Supplement of

Current estimates of $K_1^*$ and $K_2^*$ appear inconsistent with measured CO$_2$ system parameters in cold oceanic regions

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Table of contents

S1 Overview of past studies and derivations of the carbonic acid dissociation constants…. p.2
S2 Additional derivation of expressions for $K_1^*$ and $K_2^*$ …………………………… p.4
S3 Reasons for discarding data from cruises #33AT20120419 and #49NZ20010828 …… p.5
S4 Alternative iterative procedure …………………………………………………………… p.7
Supplementary references…………………………………………………………………p.8
S1 Overview of past studies and derivations of the carbonic acid dissociation constants

Table S1. Overview of most commonly used (i.e. included in most popular carbonate system calculation software) and recently published stoichiometric equilibrium constants at atmospheric pressure, and some of their properties and methodological details. Studies in italic indicate refits of previous studies.

<table>
<thead>
<tr>
<th>Reference</th>
<th>T range (°C)</th>
<th>S_p range</th>
<th>pH scale</th>
<th>σ of fit</th>
<th>Medium</th>
<th>Method</th>
</tr>
</thead>
<tbody>
<tr>
<td>Mehrbach et al., 1973</td>
<td>2 to 35</td>
<td>19 to 43</td>
<td>NBS</td>
<td>lnK_1</td>
<td>Natural seawater (filtered at 0.45 µm)</td>
<td>Electrochemical cell with glass electrode and Hg–Hg_2Cl_2 (calomel) reference electrode</td>
</tr>
<tr>
<td>M1973 refit by Dickson and Millero, 1987</td>
<td></td>
<td></td>
<td>SWS</td>
<td></td>
<td></td>
<td>Recalculation of K_2; reformulation on SWS scale</td>
</tr>
<tr>
<td>M1973 refit by Lueker et al., 2000</td>
<td></td>
<td></td>
<td>T</td>
<td></td>
<td></td>
<td>K_2 determined as by Dickson and Millero (1987); reformulated to total scale</td>
</tr>
<tr>
<td>Hansson, 1973</td>
<td>5 to 30</td>
<td>20 to 40</td>
<td>SWS</td>
<td></td>
<td>Artificial seawater (no Na_2CO_3)</td>
<td>Electrochemical cell with glass electrode and Ag–AgCl reference electrode</td>
</tr>
<tr>
<td>H1973 refit by Dickson and Millero, 1987</td>
<td></td>
<td></td>
<td>SWS</td>
<td></td>
<td></td>
<td>Corrected for deviations of the sulfate concentration and lack of fluoride in medium</td>
</tr>
<tr>
<td>M1973 and H1973 refit by Dickson and Millero, 1987</td>
<td>2 to 35</td>
<td>0 to 40</td>
<td>SWS</td>
<td></td>
<td></td>
<td>Pooling of 1973 and H1973 data sets at SWS scale</td>
</tr>
<tr>
<td>Goyet and Poisson, 1989</td>
<td>−1 to 40</td>
<td>10 to 50</td>
<td>SWS</td>
<td></td>
<td>Artificial seawater (incl. Na_2CO_3)</td>
<td>Electrochemical cell with glass electrode and Hg–Hg_2Cl_2 (calomel) reference electrode</td>
</tr>
<tr>
<td>Roy et al., 1993</td>
<td>0 to 45</td>
<td>5 to 45</td>
<td>T</td>
<td>±0.0048 (lnK_1) ±0.0070 (lnK_2)</td>
<td>Artificial seawater (no Na_2CO_3)</td>
<td>Electrochemical cell (no liquid junction) with Pt–H_2 and Ag–AgCl electrodes</td>
</tr>
<tr>
<td>Mojica Prieto and Millero, 2002</td>
<td>0 to 45</td>
<td>5 to 42</td>
<td>SWS</td>
<td></td>
<td>Artificial seawater (incl. Na_2CO_3); natural seawater (filtered at 0.45 µm)</td>
<td>Electrochemical cell with glass electrode and Ag–AgCl reference electrode; spectrophotometer</td>
</tr>
<tr>
<td>Reference</td>
<td>T range</td>
<td>S range</td>
<td>pH scale</td>
<td>σ of fit</td>
<td>Medium</td>
<td>Method</td>
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<tr>
<td>Millero et al., 2002</td>
<td>−1.6 to 35</td>
<td>34 to 37</td>
<td>SWS</td>
<td></td>
<td>Natural seawater</td>
<td>Concurrent measurements of TA, DIC, pH and pCO₂</td>
</tr>
<tr>
<td>Millero et al., 2006</td>
<td>0 to 50</td>
<td>1 to 50</td>
<td>SWS</td>
<td></td>
<td>Natural seawater (filtered at 0.45 µm)</td>
<td>Electrochemical cell with glass electrode and Ag–AgCl reference electrode</td>
</tr>
<tr>
<td>Millero, 2010</td>
<td>0 to 50</td>
<td>1 to 50</td>
<td>SWS, T, F</td>
<td></td>
<td>Pooling of M1973, MPM2002 and M2006 data, recalculations on three different pH scales</td>
<td></td>
</tr>
<tr>
<td>Waters et al., 2013, 2014</td>
<td>0 to 45</td>
<td>5 to 45</td>
<td>SWS, T, F</td>
<td></td>
<td>Update from M2010 using a Pitzer ion-interaction model</td>
<td></td>
</tr>
<tr>
<td>Tishchenko et al., 2013</td>
<td>0 to 30</td>
<td>1.5 to 40</td>
<td>T</td>
<td></td>
<td>Artificial seawater (incl. NaHCO₃)</td>
<td>Electrochemical cell (no liquid junction) with pH-glass and Ag–AgCl electrodes</td>
</tr>
<tr>
<td>Papadimitriou et al, 2018</td>
<td>−6 to 25</td>
<td>33 to 100</td>
<td>T</td>
<td></td>
<td>Natural seawater, seawater-derived brines (filtered at 0.2 µm)</td>
<td>Concurrent measurements of TA, DIC, pH and pCO₂</td>
</tr>
</tbody>
</table>
S2 Additional derivation of expressions for $K_1^*$ and $K_2^*$

