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CALCIUM CARBONATE RETENTION IN SUPERSATURATED SEAWATER*

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ABSTRACT. It is shown that magnesium ions inhibit the spontaneous precipitation of calcium carbonate from supersaturated seawater to such an extent that only biogenic removal is possible from the open oceans. Citric acid and inorganic phosphate also have retarding effects, but stearic acid does not. Inorganic precipitation can occur only in special environments such as the Bahama Banks where there is an abundance of nuclei.

INTRODUCTION

This work represents a study of why near-surface oceanic waters can remain supersaturated with $CaCO_3$ without the occurrence of massive inorganic precipitation and is an extension of the results of Pytkowicz (1965a). The stability of dissolved carbonates is one example of how the behavior of geologic materials in seawater may differ from that in freshwater.

Near-surface seawater is known to be supersaturated (for example, Wattenberg and Timmerman, 1936; Pytkowicz, 1965b, 1970; Chave and Suess, 1967), and one could expect *a priori* either spontaneous precipitation within the water, as would occur if it were distilled, or on particles present in seawater. Theoretical calculations by Wollast (1969) indicate that homogeneous nucleation is not likely, as exceedingly long times are required. The observations of Chave (1965) and Chave and Suess (1967) show that precipitation on existing particles is inhibited by the presence of protective organic coatings. In addition there may not be enough particles for them to come in contact with most of the seawater in which they are suspended.

Pytkowicz (1965a) studied the problem of spontaneous precipitation. He found that magnesium in seawater inhibits the precipitation of $CaCO_3$ and concluded that magnesium precludes inorganic precipitation from the open oceans, although it may occur in special environments, and that the removal of $CaCO_3$ from the ocean is biogenic. Weyl (1967) showed that magnesium affects the solution behavior of carbonate materials in seawater. Chave and Suess (1970) found that organic matter in seawater also acts as a precipitation inhibitor.

In this work the relative effects of magnesium, phosphate (Simkiss, 1964), stearic acid, and citric acid upon the time required for precipitation were examined. Artificial seawater was used exclusively, in contrast to the earlier work (Pytkowicz, 1965a), to isolate better the effects of the various retardants.

METHODS

Three artificial seawaters were prepared by diluting the salts presented in table 1 to 1 liter with distilled water. Air was then diffused

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TABLE 1

Composition of the artificial seawater

Salt	ASW-1	ASW-2	ASW-3
NaCl	34.06 g/*l*	24.49 g/*l*	14.93 g/*l*
$MgCl_2 \cdot 6H_2O$	0.00	11.09	22.18
$CaCl_2 \cdot 2H_2O$	1.55	1.55	1.55
Na_2SO_4	4.10	4.10	4.10
KBr	0.10	0.10	0.10
KCl	0.69	0.69	0.69
$NaHCO_3$	0.20	0.20	0.20
H_3BO_3	26.55 mg/*l*	26.71 mg/*l*	26.60 mg/*l*
$SrCl_2 \cdot 6H_2O$	24.90	24.69	24.85
NaF	0.40	0.40	0.32

through the seawaters for 48 hours for equilibration with atmospheric CO_2. When indicated, $CaHPO_4$, stearic acid, or citric acid was added to aliquots of seawater. Then, varying amounts of 0.10 molar Na_2CO_3 from a freshly prepared stock solution were added to the seawaters to promote precipitation.

Artificial seawater no. 2(ASW-2) corresponds roughly to natural seawater of 35‰, in ASW-1 $MgCl_2 \,.\, 6H_2O$ was replaced by approximately the same weight of NaCl, while in ASW-3 the excess $MgCl_2 \,.\, 6H_2O$ replaced part of the NaCl. Magnesium and calcium were not determined by titration, as this was not considered necessary due to the rough nature of the required data. Broad trends in the data rather than exact numbers were sought, because they are sufficient to warrant our conclusions, and as it is difficult to reproduce heterogenous kinetics with great precision.

The experiments were carried out in an air conditioned room at temperatures between 23° and 25°C. The runs were made by placing 100 ml of artificial seawater in Erlenmeyer flasks with glass stoppers, adding $CaHPO_4$, stearic acid, or citric acid when indicated, shaking and waiting 10 minutes, and then adding the desired amount of Na_2CO_3 with stirring.

Zero time was when the Na_2CO_3 was added, and the aliquots were then examined periodically for signs of precipitation. The time ranges for the onset of precipitation used in this work correspond to the interval between when a solution was last clear and when precipitation was first observed. The occurrence of precipitation in highly supersaturated solutions was obvious as it was indicated by the fairly fast formation of a massive white precipitate. This corresponded to an abrupt decrease in pH (Pytkowicz, 1965a). At low supersaturations there was a period of uncertainty, which was included in the accepted time ranges. The precipitate was usually observed at the bottom of the flasks, by vertical viewing over a black background, although some of it floated at the surface of the seawater.

