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Dissociation constants for carbonic acid determined from field measurements

Frank J. Millero[a,*], Denis Pierrot[a], Kitack Lee[a,b], Rik Wanninkhof[b], Richard Feely[c], Christopher L. Sabine[c], Robert M. Key[d], Taro Takahashi[e]

[a] *Rosenstiel School of Marine and Atmospheric Science, University of Miami, 4600 Rickenbacker Causeway, Miami, FL 33149-1098, USA*
[b] *NOAA Atlantic Oceanographic and Meteorological Laboratory, 4301 Rickenbacker Cswy, Miami, FL 33149, USA*
[c] *NOAA Pacific Marine and Environmental Laboratory, 7600 San Point Way NE, Seattle, WA 98115, USA*
[d] *Atmospheric and Ocean Science Program, Princeton University, Princeton, NJ 08544, USA*
[e] *Lamont-Doherty Earth Observatory, Columbia University, Palisades, NY 10964-8000, USA*

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Abstract

A number of workers have recently shown that the thermodynamic constants for the dissociation of carbonic acid in seawater of Mehrbach et al. are more reliable than measurements made on artificial seawater. These studies have largely been confined to looking at the internal consistency of measurements of total alkalinity (TA), total inorganic carbon dioxide (TCO_2) and the fugacity of carbon dioxide (fCO_2). In this paper, we have examined the field measurements of pH, fCO_2, TCO_2 and TA on surface and deep waters from the Atlantic, Indian, Southern and Pacific oceans to determine the pK_1, pK_2 and $pK_2 - pK_1$. These calculations are possible due to the high precision and accuracy of the field measurements. The values of pK_2 and $pK_2 - pK_1$ over a wide range of temperatures (−1.6–38°C) are in good agreement (within ±0.005) with the results of Mehrbach et al. The measured values of pK_1 at 4°C and 20°C are in reasonable agreement (within ±0.01) with all the constants determined in laboratory studies. These results indicate, as suggested by internal consistency tests, that the directly measured values of pK_1+pK_2 of Mehrbach et al. on real seawater are more reliable than the values determined for artificial seawater. It also indicates that the large differences of $pK_2 - pK_1$ (0.05 at 20°C) in real and artificial seawater determined by different investigators are mainly due to differences in pK_2. These differences may be related to the interactions of boric acid with the carbonate ion.

The values of $pK_2 - pK_1$ determined from the laboratory measurements of Lee et al. and Lueker et al. at low fCO_2 agree with the field-derived data to ±0.016 from 5°C to 25°C. The values of $pK_2 - pK_1$ decrease as the fCO_2 or TCO_2 increases. This effect is largely related to changes in the pK_2 as a function of fCO_2 or TCO_2. The values of fCO_2 calculated from an input of TA and TCO_2, which require reliable values of $pK_2 - pK_1$, also vary with fCO_2. The field data at 20°C has been used to determine the effect of changes of TCO_2 on pK_2 giving an empirical relationship:

$$pK_2^{TCO_2} = pK_2 - 1.6 \times 10^{-4}(TCO_2 - 2050)$$

which is valid at $TCO_2 > 2050\,\mu mol\,kg^{-1}$. This assumes that the other dissociation constants such as K_B for boric acid are not affected by changes in TCO_2. The slope is in reasonable agreement with the laboratory studies of Lee et al. and Lueker et al. (-1.2×10^{-4} to -1.9×10^{-4}). This equation eliminates the dependence of the calculated fCO_2 on the level

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*Corresponding author. Tel.: +1-305-361-4706; fax: +1-305-361-4144.
E-mail addresses: fmillero@rsmas.miami.edu (F.J. Millero).

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of $f\mathrm{CO_2}$ or $\mathrm{TCO_2}$ in ocean waters ($\sigma = 29.7$ µatm in $f\mathrm{CO_2}$). An input of pH and $\mathrm{TCO_2}$ yields values of $f\mathrm{CO_2}$ and TA that are in good agreement with the measured values (± 22.3 µatm in $f\mathrm{CO_2}$ and ± 4.3 µmol kg^{-1} in TA). The cause of the decrease in pK_2 at high $f\mathrm{CO_2}$ is presently unknown. The observed inconsistencies between the measured and computed $f\mathrm{CO_2}$ values may be accounted for by adding the effect of organic acid (~ 8 µmol kg^{-1}) to the interpretation of the TA. Further studies are needed to elucidate the chemical reactions responsible for this effect.

1. Introduction

The carbon dioxide system in the oceans can be characterized using any two of the four measurable parameters, pH, total alkalinity (TA), fugacity of carbon dioxide ($f\mathrm{CO_2}$) and the total inorganic carbon dioxide ($\mathrm{TCO_2}$) providing that constants are available for the other acid/base species in seawater. Dissociation constants of carbonic acid are needed to calculate the components of the $\mathrm{CO_2}$ system from these measurements. The stoichiometric dissociation of carbonic acid in seawater are given by

$$\mathrm{CO_2 + H_2O \Leftrightarrow H^+ + HCO_3^-}, \tag{1}$$

$$\mathrm{HCO_3^- \Leftrightarrow H^+ + CO_3^{2-}}. \tag{2}$$

The dissociation constants K_1 and K_2 are defined by

$$K_1 = [\mathrm{H^+}][\mathrm{HCO_3^-}]/[\mathrm{CO_2}], \tag{3}$$

$$K_2 = [\mathrm{H^+}][\mathrm{CO_3^{2-}}]/[\mathrm{HCO_3^-}], \tag{4}$$

where the brackets are used to denote the concentration in mol kg^{-1} of seawater and the proton concentration is on the seawater scale, $[\mathrm{H^+}]_{\mathrm{SWS}} = [\mathrm{H^+}]_{\mathrm{F}}\{1 + [\mathrm{SO_4^{2-}}]_{\mathrm{T}}/K_{\mathrm{HSO_4}} + [\mathrm{F^-}]_{\mathrm{T}}/K_{\mathrm{HF}}\}$ ($K_{\mathrm{HSO_4}}$ and K_{HF} are the dissociation constants for $\mathrm{HSO_4^-}$ and HF, respectively, and the subscripts F and T represent the concentration of the free and total proton).

The stoichiometric dissociation constants pK_1 and pK_2 have been determined by a number of workers (Mehrbach et al., 1973; Hansson, 1973; Goyet and Poisson, 1989; Roy et al., 1993). A summary of these results is given in Table 1. The standard errors (1σ) of the fits of the experimental measurements to functions of temperature and salinity are 0.002–0.007 for pK_1 and 0.006–0.013 for pK_2. The measurements made by Mehrbach et al. (1973) were made on real seawater; while the other studies were made in artificial seawater. Mehrbach et al. (1973) determined pK_1 from potentiometric titrations and pK_1 + pK_2 by additions of $\mathrm{NaHCO_3}$ to seawater devoid of $\mathrm{CO_2}$ until the pH was constant (pH = [pK_1 + pK_2]/2, when $\mathrm{TCO_2}$ = CA, the carbonate alkalinity). They calculated pK_2 by subtracting the pK_1 from the measured values of pK_1 + pK_2. Hansson (1973) determined the values of pK_1 and pK_2 from potentiometric titrations of $\mathrm{Na_2CO_3}$ in artificial seawater (without $\mathrm{F^-}$ and $\mathrm{B(OH)_3}$). Goyet and

Table 1
Summary of measurements made on the dissociation constants of carbonic acid in seawater by various workers[a]

Author	Temp. range (°C)	Salinity range	Std. Error[b]		Values at $S = 35$ and 25°C	
			pK_1	pK_2	pK_1	pK_2
Hansson (1973)	5–30	20–40	0.007	0.009	5.850	8.942
Mehrbach et al. (1973)	2–35	26–43	0.006	0.010	5.837	8.955
Goyet and Poisson (1989)	−1–40	10–50	0.007	0.011	5.848	8.919
Dickson and Millero (1987)	0–35	20–43	0.008	0.013	5.845	8.945
Roy et al. (1993)	0–45	5–45	0.002	0.006	5.847	8.916

[a] All the constants have been converted to the seawater scale.

[b] The standard errors are 1σ from fits of pK_1 and pK_2 as a function of temperature and salinity.

Poisson (1989) determined the values of $\mathrm{p}K_1$ and $\mathrm{p}K_2$ from potentiometric titrations of Na_2CO_3 in artificial seawater (without $B(OH)_3$). Roy et al. (1993) determined the values of $\mathrm{p}K_1$ in artificial seawater (devoid of F^- and $B(OH)_3$) measuring the cell potential with a hydrogen silver–silver chloride electrode system. These measurements were made on solutions with various amounts of $NaHCO_3$ that were equilibrated with gas mixtures of CO_2 and H_2. Roy et al. (1993) determined the values of $\mathrm{p}K_2$ from potentiometric measurements in artificial seawater with mixtures of $NaHCO_3$ and Na_2CO_3.

Millero (1979) examined the $\mathrm{p}K_1$ and $\mathrm{p}K_2$ determined by Hansson (1973) and Mehrbach et al. (1973) using thermodynamic equations that could be extrapolated to pure water. Dickson and Millero (1987) combined the measurements of Mehrbach et al. (1973) and Hansson (1973) to produce constants that were suggested for general use in oceanography. The more recent measurements of Goyet and Poisson (1989) and Roy et al. (1993) were in reasonable agreement and were combined by Millero (1995). More recently the examination of the internal consistency of laboratory (Lee et al., 1996; Lueker et al., 2000) and field (Wanninkhof et al., 1999; Lee et al., 2000) measurements of $f\mathrm{CO}_2$, TCO_2 and TA have indicated that the constants of Mehrbach et al. (1973) are more reliable than those of other workers. The calculation of $f\mathrm{CO}_2$ from an input of TA and TCO_2 and calculations of other parameters from an input of $f\mathrm{CO}_2$ and TA or TCO_2 require reliable values of $\mathrm{p}K_2 - \mathrm{p}K_1$ (or K_2/K_1). Thus, the field measurements suggest that the values $\mathrm{p}K_2 - \mathrm{p}K_1$ from Mehrbach et al. (1973) are more reliable than other laboratory studies.

