Speciation of metals in natural waters

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Article

The form or speciation of a metal in natural waters can change its kinetic and thermodynamic properties. For example, Cu(II) in the free ionic form is toxic to phytoplankton, while copper complexed to organic ligands is not toxic. The form of a metal in solution can also change its solubility. For example, Fe(II) is soluble in aqueous solutions while Fe(III) is nearly insoluble. Natural organic ligands interactions with Fe(III) can increase the solubility by 20-fold in seawater. Ionic interaction models that can be used to determine the activity and speciation of divalent and trivalent metals in seawater and other natural elements will be discussed. The model is able to consider the interactions of metals with the major (Cl^-, SO_4^{2-}, HCO_3^-, CO_3^{2-}, Br^-, F^-) and minor (OH^-, $H_2PO_4^-$, HPO_4^{2-}, PO_4^{3-}, HS^-) anions as a function of temperature (0 to 50 °C), ionic strength [0 to 6 m (m = mol kg^{-1})] and pH (1 to 13). Recently, it has been shown that many divalent metals are complexed with organic ligands. Although the composition of these ligands is not known, a number of workers have used voltammetry to determine the concentration of the ligand [L^n] and the stability constant (K_{ML}) for the formation of the complex

$$M^{2+} + L^n \rightarrow ML^{n+2} \quad K_{ML} = [ML^{n+2}]/[M^{2+}][L^n]$$

We have added the experimental values of K_{ML} for the formation of complexes of natural organics in seawater of known concentration ([L^n]) with Cu^{2+}, Zn^{2+}, Cd^{2+}, Co^{2+}, and Fe^{3+}. The model can be used to examine the competition of inorganic and organic ligands for divalent metals as a function of ionic strength. The importance of organic ligands in controlling the solubility of Fe(III) in seawater will be discussed. New experimental studies are needed to extend the model to higher temperatures and ionic strength.

Introduction

The formation of ion-pairs or ion-complexes in natural waters can have a major effect on the rates of redox processes,[1,2] mineral solubility[3] and biochemical availability.[4] An example of the importance of the formation of ion-pairs can be demonstrated by considering the reduction of Fe(III) with S(IV)

$$\text{Fe(III)} + \text{S(IV)} \Rightarrow \text{Products} \quad (1)$$

$$-d[\text{Fe(III)}]/dt = k[\text{Fe(III)}][\text{S(IV)}] \quad (2)$$

The rate constants (k) for the reduction of Fe(III) in NaCl and seawater solutions as a function of ionic strength (I) are shown in Fig. 1.[5] The rates in seawater are lower than the rates in NaCl at the same ionic strength (I). To examine why the values are lower in seawater than NaCl at the same ionic strength, we determined the rates (Fig. 2) in solutions of NaCl with added amount of the major cations (Mg^{2+}, Ca^{2+}, K^+, Sr^{2+}) and anions (SO_4^{2-}, HCO_3^-, Br^-, F^-) at their concentrations in seawater.[6] We were surprised to find that F^- at 70 μM was largely responsible for the lower values in seawater.

We also determined the effect of pH on the reduction of Fe(III) with S(IV) in seawater. The results are shown in Fig. 3.

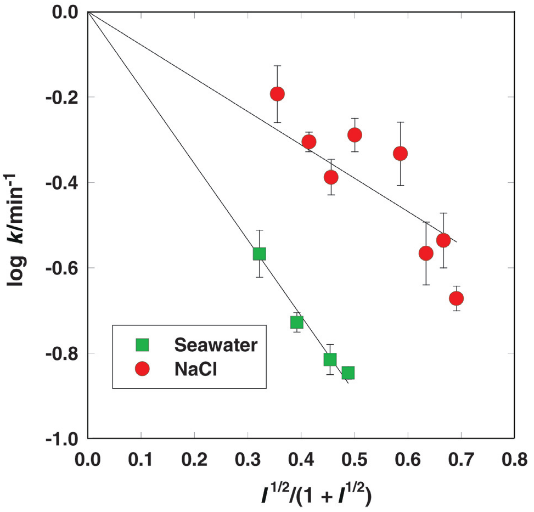

Fig. 1 The reduction of Fe(III) with S(IV) in NaCl and seawater at 25 °C.[5]

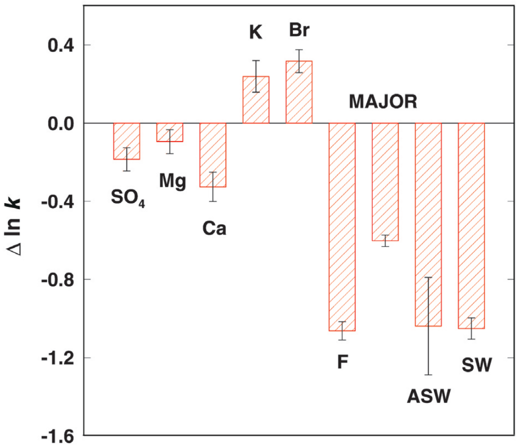

Fig. 2 The effect of the major seasalts on the reduction of Fe(III) with S(IV) at 25 °C.[5]

