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Adsorption and Desorption of Phosphate on Calcite and Aragonite in Seawater

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Abstract. The adsorption and desorption of phosphate on calcite and aragonite were investigated as a function of temperature (5–45 °C) and salinity (0–40) in seawater pre-equilibrated with $CaCO_3$. An increase in temperature increased the equilibrium adsorption; whereas an increase in salinity decreased the adsorption. Adsorption measurements made in NaCl were lower than the results in seawater. The higher values in seawater were due to the presence of Mg^{2+} and Ca^{2+} ions. The increase was 5 times greater for Ca^{2+} than Mg^{2+}. The effects of Ca^{2+} and Mg^{2+} are diminished with the addition of SO_4^{2-} apparently due to the formation of $MgSO_4$ and $CaSO_4$ complexes in solution and/or SO_4^{2-} adsorption on the surface of $CaCO_3$. The adsorbed Ca^{2+} and Mg^{2+} on $CaCO_3$ (at carbonate sites) may act as bridges to PO_4^{3-} ions. The bridging effect of Ca^{2+} is greater than Mg^{2+} apparently due to the stronger interactions of Ca^{2+} with PO_4^{3-}.

The apparent effect of salinity on the adsorption of PO_4 was largely due to changes in the concentration of HCO_3^- in the solutions. An increase in the concentration of HCO_3^- caused the adsorption of phosphate to decrease, especially at low salinities. The adsorption at the same level of HCO_3^- (2 mM) was nearly independent of salinity. All of the adsorption measurements were modeled empirically using a Langmuir-type adsorption isotherm

$$[PO_4]_{ad} = K_m C_m [PO_4]_T / (1 + K_m [PO_4]_T),$$

where $[PO_4]_{ad}$ and $[PO_4]_T$ are the adsorbed and total dissolved phosphate concentrations, respectively. The values of C_m (the maximum monolayer adsorption capacity, (mol/g) and K_m (the adsorption equilibrium constant, g/(mol) over the entire temperature (t, °C) and salinity (S) range were fitted to

$$C_m = 17.067 + 0.1707t - 0.4693S + 0.0082S^2 \quad (\sigma = 0.7)$$

$$\ln K_m = -2.412 + 0.0165t - 0.0004St - 0.0008S^2 \quad (\sigma = 0.1)$$

These empirical equations reproduce all of our measurements of $[PO_4]_{ad}$ up to 14 μmol/g and within ± 0.7 μmol/g.

The kinetic data showed that the phosphate uptake on carbonate minerals appears to be a multi-step process. Both the adsorption and desorption were quite fast in the first stage (less than 30 min) followed by a much slower process (lasting more than 1 week). Our results indicate that within 24 hours aragonite has a higher sorption capacity than calcite. The differences between calcite and

aragonite become smaller with time. Consequently, the mineral composition of the sediments may affect the short-term phosphate adsorption and desorption on calcium carbonate. Up to 80% of the adsorbed phosphate is released from calcium carbonate over one day. The amount of PO_4 left on the $CaCO_3$ is close to the equilibrium adsorption. The release of PO_4 from calcite is faster than from aragonite. Measurements with Florida Bay sediments produced results between those for calcite and aragonite. Our results indicate that the calcium carbonate can be both a sink and source of phosphate in natural waters.

1. Introduction

It is well known that increased nutrient concentrations and altered nutrient ratios can result in phytoplankton blooms and degradation of the water quality (Smayda, 1989, 1990). It is particularly important in Florida Bay due to the runoff of nutrients from the Everglades. As a result of increased fertilizer and sewage input, Si : N and Si : P ratios have declined in many coastal waters (Smayda, 1989, 1990; Turner and Rabalais, 1991, 1994; Sommer, 1994; Justic et al., 1995). This tends to lead to a shift from diatoms (a preferred food source for many marine herbivores) to small flagellates (which are often poor foods) within the phytoplankton community (Schelske and Stoermer, 1971; Officer and Ryther, 1980). Florida Bay sediments are mainly composed of calcium carbonate (cf. Table I). Measurements of soluble reactive phosphate in the pore waters of calcium carbonate-rich sediments are much lower than in sediments with little or no calcium carbonate (Morse et al., 1985). Therefore calcium carbonate minerals may exert significant control on phosphate chemistry in marine waters (Ames, 1959; de Kanel and Morse, 1978). Phosphate has been shown to be the limiting nutrient in part of Florida Bay due to adsorption to biogenic carbonate sediments (Fourqurean et al., 1992). The retention of phosphate by carbonate affects the growth of primary producers such as seagrasses (Short, 1987). Some researchers have suggested that adsorption of phosphate on calcium carbonates may lead to the formation of apatite (Ames, 1959; Simpson, 1964, Martens and Harriss, 1970). In contrast, recent work by Louchouarn et al. (1997) indicates that high carbonate ion concentrations and the presence of calcite in marine sediments may inhibit the formation of carbonate fluorapatite.

The mechanism of the adsorption of PO_4 (phosphate) to $CaCO_3$ (calcium carbonate) has been studied previously by Stumm and Leckie (1970) and de Kanel and Morse (1978). Stumm and Leckie (1970) suggested that the initial uptake of phosphate on calcite occurs by chemisorption, followed by a slow transformation of amorphous calcium phosphate to crystalline apatite. The rate of apatite crystal growth depends strongly on the phosphate to carbonate ratio and the authors suggested that this is due to the competition for growth sites. In their experiments, they also found that fluoride increased the rate of phosphate uptake whereas magnesium strongly inhibited the adsorption. de Kanel and Morse (1978) investigated the kinetic behavior of phosphate adsorption on calcite carbonate and their results

indicated that fluoride and magnesium have only a minor effect on the rate of phosphate uptake.

While many studies have focused on phosphate uptake on calcium carbonate, few studies have examined the adsorptive behavior over a wide range of environmental conditions such as temperature and salinity. Little data are available for the desorption of phosphate from calcium carbonates. In this study, we examine the adsorption and desorption of phosphate on calcium carbonates (calcite and aragonite) as a function of temperature (5–45 °C), salinity (0 –41), pH (7.2–9.0) and solution composition. The adsorption and desorption on natural carbonate sediments from Florida Bay are also studied. The purpose of this work is to model the turnover of the phosphate on suspended $CaCO_3$ in seawater, especially in Florida Bay waters that experience a wide range of salinity and temperature.

2. Experimental

2.1. MATERIALS

Stock solutions of phosphate (1 mM) were prepared with reagent grade Na_2HPO_4 (Fisher Scientific). Seawater from the Gulf Stream (S = 36.4) (5 meters below the surface) filtered through 0.2 μm filters was used throughout the experiments. The phosphate levels in Gulf Stream waters are below 0.05 μmol kg^{-1}. Since the seawater is supersaturated with respect to calcite and aragonite all of the measurements were made after a pre-equilibration of at least one hour. Reagent grade calcite was obtained from Mallinckrodt. The aragonite used in this study was synthesized at 70 °C by the method of Wray and Daniels (1957) as modified by Katz et al. (1972). The equilibrium experiments were carried out in Nalgene HDPE bottles. Phosphate added to these bottles without calcium carbonate showed no noticeable loss due to adsorption. The natural carbonate sediments used in this work were collected in Florida Bay. Florida Bay is a triangular area on the southern tip of the Florida peninsula. The mainland borders it on the north and both of its southern and eastern portions merge into the reef ridge of the Florida Keys. It opens its western side to the Gulf of Mexico and receives fresh-water runoff from the Everglades. In all but the wettest years, it is a negative estuary, with hypersalinity caused by evaporation exceeding freshwater inputs. The salinity in Florida Bay can be as high as 50 (Fourqurean et al. 1992). The location and mineral compositions of the sediments are given in Table I. Large debris was removed from the sediments by passing them through a 60-mesh sieve. The sediments were dried at 60 °C and stored at 5 °C before use. The fraction of $CaCO_3$ in the sediments was determined by subtracting the acid non-dissolvable component from the total weight of the sediment after dissolving a portion of the sample in 10% HCl solution. After filtration through a pre-weighed 0.45 μm Nucleopore® filter, the weight of the non-carbonate material retained on the filter was determined after the filter was dried at 60 °C overnight. The phosphate and iron concentrations in the sediments

Table I. The mineral composition of the Florida Bay sediments.

