BY FRANK J. MILLERO, RYAN WOOSLEY, BENJAMIN DITROLIO, AND JASON WATERS

Effect of Ocean Acidification on the Speciation of Metals in Seawater

ABSTRACT. Increasing atmospheric CO_2 over the next 200 years will cause the pH of ocean waters to decrease further. Many recent studies have examined the effect of decreasing pH on calcifying organisms in ocean waters and on other biological processes (photosynthesis, nitrogen fixation, elemental ratios, and community structure). In this review, we examine how pH will change the organic and inorganic speciation of metals in surface ocean waters, and the effect that it will have on the interactions of metals with marine organisms. We consider both kinetic and equilibrium processes. The decrease in concentration of OH^- and CO_3^{2-} ions can affect the solubility, adsorption, toxicity, and rates of redox processes of metals in seawater. Future studies are needed to examine how pH affects the interactions of metals complexed to organic ligands and with marine organisms.

INTRODUCTION

With continued emissions of anthropogenic CO_2 from the burning of fossil fuels, changing land use, and cement production, the partial pressure of CO_2 (pCO_2) in the atmosphere is expected to reach 2000 µatm (Caldeira and Wickett, 2003) in ~ 150 years. As Figure 1 shows, equilibration of atmospheric CO_2 with the surface ocean will decrease the pH of seawater from its current value of 8.1 to 7.4 (Caldeira and Wickett, 2003). This decrease in pH will result in a reduction in the concentrations of both hydroxide and carbonate (OH^- and CO_3^{2-}) in most natural surface waters (Figure 2).

The decrease in carbonate ion concentration has spurred considerable work on how it affects the production of calcium carbonate ($CaCO_3$) by calcifying organisms (Orr et al., 2005; Gattuso et al., 1998; Kleypas, et al., 1999; Langdon et al., 2003). However, few studies have considered the effect that this lower pH will have on the speciation of metals in natural waters (Turner et al., 1981; Byrne et al., 1988; Byrne, 2002). Both OH^- and CO_3^{2-} form strong complexes in ocean water with metals that are divalent (Baes and Mesmer, 1976; Byrne et al., 1988; Millero and Hawke, 1992) and trivalent (Millero, 1992; Millero et al., 1995; Cantrell and Byrne, 1987; Millero 2001b). These anions are expected to decrease in surface waters by 82% and 77%, respectively (Figure 2). Such a decrease in these ions is expected to change the speciation of a number of metal ions in seawater (Byrne, 2002; Millero, 2001a,b). Metals that form strong complexes with OH^- and CO_3^{2-} will have a higher fraction in their free forms at lower pH. These changes in speciation will also increase the thermodynamic (Millero, 2001a) and kinetic (Millero, 2001b) activity of the metals. The lower pH will also affect the adsorption of metals to organic material. Most organic particles in seawater are negatively charged. As pH decreases, the surface sites will become less available to adsorb metals

(Crist et al., 1988; Wilde et al., 2006). Most metals are more soluble in acidic waters so their concentrations are expected to change as well.

In this review, we examine how the decreasing pH of ocean and estuarine waters affects the interaction of metals in surface waters.

EFFECT OF OCEAN ACIDIFICATION ON INORGANIC METAL SPECIATION

Trace metals in seawater can be classified into five groups according to the dominant inorganic ligand that complexes them (Byrne et al., 1988):

a) Hydrolyzed (OH^-): Al(III), Fe(III), In(III), Th(IV), U(IV)

b) Carbonate (CO_3^{2-}): Cu(II), UO^{2+}, Rare Earths, Y(III)

c) Chloride (Cl^-): Ag(I), Au(I), Cu(I), Hg(II)

d) Free: Mn(II), Fe(II), Co(II)

e) Transition/Mixed: Pb(II), Y(III), Sc(III), Ac(III)

Although the metals in the transition/mixed category could be placed in the other categories, they are separated because of their unique behavior (Byrne et al., 1988; Byrne, 2002). Metals that form strong complexes with chloride or are mainly in the free form will not be strongly influenced by a change in pH, but metals that form strong complexes with hydroxide and carbonate will undergo significant changes in speciation as the pH of seawater decreases.

The ionic Pitzer (1991) interaction model can be used to examine the effect of pH on metal speciation (Millero and Pierrot, 1998, 2002). The model depends on the stability constants (β) for the formation of complexes in pure water (Millero, 1992; Millero and Hawke,
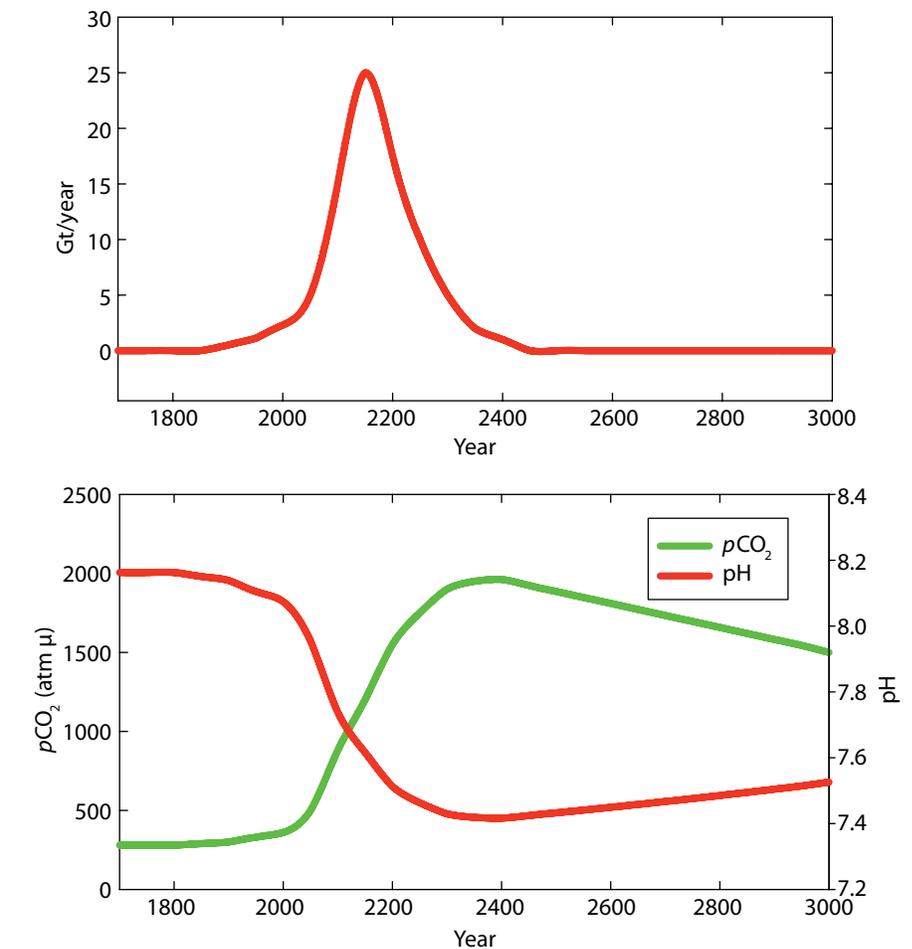
Figure 1. The top graph shows the expected emissions of carbon in GtC yr^{-1}. The bottom graph shows expected pCO$_2$ in the atmosphere (green line), and the change in pH (red line) as a function of time (Caldeira and Wickett, 2003).

1992). For hydroxide, the formations of complexes are expressed as the stepwise hydrolysis of the metal:

$$M^{n+} + iH_2O = M(OH)_i^{(n-i)} + iH^+, \quad (1)$$

where M is the metal, n is the charge (2, 3, or 4), and i is the number of hydroxides (1 to 4). The hydrolysis constants are given by

$$\beta_i = [M(OH)_i^{(n-i)}] [H^+]^i / [M^{n+}], \quad (2)$$

where brackets denote the concentrations. Because the ratio of total carbonate, $[CO_3^{2-}]_T$, to free carbonate is constant at a constant salinity and temperature, the formation constant

for carbonate complexation can be expressed in terms of the total ion concentration (Byrne et al., 1988; Byrne, 2002):

$$_{CO3}\beta_k = [M(CO_3)_k]/([M^{n+}] [CO_3^{2-}]_T^k), \quad (3)$$

where k is the number of carbonate ions. The stability constants needed for the various metals were taken from literature (Baes and Mesmer, 1976; Cantrell and Byrne, 1987; Byrne et al., 1988; Millero and Hawke, 1992; Millero, 1992, 2001a). A Microsoft Excel program is available to examine the speciation of metal from 0° to 50°C and 0 m to 6 m ionic strength (Millero and Pierrot, 1998,

2002). It should be pointed out that the Pitzer (1991) ionic interaction model only considers the formation of strong complexes and neglects the formation of weak complexes with chloride and sulfate (Cl^- and SO_4^{2-}). This model estimates the effect of the major components of seawater on metal ions and their complexes. The resultant activity coefficients are used to determine the stability constants in seawater. This approach is different than the methods used in other studies (Millero and Hawke, 1992; Byrne et al., 1988; Byrne, 2002) and can lead to differences in the calculated speciation of a given metal. The effect of pH on the speciation will not be strongly affected because the changes are largely related to changes in the OH^- and CO_3^{2-} ions.

