

The effects of magnesium-to-calcium ratios in artificial seawater, at different ionic products, upon the induction time, and the mineralogy of calcium carbonate: a laboratory study

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With 4 figures and 2 tables

Zusammenfassung

Die Wirkung der Mg^{2+} -Ionenkonzentration und des Ionenprodukts von Karbonaten wurde in Abhängigkeit von der Induktionszeit für den Beginn der Ausfällung und der unterschiedlichen Mineralogie von Kalziumkarbonaten untersucht. Es konnte gezeigt werden, daß Mg^{2+} -Ionen die spontane Ausfällung von Kalziumkarbonat aus einer übersättigten Lösung (z. B. Meerwasser), im Vergleich zu Kalziumkarbonatmineralien derart verzögert, daß nur noch der biogene Entzug für skelettbildendes Kalziumkarbonat aus dem Meerwasser möglich ist. Niedrige Konzentrationen von Magnesiumionen in der Lösung fördern die Kalzitbildung, während Aragonit bei hohen Magnesiumkonzentrationen gebildet wird. Die Mol% $MgCO_3$ in Magnesiumkalzit steigen mit der Zunahme von (Mg^{2+}) und mit der Zunahme von (CO_3^{2-}) bei Gegenwart von (Mg^{2+}) in der Lösung.

Daher würde man erwarten, daß Hochmagnesiumkalzit in erwärmten Küstengebieten gebildet wird, wo hohe Temperaturen, und/oder die Zunahme der Photosyntheseaktivität dazu führen, daß CO_2 frei wird, und damit die Übersättigung ansteigen lassen. Niedrigmagnesiumkalzit wird bevorzugt in meteorische-vadosen Gebieten mit niedriger Magnesiumionenkonzentration oder in Versenkungsgebieten gebildet, wo die Respiration und die Oxidation hoch ist, bei sinkender Übersättigung.

Abstract

The effects of the Mg^{2+} ion concentration and the ionic products of carbonate upon the induction time for the onset of precipitation and the different mineralogies of calcium carbonates were studied. It was shown that Mg^{2+} ions delay the spontaneous precipitation of calcium carbonate from supersaturated solutions (e.g. seawater) with respect to calcium carbonate mineral to such an extent that only biogenic removal of skeletal calcium carbonate is possible from the open ocean. Low concentrations of magnesium ions in solution favor calcite formation while aragonite is formed at high magnesium concentrations. The mole % of $MgCO_3$ in magnesian calcite increases with the increase of (Mg^{2+}) in solution and with the increase of (CO_3^{2-}) in the presence of (Mg^{2+}) in solution.

Therefore, one would expect that high Mg-calcite is formed in warmed coastal regions, where high temperature and or the increase of photosynthesis activities tend to expel CO_2 and increase supersaturation, and low-magnesian calcite is favored in meteoric-vadose environment where low concentration of magnesium ions or in burial environment where respiration and oxidation is high and decrease supersaturation.

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Résumé

Une étude a été menée sur l'effet de la concentration en ions Mg^{2+} et des produits ioniques des carbonates sur le temps d'induction du début de la cristallisation et sur la nature minéralogique du carbonate de calcium formé. On a pu montrer que les ions Mg^{2+} retardent la précipitation spontanée du carbonate de Ca à partir de solutions sursaturées par rapport aux minéraux de $CaCO_3$ (par exemple l'eau de mer) et ce à un point tel que seule la précipitation biogénique du carbonate de Ca dans les squelettes est possible à partir de l'eau de mer. Les faibles concentrations en ions Mg^{2+} dans les solutions favorisent la formation de calcite, l'aragonite se formant pour des concentrations plus élevées. Le pourcentage molaire de $MgCO_3$ dans la calcite magnésienne augmente avec la teneur, dans la solution, de Mg^{2+} et de CO_3^{2-} en présence de Mg^{2+} .

On présume donc que la calcite riche en Mg se forme dans des milieux côtiers chauds dans lesquels la haute température et/ou la forte activité photosynthétique provoquent la libération de CO_2 , ce qui augmente la sursaturation. La calcite pauvre en Mg se forme de préférence dans des milieux météoriques vadoses à faible concentration en ions Mg^{2+} ou dans des milieux d'enfouissement où la respiration et l'oxydation importantes abaissent le degré de sursaturation.

