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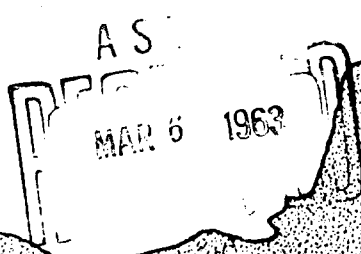


THE RESISTANCE OF RECENT MARINE CARBONATE SEDIMENTS TO SOLUTION

Office of Naval Research
Contract Nonr 2119 (04)
A & M Project 286-A

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SOLUTION

Technical Report
Ref. 62-18T

Prepared by

John F. Jansen, Yasushi Kitano, Donald W. Hood & Louis S. Kornicker

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C H A P T E R I

INTRODUCTION

Objectives (Statement of the Problem)

The objective of this study is to determine the effect of the particle size, mineralogy and chemical composition of recent marine carbonate sediments on their resistance to solution in the ion pairs of sea water and distilled water.

Summary of Past Research

The polymorphs of calcium carbonate to be investigated in this research are calcite and aragonite. Seidell (1940) showed that the difference in solubility between those polymorphs is associated with their difference in crystal form. Much of the published literature on the solubility of carbonates up to the time of Seidell's work is confusing and contradictory and is based on insufficient data and little control.

The most stable polymorph of calcium carbonate is calcite. Calcite is known to be more resistant to solution than aragonite; however, co-existing material or impurities in the crystal structures of calcium carbonate greatly affects its solubility. Chave (1954) and Kitano and Furutsu (1959) have shown

that magnesium, the major impurity in marine carbonates, exists in the calcite crystal structure as a solid solution series between calcite and dolomite, and that as the magnesium content increases in the solid solution series, the solubility of calcite eventually becomes greater than aragonite. As magnesium exists in the calcite crystal form and is incompatible with aragonite (Chave, 1954), the crystal form of calcium carbonate, as well as the availability of magnesium, exerts a major control on the solution of carbonates in nature.

The majority of the published research, in the past two decades, on the stability of carbonates has been carried out under higher than normal temperature and $p\text{CO}_2$ conditions. An excellent study of the stability of a few carbonates is presented by Garrels, et al. (1960), near room temperature conditions. This study was, however, carried out under one atmosphere pressure of CO_2 with the major emphasis placed on changes in pH during equilibration.

Other investigations on the solution of carbonates have also emphasized pH changes (Holland, et al., 1960; Weyl, 1961). The effect of magnesium on the solution of carbonates in natural samples and the effects of solutions other than distilled water have not been investigated.

CHAPTER II

EXPERIMENTAL

Reagents Used in Experimental Procedures.

- 1) Buffer Solution: Beckman pH 7 buffer solution was prepared.
- 2) Synthetic Sea Water: Solutions of the following ion pairs of sea water were prepared from reagent grade chemicals.

	NaCl (g/l)	MgCl ₂ (g/l)	NaHCO ₃ (g/l)
Sodium Chloride	23.70		
Magnesium Chloride		4.975	
Sodium Hydrogen Carbonate			0.194
Sodium Chloride + Magnesium Chloride	23.70	4.975	

Equipment Used in Experimental Procedures.

- 1) Electrodes: Beckman calomel electrodes and glass electrodes were used as furnished with the "Zeromatic".
- 2) Glassware: All glassware used was of the standard laboratory variety as no special apparatus was needed. Several gross of 250 ml erlenmeyer flasks and at

least a dozen long stem funnels and 150 ml beakers were needed.

- 3) Mortar and Pestle: A motor driven agate mortar and pestle was used to reduce sediment samples to approximately 325 mesh.
- 4) pH Meter: A Beckman Zeromatic pH Meter was employed to establish the pH of the suspensions.
- 5) Sieves: U. S. Standard Sieves of 8, 10, 18, 35, 60, 120, 230, and 325 mesh were used to subdivide several of the sediment samples.
- 6) Stirrer: To aid the solution of sediment samples, a magnetic stirrer and teflon covered stirring bar were used.
- 7) Stoppers: Cotton, covered with cotton gauze, stoppers were used to permit the experiment to be conducted open to the atmosphere.

Natural Carbonate Samples Used. The natural carbonate samples used in this study were collected on and about the reefs on the Campeche Bank in the Gulf of Mexico. The samples include:

- #1 - Montastrea annularis plus encrusting foraminifera
- 2 - Coral and shell sand from Alacran Reef
- 3 - Montastrea annularis
- 4 - Bottom sediment

- 5 - Strombus gigas Linne'
- 6F - Lucina pensylvanica Linne' (fresh and unweathered)
- 6W - Lucina pensylvanica Linne' (worn and weathered)
- 7 - Glycymeris pectinata Gmelin
- 13 - Bottom sediment containing algal material.

Sample numbers 1 and 3 were collected by Dr. Brian Logan on Campeche Bank in the Gulf of Mexico. Sample numbers 2, 5, 6F, 6W, and 7 were collected on cruise 61-H-5 at Isla Desertora, Alacran Reef, Campeche Bank, in the Gulf of Mexico. Sample numbers 4 and 13 were bottom samples collected off the Campeche Bank on cruise 59-H-7.

Sample numbers 2, 4, and 13 were subdivided by sieving into 10, 18, 35, 60, 120, 230, and pass 230 mesh fractions. Sample number 13 was further subdivided into 1/2", 3/8", 1/4", and 8 mesh fractions. See Table 1.

TABLE 1
Size Analyses

Mesh $\frac{1}{\text{inch}}$	Diameter mm	Sample #2 %	Sample #4 %	Sample #13 %
10	>2	4.92	61.1	73.1
18	1-2	4.85	3.82	16.4
35	1/2-1	75.5	11.5	8.32
60	1/4-1/2	14.5	11.9	1.10
120	1/8-1/4	0.22	5.94	0.27
230	1/16-1/8	trace	4.61	0.41
<230	<1/16	-----	1.00	0.44

$\frac{1}{\text{inch}}$ U. S. Standard Sieve Sizes

Each of the above samples or fractions of a sample were split and a portion ground in an agate mortar and pestle for two hours. The ground portions were used for the determination of the Ca^{++} and Mg^{++} in each sample, and also for the solution experiments.

A summary of the analyses of the recent marine carbonate sediments used in this study may be found in Tables 2, 3, and 4. Table 2 shows the percentage of CaCO_3 and MgCO_3 present in each of the unground natural sediment samples.

TABLE 2
 Ca^{++} and Mg^{++} Content of Unground Natural
Carbonate Sediments^{2/}

Sample # Mesh Size	% CaCO_3	% MgCO_3	Sample # Mesh Size	% CaCO_3	% MgCO_3
2-18 X	94.50	4.39	4-18 X	90.27	6.90
2-35 X	93.82	2.03	4-35 X	91.96	5.27
2-60 X	93.48	2.28	4-60 X	95.57	2.91
4-10 X	90.16	6.09	4-230 X	94.07	2.28

Table 3 reports the percentage of CaCO_3 and MgCO_3 present in each of the ground sediment samples. All analyses are reported by mesh size fractions whether it has undergone grinding or not.

^{2/} Average of three analyses

A comparison between Tables 2 and 3 indicate different values of MgCO_3 content exist for ground and unground samples of the same size fraction. It is felt that this difference is due to the heterogeneous nature of the sample. Binocular examination of the samples reveal a number of echinoid spines which are known to be very high in magnesium. It is felt that the ground sample gives a better indication of the average MgCO_3 present in each size fraction of each sample. This suggestion is borne out as the difference in MgCO_3 content decreases with decreasing sediment size.

TABLE 3
 Ca^{++} and Mg^{++} Content of Ground Natural
 Carbonate Sediments^{3/}

Sample # Mesh Size	% CaCO_3	% MgCO_3	Sample # Mesh Size	% CaCO_3	% MgCO_3
1	87.32	6.95	5	96.23	0.00
2-18	93.39	2.87	6F	97.76	0.00
2-35	93.02	2.72	6W	96.66	0.00
2-60	92.64	2.93	7	96.12	0.00
3	95.19	0.00	13-1/2"	84.38	9.90
4-10	90.16	6.09	13-3/8"	84.88	9.52
4-18	89.70	6.53	13-1/4"	85.57	12.1
4-35	91.25	5.36	13-8	85.13	12.0
4-60	93.34	3.39	13-18	85.23	11.8
4-230	94.07	2.28			

^{3/} Average of two analyses

Table 4 shows the mineralogical composition of the samples as determined by X-ray diffraction. X-ray analyses of sample number 4 at the onset of grinding and after 2 hours of grinding show no significant alteration of calcite to aragonite.

TABLE 4
Mineralogical Composition of Ground Natural
Carbonate Sediments

Sample #	%	%	Sample #	%	%
Mesh Size	Aragonite	Calcite	Mesh Size	Aragonite	Calcite
1	53	47	4-120	82	13
2-18	95	5	4-120 ^{4/}	87	13
2-35	97	3	4-230	84	16
2-60	95	5	5	100	--
3	100	--	6F	100	--
4-10	74	26	6W	100	--
4-10 ^{4/}	74	26	7	100	--
4-18	70	30	13-1/2"	31	69
4-18 ^{4/}	71	29	13-3/8"	32	68
4-35	72	28	13-1/4"	34	66
4-35 ^{4/}	72	28	13-8	31	69
4-60	86	14	13-10	41	59
4-60 ^{4/}	86	14	13-18	43	57

Lowenstam (1954) assigns a rather large error, ⁺10 per cent, to the analysis of calcite : aragonite ratios. The relationship between the percentages of MgCO_3 and aragonite

^{4/}Mineralogical composition at the onset of the grinding

in the sediment samples is shown in Figure 1. As the percentage of aragonite increases in the samples, less MgCO_3 is found. This can be easily explained as the MgCO_3 is found as a calcite type structure, being present in a solid solution series between calcite and dolomite, and the percentage of MgCO_3 present would decrease as the ratio of calcite to aragonite decreases.

Solution Experiment.

Introduction.

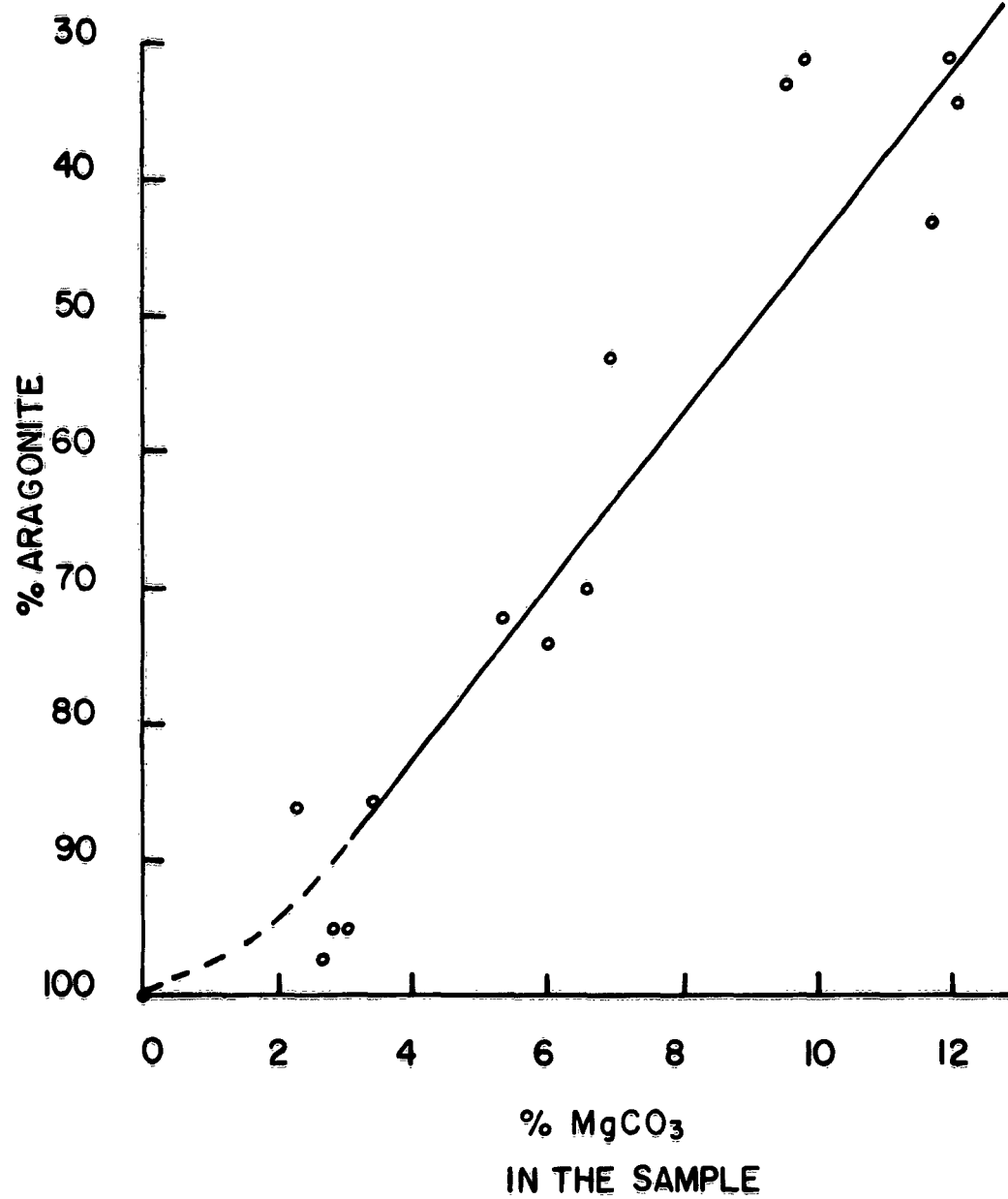
In order to measure the resistance of recent natural marine carbonate sediments to solution, sediment samples were suspended in various salt solutions and after a number of months, the amount of calcium and magnesium given up to the solution was determined. The degree of solution of each sample in the various salt solutions was then related to sample composition, mineralogy, and the particle size.

Procedure.

Five 0.5 gram samples of each of the sediment fractions listed in Tables 2 and 3 were weighed out on glazed weighing paper, folded, and set aside. One-hundred milliliters of distilled water were pipetted into a 250 ml beaker, placed on a magnetic stirrer, and after the stirring bar was added, the pH was recorded. Then a 0.5 gram sample of a sediment

FIGURE 1

The Relationship Between Aragonite and MgCO_3 in Recent
Marine Carbonate Sediment Samples



was added and the change in pH recorded continuously for about 10 to 15 minutes. The suspension was then transferred to a 250 ml erlenmeyer flask and stoppered with cotton and gauze. This procedure was repeated until one 0.5 gram sample of each sediment sample was placed in distilled water and the pH measurements recorded continuously.

The process was then repeated for the NaCl , MgCl_2 , $\text{NaCl} + \text{MgCl}_2$, and NaHCO_3 ion pairs of synthetic sea water. The solution experiments for each sediment sample were not run in duplicate; however, the analyses for Ca^{++} and Mg^{++} were the average of two determinations each. Duplicate blanks of each solution, minus the sediment sample, were also prepared.

The pH of each suspension was recorded after 1, 2, 3, 4, and 10 weeks, and at the end of the experiment. The pH results are given in Appendix III.

After the final pH was recorded, the solution was analyzed for dissolved Ca^{++} and Mg^{++} , using the procedure given in Appendix I, Part F. The results of these analyses are given in Appendix II.

CHAPTER III

RESULTS AND DISCUSSION

NaHCO_3 Solution Experiment

The amounts of Ca^{++} and Mg^{++} dissolved out of the marine carbonate sediments in NaHCO_3 are recorded in Appendix II, Table 1. These analyses were obtained after the sediments had been in contact with the NaHCO_3 solution for eight months. Figure 2 relates the dissolved amounts of Ca^{++} and Mg^{++} in millimoles to the percentage of MgCO_3 in the sediments.

From Figure 2, it is evident that little change occurs in the amount of dissolved Ca^{++} , averaging about 0.15 millimoles per liter, from the ground sediment samples regardless of MgCO_3 content. The amount of dissolved Mg^{++} , on the other hand, increases with increasing MgCO_3 content only to begin to level off around 0.6 millimoles per liter at higher MgCO_3 percentages. The amount of dissolved Ca^{++} from unground sediments is also about 0.15 millimoles per liter; however, no dissolved Mg^{++} is found in solution.

Figure 4 indicates that the carbonate alkalinity^{1/} of the solution of ground sediment samples in NaHCO_3 is 2 to 3

^{1/}Carbonate alkalinity = the HCO_3^- plus CO_3^{--} contributed to the solution by the dissolving CaCO_3 and MgCO_3 .

C.A. = $\text{C}_{\text{HCO}_3^-} + 2\text{C}_{\text{CO}_3^{--}}$ (expressed as equivalents).

