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THE INFLUENCE OF Mg^{2+} ON THE ADSORPTION OF FLUORIDE BY HYDROUS OXIDES IN SEAWATER

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ABSTRACT. The interpretation of changes in dissolved fluoride concentrations in marine pore water as being an indicator of fluorapatite precipitation, carbonate mineral reactions, and alumino-silicate reactions has led to the need for a more detailed understanding of the marine geochemistry of fluorine. The speciation of F^- in seawater is dominated by the free ion (51 percent) and the MgF^+ ion pair (47 percent). The involvement of an ion in complexes or ion pairs in aqueous solution has profound effects on its adsorption behavior. In this paper we present experiments exploring the influence of MgF^+ formation on the adsorption of F^- in NaCl and major ion seawater solutions onto representative forms of amorphous iron oxyhydroxide, aluminum hydroxide, $SiO_2 \cdot nH_2O$, and hydrous manganese oxide. Experiments demonstrate that F^- adsorption in seawater is predominantly reversible and dependent on formation of MgF^+ in solution and adsorption of free F^- and co-adsorption of Mg^{2+} and F^- at particle surfaces. At pH values where little free F^- adsorbs without Mg^{2+} present (generally pH ≥ ZPC), F^- adsorption by FeOOH, δMnO_2, and $SiO_2 \cdot nH_2O$ is greatly enhanced by the presence of Mg^{2+}. The enhancement of F^- adsorption correlates with the adsorption of Mg^{2+}. At lower pH, where Mg^{2+} adsorption is minimal, F^- adsorption is reduced in the presence of Mg^{2+} compared to Mg^{2+}-free solutions. The enhanced total F^- adsorption observed for these phases can be explained by co-adsorption or ternary surface complex formation. Reduced F^- adsorption with Mg^{2+} present at low pH is due to competition between dissolved Mg^{2+} and surface sites for free F^-. Magnesium fluoride ion pair formation in seawater and its influence on F^- adsorption has important implications for the mobility and distribution of F^- in marine sedimentary and other aqueous environments.

INTRODUCTION

Changes in the concentration of the fluoride ion in marine sediment pore water have been used to indicate fluorapatite precipitation (Gaudette and Lyons, 1980; Jahnke and others, 1983; Froelich and others, 1983; Froelich and others, 1988; Ruttenberg, ms), precipitation or dissolution of calcium carbonate (Rude and Aller, 1991; Froelich and others,

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1991), and alumino-silicate mineral reactions (Shishkina, Baturin, and Bykova, 1972; Rude and Aller, 1992). Fluoride also undergoes surface sorption reactions, which are dependent on pH, particle surface composition and charge and the presence or absence of complexing ions. Variations in these properties due to diagenesis could change the amount of F^- in the dissolved pool and complicate interpretation of interstitial F^- profiles. Such release or uptake of F^- may also represent an important source or sink for dissolved F^- within the context of the global fluorine cycle.

The inorganic speciation of F^- in seawater is dominated by the MgF^+ ion pair. Here a study has been undertaken of the effect of MgF^+ formation on the sorption of F^- in NaCl and major ion seawater solutions, onto representative forms of amorphous iron oxyhydroxide, aluminum hydroxide, $SiO_2 \cdot nH_2O$, and hydrous manganese oxide. The results of this study demonstrate that F^- sorption behavior in seawater is predominantly reversible and occurs by adsorption of both free F^- and the MgF^+ ion pair (co-adsorption). MgF^+ formation in solution competes with surface sites for free F^-. The behavior is consistent with simple models of ion pairing and co-adsorption and has important implications for the mobility and distribution of F^- in diagenetic environments where pH and/or magnesium ion concentration are changing.

BACKGROUND

Fluoride forms relatively weak alkaline earth monofluoride complexes in aqueous solution, the strongest being that with magnesium ion (Tanner, Walker, and Chopin, 1968):

$$F^- + Mg^{2+} \leftrightarrow MgF^+ \tag{1}$$

$$K = \frac{[MgF^+]}{[F^-][Mg^{2+}]}. \tag{2}$$

$[F^-]$, $[Mg^{2+}]$, and $[MgF^+]$ are the free solution concentrations, and $K = 18.8$ for seawater at 25°C (Elgquist, 1970). The inorganic speciation of total F^- dissolved in seawater (salinity = 35 permil, pH = 8) is approximately divided between the free ion (51 percent) and the MgF^+ ion pair (47 percent) with minor percentages as CaF^+ (~2 percent), HF (<1 percent), and HF_2^- (<1 percent) (Elgquist, 1970; Stumm and Morgan, 1981). The concentration of Mg^{2+} in seawater (~50 mM) is 3 orders of magnitude greater than that of F^- (~70 μM) so that while speciation and, as will be shown, the adsorption of F^- are greatly influenced by the presence of Mg^{2+}, the speciation and adsorption of total Mg^{2+} is influenced negligibly by F^-.

The sorption behaviors of F^- in solutions that contain no species capable of forming solution complexes with F^- have been studied for many mineral phases. These include clays (Slavek, Farrah, and Pickering, 1984; Bar-Yosef, Afik, and Rosenberg, 1988), aluminum and iron oxides and hydroxides (Farrah, Slavek, and Pickering, 1987; Hingston,

Posner, and Quirk, 1972), calcium carbonate, humic acid, manganese dioxide, and silica (Farrah, Slavek, and Pickering, 1985), and various other soil minerals (Bower and Hatcher, 1967). Much of the existing information on F^- sorption by representative sedimentary (or soil) particle surfaces has been acquired at pH values substantially lower than that found in seawater or marine pore fluids (the marine environment has a pH range of ~6.5 to 8.5), and little work has been done in seawater. Ruttenberg (ms) performed F^- sorption experiments in artificial seawater with a variety of adsorbents in a limited pH range, although specific interactions with Mg^{2+} or reversibility were not addressed.

Fluoride adsorption is best understood in the case of hydrous iron oxides (Hingston, Posner, and Quirk, 1972; Hingston, Posner, and Quirk, 1974; Parfitt and Russell, 1977; Stumm, Kummert, and Sigg, 1980; Sigg and Stumm, 1981; Farrah and Pickering, 1986). Metal hydroxide and oxide particles in water are generally covered with surface hydroxyl groups (Schindler, 1981). pH-dependent surface charge develops at the particle surface by proton transfers:

$$\equiv SOH_2^+ \leftrightarrow \equiv SOH + H^+ \tag{3}$$

$$\equiv SOH \leftrightarrow \equiv SO^- + H^+ \tag{4}$$

where $\equiv S$ represents a surface metal atom. Adsorption or surface complex formation involving aqueous ions in many cases is then dependent on the development of surface charge and coulombic attraction between surface binding sites and aqueous ions. In other cases, specific, chemical interactions between aqueous ions and surface metal atoms dominate adsorption behavior. The phenomenon of ion complex formation in solution is comparable to the formation of surface complexes, the major difference being the electrostatic effects caused by electrical double layer formation at particle surfaces (Stumm, Kummert, and Sigg, 1980).

The pH-dependent, non-specific adsorption behavior of dissolved cations by metal hydroxides and oxides follows a pattern of minimal or no adsorption at low pH values (positive surface charge), an abrupt increase in adsorption as pH increases (more negative surface charge) called the adsorption edge, and maximum adsorption at high pH (see, for example, Schindler, 1981). Anion adsorption behavior is a mirror image with respect to pH of the cation behavior showing maximum adsorption at low pH, a decreasing adsorption edge as pH increases, and minimal or no adsorption at high pH. The exact pH dependence of these patterns will depend on the nature of the adsorbent, the adsorbate and adsorbent concentrations, and the solution composition. These patterns will also be affected when specific, chemical interactions are involved in the adsorption reaction.

The involvement of an ion in complexes or ion pairs in aqueous solution can profoundly influence the adsorption behavior of that ion (Benjamin and Leckie, 1981; Schindler, 1990), and many studies demonstrating this influence have been reported (MacNaughton and James, 1974; Davis and Leckie, 1978a; Theis and Richter, 1980; Balistrieri and

Murray, 1982a; Benjamin and Leckie, 1982; Bowers and Huang, 1987). Complexation in solution of an adsorbate can enhance or reduce its adsorption depending on the stability of the complex in solution or at the surface and the affinity of the complex for surface sites.

Benjamin and Leckie (1981) described three simple, end-member ways in which adsorption of a solution complex or ion pair may depend on pH: (1) adsorption of the complex or ion pair is analogous to and has similar pH dependence as the free cation, (2) adsorption of the complex or ion pair is similar to that of the free anion, and (3) the complex or ion pair does not adsorb at all. Adsorption of a complex or ion pair in the pH region where the free cation or metal adsorbs can be called cation-like:

$$\equiv SOH + MeL \leftrightarrow \equiv SO—MeL^- + H^+ \quad (5)$$

where MeL is the metal-ligand or cation-anion complex. Adsorption of a complex or ion pair in the pH region where the free anion adsorbs can be called anion-like:

$$\equiv SOH + H^+ + MeL \leftrightarrow \equiv SOH_2—LMe^+ \quad (6)$$

Specific adsorption (as defined by Parks, 1990) of F^- by goethite (a hydrous iron oxide) is modeled as a two-step ligand exchange reaction (Stumm, Kummert, and Sigg, 1980; Sposito, 1984):

$$\equiv SOH + H^+ \leftrightarrow \equiv SOH_2^+$$

$$\equiv SOH_2^+ + F^- \leftrightarrow \equiv SF + H_2O$$

which, combined, gives:

$$\equiv SOH + H^+ + F^- \leftrightarrow \equiv SF + H_2O \quad (7)$$

where $\equiv S$ represents a surface iron atom. This mechanism predicts greatest adsorption around the pK_a of the conjugate acid with decreasing adsorption as pH increases. This behavior has been observed experimentally (Hingston, Posner, and Quirk, 1972; Stumm, Kummert, and Sigg, 1980; Sigg and Stumm, 1981; Farrah and Pickering, 1986). Because F^- is the conjugate base of a monoprotic acid, it exhibits only one adsorption maximum as a function of pH and in general adsorbs little above the ZPC (zero point of charge; here defined as the pH value of a solution when the total net particle charge vanishes) in contrast to a multiprotic acid such as phosphoric acid (Stumm, Kummert, and Sigg, 1980). Adsorption of other anions such as Cl^- by goethite occurs due to predominantly electrostatic interactions, where the surface metal hydration is maintained:

$$\equiv FeOH + Cl^- + H^+ \leftrightarrow \equiv FeOH_2—Cl^0. \quad (8)$$

Magnesium adsorption by hydrous metal oxides is predominantly electrostatic and restricted to surfaces above the ZPC, where the surface charge

is negative (Balistrieri and Murray, 1982b; Balistrieri and Murray, 1981; McBride, 1978; Kinniburgh, Jackson, and Syers, 1976; Huang and Stumm, 1973):

$$\equiv SOH + Mg^{2+} \leftrightarrow \equiv SO—Mg^{+} + H^{+}. \quad (9)$$

Given the ion pairing behavior of F^- and Mg^{2+} in aqueous solution, we hypothesize that in addition to eq 7, the adsorption of F^- by metal hydroxides or oxides from solutions containing Mg^{2+} can take place by the following representative reaction (compare eq 5):

$$\equiv SOH + MgF^{+}_{aq} \leftrightarrow \equiv SO—MgF^{0} + H^{+} \quad (10)$$

Anion-like adsorption of the MgF^+ ion pair (see eq 6) is probably unimportant given that in this case such a reaction would increase the surface charge.

