The recommended dissociation constants for carbonic acid in seawater

Kitack Lee,[1,2] Frank J. Millero,[3] Robert H. Byrne,[4] Richard A. Feely,[5] and Rik Wanninkhof[1]

Abstract. A coherent representation of carbonate dissociation constants and measured inorganic carbon species is essential for a wide range of environmentally important issues such as oceanic uptake of anthropogenic CO_2 and carbon cycle depictions in ocean circulation models. Previous studies have shown varying degrees of discordance between calculated and measured CO_2-system parameters. It is unclear if this is due to errors in thermodynamic models or in measurements. In this work, we address this issue using a large field dataset (15,300 water samples) covering all ocean basins. Our field data, obtained using laboratory-calibrated measurement protocols, are most consistent with calculated parameters using the dissociation constants of *Mehrbach et al.* [1973] as refit by *Dickson and Millero* [1987]. Thus, these constants are recommended for use in the synthesis of the inorganic carbon data collected during the global CO_2 survey during the 1990s and for characterization of the carbonate system in seawater.

Introduction

The carbon dioxide system in seawater can be defined by specifying temperature, salinity, nutrient and boron concentrations, and two of the four inorganic CO_2-system parameters: pH ($-\log [H^+]$), total inorganic carbon (C_T), total alkalinity (A_T), and CO_2 fugacity (fCO_2). The CO_2 fugacity is expressed by the relationship, $fCO_2 = [CO_2]/K_0$ where K_0 is the solubility of CO_2 and $[CO_2] = [CO_{2aq}] + [H_2CO_3]$. Measurement of all four of the CO_2-system parameters allows an evaluation of the accuracy of available carbonic acid dissociation constants by the so-called "system overdetermination." Agreement between measurements and thermodynamic calculations (model closure) is fundamental to our understanding of important geochemical issues such as the determination of the calcium carbonate compensation depth and the distribution of fossil fuel CO_2 in the oceans. It is par-

ticularly important in numerical ocean circulation models where surface ocean fCO_2 is calculated from A_T and C_T fields. Different carbonate-system equilibrium models yield differences in calculated fCO_2 as large as 30 μatm.

Several determinations of carbonic acid dissociation constants have been made as a function of temperature and salinity in natural seawater [*Mehrbach et al.*, 1973] and in artificial seawater without fluoride [*Hansson*, 1973; *Goyet and Poisson*, 1989; *Roy et al.*, 1993]. *Dickson and Millero* [1987] refit the experimental datasets of *Mehrbach et al.* [1973] (referred to as MEHR-DM87) and of *Hansson* [1973]. Additional sets of constants have been created by fitting the pooled data of *Hansson* and *Mehrbach et al.* [*Dickson and Millero*, 1987], and the pooled data of *Goyet and Poisson* and *Roy et al.* [*Millero*, 1995]. Average differences in various equations for pK_1 and pK_2 are in a range of 0.001-0.008 in pK_1 and of 0.005-0.03 in pK_2 [*Millero*, 1995]. These differences are similar to the 2σ experimental precision (0.01-0.017 in pK_1 and 0.015-0.026 in pK_2) and probably are not strongly significant. However, the different equations derived from original experimental datasets yield significant differences in calculated parameters. Here we present the equations that yield the best agreement with a large field dataset.

Over the last 10 years, significant improvements have been made in the measurement of inorganic CO_2 parameters [*DOE*, 1994]. The use of certified reference material (CRM), developed by Dr. A. Dickson (Scripps Institution of Oceanography), greatly contributed to improved precision and accuracy in at-sea A_T and C_T measurements. These improvements have motivated a number of investigators to re-examine the internal consistency of the CO_2 parameters measured in the laboratory [*Lee et al.*, 1996; *Murphy*, 1996; *Lueker*, 1998] and at sea [*Millero et al.*, 1993; *Clayton et al.*, 1995; *Lee et al.*, 1997; *McElligott et al.*, 1998; *Wanninkhof et al.*, 1999; *Byrne et al.*, 1999]. These studies have resulted in conflicting conclusions regarding the optimal set of carbonic acid dissociation constants. The differing conclusions drawn from previous studies have a variety of experimental origins: (1) A_T measurement uncertainties: A_T data obtained during the U.S. JGOFS Equatorial Pacific Process Study in 1992 (EqPac92) were overestimated by about 8 μmol kg^{-1} due to inaccurately assigned titrant concentrations. This affects the conclusions drawn by *Millero et al.* [1993]. (2) pH scale uncertainties: *McElligott et al.* [1998] noted that all four CO_2 parameters measured during the EqPac92 program would be internally consistent with the constants of MEHR-DM87 at 20°-25°C if spectroscopic pH values were increased by 0.0038. *DelValls and Dickson* [1998] determined that the pH values assigned to "tris" buffers needed to be increased by 0.0047 for all temperatures and salinities. The reported pK_2 of the indicator m-cresol purple [*Clayton and Byrne*, 1993] is based on the "tris" characterization of *Dickson* [1993] who used the reported e.m.f.