The following section describes expressions for $K_1^*$ and $K_2^*$ as functions of any three variables of the set carbonate alkalinity (CA), dissolved inorganic carbon (DIC), partial pressure of CO$_2$ ($p$CO$_2$) and proton concentration ($[H^+]$), and $K_1^*$ (for $K_2^*$) or $K_2^*$ (for $K_1^*$). These expressions were derived based on equations given by Dickson et al. (2007), who provide a comprehensive overview of carbonate system equations, based on CA, DIC, $p$CO$_2$ and $[H^+]$, in their Chapter 2. Here, for brevity, their equations are not repeated, but are referred to as Eq. (D#), where # represents the equation number used in their chapter. Note that, in comparison to Dickson et al. (2007), we use $H_2CO_3^*$ instead of CO$_2^*$ to represent the sum of $H_2CO_3$ and solvated CO$_2$. We also use $p$CO$_2$ instead of $f$CO$_2$; this difference is accounted for in the calculation of $K_0$.

Recall that $K_1^*$ and $K_2^*$ are normally defined in terms of $[H^+]$, and the acid-base species for which equilibrium they describe:

$$K_1^* = \frac{[HCO_3^-][H^+]}{[H_2CO_3^2]} \quad (S1)$$

$$K_2^* = \frac{[H^+][CO_3^{2-}]}{[HCO_3^-]} \quad (S2)$$

S2.1 Expressions for $K_1^*$ and $K_2^*$ as a function of DIC, CA and $[H^+]$

To derive $K_1^*$ as a function of this set of variables, we use Eq. (S1) and express $[HCO_3^-]$ and $[H_2CO_3^2]$ in terms of DIC, CA, $[H^+]$ and $K_2^*$. For this, we use Eq. (D58) and Eq. (D87) for $[HCO_3^-]$ and $[H_2CO_3^2]$, respectively. Upon substituting these equations into Eq. (S1) and multiplying the numerator and denominator by $([H^+] + 2K_2^*)$, we obtain the final expression for $K_1^*$:

$$K_1^* = \frac{CA[H^+]^2}{([H^+] + 2K_2^*)DIC - CA([H^+] + K_2^*)} \quad (S3)$$

The derivation of $K_2^*$ is done in a similar manner. We use Eq. (S2) and replace $[CO_3^{2-}]$ and $[HCO_3^-]$ by Eq. (D85) and Eq. (D84), respectively. Both the numerator and denominator were then multiplied by $(2[H^+] + K_1^*)$, and the expression for $K_2^*$ becomes:

$$K_2^* = \frac{[H^+][CA + K_1^*CA - K_1^*DIC]}{K_1^*(2DIC - CA)} \quad (S4)$$

S2.2 Expressions for $K_1^*$ and $K_2^*$ as a function of CA, $[H^+]$ and $p$CO$_2$

