

Use of Thermodynamics in Examining the Effects of Ocean Acidification

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The first author beside the CTD (conductivity, temperature, depth) system used to collect seawater samples at different depths. CO₂ is measured to determine the saturation state of seawater.

The burning of fossil fuels has increased the concentration of carbon dioxide (CO₂) in the atmosphere from 280 ppmv (volume parts per million) to 385 ppmv over the last 200 years. This increase is larger than has occurred over the past 800,000 years. Equilibration of increasing amounts of CO₂ with surface waters will decrease the pH of the oceans (called ocean acidification) from a current value of 8.1 to values as low as 7.4 over the next 200 years. Decreasing the pH affects the production of solid CaCO₃ by microorganisms in surface waters and its subsequent dissolution. CO₂ dissolution in the ocean can also affect acid–base equilibria, metal complex formation, solid–liquid equilibria, and the adsorption of ions to charged surfaces. Thermodynamic principles can be used to understand these processes in natural waters.

KEYWORDS: pH, ocean acidification, carbonate system, metal complex formation

INTRODUCTION

Over the last 200 years the concentration of CO₂ in the atmosphere has been increasing due to the burning of fossil fuels. This increase is shown in FIGURE 1, which is based on the CO₂ measurements of Keeling and Whorf (2004) in Hawai'i and the ice-core measurements of Neftel et al. (1994). CO₂ levels were 280 ppmv prior to the industrial revolution and have increased to the current level of 388 ppmv over the last 200 years. Levels of CO₂ over the past 800,000 years (FIG. 2) have varied between 200 ppmv during glacial times and 300 ppmv during interglacial times (Siegenthaler et al. 2005). Present levels of CO₂ in the atmosphere are ~23% higher than at any point in the past 800,000 years. Caldeira and Wickett (2003) have suggested that over the next 200 years atmospheric CO₂ concentrations may increase to as much as 2000 ppmv due to the burning of fossil fuels (FIG. 3). These authors suggest that the increase in the concentration of CO₂ in ocean surface waters will decrease the pH from a present value of 8.1 to as low as 7.4. As shown in Equation (2), below, the decrease in pH is due to the CO₂ reacting with water to form H⁺ and HCO₃⁻. Due to CO₂ uptake since the year 1750, the surface pH has already decreased by 0.1 unit, which corresponds to a 30% increase in the concentration of H⁺ ions (Sabine et al. 2004). A continued decrease in the pH of the surface ocean will affect the carbonate system and the speciation of metals in seawater. Because the uptake of CO₂ by the oceans is a slow process, ocean pH will remain low for thousands of years.

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FIGURE 4 shows pH profiles with depth for the Atlantic and Pacific oceans. Currently ocean surface waters are in near equilibrium with the atmosphere and have the pH that is expected for surface waters for nearly constant normalized total alkalinity (NTA = TA•35/S, where TA is the total alkalinity and S is the salinity). Deep waters have a lower pH and a higher total alkalinity as a result of the dissolution of solid CaCO₃ [CaCO₃(s)] and oxidation of organic carbon by bacteria produced by phytoplankton near the ocean surface. Values for pH are as low as 7.4 at a depth of about 1000 m in the Pacific Ocean.

Decreasing pH lowers the concentrations of the OH⁻ and CO₃²⁻ ions in the oceans. The decrease in these anions is due to the equilibrium of OH⁻ with water ($10^{-14}/[H^+] = [OH^-]$) and the reaction of H⁺ with CO₃²⁻ to form HCO₃⁻. For surface waters, the projected effect of ocean acidification on these two species is shown in FIGURE 5. This calculation is made by assuming that the NTA in surface waters does not change significantly with time. Direct measurements over time in Atlantic surface waters have not changed more than 10–20 μmol kg⁻¹ over the last 70 years (Bustos-Serrano et al. 2009). Decreased concentrations of these ions will affect the carbonate system and the speciation of metals. The lower concentrations of the CO₃²⁻ ion will result in a decrease in the saturation state of aragonite (FIG. 6).

