



## The stoichiometric dissociation constants of carbonic acid in seawater brines from 298 to 267 K

Papadimitriou, Efsthios; Loucaides, Socratis; Rerolle, Victoire; Kennedy, David; Achtberberg, Eric P.; Dickson, Andrew G.; Mowlem, Matthew; Kennedy, Hilary

### Geochimica et Cosmochimica Acta

DOI:  
[10.1016/j.gca.2017.09.037](https://doi.org/10.1016/j.gca.2017.09.037)

Published: 01/01/2018

Peer reviewed version

[Cyswllt i'r cyhoeddiad / Link to publication](#)

*Dyfyniad o'r fersiwn a gyhoeddwyd / Citation for published version (APA):*  
Papadimitriou, E., Loucaides, S., Rerolle, V., Kennedy, D., Achtberberg, E. P., Dickson, A. G., Mowlem, M., & Kennedy, H. (2018). The stoichiometric dissociation constants of carbonic acid in seawater brines from 298 to 267 K. *Geochimica et Cosmochimica Acta*, 220, 55-70.  
<https://doi.org/10.1016/j.gca.2017.09.037>

#### Hawliau Cyffredinol / General rights

Copyright and moral rights for the publications made accessible in the public portal are retained by the authors and/or other copyright owners and it is a condition of accessing publications that users recognise and abide by the legal requirements associated with these rights.

- Users may download and print one copy of any publication from the public portal for the purpose of private study or research.
- You may not further distribute the material or use it for any profit-making activity or commercial gain
- You may freely distribute the URL identifying the publication in the public portal ?

#### Take down policy

If you believe that this document breaches copyright please contact us providing details, and we will remove access to the work immediately and investigate your claim.



21 **Abstract**

22 The stoichiometric dissociation constants of carbonic acid ( $K_{1C}^*$  and  $K_{2C}^*$ ) were determined  
 23 by measurement of all four measurable parameters of the carbonate system (total alkalinity, total  
 24 dissolved inorganic carbon, pH on the total proton scale, and CO<sub>2</sub> fugacity) in natural seawater  
 25 and seawater-derived brines, with a major ion composition equivalent to that Reference Seawater,  
 26 to practical salinity ( $S_P$ ) 100 and from 25 °C to the freezing point of these solutions and -6 °C  
 27 temperature minimum. These values, reported in the total proton scale, provide the first such  
 28 determinations at below-zero temperatures and for  $S_P > 50$ . The temperature ( $T$ , in Kelvin) and  $S_P$   
 29 dependence of the current  $pK_{1C}^*$  and  $pK_{2C}^*$  (as negative common logarithms) within the salinity  
 30 and temperature ranges of this study ( $33 \leq S_P \leq 100$ ,  $-6 \text{ °C} \leq t \leq 25 \text{ °C}$ ) is described by the  
 31 following best-fit equations:  $pK_{1C}^* = -176.48 + 6.14528 S_P^{0.5} - 0.127714 S_P + 7.396 \times 10^{-5} S_P^2 +$   
 32  $(9914.37 - 622.886 S_P^{0.5} + 29.714 S_P) T^{-1} + (26.05129 - 0.666812 S_P^{0.5}) \ln T$  ( $\sigma = 0.011$ ,  $n = 62$ ),  
 33 and  $pK_{2C}^* = -323.52692 + 27.557655 S_P^{0.5} + 0.154922 S_P - 2.48396 \times 10^{-4} S_P^2 + (14763.287 -$   
 34  $1014.819 S_P^{0.5} - 14.35223 S_P) T^{-1} + (50.385807 - 4.4630415 S_P^{0.5}) \ln T$  ( $\sigma = 0.020$ ,  $n = 62$ ). These  
 35 functions are suitable for application to investigations of the carbonate system of internal sea ice  
 36 brines with a conservative major ion composition relative to that of Reference Seawater and  
 37 within the temperature and salinity ranges of this study.

38

39

## 40 **1. Introduction**

41 The investigation of the carbonate system in aquatic environments is essential in the  
42 understanding and monitoring of the carbon cycle in the hydrosphere. Such investigations have  
43 intensified in the marine environment because of the crucial role the ocean plays in the absorption  
44 and storage of the anthropogenic CO<sub>2</sub> emitted to the atmosphere during the Industrial era  
45 (Takahashi et al., 1997; Sabine et al., 2004). Through this process, the ocean is a major repository  
46 of anthropogenic CO<sub>2</sub> (Takahashi, 2004), with consequent chemical and ecosystem functioning  
47 effects from the acidification of surface oceanic waters (decreased oceanic pH relative to pre-  
48 industrial era values) (Caldeira and Wickett, 2003; Feely et al., 2004; Takahashi et al., 2014;  
49 Gattuso et al., 2015). The acidification effect on the oceanic carbonate system by atmospheric  
50 CO<sub>2</sub> absorption (Takahashi, 2004; Sabine et al., 2004) has been observed in surface coastal and  
51 pelagic waters (Takahashi et al., 2014), including large areas of the Arctic Ocean (Feely et al.,  
52 2008; Yamamoto-Kawai et al., 2009; Cai et al., 2010; Semiletov et al., 2016).

53 One of the challenges that remain in the high latitude (polar) oceans of the Earth's cryosphere  
54 is reliable determination of the carbonate system in the brine-ice system in the extensive seasonal  
55 sea ice cover of these environments (Brown et al., 2014; Miller et al., 2015; Papadimitriou et al.,  
56 2016). Early investigations in the composition and activity of the ice-associated (sympagic)  
57 microbial community in sea ice have uncovered the role of this multi-phase system on the surface  
58 of high latitude oceans as a habitat akin to other large-scale biomes, such as the deserts and  
59 tundra (Fritsen et al., 1994; Gleitz et al., 1995; Arrigo et al., 1997; Thomas and Dieckmann,  
60 2002; Kennedy et al., 2002). Subsequent investigations have revealed a complex internal carbon  
61 cycle driven not only by the sympagic autotrophic and heterotrophic microbial communities, but  
62 also by two other major chemical reactions in the surface ocean, CO<sub>2</sub> gas exchange and hydrated  
63 CaCO<sub>3</sub> authigenesis (Papadimitriou et al., 2004; Delille et al., 2007; Dieckmann et al., 2008;  
64 Munro et al., 2010; Papadimitriou et al., 2012; Fischer et al., 2013). The internal carbon cycling  
65 in sea ice is complemented by measurable CO<sub>2</sub> fluxes to and from the atmosphere as a function of  
66 ice temperature (Delille et al., 2014) and to the underlying ocean by gravity drainage of the  
67 internal brines (Rysgaard et al., 2007; Rysgaard et al., 2011). These past investigations have  
68 culminated in a keen interest in the carbonate system of sea ice brines (Brown et al., 2014; Miller  
69 et al., 2015), the residual internal solution where all biogeochemical reactions occur either in  
70 isolation from, or in direct exchange with, the adjacent seawater column and the atmosphere

71 depending on the temperature- and salinity-dependent permeability of the medium (Golden et al.,  
72 1998). Sea ice brines are derived from the frozen surface seawater by physical concentration of  
73 the dissolved sea solutes following their expulsion from the ice crystal matrix. Along with  
74 degassed components, the brines can become trapped in pockets and channels in the sea ice  
75 structure. As a result of internal thermal equilibrium in sea ice along temperature gradients  
76 extending seasonally slightly above or far below the freezing point of seawater ( $-1.92\text{ }^{\circ}\text{C}$  at 0  
77 dbar pressure and salinity 35; UNESCO, 1983), the salinity of internal brines can vary from the  
78 hyposaline to values in excess of 100 below  $-6\text{ }^{\circ}\text{C}$ , and the concentration of brine solutes can  
79 likewise vary (Gleitz et al., 1995; Miller et al., 2011a, 2011b; Papadimitriou et al., 2012; Geilfus  
80 et al., 2012a).

81 The carbonate system in the marine environment is defined by pressure, temperature, salinity,  
82 the total concentration of boron and the dissociation constant of boric acid, the total  
83 concentrations of sulfate and fluoride, along with the equilibrium constants for the formation of  
84 the bisulfate ion and HF, respectively, the dissociation constants of carbonic acid, the value of  
85 two of its four measurable parameters [total alkalinity ( $A_T$ ), total dissolved inorganic carbon ( $C_T$ ),  
86 pH, and the fugacity of  $\text{CO}_2$  ( $f\text{CO}_2$ )] and, lastly, the weak acid-base systems in the dissolved  
87 macro-nutrient and metabolite pools (phosphate, silicate, ammonium, sulphide) and their  
88 respective dissociation constants (Millero, 1995; Dickson et al., 2007). To date, all relevant  
89 dissociation constants have been adequately constrained empirically as a function of temperature  
90 and salinity for above-zero temperatures and practical salinity ( $S_P$ ) up to 50 (Millero, 1995, and  
91 references there-in). Great investigative effort has been invested in the experimental  
92 determination of the first and second stoichiometric (concentration-based) dissociation constants  
93 of carbonic acid in seawater and solutions derived from seawater by dilution or evaporation, both  
94 in natural and artificial media with the mean stoichiometric composition of seawater (Hansson,  
95 1973; Mehrbach et al., 1973; Goyet and Poisson, 1989; Roy et al., 1993; Mojica-Prieto and  
96 Millero, 2002; Millero et al., 2006). The determination of the carbonate system in the complex  
97 and sparsely accessible sea ice system is currently limited to direct measurements of  $A_T$  and  $C_T$   
98 (Miller et al., 2015) and is further compounded by the large uncertainty in the values of the  
99 relevant acid-base dissociation constants as they are currently estimated via extrapolation of the  
100 existing different salinity-temperature functions to the physical sea ice conditions (temperature  $<$   
101  $0\text{ }^{\circ}\text{C}$ ,  $S_P > 50$ ) (Brown et al., 2014). Direct in-situ measurements of  $f\text{CO}_2$  in the sea ice system are

102 still rare either in bulk sea ice (Miller et al., 2011a, b; Geilfus et al., 2012b) or in brines, which  
103 are, moreover, subject to the sparse spatial resolution afforded by brine collection in boreholes  
104 through the ice surface (Delille et al., 2007; Geilfus et al., 2012a; Delille et al., 2014). In addition,  
105 direct brine pH measurement has not been possible so far at below-zero temperatures and high  
106 salinities as a result of sampling and analytical difficulties in this complex system. As a first step  
107 towards the implementation of direct pH measurement in sea ice brines, the pH of Tris buffers  
108 (Papadimitriou et al., 2016) and the  $p(K_2e_2)$  of the pH-indicator dye *meta*-Cresol Purple  
109 (Loucaides et al., 2017) have recently been characterized electrometrically with the Harned cell  
110 and spectrophotometrically, respectively, to  $S_P = 100$  and  $-6$  °C. Sea ice geochemists, therefore,  
111 have so far relied on indirect determination of brine  $fCO_2$  and pH from the solution of the system  
112 of equations that describe the acid-base equilibria of the oceanic carbonate system using  
113 temperature, salinity, nutrient concentrations (if available), and the direct measurements of  $A_T$   
114 and  $C_T$  as input parameters, with the caveats of extrapolation mentioned above (Brown et al.,  
115 2014).