Table 1 summarizes the inorganic speciation of metals in seawater as a function of pH and time (estimated from Caldeira and Wickett, 2003). In most cases, only species found to contribute 5% or more are considered. Because the pH is expected to decrease to 7.7 by 2100, the most rapid change will occur over the latter half of this century. Figure 3 provides an example of the

Figure 2. The decrease in the concentrations of OH^- and CO_3^{2-} ions in seawater due to ocean acidification (calculated using the Millero et al., 2006, carbonate constants).

Frank J. Millero (fmillero@rsmas.miami.edu) is Professor of Marine and Physical Chemistry, and Associate Dean, Rosenstiel School of Marine and Atmospheric Science, University of Miami, Miami, FL, USA. Ryan Woosley is PhD Candidate, Rosenstiel School of Marine and Atmospheric Science, University of Miami, Miami, FL, USA. Benjamin DiTrolio is PhD Candidate, Rosenstiel School of Marine and Atmospheric Science, University of Miami, Miami, FL, USA. Jason Waters is PhD Candidate, Rosenstiel School of Marine and Atmospheric Science, University of Miami, Miami, FL, USA.

changes in Cu^{2+} as a function of time. The effect of changes in CO_3^{2-} on the speciation of Cu^{2+} is representative of all metals, although the magnitude of the change varies.

Metals that form strong complexes with chloride will see little if any change in speciation because decreasing the pH will not change the chloride concentration. These metals include Cu^+, Cd^{2+}, and Hg^{2+}. The decrease in pH is not expected to strongly influence metals that are predominantly in the free form. The metals Co^{2+}, Zn^{2+}, and Mn^{2+} will only increase by a few percent. There will be much larger increases in Iron(II) and Ni^{2+} in their ionic forms (4% and 13%, respectively) because they form carbonate complexes to a larger degree than the other free metals.

Metals that are strongly complexed with hydroxide include Al^{3+}, Ga^{3+}, In^{3+}, and Be^{2+}. These metals form strong enough complexes with hydroxide such that the change in pH will not cause significant increases in their free forms. However, there will be a shift to fewer

hydroxides per metal ion (i.e., $Al(OH)_4^+$ to $Al(OH)_3$). The largest change will be to the $Al(OH)_3$ complex, which will increase by 36%. There will be a small but significant increase (~ 5%) in the free form of Be^{2+}.

Metals that form strong complexes with carbonate include Cu^{2+}, UO_2^{2+}, and the rare earths. These metals will be most strongly affected by the change in pH, resulting in an increase in their free ionic forms. The largest percentage increase for carbonate-dominated metals is for Cu^{2+} (30%). This large change is significant not only in its magnitude but also because free copper is known to be toxic to organisms (Steeman-Nielsen and Wium-Anderson, 1970; Sunda and Ferguson, 1983). The free form of the rare earths (RE) from La to Lu will increase by 15–24%. The rare earths also show a small but significant increase in complexes with chloride and sulfate (< 10%) as well as an initial increase in the fraction of $RE(CO_3)$ as $RE(CO_3)_2$ becomes $RE(CO_3)$, and then decreases in $RE(CO_3)$ as it converts to the ionic

Table 1. The fraction forms of metals in seawater as a function of pH and time (Caldeira and Wickett, 2003) at 25°C and salinity of 35. Species contributing less than 5% are not included. All the calculations are made on the free pH scale.

	YEAR	2000	2050	2070	2085	2100	2150	2200	2250
	pH	8.1	8	7.9	7.8	7.7	7.6	7.5	7.4
	MAJOR SPECIES								
HYDROXIDE DOMINATED	$Al(OH)_3$	32.18	37.34	42.76	48.32	53.82	59.10	63.98	68.30
	$Al(OH)_4^-$	67.53	62.24	56.63	50.81	44.96	39.22	33.72	28.59
	$Ga(OH)_3$	0.94	1.18	1.48	1.86	2.33	2.92	3.65	4.55
	$Ga(OH)_4^-$	99.06	98.82	98.51	98.14	97.66	97.08	96.35	95.44
	$In(OH)_3$	95.64	96.48	97.14	97.67	98.08	98.39	98.61	98.76
	$In(OH)_4^-$	4.29	3.44	2.75	2.20	1.75	1.40	1.11	0.88
	Be^{2+}	0.24	0.32	0.40	0.55	0.70	0.91	1.18	1.50
	$BeOH^-$	59.10	62.36	65.20	67.62	69.65	71.31	72.64	73.68
	$Be(OH)_2$	27.32	22.90	19.02	15.67	12.08	10.42	8.43	6.79
	$Be(OH)_3$	2.38	1.58	1.04	0.68	0.45	0.28	0.18	0.11
	$Be(CO_3)$	13.32	14.40	15.34	16.14	16.80	17.33	17.73	18.00
CARBONATE DOMINATED	Cu^{2+}	7.67	9.64	12.04	14.92	18.32	22.26	26.75	31.76
	$CuOH^+$	4.70	4.70	4.66	4.59	4.47	4.30	4.12	3.88
	$CuCO_3$	66.98	68.51	69.25	69.14	68.14	66.25	63.50	59.96
	$Cu(CO_3)_2^{2-}$	18.34	15.26	12.49	10.05	7.95	6.18	4.70	3.55
	$CuSO_4$	-	-	-	-	-	-	-	-
	$UO_2(CO_3)_2^{2-}$	13.83	16.47	19.59	23.21	27.34	31.91	37.04	42.46
	$UO_2(CO_3)_3^{4-}$	86.14	83.46	80.35	76.70	72.52	67.86	62.71	57.19
	La^{3+}	16.99	20.51	24.40	28.59	32.96	37.39	41.74	45.90
	$LaCO_3^+$	56.18	55.15	53.12	50.15	46.42	42.13	37.52	32.82
	$La(CO_3)_2^-$	19.17	15.31	11.94	9.08	6.75	4.90	3.48	2.42
	$LaSO_4^-$	3.88	4.68	5.56	6.52	7.52	8.53	9.52	10.47
	$LaCl^{2+}$	2.45	2.95	3.51	4.12	4.75	5.39	6.01	6.61
	Ce^{3+}	12.62	15.49	18.79	22.47	26.45	30.63	34.89	39.11
	$CeCO_3^+$	57.15	57.15	56.13	54.09	51.11	47.35	43.03	38.36
	$Ce(CO_3)_2^-$	22.39	18.22	14.48	11.25	8.53	6.32	4.58	3.25
	$CeSO_4^+$	3.51	4.32	5.24	6.27	7.38	8.54	9.73	10.91
	$CeCl^{2+}$	1.93	2.38	2.88	3.45	4.06	4.70	5.35	6.00
	Pr^{3+}	10.59	13.20	16.25	19.72	23.56	27.68	31.97	36.31
	$PrCO_3^+$	56.82	57.63	57.43	56.16	53.86	50.62	46.64	42.14
	$Pr(CO_3)_2^-$	26.16	21.58	17.41	13.72	10.56	7.94	5.84	4.20
	$PrSO_4^+$	2.78	3.46	4.26	5.17	6.17	7.25	8.38	9.52
	$PrCl^{2+}$	1.64	2.04	2.51	3.05	3.64	4.28	4.94	6.61
	Nd^{3+}	8.45	10.68	13.34	16.44	19.95	23.83	27.99	32.31
	$NdCO_3^+$	56.87	58.47	59.11	58.71	57.21	54.67	51.22	47.04
	$Nd(CO_3)_2^-$	29.38	24.57	20.11	16.09	12.59	9.63	7.19	5.26

Table continued next page...

Table 1 continued...