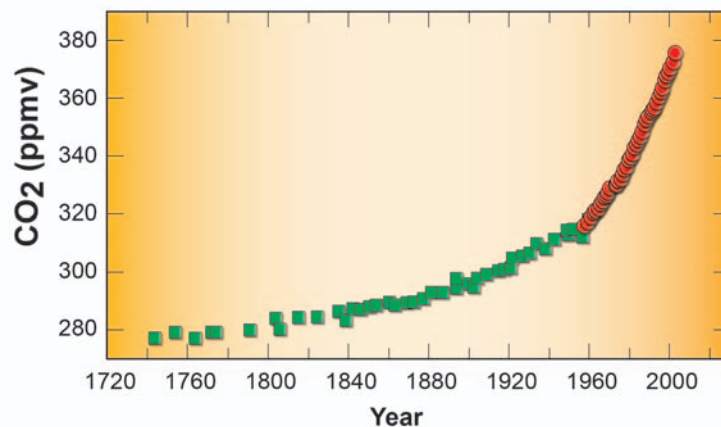


FIGURE 1 The increase of carbon dioxide in the atmosphere as determined from atmospheric samples at Hawai'i (Keeling and Whorf 2004; red circles) and from air trapped in ice cores (Neftel et al. 1994; green squares) as a function of time.

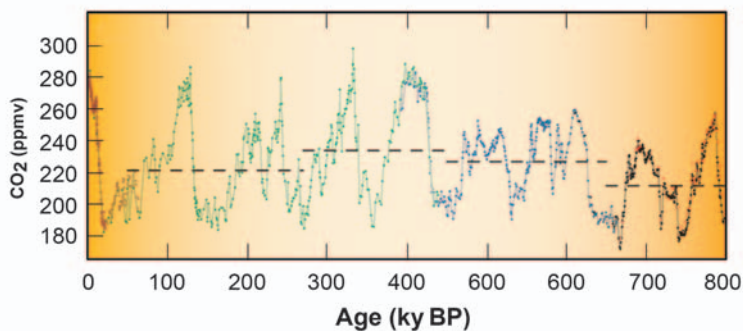


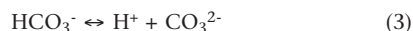
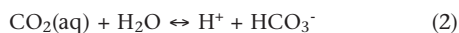
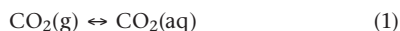
FIGURE 2 The variations of carbon dioxide concentration (in volume parts per million) since the Holocene, as recorded in the Vostok ice core. ADAPTED FROM SIEGENTHALER ET AL. (2005)

Most of the recent interest in ocean acidification has concentrated on how the decrease in the saturation state affects the production and dissolution of $\text{CaCO}_3(\text{s})$ formed by marine organisms (Guinotte and Fabry 2008; Fabry et al. 2008). As pH decreases, the growth of calcifying organisms will slow down and eventually the shells of these calcifiers and coral reefs may dissolve (Kleypas et al. 1999; Langdon and Atkinson 2005; Hoegh-Guldberg et al. 2007).

CO_3^{2-} and OH^- ions are known to form strong complexes with divalent, trivalent, and tetravalent counter ions in natural waters. Thus, decreased concentrations of these ions, as well as of some organic ligands, will affect the speciation or form of metals in seawater. We show below how thermodynamic equilibrium can be used to understand the effects of ocean acidification on the carbonate system and on the speciation of metals in ocean waters.