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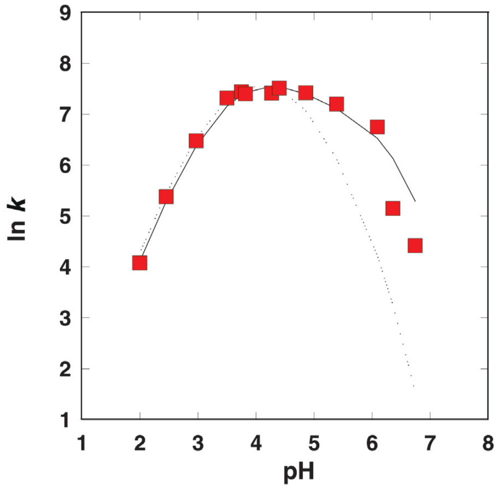

Fig. 3 The effect of pH on the reduction of Fe(III) with S(IV) in seawater at 25 °C.[5]

The rates go through a maximum near a pH of 4. We have attributed the changes in the rates as a function of pH, as being related to the hydrolysis of Fe(III)[7]

$$Fe^{3+} + H_2O \overset{\beta_1}{\Leftrightarrow} Fe(OH)^{2+} + H^+ \tag{3}$$

$$Fe^{3+} + 2H_2O \overset{\beta_2}{\Leftrightarrow} Fe(OH)_2^+ + 2H^+ \tag{4}$$

$$Fe^{3+} + 3H_2O \overset{\beta_3}{\Leftrightarrow} Fe(OH)_3 + 3H^+ \tag{5}$$

where β_i are the step-wise hydrolysis constants. The measured rate constant can be attributed to

$$\begin{aligned} k = {} & k_0\alpha(Fe^{3+}) + k_1\alpha(FeOH^{2+}) + k_2\alpha(Fe(OH_2^+)) \\ & + k_3\alpha(Fe(OH)_3) \end{aligned} \tag{6}$$

where the values of k_i are the rate constants respectively for the reduction of the various species

$$-d[Fe^{3+}]/dt = k_0[Fe^{3+}] \tag{7}$$

$$-d[FeOH^{2+}]/dt = k_1[FeOH^{2+}] \tag{8}$$

$$-d[Fe(OH)_2^+]/dt = k_2[Fe(OH)_2^+] \tag{9}$$

$$-d[Fe(OH)_3]/dt = k_3[Fe(OH)_3] \tag{10}$$

An analysis of the rates using the hydrolysis constants for seawater[7] indicated that at low pH (1.8 to 4) the species $Fe(OH)^{2+}$ is reduced (the dotted line in Fig. 3) while at higher pH (4 to 7) the $Fe(OH)_2{}^+$ ion pair is reduced (the solid line in Fig. 3). An examination of the effect of pH on the speciation of Fe^{3+} in seawater shown in Fig. 4 demonstrates that the FeF^{2+} species, which maximizes at pH 2.5 is important and is responsible for the lower rate of reduction in seawater. At a pH near 4 the $FeOH^{2+}$ species is dominant and is responsible for the maximum rate near a pH of 4. So the FeF^{2+}, Fe^{3+} and $Fe(OH)_3$ species appear to be non-labile; while the $FeOH^{2+}$ and $Fe(OH)_2{}^+$ species appear to be labile to reduction with S(IV). The importance of the speciation in the oxidation and reduction of metals (Cu, Fe, Cr, *etc.*) and non-metals (H_2S, H_2SO_3) is examined in more detail elsewhere.[2]

Modeling speciation

A quantitative model is needed to examine the speciation of metals in natural waters as a function of temperature, ionic strength and composition. The speciation of cations (M) and anions (X) in solution can be determined by a series of iterations of the equations

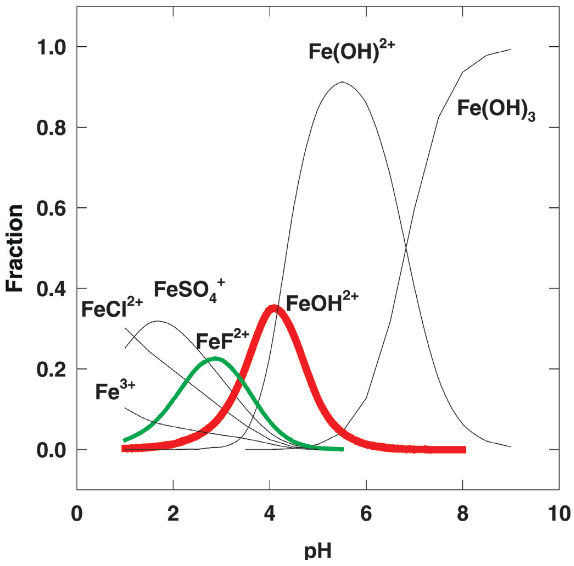

Fig. 4 The speciation of Fe(III) in seawater as a function of pH at 25 °C.[5]

$$[M]_F/[M]_T = \{1 + \textstyle\sum_i [X]_F K^*_{MXi}\}^{-1} \tag{11}$$

$$[X]_F/[X]_T = \{1 + \textstyle\sum_i [M]_F K^*_{MiX}\}^{-1} \tag{12}$$

where [i] is the concentration of ion i, F is the free and T is the total concentration and K^*_{MX} are the stoichiometric association constants for the formation of simple 1–1 complexes MX