Year	2000	2050	2070	2085	2100	2150	2200	2250
pH	8.1	8	7.9	7.8	7.7	7.6	7.5	7.4
$NdSO_4^+$	2.16	2.72	3.40	4.19	5.09	6.08	7.14	8.25
$NdCl^{2+}$	1.30	1.64	2.05	2.53	3.07	3.67	4.31	4.97
Pm^{3+}	6.65	8.52	10.79	13.48	16.60	20.12	23.98	28.08
$PmCO_3^+$	55.09	57.38	58.82	59.25	58.57	56.80	53.98	50.29
$Pm(CO_3)_2^-$	33.43	28.33	23.51	19.08	15.14	11.75	8.91	6.60
$PmSO_4^+$	2.04	2.61	3.31	4.14	5.09	6.17	7.36	8.61
$PmCl^{2+}$	1.00	1.28	1.62	2.03	2.50	3.03	3.61	4.22
Sm^{3+}	5.25	6.82	8.87	11.13	13.94	17.18	20.84	24.83
$SmCO_3^+$	53.12	56.12	58.40	59.77	60.08	59.00	57.31	54.33
$Sm(CO_3)_2^-$	37.87	32.50	27.42	22.61	18.25	14.40	11.11	8.38
$SmSO_4^+$	1.43	1.85	2.38	3.02	3.78	4.67	5.66	6.74
$SmCl^{2+}$	0.78	1.02	1.31	1.66	2.08	2.57	3.11	3.71
Eu^{3+}	4.24	5.56	7.23	9.28	11.76	14.66	17.98	21.67
$EuCO_3^+$	50.82	54.25	57.06	59.05	60.03	59.89	58.60	56.18
$Eu(CO_3)_2^-$	41.60	36.13	30.76	25.65	20.94	16.71	13.04	9.95
$EuSO_4^+$	1.43	1.87	2.44	3.13	3.96	4.94	6.06	7.30
$EuCl^{2+}$	0.61	0.80	1.04	1.34	1.69	2.11	2.59	3.12
Gd^{3+}	3.37	4.48	5.91	7.71	9.93	12.59	15.71	19.27
$GdCO_3^+$	47.53	51.46	54.95	57.77	59.71	60.59	60.31	58.84
$Gd(CO_3)_2^-$	46.78	41.20	35.61	30.17	25.03	20.33	16.14	12.52
$GdSO_4^+$	0.86	1.15	1.51	1.98	2.54	3.23	4.02	4.94
$GdCl^{2+}$	0.49	0.65	0.85	1.11	1.43	1.82	2.27	2.78
Tb^{3+}		3.64	4.86	6.41	8.37	10.76	13.61	16.93
$TbCO_3^+$	44.10	48.28	52.18	55.56	58.18	59.85	60.41	59.77
$Tb(CO_3)_2^-$	51.00	45.42	39.73	34.09	28.66	23.59	18.99	14.95
$TbSO_4^+$	0.62	0.84	1.12	1.47	1.92	2.47	3.13	3.89
$TbCl^{2+}$	0.38	0.52	0.69	0.91	1.19	1.53	1.93	2.40
Dy^{3+}	2.18	2.97	4.02	5.38	7.11	9.27	11.90	15.01
$DyCO_3^+$	40.14	44.47	48.67	52.52	55.76	58.17	59.54	59.75
$Dy(CO_3)_2^-$	55.81	50.30	44.56	38.74	33.02	27.56	22.51	17.96
$DySO_4^+$	0.45	0.61	0.83	1.11	1.46	1.91	2.45	3.09
$DyCl^{2+}$	0.31	0.42	0.57	0.77	1.01	1.32	1.70	2.14
Ho^{3+}	1.78	2.45	3.35	4.54	6.09	8.04	10.45	13.35
$HoCO_3^+$	36.14	40.48	44.82	48.97	52.66	55.64	57.70	58.63
$Ho(CO_3)_2^-$	60.41	55.04	49.33	43.43	37.49	31.70	26.22	21.19
$HoSO_4^+$	0.38	0.52	0.71	0.96	1.29	1.70	2.22	2.83
Er^{3+}	1.48	2.06	2.84	3.89	5.28	7.05	9.28	11.99
$ErCO_3^+$	32.74	37.01	41.40	45.72	49.73	53.18	55.79	57.37
$Er(CO_3)_2^-$	64.30	59.13	53.54	47.64	41.60	35.59	29.79	24.37

(row label at left, rotated: CARBONATE DOMINATED, CONT.)

Table 1 continued...

	YEAR	2000	2050	2070	2085	2100	2150	2200	2250
	pH	8.1	8	7.9	7.8	7.7	7.6	7.5	7.4
CARBONATE DOMINATED, CONT.	Tm^{3+}	1.21	1.70	2.37	3.29	4.53	6.14	8.20	10.76
	$TmCO_3^+$	28.56	32.64	36.97	41.37	45.65	49.54	52.77	55.09
	$Tm(CO_3)_2^-$	69.00	64.16	58.81	53.04	46.98	40.80	34.67	28.79
	Yb^{3+}	1.05	1.49	2.11	2.96	4.10	5.63	7.60	10.09
	$YbCO_3^+$	25.49	29.37	33.55	37.91	42.27	46.37	49.96	52.74
	$Yb(CO_3)_2^-$	72.36	67.81	62.71	57.11	51.11	44.87	38.56	32.38
	Lu^{3+}	0.85	1.21	1.72	2.45	3.45	4.80	6.58	8.88
	$LuCO_3^+$	21.88	25.45	29.40	33.63	38.02	42.34	46.34	49.74
	$Lu(CO_3)_2^-$	76.41	72.30	67.60	62.33	56.56	50.40	44.00	37.57
TRANSITION/MIXED	Pb^{2+}	2.89	3.29	3.70	4.13	4.56	4.99	5.39	5.77
	$PbOH^+$	4.24	3.83	3.40	3.03	2.66	2.31	1.98	1.68
	$PbCO_3$	59.03	54.53	49.72	44.71	39.64	34.65	29.88	25.43
	$PbCl^+$	13.09	14.86	16.74	18.68	20.63	22.54	24.37	26.07
	$PbCl_2$	14.09	16.00	18.02	20.10	22.21	24.60	26.23	28.06
	$PbCl_3^-$	6.40	7.27	8.19	9.14	10.09	11.03	11.93	12.76
	Y^{3+}	9.49	10.65	11.84	13.02	14.17	15.26	16.27	17.18
	YOH^{2+}	14.82	13.21	11.67	10.19	8.81	7.54	6.38	5.35
	YCO_3^+	41.51	37.96	34.19	30.34	26.53	22.88	19.47	16.37
	YSO_4^+	9.32	10.46	11.63	12.79	13.92	14.99	15.98	16.87
	YCl^{2+}	16.91	18.98	21.10	23.21	25.26	27.20	28.99	30.62
	YF^{2+}	5.32	5.97	6.64	7.30	7.95	8.56	9.12	9.63
CHLORIDE DOMINATED	Cd^{2+}	20.15	20.17	20.18	20.19	20.20	20.21	20.21	20.22
	$CdCl^+$	43.71	43.75	43.78	44.10	43.82	43.80	43.85	43.86
	$CdCl_2$	27.70	27.72	27.74	28.07	27.77	27.78	27.79	27.79
	$CdCl_3^-$	7.95	7.95	7.96	7.97	7.96	7.97	7.97	7.97
	$HgCl_2$	11.80	11.80	11.80	11.80	11.80	11.80	11.80	11.80
	$HgCl_3^-$	88.20	88.20	88.20	88.20	88.20	88.20	88.20	88.20
FREE	Fe^{2+}	65.99	70.42	74.57	78.36	81.76	84.75	87.33	89.53
	$FeCO_3$	32.00	27.78	23.81	20.16	16.89	14.00	11.51	9.39
	$FeOH$	1.40	1.20	1.01	0.84	0.69	0.57	0.47	0.38
	Ni^{2+}	68.29	72.48	76.37	79.91	83.10	85.79	88.15	90.12
	$NiCO_3$	30.29	26.15	22.30	18.80	15.69	12.97	10.63	8.64
	Co^{2+}	92.58	93.81	94.84	95.69	96.39	96.97	97.44	97.82
	$CoCO_3$	5.30	4.37	3.57	2.91	2.35	1.89	1.51	1.21
	$CoOH$	1.45	1.16	0.93	0.75	0.60	0.48	0.38	0.30
	Zn^{2+}	80.58	84.41	87.45	89.85	91.74	93.22	94.38	95.29
	$ZnOH^+$	5.65	4.70	3.87	3.15	2.56	2.06	1.66	1.33
	$ZnCO_3$	7.16	6.10	5.10	4.20	3.47	2.82	2.28	1.83
	Mn^{2+}	97.34	97.70	98.08	98.36	98.60	98.77	98.93	99.05

form when pH decreases further. This is probably only significant from a purely chemical standpoint and not from a biogeochemical standpoint.

Lead and yttrium have been placed in a separate category, transition or mixed, based on their unique behaviors. Lead forms significant complexes with both chloride and carbonate. As pH decreases, the free form of lead will increase by approximately 10%, and there will be a large increase in its complexation with chloride (15% among PbCl, $PbCl_2$,

and $PbCl_3$). Yttrium has a much more complex speciation, forming complexes with hydroxide, carbonate, chloride, and sulfate (Cantrell and Byrne, 1987). The pH decrease will cause yttrium to change from a carbonate-dominated metal to a chloride-dominated metal. The free form will increase by about 7%.

The pH of estuarine waters will also be affected by ocean acidification. When seawater of low pH (7.4) mixes with river water of low pH (6) without inorganic carbon, estuarine waters will have a much

lower pH that may affect biogeochemical processes in the estuary (Hofmann et al., 2009). Metals such as Cu^{2+} may be more toxic in these waters. Because the ocean may be a carbonate source for some estuaries, the lower pH of seawater will decrease the available carbonate (Figure 4). In these areas, this situation will result in greater speciation changes than those discussed in this paper.