THERMODYNAMICS OF THE CARBONATE SYSTEM IN NATURAL WATERS

The thermodynamics of the carbonate system in natural waters are governed by the following equilibria [(g), (aq), and (s) refer to gaseous, aqueous, and solid forms, respectively]:



To examine the carbonate system in seawater, ocean chemists use stoichiometric equilibrium constants, which are given by (values are for $S = 35.165$ g/kg seawater at 25°C):

$$K_0^* = K_0 a(\text{H}_2\text{O}) p\text{CO}_2/\gamma(\text{CO}_2) = [\text{CO}_2] p\text{CO}_2 \approx 10^{-1.55} \quad (5)$$

$$K_1^* = K_1 \gamma(\text{H}^+) \gamma(\text{HCO}_3^-)/[\gamma(\text{CO}_2) a(\text{H}_2\text{O})] = [\text{H}^+] [\text{HCO}_3^-]/[\text{CO}_2] \approx 10^{-5.82} \quad (6)$$

$$K_2^* = K_2 \gamma(\text{H}^+) \gamma(\text{CO}_3^{2-})/\gamma(\text{HCO}_3^-) = [\text{H}^+] [\text{CO}_3^{2-}]/[\text{HCO}_3^-] \approx 10^{-8.95} \quad (7)$$

$$K_{\text{sp}}^* = K_{\text{sp}}/[\gamma(\text{Ca}^{2+}) \gamma(\text{CO}_3^{2-})] = [\text{Ca}^{2+}] [\text{CO}_3^{2-}] \approx 10^{-6.3} \quad (8)$$

The values of K_i are the thermodynamic constants in pure water, the values of $[i]$ are the total concentrations (g/kg_{soln}), the values of $\gamma(i)$ are the activity coefficients of species i , and $a(\text{H}_2\text{O})$ is the activity of water in the solution. These constants are a function of temperature and ionic strength or salinity of seawater (Millero 2007; Millero et al. 2006). The constants are also available for NaCl solutions at ionic strengths up to 5 molar (M) from 0 to 250°C (Millero et al. 2007). Ionic interaction models can also be

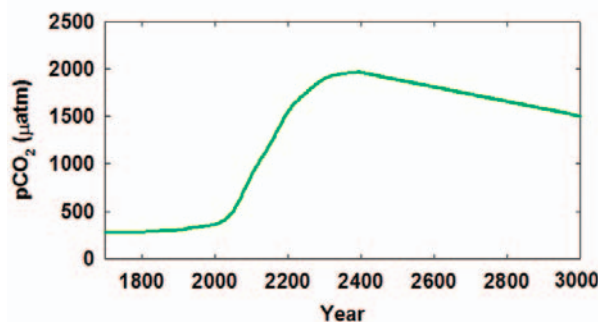
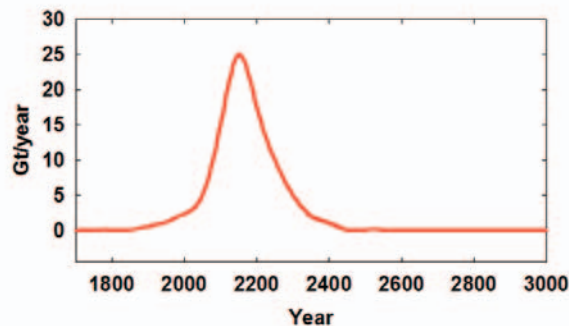


FIGURE 3 Long-term estimates of the input of fossil fuel CO_2 to the atmosphere (in gigatonnes carbon per year), and resultant increase of $p\text{CO}_2$ (in volume parts per million). ADAPTED FROM CALDEIRA AND WICKETT (2003)

used to estimate the constants in solutions made up of the major components of seawater (Na, Mg, Ca, Cl, SO_4) from 0 to 100°C and ionic strengths of 6 M (Millero and Pierrot 1998). These models calculate stoichiometric constants that are in good agreement with the measured values.

To unravel the CO_2 system in the oceans, it is necessary to measure at least two of the following parameters: pH, TA (total alkalinity), TCO_2 (total inorganic CO_2), and $p\text{CO}_2$ (partial pressure of CO_2). These parameters are mutually related by the following equations (species concentrations are in square brackets):

$$\text{pH} = -\log [\text{H}^+] \quad (9)$$

$$\text{TA} = [\text{HCO}_3^-] + 2[\text{CO}_3^{2-}] + [\text{B}(\text{OH})_4^-] + \text{other minor bases} \quad (10)$$