Date	Station	Latitude	Longitude	Description	$CaCO_3$ wt %	$[PO_4]$ μmol/g	[Fe] μM	Arag. %	LMC[a] %	HMC[b] %
14 May 1997	10	25.0172	−80.5597	White mud	95.2	0.51	1.0	31.1	9.9	59
13 May 1997	11	25.0788	−80.7477	Fine particle w/shell	85.8	1.80	0.11	31.9	10.5	57.6
13 May 1997	15	25.0463	−80.9167	Fine particle	85.8	2.83	0.27	30.3	29.9	39.8
14 May 1997	21	24.9103	−80.661	Mud w/debris	93.8	1.26	0.71	23.6	16	60.4

[a]LMC: Low Magnesium Calcite.
[b]HMC: High Magnesium Calcite.

were measured from the filtered solution. The iron in the solutions was determined using the ferrozine method (Stookey, 1970). The precision of the Fe measurements was ($\pm$30 nM. All the sediments contained greater than 86% of $CaCO_3$ and 0.5–2.8 (mol/g of PO_4 and 0.1–1.0 (mol/g of Fe. The composition of the calcium carbonates determined by XRD was 24 to 32% aragonite, 10–30% low Mg calcite (LMC) and 40–60% high Mg calcite (HMC). The cutoff point between low Mg calcite was 10% and for high Mg calcite was 40%.

Phosphate concentrations ($PO_4 = H_3PO_4 + H_2PO_4^- + HPO_4^{-2} + PO_4^{3-}$) in the solutions were analyzed using the phosphomolybdic colorimetric method (Murphy and Riley, 1962) at 880 nm on a HP 8453A spectrophotometer. The precision of the phosphate measurements was ± 0.1 μM with 1 cm length cell. Potassium molybdate, potassium antimonyl tartrate and ascorbic acid were obtained from Sigma Chemical.

2.2. KINETICS OF PHOSPHATE ADSORPTION ON ARAGONITE AND CALCITE

For the adsorption kinetic studies, 5 μmol of phosphate was added to 500 cm^3 of seawater in a 1000 cm^3-capacity jacketed beaker maintained at 25 $\pm$ 0.02 °C by a Neslab constant temperature bath. While vigorously stirring, 1 gram of either aragonite or calcite powder (<200 mesh) was added to the seawater.

For the desorption kinetic studies, phosphate was pre-adsorbed onto calcium carbonate by equilibrating two grams of calcium carbonate (aragonite or calcite) with 225 cm^3 of a 110 μM phosphate solution. After being subjected to either a 24-hour (short-term) or 1-week (long-term) equilibrium period, the solids were filtered through a 0.4 μm filter and dried at 60 °C overnight. The total amount of phosphate adsorbed was calculated based on the difference in phosphate concentrations in solution before and after the addition of the solids. One gram of calcium carbonate (calcite or aragonite) pretreated in this matter was added to 500 cm^3 of seawater.

For both kinetic experiments, 10 cm^3 of slurry were taken with a 10-cm^3 syringe at time intervals from 1 minute up to 4 hours. The samples were immediately filtered through 0.2 μm filters (Supor Acrodisc, Gilman). The amount of phosphate adsorbed on calcium carbonate was calculated by subtracting the remaining phosphate concentration in the solution from the initial total phosphate concentration.

2.3. ADSORPTION OF PHOSPHATE ON ARAGONITE AND CALCITE: ISOTHERM STUDIES

For the adsorption equilibrium studies, 50 cm^3 of solutions with different initial phosphate concentrations from 1 μM to 60 μM were combined with 0.1 gram of either calcite or aragonite in 60-cm^3 capacity HDPE bottles. As discussed later all the solutions were pre-equilibrated with $CaCO_3$ for at least 1 h before the addition of PO_4. After the pre-equilibrium, the solutions were kept at a constant temperature

with intermittent shaking for a given period of time. The effect of temperature (5–45 °C) and salinity (0–45) on the adsorption of phosphate on calcium carbonate were studied in a similar manner. Dilution with Milli-Q water or evaporation of the Gulf Stream seawater was used to obtain solutions with salinities other than 36.4. The salinities of the samples were determined on the Practical Salinity Scale using an AutoSal Salinometer to ±0.003.

The effect of pH on the phosphate adsorption was examined in 50 cm^3 of seawater with 4 μM of phosphate and 0.1 g of aragonite. The pH of the seawater was pre-adjusted to a value between 7.2 and 9.5 by adding HCl or NaOH to the sample. Phosphate was then added to obtain a final concentration of 4 μM. The pH was measured with an Orion 720A pH meter and a Ross combination electrode. The electrode was calibrated with a Tris seawater buffer (Millero, 1986) on the free proton scale. After the equilibration, the solutions were analyzed for the adsorbed phosphate.

3. Results

In our first series of experiments, we examined the effect that the precipitation of $CaCO_3$ can have on the adsorption of phosphate (PO_4) on calcium carbonate in seawater. These measurements were made to examine the possible co-precipitation of phosphate with $CaCO_3$. The addition of aragonite to supersaturated seawater results in a decrease in the total alkalinity (TA) of the solution due to the precipitation of $CaCO_3$. This is demonstrated in Figure 1 for the addition of aragonite (2 g L^{-1}) to Gulf Stream seawater (Millero et al., 1999). The TA decreases from 2468 to 1800 μmol kg^{-1} in the first two hours followed by a slower loss of TA to its equilibrium value ($\sim$1100 μmol kg^{-1} when pCO_2 = 365 μatm for aragonite at equilibrium). We have made a series of measurements to see if this precipitation of $CaCO_3$ affects the equilibrium adsorption of PO_4 to aragonite.

The adsorption of PO_4 to aragonite was measured by first pre-equilibrating the aragonite with seawater for a set period of time (pre-equilibration time), followed by adding phosphate. The solutions were then equilibrated for one day. The results at different levels of phosphate are shown as a function of the pre-equilibration time in Figure 2. The addition of 40 μM of phosphate immediately after addition of the aragonite to the seawater yields a higher adsorption than those additions with pre-equilibration time longer than 60 min. The effect is nearly undetectable at levels below 30 μM of added PO_4 or at pre-equilibration times over one hour. These experiments suggested that the apparent co-precipitation of PO_4 with $CaCO_3$ is diminished as the seawater approaches equilibrium with aragonite. This is partly due to PO_4 retarding the precipitation of $CaCO_3$. To avoid the possible co-precipitation of PO_4 with $CaCO_3$, we waited at least one hour before the addition of PO_4 in all of our subsequent measurements.

In our second series of measurements, we examined the adsorption and desorption of phosphate on aragonite and calcite in seawater as a function of time. The

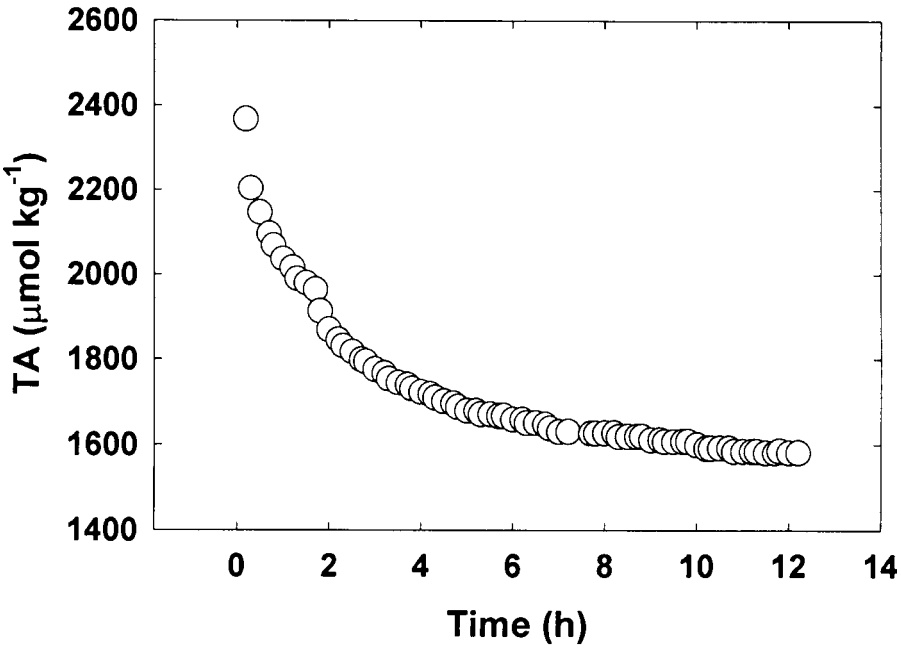


Figure 1. The decrease in the total alkalinity of seawater after the addition of aragonite (2 g L^{-1}) to Gulf Stream seawater.

