method (Gran 1952; Dyrssen and Sillen 1967; Mehrbach *et al.* 1973) and by single acid addition (Anderson and Robinson 1946) developed by Culberson *et al.* (1970) to a pH of  $4.15 \pm 0.10$ . The standard deviation of the total alkalinity determination by both methods was  $\pm 5.8 \mu$  equivalent  $\cdot \text{ kg}^{-1}$  ASW. Also the initial pH was measured for each test solution. The initial total carbon dioxide, TCO<sub>2 (i)</sub>, was calculated from these two known parameters and the values of the first and second dissociation constant carbonic acid which were determined at different magnesium concentration as described by Rushdi (1989).



FIG.1. The closed system reaction cell.

The reaction cell was, completely, filled with the test solution and the combination electrode was allowed to equilibrate until the measured pH changed by less than 0.002 pH unit per hour at 25°C. Two different degree of saturations were obtained by selecting two pH values (pH = 8.1 and pH = 8.6). This has been achieved by adding drops of 0.1 N NaOH to the test solution from a syringe of a long needle through the hole in the stop cock while stirring. Then the piston was pushed half-way into the solution to flush some of the excess solution. The pH was recorded every five minutes until obtaining a similar three successive reading, then the calcite was added. The required weight of grade calcite was placed in a 2.5 ml Hamilton syringe with a long needle, then stirring was stopped and through the hole of the stop cock about 1.5 ml of ASW of the test solution was withdrawn into the syringe to form a slurry of calcite. which was then injected slowly into the solution without stirring. This step was done carefully to avoid any bubble trapping in the cell and it was done, at least, three times to insure that all the amount of calcite was delivered into the solution and settled to the bottom of the reaction cell. The piston was then pushed all-the-way down to displace the excess volume of ASW through the stop cock hole. The stop cock was immediately closed to prevent CO<sub>2</sub> exchange and the solution was stirred. The pH was recorded with time until it showed steady-state. The steady-state pH value was assumed when the change in pH was again less than 0.002 pH unit per hour.

#### **General Principle**

The following reactions are expected during growth or dissolution of  $CaCO_{3(s)}$  in simple solutions :

$$CO_{2(g)} \xrightarrow{H_2O} CO_{2(l)}$$
(1)

$$H_2O + CO_{2(1)} \rightarrow \leftarrow H_2CO_3$$
 (2)

$$H_2CO_3 \longrightarrow \leftarrow H^+ + HCO_3^-$$
 (3)

$$HCO_{3}^{-} \longrightarrow \leftarrow H^{+} + CO_{3}^{2-}$$
(4)

$$H_2O \longrightarrow \leftarrow H^+ + OH^-$$
 (5)

$$CaCO_{3(s)} \rightarrow \leftarrow Ca^{2+} + CO_3^{2-}$$
 (6)

$$\operatorname{Ca}^{2^+} + \operatorname{HCO}_3^- \longrightarrow \leftarrow \operatorname{CaHCO}_3^+$$
(7)

$$Ca^{2+} + CO_3^{2-} \longrightarrow \leftarrow CaCO_3^{\circ}$$
(8)

$$a^{2+} + OH^{-} \longrightarrow \leftarrow CaOH^{-}$$
(9)

The H<sup>+</sup> ion has an important effect on the growth or the dissolution of CaCO<sub>3(s)</sub> and its speciation. The presence of excess H<sup>+</sup> in solution will convert Ca<sup>2+</sup> + CO<sub>3</sub><sup>2-</sup> into highly soluble Ca<sup>2+</sup> and H<sub>2</sub>CO<sub>3</sub> from equation 3. Equation 4 and 6 represent growth or dissolution depending on the conditions of the processes. According to the above equilibrium and mass balance equations, the pH decreases and pCO<sub>2</sub> increases in the solution during the growth of calcium carbonate. One can trace the rate of growth or the rate of dissolution by following the change in the pH of the solution. This pH-drift method has been used by many investigators (for example Chave *et al.*, 1962; Land 1979; Plummer and Mackenzie 1974, Wollast and Reinh-Derie 1977). In a solution with (Ca<sup>2+</sup>) and (CO<sub>3</sub><sup>2-</sup>) concentrations similar to that in natural seawater, the change in (Ca<sup>2+</sup>) during growth or dissolution is very small and depends on the degree of saturation, but the change in (H<sup>+</sup>) is about 100-times the changes of (Ca<sup>2+</sup>). Therefore, the pH which influences the carbonate alkalinity, is sensitive indicator to follow the rate of growth or the rate<sup>6</sup> of dissolution. The following equation can be used to study the kinetics of CaCO<sub>3(s)</sub> overgrowth mechanism :