$$\text{TCO}_2 = [\text{CO}_2] + [\text{HCO}_3^-] + [\text{CO}_3^{2-}] \quad (11)$$

$$\text{CO}_2 = K_0^* [\text{CO}_2] \quad (12)$$

To evaluate the concentration of the borate ion in Equation (10), one needs to know the dissociation constant for the dissociation of boric acid (Millero 2007). The methods used to determine these parameters in oceanography are available from the Carbon Dioxide Information Analysis Center, CDIAC (Dickson et al. 2007). Pairs of parameters used in most ocean studies include $p\text{CO}_2$ and TCO_2 , pH and TA or TCO_2 , and TA and TCO_2 .

These input parameters, combined with the stoichiometric thermodynamic constants, are used to determine the two unknown parameters not measured (pH, $p\text{CO}_2$, TA, TCO_2) and the concentrations of HCO_3^- , CO_3^{2-} and CO_2 needed to examine the carbonate system in ocean waters. Computer programs are available to calculate all the components of the CO_2 system in the oceans (Dickson et al. 2007) and in brines (Millero and Roy 1997) using any possible input of the four parameters that can be measured.

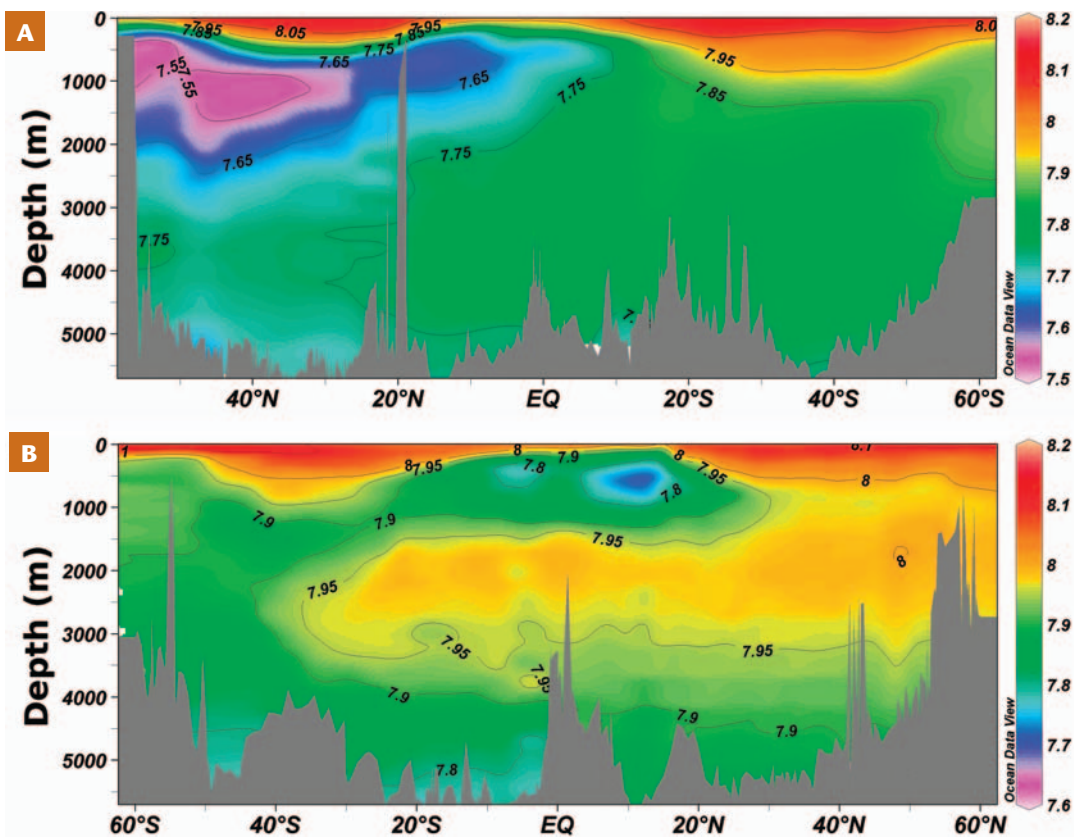


FIGURE 4 pH sections in the Pacific (A) and Atlantic (B) oceans. Bathymetry is shown in grey. The north-south transit in the Atlantic is along 30° W and in the Pacific along 150° W.