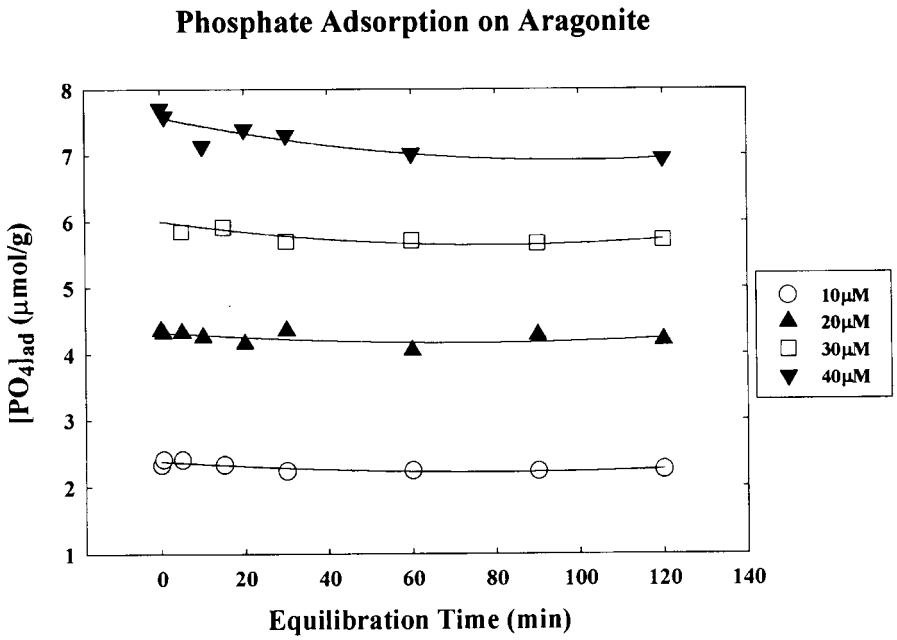


Figure 2. The adsorption of phosphate on aragonite (2 g L^{-1}) following a one hour pre-conditioning with the solid.

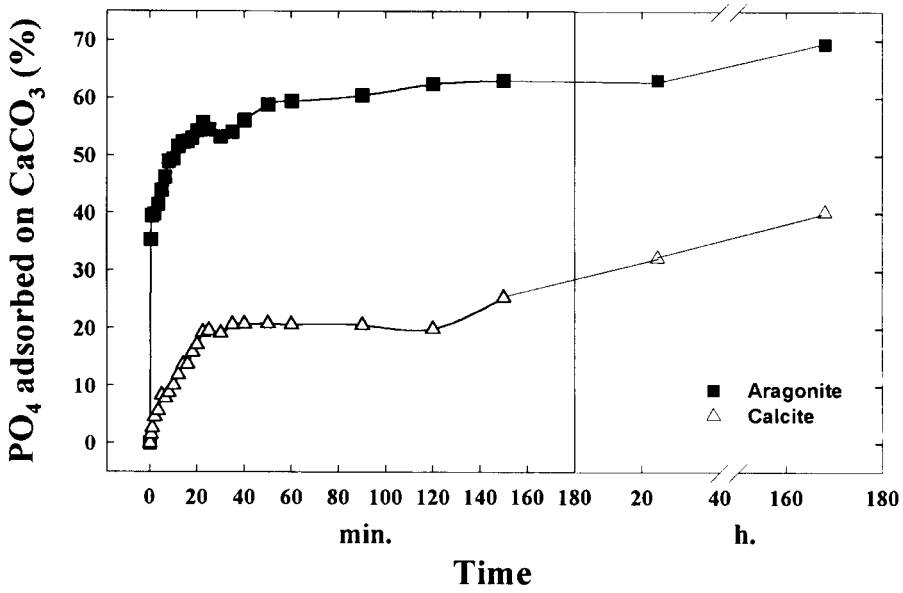


Figure 3. The percentage of phosphate adsorbed on aragonite and calcite (2 g L^{-1}) in seawater at 25 °C as a function of time ($[PO_4]_0$ = 10 μM).

results for the adsorption of phosphate to calcite and aragonite as a function of time are shown in Figure 3. The adsorption of both aragonite and calcite appears to be a two step process in agreement with the results of Stumm and Leckie (1970). In the first 30 minutes, the dissolved phosphate concentration decreased sharply and reached a relative constant concentration within two hours. After this initial fast adsorption period, the uptake rate of phosphate on calcium carbonate was much slower. A comparison of the adsorption of phosphate to aragonite and calcite after one and seven days is shown in Figure 4. The adsorption on aragonite is similar for the one-day and 7-day equilibrations. The adsorption on calcite increases with the longer equilibration. The differences in the extent of the adsorption on the two minerals may be related to the differences in the specific surface areas.

The rates of desorption of phosphate from aragonite and calcite were also studied. These measurements were made on $CaCO_3$ minerals that had been subjected to either a one-day or one-week pre-sorption of phosphate with constant shaking. The initial phosphate adsorbed was 10.5 and 9.9 μmol/g on aragonite and 3.5 and 4.1 μmol/g on calcite, respectively, after one-day equilibration and one-week equilibrations. Figure 5 shows that a fraction of the sorbed phosphate was quickly released from both calcite and aragonite (20–30 min) that had been pre-equilibrated for one day. The amount of phosphate released from aragonite was the nearly the same for the samples equilibrated for one and seven days. The phosphate released from calcite, however, was lower for the sample equilibrated for seven days. The equilibrium levels of the desorbed phosphate from aragonite and calcite are nearly

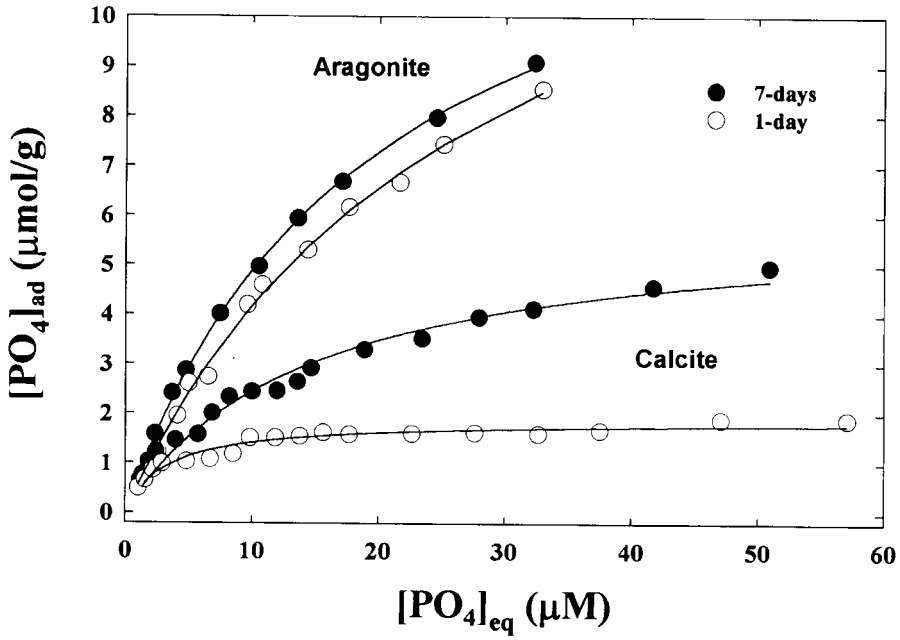


Figure 4. Comparison of adsorption of phosphate on aragonite andcalcite (2 g L^{-1}) in seawater at 25 °C at different equilibration times.

equal to the values found from adsorption measurements for the one or seven day equilibration.

To examine the effect of composition on the adsorption, we carried out a number of measurements of the adsorption of PO_4 to aragonite in seawater and the major seasalts at 25 °C. Measurements made in 0.7 M NaCl (with 0.002 M $NaHCO_3$) and seawater after a one day equilibration are compared in Figure 6. Adsorption of phosphate from seawater was higher than from the 0.7 M NaCl solution. Measurements carried out in artificial seawater composed of the major components (Na^+ = 0.47 M, Mg^{2+} = 0.053 M, Ca^{2+} = 0.010 M, K^+ = 0.0109 M, Cl^- = 0.54 M, HCO_3^- = 0.002 M, SO_4^{2-} = 0.028 M; Millero, 1996) are identical to those obtained in natural seawater within the experimental error of the measurements (0.1 μM). To further investigate the cause of the differences we have made adsorption measurements in mixtures of NaCl (0.002 M $NaHCO_3$) and some of the major seasalts.

