CHAPTER IV: CARBONATE CHEMISTRY

A. ACIDS AND BASES IN SEAWATER

B. CARBONATE EQUILIBRIA - CALCULATING THE pH OF SEAWATER

C. KINETICS OF CO_2 REACTIONS IN SEAWATER

D. PROCESSES THAT CONTROL ALKALINITY AND DIC OF SEAWATER

REFERENCES

APPENDIX IV-1. THE CARBONATE SYSTEM EQUATIONS IN SEAWATER

APPENDIX IV-2 EVALUATING THE CARBONATE SYSTEM EQUILIBRIUM CONSTANTS

TABLES

FIGURES

CHAPTER IV. THE MARINE CARBONATE SYSTEM

One of the most important components of the Chemical Perspective of Oceanography is the carbonate system, primarily because it controls the acidity of seawater and acts as a governor for the carbon cycle. Within the mix of acids and bases in the Earth-surface environment, the carbonate system is the primary buffer for the acidity of water, which determines the reactivity of most chemical compounds and solids. The carbonate system of the ocean plays a key role in controlling the pressure of carbon dioxide in the atmosphere, which helps to regulate the temperature of the planet. The formation rate of the most prevalent authigenic mineral in the environment, $CaCO_3$, is also the major sink for dissolved carbon in the long-term global carbon balance.

Dissolved compounds that make up the carbonate system in water (CO_2, HCO_3^- and CO_3^{2-}) are in chemical equilibrium on time scales longer than a few minutes. Although this is less certain in the heterogeneous equilibrium between carbonate solids and dissolved constituents, to a first approximation $CaCO_3$ is found in marine sediments that are bathed by waters that are saturated or supersaturated thermodynamically ($Q > K$) and absent where waters are undersaturated ($Q < K$). It has become feasible to test models of carbonate thermodynamic equilibrium because of the evolution of analytical techniques for the carbonate system constituents and thermodynamic equilibrium constants. During the first major global marine chemical expedition, Geochemical Sections (GEOSECS) in the 1970s, marine chemists argued about concentrations of dissolved inorganic carbon, DIC (= $HCO_3^- + CO_3^{2-} + CO_2$), and alkalinity at levels of 0.5 - 1 %, and the fugacity of CO_2, f_{CO_2}, at levels of $\pm$ 20 %. pH (the negative log of the hydrogen ion concentration) was a qualitative property because its accuracy was uncertain when measured by glass electrodes, which could not be adequately standardized. By the time of the chemical surveys of the 1980s and 1990s, the world ocean circulation experiment (WOCE) and the joint global ocean survey (JGOFS), the accuracy of the carbonate system measurements improved dramatically. Part of the improvement was due to new methods such as coulometry for DIC and colorimetry for pH. Another important advance was the development of certified, chemically-stable DIC standards that resulted from both greater community organization, and the where-with-all to make stable standards. Since it was now possible to determine DIC and alkalinity to within several tenths of 1 % and f_{CO_2} to within a

couple of microatmospheres, it became necessary to improve the accuracy of equilibrium constants used to describe the chemical equilibria among the dissolved and solid carbonate species.

Homogeneous reactions of carbonate species in water are reversible and fast so they can be interpreted in terms of chemical equilibrium, which is the primary focus of the first section of this chapter.   Applications of these concepts to $CaCO_3$ preservation in sediments and the global carbon cycle are presented in Chapters XI and XII . The following discussion uses terminology and concepts introduced in Chapter III on thermodynamics. We deal almost exclusively with *apparent* equilibrium constants (denoted by the prime on the equilibrium constant symbol, K') instead of *thermodynamic* constants which refer to solutions with ionic strength approaching zero. Since seawater chemistry is for the most part extremely constant (see Chapter I) it is feasible for chemical oceanographers to determine equilibrium constants in the laboratory in seawater solutions with chemistries that represent more than 99 % of the ocean. The equilibrium constants have been determined as a function of temperature and pressure in the seawater medium. With this approach one forgoes attempts to understand the interactions that are occurring among the ions in solution for a more empirical, but also more accurate, description of chemical equilibria. We begin our discussion of the carbonate system by describing acids and bases in water, and then evolve to chemical equilibria and kinetic rates of CO_2 reactions. The chapter concludes with a discussion of the processes controlling alkalinity and DIC in the ocean.

IV-A. ACIDS AND BASES IN SEAWATER

The importance of the many acid/base pairs in seawater in determining the acidity of the ocean depends on their concentrations and equilibrium constants. Evaluating the concentrations of an acid and its conjugate anion (base, Ba) as a function of pH (pH = -log [H$^+$]) requires knowledge of the equation describing the acid/base equilibrium (hydrogen ion exchange), the apparent equilibrium constant, K', and information about the total concentration, Ba$_T$, of the acid in solution

$$HBa \underset{\longleftarrow}{\overset{\longrightarrow}{\rule{0pt}{0pt}}} H^+ + Ba^- \tag{IV-1}$$

$$K' = \frac{[H^+] \times [Ba^-]}{[HBa]} \tag{IV-2}$$

$$Ba_T = [HBa] + [Ba^-] . \tag{IV-3}$$

Combining eqs. (IV-2) and (IV-3) gives expressions for the concentration of the acid, HBa, and its conjugate base, Ba⁻, as functions of the apparent equilibrium constant, K', and the hydrogen ion concentration, [H⁺]:

$$[HBa] = \frac{Ba_T \times [H^+]}{K' + [H^+]} \quad \text{or} \quad \log[HBa] = \log C_T + \log[H^+] - \log(K' + [H^+]) \tag{IV-4}$$

and

$$[Ba^-] = \frac{Ba_T \times K'}{K' + [H^+]} \quad \text{or} \quad \log[Ba^-] = \log Ba_T + \log[K'] - \log(K' + [H^+]) . \tag{IV-5}$$

A plot of these logarithmic equations (Fig. IV-1) illustrates that the concentration of the acid dominates the solution concentration below pH = pK' (on the acid side), and in the region where pH is greater than pK' (the basic side), the conjugate base, A⁻, dominates. At a pH equal to pK' the concentrations of the acid and basic forms are equal, [HBa] = [Ba⁻].

The final constraint is that of charge balance, which in this simple solution involves the only two ions:

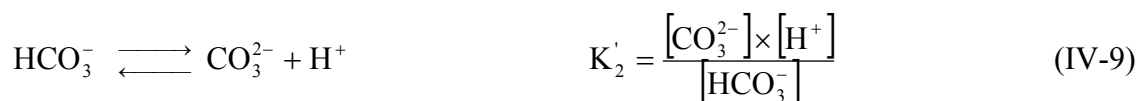$$0 = [H^+] - [Ba^-] . \tag{IV-6}$$

This equation constrains the system to a single location on the plot (where the lines for these two concentrations cross in Fig. IV-1), which uniquely fixes the pH and concentrations of acids and bases in the system. In this simple system the solution is acidic (pH = 4) because the concentration of the hydrogen ion and anion must be equal.

These simple equations and ideas provide the basis for describing the carbonate system in terms of the f_{CO_2}, DIC, pH, and alkalinity of seawater. We will build up a plot similar to that in Fig. IV-1 for the important acids and bases in seawater. These are listed along with their concentrations and apparent equilibrium constants in Table IV-1. It will then be demonstrated how the constraint of charge balance (called alkalinity) determines the pH of seawater.

IV-A.1. THE IMPORTANT ACIDS AND BASES IN SEAWATER

Carbonic Acid. In water inorganic carbon exists in four distinct forms; the gas in solution or aqueous carbon dioxide, $CO_{2(aq)}$, and the three products of hydration reactions which are carbonic acid H_2CO_3, bicarbonate HCO_3^-, and carbonate CO_3^{2-}. Concentrations are in moles
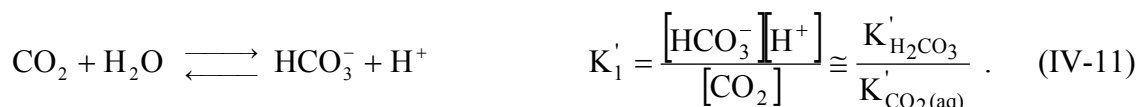
kg^{-1}. Chemical equilibria among these species in seawater is described by the apparent constants which have units necessary to make the dimensions of the equilibrium expressions correct

$$H_2CO_3 \underset{\longleftarrow}{\longrightarrow} CO_{2(aq)} + H_2O \qquad\qquad K'_{CO2(aq)} = \frac{[CO_2]_{aq}}{[H_2CO_3]} \qquad\qquad \text{(IV-7)}$$

$$H_2CO_3 \underset{\longleftarrow}{\longrightarrow} HCO_3^- + H^+ \qquad\qquad K'_{H_2CO_3} = \frac{[HCO_3^-] \times [H^+]}{[H_2CO_3]} \qquad\qquad \text{(IV-8)}$$

$$HCO_3^- \underset{\longleftarrow}{\longrightarrow} CO_3^{2-} + H^+ \qquad\qquad K'_2 = \frac{[CO_3^{2-}] \times [H^+]}{[HCO_3^-]} \qquad\qquad \text{(IV-9)}$$

where the equilibrium constant, K'_2, indicates the second dissociation constant of carbonic acid. Because only a few tenths of one percent of the neutral dissolved carbon dioxide species exists as H_2CO_3 at equilibrium, and because it is difficult to analytically distinguish between $CO_{2(aq)}$ and H_2CO_3, these neutral species are usually combined and represented with either the symbol $[CO_2]$ or $H_2CO_3^*$ (see Chapter IX, Table IX-2). We use the former here

$$[CO_2] = [CO_{2(aq)}] + [H_2CO_3] . \qquad\qquad \text{(IV-10)}$$

Equations (IV-7) and (IV-8) can be combined to eliminate $[H_2CO_3]$ and give a new composite first dissociation constant of CO_2 in seawater. If one assumes that $[CO_{2(aq)}] = [CO_2]$, the first dissociation constant of carbonic acic, K'_1, is

$$CO_2 + H_2O \underset{\longleftarrow}{\longrightarrow} HCO_3^- + H^+ \qquad\qquad K'_1 = \frac{[HCO_3^-][H^+]}{[CO_2]} \cong \frac{K'_{H_2CO_3}}{K'_{CO2(aq)}} . \qquad \text{(IV-11)}$$

The approximation involved in combining $[CO_2](aq)$ and $[H_2CO_3]$ as $[CO_2]$ is illustrated by solving eqs. (IV-7), (IV-8), (IV-10) and (IV-11) to derive a relationship among the equilibrium constants, K'_1, $K'_{CO_2(aq)}$, and $K'_{H_2CO_3}$

$$K'_1 = \frac{K'_{H_2CO_3}}{K'_{CO2(aq)} + 1} . \qquad\qquad \text{(IV-12)}$$

Because $K'_{CO2(aq)} \gg 1$ (the thermodynamic value for $K'_{CO_2(aq)}$ is 350 to 990, Stumm and Morgan, 1996):

$$K'_1 \approx \frac{K'_{H_2CO_3}}{K'_{CO_2(aq)}} . \qquad\qquad \text{(IV-13)}$$

Since it is the value $K_1^{'}$ that is measured by laboratory experiments, analytical measurements and theoretical equilibrium descriptions are consistent.

At equilibrium the gaseous CO_2 in the atmosphere, expressed in terms of the fugacity, $f_{CO_2}^{a}$ (in atmospheres, atm), is related to the aqueous CO_2 in seawater, $[CO_2]$ (mol kg^{-1}), via the Henry's Law coefficient, K_H (mol kg^{-1} atm^{-1}; see Chapter III):

$$K_{H,CO2} = \frac{[CO_2]}{f_{CO_2}^{a}}$$ (IV-14)

The partial pressure and fugacity are equal only when gases behave ideally; however, Weiss (1974) has shown that the ratio of $f_{CO_2}^{a}$, to its partial pressure, pCO$_2$, is between 0.995 and 0.997 for the temperature range of 0-30 C, indicating that the differences are not large. The term pCO$_2$ is often used in the literature because of the small non-ideal behavior of CO_2 gas in the atmosphere.

The content of CO_2 in surface waters is often presented as the fugacity (or partial pressure) in solution, $f_{CO_2}^{w}$. An example of this application is that the difference in the fugacities of CO_2 between the atmosphere and the ocean ($f_{CO_2}^{a}$ - $f_{CO_2}^{w}$) are often used in gas exchange rate calculations (Chapter X). The fugacity of CO_2 in water is calculated using Eq. IV-14.

With the above equilibria we are now prepared to define the total concentration of dissolved inorganic carbon and construct a diagram of the variation of the carbonate species concentrations as a function of pH. For simplicity we begin by assuming there is no atmosphere overlying the water, so Eq. IV-14 is not necessary to describe the chemical equilibria in this example. The total concentration, C_T, for inorganic carbon in seawater is called dissolved inorganic carbon (DIC) or total CO_2 (ΣCO_2). As the first term is more descriptive, we will adopt it here. The DIC of a seawater sample is the sum of the concentrations of the dissolved inorganic carbon species:

$$DIC = [HCO_3^-] + [CO_3^{2-}] + [CO_2] \ .$$ (IV-15)

Since this is a total quantity, it has the advantage that it is independent of temperature and pressure unlike the concentrations of its constituent species. Experimentally DIC is determined by acidifying the sample, so that all the HCO_3^- and CO_3^{2-} react with H$^+$ to become CO_2 and H$_2$O, and then measuring the amount of evolved CO_2 gas. To create a plot of the concentrations

of the three dissolved carbonate species as a function of pH we assign the DIC its average value in seawater (Table IV-1). Combining Eq. IV-15 with Eqs. IV-9 and IV-11 yields separate equations for the carbonate species as a function of equilibrium constants, DIC and pH

$$[CO_2] = \frac{DIC}{1 + \dfrac{K_1'}{[H^+]} + \dfrac{K_1'K_2'}{[H^+]^2}}$$

(IV-16)

$$[HCO_3^-] = \frac{DIC}{\dfrac{[H^+]}{K_1'} + 1 + \dfrac{K_2'}{[H^+]}}$$

(IV-17)

$$[CO_3^{2-}] = \frac{DIC}{1 + \dfrac{[H^+]^2}{K_1'K_2'} + \dfrac{[H^+]}{K_2'}} .$$

(IV-18)

The plot in Fig. IV-2 demonstrates the relative importance of the three carbonate species in seawater as a function of pH. At $pH = pK_1'$ the concentrations of CO_2 and HCO_3^- are equal and at $pH = pK_2'$ the concentrations of HCO_3^- and CO_3^{2-} are equal. Since we know that the pH of surface waters is about 8.2, it is clear that the dominant carbonate species is HCO_3^-. What has been done so far, however, does not yet explain why the pH of seawater is between 7.6 and 8.2, and we will return to this question.

