The Marine Inorganic Carbon Cycle

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1. Introduction

Over the last 200 years a number of greenhouse gases (e.g., CO_2, CH_4, N_2O, chlorofluorocarbons (CFCs)) have been increasing in the atmosphere.[1] These gases adsorb infrared energy radiated from the earth, which results in an increase in the temperature of the troposphere. At the present time, the most important greenhouse gas is CO_2. The continued burning of fossil fuels has and will continue to increase the CO_2 in the atmosphere. It is quite clear from the pioneering CO_2 measurements of Keeling and Whorf[2] at Hawaii and the ice core measurements[3] that the CO_2 is increasing (Figure 1). The preindustrial levels were 280 ppmv and have increased to the current levels of 370 ppmv. Over the next 200 years, the levels may increase as high as 2000 ppmv.[4] The levels of CO_2 in the past (Figure 2) have varied between 200 ppmv during glacial times and 300 ppmv during interglacial times over 350 ky (ky = 1000 years).[5] More recent ice core measurements indicate that these levels have been similar for 600 ky.[6] Before 450 ky BP (BP = before present), the CO_2 varied between 260 and 180 ppmv. These results indicate that the present levels of CO_2 in the atmosphere are 23% higher than 280 ppmv in the past 600 ky.

The rates of CO_2 increases in the atmosphere are nearly the same as the increase in the use of fossil fuels. However, the amounts remaining in the atmosphere are only about one-half of the expected values. This is shown in Figure 3 where the rates of fossil fuel emissions and rates accumulated in the atmosphere are compared.[1] The differences are related to the accumulation of CO_2 in the oceans and on land. The variations in the accumulation rates in the atmosphere are thought to be related to El Nino. During El Nino years, the ocean and land have lower accumulation rates.

The estimates[1] of the sources and sinks of CO_2 in the atmosphere are given in Table 1. The differences between the sources (7.0 Gt year^{-1}) and sinks (5.4 Gt year^{-1}) of 1.6 Gt year^{-1} are close to the overall uncertainty (1.4 Gt year^{-1}). These earlier estimates of the ocean sink of 2 Gt year^{-1} have been determined using ocean models. The oceans are thought to take up about 40% of the CO_2 produced from the burning of fossil fuels (Table 1). This has led to a great interest in understanding the cycling of CO_2 between the atmosphere

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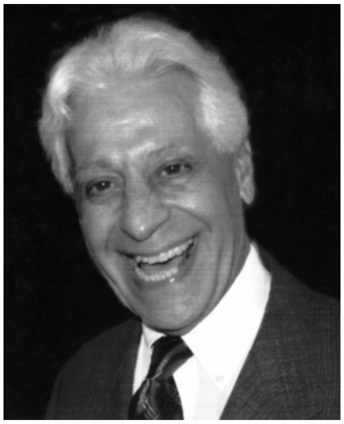

Over a 40-year career, Frank J. Millero has contributed greatly to chemical oceanography. His research toward understanding the physical chemistry of seawater has been recognized with numerous awards. Millero's research includes the global carbon dioxide cycle in the world's oceans, studies of ionic interactions in seawater, and the study of trace metals in natural waters. Dr. Frank J. Millero received his B.S. (1961) from The Ohio State University and his M.S. (1964) and Ph.D. (1965) from Carnegie-Mellon University in physical chemistry. After a brief interval in industry, he came to the University of Miami in 1966. He has been a professor in marine and physical chemistry since that time. From 1986 to 2006, he was Associate Dean of Academic Studies at the School. He serves as an associate editor for a number of journals, and since 1993 has been Editor-in-Chief of *Marine Chemistry*.

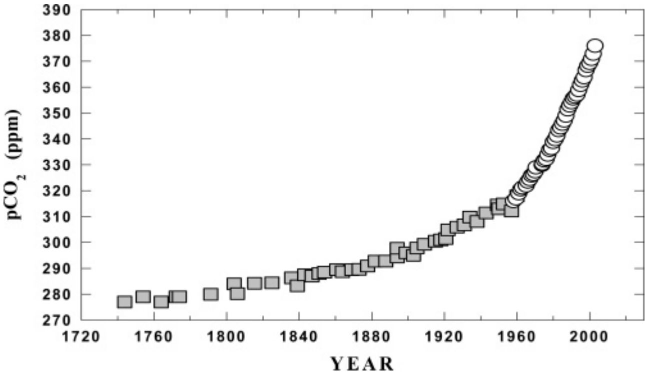

Figure 1. The increase of carbon dioxide in the atmosphere at Hawaii from atmospheric[2] sources and trapped in ice cores.[3]

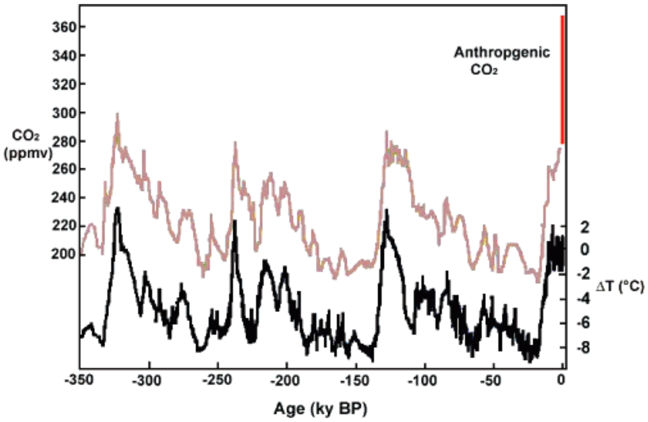

Figure 2. The variations of carbon dioxide and temperature as recorded in the Vostok ice core during the last climate cycle.[5]

and the oceans. The increase in the concentration of CO_2 in the atmosphere will increase its flux across the air–sea interface. This will result in a decrease in the pH of ocean water from the present level of 8.0 to 7.4. This decrease in the pH is expected to cause large changes in the carbonate system in the oceans. For example, organisms that make shells (pterpods, foraminifera, cocolithophores) will have difficulty precipitating $CaCO_3$; coastal corals may have difficulty growing and may eventually dissolve.[7,8] More will be said about this later in the paper.

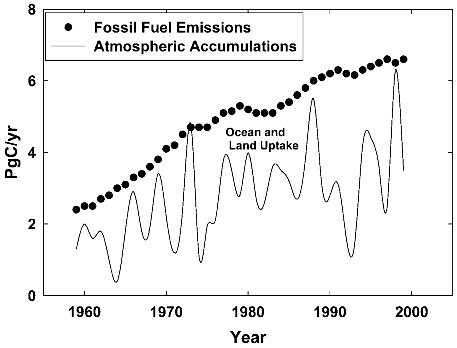

Figure 3. The annual rate of input of fossil fuel CO_2 to the atmosphere compared with the measured values. Copyright 2006 from ref 1. Reproduced by permission of Routledge/Taylor & Francis Group, LLC.

Table 1. Budget for the Global CO_2 System (1980–1989)[1]

	average perturbation (Pg of C year^{-}1)
Sources	
fossil fuel combustion	5.4 ± 0.5
deforestation	1.6 ± 1.0
total	7.0 ± 1.2
Sinks	
atmosphere	3.4 ± 0.2
oceans (models)	2.0 ± 0.8
total	5.4 ± 0.8
unaccounted for sinks	1.6 ± 1.4

1.1. Effects of Global Change

At the present time, most scientists agree that the atmospheric concentrations of greenhouse gases are increasing, and this will increase the average global temperature. Questions remain, however, to the timing and severity of the warming, its regional impacts, and the magnitude of feedback processes. Some of the expected effects include the following.

1.1.1. Sea Level Rise

The increase in the global temperature will increase the volume of seawater and subsequent sea level. Some estimate that a 3 °C change over the next 50 years will raise sea level by 80 cm or 32 in. The increase in the temperature can also melt ice on land, which would also increase the sea level. The melting of land ice on Antarctica could increase the level by as much as 70 m (~200 ft). This increase in sea level can cause serious flooding of coastal areas due to hurricanes, typhoons, and tsunamis. Although current measurements indicate that the sea level is rising, we cannot accurately predict what the levels will be in the future.

1.1.2. Extreme Weather Events

Some have speculated that if the temperatures of North Atlantic surface waters become too warm, they will not be able to sink to form North Atlantic deep water.[9] This could have large scale climate effects on the earth. Since hurricanes are known to get their energy from warm surface waters,[10] one might expect that global warming may cause an increase in the intensity of hurricanes. Sun et al.[11] have suggested that the warm waters in the Loop Current of the Gulf of Mexico caused the intensification of the recent hurricane Katrina. Scharroo et al.[12] stress that dynamic topography (depth of the thermocline), as well as surface temperature, may also play a role in agreement with the work by Shay et al.[13] and Goni and Trinanes.[14]

1.1.3. Spread of Tropical Diseases

The warmer waters in tropical regions of the earth may result in an increase in tropical diseases such as malaria and typhoid fever. This could cause some serious problems to the highly populated areas in tropical regions.

1.1.4. Species Extinctions

The increase in the temperature may cause the extinction of animals[15] and increased bleaching and dissolution of coral reefs.[8] There is present evidence that increasing temperatures in tropical regions are affecting corals.

1.1.5. Changes in Ecosystems

The increased warming of coastal waters may result in the movement of species of fish and plankton.[16] There is some evidence that the ice cover in the Arctic Ocean is thinning due to global warming. Submarine measurements made from 1957 to 1997 indicate that the Arctic ice has decreased by as much as 3 m over the last 40 years. Some predict that the ice will completely disappear in the Arctic in the summer in 50 years. There is also some evidence that the temperature of surface ocean waters have increased over the last 50 years.[17] This means that part of the increase in the temperature of the atmosphere has been used to heat up the surface waters of the oceans. Some web sites for more information on global warming are www.ipcc.ch, www.ucsusa.org, and www.iclei.org.

With these issues in mind, this review will examine the chemistry of the inorganic carbon dioxide system in natural waters with an emphasis on the oceans. I will review the thermodynamics of the CO_2 system in seawater, describe how ionic interaction models can be used to model the carbonate system, illustrate the methods that can be used to measure CO_2 parameters in seawater, explain the distribution of carbonate parameters in the oceans, and examine the input of fossil fuel CO_2 into the oceans and some of the effects of the future lowering of the pH of the oceans.

2. The Thermodynamics of the Carbonate System in Natural Waters

The thermodynamics of the carbonate system in natural waters is governed by the following equilibria

$$CO_2(g) \Leftrightarrow CO_2(aq) \qquad (1)$$

$$CO_2(aq) + H_2O \Leftrightarrow H^+ + HCO_3^- \qquad (2)$$

$$HCO_3^- \Leftrightarrow H^+ + CO_3^{2-} \qquad (3)$$

$$Ca^{2+} + CO_3^{2-} \Leftrightarrow CaCO_3(s) \qquad (4)$$

The equilibrium constants for these equilibria are given by

$$K_0 = [CO_2]\gamma(CO_2)/f_{CO_2} \qquad (5)$$

$$K_1 = [H^+][HCO_3^-]/([CO_2]\gamma(H^+)\gamma(HCO_3)/(\gamma(CO_2)\gamma(H_2O))) \qquad (6)$$

$$K_2 = [H^+][CO_3^{2-}]/([HCO_3^-]\gamma(H^+)\gamma(CO_3)/\gamma(HCO_3^-)) \qquad (7)$$

$$K_{sp} = [Ca^{2+}][CO_3^{2-}]\gamma(Ca^{2+})\gamma(CO_3^{2-}) \qquad (8)$$

The bracketed values $[i]$ are the total concentrations of species i, the values of γ_i are the activity coefficients, and $a(H_2O)$ is the activity of water (the approximate ratio of the vapor pressure of the solution divided by the value for pure water). Ocean chemists use stoichiometric constants to examine the carbonate system

$$K_1^* = [H^+][HCO_3^-]/[CO_2] = K_1\gamma(CO_2)a(H_2O)/(\gamma(H^+)\gamma(HCO_3)) \qquad (9)$$

$$K_2^* = [H^+][CO_3^{2-}]/[HCO_3^-] = K_2\gamma(HCO_3^-)/(\gamma(H^+)\gamma(CO_3)) \qquad (10)$$

$$K_{sp}^* = [Ca^{2+}][CO_3^{2-}] = K_{sp}/(\gamma(Ca^{2+})\gamma(CO_3^{2-})) \qquad (11)$$

These stoichiometric constants are a function of ionic strength, temperature, and pressure and are expressed in moles per kilogram of solution. Since the relative composition of seawater is constant,[1] the composition is expressed in terms of the mass of seasalts in a kilogram of seawater called the salinity. The salinity is a ratio of the mass of salts in a kilogram of solution. It varies from place to place due to evaporation and precipitation. The ratio of the masses of salt to solution are given in parts per thousand ($S = 35$ ppt or 35‰). Since it is difficult to measure directly the mass of salts in seawater, a Practical Salinity Scale is used to determine the salinity. The Practical Salinity is determined by measuring the conductivity ratio between seawater and a KCl solution. The practical salinity $S = 35.000$ when the conductivity is equal to a solution with 32.4356 g of KCl in a kilogram of solution at 15 °C. The evaporation salinity and the Practical Salinity are ratios of masses or conductivity and do not have units. This scale was set up so that it would be consistent with earlier estimates of salinity obtained by the evaporation of seawater. The average practical salinity of seawater is 35.0 and is related to the molal ionic strength by $I = 19.920S/(1000 - 1.0049S)$. The true or absolute salinity, which is related to the actual mass of seasalts is higher than the practical salinity ($S_T = 35.17$ ppt when $S = 35.00$) due to the loss of carbonate and borate during evaporation.[18]

These stoichiometric constants have been determined in real and artificial seawater as a function of salinity and temperature. This review will first examine the present status of the appropriate constants needed to unravel the components of the carbonate system in the oceans.

2.1. Carbonic Acid in Seawater

The earlier work on the thermodynamics of the carbonate system in seawater was reviewed by Edmond and Gieskes.[19] More recent reviews have been made by Millero in 1979[20] and 1995.[21] The modern measurements of the values of K_1^* and K_2^* of artificial seawater were made by Hansson,[22] Goyet and Poisson,[23] and Roy et al.[24] Measurements made on real seawater were made by Mehrbach et al.,[25] Mojica-Prieto and Millero,[26] and Millero et al.[27] These measurements were made as a function of temperature and salinity (see Table 2). The standard errors reported in the table are based upon fitting the measurements to the same function of temperature and salinity. The errors for pK_1^* (1σ) are 0.003 to 0.007, while the errors for pK_2^* are larger (0.002 to 0.02). The compositions of artificial and real seawaters[27] used by the various workers are given in Table 3. Hansson,[22] Goyet and Poisson,[23] and Millero et al.[27] determined pK_1^* and pK_2^* by titrating the seawater with HCl to the carbonic end point.[28,29] The constants were evaluated using computer programs using chemical models for the carbonate system in seawater.[28,30−32] The programs used in our recent studies[27] are an extension of the programs developed by Dickson[28] and Millero et al.[29] used to determine the pH, total alkalinity (TA), and total inorganic carbon (TCO_2). Roy et al.[24] made their pK_1^* and pK_2^* measurements using a Pt(s)|H_2(g,)|soln|AgCl(s)|Ag(s)|Pt(s) electrode system pioneered by Harned and co-workers[33−35] in the 1940s and by Bates and co-workers.[36−41] This method is normally more accurate and precise than making the electromotive force (emf) measurements with glass and reference electrodes but cannot be used in real seawater because Br^- interferes with the Ag−AgCl electrode. Mehrbach et al.[25] and Mojica-Prieto and Millero[26] determined pK_1^* by titrating the sample, but determined pK_2^* by stripping the CO_2 from the seawater with HCl and adding $NaHCO_3$ until the pH was constant. This pH is equal to 0.5(pK_1^* + pK_2^*). Both use a glass pH electrode to measure the emf, but Mojica-Prieto and Millero[24] also used spectrophotometric pH methods.[42]

Table 2. A Summary of the Measurement Made on the Dissociation Constants of Carbonic Acid in Real (SW) and Artificial (ASW) Seawater by Various Workers

media	salinity range	temperature range (°C)	σ(pK_1^*)[a]	σ(pK_2^*)[a]	ref
ASW	5−40	5−35	0.0070 (62)	0.010 (62)	22
SW	19−43	2−35	0.0043 (30)	0.010 (33)	25
ASW	10−50	−1−40	0.0057 (84)	0.010 (90)	23
ASW	5−45	0−45	0.0044 (80)	0.002 (80)	24
SW	12−45	5−45	0.0040 (80)	0.008 (80)	26
SW	1−50	0−50	0.0053 (466)	0.011 (459)	27

[a] The values in parentheses are the number of measurements made and the standard errors are based upon fitting the measurements to the same functional form (Millero et al.[27]).

Table 3. The Composition (mol/(kg of Soln) of Artificial Seawater Used by Various Authors

	Hansson[22]	Roy et al.[24]	Goyet and Poisson[23]	seawater[1]
NaCl	0.422	0.412598	0.409411	0.41040
Na_2SO_4	0.028	0.02824	0.028217	0.02824
KCl		0.010208	0.00908	0.00937
$CaCl_2$	0.010	0.010372	0.01033	0.01028
$MgCl_2$	0.054	0.052815	0.05327	0.05282
NaF			0.000071	0.00007
KBr			0.000823	0.00084
$SrCl_2$			0.00009	0.00009
Na_2CO_3			0.001	
$NaHCO_3$				0.00205
$B(OH)_3$				0.00042

Our recent measurements[27] on the pK^*'s in real seawater have been fitted to the equations of the form

$$\mathrm{p}K_i - \mathrm{p}K_i^0 = A_i + B_i/T + C_i \ln T \tag{12}$$

The values of pK_1^0 and pK_2^0 in pure water are taken from the early work of Harned and Bonner[35] and Harned and Scholes[34] as refit by Peiper and Pitzer[43]

$$\mathrm{p}K_1^0 = -126.34048 + 6320.813/T + 19.568224 \ln T \tag{13}$$

$$\mathrm{p}K_2^0 = -90.18333 + 5143.692/T + 14.613358 \ln T \tag{14}$$

The value of the adjustable parameters A_i, B_i, and C_i for pK_1^* are given by ($\sigma = 0.0054$ and $N = 466$)

$$A_1 = 13.4191S^{0.5} + 0.0331S - (5.33 \times 10^{-5})S^2 \tag{15}$$

$$B_1 = -530.123S^{0.5} - 6.103S \tag{16}$$

$$C_1 = -2.06950S^{0.5} \tag{17}$$

For pK_2^*, the parameters are given by ($\sigma = 0.011$ and $N = 458$)

$$A_2 = 21.0894S^{0.5} + 0.1248S - (3.687 \times 10^{-4})S^2 \tag{18}$$

$$B_2 = -772.483S^{0.5} - 20.051S \tag{19}$$

$$C_2 = -3.3336S^{0.5} \tag{20}$$

A summary of a comparison of the values of pK_1^* and pK_2^* calculated from these equations with the direct measurements of others is given in Table 4. A comparison at $S = 35$ as a function of temperature of our work with others is shown in Figures 4 and 5. It should be pointed out that all these comparisons are made on the seawater pH scale (discussed later).[44] Our measurements of pK_1^* are in good agreement with the measurements in artificial seawater of Goyet and Poisson[23] and Roy et al.[24] and real seawater of Mehrbach et al.[25] and Mojica-Prieto and Millero.[26] The early pK_1^* measurements of Hansson[22] do not agree with our studies (see Table 4). Our measurements of pK_2^* are in good agreement with the seawater results of Mehrbach et al.[25] and Mojica-Prieto and Millero,[26] but show large deviations at higher temperatures with the measurements in artificial seawater of Goyet and Poisson,[23] Roy et al.,[24] and Hansson.[22] It is

Table 4. Comparisons of the Standard Deviations of the Differences between Our Measurements and Other Authors

	σ (pK_1^*)		σ (pK_2^*)	
author	all	$S = 35$	all	$S = 35$
Mehrbach et al.[25]	0.0066	0.0036	0.013	0.010
Hansson[22]	0.021	0.011		0.11
Goyet and Poisson[23]	0.0084[a]	0.0078		0.04
Roy et al.[24]	0.0098[b]	0.0081		0.05
Mojica-Prieto and Millero[26]	0.0086[b]	0.0030	0.014	0.009

[a] Minus the measurements at 10 °C. [b] Minus the measurements at $S = 5$.

