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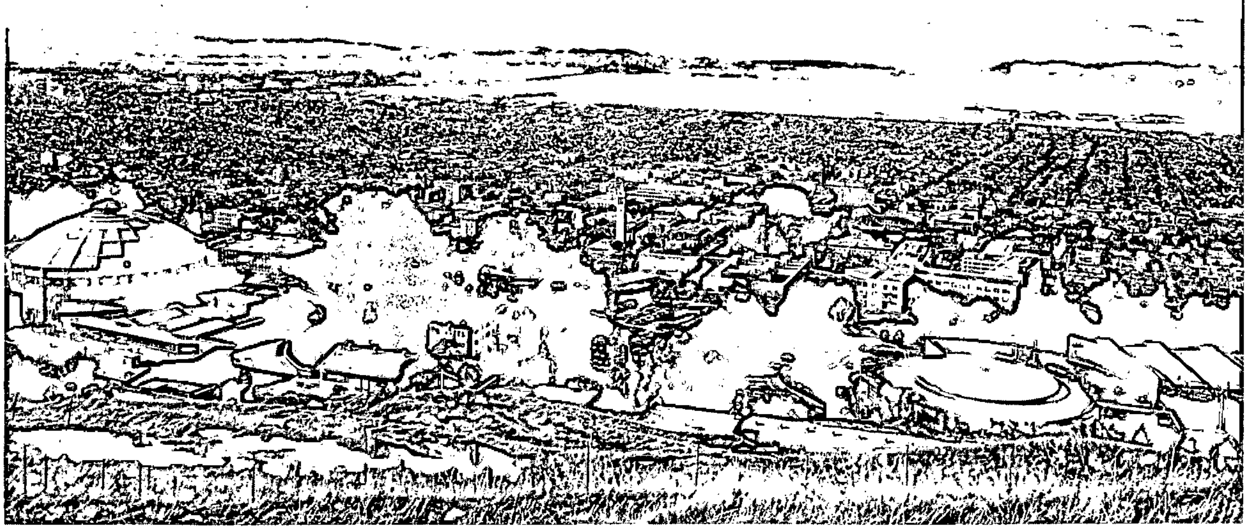

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THE INTERACTION OF MANGANESE(II) WITH THE SURFACE OF CALCITE IN DILUTE SOLUTIONS AND SEAWATER

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PREAMBLE

The interaction between Ocean Thermal Energy Conversion (OTEC) plants and the oceanic environment in which they will be operating must be considered both in terms of plant design and operation, and in regard to the potential impact of an operating plant on the marine environment. One area of concern is the release of metals from the plant, both inadvertently as corrosion products or directly through operations such as anti-fouling control. It is, therefore, important to acquire information on the probable behavior of potential metal pollutants in the area of an operating OTEC plant.

Manganese is among the most reactive and abundant transition metals in the marine environment. Much of its reactivity is derived from the fact that it is readily oxidized and reduced under conditions commonly found in marine waters and sediments. The formation of Mn(IV) oxides and oxyhydroxides is important for the removal of other less abundant transition metals, which are readily adsorbed on the oxide surfaces. It is probable that in an operating OTEC plant anoxic microenvironments will exist under normal operating conditions. Anoxic macroenvironments could also be created, if flow through the heat exchangers is interrupted. Mn(IV) will be reduced to (Mn(II) under such conditions and metal associated with the Mn(IV) oxides and oxyhydroxides released. If the Mn(II) is removed from solution before it can reach oxic conditions, this potential scavenger for metal pollutants, such as copper, will be lost.

There is increasing evidence that in many marine environments the Mn(II) concentration is controlled by interaction with carbonate mineral surfaces. This study was undertaken in order to quantify the extent and rate of this interaction.

ABSTRACT

The interaction of Mn^{2+} with the surface of calcite in aqueous solutions is complex. In dilute solutions the Mn^{2+} is rapidly adsorbed, $MnCO_3$ nucleates on the calcite surface and then grows by a first order reaction with respect to the initial Mn^{2+} concentration. At higher ionic strengths, in NaCl solutions, the rate of these processes is slower, but the same general pattern persists. In solutions containing Mg^{2+}, at the concentration of seawater and in seawater, the nucleation phase of the uptake process does not appear to occur. The long term uptake rate of Mn^{2+} on the surface of calcite in seawater is first order with respect to the dissolved Mn^{2+} concentration. The rate constant is over 3 orders of magnitude smaller than that found in dilute Mg^{2+}-free solutions. A probable explanation for the slower growth rate in seawater is that $MnCO_3$ is not nucleated on the calcite surface due to the presence of high Mg^{2+} concentrations. These, through site competition, prevent enough Mn^{2+} from being adsorbed to reach a critical concentration for $MnCO_3$ nucleation. This behavior is similar to that found for orthophosphate with calcite surfaces in dilute solutions and seawater.

Measurements of the solubility of rhodochrosite in seawater gave results from an undersaturation approach to equilibrium in excellent agreement with those found in previous studies in dilute solutions. When equilibrium was approached from supersaturation, approximately 50 times more calcium was precipitated than Mn^{2+}. The measured solubility was over twice that determined from undersaturation. It is possible that a Mn-calcite containing 25 to 30 mole percent $MnCO_3$ formed on the rhodochrosite from the supersaturated solutions. Consequently, it is doubtful that rhodochrosite controls the concentration of Mn^{2+} in calcium carbonate rich marine environments.

INTRODUCTION

Manganese is one of the most abundant and chemically reactive transition metals in sediments and soils. In oxic environments it is present primarily as Mn(IV) oxides and oxyhydroxides, which can form as colloidal suspensions, coatings on other minerals or as nodules. Mn(IV) oxides and oxyhydroxides are readily reduced to Mn^{2+} in anoxic waters, sediments and soils. The Mn^{2+} is often found to diffuse or be advected into oxic environments where it can be oxidized back to Mn^{4+}. Because the oxidation of Mn^{2+} is a relatively slow process (Wilson, 1980), Mn^{2+} can be found at concentrations higher than those predicted by equilibrium thermodynamic redox considerations.