Comparisons of dissociation constants measured in the laboratory as a function of temperature ($t = 0$–$40°\mathrm{C}$ at $S = 35$) and salinity ($S = 15$–42 at 25°C) are shown in Figs. 1 and 2. The values of $\mathrm{p}K_1$ as a function of temperature and salinity are in reasonably good agreement. All the values of $\mathrm{p}K_1$ determined in the laboratory studies as a function of temperature (T°K) and salinity (Hansson, 1973; Mehrbach et al., 1973; Goyet and Poisson, 1989; Roy et al., 1993) can be represented by (ln is log to the base e and T is the absolute temperature in Kelvin)

$$\mathrm{p}K_1 = -8.712 - 9.460 \times 10^{-3}S + 8.56 \times 10^{-5}S^2 + 1355.1/T + 1.7976\ln(T) \qquad (5)$$

with a standard error $\sigma = 0.0064$. This fit indicates that all the measurements of $\mathrm{p}K_1$ are internally consistent to 0.01, which is close to the standard error of the individual fits (see Table 1). A closer look of the individually fitted data indicates that the values of $\mathrm{p}K_1$ of Mehrbach et al. (1973) are in good agreement with the measurements of Goyet and Poisson (1989) and Roy et al. (1993) at low temperatures, but differ by as much as 0.01 near 20°C.

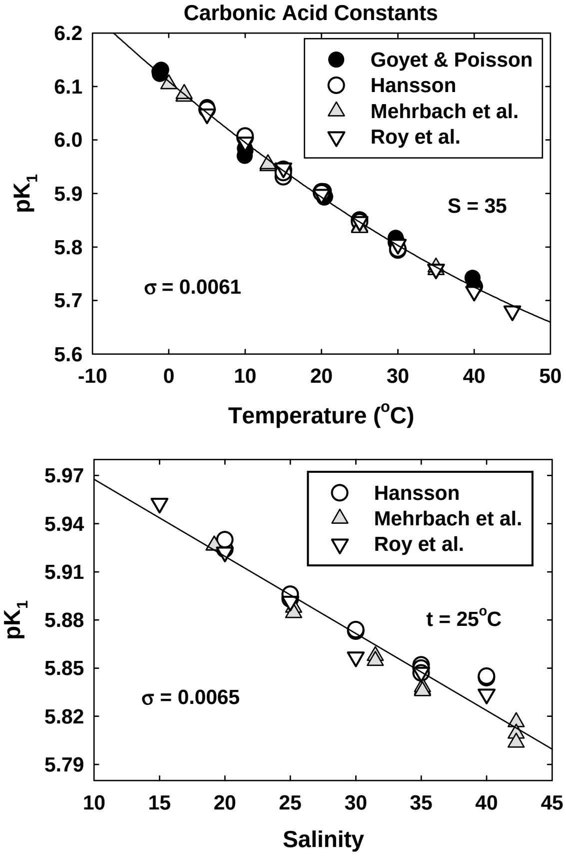

Fig. 1. Values of $\mathrm{p}K_1$ of various workers for carbonic acid (Mehrbach et al., 1973; Hansson, 1973; Goyet and Poisson, 1989; Roy et al., 1993) as a function of temperature ($S = 35$) and salinity (25°C). Goyet and Poisson (1989) did not make any measurements at 25°C so these results are not shown as a function of salinity. The smooth curve is calculated from Eq. (5).

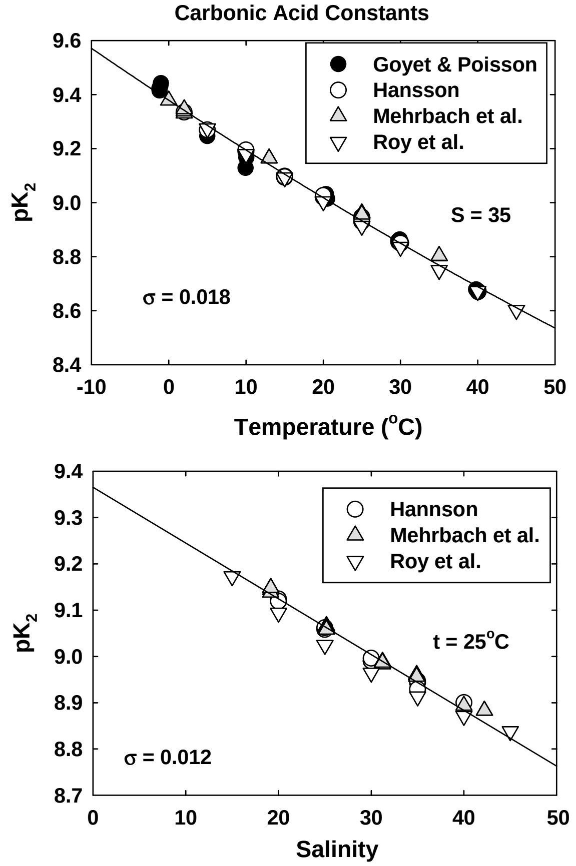

Fig. 2. Values of pK_2 of various workers for carbonic acid (Mehrbach et al., 1973; Hansson, 1973; Goyet and Poisson, 1989; Roy et al., 1993) as a function of temperature ($S = 35$) and salinity (25°C). Goyet and Poisson (1989) did not make any measurements at 25°C so these results are not shown as a function of salinity. The smooth curve is calculated from Eq. (6).

A comparison of the laboratory measurements of pK_2 as a function of temperature ($t = 0$–40°C at $S = 35$) and salinity ($S = 15$–42 at 25°C) is shown in Fig. 2. All the values of pK_2 determined in the laboratory studies (Hansson, 1973; Mehrbach et al., 1973; Goyet and Poisson, 1989; Roy et al., 1993) can be represented by (T/K)

$$\begin{aligned} \mathrm{p}K_2 = {} & 17.0001 - 0.01259S - 7.9334\times10^{-5}\,S^2 \\ & + 936.291/T - 1.87354\ln(T) \\ & - 2.61471\,S/T + 0.07479\,S^2/T \qquad (6) \end{aligned}$$

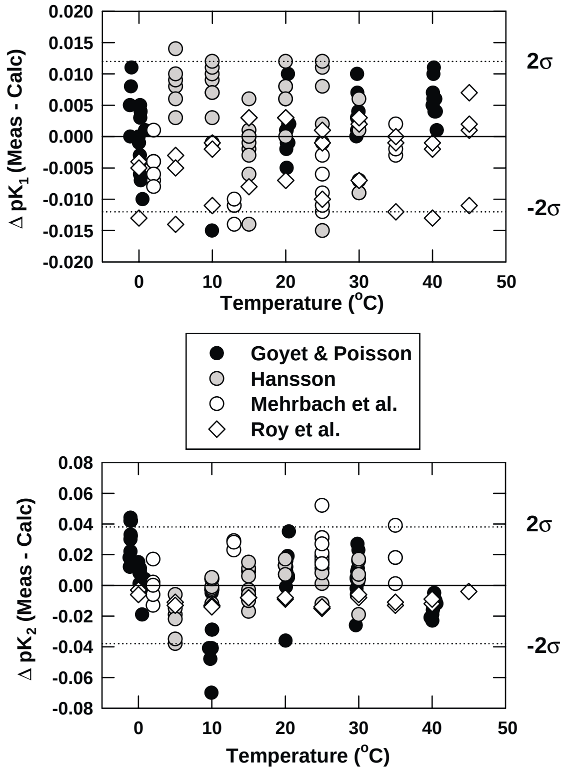

Fig. 3. Differences between the measured (Mehrbach et al., 1973; Hansson, 1973; Goyet and Poisson, 1989; Roy et al., 1993) and the calculated values of the combined equation (Eqs. (5) and (6)) of pK_1 and pK_2 as a function of temperature ($S = 20$–42).

with a $\sigma = 0.019$. The overall standard error of the fit to Eq. (6) is close to two times the standard error of the individual fits (Table 1).

The deviations of the individual measurements of pK_1 and pK_2 from the values calculated from Eqs. (5) and (6) are shown in Fig. 3 (on the seawater pH scale, mol kg^{-1}). Most of the deviations in pK_1 are within 2σ of the individual fits. The deviations in pK_2 are much larger, but within 2σ of the individual fits. The values of pK_2 − pK_1 determined in artificial seawater are also compared to the results of Mehrbach et al. (1973) in Fig. 4 (on the seawater pH scale, mol kg^{-1}). Except at low temperatures, the seawater results of Mehrbach et al. (1973) are all higher by about 0.04–0.05 than those determined in artificial seawater. Since the field and laboratory internal consistency

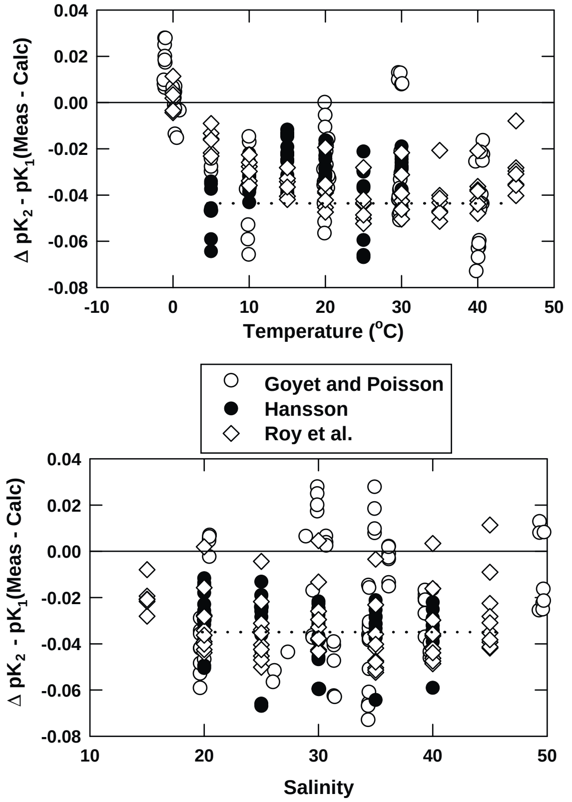

Fig. 4. Differences between the measured (Hansson, 1973; Goyet and Poisson, 1989; Roy et al., 1993) values of pK_2 − pK_1 for carbonic acid with the results of Mehrbach et al. (1973) as fitted by Dickson and Millero (1987) as a function of temperature and salinity. The dotted line shows the approximate offset in the values determined in artificial seawater and real seawater.

calculations support the pK_2 − pK_1 measurements of Mehrbach et al. (1973), the measurements by others (Hansson, 1973; Goyet and Poisson, 1989; Roy et al., 1993) appear to be in error. Since the pK_1 measurements of all the laboratory studies are in reasonable agreement, the values of pK_2 determined from potentiometric titrations in artificial seawater also appear to be in error.