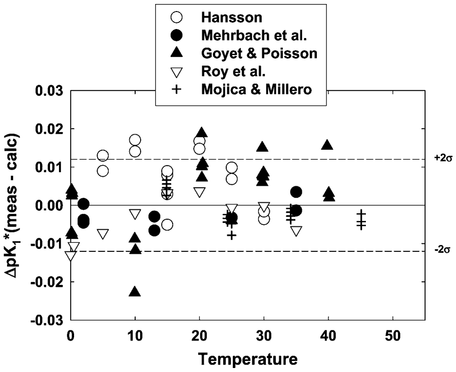

Figure 4. Comparison of the measure values of pK_1^* with those calculated from the equations of Millero et al.[27]

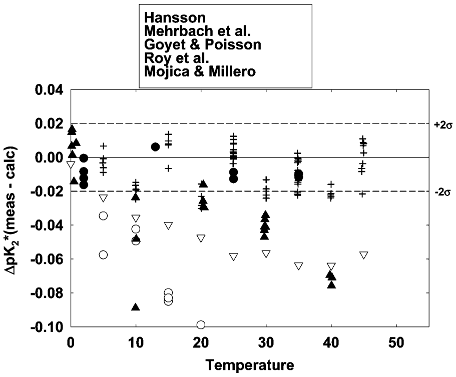

Figure 5. Comparison of the measure values of pK_2^* with those calculated from the equations of Millero et al.[27]

not clear at the present time what is causing these difference of pK_2^* in real and artificial seawater. Mojica-Prieto and Millero[26] have made measurements that suggest that the difference may be due to the borate in real seawater. Possibly this may be due to some ionic interaction of CO_3^{2-} with $B(OH)_3$ or $B(OH)_4^-$. Future work is needed to determine the exact cause of this difference in pK_2^* between real and artificial seawater. As shown by a number of laboratory[26,27,45,46] and field[47−52] measurements, the values of the carbonate constants in real seawater are more consistent with measurements of pH, TA, TCO_2, and partial pressure of CO_2 (pCO_2) in seawater and should be used in calculation of the CO_2 system in the oceans.

Laboratory[45,46] and field measurements[52] indicate that the measured values of K_2^*/pK_1^* or K_2^* determined from over-determining the system (i.e., from TA, TCO_2, and pCO_2 or pH, TA, TCO_2, and pCO_2) appear to rise with an increasing concentration of TCO_2 or pCO_2. The laboratory studies are shown in Figures 6 and 7 as a function of temperature and partial pressure of CO_2. The values of $pK_2^* - pK_1^*$ from the laboratory measurements of Lee et al.[45] and Lueker et al.[46] also show the increase in K_2^* with increasing pCO_2. The effect appears to be larger at lower temperatures. The values of $pK_2^* - pK_1^*$ as a function of temperature are linear. The spread of some of the results at a given temperature are related to changes in the values as a function of CO_2 fugacity (f_{CO_2}). The scatter is much higher in the Lueker et al.[46] data. The results of both studies at low f_{CO_2} are in reasonable agreement. The effect of f_{CO_2} on the values of $pK_2^* - pK_1^*$ is hard to explain. The data of Lee et al.[45] indicate that the dependence on f_{CO_2} is largely due to the variation of K_2^*. This tends to point to changes in the interactions of CO_3^{2-} as a function of f_{CO_2} or TCO_2. The value of pK_2^* decreases and the value of K_2^* increases as the f_{CO_2} or TCO_2 increases. The increase in K_2^* can be attributed to an increase in $\gamma(HCO_3^-)$ or a decrease in $\gamma(CO_3^{2-})$ (see eqs 9 and 10). Since the value[47] of pK_1^* is not strongly dependent on f_{CO_2}, the changes in $\gamma(HCO_3^-)$ cannot be very great. This rules out an effect of borate on pK_1, in agreement with the studies of McElligott and Byrne.[53] Model calculations of the CO_2 system in seawater[54,55] as a function of TCO_2 do not yield large changes in $\gamma(HCO_3^-)$ or $\gamma(CO_3^{2-})$. This indicates that our present understanding of the ionic interactions affecting the carbonate system in seawater is deficient.

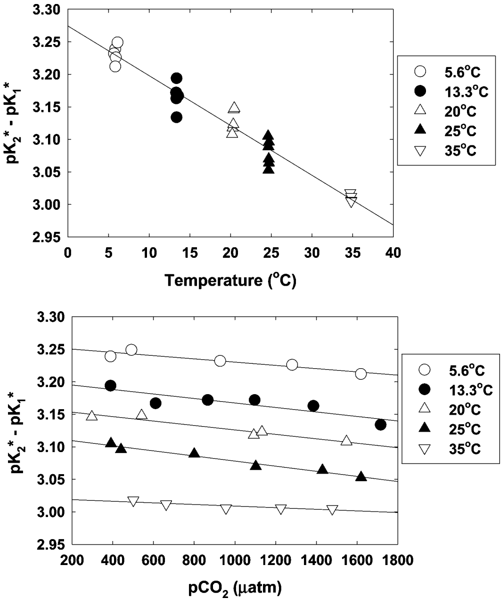

Figure 6. The values of $pK_2^* - pK_1^*$ of carbonic acid in seawater as a function of the partial pressure of CO_2.[45]

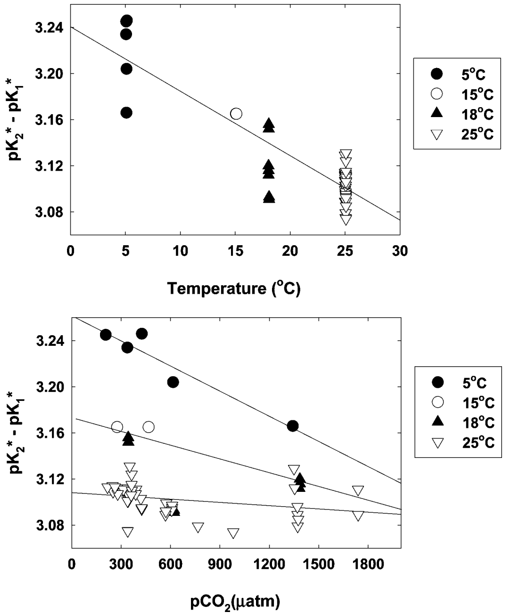

Figure 7. The values of $pK_2^* - pK_1^*$ of carbonic acid in seawater as a function of the partial pressure of CO_2.[46]

The differences in the measured and calculated values of f_{CO_2} using an input of TA and TCO_2 (which require reliable values of $pK_2^* - pK_1^*$) are shown in Figure 8 for all of the stations where all four parameters were made during the

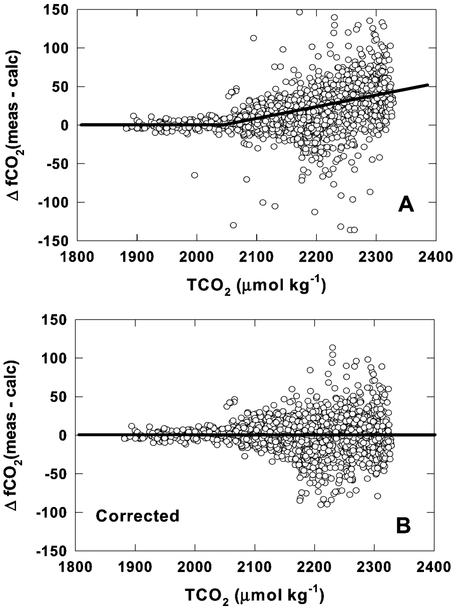

Figure 8. The differences in the calculated values of f_{CO_2} with an input of TA−TCO$_2$ compared with the measured values[52] as a function of TCO$_2$. The figure shown in panel B uses a corrected value of pK_2^* using eq 21.

World Ocean Circulation Experiment (WOCE). As found by Lee et al.,[45] an offset occurs at high f_{CO_2} for some of the cruises where f_{CO_2} was measured by the gas chromatography flame ionization detector (GC-FID) system.[56] The average difference in f_{CO_2} is 15.8 μatm. The deviations at f_{CO_2} above ∼600 μatm are greater than those at low f_{CO_2}, apparently due to changes in the values[45,52] of pK_2^* − pK_1^*. By adjusting the values of pK_2^* above TCO$_2$ = 2050 μmol kg^{-1}, it was possible to lower the deviations pCO$_2$. This resulted in the relationship

$$\mathrm{p}K_2^{\mathrm{TCO_2}} = \mathrm{p}K_2^* - 1.6 \times 10^{-4}(\mathrm{TCO_2} - 2050) \quad (21)$$

which is valid at 20 °C and at TCO$_2$ > 2050 μmol kg^{-1}. The slope is in reasonable agreement with the values determined from the laboratory measurements of Lee et al.[45] and Lueker et al.[46] ((1.2−1.9) × 10^{-4}). The values at other temperatures can be estimated from the linear fit of the results of Lee et al.[45] and Lueker et al.,[46] $\Delta(\mathrm{p}K_2^* - \mathrm{p}K_1^*)/\Delta\mathrm{TCO_2} = -2.65 \times 10^{-4} + 5.74 \times 10^{-6}t$. The input of pH and TCO$_2$ or TA is not as strongly affected by uncertainties in pK_1^* and pK_2^*. The errors in the calculated values of f_{CO_2} from an input of pH and TCO$_2$ are much lower (∼7 μatm). Thus, when using an input of pH and TCO$_2$, the correction of pK_2^* at high TCO$_2$ does not strongly influence the calculated values of f_{CO_2}. As suggested elsewhere,[52] the offset of f_{CO_2} at high TCO$_2$ calculated from an input of TA and TCO$_2$ may be due to an unknown base with an alkalinity of about 6−8 μmol kg^{-1} (see Figure 9). This is unlikely since it would have to be the same concentration in all the ocean waters studied in the laboratory and field measurements. Since the Lee et al.[45] and Lueker et al.[46] measurements were made on surface waters, one cannot attribute the effect to organic anions that one might expect to be higher in the oxygen minimum near 500−1000 m in field measurements. Further studies are needed to elucidate the cause or causes of the dependence of pK_2^* on TCO$_2$ or f_{CO_2}.

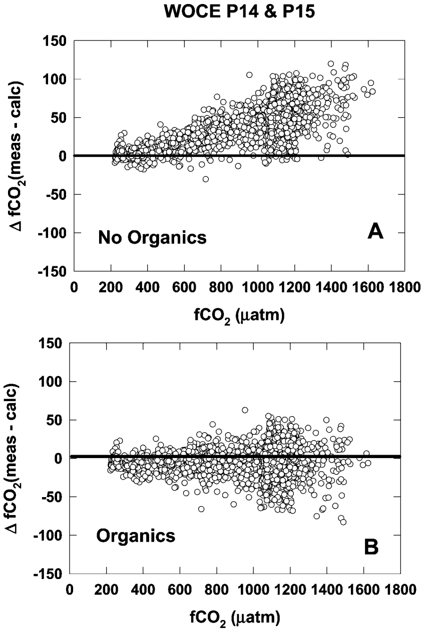

Figure 9. The differences in the measured and calculated values of f_{CO_2} from an input of TA−TCO$_2$ as a function of f_{CO_2}.[52] The figure shown in panel B uses values of TA increased by 8 μmol kg^{-1}.

2.2. Dissociation of Other Acids in Seawater

The dissociation constants for a number of other acids are needed to examine the carbonate system in seawater (see section 3). A brief review of the work on these acids is discussed below.

2.2.1. Boric Acid

Boric acid is the major component of seawater and significantly contributes to the TA of seawater. The early measurements of the dissociation of boric acid were made by Hansson.[22] He determined the boric acid constant from potentiometric titrations with a glass electrode and provided the first extensive temperature and salinity measurements in seawater. Dickson[57] used the H$_2$−Pt|AgCl−Ag electrode system to determine the dissociation of boric acid in seawater as a function of temperature and salinity. These measurements were more accurate and precise than the earlier measurements of Hansson.[22] Dickson[57] fit his measurements to the equation (mol {kg of H$_2$O}$^{-1}$)

$$\ln K_\mathrm{B} = (-8966.90 - 2890.51S^{0.5} - 77.942S + 1.726S^{1.5} - 0.0993S^2)/T + (148.0248 + 137.194S^{0.5} + 1.62247S) + (-24.4344 - 25.085S^{0.5} - 0.2474S)\ln T + 0.053105S^{0.5}T \quad (22)$$

where the standard error is 0.0042 in ln K_B. The boric acid measurements of Roy et al.[58] agree with these measurements to 0.001 in ln K_B from 0 to 50 °C and S = 35, thus confirming the validity of eq 22. The contribution of B(OH)$_4^-$ to the total alkalinity can be determined from

$$[\mathrm{B(OH)_4}^-] = B_\mathrm{T}K_\mathrm{B}/\{[\mathrm{H}^+] + K_\mathrm{B}\} \quad (23)$$

where the total boric acid in seawater B_T = 0.000412(S/35).[59]

At pH = 8, the contribution of $B(OH)_4^-$ to TA for seawater (S = 35 and T = 25 °C) is 667 mol kg^{-1}.

2.2.2. Water

The dissociation of water in seawater has been determined by a number of workers (Hansson;[22] Culberson et al.;[60] Dickson and Riley[61]). Since these results are in good agreement when adjusted to the same pH scale, they have been combined to yield (mol {kg of soln}$^{-1}$)[21]

$$\ln K_W = 148.9802 - 13847.26/T - 23.6521 \ln T + (-5.977 + 118.67/T + 1.0495 \ln T)S^{0.5} - 0.01615S \quad (24)$$

with a standard error of 0.01 in ln K_W. The contribution of OH^- to the total alkalinity is determined from

$$[OH^-] = K_W/[H^+] \quad (25)$$

At pH = 8, the contribution of OH^- for seawater (S = 35 and T = 25 °C) to the alkalinity is 1.6 μmol kg^{-1}.

2.2.3. Phosphoric Acid

The dissociation constants for phosphoric acid in seawater have been determined by a number of workers (Kester and Pytkowicz;[62] Dickson and Riley;[63] Johansson and Wedborg[64]). The values at various temperatures and salinity can be determined from[65] (mol {kg of soln}$^{-1}$)

$$\ln K_{P_1} = 115.54 - 4576.752/T - 18.453 \ln T + (0.69171 - 106.736/T)S^{0.5} + (-0.01844 - 0.65643/T)S \quad (26)$$

$$\ln K_{P_2} = 172.1033 - 8814.715/T - 27.927 \ln T + (1.3566 - 160.340/T)S^{0.5} + (-0.05778 + 0.37335/T)S \quad (27)$$

$$\ln K_{P_3} = -18.126 - 3070.75/T + (2.81197 + 17.27039/T)S^{0.5} + (-0.09984 - 44.99486/T)S \quad (28)$$

where the standard errors are 0.09, 0.03, and 0.20, respectively, in pK_{P_1}, pK_{P_2} and pK_{P_3}.

At pH = 8, the contribution of HPO_4^{2-} and PO_4^{3-} to the total alkalinity are, respectively, equal to 0.792$[P]_T$ and 2 × 0.204$[P]_T$. The maximum concentration in the Pacific Ocean (3.2 μmol kg^{-1}) gives a contribution of phosphate to TA in the Pacific of 4 μmol kg^{-1}.

2.2.4. Silicic Acid

The dissociation constant of silicic acid has not been measured in seawater. Reasonable values can be estimated from the measurements made in NaCl at the same ionic strength of seawater.[66−68] Yao and Millero[65] have used these studies to estimate the dissociation constant of $Si(OH)_4$ from ((mol {kg of H_2O}$^{-1}$)

$$\ln K_{Si} = 117.40 - 8904.2/T - 19.334 \ln T + (3.5913 - 458.79/T)I^{0.5} + (-1.5998 + 188.74/T)I + (0.07871 - 12.1652/T)I^2 \quad (29)$$

where the standard error is 0.02 in pK_{Si}. The contribution of silicate to the total alkalinity at a total silicate concentration of $[Si]_T$ can be estimated from

$$[Si(OH)_3O^-] = [Si]_T/\{1 + [H^+]/K_{Si}\} \quad (30)$$

At pH = 7.5, T = 25 °C, and I = 0.7 (pK_{Si} = 9.47), the contribution is about 0.0127$[Si]_T$. The maximum concentration of $[Si]_T$ = 170 μmol kg^{-1} in the Pacific Ocean gives a contribution to the TA of 4.6 μmol kg^{-1}.

For anoxic waters, one also has to consider the contributions of NH_3 and H_2S to the TA of seawater.

2.2.5. Hydrogen Sulfide

In anoxic waters,[65,69] it is necessary to consider the effects of HS^- and NH_3 on the total alkalinity of seawater. The dissociation constants of hydrogen sulfide in seawater can be estimated from[70] (mol {kg of soln}$^{-1}$)

$$\ln K_{1S} = 225.838 - 13{,}275.3/T - 34.6435 \ln T + 0.3449S^{0.5} - 0.0274S \quad (31)$$

The contribution of HS^- to the total alkalinity can be determined from

$$[HS^-] = [H_2S]_T/\{1 + [H^+]/K_{1S}\} \quad (32)$$

At pH = 7.5, T = 25 °C, and S = 35 (pK_{1S} = 6.98), the contribution is 0.768$[H_2S]_T$. The contribution due to HS^- can be quite large for some anoxic waters.[65,69] The $[H_2S]_T$ = 6000 μmol kg^{-1} in the Framvaren[65] gives a contribution to TA of 4600 μmol kg^{-1}. It should be pointed out that the measurements of TA in anoxic waters should be made on samples that are kept free of oxygen. This will prevent the oxidation of H_2S and loss of its effect on TA.

2.2.6. Ammonium

The dissociation constant for NH_4^+ has been determined in seawater.[71,72] These results have been adjusted to the same pH scale and fitted to the equation[65] (mol {kg of soln}$^{-1}$)

$$\ln K_{NH_4} = -6285.33/T + 0.0001635T - 0.25444 + (0.46532 - 123.7184/T)S^{0.5} + (-0.01992 + 3.17556/T)S \quad (33)$$

where the standard error is 0.01 in pK_{NH_4}. The contribution of NH_3 to the total alkalinity can be determined from

$$[NH_3] = [NH_4]_T/\{1 + [H^+]/K_{NH_4}\} \quad (34)$$

At pH = 7.5, T = 25 °C, and S = 35 (pK_{NH_4} = 9.19), the contribution is 0.020$[NH_4]_T$.

The contribution due to NH_4^+ can be quite large for some anoxic waters.[65] The $[NH_4]_T$ = 1600 μmol kg^{-1} in the Framvaren gives a contribution to TA of 32 μmol kg^{-1}.

2.2.7. Solubility of $CaCO_3$

The solubility of $CaCO_3$ in seawater has been measured by a number of workers, which is reviewed by Mucci.[73] The equations of Mucci[73] are considered to be the most reliable for pure calcite and aragonite

$$\ln K^*_{SP} = \ln K_{SP}(i) + AS^{0.5} + BS + CS^{1.5} \quad (35)$$

where

$$A_{\text{cal}} = -0.77712 + 0.0028426T + 178.34/T$$

$$B_{\text{cal}} = -0.07711$$

$$C_{\text{cal}} = 0.0041249$$

$$A_{\text{arag}} = -0.068393 + 0.0017276T + 88.135/T$$

$$B_{\text{arag}} = -0.10018$$

$$C_{\text{arag}} = 0.0059415$$

The thermodynamic values of K_{SP} for calcite and aragonite are given by

$$\ln K_{\text{SP}}(\text{calcite}) = -171.9065 - 0.077993T + 2839.319/T + 71.595 \log T \quad (36)$$

$$\ln K_{\text{SP}}(\text{aragonite}) = -171.945 - 0.077993T + 2903.293/T + 71.595 \log T \quad (37)$$

Since the natural $CaCO_3$ made by organisms frequently has concentrations of Mg incorporated in the shell,[74] the solubilities calculated from these equations may be in the upper limit. Recent studies[75] in the precipitation of $CaCO_3$ in the Bahamas demonstrate a high magnesium calcite that is two times more soluble than aragonite. More will be said about carbonate minerals in the paper by Dr. John Morse in this issue.