Figure 7 shows the comparisons of the effects of different seasalts on the adsorption of phosphate using 0.7 M NaCl as reference. Adsorption of PO_4 onto aragonite in NaCl (0.505 M) with Mg^{2+} (0.053 M) and Ca^{2+} (0.010 M) (as chlorides) increased the adsorption above the values for seawater. The effects of Mg^{2+} and Ca^{2+} at their seawater concentrations are similar. This means that the effect of Ca^{2+} is about five times greater than Mg^{2+}. The addition of both Mg^{2+} and Ca^{2+} to NaCl increases the sorption further, but not as much as the sum of the individual effects. The addition of Na_2SO_4 (0.0028 M) decreases the effects of both Mg^{2+}

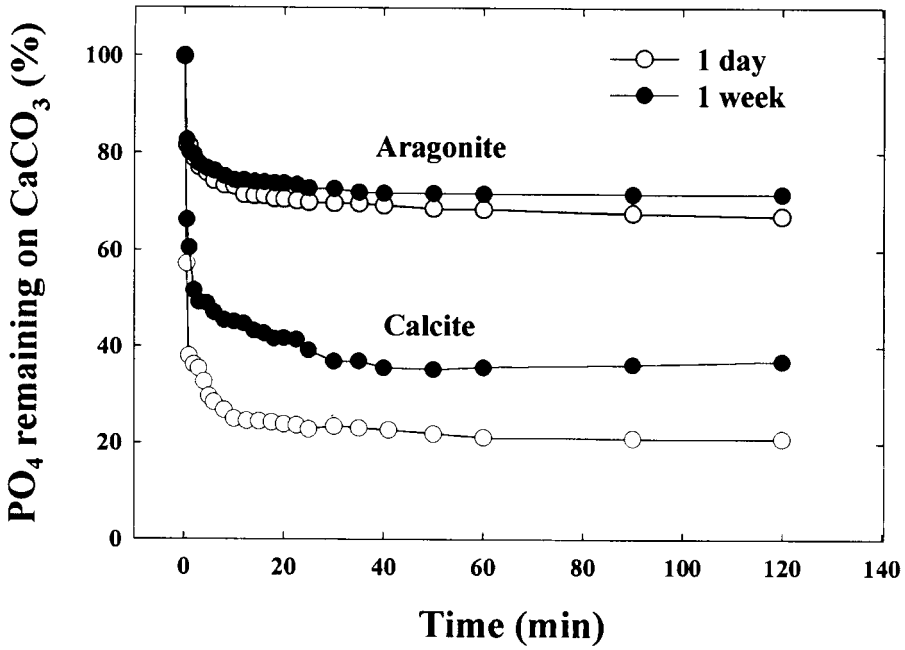


Figure 5. The percentage of phosphate remaining on aragonite and calcite (2 g L^{-1}) in seawater at 25 °C after a one day and one week pre-sorption equilibrium. The initial phosphate adsorbed was 10.5 and 9.9 μmol/g on aragonite and 3.5 and 4.1 μmol/g on calcite, respectively, after one-day equilibration and one-week equilibration.

and Ca^{2+}. These results suggest that the formation of $MgSO_4$ and $CaSO_4$ ion pairs decrease the adsorption effect of Mg^{2+} and Ca^{2+} or SO_4^{2-} competes with PO_4 for the adsorption sites on the carbonate minerals. The additions of some of the minor components at their seawater concentrations (K^+ = 0.009 M, Br^- = 0.0008 M, $B(OH)_3$ = 0.0004 M and F^- = 0.0007 M) do not affect the adsorption. Our results and those of de Kanel and Morse (1978) in seawater indicate that F^- does not affect the adsorption in contrast to the dilute solution results of Stumm and Leckie (1970). The formation of MgF^+ and CaF^+ complexes in seawater (Millero and Schreiber, 1982) may explain this discrepancy. Measurements made in solutions of the major seawater cations and anions (Na^+, Mg^{2+}, Ca^{2+}, Cl^- and SO_4^{2-}) yield adsorptions that are similar to that of natural seawater within the experimental error of the measurements (Figure 7). The effect of Mg^{2+} on the equilibrium adsorption of PO_4 to $CaCO_3$ agrees with the earlier studies of Stumm and Leckie (1970) and de Kanel and Morse (1978).

The effect of temperature (5–45 °C) on the adsorption of phosphate on aragonite was examined in seawater as a function of salinity (S = 0, 15 and 36). The results at S = 36 are shown in Figure 8. The adsorption increases with increasing temperature for all of the salinities studied. The effect of salinity (S = 0–41) on the adsorption of phosphate on aragonite was also examined at different temperatures. The results

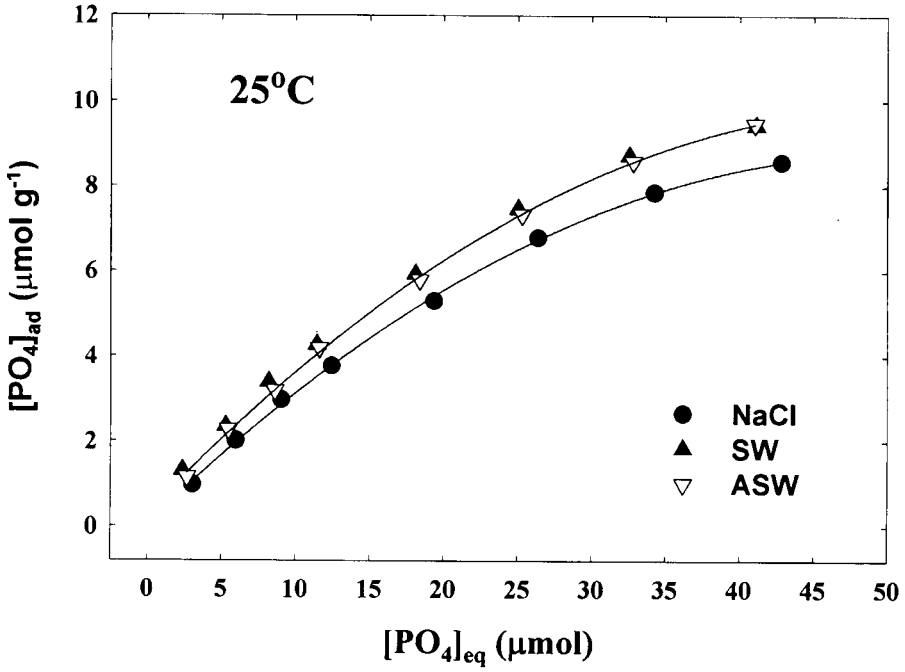


Figure 6. Comparisons of the adsorption of phosphate to aragonite in 0.7 M NaCl with 0.002 M $NaHCO_3$ and seawater at 25 °C.

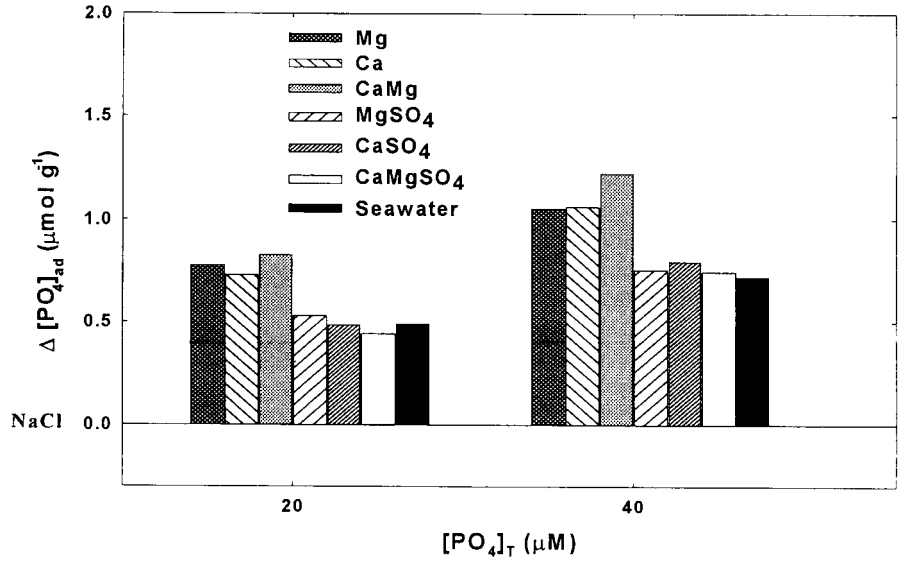


Figure 7. The difference in the adsorption of phosphate to aragonite in 0.7 M NaCl, NaCl + $MgCl_2$, NaCl + $CaCl_2$, NaCl + $MgCl_2$ + $CaCl_2$, NaCl + $MgCl_2$ + Na_2SO_4, NaCl + $CaCl_2$ + Na_2SO_4 and seawater at 25 °C. The concentrations of all the components are the same as in average seawater (Millero, 1996). $NaHCO_3$ (0.002 M) was added to all the solutions except seawater.

