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3

Redox Reactions and Solution Complexes of Iron in Marine Systems

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The chemistry of iron in natural waters has considerable effect on a variety of environmental processes. Iron plays a unique role in many biological systems due to its ability to form porphyrin molecules which participate in biochemical oxidation-reduction reactions. Changes in the oxidation state of iron in response to environmental changes in redox potential is a significant factor for geochemical processes such as the formation of pyrite ores and ferro-manganese nodules. The chemical behavior of iron in natural waters is also important because of its prevalent use in structural materials and its subsequent deterioration through corrosion reactions. The tendency of iron to form colloidal and particulate phases provides a mechanism for the removal of dissolved trace elements from natural waters by adsorption and coprecipitation. Due to this diverse range of chemical processes, it is important to establish a reliable understanding of the redox reactions of iron in marine waters.

Analytical measurements of the concentration of iron in natural waters provides a basis for evaluating the significance of this element in various chemical systems. The distinction between dissolved and particulate iron has generally been made on the basis of filtration using a 0.5 μm pore size filter. This procedure leads to an operationally defined separation of iron into soluble and solid phases which can be difficult to relate to chemically defined forms such as aqueous ions, solution complexes, and colloidal particles. It is important for this reason to qualify analytical observations according to the separation techniques employed. Table I provides a brief example of the concentrations of iron found in some natural waters. These results do not show the variability which occurs in the amount of iron in natural waters, but they represent the magnitudes which are encountered and they suggest the significance of a removal mechanism for iron as waters pass from fresh to estuarine to oceanic environments.

A second step in defining the chemical processes involving iron is to distinguish between Fe(II) and Fe(III) and to deter-

Table I. Concentrations of iron in some natural waters.

Environment	Iron (mol/kg)	Form	Reference
River	1.2×10^{-5}	Dissolved and particulate not specified	(1)
Estuarine	5×10^{-6}	Particulate	(2)
Estuarine (1°/₀₀ Salinity)	3×10^{-6}	Dissolved	(3)
Estuarine (20°/₀₀ Salinity)	6×10^{-7}	Dissolved	(3)
Oceanic	2×10^{-8}	Dissolved	(4)
Oceanic	3×10^{-9}	Particulate	(5)

mine the tendency of these two oxidation states to form solution complexes and solid phases. At the present time techniques do not exist which can reveal the specific chemical forms in aqueous samples containing less than 10^{-6} mol/kg iron. It is therefore necessary to pursue a less direct approach in which a chemical model for iron in natural waters is developed from thermodynamic and kinetic information. Some of the general characteristics of chemical models and their relationship to natural systems were considered by Morgan (6). Previous considerations of iron chemistry in marine systems have examined the importance of hydroxide, phosphate, and organic ligands (7-13). In this paper we will incorporate data recently obtained in our laboratory into a consideration of iron in marine waters giving particular attention to the effects of salinity and pH. It is possible to identify from this model the most significant forms and reactions of iron, and techniques may then be devised to characterize these chemical systems under natural conditions. A chemical model is limited by its inability to account for the effects of biochemical processes on the chemistry of a constituent such as iron. Nevertheless, deviations between the predictions from chemical models and the environmental observations can indicate the existence of additional factors which require consideration.

This paper presents a chemical model for iron in marine systems based on thermodynamic and kinetic information. Emphasis will be placed on the redox reactions of iron because of their unique importance in this metal's environmental chemistry. An Eh-pH diagram (Figure 1) provides a useful orientation for the material to be presented. The two broken lines delineate the stability range for water molecules relative to oxygen and hydrogen gases; all stable aqueous systems fall within these bounds. The redox potential (Eh) of marine systems appears to be controlled by either oxygen or sulfide. Thermodynamically, the oxygen-water reaction should control the Eh of aerated systems (line ABC in Figure 1), but due to kinetic factors it is possible that the oxygen-hydrogen peroxide reaction regulates the Eh in these systems (14, 15). For marine environments devoid of oxygen the sulfate-sulfide reaction (line DEF in Figure 1) controls the Eh. A chemical model for ferrous iron will be developed which applies along line DEF. A similar model for ferric iron applicable to line ABC will be presented next. It will then be possible to examine the redox equilibrium between these two oxidation states, and finally the kinetics of ferrous oxygenation in natural waters will be considered.

Solution Equilibria of Ferrous Ions

The first step in formulating a chemical model in natural waters is to consider the composition of the medium and the tendency for these components to form metal complexes. Table II lists the molalities of the major constituents in river water (1), ocean water (16, 17) and mixtures of these two waters. This information may be combined with data on the formation of solution complexes (18, 19) to obtain a chemical model for a constituent. The lack of knowledge about the organic constituents in marine waters and of their ability to form iron-organic complexes is a limiting factor in developing a quantitative model. One approach to this problem is to consider the inorganic speciation of iron and then assess the possible significance of organic ligands relative to the inorganic ones. There are two areas in which the present knowledge of inorganic iron complexes is inadequate for marine systems: the possible formation of bicarbonate, carbonate, and sulfide complexes can not be incorporated into the model with existing data; and the possible significance of mixed ligand complexes has not been established. The role of mixed ligand complexes such as chloro-hydroxy species is a chemical problem of special importance to multicomponent natural waters which chemists studying single salt solutions have avoided. Some considerations have indicated that mixed ligand complexes may be important for copper, zinc, and mercury in seawater (20). A chemical model for iron can be developed within these limitations.

Stability constants for hydroxide, chloride, and sulfate complexes of ferrous iron were selected in the following manner. These equilibrium constants have been measured in a variety of ionic media such as sodium perchlorate solutions with ionic

Table II. Molality of constituents and ionic strength (I) parameters in mixtures of surface oceanic seawater and world average river water (RW).