$$M^+ + X^- \Leftrightarrow MX \tag{13}$$

$$K^*_{MX} = [MX]/[M^+]_F[X^-]_F \tag{14}$$

The values of K^*_{MX} are a function of ionic strength, temperature, pressure and composition of the media. Thus, they need to be determined for each solution of interest. Our modeling of the speciation is based on estimating the values of K^*_{MX} in the media of interest at a given temperature and ionic strength. The thermodynamic association constant (K_{MX}) for the formation of an ion-pair like $CaCO_3$ is related to the stoichiometric constants by

$$\begin{aligned} K_{CaCO_3} & = a_{CaCO_3}/a_{Ca}a_{CO_3} \\ & = \{\gamma(CaCO_3)_T/\gamma(Ca^{2+})_T\gamma(CO_3^{2-})_T\} \\ & \quad \{[CaCO_3]_T/[Ca^{2+}]_T[CO_3^{2-}]_T\} \\ & = K^*_{CaCO_3}\{\gamma(CaCO_3)_T/\gamma(Ca^{2+})_T\gamma(CO_3^{2-})_T\} \end{aligned} \tag{15}$$

where a_i is the activity, $\gamma(i)_T$ is the total activity coefficient and $[i]_T$ the total concentration of i. The value of K^*_{MX} in any natural water can be estimated from the values in pure water providing that reliable estimates can be made of the total activity coefficients.

The activity of a metal ion is related to the total and free metal concentration by

$$a_{Ca} = \gamma(Ca^{2+})_T[Ca^{2+}]_T = \gamma(Ca^{2+})_F[Ca^{2+}]_F \tag{16}$$

where $\gamma(Ca^{2+})_F$ is the activity of free $[Ca^{2+}]_F$. The total activity coefficient is related to the free value by

$$\begin{aligned} \gamma(Ca^{2+})_T & = \{[Ca^{2+}]_F/[Ca^{2+}]_T\}\gamma(Ca^{2+})_F \\ & = \alpha(Ca^{2+})\gamma(Ca^{2+})_F \end{aligned} \tag{17}$$

where $\alpha(Ca^{2+}) = \{[Ca^{2+}]_F/[Ca^{2+}]_T\}$ is the fraction of free Ca^{2+} in the solution which can be determined from the speciation of Ca^{2+} [eqn. (11)]. The values of $\gamma(Ca^{2+})_F$ can be estimated in a given ionic media for the interactions of Ca^{2+} with all the anions in the solution that do not form strong complexes (Cl^-, $SO_4{}^{2-}$, $HCO_3{}^-$, Br^-).

The MIAMI ionic interaction model

Earlier workers estimated the activity coefficients of ions and speciation of metals in natural waters using the ion-pairing model.[8,9] Others[10,11] have extended this work. Byrne *et al.*[12] extended these calculations from 0 to 50 °C for a number of metals. Millero and Hawke[13] have added the divalent metals (Ba^{2+}, Mn^{2+}, Fe^{2+}, Co^{2+}, Pb^{2+}, Ni^{2+}, Zn^{2+}) to the major ion-pairing model of Millero and Schreiber.[11] A number of computer codes have been developed to aid in the use of this model to determine the speciation of metals in natural waters.[14,15] Although these programs are useful in rapidly calculating the speciation, the data are generally limited to 25 °C and low ionic strengths [<1 m (m = mol kg^{-1})].

In more recent years, the specific interaction model of Pitzer[16] has been combined with the ion-pairing model to yield activity coefficients of ionic and non-ionic solutes over a wide range of temperatures and ionic strengths. The model was first used by Whitfield[17,18] to estimate the activity coefficients of ions in seawater. Weare and co-workers[19–24] and others[25–30] have extended the model.

Most of the Pitzer[16] models used for the major components of natural waters are based on the 25 °C model of Weare and coworkers[19,20] which accounts for the interactions of the major cations and anions (H^+, Na^+, K^+, Mg^{2+}, Ca^{2+}, Cl^-, OH^-, $HCO_3{}^-$, $SO_4{}^{2-}$, $CO_3{}^{2-}$, CO_2) over a wide range of temperatures (0 to 250 °C) to high ionic strengths (<6 m). The extension of these models to trace ions at 25 °C has been made by a number of workers.[7,27–31] Campbell *et al.*[32] have developed a Pitzer[16] model for the major sea salts that considers the ionic interactions of H–Na–K–Mg–Ca–Sr–Cl–Br–OH–HSO_4–SO_4–H_2O from 0 to 50 °C and ionic strengths from 0 to 2 m. Clegg and Whitfield[28] have developed a major seawater model that they use to examine the dissociation of ammonia over the same temperature range. The extension of the Pitzer[16] model for divalent and trivalent metals[7,31] has been made at 25 °C. Millero and Roy[29] extended the model to include the components needed to evaluate the carbonate system in natural waters from $I = 0$ to 6 m and 0 to 50 °C. More recently, Millero and Pierrot[30] have extended the model to include a number of divalent and trivalent metals from 0 to 50 °C. This latter model can be used to estimate the stability constants for the formation of inorganic metal complexes and the speciation of metals in natural waters from 0 to 50 °C and high ionic strengths.