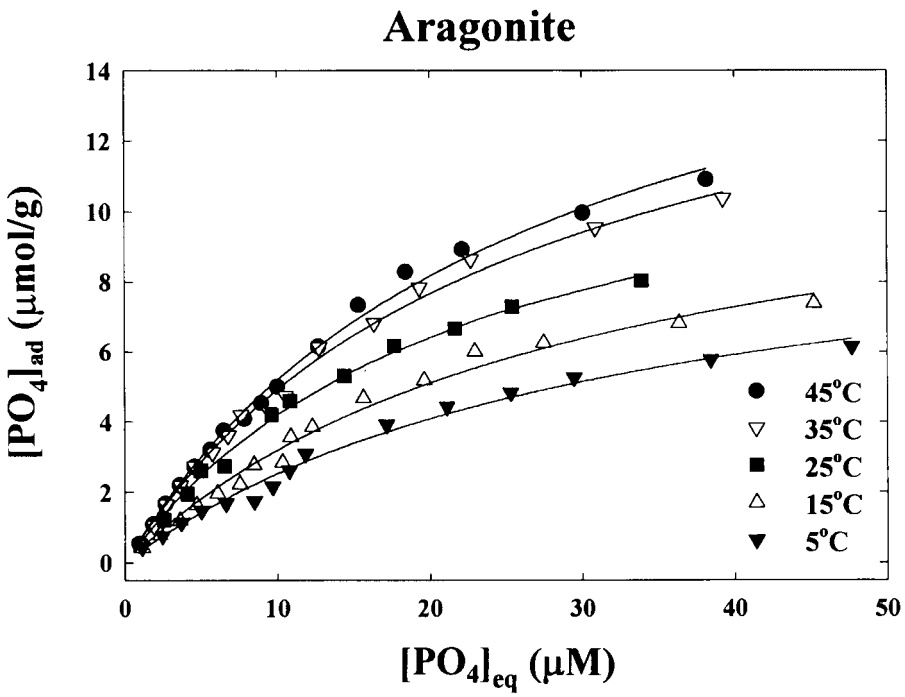


Figure 8. The effect of temperature on the adsorption of phosphate on aragonite in seawater (S = 36).

at 35 °C are shown in Figure 9. The adsorption increases as the salinity decreases. A decrease in the salinity from 41 to 36 results in a 9% increase in the observed phosphate adsorption. The effect is much larger at the lower salinities. For example, the adsorption increased by 29% when the salinity was lowered from 5 to 0.

To elucidate the effects of salinity on the adsorption of phosphate, we examined the effect of composition on the adsorption. Measurements in pure water with added HCO_3^- serving as a buffer showed that the adsorption was strongly affected by the amount of HCO_3^- added to the solution (see Figure 10a). Measurements made at the same HCO_3^- concentration or carbonate alkalinity (Figure 10b) give an adsorption that is nearly independent of ionic strength or salinity.

The effect of pH (7.4–9) on the adsorption of phosphate to aragonite was examined in seawater (S = 36) at 25 °C. The results given in Figure 11 show that the adsorption increases to a maximum at a pH of 8.6. The effect of pH on the adsorption can be related to changes in the surface sites or changes in the speciation of phosphate in the solution. At a pH near 8.6 the fractions of HPO_4^{2-} and PO_4^{3-} are nearly equal (Millero, 1996) and do not go through a maximum near this pH. This leads us to believe that the effect of pH on the adsorption is not related to the speciation of PO_4 in solution, but to changes in the surface speciation.

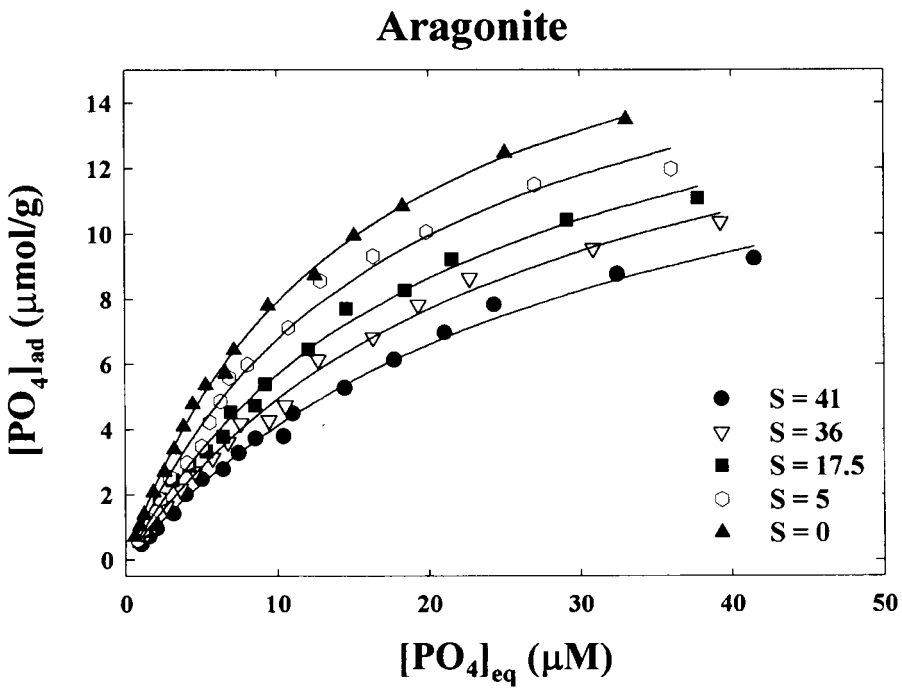


Figure 9. The effect of salinity on the adsorption of phosphate on aragonite in seawater at 35 °C.

4. Discussion

The results of our adsorption and desorption kinetics study indicate that calcium carbonate can act as both a source and sink of phosphate in natural waters. The rapid adsorption and desorption of phosphate is similar to the chemisorption reported by Stumm and Leckie (1970) in their phosphate kinetics studies. The crystal structure of the $CaCO_3$ can significantly change the adsorption behavior during the chemisorption stage. During this stage, the initial uptake rate of aragonite is much larger than calcite. This is in agreement with the results of de Kanel and Morse (1978). This difference in the rates of adsorption may be related to differences in the reaction sites in the crystal lattice or in the specific surface area (Walter and Burton, 1986). Burton and Walter (1990) for example have found that $CaCO_3$ with different specific surface areas can cause phosphate adsorption to vary by 3 to 7 fold.

The Mg^{2+} and Ca^{2+} present in natural waters increase the adsorption of PO_4 on $CaCO_3$. Since the addition of both cations lowers the activity of free PO_4^{3-} (Millero and Schreiber, 1982) that is thought to be the species adsorbing onto $CaCO_3$ (Burton and Walter, 1990), the increase in the adsorption appears to be a surface effect. This could be related to the adsorption of Mg^{2+} and Ca^{2+} to carbonate sites on the mineral surface. Since the strength of interactions of Mg^{2+} and Ca^{2+} with CO_3^{2-}

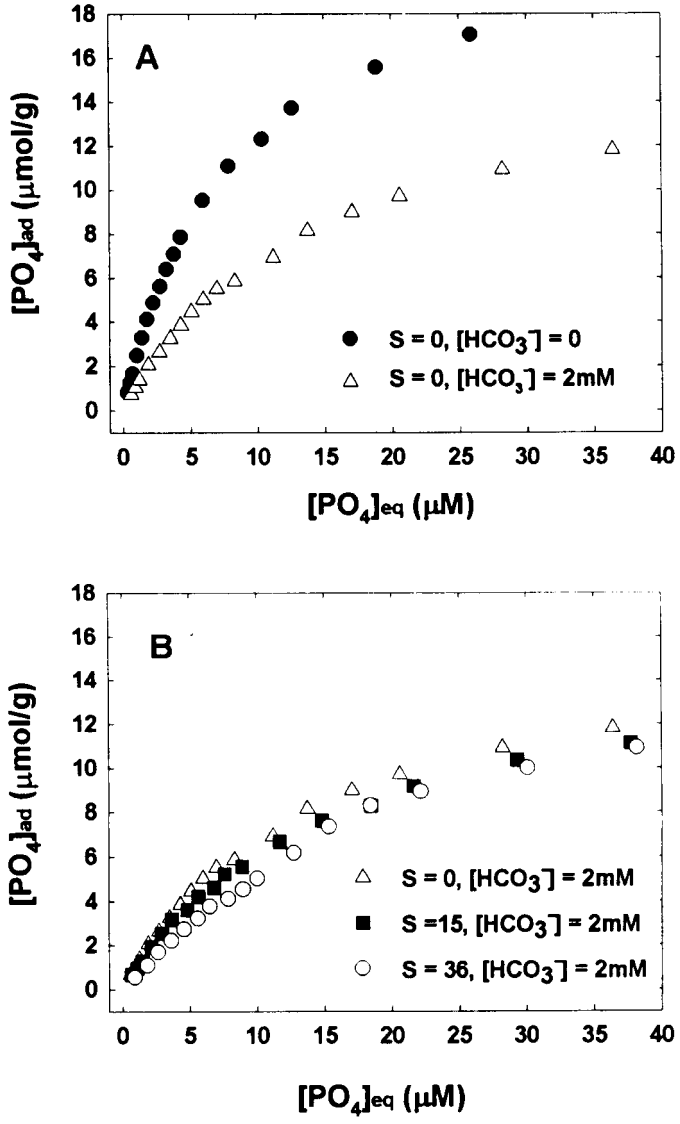


Figure 10. The effect of bicarbonate on the adsorption of phosphate on aragonite at 25 °C.

