Kinetics of Calcite Over Growth Precipitation

By

Ahmed I. Rushdi

Department of Oceanography, Faculty of Science, Sana'a University, Sana'a, Republic of Yemen

Abstract

The effects of different mangnesium-to-calcium concentration ratios and the degree of saturation in artificial seawater (ASW) upon the kinetics of calcium carbonate solid overgrowth have been investigated. It is shown that the mechanism of calcite overgrowth precipitation is a surface-controlled (interface) reaction in the presence as well as in the 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 ASW. The overgrowth reaction rates decrease with the increasing Mg^{2+} concentration in ASW. The decrease of reaction rate and shift from second order to third order reaction confirm the involvement of magnesium ions in overgrowth reaction by magnesian calcite overgrowth precipitation. Surprisingly, the degree of saturation as well as the surface area are found to affect the order of the reation. The reaction order, in presence of Mg^{2+} tends 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 behavior. The unique characteristics of carbonates, such as retention of supersaturation, metastablility 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 behavior 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 reaction rates include theoretical and experimental laboratory studies of calcite dissolution and precipitation (Sjoberg, 1976; Plummer et al., 1978; Reddy et al., 1981), but the laboratory reaction rate laws are still to be tested in field situations (Plummer and Back, 1982). Most of the investigations of reaction kinetics have been focused oh calcite and aragonite in simple or mixed electrolyte and in seawater solutions (Reddy and Nancollas, 1971; Nancollas and Reddy, 1971, 1971; Plummer et al., 1979; Morse and Berner, 1979) because they are the most common carbonate minerals in sediments and soils. However, the majority of studies have been focused on the dissolution kinetics in the ocean, because of the interest on 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 be-

cause 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), Reddy and Nancollas, (1971). The precipitation rate was interpreted as a second order surface controlled process expressed by:

$$\frac{T\,Ca^{2+}}{t} = -k_n A\,[\,(Ca^{2+})\,(CO3^{2-}) - \frac{K_{sp}}{f\,(2)^2}\,] \tag{1}$$

Where TCa^{2+} is the total concentration, t is the time, and kn is the rate constant, A is the surface area, and $f_{(2)}$ is the divalent ion activity coefficient. They found that precipitation rate was independent of stiring 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 equations could not be used (Reddy **et al.**, 1981). House (1981), tested the equation of Davies and Jones (1955), Nanocollas and Reddy (1971) and the spiral growth mechanism model, and concluded that 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 equqtions 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 precipitation at high pH (e.g. pH > 8) is the Nancollas and Reddy model.

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

General Principles

The law of mass action at equilibrium between solid and solution is achieved when the dissolution rates, k_d. and the precipitation rates, k_p, are equal and there is no net change in the reaction. The definition for $CaCO3_{(s)}$ solid is represented by:

$$CaCO3\,(s) \quad \underset{K_p}{\overset{K_d}{\rightleftharpoons}} \quad Ca^{2+} + CO3^{2-} \tag{2}$$

and

$$\frac{K_d}{K_p} = Keq = \frac{(Ca^{2+})_{T,e}\,(CO_3^{2-})_{T,e}}{(CaCO3_{(s)})} \tag{3}$$

Where the parenthesis represents the concentration and the subscripts T and e refer to total and equilibrium state respectively. The thermodynamic equilibrium equation is:

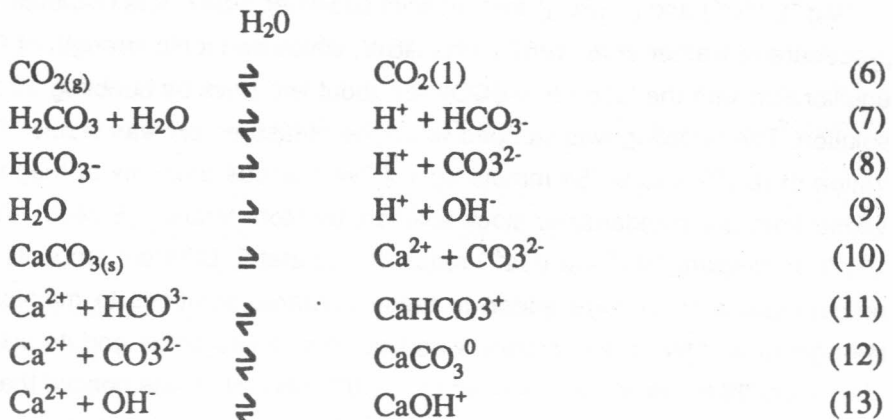$$K_{eq} = \frac{aCa^{2+}\,aCO3^{2-}}{aCaCO3_{(s)}} \tag{4a}$$

$$K_{eq} = \frac{(Ca^{2+})\,(Ca^{2+})\,(CO3^{2-})\,(CO3^{2-})}{CaCO3_{(s)}\,(CaCO3_{(s)})} \tag{4b}$$