METHODS

1. Experimental procedure.—The experiments reported in this paper were designed to evaluate (1) the pH-dependence of F^- adsorption by 4 different hydrous oxides in NaCl and major ion seawater solutions, (2) the rate of F^- adsorption uptake by FeOOH in the presence and absence of Mg^{2+}, (3) the distribution of MgF^+ between the FeOOH surface and solution, (4) the F^- concentration dependence of adsorption by FeOOH and δMnO_2 in major ion seawater, and (5) the desorption of F^- by FeOOH and δMnO_2 in major ion seawater.

The choices of solid phases for these experiments were based on several factors. Amorphous iron oxyhydroxide and manganese oxide were chosen because they commonly coat particle surfaces in the marine environment, and their surface properties and general adsorption characteristics are well studied. The Si and Al compounds chosen represent other common types of inorganic surface groups found in the marine environment.

The conditions of the various experiments, including the pH-range, adsorbent concentration, F^- and Mg^{2+} concentration, and solution type, are presented in table 1. Adsorbent characteristics are shown in table 2. Further information about adsorbents, solution preparations, and experimental procedures is given below.

2. Solutions and adsorbents.—Deionized water, which was subsequently sterilized by heating, was used for the solutions of this study. The major ion artificial seawater (ASW) preparation contained Na^+, K^+, Mg^{2+}, Ca^{2+}, Sr^{2+}, Cl^-, SO_4^{2-}, CO_3^{2-}, Br^-, and borate (reagent grade salts; Parsons, Yoshiaki, and Lalli, 1984). NaCl was used to adjust solutions without Mg^{2+} to the proper ionic strength.

Amorphous iron oxyhydroxide (FeOOH) was precipitated by either adding KOH to a $Fe(NO_3)_3$ solution (pH-dependence, adsorption uptake rate, and MgF^+ distribution experiments) or adding NaOH to a $FeCl_3$ solution (desorption and concentration dependence experiments). Hydrous manganese oxide (δMnO_2) was prepared following the procedure

of Murray (1974). $MnCl_2$ solution was added dropwise to a solution of $KMnO_4$ maintained at pH ~ 9 with KOH. The O:Mn ratio of this solid is 2.0 (Aller and Rude, 1988). $SiO_2 \cdot nH_2O$ (CAS no. 1343-98-2) and $Al(OH)_3 \cdot nH_2O$ (CAS no. 21645-51-2) were reagent grade compounds

TABLE 1

Experimental conditions for adsorption experiments. $[Mg^{2+}]$ and $[F^-]$ indicate the total (dissolved and adsorbed) concentrations of these species

Experiment	Solid	Solution	$[Mg^{2+}]$ (mM)	$[F^-]$ (μM)
pH-dependence	FeOOH	1.) NaCl (I = 0.7)	0	200
	14.5 g/l	2.) NaCl (I = 0.7)	66	200
	pH = 4.9–9.5	3.) ASW (I = 0.7)	0	200
		4.) ASW (I = 0.7)	66	200
	δMnO_2	1.) NaCl (I = 0.7)	0	200
	34.8 g/l	2.) NaCl (I = 0.7)	70	200
	pH = 3–9	3.) ASW (I = 0.7)	0	200
		4.) ASW (I = 0.7)	70	200
	$SiO_2 \cdot nH_2O$	1.) NaCl (I = 0.7)	0	200
	33.3 g/l	2.) NaCl (I = 0.7)	53	200
	pH = 3–9	3.) ASW (I = 0.7)	0	200
		4.) ASW (I = 0.7)	53	200
	$Al(OH)_3$	1.) NaCl (I = 0.7)	0	200
	50 g/l	2.) NaCl (I = 0.7)	53	200
	pH = 3.3–9.3	3.) ASW (I = 0.7)	0	200
		4.) ASW (I = 0.7)	53	200
Adsorption uptake rate	FeOOH	1.) ASW (I = 0.6)	0	200
	14.5 g/l	2.) ASW (I = 0.6)	57.5	200
	pH = 8.1			
MgF^+ distribution	FeOOH	1.) NaCl (I = 0.7)	31.5	310–6150
	14.5 g/l			
	pH = 8.8			
Desorption and concentration dependence	FeOOH	1.) ASW (I = 0.6)	60	50–250
	17.4 g/l			
	pH = 7–8			
	δMnO_2	1.) ASW (I = 0.6)	57	50–250
	24.1 g/l			
	pH = 7–8			

TABLE 2

Adsorbent descriptions. ZPC = zero point of charge. Numbers in parenthesis refer to references below

Solid	ZPC	Surface area (m^2/g)
FeOOH	~8 (1)	600 (1)
δMnO_2	~1.5 (2)	290 (3)
$SiO_2 \cdot nH_2O$	?	456 (4)
$Al(OH)_3 \cdot nH_2O$	~8–9 (5, 6)	—

(1) Davis and Leckie, 1978b.
(2) Balistrieri and Murray, 1982.
(3) Catts and Langmuir, 1986.
(4) Mackin and Swider, 1987.
(5) Kinniburgh and Jackson, 1981.
(6) Huang and Stumm, 1973.

(Fisher) and have water of hydration equal to 8 and 35 percent respectively (based on loss on ignition). Each experiment used one batch of precipitate (FeOOH and δMnO_2) or reagent powder ($SiO_2 \cdot nH_2O$ and $Al(OH)_3$) as adsorbent. Repeats of some experiments (not shown) indicate no noticeable difference between batches. The point of zero charge and surface area parameters were not determined on the actual adsorbents used in this study; these parameters were determined by previous workers on similarly prepared adsorbents (see table 2). Characterization of Mg^{2+} adsorption behavior on these adsorbents largely substantiates these assumed values and acts as an internal experimental "standard."

3. pH-dependence experiments.—This experiment was designed to examine the uptake (presumably adsorption) of F^- and Mg^{2+} by the four adsorbents over a range of pH. NaCl and ASW solutions, with and without Mg^{2+} at seawater concentration, were used to demonstrate the effect of Mg^{2+} on F^- adsorption behavior and to determine the effect of other seawater components on the relationship between F^- adsorption and the presence or absence of Mg^{2+}.

Solid phases were rinsed with distilled water and then 'equilibrated' over 2 to 3 days with one of four solutions described in table 1. Freshly precipitated, hydrous material can undergo changes in crystallinity and mineralogy on a week or month time scale (Davis and Leckie, 1978b). On the time scale of these experiments, however, the mineral surfaces are assumed to be changing negligibly and a quasi-equilibrium state was reached on the time scale of hours (see uptake rate experiment below). Repeats of the experiments (not shown) suggest that this assumption is valid with respect to the properties measured here. In solutions with Mg^{2+} added, Mg^{2+} uptake was monitored during equilibration and was complete within ~1 to 2 days at the solution/solid ratios used. The amount of Mg^{2+} adsorbed after equilibration with solutions (before addition of F^-) was determined by separate experiments of Mg^{2+} uptake. Total Mg^{2+} (dissolved and adsorbed) was calculated by adding the amount adsorbed during equilibration to the dissolved mass remaining in solution.

The pH of adsorbent slurries was adjusted to a range of values by addition of small volumes of concentrated NCl or NaOH and rechecked ~5 and 24 hrs later. A total concentration of 200 μM F^- in each reaction vial containing 15 ml of slurry was then achieved by addition of 30 μl of 100 mM NaF. Vials were shaken regularly over ~24 hrs. An aliquot of solution was filtered (0.45 μ) and analyzed for F^- and Mg^{2+}; final pH was measured on the remaining solution. The amounts of F^- and Mg^{2+} adsorbed were determined by difference. Blank runs without adsorbent yielded ≥95% F^- recovery. $Mg(OH)_2$ and MgF_2 precipitation were ruled out by solubility calculations.

4. Adsorption uptake rate experiment.—This experiment was designed to examine F^- adsorption uptake rate and determine if the effect of Mg^{2+} on the amount of F^- adsorption is a function of experiment duration. A series of vials containing equal amounts of FeOOH were equilibrated with artifical seawater with and without Mg^{2+} and adjusted to pH 8.1 (see

table 1). A pH of 8.1 was chosen so that Mg^{2+}-F^- co-adsorption would be significant in the ASW treatment with Mg^{2+}. F^- was added to give a total concentration of 200 μM, and its loss from solution by adsorption was monitored over ~ 14 days.

5. MgF^+ distribution between solution and adsorbent surface.—The distribution of MgF^+ between the FeOOH surface and solution at pH = 8.8 was examined in an experiment where the total Mg^{2+} concentration was held constant and the total F^- concentration was varied. At a pH of 8.8, it is assumed that all the F^- adsorbed is co-adsorbed with Mg^{2+}. Vials containing equilibrated FeOOH suspensions were spiked with Mg^{2+} to give $[Mg^{2+}]_T$ = 31.5 mM. F^- was added to give a range of $[F^-]_T$ = 310 – 6,150 μM. After ~ 24 hrs, solutions were filtered, and dissolved Mg^{2+} and F^- were measured.

6. F^- adsorption concentration dependence and desorption.—Artificial seawater slurries of FeOOH and δMnO_2, adjusted to a range of pH values typical of the marine environment, were spiked with F^- and left over night. Adsorption of F^- was determined as in the earlier experiments. Desorption of F^- was measured by rinsing the slurries from the adsorption concentration dependence experiments (previously concentrated by centrifugation) with F^--free artificial seawater and analyzing for F^- in the rinse solutions. Rinsing time and desorption procedure followed that of the initial adsorption procedure.

7. Analytical techniques.—Fluoride was measured with an ion selective electrode (Frant and Ross, 1966) by a method of standard additions (Rix, Bond, and Smith, 1976) modified for use with small sample volumes. Total ionic strength adjustment buffer (TISAB III, Orion) was added as a decomplexer and pH adjuster; further pH adjustments were done with sodium acetate. Samples were allowed to stand for ~ 1 to 2 hrs to allow any F^- solution complexes to decompose. Ten replicates of Long Island Sound seawater ($[Cl^-]$ = 0.417 M) gave 1.4 percent precision (1 σ) and a F/Cl of 129 μmole/mole (Stumm and Morgan, 1981, report a seawater F/Cl of 124 μmole/mole). Mg^{2+} was determined by atomic adsorption spectroscopy (air/acetylene flame, samples diluted in 1 mg La/ml in 0.6 M HCl, precision is better than 3 percent). pH was determined by glass electrode (Ag/AgCl reference) with NBS traceable buffers.