Uncertainties of ±0.01 in pK_1 and ±0.04 in pK_2 can lead to significant errors in the calculated parameters of the CO_2 system (Mojica Prieto and Millero, 2002). For example, an uncertainty of ±0.01 in pK_1 (±2.5% in K_1) can lead to errors of ±10 μatm in $f$$CO_2$ from an input of TA and TCO_2 or pH and TCO_2. Uncertainties of ±0.04 in pK_2 (±9.7% in K_2) can lead to errors of ±26 μatm in $f$$CO_2$ from an input of TA and TCO_2 (Mojica Prieto and Millero, 2002).

In this paper, we derive values of pK_1, pK_2 and pK_2 − pK_1 from 6000 sets of field measurements of pH, TA, TCO_2 and $f$$CO_2$ on the NSF/JGOFS, NOAA/OACES and DOE/WOCE cruises in the Atlantic, Pacific, Southern and Indian oceans. The results will be used to examine the reliability of the measured values of pK_1, pK_2 and pK_2 − pK_1 from various laboratory studies.

2. Quality of the field data used

The field measurements used in this study were taken from the cruises listed in Table 2. The data are available from Carbon Data Information Analysis Center (CDIAC-http://cdiac.ornl.gov/oceans/woce. All the Principal Investigators that made the measurements are listed in a Table on the web site. Surface data from the Southern Ocean JGOFS cruises from Hawaii to New Zealand and New Zealand to the Ross Sea were also used (Millero et al., 1999). We examined only the samples where all four parameters were measured. The pH measurements were made by spectroscopic methods (Clayton and Byrne, 1993) for all the stations except for the potentiometric measurements made on the S4I cruise in the Southern Ocean. The spectroscopic pH measurements were made at 25°C except for the N. Atlantic measurements made at 20°C. All the pH measurements have been converted to the seawater scale (Dickson, 1984; Millero, 1995). The pK of the pH indicator was calibrated by Clayton and Byrne (1993) with TRIS buffers (Khoo et al., 1977). Recently, DeValls and Dickson (1998) have shown that the values of pH assigned to the TRIS buffer by Khoo et al. (1977) are too low by 0.0047. Because it is uncertain that this correction should be made to the pK of the indicator and the pH measurements, it has not been made to the field data. This could result in a bias of 0.005 in the pH measurements and resultant values of pK_1 and pK_2. Recent potentiometric and spectroscopic measurements on seawater (Mojica Prieto and

Table 2
Cruise data used to determine the dissociation constants of carbonic acid

Location	Number	Temp. (°C)	Salinity	Parameters
Deep waters				
N. Atlantic Ocean				
(A16R)	1368	20	34.3–35.5	pH[a], TA, TCO_2, fCO_2
(A20)	420	20	34.3–35.5	
(A22)	340	20	34.3–35.5	
(24N)	773	20	34.3–37.3	
Indian Ocean				
(I8N R)	1368	20	34.5–35.1	
S. Pacific Ocean[b]				
(P14/P15)	2146	20	34.2–35.0	
Total	6415	20	34.3–37.3	
Southern Ocean (S4I)	1065	4	34.2–34.8.	pH[c], TA, TCO_2[d], fCO_2[d]
Surface waters[e]				
Atlantic Ocean	193	8.6–29	33–37	pH[a], TA, TCO_2, fCO_2
Indian Ocean	128	10–29	33–36	
Southern Ocean	30	−1.7–4.2	33–35	
Total	321	8.6–29	35.5 ± 0.6	

[a] Spectroscopic pH measurements made at 25°C except for A16R where the measurements were made at 20°C. They have been converted to the seawater scale.

[b] Data from the Pacific WOCE P16, P17, P18 and P19 have not been used in this study. For the first two expeditions, very few alkalinity samples were analyzed without using the CRM solutions for the alkalinity. During P18, fCO_2 was measured using a shaker bottle method of Neill et al. (1997), whereas it was measured using a gas recirculation method of Chipman et al. (1993) for all other expeditions. The P18 fCO_2 data appear to be inconsistent with the data from all other expeditions. During P19, no alkalinity was measured.

[c] Potentiometric pH measurements at 25°C on the seawater scale.

[d] The TCO_2 and fCO_2 were measured at 4°C by the Lamont group (Takahashi et al., 2002).

[e] The surface values of pH, TA and TCO_2 were determined on samples collected from CTD casts at depths between 0 and 30 m. The values of fCO_2 were made on line (~5–6 m) near the in situ temperature.

Millero, 2002) indicate that the differences between the potentiometric and spectroscopic methods are within ±0.002. The fCO_2 measurements were made in a batch mode at 4°C or 20°C (Chipman et al., 1993) for deep waters or in a continuous mode (Wanninkhof and Thoning, 1993) near the in situ temperature for surface waters. The concentration of CO_2 in the air equilibrated with seawater at a known temperature was measured using an IR analyzer or gas chromatograph, which were repeatedly calibrated using several standard gas mixtures of known CO_2 concentrations up to 1400 ppm (determined by P. Tans of NOAA/CMDL). The conversions of the measured partial pressure of CO_2, (pCO_2) to the fugacity (fCO_2) were made using the equations listed in Wanninkhof and Thoning (1993), which are based on the earlier equations developed by Weiss (1974). Differences in these quantities are small (~1 μatm) compared to the precision of measurements. The TA measurements were made by potentiometric titrations (Millero et al., 1993) and the TCO_2 was measured by coulometry (Johnson et al., 1993). Certified reference materials (CRMs) were used to adjust all the TA and TCO_2 measurements (Dickson, 1997), except the TCO_2

measurements on S4I. CRMs measured on this cruise were within 2 μmol/kg from the certified value. The precisions of the field measurements are ±0.001 for pH, ±1% for $f\mathrm{CO_2}$, $\pm 4\,\mu\mathrm{mol\,kg^{-1}}$ for TA and $\pm 2\,\mu\mathrm{mol\,kg^{-1}}$ for $\mathrm{TCO_2}$. The accuracy of the TA and $\mathrm{TCO_2}$ measurements are close to the precision because all the field measurements used standards that were reproduced to near the precision of the measurements. The uncertainties of the pH measurements are larger than the precision due to the uncertainties in the pH assigned to the TRIS buffers used in the calibration and the errors involved in the corrections to in situ temperatures. We estimate that the errors in field pH measurements could be as large as ±0.01 due to these calibration problems. The accuracy of $f\mathrm{CO_2}$ measurements for the water samples is assumed to be close to the precision.

3. Calculations

The methods used to determine the values of $\mathrm{p}K_1$, $\mathrm{p}K_2$ and $\mathrm{p}K_2 - \mathrm{p}K_1$ have been given by Lee et al. (1996). The calculations require the determination of the carbonate alkalinity (CA), which is defined by (Dickson, 1984)

$$\begin{aligned}\mathrm{CA} &= [\mathrm{HCO_3^-}] + 2[\mathrm{CO_3^{2-}}] \\ &= \mathrm{TA} - [\mathrm{B(OH)_4^-}] + [\mathrm{H^+}] - [\mathrm{OH^-}] \\ &\quad - [\mathrm{HPO_4^{2-}}] - 2[\mathrm{PO_4^{3-}}] - [\mathrm{Si(OH)_3O^-}]. \qquad (7)\end{aligned}$$

Contributions from minor weak acids including organic acids are assumed to be negligible. The concentrations of the individual components ($\mathrm{mol\,kg^{-1}}$) are determined from the appropriate dissociation constants for boric acid (K_B, Dickson, 1990), water (K_W, Millero, 1995), phosphoric ($K_{\mathrm{P}i}$, Millero, 1995), and silicic acid (Millero, 1995) on the seawater pH scale:

$$[\mathrm{B(OH)_4^-}] = [\mathrm{B}]_\mathrm{T}/\{1 + [\mathrm{H^+}]/K_\mathrm{B}\}, \qquad (8)$$

$$[\mathrm{OH^-}] = K_\mathrm{W}/[\mathrm{H^+}], \qquad (9)$$

$$\begin{aligned}[\mathrm{HPO_4^{2-}}] = \{[\mathrm{P_T}][\mathrm{H^+}]/K_\mathrm{P3}\}/\{1 + [\mathrm{H^+}]/K_\mathrm{P3} \\ + [\mathrm{H^+}]^2/(K_\mathrm{P2}K_\mathrm{P3}) \\ + [\mathrm{H^+}]^3/(K_\mathrm{P1}K_\mathrm{P2}K_\mathrm{P3})\}, \qquad (10)\end{aligned}$$

$$\begin{aligned}[\mathrm{PO_4^{3-}}] = [\mathrm{P}]_\mathrm{T}/\{1 + [\mathrm{H^+}]/K_\mathrm{P3} + [\mathrm{H^+}]^2/(K_\mathrm{P2}K_\mathrm{P3}) \\ + [\mathrm{H^+}]^3/(K_\mathrm{P1}K_\mathrm{P2}K_\mathrm{P3})\}, \qquad (11)\end{aligned}$$

$$[\mathrm{Si(OH)_3O^-}] = [\mathrm{Si}]_\mathrm{T}/\{1 + [\mathrm{H^+}]/K_\mathrm{Si}\}, \qquad (12)$$

where the concentration of boron, $[\mathrm{B}]_\mathrm{T} = 0.000416(S/35)\,\mathrm{mol\,kg^{-1}}$ (Uppström, 1974) and the concentrations of total phosphate $[\mathrm{P}]_\mathrm{T}$ and silica $[\mathrm{Si}]_\mathrm{T}$ are taken from the at-sea measurements ($\mathrm{mol\,kg^{-1}}$). As mentioned earlier, the seawater pH scale was used throughout this paper and all the constants used have been converted to this scale (Dickson and Millero, 1987; Millero, 1995). The required dissociation constants for $\mathrm{HSO_4^-}$ and HF are taken, respectively, from Dickson (1990) and Dickson and Riley (1979). The values of $[\mathrm{SO_4^{2-}}]_\mathrm{T} = 0.0293(S/35)\,\mathrm{mol\,kg^{-1}}$ and $[\mathrm{F^-}]_\mathrm{T} = 0.00007(S/35)\,\mathrm{mol\,kg^{-1}}$ (Millero, 1996). The concentrations of $\mathrm{OH^-}$, $\mathrm{HPO_4^{2-}}$, $\mathrm{Si(OH)_3O^-}$ in deep waters contribute less than 0.3% to TA; while $\mathrm{B(OH)_4^-}$ can contribute 4% to TA in surface waters and 2% in deep waters (Millero, 1996).