Boric Acid. The acid/base pair with the second highest concentration in seawater is boric acid which has a pK' near the pH of seawater (Table IV-1). The carbonate system and boric acid turn out to be by far the most important contributors to the acid/base chemistry of seawater. They contrast greatly in their reactivity in the ocean since carbon is involved in all metabolic processes and varies in concentration from place to place, while borate is conservative and maintains a constant ratio to salinity. The equilibrium reaction and total boron, B_T, equations are:

$$B(OH)_3 + H_2O \;\rightleftharpoons\; B(OH)_4^- + H^+ \qquad K_B' = \frac{[B(OH)_4^-][H^+]}{[B(OH)_3]}$$

(IV-19)

$$B_T = B(OH)_3 + B(OH)_4^-$$

(IV-20)

The equations for the boron species as a function of pH and K_B' are thus

$$[B(OH)_3] = \frac{B_T \times [H^+]}{[H^+] + K'_B} \qquad\qquad (IV\text{-}21)$$

$$[B(OH)_4^-] = \frac{B_T \times K'_B}{[H^+] + K'_B} \quad . \qquad\qquad (IV\text{-}22)$$

From the graph of these two equations shown in Fig. IV-2, it is clear why boric acid plays a role as a pH buffer in seawater. The two species that exchange hydrogen ions are nearly equal at a pH between 8 and 9. One does not need a graph to determine this since the two species that exchange hydrogen ions are equal when the pK' = pH, which in this case is pH = 8.6 (Table IV-1).

It is now clear that the most important criteria for describing the role of an acid/base pair in determining the pH of seawater is the total concentration, C_T, and the apparent equilibrium constants. For example, hydrochloric acid, HCl, and sulfuric acid, H_2SO_4, are well known acids because we use them frequently in the laboratory. We know, also, that Cl^- and SO_4^{2-} ions are the two most concentrated anions in seawater. Why, then, are these acid/base pairs not considered in our discussion? The answer is because of their extremely low pK' values; e.g., $pK_{HSO4}{}' = 1.0$ (Table IV-1). The pH where the HSO_4^- and SO_4^{2-} ions are at equal concentration is so low that SO_4^2 ion may be considered totally unprotonated at the pH of seawater.

The rest of the acids in seawater with pK' values in the vicinity of 8 to 9, silicic acid and phosphoric acid, have low and variable concentrations (1-200 μmol kg^{-1}), but they must be considered to have a complete representation of the acid/base components of seawater. The acid-base plot of Figure IV-2 includes only the first four equations in Table IV-1, which are the most important acids in seawater. With this figure one can determine which species are most involved in the exchange of protons in seawater. Any constituent for which the lines are curved in the pH range 7 – 9 contributes to the seawater buffer system. Before we can answer the question of why the sea has a pH of between 7.6 and 8.2, we must deal with an extremely important but somewhat troublesome constituent of the carbonate system; the modern concept the alkalinity of seawater.

IV-A.2. THE ALKALINITY OF SEAWATER

Just as the charge balance had to be identified in order to determine the pH at equilibrium on the simple acid/base plot in Fig. V-1 so must the charge balance be evaluated to determine the pH at equilibrium on the acid/base plot for seawater (Fig. IV-2). Presently, the system of equations includes the equilibria and total concentration (Eqs. IV-9, IV-11 and IV-15 for the carbonate species; Eqs. IV-21 and IV-22 for borate, and so on for the minor players in oxic seawater S, F, P, and Si) which describe the predominant acid/base species over the entire pH range. There are as yet insufficient constraints to evaluate the equilibrium position on the plot in Fig. IV-2. One is free to move left and right on the pH scale. For example, in the case of the carbonate system there are five unknowns (DIC, [HCO_3^-], [CO_3^{2-}], [CO_2] and pH) and only three equations. If the concentration of DIC is designated, we are still one equation shy of being able to solve the system of equations uniquely and exactly define the pH. The missing equation is the expression for total alkalinity, A_T, which represents the charge balance of the mixed electrolyte system of seawater. The practical advantage for this new constraint is that it is measurable, and it is a total quantity like DIC, which is independent of temperature and pressure.

The alkalinity in a mixed electrolyte solution is the excess in bases (proton acceptors) over acids (proton donors) in the solution. The alkalinity is measured by adding acid to seawater to an end point where most all proton acceptors have reacted. When one adds acid the hydrogen ion concentration does not increase as much as it would in the absence of alkalinity because some of the added hydrogen ions react with the excess bases (CO_3^{2-} , HCO_3^- , $B(OH)_4^-$, …). Since it is possible to precisely determine the hydrogen ion concentration change in solution, the difference between the amount of H^+ added and the measured change can be accurately determined by titration. The units of alkalinity are equivalents per kilogram (eq kg^{-1}). This value is the molar "equivalent" to the charge of the hydrogen ion (Chapter I).

One way of defining the alkalinity is by separating the anions that exchange protons during the titration from those that do not. For neutrality the alkalinity must equal the difference in charge between cations and anions that do *not* exchange protons to any significant extent during the titration. One can calculate the alkalinity of standard seawater using the concentrations of conservative ions at a salinity of 35 ‰ presented in Table I-4 and Table IV-2. SO_4^{2-} and F^- ions are included among the species that do not exchange protons because their

reaction with H^+ is so small during the titration that they are conservative to the five decimal places presented in the table. By this definition, the numerical value for Total Alkalinity, A_T, is equal to

A_T = Cation charge – Anion charge = 0.60567 – 0.60325 (eq kg^{-1}) = 0.00242 (eq kg^{-1}).

Acids and bases that make up the total alkalinity must protonate in solution in a way that achieves charge balance. For example, the difference in equivalents evaluated in Table IV-2 determines the relative abundances of $[HCO_3^-]$ and $[CO_3^{2-}]$ that are required for charge balance. As the difference between A_T and DIC increases (becomes a larger positive number) there must be a higher carbonate concentration to achieve charge balance because CO_3^{2-} carries two equivalents and HCO_3^- only one.

The concentrations of the species that make up the charge difference evaluated in Table IV-2 are bases that react with H^+ at pH = 8.2 in Fig. IV-2. The concentrations of the species that make up the bulk of the alkalinity in surface seawater are presented in Table IV-3. Values in this table are for surface seawater which is low in nutrient concentrations. In regions of the ocean where silicate and phosphate concentrations are measurable they must also be included in the definition of total alkalinity

$$A_T = [HCO_3^-] + 2 \cdot [CO_3^{2-}] + [B(OH)_4^-] + [H_3SiO_4^-] + [HPO_4^{2-}] + 2 \cdot [PO_4^{3-}] + [OH^-] . \text{(IV-23)}$$

Notice that the coefficients on the concentrations on the right hand side of Eq. IV-23 are equal to the charge of the ions except in the cases of HPO_4^{2-} and PO_4^{3-}. The reason for this is that the precise definition of the alkalinity of seawater is based on the method by which it is determined and the species that exchange protons during the titration.

As stated previously the alkalinity is determined by adding acid to the seawater solution and measuring the pH during the process. The equivalence point, the pH at which the amount of acid equals the alkalinity of the solution is accurately defined so it is possible to state precisely which base species will except protons in this range. Dickson (1981) describes the alkalinity as, "The number of moles of hydrogen ion equivalent to the excess of proton acceptors (bases formed from weak acids with a dissociation constant $K \leq 10^{-4.5}$ at 25 C and zero ionic strength) over the proton donors (acids with $K > 10^{-4.5}$) in one kilogram of sample."

Proton acceptors with $K \leq 10^{-4.5}$ ($pK \geq 4.5$) in Table IV-1 include HCO_3^-, CO_3^{2-}, $B(OH)_4^-$, OH^-, $H_3SiO_4^-$, HPO_4^{2-}, and PO_4^{3-}, but not $H_2PO_4^-$, which means that HPO_4^{2-}, and PO_4^{3-} will be titrated to $H_2PO_4^-$, but not to H_3PO_4. This is the reason that the stoichiometric coefficients of the phosphate species in Eq. IV-23 are one less than the charge. To complete the precise definition of alkalinity we subtract H^+ and the acids in Table V-1 with $K > 10^{-4.5}$, HSO_4^-, HF and H_3PO_4

$$A_T = \left[HCO_3^-\right] + 2 \cdot \left[CO_3^{2-}\right] + \left[B(OH)_4^-\right] + \left[H_3SiO_4^-\right] + \left[HPO_4^{2-}\right] + 2 \cdot \left[PO_4^{3-}\right]$$
$$+ \left[OH^-\right] - \left[H^+\right] - \left[HSO_4^-\right] - \left[HF\right] - \left[H_3PO_4\right] \qquad \text{(IV-24)}$$

This rather long expression includes all known inorganic proton acceptors and donors in oxic seawater that follow Dickson's definition of the titration alkalinity. It includes two uncharged species at the very end, so it is not exactly consistent with the previous charge balance definition; however, in practice, the acidic species concentrations in seawater (H^+, HSO_4^-, HF, and H_3PO_4) are too low in the pH range of 7.0-8.0 to be significant and are not frequently not included in the alkalinity definition. Including them here demonstrates the fate of protons during the course of acid addition to determine total alkalinity. (These species also play a more important role in more dilute environmental solutions like rain water and in many freshwater lakes.) The concentrations in Table IV-3 indicate that the ions of carbonate and borate define about 99 % of the total alkalinity. Thus, calculations are sometimes made which include only these two species, and we define this as the carbonate and borate alkalinity, $A_{C\&B}$,

$$A_{C\&B} = \left[HCO_3^-\right] + 2 \cdot \left[CO_3^{2-}\right] + \left[B(OH)_4^-\right]. \qquad \text{(IV-25)}$$

Another shortened from of the alkalinity consists only of the carbonate species which make up about 96 % of the total alkalinity and is termed the carbonate Alkalinity, A_C,

$$A_C = \left[HCO_3^-\right] + 2 \cdot \left[CO_3^{2-}\right]. \qquad \text{(IV-26)}$$

This definition is sometimes used for illustration purposes because of the simplicity of the calculations involved.

In anoxic waters a whole new set of acids are created by the lower redox conditions. The most prevalent are the different forms of sulfide and ammonia (Table IV-1). Clearly, these species meet the criteria to be included in the titration alkalinity and their concentrations can become as high as hundreds of $\mu mol\ kg^{-1}$ in some highly reducing environments. For normal

situations in which the water contains oxygen these species are too low in concentration to be considered.

IV-B. CARBONATE EQUILIBRIA: CALCULATING THE pH OF SEAWATER

We have now described the system of equations necessary for determining the pH of seawater and the distribution of carbonate species. By including the definition and numerical value of the alkalinity to the system of equations used to determine the curves in Fig. IV-2, we have constrained the location on the plot to a single pH. The equations necessary to determine this location are summarized in Appendix IV-1 for the progressively more complicated definitions using the three forms of the alkalinity, A_C, $A_{C\&B}$, and A_T.

In order to solve the equations and determine pH and the concentrations of the species that make up the alkalinity, the apparent equilibrium constants, K' must be accurately known. These constants have been evaluated and reevaluated in seawater over the past 50 y. The pH scales and methods of measuring pH during these experiments have been different which has complicated comparisons of the data until recently when many have been converted to a common scale. Equations for the best fit to carbonate system equilibrium constants as a function of temperature and salinity are presented by Leuker et al. (2000), DOE (1994) and Millero (1995) (see Appendix IV-2.)

The pH and carbonate species distribution for waters from different locations in the ocean (Table IV-4) are calculated using data for A_T and DIC and the equilibrium constants. The equilibrium equations were solved with the computer program of Lewis and Wallace (1998) using the carbonate equilibrium constants K'_1 and K'_2 of Mehrbach et al. (1973) as redetermined by Dickson and Millero (1987). This program allows one to calculate the carbonate species at equilibrium from any two of the species measured using the complete description of the alkalinity, A_T, including the contributions from silicate and phosphate. The results are presented in columns labeled 'I' of Table IV-4. We have also solved a simplified version of the equilibrium equations using the approximation that the total alkalinity includes only the carbonate and borate alkalinity, $A_{C\&B}$. Carbonate species determined by this approach are presented in columns labeled 'II' of Table IV-4, and the program is listed in Appendix IV-1(B). Ideally, the solutions using these two methods would be identical in surface waters because concentrations of Si and P are below detection limits. They are slightly different (compare

columns I and II) because of the different values used for $K_1^{'}$ and $K_2^{'}$ in the different computer programs. The values presented by Leuker et al. (2000) and presented in Appendix IV-2 are recommended for surface water calculations (see later).

Both DIC and A_T increase from surface waters to the Deep Atlantic, Antarctic and Pacific Oceans as one follows the route of the ocean "conveyor belt" (Fig. I-12). Along this transect pH changes from about 8.2 in surface waters to 7.8 in the deep Pacific Ocean and CO_3^{2-} decreases from nearly 250 μeq kg^{-1} to less than a third of this value, 75 μeq kg^{-1}. The reason for this change has to do with the ratio of the change in A_T and DIC in the waters and is discussed in the final section of this chapter. Notice that the contribution of the nutrients Si plus P to the total alkalinity is only between 0-5 μeq kg^{-1} or at most 0.2 % of the total alkalinity. Although Si concentrations are much greater than those of P, the two nutrients have nearly equal contributions to the alkalinity (Table IV-4) because the pK's for two phosphate reactions are closer to the pH of seawater than is the pK for silicate (see Table IV-1).