CALCIUM CARBONATE THERMODYNAMICS

The dissolution and precipitation of $\text{CaCO}_3(\text{s})$ in the ocean is examined using the saturation state of the mineral, defined as

$$\Omega = [\text{Ca}^{2+}] [\text{CO}_3^{2-}] / K_{\text{sp}}^* \quad (13)$$

The concentration of Ca^{2+} , a major constituent of seawater, changes only when the total salts are increased or decreased. K_{sp}^* in Equation (13) is the measured solubility of $\text{CaCO}_3(\text{s})$ in seawater at a given temperature, salinity, and pressure. Calcite and aragonite are the two forms of $\text{CaCO}_3(\text{s})$ present in ocean waters. They differ in crystal structure, with calcite being the more thermodynamically stable. Due to its relative thermodynamic instability, aragonite has a lower saturation state, Ω_A , than calcite. Calcareous organisms secrete aragonite; thus it is Ω_A that must be considered when assessing future conditions for them. When $\Omega_A > 1$, the waters are supersaturated; when $\Omega_A < 1$, they are undersaturated; and when $\Omega_A = 1$, they are in equilibrium. Most ocean surface waters are supersaturated in aragonite, and deep waters are undersaturated due to the decrease of CO_3^{2-} and increase of K_{sp}^* with depth. As the surface oceans become more acidic, the values of Ω_A in surface waters will decrease (FIG. 6). Experimental measurements show that a decrease in Ω_A or $[\text{CO}_3^{2-}]$ makes it more difficult for calcareous organisms like corals to make $\text{CaCO}_3(\text{s})$ (Langdon and Atkinson 2005; Fabry et al. 2008). It is important to note that Ω_A must not drop below 1, otherwise organisms will be negatively affected. Langdon and Atkinson (2005) showed that, in the past, the rates of growth of corals forming aragonite were slower when the saturation state decreased (SEE FIG. 7). The calcification rates for different coral species were different, but they all decreased as Ω_A decreased. In addition to the stress on the growth of calci-

fying organisms due to decreases in Ω_A , if the values fall below 1.0, aragonite skeletal structures of these organisms may dissolve (Kleypas et al. 1999; Hoegh-Guldberg et al. 2007; Fabry et al. 2008; Guinotte and Fabry 2008). The warming of the surface oceans is also a threat to corals, as an increase in temperature beyond the summer maximum can decrease aragonite production by corals (Marshall and Clode 2004).

Corals are not the only calciferous organisms threatened by the prospect of ocean acidification. Planktonic species, such as pteropods, also form shells from aragonite. These organisms have been found to make up a substantial fraction of the biomass in high-latitude regions (Urban-Rich et al. 2001), particularly in the Southern Ocean. Using the IPCC IS92a “business as usual” CO_2 -emission scenario, Orr et al. (2005) modeled Ω_A in this region and calculated that these waters will be undersaturated in aragonite by the year 2050. These workers measured the effects of undersaturated conditions on native pteropods and observed prominent shell dissolution. Pteropods in this region are thought to have a significant role in the export of carbon to the deep ocean (Hunt et al. 2008). If these calcifiers are unable to exist in undersaturated conditions, the global carbon cycle may change significantly. Pteropods, for example, are a food source for other organisms in surface waters. The saturation state of calcite is not expected to be less than 1.0 in most surface waters, so organisms utilizing calcite, like foraminifera, should not have their production rates affected by the expected changes in pH. These organisms are the major contributors of $\text{CaCO}_3(\text{s})$ to the deep oceans and sediments.