Where a; is the activity of the component i and (i) is the activity coefficients of component i and i is the activity of the solid i. Usually the activity of pure solid is assigned a value of one. The saturation state, Ω , of the solution is determined from the ratio of the measured activity ionic products to the equilibrium constants by:

$$\Omega = \frac{aCa^{2+}\,aCO3^{2-}}{KO_{eq}} \tag{5}$$

when Ω . 1, the precipitation reaction is favored because the solution is supersaturated with respect to $CaCo3_{(s)}$. The dissolution of $CaCO3_{(s)}$ is favored when $\Omega < 1$.

The following reactions are expected during growth or dissolution of $CaCO3_{(s)}$ in Simple Solutions:

$$H_2O$$

$CO_{2(g)}$	$\rightleftharpoons$	$CO_2(1)$	(6)
$H_2CO_3 + H_2O$	$\rightleftharpoons$	$H^+ + HCO_3-$	(7)
HCO_3-	$\rightleftharpoons$	$H^+ + CO3^{2-}$	(8)
H_2O	$\rightleftharpoons$	$H^+ + OH^-$	(9)
$CaCO3_{(s)}$	$\rightleftharpoons$	$Ca^{2+} + CO3^{2-}$	(10)
$Ca^{2+} + HCO^{3-}$	$\rightleftharpoons$	$CaHCO3^+$	(11)
$Ca^{2+} + CO3^{2-}$	$\rightleftharpoons$	$CaCO_3^{\,0}$	(12)
$Ca^{2+} + OH^-$	$\rightleftharpoons$	$CaOH^+$	(13)

The H^+ ion has an important effect on the growth or the dissolution of $CaCO_{3(s)}$ and its ionc speciation. The presence of excess H^+ in solution will convert $Ca^{2+} + CO3^{2-}$ into highly soluble Ca^{2+} and H_2CO_3 from equation 7. Equations 8 and 10 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_2 increases in the solution during the growth of calcium carbonate. One can trace the rate of growth of 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, 1967; Plummer and Mackenzie, 1974; Wollast and Reint-Derie, 1979; and many others). In a solution with (Ca^{2+}) and $(CO3^{2-})$ concentrations similar to that in natural seawater, the change in (Ca^{2+}) during growth or dissolution is very small and depends on the degree of saturation, but the change in (H^+) is about 100-times the change of (Ca^{2+}). Therefore, the pH, which influences the carbonate alkalinity, is a sensitive indicator to follow the rate of growth or the rate of dissolution. The following equation:

$$\frac{CO_3}{t} = - K_n A [(Ca^{2+})_t (CO_3^{2-})t - (Ca^2+)e (CO32-)e]n \qquad (14)$$

can be used to study the kinetics of $CaCO_{3(s)}$ overgrowth mechanism. Later, equation(14) will be modified and expressed in terms of the change of carbonate alkalinity with time as a result of calcite overgrowth.

Experimental Procedure

Experiment

(Mg^{2+}), (Sr^{2+}) and (H_3BO_4)-free artificial seawater, ASW, was prepared following the procedure of Kester et al (1967). This ASW, which had ionic strength of 0.526M was equilibrated with the laboratory pCO2 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+}) was 9.754 mmole kg-1 ASW. Various amounts of magnesium were added from pre-standardized stock solution, by Mohr titration (Blaedel and Meloche, 1957), to prepare (Mg^{2+})-to-(Ca^{2+}) ratios of; 1,2 and 5. Different amounts of pre-dried reagent grade NaCl were added to these prepared solutions to maintain the ionic strength of 0.718M. Each solution was kept in a closed bottle and its pH was measured every 24 hours, it only changed by ± 0.005 pH unit. It was noticed that the pHs of the solutions were decreasing with increasing magnesium concentrations.