116 Here, we present measurements that allowed the determination of the dissociation constants  
117 of carbonic acid in seawater and seawater-derived brines at below-zero temperatures to the  
118 freezing point of these solutions up to  $S_P = 100$  and a temperature minimum of  $-6$  °C. The  $S_P$  and  
119 temperature ranges of this study were set because the ionic composition and inter-ionic ratios in  
120 surface oceanic water are conserved in the natural sea ice brines over these temperature and  
121 salinity ranges. More concentrated, cooler sea ice brines ( $S_P > 100$  and  $t < -6$  °C) become  
122 supersaturated with respect to a suite of hydrated solid phases, including mirabilite, hydrohalite,  
123 and gypsum (Butler and Kennedy, 2015; Butler et al., 2016; Butler et al., 2017), thus altering the  
124 chemical composition and ionic ratios of the brines from those in surface oceanic water (Marion,  
125 2001). Determination of equilibrium constants beyond the current salinity-temperature range  
126 must account for these compositional modifications (Hain et al., 2015) by solid-solution  
127 reactions, and so, it requires custom experimental protocols in a separate investigation.

128

## 129 2. Materials and Methods

130 The stoichiometric first ( $K_{1C}^*$ ) and second ( $K_{2C}^*$ ) dissociation constants of carbonic acid  
131 describe the equilibrium of the reactions,  $CO_2^* + H_2O \leftrightarrow H^+ + HCO_3^-$  and  $HCO_3^- \leftrightarrow H^+ + CO_3^{2-}$ ,  
132 respectively, with  $[CO_2^*] = [CO_2(aq)] + [H_2CO_3]$  (Dickson et al., 2007). In this study, they were

133 determined in natural high ionic strength solutions (seawater, seawater-derived brines) from  
 134 measurements of  $A_T$ ,  $C_T$ ,  $fCO_2$ , and  $pH_T = -\log[H^+]_T$  (total proton scale) as follows (Millero et  
 135 al., 2002):

136

$$137 \quad K_{1C}^* = [H^+]_T \frac{2C_T - A_C - 2[CO_2^*]}{[CO_2^*]}, \quad (1)$$

$$138 \quad K_{2C}^* = [H^+]_T \frac{A_C - C_T + [CO_2^*]}{2C_T - A_C - 2[CO_2^*]}, \quad (2)$$

139

140 In the above equations,  $A_C = \text{carbonate alkalinity} = [HCO_3^-] + 2[CO_3^{2-}]$ ,  $C_T = [CO_2^*] + [HCO_3^-] +$   
 141  $[CO_3^{2-}]$ , and  $[CO_2^*] = K_o fCO_2$ , with  $K_o = CO_2$  solubility constant as a function of salinity and  
 142 temperature (Weiss, 1974), and brackets denoting total concentrations (single ion plus ion pairs  
 143 in the case of pair-forming ionic species).

144 Carbonate alkalinity was determined from the measured  $A_T$  and  $pH_T$  as described in Millero  
 145 et al. (2002). To this end, the contributions of dissolved phosphate and silicic acid to  $A_T$  were  
 146 computed from their measured total concentrations, the measured  $pH_T$ , and the relevant  
 147 stoichiometric equilibrium dissociation constants computed from the available salinity-  
 148 temperature functions (Millero, 1995; Dickson et al., 2007). For the contribution of boron  
 149 alkalinity to  $A_T$ , the mean total boron concentration,  $[B_T] = 0.000432578 \text{ mol kg}_{\text{solution}}^{-1}$  (hereafter,  
 150  $\text{mol kg}^{-1}$ ), in  $S_P = 35$  seawater as computed from the data in Lee et al. (2010) was used as a linear  
 151 function of salinity (Millero, 1995), along with the measured  $pH_T$  and the stoichiometric  
 152 equilibrium dissociation constant of boric acid in Dickson (1990). The contributions to  $A_T$  of  
 153  $OH^-$  (positive),  $H^+$  (total proton scale), and  $HF$  (both negative and negligible in the pH range of  
 154 this study) were determined using the measured  $pH_T$ , the concentration of  $SO_4^{2-}$  and  $F^-$  in  
 155 Reference Seawater as a linear function of salinity (Millero et al., 2008), and the relevant  
 156 equilibrium constants from the available oceanographic functions (Millero, 1995; Dickson et al.,  
 157 2007). The oceanographic functions for the equilibrium constants used for these computations  
 158 were extrapolated outside their empirical salinity-temperature ranges ( $t \geq 0 \text{ }^\circ\text{C}$ ,  $S_P < 50$ ; Dickson,  
 159 1990; Millero, 1995) when the experimental conditions extended beyond them ( $t \leq 0 \text{ }^\circ\text{C}$ ,  $S_P >$   
 160  $50$ ). Locally sourced seawater (Menai Strait; 53.1806N 4.2333W), UV-sterilized and filtered  
 161 through a  $0.2 \text{ }\mu\text{m}$  filter, was used as the experimental medium ( $S_P = 33 - 34$ ) and for the

162 preparation of the experimental brines ( $S_P = 40 - 100$ ) by variable freezing and gravimetric  
163 dilution, when needed, with ultrapure (18 M $\Omega$ -cm) Milli-Q™ water. The brines were filtered  
164 through pre-combusted (500 °C, 3 hrs) GF/F filters (0.7  $\mu$ m, WHATMAN); they were then  
165 sampled for the determination of major ion concentrations ( $\text{Na}^+$ ,  $\text{K}^+$ ,  $\text{Ca}^{2+}$ ,  $\text{Mg}^{2+}$ ,  $\text{Cl}^-$  and  $\text{Br}^-$ ,  
166  $\text{SO}_4^{2-}$ ) and were kept stored at room temperature in the dark in acid-washed glass media bottles  
167 (DURAN) capped (gas-tight) with Teflon-lined screw-caps.

168 The experiments were conducted at zero and below-zero temperatures to very near the  
169 freezing point of seawater and seawater-derived brines, as well as at above-zero temperatures to  
170 25 °C, in order for our experimental results to span the existing data sets for the stoichiometric  
171 equilibrium dissociation constants of carbonic acid in natural seawater and brines for validation.  
172 The freezing point ( $t_{FP}$ , in °C) of the experimental brines was estimated from the empirical  
173 temperature function for the weight-based salinity ( $S_W$ , in g kg<sup>-1</sup>) of thermally equilibrated sea ice  
174 brines,  $S_W = 1000 [1 - (54.11/t_{FP})]^{-1}$  (Assur, 1958). For  $S_W$  to  $S_P$  conversion, the recent absolute  
175 salinity ( $S_A$ ) and (conductivity-based)  $S_P$  relationship,  $S_A = 1.004715 S_P$  (Millero and Huang,  
176 2009), was used. The estimated  $t_{FP}$  was within  $\pm 0.05$  °C to  $-5$  °C and  $-0.15$  °C to  $-6$  °C from the  
177 values computed from the  $S_P$ - $t_{FP}$  standard oceanographic relationship for seawater in UNESCO  
178 (1983) extrapolated to  $S_P > 40$ .

179 Each salinity-temperature experiment was conducted with  $\sim 1.1$  L seawater or brine in a  
180 Teflon-lined-capped media bottle (DURAN), which was thermally equilibrated by immersion in  
181 a thermostated ethylene-glycol/water bath (GRANT TX150) and was kept at constant  
182 temperature during measurement and sampling for the analysis of the required parameters. The  
183 experimental temperature was monitored with a Fluke 5609 Platinum Resistance Probe on a Hart  
184 Scientific 1502A Thermometer and is reported as the mean of the values recorded for the  
185 duration of each experiment. Throughout the experiment, the sample was gently stirred (50 rpm)  
186 with an overhead stainless steel stirrer through the cap. Each experiment required about 70  
187 minutes to complete the necessary measurements ( $f\text{CO}_2$  and  $\text{pH}_T$ ) at the experimental temperature  
188 and the sample collection for the remainder of analyses. First, the  $f\text{CO}_2$  and  $\text{pH}_T$  measurements  
189 were conducted simultaneously in separate aliquots of the sample, drawn through Tygon®  
190 tubings with a Watson Marlow 520U peristaltic pump towards the  $\text{CO}_2$  Analyzer unit and the pH  
191 unit. Upon completion of these measurements, samples for  $C_T$  determination were pump-drawn  
192 and flame-sealed into pre-weighed 10 mL glass ampoules poisoned with saturated mercuric

193 chloride. Subsequently, samples for soluble reactive phosphorus (SRP, hereafter, phosphate) and  
194 molybdenum reactive silicon [hereafter, silicic acid,  $\text{Si}(\text{OH})_4$ ] were removed and the remaining  
195 sample was used for replicate  $A_T$  determinations.