RESULTS AND DISCUSSION

Final solution concentrations of F^- and Mg^{2+}, pH, K_F, and K_{Mg} in the pH-dependence experiments with FeOOH, δMnO_2, $SiO_2 \cdot nH_2O$, and $Al(OH)_3$ are given in tables 3 to 6. The distribution coefficients, K_F and K_{Mg}, were calculated for the experimental solutions by:

$$K_i = \frac{\text{mass of adsorbed species/mass of adsorbent}}{\text{mass of solute species/volume of solution}} \qquad (11)$$

This formulation accounts for F^- adsorption taking place by any of the mechanisms described in eqs 7 or 10. It is not a thermodynamic constant.

Nevertheless, the degree of F^- adsorption is directly related to the total analytical concentration of dissolved F^- and the presence or absence of Mg^{2+}, and thus, K_F and K_{Mg} are useful for internal comparison.

1. pH dependence of free F^- and Mg^{2+} adsorption.—The pH-dependence of free F^- adsorption generally agrees with the behavior indicated by eq 7 or an analogous outer-sphere reaction. Adsorption of F^- in NaCl and major ion artificial seawater solutions by FeOOH and $Al(OH)_3$ in the absence of Mg^{2+} exhibits a regular pattern of negligible adsorption above the ZPC and increasing adsorption below the ZPC (figs. 1A and 4A). Adsorption of F^- by δMnO_2 exhibits a similar pattern to FeOOH and $Al(OH)_3$ (fig. 2A) except that there is significant adsorption above the ZPC (the assumed ZPC is substantiated by Mg^{2+} behavior). This suggests that other than electrostatic interactions influence F^- adsorption by δMnO_2. Adsorption of F^- by $SiO_2 \cdot nH_2O$ is restricted to pH values below ~6.5 (fig. 3A). The ZPC of $SiO_2 \cdot nH_2O$ used in this study is not well defined (but see below). Adsorption of F^- by $Al(OH)_3$ exhibits a maximum at pH = 5 (fig. 4A) and then decreases at lower pH probably due to formation of soluble Al-F complexes (see, for example, Farrah, Slavek, and Pickering, 1987).

Adsorption of Mg^{2+} by FeOOH, and δMnO_2 is generally restricted to pH values greater than the ZPC and increases with increasing pH (figs. 1B and 2B). Adsorption of Mg^{2+} by $SiO_2 \cdot nH_2O$ (fig. 3B), which is predominantly electrostatic, is restricted to pH values greater than ~7 suggesting that the ZPC of this material is near this value. Significant Mg^{2+} adsorption by FeOOH below the ZPC occurs (K_{Mg} = 16, see table 3), which agrees with site-binding models predicting adsorption of Mg^{2+} by goethite down to at least a pH of 5 (Balistrieri and Murray, 1981). Previous experiments with Al-hydroxides at adsorbent concentrations comparable to those reported here show that Mg^{2+} is adsorbed by Al-hydroxides at a pH of ~8 to 9 (McBride, 1978; Kinniburgh, Jackson, and Syers, 1976; Huang and Summ, 1973). This suggests that the lack of Mg^{2+} adsorption by $Al(OH)_3$ in the present experiments (fig. 4B) indicates a ZPC greater than ~9.

2. The influence of Mg^{2+} on F^- adsorption.—The presence of Mg^{2+} in solution affects the degree of F^- adsorption relative to solutions without Mg^{2+} in two ways. First, at pH values greater than 8, 5.5, and 7 for FeOOH, δMnO_2, and $SiO_2 \cdot nH_2O$ respectively, F^- adsorption is enhanced by the presence of Mg^{2+} compared to solutions without Mg^{2+} (figs. 1A, 2A, and 3A). For example, K_F for FeOOH equals 33 with Mg^{2+} present compared to 3.4 without Mg^{2+} present in the NaCl solution at pH 8.5 (table 3 and fig. 1A). A comparable difference in K_F at high pH is observed in the ASW treatment (table 3). Comparably greater K_F's (and the percent adsorbed) are observed for F^- adsorption with Mg^{2+} present by δMnO_2 and $SiO_2 \cdot nH_2O$ at high pH (tables 4 and 5; figs. 2A and 3A). The enhancement of F^- adsorption by FeOOH, δMnO_2, and $SiO_2 \cdot nH_2O$ (figs. 1–3) at high pH in both the NaCl and ASW solutions correlates with the pH-dependent adsorption of Mg^{2+} in the same solution. The lack of

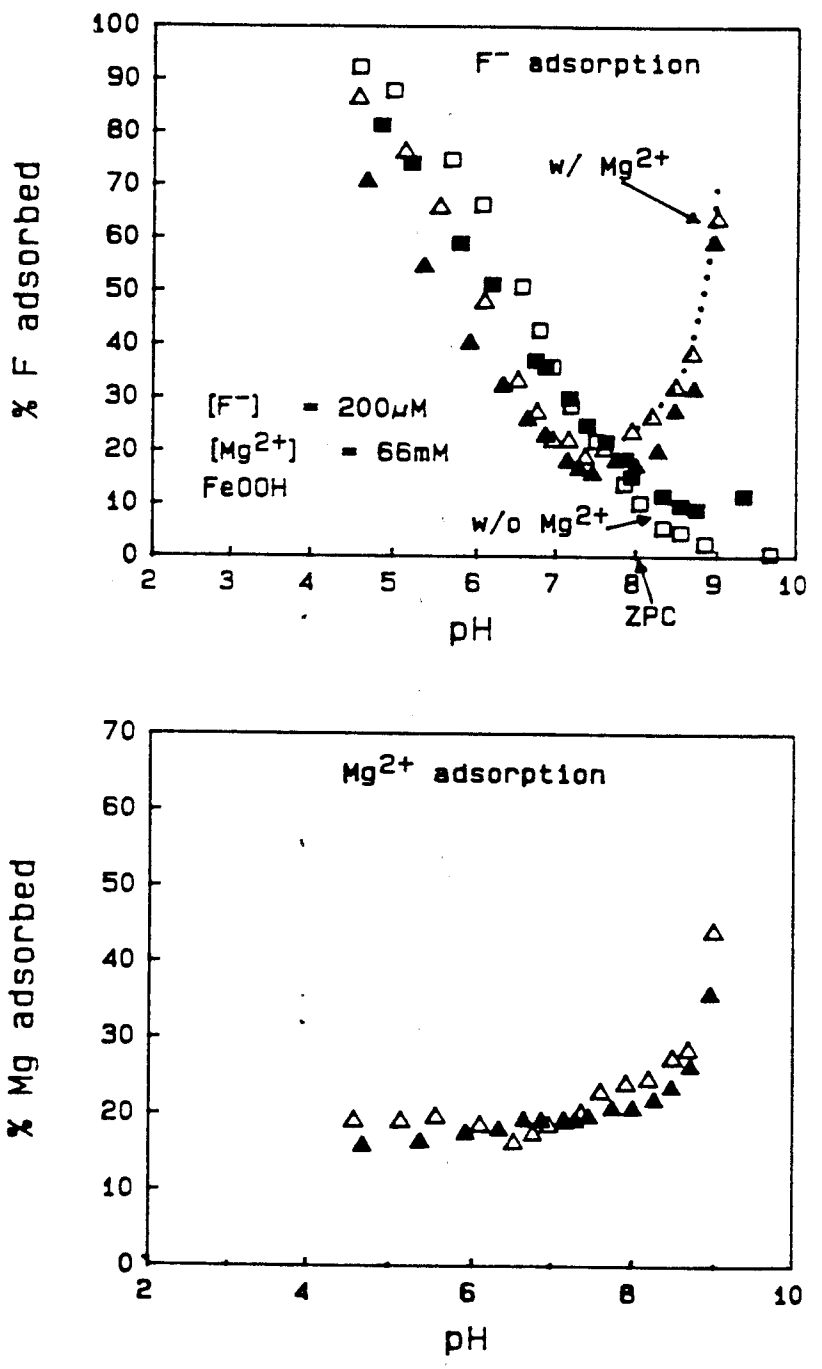


Fig. 1(A) pH-dependence of fluoride adsorption by amorphous iron oxyhydroxide (FeOOH) in the presence and absence of Mg^{2+}. (B) Mg^{2+} adsorption by FeOOH from the same experiment. The presence of Mg^{2+} in solution greatly enhances F^- adsorption at pH ≥ ZPC presumably by co-adsorption. At pH below the apparent ZPC, F^- adsorption is reduced in the presence of Mg^{2+} by MgF^+ formation in solution. Symbols: open square = NaCl; open triangle = NaCl with 53 mM Mg^{2+}; solid square = ASW without Mg^{2+}; solid triangle = ASW with Mg^{2+}; ionic strength in all solutions is 0.7, adjusted with NaCl. $[F^-]$ = 200 μM and $[Mg^{2+}]$ = 66 mM (dissolved and adsorbed); [FeOOH] = 14.5g/l; ZPC = zero point of charge (see text).