Here, we again use Eq. (S1) to express $K_1^*$ and replace $[HCO_3^-]$ with Eq. (D58) and $[H_2CO_3^2]$ with Eq. (D61). Upon multiplying the numerator and denominator by $([H^+] + 2K_2^*)$, we obtain:

$$K_1^* = \frac{CA[H^+]^2}{K_0pCO_2([H^+] + 2K_2^*)} \quad (S5)$$

In case of $K_2^*$, in Eq. (S2) $[CO_3^{2-}]$ and $[HCO_3^-]$ were replaced with Eq. (D90) and Eq. (D89), respectively. The numerator and denominator were then multiplied by $2[H^+]$, resulting in:
\[ K_2^* = \frac{[H^+](CA[H^+] - K_0 K_1^* pCO_2)}{2K_0 K_1^* pCO_2} \]  

(S6)

**S2.3 Expressions for \( K_1^* \) and \( K_2^* \) as a function of DIC, [\( H^+ \)] and \( pCO_2 \)**

In this variable set, to derive an equation for \( K_1^* \), \( [HCO_3^-] \) can be expressed by Eq. (D93), while \( [H_2CO_3^+] \) is again replaced with Eq. (D61). Upon substituting this into Eq. (S1) and multiplying both the numerator and denominator by \(([H^+] + K_2^*)\) we obtain:

\[ K_1 = \frac{[H^+]^2(DIC - K_0 pCO_2)}{K_0 fCO_2([H^+] + K_1^*)} \]  

(S7)

For \( K_2^* \), we replace \([CO_3^{2-}]\) by Eq. (D94) and \([HCO_3^-]\) by Eq. (D92). Upon multiplying the numerator and denominator by \([H^+]\), we obtain:

\[ K_2^* = \frac{[H^+](DIC[H^+] - K_0 pCO_2[H^+] - K_0 K_1^* pCO_2)}{K_0 K_1^* pCO_2} \]  

(S8)

**S2.4 Expressions for \( K_1^* \) and \( K_2^* \) as a function of DIC, CA and \( pCO_2 \)**

This set of variables does not allow for separate expressions for \( K_1^* \) and \( K_2^* \). Rather, a single equation is derived, which should be solved for \( K_1^* \) and \( K_2^* \) sequentially using a Newton-Raphson technique. This single equation is derived by combining Eq. (D17) and Eq. (D53), the respective definitions of DIC and CA, into:

\[ 2DIC - CA = 2[H_2CO_3^+] + [HCO_3^-] \]  

(S9)

Then, we subtract \((2DIC - CA)\) from both the left- and right-hand sides of Eq. (S9), replace \([HCO_3^-]\) by Eq. (D79) and express \([H_2CO_3^+]\) again through Eq. (D61), leading to:

\[ 2K_0 pCO_2 + \frac{1}{2} \left( \frac{K_1^*}{K_2^*} K_0 pCO_2 + \sqrt{\left( \frac{K_1^*}{K_2^*} K_0 pCO_2 \right)^2 - 4 \frac{K_1^*}{K_2^*} K_0 pCO_2 (K_0 pCO_2 - DIC)} \right) - 2DIC + CA = 0 \]  

(S10)

**S3 Reasons for discarding cruises #33AT20120419 and #49NZ20010828**

In Fig. S1, we show \([H_2CO_3^+], [HCO_3^-] \) and \([CO_3^{2-}]\) as a function of temperature and salinity as computed using the Lueker et al. (2000) dissociation constants and with six different carbonate variable pairs, to study carbonate system interconsistency in the different cruises that constitute our dataset. All data are from the top 5 meters of the water column, quality-controlled, and associated with a WOCE flag of 2 (i.e., “acceptable”). From Fig. S1, we see that for cruises #33AT20120419 and #49NZ20010828, the computed concentration of carbonate species can be very different depending on the input pair.

For cruise #49NZ20010828, the three pairs involving \( pCO_2-pH, DIC-pH \) and \( TA-pH \) yield very different results, while the three pairs that do not include \( pH \) appear to be interconsistent. Cruise #49NZ20010828 (GLODAP code #478) was not considered for carbon interconsistency checks, as seen in the GLODAP adjustment table (accessible on https://glodapv2.geomar.de/adjustments/list), because according to the adjustment table, there were
only a few shallow profiles to compare. The quality controller for this cruise noted that there “seem to be an offset” in the pH data and that perhaps the correct flag should be “poor data”.

For cruise #33AT20120419, we see in Fig. S1 that the three pairs that include pCO₂ as a variable yield very different [H₂CO₃], [HCO₃⁻] and [CO₃²⁻] values than the three pairs without pCO₂ data. This would go in the sense of an erroneous pCO₂ dataset for this cruise. During carbon interconsistency checks, the pH from cruise #33AT20120419 (GLODAP code #330) was corrected by adding a constant value of 0.012. This procedure is quite common for GLODAP data and we did not see any particular comment or warming for this dataset in the GLODAP adjustment table. Given the apparent inconsistency of the carbonate system highlighted here for this cruise, it was not included in the dataset that we used to derive the dissociation constants.