Much of the interest in Mn^{2+} chemistry in natural waters has centered on its interaction with dissolved bicarbonate and carbonate ions, and carbonate minerals (e.g. Morgan, 1967). This is because Mn^{2+} forms strong ion pairs with these ions, coprecipitates with calcite, and rhodochrosite ($MnCO_3$) has a low solubility of $3(\underline{+}1) \times 10^{-11}$ (Sillen and Martel, 1964; Morgan, 1967; Robie <u>et</u> <u>al</u>., 1979). It has also been noted that in the reducing zone of many sediments Mn^{2+} is associated with calcium carbonate (e.g. Wangersky and Joensuu, 1964; Lynn and Bonatti, 1965; Calvert and Price, 1972; Robbins and Callender, 1975), and that it is strongly partitioned into calcite during carbonate diagenesis (Pingatore, 1978). Recently it has been demonstrated that rhodochrosite may play an important role in controlling the carbonate chemistry (Emerson et al., 1980) and the concentration of dissolved Mn^{2+} (Sayles, 1981) in certain deep sea sediments. Michard (1971) has also noted the importance of Mn^{2+} adsorption on calcium carbonate surfaces to the diffusive flux of Mn^{2+} from anoxic sediments.

Chemical studies of the interaction between Mn^{2+} and carbonates have been primarily focused on rhodochrosite solubility, the coprecipitation of Mn^{2+} with calcite and aragonite, and the adsorption of Mn^{2+} on carbonate mineral surfaces. Values reported for rhodochrosite solubility products are; 1.8×10^{-11} (Sillen and Martel, 1964), 3.9×10^{-11} (Morgan, 1967) and 3.0×10^{-11} (Robie et al., 1979). $MnCO_3$ has been found to occur in solid solution with calcite up to 40 mole percent (Berry and Mason, 1959). Its presence in the calcite as $Mn(II)CO_3$ has been confirmed by electron paramagnetic resonance studies (Wildeman, 1970). Reported values for the distribution coefficient of Mn^{2+} in calcite and aragonite are presented in Table 1. Mn^{2+} is partitioned into calcite approximately 10 times stronger than into aragonite where the partition coefficient is close to unity. An anomolously high value (1700) for the Mn^{2+} distribution coefficient in calcite was reported by Crocket and Winchester (1966) based on erroneous theoretical considerations (see Pingatore, 1978, for discussion). Other values of the distribution coefficient range between approximately 6 and 20 (Bodine et al., 1965; Michard, 1968; Kinsman and Holland, 1969; Ichikuni, 1973; Pingatore, 1978). Recently, Lorens (1981) has found that the distribution coefficient for Mn^{2+} in calcite is dependent on the precipitation rate at which the calcite is formed. His value for the distribution coefficient for zero growth rate is 22.4 and decreases as the growth rate increases. Lorens' results may explain the previous differences in reported values for distribution coefficients.

Early studies of Mn^{2+} adsorption on calcite indicated that Mn^{2+} was strongly adsorbed by calcium carbonate at concentrations below that required for $MnCO_3$ solubility control. The lack of an adsorption maximum was interpreted as indicating that precipitation as well as adsorption was involved with the uptake of Mn^{2+} from solution onto the surface of calcite (Boischot et al., 1950; Leeper, 1952). McBride (1979) has carried out a study of the interaction of Mn^{2+} with the surface of calcite in dilute aqueous solutions. He found that the relation between adsorption and the solid to solution ratio was not linear, and that the Mn^{2+} uptake was approximately balanced by Ca^{2+} release. It was suggested that the calcium release may not be the result of direct displacement, but rather results from the following equilibrium reactions.

$$Mn^{2+} + HCO_3^- \longrightarrow MnCO_3 + H^+$$

$$H^+ + CaCO_3 \longrightarrow Ca^{2+} + HCO_3^-$$

McBride also found that Mn^{2+} replaced more than the available number of adsorption sites, based on surface area measurements and unit cell size. This observation further substantiated his hypothesis that a precipitation reaction was occurring. Electron spin resonance (ESR) studies indicated that no discrete new phase formed at low Mn^{2+} surface concentrations, but that at high concentrations of Mn^{2+} on the calcite surface $MnCO_3$ was nucleated. The pattern of uptake indicated that there is an initial rapid adsorption, followed by a period of little uptake, during which $MnCO_3$ nucleation occurs, and finally a slow but steady growth of $MnCO_3$. By considering the calcite surface a two dimensional solid,* McBride was able to calculate a surface distribution coefficient of 10 to 25, which is in good agreement with those determined for the solid. This surface distribution coefficient decreased as surface Mn^{2+} concentration increased.

This investigation was undertaken to further study the kinetics of Mn^{2+} interaction with the surface of calcite. Of particular interest were

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* A monolayer of unit calcite cell dimensions.

the influence of ionic strength and site competition from Mg^{2+}. As part of this study the solubility of rhodochrosite in seawater has been determined.

MATERIALS & METHODS

Two aqueous solutions were used for the Mn^{2+} adsorption studies. The first solution was distilled water equilibrated with calcite at a pH of 8.2. The second solution was filtered (0.4 μm Nuclepore®) surface Gulf Stream seawater with a salinity of 36°/oo. The seawater was equilibrated with calcite by alkalinity adjustment using HCl and equilibration with atmospheric P_{CO_2}. The pH of the resulting solution was 7.9.

The Gulf Stream seawater was also used for the $MnCO_3$ solubility studies. The seawater was purged with 99.99% pure N_2 to remove dissolved O_2 and equilibrated with a 0.330% CO_2 in N_2 mixture. Both the N_2 and the CO_2/N_2 mixtures were presaturated with water vapor to prevent evaporation of the seawater.