The shift in speciation will also cause a change in the solubility of many metals. Metal solubility in seawater is a strong function of pH. Most trivalent metals like Fe(III), Al(III), and As(III) are more soluble in acidic and basic solutions with a minimum somewhere in between. The location of that minimum will determine whether the metal will increase or decrease in solubility with the expected change in pH. Figure 5 shows the solubility of Fe(III) in seawater. At the current pH of seawater, Fe(III) is at its minimum solubility. Fe(III) solubility is strongly influenced by organic ligands at a pH near 8 (Liu and Millero, 2002). This solubility is much higher than in artificial seawater due to the formation of strong organic complexes (Liu and Millero, 2002). As pH decreases, solubility increases. A decrease in pH from 8.1 to 7.4 will increase the solubility of Fe(III) by about 40%, which could have a large impact on biogeochemical cycles because iron is an important micro-nutrient (Brand, 1991). The increased solubility along with changes in kinetics (discussed later) will make iron more available to phytoplankton, which could lead to an increase in primary production (Martin, 1990). The solubility of Al(III) has not been measured in seawater. However, because aluminum is very strongly hydrolyzed, the solubility should be similar to the solubility in
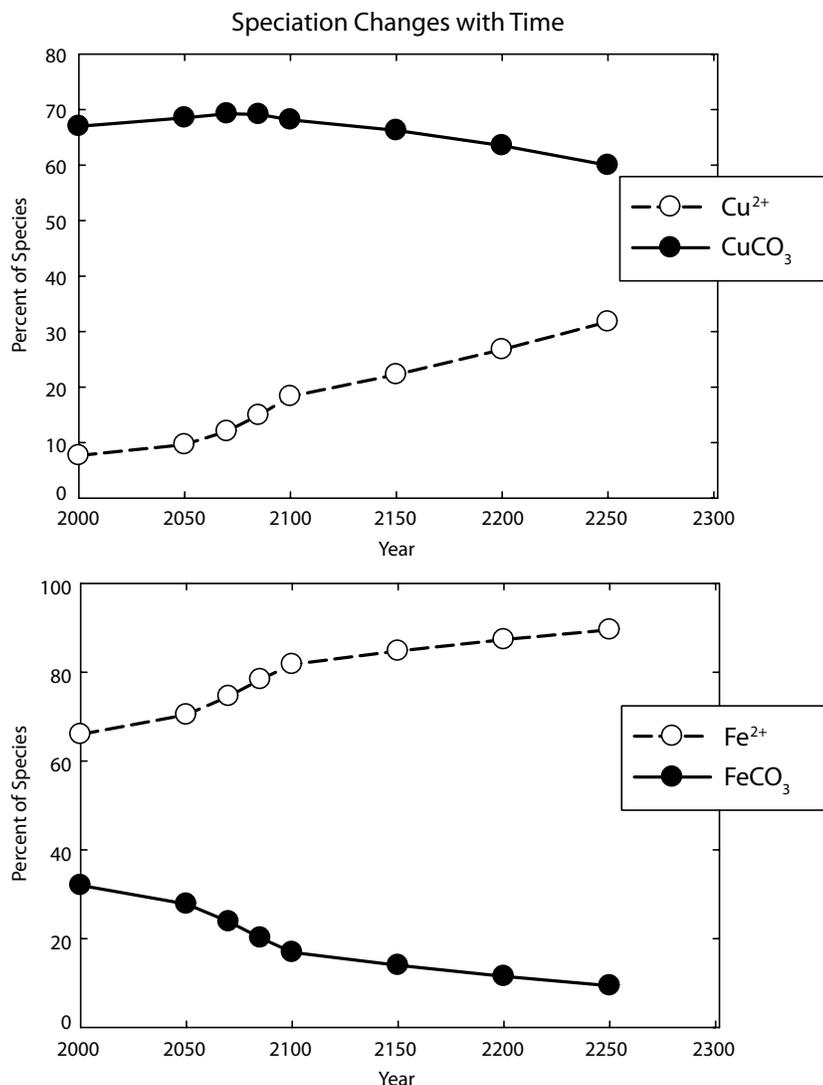
Figure 3. The expected change in the inorganic speciation of Cu(II) and Fe(II) as a function of time. The Millero et al. (2006) carbonate constants were used to calculate the carbonate ion concentration.

NaCl. The shape of the solubility curve as a function of pH is very similar to that of Fe(III) except that the minimum is shifted to a pH of approximately 5.5. This shift will cause a 30% decrease in solubility as the pH changes from 8.1 to 7.4. If there is a similar influence of organics on Al(III), the actual decrease may be less in NaCl solutions (Woosley and Millero, in press). New measurements are needed to show if this is the case in seawater. These changes in solubility could influence the distribution and cycling of metals in seawater.

Ocean acidification could have potentially harmful effects on primary productivity by increasing the concentration of free ionic copper, but acidification could also increase the concentrations of dissolved iron to stimulate primary productivity. The effect of ocean acidification on different metals may also affect the competition of various metals for surface sites (Bruland et al., 1991). Future measurements are needed to examine the effect of ocean acidification on biogeochemical processes in the ocean.

EFFECT OF OCEAN ACIDIFICATION ON ORGANIC METAL SPECIATION

The inorganic speciation of many divalent metals in seawater only affects a small fraction of the total metal. Significant fractions of the total concentrations (most > 99%) of metals such as iron, cobalt, copper, zinc, and lead are in the form of metal-organic complexes (van den Berg, 1984; Hering et al., 1987; Sunda and Hanson, 1987; Coale and Bruland, 1988; Donat and van den Berg, 1992). This observation is important, particularly for assessing the bioavailability of metals in the surface ocean. The role of metals in biological

Figure 4. The change in $[CO_3^{2-}]$ as seawater (S = 35) mixes with river water (S = 0) at the present time (pCO_2 = 380 µatm) and in 2300 (pCO_2 = 2000 µatm, calculated using the carbonate constants of Millero et al., 2006). The river is assumed to have little or no carbonate alkalinity.
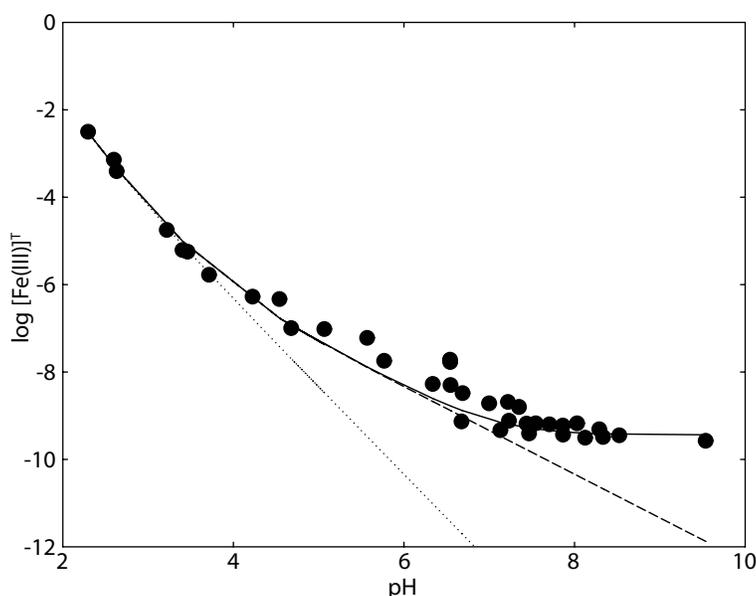
Figure 5. Solubility of Iron(III) in seawater. *From Liu and Millero, 2002*

processes is quite significant. In the surface ocean, the biochemically significant metals for microorganisms are manganese, iron, nickel, cobalt, copper, zinc, and cadmium (Morel et al., 2003). These trace metals are needed for the growth and survival of photosynthetic organisms. Low concentrations of these metals, primarily iron, have been linked to the paucity of primary producers observed in areas of the ocean with otherwise high nutrient concentrations (Martin and Fitzwater, 1988; Landry et al., 1998). Above a certain threshold, unique for each organism and metal, a number of trace metals are toxic.

Copper, cadmium, and lead have all been shown to be toxic at sufficient concentrations in the marine environment (Casas and Crecelius, 1994; Paytan et al., 2009). Ambient trace metal concentrations in the open ocean are low, and as a result, marine organisms have evolved efficient mechanisms, many of which are yet to be characterized, of concentrating these metals for their needs (Morel et al., 2003). Thus, small increases in concentration of normally scarce metals often result in toxic effects to organisms unaccustomed to the higher concentrations (Sunda and Huntsman, 1992). This has been observed with the free form of Cu(II) at concentrations as low as 10^{-12} M, which are reported to be toxic to marine phytoplankton (Brand et al., 1986). It is important to note that it is the labile or free concentration of copper that is toxic to marine organisms, not the total copper. The fraction(s) of metal(s) forming strong complexes with ligands may not be thermodynamically or kinetically available to organisms. The bioavailable, or labile, fraction of the total metal concentration is operationally defined with respect to a particular organism or analytical measurement, such that the labile forms of the metal include the free, or uncomplexed, metal and weak metal-ligand complexes (Schreiber et al., 1985; Gonzalez-Davila et al., 1995). Because the speciation of many metals is controlled by pH, a more acidic ocean will alter the bioavailable fractions of these metals. The effect of pH on inorganic ligands was discussed earlier. In this section, we consider the effect of pH on the formation of organic complexes with metals.