All the solutions were supersaturated as, even without addition of Na_2CO_3, seawater is at least 200 percent saturated. The degree of saturation of the samples used in this work can be estimated roughly from the expression

$$\text{Percent saturation} = (\text{Na}_2\text{CO}_3 \text{ added} + 0.2) \times 10^3 \text{ percent} \qquad (1)$$

in which the Na_2CO_3 added is in mmoles/*l*. This is a maximum value as some conversion of CO_3^{2-} should occur by reaction of the CO_3^{2-} with CO_2 present in the seawater and in the air gap above the solutions.

RESULTS AND DISCUSSION

The results for the addition of only Na_2CO_3 to ASW-1, ASW-2, and ASW-3 are presented in table 2 and those for ASW-2 are also presented in figure 1. Note that the results for ASW-1 are in minutes, whereas the other ones are in hours.

TABLE 2
Effect of magnesium on the precipitation time of calcium carbonate

		Time for precipitation	
Na_2CO_3 added	ASW-1*	ASW-2**	ASW-3***
0.70		700-800 hrs	
0.80		341-523	
0.98	31-158 min	81-111	
1.48		40-58	70-92 hrs
1.96	29-36	15-25	31-47
2.92	18-28	4.9-6.7	18-24
4.76	2-7	3.8-4.9	6.2-15
5.65			7.6-9.0
6.54		4.1-4.8	
7.41	0-1		10-15
9.10		13-20	22-29

* no magnesium; ** normal seawater magnesium; *** twice normal magnesium.

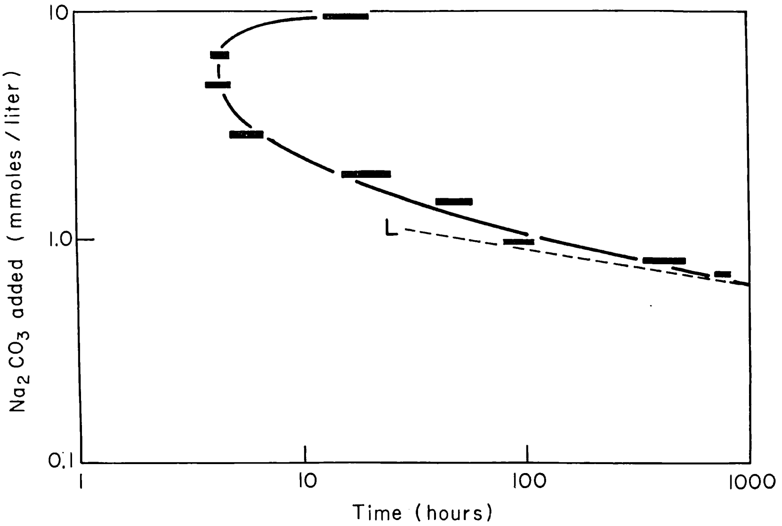

Fig. 1. Time for the onset of $CaCO_3$ precipitation versus mmoles/*l* of Na_2CO_3 added to artificial seawater #2.

It can be seen from table 2 that magnesium delays precipitation from minutes to hours or even weeks and that the effect is most pronounced in going from zero to normal seawater magnesium.

The data in figure 1 reveal two features of interest: the fast increase in the time for the onset of precipitation with decreasing supersaturation and the minimum precipitation time at about 6 mmoles/*l* of Na_2CO_3.

The fast increase in the time of precipitation has a special geochemical significance. The curve in figure 1 must approach the 100 percent saturation level asymptotically and, therefore, must curve upward. Thus, the extrapolation of the curve by line L (see fig. 1), which is tangent to the curve at 0.65 mmoles/*l* of added Na_2CO_3, will yield a minimum time for homogeneous precipitation from seawater when it intercepts the 0.10 mmoles/*l* line. This will be a minimum time, because 0.10 mmoles/*l* of added Na_2CO_3 leads to a seawater that is at least 300 percent supersaturated as a result of the straight line extrapolation and because precipitation in ASW-2 is heterogeneous due to the glass surface and dust particles.

The time for the onset of precipitation found at 0.10 mmoles/*l* of added Na_2CO_3 in seawater which already contained the usual carbonate alkalinity was 30,000 years which is well in excess of the residence time of nearsurface waters. This result, obtained in seawater free from organic matter and phosphates, in conjunction with the data in table 1, means that magnesium can inhibit the precipitation of $CaCO_3$ from supersaturated seawater to such an extent that spontaneous precipitation will not occur in the open oceans. It is likely that the inhibition results from two factors: the impingement of magnesium on the aragonite lattice of the nuclei which disrupts the crystal growth, as will be discussed later, and the ion-pairing of magnesium with carbonate ions which effectively enhances the solubility of calcium carbonate by depressing the activity coefficient of carbonate ions.