Mallinckrodt brand reagent grade $CaCO_3$ was used as the calcite source for all experiments. X-ray diffraction analysis indicated the $CaCO_3$ to be greater than 99% calcite. Absolute surface area of the calcite was determined by the multi-point Kr-BET method of de Kanel and Morse (1979) and was found to be $0.55\ m^2\ g^{-1}$.

The Mn^{2+} carbonate used was Fisher Scientific Company certified reagent grade. X-ray diffraction analysis indicated the $MnCO_3$ to be greater than 99% rhodochrosite.

In the uptake experiments, Mn solutions were prepared in the medium to be studied by successive dilutions of a 1,000 ppm atomic absorption standard. 50 to 150 ml solutions were spiked with a radioactive ^{54}Mn

standard (4.6×10^{-8}M) to give solutions with an initial activity on the order of 10^4 cpm. Addition of these weakly acidified Mn standards caused a negligible change in the pH and alkalinity of the resulting solutions.

Suspension of the calcite for the uptake experiments was maintained by stirring with teflon-coated magnetic stirring bars or by continuous shaking with an orbital shaker. The solution was separated from the solid phase by centrifugation. The fraction of Mn lost from the solution was determined by the change of the activity before and after addition of calcite. The validity of using the initial activity for the total Mn^{2+} in solution was checked for two possible extraneous losses: 1) the loss of Mn ions to the surface of the reaction vessels, and 2) the loss due to oxidation of the Mn^{2+} ions to Mn(IV) O_2. The loss of Mn ions to the surface of the reaction vessels was determined in vessels constructed from a variety of different materials (Teflon®, polyethylene and glass) and found to be <1% in the distilled water medium and <5% in the seawater medium. This small a loss of Mn ions to the container surface was uniform in all materials, and as a result, pyrex glass was employed for the uptake and solubility experiments. Initial concentrations were taken as those found in solution after 30 min exposure (time for equilibration of the solution with the reaction vessel). Loss of Mn^{2+} from solution by oxidation was checked in the solution studied by comparing continually purged N_2 solutions with solutions open to the atmosphere. Less than 2% of the Mn^{2+} was lost due to oxidation for a time period of 33 days, at 10^{-6}M Mn and a pH of 8.5. The negligible loss due to oxidation has been previously reported by Wilson (1980). The loss of Mn^{2+} due to oxidation has, therefore, been neglected in the uptake results.

The ^{54}Mn activity was determined on two 1 ml aliquots of the centrifuged samples using a Packard gamma scintillation counter, model 5975. Long term samples were corrected for ^{54}Mn decay and a standard ^{54}Mn sample was counted daily for checking alignment of the high voltage units.

$MnCO_3$ solubility in seawater was determined by continuous stirring, with a glass stirrer, to prevent grinding, of 5 g $MnCO_3$/l in 85 ml of seawater at 25°C. Continuous bubbling of CO_2 was maintained throughout the solubility experiments. Equilibrium was defined as when the pH remained constant ($\pm$ .002 pH units) for at least 4 hrs. A minimum of 50 hrs was used to reach equilibrium. Solubility was determined from both undersaturation and supersaturation. The solubility was determined from the supersaturated side by spiking an equilibrium solution obtained from undersaturation with sufficient Mn^{2+} to increase the Mn^{2+} concentration by a factor of 3. When equilibrium was established, the pH was recorded, and aliquots were withdrawn for measurement of carbonate alkalinity, Ca and Mn concentrations.

Mn analysis for the solubility determinations was performed on a Hitachi-Zeeman effect AA unit, model 170-70 with an autosampler. The analytical precision for a given sample was approximately 95%. Reproducibility from sample to sample was generally better than 90%. Samples were diluted with acidified seawater before analysis to bring the concentration in the range of 20-50 ppb.

Ca concentration was determined by EGTA (ethylenglycol-bis-(β-aminoethyl ether)-N,N'-tetraacetic acid) titration using a GHA (2,2'-Ethanediylidene-dinitrilo diphenol) indicator as described by Gieskes (1974).

RESULTS

Initial experiments indicated that the sorption of Mn^{2+} onto calcite from distilled water and seawater, in equilibrium with calcite, occurs rapidly. Results for the change in Mn^{2+} concentration in a solution of calcite suspended in distilled water are presented in Figure 1 for 8 typical samples. These samples represent a range in Mn^{2+} concentration from 1×10^{-6} to 1×10^{-9}M, and solid to solution ratios of 1.0, 4.0, and 6.0 g $CaCO_3$/l. All reactions displayed a three stage process for the removal of Mn^{2+} from solution. An initial rapid uptake occurred in the first 10 minutes. The rate of uptake was dependent on the amount of suspended calcite present, but independent of the initial concentration of Mn^{2+}, 10 to 15% of the total Mn^{2+} present was removed from the solution per gram of calcite in this initial rapid uptake. During the second stage, there was a relative slowing of the uptake process. This lasted from 10 to 30 minutes depending upon the amount of calcite present. During the third stage there was again a rapid loss of Mn^{2+} from solution, to a total of 90 to 99% Mn^{2+} removal from solution. These results are similar to those found by McBride (1979). This third reaction phase followed a first order rate law with respect to the initial Mn^{2+} concentration. The rate constant was independent of the initial concentration of Mn^{2+} but did depend on the solid to solution ratio. The values obtained for the rate constant, k, corrected for the solid to solution ratio, are presented in Table 2. The 20 samples represent a range of Mn^{2+} concentrations from 10^{-6} to 10^{-9} M and a solid to solution ratio range from 1.0 to 10.0 g $CaCO_3$/l. All the solutions maintained a constant pH during the uptake of 8.2 ($\pm$ 0.1). The average value for k is 3.0 ($\pm$ 0.8) $\times 10^{-3}$ l min^{-1}

$(\text{g CaCO}_3)^{-1}$.