The activity coefficients of ions are estimated by the Pitzer[16] equations using equations of the form

$$\ln \gamma_i = DH + \sum{}_{ij} m_i m_j B^{\gamma}_{ij} + \sum{}_{ijk} m_i m_j m_k C^{\gamma}_{ijk} \qquad (18)$$

where DH is some form of the Debye–Hückel limiting law; m_i, m_j and m_k are the molalities of i, j and k, respectively. The B^{γ}_{ij} and C^{γ}_{ijk} parameters are related to the binary (ions i and j) and ternary (ions i, j and k) interactions and can be a function of ionic strength. In more simplistic terms the equation for the activity coefficient of a metal (M) is given by

$$\ln \gamma_M = DH + \sum (M\text{–}X) + \sum (M\text{–}N) + \sum (M\text{–}N\text{–}X) \qquad (19)$$

where M–X is related to cation–anion interactions (Mg^{2+}–$CO_3{}^{2-}$), M–N is related to cation–cation interactions (Mg^{2+}–Ca^{2+}) and (M–N–X) is related to triplet interactions (Mg^{2+}–Ca^{2+}–Cl^-). The sum is the molal weighted interactions of all the components in the solution

$$\sum (M\text{–}X) = (M\text{–}Cl^-) + (M\text{–}SO_4^{2-}) + (M\text{–}HCO_3^-) + \ldots \qquad (20)$$

$$\sum (M\text{–}N) = (M\text{–}Na^+) + (M\text{–}Mg^{2+}) + (M\text{–}Ca^{2+}) + \ldots \qquad (21)$$

$$\sum (M\text{–}N\text{–}X) = (M\text{–}Na^+\text{–}Cl^-) + (M\text{–}Mg^{2+}\text{–}Cl^-) + (M\text{–}Na^+\text{–}SO_4^{2-}) + \ldots \qquad (22)$$

The interaction parameters ($\beta^{(0)}_{NaCl}$, $\beta^{(1)}_{NaCl}$, C^{ϕ}_{NaCl}) are determined from binary solutions (NaCl). The ternary interaction terms (Θ_{NaMg} Ψ_{NaMgCl}) are determined from mixtures with a common ion (NaCl + $MgCl_2$). For trace metals that do not contribute to the composition of the solution the activity coefficient can be determined from six contributions:

(i) The Debye–Hückel limiting law, which is only a function of ionic strength.

(ii) The interaction parameters of M with the major anions (Cl^-, $SO_4{}^{2-}$, *etc.*) in the solution.

(iii) The interaction parameters of M with the major cations (Na^+, Mg^{2+}, *etc.*).

(iv) The triplet interaction parameters of M with the major cations and anions (M–Na–Cl).

(v) The media terms for the major components determined from binary solutions of the major components of the solution.

(vi) The higher order electrical terms for the interactions of ions of different charge (Mg–Na) are a function of ionic strength.

For most trace metals only the contributions from (ii) are needed to make reasonable estimates of the "trace" activity coefficients.[25] The trace components of the solution do not contribute significantly to the media terms. Although this simplifies the estimation of the activity coefficients of trace constituents, many trace constituents form strong interactions with the components (OH^-, $CO_3{}^{2-}$, *etc.*) of the solution and cannot easily be accounted for using values for the Pitzer interaction parameters. To correct for these strong interactions one must consider the formation of an ion-pair between the cation and anion. This leads to parameters for the ion-pairs that are model-dependent. The major ion model includes the formation of a number of ion pairs ($HSO_4{}^-$, HF, $MgOH^+$, $MgCO_3$, $CaCO_3$, $MgB(OH)_4{}^+$ and $CaB(OH)_4{}^+$ ion-pairs). The addition of trace metals to the model[30] includes terms for the formation of metal complexes with Cl^-, $SO_4{}^{2-}$, OH^- and $CO_3{}^{2-}$.

Reliability of the model

The reliability of the model in natural waters can be examined by comparing the calculated activity and osmotic coefficients with those determined by direct measurements. A comparison[30] between the measured and calculated total activity coefficients for a number of ions in seawater is shown in Fig. 5. The agreement is quite good for most of the ions. As shown[29] in Fig. 6 the model yields reliable dissociation constants for the dissociation of carbonic acid in seawater from 0 to 50 °C. Comparisons of the measured and calculated values of the p*K* for a number of acids in seawater at 25 °C are shown in Fig. 7. The differences are quite reasonable and are close to the experimental error for most of the acids. It is interesting to note

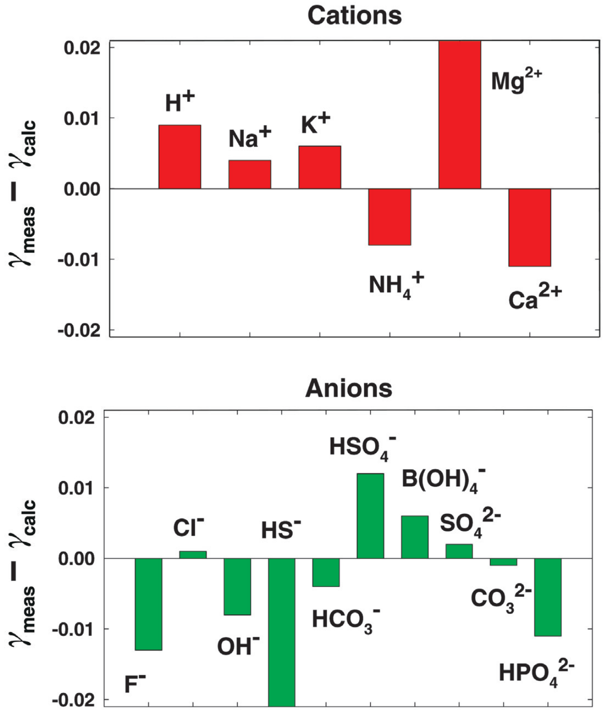

Fig. 5 A comparison of the measured and calculated activity coefficients of cations and anions in seawater at 25 °C.[30]

that the calculated pK_1 and pK_2 for carbonic acid are in better agreement with the measurements of Mehrbach *et al.*[33] at 25 °C in accord with our earlier Pitzer model[25] and more recent studies.[34]