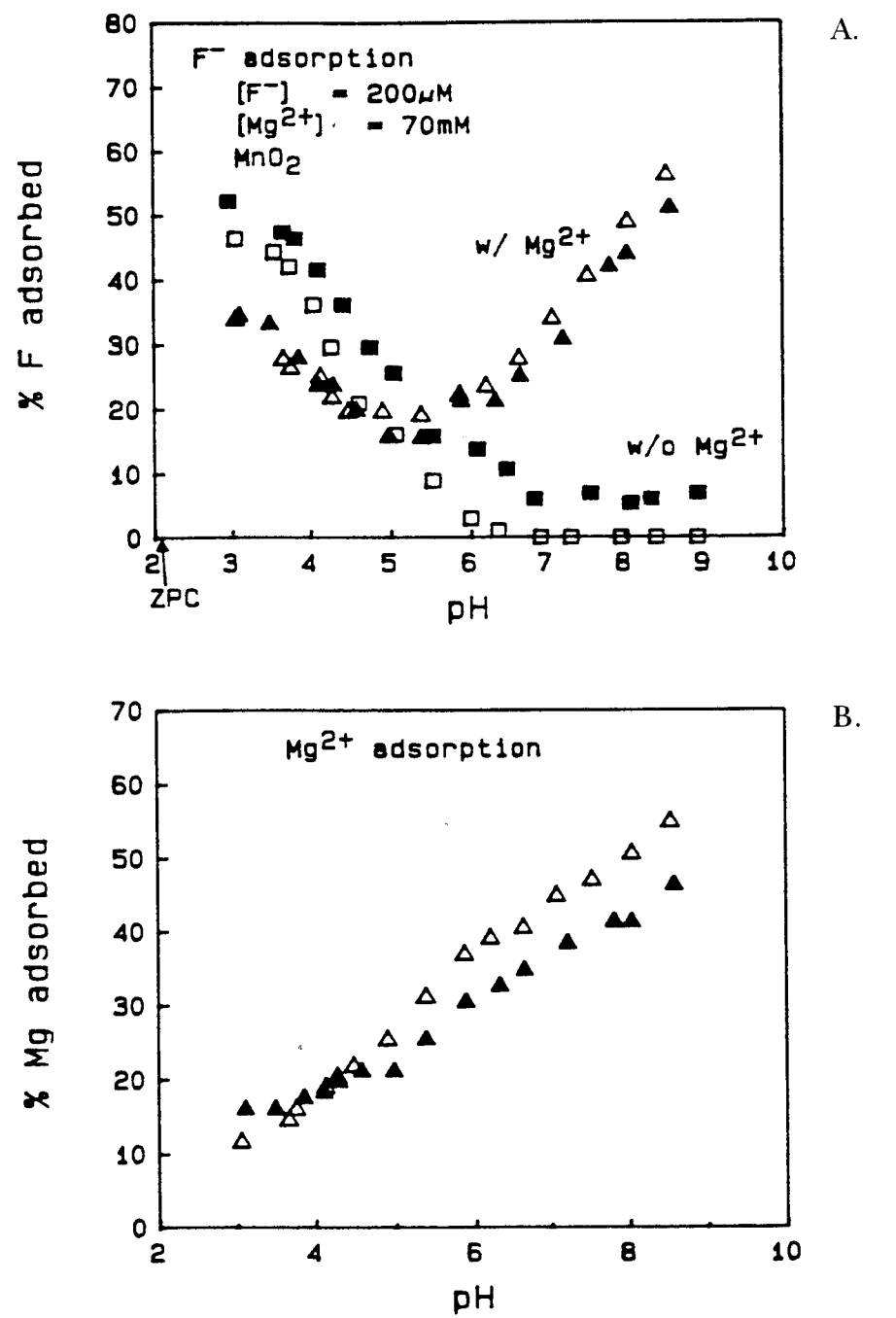


Fig. 2(A) pH-dependence of fluoride adsorption by hydrous manganese oxide (δMnO_2) in the presence and absence of Mg^{2+}. (B) Mg^{2+} adsorption by δMnO_2 from the same experiment. The presence of Mg^{2+} in solution greatly enhances F^- adsorption at pH $\geq$ 5 by co-adsorption of Mg^{2+} and F^-. At pH $\leq$ 5, F^- adsorption is reduced in the presence of Mg^{2+} by MgF^+ formation in solution. Symbols as in figure 1. [F^-] = 200 μM and [Mg^{2+}] = 70 mM (dissolved and adsorbed); [δMnO_2] = 34.8 g/l; ZPC = zero point of charge (see text).

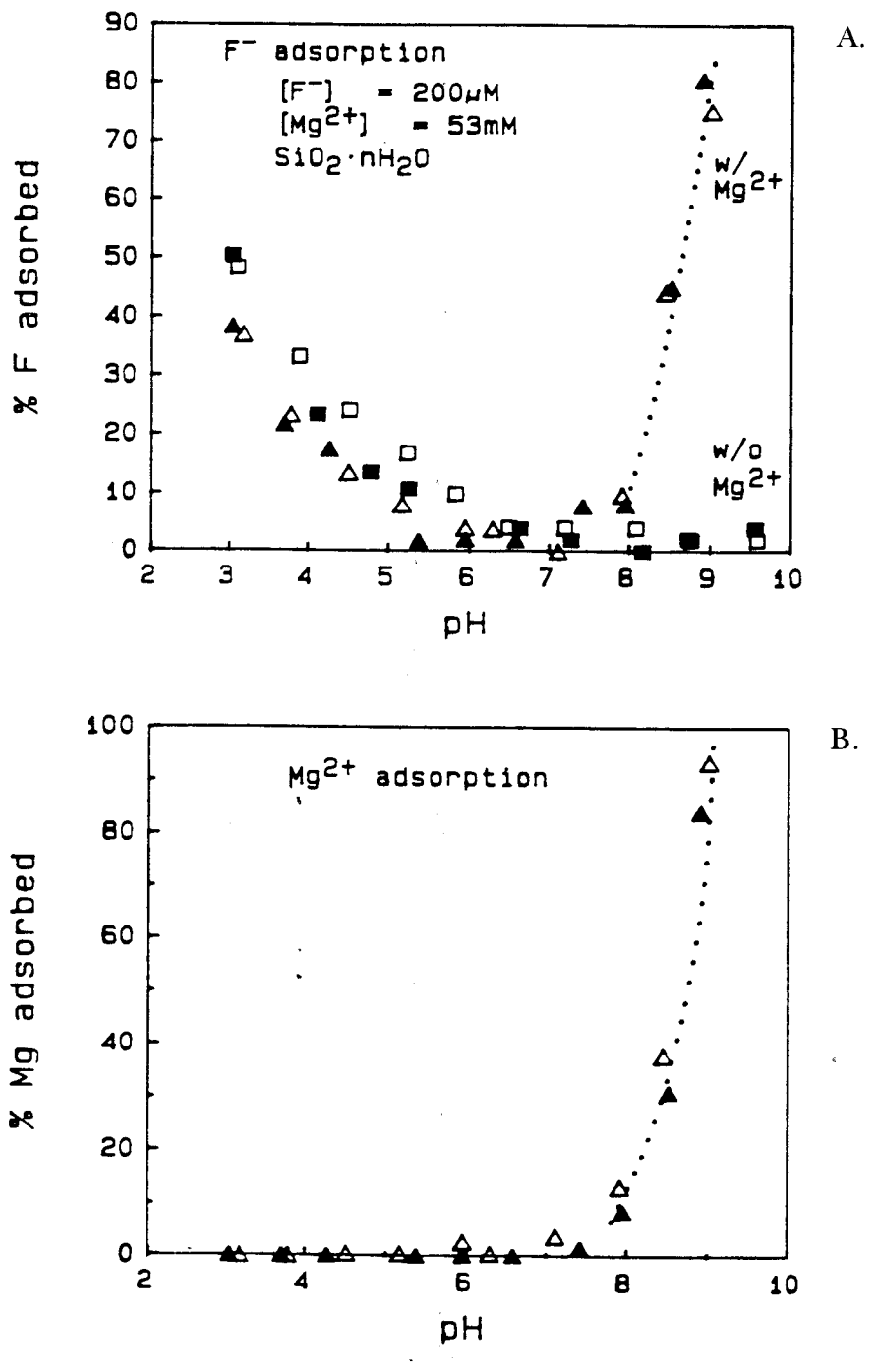


Fig. 3(A) pH-dependence of fluoride adsorption by $SiO_2 \cdot nH_2O$ in the presence and absence of Mg^{2+}. (B) Mg^{2+} adsorption by $SiO_2 \cdot nH_2O$ from the same experiment. The presence of Mg^{2+} in solution greatly enhances F^- adsorption at pH $\geq$ 7 by co-adsorption with Mg^{2+}. At pH $\geq$ 7, F^- adsorption is slightly reduced in the presence of Mg^{2+} by formation of MgF^+ in solution. Symbols as in figure 1. $[F^-]$ = 200 μM and $[Mg^{2+}]$ = 53 mM (dissolved and adsorbed); $[SiO_2 \cdot nH_2O]$ = 33.3 g/l; ZPC $\approx$ 7 (see text).

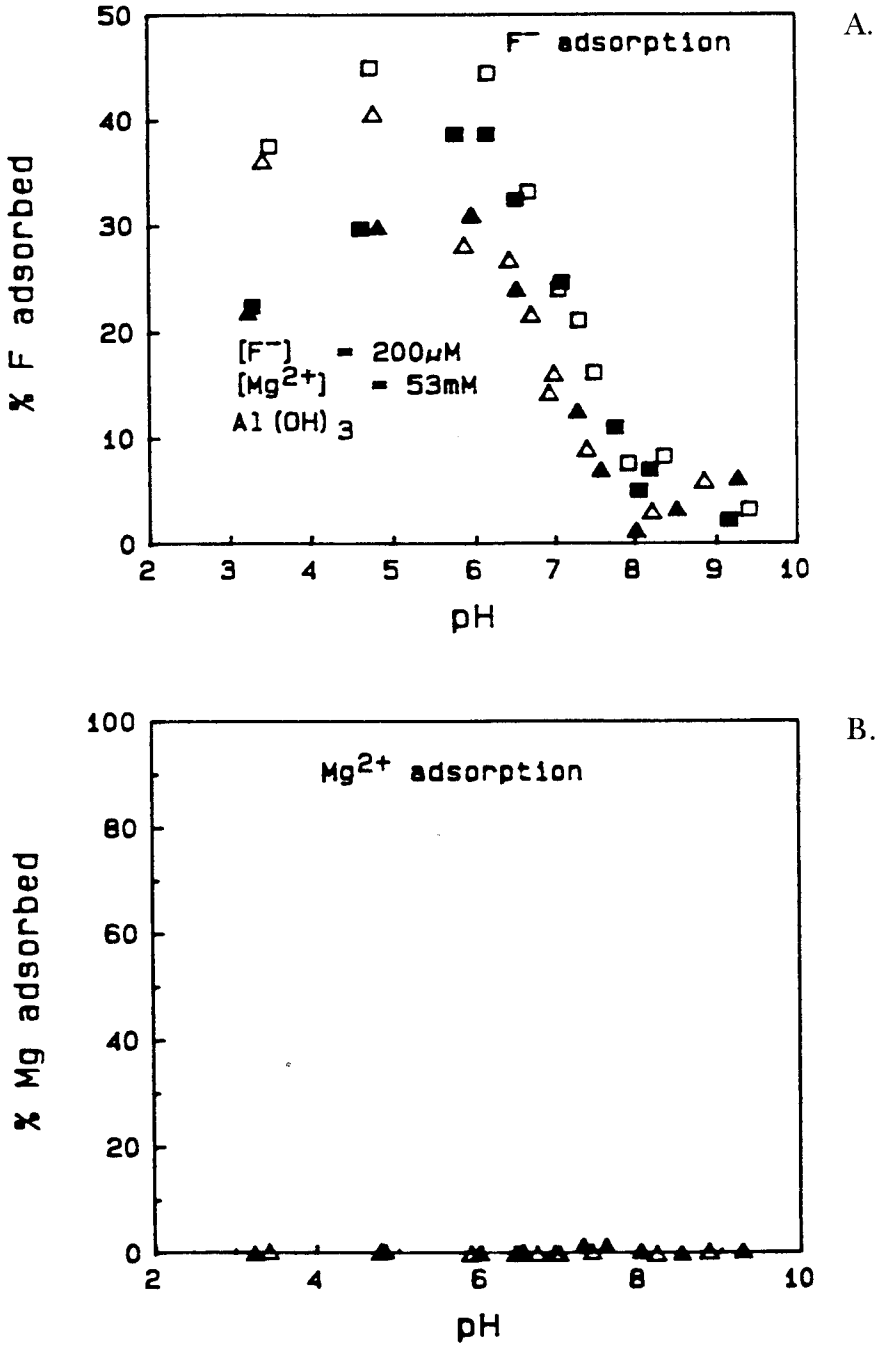


Fig. 4(A) pH-dependence of fluoride adsorption by $Al(OH)_3 \cdot nH_2O$ ($Al(OH)_3$) in the presence and absence of Mg^{2+}. (B) Mg^{2+} adsorption by $Al(OH)_3$ from the same experiment. The presence of Mg^{2+} in solution does not enhance F^- adsorption, but it does reduce adsorption in the pH range 5 to 8 by MgF^+ formation in solution. Symbols as in figure 1. $[F^-] = 200$ μM and $[Mg^{2+}] = 53$ mM (dissolved and adsorbed); $[Al(OH)_3] = 50$ g/l; ZPC ≈ 9 (see text).