The present high level of analytical accuracy makes the choice of appropriate equilibrium constants to use for the carbonate system an important consideration. The most rigorous test of how well the carbonate equilibrium in seawater is known is to calculate a third parameter from two known values and compare the calculated value with an independent measurement of that parameter. Millero (1995) compared the estimated accuracy of measured and calculated values of carbonate system parameters and his results are summarized in Table IV-5. In addition to the error associated with the accuracy of the analytical measurements, there are two estimates of calculation errors listed in the table. The first row (I) is the error to be expected from compounding the errors of the analytical measurements used to calculate the parameter assuming the equilibrium constants are perfectly known. The second row (II) is the error determined from compounding the errors of the equilibrium constants, which Millero estimates to be accurate to within $\pm$ 0.002 for $pK_1^{'}$ and $\pm$ 0.005 for $pK_2^{'}$. This analysis assumes that there are no systematic offsets in the estimation of $K_1^{'}$ and $K_2^{'}$ other than this scatter about the mean. There are two clear messages from Table IV-5. The first is that the contributions of the analytical uncertainty and the errors in the equilibrium constants to the uncertainty in calculated parameters are nearly equal. The second is that one can measure and calculate the individual parameters about equally well if you can choose the correct measured values.

While the accuracies of all the parameters are impressive (approaching 0.1 % in the cases of DIC and A_T), ones ability to calculate carbonate system concentrations varies depending on which species are measured. For example $f_{CO_2}^w$ and pH are presently the most readily determined, continuous measurements of the carbonate system by unmanned moorings and drifters. This is good for gas exchange purposes because it will become less expensive to derive large data bases of surface ocean $f_{CO_2}^w$, but very poor for defining the rest of the carbonate system using remote measurements because of the large errors in calculating A_T and DIC from this analytical pair (Table IV-5). The error analysis in Table IV-5, also, is not the whole story, because it does not address the possibility of systematic errors in the equilibrium constants. This has been assessed recently by comparing the $f_{CO_2}^w$ measured in seawater solutions at equilibrium with standard gases with $f_{CO_2}^w$ calculated from A_T and DIC (Lueker et al., 2000). They found that the constants of Mehrbach et al. (1973), reinterpreted to the "total" pH scale (Appendix IV-2), were most accurate if the $f_{CO_2}^w$ was less than 500 µatm kg^{-1}. $f_{CO_2}^w$ calculated from A_T and DIC, with accuracies of 1 µmol kg^{-1} and 2 µeq kg^{-1}, respectively (about 0.05 and 0.1 %), agreed with measured $f_{CO_2}^w$ values to within ± 3 µatm. However, the ability to distinguish the correct equilibrium constants by comparing measured and calculated values deteriorated as the $f_{CO_2}^w$ increased above 500 µatm kg^{-1}.

At the time of writing this book we are in the situation where it has been demonstrated that there is one set of preferred constants for calculating surface water $f_{CO_2}^w$ from A_T and DIC, but these values are not necessarily preferred for deeper waters where $f_{CO_2}^w$ exceeds 500 µatm. The best agreement is in the most important region from the point of view of air-sea interactions and errors deeper in the ocean are not very large. The reason for the variability may be that there are unknown organic acids and bases in the dissolved organic matter of seawater that alter the acid-base behavior, but this has not been experimentally demonstrated. While great advances in our understanding of the carbonate system have occurred relatively recently, it is also true that a version of the carbonate equilibrium constants determined more than 30 years ago (Mehrbach et al. (1973) are still preferred.

IV-C. KINETICS OF CO_2 REACTIONS IN SEAWATER

  While most of the reactions between carbonate species in seawater are nearly instantaneous, the hydration of CO_2

$$CO_2 + H_2O \; \underset{\longleftarrow}{\longrightarrow} \; H_2CO_3 \tag{IV-27}$$

is relatively slow, taking tens of seconds to minutes at the pH of most natural waters. This slow reaction rate has consequences for understanding the processes of carbon dioxide exchange with the atmosphere and the uptake of CO_2 by surface water algae. The rate equation for CO_2 reaction has four terms (eq. (b) of Table IX-2)

$$\frac{d[CO_2]}{dt} = (k_{CO_2} + k_{OH^-}[OH^-]) \cdot [CO_2] + (k_{CO_2,r}[H^+] + k_{HCO_3}) \cdot [HCO_3^-]. \tag{IV-28}$$

 The mechanisms for this reaction are discussed in the Chapter on Kinetics (Chapter IX). It is a combination of first and second order reactions, which is not solvable analytically because of the nonlinear terms following the rate constants k_{OH^-} and $k_{CO_2,r}$. The rate constants were determined in the laboratory by choosing the experimental conditions in which one of the two mechanisms predominated. pHs of natural waters, however, often fall in the range (8-10) in which both the reaction with water and OH^- can be important. To determine the lifetime of CO_2 as a function of pH one must derive the solution to the reaction rate equation. This is facilitated by employing the DIC and carbonate alkalinity, A_C, (Eqs. IV-15 and IV-26) to eliminate the concentration of bicarbonate [HCO_3^-], in the CO_2 reaction rate equation. This substitution results in an expression

$$\frac{d[CO_2]}{dt} = -A[CO_2] + B \tag{IV-29}$$

where

$$A = -\left(k_{CO_2} + k_{OH^-}[OH^-]\right) + 2 \cdot k_{CO_2,r} \cdot \frac{K_W}{[OH^+]} + 2 \cdot k_{HCO_3^-}$$

$$B = \left(2 \times DIC - A_C\right) \cdot k_{CO_2,r} \cdot \frac{K_W}{[OH^+]} + k_{HCO_3^-}. \tag{IV-30}$$

that has an analytical solution if we assume that not only A_C, and DIC, but also pH is constant

$$[CO_2](t) = [CO_2]^0 - \frac{B}{A} \exp(-A \times t) + \frac{B}{A} \, . \tag{IV-31}$$

This is an approximation because the OH^- concentration does change during the reaction, but since the change is not very great, the equation is adequate to illustrate the importance of the two reaction mechanisms. Eq. IV-31 is the solution for a reversible reaction that begins with an initial concentration of $[CO_2]^0$ and progresses toward an equilibrium value of $[CO_2]^0 + B/A$. The value represented in A is the reciprocal of the residence time of CO_2 with respect to chemical reaction and incorporates both mechanisms of reaction.
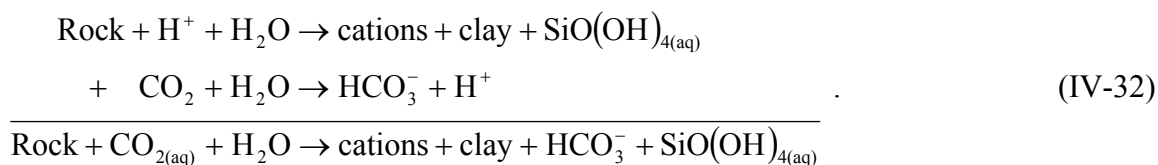
      To evaluate the importance of the two mechanisms, one has to know the reaction rate constants. These values have been determined as a function of temperature and salinity by Johnson (1982). Values in Table IV-6 are calculated from the best-fit equations for his experiments. After a small correction to the data noted by Emerson (1998) the values in Table IV-6 are consistent with those presented in Zeebe and Wolf-Gladrow (2000). The residence time of CO_2 in seawater, calculated from eq. IV-31 and the rate constants in Table IV-6, is presented in Fig. IV-3 (for seawater at 25 C). The reaction of CO_2 with water dominates in the lower pH range, <8.0, and the direct combination with hydroxyl ion is most important at pH >10. Between $8 < pH < 10$ both reaction mechanisms are operative.

      The most important applications of these rate equations are in calculating the flux of CO_2 across the air-water interface and across the diffusive boundary layer surrounding phytoplankton. In these cases the residence times with respect to CO_2 transport (across a diffusive boundary layer) are similar to the reaction residence times. If there is enough time for reaction, a gradient in HCO_3^- is created across the boundary layer which enhances the carbon transport over that which would be expected from a linear gradient of CO_2 across the layer. In practice, it is not possible to determine the structure of the concentration gradients across the layer so they must be calculated. We discuss this problem as it applies to CO_2 exchange across the air-water interface in Chapter X. The excellent book by Zeebe and Wolf-Gladrow (2000) describes the application of the CO_2 reaction and diffusion kinetics to problems of plankton growth.

IV-D. PROCESSES THAT CONTROL THE ALKALINITY AND DIC OF SEAWATER

IV-D.1. GLOBAL OCEAN, ATMOSPHERE, AND TERRESTRIAL PROCESSES

On the global spatial scales and over time periods comparable to, and longer than, the residence time of bicarbonate in the sea (~100 ky), the alkalinity and DIC of seawater are controlled by the species composition of rivers, which are determined by weathering. The imbalance of non-protonating cations and anions in seawater is caused by the reactions of rocks with atmospheric CO_2 that are described in Chapter II. In the generalized weathering reaction, hydrogen ion reacts with rocks and when this reaction is combined with the hydration reaction for CO_2 (Eq. IV-4) bicarbonate is formed

$$\text{Rock} + H^+ + H_2O \rightarrow \text{cations} + \text{clay} + SiO(OH)_{4(aq)}$$
$$\underline{+ \quad CO_2 + H_2O \rightarrow HCO_3^- + H^+}$$
$$\text{Rock} + CO_{2(aq)} + H_2O \rightarrow \text{cations} + \text{clay} + HCO_3^- + SiO(OH)_{4(aq)}$$

(IV-32)

Bicarbonate is the main anion in river water because of the reaction of CO_2-rich soil water with both calcium carbonate and silicate rocks (see Chapter II). Thus, neutralization of acid in reactions with more basic rocks during weathering creates cations that are balanced by anions of carbonic acid. In this sense the composition of rocks and the atmosphere determine the overall alkalinity of the ocean.

Seawater has nearly equal amounts of alkalinity and DIC because the main source of these properties is riverine bicarbonate ion, which makes equal contributions to both constituents. The processes of $CaCO_3$ precipitation, hydrothermal circulation, and reverse weathering in sediments remove alkalinity and DIC from seawater and maintain present concentrations at about 2 mmol (meq) kg^{-1}. Reconciling the balance between river inflow and alkalinity removal from the ocean is not well understood, and is discussed in much greater detail in Chapter II.

IV-D.2. ALKALINITY CHANGES WITHIN THE OCEAN

On time-scales of oceanic circulation (1,000 y and less) the internal distribution of carbonate system parameters, is modified primarily by biological processes. Cross sections of the distribution of A_T and DIC in the world's oceans (Fig. IV-4) and scatter plots of the data for

these quantities as a function of depth in the different ocean basins (Fig. IV-5) indicate that the concentrations increase in Deep Waters (1-4 km) from the North Atlantic to the Antarctic and into the Indian and Pacific oceans following the "conveyer belt" circulation (Fig. I-12). Degradation of organic matter (OM) and dissolution of $CaCO_3$ cause these increases in the deep waters. The chemical character of the particulate material that degrades and dissolves determines the ratio of A_T to DIC.

The stoichiometry of the phosphorous, nitrogen, and carbon in OM that degrades in the ocean (see Table I-5 and Chapter VI) is about

$$P:N:C = 1:16:106 .$$ (IV-33)

Organic carbon degradation and oxidation creates CO_2 which is dissolved in seawater. This increases DIC but does not change the alkalinity of the water. Alkalinity is a measure of charged species and since there is no charge associated with CO_2, its release to solution does not alter the alkalinity. The case for the nitrogen component in organic matter is not so simple because ammonia in OM is oxidized to dissolved NO_3^- during oxic degradation. This is a redox reaction, that involves the transfer of hydrogen ions into solution, and therefore results in an alkalinity change:

$$NH_3(OM) + 2O_2 \; \underset{\longleftarrow}{\longrightarrow} \; NO_3^- + H^+ + H_2O .$$ (IV-34)
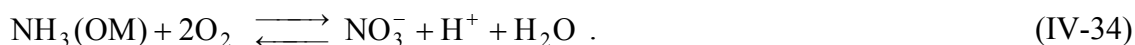
Since a proton is released into solution during this reaction the alkalinity decreases (see Eq. IV-24). Thus, when a mole of organic carbon as OM is degraded it causes the DIC to increase by one mole and the alkalinity to decrease by $16/106 = 0.15$ eq,

$$\Delta DIC_{OM} = 1; \; \Delta A_T = -0.15 .$$ IV-(35)

The change in DIC and A_T of the solution during $CaCO_3$ dissolution is very different from that resulting from organic matter degradation and oxidation. One mole of calcium carbonate dissolution

$$CaCO_3(s) + H_2O \; \underset{\longleftarrow}{\longrightarrow} \; Ca^{2+} + CO_3^{2-}$$ (IV-36)
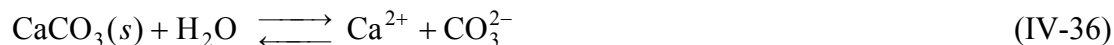
causes an increase in alkalinity that is twice that of DIC because CO_3^{2-} introduces two charge equivalents for each mole of carbon change in solution. Thus:

$$\Delta DIC_{CO_3^{2-}} = 1; \;\; \Delta A_{T,CO_3^{2-}} = 2.0 .$$ IV-(37)

It is thus pretty clear that the change in alkalinity and DIC in seawater during degradation and dissolution of algae created in the surface ocean during photosynthesis depends greatly on the chemical character of that particulate material. The ecology in the ocean euphotic zone greatly influences the chemical changes observed in the sea.