2.3. Effect of Pressure on the Thermodynamic Constants

It is necessary to know the effect of pressure on the various constants used to examine the *in situ* properties of the carbonate system in the ocean. It is possible to make the pressure correction two ways, from direct measurements of the constants[76] or using partial molal volume and compressibility data.[20,21,77−79] These two methods are in good agreement for the components of the carbonate system in water and aqueous solutions.[78,79] The effect of pressure on the dissociation constants of acids can be made to pressures of 1000 bar using equations of the form[78,79]

$$\ln(K_i^{\text{P}}/K_i^0) = -(\Delta V_i/(RT))P + (0.5\Delta\kappa_i/(RT))P^2 \quad (38)$$

where P is the applied pressure in bar and ΔV_i and $\Delta\kappa_i$ are the molal volume and compressibility change for the association or dissociation reactions ($R = 83.131$ mol bar deg). The values of ΔV_i and $\Delta\kappa_i$ for the ionization of acids have been fit to equations of the form for seawater of $S = 35$

$$\Delta V_i = a_0 + a_1(T - 298) + a_2(T - 298)^2 \quad (39)$$

$$\Delta\kappa_i = b_0 + b_1(T - 298) + b_2(T - 298)^2 \quad (40)$$

The coefficients in eqs 39 and 40 for the dissociation of a number of acids and the solubility of calcium carbonate are given in Table 5.[20,21,78,79] The results for carbonic and boric acid are taken from the measurements of Culberson and Pytkowicz.[76] The effect of pressure on the solubility of calcite and aragonite is from the measurements of Ingle[80] and volume estimates.[78,79] The direct measurements[76] are in good agreement with the values estimated from volume and compressibility data.[78] The effect of pressure on the dissociation constants of water, hydrogen sulfate, hydrogen sulfide, ammonia, and hydrofluoric and phosphoric acids have been estimated from molal volume and compressibility data.[78] The values of $\Delta V_{\text{Si(OH)}_4}$ and $\Delta\kappa_{\text{Si(OH)}_4}$ for silicic acid have been estimated from the values for boric acid.

Table 5. Coefficients for the Effect of Pressure on the Dissociation Constants of Acids in Seawater[21]

acid	$-a_0$	a_1	10^3a_2	$-b_0$	b_1
H_2CO_3	25.50	0.1271		3.08	0.0877
HCO_3^-	15.82	−0.0219		−1.13	−0.1475
$B(OH)_3$	29.48	0.1622	2.608	2.84	
H_2O	25.60	0.2324	−3.6246	5.13	0.0794
HSO_4^-	18.03	0.0466	0.316	4.53	0.0900
HF	9.78	−0.0090	−0.942	3.91	0.054
H_2S	14.80	0.0020	−0.400	−2.89	0.054
NH_4^+	26.43	0.0889	−0.905	5.03	0.0814
H_3PO_4	14.51	0.1211	−0.321	2.67	0.0427
$H_2PO_4^-$	23.12	0.1758	−2.647	5.15	0.09
HPO_4^{2-}	26.57	0.2020	−3.042	4.08	0.0714
$CaCO_3$(cal)	48.76	0.5304		11.76	0.3692
$CaCO_3$(arag)	35	0.5304		11.76	0.3692

2.4. Effect of Temperature on CO_2 fugacity (f_{CO_2}) in Seawater

The vapor pressure of CO_2 in seawater is a function of salinity and temperature. A number of workers have estimated the effect of temperature on the pCO_2, which is important in separating the field signals from biological effects. Gordon and Jones[81] were the first to give an empirical equation that could be used to estimate the effect of temperature on f_{CO_2}. Weiss et al.[82] proposed a more accurate equation based on the carbonic acid measurements of Hansson[22] as formulated by Millero[20] and the solubility measurements of Weiss.[83] Copin-Mantegut[84] gave an equation based on the carbonic acid constants of Dickson and Millero.[44] Goyet et al.[85] have derived an equation based on the constants of Goyet and Poisson,[23] and Millero[20] has derived an equation based on the constants of Roy et al.[24] Since the pK_1^* artificial seawater measurements of Roy et al.[24] are in reasonable agreement with measurements made in real seawater, the equations should provide a reasonable estimate for the oceans. The values of $\ln f_{CO_2}$ generated[20] from the equations of Roy et al.[24] can be fit to linear or quadratic equations of temperature. A near-linear equation with a slope of 0.0418 ± 0.001 deg^{-1} was found[20] (TA = 2400 and $TCO_2 = 2200$ μmol kg^{-1}). Similar calculations using the carbonate constants of other workers are shown in Table 6. The calculated results with the exception of the Hansson[22] and Dickson and Millero[44] values are in reasonable

Table 6. Values of d ln f_{CO_2}/dT (deg^{-1}) Calculated Using Various Thermodynamic Constants for the Dissociation of Carbonic Acid ($S = 35$ and $X = TA/TCO_2 = 1.09$, from 0 to 35 °C)

(d ln fCO_2/dT)10^2	author
Calculated from K_1 and K_2	
4.09	Hansson[22]
4.12	Mehrbach et al.[25]
4.06	Dickson and Millero[44]
4.22	Goyet and Poisson[23]
4.18	Roy et al.[24]
Measured	
4.23	Takahashi[85]
4.14	Wong[86]
4.21	Millero et al.[87]
3.8−4.1	Goyet et al.[88]

agreement with each other and the experimental measurements[85−88] of others. The effect of salinity on the slope has also been calculated by Millero[20] and measured by Wong.[86] The values of $d(\ln f_{CO_2})/dT$ (deg^{-1}) were found to be a near-linear function of salinity (17−36)

$$d(\ln f_{CO_2})/dT\ (\text{deg}^{-1}) = 0.044 - (8 \times 10^{-5})S \quad (41)$$

2.5. Effect of Temperature on pH in Seawater

The pH of seawater is normally measured at a fixed temperature (25 °C), and it is sometimes desirable to calculate the pH at the *in situ* temperature. The most reliable way to calculate the effect of temperature on pH is to use the value at a fixed temperature with another carbonate parameter such as TA or TCO_2. These experimental parameters can be used to determine the pH at another temperature using thermodynamic relationships. If only the pH is determined, one can make an estimate of the pH at another temperature using equations derived from thermodynamic equations[20,21] for waters at a fixed TA and TCO_2. Millero[20] estimated the effect of temperature on pH using the constants of Mehrbach et al.[25] and Hansson.[22] Millero[21] made similar estimates using the thermodynamic constants of Roy et al.[24] The values of pH_{sws} have been fit to linear and quadratic functions of temperature ($S = 35$, $X = TA/TCO_2 = 1.09$). A linear equation ($dpH/dT = -1.582 \times 10^{-2}$) can be used to correct for changes in pH over a small range of temperatures (10 °C). The effect of temperature on pH_{sws} is not a strong function of salinity. The values of pH_{sws} from 0 to 40 °C, $S = 30-40$, and pH from 7.5 to 8.5 can be estimated from

$$pH_T = pH_{298} + A + B(T - 298) + C(T - 298)^2 \quad (42)$$

where

$$A = -2.6492 - 0.0011019S + 4.9319 \times 10^{-6}S^2 + 5.1872X - 2.1586X^2$$

$$B = 0.10265 - 0.20322X + 0.084431X^2 + 3.1618 \times 10^{-5}S$$

$$C = 4.4528 \times 10^{-5}$$

with a standard error of 0.003 in pH.

A comparison of the calculated and measured values of dpH/dT for seawater from 0 to 35 °C is given in Table 7.

Table 7. Values of dpH/dT (deg^{-1}) Calculated Using Various Thermodynamic Constants for the Dissociation of Carbonic Acid ($S = 35$ and $X = TA/TCO_2 = 1.09$, from 0 to 35 °C)[21]

$(dpH/dT)10^2$	source	author
	Calculated from K_1 and K_2	
1.51 ± 0.02		Hansson[22]
1.52 ± 0.02		Mehrbach et al.[25]
1.51 ± 0.02		Dickson and Millero[44]
1.62 ± 0.02		Goyet and Poisson[23]
1.60 ± 0.02		Roy et al. [24]
	Measured	
(1.58−1.61) ± 0.01	certified reference material	Millero et al.[87]
(1.61−1.63) ± 0.01	gulf stream seawater	Millero et al.[87]

As for the results on the effect of temperature on f_{CO_2}, the calculated results from the constants of Goyet and Poisson[23] and Roy et al.[24] yield results that are in good agreement with the measured values.

2.6. Dissociation of Buffers in Seawater

Hansson[89] was the first to determine the dissociation constants of the buffer Tris in artificial seawater using a pH meter. Bates and co-worker[37−41] have determined the dissociation constants of a number of buffers in artificial seawater. The buffers include AP = 2-aminopyridine (pH = 6.77); Tris = 2-amino-2-hydroxymethyl-1,3-propanediol (pH = 8.07); MOR = tetrahydro-1,4-isoxazine (morpholine) (pH = 8.57); Bis = 2-amino-2-methyl-1,3-propanediol (pH = 8.50) at 25 °C. The buffers are very useful in calibrating glass electrodes and spectroscopic indicators. The buffers are prepared in artificial seawater with the protonated and unprotonated form of a given buffer (0.04 m). The pK of the seawater buffers were determined using the $H_2-Pt|AgCl-Ag$ electrode system similar to those used in dilute solutions. The original pK calculations were made on the free proton scale ($m(H^+)_F$). Millero[90] has produced equations that can be used to determine the free pH equation for Tris[38] in estuarine waters. The free proton scale is useful in examining the effect of the proton on rate processes in natural waters. The values for the pH_F for the Tris buffer are given by (molality)[90]

$$pH_F(\text{Tris}) = pK^* + (-9.73 \times 10^{-5}S + 6.988 \times 10^{-5}S^2)m_{\text{Tris}} \quad (43)$$

The value of pK* is given by

$$pK^* = -22.5575 + 3477.5496/T + 3.32867 \ln T + 2.065 \times 10^{-3}S - 1.770 \times 10^{-5}S^2 + 0.64S/T \quad (44)$$

Dickson[91,92] has redetermined the pK* and pH for the Bates buffers[29−32] on the total proton scale, pH_T. Del Valls and Dickson[93] used the hydrogen electrode system to determine pH_T of Tris buffers given by (molality)

$$pH_T(\text{Tris}) = (11911.08 - 18.2499S - 0.039336S^2)/T - 366.27059 + 0.53993607S + 0.00016329S^2 + (64.52243 - 0.084041S)\ln(T) - 0.11149858T \quad (45)$$

The pH_T on the total scale in molality can be converted to the seawater scale in moles per kilogram of solution using

$$pH_{sws} = pH_T - \log\{[H^+]_{sws}/[H^+]_T\} - \log(1 - S1.0005) \quad (46)$$

where $[H^+]_{sws}/[H^+]_T = (1 + [SO_4^{2-}]/K_{HSO_4} + [F^-]/K_{HF})/(1 + [SO_4^{2-}]/K_{HSO_4})$.

3. Methods Used To Measure Carbonate Parameters

The components of the carbonate system in natural waters can be characterized[94] by measuring at least two of the measurable parameters, pH, total alkalinity (TA), total inorganic carbon (TCO_2), and the partial pressure of CO_2. Over the past 20 years or so, a number of investigators have developed methods that can be used to measure these parameters. Some that have been used in recent years have been published in a Department of Energy (DOE) handbook.[95] This section will review some of the methods that have been and are currently being used to examine the CO_2 system in natural waters. The current estimates of the precision and accuracy of making pH, TA, TCO_2, and pCO_2 measurements are given in Table 8.[29,43,96,97] Measurements made in the laboratory can be made with a higher precison than those at sea.

Table 8. Estimates of the Analytical Precision and Accuracy of Measurements of pH, TA, TCO_2, and pCO_2

analysis	precision	accuracy	ref
pH (spectrophometric)	±0.0004	±0.002	42
TA (potentiometric)	±1 μmol kg^{-1}	±3 μmol kg^{-1}	29
TCO_2 (coulometric)	±1 μmol kg^{-1}	±2 μmol kg^{-1}	96
f_{CO_2} (infrared)	±0.5 μatm	±2 μatm	97

3.1. Methods Used To Measure pH

The pH of seawater has been measured using potentiometry[89,98−101] and spectrophotometry.[102−117] The pH measurements have been made on batch[98,101,104,110,111,113] and flowing[99,100,109,112,115,116] systems. Both are connected with the early pH methods developed by Bates.[36] The concentration of the proton, $[H^+]$, in seawater is defined differently than that in dilute solutions. The original definition of pH was related to measurements for the cell

$$H_2(Pt)|soln(X)||salt\ bridge|reference\ electrode| \quad (47)$$

The Nernst equation gives

$$E = E^0 + (2.303RT/F)pH(X) \quad (48)$$

The value of $E°$ was determined by measuring the emf (E) in NaCl−HCl solutions of known $[H^+]$ determined using conductivity. Due to this cell having a liquid junction, a practical pH scale was developed at the National Bureau of Standards (now National Institute of Standards and Technology, NIST). The NBS pH is defined by

$$pH_{NBS} = -\log a_H \quad (49)$$

Since it is not possible to determine individual activities of ions, this scale is based on a conventional definition of activity coefficients.[118] A number of buffers were developed that fixed the values of pH on this scale at a given temperature.[36] The values of pH for these buffers were determined using the Harned cell without liquid junction.

$$Pt, H_2\ (1\ atm)|HA(m), KCl(m')|AgCl, Ag \quad (50)$$

The emf of this cell is given by

$$E = E^0(AgCl, Ag) - (RT/F)\ln[m_H m_{Cl} \gamma_H \gamma_{Cl}] \quad (51)$$

The value of E^0(AgCl, Ag) is determined using the cell

$$Pt, H_2\ (1\ atm)|HCl(m)|AgCl, Ag \quad (52)$$

Since the individual cells do not always agree, the values of E^0 are adjusted by assuming that the emf for a 0.01 m solution of HCl has an $E^0 = 0.22244$ V.

The practical pH is generally determined by measuring the emf in a cell of the type

$$pH\ glass\ electrode|solution(X)|KCl\ (aq)|reference\ electrode \quad (53)$$

where the reference electrode is normally a calomel electrode. The pH_{NBS} of a solution is determined from emf measurements in solution X and the buffer. The values are determined from

$$pH(X) = pH(S) + [E(X) - E(S)]/(2.303RT/F) \quad (54)$$

In solutions of high ionic strength, this scale does not give reliable values due to differences in liquid junction potentials in the dilute buffers and the ionic media.[90,91]

As mentioned earlier, Bates and co-workers[29−32] have determined the dissociation constants of a number of buffers in artificial seawater using the Pt−H_2/AgCl−Ag cell. These buffers are very useful in calibrating glass electrodes[89,90] and spectroscopic indicators.[108,112] The buffers are made up in artificial seawater (without F and borate) using methods similar to the dilute solution buffers.[87,119−121] The more recent measurements of Del Valls and Dickson[93] gave values for the pH of Tris buffers (0.04 m) as a function of temperature and salinity given by eq 45. The Del Valls and Dickson[193] values of pH calculated from eq 45 are ∼0.0047 pH units higher than the earlier results of Ramette et al.[38] The earlier buffer measurements of Millero et al.[39] did not show an offset with the Bates Tris buffer.[29] Nemzer and Dickson[122] have shown that bottled Tris buffers made up in artificial seawater are quite stable and reproducible for over a year. This allows one to examine the precision of pH measurements throughout a cruise.

The free and total pH scales are related by

$$pH_T = pH_F - \log(1 + [SO_4^{\ 2-}]/K_{HSO_4}) \quad (55)$$

The values of K_{HSO_4} are given elsewhere.[92] This equation can be used to convert from one scale to the other when the concentration of H^+ is in moles per kilogram. Since seawater contains F^-, the pH is also determined on the seawater scale, which is defined by

$$[H^+]_{SWS} = [H^+]_F + [HSO_4^{\ -}] + [HF] \quad (56)$$

$$[H^+]_{SWS} = [H^+]_F(1 + [SO_4^{\ 2-}]/K_{HSO_4} + [F^-]/K_{HF}) \quad (57)$$

The values of K_{HF} are given elsewhere.[61] The seawater scale is related to the total and free scales by

$$pH_{SWS} = pH_T - \log\{(1 + [SO_4^{\ 2-}]/K_{HSO_4} + [F^-]/K_{HF})/(1 + [SO_4^{\ 2-}]/K_{HSO_4})\} \quad (58)$$

$$pH_{SWS} = pH_F - \log\{(1 + [SO_4^{\ 2-}]/K_{HSO_4} + [F^-]/K_{HF})\} \quad (59)$$

Using an input of TA = 2300 μmol kg^{-1} and $f_{CO_2} = 370$ μatm, the pH_T is 8.07 for seawater ($S = 35$ and $T = 25$ °C). The equivalent values on the other scales are $pH_{SWS} = 8.06$ and $pH_F = 8.18$. Since the activity of the proton in a mixed electrolyte solution is equal to the stoichiometric concentration times, the total activity coefficient calculated from Pitzer models, I prefer to use the seawater scale. The value of pH on the total scale in molality can be converted to the seawater scale in moles per kilogram of solution using eq 46.

The pH of seawater, estuarine, and brine can be determined by titrating the solution with HCl and fitting the titration using a Gran[123] technique to determine E^0 for the media.

For solutions containing SO_4^{2-} and F^-, one needs to use a chemical model that accounts for these species (more will be said about this in the next section). It is also possible to estimate the pK^* of Tris in a media of interest[124] and use that buffer to measure the pH in the media. It is better to estimate the pH of brines by these methods than by estimating the activity coefficient of the proton using the Pitzer equation.[125]

More precise measurements of the pH can be made using indicators that absorb light. The use of indicators to measure the pH of seawater has been developed by Byrne and co-workers.[102−104,106,108,111] The use of these indicators allows one to measure the pH of seawater to a precision of 0.0004 and an accuracy of 0.002. The indicator used in most seawater studies is *m*-cresol purple.[108] The pH of samples using the *m*-cresol purple (*m*CP) is determined from (molality)

$$\mathrm{pH_T} = \mathrm{p}K_{\mathrm{ind}} + \log[(R - 0.0069)/(2.222 - 0.133R)] \tag{60}$$

where K_{ind} is the dissociation constant for the indicator and R is the ratio of indicator absorbances at molar absorptivity maxima (i.e., $R = A_{578}/A_{434}$). The value of R is corrected for baseline absorbance at 730 nm over the range of temperature. Since the addition of the indicator perturbs the pH, one needs to make a correction for this effect.[106] Clayton and Byrne[108] calibrated the *m*-cresol purple indicator using Tris buffers[29] and the pH equations of Dickson.[91] They found that the indicator pK_{ind} could be represented by

$$\mathrm{p}K_{\mathrm{ind}} = 1245.69/T + 3.8275 + (2.11 \times 10^{-3})(35 - S) \tag{61}$$

where temperature is in kelvin and is valid from 20 to 30 °C and $S = 30-37$. Lee and Millero[126] used a 0.04 *m* Tris buffer[29] to measure the pK_{ind} of the indicator using a H_2-Pt|AgCl−Ag electode system.[87] At 25 °C, the buffer has a $\mathrm{pH_T}$ of 8.076 and yields spectrophotometric values of pH that agree (within 0.001) with eqs 60 and 61. These results from 0 to 40 °C were fitted to the equation ($S = 35$)

$$\mathrm{p}K_{\mathrm{ind}} = 35.9130 - 216.404/T - 10.9913 \log(T) \tag{62}$$

with the standard error of 0.001 in pK_{ind} where the constants are on the total proton scale {mol (kg of H_2O)$^{-1}$}. It should be pointed out that use of this equation makes the assumption that molar absorptivity ratios are independent of temperature. The conversion of the $\mathrm{pH_T}$ {mol (kg of H_2O)$^{-1}$} to the seawater $\mathrm{pH_{SWS}}$ {mol (kg of soln)$^{-1}$} can be made using eq 46.

Zhang and Byrne[111] have calibrated the thymol blue indicator that is frequently used to measure spectrophotometric pH in surface seawaters. Yao and Byrne[114] have used bromocresol purple and phenol red to determine the pH of freshwaters. Other workers[116,127] have developed submersible *in situ* spectrophotometric pH systems. Zhang et al.[111] have determined the effect of pressure on thymol blue indicator pK_{ind} so that it can be used to make *in situ* measurement of pH. These systems may be placed on moorings in the future to make continuous pH measurements in the surface and deep waters. Most of the present batch and flow pH measurements are made using the spectroscopic methods of Byrne and co-workers.[102−104,106,108,111] Once the indicator is calibrated with a buffer of known pH, it does not need to be recalibrated for use at sea.

Finally, it should be pointed out that the comparisons of titration derived and spectroscopic pH[26] have been shown to be in good agreement (±0.002) over a wide range of salinity and temperature. Recent laboratory spectroscopic measurements by Millero's and Byrne's groups on the *m*-cresol purple indicator in Tris 0.04 *m* prepared by Dickson gave values of pH that agreed with the assigned value of Del Valls and Dickson.[93] Thus, spectroscopic pH measurements using *m*-cresol purple[108] do need a correction of 0.0047.