THERMODYNAMICS OF METAL SPECIATION

Metals in natural water systems interact with organic and inorganic ligands, resulting in fractionation of the total metal concentration among a number of different species. The distribution of species for a given metal is governed

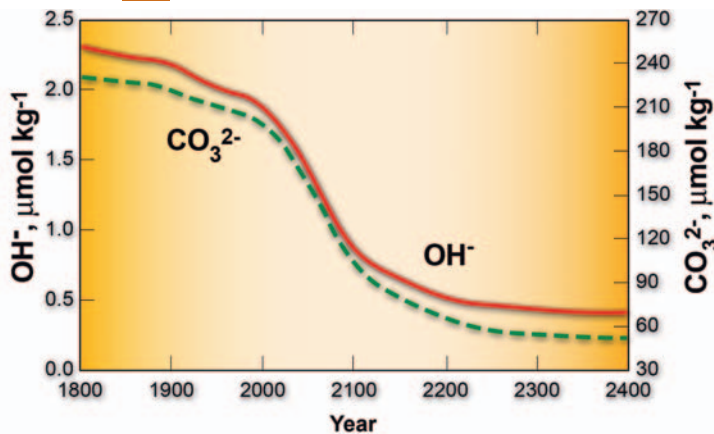


FIGURE 5 The estimated decreases in the concentrations of OH^- and CO_3^{2-} ions in surface seawater as a function of time. OH^- and CO_3^{2-} are given in terms of micromoles per kilogram of seawater. The calculations were made assuming surface waters have a normalized total alkalinity ($\text{NTA} = \text{TA} \cdot 35/S$, where TA is the total alkalinity and S the salinity) of $2300 \mu\text{mol kg}^{-1}$ and the waters are in equilibrium with the atmosphere (Caldeira and Wickett 2003).

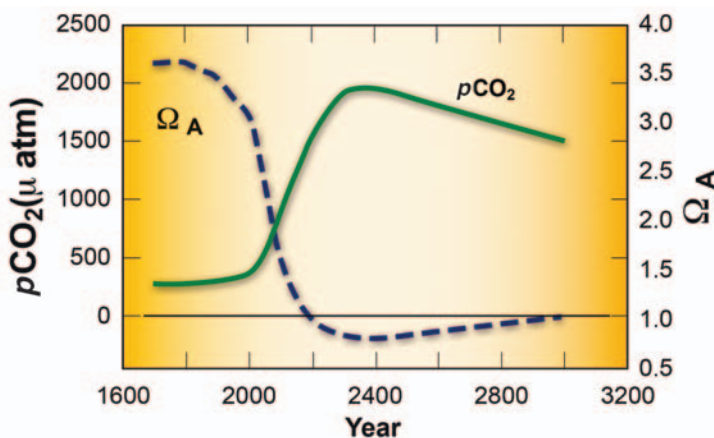


FIGURE 6 Estimated changes in $p\text{CO}_2$ and the saturation state of aragonite, Ω_A , as a function of time

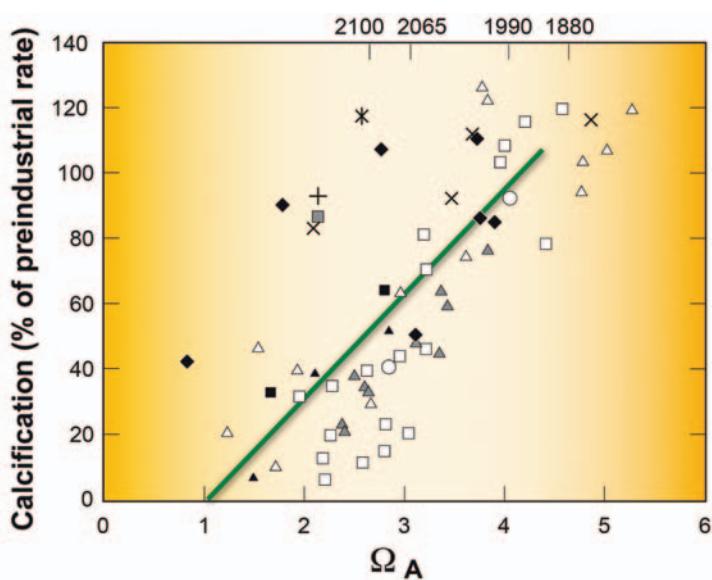


FIGURE 7 Percentage of the preindustrial rate of coral calcification (secretion of aragonite) as a function of the saturation state of aragonite (Ω_A) in seawater. Overlaid is a timescale showing the saturation state as a function of time. DATA FIT AND SUMMARIZED BY LANGDON AND ATKINSON (2005)