FIGURE 2

Dissolved Ca^{++} and Mg^{++} in 0.0023 M NaHCO_3 with Respect
to Percent MgCO_3 in Sediment Samples

LEGEND

- Dissolved Ca^{++} from ground marine carbonate sediment samples
- Dissolved Ca^{++} from unground marine carbonate sediment samples
- Dissolved Mg^{++} from ground marine carbonate sediment samples
- Dissolved Mg^{++} from unground marine carbonate sediment samples

FIGURE 3

Dissolved Ca^{++} and Mg^{++} in Distilled Water with Respect
to Percent MgCO_3 in Sediment Samples

LEGEND

- Dissolved Ca^{++} from ground marine carbonate sediment samples
- Dissolved Ca^{++} from unground marine carbonate sediment samples
- Dissolved Mg^{++} from ground marine carbonate sediment samples
- Dissolved Mg^{++} from unground marine carbonate sediment samples

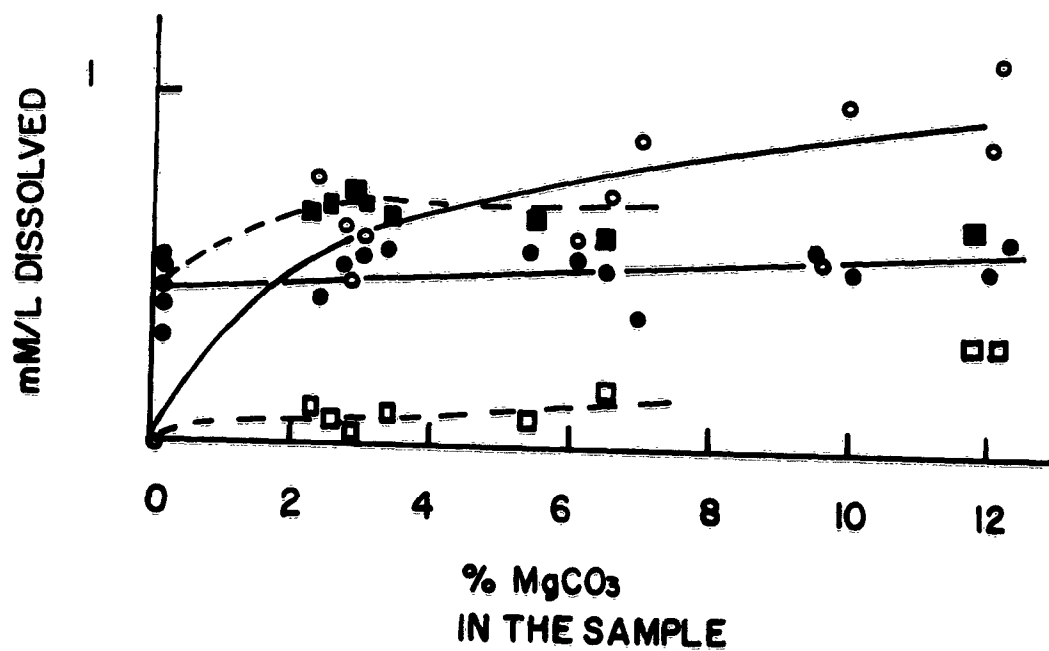
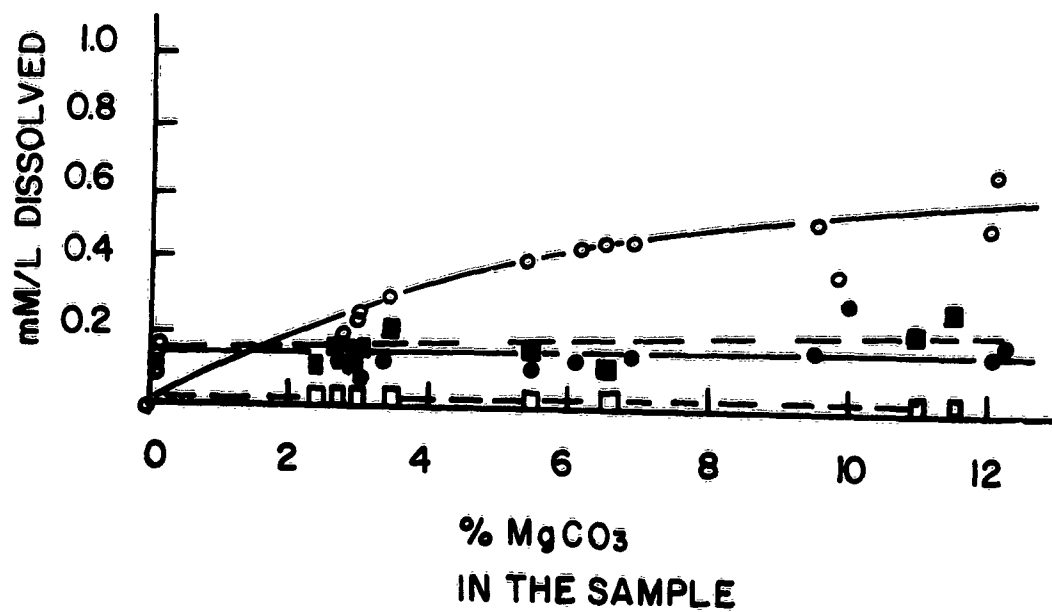
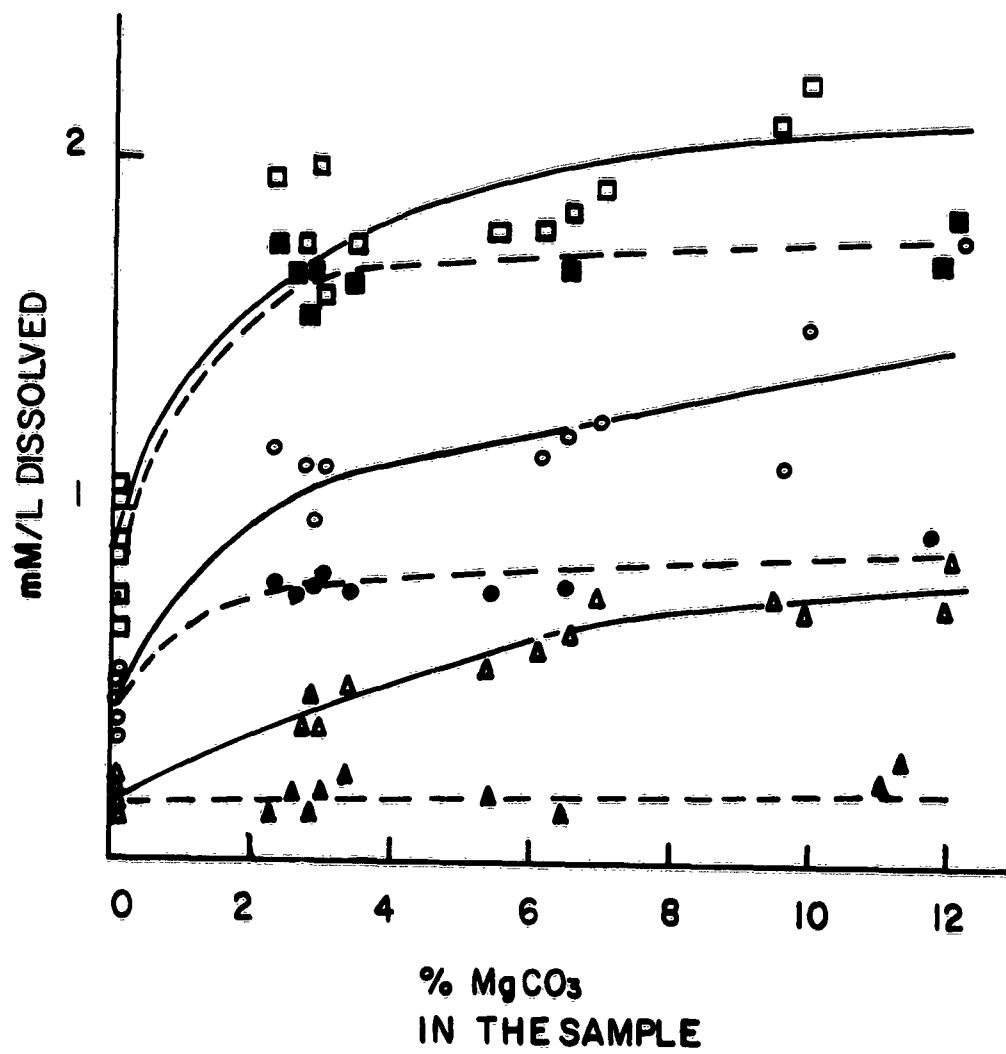


FIGURE 4

Carbonate Alkalinity Resulting from the Solution
of Sediment Samples in NaHCO_3 , Distilled Water,
and NaCl with Respect to Percent MgCO_3
in Sediment Samples

LEGEND

- $\triangle$ C.A. from ground marine carbonate
sediment samples in NaHCO_3
- $\blacktriangle$ C.A. from unground marine carbonate
sediment samples in NaHCO_3
- $\circ$ C.A. from ground marine carbonate
sediment samples in distilled water
- $\bullet$ C.A. from unground marine carbonate
sediment samples in distilled water
- $\square$ C.A. from ground marine carbonate
sediment samples in NaCl
- $\blacksquare$ C.A. from unground marine carbonate
sediment samples in NaCl



times that of the unground carbonate sediments, and approaches a constant value at the higher percentages of MgCO_3 .

Figure 5 indicates that the carbonate ion concentration resulting from the solution of ground carbonate samples in NaHCO_3 solution is not leveling off with greater percentages of MgCO_3 present in the samples. In NaHCO_3 solution, the ion products of $[\text{Ca}^{++}] [\text{CO}_3^{--}]$ and $[\text{Mg}^{++}] [\text{CO}_3^{--}]$ change very little as MgCO_3 increases in the sample (Figure 6).

The indication from Figure 2 is that Mg^{++} may have some influence on the solubility of CaCO_3 in ground carbonate sediments. The solubility of Ca^{++} from aragonite and magnesium calcite appears the same regardless of the amount of dissolved Mg^{++} present.

The situation with regard to the coarse, unground carbonate sediments is more complex. Magnesium from the coarse sediments is not going into solution (Figure 2). The reason for this is not known with certainty; however, there are 2 possible explanations.

The first explanation is derived from the fact that the sediments were washed prior to any subdivision or grinding. During the removal of the sea salts from the sediment surfaces by distilled water, it is possible that the limited amount of Mg^{++} at the surface was removed. Subsequent solution of the unground sediment samples would result in lower dissolved

FIGURE 5

Carbonate Ion Concentration of the Solution of Sediment
Samples with Respect to Percent MgCO_3
in Sediment Samples*

LEGEND

$\Delta [\text{CO}_3^{=}]$ of dissolved marine carbonate
sediment samples in NaHCO_3

$\circ [\text{CO}_3^{=}]$ of dissolved marine carbonate
sediment samples in distilled water

$\square [\text{CO}_3^{=}]$ of dissolved marine carbonate
sediment samples in NaCl

$\times [\text{CO}_3^{=}]$ of dissolved marine carbonate
sediment samples in MgCl_2

$+ [\text{CO}_3^{=}]$ of dissolved marine carbonate
sediment samples in $\text{NaCl} + \text{MgCl}_2$

*See Appendix II, Tables 6 and 7

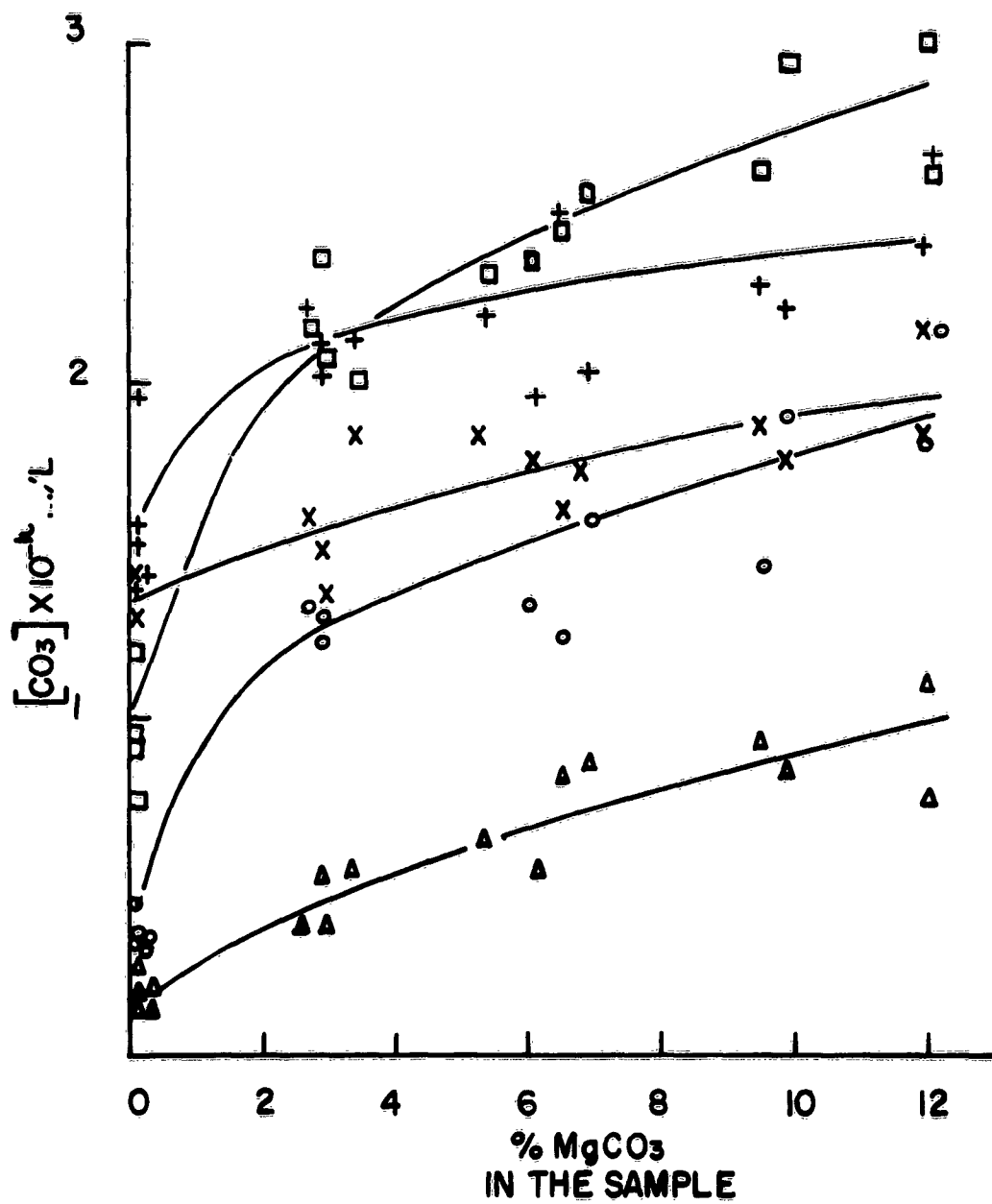


FIGURE 6

Ion Products of the Solution of Sediment Samples
in NaHCO_3 , Distilled Water, and NaCl with Respect
to Percent MgCO_3 in Sediment Samples*

LEGEND

Δ $[\text{Ca}^{++}] [\text{CO}_3^{--}]$ of dissolved marine carbonate
sediment samples in NaHCO_3

$\blacktriangle$ $[\text{Mg}^{++}] [\text{CO}_3^{--}]$ of dissolved marine carbonate
sediment samples in NaHCO_3