3.2. Methods Used To Measure Total Alkalinity

The total alkalinity of seawater is defined as the concentration of all the bases that can accept H^+ when a titration is made with HCl to the carbonic acid end point. The value of TA is given by[28]

$$\mathrm{TA} = [\mathrm{HCO_3}^-] + 2[\mathrm{CO_3}^{2-}] + [\mathrm{B(OH)_4}^-] + [\mathrm{OH}^-] - [\mathrm{H}^+] + [\mathrm{SiO(OH)_3}^-] + [\mathrm{MgOH}^+] + [\mathrm{HPO_4}^{2-}] + 2[\mathrm{PO_4}^{3-}] \tag{63}$$

For most seawaters, $[HCO_3^-]$, $[CO_3^{2-}]$, and $[B(OH)_4^-]$ are the most important bases. For anoxic waters, HS^- and NH_3 can also contribute to the total alkalinity.

The carbonate alkalinity, A_C, is defined by

$$A_C = [\mathrm{HCO_3}^-] + 2[\mathrm{CO_3}^{2-}] = \mathrm{TA} - \sum \mathrm{bases} \tag{64}$$

where $\sum$bases is the sum of all the bases that can accept a proton when the solution is titrated to a pH of ∼4.5. This may include organic bases[52,128] and bacteria[129] in the waters.

The TA for seawater is determined by titrating a given amount of seawater to the carbonic acid end point. The titration is followed by measuring the emf of a glass pH and reference electrode or measuring another property such as the heat of the reaction.[130] A full potentiometric titration can be used to determine E^*, pK_1^*, pH, TA, and TCO_2 using a chemical model for seawater by a computer.[28,29,31,131−136] A series of iterations are carried out to fit the titration curve. The increased accuracy in determining TA in seawater has greatly improved due the development of certified reference material by Dickson.[137] Laboratory measurements[28,112,126] with titration systems can be made with a precision of ±1 μmol kg^{-1}, while field measurements[138] have a precision of ±2 μmol kg^{-1} and accuracy of ±3 μmol kg^{-1}.

The TA of seawater can be determined by a number of other techniques.[138−144] Anderson and Robinson[139] developed the one point potentiometric method to determine TA. Culberson et al.[140] made some improvements in the method. Graneli and Anfalt[141] developed an automatic phototitrator to measure TA. Byrne and co-workers[142,143] developed spectroscopic methods that can be used to determine TA. Roche and Millero[144] developed a continuous flowing spectrophotometric method to measure TA. A number of recent studies of TA have been made in the Mediterranean Sea,[145] Bahama Banks,[146,147] Cariaco Trench,[148] Red Sea and Persian Gulf,[149] Sargasso Sea,[150] Indian Ocean,[151] Florida Bay,[152] Galapagos Islands,[153] Arabian Sea,[154] Canary Islands,[155] and Black Sea[69,156] (to mention a few areas). The TA and TCO_2 measurements made on JGOFS (Joint Global Ocean Flux Studies), WOCE (World Ocean Circulation

Experiment), and the present CLIVAR (Climate Variability) Repeat Hydrography programs are available at CDIAC (Carbon Dioxide Information Analysis Center, http://cdiac.esd.ornl.gov/oceans).

Recently, Kim et al.[129] examined the effect that plankton, bacteria, and particulate organic carbon, PIC ($CaCO_3$), have on the TA in some coastal waters. They found that the effect of PIC and plankton was not significant (<2 μmol kg^{-1}). Bacteria however contribute 2−5.5 μmol kg^{-1} to TA. The effect of plankton was similar to what we found during the iron enrichment experiments (IronEx I, II) and Southern Ocean Iron Experiment (SOFeX) studies inside and outside the Fe enriched patches. During IronEx I,[153] we did find changes as high as 10 μmol kg^{-1} in the bottle experiments a few days after the addition of Fe. On our recent Atlantic A16 cruises, we measured the TA on filtered (0.2 μm) and unfiltered surface and deep waters. We found maximum differences of 4 μmol kg^{-1} independent of depth. On measurements made on the Pacific P16 cruises, we found average differences between filtered and unfiltered samples of ±2 μmol kg^{-1}. Thus, filtration is not necessary when making TA measurements on open ocean samples.

3.3. Methods Used To Measure Total Inorganic CO_2

The total inorganic carbon dioxide (TCO_2) is defined by

$$TCO_2 = [CO_2{}^*] + [HCO_3{}^-] + [CO_3{}^{2-}] \qquad (65)$$

where $CO_2{}^* = CO_2 + H_2CO_3$. It can be determined from potentiometry (described in the last section), coulometry, and spectrometry. The latter two methods are based on the acidification of seawater with H_3PO_4, followed by stripping the CO_2 out of the solution with N_2 and the subsequent measuring of the emitted CO_2. The SOMMA (single-operator multiparameter metabolic analyzer) system used in most recent studies was developed by Johnson et al.[157−161] The carbon dioxide stripped from seawater is collected in a solution containing ethanolamine, which reacts with the CO_2, which is then determined by a coulometric titration. The coulometric system is calibrated with gas loops with pure CO_2 and has a precision of ±1 μmol kg^{-1}. The spectrometric method utilizes a nondispersive infrared analyzer[162] as a detection of the CO_2. This system is fully automated and can be used to measure batch samples or to map the TCO_2 in surface water.[163] The system was recently modified and used in the recent SOFeX experiments.[117] The system can make measurements every 10 min with a precision of 0.1% on a sample volume of 5 cm^3. Both systems are calibrated using certified reference material (CRM) throughout a cruise.[164] The CRM measurements normally agreed with the assigned values to ±2 μmol kg^{-1}.

Recently a sensitive IR absorption system has been developed that can make very accurate and precise measurements of CO, CO_2, CH_4, C_2H_2, and NH_3 gases.[165] The system uses an off-axis trajectory of a laser beam through the cell to yield an optical path length of several kilometers without significant unwanted cavity resonances. The minimum detectable absorption of $\sim 1.4 \times 10^{-5}$ can be determined over an effective optical path of 4.2 km. The instrument may be used in the future to make sensitive measurements of ^{14}C and CO_2 in natural waters. The system could be adapted to replace the IR detectors presently being used for measurements of TCO_2 and pCO_2 in ocean waters.

3.4. Methods Used To Measure Partial Pressure of CO_2 (pCO_2)

The continuous partial pressure of CO_2 of surface water is measured using an equilibration system. Measurements are made on air equilibrated with the seawater in a shower head. The first equilibrator used to measure large areas of the oceans was developed by Weiss.[166] He analyzed the CO_2 using a flame ionization chromatography system and a 10 L shower head. Goyet and Peltzer[167] and our system use a 4 L shower to equilibrate the seawater with air. Most of the present systems analyze the CO_2 gas using an IR detector[97,163,167−170] and use two or three standard gases to calibrate the system every hour or so. Frequent measurements of the pCO_2 of air are also made so that the flux of CO_2 between the air and surface waters can be determined. A number of the systems being used by various groups have been compared at sea.[171] Merlivat and co-workers[172−173] have used an optical sensor to measure the pCO_2 in surface waters using the CARIOCA bouy. DeGrandpre et al.[174] and Cai and co-workers[175,176] developed pCO_2 systems to study surface waters. Friederich et al.[177] have developed a system using an IR detector that can be put on moorings. Batch measurements of pCO_2 in deep waters have been described that used an IR detector[168] and gas chromatography.[56] Both systems equilibrate the sample with a standard gas and measure the head space. Standard gases are used to calibrate the pCO_2 systems. The precision of the continuous surface water f_{CO_2} measurements is estimated to be ±1 μatm.

3.5. Internal Consistency

By measuring two or more of the CO_2 parameters, it is possible to calculate those not measured. This fact allows one to examine the internal consistency of the measurements.[178] For example, if parameters pCO_2, TA, and TCO_2 are measured, one can determine the ratio of K_1^*/K_2^* for carbonic acid in the solution. If all of the four parameters are measured, it is possible to determine pK_1^* and pK_2^* in the solution. One can also use two of the parameters, pH and TCO_2, to determine the other two, TA and pCO_2. These calculated values can be compared with the measured values and act as a test of the internal consistency of the measurements. These kinds of calculations have been used by a number of workers to examine the reliability of field measurements. One can also use this analysis to examine the propagation of error due to the measured parameters and the stoichiometric constants.[179] The uncertainties due to experimental errors (Table 8) in the input parameters are given in Table 9. An input of TA−TCO_2 gives the largest errors in the calculated values of pH and f_{CO_2}. The selection of the appropriate two parameters gives uncertainties in pH (0.003), TA (3 μmol kg^{-1}), TCO_2 (3 μmol kg^{-1}), and f_{CO_2} (2

Table 9. Estimated Probable Errors in the Calculated Parameters of the Carbonate System Using Various Input Measurements

input	pH	TA (μmol kg^{-1})	TCO_2 (μmol kg^{-1})	f_{CO_2} (μatm)
pH−TA			±3.8	±2.1
pH−TCO_2		±2.7		±1.8
pH−f_{CO_2}		±21	±18	
f_{CO_2}−TCO_2	±0.0025	±3.4		
f_{CO_2}−TA	±0.0026		±3.2	
TA−TCO_2	±0.0062			±5.7

μatm) that are the same order of magnitude as the experimental errors. The uncertainty due to errors in the values of pK_1^* and pK_2^* are shown in Table 10. An input of TA−TCO_2 causes the largest error of 0.006 in pH and 6 μatm in f_{CO_2}. This uncertainty is due to errors in pK_2^*. An input of pH−TA or pH−TCO_2 gives the best estimates for both pH and f_{CO_2} because they do not require reliable estimates of pK_2^*. Direct measurements should be made if one requires parameters with a smaller uncertainty than can be calculated.

Table 10. Estimated Probable Errors in the Calculated Parameters of the Carbonate System Caused by Errors in pK_1^* (0.002) and pK_2^* (0.005) Using Various Input Measurements

input	parameter	pK_1^*	pK_2^*	both[a]	exptl error
pH−TA	f_{CO_2} (μatm)	1.5−7.6	0.9−1.3	1.7−7.7	2.1
pH−TCO_2		1.5−6.6	0.5−0.6	1.6−6.6	1.8
TA−TCO_2		1.4−4.7	2.5−8.2	2.9−9.4	5.7
f_{CO_2}−TCO_2	pH	0.002	0.0004	0.002	0.0025
f_{CO_2}−TA		0.002	0.0006	0.002	0.0026
TA−TCO_2		0.0003	0.005	0.004	0.0062
pH−TA	TCO_2 (μmol kg^{-1})	0.1−0.2	2.4−0.9	2.4−0.9	3.8
f_{CO_2}−TA		1.0−0.4	1.8−0.8	2.1−0.9	3.2
pH−TCO_2	TA (μmol kg^{-1})	0.04−0.2	2.6−0.8	2.6−0.8	2.7
f_{CO_2}−TCO_2		1.3−0.4	2.3−0.7	2.6−0.8	3.4

[a] The total error is the square root of the sum of the squared errors due to pK_1^* and pK_2^*.

4. Modeling the Ionic Interactions for the Carbonate System

Most of the recent ionic interaction models that can be used to estimate activity coefficients of solutes in natural waters are based on the specific interaction model developed by Pitzer.[180] The model was first used by Whitfield[181−183] to estimate the activity coefficients of a number of ions in a simple seawater solution (NaCl + $MgSO_4$). Weare, Møller, and co-workers[184−190] and others[54,55,191−197] have extended the model for the major components of seawater. The formation of complexes of divalent[55] and trivalent metals[197] with OH^-, HCO_3^-, CO_3^{2-}, $H_2PO_4^-$, and HPO_4^{2-} has been added to the model at 25 °C. The model was expanded from 0 to 50 °C[54,55] using heat capacity data.[198,199]

Our current formulation of the Pitzer model[55] is based on the earlier work of Weare et al.[184−190] and Pitzer et al.[180,192,200−213] The model can be used to make reliable estimates of the activity coefficients of the major components (Na^+, K^+, Mg^{2+}, Ca^{2+}, Cl^-, OH^-, SO_4^{2-}) of natural waters over a wide range of temperatures (0 to 250 °C) to high ionic strengths (<6 *m*). We recently[195] have extended the model over this same temperature range by adding $NaHCO_3$, Na_2CO_3, and CO_2 Pitzer parameters. The model from 0 to 50 °C[54,55] can be used to make reliable estimates for the components of the carbonate system in solution of the major components of seawater (Na, K, Mg, Ca, Sr, F, Cl, Br, HCO_3, CO_3, $B(OH)_4$, CO_2, $B(OH)_3$, SO_2, H_2S, NH_3). The model can estimate the pK^* of a number of acids (H_2CO_3, H_2O, HF, H_2SO_4, H_2SO_3, NH_4^+, H_2S, H_3PO_4) needed to analyze the carbonate system in natural waters 0 to 50 °C and ionic strengths from 0 to 6 *m*.[54,55,195,214] Much of the needed parameters were determine from the behavior of acids in NaCl solutions with added Ca^{2+} and Mg^{2+}, which form strong interactions with the acid anions (F^-, OH^-, HCO_3^-, CO_3^{2-}, HS^-, $B(OH)_4^-$, HSO_3^-, SO_3^{2-}).[191,195,214−243] Copies of the Pitzer model that we have developed in Miami are available on request (fmillero@rsmas.miami.edu). Plummer et al.[244] have developed a Pitzer program that can be used to determine the solubility of minerals in natural waters.

The general equation of the Pitzer equations used to estimate the activity coefficients of ions is given by

$$\ln \gamma_i = \mathrm{DH} + \sum_{ij} m_i m_j B_{ij}^{\gamma} + \sum_{ijk} m_i m_j m_k C_{ijk}^{\gamma} \quad (66)$$

where DH is some form of the Debye−Hückel limiting law. The B_{ij}^{γ} and C_{ijk}^{γ} parameters are related to the binary (ions *i* and *j*) and ternary (ions *i*, *j*, and *k*) interactions and can be a function of ionic strength. Binary solutions are used to estimate the Pitzer parameters ($\beta_{MX}^{(0)}$, $\beta_{MX}^{(1)}$, and C_{MX}^{ϕ}), which are used to fit the activity coefficients of individual electrolytes (MX). A $\beta_{MX}^{(2)}$ term is needed for 2−2 electrolytes. The $\beta_{MX}^{(0)}$ and $\beta_{MX}^{(1)}$ parameters account for the binary interactions of the ionic components of each electrolyte (Na−Na, Cl−Cl, and Na−Cl, for NaCl) in the solution as a function of ionic strength.[213,245] The C_{MX}^{ϕ} term accounts for the triplet interactions (Na−Cl−Na, Cl−Na−Cl) in the solution. Ternary solution properties of like sign ions in mixed electrolytes (NaCl + $MgCl_2$) are used to examine the interactions of cations (Θ_{Mg-Na}), anions (Θ_{Cl-SO_4}), and triple ions ($\Psi_{Na-Mg-Cl}$).[202,213,245] The Pitzer parameters for binary and ternary solution can be used to determine reliable activity coefficients for ions in mixed electrolyte solutions over a wide range of conditions. The activity coefficients for cation M and anion X can be calculated from

$$\begin{aligned}\ln \gamma_M = {} & Z_M{}^2 f^{\gamma} + 2\sum_a m_a (B_{Ma} + EC_{Ma}) + Z_M{}^2 R + \\ & Z_M S + \sum_c m_c \left(2\Theta_{Mc} + \sum_a m_a \Psi_{Mca}\right) + \\ & \sum_a \sum_{a'} m_a m_{a'} \Psi_{aa'M} + \sum_c m_c 2^E\Theta_{Mc} + Z_M{}^2 R_1 + Z_M{}^2 R_2\end{aligned} \quad (67)$$

$$\begin{aligned}\ln \gamma_X = {} & Z_X{}^2 f^{\gamma} + 2\sum_c m_c (B_{Xc} + EC_{Xc}) + Z_X{}^2 R + Z_X S + \\ & \sum_a m_a \left(2\Theta_{Xa} + \sum_c m_c \Psi_{Xac}\right) + \sum_c \sum_{c'} m_c m_{c'} \Psi_{cc'X} + \\ & \sum_a m_a 2^E\Theta_{Xa} + Z_X{}^2 R_1 + Z_X{}^2 R_2\end{aligned} \quad (68)$$

The values of *R*, *S*, R_1, and R_2 in eqs 67 and 68 are given by

$$R = \sum_c \Sigma_a m_c m_a B'_{ca} \quad (69)$$

$$S = \sum_c \sum_a m_c m_a C_{ca} \quad (70)$$

$$R_1 = \sum_c \sum_{c'} m_c m_{c'} {}^E\Theta'_{cc'} \quad (71)$$

$$R_2 = \sum_a \sum_{a'} m_a m_{a'} {}^E\Theta'_{aa'} \quad (72)$$

The f^{γ} is the Debye−Hückel limiting law, Z_i is the charge of M or X, *c* and *a* are the cations and anions in the solution. The parameters B_{Mc}, B_{Xa}, C_{Mc}, and C_{Xa} are a function of the ionic strength

$$B_{Mc} = \beta_{Mc}^{(0)} + (\beta_{Mc}^{(1)}/(2I))[1 - \exp(-2I^{0.5})(1 + 2I^{0.5})] \quad (73)$$

$$B'_{Mc} = (\beta_{Mc}^{(1)}/(2I^2))[-1 + \exp I - 2I^{0.5}](1 + 2I^{0.2} + 2I) \quad (74)$$

$$C_{Mc} = C^{\phi}_{Mc}/(2|Z_M Z_X|^{0.5}) \tag{75}$$

The parameters Θ_{Mc} and Θ_{Xa} are related to the interaction of cations M and c and anions X and a. The $\Psi_{cc'X}$ and $\Psi_{aa'M}$ are related to the triplet interactions of c and c' with X and a and a' with M.

Pitzer activity coefficient parameters for a number of electrolytes important in natural systems (HCl, NaCl, KCl, NaOH, $MgCl_2$, $CaCl_2$, Na_2SO_4, K_2SO_4, $MgSO_4$, $CaSO_4$) are known[245] over a wide range of temperatures (0−250 °C). Data over a more limited temperature range (0−50 °C) determined using enthalpy and heat capacity data[198,199] are also available.[55,245] The interaction parameters for like charge ions (Θ_{MN} and Θ_{XY}) and triplet interactions ($\Psi_{cc'X}$ and $\Psi_{aa'M}$) of cations c and c' with X and anions a and a' with M are also available.[55,202,203,245]

It should be pointed out that the Θ and Ψ terms are normally not large and do not contribute much in dilute solutions.[191] The values of Θ_{MN} and Ψ_{MNX} are model dependent since they require known values of $\beta^{(0)}_{MX}$, $\beta^{(1)}_{MX}$, $\beta^{(2)}_{MX}$, C^{ϕ}_{MX}, $\beta^{(0)}_{NX}$, $\beta^{(1)}_{NX}$, $\beta^{(2)}_{NX}$, and C^{ϕ}_{NX} and depend on the experimental data used for their evaluation (activity or solubility). It is thus important to take care in mixing the parameters determined by various workers.

For dilute solutions the activity of neutral solutes (N) in electrolyte solutions are determined from the ratio of the solubility in a salt solution (S) and in water (S^0)

$$\gamma_N = S^0/S \tag{76}$$

The ionic strength dependence is given by[213,246]

$$\ln \gamma_N = 2\sum_c m_c \lambda_{Na} + 2\sum_a m_a \lambda_{Nc} + \sum_a m_c m_a \zeta_{Nca} \tag{77}$$

The equation considers the interaction of the nonelectrolyte N with the cations c (λ_{Nc}) and anions a in the solution (λ_{Na}) at a molality m_c and m_a. For a concentrated solution, a second-order term is needed to account for the interactions of N with cations and anions ($\sum_a m_c m_a \zeta_{Nca}$).