196

## 197 **2.1 $f\text{CO}_2$ measurement**

198 The  $f\text{CO}_2$  was determined from the  $\text{CO}_2$  mole fraction ( $x_{\text{CO}_2}$ ) measured on a LICOR 840A  
199  $\text{CO}_2/\text{H}_2\text{O}$  analyzer of the dry gas generated in a closed loop by exchange with the sample via a  
200  $0.5 \times 1$  MicroModule™ Membrane Contactor (Liqui-Cell; [www.liquicell.com](http://www.liquicell.com)), used here as the  
201 gas exchange unit (Hales et al., 2004a). The gas was circulated in the closed loop at  $48 \text{ mL min}^{-1}$   
202 through a custom-made DRIERITE desiccant column ([www.drierite.com](http://www.drierite.com)) with a custom-made  
203 gas micro-pump. The contactor was immersed in a custom-made housing in the same water bath  
204 as the sample, which was pumped through the contactor at  $9 \text{ mL min}^{-1}$  in Tygon® tubing via the  
205 Watson Marlow 520U peristaltic pump. The temperature of the sample in the bottle and at the  
206 exit of the contactor was monitored with type K thermocouple probes by continuous logging on a  
207 Pico Technology USB TC-08 thermocouple data logger. In this set-up, a plateau in  $x_{\text{CO}_2}$  was  
208 achieved in 50 min, and the  $x_{\text{CO}_2}$  used for  $f\text{CO}_2$  determination in each thermostated sample was a  
209 5 min average of recorded values within the plateau phase. These values were within 1 ppm for  
210  $x_{\text{CO}_2} < 1000$  ppm and within 3 ppm for  $x_{\text{CO}_2} > 1000$  ppm. The measurements were calibrated  
211 against  $\text{CO}_2/\text{N}_2$  mixtures with a certified  $x_{\text{CO}_2}$  (0, 20, 100, 400, 1000, and 2000 ppm; uncertainty  
212  $\leq 5\%$ , BOC, [boc.com](http://boc.com)). The calibrations were conducted between two consecutive experiments.  
213 The sample  $f\text{CO}_2$  was computed from the measured  $x_{\text{CO}_2}$  as in SOP 5 in Dickson et al. (2007),  
214 using the pressure readings from the built-in barometer in the LICOR gas cell.

215 An estimate of the uncertainty of these measurements was possible at above-zero  
216 temperatures by analyzing, with this protocol, samples of  $\text{CO}_2$  in Seawater Certified Reference  
217 Materials (CRM, Batches #112, #124, and #125; Scripps Institution of Oceanography) and  
218 comparing the measured  $f\text{CO}_2$  with that computed from the certified  $C_T$  and  $A_T$ , as well as the  
219 salinity and the phosphate and silicic acid concentrations reported in the certificate. The CRM  
220  $f\text{CO}_2$  analyses were thus conducted every  $1 - 4$  °C in the temperature range from  $3.16$  °C to  $24.99$   
221 °C (batch #112:  $n = 11$ ; batch #124,  $n = 1$ ; batch #125,  $n = 1$ ). For the calculations, the first and  
222 second dissociation constants of carbonic acid were computed from the salinity-temperature

223 functions based on the measurements of Mehrbach et al. (1973) as refitted on the total proton  
224 scale by Lueker et al. (2000). The dissociation constants of the remainder of the weak acids and  
225 bases of the oceanic carbonate system, the solubility of CO<sub>2</sub> in seawater, and the B<sub>T</sub> and the total  
226 dissolved sulphate and fluoride concentrations were computed as described earlier. All  
227 computations were conducted on the total proton scale by solving for pH the system of equations  
228 that describe the equilibria of the marine carbonate system using the Solver routine on Microsoft  
229 Excel. At the computed CRM *f*CO<sub>2</sub> from 225 μatm at 3.16 °C to 567 μatm at 24.99 °C for batch  
230 #112 and 537 μatm at 22.03°C for batch #124, the measured *f*CO<sub>2</sub> differed by (mean ± 1σ) −9 ±  
231 10 μatm (*n* = 12). This estimated uncertainty is equivalent to −2 ± 3% relative to the computed  
232 *f*CO<sub>2</sub> and consists of the measurement uncertainty and the computational uncertainty. The  
233 computational uncertainty is due to the combined uncertainties in the certified parameters and in  
234 the acid-base dissociation constants used in the computations, including the uncertainty in pK<sub>1C</sub><sup>\*</sup>  
235 and pK<sub>2C</sub><sup>\*</sup> (0.0055 and 0.0100 pK unit, respectively; Lueker et al., 2000). Based on the  
236 assessment in Lueker et al. (2000), the computational *f*CO<sub>2</sub> uncertainty has been estimated to be  
237 1.6% for the uncertainty in the certified A<sub>T</sub> and C<sub>T</sub> concentrations (3 μmol kg<sup>-1</sup> for both A<sub>T</sub> and  
238 C<sub>T</sub>; Bockmon and Dickson, 2015). This indicates that the computational uncertainty was a  
239 significant contributor to the estimated uncertainty in the current methodology for up to 600 μatm  
240 *f*CO<sub>2</sub>. The measured *f*CO<sub>2</sub> differed by −85 μatm at CRM *f*CO<sub>2</sub> = 1062 μatm at 18.06 °C for batch  
241 #125, equivalent to −8% relative to the computed *f*CO<sub>2</sub>. In contrast, in the assessment of Lueker  
242 et al. (2000), the measured *f*CO<sub>2</sub> was systematically higher by +3.35 ± 1.22% than the computed  
243 *f*CO<sub>2</sub> at *f*CO<sub>2</sub> > 500 μatm. In comparison, the uncertainty based on the single high-*f*CO<sub>2</sub> CRM  
244 measurement (batch #125) available during this study suggests an increased negative bias at high  
245 *f*CO<sub>2</sub> (~ 1,000 μatm, or higher) with the current methodology.

246

## 247 2.2 pH measurement

248 The pH<sub>T</sub> (total proton scale) was determined spectrophotometrically using purified *meta*-  
249 Cresol Purple (mCP) indicator dye, the salinity and temperature functions of its optical  
250 parameters and second stoichiometric equilibrium dissociation constant (on the total proton scale)  
251 as determined in the same temperature and salinity ranges as in this study by Loucaides et al.  
252 (2017), and the custom-made micro-opto-fluidic Lab-On-Chip (LOC) pH system described in  
253 Rérolle et al. (2013). The LOC unit with its sample and dye inlets, as well as the optics

254 (photodiode detector and light source) were all custom-housed and immersed as a separate micro-  
255 unit in the same thermostated water bath as the sample and the  $f\text{CO}_2$  contactor described in the  
256 previous section. The electronics, pumps, and reagent stores were outside the water bath. The  
257 mCP solutions used in this study were prepared from the same batch of HPLC-purified dye that  
258 was used for the characterization of the dye as reported in Loucaides et al. (2017). The  $\text{pH}_T$  is  
259 reported as the mean of several injections (5 – 10) per sample through the LOC pH system. In the  
260 case of the  $\text{pH}_T$  measurements used in the determination of  $K_{1C}^*$  and  $K_{2C}^*$  (eqs. 1 and 2), these  
261 multiple injections occurred over the course of the simultaneous  $f\text{CO}_2$  determination, with a  
262 reproducibility better than 0.004 pH unit (as  $1\sigma$ ). The uncertainty associated with the  $\text{pH}_T$   
263 measurement protocol was assessed against the  $\text{pH}_T$  computed for CRMs as described in the  
264 previous section for  $f\text{CO}_2$ . The CRM pH analyses were thus conducted every 1 – 2 °C in the  
265 temperature range from 1.52 °C to 25.15 °C using CRM batches #112 ( $n = 5$ ), #124 ( $n = 1$ ), and  
266 #125 ( $n = 1$ ), which were also used for the  $f\text{CO}_2$  protocol validation described in the previous  
267 section, as well as batch #138 ( $n = 15$ ), used here only for the validation of the pH measurement  
268 protocol. At the computed CRM  $\text{pH}_T$  for batches #112 (7.908 at 24.99 °C to 8.264 at 1.97 °C),  
269 #124 (7.927 at 22.03 °C), and #138 (7.852 at 25.15 °C to 8.215 at 1.52 °C), the measured  $\text{pH}_T$   
270 differed by (mean  $\pm 1\sigma$ )  $-0.013 \pm 0.011$  pH unit ( $n = 21$ ). For the high- $f\text{CO}_2$  CRM batch #125  
271 (CRM  $\text{pH}_T = 7.659$  at 18.06 °C), the measured  $\text{pH}_T$  differed by +0.015 pH unit. Numerical  
272 evaluation yielded a computational uncertainty of  $\pm 0.010$  pH unit due to the combined  
273 uncertainties in the certified parameters (3  $\mu\text{mol kg}^{-1}$  for both  $A_T$  and  $C_T$ ; Bockmon and Dickson,  
274 2015) and in the  $\text{p}K_{1C}^*$  and  $\text{p}K_{2C}^*$  (0.0055 and 0.0100 pK unit, respectively; Lueker et al., 2000)  
275 used in the computation of the CRM  $\text{pH}_T$ . This suggests that about half of the overall uncertainty  
276 evaluated on the CRM  $\text{pH}_T$  determinations ( $\sim 0.020$  pH unit as  $2\sigma$ ) can be attributable to  
277 computational uncertainty. A similar uncertainty of 0.010 – 0.020 pH unit was evaluated for the  
278  $\text{pH}_T$  measurement on the same batch of purified mCP and analytical set-up throughout the current  
279 experimental temperature and salinity ranges by Loucaides et al. (2017) based on relevant,  
280 electrochemically characterized Tris-HCl buffer solutions (Papadimitriou et al., 2016).