TABLE 3

Final solution concentrations of $[F^-]$ (μM) and $[Mg^{2+}]$ (mM), pH, K_F, and K_{Mg} in the pH-dependent adsorption experiment with FeOOH. K_F and K_{Mg} are the adsorption coefficients for F^- and Mg^{2+} (ml/g FeOOH, see text). The total F^- and Mg^{2+} concentrations (adsorbed and dissolved), were 200 μM and 66 mM, respectively. These data are plotted in figure 1, but percent adsorbed is used instead of K_F and K_{Mg}

FeOOH														
NaCl								Artificial Seawater						
Without Mg			With Mg					Without Mg			With Mg			
pH	$[F^-]$	K_F	pH	$[F^-]$	$[Mg^{2+}]$	K_F	K_{Mg}	pH	$[F^-]$	K_F	pH	$[F^-]$	$[Mg^{2+}]$	K_F	K_{Mg}
4.60	15.9	800	4.58	26.5	53.1	450	17	4.86	37.6	270	4.65	58.1	55.3	170	13
5.00	24.9	490	5.14	46.7	53.1	230	17	5.21	51.9	200	5.37	90.1	55.0	84	14
5.69	51.0	200	5.55	67.8	52.8	140	17	5.79	82.2	99	5.91	119	54.2	47	15
6.06	65.0	140	6.09	103	53.5	65	16	6.19	97.6	73	6.33	135	53.9	33	16
6.56	98.9	71	6.51	133	55.0	35	14	6.74	126	41	6.64	148	53.1	25	17
6.79	115	51	6.76	145	54.2	26	15	6.87	128	39	6.87	154	53.1	21	17
6.96	129	38	6.96	155	53.5	20	16	7.17	140	30	7.15	163	53.1	16	17
7.19	144	27	7.16	155	53.1	20	17	7.39	150	23	7.30	166	53.1	14	17
7.51	157	19	7.37	162	52.4	17	17	7.63	157	19	7.46	168	52.8	13	17
7.86	173	11	7.60	162	50.6	18	21	7.87	163	16	7.75	163	52.0	16	19
8.06	180	7.9	7.95	152	49.9	22	22	7.95	170	12	8.00	165	52.0	15	19
8.34	189	4.1	8.20	146	49.5	25	23	8.33	177	9.1	8.27	160	51.3	18	20
8.56	191	3.4	8.49	135	47.7	33	27	8.55	181	7.5	8.48	144	50.2	27	22
8.85	195	1.8	8.68	123	46.9	44	28	8.75	182	6.8	8.71	136	48.4	32	25
9.66	199	0.4	8.99	72.0	36.7	120	55	9.33	177	9.1	8.95	81.3	42.2	100	39

enhanced F^- adsorption by $Al(OH)_3$ is consistent with the lack of Mg^{2+} adsorption.

Secondly, at pH values where Mg^{2+} adsorption is a minimum or does not occur, F^- adsorption is reduced by the presence of Mg^{2+} compared to solutions without Mg^{2+} (figs. 1A, 2A, 3A, and 4A); this is observed for both NaCl and ASW solutions. The reduction in adsorption corresponds to about a factor of 2 difference in K_F (tables 3-6). There are only slight differences (typically 0.5 pH unit shifts) in the pH-dependent adsorption behavior of F^- between the NaCl and major ion artificial seawater treatments for all adsorbents indicating that Mg^{2+} is the dominant influence on the F^- adsorption behavior observed. The slightly elevated K_F for FeOOH and δMnO_2 in ASW without Mg^{2+}, above pH values where free F^- adsorbs, is probably due to adsorption of the weaker CaF^+ ion pair (fig. 1A and 2A; $[Ca^{2+}] = 10$ mM).

The possibility that the relative enhancement of F^- adsorption at high pH in these experiments was due to different uptake rates of F^- and MgF^+ during adsorption was tested by examining a time series of F^- adsorption by FeOOH with and without Mg^{2+} present in the solutions (fig. 5). Adsorption of F^- in solutions with and without Mg^{2+} (pH = 8.1) was essentially complete and stable in ~30 min. The enhancement of F^- adsorption with Mg^{2+} present in solution existed throughout the 14 day experiment.

TABLE 4

Final solution concentrations of $[F^-]$ (μM) and $[Mg^{2+}]$ (mM), pH, K_F, and K_{Mg} in the pH-dependent adsorption experiment with δMnO_2. K_F and K_{Mg} are the adsorption coefficients for F^- and Mg^{2+} (ml/g δMnO_2, see text). The total F^- and Mg^{2+} concentrations (adsorbed and dissolved), were 200 μM and 70 mM, respectively. These data are plotted in figure 2, but percent adsorbed is used instead of K_F and K_{Mg}

δMnO_2														
NaCl								Artificial Seawater						
Without Mg			With Mg					Without Mg			With Mg			
pH	$[F^-]$	K_F	pH	$[F^-]$	$[Mg^{2+}]$	K_F	K_{Mg}	pH	$[F^-]$	K_F	pH	$[F^-]$	$[Mg^{2+}]$	K_F	K_{Mg}
3.05	107	25	3.05	132	61.8	15	3.8	2.96	95.7	31	3.10	131	58.7	15	5.5
3.55	112	23	3.66	144	59.7	11	5.0	3.66	106	26	3.49	133	58.7	15	5.5
3.75	116	21	3.75	147	58.7	11	5.5	3.81	107	25	3.85	144	57.7	11	6.1
4.05	128	16	4.13	149	56.7	9.7	6.7	4.10	117	20	4.11	152	57.2	9.0	6.4
4.27	141	12	4.27	156	55.7	8.2	7.4	4.41	128	16	4.29	152	56.2	9.0	7.1
4.61	158	7.6	4.47	160	54.7	7.1	8.0	4.75	141	12	4.57	160	55.2	7.2	7.7
5.06	168	5.5	4.89	160	52.1	7.1	9.9	5.04	149	9.9	4.98	168	55.2	5.4	7.7
5.52	182	7.8	5.37	161	48.1	6.9	13	5.52	168	5.4	5.38	168	52.1	5.4	9.9
6.00	194	0.9	5.86	155	44.1	8.3	17	6.08	173	4.6	5.88	157	48.6	7.9	13
6.34	198	0.3	6.19	152	42.5	9.0	19	6.46	179	3.4	6.31	157	47.1	7.9	14
6.91	202	0	6.63	144	41.5	11	20	6.83	188	1.8	6.64	149	45.6	9.8	15
7.31	206	0	7.08	132	38.5	15	24	7.56	186	2.1	7.22	138	43.0	13	18
7.95	211	0	7.53	118	37.0	20	26	8.07	189	1.7	7.81	116	41.0	21	20
8.39	206	0	8.04	102	34.4	28	30	8.33	188	1.8	8.03	112	41.0	23	20
8.91	202	0	8.53	87.0	31.4	37	35	8.92	186	2.1	8.58	97.5	37.5	30	25

TABLE 5

Final solution concentrations of $[F^-]$ (μM) and $[Mg^{2+}]$ (mM), pH, K_F, and K_{Mg} in the pH-dependent adsorption experiment with $SiO_2 \cdot nH_2O$. K_F and K_{Mg} are the adsorption coefficients for F^- and Mg^{2+} (ml/g $SiO_2 \cdot nH_2O$, see text). The total F^- and Mg^{2+} concentrations (adsorbed and dissolved), were 200 μM and 53 mM, respectively. These data are plotted in figure 3, but percent adsorbed is used instead of K_F and K_{Mg}

$SiO_2 \cdot nH_2O$														
NaCl								Artificial Seawater						
Without Mg			With Mg					Without Mg			With Mg			
pH	$[F^-]$	K_F	pH	$[F^-]$	$[Mg^{2+}]$	K_F	K_{Mg}	pH	$[F^-]$	K_F	pH	$[F^-]$	$[Mg^{2+}]$	K_F	K_{Mg}
3.10	104	19	3.17	126	53.5	18	0	3.03	100	30	3.03	124	53.5	19	0
3.90	134	15	3.79	154	53.5	9.0	0	4.13	154	9.0	3.71	157	54.1	8.2	0
4.53	152	9.4	4.51	173	52.8	4.6	0.1	4.78	173	4.7	4.28	165	54.7	6.3	0
5.24	167	6.0	5.17	184	52.8	2.6	0.1	5.25	179	3.6	5.37	197	54.7	0.5	0
5.83	180	3.3	5.95	192	51.6	1.3	0.8	—	—	—	5.95	196	54.7	0.6	0
6.48	192	1.3	6.28	192	52.8	1.2	0.1	6.63	192	1.2	6.57	196	54.7	0.6	0
7.20	192	1.3	7.11	201	51.0	0	1.2	7.28	196	0.6	7.42	184	52.2	2.5	0.5
8.09	192	1.2	7.91	181	46.0	3.2	4.6	8.17	205	0	7.95	184	48.5	2.6	2.8
8.77	196	0.6	8.45	162	32.9	16	18	8.74	196	0.7	8.52	110	36.6	25	13
9.58	196	0.6	9.01	49.6	3.50	91	424	9.56	192	1.2	8.91	39	8.49	120	157

TABLE 6

Final solution concentrations of $[F^-]$ (μM) and $[Mg^{2+}]$ (mM), pH, K_F, and K_{Mg} in the pH-dependent adsorption experiment with $Al(OH)_3$. K_F and K_{Mg} are the adsorption coefficients for F^- and Mg^{2+} (ml/g $Al(OH)_3$, see text). The total F^- and Mg^{2+} concentrations (adsorbed and dissolved), were 200 μM and 53 mM, respectively. These data are plotted in figure 4, but percent adsorbed is used instead of K_F and K_{Mg}