One can use the Pitzer model to estimate all the values of K^*_{HX} needed to study the carbonate system in natural waters from 0 to 50 °C.[54,55] The equilibrium constants for the acids in a given media can be estimated from

$$\ln K^*_{HX} = \ln K_{HX} - \ln \gamma(H^+) - \ln \gamma(X^-) + \ln \gamma(HX) \tag{78}$$

The values of ln K_{HX} in pure water as a function of temperature can be estimated from

$$\ln K = A + B/T + C \ln T + DT \tag{79}$$

The coefficients for eq 79 are given in Table 11.[13,20,33,34,43,61,70,73,241,245,247−254] The stability constants for the ion complexes needed in the program are determined from

$$pK = A + B/T + CT \tag{80}$$

The coefficients are given in Table 12.[54] The activity coefficients of the proton (H^+), the acid (HX), and the anion (X^-) can be estimated from the Pitzer equation from 0 to 50 °C. Comparisons of the measured and calculated values of pK for a number of acids are given in Table 13. The estimates are in good agreement with the measured values.

Table 11. Coefficients for the Thermodynamic Constants for the Dissociation of Acids and Solubility of Gases in Water Fit to Eq 79

acid	A	B	C	D	ref
HF	−12.641	1590.2			6
H_2S	225.8375	−13275.324	−34.64354		70
H_2O	148.9802	−13847.26	−23.6521		247[a]
$B(OH)_3$	148.0248	−8966.901	−24.4344		248, 249[a]
HSO_4^-	141.411	−4340.704	−23.4825	0.016637	241
NH_4^+	−0.25444	−6285.33		0.0001635	250
H_2CO_3	290.9097	−14554.21	−45.0575		34[b]
HCO_3^-	207.6548	−11843.79	−33.6485		33[b]
H_2SO_3	554.963	−16700.1	−93.67	0.1022	251
HSO_3^-	−358.57	5477.1	65.31	−0.1624	251
H_3PO_4	115.54	−4576.7518	−18.453		252
$H_2PO_4^-$	172.1033	−8814.715	−27.927		253
HPO_4^{2-}	−18.126	−3070.75			13
CO_2	−60.2409	9345.17	18.7533		34[b]
SO_2	−142.679	8988.76	19.8967	−0.0021	251
aragonite	303.5363	−13348.09	−48.7537		78
calcite	303.1308	−13348.09	−48.7537		78

[a] Refit by Millero.[20] [b] Refit by Peiper and Pitzer[43]

Table 12. Coefficients for the Formation of Ion Pairs in Water Fitted to Eq 80[54]

ion pair	A	B	C
$MgOH^+$	3.87	−501.6	
MgF^+	3.504	−501.6	
CaF^+	3.014	−501.6	
$MgCO_3$	1.028		0.0066154
$CaCO_3$	1.178		0.0066154
$SrCO_3$	1.028		0.0066154
$MgH_2PO_4^+$	1.13		
$CaH_2PO_4^+$	1.0		
$MgHPO_4$	2.7		
$CaHPO_4$	2.74		
$MgPO_4^-$	5.63		
$CaPO_4^-$	7.1		

Table 13. Comparison of Measured and Calculated Values of pK* (Total Scale) in Seawater at 25 °C and S = 35

acid		meas	calcd	D	ref (meas)
H_2CO_3	pK^*_0	1.547	1.546	0.001	83
	pK^*_1	5.837	5.832	0.005	25
		5.850		0.018	22
		5.849		0.017	44
		5.846		0.014	23
		5.847		0.015	24
	pK^*_2	8.955	8.954	0.001	25
		8.942		−0.012	22
		8.945		−0.009	44
		8.919		−0.035	23
		8.915		−0.039	24
NH_4^+		9.256	9.235	0.021	65
H_2O		13.211	13.218	−0.007	21
H_2S	pK^*_1	6.510	6.533	−0.023	70
HF		2.611	2.552	0.059	6
H_2SO_3	pK^*_1	1.58	1.477	0.103	234
	pK^*_2	6.13	6.159	−0.029	234
$B(OH)_3$		8.582	8.596	−0.014	57
H_3PO_4	pK^*_1	1.591	1.605	−0.014	65
	pK^*_2	5.955	6.003	−0.048	65
	pK^*_3	8.783	8.746	0.037	65
HSO_4^-		0.983	0.993	−0.010	92
calcite		6.367	6.397	−0.030	78
aragonite		6.186	6.221	−0.035	78

We recently[195] have determined equations for pK_1 and pK_2 for carbonic acid from 0 to 250 °C using literature values from 0 to 50 °C and the Patterson et al.[255,256] data from 50 to 250 °C. The values of pK_0 for the solubility of CO_2 in water has also been estimated[195] from the results of Duan and co-workers.[257,258]

The effect of pressure on activity coefficients in a solution can be determined from[77,78]

$$\ln (\gamma_{\pm}^{P}/\ln \gamma_{\pm}^{0}) = (\bar{V} - \bar{V}^0)P/(\upsilon RT) - 0.5(\bar{K} - \bar{K}^0)P^2/(\upsilon RT) \quad (81)$$

where P is the applied pressure, R and T have their normal meaning, υ is the number of ions in a given electrolyte, and $\bar{V}$ and $\bar{K}$ are the partial molal volume and compressibility (the parameters with asuperscript zero are the values in pure water). Tabulations of the partial molal volume and compressibility of ions in pure water are given elsewhere.[77,245,259−261,269] The values of $\bar{V}$ and $\bar{K}$ in a given ionic media can be estimated from the apparent molal volume and compressibility of electrolytes.[245] A number of workers have fit the volume properties of electrolytes to the Pitzer equations.[262−271] Connaughton,[266] Monnin,[267,268] Krumgalz et al.[269,270] and Pierrot and Millero[271] have used the Pitzer equations to estimate the properties of mixed electrolyte solutions. The ionic values of $\bar{V}_i^0$ and the Pitzer parameters for the major seasalts are available[271] at 25 °C and have been summarized in Table 14. The Pitzer parameters that are related to the effect of pressure on the activity coefficient parameters are given by

$$\beta^{(i)V} = (\partial \beta_{ca}^{(i)}/\partial P)_T \quad (82)$$

$$C^V = (\partial C_{ca}^{(i)}/\partial P)_T \quad (83)$$

$$C_{ca}^V = (\partial C_{ca}/\partial P)_T = (\partial C_{ca}^{\phi}/\partial P)_T/(2|z_c z_a|^{1/2}) \quad (84)$$

The addition of these parameters for the major seasalts makes it possible to yield reasonable estimates of the effect of pressure on the major components of seawater.

5. Distribution of Carbonate Species in the Oceans

The distribution of the various components of the CO_2 system in the oceans has been studied by many workers. Skirrow[272] has reviewed much of the earlier work. The earlier 1970s studies of the carbonate system during the Geochemical Ocean Section Study (GEOSEC) program have yielded the first global look of the CO_2 system. The published atlas gives detailed profiles. The more recent Joint Global Ocean Flux Study (JGOFS) CO_2 measurements made in the 1990s as part of the World Ocean Circulation Experiment (WOCE) hydrographic program present a much more reliable and global picture of the CO_2 system that will serve as a benchmark for the future. These synthesized results are available on the web (http://cdiac.esd.ornl.gov) and will be discussed in this section. The distribution of the CO_2 parameters is discussed in this section. In recent years, a number of workers have studied the CO_2 system in coastal waters, estuaries, and rivers. This includes studies in the coastal waters[273−279] of North America,[280−297] South America,[298−301] Europe,[302−305] Asia,[306−313] Africa,[314−318] and Antarctica.[319−322] Studies have also been made on a number of rivers in Europe.[323−330] These trends will continue in the future because of the interest in how coastal waters contribute to the global carbon budget.[273−275]

Table 14. Compilation of Volumetric Pitzer Parameters of Salts Obtained by Different Authors at 25 °C[55]

electrolyte	$\bar{V}^0$	$10^5\beta^{(0)V}$	$10^5\beta^{(1)V}$	$10^2\beta^{(2)V}$	10^6C^V	m (max)
HCl	17.824	0.055039	−0.74008		0.023984	17.48
NaCl	16.68	1.2414			−0.662	6
	16.62	1.2335	0.43543		−0.6578	6
	16.68	1.234			−0.645	5.5
	16.58	1.14	1.15		−0.555	4
	16.681	1.255			−0.688	6
Na_2SO_4	11.48	4.9790	16.1		−2.308	1.5
	11.487	4.466	18.02		−1.313	1.47
	11.787	5.308	12.34		−2.794	2.2
	11.776	5.325	12.932		−2.914	1.5
$NaHCO_3$	23.181	−1.162	17.8			1
Na_2CO_3	−6.48	5.98	8.16		−3.25	1.7
NaBr	23.479	0.76074	0.95252		−0.34908	8
$NaB(OH)_4$	20.673					
NaF	−2.34	2.32766				
KCl	26.91	1.55	−0.11		−1.37	4.5
	26.87	1.3949	0.235		−0.87	4.7
	26.93	1.5030			−1.023	4.5
	26.848	1.2793	0.89477		−0.7131	4.7
K_2SO_4	32.167	3.348	23.8			0.65
	31.98	2.14	28.85			0.4
	32.05	−2.3199	36.414		29.11	0.7
$KHCO_3$	33.448	−1.9568	21.604			1.0
	33.371	−0.2705	16.95			1.0
	34.34	7.0283	−8.4507		−16.738	1.0
K_2CO_3	14.054	3.4471	18.043		−0.824	5.6
	12.327	3.0758	33.269		−0.6468	7.6
KBr	33.746	1.066	0.8337		−0.7017	5.6
	33.689	1.0259	1.1021		−0.6641	5.6
$KB(OH)_4$	30.94					
KF	7.76	2.7663			−6.065	
$MgCl_2$	14.4	1.6992	−7.44		−0.56748	6
	14.395	1.844	−8.46		−0.6887	5.8
	14.16	1.78	−6.38		−0.643	
	13.734	1.3833			−0.357	
	14.083	1.6933	−5.2068		−0.5698	5.8
$MgSO_4$	−7.48	4.323	19.636	1.3405	0.86	2.4
	−7.485	5.137	13.19	1.495		2.4
	−7.839	4.9329	14.838	1.679	0.192	2.9
	−6.551	4.2551	18.439	0.8889	1.3198	2.5
$Mg(HCO_3)_2$	27.402					
$MgCO_3$	−25.44					
$MgBr_2$	27.998	−0.0468	14.569		1.0696	4.4
	28.788	0.60798	3.1073		0.5359	4.4
$MgB(OH)_4$	22.387					
MgF_2	−23.64					
$CaCl_2$	17.612	1.3107	−2.4575		−0.1265	7.7
	18.53	1.564	−10.48		−0.882	7.4
	17.419	1.3287			−0.217	NR
$CaSO_4$	−4.268					
$Ca(HCO_3)_2$	30.614					
$CaCO_3$	−22.228					
$CaBr_2$	31.21	2.1496	−5.2328		−0.8976	5.0
	32.3	2.6894	−16.029		−1.2951	5.0
$SrCl_2$	16.29	4.3451			−5.404	
	18.4	3.2044	−9.8894		−2.1913	3.0
$SrSO_4$	−5.59					
$Sr(HCO_3)_2$	29.292					
$SrCO_3$	−23.55					
$SrBr_2$	29.888	1.7931	13.073		−1.2458	3.3
$SrB(OH)_4$	24.277					
SrF_2	−21.75					

5.1. Partial Pressure of CO_2

Unfortunately no historical data of sufficient accuracy is available for pCO_2 in surface waters of the oceans as is the case in the atmosphere. More recent measurements of pCO_2 as a function of time are available from two time series stations called HOT (off Hawaii)[331,332] and BATS (off Bermuda).[333−338] The values of pCO_2 in surface waters

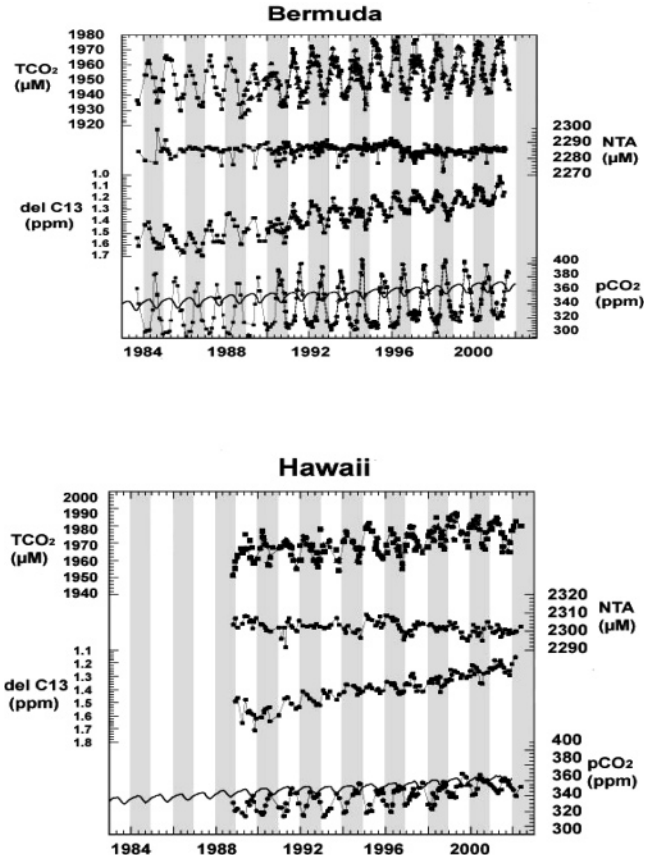

Figure 10. The measurements of pCO_2, TCO_2, NTA, and $\delta^{13}C$ at the Bermuda and Hawaii time series stations. The lines are the changes in the values of pCO_2 in the atmosphere as a function of time. Copyright 2006 from ref 1. Reproduced by permission of Routledge/Taylor & Francis Group, LLC.

determined at these two sites are shown in Figure 10. The lines show the variation of pCO_2 in the atmosphere. Both show an increase in the levels of pCO_2, TCO_2, and $\delta^{13}C$ with time. TA does not show any large changes with time since it is not affected by the addition of CO_2 to ocean waters. The pCO_2 is lower in the winter and higher in the summer largely due to changes in the temperature of the waters. The annual cycle of pCO_2 is much greater in Bermuda than Hawaii due to the larger variations in temperature. The annual increase in the pCO_2 is 1.5 ppm year^{-1} in Bermuda and 2.3 ppm year^{-1} in Hawaii, which is the same order of magnitude as the increase in the atmosphere. The TA in the surface water does not change significantly in the waters. The TCO_2 increases by 0.68 and 1.26 μmol kg^{-1} year^{-1} and the $\delta^{13}C$ decreases by 0.024 and 0.027 ppm year^{-1}, respectively, at the Bermuda and Hawaii Time series stations.

The changes in pCO_2 in surface waters are related to the flux of fossil fuel into the surface oceans. The flux of CO_2 across the air−sea interface has been examined by a number of workers. Takahashi et al.[339] have estimated the global flux of CO_2 into the oceans. The global atmospheric gradient of CO_2 across the air−sea interface needed to take up 2 Pg year^{-1} (2×10^{14} mol year^{-1}) is between 6 and 8 ppmv. A number of international programs[340−342] are involved in improving the uncertainty in the estimates of the global and regional air−sea fluxes of CO_2. The theoretical framework for estimating the flux has recently been discussed by McGillis and Wanninkhof.[343]

The flux (F) of a slightly soluble gas across the air−sea interface is the rate-limiting step and is given by

$$F = k\Delta C = k\{C_W - C_A\} \qquad (85)$$

where k is the gas transfer velocity and C_W and C_A are the concentrations in water at the bottom and top of the boundary layer. In water, the concentration is mostly in the undissociated form CO_2.[344,345] As discussed earlier, the solubility constant of CO_2 in seawater (K_0) as a function of temperature and salinity is based on the equations of Weiss.[83] He used the measurements of Murray and Riley,[346] which are more reliable than the measurements of Li and Tsu.[347] The introduction of the solubility constant ($K_0 = C/f_{CO_2}$, where C is the equilibrium concentration) allows one to express the gradient across the boundary layer in terms of the fugacity (f_{CO_2})

$$F = k(K_{0W}f_{CO_2W} - K_{0A}f_{CO_2A}) = kK_0\Delta f_{CO_2} \qquad (86)$$

W and A indicate the values of f_{CO_2} and K_0 at the top (A) and bottom (W) of the boundary layer. The values of f_{CO_2} are similar to the partial pressure of pCO_2 and can be determined from the equations of Weiss.[83] Since the atmospheric values of CO_2 are frequently expressed as the fraction, X_{CO_2}, in ppm in air, the fugacity is related to the mole fraction in dry air by

$$f_{CO_2} = (P - p_{H_2O})X_{CO_2}f(g) \qquad (87)$$

where the fugacity coefficient, f(g), is for the nonideal gas behavior[83]

$$f(g) = \exp(B_{11} + 2\delta_{12}) \qquad (88)$$

The second virial coefficient, B_{11}, and the correction for air−CO_2 mixing, δ_{12}, are given by[83]

$$B_{11} = -1636.75 + 12.0408T - 0.0327957T^2 + 3.16528T^3 \qquad (89)$$

$$\delta_{12} = 57.7 - 0.118T \qquad (90)$$

The effect of temperature and salinity on the vapor pressure of H_2O can be estimated from[343]

$$p_{H_2O} = \exp\{24.4543 - 67.4509(100/T) - 4.8489 \ln (T/100) - 0.000544S) \qquad (91)$$

Weiss and Price[348] have suggested that one can avoid some of the problems of estimating f(g), the nonideal gas correction, using the values of X_{CO_2} in the atmosphere in terms of ppt by using

$$F = kK_0(P - p_{H_2O})\Delta X_{CO_2} \qquad (92)$$

where X is reported in mole fraction in both air and water (assuming $f(g) = 0$). Equations 86 and 92 do not account for the differences in the solubility above and below the boundary that result from differences in temperature. Film models account for these differences.[343,349−352] Minnett,[353] for example, has measured skin temperature changes of 0.2 °C near the interface. McGillis and Wanninkhof[343] have examined the effect of 1 °C in the temperature above and below the boundary layer and found significant differences in the fluxes. Robertson and Watson[354] and Van Scoy et al.[355] have estimated global effects of 0.4−0.6 pG °C^{-1} due to differences in the skin temperature. This may be an overestimate of the global effect.[343]

Reliable values of the exit coefficient or transfer coefficient k are needed to make accurate estimates of the flux of CO_2 across the air−sea interface. A number of workers[356−361] have used laboratory and field measurements to determine k. They have examined the effects of wind, bubbles, boundary layer stability, and drag coefficients on the transfer coefficient. The most used relationships between k and wind speed are those developed by Liss and Merlivat[358] and Wanninkhoff.[362] These models assume that the value of k is related to the friction velocity yielding

$$k = \beta^{-1} Sc^{-n} U_W{}^m \tag{93}$$

where Sc is the Schmidt number equal to the kinematic viscosity of water divided by the molecular diffusivity of the gas in water, β is dependent on the hydrodynamic turbulence (varying from 16 to 11 with increasing turbulence based on tank studies),[363] and U_W is wind speed raised to the power m. The exponent n for the Schmidt number varies from 0.67 for a smooth surface to 0.4 for a system with bubbles.[364−367] McGillis and Wanninkhof[343] have recently examined the Gas X-98 field data using dual tracers ^{3}He and SF_6. They examined the quadratic and cubic dependence of k on wind speed. The values of k normalized to $Sc = 660$ at 20 °C are given by

$$k_{660}\ (\text{cm hr}^{-1}) = 0.312 U_{10}{}^2 \tag{94}$$

$$k_{660}\ (\text{cm hr}^{-1}) = 0.028 U_{10}{}^3 \tag{95}$$

with standard errors of ±9.1 and ±8.3 in k_{660}, respectively. The value of U_{10} is the velocity at 10 m. These equations have been compared to the ^{14}C inventory value of Broecker et al.[368] of $U_{10} = 7.4$ m s^{-1} and $k = 22$ cm h^{-1}. Using an estimate of the global wind speed[349] for steady short term average winds (less than 1 day), they found

$$k_{660}\ (\text{cm hr}^{-1}) = (Sc/660)^{-0.5} 0.028 U_{10}{}^3 \tag{96}$$

which is in good agreement with the Gas Exchange results. They[343] attribute the stronger dependence at high wind speeds to bubble entrainment while the lower winds may be related to retardation by surfactants.[369] For long term average winds, they derived

$$k_{avg} = (109 U_{10} - 0.33 U_{10}{}^2 + 0.78 U_{10}{}^3)(Sc/660)^{0.5} \tag{97}$$

The monthly values of ΔpCO_2 of Takahashi et al.[370] give a global flux of CO_2 equal to 1.7 Gt year^{-1} using the second degree equation of Wanninkhof.[362] The new cubic equation[371] gives a flux of 1.9 Gt year^{-1}, which is closer to the values determined by other techniques.