	Salinity				
Constituent	RW	4°/oo	10°/oo	20°/oo	35°/oo
Na^+	0.00027	0.05426	0.13731	0.27574	0.48614
Mg^{2+}	0.00017	0.00623	0.01556	0.03110	0.05473
Ca^{2+}	0.00037	0.00151	0.00327	0.00620	0.01065
K^+	0.00006	0.00123	0.00303	0.00627	0.0106
Cl^-	0.00022	0.06306	0.15973	0.32086	0.56577
SO_4^{2-}	0.00011	0.00335	0.00833	0.01664	0.02926
HCO_3^-	0.00096	0.00113	0.00139	0.00182	0.00247
F^-	0.00001	0.00002	0.00003	0.00004	0.00007
I	0.0021	0.0820	0.2051	0.4102	0.7218
$\sqrt{I}/(1 + \sqrt{I})$	0.0434	0.2226	0.3117	0.3904	0.4593

strengths (I) between 0.1 and 3.0 molal (18, 19). In some cases these equilibrium constants were evaluated at infinite dilution or zero ionic strength. A plot of the logarithm of the stability constant for each complex versus $\sqrt{I}/(1 + \sqrt{I})$ was constructed in order to examine the consistency of the various values and to obtain their ionic strength dependence. The functional form $\sqrt{I}/(1 + \sqrt{I})$ provides a convenient means of interpolating between different ionic strengths and of extrapolating data to infinite dilution (21, 22).

The resulting stability constants are summarized in Table III. The values which have been reported for log $^*\beta_2(Fe(OH)_2)$ range from -17.6 to -5.85 for $0 \leq I \leq 1$. Such wide discrepancies may occur between different studies when in one case the formation of related complexes such as $FeOH^+$ is taken into account while in another case these complexes are not considered and their effects thus become associated with the $Fe(OH)_2{}^\circ$. Alternatively, measurements of this constant may be particularly difficult due to the tendency of Fe(II) to oxidize to Fe(III) which undergoes much more extensive hydrolysis. The systematic selection of free energy data by Langmuir (23) provides a consistent set of values for hydroxy species at infinite dilution. Other data for $^*\beta_2(Fe(OH)_2{}^\circ)$ would require that this constant increase by six to twelve orders of magnitude between I = 0 and

Table III. Stability constants selected for the calculation of ferrous complexes in natural waters.

Constant	Value	Reference
$*\beta_1(FeOH^+) = \frac{[FeOH^+][H^+]}{[Fe^{2+}]}$	$\log *\beta_1 = -8.30 + 3.58\sqrt{I}/(1 + \sqrt{I})$	(23, 24)
$*\beta_2(Fe(OH)_2{}^\circ) = \frac{[Fe(OH)_2{}^\circ][H^+]^2}{[Fe^{2+}]}$	$\log *\beta_2 = -17.6$	(23)
$\beta_1(FeCl^+) = \frac{[FeCl^+]}{[Fe^{2+}][Cl^-]}$	$\log \beta_1 = 0.79 - 0.73\sqrt{I}/(1 + \sqrt{I})$	(25)
$\beta_2(FeCl_2{}^\circ) = \frac{[FeCl_2{}^\circ]}{[Fe^{2+}][Cl^-]^2}$	$\log \beta_2 = 0.21 - 0.29\sqrt{I}/(1 + \sqrt{I})$	(25)
$\beta_1(FeSO_4{}^\circ) = \frac{[FeSO_4{}^\circ]}{[Fe^{2+}][SO_4{}^{2-}]}$	$\log \beta_1 = 2.12 - 2.47\sqrt{I}/(1 + \sqrt{I})$	(26)
$\beta_1(HSO_4{}^-) = \frac{[HSO_4{}^-]}{[H^+][SO_4{}^{2-}]}$	$\log \beta_1 = 1.99 - 1.06\sqrt{I}/(1 + \sqrt{I})$	(27-30)

I, which is totally contrary to the ionic strength dependence which can be associated with the various species. For example:

$$*\beta_2(\mathrm{Fe(OH)_2}^\circ,\ I = 0.7) = *\beta_2(\mathrm{Fe(OH)_2}^\circ,\ I = 0)\ \frac{g_{\mathrm{Fe}^{2+}}}{g_{\mathrm{Fe(OH)_2}^\circ}\ g^2_{\mathrm{H}^+}} \qquad (1)$$

where the g factors represent the free activity coefficients of each species at $I = 0.7$. Even though accurate values can not be assigned to individual ionic activity coefficients, limits can be placed on their variation with I such that the quotient of g-values in equation (1) can not be expected to vary by six orders of magnitude between $I = 0$ and 1. In fact "rule of thumb" values for these activity coefficients (31) suggest that $*\beta_2(\mathrm{Fe(OH)_2}^\circ)$ should be relatively insensitive to variations in I; this rationale yielded the value for this constant selected in Table III. The equilibrium constants for ferrous chloride and sulfate complexes were not available over a range of ionic strengths, so their ionic strength dependences were estimated also from a relationship analogous to equation (1) and from information on the typical behavior of activity coefficient variations between $I = 0$ and 1 (31).

The calculation of ferrous iron speciation is based on the expression for total Fe(II):

$$T(\mathrm{Fe(II)}) = [\mathrm{Fe}^{2+}] + [\mathrm{FeCl}^+] + [\mathrm{FeCl_2}^\circ] + [\mathrm{FeSO_4}^\circ] + [\mathrm{FeOH}^+] + [\mathrm{Fe(OH)_2}^\circ] \qquad (2)$$