Краткое содержание

Исследовали влияние концентрации ионов Mg^{2+} на появление их в карбонатах в зависимости от времени индукции начала выпадения и от различия минерального состава карбонатов кальция. Доказано, что ионы магния настолько задерживают спонтанное выпадение карбоната кальция из пересыщенного раствора, (напр.: морской воды), по сравнению с другими минералами карбоната кальция, что $CaCO_3$ может извлекаться из морской воды только биогенно. Низкие концентрации ионов магния в растворе усиливают образование кальцита, а арагонит образуется только при высоких концентрациях его. В растворах, в которых присутствуют ионы магния, с увеличением их числа и ионов CO_3 содержание $MgCO_3$ в магниевом кальците возрастает. Поэтому следует ожидать, что кальцит с высоким содержанием магния образуется в прибрежных регионах, где вода теплая и усиление фотосинтеза приводит к освобождению CO_2 и возрастанию перенасыщенности.

Кальцит с низким содержанием магния образуется гл. обр. в регионах, где часты дожди и концентрация ионов магния низка, или же в регионах осадения, где при понижающейся перенасыщенности господствует высокая окисляемость и респирация.

Introduction

The precipitation, conversion of minerals, and the cementation of carbonate rocks in an aqueous solution at the temperatures and pressures of the upper crust are mainly affected by the dissolution and reprecipitation of different calcium carbonate minerals due to the biogenic and inorganic factors. The rates of dissolution and reprecipitation are controlled by the nucleation and the growth of the solid phases. These, in turn, depend upon a large number of factors (PYTKOWICZ, 1983). PYTKOWICZ (1965, and 1973) studied the problem of spontaneous precipitation and found that Mg^{2+} ions in seawater inhibit the precipitation of calcium carbonate. He concluded that the slow step was due to the adsorption which inhibited the nucleation. BISCHOFF (1968) and BISCHOFF & FYFE (1968) suggested that the presence of Mg^{2+} ions in solution retards the nucleation of calcite during the dissolution of aragonite and precipitation of calcite. MOLLER & RAJAGAPOLAN (1975) showed that the induction time increased with the increase of Mg^{2+} ions in solution.

It has been concluded that the magnesian content of calcite is dominantly influenced by the Mg:Ca ratio in the water from which it precipitates (MUCCI & MORSE, 1983). It has also been suggested that magnesian calcite composition is controlled by growth rates (BERNER, 1975, 1978; THORSTENSON & PLUMER, 1977).

It was observed that aragonite is the polymorph that precipitates spontaneously from seawater at high supersaturation (KITANO et al., 1962; KITANO & HOOD, 1962; LEITMEIR, 1910; PYTKOWICZ, 1975; TAFT & HARBAUGH, 1964). KITANO et al. (1962) could synthesize pure aragonite at Mg:Ca ratios > 3.82 and MOLLER & RAJAGAPOLAN (1975) found that aragonite precipitates when the $Mg^{2+}:Ca^{2+}$ ratio > 4 . Furthermore, Mg^{2+} concentration affects the mineralogy of bulk solids or of overgrowth on calcite (MORSE et al., 1979; MUCCI & MORSE, 1983, 1984).

Crystallization of salts from supersaturated solutions, as in seawater, involves two steps: nucleation and growth. Nucleation is the process in which initially small clusters of ions or molecules build up to

a critical size beyond which growth can occur (NEWKIRK, 1957; DUFOUR & DEFAY, 1963; NANCOLLAS & PURDIE, 1964; STUMM & MORGAN, 1970; and PYTKOWICZ, 1983).

Spontaneous crystallization or precipitation is a process that occurs in the intentional absence of an initial solid phase which serves as nucleus. In theory, there are two steps: spontaneous nucleation which occurs in the body of solution and subsequent growth. Dust and other particles provide nucleation sites, so that nucleation usually is not homogeneous (STUMM & MORGAN, 1970 and PYTKOWICZ, 1983).

There is often a delay between the preparation of supersaturated solution and the onset of crystal growth, that is, the time of nucleation. This delay is known as the induction period (KASHICHEV, 1969). This period is generally due to the time required to reach a steady-state distribution of clusters, with one large enough to act as nucleus for continued growth (CHRISTIANSEN & NIELSEN, 1951).