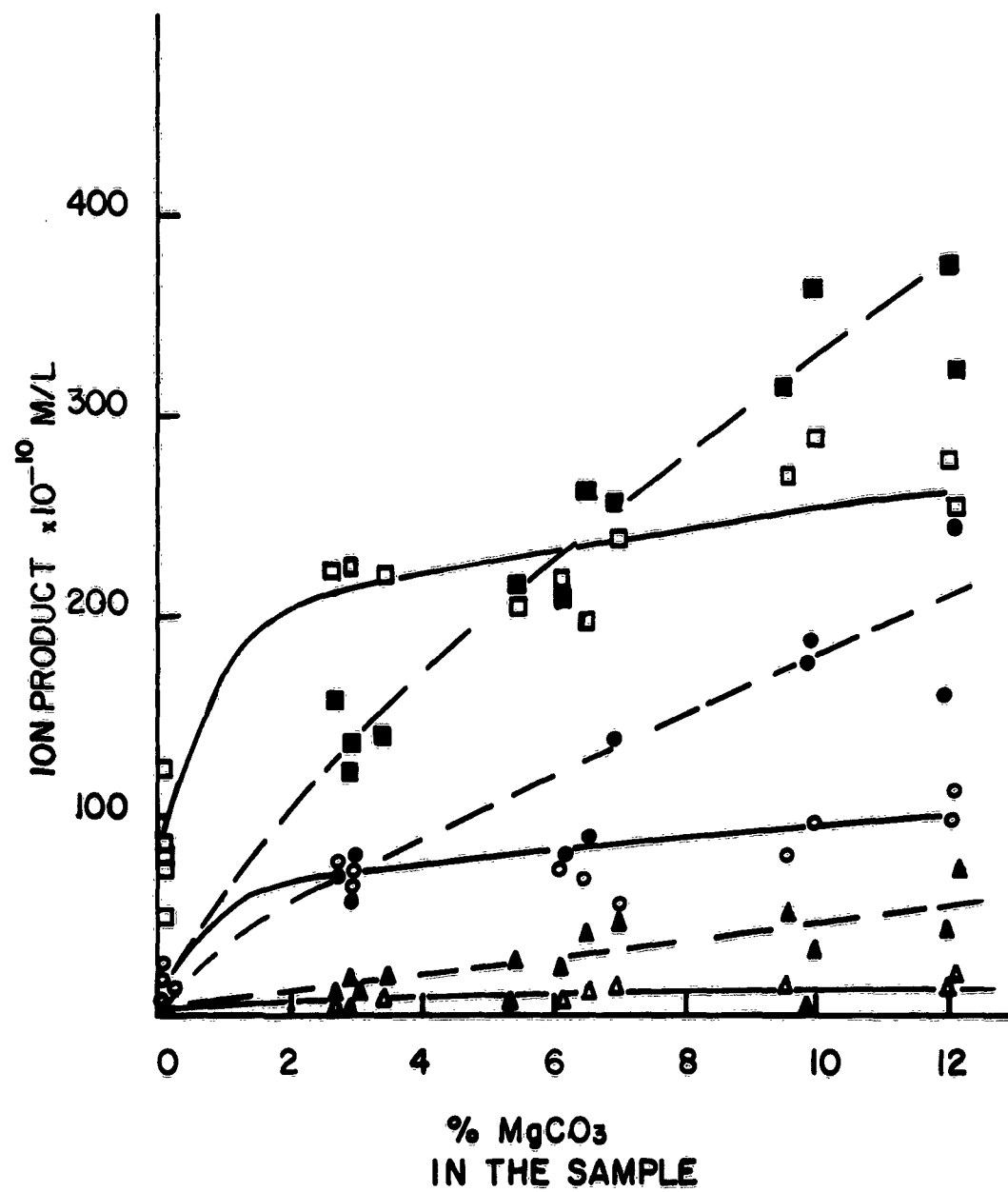
$\circ$ $[\text{Ca}^{++}] [\text{CO}_3^{--}]$ of dissolved marine carbonate
sediment samples in distilled water

$\bullet$ $[\text{Mg}^{++}] [\text{CO}_3^{--}]$ of dissolved marine carbonate
sediment samples in distilled water

$\square$ $[\text{Ca}^{++}] [\text{CO}_3^{--}]$ of dissolved marine carbonate
sediment samples in NaCl

$\blacksquare$ $[\text{Mg}^{++}] [\text{CO}_3^{--}]$ of dissolved marine carbonate
sediment samples in NaCl

*See Appendix II, Tables 6 and 7



Mg^{++} values than for ground samples. It is further suggested that the washing would not remove all available surface Ca^{++} as the samples are composed of 88 percent plus CaCO_3 . No change in dissolved Ca^{++} would therefore be expected.

The second explanation stems from the possibility that in the marine environment, the sediments, or actually the sediment surfaces, are in equilibrium with sea water. Upon solution in NaHCO_3 , an "equilibrium shift" results in the observed value of dissolved Ca^{++} and Mg^{++} . The inner parts of the sediments are not in equilibrium with sea water and grinding exposed a great number of these surfaces. Therefore, upon solution of the ground sediments, different values of dissolved Ca^{++} and Mg^{++} result.

Figure 4 indicates that the carbonate alkalinity for the ground carbonate samples in NaHCO_3 is 2 times greater than for the unground sediment samples when more than 2 percent MgCO_3 is in the sediment sample. This also may be due to washing the sediments, as CO_3^{--} and HCO_3^- from the dissolving MgCO_3 of the unground sediments would be lost to the distilled water wash.

The carbonate alkalinity resulting from the solution of the ground samples approaches constancy with increasing MgCO_3 content in the sediment, indicating that additional HCO_3^- and CO_3^{--} ions are not going in solution (Figure 4).

The $[\text{CO}_3^{2-}]^2/$ of the solution, which takes K_2' and pH into consideration, may be approaching a constant value (Figure 5). This value gives some indication as to the status of equilibrium; however, only the ion product attaining a constant value will tell whether equilibrium is reached. In the case of NaHCO_3 , CaCO_3 equilibrium is approached in eight months by sediments with high MgCO_3 content (Figure 6); however, MgCO_3 equilibrium is not yet reached as indicated by the increasing $[\text{Mg}^{++}] [\text{CO}_3^{2-}]$ ion product.

Distilled Water Solution Experiment

The amounts of Ca^{++} and Mg^{++} dissolved out of the marine carbonate sediments in distilled water are recorded in Appendix II, Table 2. These analyses were obtained after the sediments were in contact with distilled water for six months. Figure 3 relates the dissolved amounts of Ca^{++} and Mg^{++} in millimoles to the percentage of MgCO_3 in the sediment samples.

The dissolved amounts of Ca^{++} from the ground sediment samples increase from 0.45 to 0.55 millimoles per liter with increasing MgCO_3 . The dissolved amounts of Mg^{++} , meanwhile, increase from 0 to almost 1 millimole, and there is only

$$\frac{2}{[\text{CO}_3^{2-}]} = [\text{C.A.}] \frac{K_2'}{\text{H}^+ + 2K_2'}$$

a slight suggestion that it is beginning to level off for the same ground sediment samples.

Comparing Figures 2 and 3, it is observed that for the ground samples, the dissolved Ca^{++} is greater in distilled water (0.6 mM/L) than in NaHCO_3 (0.2 mM/L). Likewise, the dissolved Mg^{++} has reached almost 1 millimole per liter in distilled water while reaching only 0.6 millimoles per liter in NaHCO_3 .

Figure 4 indicates that the carbonate alkalinity for ground samples in distilled water is 50 percent higher than the carbonate alkalinity for unground sediment samples in distilled water. For ground sediment samples in distilled water, the carbonate alkalinity (Figure 4) and the carbonate ion concentration (Figure 5) are both steadily increasing with greater percentages of MgCO_3 present. The ion products of $[\text{Ca}^{++}] [\text{CO}_3^{=}]$ and $[\text{Mg}^{++}] [\text{CO}_3^{=}]$ also continue to increase with higher percentages of MgCO_3 in the sediment for the distilled water solution experiment (Figure 6).

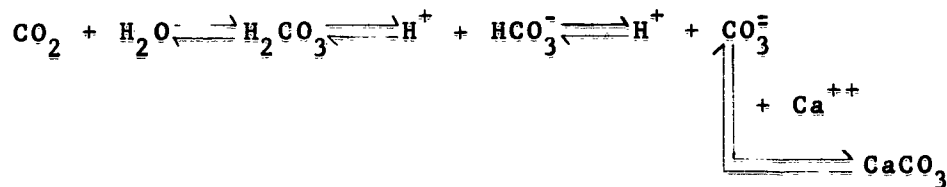
Figure 3 is interpreted as indicating that the Mg^{++} in the ground samples has influenced the solubility of Ca^{++} dissolving from calcite. This has resulted in there being a slight increase in the solubility of calcite over aragonite. The fact that a considerable amount of the calcite is dissolving is indicated by the rapidly increasing amounts of

Mg^{++} going into solution. The absolute value of Ca^{++} dissolved appears to increase slightly with increasing MgCO_3 in the sediment. The presence of Mg^{++} has increased the overall solubility of calcite in natural marine carbonates.

The interpretation of the dissolved Ca^{++} and Mg^{++} from the unground carbonate sediments is more complex. The indication from Figure 3 is that the Mg^{++} dissolved from unground sediments is depressed, and the Ca^{++} dissolved is increased. Two possible explanations have been outlined in the previous section.

The first explanation, derived from the washing history of the coarse sediment samples after removal from the marine environment, does explain the low values of dissolved Mg^{++} from unground sediment samples. From this explanation the value of dissolved Ca^{++} is not expected to change from ground to unground sediment samples; however, Figure 3 indicates that the dissolved Ca^{++} from unground sediments is 0.1 to 0.2 millimoles per liter greater than dissolved Ca^{++} from ground sediment samples. This is reasonable when the chemistry of the CO_2 system is taken into consideration.

The CO_2 system can be represented by the following:



In distilled water, the CO_2 system is established upon the solution of CaCO_3 and a specific carbonate alkalinity is maintained. In the case of the ground samples, $\text{CO}_3^{=}$ and HCO_3^- is contributed to the solution through dissolving CaCO_3 and MgCO_3 . For the unground samples, however, less MgCO_3 is available for solution which results in more CaCO_3 dissolving to make up the $\text{CO}_3^{=}$ deficiency.

The second explanation suggesting an "equilibrium shift" could result in decreased Mg^{++} solution and increased Ca^{++} solution.

The differences in solution between distilled water and NaHCO_3 can be attributed to the common ion effect in the NaHCO_3 solution. At pH values of around 8, the major contributing ion in the CO_2 system is HCO_3^- , and the concentration of $\text{CO}_3^{=}$ present will therefore depend upon the HCO_3^- concentration. As CaCO_3 is added to NaHCO_3 , the system will establish equilibrium with less carbonate from CaCO_3 , as $\text{CO}_3^{=}$ is already present from the dissolved NaHCO_3 . For this reason, Ca^{++} and Mg^{++} are dissolved more readily in distilled water than NaHCO_3 .

The steady increase in carbonate alkalinity with higher percentages of MgCO_3 in the sample for ground sediment samples indicates that more HCO_3^- and $\text{CO}_3^{=}$ are being added to the distilled water, when pH and K_2' are taken into consideration, as shown by Figure 5.

The changing $[Ca^{++}] [CO_3^{--}]$ and $[Mg^{++}] [CO_3^{--}]$ ion products in distilled water indicate that equilibrium is not yet reached, although the $[Ca^{++}] [CO_3^{--}]$ ion product appears to be much closer to attaining it (Figure 6).

NaCl Solution Experiment

The amounts of Ca^{++} and Mg^{++} dissolved out of the marine carbonate sediments in NaCl are recorded in Appendix II, Table 3. These analyses were obtained after the sediments were in contact with NaCl for 3 months. Figure 7 relates the dissolved amounts of Ca^{++} and Mg^{++} in millimoles to the percentage of $MgCO_3$ in the sediment samples.

From Figure 7, it can be seen that the dissolved amounts of Ca^{++} from the ground sediment samples are relatively constant, averaging between 0.9 and 1.0 millimoles per liter regardless of the $MgCO_3$ content. The dissolved amounts of Mg^{++} , however, increase rapidly at first, and begin to level off around 1.2 millimoles per liter at higher $MgCO_3$ contents. The dissolved amounts of Mg^{++} for unground sediment samples average about 0.1 millimoles per liter, and Ca^{++} about 1.55 millimoles per liter (Figure 7).

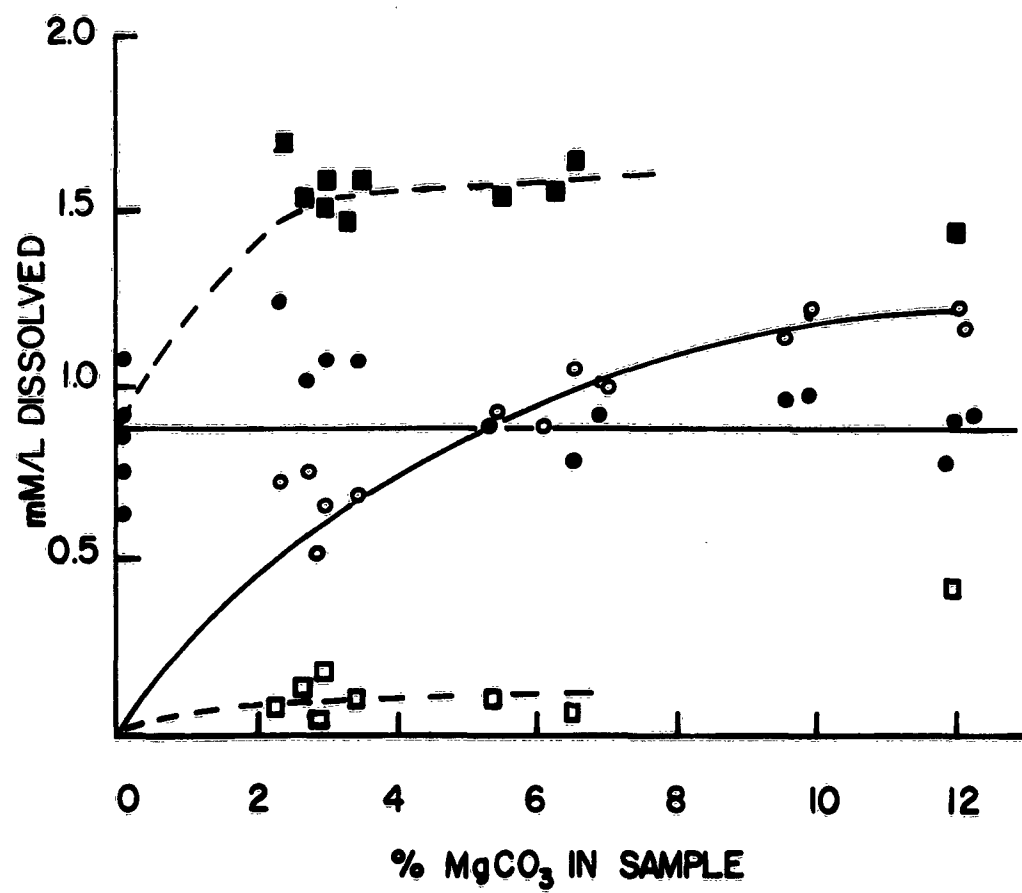
The dissolved Ca^{++} and Mg^{++} for ground samples in NaCl are greater than the dissolved Ca^{++} and Mg^{++} for ground samples in distilled water (Figures 3 and 7).

FIGURE 7

Dissolved Ca^{++} and Mg^{++} in 0.405 M NaCl with Respect
to Percent MgCO_3 in Sediment Samples

LEGEND

- Dissolved Ca^{++} from ground marine
carbonate sediment samples
- Dissolved Ca^{++} from unground marine
carbonate sediment samples
- Dissolved Mg^{++} from ground marine
carbonate sediment samples
- Dissolved Mg^{++} from unground marine
carbonate sediment samples



The carbonate alkalinity for the ground samples in NaCl is somewhat higher than for the unground carbonate samples with some indication of leveling off at higher percentages of MgCO_3 (Figure 4).

Figure 5 shows the carbonate ion concentration for NaCl to be quite high with the absolute value not yet approaching constancy.

Figure 6 indicates that the $[\text{Ca}^{++}] [\text{CO}_3^{=}]$ ion product for the NaCl solution experiment may be beginning to level off; however, the $[\text{Mg}^{++}] [\text{CO}_3^{=}]$ ion product is still rapidly increasing at almost a linear rate.

A considerable amount of calcite is dissolving as indicated by the rapidly increasing Mg^{++} in solution (Figure 7). Much of the dissolved Ca^{++} must therefore come from the calcite present in the carbonate samples. The absolute value of Ca^{++} dissolved appears to be little changed by increasing Mg^{++} , suggesting that there is little difference in the solubility of aragonite and the magnesium calcite present in NaCl solution. Seidell (1940) reports that aragonite is somewhat more soluble than calcite in NaCl. The indication is, then, that Mg^{++} does influence the solubility of CaCO_3 as seen in Figure 7.

Figure 7 indicates that between 1.5 and 1.6 millimoles per liter of Ca^{++} dissolved from unground natural size

sediments, whereas only about 1 millimole per liter of Ca^{++} dissolves from the ground sediments. Likewise, only a very small amount of Mg^{++} dissolves from the unground sediments, about 0.1 millimoles per liter, whereas from 0.5 to 1.2 millimoles per liter of Mg^{++} dissolves from the ground sediments (Figure 7). The reason for these differences again is not known with absolute certainty; however, there are 2 possible explanations, one involving washing history, and the other involving equilibrium, both of which have been previously outlined under the distilled water discussion.

The increase in the solubility of CaCO_3 by alkali chlorides have long been recognized (Seidell, 1940). This has been reaffirmed in the present study; however, it is difficult to say whether the solution of Mg^{++} is ultimately greater or less in NaCl than in distilled water. A comparison between Figures 3 and 7 indicates that at 10 to 12 percent MgCO_3 in the sample, 1.2 millimoles per liter of Mg^{++} are dissolved in the NaCl solution compared to just under 1 millimole per liter of Mg^{++} present in distilled water.

The carbonate alkalinity plot (Figure 4) for ground sediment samples in NaCl indicates that the total HCO_3^- and CO_3^{--} content of the solution is not yet beginning to show signs of leveling off at high percentages of MgCO_3 . The carbonate ion concentration in the NaCl solution, from

Figure 5, is continuing to rise as MgCO_3 increases in the sediments. The latter value takes into account any pH difference as it was previously seen.

Figure 6 indicates, however, that the $[\text{Mg}^{++}] [\text{CO}_3^{--}]$ ion product is still rapidly increasing at 12 percent MgCO_3 . The $[\text{Ca}^{++}] [\text{CO}_3^{--}]$ ion product on the other hand, may be approaching equilibrium with increasing MgCO_3 . It is evident that NaCl does favor the solution of Mg^{++} , and the dissolved Mg^{++} does not approach equilibrium in the NaCl solution (Figure 6).