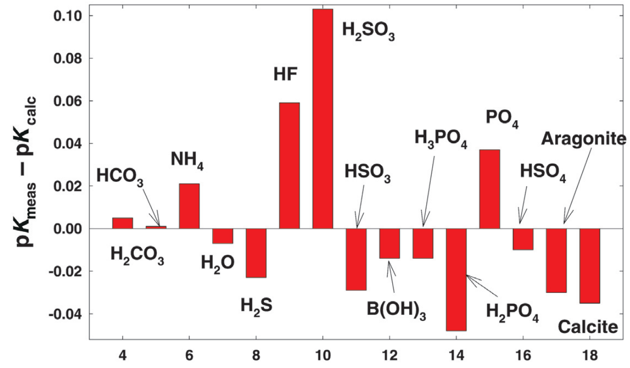

Fig. 7 A comparison of the measured and calculated p*K* of acids and solubility of $CaCO_3$ in seawater at 25 °C.[29]

The present model provides reliable activity coefficients for all the major components of seawater from 0 to 50 °C. It has also been shown to provide reliable estimates of the p*K* of acids in seawater from 0 to 50 °C.[29] More recently, the model includes divalent and trivalent metals from 0 to 50 °C using enthalpy and heat capacity data. A number of workers have started to derive Pitzer[16] coefficients for the interactions of actinides with the major inorganic anions of natural waters.[35] More reliable measurements of the stability constants for the formation of OH^-, CO_3^{2-}, *etc.* with divalent and trivalent metals in NaCl are needed (0 to 50 °C) and ionic strength (0 to 6 m) to derive Pitzer[16] coefficients of ion-pairs. These fundamental data are needed to examine the competition of inorganic and organic ligands for trace metal in natural waters. Extensions of the model for the minor anions of natural waters at the present time are difficult due to the lack of reliable activity coefficient data for Na, K, Mg and Ca salts over a wide range of temperatures.

An example of the output of the model is shown for the speciation of La(III) in seawater in Fig. 8. As found in earlier work[31] most of La(III) is complexed with carbonate ions in seawater. The model can also easily determine the effect of pH on the speciation of Fe(III) in seawater[7] (Fig. 4) and NaCl solutions[3] (Fig. 9). The importance of the formation of metal organic complexes is discussed in the next section.

Organic complexes

Recent workers[36–55] have shown that many trace metals can form strong complexes with natural organic ligands. Before we discuss these results it is useful to examine the methods used to study the formation of the complexes in natural waters between a metal (M) and organic ligand (L)

$$M + L = ML \tag{23}$$

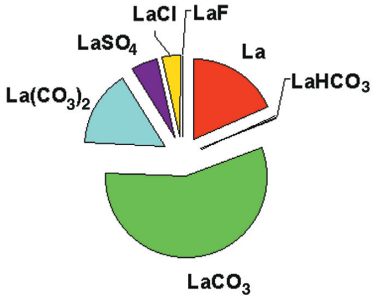

Fig. 8 The speciation of La(III) in seawater at 25 °C.[31]

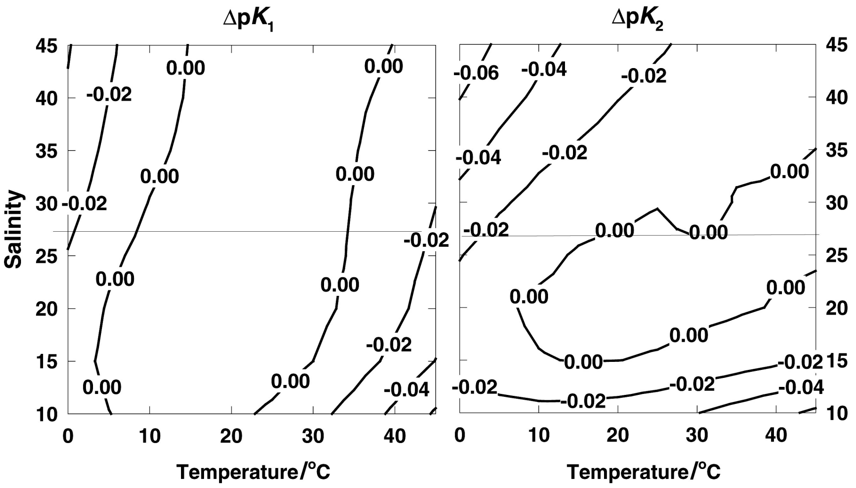

Fig. 6 A comparison of the measured[33] and calculated ($\Delta pK = pK_{meas} - pK_{calc}$) pK_1 and pK_2 of carbonic acid in seawater at 25 °C.[29]