by the strength of the stoichiometric stability constant, K_{MX}^* . For a single complex, MX, between a metal, M, and an inorganic ligand, X, the stability constant can be determined from

$$K_{\text{MX}}^* = K_{\text{MX}} \gamma(\text{M}) \gamma(\text{X}) / \gamma(\text{MX}) = [\text{MX}] / [\text{M}] [\text{X}] \quad (14)$$

As described above, K_i , $\gamma(I)$, and $[i]$ are, respectively, thermodynamic constants in pure water, activity coefficients, and stoichiometric concentrations. In order to account for the competitive speciation between a metal and multiple ligands, K_{MX}^* must be known for all relevant metal–ligand interactions. It is then possible to determine the fraction of each metal–ligand species by determining the fraction of the free metal in solution, $\alpha(\text{M}^{x+})$, and the fraction of the free ligand, $\alpha(\text{X}^{y-})$, through a series of iterations. A number of methods have been used to calculate the speciation of metals using these relations. These methods have traditionally involved the use of an ion-pairing model (Millero and Schreiber 1982), a Pitzer (1991) formulation, or a hybrid of the two (Millero and Pierrot 2002). A comprehensive review of these methods and their applications is provided by Millero (2001).

Inorganic ligands in seawater consist of both pH-dependent species, such as OH^- , CO_3^{2-} , and HCO_3^- , and pH-independent species, such as Cl^- and the less abundant halides. Metals that form strong complexes with halides (Cd^{2+} , Hg^{2+}) are not affected by decreases in pH. FIGURE 8 shows the inorganic speciation in seawater for Cu^{2+} at the current pH of 8.1 and at the projected future level of 7.4. Free Cu^{2+} will increase by 30% if pH decreases from 8.1 to 7.4, resulting in 45% of the total copper concentration not complexed with organic material being in the free form. This may increase the toxicity of Cu^{2+} in surface ocean waters.

Surface concentrations of total Cu^{2+} in the open ocean range on average between 0.6 and 2.5 nanomolar (nM) (Coale and Bruland 1988; Donat and van den Berg 1992). Inorganically complexed and free forms generally represent <1% of the total Cu^{2+} present in surface waters (Coale and Bruland 1988; Donat and van den Berg 1992). The remaining Cu^{2+} is strongly complexed with organic matter. This fact is important to note as Cu^{2+} bound by organic ligand(s) is not bioavailable (Schreiber et al. 1985; Gonzalez-

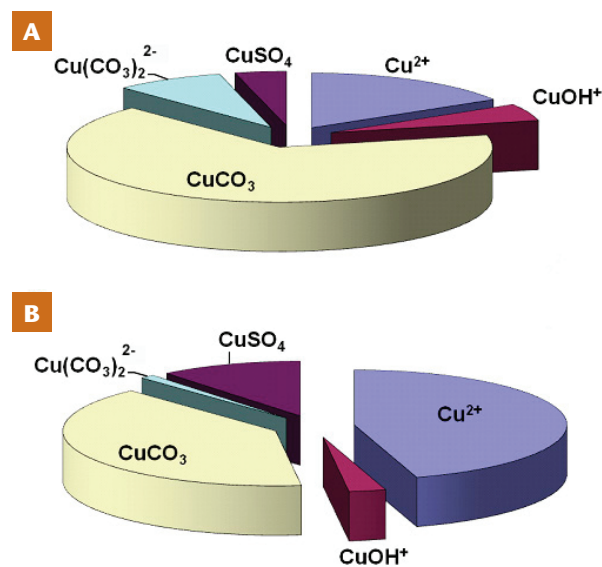


FIGURE 8 Inorganic speciation of $\text{Cu}(\text{II})$ in seawater at pH 8.1 (A) and at pH 7.4 (B). The changes in going from 8.1 to 7.4 for the various species are as follows: Cu^{2+} : 16 to 45%; $\text{Cu}(\text{OH})^+$: 5 to 2.8%; CuCO_3 : 65 to 40%; $\text{Cu}(\text{CO}_3)_2^{2-}$: 8 to 1%; CuSO_4 : 4 to 11%.