Fig. IV-6 is a plot of the salinity-normalized alkalinity, $A_{T,N}$, versus salinity-normalized dissolved inorganic carbon, DIC_N, for the ocean between Atlantic surface water and the deep North Atlantic (100 – 2000 m) and then along the Deep Water conveyor belt circulation between 2-4 km. The lines in the figure illustrate that the $DIC_N : A_{T,N}$ ratios during the "aging" of subsurface seawater are not constant throughout the ocean. Between the surface Atlantic and the base of the thermocline the change in $DIC_N : A_{T,N}$ is about 10:1 whereas in the depth range of 2 – 4 km., from the deep N. Atlantic to deep Indian and Pacific Oceans, the ratio is between 1:1 and 2:1. The difference is due to the high OM : $CaCO_3$ ratio in particles that exit the euphotic zone and more rapid degradation of organic matter than dissolution of $CaCO_3$ as particles fall through the water. More organic matter degrades than $CaCO_3$ dissolves in the upper portion of the ocean. In the deeper waters the $DIC_N : A_{T,N}$ ratio is close to that expected for the addition of HCO_3^- to the water ($DIC : A_T = 1:1$) except in the Antarctic where the trend is relatively richer in DIC (the dashed line in Figure IV-6). Mineral secreting plankton in the Southern Ocean are dominated by diatoms which form opal rather than $CaCO_3$ shells. Thus, particle dissolution at depth in this part of the ocean releases DIC and H_4SIO_4 to the water but little alkalinity. The general 1:1 increase in DIC_N and $A_{T,N}$ in ocean deep waters is probably strongly influenced by reactions at the sediment-water interface (see Chapter VI and Jahnke and Jackson, 1987). In carbonate-rich sediments a large percentage of the CO_2 produced by organic matter degradation reacts with $CaCO_3$ to produce HCO_3^-, which translates to an equal increase in DIC and A_T in solution.

The relationship between the relative changes of DIC and A_T in seawater and the OM degradation to $CaCO_3$ dissolution ratio in particulate matter is illustrated in Table IV-7. The DIC : A_T ratio to be expected is calculated assuming one part $CaCO_3$ dissolution and progressively greater parts of O.M. degradation using the stoichiometry in Eqs. IV-35 and IV-37. Solid phase OM : $CaCO_3$ ratios necessary to create the observed $\Delta DIC : \Delta A_T$ ratios vary from about 8:1 for the transition from the upper ocean through the thermocline in the North Atlantic to about 2:1 in the deeper waters of the world's ocean. The higher values are less than the ratio exiting the

upper ocean (Sarmiento et al., 2002, determine an export flux of DIC : $A_T \sim 15$.) presumably because much of the organic matter is respired in the top few hundred meters below the euphotic zone and the data along the 10:1 line in Fig. IV-6 are from a much greater depth range (100 – 2000m). The deeper values are less than the ratio of 4:1 that derives from box models (Broecker and Peng, 1982) where the entire deep ocean is a weighted average of the data presented in Figure IV-6.

It was demonstrated in Table IV-4 how the DIC and A_T changes observed in deep waters alter the carbonate system constituents. One can predict the relative change in carbonate ion concentration resulting from solubilization of particulate matter with an OM : $CaCO_3$ molar ratio of between 10 and 1.5 by focusing on the changes in alkalinity and DIC. We use carbonate alkalinity, A_C in this calculation for simplicity. In all cases of Table IV-7 the composite change of DIC is greater than that for A_C . Subtracting the equation for DIC from that for carbonate alkalinity gives:

$$
\begin{aligned}
A_C - DIC &= \left(\left[HCO_3^- \right] + 2 \cdot \left[CO_3^{2-} \right] \right) - \left(\left[HCO_3^- \right] + \left[CO_3^{2-} \right] + \left[CO_2 \right] \right) \\
&= \left[CO_3^{2-} \right] - \left[CO_2 \right] \\
&\cong \left[CO_3^{2-} \right]
\end{aligned}
\qquad \text{(IV-38)}
$$

(Note that the approximation in the last step is only accurate in ocean waters with pH equal to or greater than 8.0. This is seen in Table IV-4 where CO_3^{2-} and CO_2 concentrations are evaluated in different water masses.) The above approximation indicates that addition of more DIC than A_C to the water results in a decrease in carbonate ion concentration ($\Delta A_C - \Delta DIC = \Delta CO_3^{2-}$). Essentially more acid, in the form of CO_2 than base in the form of CO_3^{2-} is added to the water during the solubilization of particulate matter. These trends are born out in Table IV-4 where the actual carbonate species changes are calculated using the complete carbonate equilibrium equations.

In the above discussion of the response of the carbonate system to changes caused by OM degradation (addition of CO_2) or $CaCO_3$ dissolution (addition of CO_3^{2-}) we relied almost exclusively on changes in the total quantities DIC and A_T (or A_C) to gain insight into how the system responds. The reason for this is that it is possible to predict exactly how the total quantities will change due to organic carbon degradation or $CaCO_3$ dissolution whereas it is not clear how the equilibria will react without solving the entire set of equations (Fig. IV-2).

As an example, let's start with surface seawater and add 20 μmol kg^{-1} of CO_2 only. DIC in the solution increases by 20 μmol kg^{-1} but A_C does not change, which is roughly analogous to organic matter degradation with no $CaCO_3$ dissolution. We will approximate the change in CO_3^{2-} and HCO_3^- and then see how correct this turns out to be. From the carbonate equilibrium program we find that the distribution of carbonate species is as given in Table IV-8 (a) for A_T = 2300 μeq kg^{-1} and DIC = 2188 μmol kg^{-1} at 25 C and S=35. To predict the change in HCO_3^- and CO_3^{2-} in response to the addition of CO_2 we could take two different routes. First, by the laws of mass action we would predict from the CO_2 hydration equation that bicarbonate would be formed

$$CO_{2(aq)} + H_2O \;\xrightleftharpoons{}\; HCO_3^- + H^+ . \tag{IV-11}$$

However, there is no way to know how much this would affect the CO_3^{2-} concentration formed by the second carbonate dissociation reaction

$$HCO_3^- \;\xrightleftharpoons{}\; CO_3^{2-} + H^+ . \tag{IV-9}$$

We are stuck unless we do the entire equilibrium/mass balance calculation or refer to Fig. IV-2 to find the answer. The lines in the figure indicate that as CO_2 increases CO_3^{2-} decreases, but we get very little information about the fate of HCO_3^-.

The other route is to think in terms of mass and charge balance. By subtracting the change in dissolved organic matter, ΔDIC from the change in carbonate alkalinity, ΔA_C, and realizing that CO_2 is a very small component of DIC and can be neglected in the DIC formula (Again, this is true for surface waters but not for those in the deep ocean.), the CO_3^{2-} concentration must decrease by about 20 μmol kg^{-1} (Eq. IV-37)

$$\Delta A_C - \Delta DIC = \Delta\left[CO_3^{2-}\right] - \Delta\left[CO_2\right] \cong \Delta\left[CO_3^{2-}\right] \cong -20 \;\mu mol\; kg^{-1} .$$

Since the only carbonate species added was CO_2, it is reasonable to assume A_C cannot have changed much (We are going to check this below.). Thus, any change in CO_3^{2-} will require an opposite change in HCO_3^- of twice the magnitude to maintain a neutral solution. The only way both of these can happen is if HCO_3^- grows by 40 μmol kg^{-1} as CO_3^{2-} decreases by 20 μmol kg^{-1} (Table IV-8(a)).

Calculated changes in HCO_3^- and CO_3^{2-} after the addition of 20 μmol kg^{-1} of CO_2 using the carbonate equilibrium equations with the assumption that A_C remains constant are presented in line 2b of Table IV-8. We see that the mass balance calculation is approximately correct (Compare the changes under (2a) and (2b) of Table IV-8.) Taking the final step towards reality by stipulating that it is carbonate + borate alkalinity that does not change rather than the carbonate alkalinity ($\Delta A_{C\&B}$=0, 2c in Table IV-8) reveals that the bicarbonate and carbonate changes are somewhat smaller than predicted by the simple calculation represented by Equation IV-37. The reason for the differences between the changes in 2b and 2c is that addition of the acid CO_2 caused the borate equilibrium in Eq. IV-19 to shift to the left decreasing the borate concentration, which required an increase in carbonate alkalinity, A_C, for $A_{C\&B}$ to remain constant. The bottom line is that the approximation in Eq. IV-37 overestimates the HCO_3^- and CO_3^{2-} changes by ~25 and 50 %, respectively.

We can try this again by estimating the HCO_3^- and CO_3^{2-} changes from the addition of 20 μmol kg^{-1} of $CaCO_3^{2-}$ to the same surface water (Table IV-8(3)). In this case the carbonate alkalinity increases by 40 μeq kg^{-1} and the DIC by 20 μmol kg^{-1}. Using the approximation in Eq. IV-37, leads to a change in CO_3^{2-} of + 20 μmol kg^{-1} ($\Delta A_C - \Delta DIC = \Delta CO_3^{2+} = +20$ μmol kg^{-1} = 40 μeq kg^{-1}). Since the change in A_C is 40 μ eq kg^{-1} there can be virtually no change in HCO_3^-. We see that removing the successive approximations in Table IV-8 (3b and c) reveals errors that are of the same magnitude as when we did this for the CO_2 addition in section (2) of the table.

Generally, when estimating the changes to be expected in the carbonate system by organic matter degradation, $CaCO_3$ dissolution or exchange with the atmosphere, it is much safer to deal with changes in the total properties A_C and DIC rather than trying to guess the response of the carbonate equilibrium equations. One can predict precisely how the total quantities change, and then it is possible to show the change in direction and approximate concentration of

both CO_3^{2-} and HCO_3^-. Absolute values of the carbonate species change, however, must wait till you consult the simultaneous solution of the carbonate equilibrium equations.

REFERENCES

Broecker, W. S. and T.-H. Peng (1982) *Tracers in the Sea,* ELDIGIO Press, Palisades, N.Y., 690 p.

Dickson A. G. (1981) An exact definition of total alkalinity and a procedure for estimation of alkalinity and total inorganic carbon from titration data. *Deep-Sea Research,* 28A(6), 609-623.

Dickson A. G. (1984) pH scales and proton-transfer reactions in saline media such as sea water. *Geochimica et Cosmochimica Acta,* 48, 2299-23089.

Dickson A. G. (1990) Thermodynamics of the dissociation of boric acid in synthetic seawater from 273.15 to 298.15 K. *Deep-Sea Research,* 37, 755-766.

Dickson A. G. (1993) pH buffers for sea water media based on the total hydrogen ion concentration scale. *Deep-Sea Research I,* 40, 107-118.

Dickson A. G., and Millero, F. J. (1987) A comparison of the equilibrium constants for the dissociation of carbonic acid in seawater media. *Deep-Sea Research,* 34, 1733-1743.

Dickson A. G. and Riley J. P. (1979) The estimation of acid dissociation constants in seawater media from potentiometric titrations with strong base I. The ionic product of water (K_w). *Marine Chemistry,* 7, 89-99.

DOE (1994) *Handbook of methods for the analysis of the various parameters of the carbon dioxide system in sea water; version 2.* Dickson A. G. and Goyet C., editors, ORNL/CDIAC-74.

Emerson, S.(1995) Enhanced transport of carbon dioxide during gas exchange, In: B. Jahne and E. C. Monahan, editors, *Air-Water gas transfer. Selected papers form the Third International Symposium on Air-Water Gas Transfer July 24-27, 1995 Heidelberg University*, pg. 23-36. AEON Verlag, Hanau, Germany.

Harned H. S. and Davis R. (1943) The ionization constant of carbonic acid in water and the solubility of CO2 in water and aqueous salt solution from o to 50 C. *Journal of American Chemical Society,* 65, 2030-2037.

Harned H. S. and Owen B. B. (1958) *The Physical Chemistry of Electrolyte Solutions*. Reinhold.

Jahnke, R. J. and G. A. Jackson (1987) Role of sea floor organisms in oxygen consumption in the deep North Pacific Ocean, *Nature*, 329, 621-623.

Johnson, K. S. (1982) Carbon dioxide hydration and dehydration kinetics in seawater, *Limnol. Oceanogr.,* 27, 849-855.

Keir R. S. (1980) The dissolution kinetics of biogenic calcium carbonates in seawater. *Geochimica et Cosmochimica Acta,* 44, 241-252.

Key, R. M., A Kozar, C. L Sabine, K. Lee, R. Wanninkhov, J. L. Bullister, R. A. Feely, F. J. Millero, C. Mordy and T.H. Peng (2004) A global ocean carbon climatololgy: Results from Global Data Analysis Project (GLODAP), *Glob. Biogeochem. Cycles,* 18, GB4031, doi: 10.1029/2004GB002247.

Lewis E. and Wallace, D. (1998) Program developed for CO2 system calculations. ORNL/CDIAC - 105. *Carbon Dioxide Information Analysis Center, Oak Ridge National Laboratory, U. S. Department of Energy, Oak Ridge, Tenn*.

Lueker T. J., Dickson A. G., and Keeling C. D. (2000) Ocean pCO2 calculated from dissolved inorganic carbon, alkalinity, and the equations for K1 and K2: validation based on laboratory measurements of CO_2 in gas and seawater at equilibrium. *Marine Chemistry,* 70, 105-119.

Mehrbach C., Culberson, C. H., Hawley, J. E., Pytkowicz, R. M. (1973) Measurements of the apparent dissociation constants of carbonic acid in seawater at atmospheric pressure. *Limnology and Ocenography,* 18, 897-907.

Millero F. J. (1995) Thermodynamics of the carbon dioxide system in the oceans. *Geochimica et Cosmochimica Acta,* 59, 661-677.

Sarmiento, J. L., J. Dunne, A. Gnanadesikan, R. Key, K. Matsumoto and R. Slater (2002) A new estimate of the $CaCO_3$ to organic carbon export ratio, *Glob. Biogeochem. Cycles*, 16, doi:10.1029/2002GB001010

Stumm W. and Morgan J. J. (1996) *Aquatic Chemistry*. Wiley Interscience, New York, N. Y., 780 p.

Weiss R. F. (1974) Carbon dioxide in water and seawater: The solubility of a non-ideal gas. *Marine Chemistry* **2**, 203-215.

Zeebe R. E. and Wolf-Gladrow D. A. (2000) *CO₂ in Seawater: Equilibrium, Kinetics, Isotopes*.
      Elsevier, 346 p.