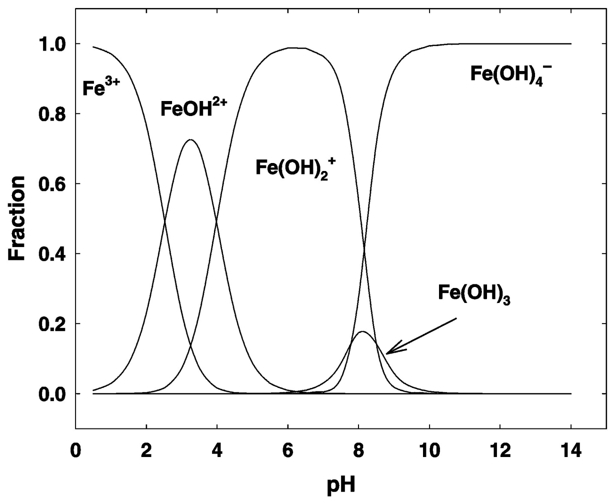

Fig. 9 The speciation of Fe(III) in 0.7 m NaCl at 25 °C.[3]

Because the measurements are made directly in seawater, the formation constant used is defined in terms of easily measurable quantities

$$K'_{ML} = [ML]/[M'][L'] \tag{24}$$

where [ML] is the concentration of the complex, [M′] is the concentration of the metal not complexed by L, and [L′] is the concentration of the free ligand not complexed by M. The values of [M′] and [L′] are related to the total concentrations by

$$[M]_T = [M'] + [ML] \tag{25}$$

$$[L]_T = [L'] + [ML] \tag{26}$$

where the subscript T is used to denote the total analytical concentrations. The values of [M′] and [L′] are related to the free metal and ligand by

$$[M'] = [M^{n+}] + \sum MX_i \tag{27}$$

$$[L'] = [L^{n-}]_T + \sum N_iL \tag{28}$$

where X_i are the inorganic ligands (OH^-, CO_3^{2-}, *etc.*) that can complex the metal and N_i are the cations that can complex the ligand (Mg^{2+}, Ca^{2+}, and other trace metals). Since natural organic ligands cannot normally be studied in simple solutions, it is not possible to determine the free ligand concentrations [L^{n-}], and the values of [L′] are normally reported. The concentration of the free metal not complexed to inorganic ligands can be determined by the methods discussed above

$$[M^{n+}] = [M']\alpha_M \tag{29}$$

where α_M is the fraction of free metal in the solution without the organic ligand determined from

$$\alpha_M = 1/(1 + \sum K_{MXi}\,[X_i]) \tag{30}$$

To examine the competition between organic and inorganic ligands it is more appropriate to use the stability defined in terms of the free metal

$$K_{ML} = [ML]/[M^{n+}][L'] \tag{31}$$

where

$$\alpha*_M = 1/(1 + \sum K_{MXi}[X_i] + K_{ML}[L']) \tag{32}$$

Because the concentrations of the inorganic ligands are normally much higher than those of the organic ligands, one can use the fraction of free metals determined in seawater without organics to make a reasonable estimate of the value from

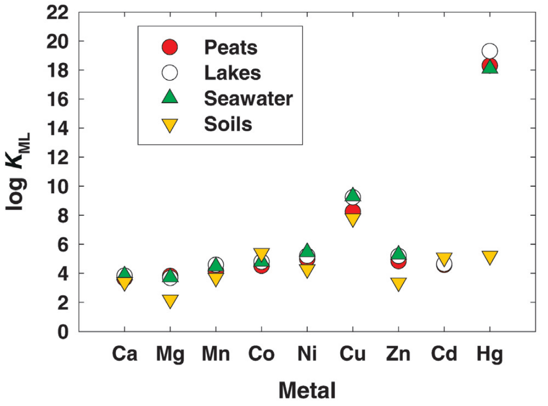

Fig. 10 The p*K* for the formation of metal complexes with humics collected from various areas.[2]

$$K_{ML} \approx K'_{ML}/\alpha^*{}_M \tag{33}$$

The values of α^*_M, the fraction of free metal in seawater, with various concentrations of inorganic and organic ligands can be estimated from eqn. (32). For the organic complexes to dominate, the speciation of a metal $K_{ML}[L'] > \sum K_{MX_i}[X_i]$. This can occur when K_{ML} or [L′] is large. In more simple terms, if the value of $[L'] > 1/K_{ML}$ or $K_{ML} > 1/[L']$ organic complexation can be important. For example, if $K'_{ML} = 10^9\ M^{-1}$, the concentration of [L′] must be greater than 1 nM to start to affect the speciation.

Because humic materials are the most abundant organic material in natural waters, a number of workers have determined the stability constants for the formation of metal complexes with extracted humics. Some of these results[56] for humic material collected from water, soils, sediments, peats *etc.* as a model organic ligand are shown in Fig. 10. The stability constants for individual metals with different source material are in reasonable agreement. With the exception of Cu(II) and Hg(II) the stability constants are not very large and indicate that organic complexes may not be important except at high concentrations of humics in coastal and estuarine waters.

Much of our recent knowledge of the concentration and strength of metal organic ligands in seawater comes from voltammetric measurements. The stability constants[36–55] found using these methods are shown in Table 1. These constants are quite large and indicate that most of the metals are strongly complexed with organic ligands in ocean waters. An example of the importance of organic complexes is shown in Fig. 11 for Cu(II).[6] Cu(II) can form complexes with two organic ligands.[41] The concentrations $L_1 = 5$ and $L_2 = 150$ nM with stability constants of log $K_1 = 12$ and log $K_2 = 9$ have been used in these calculations. The results are quite striking as the fraction of free Cu(II) goes from 0.03 to 0.0002 at a pH of 8.1.