MgCl_2 Solution Experiment

The amounts of Ca^{++} and Mg^{++} dissolved out of the marine carbonate sediments in MgCl_2 are recorded in Appendix II, Table 4. These analyses were obtained after the sediments were in contact with MgCl_2 for eight months. Figure 8 relates the dissolved amounts of Ca^{++} and Mg^{++} in millimoles to the percentage of MgCO_3 in the sediments.

From Appendix II, Table 4, it is evident that something unusual is taking place. The Mg^{++} content of the MgCl_2 solution is not increased by either the dissolving ground or unground samples.

The dissolved amount of Ca^{++} from the ground sediment samples is relatively constant for those carbonate samples

FIGURE 8

Dissolved Ca^{++} in MgCl_2 and $\text{NaCl} + \text{MgCl}_2$ with Respect
to Percent MgCO_3 in Sediment Samples

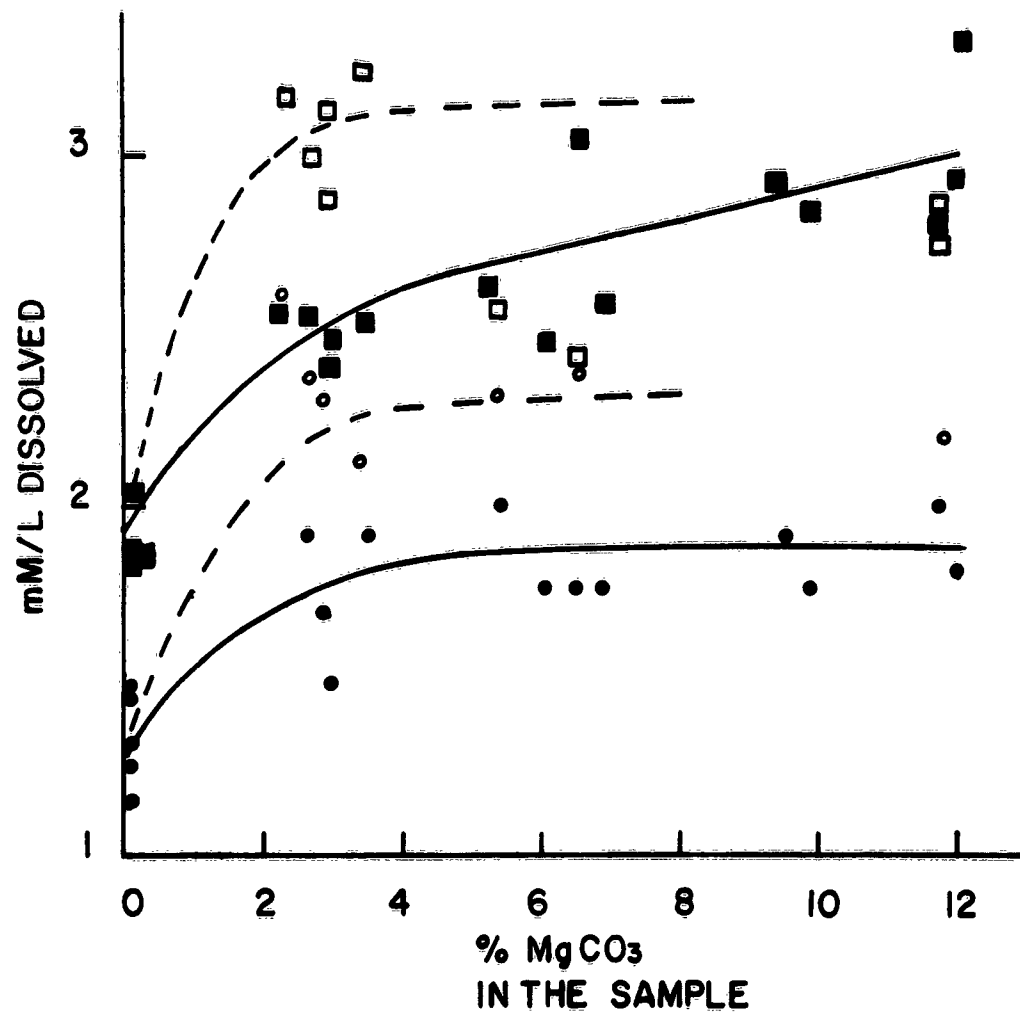
and

Carbonate Alkalinity Resulting from the Solution
of Sediment Samples in MgCl_2 and $\text{NaCl} + \text{MgCl}_2$
with Respect to Percent MgCO_3
in Sediment Samples*

LEGEND

- Dissolved Ca^{++} from ground marine carbonate
sediment samples in MgCl_2
- Dissolved Ca^{++} from unground marine carbonate
sediment samples in MgCl_2
- Dissolved Ca^{++} from ground marine carbonate
sediment samples in $\text{NaCl} + \text{MgCl}_2$
- Dissolved Ca^{++} from unground marine carbonate
sediment samples in $\text{NaCl} + \text{MgCl}_2$

*Carbonate Alkalinity is equal to dissolved Ca^{++} , as no additional Mg^{++} is contributed to the solution from the sediment.



containing calcite, with the dissolved amount of Ca^{++} from pure aragonite being much lower (Figure 8). The amount of Ca^{++} dissolved from unground carbonate sediments is greater than the amount of Ca^{++} dissolved from the ground sediment samples for the MgCl_2 solution experiment (Figure 8).

Figure 8 indicates that the carbonate alkalinity from the dissolving ground sediment samples in MgCl_2 is on the average 0.4 millimoles per liter less than the carbonate alkalinity of the unground sediment samples. The carbonate ion concentration of the ground carbonate sediments in MgCl_2 may be beginning to level off according to Figure 5, and the $[\text{Ca}^{++}] [\text{CO}_3^{--}]$ ion product from Figure 9 has about reached a constant value.

The absence of Mg^{++} in solution can not be explained either by washing or equilibrium as in the case of NaHCO_3 , distilled water, or NaCl . One very possible explanation, however, is that the high concentration of MgCl_2 in solution inhibits Mg^{++} from dissolving. Common ion effects such as these are well known in solution chemistry.

Seidell (1940) reported that alkaline earth chlorides depress the solution of CaCO_3 . A comparison between Figures 3 and 8 shows quite convincingly that the solubility of Ca^{++} is greater in MgCl_2 solution than in distilled water. The increase in the dissolved amount of Ca^{++} , above that

FIGURE 9

Ion Products of the Solution of Sediment Samples
in MgCl_2 and $\text{NaCl} + \text{MgCl}_2$ with Respect
to Percent MgCO_3 in Sediment Samples*

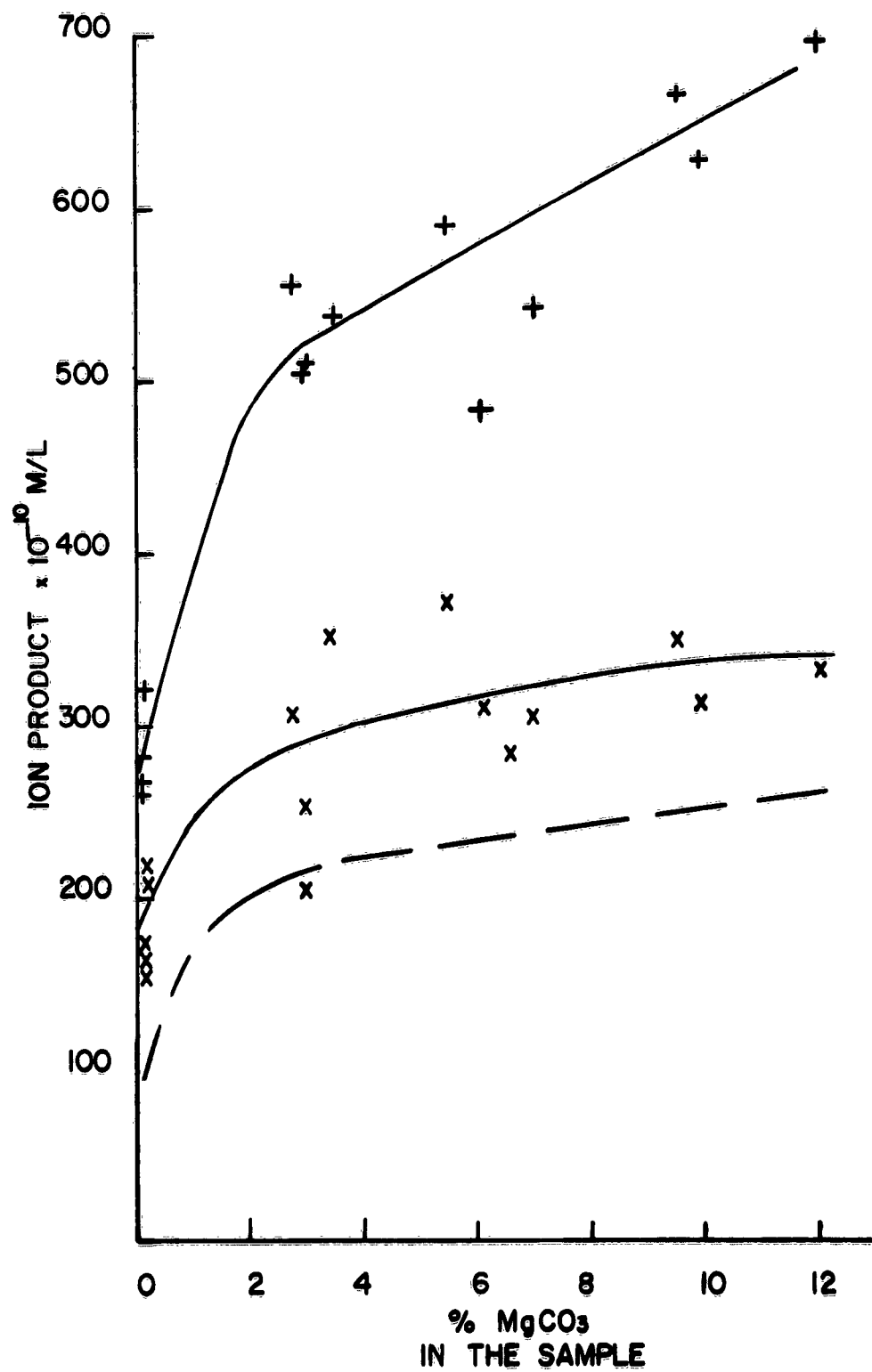
LEGEND

-- $[\text{Ca}^{++}] [\text{CO}_3^{=}]$ of dissolved marine carbonate
sediment samples in NaCl
(from Figure 6)

X $[\text{Ca}^{++}] [\text{CO}_3^{=}]$ of dissolved marine carbonate
sediment samples in MgCl_2

+ $[\text{Ca}^{++}] [\text{CO}_3^{=}]$ of dissolved marine carbonate
sediment samples in $\text{NaCl} + \text{MgCl}_2$

*See Appendix II, Table 7



which dissolves from pure aragonite, can be attributed to the high magnesium calcite.

In order to justify the difference in the amounts of Ca^{++} dissolved from ground and unground sediments, we must return to the alternatives presented under the discussion of NaHCO_3 . The most likely explanations, derived from either preliminary washing or differences due to an equilibrium shift, seem to apply.

It is evident from Figure 5 that the $[\text{CO}_3^{=}]$, from the dissolving ground carbonate sediments in MgCl_2 , may have begun to level off so that further increase in available MgCO_3 will result in very little additional carbonate being added to solution.

The $[\text{Ca}^{++}] [\text{CO}_3^{=}]$ ion product has nearly reached equilibrium for ground sediments in MgCl_2 indicating that the solution will not dissolve greater quantities of CaCO_3 (Figure 9).

$\text{NaCl} + \text{MgCl}_2$ Solution Experiment

The amounts of Ca^{++} and Mg^{++} dissolved out of marine carbonate sediments in $\text{NaCl} + \text{MgCl}_2$ are recorded in Appendix II, Table 5. These analyses were obtained after the sediments were in contact with $\text{NaCl} + \text{MgCl}_2$ for eight months. Figure 8 relates

the dissolved amounts of Ca^{++} and Mg^{++} in millimoles to the percentage of MgCO_3 in the sediments.

As in the case of MgCl_2 , Appendix II, Table 5, indicates unusual behavior on the part of sediment solution. Again Mg^{++} is not dissolved from either the unground or ground sediment samples.

Figure 8 indicates that the amount of Ca^{++} dissolved from the ground sediment samples slowly increases at a rather constant rate from just under 1.9 millimoles per liter to more than 3 millimoles per liter for 0 percent MgCO_3 to 12 percent MgCO_3 , respectively. A comparison between Figures 7 and 8 indicates that the total Ca^{++} dissolved by $\text{NaCl} + \text{MgCl}_2$ is roughly the same as the Ca^{++} dissolved from NaCl and MgCl_2 added separately.

Figure 5 indicates that the $[\text{CO}_3^-]$ for $\text{NaCl} + \text{MgCl}_2$ continues to rise with increase in MgCO_3 in the sediment, and Figure 9 shows that the rapidly increasing $[\text{Ca}^{++}] [\text{CO}_3^-]$ ion product for $\text{NaCl} + \text{MgCl}_2$ does not level off and reach a constant value.

Figure 7 indicates that NaCl dissolves over 1 millimole of Mg^{++} per milliliter; however, when NaCl is combined with MgCl_2 , no Mg^{++} is in solution after eight months (Figure 8). Magnesium chloride exerts greater control over the solution of carbonates than NaCl . It is again suggested that the MgCl_2 in solution tends to inhibit the solution of Mg^{++} from the sediments.

The differences in amount of Ca^{++} dissolved from ground and unground sediments for the $\text{NaCl} + \text{MgCl}_2$ solution experiment are attributed to either preliminary washing, or to the equilibrium shift.

Figure 5 indicates that the $[\text{CO}_3^{--}]$ for $\text{NaCl} + \text{MgCl}_2$ may be leveling off. With increasing MgCO_3 in the sample the carbonate ion concentration in $\text{NaCl} + \text{MgCl}_2$ solution may become constant. The $[\text{Ca}^{++}] [\text{CO}_3^{--}]$ ion product from Figure 9, however, shows that equilibrium is not being reached in the case of $\text{NaCl} + \text{MgCl}_2$. It is also evident that the $[\text{Ca}^{++}] [\text{CO}_3^{--}]$ ion product in $\text{NaCl} + \text{MgCl}_2$ is merely the additive effect of the ion products for NaCl and MgCl_2 added individually.

Figures 10 and 11 summarize the dissolved amounts of Ca^{++} and Mg^{++} with respect to the percent MgCO_3 in the sediment samples for each of the solutions used in the experiment. The solution of Ca^{++} is inhibited by NaHCO_3 , followed by distilled water, NaCl , MgCl_2 , and $\text{NaCl} + \text{MgCl}_2$. The solution of Mg^{++} is inhibited by MgCl_2 and $\text{NaCl} + \text{MgCl}_2$, followed by NaHCO_3 , distilled water and NaCl . Figures 10 and 11 show the relationship between dissolved amounts of Ca^{++} and Mg^{++} with increasing MgCO_3 content in the sediments for each solution.