$$\frac{\delta_{\text{CO}_3^{2-}}}{\delta T} = -k_n A \left[ (\text{Ca}^{2+})_t (\text{CO}_3^{2-})_t - (\text{Ca}^{2+})_e (\text{CO}_3^{2-})_e \right]^n$$
(10)

Later equation (10) will be modified and expressed in terms of the change of carbonate alkalinity with time as a result of calcite.

#### Calculation

From the initial pH,  $pH_{(i)}$ , and initial total alkalinity  $TA_{(i)}$ , of the solution, the initial total carbon dioxide,  $TCO_{2(i)}$ , of each test solution was calculated using the following equation :

$$TCO_{2(i)} = CA_{(i)} \left[ \frac{(x)^{2} + (x) K_{1}^{'} + K_{1}^{'} K_{2}^{'}}{(x) K_{1}^{'} + 2K_{1}^{'} K_{2}^{'}} \right]_{(i)}$$
(11)

where (x) is (H<sup>+</sup>) and Ca<sub>(i)</sub> is the initial carbonate alkalinity (=  $TA_{(i)} - (OH^-) + (H^+)$ , in the case of this study). The values of K<sub>1</sub> and K<sub>2</sub> of different magnesium : calcium concentration ratios were experimentally determined (Rushdi 1989). Because each test solution was kept in a closed bottle, the total carbon dioxide was, actually, constant before the introduction of calcite. This was also confirmed by the steady state pH measurements of the test solution.

The initial carbonate alkalinity,  $CA_{(i)}$ , of each experiment at the two pH values was calculated from the initial pH and the initial carbon dioxide :

$$TCA_{(i)} = TCO_{2(i)} \left[ \frac{(x) K_1' + 2K_1' K_2'}{(x)^2 + (x) K_1' + K_1' K_2'} \right]_{(i)}$$
(12)

The number of moles of  $(CO_3^{2-})$ ,  $\Delta$ , which was involved in  $CaCO_{3(s)}$  overgrowth at time t was calculated from :

$$\Delta = CA_{(i)} \frac{\left\{ \left[ \frac{(x)^2 + (x) K_1' + K_1' K_2'}{(x) K_1' + 2K_1' K_2'} \right]_i - \left[ \frac{(x)^2 + (x) K_1' + K_1' K_2'}{(x) K_1' + 2K_1' K_2'} \right]_i \right\}}{\left\{ \left[ \frac{(x)^2 + (x) K_1' + K_1' K_2'}{(x) K_1' + 2K_1' K_2'} \right]_i - 1 \right\}}$$
(13)

The concentration of  $(CO_3^{2-})$  at time t, was calculated accordingly :

$$(CO_3^2)_{(t)} = (CA_{(i)} + 2\Delta) \left[ \frac{K_2}{(x) + 2K_2} \right]_t$$
 (14)

The rate of the reaction could be expressed, in terms of the driving force between equilibrium and ionic products, by the following equations :

$$\frac{\delta CA}{\delta T} = -2K_n A \left[ (Ca^{2+})_t (CO_3^{2-})_t - (Ca^{2+})_e (CO_3^{2-})_e \right]^n$$
(15)

where  $\delta CA/\delta T$  is the change in carbonate alkalinity with time. Since the change in  $(Ca^{2+})$  is very small, which was found to be less than 3% of the total  $(Ca^{2+})$  concentration in solution, while the change in  $(CO_3^{2-})$  was more than 80% of the total  $(CO_3^{2-})$  concentration in solution, hence the following equation could be used :

$$\frac{\delta CA}{\delta T} = -2k_n A \left[ \frac{(CO_3^{2-})_t}{(CO_3^{2-})_e} - 1 \right]^n$$
(16)