281

### 282 **2.3 $A_T$ and $C_T$ measurements**

283 Total alkalinity was determined by open-cell potentiometric titration with 0.1 N HCl at 20 °C  
284 using the Gran function for  $\text{pH} < 3.5$  (Gleitz et al., 1995; Papadimitriou et al., 2013) with a

285 Metrohm Titrand 888 unit of automatic burette, pH meter, Pt temperature probe, Ag/AgCl/KCl  
286 reference electrode, and glass indicator electrode calibrated with buffers traceable to SRM from  
287 NIST and PTB (Merck, pH 2.00, 4.01, 7.00, 9.00, and 10.00 at 25 °C). The titration was  
288 conducted in replicate ~100 mL aliquots of known weight at constant pCO<sub>2</sub> (400 ppm CO<sub>2</sub>)  
289 provided at a controlled rate (200 mL min<sup>-1</sup>) via a CHELL CMD100 microprocessor controller  
290 and Hastings Mass Flow Control Valve. The rigour of the technique was assessed from several  
291 titrations of CRM batch #112 ( $A_T = 2223.26 \mu\text{mol kg}^{-1}$ ) with a coulometry-characterized HCl  
292 solution (0.100171 mol HCl kg<sup>-1</sup>, ~0.7 M NaCl; Scripps Institution of Oceanography), yielding a  
293 difference of measured from certified  $A_T$  of  $-1.9 \pm 1.7 \mu\text{mol kg}^{-1}$  ( $n = 23$ ), equivalent to 0.08%  
294 reproducibility and accuracy. Batches of 0.1 N HCl were also prepared gravimetrically in the  
295 course of this study to a total ionic strength of 0.72 molal using NaCl, and the HCl concentration  
296 was calibrated against the  $A_T$  of CRM batches #112 and #138. The difference between the  $A_T$   
297 measured with these acid batches and the certified concentrations was  $-1.1 \pm 2.8 \mu\text{mol kg}^{-1}$  ( $n =$   
298 99) in good agreement with that determined with the Scripps CRM and acid. Because the acid  
299 batches were calibrated against seawater CRMs and the response of commercial glass electrodes  
300 may be unreliable in hypersaline solutions, the  $A_T$  in brines was determined in samples diluted  
301 gravimetrically to a salinity of 34 with ultrapure (18 MΩ·cm) Milli-Q™ water. The  $A_T$  of the  
302 brine batches (Table 2), normalized to salinity 35, was  $A_{T,35} = 2424 \pm 39 \mu\text{mol kg}^{-1}$  ( $n = 10$ ),  
303 while the local seawater had a two-year (2014-2015) average  $A_{T,35} = 2398 \pm 22 \mu\text{mol kg}^{-1}$  ( $n =$   
304 37).

305 The  $C_T$  concentration was determined manometrically in 3 – 10 replicate sample aliquots  
306 (~10 mL) from the CO<sub>2</sub> generated and extracted in vacuo in a glass manifold following reaction  
307 of a weighed sample aliquot with H<sub>3</sub>PO<sub>4</sub> and cryogenic CO<sub>2</sub> gas distillation in successive cold (–  
308 95 °C) methanol and liquid nitrogen traps, using an in-line manometer (CHELL) and a virial  
309 equation of state (Bockmon and Dickson, 2015). The reproducibility of these measurements was  
310 better than 0.4% in the 2000 to 5600  $\mu\text{mol kg}^{-1}$  concentration range. Determination of  $C_T$  on  
311 CRM batches #112, #124, #125, and #138 (Scripps Institution of Oceanography) yielded a  
312 difference between the measured and certified  $C_T$  of (mean  $\pm 1\sigma$ )  $+0.7 \pm 8.8 \mu\text{mol kg}^{-1}$  ( $n = 111$ ).

313

## 314 2.4 Other measurements

315 The salinity of the experimental solutions was measured at laboratory temperature ( $\sim 20$  °C)  
 316 using a portable conductivity meter (WTW Cond 3110) with a WTW Tetracon 325 probe. When  
 317 salinities exceeded 70, they were determined following gravimetric dilution with distilled water.  
 318 The initial major ion composition of the brines was determined as follows: (i) potentiometric  
 319 titration with EDTA as titrant and Tris-buffered acetylacetone (0.1 M) as the complexing agent at  
 320 pH  $\sim 8.5$  for  $\text{Ca}^{2+}$  and  $\text{Mg}^{2+}$  as described in Papadimitriou et al. (2012), (ii) ion chromatography  
 321 on a Dionex Ion Exchange Chromatograph ICS 2100 for  $\text{Na}^+$  and  $\text{K}^+$ , (iii) gravimetric Mohr  
 322 titration for total halides (except  $\text{F}^-$ , but mostly  $\text{Cl}^-$ , with comparatively small contributions from  
 323 bromide and smaller by iodine; hereafter termed:  $[\text{Cl}^-] + [\text{Br}^-]$ ) with  $0.3 \text{ mol kg}^{-1} \text{ AgNO}_3$   
 324 standardized against NaCl purified by re-crystallization (Dickson, 1990; Millero et al., 1993), and  
 325 (iv) for  $\text{SO}_4^{2-}$ , precipitation as  $\text{BaSO}_4$  in EDTA followed by titration with  $\text{MgCl}_2$  (Howarth,  
 326 1978). The phosphate and silicic acid concentrations were determined within 4 to 8 weeks from  
 327 collection on refrigerated aliquots stored in acid-washed (2 N HCl) 20 mL PE vials. These  
 328 analyses were conducted on a SEAL AA3 MR continuous segmented flow autoanalyzer using  
 329 standard colorimetric methodology (Hales et al., 2004b).

330

### 331 2.5 Error analysis

332 The error in the experimental  $K_{1C}^*$  and  $K_{2C}^*$  values was computed as  $\sigma_{K_c}^2 = \sum[(dK_{ic}^*/dX) \sigma_X]^2$   
 333 (Barford 1985), with  $X = \text{H}^+$ ,  $C_T$ ,  $A_C$ ,  $\text{CO}_2(\text{aq})$  (all in  $\text{mol kg}^{-1}$ ). The maximum measurement  
 334 uncertainty ( $\sigma_X$ ) was 0.020 pH unit for the pH measurements, 0.4% for the  $C_T$  determinations, 20  
 335  $\mu\text{atm}$  for  $f\text{CO}_2 < 1000 \mu\text{atm}$ , 90  $\mu\text{atm}$  for  $f\text{CO}_2 > 1000 \mu\text{atm}$ , and 0.1% for the  $A_C$  estimates based  
 336 on the uncertainty of the  $A_T$  measurement. The magnitude of the extrapolation error for the  
 337 estimates of the non-carbonate  $A_T$  components is unknown at this stage. The available  
 338 measurement uncertainties in  $\text{pH}_T$ ,  $C_T$ ,  $f\text{CO}_2$ , and  $A_C$  determinations indicated that  $K_{1C}^*$  is most  
 339 sensitive to uncertainties in the pH and  $f\text{CO}_2$  measurements, while  $K_{2C}^*$  is most sensitive to the  
 340 uncertainties in the  $A_C$  estimates and the  $C_T$  and pH measurements. The  $K_{1C}^*$  uncertainty was  
 341 thus calculated to range from 0.020 – 0.040 pK unit at  $f\text{CO}_2 > 250 \mu\text{atm}$  to 0.050 pK unit at  $f\text{CO}_2$   
 342  $< 250 \mu\text{atm}$ . The  $K_{2C}^*$  uncertainty was calculated to be 0.040 pK unit for our experiments. The  
 343 uncertainties of both constants in this study are therefore estimated to be about twice those

344 reported for standard oceanographic conditions (0.020 pK unit for  $K_{1C}^*$  and 0.030 pK unit for  
345  $K_{2C}^*$ ; Dickson and Millero, 1987).

346

## 347 2.6 Data evaluation

348 The  $K_{1C}^*$  and  $K_{2C}^*$  determinations in seawater at above-zero temperatures were evaluated  
349 against the existing major data sets in natural seawater, i.e., the Mehrbach et al. (1973) data set  
350 (experimental ranges:  $S_P = 19 - 43$ ,  $t = 2 - 35$  °C) as refitted on the total proton scale by Lueker  
351 et al. (2000) and the Millero et al. (2006) data set (experimental ranges:  $S_P = 1 - 51$ ,  $t = 1.0 - 50.5$   
352 °C). Because the latter data set has been reported on the seawater proton scale, it was converted  
353 to the total proton scale as described in Millero (1995) and was re-fitted here using the same  
354 equation format as in the original study:

355

$$356 \text{p}K_{iC}^* = \text{p}K_{iC}^o + A_i + B_i/T + C_i \ln T \quad (i = 1, 2), \quad (3)$$

357

358 In the above equation,  $T$  = temperature (in Kelvin),  $A_i = a_0 S_P^{0.5} + a_1 S_P + a_2 S_P^2$ ,  $B_i = a_3 S_P^{0.5} + a_4 S_P$ ,  
359  $C_i = a_5 S_P^{0.5}$ , and  $\text{p}K_{iC}^o = b_0 + b_1/T + b_2 \ln T$  = thermodynamic equilibrium dissociation constant,  
360 with  $a_0, a_1, a_2, a_3, a_4, a_5$  = best-fit parameters (Table 3) determined by non-linear regression using  
361 the Excel regression routine, while  $b_0, b_1$ , and  $b_2$  are from Millero et al. (2006). The standard  
362 error of the fit was the same as in the original study ( $\sigma_{\text{p}K_{1C}^*} = 0.006$  and  $\sigma_{\text{p}K_{2C}^*} = 0.011$ ).