A number of researchers have shown that many biologically significant metals form strong complexes with organic ligands in seawater, including:

Copper(II): van den Berg, 1982, 1984; Sunda and Ferguson,1983; Kramer and Duinker, 1984; Sunda et al., 1984; Hering et al., 1987; Moffett and Zika, 1987; Sunda and Hanson, 1987; Coale and Bruland, 1988; Donat and van den Berg, 1992; Croot et al., 1999; Louis et al., 2009
Iron(III): Gledhill and van den Berg, 1994; Rue and Bruland, 1995; Wu and Luther, 1995
Cobalt(II): Zhang et al., 1990; Ellwood and van den Berg, 2001; Saito and Moffett, 2001
Zinc(II): Bruland, 1989
Cadmium(II): Bruland, 1992
Lead(II): Capodaglio et al., 1990
Nickel(II): van den Berg and Nimmo, 1987; Donat and van den Berg, 1992; Gledhill and van den Berg, 1994; Gonzalez-Davila et al., 1995; Croot et al., 1999; Morel et al., 2003

Table 2 provides some of the stability constants for the formation of metal organic complexes (Millero, 2001b).

The fractional composition of a metal complexed by an organic ligand can be assessed by evaluating the conditional ligand-binding constant, K_c, for the relevant ligands in solution. For a metal species, M, and a ligand species, L, the relationship to K_c is given by:

$$M^{x+} + nL^{y-} \xleftrightarrow{K_c} ML_n^{x-ny}$$

$$K_c = \frac{[ML_n^{x-ny}]}{[M^{x+}]_F \, [L^{y-}]_F^n} \tag{4}$$

where the variables x and y are charges on the metal and ligand, respectively, the subscript *F* denotes that the concentrations of each are free (labile), and *n* is the number of ligands complexing the metal. As discussed earlier, the inorganic carbonate and hydroxide ligands are pH dependent, and these, as with most of the inorganic metal-ligand complexation constants, can be estimated for seawater. This allows reasonable estimation of the inorganic form for most natural waters.

Whether the labile fraction of the inorganic metal complexes is available in nutrient form or contributes to a toxic response is difficult to determine and is not consistent for all organisms (Croot et al., 1999). Metal-organic complexes, however, are for the most part sufficiently strong that this fraction of the total metal concentration is rendered nonlabile and cannot interact with organisms (Schreiber et al., 1985;

Table 2. Conditional stability constants for metals in seawater (Millero, 2001b)

Metal	[M]	[L]	log K_c
Cu(II)	1–10 nM	2–60 nM	8.5
Zn(II)	0.1–2 nM	1.2 nM	12
Cd(II)	2–800 pM	100 pM	12
Pb(II)	17–49 pM	200–500 pM	11
Ni(II)	1.7–4.3 nM	2–4 nM	17–19
Co(II)	10–103 pM	9–83 pM	11–16
Fe(III)	0.2–8 nM	0.4–13 nM	19–23

Table 3. Literature data for Cu(II) complexation with L_1 and estimated values of the free $[Cu(II)]_F$ at pH 8.1 and 7.4

Location	$[Cu]_T$ (nM)	$[L]_T$ (nM)	log K_c	pH 8.1[*] $[Cu]_F$ (pM)	pH 7.4[*] $[Cu]_F$ (pM)	Reference
NE Pacific	0.59	1.6	11.8	1.1	1.7	Coale and Bruland (1988)
Biscayne Bay	2.7	5.1	12.0	1.1	2.4	Moffett and Zika (1987)
Montauk Point	5.9	20	11.7	0.84	1.3	Hering et al. (1987)
Narragansett Bay	21	35.	12.3	0.70	1.9	Sunda and Hanson (1987)
Indian Ocean	1.7	3.1	12.6	0.42	1.2	Donat and van den Berg (1992)
North Sea	3.2	16.	12.4	0.10	0.14	Donat and van den Berg (1992)
South Atlantic	2.3	11	12.2	0.17	0.24	van den Berg (1984)
Balaguier Bay	14.8	138	9.9	15.1[‡]	20.9[‡]	Louis et al. (2009)

[*] Estimated values using $pK_a = 8.6$ (Louis et al., 2009) for L_1.

[‡] When a value of log K_c of 12 is used to compute $[Cu]_F$, the pH 8.1 and 7.4 values are 0.12 and 0.17 nM, respectively.

Gonzalez-Davila et al., 1995). Using the stability constants for the formation of organic complexes, it is possible to examine the competition of the inorganic and organic complexes to assess the fractionation of a metal. This can be done if the organic complexing constants and concentration of the ligand are known. A number of scientists (given above) have studied the formation of Cu(II) organic complexes. Most studying Cu(II) speciation have observed two ligand classes, L_1 and L_2, in seawater collected from a number of locations. Table 3 tabulates the total concentration of the strongest ligand $[L_1]_T$ and its values, determined by a number of scientists, along with the concentrations of $Cu(II)_T$ and the conditional stability constants K_c. The fraction of the free ligand (αL_F) and free copper (αCu_F) can be estimated from the following:

$$\alpha L_F = \frac{1}{(1 + K_c \alpha Cu_F [Cu]_T)} \quad (5)$$

$$\alpha Cu_F = \frac{1}{(1 + K_c \alpha L_F [L]_T)} \quad (6)$$

Table 3 provides the iterative values of αCu_F and αL_F determined from these equations. The free concentrations of copper $[Cu]_F$ vary from 0.1 to 1.1 pM at a pH equal to 8.1.

The effect of pH on the speciation of metal organic complexes in the marine environment is not as well characterized as the inorganic ligands due to the nonhomogenous composition and unknown structures of the organic ligands. Characterizing organic material capable of complexing metals in the marine environment has proven to be a daunting analytical task, but a number of scientists have made progress (Dittmar and Paeng, 2009; Sleighter and Hatcher, 2007). They find that marine organic material has similar properties to the better-characterized metal complexing organics in freshwater systems (Ritchie and Perdue, 2003). It is highly likely that the marine dissolved organic material that can complex metals will be a function of pH. This relationship is due to the presence of phenolic and carboxylic functional groups present on organic material that may be responsible for the chelation of metals. These moieties exhibit a charge dependence that is a function of pH, and each bind metals with varying degrees of strength.

There has been little comprehensive work assessing the effect of pH on the stability constants for the formation of organic complexes. Louis et al. (2009) recently characterized the acid-base properties of dissolved organic material in waters collected off the southern coast of France. They report a lower Cu(II) organic complex constant (log K_c = 9.9) than found by other researchers. They did, however, determine the effect of pH on the major L_1 ligand. Figure 6 shows the fractional composition of the L_1 ligand as a function of pH using their acid dissociation constant of $pK_a = 8.6$. Between pH 8.1 and 7.4, the concentration of this ligand decreases by 25%. We used this decrease in concentration of L_1 to estimate the effect of pH on the speciation of Cu(II) in seawater (see Table 3). The levels for free copper may surpass the 1 pM threshold, levels at which some organisms have exhibited a toxic response. It should be emphasized, however, that this estimate is very rudimentary. Its primary purpose is to demonstrate the need for empirical inquiry into the area of the
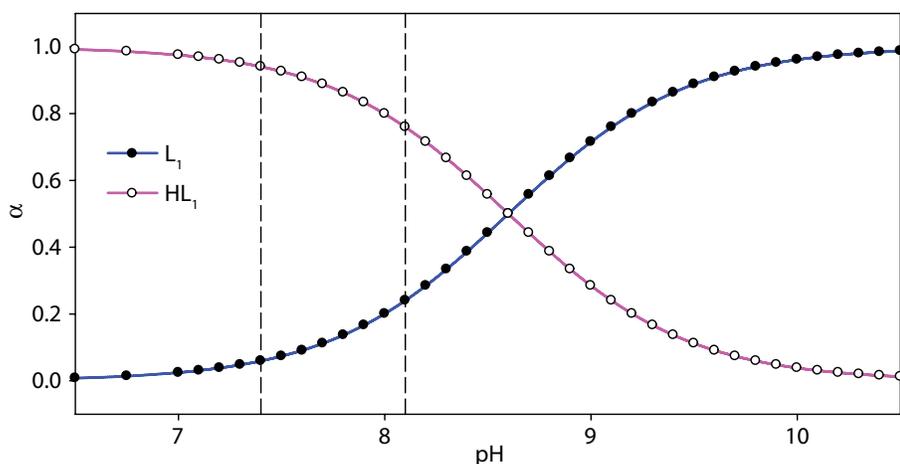
Figure 6. The effect of pH on the fraction (α) of the natural organic ligand that complexes Cu(II) in seawater (Louis et al., 2009).

pH dependence of organic speciation of metals in seawater. Because upwelling waters frequently have a similarly lower pH due to ocean acidification, metal complexing studies in these areas may be useful in studying the organic speciation of metals.