FIGURE 10
Dissolved Amounts of Ca^{++} with Respect to Percent MgCO_3
in Sediment Samples in the Ion Pairs of Synthetic
Sea Water

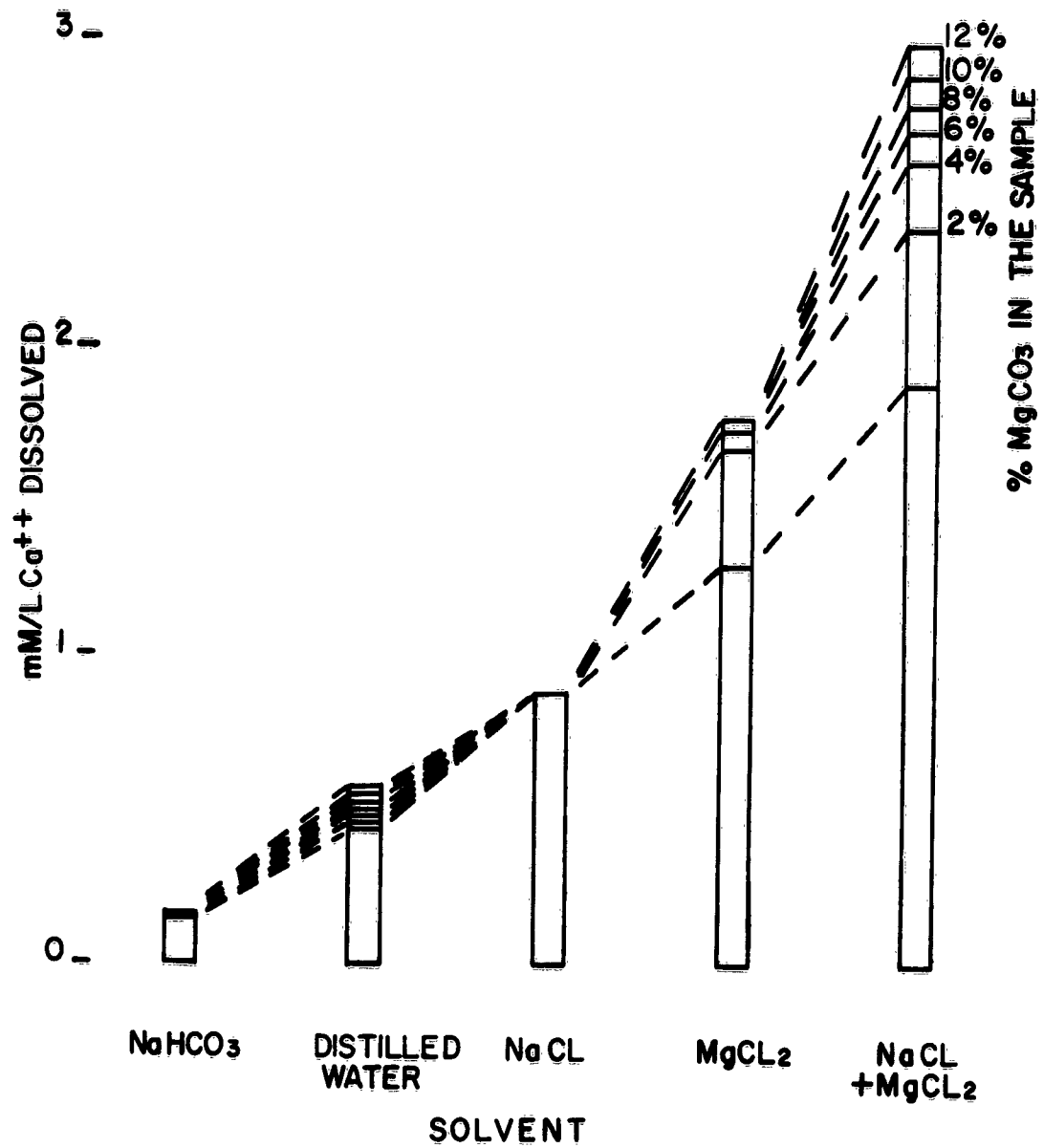
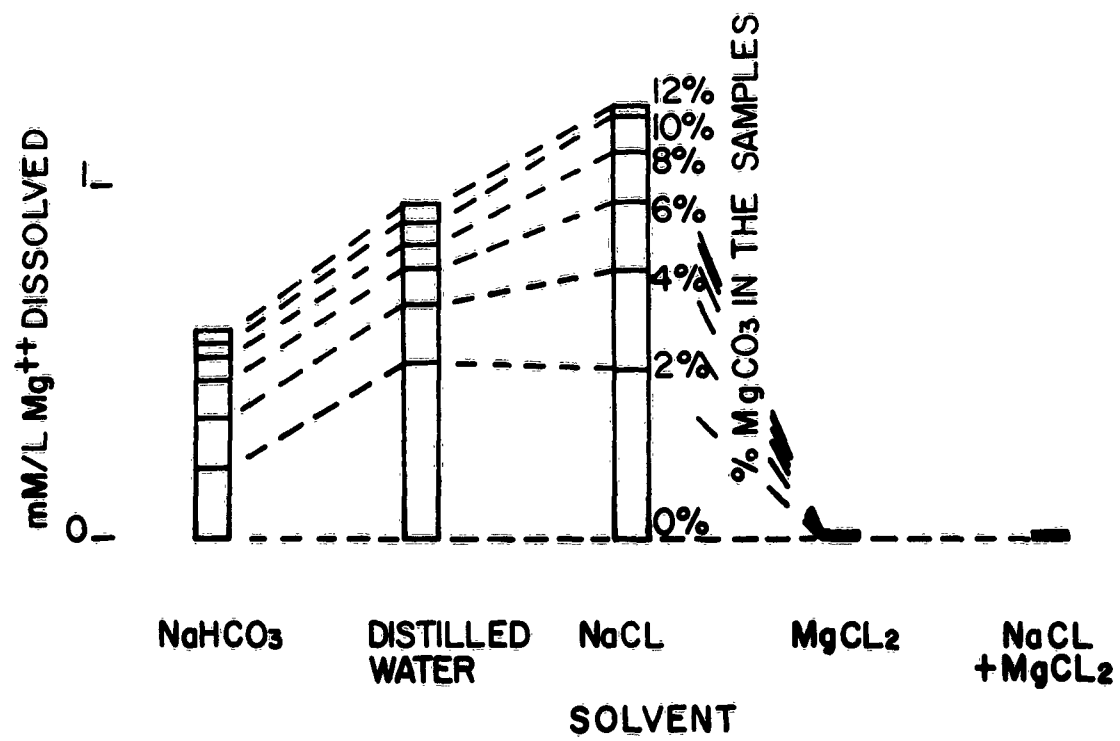


FIGURE 11.
Dissolved Amounts of Mg^{++} with Respect to Percent MgCO_3
in Sediment Samples in the Ion Pairs of Synthetic
Sea Water



The Effects of Particle Size and pH

From the pH values observed during the first 10 or 15 minutes as each sediment went into solution, it was evident that particle size did affect the rate of solution. The ground samples, in almost every case, go into solution very rapidly as indicated by the immediate rise in pH. For the unground samples the rate of pH change decreases with increasing grain size. This indicates that the initial rate of solution is dependent upon grain size. Figure 12 shows a typical family of pH curves for various size carbonate sediments as they dissolve. Appendix III contains the pH values of each dissolving carbonate with time.

All differences in pH, with respect to particle size, disappear as the solution approaches equilibrium. No correlation appears to exist between particle size and ultimate solubility in any of the solutions used.

It is apparent that the final pH values do not reflect solubility in NaHCO_3 , distilled water, and NaCl . For MgCl_2 and $\text{NaCl} + \text{MgCl}_2$, however, the final pH values of the unground sediment samples are higher than the final pH values of the ground sediment samples.

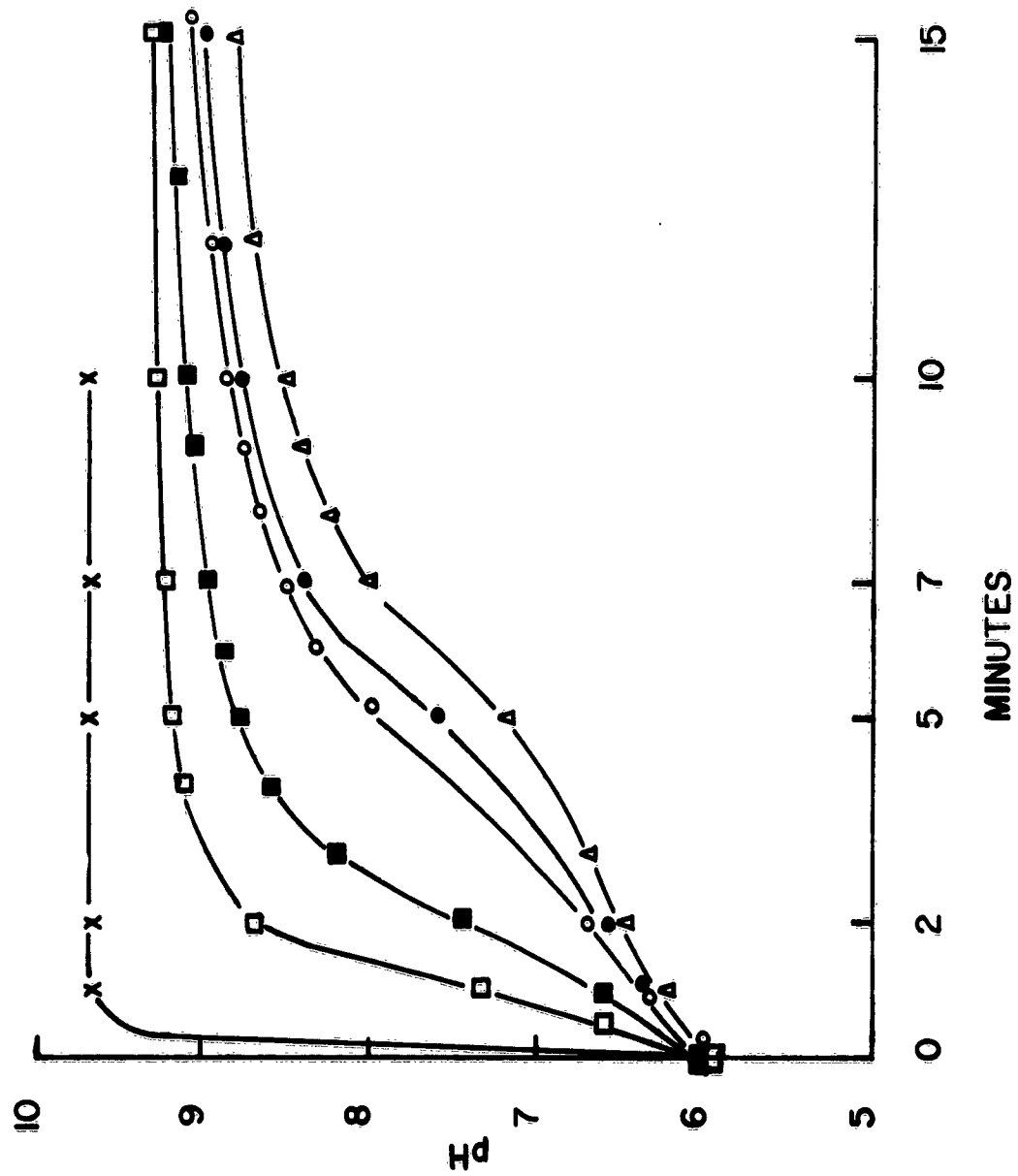
Figure 8 indicates that the dissolved Ca^{++} from unground carbonate sediments is greater than the dissolved Ca^{++} from ground carbonate samples. Inasmuch as no CO_3^{--} is contributed

FIGURE 12

Typical Variations in pH for Various Grain
Size Carbonate Sediments

LEGEND

- Δ pH variations for 18 mesh size
sediments
- pH variations for 35 mesh size
sediments
- pH variations for 60 mesh size
sediments
- pH variations for 120 mesh size
sediments
- pH variations for 230 mesh size
sediments
- X pH variations for all sediments
ground for 2 hours



to the solution from dissolving MgCO_3 in either MgCl_2 or $\text{NaCl} + \text{MgCl}_2$, dissolved Ca^{++} and $\text{CO}_3^{=}$ are directly related. As dissolved Ca^{++} increases in a solution, $\text{CO}_3^{=}$ also increases. The relationship between pH and $\text{CO}_3^{=}$ can be written as:

$$\text{pH} = \text{pK}'_2 + \log \frac{\text{CO}_3^{=}}{\text{HCO}_3^{-}}$$

The higher values of dissolved Ca^{++} for the unground samples are thus accompanied by higher pH values in both MgCl_2 and $\text{NaCl} + \text{MgCl}_2$ solution experiments, indicating that a relationship between pH and the solution of Ca^{++} exists. An understanding of the mechanisms underlying this relationship will require further work.

The pH values reached during the initial stages of solution are as high as 9.7, which are considerably greater than the final equilibrium pH values of 8.2 to 8.4 (Appendix III, Tables 1-5). It is suggested here that supersaturation occurs during initial solution of marine carbonate sediments in the ion pairs of sea water. Reprecipitation of the cations is indicated by the lower pH values after 1 week.

The situation with regard to sea water is somewhat different. The pH of each sediment sample going into solution was followed for eight months (Appendix III, Table 6). No significant change in pH occurs during the first 15 minutes

except for pure aragonite samples which decrease somewhat. Little change in pH occurs during the entire experiment for ground sediment samples. The unground sediment samples, however, raise the pH of the solution from about 8.0 at 1 week to 8.2 at 10 weeks.

CHAPTER IV

CONCLUSIONS

The results of this study indicate:

1. The grain size of recent marine carbonate sediments have no relationship to the amount of Ca^{++} or Mg^{++} dissolved by the major ion pairs of synthetic sea water and distilled water.
2. The pH of solutions containing MgCl_2 reflect, to some extent, the amount of Ca^{++} dissolved.
3. The presence of MgCl_2 in solution inhibits Mg^{++} from dissolving out of sediments, and promotes the solution of Ca^{++} . The indication is that MgCl_2 is the major controlling ion pair of synthetic sea water, and the effects of the other ion pairs are relatively unimportant on the solution of Ca^{++} and Mg^{++} .
4. The magnesium calcites present in the marine carbonate sediments of this study are more soluble than 100 percent aragonite in MgCl_2 and $\text{NaCl} + \text{MgCl}_2$, but are not noticeably different than pure aragonite in NaHCO_3 , distilled water, and NaCl .

5. At the conclusion of the solution experiments, it is evident that when large amounts of MgCO_3 are present in the sediment, the ion product of $[\text{Ca}^{++}] [\text{CO}_3^{=}]$ in the MgCl_2 solution nearly reaches equilibrium, and the ion products of $[\text{Ca}^{++}] [\text{CO}_3^{=}]$ and $[\text{Mg}^{++}] [\text{CO}_3^{=}]$ do not reach equilibrium in NaHCO_3 , distilled water, NaCl , or $\text{MgCl}_2 + \text{NaCl}$.

6. The pH values of the suspensions increase rapidly to a maximum during the first 15 minutes in most cases and decrease to a constant lower value after the first week. This is considered as evidence that during the first 15 minutes of solution, more cations are in solution than are present after a week. It is suggested that the initial solution of each sediment is followed by reprecipitation until an equilibrium value is reached.

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A P P E N D I X I

APPENDIX I

A. Preparation of Calcium Ion Standard Solution

Reagents.

- 1) 6N Hydrochloric Acid. Dilute 485 ml of reagent grade concentrated HCl (S.G. 1.19) to 1 liter.

Equipment.

- 1) Hot plate.
- 2) Glassware:
 - 1-200 ml tall form beaker
 - 1-1 liter volumetric flask
 - 1 short stem funnel (slightly greater in width than the tall form beaker).

Dry several gm reagent grade CaCO_3 overnight in a low temperature (85°C) drying oven. Cool in a desiccator and weight-out 1.000 gm. Quantitatively transfer the weighed CaCO_3 to a 200 ml tall form beaker and add 20 ml of distilled water. Place the short stem funnel in the beaker^{1/}. Through the funnel add several ml of 6N HCl to dissolve the CaCO_3 completely. The solution is carefully boiled for 5 minutes to remove CO_2 completely. Cool the solution and quantitatively transfer to a 1 liter volumetric flask. Dilute the solution

^{1/}The funnel prevents any loss of Ca^{++} either due to the effervescence of the carbonate while dissolving, or due to the bubbling of the solution during boiling.

to 1 liter with boiled distilled water and stopper. The titer of the calcium ion standard is 0.4008 mg Ca^{++} /ml.

B. Standardization of EDTA for Ca^{++} Analysis

Reagents.

- 1) Methyl Red Indicator (0.02 percent dissolved in ethanol).
- 2) 2N Sodium Hydroxide. Dissolve 80 gm of reagent grade NaOH pellets in distilled water and make to volume of 1 liter.
- 3) Calcium Red Indicator. One gram of 2-hydroxy-1-(2-hydroxy-4-sulfo-1-naphthylazo)-3-naphthoic acid is ground and mixed with 100 gm of reagent grade NaCl in a mortar and stored in the dry form in a dark colored bottle.
- 4) EDTA Standard Solution. Dissolve 80 gm of the di-sodium salt of ethylenediaminetetraacetic acid in 20 liters and allow to stand at room temperature with occasional stirring, for several days.

Equipment.

1) Glassware:

- 1-50 ml automatic burette with automatic zero point
- 1-10 ml pipette
- 3-250 ml erlenmeyer flasks.

With the volumetric pipette, transfer 1-10 ml aliquot of the calcium ion standard into each of the 3-250 ml erlenmeyer flasks. Adjust the total volume of solution to about 50 ml with distilled water. Add 1 drop of methyl red and then add 2N NaOH dropwise until the solution just becomes

basic (methyl red turns to yellow). Add an excess of 15 ml of 2N NaOH (the titration must be carried out at a pH of about 13). With a spatula, add approximately 100 mg of the solid calcium red indicator and titrate with EDTA until 1 drop turns the indicator from red to blue. The triplicate titrations should agree within 0.05 ml.

The EDTA titer is calculated as follows:

$$\text{Titer (mg/ml)} = \frac{(10.00) (0.4008 \text{ mg Ca/ml})}{(\text{ml EDTA required})}$$

C. Standardization of Mg-EDTA for Total Ca^{++} + Mg^{++} Analysis

Reagents.

- 1) Methyl Red (0.02 percent dissolved in ethanol).
- 2) Ammonium Hydroxide-Ammonium Chloride Buffer. Mix 570 ml of reagent grade NH_4OH and 67.5 gm of reagent grade NH_4Cl and dilute to 1 liter.
- 3) Eriochrome Black T Indicator (EBT). Add 0.4 gm of EBT to a mixture of 10 ml of 95 percent ethanol and 30 ml 2, 2', 2" nitrilotriethanol. The indicator should be stored under refrigeration when not in use.
- 4) Mg-EDTA Standard Solution. Mix 160 gm of the disodium salt of ethylenediaminetetraacetic acid and 40 gm of reagent grade $\text{MgCl}_2 \cdot 6\text{H}_2\text{O}$, dilute to 20 liters, and allow to stand at room temperature, with occasional stirring, for several days.