363 The current  $\text{p}K_{1C}^*$  and  $\text{p}K_{2C}^*$  determinations in natural seawater ( $S_P = 33 - 34$ ; mean  $S_P =$   
364  $33.66 \pm 0.36$ ,  $n = 5$ ) over the temperature range from 0 to 25 °C (Table 2) are in very good  
365 agreement with the previously published data sets (Fig. 1). Specifically, in the 0 – 25 °C  
366 temperature range, the current observations ( $n = 23$ ) differed by  $\Delta \text{p}K_{1C}^* = -0.009 \pm 0.016$  and  
367  $\Delta \text{p}K_{2C}^* = +0.002 \pm 0.018$  relative to the Mehrbach et al. (1973) data set, and  $\Delta \text{p}K_{1C}^* = -0.014 \pm$   
368  $0.016$  and  $\Delta \text{p}K_{2C}^* = -0.003 \pm 0.022$  relative to the Millero et al. (2006) data set, all within  
369 experimental error. The determinations beyond the salinity-temperature bounds of the available  
370 oceanographic data sets ( $t < 0$  °C,  $S_P > 50$ ) were compared with the extrapolated values of the  
371 oceanographic equations as will be discussed in the *sections 3 and 4*. In addition, the  $K_{1C}^*$  and

372  $K_{2C}^*$  determinations near the freezing point of seawater and seawater-derived brines from this  
 373 study were compared with the values calculated from appropriate thermodynamic data as follows.  
 374 Stoichiometric equilibrium constants are related to the thermodynamic equilibrium constants at  
 375 infinite dilution (pure water) via the activity coefficients of the reacting ions. In the case of  $K_{1C}^*$   
 376 and  $K_{2C}^*$ , this relationship is given by the following equations (Millero et al., 2006):

377

$$378 \quad K_{1C}^* = K_{1C}^o \frac{\gamma_{CO_2} \alpha_{H_2O}}{\gamma_{H^+} \gamma_{HCO_3^-}} \Theta, \quad (4)$$

$$379 \quad K_{2C}^* = K_{2C}^o \frac{\gamma_{HCO_3^-}}{\gamma_{H^+} \gamma_{CO_3^{2-}}} \Theta, \quad (5)$$

380

381 where  $K_{1C}^o$ ,  $K_{2C}^o$  = thermodynamic equilibrium dissociation constants of carbonic acid,  $\alpha_{H_2O}$  =  
 382 activity of water,  $\gamma_i$  = total ion activity coefficient ( $i = CO_2(aq), H^+, HCO_3^-, CO_3^{2-}$ ) (in mol  
 383  $kg_{H_2O}^{-1}$ ), and  $\Theta = 1 - 0.001005 S_P$  = conversion factor from mol  $kg_{H_2O}^{-1}$  to mol  $kg_{solution}^{-1}$  (Millero,  
 384 1995). For the calculation of the required thermodynamic equilibrium dissociation constants,  
 385  $\alpha_{H_2O}$ , and  $\gamma_i$  at below-zero temperatures, the database of the FREZCHEM code (version 15.1)  
 386 was used here, which is frequently used to examine geochemical processes in the cryosphere and  
 387 is based on the Pitzer formalism of ionic interactions in strong electrolyte solutions (Marion,  
 388 2001; Marion et al., 2010). The FREZCHEM v15.1 includes some of the equilibria of the  
 389 aqueous carbonate system (boron and fluoride chemistry,  $CaCO_3$ -solution equilibrium) and is  
 390 rooted in the extant above-zero temperature data of the relevant thermodynamic equilibrium  
 391 constants and Pitzer coefficients, with additional validation at below-zero temperatures from the  
 392 metal-carbonate solubility data of the early 20<sup>th</sup> century Russian literature mostly at the eutectic  
 393 point of these salt solutions (Marion, 2001). The model was run in the freezing mode (ice-water  
 394 equilibrium) at 0.1 °C steps from 0 to -6 °C at 1 atm and a fixed  $pCO_2$  at 400  $\mu atm$  (non-  
 395 conservative  $C_T$ ) for a starting ionic composition equivalent to the composition of Reference  
 396 Seawater of salinity 35 (Millero et al., 2008), with all other solid phases disabled (conservative  
 397 major ionic composition and  $A_T$ ). Total ion activity coefficients are directly proportional to the  
 398 free ion activity coefficients, with the concentration ratio of the free ion to the sum of the free ion

399 and ion pairs as the proportionality factor (Pytkowicz and Kester, 1969). In the case of the total  
 400 proton scale used in this study,  $\gamma_{\text{H}^+} = \gamma_{\text{H}^+, \text{free}} m_{\text{H}^+, \text{free}} / (m_{\text{H}^+, \text{free}} + m_{\text{HSO}_4^-})$  (Millero, 1995), with  $m$   
 401 = molality (in mol kg<sub>H<sub>2</sub>O</sub><sup>-1</sup>) and all quantities in the right side of this equation obtained from the  
 402 output of the code. The FREZCHEM code output provides the ionic strength ( $I$ ) of model brines,  
 403 and their  $S_P$  was estimated from the relationship,  $I = 19.924 S_P / (1000 - 1.005 S_P)$  (Dickson et al.  
 404 2007). The code also computes  $\alpha_{\text{H}_2\text{O}}$ ,  $\gamma_{\text{CO}_2}$ , and the single ion activity coefficients of  $\text{HCO}_3^-$  and  
 405  $\text{CO}_3^{2-}$  from the Pitzer equations (Pitzer, 1973) and relevant Pitzer parameters. All ion pairs for  
 406  $\text{HCO}_3^-$  are considered adequately represented in the Pitzer computation (He and Morse, 1993)  
 407 and so, the single ion activity coefficient of  $\text{HCO}_3^-$  in the code output is equivalent to  $\gamma_{\text{HCO}_3^-}$  in  
 408 eqs. (3) and (4). The code takes into account explicitly ion pair formation for  $\text{CO}_3^{2-}$  in the form of  
 409  $\text{CaCO}_3^0$  and  $\text{MgCO}_3^0$  (He and Morse, 1993; Marion, 2001). The molalities of these ion pairs were  
 410 taken into account along with the molality and activity coefficient of  $\text{CO}_3^{2-}$  as a single ion in the  
 411 code output to compute the total activity coefficient of  $\text{CO}_3^{2-}$  ( $\gamma_{\text{CO}_3^{2-}}$ ) for use in eqs. (3) and (4) by  
 412 applying the same principle as outlined above for  $\gamma_{\text{H}^+}$ .

413

## 414 2.7 Application to sea ice brines

415 A simple numerical model was used to illustrate the changes in the parameters of the  
 416 carbonate system in seawater-derived brines with (i) conservative major ionic composition,  $A_T$ ,  
 417 and  $C_T$ , and (ii) brines of otherwise conservative chemical composition but at constant  $f\text{CO}_2$  and,  
 418 hence, non-conservative  $C_T$ , such as that which will occur as a result of dissolved-gaseous  $\text{CO}_2$   
 419 exchange to atmospheric equilibrium. These scenarios are chosen for their simplicity for  
 420 illustration purposes and cannot reflect the complexity of the carbonate system in sea ice brines  
 421 as it is driven by several internal brine reactions at different and varying rates (Papadimitriou et  
 422 al., 2004; Papadimitriou et al., 2007; Delille et al., 2007; Dieckmann et al., 2008; Munro et al.,  
 423 2010; Geilfus et al., 2012a; Papadimitriou et al., 2012; Delille et al., 2014). The model was  
 424 described in detail in Papadimitriou et al. (2014); briefly, it uses as a system of equations the  
 425 weak acid-base equilibria in seawater, the salinity-normalized measured concentrations of  
 426 phosphate,  $\text{Si(OH)}_4$ ,  $C_T$ , and  $A_T$  in surface waters of the seasonal sea ice zone (SIZ) in the

427 western Weddell Sea, Antarctica, reported in Papadimitriou et al. (2012), along with the  
428 concentrations of  $\text{SO}_4^{2-}$  and  $\text{F}^-$  in Reference Seawater (Millero et al., 2008) and the mean total  
429 boron concentration in oceanic waters from Lee et al. (2010). In scenario (i) above, all these  
430 concentrations are conserved as a linear function of salinity, and the set of equations is solved for  
431  $\text{pH}_T$  from  $A_T$  and  $C_T$  at each salinity-temperature pair at the freezing point of brines, allowing  
432 computation of the  $C_T$  speciation. In scenario (ii) above, all concentrations are conserved except  
433  $C_T$ , and the system is solved for  $\text{pH}_T$  from  $f\text{CO}_2$  and  $A_T$ , yielding  $C_T$  and its speciation. In this  
434 case, the  $f\text{CO}_2$  was set at a constant value computed for 1 atm total pressure as described in  
435 Pierrot et al. (2009) from the average 2015 atmospheric  $\text{CO}_2$  molar ratio  
436 ([www.esrl.noaa.gov/gmd/ccgg/trends/](http://www.esrl.noaa.gov/gmd/ccgg/trends/)). These calculations were done using the  $K_{1C}^*$  and  $K_{2C}^*$   
437 determined in this study, as well as the values computed by extrapolation beyond their salinity  
438 maximum and temperature minimum of the salinity-temperature oceanographic functions  
439 described in the previous section.

440

### 441 3. Results

442 The initial composition of the brines for all major ions (Table 1), normalized to salinity 35,  
443 was in very good agreement with that of Reference Seawater (Millero et al. (2008) except for  $\text{K}^+$ ,  
444 which was less by  $1 \text{ mmol kg}^{-1}$  on average, likely as a result of shading of the  $\text{K}^+$  peak by the  
445 much greater  $\text{Na}^+$  peak during ion chromatographic analysis. The conservative composition of the  
446 brines relative to that of Reference Seawater indicates no measurable alteration due to production  
447 of authigenic  $\text{CaCO}_3$ ,  $\text{CaSO}_4$ , or  $\text{Na}_2\text{SO}_4$  polymorphs over the short time scales of variable  
448 freezing of the seawater (6 – 15 hours) used here for brine preparation. It also justifies the use of  
449 the ionic composition of Reference Seawater in the thermodynamic evaluation of the current  
450 determinations of the stoichiometric equilibrium dissociation constants of carbonic acid.