The components of the carbonate system are determined from

$$[\mathrm{CO_2}] = f\mathrm{CO_2}\mathrm{K_0}, \qquad (13)$$

$$[\mathrm{HCO_3^-}] = 2\mathrm{TCO_2} - \mathrm{CA} - 2[\mathrm{CO_2}], \qquad (14)$$

$$[\mathrm{CO_3^{2-}}] = \mathrm{CA} - \mathrm{TCO_2} + [\mathrm{CO_2}], \qquad (15)$$

where K_0 is the solubility constant for $\mathrm{CO_2}$ (Weiss, 1974). The constants are determined from

$$\begin{aligned}K_1 &= [\mathrm{H^+}][\mathrm{HCO_3^-}]/[\mathrm{CO_2}] \\ &= [\mathrm{H^+}]\{2\mathrm{TCO_2} - \mathrm{CA} - 2[\mathrm{CO_2}]\}/[\mathrm{CO_2}], \qquad (16)\end{aligned}$$

$$\begin{aligned}K_2 &= [\mathrm{H^+}][\mathrm{CO_3^{2-}}]/[\mathrm{HCO_3^-}] \\ &= \frac{\{[\mathrm{H^+}](\mathrm{CA} - \mathrm{TCO_2} + [\mathrm{CO_2}])\}}{\{2\mathrm{TCO_2} - \mathrm{CA} - 2[\mathrm{CO_2}]\}}, \qquad (17)\end{aligned}$$

$$\begin{aligned}K_2/K_1 &= [\mathrm{CO_2}][\mathrm{CO_3^{2-}}]/[\mathrm{HCO_3^-}]^2 \\ &= \frac{\{[\mathrm{CO_2}](\mathrm{CA} - \mathrm{TCO_2} + [\mathrm{CO_2}])\}}{\{(2\mathrm{TCO_2} - \mathrm{CA} - 2[\mathrm{CO_2}]\}^2}. \qquad (18)\end{aligned}$$

As is clear from Eq. (18), the ratio of K_2/K_1 is nearly independent of the pH and can be determined from measurements of TA, $\mathrm{TCO_2}$ and $f\mathrm{CO_2}$. This is important since errors in the

Table 3
Effect of temperature (25–0°C) on the pH of seawater ($S = 30$–40, $TA = 2300\,\mu mol\,kg^{-1}$ and $TCO_2 = 2100\,\mu mol\,kg^{-1}$)

$-\Delta pH/\Delta T$ (°C^{-1})					
Salinity	Mehrbach[a]	Hansson[b]	D & M[c]	G & P[d]	Roy[e]
30	0.0158	0.0149	0.0156	0.0165	0.0166
35	0.0157	0.0148	0.0155	0.0164	0.0166
40	0.0156	0.0148	0.0154	0.0163	0.0164
Effect of change in temperature (25–4°C) *on the calculated* pK_1					
	—	−0.0168	−0.0042	+0.0147	+0.0165

[a] Mehrbach et al. (1973).
[b] Hansson (1973).
[c] Dickson and Millero (1987).
[d] Goyet and Poisson (1989).
[e] Roy et al. (1993).

measurement of pH do not strongly affect the estimates of $pK_2 - pK_1$.

Since most of the measurements of pH were made at 25°C, it is necessary to estimate their values at lower or higher temperatures. This requires knowledge of the constants K_0, K_1 and K_2 for the CO_2 system. The values of $\Delta pH/\Delta T$ determined from the presently available constants are given in Table 3 (Mehrbach et al., 1973; Hansson, 1973; Goyet and Poisson, 1989; Roy et al., 1993). The values of $\Delta pH/\Delta T$ are nearly independent of salinity and temperature from 25°C to 0°C (Millero, 1995) and range from 0.0148 to 0.0166 at $S = 35$. These can be compared to directly measured values of $\Delta pH/\Delta T$ of 0.0150–0.0165 for seawater with the same ratio of TA/TCO_2 (Millero, 1995). The differences in the values of $\Delta pH/\Delta T$ calculated using different constants are not important for small changes in temperature (5°C), but are quite important for large changes in temperature (25°C) (see Table 3 for calculations of pK_1). Since the values of $\Delta pH/\Delta T$ can differ, we have determined their values using the CO_2 Sys program (Lewis and Wallace, 1998) for each sample. Since the Mehrbach et al. (1973) constants appear to be more internally consistent with field measurements (Clayton et al., 1995; McElligott et al., 1998; Wanninkhof et al., 1999; Lee et al., 1997, 2000), we have used these constants to determine the values of $\Delta pH/\Delta T$ from the measured values of TA and TCO_2. This is supported by the fact that the Mehrbach et al. (1973) values of $pK_2 - pK_1$ are more reliable than the measurements made on artificial seawater (Mojica Prieto and Millero, 2002).

Uncertainties in the measured parameters result in values of pK_1, pK_2 and $pK_2 - pK_1$ with deviations of ± 0.006 in pK_1, ± 0.010 in pK_2 and ± 0.010 in $pK_2 - pK_1$. Larger errors in pH will affect the uncertainty of the values determined for pK_1 and pK_2 by ± 0.01, but not seriously affect the values of $pK_2 - pK_1$ (see Eq. (18)). It should be pointed out that all the calculations were made at 1 atm and not at the in situ pressure.

4. Measurements made on deep waters at a constant temperature

4.1. Measurements of fCO$_2$ at 20°C

We have first examined the results where the fCO_2 was measured at 20°C and the pH at 20°C or 25°C for surface and deep waters (see Table 2). The adjustments of the pH measurements from 25 to 20°C have been made using the CO_2 Sys program (Lewis and Wallace, 1998) as discussed above. The resulting values of pK_1, pK_2 and $pK_2 - pK_1$ are shown as a function of depth (expressed in terms of hydrostatic pressure) where water samples were collected, in Fig. 5 and tabulated in Table 4. The values with deviations

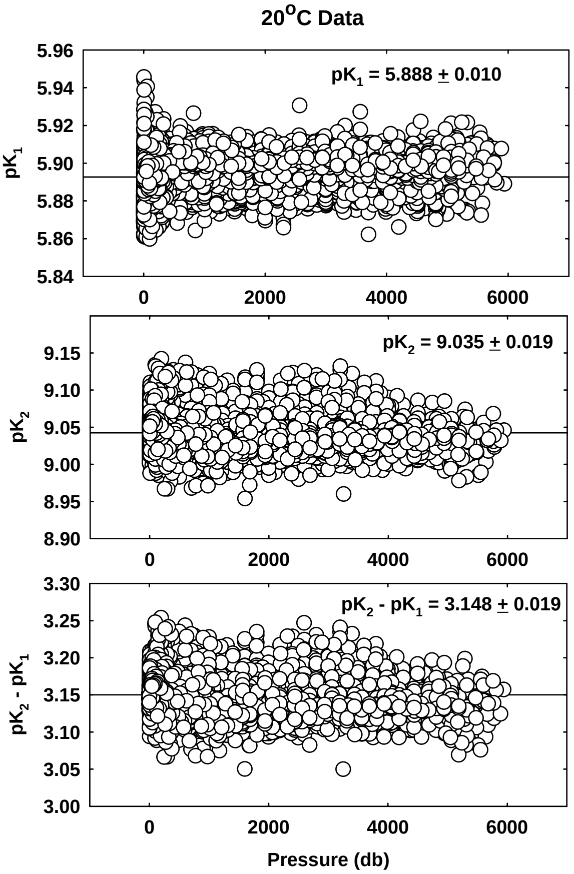

Fig. 5. Calculated values of pK_1, pK_2 and pK_2−pK_1 at 20°C as a function of depth for deep waters from the Atlantic, Indian, Pacific and Southern oceans. The value listed is the average of all the data and is depicted by the horizontal line.

greater than 2σ (0.04 for pK_1 and 0.08 for pK_2) have been eliminated (~3.8%) from the plots. This cuts down the scatter in the data, but does not change the average values of p$K_1 = 5.888 \pm 0.010$, p$K_2 = 9.035 \pm 0.019$ and p$K_2 -$ p$K_1 = 3.148 \pm 0.019$. The average salinity for all the samples was $S = 34.9 \pm 0.5$ which is the same as the deep waters. As shown in Eqs. (5) and (6) and Figs. 1 and 2, the values of pK_1 and pK_2 are not a strong function of salinity (Δp$K_1/\Delta S \approx 0.0048$ and Δp$K_2/\Delta S \approx 0.012$). The p$K_1$ changes by 0.003 and pK_2 changes by 0.006 for a change in salinity of 0.5, which is within the experimental error. A comparison of the calculated values of pK_1 and pK_2 with those obtained in earlier studies (Mehrbach et al., 1973; Hansson, 1973; Goyet and Poisson, 1989; Roy et al., 1993) is shown in Fig. 6. The measured values of pK_1 at 20°C agree with the constants of Mehrbach et al. (1973), Dickson and Millero (1987), Goyet and Poisson (1989) and Roy et al. (1993) to within 0.007. The pK_1 values of Hansson (1973) show much larger deviations (0.01). The values of pK_2 and p$K_2 -$ pK_1 at 20°C are in excellent agreement (0.005) with the results of Mehrbach et al. (1973) (p$K_2 = 9.035$ and p$K_2 -$ p$K_1 = 3.153$). The values of pK_2 and p$K_2 -$ pK_1 agree to within 0.02 with the measurements of Hansson (1973) and the equations of Dickson and Millero (1987). The studies of Goyet and Poisson (1989) and Roy et al. (1993) show much larger deviations (0.03).

Table 4
Calculated values of pK_1, pK_2 and p$K_2 -$ pK_1 ($S = 35$) at various temperatures (on the seawater pH scale)

Data	Waters	pK_1	pK_2	p$K_2 -$ pK_1
4°C	Deep[a]	6.062 ± 0.009	9.321 ± 0.020	3.257 ± 0.020
	Surface[b]	6.057 ± 0.005	9.324 ± 0.008	3.258 ± 0.008
	Lee et al.[c]	6.058 ± 0.006	9.303 ± 0.011	3.245 ± 0.011
	Lueker et al.[c]	—	—	3.241 ± 0.013
20°C	Deep[d]	5.888 ± 0.010	9.035 ± 0.019	3.148 ± 0.019
	Surface[b]	5.879 ± 0.005	9.032 ± 0.008	3.152 ± 0.008
	Lee et al.[c]	5.888 ± 0.006	9.011 ± 0.011	3.139 ± 0.014
	Lueker et al.[c]	—	—	3.141 ± 0.013

[a] Adjustments of 0.002 in pK_1 and 0.006 in pK_2 were made to correct the values from an average salinity of 34.5 ± 0.3 to 35.00 using Eqs. (5) and (6).