A reaction cell 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^{2+})-to-(Ca^{2+}) concentration ratios and constant ionic strength of 0.718 at 25°C. The cell invoived a combination electrode (Radiometer GK2401C), a stopcock for flushing excess solutions, a ground glass syringe piston for displacement of the excess solution and an stirring bar. The closed system reaction cell is shown in Figure 1. The volume of the cell was 103.761±0.027 ml.

The seeds used in this experiment were reagent grade artificial calcite (J.T.Baker). The synthetic calcite was washed with double deionized distilled water, three times, filtered and dried at 110-130°C for about four hours, and kept in vacum desiccator after cocling down, before being exposed to ASW. The x-ray diffraction showed that they was pure calcite by 2 = 29.40. The specific surface area of calcite seeds was estimated from its density and the seed mean volume, determined by SEM images. It was 0.589 m^3g^{-1}.

The combination electrode was calibrated with NBS buffers, 185f (pH = 4.006 at 25°C) and 186-IC and 186-II-C (pH = 7.415 at 25°C). The stope of the electrode was as in the PHM64 Research pHmeter Operating Instructions. Usually the slope was 99.00±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±0.10. The standard deviation of the total alkalinity determined by both methods was ±5.8 uequivalent kg-1ASW, The initial pH was measured for each test solution. The initial total carbon dioxide, $\Sigma CO2(i)$ was calculated from these two known parameters and the values of first and second dissociation constants of carbonic acid which were determined at different magnesium concentration as described by Rushdi (1989).

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. They were pH = 8.1 and pH = 8.6, and were achieved by adding drops of 0.1N NaOH to the test solution from a syringe of a long needle through the hole in the stopcock 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 three successive reading were the same 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 stopcock 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
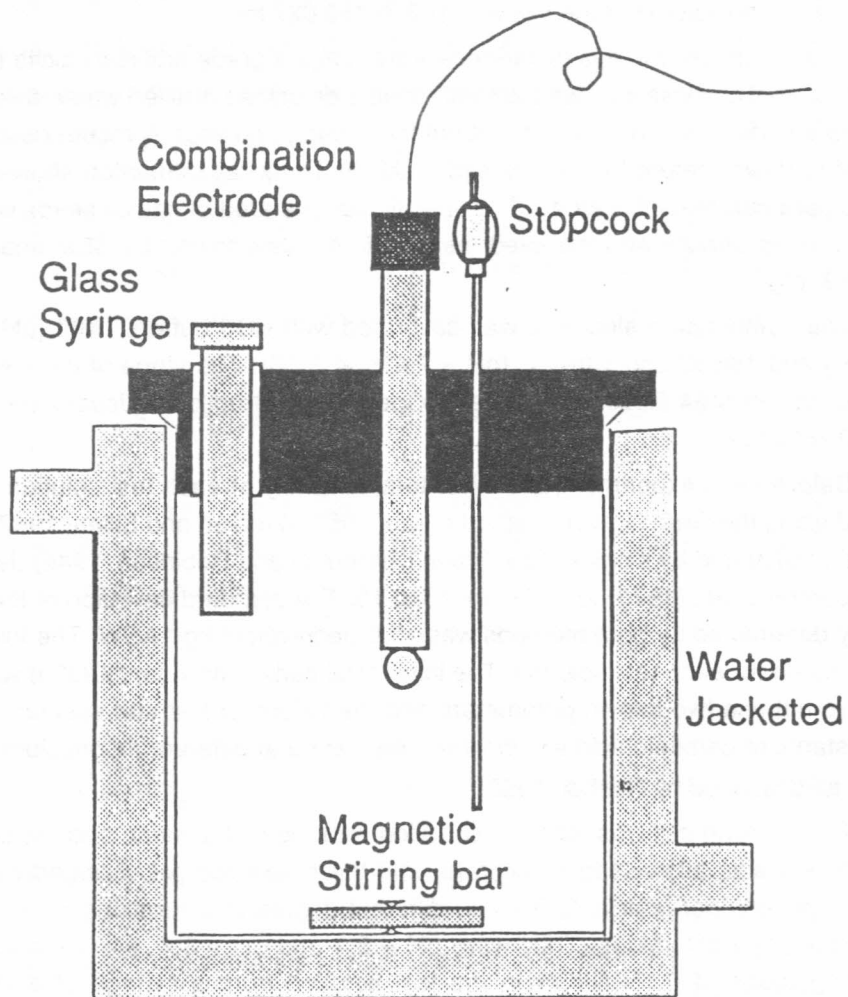
Fig. (1)