The purposes of the present work are: (a) to study the effects of Mg^{2+} ions in solution upon the induction time for spontaneous nucleation, (b) to show why near-surface oceanic waters can remain supersaturated with respect to calcium carbonate without spontaneous precipitation such as occurs in seawater rendered supersaturated, and (c) to study the mineralogy of calcium carbonate and its control by Mg^{2+} ions in solution and by the degree of supersaturation.

Methods

Ten liters of Mg-free artificial seawater (ASW) were prepared using the method of KESTER et al., (1967). Air was bubbled through the solution for two days to equilibrate the solution with atmospheric carbon dioxide. Varying quantities of Mg^{2+} ion were added to test their effect upon the induction time, and upon the mineralogy of calcium carbonate. Different amount of 0.1 molar Na_2CO_3 from a freshly prepared stock solution were added to the artificial seawater to increase the rate of the reaction.

Artificial seawater was used to avoid, in part, the presence of organic matter and the presence of the small particles which may serve as surface sites for calcium carbonate precipitation. Still, the nucleation was at least partly heterogeneous due to the glass of the container and to particles and because homogeneous nucleation requires an exceedingly long time. NaCl was added to replace $MgCl_2 \cdot 6H_2O$ and to maintain the ionic strength at 0.7. This avoided in part the effect of the ionic strength on the rate of

the reaction when Mg^{2+} is reduced (BISCHOFF, 1969 and SAYLES & FYFE, 1973). The artificial seawater corresponds roughly to natural seawater of 35.00 salinity. The experiment was carried out in a water bath (Aminco Constant Temperature bath, # 4-8605) at 25.0 ± 0.4 °C.

The runs were made by placing 100 ml of artificial seawater in Erlenmeyer flasks to which varying amounts of $MgCl_2$ and NaCl were added. Then, the desired amount of Na_2CO_3 was added with stirring. The initial time was set when Na_2CO_3 was added. The pH was followed with a Corning Semi-Micro combination pH-electrode, a research pH meter and strip Chart Recorder. The time ranges for the onset of the precipitation used in this work correspond to the interval between the addition of Na_2CO_3 and the time when cloudiness in the solution occurred. We detected the cloudiness by observing an applied light beam through the solution with a black background. We also used the discontinuity in the pH against time by an extrapolation of the initial horizontal segments and the pH decay curves segments to a common point. The time of this point is TN (Time of Nucleation) and is also the onset of precipitation, which we illustrate in Figures 1a, b, c, d and e. The uncertainty of this method increase at low supersaturation where it is hard to determine the first appearance of the cloudiness. Then, the discontinuity of the pH against time is used primarily. All solutions are at least 250% saturation like warm near surface oceanic waters even without the addition of Na_2CO_3 .

The precipitates were filtered, washed with distilled water, dried, and identified by X-ray diffraction (XRD) immediately after the first massive precipitations. The mole % of $MgCO_3$ in calcite was calculated from the empirical relationship (CHAVE, 1952):

$$\text{Mole \% } MgCO_3 = 376.6 X (3.303 - d_{100}) \quad (1)$$

where d_{100} is the d-spacing of the major reflector (100). It is directly proportional to the amount of substitution of the smaller Mg^{2+} for Ca^{2+} in the crystal lattice.

Subsequent to XRD analysis each precipitate was dissolved in HCl (0.10 mole l^{-1}) and the amount of Mg^{2+} was determined by standard atomic adsorption spectroscopy (AAS).

The wt % of calcite was calculated for each sample from the following equation:

$$\begin{aligned} \text{wt \% calcite} = & [(b X 84.32/24.31) + \\ & + (b X 100.09/24.31)] X \\ & X [(100 - a)/a] \quad (2) \end{aligned}$$