[1]K. Lee and R. Wanninkhof, Ocean Chemistry Division, NOAA/AOML, 4301 Rickenbacker Causeway, Miami, FL 33149.

[2]K. Lee, Cooperative Institute of Marine and Atmospheric Studies, University of Miami/Rosenstiel School of Marine and Atmospheric Science, 4600 Rickenbacker Causeway, Miami, FL 33149.

[3]F.J. Millero, Division of Marine and Atmospheric Chemistry, University of Miami/Rosenstiel School of Marine and Atmospheric Science, 4600 Rickenbacker Causeway, Miami, FL 33149.

[4]R.H. Byrne, Department of Marine Science, University of South Florida, 140 7th Avenue S, St. Petersburg, FL 33701.

[5]R.A. Feely, Ocean Climate Research Division, NOAA/PMEL, 7600 Sand Point Way N.E., Seattle, WA 98115.

values of *Ramette et al.* [1977]. Consequently, spectroscopic pH values obtained in the laboratory [*Lee et al.*, 1996] and in field studies [*Millero et al.*, 1993; *Clayton et al.*, 1995; *Lee et al.*, 1997] may need to be revised upward by 0.0047 pH units. (3) Limited scope of previous studies: Previous investigations of thermodynamic CO_2-system consistency often involved two or three carbon system parameters over a narrow range of temperature (t) and fCO_2, or specific ocean regions.

This work is distinct from previous studies in that it uses a large, well-calibrated field dataset covering a 5°-30°C range of temperature, a 33-37 range of salinity, and a 250-1700 µatm range of fCO_2. Field measurements were made in all major ocean basins from the equator to high latitudes. The data were obtained by many investigators over a four-year period. Laboratory measurements made over a similar range of temperature and fCO_2 are also included in this analysis. The internal consistency of all data used in this study was carefully examined on a per cruise basis: A_T and C_T data were normalized to CRM values [*Dickson*, 1997] and pH data were adjusted upward by 0.0047 pH units for consistency with the revised "tris" buffer characterization of *DelValls and Dickson* [1998]. This dataset, which represents our current achievable level of accuracy on a routine basis at sea and in the laboratory, is used to determine which set of carbonic acid dissociation constants is optimal for use in characterizing the oceanic CO_2-system.

Sources of Laboratory and Field Data

Laboratory measurements of all four CO_2 parameters were made on a single seawater sample (S=35) as a function of temperature (5°-35°C) and fCO_2 (300-1700 µatm). The analytical techniques and data are documented in *Lee et al.* [1996]. Field data were obtained on cruises conducted by the National Oceanic and Atmospheric Administration/Ocean-Atmosphere Carbon Exchange Study (NOAA/OACES) in the Atlantic, Indian, and Pacific Oceans (Table 1). The NOAA/OACES CO_2 dataset is unique in that all four CO_2 parameters were measured throughout the water column from the surface to 6000 m. Samples were analyzed for fCO_2 and C_T at 20°C, and for A_T and pH at 25°C except for the North Atlantic study where pH was measured at 20°C. Detailed procedures for analysis of fCO_2, pH, C_T, and A_T can be found in *DOE* [1994]. Analysis protocols differed for pH and fCO_2 measurements on different cruises. The fCO_2 of discrete samples was measured by an infrared analyzer (IR) [*Wanninkhof and Thoning*, 1993] on the EQPAC, A20R, and P18 cruises, and by gas chromatographic analysis with flame-ionization detection (GC-FID) after catalytic reduction of CO_2 to CH_4 [*Neill et al.*, 1997] on the I8R and P15S cruises. Spectroscopic pH measurements using the indicator m-cresol purple were made at 20°C on the A20R and at 25°C on the I8R by the University of Miami group, and at 25°C on the EQPAC, P15S, and P18 cruises by the University of South Florida group.