[b] At $S = 35$ and estimated from Eqs. (19)–(21).

[c] Values at low fCO$_2$ less than 600 μatm.

[d] Adjustments of 0.0005 in pK_1 and 0.001 in pK_2 to correct for an average salinity of 34.9 ± 0.6 to 35.0 using Eqs. (5) and (6).

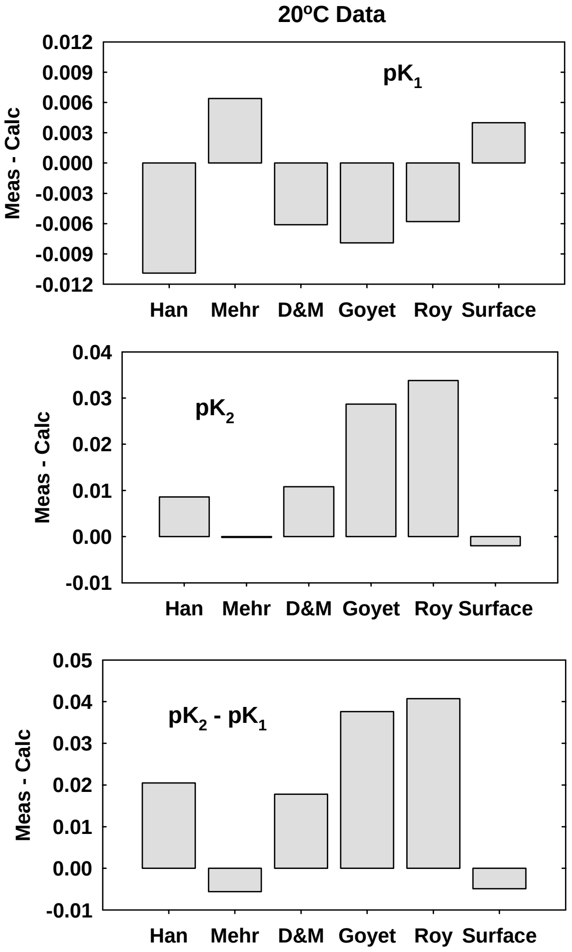

Fig. 6. Comparisons of the field calculated values of pK_1, pK_2 and pK_2 − pK_1 at 20°C with the smoothed literature values and the average value for surface measurements. The surface values were calculated from Eqs. (19)–(21).

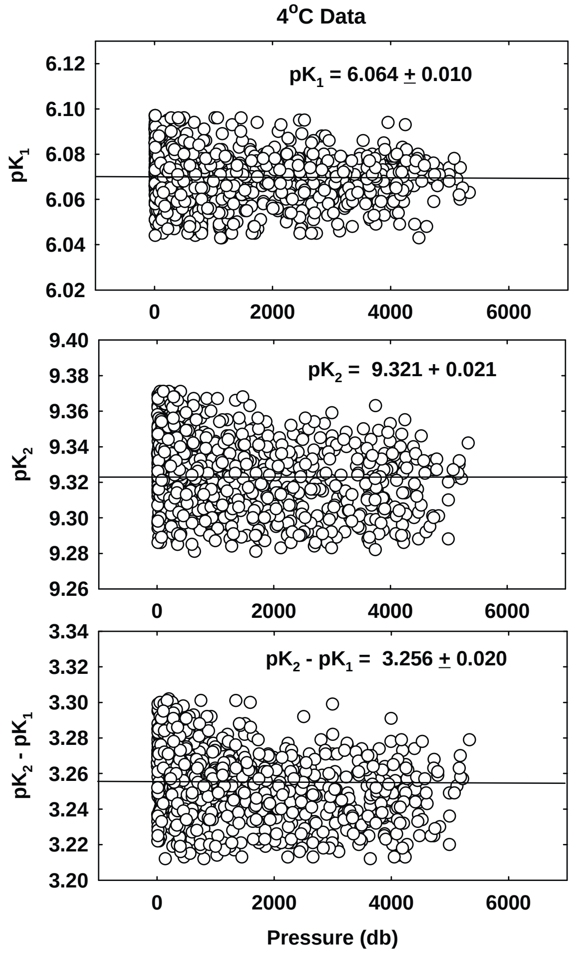

Fig. 7. Calculated values of pK_1, pK_2 and pK_2 − pK_1 at 4°C as a function of depth for deep waters from the Atlantic, Indian, Pacific and Southern oceans. The value listed is the average of all the data and is depicted by the horizontal line.

4.2. Measurements of fCO$_2$ at 4°C

We next examined the measurements made in the Southern Ocean where the TCO$_2$ and fCO$_2$ were determined at 4°C by the Lamont Group (Takahashi et al., 2002). The measurements of pH and TA on this cruise were made by potentiometric methods (Millero et al., 1993) corrected using measurements on CRM. The pH measurements were made at 25°C; thus, the corrections to 4°C are quite large and a function of the constants used. Since the conversion with the constants of Mehrbach et al. (1973) gave values of pK_1 at 4°C that were in good agreement with the literature values; while the others did not, we used them in all the conversions. These large corrections in pH lead to uncertainties in the calculated values of pK_1 and pK_2 at 4°C, but do not affect the calculated values of p$K_2 -$ pK_1. The calculated values of pK_1, pK_2 and p$K_2 -$ pK_1 are shown in Fig. 7. The average values found are p$K_1 = 6.064 \pm 0.010$, p$K_2 = 9.321 \pm 0.021$ and p$K_2 -$ p$K_1 = 3.256 \pm 0.020$. The values of pK_2 and p$K_2 -$ pK_1 at 4°C adjusted to $S = 35$ are shown in Fig. 8.

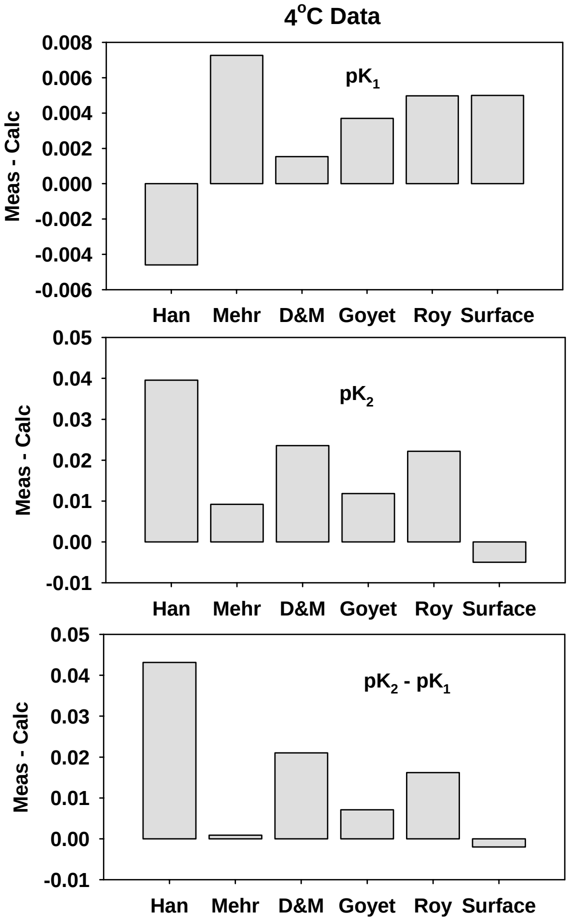

Fig. 8. Comparisons of the field calculated values of pK_1, pK_2 and $pK_2 - pK_1$ at 4°C with the smoothed literature values. The surface values were calculated from Eqs. (19)–(21).

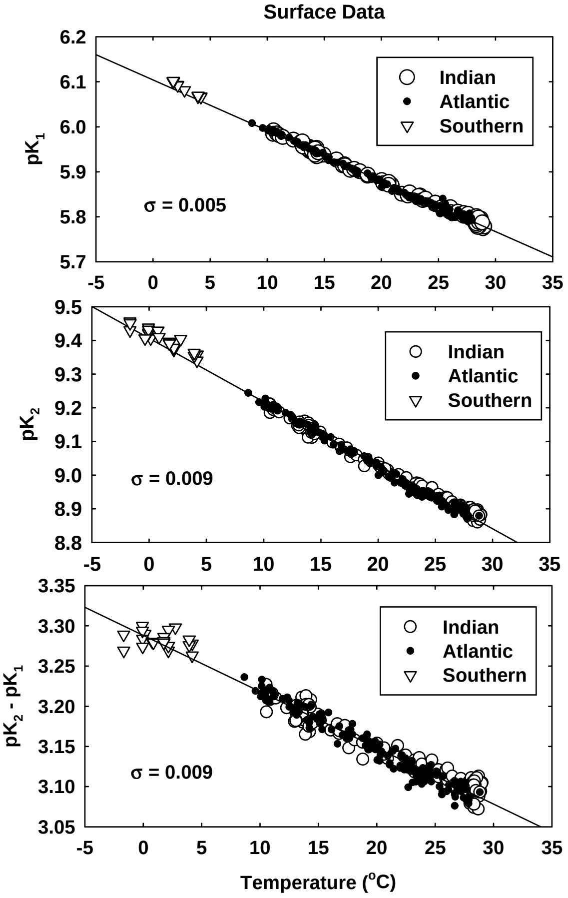

Fig. 9. Calculated values of pK_1, pK_2 and $pK_2 - pK_1$ for surface waters from the Indian, Atlantic, and Southern oceans as a function of temperature. The lines were calculated from Eqs. (19)–(21).

The results are in reasonable agreement with the results of Mehrbach et al. (1973) ($pK_2 = 9.315$ and $pK_2 - pK_1 = 3.258$) and Goyet and Poisson (1989) ($pK_2 = 9.307$ and $pK_2 - pK_1 = 3.249$). The measured values of pK_1 at 4°C are all in reasonable agreement (0.007) with the laboratory studies.