$Al(OH)_3$														
NaCl								Artificial Seawater						
Without Mg			With Mg					Without Mg			With Mg			
pH	$[F^-]$	K_F	pH	$[F^-]$	$[Mg^{2+}]$	K_F	K_{Mg}	pH	$[F^-]$	K_F	pH	$[F^-]$	$[Mg^{2+}]$	K_F	K_{Mg}
3.52	125	12	3.43	128	52.8	11	0.1	3.29	155	5.8	3.24	156	53.5	5.6	0
4.75	110	16	4.78	119	52.8	14	0.1	4.62	141	8.4	4.83	140	52.8	8.5	0.1
6.17	111	16	5.87	144	53.5	7.8	0	5.77	123	13	5.96	138	52.8	10	0.1
6.67	134	9.9	6.42	146	53.5	7.3	0	6.15	123	12	5.97	138	52.8	9.0	0.1
7.05	152	6.3	6.70	157	53.5	5.5	0	6.51	135	9.6	6.52	152	52.8	6.3	0.1
7.31	158	5.3	6.92	171	53.5	3.3	0	7.09	151	6.6	7.29	175	52.8	2.9	0.1
7.50	168	3.9	6.98	168	54.1	3.8	0	7.76	178	2.5	7.58	186	52.8	1.5	0.1
7.93	185	1.6	7.40	182	52.8	2.0	0.1	8.05	190	1.1	8.02	197	52.8	0.3	0.1
8.36	184	1.8	8.21	194	53.5	0.6	0	8.19	186	1.5	8.5	193	52.8	1.7	0.1
9.39	194	0.7	8.85	188	52.8	1.3	0.1	9.15	196	0.5	9.26	188	52.8	1.3	0.1

Whether the adsorption reaction depicted in eq 10 occurs for these adsorbents can be evaluated with the data collected. Rigorous, thermodynamic analysis demands better characterization of adsorbent surface parameters. The enhanced total F^- adsorption (or increased K_F) observed for FeOOH, δMnO_2, and $SiO_2 \cdot nH_2O$ at high pH values (generally above the ZPC), which co-occurs with Mg^{2+} adsorption, can be explained by co-adsorption or ternary surface complex formation.

$$\equiv SOH + F^- + Mg^{2+} \leftrightarrow \equiv SO—MgF^0 + H^+ \qquad (12)$$

These experiments cannot reveal whether the ion pair adsorbs (eq 10), or Mg^{2+} adsorbs, and then F^- associates with it (eq 12). Aqueous MgF^+ probably exists as an outer sphere ion pair (Tanner, Walker, and Choppin, 1968), and this is hypothesized here for the adsorbed complex. Determining whether MgF^+ formation at the surface changes the nature of the association of Mg^{2+} with the surface (the degree of hydration) requires more detailed study.

By examining F^- adsorption over a range of total F^- concentration, the phenomenon of MgF^+ co-adsorption is further explored. The distribution of MgF^+ between the FeOOH surface and solution at pH = 8.8 is shown in figure 6. It is assumed that at this pH fluoride only adsorbs in conjunction with Mg^{2+}. The concentration of MgF^+ in solution was determined by combining eq 2 with:

$$[Mg^{2+}]_T = [Mg^{2+}] + [MgF^+] \qquad (13)$$

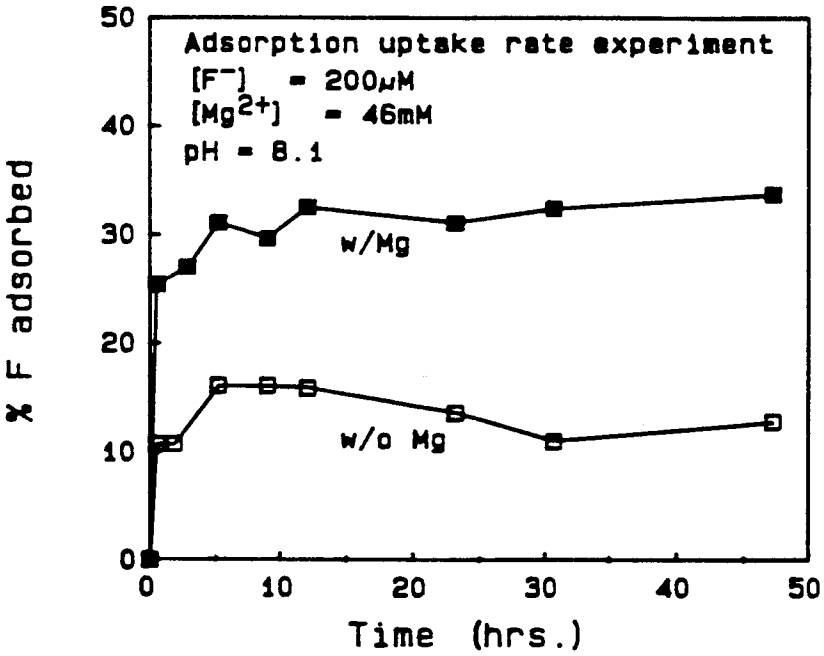


Fig. 5. Uptake of F^- by adsorption over time by FeOOH with and without Mg^{2+} present in solution. The enhancement of F^- adsorption with Mg^{2+} present in solution existed throughout the 14 day experiment (only 50 hrs are shown). pH = 8.1; $[F^-]$ = 200 μM and $[Mg^{2+}]$ = 46 mM (dissolved and adsorbed); [FeOOH] = 14.5 g/l. Solid squares = ASW with Mg^{2+}; open squares = ASW without Mg^{2+}.

and

$$[F^-]_T = [F^-] + [MgF^+] \quad (14)$$

where $[Mg^{2+}]_T$ and $[F^-]_T$ are the total aqueous concentrations of Mg^{2+} and F^- respectively. $[Mg^{2+}]_T$ and $[F^-]_T$ were measured directly. $(MgF^+/Mg_T^{2+})_{surf}$, the ratio of adsorbed MgF^+ to total Mg^{2+} adsorbed, was calculated by assuming that all F^- adsorbed at this pH is co-adsorbed with Mg^{2+} as MgF^+, and determining the amount of Mg^{2+} adsorbed by difference. Figure 6 shows that the ratio of aqueous MgF^+ to total aqueous Mg^{2+}, $[(MgF^+/Mg_T^{2+})_{aq}]$, is directly related to the corresponding surface ratio $[(MgF^+/Mg_T^{2+})_{surf}]$, consistent with eqs 10 or 12. The slope of the relationship is 2.9 suggesting that the MgF^+ ion pair is more stable at the FeOOH surface than in solution at this pH. The linear adsorption coefficient, K (the slope of a plot of $[MgF^+]_{aq}$ versus $[MgF^+]_{surf}$, see eq 11), for MgF^+ adsorption by FeOOH at pH 8.8 is 80 ml/g FeOOH. At higher adsorbate concentration (surface saturation), linearity cannot be assumed.

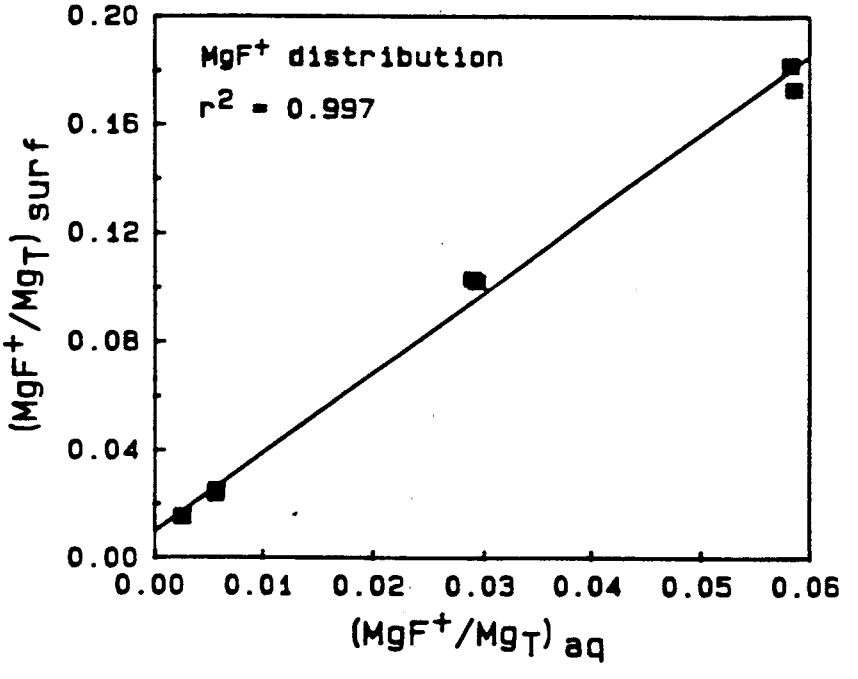


Fig. 6 The distribution of MgF^+ between solution and the surface of FeOOH at pH = 8.8. Solutions were spiked with Mg^{2+} to give a total dissolved and adsorbed concentration of 31.5 mM, and F^- to give a range of total and dissolved F^- equal to 310–6150 μM. $(MgF^+/Mg_T^{2+})_{surf}$ = the ratio of adsorbed MgF^+ to total Mg^{2+} adsorbed. $(MgF^+/Mg_T^{2+})_{aq}$ = the ratio of dissolved MgF^+ to total Mg^{2+} dissolved. The MgF^+ association is more stable at the FeOOH surface than in solution at this pH (see text).

At pH values where no or limited Mg^{2+} adsorption by the adsorbents used occurs (generally lower pH), the reduced F^- adsorption (compared to solutions without Mg^{2+}) can be explained by the formation of the MgF^+ ion pair in solution (eq 1) and adsorption of only uncomplexed F^- (eq 7). For example, if K_F for FeOOH in the solutions containing Mg^{2+} is recalculated with the free solution concentration of F^- (the denominator in eq 11) instead of the total solution concentration of F^- (F^- plus MgF^+), then the K_F's in the pH range 4.5 to 7 for the solutions with and without Mg^{2+} are nearly equal (not shown). This is also true for the other adsorbents (δMnO_2, pH = 3 to 5; $SiO_2 \cdot nH_2O$, pH = 3 to 6; $Al(OH)_3$, pH = 5 to 8) and both solution types. This can be thought of as a competition for free F^- between adsorbent surface sites and Mg^{2+} ion in solution. Anionlike adsorption of the MgF^+ ion pair is apparently not significant for these adsorbents, probably because of electrostatic repulsion of the like-charged ion pair and particle surface at low pH.