Results and Discussion

In this study, pH-C_T and A_T-C_T are used as input combinations to study the consistency between the measurements and the first and second carbonate dissociation constants. The pH-C_T combination can be used to assess the consistency between measurements and pK_1 parameterizations by comparing measured

Table 1. Summary of NOAA/OACES cruise data and thermodynamic consistency.

| Cruise	Variable	Thermodynamic Calculations Constants	
		MEHR-DM87	ROY
A20R – Atlantic	ΔfCO_2^A	-0.1 ± 0.8	-2.4 ± 0.8
Along 20°W	ΔA_T^B	2.6 ± 3.5	-7.3 ± 4.4
(5°S–63°N)	ΔfCO_2^C	0.2 ± 1.0	-1.7 ± 1.2
I8R – Indian	ΔfCO_2^A	-0.1 ± 1.1	-1.3 ± 1.0
Along 80°E	ΔA_T^B	3.8 ± 3.5	-6.4 ± 5.7
(43°S–10°N)	ΔfCO_2^C	2.1 ± 2.4	-4.6 ± 2.9
EQPAC – Pacific	ΔfCO_2^A	0.3 ± 1.1	-0.9 ± 1.4
(15°S–15°N	ΔA_T^B	1.0 ± 4.9	-8.1 ± 9.5
80°W–140°W)	ΔfCO_2^C	1.2 ± 2.7	-4.6 ± 4.0
P15S – Pacific	ΔfCO_2^A	1.4 ± 1.4	0.2 ± 1.5
Along 170°W	ΔA_T^B	4.2 ± 3.2	-5.6 ± 5.4
(67°S–equator)	ΔfCO_2^C	3.8 ± 2.5	-2.8 ± 3.3
P18 – Pacific	ΔfCO_2^A	0.5 ± 0.9	-0.6 ± 1.3
Along 103°W	ΔA_T^B	-2.5 ± 4.6	-12.2 ± 7.6
(67°S–23°N)	ΔfCO_2^C	-1.0 ± 2.8	-7.6 ± 3.0

$^{A,C}\Delta fCO_2$ (%) = [(measured – calculated) / measured] × 100. ΔfCO_2 represents the mean of individual differences between the measured fCO_2 and fCO_2 calculated from pH-C_T (A) and A_T-C_T (C) using the constants of MEHR-DM87 and *Roy et al.* [1993].

$^B \Delta A_T$ (µmol kg^{-1}) = (measured – calculated). ΔA_T represents the mean of individual differences between the measured A_T and A_T calculated from pH-C_T using the constants of MEHR-DM87 and *Roy et al.* [1993].

vs. calculated fCO_2 (Fig. 1a, 1b), and the consistency between measurements and pK_2 parameterizations by comparing measured vs. calculated A_T (Fig. 1c, 1d) [*Lee et al.*, 1996]. The A_T-C_T combination can be used to evaluate the consistency between measurements and log K_1/K_2 ratios by comparing measured fCO_2 and fCO_2 calculated from A_T-C_T (Fig. 1c, 1f). In these calculations we have used the constants of MEHR-DM87, along with equilibrium constants for other components (e.g., boric acid dissociation, solubility of CO_2, water hydrolysis, and phosphoric and silicic acid dissociation), necessary to characterize the carbonate system in seawater as recommended in *Millero* [1995]. Since the constants of MEHR-DM87 are expressed in terms of moles per kilogram of solution on the "seawater" scale [*Dickson and Millero*, 1987], all acid dissociation constants have been adjusted to the same scale. The effect of uncertainties in equilibrium constants on calculated parameters is discussed in the caption of Fig. 1.