Table IV-1. Compounds that exchange protons in the pH range of seawater. Equilibrium constants are for 25 C and S = 35 from the equations in Appendix IV-2 and Millero (1995) for nitrogen and sulfur species. An asterisk (*) indicates the concentration is in the μmol kg^{-1} range and variable. (pK = -log K)

Species	Reaction	Concentration (mol kg^{-1})	-log C_T	pK$^{'}$
H_2O	$H_2O \rightleftharpoons OH^- + H^+$			13.2
DIC	$CO_2 + H_2O \rightleftharpoons HCO_3^- + H^+$	$\approx 2.04 \times 10^{-3}$	2.69	5.85
	$HCO_3^- \rightleftharpoons CO_3^{2-} + H^+$			8.97
B	$B(OH)_3 + H_2O \rightleftharpoons B(OH)_4^- + H^+$	4.16×10^{-4}	3.38	8.60
Si	$H_4SiO_4 \rightleftharpoons H_3SiO_4^- + H^+$	*	*	9.38
P	$H_3PO_4 \rightleftharpoons H_2PO_4^- + H^+$	*	*	1.61
	$H_2PO_4^- \rightleftharpoons HPO_4^{2-} + H^+$	*	*	5.96
	$HPO_4^{2-} \rightleftharpoons PO_4^{3-} + H^+$	*	*	8.79
SO_4^{2-}	$HSO_4^- \rightleftharpoons SO_4^{2-} + H^+$	2.824×10^{-2}	1.55	1.00
F	$HF \rightleftharpoons F^- + H^+$	7.0×10^{-5}	4.15	2.52
Anoxic Water				
N	$NH_4^+ \rightleftharpoons NH_3 + H^+$	*	*	9.19
HS$^-$	$H_2S \rightleftharpoons HS^- + H^+$	*	*	6.98

Table IV-2. Concentrations of cation and anion
species that do not significantly exchange protons
in the pH range of seawater (35 ‰). (From the
compilation in Table I-4.)

Cation	eq kg^{-1}	Anion	eq kg^{-1}
Na^+	0.46906	Cl^-	0.54586
Mg^{2+}	0.10564	SO_4^{2-}	0.05648
Ca^{2+}	0.02056	Br^-	0.00084
K^+	0.01021	F^-	0.00007
Sr^{2+}	0.00018		
Li^+	0.00002		
Total Cations	0.60567	Total Anions	0.60325

ΣCations – ΣAnions = 0.60567 - 0.60325 = 0.00242

Table IV-3. The concentrations of the species that make up the total alkalinity ($A_T = 2420$ μeq kg^{-1}) of seawater at pH ~ 8.2 (T = 20C, S=35). Since this is the pH of surface seawater, it is presented without the contribution of silicate and phosphate.

Species	Concentration		% of A_T
	μmol kg^{-1}	μeq kg^{-1}	
HCO_3^-	1796	1796	75
CO_3^{2-}	255	510	21
$B(OH)_4^-$	108	108	4
OH^-	6	6	0.2

Table IV-4. Carbonate system parameters calculated for different conditions in the Surface and Deep Oceans at 35 ‰ salinity using two different methods. Column (I)[a] is the calculation utilizing all species in the total alkalinity, A_T. A_{Si} and A_P (bottom row) are the alkalinities due to silicate and phosphate species. Column (II)[b] is the calculation assuming the total alkalinity does not include Si and P species, $A_T = A_{C\&B}$. Concentrations and DIC are in units of $\mu mol\ kg^{-1}$ and alkalinity values, A_T, are in $\mu eq\ kg^{-1}$.

Parameter	Surface Water		North Atlantic Deep Water		Antarctic Deep Water		North Pacific Deep Water	
Measured Concentrations								
Z (km)	0.0		4.0		4.0		4.0	
T (C)	20.0		2.0		2.0		2.0	
A_T	2300		2350		2390		2460	
DIC	1950		2190		2280		2370	
[Si]	0.0		60		130		160	
[P]	0.0		1.5		2.2		2.5	
Calculated Carbonate Parameters (Models I and II)								
	I	II	I	II	I	II	I	II
pH	8.19	8.21	7.95	8.11	7.80	7.98	7.74	7.92
f_{CO_2} (atm)	256	250	316	331	462	476	562	573
HCO_3^-	1698	1694	2064	2052	2171	2161	2264	2254
$[CO_3^{2-}]$	244	249	108	119	82	92	73	83
$[CO_2]$	8	7	18	19	27	27	33	33
$[B(OH)_4^-]$	108	110	67	60	50	46	44	40
A_{Si}	0.0	0.0	1.3	0.0	2.0	0.0	2.1	0.0
A_P	0.0	0.0	1.6	0.0	2.3	0.0	2.5	0.0

[a] Calculated using the program of Lewis and Wallace (1998)) with the $K_1^{'}$ and $K_2^{'}$ of Mehrbach et al., 1973 as reinterpreted by Dickson and Millero (1987).

[b] Calculated using the program in Appendix IV-1 using the $K_1^{'}$ and $K_2^{'}$ of Mehrbach et al., 1973 as refitted by Lueker et al., 2000.

Table IV-5. Estimates of the errors in measurement and calculation of the carbonate system parameters (from Millero, 1995). All values are standard deviations about the mean. Measurement error is based on comparison to standard values. Calculated error is determined either by: (I) compounding errors in the analytical accuracy of the input values assuming equilibrium constants are perfect; or (II) compounding errors in the first and second dissociation constants assuming the measurements are perfect. The total error of the calculated estimate would involve compounding these two errors.

Parameter	Calculation method	pH	A_T (μeq kg^{-1})	DIC (μmol kg^{-1})	f_{CO_2} (μatm)
Measurement error		0.0020	4.0	2.0	2.0
Calculated error (methods I and II)					
pH-A_T	I			3.8	2.1
	II			2.4	1.7
pH - DIC	I		2.7		1.8
	II		2.6		1.6
pH $- f_{CO_2}^w$	I		21	21	
	II				
$f_{CO_2}^w$ - DIC	I	0.0025	3.4		
	II	0.0019	2.6		
$f_{CO_2}^w$ - A_T	I	0.0026		3.2	
	II	0.0019		2.1	
A_T - DIC	I	0.0062			5.7
	II	0.0036			2.9

Table IV-6. Temperature dependence of rate constants of CO_2 reaction with H_2O in pure water and seawater. The values are from the equation which best fit the data of Johnson (1982). His values for $k_{OH^-}K_W$ are reinterpreted as indicated in Emerson (1995). The equilibrium constants necessary to calculate the reverse rate constants are also tabulated.

	Pure Water					Seawater (35 ‰)				
Temperature (C)	10	15	20	25	30	10	15	20	5	30
Equilibrium constants										
[a] K_1, K_1' (mol kg^{-1}) $\times 10^7$	3.44	3.80	4.15	4.45	4.71	10.0	11.2	12.5	13.9	15.4
[b] K_W, K_W' (mol kg^{-1})$^2 \times 10^{14}$	0.29	0.45	0.68	1.01	1.47	1.4	2.4	3.8	6.1	9.4
Reaction rate constants										
[c] k_{CO_2} (s^{-1}) $\times 10^2$	0.8	1.4	2.4	3.7	5.4	0.8	1.4	2.4	3.7	5.4
[c] $k_{OH^-}K_W$, $k_{OH^-}K_W\gamma_{H^+}$ (mol kg^{-1}s^{-1}) $\times 10^{11}$	1.2	2.1	3.8	7.1	13.4	2.3	4.1	7.4	13.7	25.6
[d] k_{OH^-} (kg mol^{-1}s^{-1}) $\times 10^{-3}$	4.1	4.7	5.6	7.0	9.1	2.7	2.8	3.2	3.7	4.5
[e] $k_{H_2CO_3}$ (kg mol^{-1}s^{-1}) $\times 10^{-4}$	2.3	3.7	5.8	8.3	11.5	0.8	1.2	1.9	2.7	3.5
[e] $k_{HCO_3^-}$ (s^{-1}) $\times 10^5$	3.5	5.5	9.2	16.0	28.4	3.8	6.1	9.9	16.4	27.7

[a] K_1 (I=0) Harned and Davis (1943); K_1' (seawater) Dickson and Goyet (1994)

[b] K_W (I=0) Harned and Owen (1958); K_W' (seawater) Dickson and Goyet (1994)

[c] Johnson (1982)

[d] Calculated from (c) and (b), $\gamma_{H^+} = 0.6$, Millero (1995)

[e] $\dfrac{k_{co2}}{k_{H2CO3}} = \dfrac{k_{OH^-}K_W}{k_{HCO_3^-}} = K_1 \ (I=0) \quad : \quad \dfrac{k_{co2}}{k_{H2CO3}} = \dfrac{k_{OH^-}K_W'}{k_{HCO_3^-}} = K_1' \ (\text{seawater})$

Table IV-7. Relative changes in DIC and A_T in seawater caused by dissolution of one μmol kg^{-1} of $CaCO_3$ along with degradation of 2 to 8 μmoles kg^{-1} of organic carbon. The $\Delta DIC : \Delta A_T$ trends in Figure IV-6 are in accord with OM : $CaCO_3$ ratios of ~8:1 and ~2:1

OM degraded (μmol kg^{-1})	ΔDIC (μmol kg^{-1})			ΔA_T (μeq kg^{-1})			$\Delta DIC{:}\Delta A_T$
	From O.M.	From $CaCO_3$	Composite	From O.M.	From $CaCO_3$	Composite	
2	2	1	3	-0.3	2	1.7	1.8
4	4	1	5	-0.6	2	1.4	3.6
6	6	1	7	-0.9	2	1.1	6.4
8	8	1	9	-1.2	2	0.8	11.2

Table IV-8. The degree of approximation involved in calculations using Eq. IV-37. (1) Distribution of carbonate species in surface seawater at chemical equilibrium (25 C, S=35). (2) After the addition of 20 μmol kg^{-1} of CO_2: (a) guess using Eq.IV-37, (b) Assuming $A_T = A_C$ only, (c) assuming $A_T = A_{C\&B}$. Note differences in the changes in HCO_3^- and CO_3^{2-}. (3) The same as (2) except for dissolution of the equivalent of 20 μmol kg^{-1} $CaCO_3$. All concentrations are in μmol kg^{-1} except $A_{C\&B}$ and A_C which are μeq kg^{-1}.

	$A_{C\&B}$	A_C	DIC	HCO_3^-	CO_3^{2-}	CO_2
(1) Surf SW	2300	2188	1950	1696	246	9
(2) + 20 μmol kg^{-1} of CO_2						
(a) Eq. IV-37		2188	1970	1736	226	10
Δ(1-2a)		**0**	**20**	**+40**	**-20**	**0**
(b) A_C, DIC		2188	1970	1732	228	10
Δ(1 – 2b)		**0**	**+20**	**+36**	**-18**	**+1**
(c) $A_{C\&B}$, DIC	2300	2194	1970	1728	233	10
Δ(1 – 2c)	**0**	**+6**	**+20**	**+32**	**-13**	**+1**
(3) + 20 μmol kg^{-1} of CO_3^{2-}						
(a) Eq. IV-37		2228	1970	1696	266	8
Δ(1 – 3a)		**+40**	**+20**	**0**	**+20**	**0**
(b) A_C, DIC		2228	1970	1694	267	8
Δ(1 - 3b)		**+40**	**+20**	**-2**	**+21**	**0**
(c) $A_{C\&B}$,DIC	2340	2221	1970	1701	260	8
Δ(1 – 3c)	**+40**	**+33**	**+20**	**+5**	**+14**	**0**

APPENDIX IV-1 CARBONATE SYSTEM EQUILIBRIUM EQUATIONS IN SEAWATER

Part A describes the equations necessary for determining the concentrations of carbonate species in seawater for the three different definitions of alkalinity given in the text. Part B is a listing of the Matlab program for determining carbonate buffer species using the equations for the case where $A_T = A_{C\&B}$.

PART A. (Equation numbers refer to equations in text.)

(a) Using Carbonate Alkalinity, A_C:

(5 equations, 7 unknown chemical concentrations: A_C, DIC, HCO_3^-, CO_3^{2-}, CO_2, H^+, f_{CO_2})

$$A_C = [HCO_3^-] + 2[CO_3^{2-}] \tag{IV-26}$$

$$DIC = [HCO_3^-] + [CO_3^{2-}] + [CO_2] \tag{IV-15}$$

$$K_1' = \frac{[HCO_3^-] \times [H^+]}{[CO_2]} \tag{IV-11}$$

$$K_2' = \frac{[CO_3^{2-}] \times [H^+]}{[HCO_3^-]} \tag{IV-9}$$

$$K_H = \frac{[CO_2]}{f_{CO_2,a}} \tag{IV-14}$$

(b) Using Carbonate and Borate Alkalinity, $A_{C\&B}$

(7 equations and 10 unknown chemical concentrations)

New unknown concentrations: B_T, $B(OH)_4^-$, $B(OH)_3$

substitute eq, (IV-25) for eq. IV-26:

$$A_{C\&B} = [HCO_3^-] + 2[CO_3^{2-}] + [B(OH)_4^-] \tag{IV-25}$$

Include borate related equations (V-19,V-20):

$$B_T = [B(OH)_4^-] + [B(OH)_3] \tag{IV-20}$$

$$K_B = \frac{[B(OH)_4^-] \times [H^+]}{[B(OH)_3]} \tag{IV-19}$$

(c) Using the Total Alkalinity, A_T but no acidic species

(14 equations and 19 unknown concentrations)