5. Measurements made on surface waters

The field measurements of TA, TCO_2, pH (25°C), and pCO_2 for surface waters have been used to calculate the values of pK_1, pK_2 and $pK_2 - pK_1$. The results for waters from the Indian, Atlantic and Southern oceans are shown in Fig. 9 as a function of temperature and salinity ($t = -1.6$–35°C and $S = 34$–37) and have been fitted to the equations (T/K)

$$pK_1 = 6.359 - 0.00664S - 0.01322(T - 273.15) + 4.989 \times 10^{-5}(T - 273.15)^2, \quad (19)$$

$$pK_2 = 9.867 - 0.01314S - 0.01904(T - 273.15) + 2.4480 \times 10^{-5}(T - 273.15)^2, \quad (20)$$

$$pK_2 - pK_1 = 3.510 - 0.0064S - 0.006711(T - 273.15) \quad (21)$$

with standard deviations of $\sigma = 0.005$ in pK_1, $\sigma = 0.008$ in pK_2 and $\sigma = 0.008$ in p$K_2 - pK_1$. The effect of salinity on pK_1 and pK_2 from the surface data is slightly higher than literature data ($\Delta pK_1/\Delta S \approx 0.0048$ and $\Delta pK_2/\Delta S \approx 0.012$). This is not surprising due to the limited salinity range of the field data. The values calculated from Eqs. (19)–(21) at 4°C and 20°C are compared to the values calculated for the deep waters in Table 4 and Figs. 6 and 8. The agreement is reasonable and within the combined experimental error. The surface values of p$K_2 - pK_1$ are in excellent agreement with the deep-water values and results of Mehrbach et al. (1973) indicating that the uncertainties in pK_1 and pK_2 at 4°C and 20°C are related to errors in pH.

6. Estimations of pK_1 and pK_2 as a function of salinity and temperature

All the field measurements clearly demonstrate that the values of p$K_2 - pK_1$ from the measurements of Mehrbach et al. (1973) are more reliable than those determined in the other laboratory studies. This is largely due to differences in the values of pK_2 determined in real and artificial seawater. The values of pK_1 determined from the field data do not favor a given set of laboratory measurements. This is partly due to uncertainties in the spectroscopic pH measurements and errors in the calculation of in situ values of pH from measurements made at 25°C. The recent pK_1 and p$K_1 + pK_2$ measurements of Mojica Prieto and Millero (2002) have shown to be in good agreement with the work of Mehrbach et al. (1973). These studies have been combined (Mojica Prieto and Millero, 2002) to give (ln = the base -e logarithm)

$$\begin{aligned} pK_1 &= -43.6977 - 0.0129037S + 1.364 \times 10^{-4}S^2 \\ &\quad + 2885.378/T + 7.045159 \ln T \\ &(\sigma = 0.0056), \qquad (22) \end{aligned}$$

$$\begin{aligned} pK_2 &= -452.0940 + 13.142162S - 8.101 \times 10^{-4}S^2 \\ &\quad + 21263.61/T + 68.483143 \ln T \\ &\quad + (-581.4428S + 0.259601S^2)/T \\ &\quad - 1.967035S \ln T \\ &(\sigma = 0.010). \qquad (23) \end{aligned}$$

These equations give pK values somewhat different from those given by Eqs. (19) and (20) (within ±5% for K_1 and ±8% for K_2). However, since Eqs. (19) and (20) are based on field data with relatively narrow salinity range, we feel that these equations are the best representation of the carbonic acid dissociation constants in seawater.

7. Comparisons of p$K_2 - pK_1$ with laboratory measurements

The reliability of our values of p$K_2 - pK_1$ for deep and surface waters can be examined using the recent laboratory measurements of Lee et al. (1996) and Lueker et al. (2000) for seawater. The values of p$K_2 - pK_1$ from the measurements of Lee et al. (1996) as a function of temperature are shown in Fig. 10. The values of p$K_2 - pK_1$ appear to be a linear function of temperature as found for the field measurements (see Fig. 9). The spread of the results at a given temperature is related to changes in the values as a function of fCO$_2$ (Fig. 10b). The values of p$K_2 - pK_1$ at 4°C and 20°C at low fCO$_2$ are compared to our values in Table 4. The agreement is within 0.01 at each of these temperatures and is satisfactory. The values of p$K_2 - pK_1$ from the measurements of Lueker et al. (2000) as a function of temperature are shown in Fig. 11. The values of p$K_2 - pK_1$ also appear to be a linear function of temperature. The spread of some of the results at a given temperature are related to changes in the values as a function of fCO$_2$ (Fig. 11). The scatter is much greater in the Lueker et al. (2000) data than the results of Lee et al. (1996). The results at low fCO$_2$, however, are in reasonable agreement within 0.01 with other workers (Table 4). The effect of fCO$_2$ on the values of p$K_2 - pK_1$ is hard to explain. The data of Lee et al. (1996) indicate that the dependence on fCO$_2$ is largely due to the variation of pK_2. This tends to point to changes in the interactions as a function of fCO$_2$ being related to changes in the ratio of CO_3^{2-}/HCO_3^-.

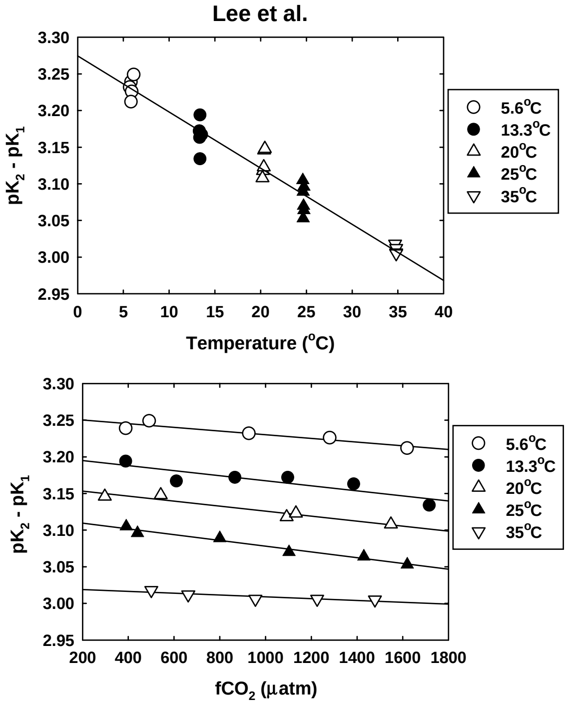

Fig. 10. Values of $pK_2 - pK_1$ determined from the measurements of Lee et al. (1996) as a function of temperature (top) and fCO$_2$ (bottom).

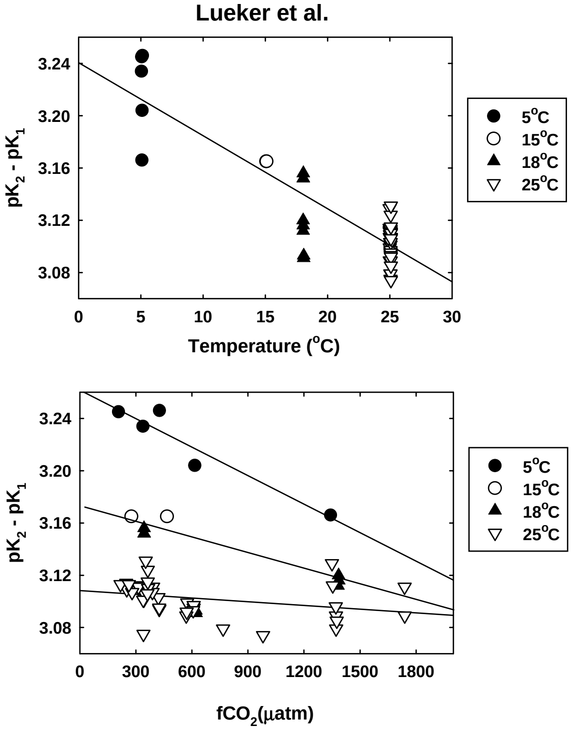

Fig. 11. Values of $pK_2 - pK_1$ determined from the measurements of Lueker et al. (2000) as a function of temperature (top) and fCO$_2$ (bottom).

The recent studies of Mojica Prieto and Millero (2002) indicate that the differences in the values of pK_1 and pK_2 in real and artificial seawater are related to interactions of the borate and carbonate system. At 25°C the values of pK_1 in artificial seawater with boric acid are ~0.01 lower than in artificial seawater without boric acid; while, the values of pK_2 in artificial seawater with boric acid are higher ~0.04 than seawater without boric acid. The interactions responsible for these differences are not clear. The increase in K_1 in real seawater can be attributed to a decrease in the activity coefficient of HCO_3^-, $\gamma(HCO_3^-)$ and the decrease in K_2 can be attributed to an increase in the activity coefficient of CO_3^{2-}, $\gamma(CO_3^{2-})$. If one assumes that the repulsive interactions between $B(OH)_4^-$ and HCO_3^- and CO_3^{2-} are small, one can attribute the changes in $\gamma(HCO_3^-)$ and $\gamma(CO_3^{2-})$ to interactions with $B(OH)_3$. McElligott and Byrne (1998) have shown the interactions of $B(OH)_3$ and HCO_3^- can be due to

$$HCO_3^- + B(OH)_3 = B(OH)_2CO_3^- + H_2O. \qquad (24)$$

Although this reaction would lower $\gamma(HCO_3^-)$, the magnitude of this interaction that they found is not large enough to lower the pK_1 by 0.01. Similar interactions between $B(OH)_3$ and CO_3^{2-} would not be expected to increase $\gamma(CO_3^{2-})$. Further studies of mixtures of boric and carbonic acid mixtures are needed to elucidate these interactions.

If the borate–carbonate ion interactions are assumed to be significant, then the following considerations may be advanced in order to account for the observed decrease in pK_2 (or increase in K_2) with increasing fCO$_2$. The value of K_2 is related to the value in water at 0 ionic strength, K_2^0, and the activity coefficients, $\gamma(i)$, by

$$K_2 = K_2^0\{\gamma(HCO_3^-)/\gamma(H^+)\gamma(CO_3^{2-})\}. \qquad (25)$$

The increase in K_2 can be attributed to an increase in $\gamma(\mathrm{HCO_3^-})$ or a decrease in $\gamma(\mathrm{CO_3^{2-}})$. Since the value of p$K_1$ is not strongly dependent on fCO$_2$, the changes in $\gamma(\mathrm{HCO_3^-})$ cannot be very great. This is in agreement with the studies of McElligott and Byrne (1998). Model calculations of CO$_2$ system in seawater (Millero and Pierrot, 1998) as a function of TCO$_2$ do not yield large changes in $\gamma(\mathrm{HCO_3^-})$ or $\gamma(\mathrm{CO_3^{2-}})$. It should be noted that the activity coefficients for B(OH)$_3$ and B(OH)$_4^-$ would also depend on the concentrations of HCO$_3^-$ and CO$_3^{2-}$ via ionic interactions. Hence, the value of K_B would vary with fCO$_2$, and the direction of its changes depends upon the nature of the interactions and ion pairs. This means that our present understanding of the ionic interactions affecting the carbonate system in seawater is deficient.