Assessment of pK_1

The difference between measured fCO_2 and fCO_2 calculated from pH-C_T is strongly dependent upon the pK_1. The fCO_2 residuals in Fig. 1a and 1b show the percentage error in fCO_2 (ΔfCO_2 = [(measured fCO_2–calculated fCO_2) / measured fCO_2] × 100) for laboratory and field data. Observations are binned into fCO_2 intervals equal to 300 µatm, and are shown as a function of sample fCO_2. The best agreement between measured and calculated fCO_2 was obtained using the constants of MEHR-DM87. The fCO_2 residuals for field measurements are mostly within ±1% over the entire fCO_2 range (Fig. 1a, 1b) and
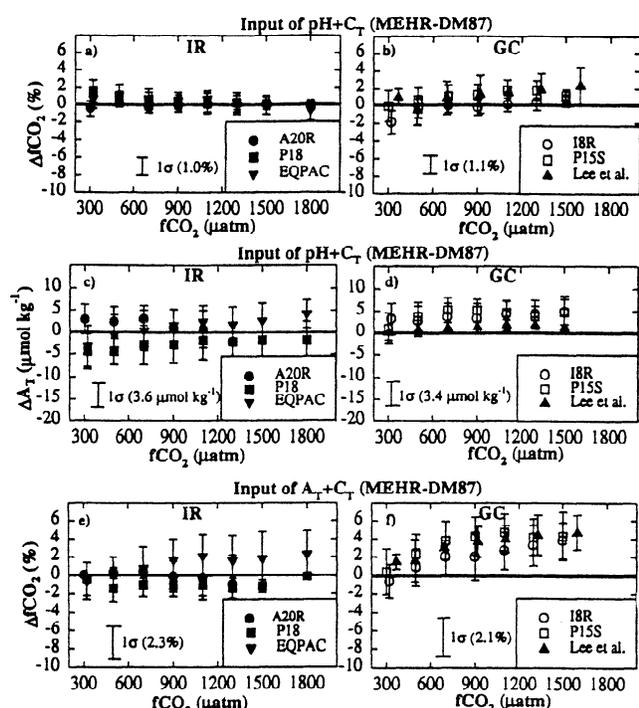
Figure 1. Comparison of laboratory [*Lee et al.*, 1996] (filled triangles) and field measurements of fCO_2 and A_T vs. those calculated using the constants of MEHR-DM87. (a,b) The ΔfCO_2 of measured values using (a) IR (A20R, P18, EQPAC) and (b) GC-FID (I8R, P15S) vs. those calculated from pH-C_T. (c,d) The ΔA_T of measured values (c) (A20R, P18, EQPAC) and (d) (I8R, P15S) vs. those calculated from pH-C_T. (e,f) The ΔfCO_2 of measured values using (e) IR (A20R, P18, EQPAC) and (f) GC-FID (I8R, P15S) vs. those calculated from A_T-C_T. The filled symbols are the field data (A20R, P18, EQPAC), during which discrete fCO_2 measurements were made using IR analysis (Fig. 1a, 1e). Open symbols are discrete fCO_2 measurements (I8R, P15S) using a GC-FID (Fig. 1b, 1f). Error bars represent standard deviations (1σ) of the differences in each bin. The probable error of the calculated A_T (Fig. 1c, 1d) due to uncertainties in equilibrium constants for minor components is ± 2.5 μmol kg^{-1} for surface water and ± 4.0 μmol kg^{-1} for deep water based on an uncertainty of ± 0.0042 in log K_B-boric acid; of ± 0.00015 in log K_0-solubility of CO_2; of ± 0.01 in log K_W-water hydrolysis; of ± 0.09 in pK_{P1}-phosphoric acid; of ± 0.03 in pK_{P2}-phosphoric acid; of ± 0.20 in pK_{P3}-phosphoric acid; of ± 0.02 in pK_{Si}-silicic acid [*Millero*, 1995]. The assessment of the consistency between the measurements and the pK_1 parameterizations is independent of the uncertainties in the equilibrium constants for minor components, since calculations of fCO_2 from pH-C_T do not include those constants. The assessment of the consistency between the measurements and the pK_2 parameterizations is sensitive to these uncertainties, since these constants are needed to convert A_T to carbonate alkalinity or vice versa. These uncertainties cannot account for the non-zero slope of A_T residuals when constants other than MEHR-DM87 are used.

are of similar magnitude to those of laboratory measurements (Fig. 1b). GC-FID based field fCO_2 measurements are in good agreement with the laboratory measurements. The residuals for the laboratory and field data are about 3% larger using

dissociation constants other than MEHR-DM87 (Table 1). The pK_1 measurements of *Goyet and Poisson, Hansson,* and *Roy et al.* agreed to within ± 0.003 in pK_1 [*Millero*, 1995] but they differ from MEHR-DM87 by about 0.01, which is equivalent to a 3% offset in calculated fCO_2.