3. Reversibility of F^- adsorption in major ion seawater and concentration dependence.—The reversibility of F^- adsorbed on goethite in 0.01 M NaCl

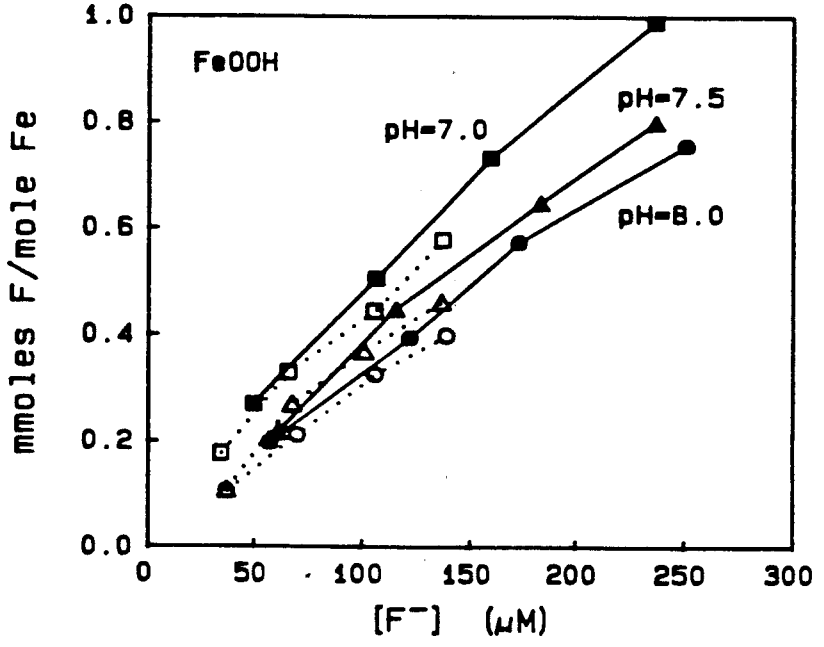
at pH 4.5 has been demonstrated by Hingston, Posner, and Quirk (1974). Few other data on F^- adsorption reversibility exist (Hingston, 1981). In the present study the adsorption of F^- by FeOOH and δMnO_2 is linearly dependent on the total solution concentration of F^- (50 to 250 μ) in the pH range 7 to 8.5 (fig. 7A, B). Fluoride adsorption can be reversed for FeOOH and $\delta Mn0_2$ (fig. 7A, B). These experiments suggest that in seawater, adsorption of F^- by FeOOH and δMnO_2 during early diagenesis can be modeled by a reversible adsorption constant, K, independent of the concentration of F^-, and dependent on pH and changes in $[Mg^{2+}]$. The constant distribution with time during the adsorption rate experiment (fig. 5) is also consistent with a reversible adsorption process rather than net incorporation into the solid.

IMPLICATIONS

Magnesium fluoride ion pair formation in the sea and its influence on F^- adsorption has important implications for the mobility of F^- and its distribution between particle surfaces and seawater. The pH range found in the marine environment ($\sim$6.5 to 8.5) falls within the range of Mg^{2+}-influenced F^- adsorption for FeOOH, δMnO_2, and $SiO_2 \cdot nH_2O$. Clay minerals (for example, kaolinite, smectite, and illite) adsorb little free F^- at seawater pH (Ruttenberg, ms; Bar-Yosef, Afik, and Rosenberg, 1988), but given the data presented in this study, Mg^{2+}-F^- co-adsorption could be an important mechanism of F^- adsorption for these phases in seawater. In addition, organic matter coatings on suspended particle surfaces in the sea (and perhaps sediment) render their surface charge negative (Neihof and Loeb, 1973; Hunter, 1980; Loder and Liss, 1985), so that adsorption of F^- via the MgF^+ ion pair may be important. This indicates that in the marine environment a major fraction of the adsorbed F^- pool is probably co-adsorbed with Mg^{2+}.

In addition to F-bearing mineral precipitation or dissolution reactions, changes in pore water pH and Mg^{2+} ion concentration and the character of particle surfaces during diagenesis will also redistribute F^- between the solid phase and solution. The results of the present study show that co-adsorption of Mg^{2+} and F^- must be considered when interpreting dissolved F^- behavior in marine sedimentary deposits. Ion pair association with surfaces may also represent an important mechanistic step in the incorporation of F^- into authigenic precipitates and deserves further study within this context.

Magnesium ion concentration can be depleted substantially during deeper sediment diagenesis due to reactions involving basaltic basement (Froelich and others, 1991; Gieskes, Kastner, and Warner, 1975) or carbonate mineral diagenesis (Baker and Burns, 1985). These variations will cause a redistribution of F^- between solution and surface, which could influence the mobility of F^-. Although CaF^+ is a relatively minor species in seawater, it may be important in hydrothermal brines where Ca^{2+} is often elevated in addition to Mg^{2+} (Hanor, 1979). The occurrence of MgF^+ and CaF^+ in such waters could significantly affect F^- mobility.



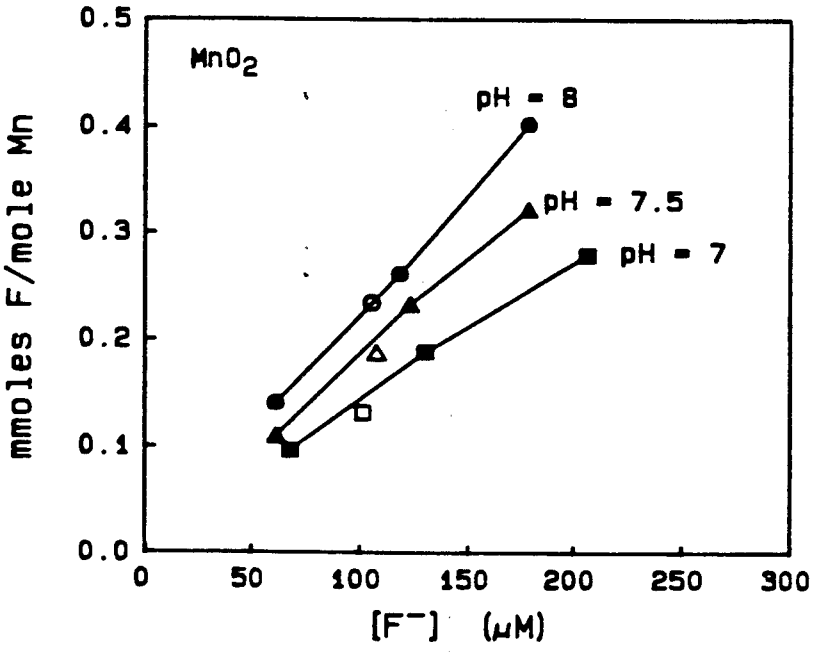


Fig. 7. The concentration dependence of F^- adsorption by FeOOH and δMnO_2, and F^- desorption in ASW with Mg^{2+}. (A) F^- adsorption and desorption isotherms for FeOOH at pH = 7, 7.5, and 8 (1 g FeOOH = 6.9 mmoles FeOOH). (B) F^- adsorption and desorption isotherms for δMnO_2 at pH = 7, 7.5, and 8 (1 g δMnO_2 = 7.5 mmoles δMnO_2). Closed symbols = adsorption; open symbols = desorption.

MgF^+ or CaF^+ ion pair formation could also affect the diffusion of total F^- independent of any adsorption affects because of inter-ion interactions brought about by ion pairing (Lasaga, 1979).

Except for chloride, a significant fraction of the other major seawater anions (sulfate, carbonate, and bicarbonate) are paired with major seawater cations (Na^+, Mg^{2+}, and Ca^{2+}). The influence of MgF^+ formation on F^- adsorption behavior suggests that the adsorption behavior of these anions could be comparably affected by ion pair formation.

CONCLUSION

The use of changes in dissolved fluoride concentrations in marine pore water as an indicator of authigenic mineral reactions has led to the need for a more detailed understanding of the marine geochemistry of fluorine. The present study demonstrates that in seawater, co-adsorption of F^- and Mg^{2+} at common inorganic particle surfaces greatly influences the distribution of F^- between surface and solution. At relatively high pH values, F^- adsorption by FeOOH, δMnO_2, and $SiO_2 \cdot nH_2O$ is enhanced due to co-adsorption or ternary complex formation involving MgF^+ and surface sites (the exact nature of this surface complex demands further study); at low pH values, free F^- adsorption is reduced by MgF^+ formation in solution (fig. 8). Adsorption of free F^- and MgF^+ by FeOOH and δMnO_2 is rapid and reversible in the pH range found in the marine environment ($\sim$6.5 to 8.5).

Discovery of the influence of Mg^{2+} on the adsorption behavior of F^- provides a more complete framework within which to interpret pore water F^- profiles from sedimentary deposits undergoing early diagenesis. Co-adsorption of F^- and Mg^{2+} as well as free F^- adsorption must be considered when interpreting F^- behavior in marine sedimentary deposits.

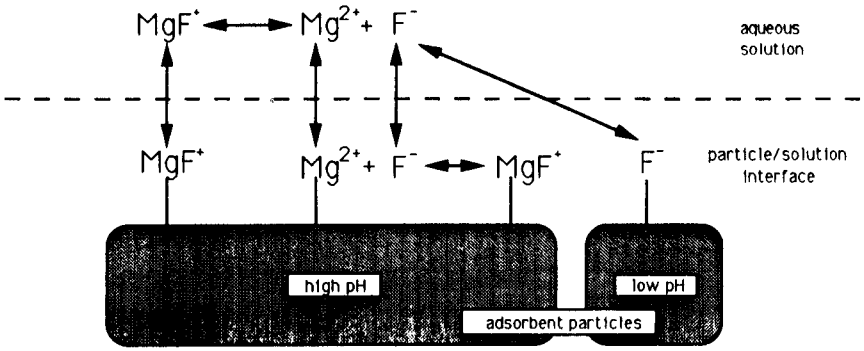


Fig. 8. A schematic representation of the influence of MgF^+ formation on the adsorption of F^- in seawater. F^- adsorbs both as the free ion and in association with Mg^{2+} (presumably co-adsorption of Mg^{2+} and F^-). MgF^+ formation in solution can compete with surface sites for F^-. The relative importance of the various reactions and the exact pH dependence depends on the nature of the solid and its surface charge.

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REFERENCES

Aller, R. C., and Rude, P. D., 1988, Complete oxidation of solid phase sulfides by manganese and bacteria in anoxic marine sediments: Geochimica et Cosmochimica Acta, v. 52, p. 751–765.

Baker, P. A., and Burns, S. J., 1985, Occurrence and formation of dolomite in organic-rich continental margin sediments: American Association of Petroleum Geologists, v. 69, p. 1917–1930.

Balistrieri, L. S., and Murray, J. W., 1981, The surface chemistry of goethite (αFeOOH) in major ion seawater: American Journal of Science, v. 281, p. 788–806.

———— 1982a, The adsorption of Cu, Pb, Zn, and Cd on Goethite from major ion seawater: Geochimica et Cosmochimica Acta, v. 46, p. 1253–1265.