In terms of logarithmic formula, equation (16) is written as :

$$\log \left[\frac{\delta CA}{\delta T}\right] = \log \left[-2k_{n} A\right] + n \log \left[\frac{(CO_{3}^{2-})_{t}}{(CO_{3}^{2-})_{e}} - 1\right]$$
(17)

By fitting log  $[\delta CA/\delta T]$  versus log  $\{[(CO_3^{2-})_t / (CO_3^{2-})_e] - 1\}$ , one obtains the rate constant of the reaction, kn, from the intercept and the order of the reaction, n, from the slope.

### **Results and Discussion**

The effects of  $(Mg^{2^+})$  ions and the amount of calcite seeds upon the change of the pH with time as a result of the overgrowth is shown in Fig. 2. It is obvious that both magnesium and surface area influence the reaction process. Generally, the plots of log  $\delta CA/\delta T$  versus log  $[(CO_3^{2^-})_t / (CO_3^{2^-})_e - 1]$  shows two types of slopes (Fig. 3). Each of the slopes values is usually, referred to the total order of the reaction, n. Therefore, two values of n's for each reaction are reported in Table 1. The first n, n<sub>1</sub>, which is the value of the slope at the beginning of the reaction, and second n, n<sub>2</sub>, is the value of the second slope. The results showed that the n<sub>1</sub> value was larger than 4, and became larger with the increase of  $(Mg^{2^+})$  concentration in solution. The n<sub>2</sub> showed a value of about 2 for Mg-free solution and a value of about 3 in presence of Mg ions in solution. The n<sub>2</sub> value was observed to decrease with the increase of the surface area of calcite seeds (Fig. 4). The effect of the availability of surface area of calcite seeds was also demonstrated by the fast decrease in pH as a function of the increase of the amount of seed in solution as shown in Fig. 2. In Mg-free artificial seawater and high initial pH, *e.g.* high ionic products, it was noticed that n<sub>1</sub> disappeared and only n<sub>2</sub> was obtained.

The reactions showed two types of orders of (>1) which indicated surface-controlled mechanisms of two types. This phenomenon was also observed by Nancollas and Reddy (1971). They suggested that the first one might be caused by the surface and the bulk nucleation. A general agreement suggests that the crystal growth proceeds by incorporation of neutral molecules, at kinks in a growth step on crystal surface (Laitinen and Harris 1975). Ions of opposite charge must combine stiochiometrically, at certain stage in the process to obtain an electrical neutrality in the crystal lattice. Doremus (1958) suggested two ways of ion grouping on surface of the crystals: (a) formation of salt "molecule" which then diffuse to growth steps; (b) alternate incorporation of oppositely charged ions directly from adsorbed layer at a kink in growth step.

Probably, the reason for the large initial values of  $n_1$  were caused by the formation of hydrated, non-neutral amorphous form of calcium and/or magnesium carbonate (or bicarbonate) as a monolayer on the surface of the crystals, then gradually, transformed to a neutral molecule of unhydrated calcium and/or magnesium carbonate which is involved in the formation of crystal overgrowth. This was suggested from the disappearance of  $n_1$  at high ionic products. This disappearance of  $n_1$ , at high pH was probably due to the presence of sufficient  $CO_3^{2-}$  species that could form  $CaCO_3^{\circ}$  ionpairs on the surface of the crystal because the stability constants of  $CaCO_3^{\circ}$  is larger



FIG. 2. Change of pH as a result of calcite overgrowth, (a) 0.5 g of calcite was added per kg of ASW, (b) about 5.0 g of calcite was added per kg ASW.



FIG. 3. Log  $\delta CA/\delta T$  versus log [( $CO_3^2$ )<sub>1</sub>/( $CO_3^2$ )<sub>e</sub>-1] for various Mg : Ca concentration ratios in ASW of pHi = 8.1 (a) about 0.5 g of calcite was added per kg ASW; (b) 1.0 g of calcite was added per kg ASW.