8. Proposed dependence of K_2 on TCO$_2$

Our determinations of pK_2 from the field data do not show any effect of fCO$_2$ on the calculated values within the experimental error of the calculations as shown in Fig. 5. This is not surprising since at 20°C, the effect is quite small (see Figs. 10 and 11). Internal consistency tests, however, do show this effect (Lueker et al., 2000; Lee et al., 2000). The differences in the measured and calculated values of fCO$_2$ using an input of TA and TCO$_2$ (which require reliable values of pK_2 − pK_1) are shown in Fig. 12A for all the stations listed in Table 2. The average differences in fCO$_2$ are 26.6 μatm while the standard errors are 29.7 μatm. The deviations at fCO$_2$ above ~600 μatm are greater than at low fCO$_2$, apparently due to changes in the pK_2 − pK_1 (Lueker et al., 2000; Lee et al., 2000). The differences of the measured and calculated values of fCO$_2$ as a function of TCO$_2$ (Fig. 13A) show larger deviation at high TCO$_2$. At values of TCO$_2$ less than 2050 μmol kg^{-1}, the deviations are independent of the TCO$_2$. By adjusting the values of pK_2 above 2050 μmol kg^{-1}, it was possible to lower the average deviations to 0 μatm and the standard error to 22.7 μatm (see Figs. 12B and 13B). This resulted in the empirical relationship

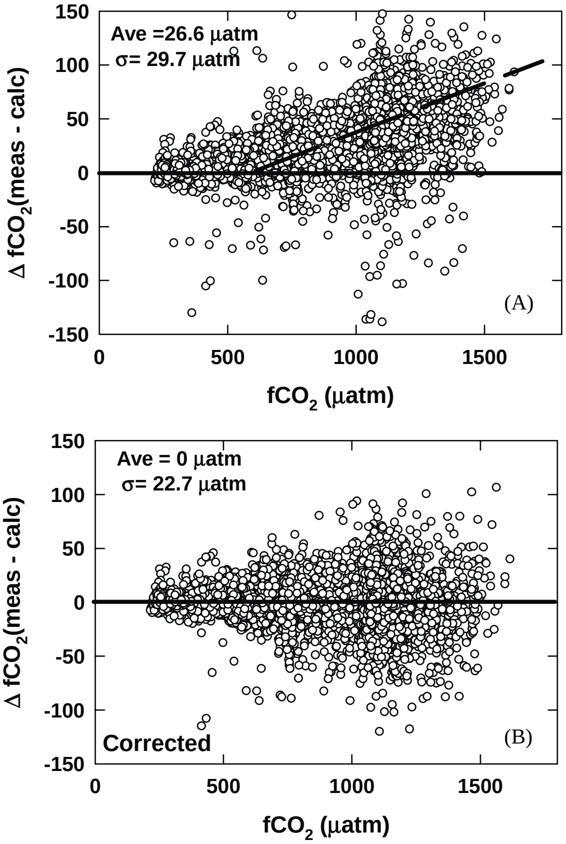

Fig. 12. Differences between the measured and calculated values of fCO$_2$ from an input of TA and TCO$_2$ as a function of fCO$_2$ using the combined constants of Mehrbach et al. (1973) and Mojica Prieto and Millero (2002) (Eqs. (22) and (23)). The values in panels (A) and (B) were determined without and with the correction for changes in pK_2 as a function of TCO$_2$ (Eq. (26)). The dotted line in (A) is an estimate of the offset at high fCO$_2$.

$$\mathrm{p}K_2^{\mathrm{TCO_2}} = \mathrm{p}K_2 - 1.6\times10^{-4}(\mathrm{TCO_2} - 2050) \qquad (26)$$

which is valid at 20°C and at TCO$_2$ > 2050 μmol kg^{-1}. Similar calculations at 4°C were not possible since the values of fCO$_2$ of all the waters are below 680 μatm. As shown in Fig. 14, the values of the slope of pK_2 as a function of fCO$_2$ at 20°C or TCO$_2$ found from the field data are in reasonable agreement with the values determined from the laboratory measurements of Lee et al. (1996) and Lueker et al. (2000) (-1.2×10^{-4} to

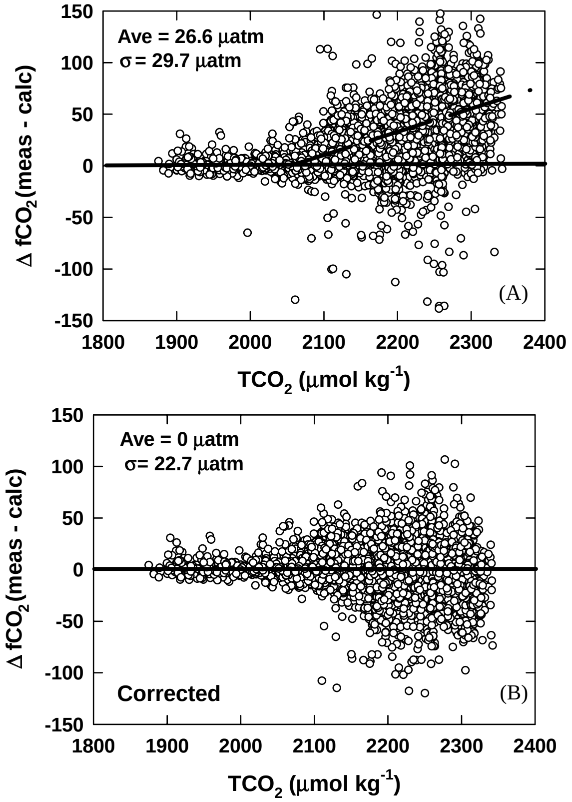

Fig. 13. Differences between the measured and calculated values of $f\mathrm{CO_2}$ from an input of TA and $\mathrm{TCO_2}$ as a function of $\mathrm{TCO_2}$ using the combined constants of Mehrbach et al. (1973) (top) and Mojica Prieto and Millero (2002) (bottom) (Eqs. (22) and (23)). The values in (A) and (B) were determined without and with the correction for changes in $\mathrm{p}K_2$ as a function of $\mathrm{TCO_2}$ (Eq. (26)). The dotted line in (A) is an estimate of the offset at high $\mathrm{TCO_2}$.

-1.9×10^{-4}). The values at other temperatures (t°C) can be estimated from the linear fit (Fig. 14) of the results of Lee et al. (1996) and Lueker et al. (2000), $\Delta(\mathrm{p}K_2-\mathrm{p}K_1)/\Delta\mathrm{TCO_2}=-2.65\times10^{-4}+5.74\times10^{-6}t$ with a unit of kg μmol^{-1}. As discussed earlier, the borate–carbonate ion interactions would affect not only the K_2 for carbonic acid, but also the K_B for boric acid. Hence, the proposed relationships include the combined effects on K_2 and K_B, and should be considered as an empirical expression which is intended to correct for imperfections of the chemical model used.

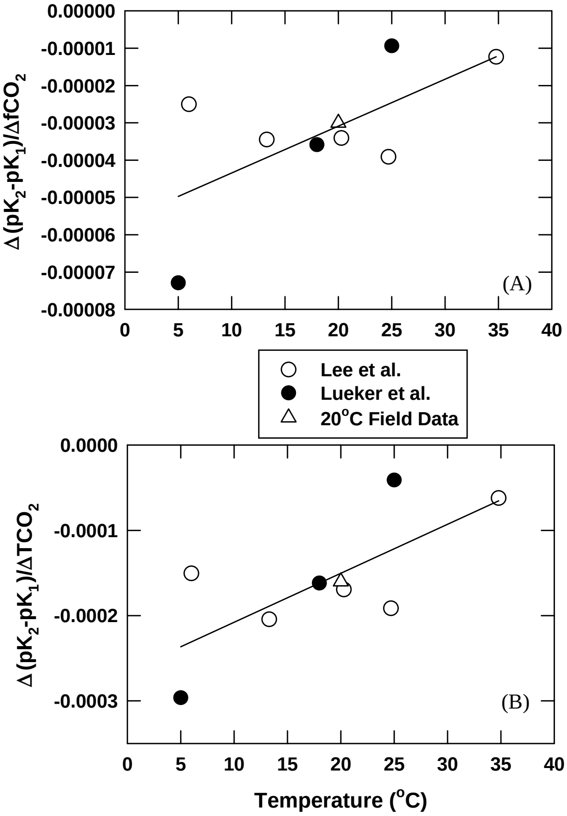

Fig. 14. Comparison of the slopes of $\mathrm{p}K_2$ as a function of $f\mathrm{CO_2}$ and $\mathrm{TCO_2}$ obtained from the field data at 20°C with the measurements of Lee et al. (1996) and Lueker et al. (2000) as a function of temperature.

When pH values are used with $\mathrm{TCO_2}$ or TA for the computation of $f\mathrm{CO_2}$, the results are not sensitively affected by the uncertainties in K_1 and K_2. For example, for an input of pH and $\mathrm{TCO_2}$ an uncertainty of 0.01 in $\mathrm{p}K_1$ yields an error of 10 μatm in $f\mathrm{CO_2}$; while an uncertainty of 0.04 in $\mathrm{p}K_2$ leads to an error of 7 μatm. The errors in the calculated values of $f\mathrm{CO_2}$ from an input of pH and $\mathrm{TCO_2}$ are examined in Fig. 15A. The average error is 9.5 μatm and the standard error is 21.8 μatm. When the value of $\mathrm{p}K_2$ using Eq. (26) is used (see Fig. 15B), the average error remains unaffected, and is 11.8 μatm with the standard error is 22.3 μatm. Thus, when using an input of pH and $\mathrm{TCO_2}$, the correction of $\mathrm{p}K_2$ at high $\mathrm{TCO_2}$ does not strongly influence the calculated values of $f\mathrm{CO_2}$. The effect of an addition of 0.0047 to

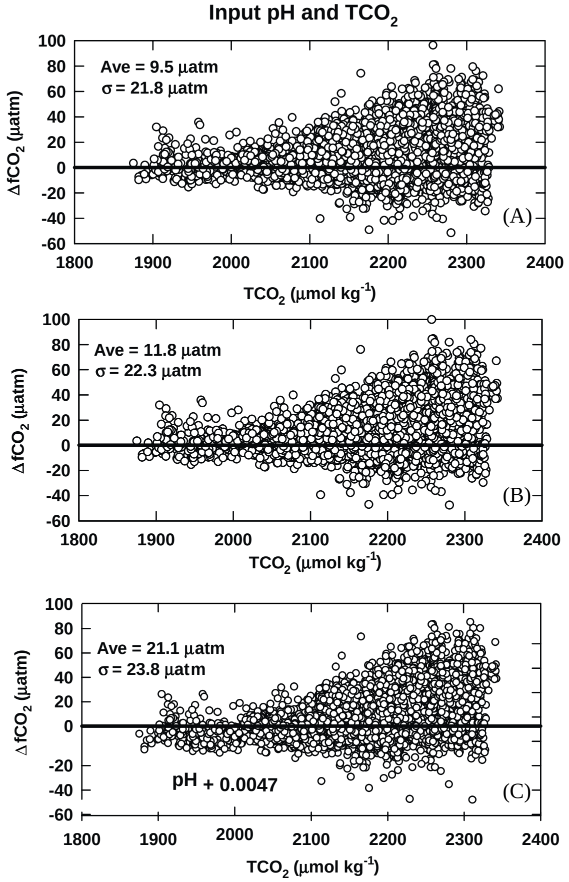

Fig. 15. Comparison of the measured and calculated values of fCO$_2$ from an input of pH and TCO$_2$ using the combined constants of Mehrbach et al. (1973) and Mojica Prieto and Millero (2002) (Eqs. (22) and (23)). The values in (A) and (B) were determined without and with the correction for changes in pK_2 as a function of TCO$_2$ (Eq. (26)). The values in (C) have been determined by increasing the pH by 0.0047.