Few similar studies are available for other metals, but a number of studies show that Fe(III) forms strong complexes with organic ligands in seawater (Gledhill and van den Berg, 1994; Rue and Bruland, 1995; Wu and Luther, 1995). Because lower pH values increase the solubility of Fe(III) in seawater (Liu and Millero. 2002), it might be inferred that these Fe(III) organic complexes may also be affected by ocean acidification. More work is needed to determine the effect of pH on other metal organic ligands in seawater.

EFFECT OF OCEAN ACIDIFICATION ON RATE PROCESSES

Chemical reaction rates are also affected by pH changes (Millero, 2001b), including the oxidation and reduction of metals (Cu(I), Cu(II), Fe(II), Fe(III), Cr(III), Cr(IV)), and of sulfur

compounds (H_2SO_3, H_2S). Changes in pH also affect photochemical processes such as the production of O_2^-, HO_2, and H_2O_2. In this section, we examine how pH changes affect kinetic processes in surface waters. We focus on the possible effects of acidification on the rates of reduction and oxidation (redox) processes concerning Cu(I)–Cu(II) and Fe(II)–Fe(III), the lifetimes of the superoxide radicals HO_2 and O_2^-,

and H_2O_2 production.

The kinetic rate constant for the reduction of Cu(II) to Cu(I) is a function of pH because the reaction is slower at high concentrations of the carbonate ion (Figure 7). As the ocean becomes more acidic, reduction of Cu(II) will increase, as the ionic form of Cu(II) is reduced faster than the Cu(II) in either the $CuCO_3^o$ or $Cu(OH)^+$ species (Millero et al., 1991; Millero, 2001a). The effect of higher concentrations of Cu(I) in surface waters on biological systems is currently unknown. The oxidation of Cu(I) with H_2O_2 is not expected to be strongly dependent on acidification, as the oxidation rates are not strongly affected by pH (Moffett and Zika, 1983; Sharma and Millero, 1988).

As discussed earlier, iron in surface waters is needed for primary productivity. For phytoplankton to use iron, it must be dissolved (Davies, 1990; Rich and Morel, 1990), making the bioavailability of iron a function of its solubility and oxidation state (Millero, 2001a).
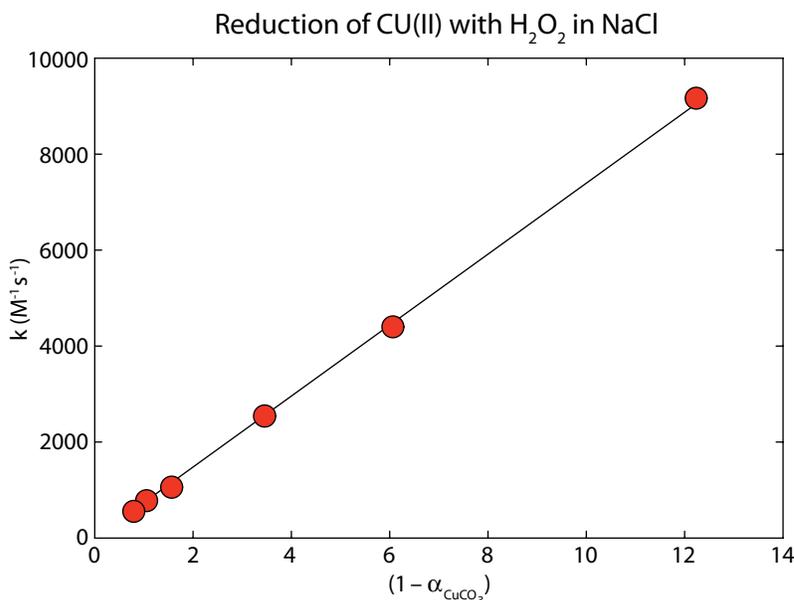
Figure 7. The rate constant for the reduction of Cu(II) with H_2O_2 as a function of the fraction of the carbonate ion.

Photochemical processes in ocean surface waters produce a number of free radicals that can change the oxidation state of a number of metals. The free radical O_2^- is produced by the adsorption of organic chromophores (Zika et al., 1985):

$$Org + hv = Org^+ + e^- \qquad (7)$$

$$e^- + O_2 = O_2^- \qquad (8)$$

$$O_2^- + H^+ = HO_2. \qquad (9)$$
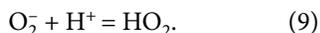
Increasing evidence also shows the production of HO_2 by a wide range of microorganisms (Rose et al., 2008). Millero (1987) estimated the overall rate constant for the disproportionation of the superoxide molecule as a function of pH. Assuming a constant value for $[HO_2^-]_T$, the half-life of the superoxide decreases by 20% at pH = 7.4. A decrease in concentration of the superoxide molecule would affect the redox equilibrium of biologically important trace metals, as it is important in the reduction of organically complexed Fe(III) (Rose and Waite, 2005) and redox reactions of organic and inorganically complexed Cu(II) and Cu(I) (Zafiriou et al., 1998; Voelker et al., 2000).

The HO_2 radical can disproportionate and form hydrogen peroxide (Bielski, 1978):

$$HO_2 + HO_2 = H_2O_2 + O_2. \qquad (10)$$

The rate of this reaction is a function of pH (log k = 12.28 - 1 pH; Millero, 1987). The concentration of HO_2 at a pH equal to 7.4 will be decreased by 30% compared to the value at a pH equal to 8.1. The photochemical production of the superoxide radical, HO_2 or O_2^-, can reduce Cu(II) and Fe(III) in surface waters:

$$Cu^{2+} + O_2^- = Cu^+ + O_2 \qquad (11)$$

$$Fe^{3+} + O_2^- = Fe^{2+} + O_2. \qquad (12)$$
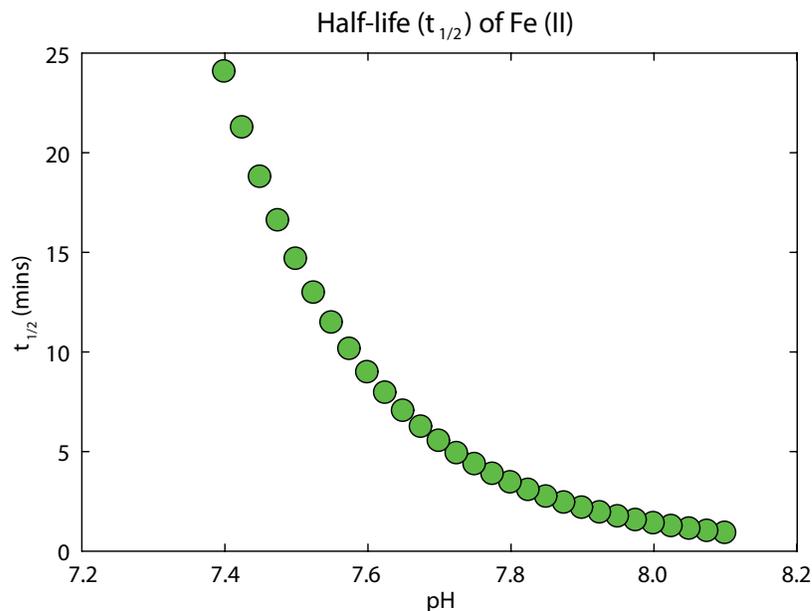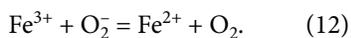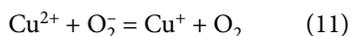
Figure 8. The calculated increase in the half life of Fe(II) as a function of pH at 25°C.

It can also oxidize dissolved organic material in seawater (Goldstone and Voelker, 2000). The destruction of the HO_2 radical in surface seawater is thought to be affected by the concentration of Cu(II) (Zafiriou et al., 1998; Voelker et al., 2000). The increase of free Cu^{2+} in surface waters due to a decrease in the pH may increase the destruction of the radical.

The peroxide formed from the disproportion of HO_2 can also react with Fe(II) and Cu(II):

$$Fe^{2+} + H_2O_2 = Fe^{3+} + OH^{\cdot} + OH^- \quad (13)$$

$$Cu^{2+} + H_2O_2 = Cu^+ + HO_2 + H^+. \quad (14)$$
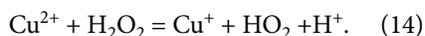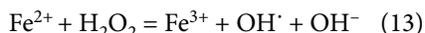
The concentration of Fe(II) in surface seawater is controlled by its oxidation with O_2 (Millero et al., 1987):

$$Fe^{2+} + O_2 = Fe^{3+} + O_2^-. \qquad (15)$$
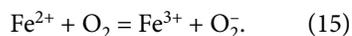
As Figure 8 shows, the oxidation of Fe(II) is a strong function of pH. At 25°C, a decrease in pH from 8.1 to 7.4 will increase the half life of Fe(II) in seawater from 1 to 24 minutes (Millero et al., 1987). So, the decrease in pH of ocean waters should increase

dissolved Fe and make it more available for primary production. In a CO_2 manipulation microcosm experiment, Breitbarth et al. (2009) showed changes in Fe(II) oxidation that agree with our expectations.