Average results for the sorption of Mn^{2+} from solution onto suspended calcite in seawater for 8 samples are presented in Figure 2 and Table 3. These samples had a solid to solution ratio of 5 g $CaCO_3$/l and a range of Mn^{2+} concentrations from 10^{-5} to 10^{-9}M. The percent of Mn^{2+} remaining in solution, as a function of time, is independent of the initial Mn^{2+} concentrations. The percentages presented in Figure 2 represent the average fraction remaining in solution after different periods of reaction, with the error bars representing 1 standard deviation. The seawater samples exhibited an uptake pattern which had only two stages. Overall uptake was much slower from seawater than from distilled water. The first stage was more rapid than the second stage, and lasted for about 25 hours. Approximately a 2% loss of Mn^{2+} from solution per g $CaCO_3$/l occurred during this period. The second stage continued for at least 350 hrs. Mn^{2+} uptake followed a first order rate law during this phase. There was no indication of a third stage in the uptake experiments even at higher solid to solution ratios. These samples had an average Mn^{2+} removal from solution at 350 hrs. of 24.0 ($\pm$ 1.8) percent and an average value of k for the second stage of sorption of 8.0 ($\pm$1) x 10^{-7} l min^{-1} $(\text{g CaCO}_3)^{-1}$. This rate constant is approximately 4000 times smaller than that found in distilled water. All the solutions maintained a constant pH during the uptake of 8.0 ($\pm$ 0.1). The uptake of Mn^{2+} onto calcite, from seawater in equilibrium with calcite, at a solid to solution ratio from 2.5 to 10.0 g $CaCO_3$/l was investigated for Mn^{2+} concentrations of 1 x 10^{-6} and 1 x 10^{-9}M. These results are presented in Table 4. In this case, k' represents the first order rate constant obtained from the plot of log [Mn^{2+}] versus time. The slope was not adjusted for the amount of suspended calcite. Data in Table 3 indicate that the rate of loss of Mn^{2+} from a seawater solution is not strongly dependent upon the amount of suspended calcite present. This result is different from that obtained in distilled water, where the rate was dependent on the solid to solution ratio. Values for k' could not be determined for the 1×10^{-9}M Mn^{2+} samples at 2.5, 7.5, and 10.0 g $CaCO_3$/l because they did not follow the normal uptake pattern for Mn^{2+} onto calcite in seawater. Instead, uptake in the first 50 hrs. removed a large fraction of the Mn^{2+} from these samples (approximately 45% in each case). This was followed by desorption of the Mn^{2+} back into solution to the values listed in Table 4 at 350 hrs. This different uptake pattern occurred even though the major variables (e.g., pH, carbonate alkalinity, etc.) were the same as in other experiments. It is possible that at these very low concentrations of Mn^{2+}, site competition with the many different seawater components or complexation with trace organic compounds may be responsible for this behavior.

Two additional solutions were prepared for studying the Mn^{2+} uptake process. A 0.7 m NaCl solution was prepared along with a solution made up of 0.05 m $MgCl_2$ plus 0.55 m NaCl. These solutions were prepared in distilled water and then equilibrated with calcite. Both solutions have the ionic strength of normal seawater ($I \simeq 0.7$). The 0.7 m NaCl solution represents a "Mg-free" solution and the $MgCl_2$ plus NaCl solution has the same Mg^{2+} concentration as average seawater. Both uptake experiments were run at a Mn^{2+} concentration of 1×10^{-8}M and a solid to solution ratio of 5 g $CaCO_3$/l. The 0.7 m NaCl solution maintained a constant pH of 8.4 (± 0.1) during Mn^{2+} uptake, while the $MgCl_2$/NaCl solution had an initial pH of 9.0, which steadily decreased to 8.3 over 100 hrs. The results of these two uptake experiments are presented in Figure 3. For the purpose of comparison, a "regular" seawater uptake ($[Mn^{2+}] = 1 \times 10^{-8}$M, 5 g $CaCO_3$/l) and a distilled water uptake ($[Mn^{2+}]$ - 1×10^{-8}M, 2 g $CaCO_3$/l) are also presented in Figure 3. The 0.7 m NaCl ("Mg-free") solution followed an uptake pattern very similar to, but slower than, that obtained in distilled water (Figure 1). The 0.05 m Mg^{2+} solution followed an uptake pattern almost identical to the seawater sample.

Results on the determination of the solubility of $MnCO_3$ in seawater are presented in Table 5. Equilibrium was established at 50 hrs. from undersaturation and at 75 hrs. from supersaturation. K_{sp} was calculated from $a_{Mn^{2+}} a_{CO_3^{2-}}$. The total activity coefficient for Mn^{2+} in seawater was calculated from the activity coefficient of the free ion, obtained from the equations and constants given by Millero and Schreiber (1981), and calculations of the fraction of Mn^{2+} in the free form in seawater. The fraction of free Mn^{2+} was calculated using the stability constants of Sillen and Martel (1964) for $MnHCO_3^+$, and $MnCl^+$, the only quantitatively important pairs. A value of 0.25 was obtained for the activity coefficient of the free ion and 0.60 for the fraction of Mn^{2+} in the free form in seawater. This results in a value of 0.15 for the Mn^{2+} total activity coefficient. Average K_{sp} values of 2.2×10^{-11} and 5.7×10^{-11} were obtained from undersaturation and supersaturation, respectively, for two separate determinations from each saturation state. The K_{sp} value obtained from undersaturation is in reasonable agreement with previously reported values from dilute solutions (1.8×10^{-11}, Sillen and Martel, 1964; 3.9×10^{-11}, Morgan, 1967; 3.0×10^{-11} by Robie, et al., 1979).

The Ca concentration decreased by 0.3×10^{-3}M in going to equilibrium from undersaturation. A much larger decrease (1.1×10^{-3}M) occurred when approaching equilibrium from supersaturation. This change is large compared with the Mn^{2+} concentration change of 2.4 x 10^{-5}, in going from the initial supersaturation Mn^{2+} concentration to the equilibrium value obtained from the supersaturated side. Consequently, much more $CaCO_3$ was precipitated than $MnCO_3$ when equilibrium was approached from supersaturation. The solubility obtained from supersaturation may, therefore, be more representative of a Mn-calcite solubility than that of rhodochrosite.