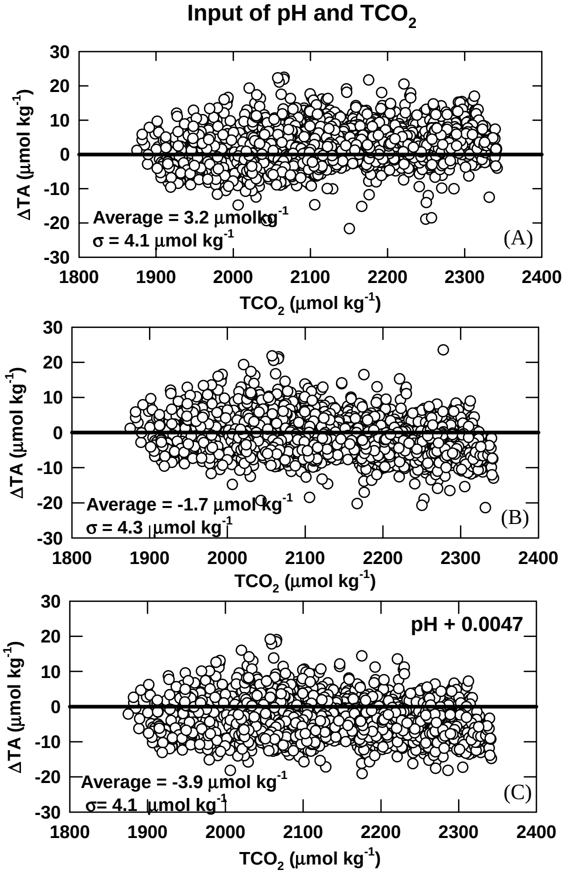

Fig. 16. Comparison of the measured and calculated values of TA from an input of pH and TCO$_2$ using the combined constants of Mehrbach et al. (1973) and Mojica Prieto and Millero (2002) (Eqs. (22) and (23)). The values in (A) and (B) were determined without and with the correction for changes in pK_2 as a function of TCO$_2$ (Eq. (26)). The values in (C) have been determined by increasing the pH by 0.0047.

the pH (DeValls and Dickson, 1998) is shown in Fig. 15C. The addition increases not only the fCO$_2$ deviations, but also the average error to 21.1 µatm. These results indicate that an increase of the pH by 0.0047 is not needed when calculating fCO$_2$.

The errors in the calculated values of TA from an input of pH and TCO$_2$ are examined in Fig. 16A. The average error is 3.2 µmol kg^{-1} and the standard error is 4.1 µmol kg^{-1}. The correction of the value of pK_2 using Eq. (26) is shown in Fig. 16B. The average error is decreased to −1.7 µmol kg^{-1} and the standard error is increased to 4.3 µmol kg^{-1}. Thus, when using an input of pH and TCO$_2$, the correction of pK_2 at high TCO$_2$ improves slightly the calculated values of TA. The effect of an addition of 0.0047 to the pH (DeValls and Dickson, 1998) is shown in Fig. 16C. The addition causes the average deviation in TA to be 3.9 µmol kg^{-1} and does not strongly affect the standard error. These results indicate that the correction of the pH by 0.0047 is not needed to make reliable calculations of fCO$_2$ and TA from an input of pH and TCO$_2$. It should be pointed out that an input of pH and TA to calculate $f\mathrm{CO}_2$ and TCO_2 yields similar results.

9. Possible effects of organic acids

The field data shown in Figs. 12 and 13 as well as the laboratory data presented by Lee et al. (1996) and Lueker et al. (2000) demonstrate that the difference between the observed and computed $f\mathrm{CO}_2$ values increase systematically for waters with greater $f\mathrm{CO}_2$ and TCO_2 concentrations. As discussed earlier, this may be accounted for by an increase in K_2 (or a combined effect of K_2 for carbonic acid and K_B for boric acid) with increasing TCO_2 for $f\mathrm{CO}_2$. The increase in K_2 may be accounted for in terms of assumed borate–carbonate ion pairs. However, since the CO_3^{2-} concentration in ocean waters decreases with increasing $f\mathrm{CO}_2$ and TCO_2, the $\gamma(\mathrm{CO}_3^{2-})$ value tends to increase and hence K_2 is expected to decrease with waters with high $f\mathrm{CO}_2$ values. Thus, this hypothesis is somewhat inconsistent with the known distribution of carbon chemistry in the oceans. Accordingly, an alternative hypothesis is considered. Of various organic matter dissolved in ocean waters ($\sim 80\,\mu\mathrm{mol\,kg}^{-1}$ in surface waters and $\sim 40\,\mu\mathrm{mol\,kg}^{-1}$ in deep waters as total dissolved organic carbon, DOC), a portion of DOC might be composed of weak organic acids. Since these acids are included in the titrimetric determination of the TA, extra terms for organic acids must be added to the definition of the alkalinity (Eq. (7)). However, since neither the detailed nature of DOC nor the dissociation constants for organic acids are well known, the effect of organic acids on the alkalinity cannot be determined rigorously in each water sample. Nevertheless, we attempt to estimate possible effects of organic acids by making the following assumptions. First, the concentration of weak organic acids in seawater is assumed to be uniformly $8\,\mu\mathrm{mol\,kg}^{-1}$ throughout water columns. In view of the fact that DOC decreases from the surface to deep waters by a factor of two to three, this assumption may be an oversimplification for the real ocean. Second, since the pK values for organic acids in lake waters are generally 3–4, they are totally dissociated at pH of normal seawater (8.2–7.9). Using the shipboard data obtained during Pacific WOCE P14/15, the effect of this hypothetical organic acid on computed $f\mathrm{CO}_2$ values is demonstrated below.

Fig. 17A shows that the difference between the observed and computed $f\mathrm{CO}_2$ values at 20°C increases systematically with increasing $f\mathrm{CO}_2$ for seawater. The computed $f\mathrm{CO}_2$ values were obtained using the observed values for TCO_2, alkalinity, salinity and the concentrations of

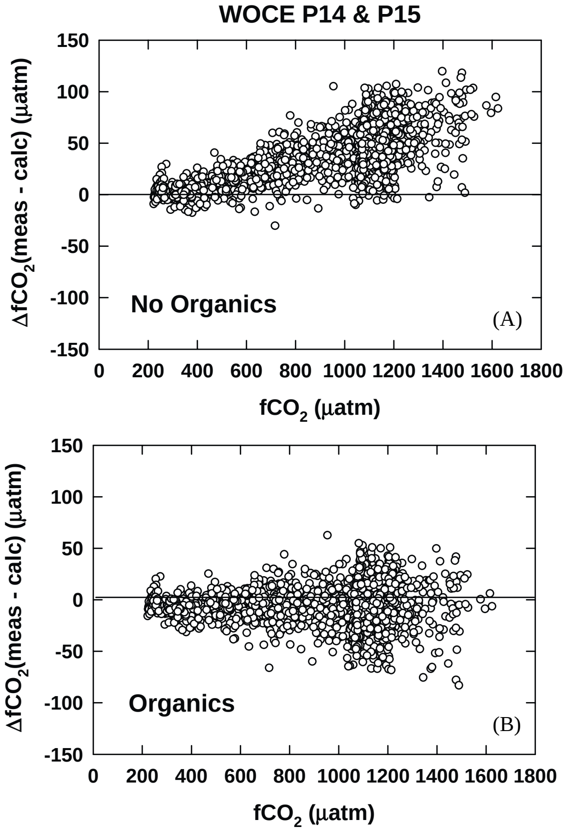

Fig. 17. (A) Differences between the measured and calculated values of $f\mathrm{CO}_2$ at 20°C from an input of the WOCE P14/P15 TA and TCO_2 data using the constants of Mehrbach et al. (1973). (B) The differences for the same data computed by the addition of an organic acid term to the definition of the alkalinity. A constant organic acid concentration of $8\,\mu\mathrm{mol\,kg}^{-1}$ and a pK of 4 have been assumed. The systematic deviation of $f\mathrm{CO}_2$ in waters with greater $f\mathrm{CO}_2$ has been eliminated.

silicate and phosphate. Fig. 17B shows the difference computed using a constant amount of organic acids (8.0 μmol kg^{-1}) by adding to the alkalinity equation (Eq. (7)) a single term for organic acid with a pK of 4. The resulting fCO$_2$ difference values scatter above and below the zero line evenly yielding a mean difference of 2.6 μatm. The magnitude of scatter is consistent with the uncertainty in computed fCO$_2$ values resulting from the stated uncertainties in the measurements of TCO$_2$ and alkalinity. Thus, the observed systematic trend for deviations of the computed fCO$_2$ values can be eliminated by this hypothesis as satisfactorily as the K_2 hypothesis. Testing of this hypothesis will require chemical characterization of organic acids dissolved in seawater, especially their changes in concentrations and properties geographically and with water depth. Furthermore, the alkalinity values hitherto reported for shipboard operations as well as for laboratory experiments using natural seawaters include unspecified contributions from dissolved organic acids. As the precision of measurements improves for the alkalinity, TCO$_2$, fCO$_2$ and pH, the effects of organic acids could manifest themselves as imperfections in the chemical models for seawater, which are commonly used for geochemical and global carbon cycle model studies.

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