New unknown concentrations: Si_T, P_T, $H_3SiO_4^-$, H_4SiO_4, PO_4^{3-}, HPO_4^{2-}, $H_2PO_4^-$, H_3PO_4, OH^-, $SO_{4,T}$, SO_4^{2-}, HSO_4^-, F_T, HF, F^-, H^+

substitute eq. IV-24 for eq. IV-25

$$A_T = [HCO_3^-] + 2[CO^{3-}] + [B(OH)_4^-] + [H_3SiO_4^-] + [HPO_4^{2-}] + 2[PO_4^{3-}] + [OH^-] - [H^+] -$$

$$[HSO_4^-] - [HF] - [H_3PO_4] \tag{IV-24}$$

Include new species related mass balance and equilibrium equations:

$$Si_T = [H_3SiO_4^-] + [H_4SiO_4] \tag{IV-39}$$

$$P_T = [H_3PO_4] + [H_2PO_4^-] + [H_2PO_4^{2-}] + [PO_4^{3-}] \tag{IV-40}$$

$$K_{Si} = \frac{[H_3SiO_4^-] \times [H^+]}{[H_4SiO_4]} \tag{IV-41}$$

$$K_{P,1} = \frac{[H_2PO_4^-] \times [H^+]}{[H_3PO_4]} \tag{IV-42}$$

$$K_{P,2} = \frac{[HPO_4^{2-}] \times [H^+]}{[H_2PO_4^-]} \tag{IV-43}$$

$$K_{P,3} = \frac{[PO_4^{3-}] \times [H^+]}{[HPO_4^{2-}]} \tag{IV-44}$$

$$K_W = [OH^-][H^+] \tag{IV-45}$$

$$K_{SO_4} = \frac{[SO_4^{2-}][H^+]}{[HSO_4^-]} \tag{IV-46}$$

$$K_{HF} = \frac{[F^-][H^+]}{HF} \tag{IV-47}$$

PART B

The following Matlab function program finds the root of the cubic equation for $[H^+]$ in terms of $A_{C\&B}$ and DIC resulting from the combination of the equations in (a) and (b) above (Zeebe and Wolf-Gladrow, 2000). Input values are temperature, salinity, depth, $A_{C\&B}$ and DIC and the outputs are fCO_2, pH, $[CO_2]$, $[HCO_3^-]$ and $[CO_3^{2-}]$. Units and equilibrium constants used are indicated in the comment statements.

```
function [fco2,pH,co2,hco3,co3] = co3eq(temp,s,z,alk,dic)

% Function to calculate fCO2, HCO3, and CO3 from ALK and DIC as a f(temp,sal,Z)
% temp=temp(deg C), sal=salinity(ppt),depth=z(m),alk=ALK(microeq/kg),
% dic=DIC(micromol/kg)
% HCO3, CO3, and CO2 are returned in moles/kg, fCO2 in atm, KH in moles/kg atm
% This program uses the equations in Zeebe and Wolf-Gladrow (2001) and
```

```
% Matlab's root finding routine
% checked for fCO2 against Luecker et al. 2000, May 2002;
% Depth dependence has not been checked


t = temp + 273.15;
Pr = z/10;
alk = alk * .000001;
dic = dic * .000001;
R = 83.131;


% Calculate total borate (tbor) from chlorinity


tbor = .000416 * s / 35.0;


% Calculate Henry's Law coeff, KH (Weiss, 1974, Mar. Chem., 2, 203)


U1 = -60.2409 + 93.4517 * (100 / t) + 23.3585 * log(t / 100);
U2 = s * (.023517 - .023656 * (t / 100) + .0047036 * (t / 100) ^ 2);
KH = exp(U1 + U2);


% Calculate KB from temp & sal (Dickson,1990,DSR, 34, 1733)


KB = exp((-8966.9 - 2890.53 * s^0.5 - 77.942 * s + 1.728 * s^1.5 - 0.0996*s^2)/t...
   + 148.0248 + 137.1942 * s^0.5 + 1.62142 * s - (24.4344 + 25.085 * s^0.5 +...
   0.2474 * s) * log(t) + 0.053105 * s^0.5 * t);


% Calculate K1 and K2 (Lueker et al., 2000, Mar Chem, 70, 105)


K1 = 10^(-(3633.86/t - 61.2172 + 9.67770 * log(t)- 0.011555*s + 0.0001152 * s^2));


K2 = 10^(-(471.78/t + 25.9290 - 3.16967 * log(t) - 0.01781*s + 0.0001122 * s^2));


% Pressure variation of K1 and K2 (Millero, 1995, GCA, 59, 661)


dvB = -29.48 - 0.1622 * temp + .002608 * (temp)^2;
dv1 = -25.50 + 0.1271 * temp;
dv2 = -15.82 - 0.0219 * temp;


dkB = -.00284;
dk1 = -.00308 + 0.0000877 * temp;
dk2 = +.00113 - .0001475  * temp;


KB = (exp(-(dvB/(R*t))*Pr + (0.5 * dkB/(R*t))*Pr^2)) * KB;
K1 = (exp(-(dv1/(R*t))*Pr + (0.5 * dk1/(R*t))*Pr^2)) * K1;
K2 = (exp(-(dv2/(R*t))*Pr + (0.5 * dk2/(R*t))*Pr^2)) * K2;


% temperature dependence of Kw (Dickson and Goyet, 1994)


KW1 = 148.96502-13847.26/t-23.65218*log(t);
KW2 = (118.67/t-5.977+1.0495*log(t))*s^.5-0.01615*s;
KW = exp(KW1+KW2);


% solve for H ion (Zeebe and Wolf-Gladrow, 2000)
```

```
a1=1;
a2=(alk+KB+K1);
a3=(alk*KB-KB*tbor-KW+alk*K1+K1*KB+K1*K2-dic*K1);
a4=(-KW*KB+alk*KB*K1-KB*tbor*K1-KW*K1+alk*K1*K2+KB*K1*K2-dic*KB*K1-2*dic*K1*K2);
a5=(-KW*KB*K1+alk*KB*K1*K2-KW*K1*K2-KB*tbor*K1*K2-2*dic*KB*K1*K2);
a6= -KB*KW*K1*K2;


p=[a1 a2 a3 a4 a5 a6];
r=roots(p);
h=max(real(r));


%calculate the HCO3, CO3 and CO2aq using DIC, AlK and H+
format short g;
hco3 = dic/(1 + h/K1 + K2/h);
co3 = dic/(1 + h/K2 + h*h/(K1*K2));
co2 = dic/(1 + K1/h + K1*K2/(h*h));
fco2 = co2 / KH;
pH=-log10(h);


%calculate B(OH)4- and OH


BOH4=KB*tbor/(h+KB);OH=KW/h;


%recalculate DIC and Alk to check calculations


Ct=(hco3+co3+co2)*1e6;
At= (hco3+2*co3+BOH4+OH-h)*1e6;
```

APPENDIX IV-2. EQUATIONS FOR CALCULATING THE EQUILIBRIUM CONSTANTS OF THE CARBONATE AND BORATE BUFFER SYSTEM

Constants are based on the "total" pH scale, pH_T (Dickson, 1984, 1993). Values are first presented at 1 atm pressure and then equations are given for calculating the pressure effect on K. (T is temperature in either degrees Kelvin (T), or degrees centigrade (T_C). Salinities are on the practical salinity scale. Equilibrium constants for the equilibria in APPENDIX IV-1.A (c) can be found in DOE, 1994, and in Zeebe and Wolf-Gladrow, 2000)

PART A. VALUES AT 1 ATMOSPHERE

(1) The Henry's Law constant for CO_2 in seawater (mol kg^{-1} atm^{-1}), eq. IV-14
(from Weiss, 1974; as reported in DOE, 1994)

$$\ln K_H = \frac{9345.17}{T} - 60.2409 + 23.3585 \ln\left(\frac{T}{100}\right)$$

$$+ S\left[0.023517 - 0.00023656\,T + 0.0047036\left(\frac{T}{100}\right)^2\right] \tag{IV-46}$$

$$= -3.5617 \ (T_C = 25\,(T = 298.15), S = 35)$$

(2) The First (eq. IV-11) and Second (eq. IV-9) Dissociation Constants for Carbonic Acid in seawater (mol kg-1) (Mehrbach's constants given on the total pH scale; Lueker et al., 2000)

$$pK_1' = \frac{3633.86}{T} - 61.2172 + 9.6777 \ln(T) - 0.011555\,S + 0.0001152\,S^2 \tag{IV-47}$$

$$= 5.847 \ (T_C = 25, \ S = 35)$$

$$pK_2' = \frac{471.78}{T} + 25.9290 - 3.16967 \ln(T) - 0.01781\,S + 0.0001122\,S^2 \tag{IV-48}$$

$$= 8.966 \ (T_C = 25, \ S = 35)$$

(3) Boric Acid in seawater, mol kg^{-1} (eq. IV-19 and IV-20) (based on Dickson, 1990 as reported in DOE, 1994)

$$B_T = [B(OH)_3] + [B(OH)_4^-] = 4.16 \times 10^{-4} \quad (S = 35) \tag{IV-49}$$

$$\ln K_B = \frac{-8966.90 - 2890.53\,S^{1/2} - 77.942\,S + 1.728\,S^{3/2} + 0.0996\,S^2}{T} + 148.0248$$

$$+ 137.1942\,S^{1/2} + 1.62142\,S - (24.4344 + 25.085\,S^{1/2} + 0.2474\,S)\ln(T) \tag{IV-50}$$

$$+ 0.053105\,S^{1/2}\,T$$

$$= -19.7964 \quad (T_C = 25,\ S = 35)$$

(4) The Dissociation Constant of Water, mol² kg⁻¹(Dickson and Riley, 1979, as reported in DOE, 1994)

$$\ln K_W = 148.96502 - \frac{13847.26}{T} - 23.6521 \ln(T)$$

$$+ \left(\frac{118.67}{T} - 5.977 + 1.0495 \ln(T) \right) S^{1/2} - 0.01615\,S \tag{IV-51}$$

$$= -30.434 \quad (T_C = 25,\ S = 35)$$

PART B. THE PRESSURE DEPENDENCE (from Millero, 1995)

The effect of pressure can be calculated from the molal volume, ΔV, and compressibility, $\Delta \kappa$, changes for any given reaction

$$\ln \frac{K_P}{K_0} = -\left(\frac{\Delta V}{RT} \right) P + \left(\frac{0.5 \Delta \kappa}{RT} \right) P^2 \tag{IV-52}$$

where K_P and K_0 are equilibrium constants for the reaction of interest at pressure P and at 0 bars (1 atm), respectively. P is pressure in bars, R = 83.131 (cm³ bar mol⁻¹ deg K⁻¹) and T is in degrees Kelvin. The molar volume (cm³ mol) and compressibility can be fit to equations of the form (S = 35)

$$\Delta V = a_0 + a_1 T_C + a_2 T_C^2 \tag{IV-53}$$

$$\Delta \kappa = b_0 + b_1 T_C \tag{IV-54}$$

where T_C is now temperature in degrees C. Values for the coefficients a and b are presented in the table below along with calculated differences in pK' and K' at two different pressures (T_C = 25 C, S = 35).

Table IVA-2. Parameters for calculating the effect of pressure change on carbonate buffer system reactions and values of equilibrium constants at P = 0 and 300 bars.

Constant	$-a_0$	A_1	$a_2 \times 10^3$	$-b_0 \times 10^3$	$b_1 \times 10^3$	P = 0	P = 300	K^{300}/K^0

pK_1'	25.50	0.1271	0.0	3.08	0.0877	5.8563	5.7397	1.31
pK_2'	15.82	-0.0219	0.0	-1.13	-0.1475	8.9249	8.8409	1.21
pK_B'	29.48	0.1622	2.608	2.84	0.0	8.5975	8.4746	1.33
pK_W'	25.60	0.2324	-3.6246	5.13	0.0794	13.2173	13.1039	1.30

FIGURE CAPTIONS

Figure IV-1. Concentrations of the acidic, [HBa], and basic, [Ba⁻], forms of an acid with total concentration, $Ba_T = 10^{-2}$ moles kg^{-1} and an equilibrium constant, $K = 10^{-6}$, as a function of pH. The concentrations are equal at the point where pH = pK. When the criteria of charge balance is included in the equations, the system is defined at a single pH where $[H^+] = [Ba^-]$ indicated by the small circle.

Figure IV-2. Concentrations of the species of the acid-base pairs of carbonate, borate and water in seawater as a function of pH. (salinity, S = 35, temperature, T = 20 $^{\circ}$C and DIC = 2.0×10^{-3} mol kg^{-1})