The Reaction Cell.

bottom of the reaction cell. Then the piston was pushed all-the-way down to displace the excess volume of ASW through the stopcock hole. The stopcock was immediately closed to prevent CO_2 exchange and the solution was stirred. The pH was recorded with time until it was at steady-state. The steady-state pH value was assumed when the change in pH was again less than 0.002 pH unit per hour.

Calculation

From the initial pH and initial TA of the test solution, the initial total carbon dioxide of each test solution was calculated using the following equation:

$$\Sigma CO_{2(i)} = (TA - OH^- + H^+)_{(i)} \left[\frac{(X) K_1' + K_1' K_2'}{(X) K_1' + 2K_1' K_2'} \right]_i \tag{15}$$

The values of K_1' and K_2' of different magnesium-to-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 of each experiment at the two pH values was calculated from the initial pH and the initial total carbon dioxide:

$$CA_{(i)} = \Sigma CO_{2(i)} \left[\frac{(X) K_1' + 2K_1' K_1'}{(X) K_1' + K_1' K_2'} \right]_i \tag{16}$$

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

$$\Delta = CA_{(i)} \frac{\left\{ \left[\frac{(X) K_1' + K_1' K_2'}{(X) K_1' + 2K_1' K_2'} \right]_i - \left[\frac{(X)^{2+} (X)K_1 + K_1' K_2'}{(X)K_1' + 2K_1' K_2'} \right]_t \right\}}{\left\{ \left[\frac{(X) K_1' + K_1' K_2'}{(X) K_1' + 2K_1' K_2'} \right]_{t-1} \right\}} \tag{17}$$

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

$$(CO_3^{2-})_t = (\Sigma CO_{2(i)} + \Delta) \left[\frac{K_1' K_2'}{(X) K_1' + K_1' K_2'} \right]_t \tag{18}$$

it could also be calculated from:

$$(CO_3^{2-})t = (CA_{(i)} + 2\Delta) \left[\frac{K_2'}{+ 2K_2'} \right]_t \tag{19}$$

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

$$\frac{CA}{t} = -2K_n A [(Ca^{2+})_t (CO3^{2-})_t - (Ca^{2+})e - (CO3^{2-})e]n \qquad (20)$$

Where CA/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 $(CO3^{2-})$ was more than 80% of the total $(CO3^{2-})$ concentration in solution, hence, the following equation could be used:

$$\frac{CA}{t} = -2K_n A [(CO3^{2-})_t - (CO_3^{2-})_e]n$$

and

$$\frac{CA}{t} = -2k_n A [\frac{(CO_3{}^{2-})_t}{(CO_3{}^{2-})_e} -1]n \qquad (21)$$

In terms of logarithmic formula equation (21) is written as:

$$\log [\frac{CA}{t}] = \log [-2K_n A] + n \log [\frac{(CO_3{}^{2-})_t}{(CO_3{}^{2-})_e} -1] \qquad (22)$$