are similar (Millero and Schreiber, 1982), one would expect that the carbonate surface sites would be equally populated with both cations. The Mg^{2+} and Ca^{2+} on the surface sites can increase the adsorption of PO_4 by forming $>CO_3$—Mg—PO_4 and $>CO_3$—Ca—PO_4 bonds. The addition of SO_4^{2-} to the solutions lowers the activity of these cations due to the formation of sulfate ion pairs ($MgSO_4$ and $CaSO_4$) decreasing the adsorption of PO_4. The higher adsorption with added Ca^{2+} may be related to its ability to form much stronger interactions with PO_4 than Mg^{2+} (K_{CaPO_4} =$10^{4.5}$ and K_{MgPO_4} = $10^{3.4}$, Millero and Schreiber, 1982). It should

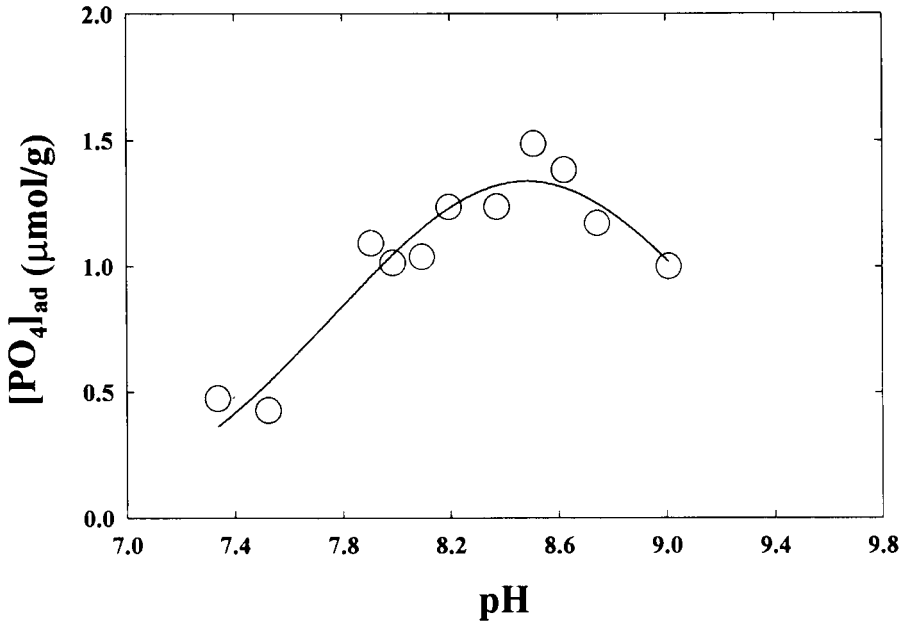


Figure 11. The effect of pH on the adsorption of phosphate on aragonite at 25 °C.

be pointed out that we cannot rule out the actual adsorption of $MgPO_4^+$ and $CaPO_4^+$ ion pairs to the surface rather than some bridged complex as discussed above. The adsorption of SO_4^{2-} to $CaCO_3$ may also decrease the adsorption of PO_4.

The adsorption of phosphate is almost independent of the salinity, but is a strong function of the bicarbonate concentration. The bicarbonate ion decreases the adsorption of phosphate by competing for positive surface sites of Ca on $CaCO_3$. Calcium carbonate at low ionic strengths with low concentrations of bicarbonate will strongly adsorb phosphate compared with waters with high bicarbonate concentrations. Since the alkalinity of most rivers is less than seawater, one would expect the adsorption to be greater in the river end member of an estuary and PO_4 would be released to seawater as the waters enter the ocean. The total alkalinity of the rivers entering Florida Bay (3.0 mM), in contrast, is greater than the alkalinity of seawater (2.3 mM) (Millero et al., 1999). The high levels of bicarbonate in the input waters to Florida Bay could result in the delivery of dissolved phosphate to the Bay.

The most commonly used empirical models to quantitatively describe the adsorption of a solute to solids are the Langmuir, Temkin and Freundlich Equations (Olsen and Watanabe 1957; Kaila, 1963; Bache and Williams, 1971; Mead, 1981). In this study, we have found that the Langmuir-type equation can be used to fit all our data even though it has a number of shortcomings (Syers et al., 1973; Holford et al., 1974). We selected this empirical equation as a convenient way to fit the data,

and examine the effects of different experimental conditions. The Langmuir-type equation for the adsorption of phosphate to calcium carbonate is given by

$$[PO_4]_{ad} = K_m C_m [PO_4]_T / (1 + K_m [PO_4]_T), \quad (1)$$

where $[PO_4]_{ad}$ and $[PO_4]_T$ are the adsorbed and total dissolved concentrations of phosphate, respectively. Although C_m and K_m are defined, respectively, as the maximum monolayer adsorption capacity and the adsorption equilibrium constant, we are treating them as empirical constants. This equation can be rearranged to give the linear equation

$$1/[PO_4]_{ad} = 1/C_m + 1/(K_m C_m [PO_4]_T). \quad (2)$$

The results at S = 36 and 25 °C fitted to Equation (2) are shown in Figure 12a. The least squares fit of the data gives $C_m = 24.45 \pm 4$ μmol/g and $K_m = 0.0205 \pm 0.0002$ g/μM. Although the data appear to be well represented by Equation (2), as shown in Figure 12b, it does not give a good fit of the experimental results (σ = 4 μmol/g in $[PO]_{ad}$). We have thus used a non-linear least squares method to fit the results directly to Equation (1). This gives $C_m = 15.48 \pm 0.7$ μmol/g and $K_m = 0.037 \pm 0.003$ g/μM and fits the experimental values of $[PO_4]_{ad}$ with a σ = 0.2 μmol/g (Figure 12b). Similar calculations for all of the measurements are given in Table II.

The effects of temperature and salinity on the values of C_m (Table II) are shown in Figure 13. The values of C_m are a linear function of temperature and a second degree function of salinity. All of the results have been fitted to (σ = 0.71)

$$C_m = 17.0607 + 0.1707t - 0.4693S + 0.0082S^2. \quad (3)$$

The effects of temperature and salinity on ln K_m are shown in Figure 14. The values of ln K_m are nearly independent of temperature, except for the results of S = 0 without HCO_3^- which are a linear function of temperature. The results have been fitted to (σ = 0.11)

$$\ln K_m = -2.4120 + 0.0165t + 0.0032S - 0.0004St - 0.0008S^2. \quad (4)$$

The enthalpies of adsorption determined from the results give values of -4 ± 4 kcal mol^{-1}. The calculated values of $[PO_4]_{ad}$ determined from Equations (1), (3) and (4) yield values of $[PO_4]_{ad}$ that agree with the measured values to ± 0.7 μmol kg^{-1} for all of our measurements.

To test the reliability of our work on aragonite and calcite, we have made a number of measurements on sediments collected from Florida Bay at the locations given in Table I. Four samples collected from different locations were used to examine the adsorption of phosphate to natural sediments. As shown in Table I, the sediments from Florida Bay are composed of a high percentage (>85%) of

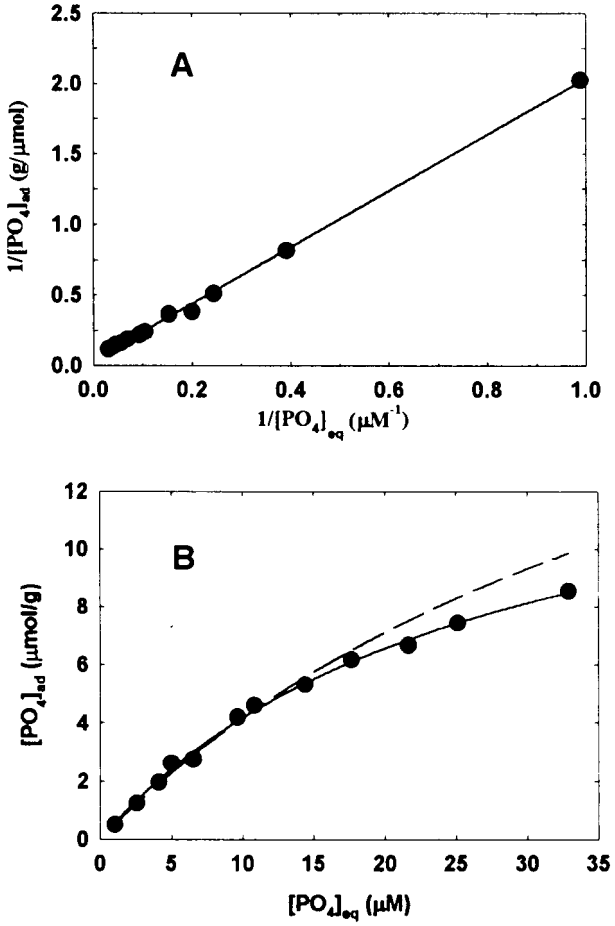


Figure 12. The Langmuir plot for the adsorption of phosphate on aragonite in seawater (S = 36) at 25 °C. (a) A fit of the results to Equation (2) with C_m = 24.45 and K_m = 0.02005. (b) A fit of the results to Equation (1) with C_m = 15.48 and K_m = 0.037. The dotted line is the calculated values using the coefficients determined from Equation (2).