![Figure S1.](image)

**Figure S1.** [H₂CO₃], [HCO₃⁻] and [CO₃²⁻] as a function of (left) in-situ temperature and (right) practical salinity, as computed with 6 different carbonate system variable pairs: TA-DIC (light green), TA-pH (light blue), DIC-pH (yellow), pCO₂-DIC (purple), pCO₂-pH (dark blue) and pCO₂-TA (red). Circles represents the 948 data points used for our analysis, squares are data from cruise #33AT20120419 (GLODAP code #330) and triangles are data from cruise #49NZ20010828 (GLODAP code #478).
S4 Alternative iterative procedure

Since there are only two pH-independent parameters (DIC, pCO₂), we can use these two parameters and one pH-dependent parameter (either pH itself or CA) to initialise the iterative procedure. This implies that either K₁⁺ or K₂⁺ must be assigned an initial value, before starting the iterations. Here, we present an alternative iterative fitting procedure, in which in situ K₁⁺ rather than K₂⁺ was initially set to Lueker et al. (2000). Again, each iteration consisted of four different steps.

(1) First, K₂⁺ was computed from in situ DIC, CA, pCO₂ and K₁⁺ from Lueker et al. (2000) and subsequently fitted (see details in the main text) to a general expression as a function of temperature and salinity of the form:

\[ pK_{1 \ or \ 2}^+ = a_1 + a_2 S_p + a_3 S_p^2 + \frac{a_4}{T} + a_5 \ln(T) \]  

(S11)

where pKᵢ⁺ corresponds to -log₁₀(Kᵢ) and aᵢ are fitting coefficients determined using nonlinear least-squares estimates (function nlsLM).

(2) Second, this new expression for K₂⁺, and CA and the expression for K₁⁺ used in step 1 were used to compute pH at in situ temperature, see details for this procedure in the main text.

(3) Third, CA – that is dependent on pH – is updated based on the new [H⁺], as per Eq. (6) of the main text and the method outlined for the initial calculation of CA.

(4) Fourth, we use Eq. (8) of the main text to calculate K₁⁺ as a function of pCO₂, DIC, and the new pH and CA, and fit these in-situ computed constants to an equation of the form of Eq. (S11).

These four steps are repeated and at each iteration, K₁⁺, CA, and pH from the previous iteration are used as initial values.

The coefficients aᵢ for pK₁⁺ and pK₂⁺ obtained with this procedure, in an equation of the form of Eq. (S11), and after 30 iterations, are reported in Table S2, along with their respective confidence intervals. In both expressions, all coefficients were significantly different from zero (p values < 0.001).

<table>
<thead>
<tr>
<th></th>
<th>pK₁⁺</th>
<th>pK₂⁺</th>
</tr>
</thead>
<tbody>
<tr>
<td>a₁</td>
<td>-170.233 ± 8.898</td>
<td>-47.191 ± 14.308</td>
</tr>
<tr>
<td>a₂</td>
<td>-0.011555</td>
<td>-0.01781</td>
</tr>
<tr>
<td>a₃</td>
<td>0.0001152</td>
<td>0.0001122</td>
</tr>
<tr>
<td>a₄</td>
<td>8421.155 ± 388.159</td>
<td>3693.155 ± 626.060</td>
</tr>
<tr>
<td>a₅</td>
<td>25.994 ± 1.333</td>
<td>7.768 ± 2.143</td>
</tr>
</tbody>
</table>

In Fig. S2, we show a comparison of our pK values when K₂⁺ is initially set to the value of Lueker et al. (2000) (as presented in the main text of this manuscript, see Table 1) with our pK values...
when $K_1^*$ is initially set to the value of Lueker et al. (2000) (as presented in this section, see Table S2). Regardless of the K value that is initially set to the value of Lueker et al. (2000), both our pK fits are statistically indistinguishable, and higher than the Lueker et al. (2000) values at low temperatures.

![Figure S2](image)

**Figure S2.** (a) $pK_1^*$ and (b) $pK_2^*$ as a function of temperature where the colour represents practical salinity ($S_p$), and the fits are fixed for a $S_p$ of 35. The solid blue line represents the pK$^*$ fits from Lueker et al. (2000), the solid red line the pK$^*$ from this study computed with the coefficients presented in Table 1, the solid green line the pK$^*$ from this study computed with the coefficients presented in Table S2. Dashed lines are overall uncertainties for each of our pK fits, as defined in section 2.4.

**Supplementary references**