By fitting $\log [- CA/ t]$ versus $\log \{[(CO_3{}^{2-})t / (CO_3{}^{2-})_e]-1\}$, one obtains the rate constant of the reaction, K_n, 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 Figure 2. The presence of magnesium in solution slows down the rate of the reaction as illustrated in figures 2a and 2b but the increase in surface area of calcite seeds exposed to the solution accelerates the reaction as shown in figure 2b. It is obvious that both magnesium and surface area influence the reaction process. Generally, the plots of $\log CA/ t$ versus $\log (CO3t/CO3e-1)$ shows two types of slopes, as is illustrated in Figure 3. Each of these values of the slopes is, usually, referred to the total order of the reaction, n.Therfore, two values of n's for each reaction are reported in Table 2. The first n, n_1, which is the value of the slope at the beginning of the reaction, and second n_2, is the value of the second slope. The results showed that the n_1 value was larger than 4, and became larger with the increase of (Mg^{2+}) concentration in solution. The n_2 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_1 value was observed to decrease with the increase of the surface area of calcite
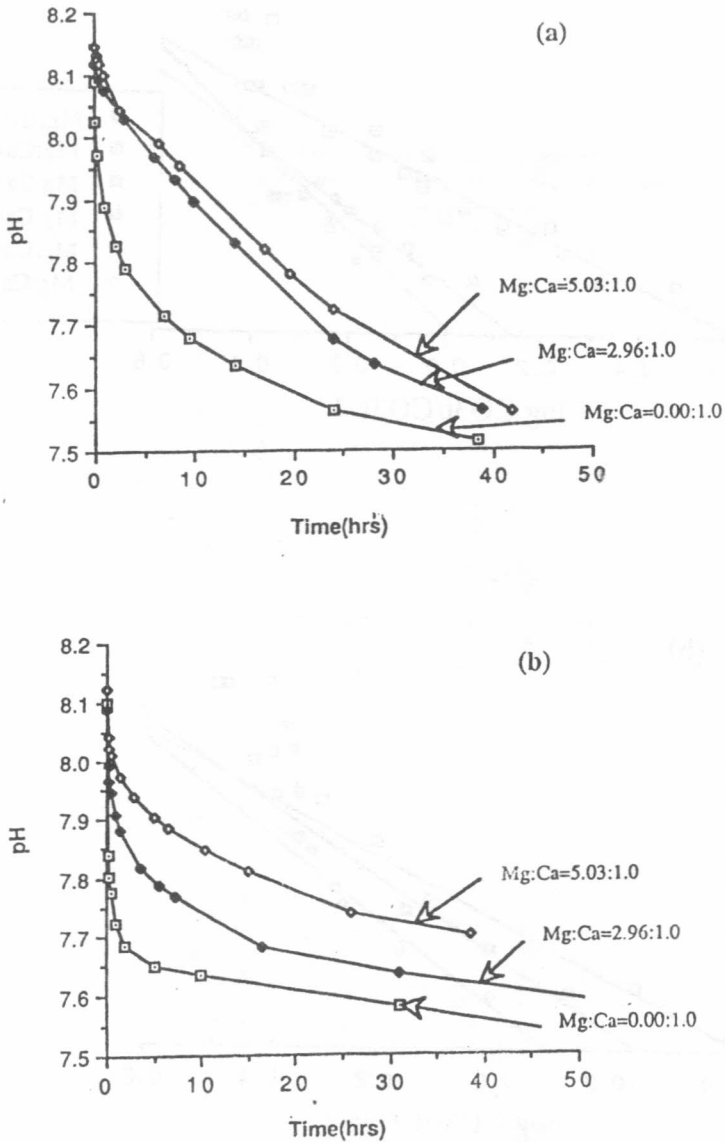
Figure (2)