Due to the low concentration of iron in natural waters it is not necessary to consider polynuclear complexes of iron. The fraction of Fe(II) which is uncomplexed may be derived from equation (2) with the definition of stability constants contained in Table III:

$$[\mathrm{Fe}^{2+}]/T(\mathrm{Fe(II)}) = 1/(1 + \beta_1(\mathrm{FeCl}^+)[\mathrm{Cl}^-] + \beta_2(\mathrm{FeCl_2}^\circ)[\mathrm{Cl}^-]^2 + \beta_1(\mathrm{FeSO_4}^\circ)[\mathrm{SO_4}^{2-}] + *\beta_1(\mathrm{FeOH}^+)/[\mathrm{H}^+] + *\beta_2(\mathrm{Fe(OH)_2}^\circ)/[\mathrm{H}^+]^2) \qquad (3)$$

and similarly the fraction of Fe(II) which occurs as the generic species FeL_n is given by:

$$[\mathrm{FeL}_n]/T(\mathrm{Fe(II)}) = \beta_n(\mathrm{FeL}_n)[\mathrm{L}]^n/(1 + \beta_1(\mathrm{FeCl}^+)[\mathrm{Cl}^-] + \beta_2(\mathrm{FeCl_2}^\circ)[\mathrm{Cl}^-]^2 + \beta_1(\mathrm{FeSO_4}^\circ)[\mathrm{SO_4}^{2-}] + *\beta_1(\mathrm{FeOH}^+)/[\mathrm{H}^+] + *\beta_2(\mathrm{Fe(OH)_2}^\circ)/[\mathrm{H}^+]^2) \qquad (4)$$

The square brackets designate the molality of the enclosed species (e.g., unassociated or free ligands) and the species in parentheses following each beta identifies the particular stability constant as defined in Table III.

The molality of free ligands was based on an ion-pairing model for seawater in which the free chloride was assumed to be equal to the total chloride (32). The free sulfate was 39% of the total sulfate at 35°/₀₀ salinity (32) and this percentage increased to 100% in river water in proportion to the decrease in salinity. The decrease in $[SO_4^{2-}]$ at low pH due to the formation of HSO_4^- was accounted for in the calculations. For the purpose of this chemical model of iron a pH scale was used such that $pH = -\log [H^+]$ so that the pH yields the free H^+ directly. This pH scale has a number of advantages for treating seawater equilibria, and it departs from the conventional National Bureau of Standards pH scale by 0.01 pH units (33, 34).

The results of these calculations for ferrous iron over the pH range of 3.0 to 10.0 for river water, 4°/₀₀ salinity, and 35°/₀₀ salinity seawater are shown in Figure 2. In river water below pH 7 the Fe(II) exists primarily as Fe^{2+} whereas between pH 7 and 10 the hydroxide complexes of Fe(II) become significant. At 35°/₀₀ salinity chloro-complexes are a major form of Fe(II) up to a pH of 7, beyond which the $FeOH^+$ species is the predominant form. The effect of salinity on the Fe(II) species distribution at pH 8 is illustrated in Figure 3. There are two factors involved in the effect of salinity on Fe(II): one is the change in concentration of the chloride and sulfate complexing ligands; the second is the change in stability constants with ionic strength. Table IV provides a more convenient quantitative representation of the net effect of these two factors at pH 7 and pH 8. These results provide an inorganic chemical model for iron which is applicable to line DEF in Figure 1 at various salinities.

It is possible to evaluate the potential significance of organic ligands in complexing ferrous iron. Marine waters typically contain a maximum of 1-5 mg of dissolved organic carbon (DOC) per liter (1, 35, 36). Assuming approximately one functional group capable of complexing Fe^{2+} per six carbon atoms and an average DOC concentration of 2 mg/l yields an effective concentration of 2.8×10^{-5} molal for the organic ligands. In order for these ligands to complex 20% of the Fe(II) in 35°/₀₀ salinity seawater at pH 8.0 they must have a stability constant on the order of 2.2×10^5 whereas in river water at pH 7 an Fe(II)-organic stability constant of 9.6×10^3 would be sufficient to complex 20% of the Fe(II). Stability constants for the formation of Fe^{2+} complexes with the functional groups of amino acids, acetate, citrate, and quinoline carboxylate are generally in the range $1\text{-}6 \times 10^3$ (18, 19) which indicates that these types of ligands could not compete with the inorganic ones for Fe(II) in seawater, but they could be significant in river water.

A second factor to consider in evaluating the effectiveness

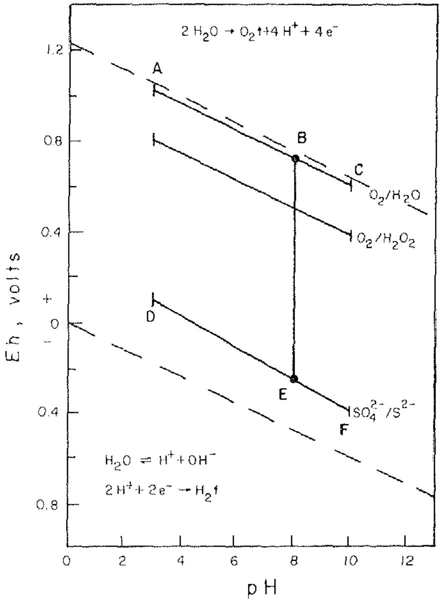

Figure 1. Eh–pH diagram for natural waters. Line ABC shows the relationship between Eh and pH when the O_2/H_2O controls the Eh. Line DEF is the relationship for the SO_4^{2-}/S^{2-} reaction in marine systems. The intermediate line shows control by the O_2/H_2O_2 reaction.

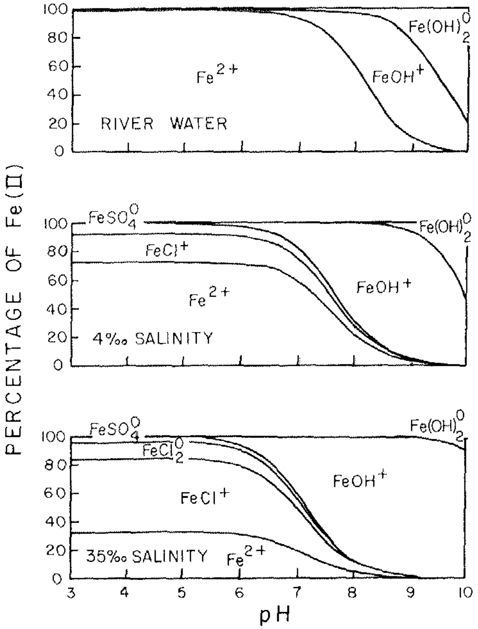

Figure 2. Distribution of Fe(II) species as a function of pH at three salinities. The vertical distance between curves represents the percentage of the species between the curves.