Figure IV-3. The residence time (τ) of CO_2 with respect to hydration and reaction with OH^- as a function of pH. The curves were determined from exponent, A, in Eq. IV-30 and the rate constants in Table IV-6. The residence times with respect to the two separate reactions are presented separately and together. CO_2 hydration is indicated by k_{CO2} and calculated for the case where $k_{OH} = k_{HCO3} = 0$. Hydroxylation is indicated by k_{OH} and calculated for the case where $k_{CO2} = k_{CO2r} = 0$. Together the reactions are indicated by $(k_{CO2} + k_{OH})$. In pH range of seawater both reactions are important in determining the reaction residence time.
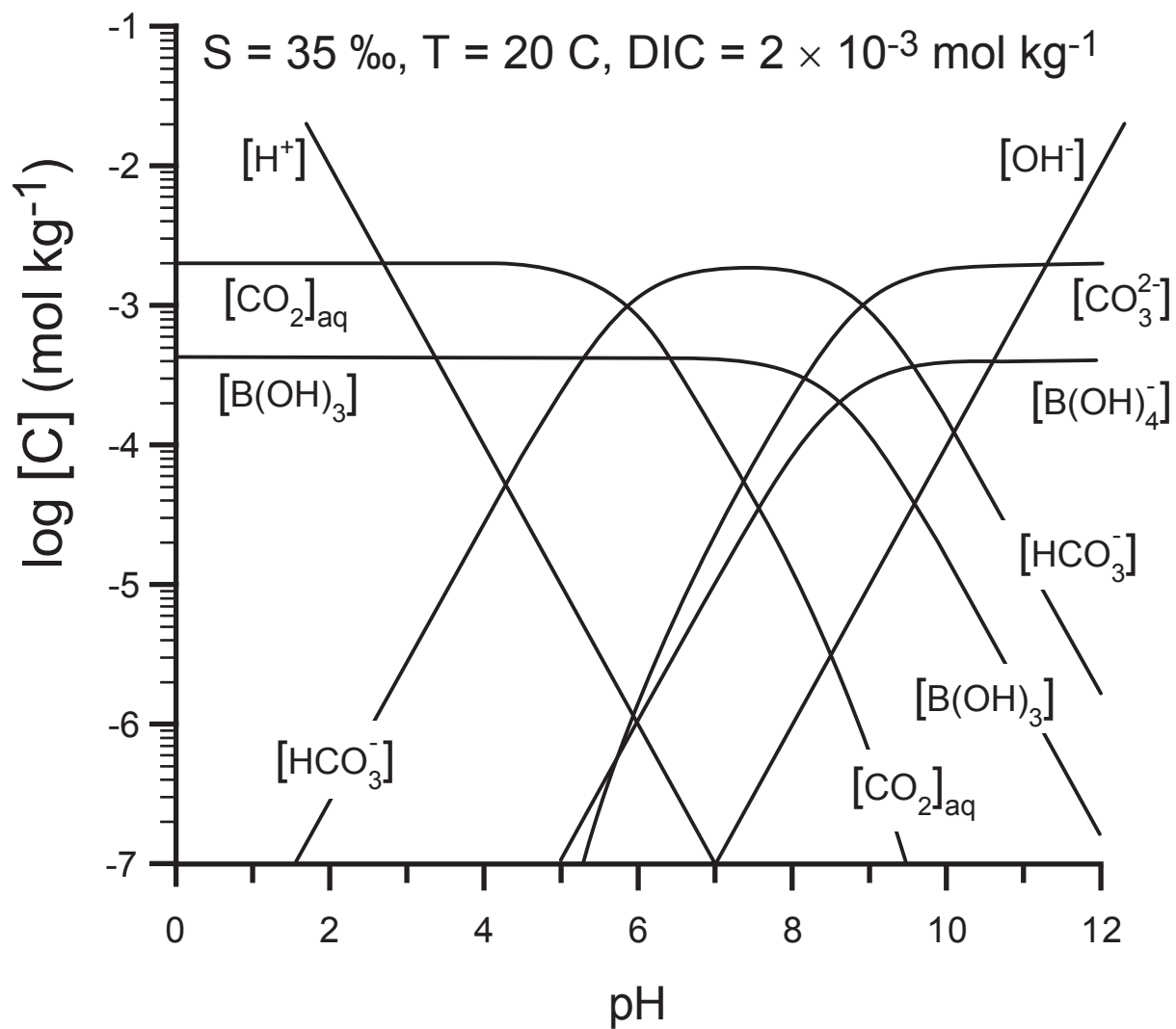
Figure IV-4. Cross sections of Total Alkalinity (a) and (b) DIC in the Atlantic, Indian and Pacific Oceans. (Modified from the figure in Key et al., 2004)

Figure IV-5. Depth profiles of total alkalinity (A_T) in the Atlantic, Antarctic, Indian and Pacific Oceans. (Plotted in Ocean Data View, using data from the e-WOCE compilation.)
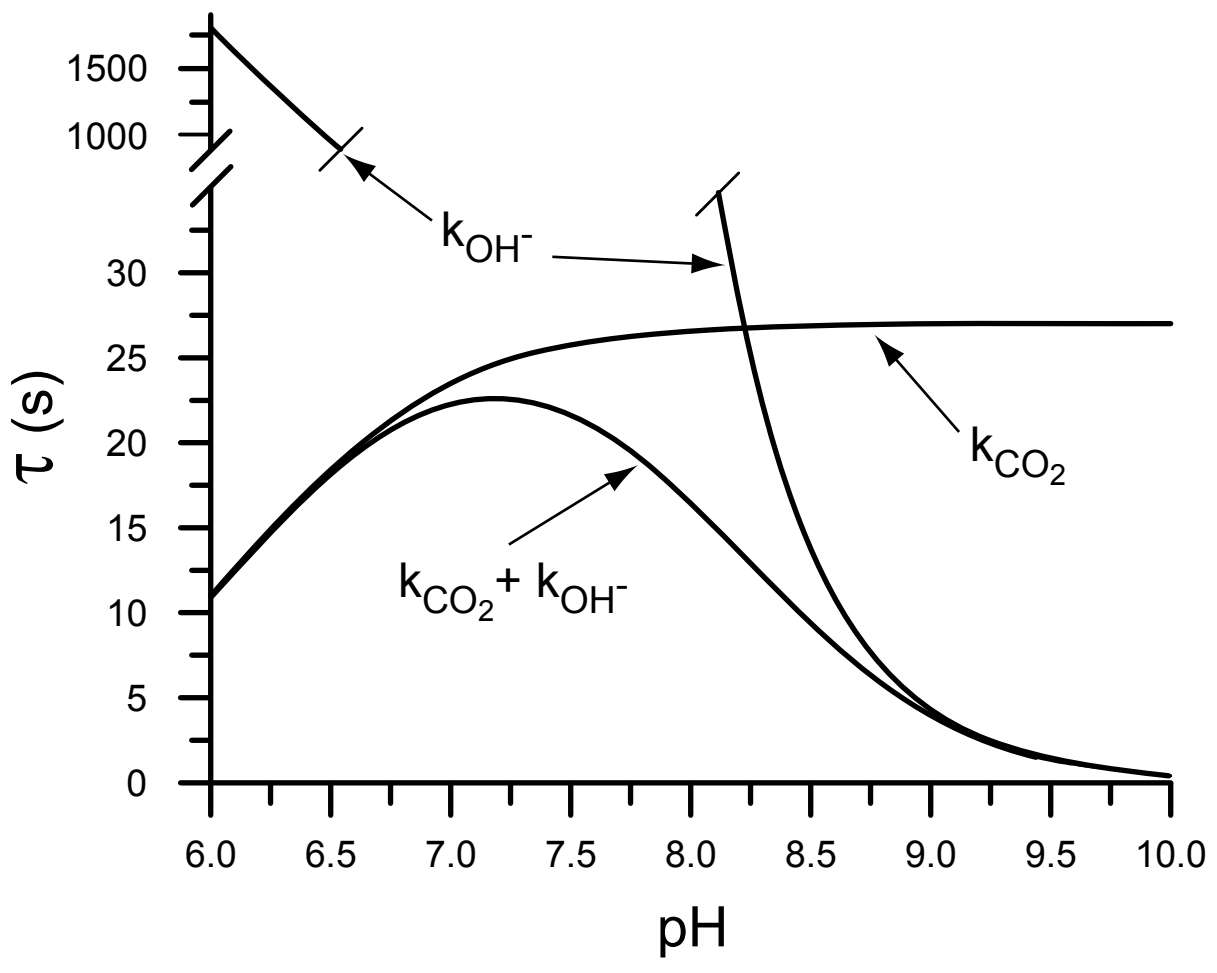
Figure IV-6. Salinity normalized (S=35) total alkalinity, $A_{T,N}$, versus salinity normalized dissolved inorganic carbon, DIC_N, for the world's ocean. Data are for the deep ocean at depths > 2.5 km except for the section labeled "North Atlantic Shallow" which is 100 – 1000 meters in the North Atlantic Ocean. Lines indicate different $DIC_N:A_{T,N}$ ratios.
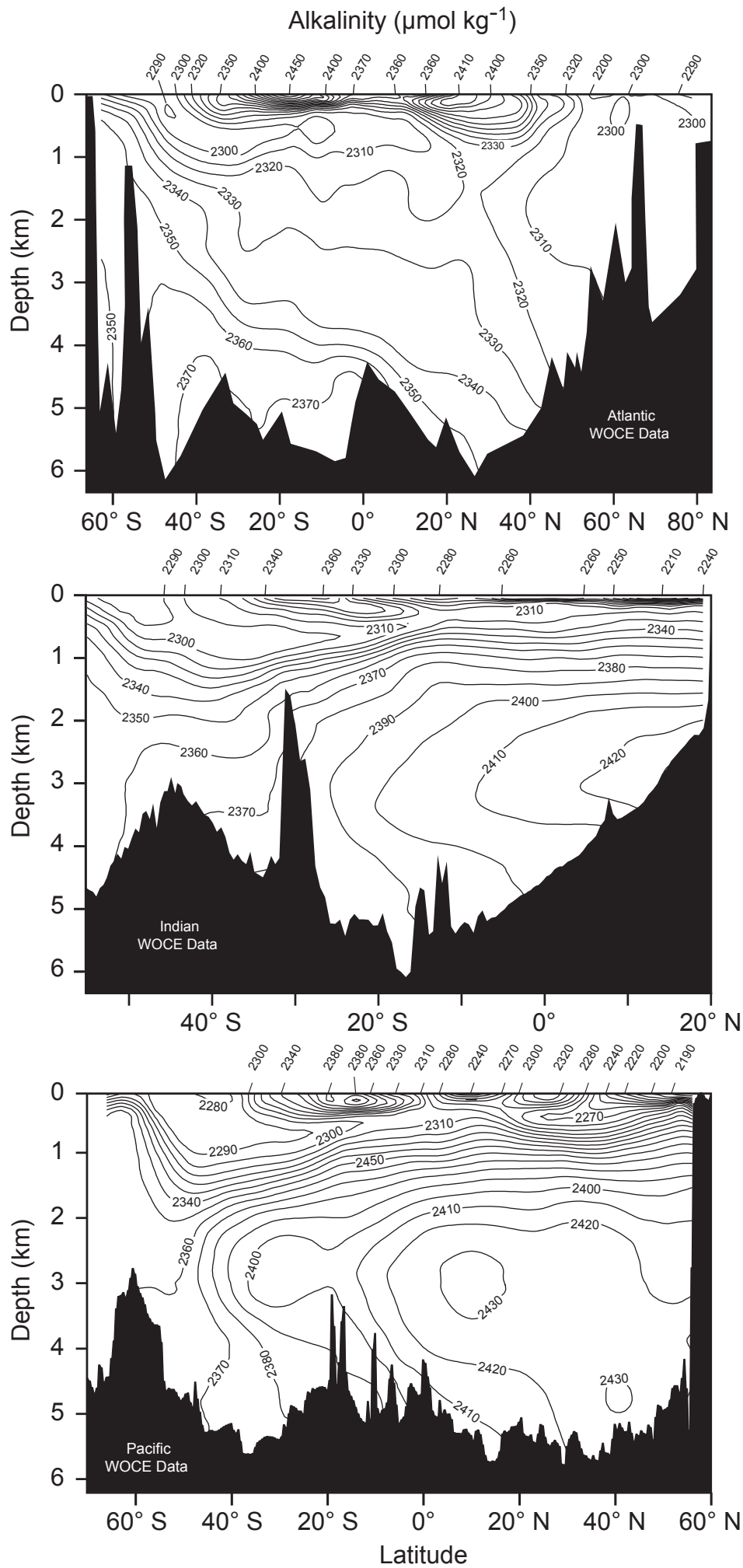
$Ba_T = 10^{-2}$ M   K' = 10^{-6} (pK' = 6)
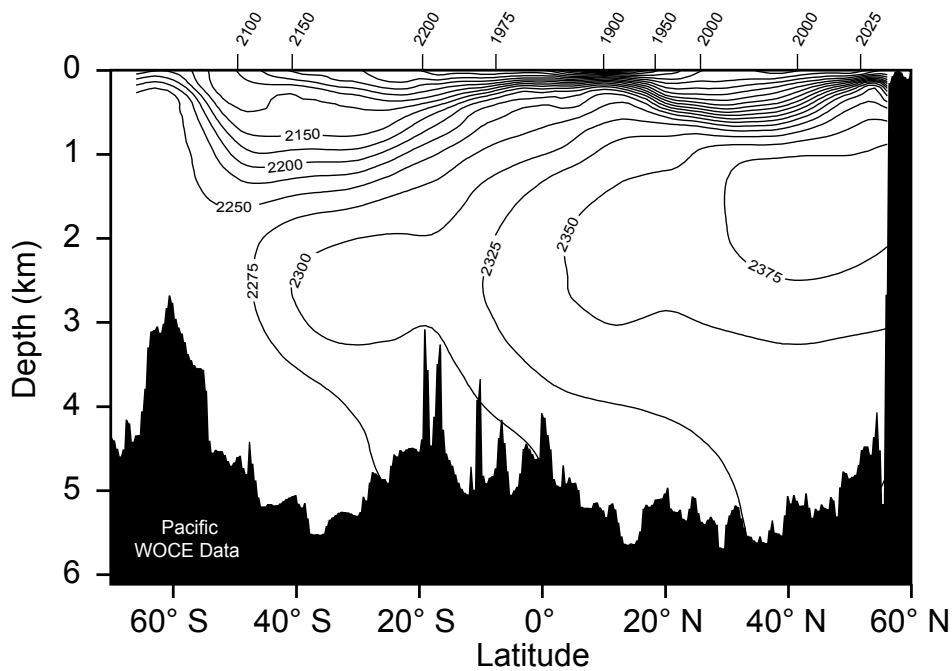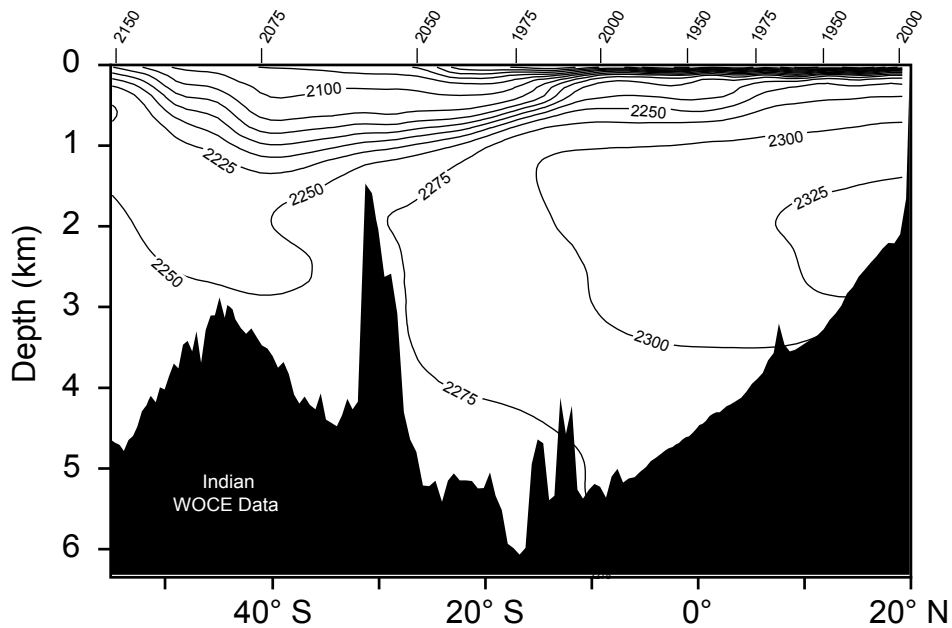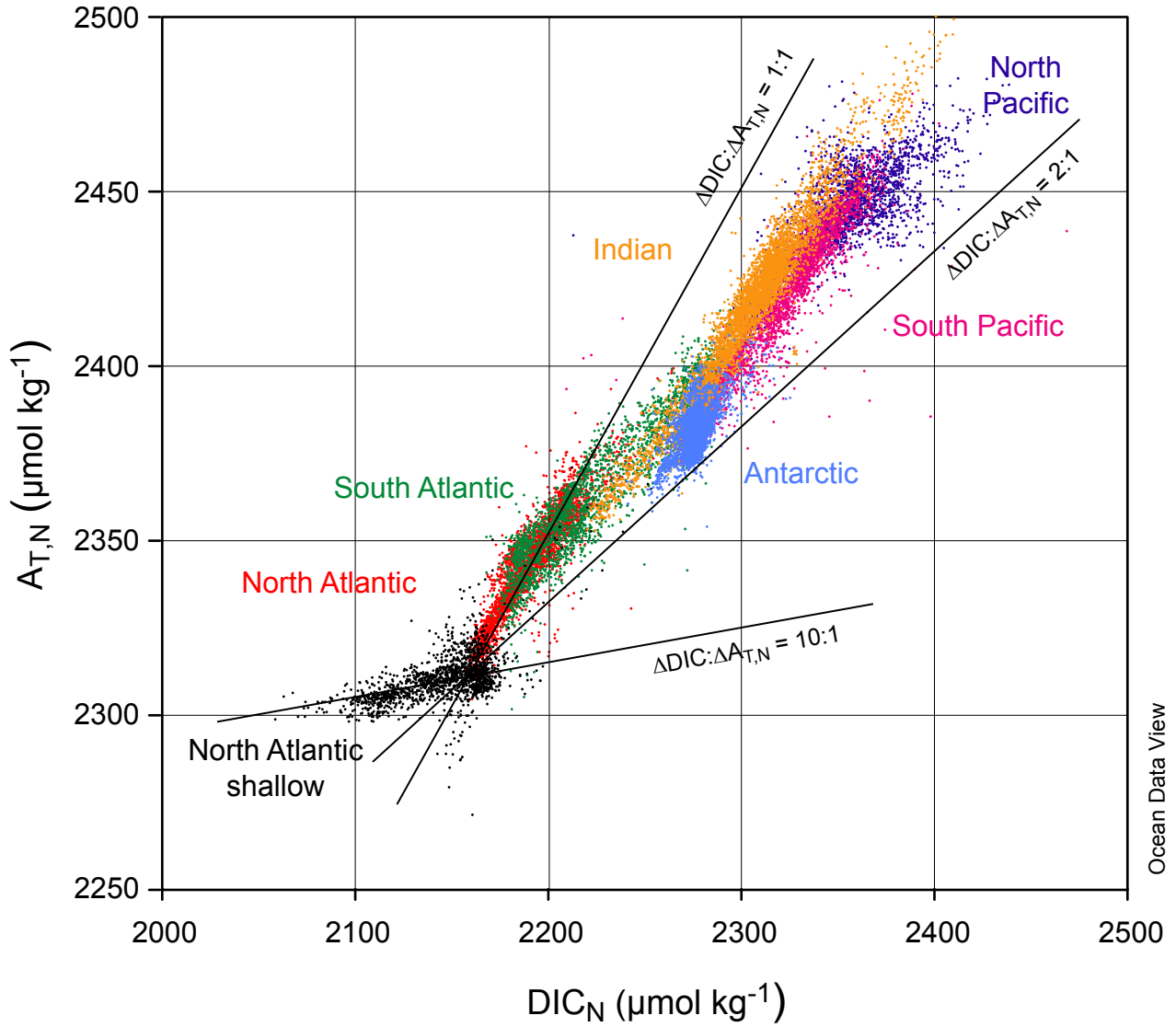
$[H^+]$