Assessment of pK_2

The difference between measured A_T and A_T calculated from pH-C_T strongly depends on the pK_2. The A_T residuals (ΔA_T = measured A_T − calculated A_T in μmol kg^{-1}) for laboratory and field data are binned and are plotted as a function of sample fCO_2 in Fig. 1c and 1d. The A_T residuals for laboratory and field data using the constants of MEHR-DM87 are about ± 3 μmol kg^{-1} (1σ) with little dependence on fCO_2. When the constants of *Roy et al.* and *Goyet and Poisson* are used, the A_T residuals are considerably larger for samples with low fCO_2. An adjustment of 0.03 in the pK_2 of *Roy et al.* would be required to produce a near zero slope in the residuals. Such an adjustment lowers the calculated A_T by about 15 μmol kg^{-1} for samples with $fCO_2 = 300$ μatm and also lowers the A_T by 4 μmol kg^{-1} for samples with $fCO_2 = 1600$ μatm.

Assessment of the log K_1/K_2 Ratio

Calculation of fCO_2 from A_T-C_T requires a reliable log K_1/K_2 ratio. The differences in the log K_1/K_2 for various parameterizations range from -0.04 to +0.06 and are primarily caused by differences in K_2. Measured fCO_2 values for samples with low fCO_2 (<500 μatm) at t = 5-30°C are most consistent with calculations using the constants of MEHR-DM87. This is not the case at high fCO_2 (>500 μatm) where fCO_2 residuals become greater as fCO_2 increases (Fig. 1f). The fCO_2 dependence of the residuals is apparent in two independent laboratory measurements [*Lee et al.*, 1996; *Lueker*, 1998], and in the field data of GC-FID based fCO_2 measurements (Fig. 1f). This trend is also evident irrespective of the carbonic acid dissociation constants used. This implies that the log K_1/K_2 ratio calculated from these measurements varies as a function of sample fCO_2, which is in contradiction with our understanding of the carbonate system. The IR based fCO_2 measurements do not show this trend (Fig. 1e), and the apparent discrepancy in fCO_2 measurements at high fCO_2 has to be resolved before we draw firm conclusions regarding the consistency between fCO_2-A_T-C_T measurements and the log K_1/K_2 at high fCO_2. *Wanninkhof et al.* [1999] showed that surface underway fCO_2 measurements, made on three OACES cruises (A20R, I8R, and P18) covering a temperature range of 5-30°C and fCO_2 range of 280-450 μatm, are most consistent with fCO_2 calculated from A_T-C_T data using the constants of MEHR-DM87. At low temperature, the constants of MEHR-DM87 and *Roy et al.* both give a reliable prediction of fCO_2, because the difference in the log K_1/K_2 between *Roy et al.* and MEHR-DM87 at t<5°C is significantly smaller (<0.02) than at other temperatures. At 25°C the difference is as large as 0.05, which leads to differences in calculated fCO_2 of 30 μatm.

Conclusions

The adjustment in the pK_2 of m-cresol purple suggested by *DelValls and Dickson* [1998] brings calculations involving pH into optimal agreement with the other CO_2-system measurements. The constants of MEHR-DM87 are most suitable for

calculations involving pH-A_T-C_T combinations over a range of $t=0°$-$35°C$, $S=33$-37, and $fCO_2=250$-1700 μatm. The constants of MEHR-DM87 also yield good agreement with measurements and calculations involving fCO_2-A_T-C_T combinations at low fCO_2. At high fCO_2, calculated fCO_2 values using the log K_1/K_2 ratio of MEHR-DM87 are less than the measured values for the laboratory and GC-FID field measurements. Definitive conclusions regarding the consistency between measurements and the log K_1/K_2 will require resolution of discrepancies in fCO_2 measurements at high fCO_2. Overall, the constants of MEHR-DM87 provide the most consistent comparisons between laboratory and field measurements over a wide range of ocean temperature, salinity, and fCO_2. This work suggests that the internal consistency of CO_2-system measurements can be achieved over long periods of time by diverse teams of investigators through the use of standard reference materials.

References

Byrne, R.H., S. McElligott, R.A. Feely, and F.J. Millero, The role of pH_T measurements in marine CO_2-system characterizations, *Deep-Sea Res., 46*, 1985-1997, 1999.

Clayton, T.D., and R.H. Byrne, Calibration of m-cresol purple on the total hydrogen ion concentration scale and its application to CO_2-system characteristics in seawater, *Deep-Sea Res., 40*, 2115-2129, 1993.