Table IV. Percentage distribution of Fe(II) species over the estuarine range of salinity at constant pH.

pH = 7

Salinity	RW	4°/oo	10°/oo	20°/oo	35°/oo
Fe^{2+}	92.2	59.1	41.7	28.3	18.8
$FeCl^{+}$	0.1	15.8	24.3	29.0	30.3
$FeCl_2^{\circ}$	--	0.3	1.4	3.6	7.2
$FeSO_4^{\circ}$	1.0	6.2	5.4	3.6	2.1
$FeOH^{+}$	6.6	18.5	27.3	35.4	41.6
$Fe(OH)_2^{\circ}$	--	0.01	0.01	--	--

pH = 8.0

Salinity	RW	4°/oo	10°/oo	20°/oo	35°/oo
Fe^{2+}	57.0	22.0	12.0	6.7	4.0
$FeCl^{+}$	0.07	5.9	7.0	6.9	6.4
$FeCl_2^{\circ}$	--	0.1	0.4	0.9	1.5
$FeSO_4^{\circ}$	0.6	2.3	1.6	0.8	0.4
$FeOH^{+}$	40.9	69.1	78.7	84.4	87.6
$Fe(OH)_2^{\circ}$	1.4	0.6	0.3	0.2	0.1

of organic ligands in complexing Fe(II) is the competition between Fe^{2+} and Mg^{2+} or Ca^{2+} for the organic functional groups (37, 38). The availability of functional groups for these divalent ions is likely to depend on the hydrogen ion dissociation equilibrium for acid groups. The estimate of organic metal complexing will be maximized by considering that all the functional groups are available for the metal ions at pH 7.0 and 8.0. Table V illustrates that most of the organic ligands capable of complexing Fe^{2+} will be complexed by the much more abundant Mg^{2+} and Ca^{2+} ions in seawater. This effect further decreases the likelihood of significant Fe(II)-organic complexes at pH 8 in seawater. In river water at pH 7 the Fe^{2+} can compete effectively with the Mg^{2+} and Ca^{2+} and about 10% of the Fe(II) could be complexed by organic ligands with a 6×10^3 stability constant. A definitive evaluation of the importance of Fe(II)-organic complexes will require measurements of β(Fe-org) using naturally derived organic matter from marine systems. Nevertheless the present analysis shows that unless the natural organic matter has a much greater selectivity for Fe^{2+} relative to Mg^{2+} it will not be significant for Fe(II) in seawater, but it could be important for Fe(II) in river water and in coastal waters of low salinity.

Table V. Evaluation of the competition between ferrous, magnesium, and calcium ions for organic ligands in 35°/₀₀ salinity seawater and in river water.

$$T(org) = [Fe\text{-}org] + [Mg\text{-}org] + [Ca\text{-}org] + [org]$$

$$\frac{[Fe\text{-}org]}{T(org)} = \frac{\beta(Fe\text{-}org)[Fe^{2+}]}{1 + \beta(Mg\text{-}org)[Mg^{2+}] + \beta(Ca\text{-}org)[Ca^{2+}] + \beta(Fe\text{-}org)[Fe^{2+}]}$$

		Seawater, pH = 8.0		River Water, pH = 7.0	
Metal	(M-org)	[M]	% T(org)	[M]	% T(org)
Fe^{2+}	6×10^3	4×10^{-8}	4×10^{-3}	1×10^{-5}	5.5
Mg^{2+}	1×10^2	5×10^{-2}	81	2×10^{-4}	1.8
Ca^{2+}	20	1×10^{-2}	3	4×10^{-4}	0.7

Solution Equilibria of Ferric Ions

An analysis for ferric iron in natural waters may be made similar to the preceding one for Fe(II). Preliminary calculations of this type considering a wide range of ligands (Cl^-,

Table VI. Stability constants selected for the calculation of ferric species in natural waters.

Constant	Value	Reference
$^*\beta_1(FeOH^{2+}) = [FeOH^{2+}][H^+]/[Fe^{3+}]$	$\log {}^*\beta_1 = -2.17 - 1.19\sqrt{I}/(1+\sqrt{I})$	(23, 40, 41)
$^*\beta_2(Fe(OH)_2{}^+) = [Fe(OH)_2{}^+][H^+]^2/[Fe^{3+}]$	$\log {}^*\beta_2 = -7.17 + 0.22\sqrt{I}/(1+\sqrt{I})$	(23, 40, 41)
$^*\beta_3(Fe(OH)_3{}^\circ) = [Fe(OH)_3{}^\circ][H^+]^3/[Fe^{3+}]$	$\log {}^*\beta_3 = -13.6$	(23, 40, 42)
$\beta_1(FeCl^{2+}) = [FeCl^{2+}]/[Fe^{3+}][Cl^-]$	$\log \beta_1 = 1.48 - 2.30\sqrt{I}/(1+\sqrt{I})$	(40, 41, 44, 45)
$\beta_2(FeCl_2{}^+) = [FeCl_2{}^+]/[Fe^{3+}][Cl^-]^2$	$\log \beta_2 = 0.65 - 2.21\sqrt{I}/(1+\sqrt{I})$	(40, 41, 45)
$\beta_2(FeSO_4{}^+) = [FeSO_4{}^+]/[Fe^{3+}][SO_4{}^{2-}]$	$\log \beta_1 = 4.04 - 4.02\sqrt{I}/(1+\sqrt{I})$	(46, 47)
$\beta_1(FeF^{2+}) = [FeF^{2+}]/[Fe^{3+}][F^-]$	$\log \beta_1 = 6.0 - 2.0\sqrt{I}/(1+\sqrt{I})$	(48, 49)
$\beta_1(HF) = [HF]/[H^+][F^-]$	$\log \beta_1 = 3.18 - 0.65\sqrt{I}/(1+\sqrt{I})$	(50-52)