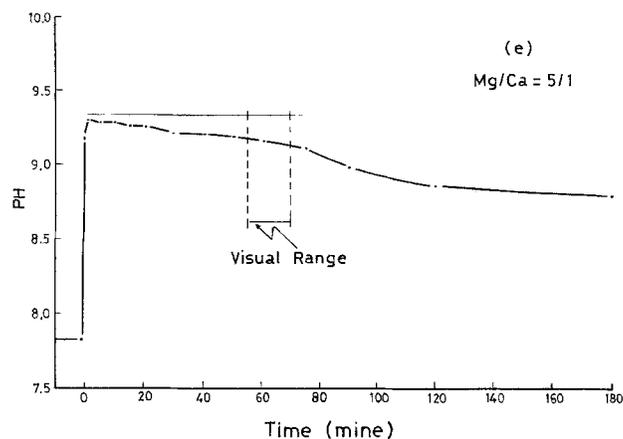
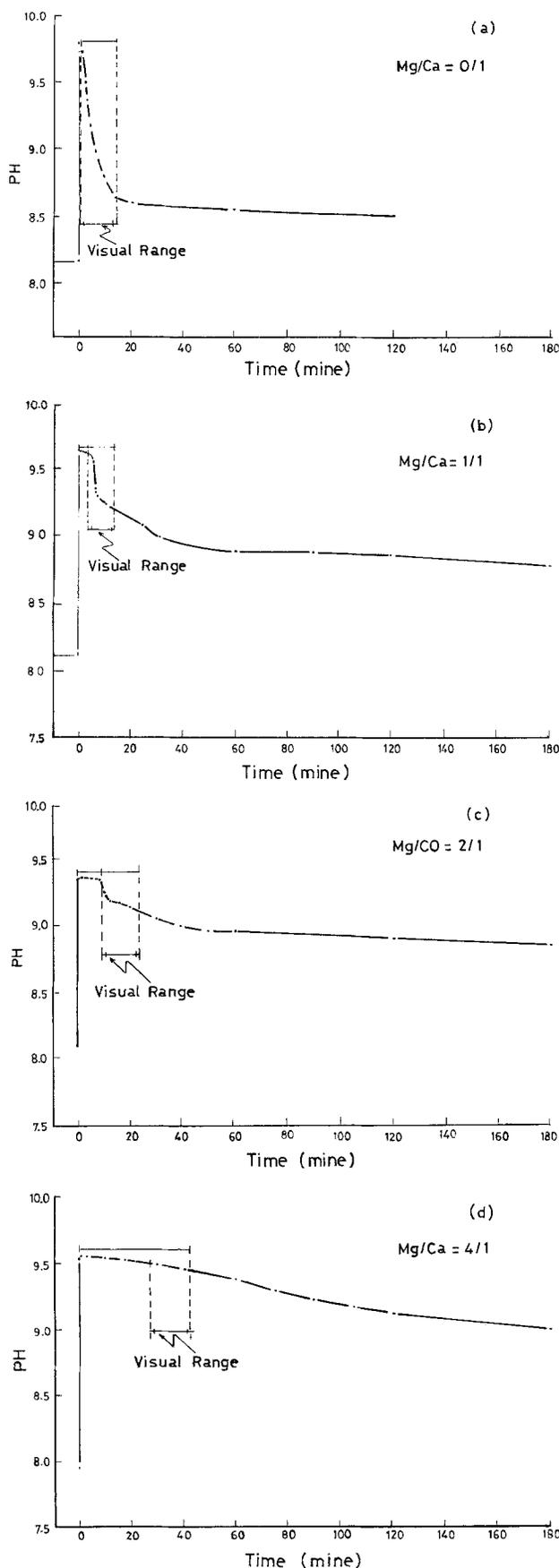


Fig. 1. Visual (cloudiness) range and pH determination of the induction time when $4.72 \text{ mmole l}^{-1} \text{ Na}_2\text{CO}_3$ is added to a solution with the $(\text{Mg}^{2+}):(\text{Ca}^{2+})$ molar ratios of 0:1, 1:1, 2:1, 3:1, 4:1 and 5:1.

where a is the mole % MgCO_3 in calcite, calculated from XRD using equation (1), and b is the wt % of Mg^{2+} in the total sample, determined by AAS. Therefore, the wt % of aragonite is $100 - \text{wt \% Calcite}$.

Results

The addition of Na_2CO_3 to ASW with varying amounts of Mg^{2+} caused changes in TN and lead to the formation of a different mineralogy (Table 1 and Fig. 2). The amount of Mg^{2+} present are shown as $(\text{Mg}^{2+}):(\text{Ca}^{2+})$ ratios, where the Ca^{2+} concentration was $0.00993 \text{ mole.l}^{-1}$ in all cases. The induction times are shown as a function of added amounts of carbonate ions from a Na_2CO_3 stock solution.