The corresponding time found by Pytkowicz (1965a) for filtered and unfiltered natural seawater was 70,000 years. The agreement with the present result is good when uncertainties in extrapolation and in attempting to reproduce heterogeneous kinetics as well as the possible effects of organics and of phosphates on the earlier results are taken into consideration.

It is also interesting that precipitation does not seem to occur to any marked extent onto calcareous tests in the open ocean, as the waters remain supersaturated in the presence of foraminifera and other carbonate particles. This may be due to three factors: the protective organic coatings on tests (Chave, 1965; Chave and Suess, 1967), the possibility of high-magnesium calcite coatings that increase the effective solubility of the particles, and the lack of contact between most of the seawater and the calcareous surfaces. Still, further work is needed to test the possibility of overgrowths. Inorganic precipitation seems to be limited to special environments, such as the Bahama Banks, where there is an abundance of nucleating surface, or to areas where intensive photosynthesis may drive the pH, and hence the degree of supersaturation, to high values.

It is important to distinguish the two problems that have been dealt with so far: the absence of precipitation within the supersaturated waters and the absence of precipitation on calcareous particles. The present measurements were oriented toward the first problem. They set an experimentally observed lower limit for homogeneous precipitation.

The second point of interest in figure 1 is the surprising increase in the time of precipitation with the degree of supersaturation at additions greater than 6 mmoles/*l*. It was tentatively ascribed (Pytkowciz, 1965a) to the enhancement of the inhibition by magnesium when the solubility of magnesite is exceeded and suggests that magnesium ions impinge upon the calcium carbonate nuclei and disrupt their growth. The data shown in figure 2 are not incompatible with this hypothesis as the minimum, if it occurs at lower than normal magnesium concentrations, appears at higher carbonate concentrations when the magnesium content is decreased.

It is interesting to observe that the results obtained in artificial seawater in 1968, at 0.5 molar magnesium, agree reasonably well with those obtained in natural seawater in 1965. The 1965 and the present results are intercompared in table 3. The faster times that occur at low supersaturations in ASW-2 may be due to the absence of phosphate and of organic matter. It will be shown later that phosphate has a retarding effect upon slow precipitation but does not seem to have time to act upon precipitation at high supersaturations. On the other hand, the differences between the earlier and the present results may be due to the irreproducibility of the data. Still, as was seen above, it is the main features of

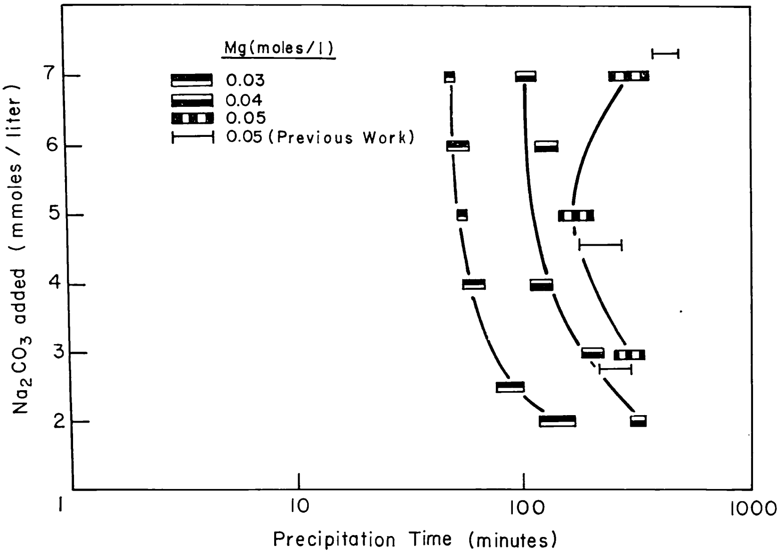

Fig. 2. The precipitation time versus added carbonate for various magnesium concentrations.