Change of pH as a result of calcite overgrowth, (a) about 0.5 g of calcite was added per kg of ASW, (b) about 5.0 g of calcite per kg ASW was added.
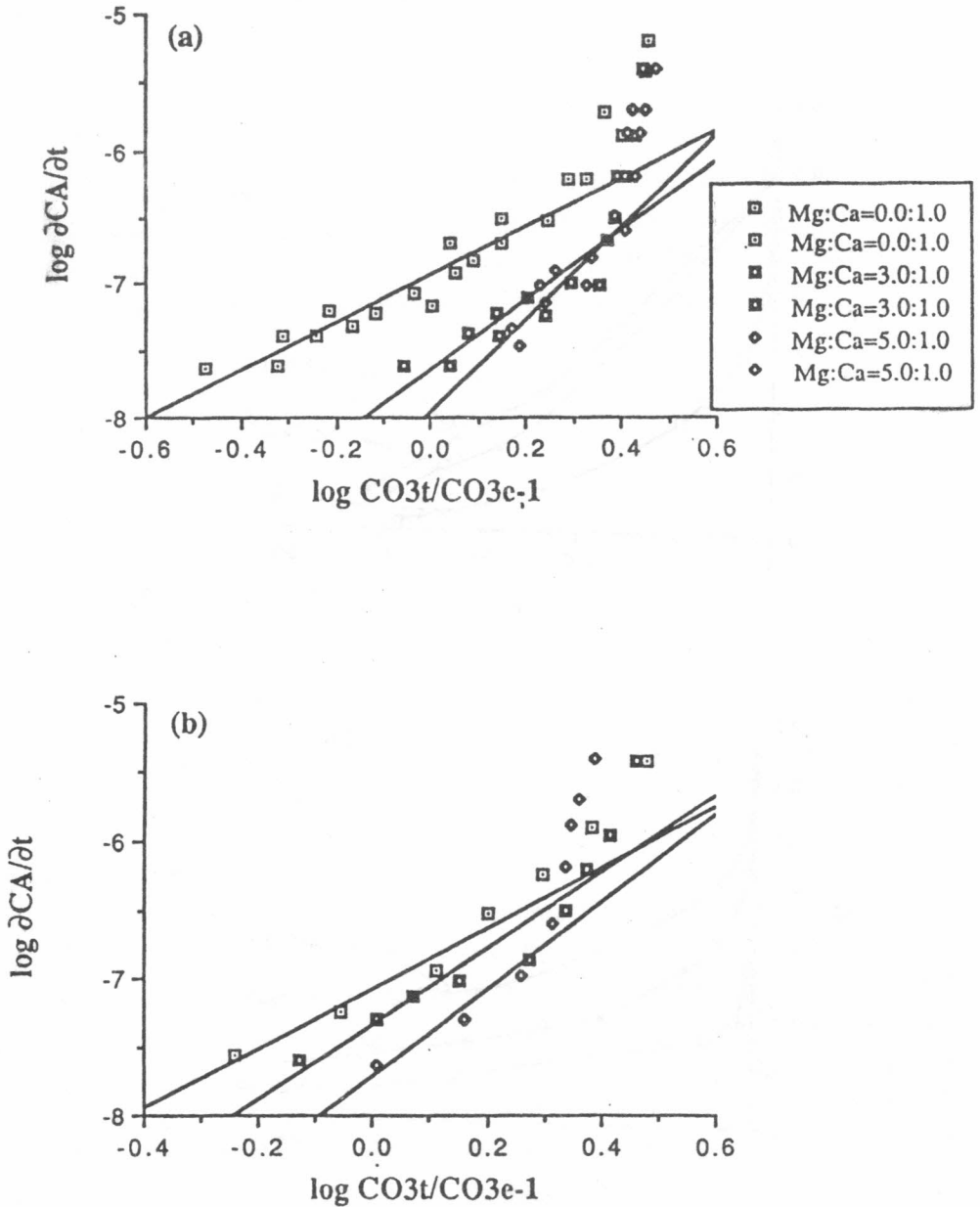
Figure (3)

Log CA/ t versus log [(CO32-)t/(CO32-)e -1] for various Mg: Ca concentration ratios in ASW of pH; = 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.
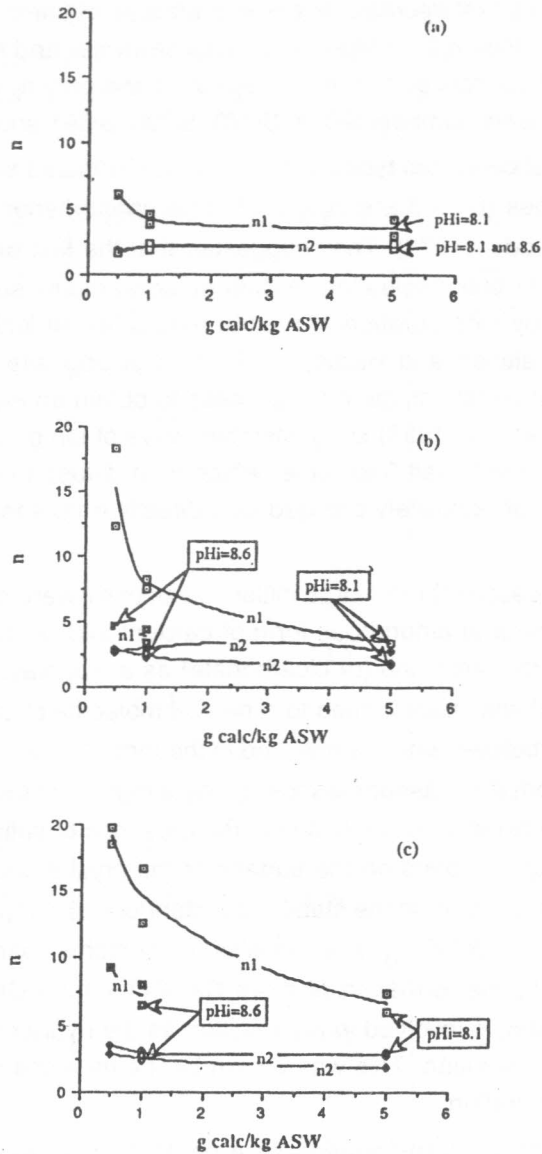
Figure (4)