$(Mg^{2+}): (Ca^{2+}) = 0.0:1.0$					
Expt #	<u>g</u> calcite kg ASW	$\Omega^1_{(initial)}$	– log k <sub>n</sub>	n	R
SC62	0.500	3.92	7.70	5.59	1.00
SC64	0.499	3.90	6.58 8.04 6.78	1.83 6.13 1.84	0.98 0.98 0.99
SC66	0.496	10.58	6.58	1.70	1.00
SC68	0.546	9.91	6.65	1.64	0.99
SC70	0.998	4.06	7.70	4.60	1.00
			7.14	2.17	0.98
SC72	0.998	4.01	7.33	3.91	0.97
			6.53	2.19	0.99
SC74	1.388	10.86	6.87	2.34	0.99
SC75	0.997	11.16	6.41	1.93	0.99
SC76	5.000	3.52	6.42	4.21	0.95
			6.72	2.27	0.99
SC77	5.005	3.44	6.27	3.05	0.98
			6.45	2.10	0.99
SC78	5.021	10.39	6.70	1.95	1.00
SC79	5.003	10.73	6.66	2.32	1.00

TABLE 1.	The results of log $\delta CA/\delta T$ versus log $[(CO_3^{2-})_t/(CO_3^{2-})_e - 1]$ fitting of calcite overgrowth in ASW
	with various Mg-to-Ca concentration ratios at 25°C and total ionic strength of 0.718 M.

Table 1. Contd.

$(Mg^{2+}): (Ca^{2+}) = 2.96:1.0$					
Expt #	<u>g</u> calcite kg ASW	$\Omega^{^{\mathrm{I}}}_{(\mathrm{initial})}$	– log k <sub>n</sub> .	n	R
SC80	4.99	3.86	11.77	16.73	1.00
			7.54	2.57	0.95
SC81	0.502	3.89	9.27	8.18	0.95
			7.34	2.67	0.93
SC82	0.499	10.65	9.13	4.60	0.99
			7.85	2.92	0.99
SC83	0.558	10.60	8.42	6.76	0.98
			7.72	2.45	0.96
SC84	1.001	3.68	8.42	6.76	0.98
			7.35	3.20	0.96
SC85	1.007	4.11	9.07	7.53	0.98
			7.41	2.75	0.96
SC86	1.003	11.31	9.63	4.39	0.98
			7.85	2.31	0.98
SC87	- 1.002	9.40	9.10	3.40	0.95
			7.94	2.49	0.98
SC88	5.005	3.37	7.37	3.41	0.99
			7.29	2.72	0.98
SC89	5.001	3.53	7.50	3.40	0.98
			7.42	2.82	1.00
SC90	5.000	10.15	7.78	1.86	0.98
SC91	5.002	10.01	7.68	1.76	0.99

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$(Mg^{2^{+}}): (Ca^{2^{+}}) = 4.99:1.0$					
Expt #	<u>g</u> calcite kg ASW	$\Omega^1_{(initial)}$	- log k <sub>n</sub>	n	R
SC92	0.499	3.91	13.44	18.51	0.99
			7.66	3.51	0.97
SC93	0.500	4.04	14.46	19.75	0.99
			7.86	3.54	0.97
SC95	0.573	8.70	12.87	9.24	0.99
			8.10	2.29	0.99
SC94	1.003	4.06	11.35	12.47	0.98
			7.81	2.80	0.97
SC97	1.003	3.58	11.84	16.59	0.98
			7.78	3.15	0.97
SC98	1.004	8.70	11.08	16.44	0.97
			8.18	2.38	0.99
SC99	0.968	8.64	11.31	7.97	1.00
			8.16	2.81	0.99
SC02	5.002	3.76	8.54	5.66	0.97
			8.02	2.47	1.00
SC03	5.002	3.77	8.92	7.35	0.95
			8.11	2.97	0.99
SC100	5.001	9.07	7.97	1.87	0.99
			7.42	2.82	1.00
SC90	5.000	10.15	7.78	1.86	0.98
SC91	5.002	10.01	7.68	1.76	0.99