Table 3

Comparison of the 1965 and the present results

1965		This work	
Na_2CO_3 added (mmoles/*l*)	Time for precipitation	Na_2CO_3 (mmoles/*l*)	Time for precipitation
	(A) No magnesium		
0.93	20 min	0.98	31 -158 min
1.83	13	1.96	29 - 36
		2.92	18 - 28
4.58	4.7	4.76	2 - 7
7.34	1.0	7.41	0 - 1
	(B) Normal seawater magnesium		
		0.70	700 -820 hrs
		0.80	341 -523
0.93	900 -940 hrs	0.98	82 -111
1.41	47 - 66	1.48	40 - 58
1.83	15 - 18	1.96	15 - 25
2.69	3.4- 4.7	2.92	4.9- 6.7
4.58	3.0- 4.5	4.76	3.8- 4.9
6.46	3.8- 5.0	6.54	4.1- 4.8
8.70	13 - 25	9.10	13 - 20
	(C) Twice normal magnesium		
		1.48	70 - 92 hrs
		1.96	31 - 47
		2.92	18 - 24
3.85	22 - 53 hrs		
4.75	22 - 53	4.76	6.2- 15
		5.65	7.6- 9.0
		7.41	10 - 15
		9.10	22 - 29

the data rather than the exact numbers that warrant the conclusions with respect to the inhibiting effect of magnesium, the non-occurrence of inorganic precipitation in open ocean waters, and the curious reversal in precipitation times at high supersaturations.

The effect of phosphate on the precipitation time is shown in table 4. Ten μg–at/*l* of inorganic phosphorus had been added in the form of $CaHPO_4$ before the addition of Na_2CO_3. This amount is in excess of that found in the oceans, where it ranges from 1 to 3 μg–at/*l*. It is apparent that phosphate has no effect if precipitation occurs within minutes, as was the case in magnesium-free artificial seawater, but that it is a retardant for the slow precipitation that occurs in the presence of magnesium. Possibly the retardation is due to the slow exchange of carbonate by phosphate on the surface of growing nuclei. Presumably this exchange does not have time to occur when the rate of precipitation is fast. The inhibiting effect by phosphate is considerably smaller than that due to magnesium as the latter can delay precipitation from minutes to hours and weeks (see table 1).

The effects of stearic acid and citric acid, both added in larger amounts than those found in natural seawater better to observe their impact, are shown in tables 5 and 6. The runs were made in the absence of magnesium to ascertain whether these organic acids have inhibiting properties comparable to that of magnesium. It can be seen from these tables that stearic acid has no effect, within the sensitivity of the results, but that citric acid, at least when present in large amounts, has a marked retarding effect which is comparable to that of magnesium. This is not due to the complexing of calcium ions by citric acid, as ($Ca^{2}+$) = 0.01 molar while the concentration of citric acid was only 3.2×10^{-4} molar, but is probably due to the coating of the incipient nuclei by the acid. The difference between the behaviors of stearic and citric acids may be due to the smaller size of the latter. Thus, dissolved organic carbon can inhibit the precipitation of $CaCO_3$, but this effect, which will require further study, appears to be specific to some organic forms. Further work should also take into consideration the possible retarding effects of proteins.

CONCLUSIONS

It has been shown that magnesium ions can prevent the inorganic precipitation of $CaCO_3$ from supersaturated seawater to such an extent that the removal of carbonates from the oceans, except in special environments is strictly biogenic. When abundant nucleating surfaces are present,

TABLE 4

Effect of phosphate on the precipitation time of calcium carbonate

Seawater	No phosphate		Phosphate present	
	CO_3 added (mmole/*l*)	Time	CO_3 added (mmole/*l*)	Time
ASW-1	1.96	29 -36 min	1.94	28-43 min
	2.92	18 -28 "	2.90	15-26 "
ASW-2	1.96	15 -25 hrs	1.94	48-63 hrs
	2.92	4.9- 6.7 "	2.90	10-22 "

TABLE 5

Effect of stearic acid on the precipitation time of calcium carbonate

Seawater	No stearic acid		Stearic acid	
	CO_3 added	Time	CO_3 added	Time
ASW-1	1.48	44-60 min	1.35	58-88 min
	1.96	29-36 "	1.79	27-42 "
	2.92	18-28 "	2.76	8-18 "
	4.76	2- 7 "	4.35	0- 7 "
ASW-2	1.96	15-25 hrs	1.79	20-24 hrs

TABLE 6

Effect of citric acid on the precipitation time of calcium carbonate

No citric acid			Citric acid	
CO_3 added	Time		CO_3 added	Time
	First run (table 1)	Second run		
0.98	31-158 min	25-183 min	0.98	22 -30 hrs
1.96	29- 36 "	0- 37 "	1.94	22 -30 "
2.92	18- 28 "	0- 32 "	2.88	8.9-12 "

then inorganic precipitation and cementation can occur. In addition, inorganic phosphate and citric acid also retard the precipitation of carbonates, but stearic acid, which is a high molecular weight organic acid, has no demonstrable effect. The absence of precipitation on the surface of calcareous tests is primarily due to protective organic coatings.

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