The values of ns as a function of the initial pHi and the amount of calcite added
in solutions of: (a) Mg-free ASW, (b) Mg:Ca = 3 and (c) Mg:Ca = 5.

seeds as is shown in Figure 4. The effect of the availability of surface area was also demonstrated by the fast decrease in pH as a function of the increase of the amount of seed in solution in Figure 2. In Mg-free artificial seawater and high initial pH, e.g. high ionic products, it was noticed that n_1 disappeared and only n_2 was obtained as shown in table 1, experiments numbers SC78, SC79, SC90, SC91 and SC100.

The reactions showed two types of orders which indicated surface-controlled mechanisms of two types ($n_1 > 3$ and $n_2 = 2$-3). 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 agreements suggests that the crystal growth proceeds by incorporation of neutral molecules, at kinks in a growth step on crystal surface (Laitinen and Harris, 1977). Ions of opposite charge must combine stoichiomtrically 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 reasons for the large initial values of n_1 were caused by the formation of hydrated, non-neutral amorphous form of calcium and or magnesium (i.e. in presence of 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 a 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 $CaCO_30$ ion-pairs on the surface of the crystal because the stability constant of $CaCO_30$ is larger than the stability constant of $CaHCO_{3+}$ (Hawely, 1973). At low pH the concentration of HCO_3- species was much higher than the concentrations of CO_3^{2-}, which led to the formation of more $CaHCO_{3+}$ than $CaCO_30$. Apparently, the (Mg^{2+}) 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_1, as well as n_2 with magnesium concentration.

Once the monolayer transformed into a neutrally charged interface between the bulk solution and the crystal surface, it regulates 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 $n_2 = 2.07\pm0.17$ for Mg-free artificial seawater; $n_2 = 2.81\pm0.18$ for $(Mg^{2+}) : (Ca^{2+}) = 2.96$ and $n_2 = 3.07\pm0.38$ for $(Mg^{2+}) : (Ca^{2+}) = 5.03$. Interestingly, at high degree of supersaturtion and large surface area the total order of the reaction approached a second order in presence of magnesium ions in solution.

Table (1): The results of log DCA/Dt versus log (CO3t/CO3e-1) fitting of calcite overgrowth in ASW with various Mg-to-Ca concentration ratios at 25°C and total ionic strength of 0.718.

		$(Mg^{2+}) : (Ca^{2+}) = 0.0:1.0$			
Expt No.	gcalcite / kg ASW	Ω (initial)	- log kn	n*	R**
SC62	0.500	3.92	7.70	5.95	1.00
			1.83	0.98	
SC64	0.499	3.90	8.04	6.13	0.98
			1.84	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
			2.17	0.98	
SC72	0.998	4.01	7.33	3.91	0.97
			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
			2.27	0.99	
SC77	5.005	3.44	6.27	3.05	0.98
			2.10	0.99	
SC78	5.012	10.39	6.70	1.95	1.00
SC79	5.003	10.73	6.66	2.32	1.00
SC80	0.499	3.86	11.77	16.73	1.00
			2.67	0.95	
SC81	0.502	3.89	9.27	8.18	0.95
			2.67	0.93	