Clayton, T.D., R.H. Byrne, J.B. Breland, R.A. Feely, F.J. Millero, D.M. Campbell, P.P. Murphy, and M. Roberts, The role of pH measurements in modern oceanic CO_2-system characterizations: Precision and thermodynamic consistency, *Deep-Sea Res., 42*, 411-429, 1995.

Dickson, A.G., pH buffers for seawater media based on the total hydrogen ion concentration scale, *Deep-Sea Res., 40*, 107-118, 1993.

DelValls, T.A., and A.G. Dickson, The pH of buffers based on 2-amino-2-hydroxymethyl-1,3-propanediol ('tris') in synthetic seawater, *Deep-Sea Res., 45*, 1541-1554, 1998.

Dickson, A.G., Reference material batch information, 1997. (http://www-mpl.ucsd.edu/people/adickson/CO2_QC/Level1/Batches.html).

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

DOE Handbook, *Handbook of Methods for the Analysis of the Various Parameters of the Carbon Dioxide System in Seawater*; v. 2, A.G. Dickson and C. Goyet (Eds.), ORNL/CDIAC-74, 1994.

Goyet, C., and A. Poisson, New determination of carbonic acid dissociation constants in seawater as a function of temperature and salinity, *Deep-Sea Res., 36*, 1635-1654, 1989.

Hansson, I., A new set of acidity constants for carbonic acid and boric acid in seawater, *Deep-Sea Res., 20*, 661-678, 1973.

Lee, K., F.J. Millero, and D.M. Campbell, The reliability of the thermodynamic constants for the dissociation of carbonic acid in seawater, *Mar. Chem., 55*, 233-246, 1996.

Lee, K., F.J. Millero, and R. Wanninkhof, The carbon dioxide system in the Atlantic Ocean, *J. Geophys. Res., 102*, 15,693-15,707, 1997.

Lueker, T.J., The ratio of the first and second dissociation constants of carbonic acid determination from the concentration of carbon dioxide in gas and seawater at equilibrium, Ph.D dissertation, 155 pp., Univ. of California at San Diego, 1998.

McElligott, S., R.H. Byrne, K. Lee, R. Wanninkhof, F.J. Millero, and R.A. Feely, Discrete water column measurements of CO_2 fugacity and pH_T in seawater: A comparison of direct measurements and thermodynamic calculations, *Mar. Chem., 60*, 63-73, 1998.

Mehrbach, C., C.H. Culberson, J.E. Hawley, and R.M. Pytkowicz, Measurement of the apparent dissociation constants of carbonic acid in seawater at atmospheric pressure, *Limnol. Oceanogr., 18*, 897-907, 1973.

Millero, F.J., Thermodynamics of the carbon dioxide system in the oceans, *Geochim. Cosmochim. Acta, 59*, 661-677, 1995.

Millero, F.J., R.H. Byrne, R. Wanninkhof, R.A. Feely, T. Clayton, P. Murphy, and M.L. Lamb, The internal consistency of CO_2 measurements in the equatorial Pacific, *Mar. Chem., 44*, 269-280, 1993.

Murphy, P., The carbonate system in seawater: Laboratory and field studies, Ph.D dissertation, 288 pp., Univ. of Washington, 1996.

Neill, C., K.M. Johnson, E. Lewis, and D.W.R. Wallace, Accurate headspace analysis of fCO_2 in discrete water samples using batch equilibration, *Limnol. Oceanogr., 42*, 1774-1783, 1997.

Ramette, R.W., C.H. Culberson, and R.G. Bates, Acid-base properties of tris (hydroxymethyl) aminomethane (tris) buffers in seawater from 5 to 40°C, *Analy. Chem., 49*, 867-870, 1977.

Roy, R.N., L.N. Roy, M. Lawson, K.M. Vogel, C. Porter-Moore, W. Davis, F.J. Millero, and D.M. Campbell, Determination of the ionization constants of carbonic acid in seawater, *Mar. Chem., 44*, 249-259, 1993.

Wanninkhof, R., and K. Thoning, Measurement of fugacity of CO_2 in surface water using continuous and discrete sampling methods, *Mar. Chem., 44*, 189-204, 1993.

Wanninkhof, R., E. Lewis, R.A. Feely, and F.J. Millero, The optimal carbonate dissociation constants for determining surface water pCO_2 from alkalinity and total inorganic carbon, *Mar. Chem, 65*, 291-301, 1999.