SO_4^{2-}, Br^-, F^-, $B(OH)_4^-$, HPO_4^{2-}, $H_2PO_4^-$, and OH^-) showed the predominant influence of hydroxide species at pH values greater than 5 (39). During the past several years a program has been carried out in our laboratory to measure the stability constants for ferric hydroxide species which are appropriate to equilibrium calculations in a seawater medium (40-43). Stability constants for the principal inorganic ferric species were obtained as a function of ionic strength in the same manner as for Fe(II). The results are summarized in Table VI. The relative amounts of ferric species were calculated using expressions analogous to equations (3) and (4). The free fluoride ligand was taken to be 50% of the total fluoride in 35°/₀₀ salinity seawater (53) in order to account for fluoride ion-pairing by Mg^{2+}, Ca^{2+}, and Na^+. This percentage increased to 100% in river water in proportion to the decrease in salinity. At low pH values the protonation of F^- was accounted for by use of the $\beta_1(HF)$ listed in Table VI.

The results of Fe(III) species distributions are shown in Figure 4. One of the major differences between the Fe(III) and Fe(II) speciation models is that Fe(III) is not substantially affected by salinity changes for pH values greater than 4 due to the predominance of hydroxide over the other inorganic ligands. Table VII illustrates the competition which exists between hydroxide and the other anions at pH 4 as salinity increases from river water to oceanic values.

Table VII. Percentage distribution of Fe(III) species over the estuarine range of salinity at pH = 4.0.

Salinity	RW	4°/₀₀	10°/₀₀	20°/₀₀	35°/₀₀
Fe^{3+}	1.3	1.8	2.1	2.5	2.7
$FeCl^{2+}$	--	1.0	2.0	3.0	4.1
$FeCl_2^+$	--	--	--	0.2	0.4
FeF^{2+}	9.4	10.5	10.9	10.0	11.2
$FeSO_4^+$	1.0	7.1	7.4	6.4	4.9
$FeOH^{2+}$	79.0	65.9	60.8	57.6	53.0
$Fe(OH)_2^+$	9.1	13.6	16.7	20.4	23.6
$Fe(OH)_3^\circ$	0.03	0.05	0.05	0.06	0.07

The requirements for significant organic complexes of Fe(III) relative to the hydroxide species at pH 8 can be formulated in a manner similar to that for Fe(II). This consideration will be made for 35°/₀₀ salinity, because it is essentially independent of the ionic strength and the anion concentrations

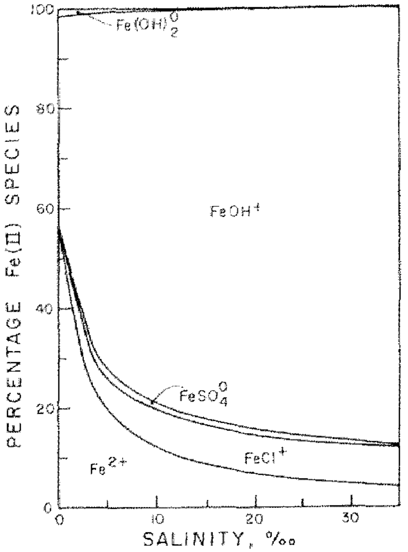

Figure 3. Effect of salinity on the distribution of Fe(II) species at pH = 8.0

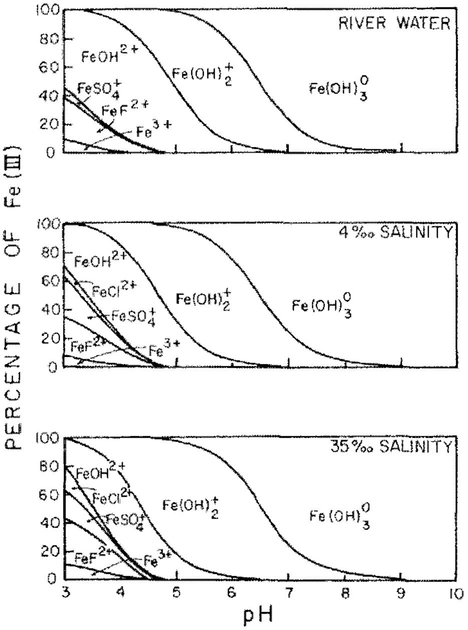

Figure 4. Distribution of Fe(III) species as a function of pH for three salinities

other than OH^-. Organic ligands such as amino acids (glutamic, aspartic, and alanine), hydroxy acids (citric), and carboxylic acids (propionic) have stability constants with Fe^{3+} of less than 1×10^{12}. Due to the extensive hydroxide complexing of Fe^{3+} at pH 8 the iron can not compete with the magnesium and calcium ions in seawater for the organic ligands (Table VIII).

Table VIII. Estimation of the ability of ferric ions to compete with the magnesium and calcium ions in seawater at pH = 8.0 for typical organic ligands. The $[Fe^{3+}]$ is based on a $T(Fe(III)) = 1 \times 10^{-7}$.

Metal	(M-org)	[M]	% T(org)
Fe^{3+}	1×10^{12}	3.9×10^{-18}	6.3×10^{-5}
Mg^{2+}	1×10^{2}	5×10^{-2}	81
Ca^{2+}	20	1×10^{-2}	3

These estimates indicate that 3.5×10^{-8}% of the T(Fe(III)) could be complexed by organic matter. In order for Fe(III)-organic complexes to be significant in seawater it would require that the natural organic matter in seawater has a stability constant with iron which is 10^{18} times greater than its stability constant with magnesium.