Equipment.

- 1) Glassware:
 - 1-50 ml automatic burette with automatic zero point
 - 1-10 ml pipette
 - 3-250 ml erlenmeyer flasks.

With the volumetric pipette, transfer 1-10 ml aliquot of the calcium ion standard into each of 3-250 ml erlenmeyer flasks. Adjust the total volume of solution to about 50 ml with distilled water. Add 1 drop of methyl red and then add $\text{NH}_4\text{OH}-\text{NH}_4\text{Cl}$ buffer solution dropwise until the solution just becomes basic (methyl red turns to yellow). Add an excess of 2 ml of the buffer (the titration must be carried out at a pH of about 9.5). Add 2 to 4 drops of EBT indicator, and titrate with Mg-EDTA until 1 drop turns the indicator from red to blue. The triplicate titrations should agree within 0.05 ml.

The Mg-EDTA titer is calculated as follows:

$$\text{Titer (mg Ca}^{++}\text{/ml)} = \frac{(10.00) (0.4008 \text{ mg Ca/ml})}{(\text{ml EDTA required})}$$

D. The Determination of Ca^{++} and Mg^{++} in Natural Carbonate Sediment Samples

Reagents.

- 1) 6N Hydrochloric Acid (see Appendix I, Part A)
- 2) Methyl Red Indicator (see Appendix I, Part B)
- 3) 2N Sodium Hydroxide (see Appendix I, Part B)
- 4) $\text{NH}_4\text{OH}-\text{NH}_4\text{Cl}$ Buffer (see Appendix I, Part C)
- 5) Calcium Red Indicator (see Appendix I, Part B)
- 6) EDTA Standard Solution (see Appendix I, Part B)
- 7) Eriochrome Black T Indicator (see Appendix I, Part C)
- 8) Mg-EDTA Standard Solution (see Appendix I, Part C)

Equipment.

1) Hot Plate.

2) Glassware:

1-20 ml pipette

2-50 ml automatic burettes.

Wash free of chlorides approximately 100 mg of the sample to be analyzed, and dry at 85°C overnight. Carefully weigh the sample and transfer to a 150 ml beaker. Add 20 ml of distilled water and several ml of 6N HCl. Boil carefully for 2 or 3 minutes and cool. Transfer the dissolved sample quantitatively to a 100 ml volumetric flask and bring to volume with distilled water. Mix thoroughly and withdraw 4-20 ml aliquots, transferring them into 4-250 ml erlenmeyer flasks. Two aliquots are for Ca^{++} analysis and 2 for Mg^{++} analysis. Reserve the remaining 20 ml in the volumetric flask in case of loss.

Calcium Determination. Add one drop of methyl red to each of the two solutions reserved for Ca^{++} analysis. Add 2N NaOH dropwise until the solution just becomes basic, and then add an excess of 15 ml NaOH. Adjust the volume of the solution with distilled water to about 50 ml. Add approximately 100 mg of the calcium red indicator with a spatula and titrate with EDTA until 1 drop turns the solution from red to blue. Duplicate analyses should agree within 0.05 ml. The calculations are as follows:

$$\text{Ca}^{++} \text{ (mg)} = (\text{ml EDTA required}) \left(\frac{100}{20} \right) (\text{EDTA titer}^{2/})$$

$$\text{CaCO}_3 \% = \frac{\text{Ca}^{++} \text{ (mg)}}{\text{Sample weight}} \times \frac{100.09}{40.08}$$

Magnesium Determination. The analysis of Mg^{++} in carbonate sediments is obtained by difference. The calcium present in the sample is subtracted from the total $\text{Ca}^{++} + \text{Mg}^{++}$ as determined by Eriochrome Black T and Mg-EDTA.

To the 2 remaining aliquots, add 1 drop of methyl red to each and $\text{NH}_4\text{OH}-\text{NH}_4\text{Cl}$ buffer until the solution just becomes basic. Add an excess of 2 ml of the buffer, and adjust the volume of solution in each flask to about 50 ml with distilled water. Add 2 to 4 drops of EBT indicator and titrate with Mg-EDTA until 1 drop turns the solution from red to blue. Duplicate analyses should agree within 0.05 ml.

The calculations are as follows:

$$\text{Mg}^{++} \text{ (mg)} = \left[(\text{ml Mg-EDTA required}) \left(\frac{100}{20} \right) (\text{Mg-EDTA titer}^{3/}) - \text{Ca}^{++} \text{ mg} \right] \frac{24.32}{40.08}$$

$$\text{MgCO}_3 \% = \frac{\text{Mg}^{++} \text{ (mg)}}{\text{Sample weight}} \times \frac{84.33}{24.32}$$

^{2/} See Appendix I, Part B

^{3/} See Appendix I, Part C

E. The Determination of the Chloride Ion in the Components of Synthetic Sea Water

Reagents.

- 1) Reagent Grade NaCl.
- 2) 0.05 M K_2CrO_4 Solution. Dissolve 1.0 gm of reagent grade K_2CrO_4 in 100 ml of distilled water.
- 3) 0.05 N $AgNO_3$ Standard Solution. Dissolve 8.5 gm of reagent grade $AgNO_3$ in distilled water and dilute to 1 liter. Store in a dark colored bottle away from light.

Equipment.

- 1) Glassware:

1-25 ml automatic burette
 1-5 ml micro-burette
 1 to 5 ml pipettes
 3-250 erlenmeyer flasks.

The $AgNO_3$ solution must be standardized before use. Weigh approximately 30 mg of NaCl accurately, and dissolve in 20 ml of distilled water. Add 1 ml of 0.05 M K_2CrO_4 as the indicator, and titrate with the $AgNO_3$ standard solution. The end point is reached when 1 drop of the $AgNO_3$ produces a red precipitate of Ag_2CrO_4 which persists. Repeat until triplicate analyses agree to within 0.05 ml. The $AgNO_3$ titer is then calculated as follows:

$$\frac{(\text{gm NaCl} \times 35.46 \times 1000)}{(\text{ml } AgNO_3 \times 58.45)} = \text{Cl } \% \text{ per ml } AgNO_3$$

To determine the chloride content of a solution, withdraw an aliquot of the unknown with a volumetric pipette calibrated to deliver 1 to 5 ml, depending on the amount of solution available, and dilute it to about 20 ml with distilled water. Add 1 ml of 0.05 M K_2CrO_4 indicator and titrate with the $AgNO_3$ standard solution until a single drop produces a red precipitate that persists. For the chloride determination of $MgCl_2$, use the 5 ml micro-burette; for the others, use the 25 ml automatic burette. The chloride content of the solution is calculated as follows:

$$\frac{\text{ml } AgNO_3}{\text{ml aliquot}} \times AgNO_3 \text{ titer} = Cl \%$$

F. The Determination of Dissolved Amounts of Ca^{++} and Mg^{++} in Various Solutions

Reagents.

- 1) 6N Hydrochloric Acid (see Appendix I, Part A)
- 2) Methyl Red Indicator (see Appendix I, Part B)
- 3) 2N Sodium Hydroxide (see Appendix I, Part B)
- 4) NH_4OH-NH_4Cl Buffer (see Appendix I, Part C)
- 5) Calcium Red Indicator (see Appendix I, Part B)
- 6) EDTA Standard Solution (see Appendix I, Part B)
- 7) Eriochrome Black T Indicator (see Appendix I, Part C)
- 8) Mg-EDTA Standard Solution (see Appendix I, Part C)
- 9) Reagent Grade NaCl
- 10) 0.05 M K_2CrO_4 Solution (see Appendix I, Part E)
- 11) 0.5N $AgNO_3$ Standard Solution (see Appendix I, Part E).

Equipment.

1) Hot Plate.

2) Glassware:

2-50 ml automatic burettes

1-25 ml automatic burette

1-5 ml micro-burette

400 ml beakers

long stem funnels

various sizes of volumetric pipettes.

Filter each natural carbonate suspension through #42 Whatman filter paper into a clean dry flask. Do not wash. Withdraw 4 equal aliquots from the flask so that at least a few ml of the solution remain, and transfer to 4 erlenmeyer flasks. Dilute the 4 aliquots to about 50 ml each with distilled water, add 2 ml of 6N HCl to each, and boil for 2 or 3 minutes. Two of the aliquots are reserved for Ca^{++} analysis, and 2 for Mg^{++} analysis.

Calcium Determination. To the 2 solutions reserved for Ca^{++} analysis, add 1 drop of methyl red. Add 2N NaOH dropwise until the solution just becomes basic, and then add 15 ml NaOH in excess. Adjust the volume of the solution to about 50 ml with distilled water. Add approximately 100 mg of the calcium red indicator from red to blue. Duplicate analyses should agree within 0.05 ml.

Magnesium Determination. The analysis of Mg^{++} in the carbonate sediments is done by difference. The calcium present in the sample is subtracted from the total $Ca^{++} + Mg^{++}$ as determined by Eriochrome Black T and Mg-EDTA.

To the 2 remaining aliquots, add 1 drop of methyl red to each and add NH_4OH-NH_4Cl buffer until the solution just becomes basic. Then add an excess of 2 ml of the buffer. Adjust the volume of solution in each flask to about 50 ml with distilled water, and add 2 to 4 drops of EBT indicator. Titrate with Mg-EDTA until 1 drop turns the indicator from red to blue. Duplicate analyses should agree within 0.05 ml.

The calculations for the sediment samples in distilled water, NaCl, and $NaHCO_3$ are as follows:

$$\text{Dissolved } Ca^{++} \left(\frac{mg}{L} \right) = \frac{(\text{ml Mg-EDTA required})}{(\text{ml aliquot})} (\text{EDTA titer}^{\frac{4}{}}) (1000)$$

$$\begin{aligned} \text{Dissolved } Mg^{++} \left(\frac{mg}{L} \right) &= \left[\frac{(\text{ml Mg-EDTA required})}{(\text{ml aliquot})} (\text{Mg EDTA titer}^{\frac{5}{}}) (1000) \right. \\ &\quad \left. - \text{Dissolved } Ca^{++} \left(\frac{mg}{L} \right) \right] \frac{24.32}{40.08} \end{aligned}$$

⁴/See Appendix I, Part B

⁵/See Appendix I, Part C

Chloride Determination. Since several of the synthetic solutions used contain Mg^{++} , any evaporation of the liquid medium will result in concentration of Mg^{++} . By determining the Mg^{++} and Cl^- contents of the original synthetic solution, and the Cl^- content at the end of the experiment, the Mg^{++} content of the solution at the end of the experiment is calculated.

From the remainder of the filtered solution, after aliquots for Ca^{++} and Mg^{++} analysis have been taken, a suitable aliquot is withdrawn with a pipette and placed in an erlenmeyer flask. Dilute to about 20 ml with distilled water, and add 1 ml of 0.05 M K_2CrO_4 indicator. Titrate with AgNO_3 standard solution until a single drop produces a red precipitate that persists. Use the 5 ml micro-burette for MgCl_2 solutions, and the 25 ml automatic burette for the others.

The calculations for the dissolved amounts of Ca^{++} and Mg^{++} in MgCl_2 and $\text{NaCl} + \text{MgCl}_2$ are as follows:

$$\text{Dissolved } \text{Ca}^{++} \left(\frac{\text{mg}}{\text{L}} \right) = \frac{(\text{ml EDTA required})}{(\text{ml required})} (\text{EDTA titer}^{6/}) (1000)$$

^{6/}See Appendix I, Part B

$$\text{Dissolved Mg}^{++} \left(\frac{\text{mg}}{\text{L}} \right) = \left[\frac{(\text{ml Mg-EDTA required})}{(\text{ml aliquot})} (\text{Mg EDTA titer}^{7/}) (1000) \right]$$

$$= \left[\text{Dissolved Ca}^{++} \left(\frac{\text{mg}}{\text{L}} \right) \right] \frac{24.32}{40.08} - \left(\frac{\text{Concentration factor}^{8/}}{\text{Mg concentration of original solution}^{9/}} \right)$$

^{7/} See Appendix I, Part C

$$\text{Concentration factor}^{8/} = \frac{(\text{ml AgNO}_3) (\text{AgNO}_3 \text{ titer}) (1000)}{(\text{Cl}^- \text{ concentration of original solution in } \%)}$$

$$\begin{aligned} \text{Mg}^{++} \text{ concentration of original solution} \left(\frac{\text{mg}}{\text{L}} \right) &= \left[\frac{(\text{ml Mg-EDTA})}{(\text{ml aliquot})} (\text{Mg-EDTA titer}) (1000) \right. \\ &\quad \left. - \left(\frac{\text{ml EDTA}}{\text{ml aliquot}} \right) (\text{EDTA titer}) (1000) \right] \frac{24.32}{40.08} \end{aligned}$$

A P P E N D I X I I

TABLE 1. Quantities of Calcium and Magnesium Dissolved in 0.0023 M NaHCO₃

Sample	Ca ⁺⁺ + Mg ⁺⁺		Ca ⁺⁺ ml**	Solubility		Solubility	
	ml*			mg Ca/L	mM Ca/L	mg Mg/L	mM Mg/L
1	0.64		0.09	6.88	0.17	14.0	0.57
2-18 X	0.08		0.14	6.02	0.15	0.00	0.00
2-18	0.39		0.16	6.88	0.17	6.92	0.28
2-35 X	0.13		0.18	7.74	0.20	0.00	0.00
2-35	0.31		0.13	5.59	0.15	5.40	0.22
2-60 X	0.12		0.16	6.88	0.17	0.00	0.00
2-60	0.31		0.09	3.87	0.10	6.43	0.26
3	0.25		0.15	6.45	0.16	3.16	0.00
4-8	0.53		0.15	6.45	0.16	11.1	0.45
4-18 X	0.04		0.12	5.16	0.13	0.00	0.00
4-18	0.55		0.14	6.02	0.15	12.0	0.49
4-35 X	0.00		0.16	6.88	0.17	0.00	0.00
4-35	0.47		0.11	4.73	0.12	10.5	0.43
4-60 X	0.00		0.20	8.60	0.21	0.00	0.00
4-60	0.41		0.14	6.02	0.15	8.01	0.33
4-120 X	0.07		0.19	8.17	0.20	0.00	0.00
4-120	0.21		0.13	5.59	0.14	2.55	0.10
4-230	0.66		0.13	5.59	0.14	15.6	0.64
5	0.00		0.19	8.17	0.20	0.00	0.00
6F	0.00		0.12	5.16	0.15	0.00	0.00
6W	0.00		0.14	6.02	0.13	0.00	0.00
7	0.06		0.17	7.31	0.18	0.00	0.00
13-1/2	0.61		0.30	12.9	0.32	9.47	0.39
13-3/8	0.63		0.17	7.31	0.18	13.5	0.55
13-1/4	0.75		0.18	7.74	0.19	16.6	0.68
13-8	0.62		0.17	7.31	0.18	13.2	0.54
13-10 X	0.41		0.29	12.5	0.31	4.07	0.16
13-18 X	0.32		0.22	9.46	0.24	3.34	0.13

*titer = 0.468; aliquot = 10 ml

**titer = 0.430; aliquot = 10 ml

TABLE 2. Quantities of Calcium and Magnesium Dissolved in Distilled Water

Sample	Ca ⁺⁺ + Mg ⁺⁺		Ca ⁺⁺		Titer	Solubility		Solubility	
	ml*	Aliquot ml	ml	Aliquot ml		mg Ca/L	mM Ca/L	mg Mg/L	mM Mg/L
1	1.07	10	0.34	10	0.430	14.6	0.36	21.5	0.88
2-18 X	1.00	15	1.00	15	0.439	29.3	0.73	1.15	0.04
2-18	0.84	10	0.46	10	0.430	19.8	0.48	11.8	0.48
2-35 X	0.97	15	0.95	15	0.439	27.8	0.69	1.52	0.06
2-35	0.96	10	0.48	10	0.430	20.6	0.51	14.8	0.61
2-60 X	1.04	15	1.00	15	0.439	29.3	0.73	1.88	0.07
2-60	0.96	10	0.51	10	0.430	21.9	0.55	14.0	0.57
2-120 X	0.76	10	0.71	10	0.430	30.5	0.76	3.10	0.12
3	0.51	10	0.48	10	0.430	20.6	0.51	2.00	0.00
4-8	0.98	10	0.51	10	0.430	21.9	0.55	14.6	0.60
4-18 X	1.02	15	0.85	15	0.439	24.9	0.62	4.19	0.17
4-18	1.06	10	0.47	10	0.430	20.2	0.50	17.8	0.73
4-35 X	0.97	15	0.91	15	0.439	26.6	0.66	2.61	0.11
4-35	1.88	10	0.53	10	0.430	22.8	0.54	39.6	1.63
4-60 X	0.92	15	0.91	15	0.439	26.6	0.69	2.71	0.11
4-60	1.84	10	0.54	10	0.430	23.2	0.57	38.2	1.57
4-120 X	1.13	15	0.92	15	0.439	26.9	0.67	5.10	0.21
4-120	0.77	10	0.59	10	0.430	25.4	0.63	6.43	0.26
4-230 X	1.02	15	0.92	15	0.439	26.9	0.67	2.97	0.12
4-230	1.01	10	0.39	10	0.430	16.8	0.42	18.5	0.76
5	0.00	10	0.30	10	0.430	12.9	0.32	0.00	0.00
6F	0.00	10	0.40	10	0.430	17.2	0.42	0.00	0.00
6W	0.20	10	0.47	10	0.430	20.2	0.50	0.00	0.00
7	0.20	10	0.37	10	0.430	15.9	0.40	0.00	0.00
13-1/2	1.30	10	0.48	10	0.430	20.6	0.51	24.4	1.00
13-3/8	1.18	10	0.53	10	0.430	22.8	0.57	13.6	0.56
13-1/4	1.51	10	0.58	10	0.430	24.9	0.62	27.8	1.15
13-8	1.24	10	0.51	10	0.430	21.9	0.55	21.9	0.90
13-10 X	1.00	10	0.70	10	0.430	30.1	0.75	10.1	0.41
13-10	1.86	10	0.21	10	0.430	9.0	0.23	47.3	1.92
13-18 X	1.21	15	0.87	15	0.439	25.5	0.64	7.47	0.30
13-18	1.91	10	0.22	10	0.430	9.5	0.24	48.5	1.99