A number of workers have measured or modeled the partial pressure or fugacity of CO_2 in surface waters of the oceans.[372−406] Most of these measurements will make their way into the global pCO_2 database compiled by Takahashi and Sutherland at Lamont and will eventually be available at CDIAC. The global results for ΔpCO_2 of Takashashi and co-workers[339] are shown in Figure 11. The flux of CO_2 is out of the oceans in regions of upwelling and into the oceans in the polar cold waters. This input of CO_2 from the atmosphere to the oceans is called the “solubility pump”.

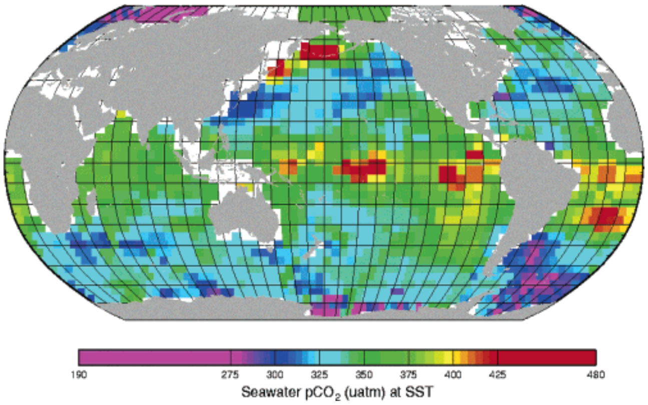

Figure 11. The surface values of pCO_2 in the world oceans for February 1995.[339]

The growth of phytoplankton also affects the levels of pCO_2 in surface waters.[407,408] The pull down of surface pCO_2 by phytoplankton and delivery of the CO_2 to deep waters after decomposition is the so-called “biological pump”. For this biological pump to take CO_2 permanently from the atmosphere, the organic carbon must sink below the thermocline and be oxidized back to CO_2, which will be stored for hundreds of years in deep waters.[409,410] The particulate organic carbon can also be stored in sediments without being oxidized. Changes in the pCO_2 are quite large in a phytoplankton bloom. This is shown for the changes that occurred during the cruises where Fe was added to the ocean to stimulate the production of phytoplankton.[117,153,410−417] The results going across the Fe-enriched patch[117] are shown in Figure 12. The pCO_2 and TCO_2 decrease in the Fe-enriched patch while the pH increases. The changes are quite significant in areas where primary production is occurring.

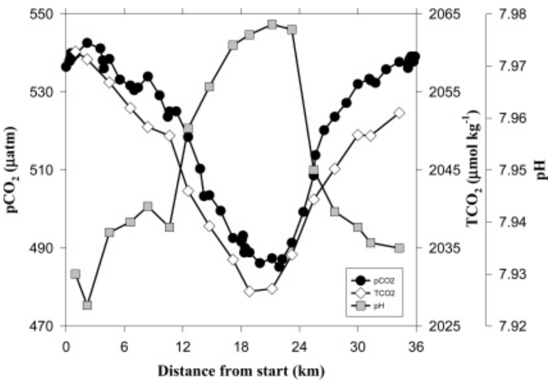

Figure 12. Values of pCO_2, pH, and TCO_2 on a transit across an Fe-enriched patch in the equatorial Pacific.[385]

Much of the deep ocean pCO_2 data acquired as part of the JGOFS and WOCE program is available at CDIAC. Typical profiles of pCO_2 in the North Atlantic and Pacific Oceans are shown in Figure 13. The surface values are similar and in near equilibrium with the atmosphere. The values increase to a maximum in the deeper waters (800−1000 m) due to the oxidation of organic carbon by bacteria at the oxygen minimum. The waters at the permanent thermocline are older and accumulate more CO_2. The levels at the maximum are much higher in the Pacific due to older age of the water. The deep waters that move from the Atlantic to the Pacific have increasing concentrations of CO_2 as the waters age. One can download the pCO_2 determined from direct measurements made across an ocean basin to construct

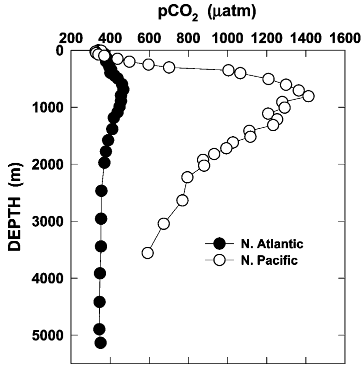

Figure 13. The pCO_2 in the North Atlantic and North Pacific oceans as a function of depth. Copyright 2006 from ref 1. Reproduced by permission of Routledge/Taylor & Francis Group, LLC.

north−south sections in the Atlantic, Pacific, and Indian oceans. A typical example for the Atlantic Ocean is shown in Figure 14. The Atlantic waters in the north sink form the surface with near-equilibrium levels of pCO_2. As the waters move south, they accumulate more CO_2. Bottom and intermediate waters are formed in the South Atlantic that have higher levels of CO_2 and move toward the north.

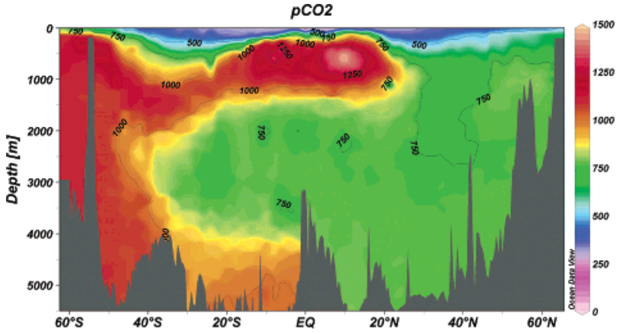

Figure 14. A section of pCO_2 in the Atlantic Ocean (A16).[501]

5.2. pH

The pH of most surface waters in near equilibrium with the atmosphere is 8.1 ± 0.1. A profile of pH in the North Atlantic and Pacific oceans is shown in Figure 15. The pH decreases due to the addition of CO_2 from the oxidation of organic carbon. The minimum values of pH in the Pacific are much lower due to the older waters accumulating more CO_2. The pH of deep water formed in the North Atlantic decreases as the waters age and move to the North Pacific. The pH increase in deep Pacific waters is partly due to the dissolution of $CaCO_3$. The CO_3^{2-} ion from the dissolution of $CaCO_3$ reacts with H^+ to form HCO_3^- causing the pH to increase. The pH of deep waters can be as low as 7.5 near 1000 m in the Pacific. In very deep waters, the pH can go through a maximum due to the effect of pressure on the ionization of carbonic acid. A section of pH in the Atlantic is shown in Figure 16. The section of pH is similar to the pCO_2 but is opposite in sign. When the pCO_2 increases, the pH decreases. The older intermediate and deep waters in the South Atlantic have a lower pH than the North Atlantic deep waters.

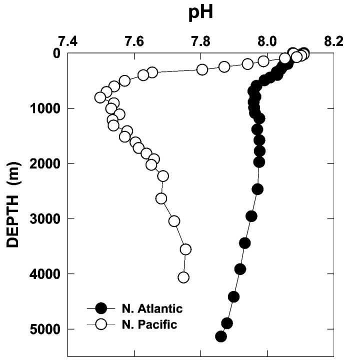

Figure 15. The pH in the North Atlantic and North Pacific oceans as a function of depth. Copyright 2006 from ref 1. Reproduced by permission of Routledge/Taylor & Francis Group, LLC.

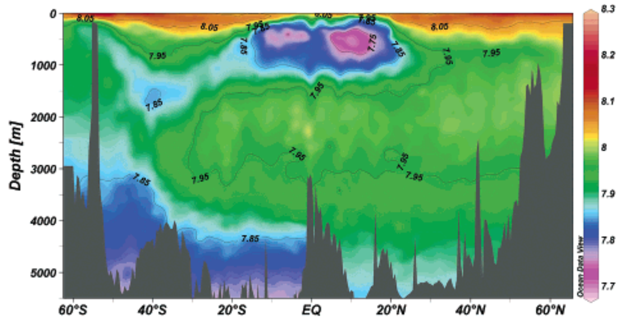

Figure 16. A section of *in situ* pH in the Atlantic Ocean (A16).[501]

5.3. Total Alkalinity

The total alkalinity (TA) of surface and deep waters was measured extensively during the WOCE and JGOFS studies. The surface values of TA are largely a function of salinity since HCO_3^- and CO_3^{2-} are major components of seawater.[418] To account for the changes in these major components as a function of salinity, the TA is normalized to a salinity of 35 (NTA = TA × 35/*S*). Typical profiles of NTA for waters in the North Atlantic and Pacific are shown in Figure 17. The surface values of NTA of surface waters in the oceans are nearly constant (~2300 to 2350 μmol kg^{-1}) except for the outcropping of deep waters in polar waters

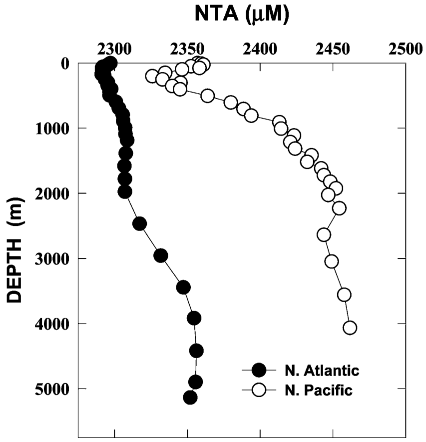

Figure 17. The normalized total alkalinity (NTA) in the North Atlantic and North Pacific oceans as a function of depth. Copyright 2006 from ref 1. Reproduced by permission of Routledge/Taylor & Francis Group, LLC.

and in coastal upwelling areas.[418] Differences of TA in warm surface waters can also be related to the growth of organisms with shells of $CaCO_3$ (formanifera and pterpods). The deep waters have a higher NTA due to the dissolution of $CaCO_3$. The maximum increases of NTA from the surface to deep are about 50 and 100 μmol kg^{-1}, respectively, in the Atlantic and Pacific oceans. For every mole of $CaCO_3$ that dissolves, the NTA increase by 2 mol. The dissolution of $CaCO_3$ in deep waters is due to the increase in pressure of the waters and the level of pH. At the same depth in both oceans, the equilibrium solubility constant of $CaCO_3$ will be nearly the same. Since the pH is much lower in the Pacific, the solubility $CaCO_3$ will be greater. A section of NTA in the Atlantic is shown in Figure 18. The distribution of TA is very similar to the salinity distributions that follow the major water masses. The values of NTA in the deep waters increase from the North Atlantic (2330 μmol kg^{-1}) to the North Pacific (2430 μmol kg^{-1}) due to the dissolution of $CaCO_3$ in the waters. The features of the patterns of NTA are similar to the other CO_2 parameters.

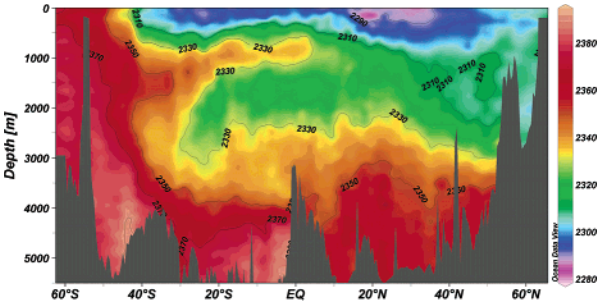

Figure 18. A section of normalized TA in the Atlantic Ocean (A16).[501]

5.4. Total Inorganic CO_2

As with TA, the effect of salinity on TCO_2 can be corrected by normalizing the results to a constant salinity ($NTCO_2 = TCO_2 \times 35/S$). If the values of TCO_2 are normalized, the surface values are about 2050 μmol kg^{-1} except for the outcropping of deep waters in the polar regions and in upwelling areas. Typical profiles of $NTCO_2$ in the North Atlantic and Pacific oceans are shown in Figure 19.

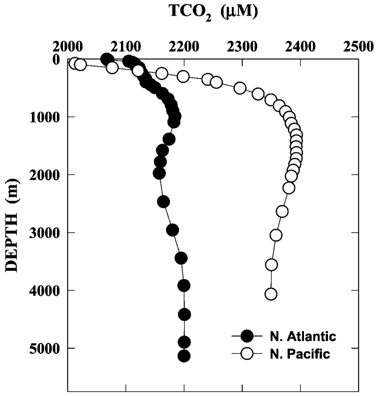

Figure 19. The normalized total carbon dioxide ($NTCO_2$) in the North Atlantic and North Pacific oceans as a function of depth. Copyright 2006 from ref 1. Reproduced by permission of Routledge/Taylor & Francis Group, LLC.

In deep waters, the TCO_2 increases due to the oxidation of plant material and the dissolution of $CaCO_3$. The TCO_2 values for deep Pacific waters are higher than those for the Atlantic because the waters are older and have had more time to accumulate CO_2 due to microbial oxidation of organic carbon. The values of TCO_2 and TA correlate very well with each other and can be used to characterize various water masses. Due to the buffering effect of seawater, only a small amount of CO_2 needs to be transferred to the oceans to restore the equilibrium between the atmosphere and surface. This buffering is called the Revelle factor (R).

$$R = (\Delta pCO_2/pCO_2)/(\Delta TCO_2/TCO_2) \qquad (98)$$

A smaller Revelle factor indicates a higher buffer capacity. It is the ratio of the fractional change in the partial pressure of carbon dioxide in the atmosphere to the fractional increase of the total carbon dioxide in the ocean. This value is about 14 for cold waters and 8 for warmer waters (the average is about 10). Thus, a 10% change in pCO_2 only results in a 1% change in TCO_2. This factor is important when considering the effect that increases of CO_2 in the atmosphere have on the carbonate system.

A section of $NTCO_2$ in the Atlantic is shown in Figure 20. The distribution of $NTCO_2$ is similar to pCO_2. The values in the deep waters increase from the North Atlantic (2180 μmol kg^{-1}) to the North Pacific (2380 μmol kg^{-1}) due to the oxidation of organic carbon and dissolution of $CaCO_3$. As for pCO_2, surface changes can be related to up welling of deep waters with high CO_2 and decreases due to primary production of organic carbon.

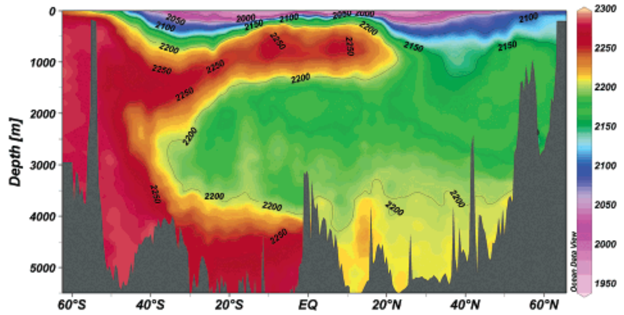

Figure 20. A section of normalized TCO_2 in the Atlantic Ocean (A16).[501]

5.5. $CaCO_3$ Dissolution in Seawater

The precipitation or formation of solid $CaCO_3$ in surface waters and the dissolution of solid $CaCO_3$ in deep waters is very important in transferring CO_2 from surface waters to deep waters. $CaCO_3(s)$ is also present in pelagic sediments of the world oceans (see review by Morse et al. in this issue). The saturation state of seawater with respect to $CaCO_3$ is determined from

$$\Omega = [Ca^{2+}][CO_3^{\ 2-}]/K^*_{sp} \qquad (99)$$

where $[Ca^{2+}][CO_3^{\ 2-}]$ is the ion product of the concentration of Ca^{2+} and $CO_3^{\ 2-}$ and K^*_{sp} is the solubility product at the "*in situ*" conditions of S, T, and P. Since Ca^{2+} is a major constituent of seawater (within 1%), its concentration (mol kg^{-1}) can be estimated from

$$[Ca^{2+}] = 2.934 \times 10^{-4} S \qquad (100)$$

The solubility product for calcite formed by foraminifera and aragonite formed by pteropods can be examined relative to the saturate state. The values of [CO_3^{2-}] can be determined from the measured carbonate parameters (pH and TA or TA and TCO_2). Typical profiles of the saturation state of calcite and aragonite are shown in Figures 21 and 22. The surface waters in both oceans are supersaturated ($\Omega > 1$). The values of Ω for calcite are near 5.0, while the surface water values of Ω are 3.0 for aragonite. Aragonite is about 1.5 times more soluble than calcite. The waters of the Pacific become undersaturated ($\Omega < 1.0$) at shallower depths than those in the Atlantic. Approximate saturation levels in North Atlantic and North Pacific waters for calcite are 4300 and 750 m, and for aragonite, the levels are 1500 and 500 m. Most of the deep Atlantic waters are supersaturated with respect to calcite (above 4500 m) and aragonite (above 2500 m). The deep waters in the North Pacific go undersaturated very close to the surface (100−200 m).

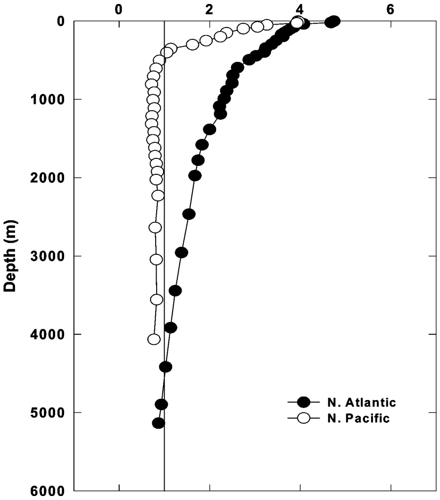

Figure 21. The saturation state of calcite in the North Atlantic and North Pacific oceans as a function of the depth. Copyright 2006 from ref 1. Reproduced by permission of Routledge/Taylor & Francis Group, LLC.

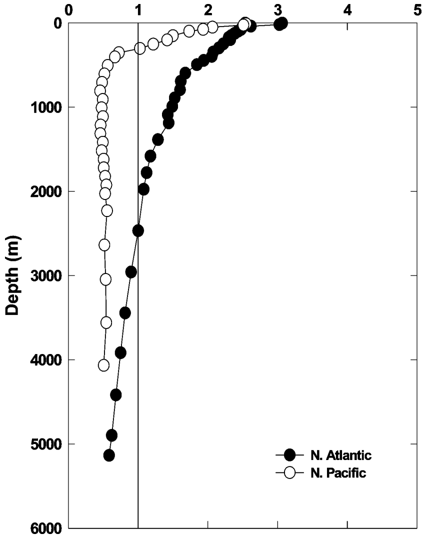

Figure 22. The saturation state of aragonite in the North Atlantic and North Pacific oceans as a function of the depth. Copyright 2006 from ref 1. Reproduced by permission of Routledge/Taylor & Francis Group, LLC.

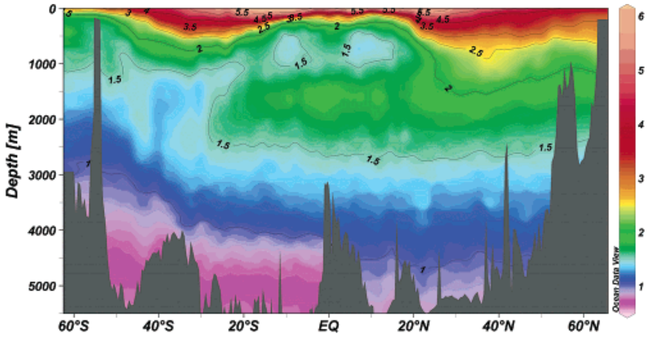

Figure 23. A section of saturation state for Calcite in the Atlantic Ocean (A16).[501]

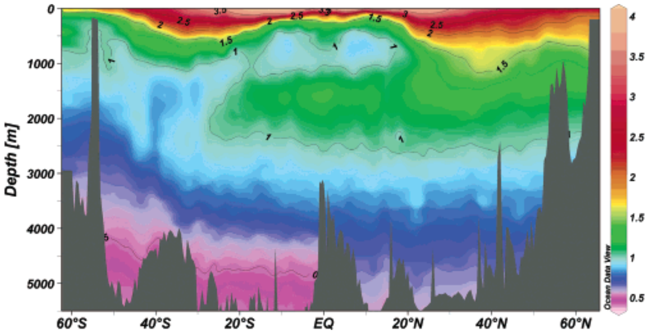

Figure 24. A section of saturation state for Aragonite in the Atlantic Ocean (A16).[501]

Sections of the saturation of calcite and aragonite in Atlantic waters are shown in Figures 23 and 24. The greater solubility (K_{sp}^*) of these minerals in deep waters is related to the effect of pressure on the solubility of $CaCO_3(s)$. Since two divalent ions are formed during the dissolution, the volume change is large and negative due to electrostriction. Pressure pushes chemical reaction to the smallest volume. The Pacific deep waters become undersaturated at shallower depths due to the lower pH or higher CO_2 formed by the oxidation of plant material. This decreases the concentration of CO_3^{2-} due to the shift in the equilibrium

$$CO_3^{2-} + H^+ \rightarrow HCO_3^- \quad \text{or} \quad CO_3^{2-} + CO_2 + H_2O \rightarrow 2HCO_3^- \tag{101}$$

The differences in Ω between the two oceans become smaller in the deep oceans due to the effect of pressure on the solubility constant. The rates of dissolution and precipitation of $CaCO_3$ in seawater are discussed in more detail in the review by Morse et al. The thermodynamic saturation state gives the depth at which $CaCO_3$ should be at equilibrium. The depth where the dissolution becomes significant in the water column or in sediments is controlled by kinetics and occurs in deeper waters and is called the lysocline.