451 The measured parameters and the determined stoichiometric equilibrium dissociation  
452 constants of carbonic acid (as negative common logarithms,  $\text{pK}_{1C}^*$  and  $\text{pK}_{2C}^*$ ) are given in Table  
453 2, with  $\text{pK}_{1C}^*$  and  $\text{pK}_{2C}^*$  reported in the total proton scale of the pH measurements. In the narrow  
454 below-zero temperature range to the freezing point of seawater [for the seawater  $S_P$  range from  
455 33.14 to 34.04 used in this study (Table 2),  $t_{FP} = -1.82^\circ\text{C}$  to  $-1.87^\circ\text{C}$  (UNESCO, 1983)], the  
456 current observations ( $n = 6$ ) were systematically higher than, but within experimental error from,

457 the values determined by below-zero temperature extrapolation of the best-fit curves on the  
 458 existing data sets, with an overall  $\Delta pK_{1C}^* = +0.015 \pm 0.005$  and  $\Delta pK_{2C}^* = +0.019 \pm 0.015$  relative  
 459 to both the Mehrbach et al. (1973) and Millero et al. (2006) data sets (Fig. 1). The measurements  
 460 from natural brines (Table 2) from  $S_P = 40$  to  $S_P = 100$  and from  $25\text{ }^\circ\text{C}$  to near their freezing point  
 461 (from  $-2.1\text{ }^\circ\text{C}$  at  $S_P = 40$  to  $-6.0\text{ }^\circ\text{C}$  at  $S_P = 100$ ) demonstrate that the determined  $pK_{1C}^*$  and  $pK_{2C}^*$   
 462 at  $S_P > 60$  differ substantially at all temperatures from the values derived from the extrapolation  
 463 of the existing oceanographic salinity-temperature functions (Fig. 2). Specifically, the current  
 464 values are between the extrapolated values derived from the two oceanographic data sets used  
 465 here for comparison. The greatest differences between measured and extrapolated values were  
 466 seen at the highest salinities in the  $pK_{2C}^*$  relative to the best-fit equation derived from the Millero  
 467 et al. (2006) data set, with  $\Delta pK_{2C}^* = +0.72 \pm 0.09$  ( $n = 5$ ) and  $+1.26 \pm 0.12$  ( $n = 6$ ) at  $S_P = 85$  and  
 468  $S_P = 100$ , respectively. For comparison, the equivalent  $\Delta pK_{1C}^*$  was  $+0.13 \pm 0.04$  and  $+0.24 \pm 0.07$   
 469 at  $S_P = 85$  and  $S_P = 100$ , respectively. The difference between the current and extrapolated values  
 470 derived from the best fits to the Mehrbach et al. (1973) data set were similar for both  $pK_{1C}^*$  and  
 471  $pK_{2C}^*$  at the highest salinities (Fig. 2) and were more modest than those from the extrapolation of  
 472 the Millero et al. (2006) data set, with  $\Delta pK_{1C}^* = -0.19 \pm 0.02$  and  $\Delta pK_{2C}^* = -0.12 \pm 0.02$  ( $n = 5$ ) at  
 473  $S_P = 85$  and  $\Delta pK_{1C}^* = -0.32 \pm 0.05$ ,  $\Delta pK_{2C}^* = -0.21 \pm 0.04$  ( $n = 6$ ) at  $S_P = 100$ .

474

## 475 4. Discussion

### 476 4.1. The stoichiometric equilibrium dissociation constants of carbonic acid

477 It is of note that  $pK_{2C}^*$  changed more dramatically (over 0.4 pK unit) than  $pK_{1C}^*$  (over 0.1 pK  
 478 unit) as a function of salinity at all temperatures in the current experiments (Fig. 2). The  $pK_{1C}^*$   
 479 computed from the output of the FREZCHEM thermodynamic code for the ionic composition of  
 480 Reference Seawater at ice-water equilibrium was in excellent agreement with the current freezing  
 481 point observations (Fig. 3). According to eq. (4), this indicates that all relevant thermodynamic  
 482 parameters ( $K_{1C}^0$ ,  $\gamma_{\text{CO}_2}$ ,  $\gamma_{\text{HCO}_3^-}$ ,  $\gamma_{\text{H}^+}$  and  $\alpha_{\text{H}_2\text{O}}$ ) are predicted reliably by the FREZCHEM code in  
 483 the temperature range from the freezing point of seawater to that of  $S_P = 100$  seawater-derived  
 484 brine:  $K_{1C}^0$ ,  $\gamma_{\text{CO}_2}$ , and  $\gamma_{\text{HCO}_3^-}$  via extrapolation of the relevant above-zero temperature data sets of

485 He and Morse (1993) and Plummer and Busenberg (1982),  $\gamma_{\text{H}^+}$  from the Pitzer parameters for the  
486 specific interaction of the proton with all other ions in the model solutions, and  $\alpha_{\text{H}_2\text{O}}$  from the  
487 Pitzer parameterization of the osmotic coefficient. This was not the case, however, for  $\text{pK}_{2\text{C}}^*$ ,  
488 with differences up to 0.2 pK unit between current determinations and FREZCHEM-derived  
489 values (Fig. 3), which is higher than experimental uncertainty. A similar discrepancy trend was  
490 observed in the study of the stoichiometric equilibrium solubility product of ikaite in  
491 Papadimitriou et al. (2013). The current  $\text{pK}_{2\text{C}}^*$  determinations are based on the  $A_{\text{C}}$  estimated from  
492 the measured  $\text{pH}_{\text{T}}$  and  $A_{\text{T}}$ , and are, therefore, affected by the (unknown) extrapolation error for  
493 the estimates of the non-carbonate  $A_{\text{T}}$  components (section 2). However, the FREZCHEM-  
494 derived values are also affected by the same extrapolation error, which thus cannot exclusively  
495 explain the discrepancy between the current  $\text{pK}_{2\text{C}}^*$  determinations and the FREZCHEM-derived  
496 values. Based on eqs. (4) and (5), the disagreement in  $\text{pK}_{2\text{C}}^*$  with the thermodynamic code  
497 suggests uncertainty in  $K_{2\text{C}}^{\circ}$  or the total activity coefficient of  $\text{CO}_3^{2-}$ , or both, at below-zero  
498 temperatures. The total activity coefficient of  $\text{CO}_3^{2-}$  depends strongly on the extent of ion pair  
499 formation in solution. Its ion pairs with  $\text{Ca}^{2+}$  and  $\text{Mg}^{2+}$  have large equilibrium association  
500 constants which have to be taken into account explicitly in Pitzer parameterization routines, such  
501 as FREZCHEM, to complement the formal Pitzer parameterization of the  $\text{CO}_3^{2-}$  interactions in  
502 multi-electrolyte solutions (He and Morse, 1993; Marion, 2001). Knowledge about the behaviour  
503 of these strong ion pairs is based on the above-zero temperature study of Plummer and Busenberg  
504 (1982), while the Pitzer parameters for the single ion activity coefficient of  $\text{CO}_3^{2-}$  are based on  
505 the above-zero temperature experiments of He and Morse (1993). It is conceivable that targeted  
506 relevant experiments that will expand the empirical thermodynamic data base for the  $\text{C}_{\text{T}}$  species  
507 to below-zero temperatures may reconcile such differences as that seen here with respect to  
508  $\text{CO}_3^{2-}$  (Fig. 3). This is in line with the objectives of the recent SCOR Working Group 145 for the  
509 update of chemical speciation modelling in seawater (Turner et al., 2016).

510 The  $\text{pK}_{1\text{C}}^*$  and  $\text{pK}_{2\text{C}}^*$  values determined in this study were fitted to the same equation format  
511 (eq. 3) as described in *Section 2.6*, and the best-fit coefficients are given in Table 3. The standard  
512 error of the fit was  $\sigma_{\text{pK}_{1\text{C}}^*} = 0.011$  and  $\sigma_{\text{pK}_{2\text{C}}^*} = 0.020$ , and the fitted residuals demonstrated no

513 significant trends as a function of salinity and temperature (Fig. 4). These equations are suitable  
 514 for interpolation within the salinity and temperature ranges of this investigation ( $33 \leq S_P \leq 100$ ,  $-$   
 515  $6 \text{ }^\circ\text{C} \leq t \leq 25 \text{ }^\circ\text{C}$ ), but not outside these ranges, in conservative seawater-derived brines only.  
 516 Specifically, they are relevant to solutions with the composition of Reference Seawater (Table 1)  
 517 and the conservative-composition brines that can be derived from it. By altering the free-ion and  
 518 total-ion activity coefficients, solution composition changes can affect the value of stoichiometric  
 519 equilibrium constants as a function of ionic strength relative to the temperature-dependent  
 520 thermodynamic value of said constants at constant temperature [e.g., He and Morse (1993) for  
 521  $pK_{1C}^*$  and  $pK_{2C}^*$  at above-zero temperatures in NaCl, Mg-Na-Cl, and Na-SO<sub>4</sub>-Cl solutions to 6  
 522 m]. Assessment of solution composition is, therefore, the first step for rigorous use of available  
 523 empirical stoichiometric equilibrium constants. More specifically, the current empirical salinity  
 524 and temperature functions of  $pK_{1C}^*$  and  $pK_{2C}^*$  (Table 3) are not recommended for extrapolation in  
 525 the hyposaline and more hypersaline regions of the salinity spectrum in sea ice, not least because,  
 526 at the coldest part of sea ice temperature ( $t < -6 \text{ }^\circ\text{C}$ ) where  $S_P > 100$ , the brine inclusions will  
 527 have non-conservative ionic composition and altered major ionic ratios as a result of reactions  
 528 with authigenic ikaite, mirabilite, gypsum, and hydrohalite (Papadimitriou et al., 2013; Butler and  
 529 Kennedy, 2015; Butler et al., 2016; Butler et al., 2017). This will affect the value of  
 530 stoichiometric equilibrium constants (Hain et al., 2015), which must be determined in the context  
 531 of authigenic mineral-brine equilibria.

532

#### 533 **4.2. The carbonate system in sea ice**

534 The simple numerical model described in *Section 2.7* was used to compute the change in  $pH_T$ ,  
 535  $fCO_2$ , and  $CO_3^{2-}$  with decreasing temperature from the freezing point of  $S = 35$  seawater to  $-6 \text{ }^\circ\text{C}$   
 536 ( $S_P = 100$ ) in sea ice brines (Fig. 5). In brines which are conservative with respect to major ionic  
 537 composition,  $A_T$ , and  $C_T$ , the  $pK_{1C}^*$  and  $pK_{2C}^*$  equations derived in this study predict a monotonic  
 538 decrease in the  $pH_T$  from 8.03 to 7.86 coupled with increase in both the internal brine  $fCO_2$  from  
 539 429 to 2262  $\mu\text{atm}$  and the  $CO_3^{2-}$  concentration from 84 to 330  $\mu\text{mol kg}^{-1}$ . These changes are  
 540 anticipated solely from the physical concentration during the expulsion of seawater solutes from  
 541 the ice crystal matrix in the process of sea ice formation and further cooling to  $-6 \text{ }^\circ\text{C}$ . If gas  
 542 exchange occurs during seawater freezing and cooling of the sea ice system with all major ions

543 and  $A_T$  conserved in the internal brines, the composition of the brines is non-conservative with  
 544 respect to  $C_T$  and, as a result, the brine  $fCO_2$  is controlled by its equilibrium solubility. In this  
 545 case, if atmospheric equilibrium is achieved in the brines, the brine  $pH_T$  is predicted to increase  
 546 from 8.06 to 8.48 and the  $CO_3^{2-}$  concentration will also increase but to a much larger extent from  
 547 89 to  $1017 \mu\text{mol kg}^{-1}$ .