$[Ba^-]$

$[HBa]$
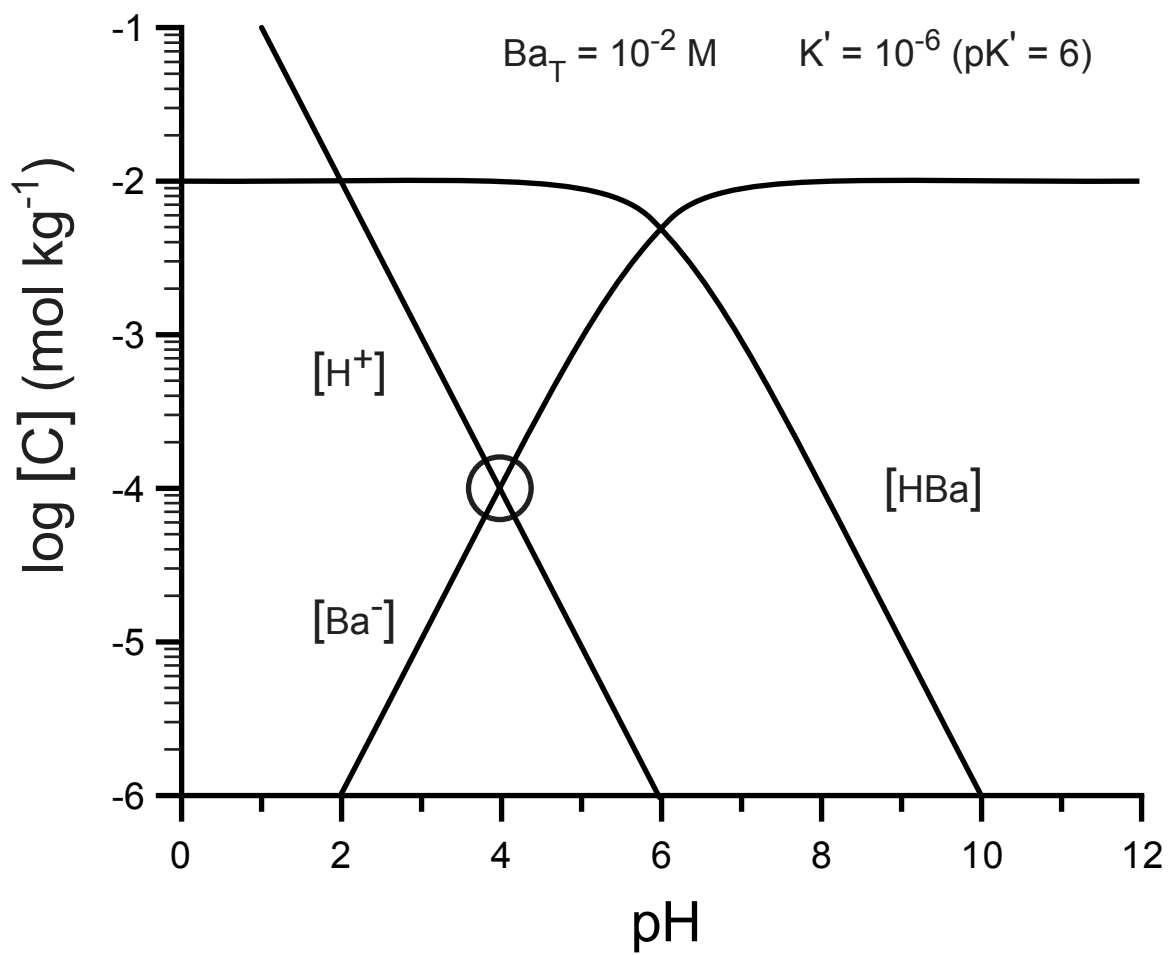
Chapter 4 Figure 1

Chapter 4 Figure 2

Chapter 4 Figure 3

Chapter 4
Figure 4A

DIC (µmol kg⁻¹)

Atlantic
WOCE Data

Indian
WOCE Data

Pacific
WOCE Data
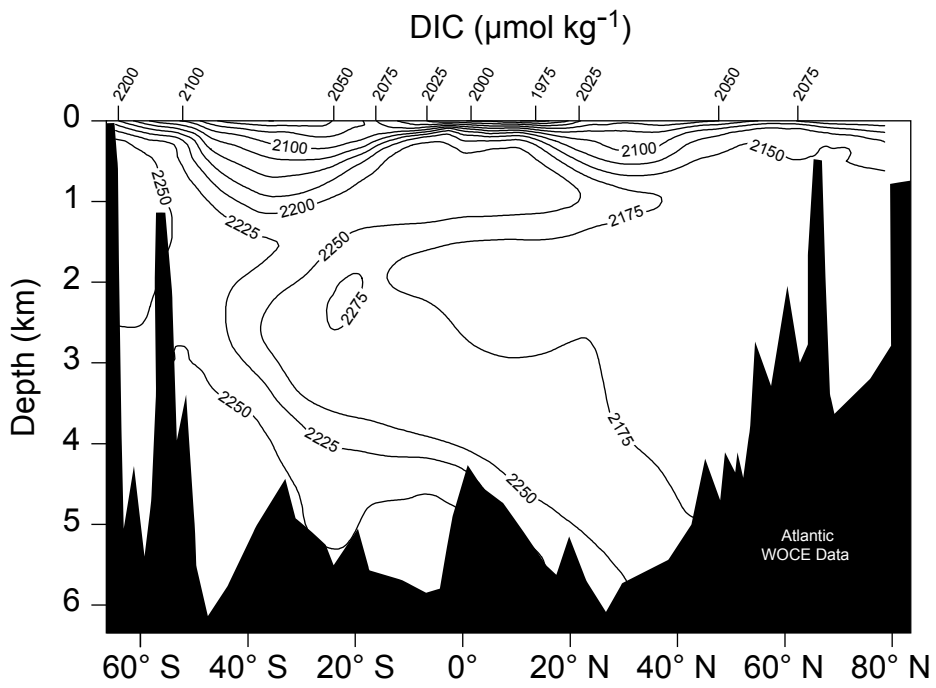
Chapter 4
Figure 4B

Latitude
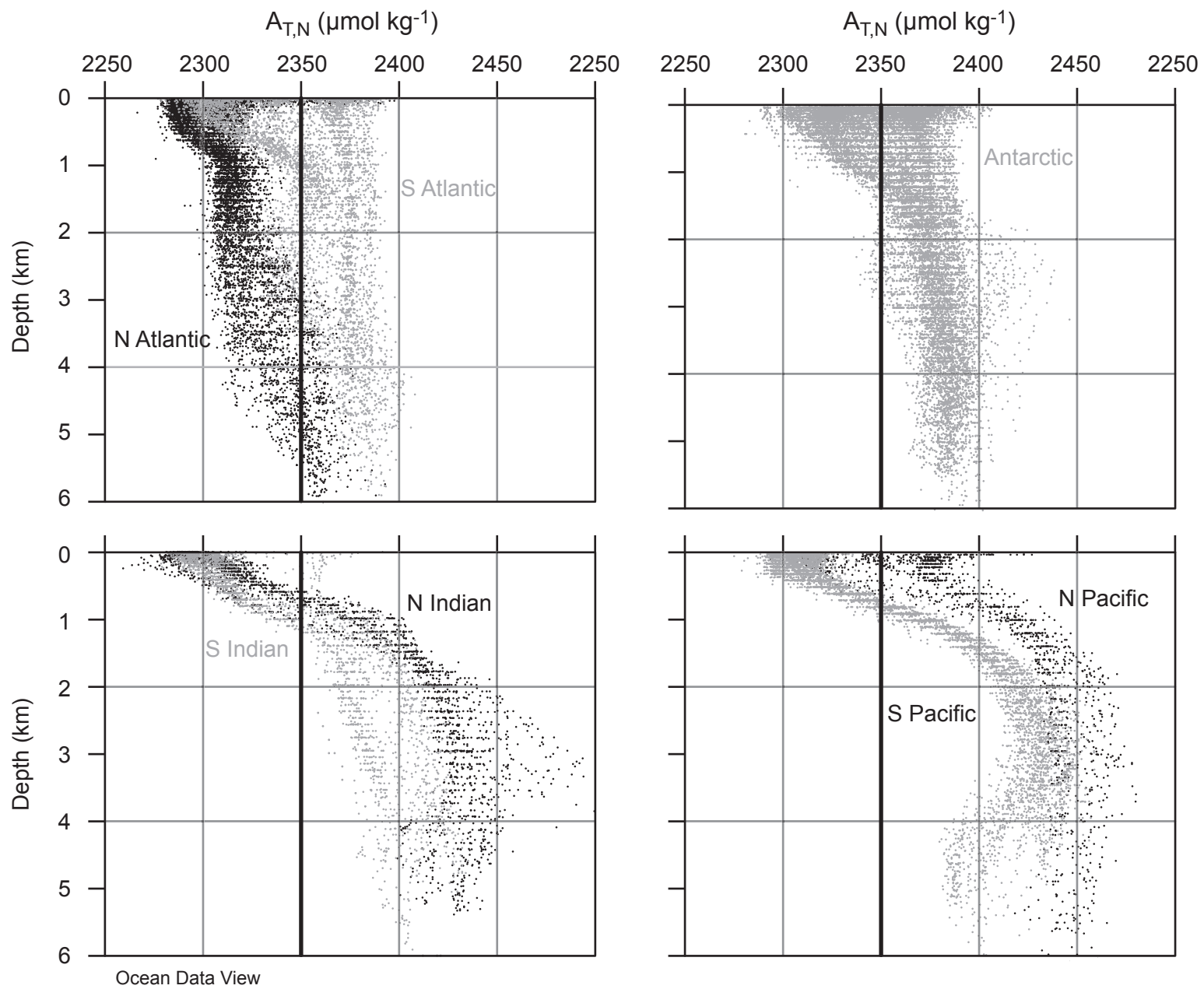
Chapter 4 Figure 5

Chapter 4 Figure 6