Feely et al.[419] have examined the saturation state of calcite and aragonite in ocean waters and the rates of dissolution of $CaCO_3$ in the oceans. They determined the aragonite and calcite saturation states in the major oceans using the new carbonate data determined over the last 10 years on the WOCE cruises (Figure 25). The values range from 3000 and 4500 m in the North Atlantic to 500 and 700 m in the North Pacific, respectively, for aragonite and calcite. The added anthropogenic CO_2 to the oceans has decreased the saturation levels by as much as 500 m. As discussed later, over the next 200 years, the surface waters of the oceans may be undersaturated with respect to aragonite.

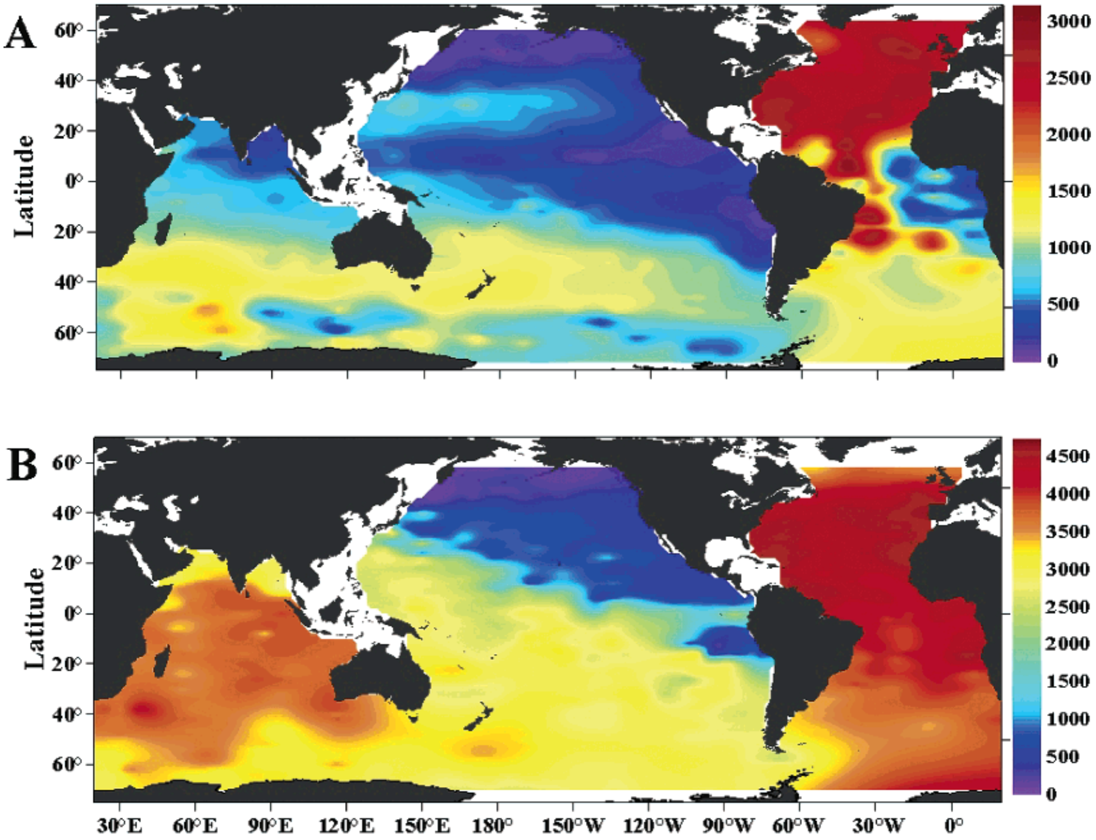

Figure 25. The depth of the aragonite (A) and calcite (B) saturation state in the oceans. Reprinted with permission from *Science* (http://www.aaas.org), ref 496. Copyright 2004 American Association for the Advancement of Science.

Feely et al.[419−421] also determined the rates of dissolution of aragonite and calcite in the oceans. They determined the amount of $CaCO_3$ dissolved from the equation

$$\Delta CaCO_3 = 0.5[TA_{meas} - TA^0] + 0.63(0.0941AOU) \quad (102)$$

The TA^0 is the preformed value of the surface alkalinity and is estimated from

$$TA^0 = 148.7 + (61.36S) + (0.0941PO) - (0.582\theta) \quad (103)$$

where S is the salinity, $PO = [O_2] - (O_2/P)[PO_4]_T$, and θ is the potential temperature.[422,423] The second term in eq 102 accounts for the decrease in TA resulting from the oxidation of organic matter using the apparent oxygen utilization (AOU)[424] and uses a N/O_2 ratio $= 0.094$.[423] The 0.63 term in eq 102 accounts for the change in TA due to the oxidation of organic nitrogen, phosphorus, and sulfur.[425] By dating the waters using CFCs or ^{14}C, one can estimate the rates of dissolution of $CaCO_3$ along constant density surfaces. The maximum dissolution rates range from 0.5 μmol kg^{-1} year^{-1} in the Atlantic to 1.2 μmol kg^{-1} year^{-1} in the Pacific. Most of the dissolution occurs near the aragonite saturation depth. This is above the lysocline level (the level where significant $CaCO_3$ dissolves). This dissolution of $CaCO_3$ in these upper waters may be related to (1) dissolution of $CaCO_3$ particles in the guts of zooplankton,[426−431] (2) dissolution of $CaCO_3$ particles in microenviroments where bacterial oxidation of organic matter can enhance the dissolution process,[432] or (3) dissolution of the more soluble forms of $CaCO_3$ in shallow waters including those from pteropods and high-Mg calcite.[433−435]

The dissolution of calcite in the guts of copepods grazing on coccolithophorids has been discounted as a major pathway for the dissolution.[432] The sharp increase in TA* near or below the aragonite saturation horizon in the Pacific[419] suggests that the more soluble carbonates dissolve quite readily and the least soluble carbonates are preserved during transit to deeper levels. This is in agreement with the earlier *in vitro* experiments on pteropod shells by Byrne and colleagues.[433,436] In summary, there is probably more than one process that contributes to the increase of TA at shallow water depths.

The marine $CaCO_3$ budget has been examined by a number of workers.[437−440] New global production[441−442] of $CaCO_3$ ranges from 0.8−1.4 Pg of $CaCO_3$-C year^{-1}. The globally averaged sediment trap data for deep waters indicates a global average flux of about 0.4 Pg of $CaCO_3$-C year^{-1}. This suggests that 40−80% of the $CaCO_3$ is rematerialized in the upper water column, which is consistent with the estimates of Feely et al.[421,443] of ∼0.5 Pg of C year^{-1} globally. It is also consistent with the fluxes of foraminifera indicating that approximately 65% of the tests are dissolved in the upper 1000 m of the water column.[444] The present accumulation of $CaCO_3$ in marine sediments is about 0.1−0.14 Pg of $CaCO_3$-C year^{-1} along the margins or deep sea and 0.13−0.17 Pg of $CaCO_3$-C year^{-1} on the continental shelf.[441,445−447] Thus, only 25% of the $CaCO_3$ is buried in shallow and deep sediments. A very large fraction of this dissolution, up to 60% or more, occurs in the upper water column above 2000 m.

6. Fossil Fuel CO_2 Input to the Oceans

Much of the interest in the carbonate system in the ocean is due to the ability of the oceans to take up a large amount

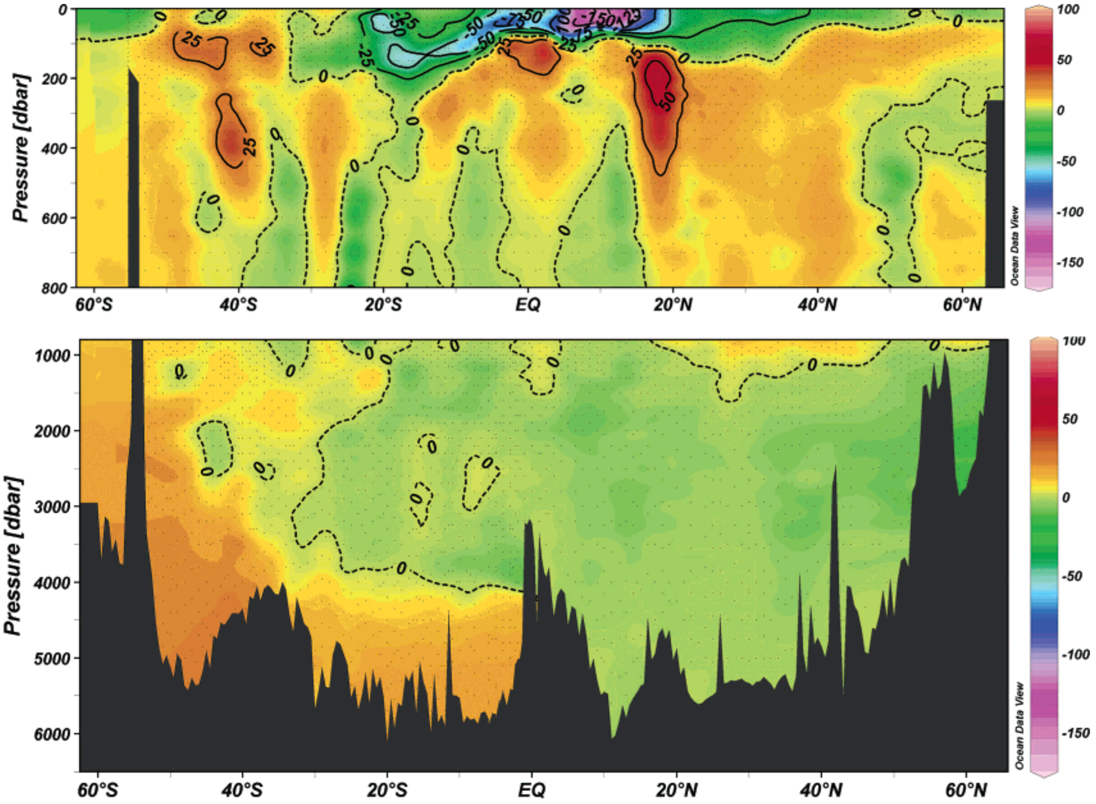

Figure 26. The differences in the $NTCO_2$ from 1989 to 2003.[501]

of the fossil fuel emitted each year. The input of this fossil fuel into the oceans has been estimated by a number of methods some are summarized below along with some examples:

1. The penetration of C^{13} into the oceans.[448]
2. The penetration of CFCs into the oceans.[449]
3. The transfer of CO_2 across the air–sea interface.[339]
4. The inferring the values from atmospheric O_2/CO_2 ratios in the atmosphere.[450]
5. Modeling the input of CO_2 into the oceans.[451]
6. Using measurements of TCO_2 as a function of time.[452]
7. Using measurements of TCO_2 and correcting for the amount added due to the oxidation of organic carbon and dissolution of $CaCO_3$.[453−456]

Many others[457−497] have used these methods to examine the input of CO_2 into the oceans. The estimates of the input of CO_2 into the oceans in Table 1 were made by early model calculations.[498] These earlier estimates were supported by ocean circulation models and indirect methods supported by observations.[448,468,499] The tracers CFC, ^{14}C, and ^{13}C are not ideal tracers for the invasion of CO_2 into the oceans because their air–sea equilibrations are not the same as CO_2. The earlier estimates based on tracers with equilibration times that were greater than CO_2 are suspect. For example,[500] the equilibration time for ^{14}C is about two times faster and that for CFCs ten times faster than that for CO_2. The equilibration of CO_2 in the oceans is controlled by the vertical transport of surface waters into the deep oceans that mix with time scales of 500−1000 years.

The direct determination of the uptake of CO_2 by the oceans over time will take years to obtain a record like the one that is known for the atmosphere. The record from the sediments gives some estimation of the past CO_2 in the oceans but is not as good as that from ice cores. The reoccupation of the world oceans and time series stations will provide us with future information, but there is a need to use indirect methods to give us some understanding of the changes that have occurred over the past 200 years and into the future. More seasonal information will come from moorings and floats capable of measuring at least two CO_2 parameters.

In this review, we will concentrate on the last two methods of determining the input of CO_2 into the oceans. The time series method simply examines the change in TCO_2 over a given time period.[452,481] For example, the changes from 1970 to 1990 can be examined using

$$\Delta(TCO_2)_{Anth} = [TCO_2(t{=}1970) - TCO_2(t{=}1990)]/20 \tag{104}$$

This method can be made by comparing the measured values in a given year with those calculated from a fit of the other year to empirical equations of the form

$$TCO_2(t{=}1970) = a_0 + a_1 S + a_2 \theta + a_3 TA + a_4 O_2 \tag{105}$$

where a_0, etc. are adjusted parameters. It is also possible to compare differences between the equations fit to the different time periods. This is much easier and yields smoother section plots for the results. This method requires reliable measurements as a function of time. Unfortunately some of the earlier global CO_2 measurements made in the 1970s were not as accurate as the more recent results. This method has been used for measurements made from 1990 to 2000[481,484,486,501] and will be used in the future as the ocean CO_2 system continues to be studied. Goyet et al.[483] developed a multiparameter approach that corrects for the mixing of water masses. The recent results[501] for the Atlantic are shown in Figure 26.

The second method determines the TCO_2 entering the oceans using an equation of the form[453,454]

$$\Delta(TCO_2)_{Anth} = (TCO_2)_{Meas} - \Delta(TCO_2)_{CaCO_3} - \Delta(TCO_2)_{Organic} \quad (106)$$

The estimation of the TCO_2 due to the dissolution of $CaCO_3$ and oxidation of organic matter can be estimated by assuming that plant material has a fixed composition. Combining this oxidation with the dissolution of $CaCO_3$ effects, one gets[502]

$$(CH_2O)_{106}(NH_3)_{16}H_3PO_4 + 138O_2 + 124CO_3^{2-} \rightarrow 16NO_3^{-} + HPO_4^{2-} + 230HCO_3^{-} + 16H_2O \quad (107)$$

The CO_3^{2-} ions formed from the dissolution of $CaCO_3$ react with the protons formed from the oxidation of plant material.[424] If x μM $CaCO_3$ and y μM organics are decomposed, the changes in TA, TCO_2, and NO_3^- are given by

$$\Delta TA = 2x - 17y \quad (108)$$

$$\Delta TCO_2 = x + 106y \quad (109)$$

$$\Delta NO_3 = 16y \quad (110)$$

A direct measure of the invasion of CO_2 in the oceans was first attempted independently by Brewer[453] and Chen and Millero[454] using these equations. Although these early methods were criticized[503] due to uncertainties associated with the mixing of water masses of poorly known initial concentrations of CO_2 and the selection of the preindustrial end members, it did yield reasonable values for the input of CO_2 into the oceans and predicted the preindustrial value of 260 ± 15 ppmv[454] in the atmosphere, which is in reasonable agreement with the value of 280 ppmv[2] later measured in ice cores. The basic assumptions of determining the anthropogenic CO_2 from the measured CO_2 and the amounts due to the oxidation of organic carbon and dissolution of $CaCO_3$ are fundamental to the method.[502]

The improvements to the model by Gruber et al.,[455] Sabine et al.,[484] and Touratier and Goyet[456] have corrected for the mixing of surface waters and different water masses and used a more conservative parameter than AOU to analyze the results. The improved method of Gruber et al.[455] defines the tracer C* given by

$$C^* = C - C_{Biol}$$

$$C^* = C - (C/O_2)O_2 - 0.5[TA + (N/O_2)O_2] \quad (111)$$

The C_{Biol} term uses stoichiometric ratios for $C/O_2 = -170$ and $N/O_2 = 0.094$, which are based on field measurements[423,504] and are closer to the values for the formation of diatoms.[415] This tracer has conservative properties for a given water mass. They assume that most of the influence of different water masses can be eliminated by considering the deviation of C^* from its preindustrial value C^{*0} defined by

$$C^{*0} = C^0 - r(C/O_2)O_2^{\,0} - 0.5[TA^0 + r(N/O_2)O_2^{\,0}] \quad (112)$$

The new quantity ΔC^*, which is not strongly affected by different water masses, is given by

$$\Delta C^* = C^* - C^{*0} \quad (113)$$

The preindustrial C^0 is determined by assuming the pCO_2 = 280 ppmv and TA^0 is estimated from

$$TA^0 = 367.5 + 54.9S + 0.074PO \quad (114)$$

where $PO = [PO_4]_{meas} + [O_2]_{meas}$.[422] The equilibrium values of C as a function of S, T (°C), and pCO_2 have been fitted to the equation

$$C_{eq}(S,T,TA)_{pCO_2=280} = 2072.0 - 8.982(C - 1)(T - 9.0\ °C) - 4.931(S35.0) + 0.842(TA - 2320) \quad (115)$$

The calculated values of C were determined using the equations of Goyet and Poisson,[23] which are not strictly valid for seawater as discussed earlier. The value of $O_2^{\,0}$ is estimated from the saturation value at the surface at a given temperature and salinity.

The final equation for ΔC^* is given by

$$\Delta C^* = C - C_{eq} - r(C/O_2)(O_2 - O_2^{\,sat}) - 0.5[TA - TA^0 + r(N/O_2)(O_2 - O_2^{\,sat})] \quad (116)$$

The anthropogenic CO_2 is calculated by

$$\Delta C_{ANT} = \Delta C^* - \Delta C_{diseq} \quad (117)$$

The ΔC_{diseq} is a term due to the air−sea disequilibrium of CO_2 before the water sinks. The calculation of ΔC^* in surface waters are corrected for changes since leaving the surface using ^3H, ^3He, and CFC-11 measurements and for the mixing of various water masses.[455,484] Gruber et al. estimate that the inventory for anthropogenic CO_2 in the North Atlantic is 20 ± 4 Gt of C, which was in reasonable agreement with some of the global circulation model estimates of 18−19 Gt of C.[475] This method has also been used to estimate the anthropogenic input of CO_2 into the Indian,[484] Pacific,[492] and Atlantic[442] oceans. The results for the world's oceans[496] will be discussed later.

A much simpler method has been developed by Touratier and Goyet.[456] It defines a tracer

$$TrOCA = O_2 + 1.2TCO_2 - 0.6TA \quad (118)$$

TrOCA[505] is a reasonable tracer of water masses, when it is corrected for the input of anthropogenic CO_2. They define a conservative tracer without a contribution of anthropogenic CO_2 by

$$TrOCA^0 = O_2^{\,0} + 1.2TCO_2^{\,0} - 0.6TA^0 \quad (119)$$

Since TA is not affected by the increase in CO_2 in the atmosphere,[454,483] TA^0 is equated to TA. They also assume that $O_2^{\,0} = O_2$ since the oxygen in the oceans is not significantly affected by the changes of oxygen in the atmosphere.[468] The final equation for the concentration of CO_2 from anthropogenic sources is given by

$$C_{ANT} = TCO_2 - TCO_2^{\,0} = (TrOCA - TrOCA^0)/1.2 \quad (120)$$

They calculate an empirical equation for the Atlantic that defines the relationship of $TCO_2^{\,0}$ with the potential temperature (Θ)

$$\mathrm{TrOCA}^0 = 1505.04\ \exp(-\Theta/89.04) \qquad (121)$$

The precision of the method has been estimated to be 3−6 μmol kg^{-1}. They estimate that the anthropogenic input into the Atlantic is 45 Gt in the 1990s and 1.97 Gt year^{-1} from 1984 to 1995. More recently Touratier et al.[497] have examined the TrOCA method in the equatorial Atlantic Ocean and compared the results to the penetration of CFCs.