548 The advantage gained by the current  $K_{1C}^*$  and  $K_{2C}^*$  data set relative to the extrapolation of the  
 549 oceanographic equations parameterized for above-zero temperatures and  $S_P < 50$  is evident in the  
 550 difference in absolute values for all parameters concerned here. Of the two major oceanographic  
 551 data sets used here for comparison, the extrapolation of the equations based on the Mehrbach et  
 552 al. (1973) data set yielded the smallest such differences (Fig. 5), especially with respect to  $CO_3^{2-}$   
 553 in the conservative brine scenario (mean difference:  $-0.2 \pm 3.8 \mu\text{mol kg}^{-1}$ ) over the temperature  
 554 range of the simulation (Fig. 5c). At the temperature minimum of this study and depending on the  
 555 set of extrapolated oceanographic  $pK_{1C}^*$  and  $pK_{2C}^*$  equations, these differences were calculated to  
 556 be up to +0.9 pH unit and  $-6000 \mu\text{atm } fCO_2$  in the conservative brine  $C_T$  scenario (Figs. 5a-c), as  
 557 well as up to  $-1300 \mu\text{mol } CO_3^{2-} \text{ kg}^{-1}$  in the non-conservative brine  $C_T$  scenario (Fig. 5f). Similar  
 558 differences have been reported as perplexing uncertainties of extrapolation in the sensitivity  
 559 analysis for the sea ice brine carbonate system within  $S_P = 50 - 70$  in Brown et al. (2014). The  
 560 differences between the current and the two sets of extrapolated oceanographic  $pK_{1C}^*$  and  $pK_{2C}^*$   
 561 equations in respect of  $pH_T$  and  $fCO_2$  computations at the freezing point for the conservative  
 562 brine  $C_T$  scenario (Fig. 5a, b) can be coupled with the differences between measured  $pH_T$  and  
 563  $fCO_2$  near the freezing point of experimental brines and their values derived from the relevant  $A_T$   
 564 and  $C_T$  measurements (Table 2) as computed using the two sets of extrapolated oceanographic  
 565  $pK_{1C}^*$  and  $pK_{2C}^*$  equations (Lueker et al., 2000; Millero et al., 2006). These are illustrated as a  
 566 function of the  $C_T$  to  $A_T$  ratio ( $C_T/A_T$ ) of the brine system (Fig. 6) and are increasingly significant  
 567 at  $S_P > 60$ , higher  $C_T/A_T$  at constant  $t_{FP}-S_P$ , and, also, when the salinity- and temperature-  
 568 extrapolated  $pK_{1C}^*$  and  $pK_{2C}^*$  equations in Millero et al. (2006) are used. The above comparisons  
 569 (Figures 5 and 6) highlight the importance of re-evaluating the coefficients of the existing  
 570 salinity-temperature functions on empirical data when applied to extended conditions.

571 Direct measurements at below-zero temperatures are rare for  $f\text{CO}_2$  in sea ice brines (Delille et  
572 al., 2007; Geilfus et al., 2012a; Delille et al., 2014) or bulk sea ice (Miller et al., 2011a, b; Geilfus  
573 et al., 2012b) and have not been possible until recently for pH (Loucaides et al., 2017) due to  
574 sampling and analytical difficulties in this complex medium. Sea ice geochemists thus far have  
575 often relied on indirect determination of brine  $f\text{CO}_2$  and pH in sea ice from direct measurements  
576 of  $A_T$  and  $C_T$  to determine the brine carbonate system, with the caveats of extrapolation (Brown  
577 et al., 2014), in order to assess the inorganic carbon budget in sea ice (Papadimitriou et al., 2007;  
578 Delille et al., 2007; Munro et al., 2010; Fransson et al., 2011; Geilfus et al., 2012a; Papadimitriou  
579 et al., 2012). The results of this study will provide confidence in the output of indirect parameter  
580 determination for the carbonate system in the below-zero temperature range in high salinity  
581 brines in parts of sea ice that are still warm enough to allow exchange with the air and the ocean.  
582 Additional studies are still required to extend the current empirical data base of the equilibrium  
583 dissociation constants of carbonic acid to the coldest temperature spectrum of sea ice to the  
584 eutectic and, also, to determine the behavior of the remainder weak acids and bases of the  
585 carbonate system in the full salinity and temperature spectrum of sea ice brines.

586

## 587 **5. Conclusions**

588 The stoichiometric equilibrium dissociation constants of carbonic acid determined in this  
589 study extended the existing oceanographic data set to below-zero temperatures and salinities  
590 greater than 50 to the freezing point of salinity 100 brines with major ionic composition and  
591 major ionic ratios equivalent to those of Reference Seawater. They are reported here in the total  
592 proton scale and each was fitted to a salinity and temperature function for interpolation in sea ice  
593 brine investigations of the internal carbonate system of the medium. This work confirmed the  
594 uncertainties of the salinity and temperature extrapolation of the existing oceanographic functions  
595 for application outside their empirical ranges. There were also indications for uncertainty in the  
596 current state of knowledge of the thermodynamic parameters (e.g., total activity coefficient of the  
597 carbonate ion) for the second equilibrium dissociation constant of carbonic acid at below-zero  
598 temperatures. Further relevant work is thus needed for accurate parameterization of the carbonate  
599 ion interactions with the remainder of sea solutes in brines at below-zero temperatures and for the  
600 dissociation constants of carbonic acid in the coldest temperature and salinity range of non-

601 conservative oceanic brines at equilibrium with authigenic cryogenic minerals to the eutectic of  
602 seawater.

603

#### 604 **Acknowledgements**

605 This work was supported by a NERC-UK grant (grant NE/J011096/1). We thank Susan  
606 Allender for the dissolved macro-nutrient analyses and Dr. Ben Butler for the analyses of the  
607 major ions in the experimental solutions. We also thank three anonymous reviewers for their  
608 supportive and insightful comments.

609

#### 610 **References**

611 Arrigo K. R., Worthen D. L., Lizotte M. P., Dixon P. and Dieckmann G. S. (1997) Primary  
612 production in Antarctic sea ice. *Science* **276**, 394-397.

613 Assur A. (1958) Composition of sea ice and its tensile strength in Arctic sea ice. U. S. National  
614 Academy of Sciences, National Research Council, Publ. 598, 106-138.

615 Barford N. C. (1985) Experimental measurements: Precision, error, and truth. John Wiley &  
616 Sons, Chichester, UK.

617 Bockmon E. E. and Dickson A. G. (2015) An inter-laboratory comparison assessing the quality  
618 of seawater carbon dioxide measurements. *Mar. Chem.* **171**, 36-43.

619 Brown K. A., Miller L. A., Davelaar M., Francois R. and Tortell P.D. (2014) Over-determination  
620 of the carbonate system in natural sea-ice brine and assessment of carbonic acid dissociation  
621 constants under low temperature, high salinity conditions. *Mar. Chem.* **165**, 36-45.

622 Butler B. M. and Kennedy H. (2015) An investigation of mineral dynamics in frozen seawater  
623 brines by direct measurement with synchrotron X-ray powder diffraction. *J. Geophys. Res.*  
624 *Oceans* **120**, 5686-5697, doi:10.1002/2015JC011032.

625 Butler B. M., Papadimitriou S., Santoro A., Kennedy H. (2016) Mirabilite solubility in  
626 equilibrium sea ice brines. *Geochim. Cosmochim. Acta* **182**, 40-54.

627 Butler B. M., Papadimitriou S., Day S. J., Kennedy H. (2017) Gypsum and hydrohalite dynamics  
628 in sea ice brines. *Geochim. Cosmochim. Acta* **213**, 17-34.

629 Cai W.-J., Chen L., Chen B., Gao Z., Lee S. H., Chen J., Pierrot D., Sullivan K., Wang Y., Hu X.,  
630 Huang W.-J., Zhang Y., Xu S., Murata A., Grebmeier J. M., Jones E. P. and Zhang H. (2010)  
631 *Science* **329**, 556-559.