Davila et al. 1995). Little is known regarding how the organic speciation of metals will change with decreasing pH, but preliminary data for Cu^{2+} suggest that the organically complexed fraction will decrease, resulting in higher concentrations of labile Cu^{2+} (Louis et al. 2009). Toxic thresholds of free Cu^{2+} for certain marine organisms have been observed to be on the order of 1 picomolar (pM) (Brand et al. 1986). This is a small percentage of the total Cu^{2+} in open-ocean surface waters (0.2–0.04%); thus subtle increases in free and inorganic copper could translate into toxic conditions (Millero et al. 2009).

The speciation and solubility of other metals significant to microorganisms—Mn, Fe, Ni, Co, Zn, and Cd—will also be affected by decreases in pH. Assessing these changes is an area in which thermodynamic research will play a significant role.

CONCLUSIONS

The continued burning of fossil fuels will increase the concentration of CO_2 in the atmosphere. The increased

solubility of this CO_2 in the oceans will lead to a decrease in the pH. This so-called “ocean acidification” will affect the thermodynamic equilibrium of the carbonate system and the speciation of metals. The lower concentrations of CO_3^{2-} will slow the production of CaCO_3 minerals by organisms and may dissolve coral reefs in some areas. The decrease in the pH will also make some metals more toxic (Cu^{2+}) and others more available (Fe^{2+}) for phytoplankton. Further studies are needed to determine the long-term effect of ocean acidification on the ecology of ocean waters. Unless dramatic changes in our use of fossil fuels are made, it will take thousands of years to return the pH of the oceans to their preindustrial levels.

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All other regions: Email: sales@geolsoc.org.uk Telephone: +44 (0)1225 445046

For more information visit: www.lyellcollection.org

New Developments for 2011

Full functionality of H2O

All Lyell collection titles will have migrated to Highwire Press' enhanced hosting platform, benefits include:

- advanced research tools
- cross journal alerts
- instant indexing
- inter-journal linking

New titles

Two new journal titles launched on the Lyell Collection in 2010 will be included for all 2011 subscribers to Lyell Collection Complete (LCC):

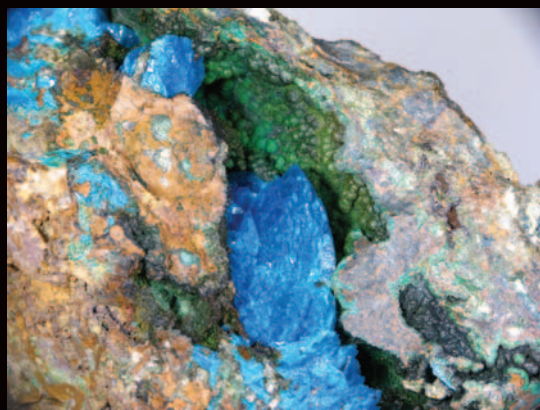
- Journal of Micropaleontology
- Petroleum Geoscience

In addition, two new archival titles will be launched on the Lyell Collection in 2011 and made available to LCC subscribers at no additional charge:

- Transactions of the Edinburgh society
- Transactions of the Glasgow society

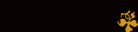


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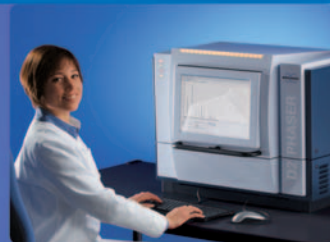
- Automated laser heating for 25 samples under computer control
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