DISCUSSION

The general patter of Mn^{2+} uptake from dilute solutions onto the surface of calcite found in this study is similar to that found by McBride (1979). The interpretation given by McBride for the uptake of Mn^{2+} from dilute solutions onto calcite is that initial rapid uptake represents an adsorption reaction. This is followed by a period of relatively little uptake during which $MnCO_3$ nucleation takes place. After nucleation, uptake resumes as $MnCO_3$ crystal growth on the calcite surface. In this study the growth phase was found to follow first order reaction kinetics with respect to the dissolved Mn^{2+} concentration. The rate constant for the reaction is 3.0 ($\pm$ 0.8) x 10^{-3} 1 min^{-1} (g $CaCO_3$)$^{-1}$ for reagent grade calcite with a surface area of 0.55 m^{-2} g^{-1}. In seawater only a two stage process was found in which initial rapid uptake was followed by steady Mn^{2+} removal, with no intervening quiescent period. The rate of uptake following the initial fast adsorption phase was found to be first order with respect to dissolved Mn^{2+} concentration with a rate constant of 8 ($\pm$ 1) x 10^{-7} 1 min^{-1} (g $CaCO_3$)$^{-1}$. The first order rate constant measured in seawater is approximately 4000 times less than the first order rate constant found in dilute solutions. Since the activity coefficient for Mn^{2+} in the two solutions differs by less than an order of magnitude, the difference in observed rate constants cannot be explained by differences in dissolved Mn^{2+} activity and must represent a change in processes occurring on the calcite surface.

It is interesting to note that the uptake patterns found for Mn^{2+} on the surface of calcite in these solutions are similar to those observed for orthophosphate uptake on calcite. Stumm and Leckie (1970) observed a 3 stage process for phosphate uptake on calcite surfaces from dilute solutions. They interpreted these different stages as representing adsorption, nucleation and apatite growth. de Kanel and Morse (1978) found a 2 stage pattern of phosphate uptake on calcite from seawater, with an initial rapid adsorption phase followed by slow but steady uptake.

McBride (1979), using ESR, found that $MnCO_3$ nucleation on the surface of calcite will not occur if high Mn^{2+} concentrations are not reached on the calcite surface during the fast adsorption phase. Approximately 7 times more adsorption occurs during the rapid uptake phase from dilute solutions than from seawater. A probable explanation for this is site competition from dissolved seawater components such as Mg^{2+}. Experiments carried out to verify this hypothesis, indicate that while increased ionic strength (0.7) slows Mn^{2+} uptake, the same general pattern is found as in dilute solutions. Adding Mg^{2+} at seawater concentration to the 0.7 ionic strength solution produced the same results found in seawater. Shanbhag and Morse (1982) were able to produce similar results for Am^{3+} uptake on the surface of calcite, where a NaCl + $MgCl_2$ solution gave the same results as seawater. It is also possible that the presence of Mg^{2+} in solution may inhibit the nucleation of $MnCO_3$, as it does the nucleation of calcite.

The results from the rhodochrosite solubility measurements in seawater were in reasonable agreement with values predicted from dilute solution solubility measurements, when equilibrium is approached from undersaturation, but approximately a factor of 2 times higher when approached from supersaturation. By monitoring the change in the dissolved calcium concentration it was found that Ca^{2+} was being removed from solution onto the surface of the rhodochrosite. Since only the net Mn^{2+} concentration change was observable, it is not possible to calculate the composition of the mixed Mn and Ca carbonate which formed on the surface of the rhodochrosite. If the same partition coefficient from Mn^{2+} as in calcite were followed (approximately 15) the resulting Mn-calcite would contain 25 to 30 mole percent $MnCO_3$. The formation of such a carbonate could occur through the reverse of the reactions suggested by McBride (1979) for Mn^{2+} replacement of calcite (see Introduction).

CONCLUSIONS

The findings of this study for the behavior of Mn^{2+} with the surface of calcite, in dilute solutions, are in good agreement with those of previous studies (e.g. McBride, 1979). The rate of Mn^{2+} uptake on the surface of calcite in dilute solutions, NaCl-$MgCl_2$ mixtures and natural seawater is first order with respect to Mn^{2+} concentrations, after initial surface reactions are completed. The rate constant for the reaction in seawater is approximately 4000 times smaller than in dilute solutions. It is hypothesized that long term Mn^{2+} uptake on the surface of calcite in dilute solutions proceeds through the growth of a distinct $MnCO_3$ phase, while in seawater a Mn-calcite is formed. These differences in behavior of Mn^{2+} with the surface of calcite are primarily the result of the high Mg^{2+} concentration in seawater which limits adsorption through site competition and may also inhibit $MnCO_3$ nucleation.

Rhodochrosite ($MnCO_3$) solubility in seawater determined from undersaturation is in good agreement with previously reported values determined in dilute solutions. When equilibrium is approached for supersaturation a mixed Ca-Mn carbonate forms which is over twice as soluble. It is, therefore, probable that a relatively pure $MnCO_3$ with the solubility of rhodochrosite does not form in seawater to control Mn^{2+} concentrations in calcium carbonate-rich marine environments. In such environments, the Mn^{2+} concentration will be controlled by reactions on the surface of calcite, in which calcites containing Mn^{2+}, as well as other components such as Mg^{2+} and Sr^{2+}, are formed.