The effects of the lowering of pH on the rates of enzymatic and other organic reactions in ocean waters are not well known. Because much of the dissolved organic material in seawater consists of –OH and –COOH groups that are affected by pH, it might be expected that the rates are also affected. Additional research is required to further characterize the effects ocean acidification will have on the kinetics of trace metals and the overall implications on biogeochemistry.

SUMMARY

Ocean acidification will have an impact on the thermodynamics and kinetics of metals in seawater. The changes in the speciation of metals due to the lower pH will result in changes in the behavior and fate of metals in seawater. These changes could possibly affect the availability

and toxicity of metals on marine organisms. We suggest how these pH changes can affect thermodynamic and kinetic processes in seawater. The impact these changes have on biogeochemical cycles in the ocean requires further study. Coastal upwelling and oxygen minimum zones, which already have a pH around 7.4 (Feely et al., 2008), would be useful areas to study in order to better understand how metals will behave under future ocean acidification scenarios.

REFERENCES

Baes, C.F., and R.E. Mesmer. 1976. *The Hydrolysis of Cations*. John Wiley & Sons Inc., 512 pp.

Bielski, B.H. 1978. Re-evaluations of the spectra and kinetic properties of HO_2 and O_2^- free radicals. *Photochemical Photobiology* 28:645–649.

Brand, L.E. 1991. Minimum iron requirements of marine phytoplankton and the implications for the biogeochemical control of new production. *Limnology and Oceanography* 36(8):1,756–1,771.

Brand, L.E., W.G. Sunda, and R.R.L. Guillard. 1986. Reduction of marine phytoplankton reproduction rates by copper and cadmium. *Journal of Experimental Marine Biology and Ecology* 96:225–250.

Breibarth E., R.J. Bellerby, C.C. Neill, M.V. Ardelan, M. Meyerhöfer, E. Zöllner, P.L. Croot, and U. Riebesell. 2009. Ocean acidification affects iron speciation in seawater. *Biogeosciences Discussions*. Available online at: http://www.biogeosciences-discuss.net/6/6781/2009/bgd-6-6781-2009.pdf (accessed October 21, 2009).

Bruland, K.W. 1989. Complexation of zinc by natural organic ligands in the central North Pacific. *Limnology and Oceanography* 34:269–285.

Bruland, K.W. 1992. Complexation of cadmium by natural organic ligands in the central North Pacific. *Limnology and Oceanography* 37:1,008–1,017.

Bruland, K.W., J.R. Donat, and D.A. Hutchins. 1991. Interactive influences of bioactive trace metals on biological production in oceanic waters. *Limnology and Oceanography* 36:1,555–1,577.

Byrne, R.H. 2002. Inorganic speciation of dissolved elements in seawater: The influence of pH on concentration ratios. *Geochemical Transactions* 3:11–16.

Byrne, R.H., L.R. Kump, and K.J. Cantrell.1988. The influence of temperature and pH on trace metal speciation in seawater. *Marine Chemistry* 25:163–181.

Caldeira, K., and M.E. Wickett. 2003. Oceanography: Anthropogenic carbon and ocean pH. *Nature* 425:365.

Cantrell, K.J., and R.H. Byrne. 1987. Rare earth complexation by carbonate and oxalate ions. *Geochimica et Cosmochimica Acta* 51(3):597–605.

Capodaglio, G., K.H. Coale, and K.W. Bruland. 1990. Lead Speciation in surface waters of the eastern North Pacific. *Marine Chemistry* 29:221–233.

Casas, A.M., and E.A. Crecelius. 1994. Relationship between acid volatile sulfide and the toxicity of zinc, lead and copper in marine sediments. *Environmental Toxicology and Chemistry* 13(3):529–536.

Coale, K.H., and K.W. Bruland. 1988. Copper complexation in the Northeast Pacific. *Limnology and Oceanography* 33:1,084–1,101.

Crist, R.H., K. Oberholser, D. Schwartz, J. Marzoff, D. Ryder, and D.R. Crist.1988. Interactions of metals and protons with algae. *Environmental Science and Technology* 22:755–760.

Croot, P.L., J.W. Moffett, and G.W. Luther III. 1999. Polarographic determination of half-wave potentials for copper-organic complexes in seawater. *Marine Chemistry* 67:219–232.

Davies, A.G. 1990. Taking a cool look at iron. *Nature* 345:114–115.

Dittmar, T., and J. Paeng. 2009. A heat-induced molecular signature in marine dissolved organic matter. *Nature Geoscience* 2:175–179.

Donat, J.R., and C.M.G. van den Berg. 1992. A new cathodic stripping voltammetric method for determining organic copper complexation in seawater. *Marine Chemistry* 38:69–90.

Ellwood, M.J., and C.M.G. van den Berg. 2001. Determination of organic complexation of cobalt in seawater by cathodic stripping voltammetry. *Marine Chemistry* 75(1–2):33–47.

Feely, R.A., C.L. Sabine, M. Hernandez-Ayon, D. Lanson, and B. Hales. 2008. Evidence for upwelling of "acidified" water onto the continental shelf. *Science* 320:1,490–1,492.

Gattuso, J.-P., M. Frankignoulle, I. Bourge, S. Romaine, and R.W. Buddemeier. 1998. Effect of calcium carbonate saturation of seawater on coral calcification. *Global and Planetary Change* 18(1–2):37–46.

Gledhill, M., and C.M.G. van den Berg. 1994. Determination of complexation of iron(III) with natural organic complexing ligands in seawater using cathodic stripping voltammetry. *Marine Chemistry* 47:41–54.

Goldstone, J.V., and B.M. Voelker. 2000. Chemistry of superoxide radical in seawater: CDOM associated sink of superoxide in coastal waters. *Environmental Science and Technology* 34:1,043–1,048.

Gonzalez-Davila, M., J. Santana-Casiano, M. Perez-Pena, and F.J. Millero. 1995. Binding of Cu(II) to the surface and exudates of the alga *Dunaliella tertiolecta* in seawater. *Environmental Science and Technology* 29:289–301.

Hering, J.G., W.G. Sunda, R.L. Ferguson, and F.M.M. Morel. 1987. A field comparison of two methods for the determination of copper complexation: Bacterial bioassay and fixed-potential amperometry. *Marine Chemistry* 20:299–312.

Hofmann, A.F., F.J.R. Meysman, K. Soetaert, and J. Middleburg. 2009. Factors governing the pH in a heterotrophic, turbid, tidal estuary. *Biogeosciences Discussion* 6:197–240.

Kleypas, J.A., R.W. Buddemeier, D. Archer, J-P. Gattuso, C. Langdon, and B.N. Opdyke. 1999. Geochemical consequences of increased atmospheric carbon dioxide on coral reefs. *Science* 284:118–120.

Kramer, C.J.M., and J.C. Duinker. 1984. Complexation capacity and conditional stability constants for copper of sea and estuarine waters, sediment extracts and colloids. Pp. 217–288 in *Complexation of Trace Metals in Natural Waters*. C.J.M. Kramer and J.C. Duinker, eds, Nijhoff/Junk, The Hague, The Netherlands.

Landry, M.R, R.T. Barber, R.R. Bidigare, F. Chai, K.H. Coale, H.G. Dam, M.R. Lewis, S.T. Lindley, J.J. McCarthy, M.R. Roman, and others. 1998. Iron and grazing constraints on primary production in the central equatorial Pacific: An EqPac synthesis. *Limnology and Oceanography* 42:405–418.

Langdon, C., W.S. Broecker, D.E. Hammond, E. Glenn, K. Fitzsimmons, S.G. Nelson, T.-H. Peng, I. Hajdas, and G. Bonani. 2003. Effect of elevated CO_2 on the community metabolism of an experimental coral reef. *Global Biogeochemical Cycles* 17:1011, doi:10.1029/2002GB001941.

Liu, X., and F.J. Millero. 2002. The solubility of iron in seawater. *Marine Chemistry* 77:43–54.

Louis, Y., C. Garnier, V. Lenoble, D. Omanovic, S. Mounier, and I. Pizeta. 2009. Characterization and modelling of marine dissolved organic matter interactions with major and trace cations. *Marine and Environmental Research* 67:100–107.

Martin, J.H. 1990. Glacial-interglacial CO_2 change: The iron hypothesis. *Paleoceanography* 5(1):1–13.

Martin, J.H., and S.E. Fitzwater. 1988. Iron deficiency limits phytoplankton growth in the north-east Pacific subarctic. *Nature* 331:341–343.

Millero, F.J. 1987. Estimate of the life time of superoxide in seawater. *Geochimica et Cosmochimica Acta* 51:351-353.