The calculation of ferric iron complexes in seawater and in river water provides a description of the solution equilibria of iron along line ABC in Figure 1. The resulting conclusions are that ferric hydroxide complexes predominate for pH values greater than 4 and that these species are insensitive to changes in salinity. Other ferric complexes are important only under extreme conditions such as acidic mine waters or the microenvironments near surfaces where the pH may decrease below 4. The uncharged $Fe(OH)_3^\circ$ species has been treated as a solution complex in this analysis. The experiments used to determine its stability constant (40, 42) provided an operational characterization of this species such as the fact that it passed through a 0.45 µm pore size filter; it was retained on a 0.05 µm filter (possibly by adsorption); it passed through a dialysis membrane; and it was much more rapidly converted to a filterable form than the bulk portion of precipitated hydrous ferric oxide when the pH was reduced from about 8 to 4. These properties are consistent with what would be expected for an uncharged complex, but they may also represent features of very small colloidal particles as indicated in ultracentrifugation experiments (54). Even though the molecular nature of this $Fe(OH)_3^\circ$ species has not been established, it is possible to differentiate it chemically and physically from other solution complexes and from bulk particulate phases (particle size greater than 0.1-0.5 μm).

Redox Equilibria of Fe(II) and Fe(III)

The preceding considerations of Fe(II) and Fe(III) speciation provide a basis for examining the redox equilibrium between these two oxidation states. These reactions frequently are expressed in terms of standard electrode potentials (relative to the conventional hydrogen scale) in which case the parameter Eh and the following expressions are useful:

$$Fe^{3+} + e^{-} \rightleftharpoons Fe^{2+} \qquad E^\circ = +0.771 \text{ volt} \tag{5}$$

$$E^\circ = \frac{RT}{F} \ln \frac{a(Fe^{2+})}{a(Fe^{3+})\ a(e)} \qquad RT/F = 0.02569 \text{ volts at } 25^\circ C \tag{6}$$

$$\ln \frac{a(Fe^{2+})}{a(Fe^{3+})} = \frac{E^\circ - Eh}{RT/F} \text{ where } Eh = -\frac{RT}{F} \ln a(e) \tag{7}$$

The a(i) represents the activity of the i constituent.

Equation (7) provides the basis for calculating the relative thermodynamic stability of Fe(II) and Fe(III) as a function of Eh. In order to relate such a calculation to analytical observations it is more useful to consider T(Fe(II)) and T(Fe(III)) than $a(Fe^{2+})$ and $a(Fe^{3+})$. These quantities are related to the activity coefficients of free metal ions, g, and to the speciation of the metal by the following:

$$a(Fe^{2+}) = g(Fe^{2+})\ [Fe^{2+}] \text{ and } a(Fe^{3+}) = g(Fe^{3+})\ [Fe^{3+}] \tag{8}$$

$$T(Fe(II)) = \frac{a(Fe^{2+})/g(Fe^{2+})}{[Fe^{2+}]/T(Fe(II))} \text{ and } T(Fe(III)) = \frac{a(Fe^{3+})/g(Fe^{3+})}{[Fe^{3+}]/T(Fe(III))} \tag{9}$$

The ratios [Fe]/T(Fe) for each oxidation state are obtained from the two preceding sections of this paper, and for the purpose of these calculations it is sufficient to assign "rule of thumb" values to $g(Fe^{2+})$ and $g(Fe^{3+})$ on the basis of solution ionic strength and ionic charge (31). For 35°/₀₀ salinity seawater $g(Fe^{2+}) = 0.25$, $g(Fe^{3+}) = 0.044$ and for river water $g(Fe^{2+}) = 0.915$, $g(Fe^{3+}) = 0.819$.

The resulting calculation of the relative magnitudes of T(Fe(III)) and T(Fe(II)) based on equations (7) and (9) is shown by the solid lines in Figure 5. The redox equilibrium between Fe(II) and Fe(III) does not change much with salinity, but a pH change from 8 to 6 alters the ratio of Fe(III) to Fe(II) by five orders of magnitude.

It is necessary to establish a value for the Eh of natural waters in order to relate Figure 5 to marine systems. For anoxic environments containing hydrogen sulfide there is general agreement between thermodynamic calculations and Eh measurements using a platinum electrode. The sulfate/sulfide reaction regulates Eh under these conditions and its effect on the Fe(III) and Fe(II) equilibrium is shown by the horizontal diamonds in Figure 5.

For waters containing dissolved oxygen, thermodynamic considerations predict that Eh should be controlled by the O_2/H_2O reaction, but measurements with a platinum electrode yield values which are not well-defined but which are several tenths of a volt lower than predicted. One possible explanation for this observation is that the O_2/H_2O reaction does not occur reversibly on a platinum surface. Another possible factor is that the breaking of the O=O bond in the O_2/H_2O reaction kinetically prevents the attainment of equilibrium and an intermediate redox couple, O_2/H_2O_2, may set the Eh of the system (14, 15). It has not been clear to what extent these factors of Eh control at electrode surfaces by dissolved oxygen reflect the mechanism of Eh control for the homogeneous solution reaction between ferrous ions and oxygen. Regardless of which oxygen reaction controls the Fe(II)/Fe(III) couple, these calculations indicate thermodynamically that ferrous iron should yield ferric iron in oxygenated natural waters having pH values greater than 6 and salinities ranging from river to ocean waters.

Kinetics of Ferrous Oxygenation in Natural Waters

The kinetics of the reaction between Fe(II) and oxygen will determine the extent to which the preceding equilibrium considerations reflect the forms of iron in oxygenated waters. In $NaHCO_3$ solutions with pH = 6.0 to 7.5 Stumm and Lee (55) found that the rate of ferrous oxygenation varied according to:

$$\frac{d\ T(Fe(II))}{d\ t} = k\ T(Fe(II))\ P_{O_2} [OH^-]^2 \qquad (10)$$

The first order dependence of the rate on the partial pressure of oxygen, P, and on T(Fe(II)) appears to be a characteristic feature of the reaction except in highly acidic solutions ($pH < 2$) where the rate is second order with respect to $[Fe^{2+}]$ (56). The second order dependence on $[OH^-]$ persists to a pH = 5, but this pH effect diminishes below this value so that for $pH < 3$ there is very little change in the rate with a further decrease in pH (57). The pH dependence of this reaction is highly significant for natural waters. At pH = 6.0 about a week is required to oxidize 95% of an initial quantity of Fe(II), whereas at pH = 8.0 the reaction is 95% complete in one minute (31).