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TABLE 1

DISTRIBUTION COEFFICIENTS OF Mn(II) IN CALCIUM CARBONATE

Mineral	Distribution Coefficeint	Remarks	Reference
Aragonite	0.86(±0.04)	30 to 60°C	Raiswell and Brimblecombe (1977)
Calcite	6.2(±2)	40°C	Bodine *et al.*(1965)
Calcite	1700	Theoretical	Crocket and Winchester (1966)
Calcite	5.4(±0.3)	0 to 25°C	Michard(1968)
Calcite	17.4	-	Kinsman and Holland(1969)
Calcite	10 to 18	40°C from travertine	Ichikuni(1973)
Calcite	15(approx.)	40°C lime-stone	Pingatore(1978)
Calcite	22.4	at ppt. rate =0, decreases with increase in rate	Lorens(1981)

TABLE 2

Manganese Uptake on Calcite in Distilled Water

Total Mn M	Suspended Calcite g ℓ^{-1}	k x 10^{-3} ℓ min^{-1} (g $CaCO_3$)$^{-1}$
1 x 10^{-6}	1.0	2.4
1 x 10^{-7}	1.0	3.8
1 x 10^{-8}	1.0	4.8
1 x 10^{-9}	1.0	3.2
1 x 10^{-9}	1.0	1.8
1 x 10^{-6}	2.0	3.2
1 x 10^{-8}	2.0	3.4
1 x 10^{-9}	2.0	3.3
1 x 10^{-6}	4.0	2.9
1 x 10^{-6}	4.0	4.0
1 x 10^{-9}	4.0	3.4
1 x 10^{-9}	4.0	3.6
1 x 10^{-6}	6.0	1.8
1 x 10^{-6}	6.0	2.2
1 x 10^{-9}	6.0	3.9
1 x 10^{-9}	6.0	2.8
1 x 10^{-6}	8.0	3.3
1 x 10^{-9}	8.0	2.7
1 x 10^{-6}	10.0	1.7
1 x 10^{-9}	10.0	2.4

TABLE 3

Fraction of Manganese Remaining in Solution for Manganese Uptake on Calcite in Seawater

Percent Mn Remaining in Solution

Initial Total → Mn^{2+}(M)	1×10^{-5}	1×10^{-6}	5×10^{-7}	1×10^{-7}	5×10^{-8}	1×10^{-8}	5×10^{-9}	1×10^{-9}	Average
Time Hrs.									
1	0.98	0.98	0.97	0.98	0.97	0.98	0.97	0.98	0.976 ± 0.005
3	0.98	0.96	0.95	0.96	0.96	0.97	0.96	0.97	0.964 ± 0.009
6	0.97	0.95	0.96	0.96	0.94	0.95	0.95	0.96	0.955 ± 0.009
10	0.95	0.95	0.93	0.95	0.94	0.94	0.95	0.94	0.944 ± 0.007
25	0.93	0.94	0.90	0.92	0.90	0.91	0.91	0.91	0.915 ± 0.014
50	0.93	0.92	0.88	0.89	0.89	0.87	0.86	0.88	0.890 ± 0.024
75	0.91	0.89	0.87	0.86	0.86	0.84	0.86	0.85	0.868 ± 0.023
100	0.89	0.87	0.86	0.84	0.84	0.83	0.81	0.83	0.846 ± 0.026
125	0.89	0.87	0.86	0.83	0.84	0.82	0.82	0.82	0.844 ± 0.027
150	0.87	0.85	0.83	0.83	0.82	0.82	0.80	0.81	0.829 ± 0.022
175	0.85	0.84	0.82	0.81	0.80	0.80	0.79	0.80	0.814 ± 0.021
200	0.85	0.84	0.82	0.81	0.82	0.79	0.80	0.81	0.818 ± 0.020
225	0.85	0.84	0.81	0.80	0.79	0.80	0.78	0.78	0.806 ± 0.026
250	0.83	0.81	0.80	0.80	0.78	0.79	0.77	0.77	0.794 ± 0.021
275	0.82	0.80	0.80	0.80	0.78	0.79	0.77	0.79	0.794 ± 0.015
350	0.77	0.79	0.77	0.76	0.75	0.76	0.73	0.75	0.760 ± 0.018

All experiments conducted with a solid to solution ratio of 5 g calcite per liter.

TABLE 4

Manganese Uptake on Calcite in Seawater

Total Mn M	Suspended Calcite g ℓ^{-1}	Percent Uptake at 350 hours	k' x 10^{-6} min^{-1}
1 x 10^{-6}	2.5	22	4.0
1 x 10^{-9}	2.5	32	-
1 x 10^{-5} to 1 x 10^{-9} (8 samples)	5.0	24 ± 2	4.0
1 x 10^{-6}	7.5	27	4.0
1 x 10^{-9}	7.5	38	-
1 x 10^{-6}	10.0	27	3.5
1 x 10^{-9}	10.0	36	-

TABLE 5

Solubility of $MnCO_3$ in Seawater

Initial Saturation	Final pH	$a_{CO_3{}^{2-}}$ (x 10^6)	Ca^{2+} (mM)	Mn^{2+} (μM)	K_{sp} ($MnCO_3$)
Undersaturated	7.33	2.4	10.31	67	2.4×10^{-11}
	7.35	2.6	-	49	1.9×10^{-11}
Supersaturated	7.29	2.0	9.21	173	5.2×10^{-11}
	7.31	2.1	-	197	6.2×10^{-11}

All measurements done at a $P_{CO_2} = 3.3 \times 10^{-3}$ atm.

FIGURE CAPTIONS

Figure 1. The uptake of Mn^{2+} onto calcite in distilled water at Mn^{2+} concentrations from 1×10^{-6} to 1×10^{-9}M and solid to solution ratios of 1, 4, and 6 g $CaCO_3/\ell$.

KEY: ● 1 g $CaCO_3/\ell$; ■ 4 g $CaCO_3/\ell$; ▲ 6 g $CaCO_3/\ell$.

Figure 2. The average percent of Mn^{2+} remaining in solution versus time for calcite in seawater at Mn^{2+} concentrations from 1×10^{-5} to 1×10^{-9}M and a solid to solution ratio of 5 g $CaCO_3/\ell$.