———— 1982b, The surface chemistry of δMnO_2 in major ion seawater: Geochimica et Cosmochimica Acta, v. 46, p. 1041–1052.

Bar-Yosef, B., Afik, I., and Rosenberg, R., 1988, Fluoride sorption by montmorillonite and kaolinite: Soil Science, v. 145, p. 194–200.

Benjamin, M. M., and Leckie, J. O., 1981, Conceptual model for metal-ligand-surface interactions during adsorption: Environmental Science and Technology, v. 15, p. 1050–1057.

———— 1982, Effects of complexation by Cl, SO_4, and S_2O_3 on adsorption behavior of Cd on oxide surfaces: Environmental Science and Technology, v. 16, p. 162–170.

Bower, C. A., and Hatcher, J. T., 1967, Adsorption of fluoride by soils and minerals: Soil Science, v. 103, p. 151–154.

Bowers, A. R., and Huang, C. P., 1987, Role of Fe(III) in metal complex adsorption by hydrous solids: Water Research, v. 21, p. 757–764.

Catts, J. G., and Langmuir, D., 1986, Adsorption of Cu, Pb, and Zn by δMnO_2: Applicability of the site binding-surface complexation model: Applied Geochemistry, v. 1, p. 255–264.

Davis, J. A., and Leckie, J. O., 1978a, Effect of adsorbed complexing ligands on trace metal uptake by hydrous oxides: Environmental Science and Technology, v. 12, p. 1309–1315.

———— 1978b, Surface ionization and complexation at the oxide/water interface. II. Surface properties of amorphous iron oxyhydroxides and adsorption of metal ions: Journal of Colloid and Interface Science, v. 67, p. 90–107.

Elgquist, B., 1970, Determination of the stability constants of MgF^+ and CaF^+ using the fluoride ion selective electrode: Journal of Inorganic and Nuclear Chemistry, v. 32, p. 937–944.

Farrah, H., and Pickering, W. F., 1986, Interaction of dilute fluoride solutions with hydrous iron oxides: Australian Journal of Soil Research, v. 24, p. 201–208.

Farrah, H., Slavek, J., and Pickering, W. F., 1985, Fluoride sorption by soil components: calcium carbonate, humic acid, manganese dioxide and silica: Australian Journal of Soil Research, v. 23, p. 429–439.

———— 1987, Fluoride interactions with hydrous aluminum oxides and alumina: Australian Journal of Soil Research, v. 25, p. 55–69.

Frant, M. S., and Ross, J. W., Jr., 1966, Electrode for sensing fluoride ion activity in solution: Science, v. 154, p. 1553–1555.

Froelich, P. N., Arthur, M. A., Burnett, W. C., Deakin, M., Hensley, V., Jahnke, R., Kaul, L., Kim, K.-H., Roe, K., Soutar, A., and Vathakanon, C., 1988, Early diagenesis of organic matter in Peru continental margin sediments: phosphorite precipitation: Marine Geology, v. 80, p. 309–343.

Froelich, P. N., Kim, K. H., Jahnke, R., Burnett, W. C., Soutar, A., and Deakin, M., 1983, Pore water fluoride in Peru continental margin sediments: Uptake from seawater: Geochimica et Cosmochimica Acta, v. 47, p. 1605–1612.

Froelich, P. N., Mortlock, A., Mefferd, M., and Powers, J., 1991, Interstitial-water chemistry: Abyssal South Atlantic and East Georgia basins, Islas Orcadas and Meteor rises: Proceedings of the Ocean Drilling Program, Scientific Results, v. 114, p. 719–731.

Gaudette, H. E., and Lyons, W. B., 1980, Phosphate geochemistry in nearshore carbonate sediments: A suggestion of apatite formation, *in* Bentor, Y. K., editor, Marine Phosphorites: Society Economic Paleontologists and Mineralogists Special Publication 29, p. 215–225.

Gieskes, J. M., Kastner, M., and Warner, T. B., 1975, Evidence for extensive diagenesis, Madagascar Basin, Deep Sea Drilling Site 245: Geochimica et Cosmochimica Acta, v. 39, p. 1385–1393.

Hanor, J. S., 1979, The sedimentary genesis of hydrothermal fluids, *in* Barnes, H. L., editor, Geochemistry of Hydrothermal Fluids: New York, John Wiley & Sons, p. 138–172.

Hingston, F. J., 1981, A review of anion adsorption, *in* Anderson, M. A, and Rubin, A. J., editors, Adsorption of Inorganics at Solid-Liquid Interfaces: Ann Arbor Science p. 51–89.

Hingston, F. J., Posner, A. M., and Quirk, J. P., 1972, Anion adsorption by goethite and gibbsite: I. The role of the proton in determining adsorption envelopes: Journal of Soil Science, v. 23, p. 177–192.

———— 1974, Anion adsorption by goethite and gibbsite II. Desorption of anions from hydrous oxide surfaces: Journal of Soil Science, v. 25, p. 16–26.

Huang, C.-P., and Stumm, W., 1973, Specific adsorption of cations on hydrous γ-Al_2O_3: Journal of Colloid and Interface Science, v. 43, p. 409–420.

Hunter, K. A., 1980, Microelectrophoretic properties of natural surface-active organic matter in coastal seawater: Limnology and Oceanography, v. 25, p. 807–822.

Jahnke, R. A., Emerson, S. R., Roe, K. K., and Burnett, W. C., 1983, The present day formation of apatite in Mexican continental margin sediments. Geochimica et Cosmochimica Acta, v. 47, p. 259–266.

Kinniburgh, D. G., and Jackson, M. L., 1981, Cation adsorption by hydrous metal oxides and clay, *in* Anderson, M. A, and Rubin, A. J., editors, Adsorption of Inorganics at Solid-Liquid Interfaces: Ann Arbor Science, p. 91–160.

Kinniburgh, D. G., Jackson, M. L., and Syers, J. K., 1976, Adsorption of alkaline earth, transition, and heavy metal cations by hydrous oxide gels of iron and aluminum: Soil Science Society of America Journal, v. 40, p. 796–799.

Lasaga, A. C., 1979, The treatment of multi-component diffusion and ion pairs in diagenetic fluxes: American Journal of Science, v. 279, p. 324–346.

Loder, T. C., and Liss, P. S., 1985, Control by organic coatings of the surface charge of estuarine suspended particles. Limnology and Oceanography, v. 30, p. 418–421.

Mackin, J. E., and Swider, K. T., 1987, Modeling the dissolution behavior of standard clays in seawater: Geochimica et Cosmochimica Acta, v. 51, p. 2947–2964.

MacNaughton, M. G., and James, R. O., 1974, Adsorption of aqueous mercury (II) complexes at the oxide/water interface: Journal of Colloid and Interface Science, v. 47, p. 431–440.

McBride, M. B., 1978, Retention of Cu^{2+}, Ca^{2+}, Mg^{2+}, and Mn^{2+} by amorphous alumina: Soil Science Society of America Journal, v. 42, p. 27–31.

Murray, J. W., 1974, The surface chemistry of hydrous manganese dioxide: Journal of Colloid and Interface Science, v. 46, p. 357–371.

Neihof, R., and Loeb, G., 1974, Dissolved organic matter in seawater and the electric charge of immersed surfaces: Journal of Marine Research, v. 32, p. 5–12.

Parfitt, R. L., and Russell, J. D., 1977, Adsorption on hydrous oxides. IV. Mechanism of adsorption of various ions on goethite: Journal of Soil Science, v. 28, p. 297–305.

Parks, G. A., 1990, Surface energy and adsorption at mineral/water interfaces: An introduction, *in* Hochella, M. F., Jr., and White, A. F., editors, Mineral-Water Interface Chemistry: Mineralogical Society of America, p. 133–169.

Parsons, T. R., Yoshiaki, M., and Lalli, C. M., 1984, A manual of chemical and biological methods for seawater analysis: Pergamon Press, 173 p.

Rix, C. J., Bond, A. M., and Smith, J. D., 1976, Direct determination of fluoride in sea water with a fluoride selective ion electrode by a method of standard additions: Analytical Chemistry, v. 48, p. 1236–1239.

Rude, P. D., and Aller, R. C., 1991, Fluorine mobility during the early diagenesis of carbonate sediment: An indicator of mineral transformations. Geochimica et Cosmochimica Acta, v. 55, p. 2491–2509.

———— 1992, Fluorine uptake by Amazon continental shelf sediment and its impact on the global fluorine cycle: Continental Shelf Research, in press.

Ruttenberg, K. C., ms, 1990, Diagenesis and burial of phosphorous in marine sediments: Implications for the marine phosphorous budget: Ph.D. dissertation, Yale University, New Haven, Connecticut.

Schindler, R. W., 1981, Surface Complexes at Oxide-Water Interfaces, *in* Anderson, M. A, and Rubin, A. J., editors, Adsorption of Inorganics at Solid-Liquid Interfaces: Ann Arbor Science, p. 1–49.

———— 1990, Co-adsorption of metal ions and organic ligands: Formation of ternary surface complexes, *in* Hochella, M. F., Jr., and White, A. F., editors, Mineral Water Interface Chemistry: Mineralogical Society of America, p. 281–307.

Shishkina, O. V., Baturin, G. N., and Bykova, V. S., 1972, Fluorine in the sediments and ooze water of highly productive parts of the oceans. Geokhimiya, v. 8, p. 988–996.
Sigg, L., and Stumm, W., 1981, The interaction of anions and weak acids with the hydrous goethite (α-FeOOH) surface: Colloids and Surfaces, v. 2, p. 101–117.
Slavek, J., Farrah, H., and Pickering, W. F., 1984, Interaction of clays with dilute fluoride solutions: Water, Air, and Soil Pollution, v. 23, p. 209–220.
Sposito, G., 1984, The Surface Chemistry of Soils: New York, Oxford, 234 p.
Stumm, W., and Morgan, J. J., 1981, Aquatic Chemistry, An introduction emphasizing chemical equilibria in natural waters. second edition: New York, Wiley Interscience.
Stumm, W., Kummert, R., and Sigg, L., 1980, A ligand exchange model for the adsorption of inorganic and organic ligands at hydrous oxide interfaces: Croatica Chemica Acta, v. 53, p. 291–312.
Tanner, S. P., Walker, J. B., and Choppin, G. R., 1968, Thermodynamic parameters of the alkaline earth monofluorides: Journal of Inorganic and Nuclear Chemistry, v. 30, p. 2067–2070.
Theis, T. L., and Richter, R. O., 1980, Adsorption reactions of nickel species at oxide surfaces, *in* Kavanaugh, M. C., and Leckie, J. O., editors, Particulates in Water: Characterization, Fate, Effects, and Removal: American Chemical Society, Advances in Chemistry Series 189, p. 73–96.