Evidence has been acquired which shows that the rate of ferrous oxidation differs for various solution complexes of Fe^{2+}

(55). The rate increases in the order of the following anions: ClO_4^-, SO_4^{2-}, Cl^-, PO_4^{3-}, and OH^-. There are several possible mechanisms for the ferrous oxygenation reaction. The Haber-Weiss mechanism has received the most attention (15) and it involves the following rate determining step:

$$FeOH^+ + O_2 + H^+ \rightarrow FeOH^{2+} + HO_2 \qquad (11)$$

This reaction would account for the first order dependence on Fe(II) and O_2, but it predicts a zero order pH dependence. The HO_2 species formed by reaction (11) would react rapidly to form H_2O_2 and possibly H_2O with the subsequent electron transfer reactions involving either additional Fe(II) or another reduced substance in the system. Goto et al. (58) proposed the following rate determining step to account for the observed dependence on Fe(II), O_2, and OH^-:

$$FeOH^+ + O_2OH^- \rightarrow Fe(OH)_2^+ + O_2^- \qquad (12)$$

The O_2^- species would undergo rapid protonation to HO_2 with subsequent reactions as suggested in the Haber-Weiss mechanism. Reaction (12) postulates the existence of an O_2OH^- species which is a hydrated oxygen molecule that has undergone proton dissociation similar to the hydrolysis reactions of transition metal ions. The O_2OH^- species must be quantitatively insignificant compared to ordinary dissolved oxygen even in 2 N NaOH solutions, because the solubility of oxygen in aqueous solution is not pH dependent.

We can suggest two possible rate determining steps which conform to the rate law of equation (10) without invoking a special form of dissolved oxygen. The first one is:

$$Fe(OH)_2^\circ + O_2 \rightarrow Fe(OH)_2^+ + O_2^- \qquad (13)$$

The calculations of Fe(II) species indicate that the $Fe(OH)_2^\circ$ complex is less than 0.02% of T(Fe(II)) at pH = 7.0, so that reaction (13) would require the rate constant for $Fe(OH)_2^\circ$ oxygenation to be several orders of magnitude greater than one for an $FeOH^+ + O_2$ reaction. The second possibility is:

$$FeOHH_2O^+ + O_2 \rightarrow Fe(OH)_2^+ + HO_2 \qquad (14)$$

in which the rate determining step involves the deprotonation of a hydrated water molecule along with the electron transfer between Fe and O_2. Both the deprotonation and the concentration of $FeOH^+$ would be favored by an increase in pH thereby leading to the second order dependence of the rate on OH^-. Reaction (14) is more consistent than (13) with the principal Fe(II) species in the neutral pH range.

The role of dissolved organic matter in natural waters is another factor which is significant in the kinetics of the Fe(II)-

Fe(III) reaction. Experiments have shown that organic substances may have several effects on iron reactions (59, 60). Tannic acid, gallic acid, and pyrogallol prevented the oxygenation of Fe(II). Other substances such as glutamic acid, tartaric acid, and glutamine produced a slower rate of oxygenation than was observed in $NaHCO_3$ solutions at the same pH = 6.3. Citric acid produced an initial rate which was greater than the one in $NaHCO_3$. Thus different organic materials can inhibit, retard, or accelerate the rate of ferrous oxygenation. Theis and Singer (60) also found that 10^{-4} molar concentrations of numerous organic compounds could reduce 10^{-6} to 10^{-5} molar concentrations of Fe(III) to Fe(II) in the presence of dissolved oxygen. The humic acid portion of organic material extracted from fresh waters exhibits some of the same characteristics with Fe(II) and Fe(III) as tannic acid. These results have significant implications which require investigation of the kinetics of iron redox reactions in marine systems.

Some initial studies of the rate of ferrous oxygenation in natural waters have been carried out in our laboratory. Two experimental approaches were used. A direct monitoring of the Fe(III) product as a function of time was performed by recording the absorbance at 295 nm of the reaction solution contained in a 10 cm cell. Approximately 5×10^{-6} moles of $FeCl_2$ was added to the reaction medium which had a pH between 7.9 and 8.3. The increase in absorbance at 295 nm with time is due to the formation of ferric hydroxy complexes and the scattering of light by colloidal and particulate hydrous ferric oxide. Because the attenuation of light intensity due to absorption and scattering may not have been directly proportional to the Fe(III) concentration a second technique was used in which scattering was not a factor. Samples were allowed to react for various periods of time, and the reaction was quenched by the addition of 1.1 N $HClO_4$ to reduce the pH to 2.5. The UV spectrum of the quenched sample was characteristic of Fe(III) complexes over the wavelength range 240-400 nm. The absorbance at 303 nm of the quenched samples varied linearly with the ferric concentration over the range of 1-8 μM.