Table 1 shows the effect of Mg^{2+} on the time of nucleation, mineralogy, and composition of precipitates. It can be seen that increasing $(\text{Mg}^{2+}):(\text{Ca}^{2+})$ ratios in ASW inhibits the precipitation and delay it from minutes to weeks.

The data in Table 1 and Fig. 2 show two features. The induction time gets shorter with increasing ionic products of carbonate. Furthermore, the minimum time of nucleation decreases when the added Na_2CO_3 increases beyond 6.5 mmole l^{-1} at $(\text{Mg}^{2+}) = 0.01 \text{ mole l}^{-1}$ and beyond about 5.0 mmole l^{-1} for $(\text{Mg}^{2+}) = (0.02-0.05)$. These features will be discussed later.

X-ray diffraction results on the precipitates (Table 1) show three different mineralogies of calcium carbonate. These are pure calcite (at zero Mg^{2+} ions in solution), mixtures of magnesian calcite and aragonite, and aragonite alone in solution.

Experiment Number	Ratio (Mg ²⁺):(Ca ²⁺)	Na ₂ CO ₃ (mmole l ⁻¹)	TN (minutes)	Mole % MgCO ₃	Wt % Calcite
F1	0:1	8.32	0.2	0	100
F2		6.52	0.4	0	100
F3		4.75	1.0	0	100
F4		2.90	4.0	0	100
F5		1.92	8.0	0	100
F6		1.48	15.0	0	100
M1-1	1:1	8.30	18.0	10.4	90
M1-2		6.50	10.0	20.1	76
M1-3		4.74	5.0	11.2	96
M1-4		2.90	7.0	6.7	61
M1-5		1.95	14.0	3.0	33
M1-6		1.45	30.0	3.0	11
M1-7		0.99	72.0	?	?
M1-8		0.79	168.0	?	?
M2-1	2:1	8.20	60.0	17.1	78
M2-2		6.50	18.0	12.7	81
M2-3		4.70	8.0	12.7	66
M2-4		2.90	9.0	12.3	89
M2-5		1.90	12.0	1.4	3
M2-6		1.50	60.0	1.4	3
M2-7		1.00	118.0	0	0
M2-8		0.80	168.0	2.1	?
M2-9		0.70	380.0	0	?
M3-1	3:1	8.10	123.0	19.3	59
M3-2		6.40	24.0	16.4	45
M3-3		4.70	10.0	11.4	65
M3-4		2.90	13.5	11.2	38
M3-5		1.90	40.0	12.7	3
M3-6		1.00	160.0	0	0
M3-7		0.80	480.0	?	?
M4-1	4:1	8.09	180.0	22.2	60
M4-2		6.40	48.0	19.3	44
M4-3		4.82	27.0	14.7	46
M4-4		2.82	39.5	12.7	3
M4-5		1.90	72.0	0	0
M4-6		1.40	96.0	0	0
M4-7		0.97	450.0	0	0
M4-8		0.78	1020.0	0	0
M5-1	5:1	8.10	480.0	0	0
M5-2		6.37	120.0	0	0
M5-3		4.64	57.0	0	0
M5-4		2.84	96.0	0	0
M5-5		1.91	120.0	0	0
M5-6		1.44	360.0	0	0
M5-7		0.78	3200.0	0	0

Tab. 1. The effect of Mg²⁺ concentration and degree of saturation on the time of nucleation (TN) and the mineralogy of calcium carbonate.

Discussion

The solubility of calcium carbonate minerals was shown to increase in the order from pure calcite, low-magnesian calcite, aragonite to high-magnesian calcite (CHAVE et al., 1962; PLUMMER & MACKENZIE, 1974 and LAND, 1967).

Our results demonstrate that the (Mg²⁺):(Ca²⁺) ratio and the initial ionic product of carbonate in solution control the time of nucleation and the mineralogy of the precipitate. Increasing the ionic product of the solution increases the number of collisions of ions so that the time to form nuclei of calcium carbonate with a critical size is shorter. An

increase in Mg²⁺ ions in solution lead to nuclei with a higher magnesium content and higher solubilities and, consequently, a longer time was required for precipitation. In other words, the formation of magnesian calcite nuclei of critical size, which serve as centers for growth, is slowed down. The effect of Mg²⁺ ions on the time of nucleation is illustrated in Fig. 3 where the ratio of (Mg²⁺):(Ca²⁺) is plotted against the time of nucleation for different ionic products.