*titer = 0.468

TABLE 3. Quantities of Calcium and Magnesium Dissolved in 0.405 M NaCl

Sample	Ca ⁺⁺ + Mg ⁺⁺		Ca ⁺⁺		Solubility		Solubility	
	ml*	Aliquot	ml**	Aliquot	mg Ca/L	mM Ca/L	mg Mg/L	mM Mg/L
1	2.49	15	1.35	15	62.5	0.93	24.5	1.1
2-18 X	2.09	15	2.30	15	63.6	1.58	0.97	0.03
2-18	2.56	15	2.13	15	58.9	1.45	12.7	0.52
2-35 X	2.15	15	2.20	15	60.9	1.58	3.76	0.15
2-35	2.28	15	1.49	15	41.2	1.02	18.1	0.74
2-60 X	2.14	15	2.16	15	59.8	1.49	4.67	0.19
2-60	2.24	15	1.57	15	43.4	1.08	16.1	0.66
2-120 X	2.19	15	2.15	15	59.5	1.49	5.34	0.22
3	1.67	15	1.30	15	36.0	0.90	9.77	0.00
4-8	2.35	15	1.34	15	37.1	0.92	22.0	0.90
4-18 X	2.21	15	2.39	15	66.1	1.62	1.76	0.09
4-18	2.39	15	1.16	15	32.1	0.80	25.8	1.06
4-35 X	2.15	15	2.27	15	62.7	1.62	2.67	0.06
4-35	2.32	15	1.30	15	36.0	0.90	22.1	0.90
4-60 X	1.43	10	3.01	20	62.5	1.56	2.67	0.06
4-60	2.27	15	1.56	15	43.2	1.02	16.8	0.69
4-120 X	1.56	10	3.01	20	62.5	1.56	6.37	0.26
4-120	2.22	15	1.52	15	42.1	1.05	16.5	0.68
4-230 X	2.28	15	2.45	15	67.8	1.69	2.00	0.08
4-230	2.52	15	1.80	15	49.8	1.24	17.5	0.72
5	1.12	15	0.94	15	26.0	0.65	5.40	0.00
6F	1.16	15	1.08	15	29.9	0.75	3.82	0.00
6W	1.32	15	1.24	15	34.3	0.85	4.19	0.00
7	1.67	15	1.55	15	42.9	1.07	5.58	0.00
13-1/2	2.86	15	1.43	15	39.6	0.99	30.1	1.24
13-3/8	2.73	15	1.41	15	39.0	0.98	28.0	1.15
13-1/4	2.73	15	1.35	15	37.4	0.94	29.0	1.19
13-8	2.80	15	1.34	15	37.1	0.88	30.5	1.25
13-10 X	2.41	15	2.10	15	58.1	1.45	10.4	0.43
13-10	3.33	15	1.11	15	30.7	0.76	44.4	1.83
13-18 X	2.23	15	1.44	15	39.8	1.00	18.1	0.75
13-18	3.25	15	1.15	15	31.8	0.80	42.2	1.74

*titer = 0.468

**titer = 0.415

TABLE 4. Quantities of Calcium and Magnesium Dissolved in 0.052 M MgCl_2

Sample	Ca ⁺⁺ + Mg ⁺⁺		Ca ⁺⁺ ml**	Solubility		Chloride ml***	Solubility	
	ml*			mg Ca/L	mM Ca/L		mg Mg/L	mM Mg/L
1	49.25		0.82	71	1.77	2.36	0.00	0.00
2-18 X	46.73		1.07	92	2.30	2.21	0.00	0.00
2-18	46.42		0.79	68	1.69	2.20	0.00	0.00
2-35 X	46.78		1.10	95	2.37	2.21	0.00	0.00
2-35	44.32		0.90	77	1.92	2.08	0.00	0.00
2-60 X	48.94		1.04	89	2.22	2.39	0.00	0.00
2-60	49.91		0.70	60	1.50	2.39	0.00	0.00
3	45.31		0.59	51	1.27	2.11	0.00	0.00
4-8	46.06		0.83	71	1.77	2.26	0.00	0.00
4-18 X	45.71		1.10	95	2.37	2.18	0.00	0.00
4-18	47.42		0.83	71	1.77	2.19	0.00	0.00
4-35 X	47.10		1.07	92	2.29	2.21	0.00	0.00
4-35	46.01		0.94	81	2.02	2.17	0.00	0.00
4-60 X	46.81		0.99	85	2.12	2.21	0.00	0.00
4-60	45.51		0.90	77	1.92	2.15	0.00	0.00
4-120 X	45.67		1.18	101	2.47	2.20	0.00	0.00
4-120	49.58		1.30	112	2.79	2.42	0.00	0.00
4-230 X	54.20		1.22	105	2.62	2.55	0.00	0.00
4-230	49.70		1.08	93	2.32	2.37	0.00	0.00
5	44.68		0.55	47	1.17	2.18	0.00	0.00
6F	43.70		0.67	58	1.45	2.12	0.00	0.00
6W	44.67		0.61	53	1.32	2.21	0.00	0.00
7	44.71		0.68	59	1.47	2.16	0.00	0.00
13-1/2	44.80		0.82	71	1.77	2.17	0.00	0.00
13-3/8	42.28		0.88	76	1.90	2.04	0.00	0.00
13-1/4	43.41		1.10	95	2.40	2.16	0.00	0.00
13-8	43.15		0.85	73	1.82	2.08	0.00	0.00
13-10 X	43.20		0.86	74	1.85	2.08	0.00	0.00
13-10	46.85		1.01	87	2.17	2.21	0.00	0.00
13-18 X	45.92		1.02	88	2.20	2.16	0.00	0.00
13-18	45.92		0.93	80	2.00	2.20	0.00	0.00

*titer = 0.468; aliquot = 10 ml

**titer = 0.430; aliquot = 5 ml

***titer = 1.76

TABLE 5. Quantities of Calcium and Magnesium Dissolved in 0.405 M NaCl
+ 0.052 M MgCl_2

Sample	$\text{Ca}^{++} + \text{Mg}^{++}$		Ca^{++} ml**	Aliquot	Solubility		Chloride ml***	Solubility	
	ml*				mg Ca/L	mM Ca/L		mg Mg/L	mM Mg/L
1	45.04		1.24	5	107	2.67	18.55	0.00	0.00
2-18 X	43.10		1.34	5	115	2.86	17.65	0.00	0.00
2-18	42.25		1.12	5	96.3	2.40	17.65	0.00	0.00
2-35 X	43.50		1.40	5	120	3.00	17.75	0.00	0.00
2-35	44.67		1.17	5	101	2.52	18.72	0.00	0.00
2-60 X	43.90		1.45	5	125	3.11	18.10	0.00	0.00
2-60	42.43		1.16	5	99.8	2.50	17.40	0.00	0.00
3	42.44		0.94	5	80.8	2.20	17.90	0.00	0.00
4-8	45.27		1.16	5	98.8	2.47	18.80	0.00	0.00
4-18 X	44.32		1.11	5	95.5	2.40	17.95	0.00	0.00
4-18	46.68		1.42	5	122	3.04	19.11	0.00	0.00
4-35 X	43.64		1.20	5	103	2.56	17.55	0.00	0.00
4-35	43.75		1.25	5	108	2.69	18.12	0.00	0.00
4-60 X	43.34		1.51	5	130	3.24	17.93	0.00	0.00
4-60	42.15		1.19	5	102	2.54	17.48	0.00	0.00
4-120 X	47.56		1.20	4	129	3.22	19.55	0.00	0.00
4-120	44.12		1.30	5	112	2.79	18.32	0.00	0.00
4-230 X	45.25		1.48	5	127	3.17	18.50	0.00	0.00
4-230	45.30		1.19	5	102	2.79	18.65	0.00	0.00
5	40.60		0.86	5	74.0	1.85	17.10	0.00	0.00
6F	43.52		1.22	5	105	2.62	17.80	0.00	0.00
6W	43.58		0.86	5	74.0	1.85	18.15	0.00	0.00
7	42.28		0.88	5	75.7	1.90	Lost	0.00	0.00
13-1/2	45.50		1.32	5	114	2.84	18.30	0.00	0.00
13-3/8	42.81		1.35	5	116	2.89	17.70	0.00	0.00
13-1/4	43.15		1.55	5	133	3.32	17.40	0.00	0.00
13-8	45.80		1.38	5	117	2.91	18.05	0.00	0.00
13-10 X	43.00		1.32	5	114	2.84	17.75	0.00	0.00
13-10	42.18		1.39	5	120	3.00	17.30	0.00	0.00
13-18 X	44.20		1.29	5	111	2.77	18.00	0.00	0.00
13-18	43.75		1.31	5	113	2.82	17.95	0.00	0.00

*titer = 0.468; aliquot = 10 ml

**titer = 0.430

***titer = 1.84

TABLE 6. The Carbonate Ion Concentration, $[Ca^{++}]$ $[CO_3^{--}]$ and $[Mg^{++}]$ $[CO_3^{--}]$ Ion Products Resulting from the Solution of Sediment Samples in $NaHCO_3$ and Distilled Water

Sample	$NaHCO_3$			H_2O		
	$CO_3^{--} \times 10^{-6}$ M/L	Ion Product $\times 10^{-10}$ M/L		$CO_3^{--} \times 10^{-5}$ M/L	Ion Product $\times 10^{-10}$ M/L	
		$CaCO_3$	$MgCO_3$		$CaCO_3$	$MgCO_3$
1	8.70	15.0	50.1	1.60	58.4	141
2-18	5.31	9.13	15.1	1.23	60.9	59.7
2-35	3.77	5.28	8.37	1.33	68.5	81.0
2-60	3.76	3.65	9.93	1.30	71.2	74.9
3	1.68	2.70	0.00	0.373	19.2	00.0
4-8	5.51	8.87	25.1	1.34	73.4	80.4
4-18	8.26	12.5	40.7	1.24	62.6	90.8
4-35	6.55	7.73	28.3	ND	ND	ND
4-60	5.45	8.23	17.9	ND	ND	ND
5	2.62	5.34	0.00	0.367	11.9	00.0
6F	1.54	2.33	0.00	0.352	15.1	00.0
6W	1.47	1.90	0.00	0.459	23.2	00.0
7	1.87	3.42	0.00	0.349	13.9	00.0
13-1/2	8.67	2.79	33.7	1.90	97.9	190
13-3/8	9.23	16.9	51.2	1.45	82.7	81.1
13-1/4	11.0	21.3	75.1	2.15	114	245
13-8	7.56	13.8	41.1	1.81	99.2	163
2-18 X	1.79	2.69	0.00	0.895	65.3	3.6
2-35 X	1.89	3.65	0.00	0.872	60.2	5.2
2-60 X	1.41	2.43	0.00	0.976	71.2	6.8
4-18 X	1.61	2.08	0.00	0.879	54.4	14.9
4-35 X	2.15	3.70	0.00	0.875	57.8	9.6
4-60 X	2.50	5.38	0.00	0.930	64.2	10.2
4-230 X	ND	ND	ND	1.04	69.7	12.5
13-10 X	ND	ND	ND	1.37	103	56.2
13-18 X	ND	ND	ND	1.15	73.6	34.5

TABLE 7. The Carbonate Ion Concentration, $[Ca^{++}]$ $[CO_3^{--}]$ and $[Mg^{++}]$ $[CO_3^{--}]$ Ion Products Resulting from the Solution of Sediment Samples in NaCl, $MgCl_2$ and NaCl + $MgCl_2$

Sample	NaCl			$MgCl_2$			NaCl + $MgCl_2$		
	Ion Product			Ion Product			Ion Product		
	$CO_3^{--} \times 10^{-5}$ M/L	$CaCO_3 \times 10^{-10}$ M/L	$MgCO_3$	$CO_3^{--} \times 10^{-5}$ M/L	$CaCO_3 \times 10^{-10}$ M/L	$CaCO_3$	$CO_3^{--} \times 10^{-5}$ M/L	$CaCO_3 \times 10^{-10}$ M/L	$CaCO_3$
1	2.55	238	258	1.74	308	308	2.03	544	544
2-18	2.36	345	123	1.49	253	253	2.11	506	506
2-35	2.16	222	161	1.60	307	307	2.21	557	557
2-60	2.07	224	137	1.36	204	204	2.04	508	508
3	0.96	86	000	1.30	165	165	1.58	319	319
4-8	2.35	218	213	1.77	313	313	1.96	484	484
4-18	2.45	196	260	1.61	285	285	2.49	757	757
4-35	2.32	208	211	1.84	372	372	2.20	592	592
4-60	2.06	222	142	1.85	355	355	2.12	538	538
5	0.76	49	000	1.33	156	156	1.52	281	281
6F	0.96	71	000	1.42	206	206	1.40	259	259
6W	0.95	81	000	1.29	170	170	1.98	519	519
7	0.12	124	000	1.47	216	216	1.41	266	266
13-1/2	2.93	289	363	1.77	313	313	2.22	630	630
13-3/8	2.72	265	313	1.86	353	353	2.29	662	662
13-1/4	2.72	254	324	2.16	512	512	2.63	873	873
13-8	3.03	281	379	1.82	331	331	2.39	698	698
2-18 X	2.06	325	6.2	2.67	614	614	2.92	835	835
2-35 X	2.06	325	30.9	2.63	623	623	3.06	918	918
2-60 X	2.05	305	39.0	2.52	559	559	3.17	986	986
4-18 X	2.09	339	18.8	2.76	654	654	2.50	600	600
4-35 X	2.00	324	12.0	2.66	609	609	2.67	684	684
4-60 X	1.98	309	11.9	2.52	534	534	3.45	1120	1120
4-230 X	2.21	373	17.7	3.20	838	838	3.45	1090	1090
13-10 X	2.54	368	109	1.89	350	350	2.96	841	841
13-18 X	2.30	230	173	2.00	440	440	2.83	784	784

A P P E N D I X I I I

TABLE 1. pH Values of Sediments Dissolving in 0.0023 M NaHCO_3 *

Sample	Minutes										10th week	Final
	1	2	5	7	10	15	1st week	2nd week	3rd week	4th week		
1							9.01	8.69	8.68	8.68	8.68	8.38
2-18 X							8.13	8.60	8.58	8.60	8.61	8.38
2-18							8.89	8.69	8.63	8.63	8.62	8.38
2-35 X							8.21	8.61	8.59	8.60	8.60	8.30
2-35							8.89	8.68	8.62	8.64	8.61	8.33
2-60 X							8.22	8.59	8.59	8.61	8.61	8.22
2-60							8.90	8.70	8.62	8.63	8.60	8.33
3							8.89	8.69	8.62	8.61	8.61	8.33
4-8							8.90	8.72	8.68	8.67	8.65	8.26
4-18 X	8.12	8.24	8.28	8.32	8.39		8.47	8.69	8.58	8.60	8.59	8.41
4-18	8.94	8.98	9.01	9.01	9.01			8.72	8.67	8.66	8.64	8.42
4-35 X	8.12	8.18	8.27	8.31	8.39	8.45		8.68	8.61	8.58	8.58	8.41
4-35	8.92	8.97	8.99	9.00	9.00			8.71	8.65	8.62	8.66	8.39
4-60 X	8.10	8.13	8.22	8.30	8.37	8.47		8.62	8.59	8.60	8.59	8.38
4-60	8.93	8.97	8.99	9.00	9.01			8.70	8.67	8.63	8.63	8.37
4-120 X	8.10	8.13	8.37	8.45	8.60			8.70	8.59	8.59	8.59	8.32
4-120	8.91	8.95	8.99	8.99	9.00			8.70	8.61	8.61	8.62	8.38
4-230	8.99	9.04	9.08	9.09	9.10			8.74	8.70	8.68	8.69	8.41
5												
6F							8.83	8.71	8.67	8.65	8.65	8.42
6W							8.79	8.70	8.61	8.62	8.61	8.32
7							8.78	8.69	8.62	8.60	8.60	8.37
13-1/2							8.79	8.70	8.61	8.61	8.60	8.32
13-3/8							9.01	8.67	8.65	8.66	8.63	8.40
13-1/4							9.01	8.71	8.67	8.68	8.67	8.41
13-8							8.99	8.72	8.68	8.67	8.63	8.41
13-10 X							8.99	8.72	8.67	8.67	8.65	8.32
13-18 X							8.22	8.63	8.58	8.58	8.62	8.40
							8.20	8.62	8.59	8.59	8.61	8.38