An example of the results obtained by the direct monitoring of absorbance at 295 nm is shown in Figure 6. For the reaction:

$$Fe(II) + O_2 \rightarrow Fe(III)$$

the pseudo first order rate law may be written

$$\frac{d\ [Fe(II)]}{d\ t} = k' \{[Fe(II)]_o - [Fe(III)]\} \qquad (15)$$

where [Fe(II)] and [Fe(III)] are the concentrations of reduced and oxidized iron at time t and $[Fe(II)]_o$ is the initial concentration of ferrous iron. The rate parameter k' will be a constant

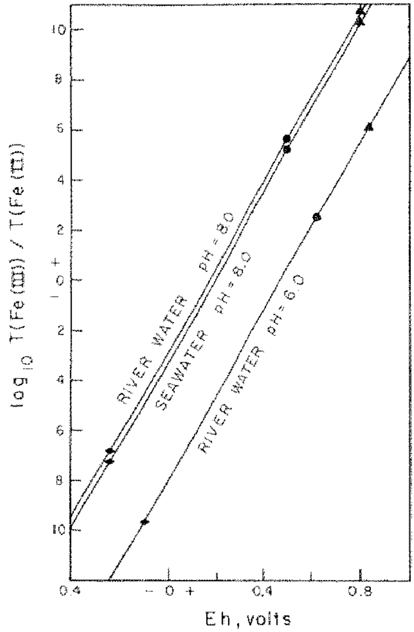

Figure 5. Variation in the ratio of total Fe(III) to total Fe(II) molality as a function of Eh for three natural water systems. ▲, *Eh control by the O_2/H_2O reaction;* ●, *Eh control by the O_2/H_2O_2 reaction;* ◆, *the control of Eh by the SO_4^{2-}/S^{2-} reaction.*

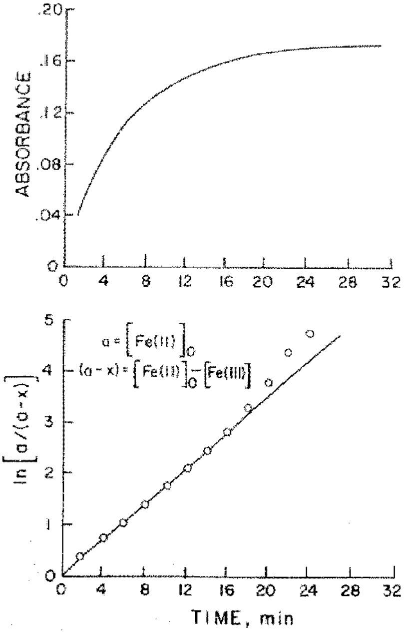

Figure 6. Rate of Fe(II) oxygenation in Narragansett Bay seawater at pH = 8.08. The upper curve shows the continuously recorded absorbance at 295 nm. The lower plot shows the logarithmic fit which is characteristic of a pseudo first order rate, the slope of which yields k′.

provided that pH and P are constant (compare equation (15) with (10)). The plot of ln $[Fe(II)]_o/([Fe(II)]_o - [Fe(III)])$ versus time yields a straight line during the initial portion of the reaction (e.g., the first 16 min in Figure 6). Deviations from this line are observed over longer periods of time which may be due to departures in a direct proportionality between [Fe(III)] and absorbance due to coagulation and scattering effects of the hydrous ferric oxide. The value of k' was obtained from the initial linear portion of the data. This rate parameter was indistinguishable from the value obtained by the quenching technique in which scattering of the light was not a factor.

The rate constant k in equation (10) was calculated from k', pH, and P. The results of our measurements in natural seawater from Narragansett Bay and surface Sargasso Seawater are shown in Table IX along with the values obtained by Singer and Stumm (57) in sodium bicarbonate solutions. The $t_{\frac{1}{2}}$ is the time required for the concentration of Fe(II) to be diminished by a factor of two. These preliminary results show that the rate of this reaction is much slower in natural marine waters than would be expected on the basis of measurements in sodium bicarbonate solutions. This observation could reflect the importance of organic matter as pointed out by Theis and Singer (60) or of other constituents in marine waters on the rate of ferrous oxygenation.

Table IX. The rate of ferrous oxygenation in marine waters and in sodium bicarbonate solutions.

Medium	k^a	$t_{\frac{1}{2}}$ at $P_{O_2} = 0.2094$ pH = 7 (min)	pH = 8 (min)	Source
$NaHCO_3$, pH = 2-6	8.0×10^{13}	4	0.04	(57)
Narragansett Bay S°/oo = 31.2°/oo, pH = 7.9 - 8.3	6×10^{11}	550	5.5	This work
Sargasso Seawater S°/oo = 36.0°/oo, pH = 8.2	10×10^{11}	330	3.3	This work

a: The units for k are liter^2 mol^{-2} atm^{-1} min^{-1}

Summary of Iron Reactions in Marine Waters

Four aspects of the chemistry of iron have been considered in this paper. The formation of ferrous solution complexes varies significantly with salinity and pH over the range of conditions encountered in coastal regions. Complexes of ferric iron are primarily hydroxide species which depend on pH and which appear not to vary greatly with salinity. The redox equilibrium between Fe(II) and Fe(III) favors the predominance of Fe(III) if the redox potential is set by either the O_2/H_2O or O_2/H_2O_2 reaction, but Fe(II) is the stable oxidation state when the redox potential is set by the SO_4^{2-}/S^{2-} reaction. The rate of oxygenation of Fe(II) in natural waters depends greatly on pH, and preliminary data indicate that this reaction is slower in marine waters than in sodium bicarbonate solutions. Knowledge of these types of chemical processes under environmental conditions provides a basis for predicting the behavior of dissolved iron in marine systems.

This analysis of iron chemistry points to several areas where additional information is needed. Data are lacking for evaluating the significance of bicarbonate and carbonate species of iron and for possible sulfide species of Fe(II). Equilibrium considerations indicate that iron organic complexes are not likely to be stable in marine systems, but this conclusion should be tested by experimental methods and it should be recognized that biochemically synthesized iron organic species may be kinetically, if not thermodynamically, stable. Additional work is required to determine the kinetics of ferrous oxygenation in marine systems. The role of dissolved organic matter appears to be of considerable importance. Observations by Lewin and Chen (61) indicate the presence of Fe(II) in coastal waters immediately after sampling and the quantity of Fe(II) decreases over a period of 30-40 hours upon storage. There may be a steady state concentration of Fe(II) in marine waters due to a balance between its rate of production by biological systems and its rate of oxygenation to Fe(III). The development of analytical techniques to determine 10^{-8} molar concentrations of organic and inorganic forms of Fe(II) and Fe(III) in marine waters would be a great asset to further work on the marine chemistry of iron.

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