Table (1) continurd

(Mg2+) : (Ca2+) = 0.0:1.0				
Expt No.	gcalcite / kg ASW	Ω (initial)	- log kn	n*	R**
SC82	0499	10.65	9.13	4.60	0.99
			2.92	0.99	
SC83	0.558	10.60	8.42	6.76	0.98
	0.496		2.45	0.96	
SC84	0.001	3.68	8.42	6.76	0.98
			3.20	0.96	
SC85	1.007	4.11	9.07	7.53	0.98
			2.75	0.96	
SC86	1.003	11.31	9.63	4.39	0.98
			2.31	0.98	
SC87	1.002	9.40	9.10	3.40	0.95
			2.49	0.98	
SC88	5.005	3.37	7.37	3.41	0.99
			2.72	0.98	
SC89	5.001	3.53	7.50	3.40	0.98
			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
SC92	0.499	3.91	13.44	18.51	0.99
			3.51	0.97	
SC93	0.500	4.04	14.46	19.75	0.99
			3.54	0.97	
SC95	0.573	8.70	12.87	9.24	0.99
			2.29	0.99	

Table (1) continurd

		$(Mg2+) : (Ca2+) = 0.0{:}1.0$			
Expt No.	gcalcite kg ASW	Ω (initial)	- log kn	n^{*}	R^{**}
SC94	1.003	4.06	11.35	12.47	0.98
			2.80	0.97	
SC97	1.003	3.58	11.84	16.59	0.98
			3.15	0.97	
SC98	1.004	8.70	11.08	6.44	0.97
			2.38	0.99	
SC99	0.968	8.64	11.31	7.97	1.00
			2.81	0.99	
SC02	5.002	3.76	8.54	5.66	0.97
			2.42	1.00	
SC03	5.002	3.77	8.92	7.35	0.95
			2.97	0.99	
SC100	5.001	9.07	7.97	1.87	0.99

The presence of magnesium ions in solution affected the reaction rate as shown in Figure 5. The rate of the reaction was slowed down by a factor of 14 by going from a Mg-free artificial seawater to a magnesium concentration that is found in natural sea-water.

Conclusion

Generally, the mechanism of calcite 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, a third order. 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 magnesiam calcite.
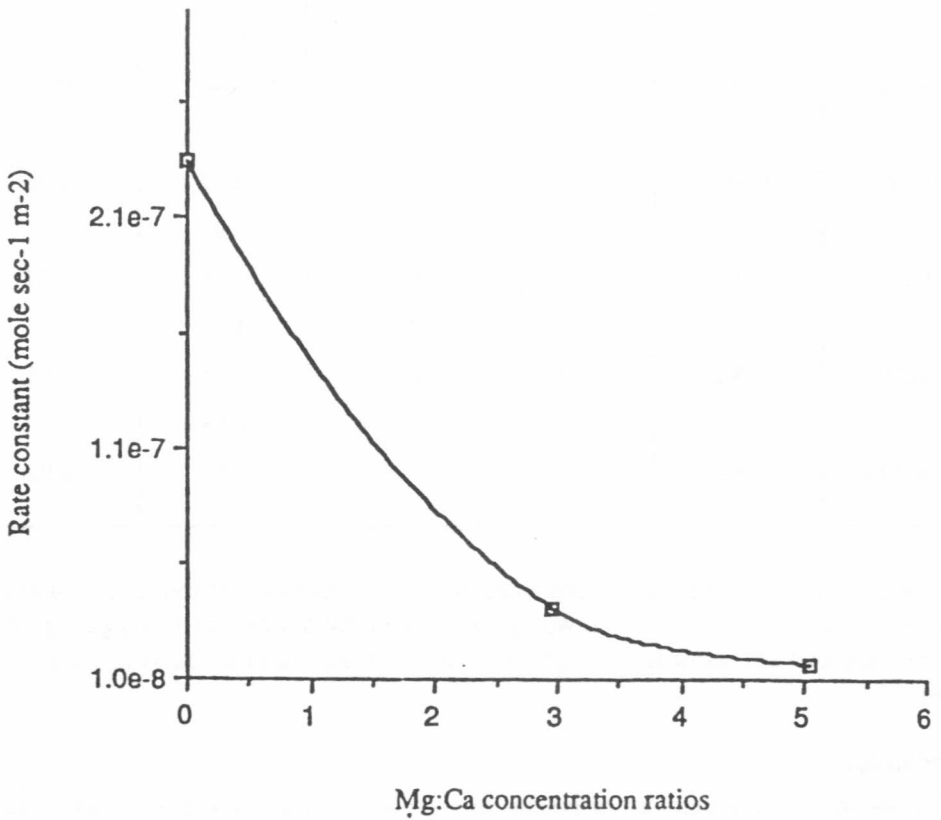
Figure (5)

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

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