The data in Table 1 and Fig. 2 show that high Na₂CO₃ added in the presence of Mg²⁺ slows precipitation and that the high ionic products favor the formation of magnesian calcite minerals over aragonite for kinetic reasons. At low ionic products, aragonite is kinetically favored. High Mg contents in solution lead to favoring the formation of aragonite over that of magnesian calcite. The increase of aragonite rather than magnesian calcite at Mg²⁺ concentration smaller than 0.03 mole l⁻¹ and at a low ionic product suggests that the nuclei of high Mg contents may be formed, but that they redissolve because they are more soluble and have a longer TN, thus providing time for the more stable aragonite to form.

It is concluded that aragonite is formed when the ratio of (Mg²⁺):(Ca²⁺) is greater than 4. This agrees with the results of KITANO et al. (1962), PYTKOWICZ (1965), MOLLER and RAJAGAPOLAN (1975), and others. Magnesian calcite precipitation is favored at (Mg²⁺):(Ca²⁺) ratios are smaller than 4. The increase of the time of nucleation upon addition of Na₂CO₃ to concentrations greater than 5.0 mmole l⁻¹ (Fig. 2) may be due to a decrease in the degree of saturation with respect to the formation of very high magnesian calcite. Our results show that, at high CO₃²⁻ in solution, high-magnesian calcite is kinetically favored.

The curves in Fig. 2 must approach the 100% saturation level asymptotically. Thus, extrapolation of the curves by lines which are tangent to the curves at about 0.79–0.69 mmole l⁻¹ of added Na₂CO₃ will yield the minimum time for precipitation from seawater, when they intercept the 0.05 mmole l⁻¹ line. This may be the lowest time for precipitation to occur in natural seawater if stayed in supersaturated near-surface layers for terms of thousands of years (PYTKOWICZ, 1965, 1973). The result of the intercept of the straight line extrapolation with the 0.05 mmole l⁻¹ line in artificial seawater with varying amounts of Mg²⁺ is shown in Table 2. The minimum time for artificial seawater with which has the same amount of Mg²⁺ as natural seawater was found to be 38,000 ± 8,000 years (Fig. 4), in agreement with PYT-