Millero, F.J. 1992. Stability constants for the formation of rare earth inorganic complexes of a function of ionic strength. *Geochimica et Cosmochimica Acta* 56:3,123–3,132.

Millero, F.J. 2001a. *Physical Chemistry of Natural Waters*. Wiley-Interscience, NY. 654 pp.

Millero, F.J. 2001b. Speciation of metals in natural water. *Geochemical Transactions* 2(8): 56–64.

Millero, F.J., and D.J. Hawke. 1992. Ionic interactions of divalent metals in natural waters. *Marine Chemistry* 40:19–48.

Millero, F.J., and D. Pierrot. 1998. A chemical model for natural waters. *Aquatic Geochemistry* 4:153–199.

Millero, F.J., and D. Pierrot. 2002. Speciation of metals in natural waters. Pp. 193–220 in *Chemistry of Marine Water and Sediments.* A. Gianguzza, E. Pellizzetti, and S. Sammartano, eds, Springer-Verlag, Berlin.

Millero, F.J., T. Graham, F. Huang, H. Bustos, and D. Pierrot. 2006. Dissociation constants for carbonic acid in seawater as a function of temperature and salinity. *Marine Chemistry* 100:80–94.

Millero, F.J., V.K. Sharma, and B. Karn. 1991. The rate of reduction of Cu(II) with hydrogen peroxide in seawater. *Marine Chemistry* 36:71–83.

Millero, F.J., S. Sotolongo, and M. Izaguirre. 1987. The kinetics of oxidation of Fe(II) in seawater. *Geochimica et Cosmochimica Acta* 51:793–801.

Millero, F.J., W. Yao, and J. Aicher. 1995. The speciation of iron(II) and (III) in natural waters. *Marine Chemistry* 50:21–39.

Moffett, J.W., and R.G. Zika. 1983. Oxidation kinetics of Cu(I) in seawater: Implications for its existence in the marine environment. *Marine Chemistry* 13:39–251.

Moffett, J.W., and R.G. Zika. 1987. Solvent extraction of copper acetylacetonate in studies of copper(II) speciation in seawater. *Marine Chemistry* 21:301–313.

Morel, F.M.M., A.J. Milligan, and M.A. Saito. 2003. Marine bioinorganic chemistry: The role of trace metals in the oceanic cycles of major nutrients. *Treatise on Geochemistry* 6:113–143.

Orr, J.C., V.J. Fabry, O. Aumont, L. Bopp, S.C. Doney, R.A. Feely, A. Gnanadesikan, N. Gruber, A. Ishida, F. Joos, and others. 2005. Anthropogenic ocean acidification over the twenty-first century and its impact on calcifying organisms. *Nature* 437:681–686.

Paytan, A., R.M. Mackey, Y. Chen, I.D. Lima, S.C. Doney, N. Mahowald, R. Labiosa, and A.F. Post. 2009. Toxicity of atmospheric aerosols on marine phytoplankton. *Proceedings of the National Academy of Sciences of the United States of America* 106:4,601–4,605.

Pitzer, K.S. 1991. Ion interaction approach: Theory and data collection. Pp. 75–153 in *Activity Coefficients in Electrolyte Solutions*, 2nd ed. CRC Press, Boca Raton, FL.

Rich, H.W., and F.M.M. Morel. 1990. Availability of well-defined iron colloids to the marine diatom *Thalassiosira weissflogii*. *Limnology and Oceanography* 35:652–662.

Ritchie, J.D., and E.M. Perdue. 2003. Proton-binding study of standard and reference fulvic acids, humic acids, and natural organic matter. *Geochimica et Cosmochimica Acta* 67:85–96.

Rose, A.L., and T.D. Waite. 2005. Reduction of organically complexed ferric iron by superoxide in a simulated natural water. *Environmental Science and Technology* 39:2,645–2,650.

Rose, A.L., E.A. Webb, T.D. Waite, and J.W. Moffett. 2008. Measurement and implications of nonphotochemically generated superoxide in the Equatorial Pacific Ocean. *Environmental Science and Technology* 42:2,387–2,393.

Rue, E.L., and K.W. Bruland. 1995. Complexation of iron(III) by natural organic ligands in the Central North Pacific as determined by a new competitive ligand equilibration/adsorptive cathodic stripping voltammetric method. *Marine Chemistry* 50:17–138.

Saito, M.A., and J.W. Moffet. 2001. Complexation of cobalt by natural organic ligands in the Sargasso Sea as determined by a new high-sensitivity electrochemical cobalt speciation method suitable for open ocean water. *Marine Chemistry* 79(1–2):49–68.

Schreiber, D.R., A.S. Gordon, and F.J. Millero. 1985. The toxicity of copper to the marine bacterium *Vibrio alginolyticus*. *Canadian Journal of Microbiology* 31:83–87.

Sharma, V.K., and F.J. Millero. 1988. The oxidation of Cu(I) with H_2O_2 in natural waters. *Geochimica et Cosmochimica Acta* 53:2,269–2,276.

Sleighter, R.L., and P.G. Hatcher. 2007. The application of electrospray ionization coupled to ultrahigh resolution mass spectrometry for the molecular characterization of natural organic matter. *Journal of Mass Spectrometry* 42:559–574.

Steemann Nielsen, E., and S. Wium-Anderson. 1970. Copper ions as poison in the sea and in freshwater. *Marine Biology* 6:93–97.

Sunda, W.G., and R.L. Ferguson. 1983. Sensitivity of natural bacterial communities to additions of copper and to cupric ion activity: A bioassay of copper complexation in seawater. Pp. 871–891 in *Trace Metals in Seawater*. C.S. Wong, E. Boyle, K.W. Bruland, J.D. Burton, and E.D. Goldberg, eds, Plenum, New York.

Sunda, W.G., and A.K. Hanson.1987. Measurement of free cupric ion concentration in seawater by a ligand competition technique involving copper sorption onto C18 SEP-PAK cartridges. *Limnology and Oceanography* 32:537–551.

Sunda, W.G., and S.A. Huntsman. 1992. Feedback interactions between zinc and phytoplankton in seawater. *Limnology and Oceanography* 37:25–40.

Sunda, W.G., D. Klaveness, and A.V. Palumbo. 1984. Bioassays of cupric ion activity and copper complexation. Pp. 399–409 in *Complexation of Trace Metals in Natural Waters*. C.J.M. Kramer and J.C. Duinker, eds, Nijhoff/Junk, The Hague, The Netherlands.

Turner, D.R., M. Whitfield, and A.G. Dickson. 1981. The equilibrium speciation of dissolved components of freshwater and seawater at 25°C and 1 atm pressure. *Geochimica et Cosmochimica Acta* 44:855–881.

van den Berg, C.M.G. 1982. Determination of copper complexation with natural organic ligands in seawater by equilibration with MnO_2. II. Experimental procedures and application to surface seawater. *Marine Chemistry* 11:323–342.

van den Berg, C.M.G. 1984. Determination of the complexing capacity and conditional stability constants of complexes of copper(II) with natural organic ligands in seawater by cathodic stripping voltammetry of copper-catechol complexions. *Marine Chemistry* 15:1,268–1,274.

van den Berg, C.M.G., and M. Nimmo. 1987. Determination of interactions of nickel with dissolved organic material in seawater using cathodic stripping voltammetry. *Science of the Total Environment* 60:185–195.

Voelker, B.M., D.L. Sedlak, and O.C. Zafiriou. 2000. Chemistry of superoxide radical in seawater: Reactions with organic Cu complexes. *Environmental Science and Technology* 34(6):1,036–1,042.

Wilde, K.L., J.L. Stauber, S.J. Markich, N.M. Franklin, and P.L. Brown. 2006. The effect of pH on the uptake and toxicity of copper and zinc in a tropical freshwater alga (*Chlorella* sp.). *Archives of Environmental Contamination and Toxicology* 51:174–185.

Woosley, R., and F.J. Millero. In press. The hydrolysis of Al(III) in NaCl solutions: A model for M(II), M(III) and M(IV) ions. *Aquatic Geochemistry*.

Wu, J., and G.W. Luther. 1995. Complexation of Fe(III) by natural organic ligands in the Northwest Atlantic Ocean by a competitive ligand equilibration method and a kinetic approach. *Limnology and Oceanography* 50:119–177.

Zafiriou, O.C., B.M. Voelker, and D.L. Sedlak. 1998. Chemistry of the superoxide radical (O_2^-) in seawater: Reactions with inorganic copper complexes. *Journal of Physical Chemistry A* 102(23):693–700.

Zhang, J., C.M.G. van den Berg, and R. Wollast. 1990. The determination of interactions of cobalt(II) with organic compounds in seawater using cathodic stripping voltammetry. *Marine Chemistry* 28:285–300.

Zika, R.G., J.W. Moffett, W.J.C. Petasne, and E.S. Saltzman. 1985. Spatial and temporal variations of hydrogen peroxide in Gulf of Mexico waters. *Geochimica et Cosmochimica Acta* 49:1,173–1,184.