A number of workers[36–55] have used these techniques to examine the concentration and strength of natural organic ligands capable of complexing Fe(III) in seawater. These studies

Table 1 Dissociation constants of metal organic complexes in seawater

Metal	[M]	[L]	log K_{ML}	Reference
Cu(II)	1–10 nM	2–60 nM	8.5	36–44
Zn(II)	0.1–2 nM	1.2 nM	12	45
Cd(II)	2–800 pM	100 pM	12.0	46
Pb(II)	17–49 pM	200–500 pM	11	47
Ni(II)	1.7–4.3 nM	2–4 nM	17–19	48
Co(II)	10–103 pM	9–83 pM	11–16	49–51
Fe(III)	0.2–8 nM	0.4–13 nM	19–23	52–55

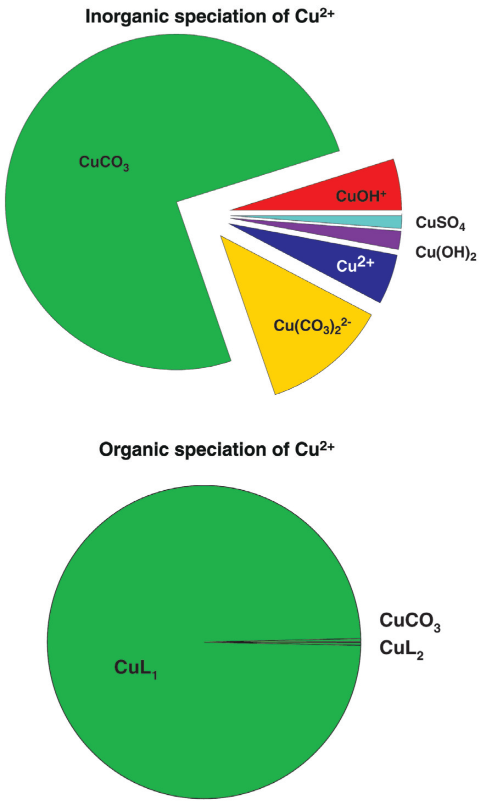

Fig. 11 The effect of natural organic ligands[41] on the speciation of Cu(II) in seawater.[30] L_1 and L_2 are weak organic ligands and strong organic ligands, respectively.

(Table 1) yield apparent stability constants of $K_{FeL} = 10^{19} - 10^{23}$. At high ligand concentrations and pH near 8, Fe(III) is almost completely complexed with this ligand.[57] The importance of the formation of metal organic complexes can be shown by examining the solubility of Fe(III) in seawater in the next section.

Solubility of Fe(III) in seawater

The solubility of Fe(III) was first measured by Byrne and Kester[58] and more recently by Kuma *et al.*[59] The solubility of Fe(III) in NaCl solutions was recently measured by Liu and Millero.[3] More recently, Liu and Millero[60] have measured the solubility of Fe(III) in seawater as a function of pH, temperature and salinity. The results of two runs in Gulf Stream seawater are shown in Fig. 12. The results can be represented using stepwise stability constants of $\beta_1 = 10^{-2.5}$, $\beta_2 = 10^{-6.5}$ and $\beta_3 = 10^{-13.6}$ for the hydrolysis constants for Fe(III) in seawater [eqn. (3) and (4)]. Our results[60] (200–300 nM) near a pH = 8 are in good agreement with the earlier measurements of Byrne and Kester[58] and Kuma *et al.*[59] A comparison of the solubilities of Fe(III) in 0.7 M NaCl[3] and seawater[60] are shown in Fig. 13. The solubilities in 0.7 M NaCl are much lower (10 pM) than the values found in average seawater (200–300 pM) at a pH near 8. The effect of ionic strength on the solubility of Fe(III) in seawater and NaCl at 25 °C shows this much clearer in Fig. 14. In dilute solutions the solubilities approach a common value in pure water. At higher concentrations the solubilities in NaCl are much lower than the values in seawater.

To examine this effect in more detail we have made a number of solubility measurements at 25 °C and pH = 8.1 in NaCl with added amounts of the major sea-salt ions at their concentration in seawater[60] (Fig. 15). None of the major sea-salt ions strongly affected the solubility of Fe(III). We also measured the solubility of Fe(III) in UV irradiated seawater and found the results were in good agreement with the results in 0.7 M NaCl. Finally, we measured the solubility in seawater diluted with 0.7 M NaCl solutions (Fig. 16). Again, the solubility in diluted seawater approached the solubility in pure NaCl solutions (10 pM).[60] These results clearly demonstrated that the solubility of Fe(III) in seawater is 20 times higher than expected due to natural organic ligands. All of these changes in the solubility can be modeled using the stability constants found by workers in seawater (Table 1) using reasonable levels for the concentration of organic ligands,[57] which may vary from place

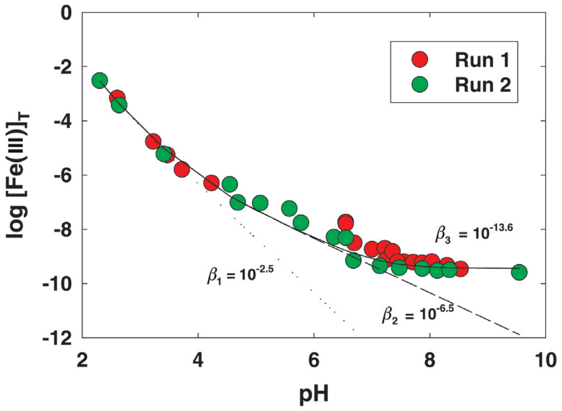

Fig. 12 The effect of pH on the solubility of Fe(III) in seawater at 25 °C.[60]