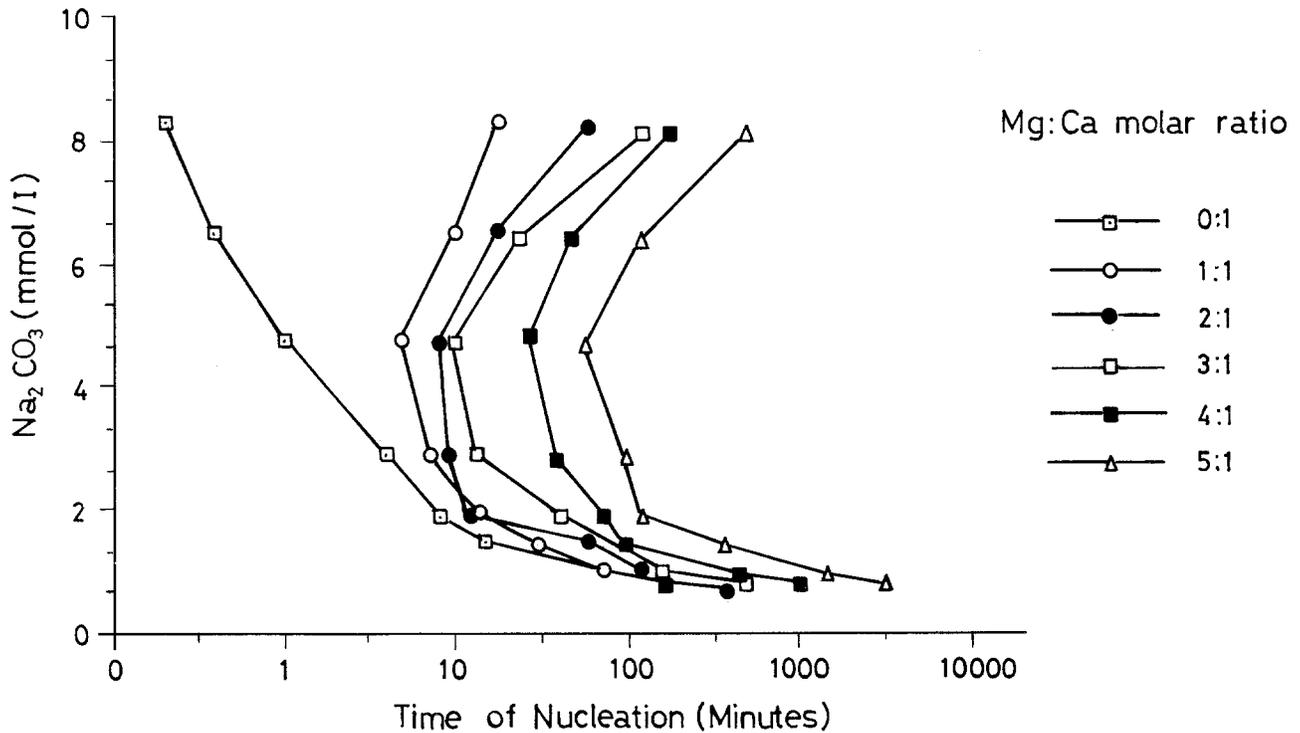


Fig. 2. Added Na_2CO_3 versus the time of nucleation for different $(\text{Mg}^{2+}):(\text{Ca}^{2+})$ molar ratios in artificial seawater.

KOWICZ (1973). This means that the Mg^{2+} can inhibit the precipitation of calcium carbonate from supersaturated seawater to such an extent that spontaneous precipitation will not occur in the open ocean.

Our experimental results show that low-magnesian calcite are dominant at low Mg:Ca ratios and low reaction rates. These conditions can be found in meteoric-vadose environments or in burial environment where respiration and oxidation is high, and the