*pH at time = 0 is 8.05 $\pm$ 0.05

TABLE 2. pH Values of Sediments Dissolving in Distilled Water*

Sample	Minutes							15	1st week	2nd week	3rd week	4th week	10th week	Final
	1	2	5	7	10	15	10th week							
1														
2-18 X	5.10	5.20	5.45	5.68	5.91	6.22	8.43	8.50	8.43	8.29	8.43	8.50	8.41	8.41
2-18	9.30	9.32	9.32	9.32	9.30	9.28	8.14	8.39	8.30	8.29	8.30	8.38	8.38	8.38
2-35 X	5.22	5.48	5.97	6.18	6.41	6.70	8.35	8.42	8.32	8.28	8.32	8.40	8.40	8.40
2-35	9.32	9.32	9.32	9.31	9.30	9.25	8.13	8.35	8.30	8.28	8.30	8.38	8.38	8.38
2-60 X	5.30	5.50	5.92	6.08	6.30	6.51	8.31	8.44	8.29	8.23	8.32	8.39	8.38	8.38
2-60	9.30	9.32	9.32	9.32	9.32	9.31	8.18	8.38	8.29	8.23	8.32	8.40	8.40	8.40
2-120 X	5.78	6.06	6.31	6.44	6.63	6.79	8.36	8.41	8.32	8.32	8.33	8.40	8.37	8.37
3							8.12	8.40	8.30	8.30	8.31	8.43	8.30	8.30
4-8							8.32	8.42	8.32	8.32	8.32	8.37	8.17	8.17
4-18 X		6.03	6.48	6.70	6.99	7.51	8.40	8.49	8.42	8.42	8.42	8.50	8.37	8.37
4-18	9.48	9.50	9.53	9.52	9.53	9.48	8.09	8.34	8.23	8.23	8.21	8.36	8.36	8.36
4-35 X		5.97	6.17	6.37	6.61	6.99	8.40	8.42	8.42	8.42	8.39	8.48	8.30	8.30
4-35	9.43	9.50	9.50	9.51	9.52	9.47	8.16	8.39	8.24	8.24	8.26	8.37	8.37	8.37
4-60 X		5.78	6.10	6.28	6.55	6.97	8.38	8.42	8.40	8.40	8.40	8.44	8.39	8.39
4-60	9.40	9.44	9.48	9.48	9.47	9.31	8.09	8.34	8.22	8.22	8.24	8.38	8.38	8.38
4-120 X	5.24	5.62	6.20	6.40	6.72	7.13	8.20	8.43	8.39	8.31	8.39	8.43	8.36	8.36
4-120	9.40	9.42	9.45	9.46	9.46	9.31	8.39	8.41	8.38	8.31	8.30	8.40	8.40	8.40
4-230 X	5.98	6.17	6.83	7.38	8.27	8.70	8.30	8.41	8.31	8.31	8.32	8.43	8.43	8.43
4-230	9.50	9.52	9.55	9.55	9.54	9.31	8.44	8.50	8.47	8.47	8.43	8.51	8.44	8.44
5							8.31	8.42	8.35	8.35	8.38	8.42	8.37	8.37
6F							8.32	8.38	8.36	8.36	8.32	8.40	8.22	8.22
6W							8.32	8.38	8.32	8.32	8.32	8.37	8.27	8.27
7							8.30	8.38	8.33	8.33	8.32	8.38	8.25	8.25
13-1/2							8.42	8.49	8.42	8.42	8.42	8.49	8.40	8.40
13-3/8							8.42	8.46	8.43	8.43	8.42	8.48	8.41	8.41
13-1/4							8.43	8.48	8.45	8.45	8.42	8.50	8.39	8.39
13-8							8.42	8.50	8.44	8.44	8.46	8.49	8.40	8.40
13-10 X	5.32	5.75	6.23	6.44	6.74	7.14	8.19	8.37	8.28	8.28	8.30	8.40	8.32	8.32
13-10	9.49	9.53	9.58	9.59	9.60	9.52	8.50	8.58	8.55	8.55	8.52	8.60	8.63	8.63
13-18 X	5.57	5.85	6.12	6.34	6.55	6.83	8.19	8.33	8.28	8.28	8.29	8.40	8.40	8.40
13-18	9.60	9.63	9.67	9.68	9.69	9.52	8.52	8.59	8.58	8.58	8.53	8.63	8.68	8.68

*pH at time = 0 is 5.10 $\pm$ 0.10

TABLE 3. pH Values of Sediments Dissolving in 0.405 M NaCl*

Sample	Minutes					15	1st week	2nd week	3rd week	4th week	Final
	1	2	5	7	10						
1											
2-18 X		6.15	6.40	6.52	6.80	9.68	8.41	8.42	8.42	8.38	8.43
2-18	9.60	9.67	9.69	9.69	9.69	7.45	8.25	8.37	8.34	8.31	8.42
2-35 X		6.50	6.85	7.10	7.82	8.45	8.38	8.38	8.38	8.33	8.39
2-35	9.63	9.66	9.66	9.66	9.65		8.29	8.32	8.32	8.30	8.39
2-60 X		6.38	6.73	7.03	7.75	8.46	8.38	8.39	8.38	8.34	8.40
2-60	9.58	9.62	9.62	9.61	9.61		8.30	8.38	8.36	8.31	8.40
2-120 X	6.40	6.60	7.13	8.20	8.63	8.89	8.39	8.39	8.38	8.34	8.39
3						9.59	8.31	8.33	8.34	8.29	8.33
4-8	9.63	9.66	9.68	9.68	9.65		8.32	8.33	8.40	8.37	8.42
4-18 X		6.39	6.76	7.12	8.12	8.61	8.41	8.37	8.37	8.32	8.42
4-18	9.67	9.70	9.70	9.70	9.69		8.27	8.41	8.40	8.38	8.43
4-35 X		6.23	6.38	6.82	7.71	8.50	8.27	8.32	8.36	8.31	8.39
4-35	9.65	9.69	9.70	9.70	9.70		8.39	8.40	8.40	8.38	8.42
4-60 X		6.31	6.60	6.88	7.48	8.40	8.28	8.33	8.37	8.32	8.40
4-60	9.63	9.68	9.70	9.70	9.70		8.39	8.39	8.39	8.31	8.38
4-120 X	6.22	6.57	6.81	7.40	8.41		8.31	8.36	8.38	8.32	8.39
4-120	9.61	9.67	9.69	9.70	9.69		8.40	8.39	8.39	8.33	8.40
4-230 X		7.00	8.47	8.77	8.95	9.10	8.32	8.39	8.40	8.35	8.41
4-230	9.60	9.63	9.65	9.66	9.64	9.63	8.40	8.41	8.42	8.38	8.42
5	9.56	9.58	9.59	9.59	9.58		8.38	8.34	8.34	8.31	8.38
6F						9.51	8.31	8.35	8.33	8.29	8.32
6W						9.51	8.30	8.33	8.32	8.29	8.36
7						9.51	8.32	8.37	8.32	8.28	8.35
13-1/2						9.69	8.43	8.44	8.43	8.39	8.43
13-3/8						9.69	8.40	8.43	8.42	8.39	8.42
13-1/4						9.68	8.40	8.43	8.40	8.37	8.42
13-8						9.69	8.43	8.48	8.42	8.39	8.46
13-10 X		6.33	6.61	6.75	7.10		8.43	8.48	8.42	8.39	8.46
13-10	9.68	9.70	9.72	9.71	9.71	8.08	8.30	8.39	8.39	8.33	8.44
13-18 X		6.42	6.80	7.12	7.90	8.48	8.50	8.50	8.50	8.46	8.51
13-18	9.71	9.75	9.77	9.77	9.77		8.30	8.39	8.38	8.32	8.43
13-18							8.49	8.51	8.46	8.46	8.52

*pH at time = 0 is 6.20 $\pm$ 0.10

TABLE 4. pH Values of Sediments Dissolving in 0.052 M MgCl₂*

Sample	Minutes					10	15	1st week	2nd week	3rd week	4th week	10th week	Final
	1	2	5	7									
1							9.40	8.40	8.38	8.32	8.32	8.38	8.30
2-18 X							8.00	8.20	8.25	8.28	8.28	8.30	8.35
2-18							9.44	8.32	8.34	8.32	8.31	8.31	8.25
2-35 X							8.44	8.19	8.23	8.28	8.24	8.30	8.36
2-35							9.44	8.33	8.38	8.32	8.31	8.31	8.23
2-60 X							8.27	8.20	8.28	8.28	8.23	8.30	8.37
2-60							9.47	8.34	8.33	8.33	8.29	8.32	8.27
3							9.49	8.39	8.32	8.31	8.31	8.36	8.32
4-8							9.43	8.40	8.36	8.31	8.30	8.38	8.31
4-18 X	5.86	6.11	6.66	6.99	7.60		8.25	8.14	8.24	8.29	8.30	8.37	8.38
4-18	9.29	9.31	9.34	9.35	9.35			8.36	9.39	8.38	8.36	8.40	8.27
4-35 X	5.95	6.22	7.00	7.77	8.24		8.72	8.21	8.28	8.30	8.30	8.36	8.38
4-35	9.30	9.32	9.36	9.36	9.36			8.36	8.39	8.38	8.36	8.38	8.39
4-60 X	6.05	6.38	7.33	8.10	8.55		8.80	8.22	8.29	8.30	8.30	8.38	8.29
4-60	9.30	9.35	9.36	9.36	9.36			8.36	8.37	8.38	8.36	8.40	8.29
4-120 X		6.23	6.31	6.55	7.41		8.05	8.23	8.30	8.30	8.30	8.35	8.39
4-120	9.31	9.36	9.38	9.38	9.38			8.38	8.39	8.39	8.38	8.40	8.24
4-230 X	6.80	7.98	8.82	8.98	9.01		9.09	8.28	8.29	8.31	8.31	8.38	8.40
4-230	9.35	9.39	9.39	9.39	9.39			8.37	8.38	8.39	8.38	8.40	8.25
5							9.43	8.39	8.37	8.32	8.32	8.39	8.37
6F							9.42	8.33	8.33	8.30	8.31	8.35	8.30
6W							9.45	8.34	8.32	8.29	8.31	8.33	8.30
7							9.44	8.32	8.33	8.30	8.31	8.33	8.31
13-1/2							8.31	8.40	8.38	8.33	8.32	8.39	8.31
13-3/8							9.40	8.38	8.37	8.35	8.31	8.39	8.30
13-1/4							9.40	8.40	8.36	8.32	8.31	8.39	8.27
13-8							9.39	8.38	8.38	8.32	8.30	8.39	8.31
13-10 X							8.30	8.13	8.20	8.22	8.22	8.28	8.32
13-10							9.37	8.38	8.38	8.36	8.34	8.31	8.33
13-18 X							8.01	8.09	8.18	8.22	8.22	8.28	8.27
13-18							9.37	8.40	8.39	8.37	8.35	8.32	8.20

*pH at time = 0 is 5.50 ± 0.05

TABLE 5. pH Values of Sediments Dissolving in 0.052 M MgCl_2 + 0.405 M NaCl *

Sample	1	2	Minutes			7	10	15	1st week	2nd week	3rd week	4th week	10th week	Final
1								9.44	8.38	8.32	8.32	8.32	8.37	8.19
2-18 X								7.47	8.28	8.22	8.21	8.28	8.31	8.32
2-18								9.40	8.38	8.34	8.30	8.31	8.32	8.25
2-35 X								7.90	8.28	8.24	8.22	8.28	8.31	8.32
2-35								9.42	8.38	8.34	8.30	8.30	8.32	8.25
2-60 X								7.70	8.30	8.21	8.22	8.29	8.32	8.32
2-60								9.42	8.39	8.33	8.33	8.30	8.32	8.22
3								9.52	8.35	8.31	8.29	8.30	8.31	8.20
4-8								9.48	8.39	8.36	8.33	8.31	8.37	8.21
4-18 X	6.22	6.40	6.90	7.40		7.40	8.06	8.49	8.22	8.24	8.22	8.26	8.30	8.33
4-18	9.39	9.42	9.45	9.46		9.46	9.46		8.39	8.36	8.31	8.34	8.32	8.22
4-35 X	6.21	6.41	7.01	7.77		7.77	8.45	8.70	8.22	8.24	8.21	8.26	8.30	8.33
4-35	9.38	9.42	9.43	9.45		9.45	9.45		8.40	8.35	8.30	8.32	8.32	8.22
4-60 X	6.28	6.50	7.72	8.19		8.19	8.58	8.84	8.27	8.27	8.23	8.24	8.30	8.34
4-60	9.39	9.42	9.43	9.46		9.46	9.47		8.40	8.37	8.31	8.33	8.33	8.23
4-120 X	6.28	6.61	8.30	8.62		8.62	8.83	8.99	8.30	8.28	8.25	8.26	8.30	8.33
4-120	9.37	9.41	9.44	9.45		9.45	9.46		8.40	8.37	8.31	8.33	8.34	8.26
4-230 X	7.02	8.30	8.90	9.01		9.01	9.10	9.18	8.30	8.30	8.27	8.29	8.32	8.35
4-230	9.43	9.47		9.49		9.49	9.49		8.41	8.38	8.32	8.37	8.37	8.24
5								9.48	8.33	8.31	8.30	8.31	8.36	8.22
6F								9.46	8.33	8.31	8.29	8.30	8.32	8.19
6W								9.48	8.33	8.31	8.30	8.31	8.36	8.19
7								9.47	8.32	8.31	8.29	8.29	8.32	8.18
13-1/2								9.47	8.38	8.36	8.32	8.33	8.38	8.20
13-3/8								9.45	8.40	8.37	8.32	8.31	8.38	8.21
13-1/4								9.44	8.38	8.37	8.33	8.32	8.37	8.21
13-8								9.42	8.40	8.37	8.34	8.34	8.38	8.22
13-10 X								7.65	8.21	8.22	8.20	8.26	8.30	8.33
13-10								9.34	8.41	8.38	8.32	8.35	8.36	8.22
13-18 X								7.65	8.15	8.20	8.20	8.26	8.32	8.32
13-18								9.49	8.42	8.36	8.33	8.37	8.35	8.22

*pH at time = 0 is 6.04⁺ -0.05

TABLE 6. pH Values of Sediments Dissolving in Sea Water*

Sample	Minutes					1st week	2nd week	3rd week	4th week	10th week	Final
	1	5	10	15							
1						8.01	8.01	8.01	8.00	7.99	7.88
2-18 X						8.00	8.12	8.14	8.19	8.12	8.21
2-18						7.95	7.97	7.97	7.97	7.93	7.88
2-35 X						8.01	8.18	8.17	8.18	8.10	8.14
2-35						7.97	7.98	7.99	7.94	7.94	7.88
2-60 X						7.99	8.19	8.14	8.18	8.14	8.13
2-60						7.99	7.99	7.96	7.98	7.95	7.89
3						7.98	7.95	7.93	7.91	7.90	7.82
4-8						7.98	7.99	8.00	7.99	7.94	7.87
4-18 X		8.05	8.06			8.06	8.18	8.13	8.17	8.20	
4-18	8.02	8.00	8.00			8.00	7.98	7.97	7.99	7.97	
4-35 X		8.05	8.06			8.07	8.18	8.14	8.14	8.20	
4-35	8.03	8.00	8.00			8.00	8.01	8.00	8.00	7.97	
4-60 X		8.05	8.05			8.05	8.18	8.13	8.19	8.20	
4-60	8.02	8.01	8.01			8.01	8.00	8.00	7.98	7.98	
4-120 X		8.05	8.06			8.05	8.15	8.17	8.18	8.20	
4-120	8.01	8.00	8.00			8.00	7.98	8.01	8.00	7.99	
4-230 X	8.09	8.09	8.09			8.09	8.14	8.18	8.16	8.20	
4-230	8.00	8.00	8.00			8.00	8.00	8.01	8.01	7.99	
5						7.76	7.91	8.91	7.89	7.88	7.77
6F						7.73	7.91	7.90	7.91	7.89	7.80
6W						7.83	7.91	7.90	7.91	7.89	7.80
7						7.79	7.91	7.90	7.91	7.89	7.81
13-1/2						8.01	8.05	8.07	8.05	8.01	7.94
13-3/8						8.10	8.07	8.06	8.05	8.20	7.91
13-1/4						8.00	8.04	8.04	8.03	8.00	7.90
13-8						8.01	8.02	8.03	8.03	8.00	7.92
13-10 X						8.01	8.17	8.13	8.19	8.18	8.11
13-10						7.99	8.01	8.03	8.03	8.00	7.91
13-18 X						8.01	8.18	8.16	8.19	8.19	8.04
13-18						8.05	8.01	8.03	8.02	7.98	7.92

*pH at time = 0 is 8.05 $\pm$ 0.04

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