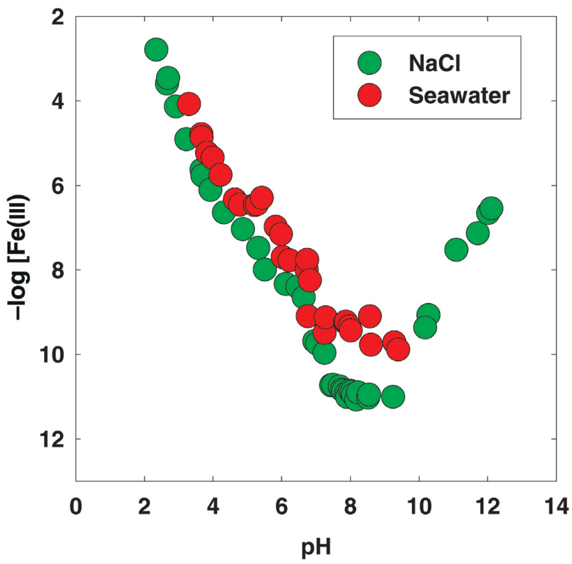

Fig. 13 A comparison of the solubility of Fe(III) as a function of pH in NaCl[3] and seawater.[60]

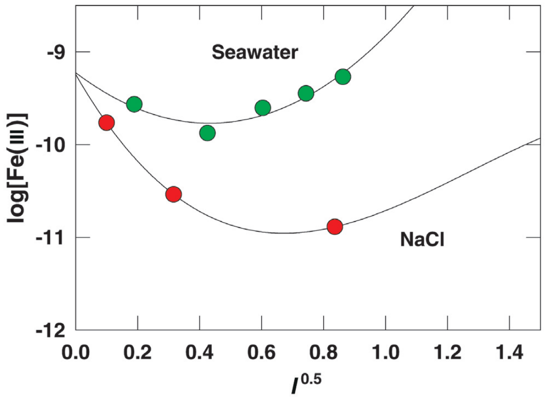

Fig. 14 The solubility of Fe(III) in NaCl and seawater as a function of ionic strength at 25 °C and pH = 8.1.[3,60]

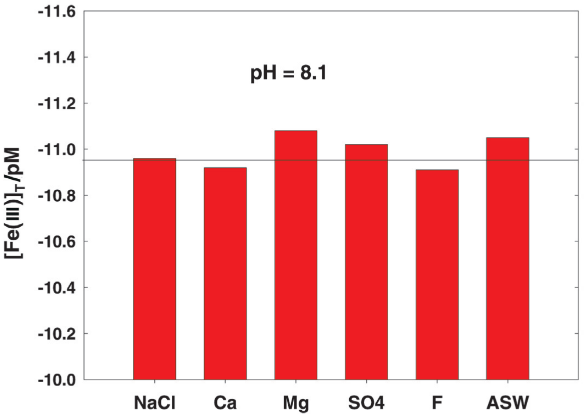

Fig. 15 The effect of the major sea salts on the solubility of Fe(III) at pH = 8.1 and 25 °C.[60]

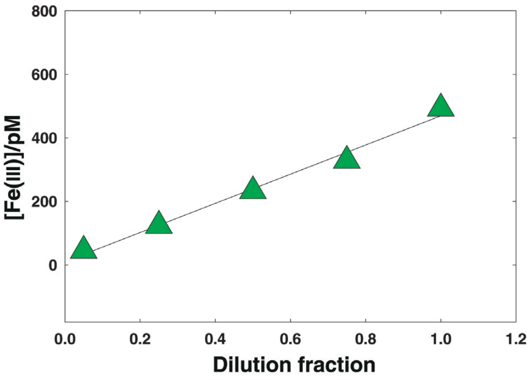

Fig. 16 The solubility of Fe(III) in seawater diluted with 0.7 m NaCl at pH = 8.1 and 25 °C.

to place. To model the interactions of divalent and trivalent metals with inorganic and organic ligands, we have made it possible to add values of K_{ML} and [L′] to our speciation codes. Future work is needed to determine the structure of the various natural organic ligands that complex trace metals in natural waters. Finally, it is important to point out that only free ions affect the thermodynamic activity in solution. I leave you with a cartoon of a free ion (Fig. 17) drawn by my son a number of years ago after I tried to tell him of its importance in equilibria in natural waters.

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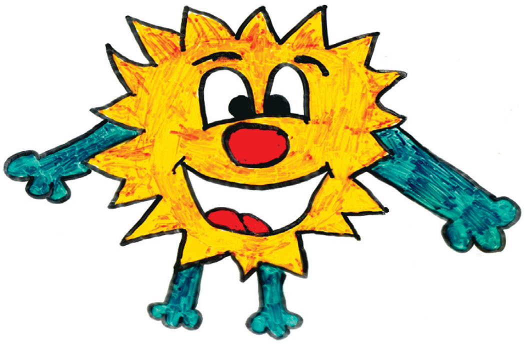

Fig. 17 A sketch of a free ion in seawater.

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