I: The initial degree of saturation with respect to calcite.

than the stability constant of CaHCO<sub>3</sub><sup>+</sup> (Hawley 1973). At low pH the concentration of HCO<sub>3</sub><sup>-</sup> species was much higher than the concentration of  $CO_{2}^{2-}$ , which led to the formation of more CaHCO<sub>3</sub><sup>+</sup> than CaCO<sub>3</sub><sup>o</sup>. Apparently, the (Mg<sup>2+</sup>) ion in solution, is involved in the reaction as the hydrated form depending upon its concentration in solution. This was shown by the increase of n<sub>1</sub>, as well as n<sub>2</sub> with magnesium concentration.

Once the monolayer transformed into a neutrally charged interface between the bulk solution and the crystal surface, it regulated the crystal overgrowth. At this stage  $n_2$  represented the real overgrowth reaction. Accordingly, by taking the overgrowth reactions at supersaturation of natural seawater, it is concluded that the order of the overgrowth reaction  $n_2 = 2.07 \pm 0.17$  for Mg-free artificial seawater,  $n_2 = 2.81 \pm 0.18$  for  $(Mg^{2+})$ :  $(Ca^{2+}) = 2.96$  and  $n_2 = 3.07 \pm 0.38$  for  $(Mg^{2+})$  ( $Ca^{2+}$ ) = 5.03. Interestingly, at high degree of supersaturation and large surface area the total order of the reaction approached a second order in presence of magnesium ions in solution.

The presence of magnesium ions in solution affected the reaction rate as shown in Fig. 5. The rate of the reaction was slowed down by a factor of 14 by going from a Mg-



FIG. 4. The values of n's as a function of the initial pH and the amount of calcite added in solutions of (a) Mg-free ASW, (b) Mg : Ca = 3 and (c) Mg : Ca = 5.



FIG. 5. The rate constants of calcite overgrowth as a function of magnesium-to-calcium concentration ratios in artificial seawater similar to natural seawater.

free artificial seawater to a magnesium concentration that is found in natural seawater.

# Conclusion

Generally, the mechanism of calcium carbonate overgrowth is a surface-controlled reaction. The total order of the reaction is a second order in Mg-free artificial seawater. In the presence of magnesium ions the order of the reaction is approximately, third order reaction. The degree of saturation as well as the surface area are found to affect the order of the reaction. The reaction order tends to approach a second order at high degree of supersaturation and large surface area of calcite.

The overgrowth reaction rates of calcite decrease dramatically, with the increase of magnesium ions in solutions, which confirms the involvement of magnesium ions in the overgrowth reaction in the form of magnesium calcite.

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حركية النمو السطحي لمعـدن الكالسيت في وجـود تركـيزات المـاغنسيوم ودرجات التشبـع المختلفـة في مـاء بحر اصطــناعي

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المستخلص . يتضمن هذا البحث دراسة لمعرفة تأثير تركيز نسبة عنصري الماغنسيوم إلى الكالسيوم ودرجات التشبع المختلفة في ماء بحر اصطناعي على حركية النمو السطحي للكالسيت . فقد دلت الدراسة على أن الترسب السطحي للكالسيت عبارة عن تفاعل سطحي التنظيم (أي يتحكم فيه السطح البيئي) في وجود أو عدم وجود عنصر الماغنسيوم في المحلول . حيث أن التفاعل من المرتبة الثانية في عدم وجود عنصر الماغنسيوم ، ومن المرتبة الثالثة عند وجوده بالمحلول . إن النقصان في معدل سرعة التفاعل والتغير من تفاعل من المرتبة الثالثة عند وجوده بالمحلول . إن النقصان في معدل سرعة التفاعل والتغير من تفاعل السطحي لعدن الكالسيت ليكون الكالسيت الماغنسيومي . كما لوحظ اقتراب تفاعل المرتبة الثالثة من تفاعل المرتبة الثانية – في وجود عنصر الماغنسيوم العابية ووجود أسطح كبيرة من معدن الكالسيت عند التفاعل .