Figure 3. The uptake of Mn^{2+} onto calcite in four aqueous mediums at a total of Mn^{2+} concentrations of 1×10^{-8}M.

KEY: ■ 0.7 m NaCℓ, 5 g $CaCO_3/\ell$; ● 0.05 m $MgC\ell_2$ + 0.55 m NaCℓ, 5 g $CaCO_3/\ell$; ▲ seawater, 5 g $CaCO_3/\ell$; □ distilled water, 2 g $CaCO_3/\ell$.

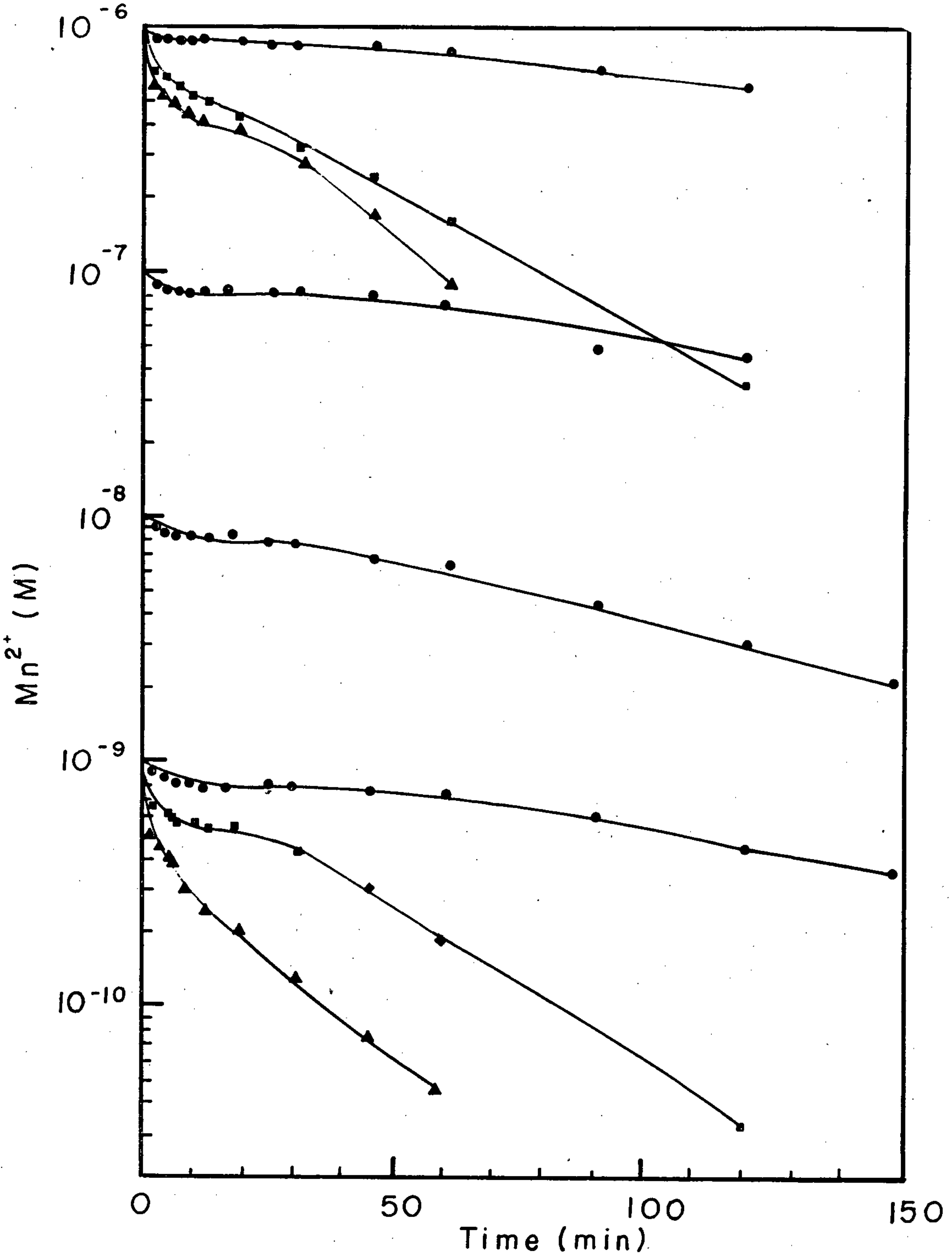

Fig. 1

XBL 8112-13066

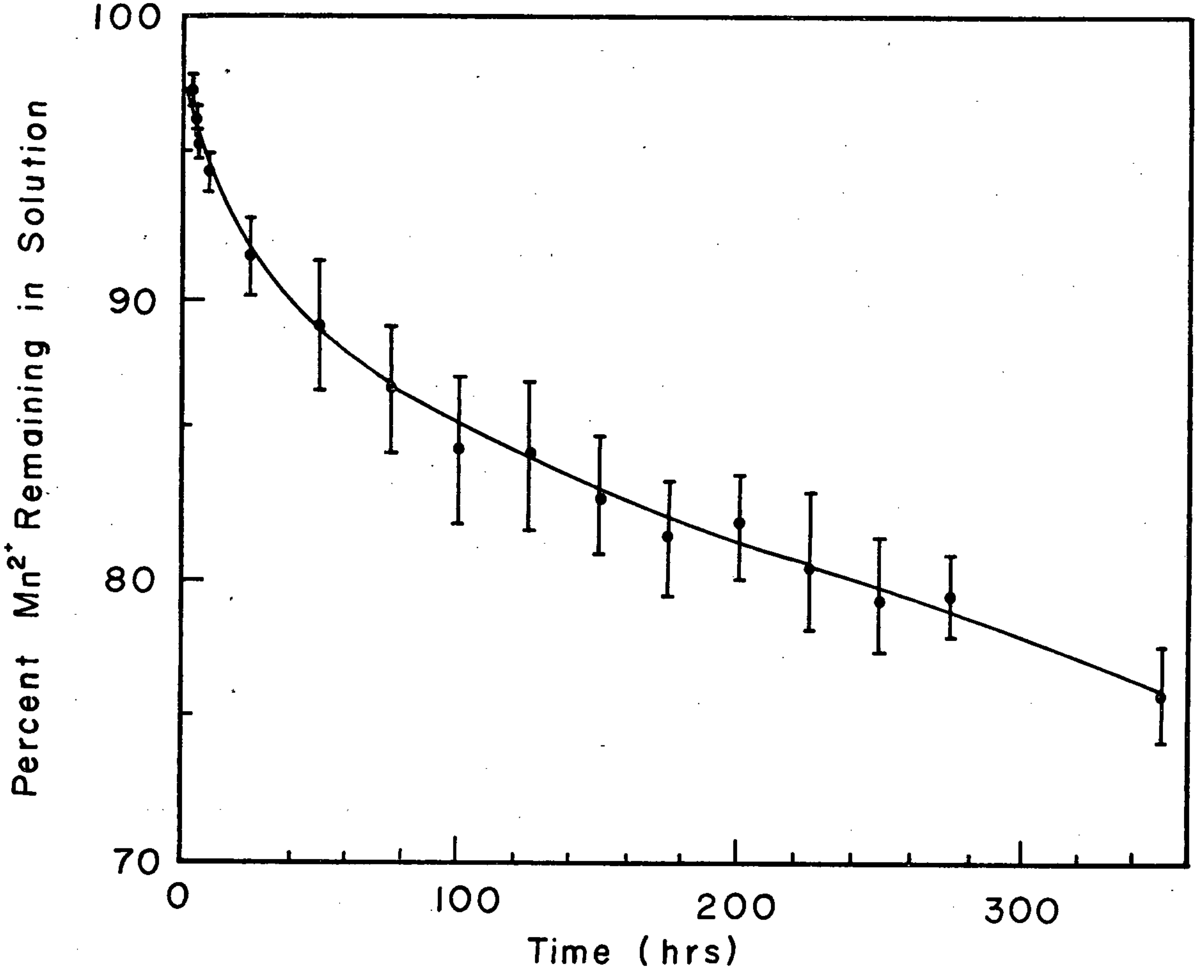

Fig. 2

XBL 8112-13067

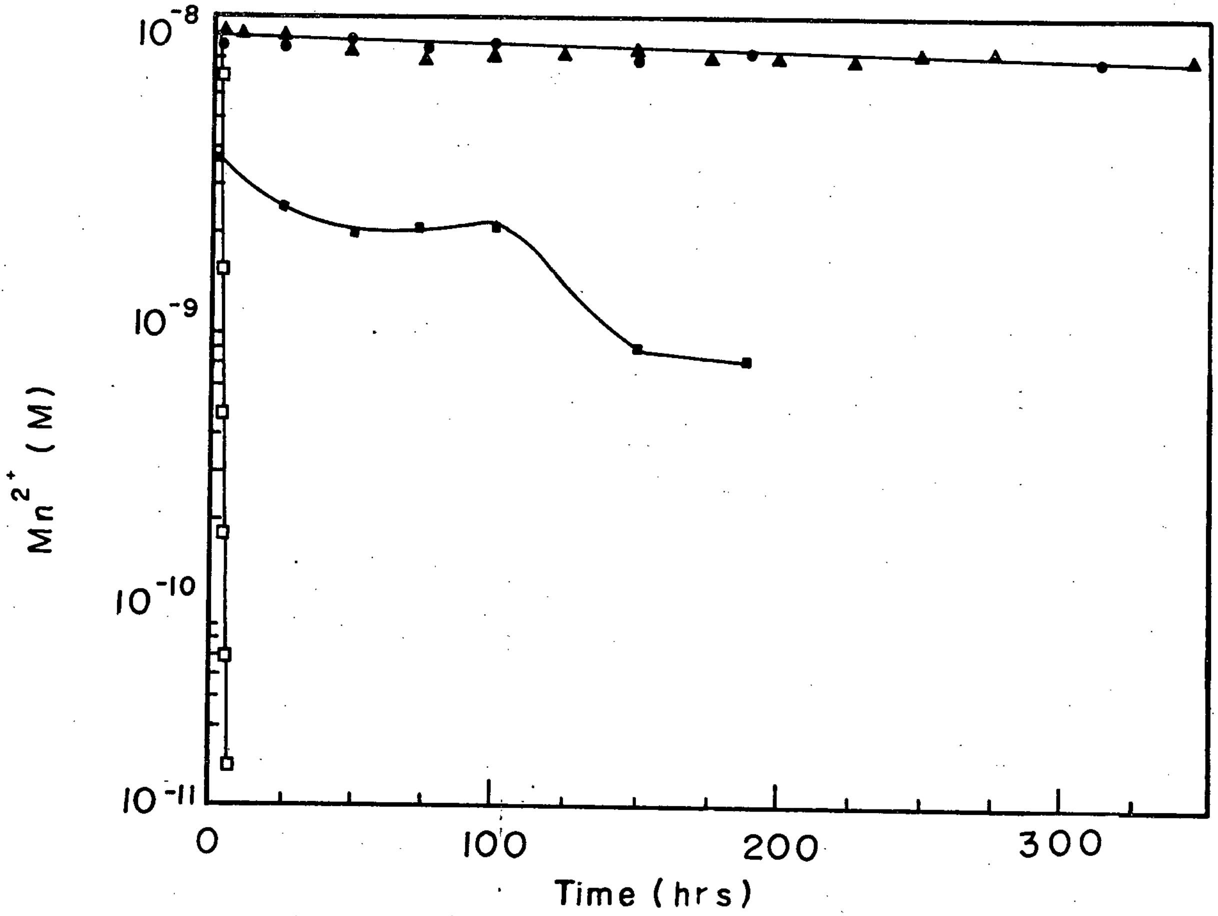

Fig. 3

XBL-8112-13068

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