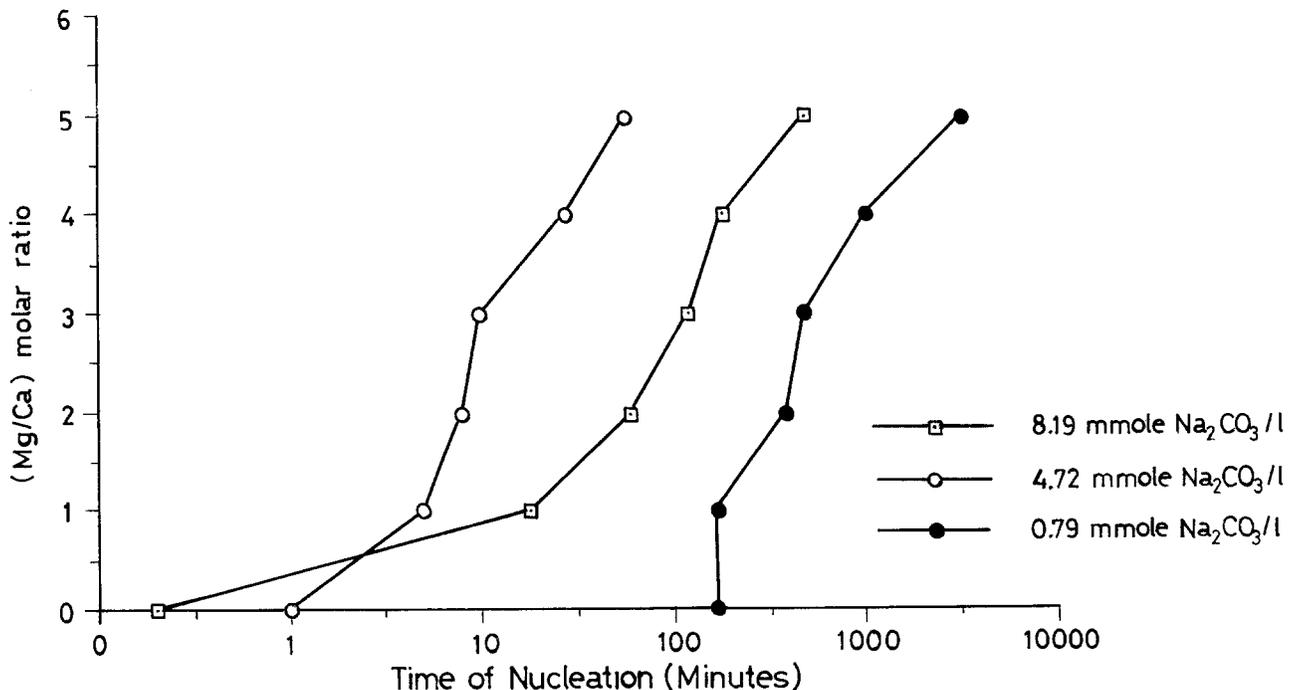


Fig. 3. $(\text{Mg}^{2+}):(\text{Ca}^{2+})$ ratios versus the time of nucleation for 4.72, 8.18 and 0.79 mmole l^{-1} of added Na_2CO_3 .

Ratio (Mg ²⁺):(Ca ²⁺)	Time of nucleation (onset)
0:1	8.3 ± 1.7 days
1:1	62.5 ± 13.1 days
2:1	15 ± 3.2 years
3:1	761 ± 160 years
4:1	21,000 ± 4,000 years
5:1	38,000 ± 8,000 years

Tab. 2. The estimated minimum times of the onset of precipitation in different ratios of (Mg²⁺):(Ca²⁺) in artificial seawater at 400% supersaturation.

low supersaturation due to the abundance of CO₂ (LONGMAN, 1980; BINKLEY et al., 1980). High-magnesian calcite can be formed in shallow marine environments where higher degree of saturation persist because of CO₂ degassing. The supersaturation is due to heat and net photosynthesis. All these factors depress the CO₂ in shallow-marine environments.

Conclusions

It has been shown that the Mg²⁺ ions can prevent the inorganic homogeneous precipitation of calcium carbonate from supersaturated seawater to such an extent that the removal of carbonate ion from the ocean is strictly biological, except in special environments, when abundant nucleating surfaces are present. Then inorganic precipitation and abiotic cementation can occur. Results suggested that homogeneous inorganic precipitation does not play a significant role in an average marine environment. However, times for the onset of precipitation would be expected in seawater containing recycling calcium carbonate seeds. Thus, oolites thrown into suspension in the Bahamas could act as seeds for the precipitation of calcium carbonate.

Rates of the reaction have significant effects on the kinetics of calcium carbonate formation in the presence of Mg²⁺ ions in solutions. There is an interaction between these two parameters (the rate of the reaction and the Mg²⁺ concentration) and one

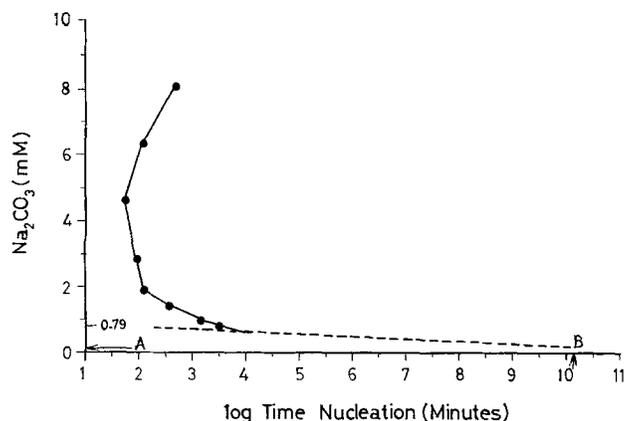


Fig. 4. Straight line extrapolation of the minimum time of spontaneous onset at (mg²⁺):(Ca²⁺) molar ratio of 5:1 in artificial seawater. The straight line is tangent at the time of nucleation when 0.79 mmole l⁻¹ Na₂CO₃ was added. Arrow at (A) corresponds to natural surface seawater CO₃²⁻ concentration and arrow at (B) indicates the log time nucleation of natural surface seawater.

will dominant over the other, depending upon its respective concentration and the conditions of the reaction.

The mineralogy of inorganic homogeneous precipitation is a result of these two parameters (e.g. Mg²⁺ ion concentration and reaction rate) at constant T and P conditions. Pure calcite is favored in Mg-free solution, low-magnesian calcite is favored at Mg:Ca < 2 and low reaction rate. These different mineralogies may affect 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.

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