calcium carbonate minerals. The phosphate concentration in the seawater near the sampling area is less than 1 μM. The adsorption of PO_4 to Florida Bay sediments is shown in Figure 15. The values of K_m and C_m for the sediments are given in Table III. For the experiments with a 24-hour equilibration time, the amounts of adsorbed phosphate for all four sediments fall between pure aragonite and calcite and suggest that the sediments could be the mixture of both minerals. This is in good agreement with the compositions of the mineral phases shown in Table II. It should be noted that biogenic calcite contain Mg in its lattice which may affect the adsorption process. Figure 16 shows the relationship of high-Mg-calcite (HMC) for the four sediments. The sediment with the greatest HMC has a higher adsorption than pure calcite and the sediments with lower HMC. These results can be attrib-

Table II. The values of C_m and K_m for the adsorption of PO_4 on aragonite in seawater.

Temp. (°C)	Salinity	C_m (μmol/g^{-1})	$\sigma(C_m)$	K_m (μmol^{-1} g))	$\sigma(K_m)$	$\sigma(PO_4)_{ad}$ (μmol g^{-1})
5	0	18..7	0.4	0.091	0.004	0.2
	15	12.7	0.2	0.100	0.003	0.1
	36	10.7	0.7	0.031	0.004	0.2
15	0	20.0	0.3	0.104	0.004	0.2
	15	14.3	0.3	0.097	0.005	0.2
	36	12.7	0.8	0.034	0.004	0.3
25	0	21.6	0.2	0.130	0.003	0.1
	0[a]	16.2	0.2	0.072	0.002	0.1
	15	16.0	0.3	0.101	0.005	0.2
	15[b]	15.8	0.2	0.063	0.002	0.1
	36	15.5	0.7	0.037	0.003	0.2
35	0	22.8	0.4	0.177	0.007	0.3
	0[a]	19.4	0.5	0.068	0.004	0.2
	5[a]	18.8	0.9	0.056	0.005	0.4
	15	18.4	0.3	0.101	0.004	0.2
	18[b]	18.0	0.7	0.046	0.003	0.2
	36	17.7	0.8	0.039	0.003	0.2
	41	16.7	0.8	0.033	0.003	0.2
45	0	23.5	0.4	0.207	0.008	0.3
	0[a]	21.1	0.4	0.069	0.003	0.2
	15	19.3	0.4	0.106	0.005	0.2
	36	19.0	0.8	0.038	0.003	0.2

[a] 2 mM of HCO_3^- added.
[b] 1 mM of HCO_3^- added.

uted to the stronger association of phosphate with Mg sites relative to Ca sites in the lattice. In our earlier experiments, we found that after a prolonged equilibration time, the phosphate adsorption onto calcite increased significantly. To test this on the real sediments, we have equilibrated the sediment samples with phosphate for 2 weeks. Figure 17 shows that the adsorption of phosphate dramatically increases with a longer equilibration time. Since the sediments from Florida Bay are high in calcite (70–80% of the total calcium carbonate phase), they show a similar behavior to our laboratory results for pure calcite.

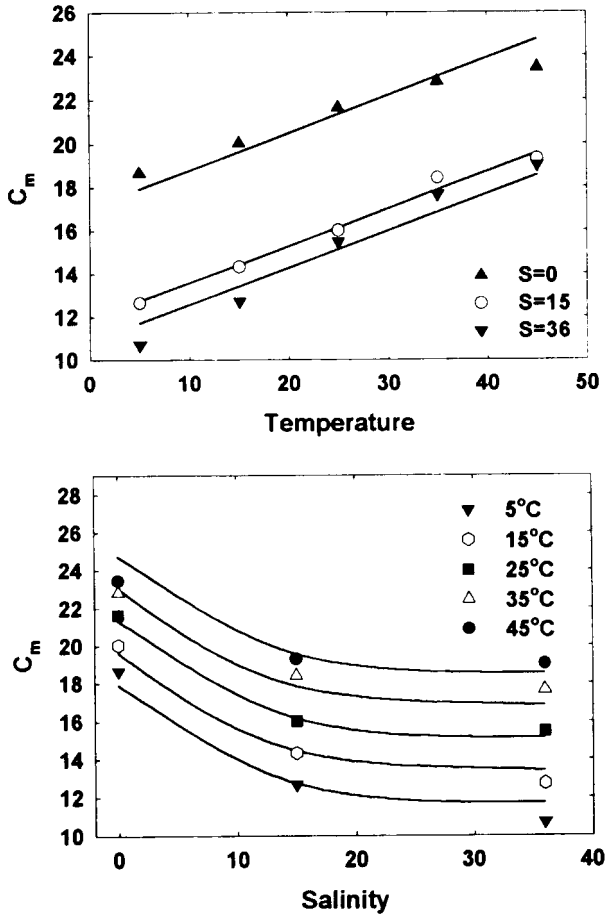


Figure 13. The effects of temperature and salinity on the Langmuir adsorption constant, C_m, for the adsorption of phosphate on aragonite in seawater.

Table III. The C_m and K_m for the sediments collected from Florida Bay.

Station	C_m (μmol/g)	$\sigma(C_m)$	K_m (g/μmol)	$\sigma(K_m)$
# 10-1	9.3	0.4	0.032	0.002
# 11-1	9.7	0.5	0.024	0.002
# 21-1	10.9	0.7	0.026	0.003
# 15-1	10.6	1.1	0.015	0.002
# 15-7	16.4	1.8	0.020	0.003
# 15-17	11.3	0.5	0.045	0.004

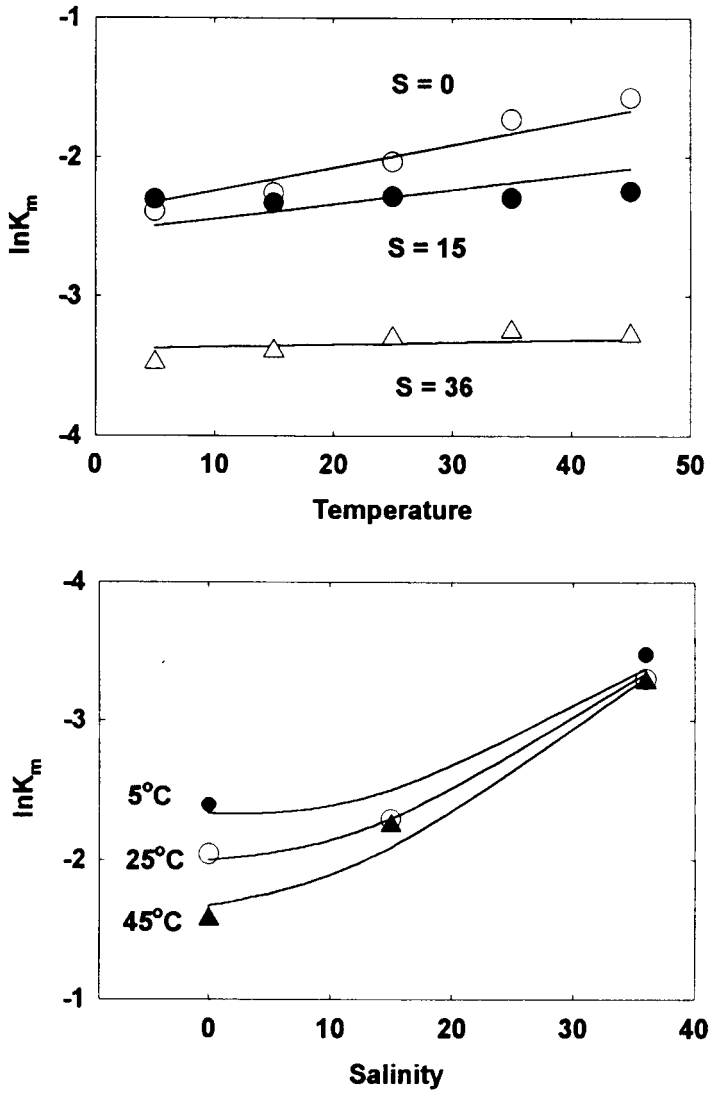


Figure 14. The effects of temperature and salinity on the Langmuir adsorption constant, K_m, for the adsorption of phosphate on aragonite in seawater.