A comparison of the ΔC^* method[455] and classical methods[453,454] of estimating the input of anthropogenic CO_2 into the oceans has been made in the Indian Ocean by a number of workers.[506,507] The methods give similar overall results but substantial differences in the distribution in the water column. Parts of these differences are related to the choice of the equations used to determine TA^0 and the stoichiometric ratios used for the biological correction. More substantial differences occur due to the reference waters used. Chen and Millero[454] use normalized preformed values as a function of potential temperature instead of the multiple references points used in the ΔC^* method. The TrOCA and ΔC^* methods have been compared in the Atlantic by Touratier and Goyet[501,505,508] and are found to be in reasonable agreement.

The CO_2 measurements made on the WOCE cruises (Figure 27) in the 1990s have been synthesized into a global database (http://cdiac.esd.ornl.gov). The synthesis group (J. L. Bullister, R. A. Feely, R. M. Key, A. Kozyr, F. J. Millero, T.-H. Peng, C. L. Sabine, and R. Wanninkhof) have examined the internal consistency of the measurements, determined the input of fossil fuel into the world oceans, and calculated the rates of dissolution of $CaCO_3(s)$ in the world oceans. The results have led to reliable TA and TCO_2 for all the major oceans, which are available to modelers and other scientists. The inventory of anthropogenic CO_2 into the oceans is shown in Figure 28. Most of the stored fossil fuel CO_2 is in the north Atlantic where deep water formation occurs. The penetration of fossil fuel CO_2 is shown in Figure 29. Except for the North Atlantic, the signal does not penetrate below 1500 m in the central gyres of the oceans. A summary of the anthropogenic budget[496] for the various oceans compared with some model results is given in Table 15. The amounts stored in the Atlantic and Pacific oceans are 71% of the total. The magnitudes in the Atlantic and Pacific are similar even though the volume of the Pacific is four times larger than the Atlantic. The calculated values for the major oceans are in reasonable agreement with estimates from models. A summary of the anthropogenic budget is given in Table 16. The oceans have taken up 48% of the anthropogenic CO_2 over the last 200 years. In recent years, the rate of uptake is 1.9 ± 0.4 Pg year^{-1}. Over the last 200 years, the land has been a source of CO_2 to the atmosphere (39 Pg), while over recent years, it has become a sink (−15 Pg). This uptake of CO_2 by terrestrial plants may be related to the regrowth of trees in North America. We are not certain whether this trend will continue in the future. Further work is needed in characterizing the role of coastal waters and the Arctic in the uptake of CO_2. The present estimates are not very reliable.

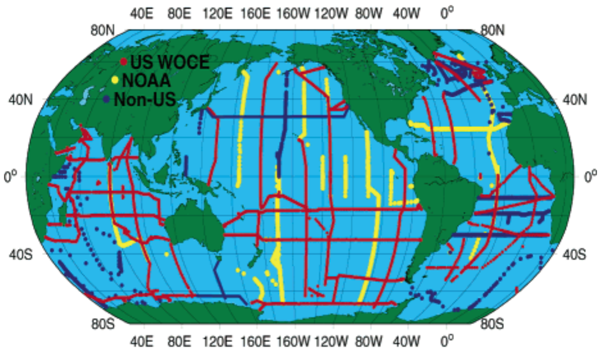

Figure 27. The CO_2 stations occupied in the world oceans during the 1990s. Copyright 2006 from ref 1. Reproduced by permission of Routledge/Taylor & Francis Group, LLC.

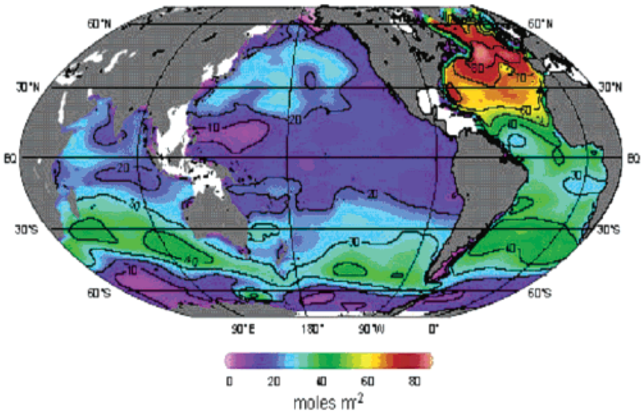

Figure 28. The column inventory of fossil fuel CO_2 in the world oceans. Reprinted with permission from *Science* (http://www.aaas.org), ref 496. Copyright 2004 American Association for the Advancement of Science.

7. Biological Effects of Increasing Levels of Partial Pressure of CO_2

It is clear that the pCO_2 in the atmosphere will increase in the future due to the continued burning of fossil fuels. Caldeiria and Wickett[4] have used a model to estimate the increase of CO_2 in the atmosphere over time if all the fossil fuel is used (see Figure 30). They examine how this increase in pCO_2 in the atmosphere would change the pH of ocean waters. They estimate that the maximum fossil fuel input of 25 Pg year^{-1} will be around 2190 and the fossil fuel will be completely spent by ~2400. This input of CO_2 will cause an increase in the atmospheric pCO_2 to a maximum of 2000 μatm near the year 2300. This high concentration of pCO_2 in the atmosphere will slowly decrease to a value of 1500 μatm by 3000. This slow decrease is due to the slow uptake of CO_2 by oceans. As the surface waters equilibrate with the high levels of pCO_2 over the next thousand years, the values of pH, TCO_2, $[CO_3^{2-}]$, and the saturation state of $CaCO_3$ will change. Over the last 200 years, the pH of the oceans has decreased by 0.11 and by the year 2400 the pH will decrease by 0.8 reaching levels of 7.4. This low pH will exist for some time and change the saturation state of $CaCO_3$.[421] The increase of CO_2 or H^+ will dissolve calcitic shells and minerals:

$$CO_2 + CaCO_3 + H_2O = 2HCO_3^- + Ca^{2+} \qquad (122)$$

$$H^+ + CaCO_3 = Ca^{2+} + HCO_3^- \qquad (123)$$

Since surface waters are supersaturated with respect to all phases of $CaCO_3$, changes in the carbonate chemistry were not previously considered to effect biogenic calcification. Carbonate skeletal structures in the future will likely be weaker and more susceptible to erosion and dissolution. With an increase in pCO_2, the future surface oceans will become

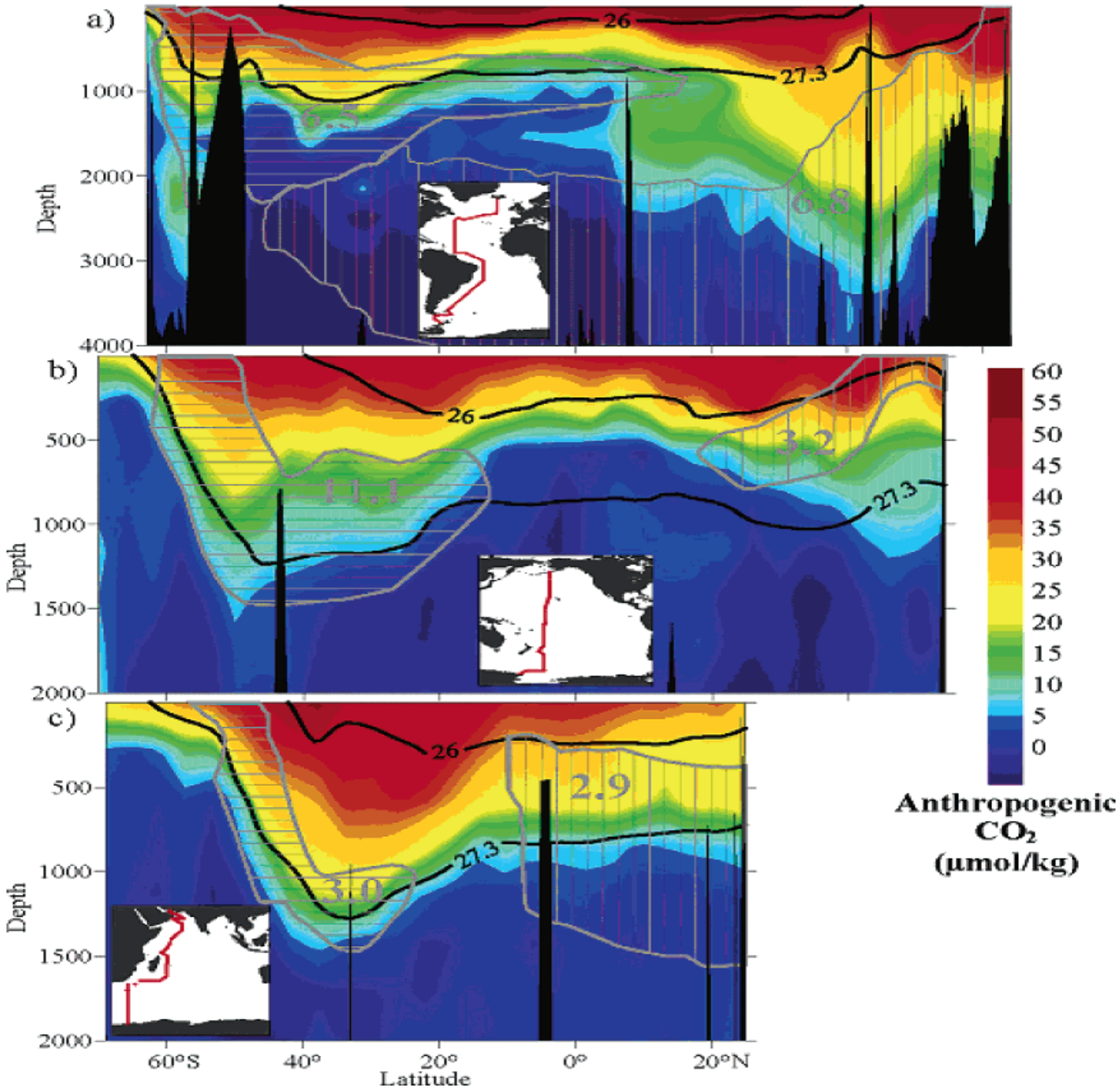

Figure 29. The penetration of anthropogenic CO_2 into the world oceans. Reprinted with permission from *Science* (http://www.aaas.org), ref 496. Copyright 2004 American Association for the Advancement of Science.

Table 15. Anthropogenic Fossil Fuel Input to the Oceans (Pg of C)[1]

ocean	location	measurements	models
Indian	>50S−20N	22 ± 2	22−27
Atlantic	>50S−50N	40 ± 5	30−40
Pacific	>50S−50N	44 ± 5	47−62
marginal seas	>65N	12 ± 5	
totals		118 ± 19	99−129

Table 16. Anthropogenic Budget (Pg of C)[496]

CO_2 sources	1800−1994	1980−1999
emissions	244 ± 20	117 ± 5
storage in atmosphere	−165 ± 5	−65 ± 1
uptake by oceans	−118 ± 19	−37 ± 8

undersaturated with respect to aragonite (Figure 31). The decreased concentration of the carbonate ion will slow down the formation of $CaCO_3$ and eventually could cause the dissolution of $CaCO_3$ in reefs and coastal sediments. The effect of the low pH on phytoplankton and other marine organisms is not known at this time, but one might expect their growth to be affected by low pH.

The biological implications of the decrease of pH in the future have been examined by a number of workers.[7,8,421,509−512]

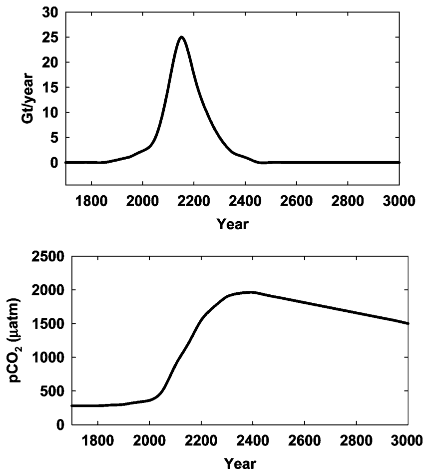

Figure 30. The long term estimates of the input of fossil fuel CO_2 in the atmosphere and resultant increases of pCO_2. Copyright 2006 from ref 1. Reproduced by permission of Routledge/Taylor & Francis Group, LLC.

Recent field and laboratory studies reveal that the degree of supersaturation has an effect on calcification rates of individual species of planktonic and benthic habitats. Some of these effects discussed by Feely et al.[421] are outline below.

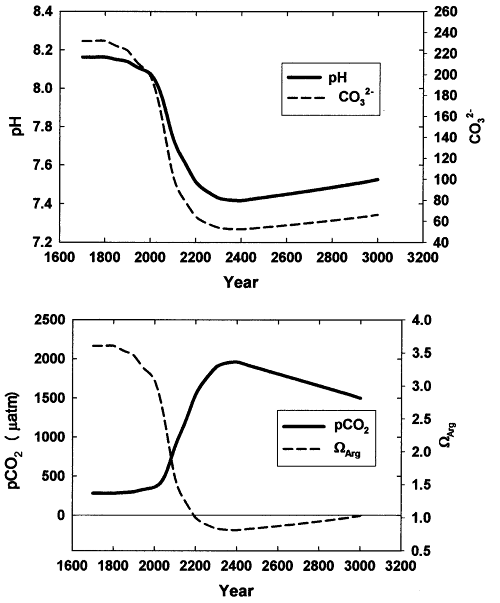

Figure 31. The changes in pH, CO_3^{2-} (μmol kg^{-1}), pCO_2 (μatm), and the saturation state for aragonite as a function of the year.

7.1. Coral Reefs

Although few studies have directly measured the effect of decreased calcification on coral reef systems, a decrease in carbonate formation and increased dissolution are likely to affect coral reefs.[513] Aragonite and magnesian calcite are at least 50% more soluble in seawater than calcite,[73,74,147] suggesting that organisms that precipitate these forms of $CaCO_3$ may be particularly affected by increasing pCO_2. Coralline algae are a major source of biogenic magnesian calcite and show a strong response to decreases in saturation state. Reef building corals produce aragonite in shallow benthic environments. Pteropod shells and heteropod molluscs are also made up of aragonite. Nearly all reef-building corals tested so far show a marked decline in calcification under reduced [CO_3^{2-}] conditions.[513−529]

7.2. Coccolithophores and Foraminifera

Coccolithophores and foraminifera have shells made of calcite. The studies of coccolithophores show decreases in the calcification rates of 25−45% when grown at pCO_2 concentrations three times greater than preindustrial values,[527−529] with one exception.[530] The production and dissolution of planktonic formaminifera shell weights have also been shown to be affected by carbonate chemistry.[531−533] As the surface waters become more undersaturated with respect to calcite, coccolithophores and foraminifera will likely precipitate undercalcified, malformed, or thinner structures.[527,534] It is not possible to state with certainty whether the calcification can exceed dissolution when the organisms live in undersaturated waters. The available empirical evidence suggests that calcification rates of coccolithophore and foraminifera are decreased even when the saturation state is greater than 1.0.

7.3. Pteropods

Quantitative data on the response of shelled pteropods to increased CO_2 are lacking. Orr et al.[8] observed the dissolution of the growing edge of shells of live *Clio pyramidata* at aragonite saturation less than one. The effects of elevated CO_2 on other producers of aragonite and magnesian calcite, including calcareous green algae, echinoderms, bryozoans, and benthic foraminifera, are largely unknown.[535] Although these labile carbonate producers are associated with benthic habitats, many of them are also found in the open ocean encrusting on *Sargassum* clumps.[536−538] Since carnivorous zooplankton and fish feed on pteropods, their loss would force them to switch to other prey types.[421] This could cause a shift of some species to other locations. The future undersaturated waters in regions that contain high amounts of pteropods would result in reduction of carbonate fluxs[539,540] and the export of organic carbon associated with fecal pellets.[540−542] Their removal from these areas would remove the only source of aragonite production and flux in the region.[543−545]

7.4. Ocean Processes

Calcium carbonate plays a dual role in regulating carbon sequestration by the oceans. An increase in the dissolution of $CaCO_3$ in the upper ocean will produce a more uniform alkalinity profile. The TA of surface waters is about 50−150 μmol kg^{-1} less than that in the deep oceans due to carbonate precipitation in surface waters and remineralization in deep waters. A decrease in carbonate precipitation in surface waters will increase the capacity of the oceans to take up CO_2 from the atmosphere. A complete shutdown of surface ocean calcification would decrease surface ocean pCO_2 by about 40 μatm.[546] A decrease in $CaCO_3$ production will affect the ratio of organic to inorganic carbon delivery to the deep sea. Uncoupled processes regulating the “rain” of organic carbon and inorganic carbon to deep-sea sediments would lead to increased dissolution of calcium carbonate sediments,[547] which would raise ocean pH and its capacity to store CO_2. If the two processes are coupled, however, such as through the process of $CaCO_3$ ballasting of organic carbon,[548] then reducing the carbonate production could result in shallower remineralization of organic carbon[549,550] and a diminished role of sediments in buffering future increases in the atmospheric CO_2. Clearly, more research on the mechanistic controls of these seemingly coupled processes is needed in the future.

8. Sequestering CO_2 in the Oceans

In recent years, a number of studies have examined the options for disposing of CO_2. The methods discussed include (1) capturing CO_2 at power stations, (2) chemical conversion, (3) terrestrial sequestration, and (4) geological sequestration. The geological disposal includes (1) use in enhanced oil recovery, (2) unmined coal beds, (3) depleted oil and gas reservoirs, (4) deep salt deposits, and (5) deep ocean.

Most of the fossil fuel power plants in the U.S. are located near many of these geological sequestration sites. The capacity to store CO_2 is given below

deep oceans	200000 Pg
deplete oil and gas reservoirs	1000 Pg
deep salt brines	800 Pg
coal seams	300 Pg
terrestrial	100 Pg

The values are quite large compared with the emissions each year. Norway Statoil has been injecting CO_2 into deep saline aquifers in the North Sea for over 10 years. Eighty percent of the production of CO_2 comes from the generation of energy. This includes 40% for electricity and 32% for transportation. The easiest way to reduce the fossil fuel used to generate energy would be to conserve. It surely is possible to double the gas mileage for automobiles in the U.S.

The recent work on sequestration for CO_2 has dealt with a number of problems and solutions to how one can dispose of CO_2 in the oceans.[551−623] Some of the problems are related to the various phases that CO_2 can be in as a function of temperature and pressure. This is shown in the phase diagram of CO_2 in seawater[623] in Figure 32. The straight line separates the gas and liquid phases, and the dotted line separates the hydrated CO_2 from the liquid at low temperatures. The red line gives the typical temperature profile as a function of depth in the ocean off the coast of Monterey, CA. At depths below 350 m, the CO_2 will be in the liquid form above ∼9 °C, and at colder temperatures, the CO_2 will be in a hydrated form. A number of researchers have examined methods of collecting CO_2 at power plants,[551,559,562] the impacts on organisms,[579,582,592,615,605,606,607,617] the effect of the lower pH,[560,569,571,582,583,589,597,599] and the formation of hydrates.[553,558,567,587,596,601,604,612−614] Rau and Caldiera[585] have considered the input of bicarbonate rather than CO_2. The CO_2 can be converted with NaOH or $CaCO_3$ to HCO_3^- which is easier to transport and does not have to be liquefied. Brewer[624] has examined some of the proposals for storing CO_2 in the oceans. More recently, White et al.[623] have used Raman spectroscopy to look at gas bubble formation in the deep ocean where liquid CO_2 was deposited. Recently, Shell Oil and Statoil have announced plans to use CO_2 for enhanced offshore oil recovery.[625] Statoil will build a gas-fired power plant. CO_2 will be separated from the exhaust gases and sent to offshore oil fields by pipeline. The addition of CO_2 will raise the oil output of the fields by as much as 85% and extend the lifetime of the field. A pilot plant in Denmark is separating CO_2 from the exhaust and storing it underground. These types of projects on the disposal of CO_2 into aquifers and the oceans will continue in the future. Studies on the environmental effects of adding CO_2 to the oceans will be an important part of the future research.

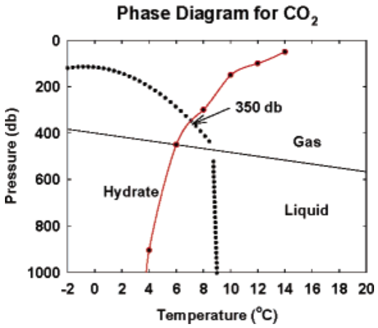

Figure 32. The phase diagram for CO_2 in seawater. The area below the dotted line represents the hydrate phase. The straight line separates the gas and liquid phases, and the red line with dots is a profile in the Pacific near Monterey, California.

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