5. Conclusions

These studies provide equations that can be used to model the adsorption of phosphate on $CaCO_3$ sediments in tropical waters. Our kinetic measurements show that the rates of adsorption and desorption are quite fast (30 min). Up to 80% of the adsorbed phosphate is released from calcium carbonate over one day. The amount of PO_4 left on the $CaCO_3$ is close to the equilibrium adsorption. For shallow waters like Florida Bay, the resuspension of the sediments may provide a short-term

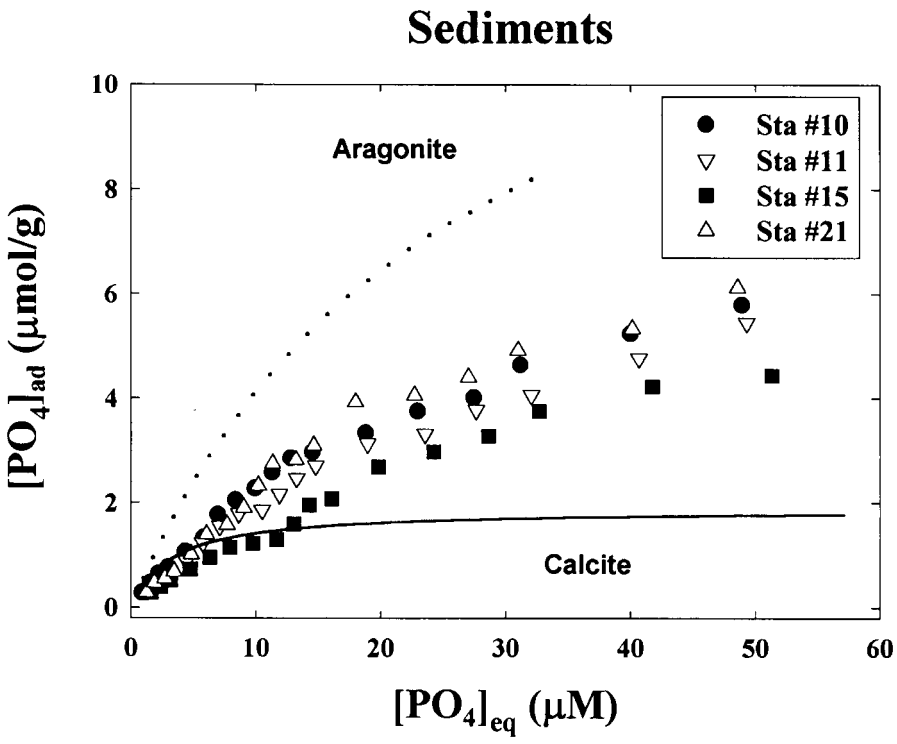


Figure 15. The adsorption of phosphate in seawater (S = 36) to carbonate sediments from Florida Bay after one day of equilibration (25 °C.

source of phosphate needed by plants, and represent a sink for excess amounts of phosphate from land sources. The effect of $CaCO_3$ precipitation on the adsorption of PO_4 to $CaCO_3$ was found to be unimportant except at high concentrations of PO_4. Measurements made after pre-equilibrating the added $CaCO_3$ with seawater for an hour were not affected by the co-precipitation of phosphate with $CaCO_3$. The solution composition affects the adsorption of phosphate on calcium carbonate. The effect of salinity on the adsorption is largely related to the dilution of the concentration of HCO_3^- in the waters. This may be important in estuaries where the alkalinity of the rivers may be high. Measurements made at the same level of HCO_3^- are nearly independent of salinity. The adsorption of PO_4 to $CaCO_3$ in NaCl solutions was less than in seawater at the same ionic strength and level of HCO_3^-. The higher values in seawater were due to Mg^{2+} and Ca^{2+} ions. The addition of Mg^{2+} and Ca^{2+} to NaCl increases the adsorption whereas the addition of SO_4^{2-} decreases the adsorption. The effects of Ca^{2+} and Mg^{2+} are diminished with the addition of SO_4^{2-} apparently due to the formation of $MgSO_4$ and $CaSO_4$ ion pairs and/or the adsorption of SO_4^{2-} on the surface of $CaCO_3$. Adsorption of PO_4 in solutions with the major seasalts (Na^+, Mg^{2+}, Ca^{2+}, Cl^-, HCO_3^- and SO_4^{2-}) were in good agreement with the values in seawater.

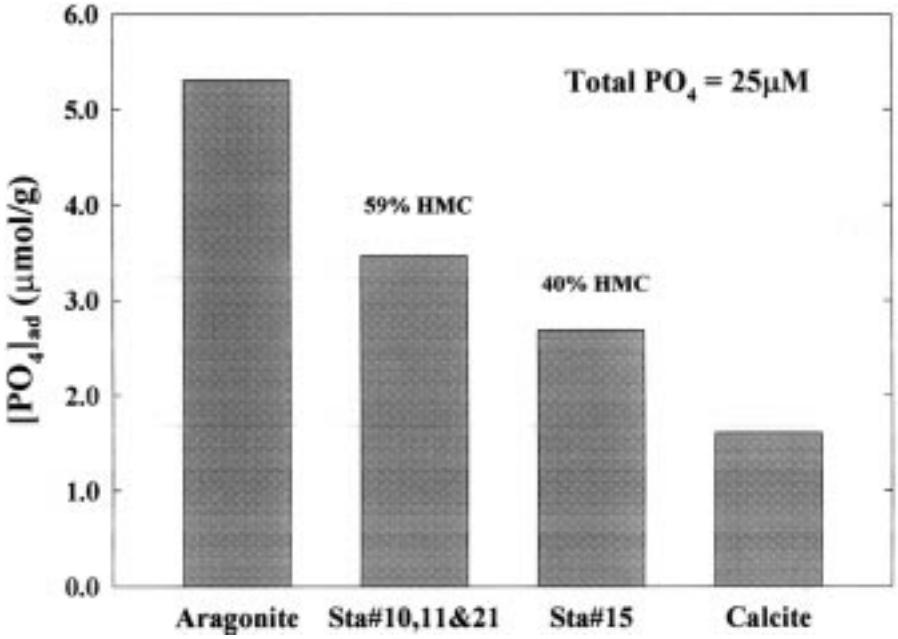


Figure 16. The comparison of adsorption of phosphate on Florida Bay carbonate sediments with pure aragonite and calcite.

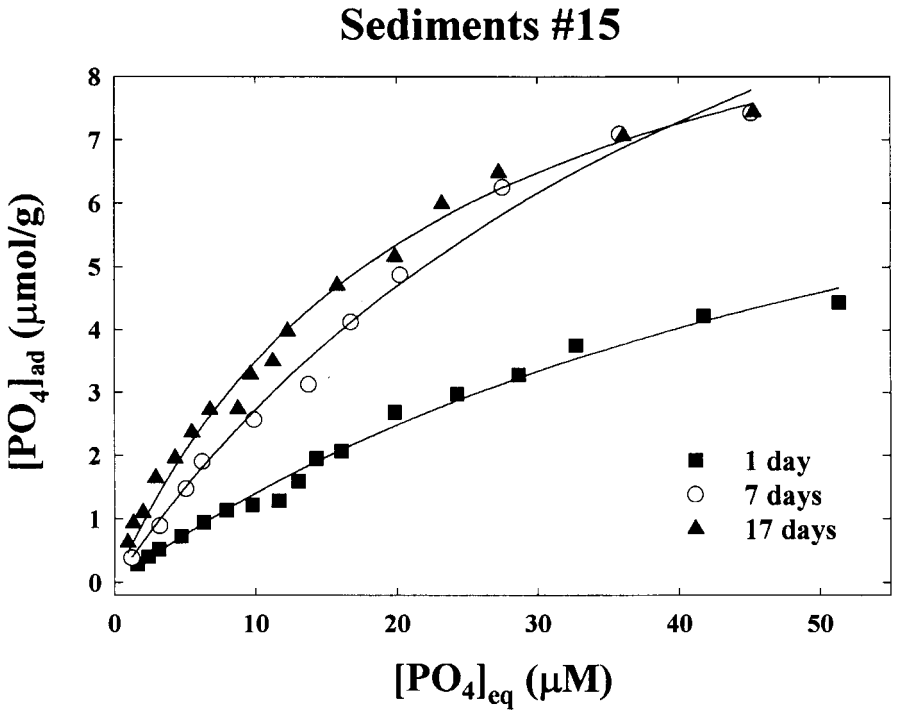


Figure 17. The effects of different equilibration time on the adsorption of phosphate on sediments from station 15.

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