- 632 Caldeira K. and Wickett M. E. (2003) Anthropogenic carbon and ocean pH. *Nature* **425**, 365.
- 633 Delille B., Jourdain B., Borges A. V., Tison J.-L. and Delille D. (2007) Biogas (CO<sub>2</sub>, O<sub>2</sub>,  
634 dimethylsulfide) dynamics in spring Antarctic fast ice. *Limnol. Oceanogr.* **52**, 1367-1379.
- 635 Delille B., Vancoppenolle M., Geilfus N.-X., Tilbrook B., Lannuzel D., Schoemann V.,  
636 Becquevort S., Carnat G., Delille D., Lancelot C., Chou L., Dieckmann G. S. and Tison J.-L.  
637 (2014) Southern ocean CO<sub>2</sub> sink: The contribution of the sea ice. *J. Geophys. Res. Oceans*  
638 **119**, 6340-6355.
- 639 Dickson A. G. (1990) Thermodynamics of the dissociation of boric acid in synthetic seawater  
640 from 273.15 to 318.15 K. *Deep-Sea Res.* **37**, 755-766.
- 641 Dickson A. G. and Millero F. J. (1987) A comparison of the equilibrium constants for the  
642 dissociation of carbonic acid in seawater media. *Deep-Sea Res.* **34**, 1733-1743.
- 643 Dickson A. G., Sabine C. L. and Christian J. R. (Eds.) (2007) Guide to best practices for ocean  
644 CO<sub>2</sub> measurements. PICES Special Publication 3, 191 pp.
- 645 Dieckmann G. S., Nehrke G., Papadimitriou S., Göttlicher J., Steininger R., Kennedy H., Wolf-  
646 Gladrow D. and Thomas D. N. (2008) Calcium carbonate as ikaite crystals in Antarctic sea  
647 ice. *Geophys. Res. Lett.* **35**, L08501, doi:10.1029/2008GL033540.
- 648 Feely R. A., Sabine C. L., Lee K., Berelson W., Kleypas J., Fabry V. J., Millero F. J. (2004)  
649 Impact of anthropogenic CO<sub>2</sub> on the CaCO<sub>3</sub> system in the oceans. *Science* **305**, 362-366.
- 650 Feely R. A., Sabine C. L., Hernandez-Ayon J. M., Janson D. and Hales B. (2008) Evidence for  
651 upwelling of corrosive “acidified” water onto the continental shelf. *Science* **320**, 1490-1492.
- 652 Fischer M., Thomas D. N., Krell A., Nehrke G., Göttlicher J., Norman L., Meiners K. M., Riaux-  
653 Gobin C. and Dieckmann G. S. (2013) Quantification of ikaite in Antarctic sea ice. *Antarct.*  
654 *Sci.* **25**, 421-432.
- 655 Fransson A., Chierici M., Yager P. L. and Smith Jr. W. O. (2011) Antarctic sea ice carbon  
656 dioxide system and controls. *J. Geophys. Res.* **116**, C12035, doi:10.1029/2010JC006844.
- 657 Fritsen C. H., Lytle V. I., Ackley S. F. and Sullivan C. W. (1994) Autumn bloom of Antarctic  
658 pack-ice algae. *Science* **266**, 782-784.
- 659 Gattuso J.-P., Magnan A., Billé R., Cheung W. W. L., Howes E. L., Joos F., Allemand D., Bopp  
660 L., Cooley S. R., Eakin C. M., Hoegh-Guldberg O., Kelly R. P., Pörtner H.-O., Rogers A. D.,  
661 Baxter J. M., Laffoley D., Osborn D., Rankovic A., Rochette J., Sumaila U. R., Treyer S. and

- 662 Turley C. (2015) Contrasting futures for ocean and society from different anthropogenic CO<sub>2</sub>  
663 emissions scenarios. *Science* **349**, 45, <http://dx.doi.org/10.1126/science.aac4722>.
- 664 Geilfus N. X., Carnat G., Papakyriakou T. N., Tison J.-L., Else B., Thomas H., Shadwick E. and  
665 Delille B. (2012a) Dynamics of pCO<sub>2</sub> and related air-ice CO<sub>2</sub> fluxes in the Arctic coastal zone  
666 (Amundsen Gulf, Beaufort Sea). *J. Geophys. Res.* **117**, C00G10, doi:10.1029/2011JC007118.
- 667 Geilfus N. X., Delille B., Verbeke V. and Tison J.-L. (2012b) Towards a method for high vertical  
668 resolution measurements of the partial pressure of CO<sub>2</sub> within bulk sea ice. *J. Glaciol.* **58**,  
669 208-212.
- 670 Gleitz M., v.d. Loeff M. R., Thomas D. N., Dieckmann G. S. and Millero F. J. (1995)  
671 Comparison of summer and winter inorganic carbon, oxygen and nutrient concentrations in  
672 Antarctic sea ice brine. *Mar. Chem.* **51**, 81-91.
- 673 Golden K. M., Ackley S. F. and Lytle V. I. (1998) The percolation phase transition in sea ice.  
674 *Science* **282**, 2238-2241.
- 675 Goyet C. and Poisson A. (1989) New determination of carbonic acid dissociation constants in  
676 seawater as a function of temperature and salinity. *Deep-Sea Res.* **36**, 1635-1654.
- 677 Hales B., Chipman D. and Takahashi T. (2004a) High-frequency measurements of partial  
678 pressure and total concentration of carbon dioxide in seawater using microporous hydrophobic  
679 membrane contactors. *Limnol. Oceanogr. Methods* **2**, 356-364.
- 680 Hales B., van Greer A. and Takahashi T. (2004b) High-frequency measurements of seawater  
681 chemistry: Flow-injection analysis of macronutrients. *Limnol. Oceanogr. Methods* **2**, 91-101.
- 682 Hain M. P., Sigman D. M., Higgins J. A. and Haug G. H. (2015) The effects of secular calcium  
683 and magnesium concentration changes on the thermodynamics of seawater acid/base  
684 chemistry: Implications for Eocene and Cretaceous ocean carbon chemistry and buffering.  
685 *Global Biogeochem. Cycles* **29**, 517-533.
- 686 Hansson I. (1973) A new set of acidity constants for carbonic acid and boric acid in seawater.  
687 *Deep-Sea Res.* **20**, 461-478.
- 688 He S. and Morse J. W. (1993) The carbonic acid system and calcite solubility in aqueous Na-K-  
689 Ca-Mg-Cl-SO<sub>4</sub> solutions from 0 to 90°C. *Geochim. Cosmochim. Acta* **57**, 3533-3554.
- 690 Howarth R. W. (1978) A rapid and precise method for determining sulfate in seawater, estuarine  
691 waters, and sediment pore waters. *Limnol. Oceanogr.* **23**, 1066-1069.

- 692 Kennedy H., Thomas D. N., Kattner G., Haas C. and Dieckmann G. S. (2002) Particulate organic  
693 matter in Antarctic summer sea ice: concentration and stable isotopic composition. *Mar. Ecol.*  
694 *Prog. Ser.* **238**, 1-13.
- 695 Lee K., Kim T.-W., Byrne R. H., Millero F. J., Feely R. A. and Liu Y.-M. (2010) The universal  
696 ratio of boron to chlorinity for the North Pacific and North Atlantic oceans. *Geochim.*  
697 *Cosmochim. Acta* **74**, 1801-1811.
- 698 Liu X., Patsavas M. C. and Byrne R. H. (2011) Purification and characterization of meta-Cresol  
699 Purple for spectrophotometric seawater pH measurements. *Environ. Sci. Technol.* **45**, 4862-  
700 4868.
- 701 Loucaides S., Rérolle V. M. C., Papadimitriou S., Kennedy H., Mowlem M. C., Dickson A. G.,  
702 Gledhill M. and Achterberg E. P. (2017) Characterization of *meta*-Cresol Purple for  
703 spectrophotometric pH measurements in saline and hypersaline media at sub-zero  
704 temperatures. *Sci. Rep.* **7**, 2481, doi:10.1038/s41598-017-02624-0
- 705 Lueker T. J., Dickson A. G. and Keeling C. D. (2000) Ocean pCO<sub>2</sub> calculated from dissolved  
706 inorganic carbon, alkalinity, and equations for K<sub>1</sub> and K<sub>2</sub>: validation based on laboratory  
707 measurements of CO<sub>2</sub> in gas and seawater at equilibrium. *Mar. Chem.* **70**, 105-119.
- 708 Marion G. M. (2001) Carbonate mineral solubility at low temperatures in the Na-K-Mg-Ca-H-Cl-  
709 SO<sub>4</sub>-OH-HCO<sub>3</sub>-CO<sub>3</sub>-CO<sub>2</sub>-H<sub>2</sub>O system. *Geochim. Cosmochim. Acta* **65**, 1883–1896.
- 710 Marion G. M., Mironenko M. V. and Roberts M. W. (2010) FREZCHEM: A geochemical model  
711 for cold aqueous solutions. *Comput. Geosci.* **36**, 10-15.
- 712 Mehrbach C., Culberson C. H., Hawley J. E. and Pytkowicz R. M. (1973) Measurement of the  
713 apparent dissociation constants of carbonic acid in seawater at atmospheric pressure. *Limnol.*  
714 *Oceanogr.* **18**, 897-907.
- 715 Miller L. A., Fripiat F., Else B. G. T., Bowman J. S., Brown K. A., Collins R. E., Ewert M.,  
716 Fransson A., Gosselin M., Lannuzel D., Meiners K. M., Michel C., Nishioka J., Nomura D.,  
717 Papadimitriou S., Russell L. M., Sørensen L. L., Thomas D. N., Tison J.-L., van Leeuwe M.  
718 A., Vancoppenolle M., Wolff E.W., Zhou J. (2015) Methods for biogeochemical studies of sea  
719 ice: The state of the art, caveats, and recommendations. *Elementa: Science of the*  
720 *Anthropocene* **3**, 000038, doi: 10.12952/journal.elementa.000038.

- 721 Miller L. A., Carnat G., Else B. G. T., Sutherland N. and Papakyriakou T. N. (2011a) Carbonate  
722 system evolution at the Arctic Ocean surface during autumn freeze-up. *J. Geophys. Res.* **116**,  
723 C00G04, doi: 10.1029/2011JC007143.
- 724 Miller L. A., Papakyriakou T. N., Collins R. E., Deming J. W., Ehn J. K., Macdonald R. W.,  
725 Mucci A., Owens O., Raudsepp M. and Sutherland N. (2011b) Carbon dynamics in sea ice: A  
726 winter flux time series. *J. Geophys. Res.* **116**, C02028, doi: 10.1029/2009JC006058.
- 727 Millero F. J. (1995) Thermodynamics of the carbon dioxide system in the oceans. *Geochim.*  
728 *Cosmochim. Acta* **59**, 661–677.
- 729 Millero F. J. and Huang F. (2009) The density of seawater as a function of salinity (5 to 70 g kg<sup>-1</sup>)  
730 and temperature (273.15 to 363.15 K). *Ocean Sci.* **5**, 91-100.
- 731 Millero, F.J., Zhang, J.Z., Fiol, S., Sotolongo, S., Roy, R.N., Lee K., Mane S. (1993) The use of  
732 buffers to measure the pH of seawater. *Mar. Chem.* **44**, 143-152.
- 733 Millero F. J., Pierrot D., Lee K., Wanninkhof R., Feely R., Sabine C. L., Key R. M. and  
734 Takahashi T. (2002) Dissociation constants for carbonic acid determined from field  
735 measurements. *Deep-Sea Res. Part I* **49**, 1705-1723.
- 736 Millero F. J., Graham T. B., Huang F., Bustos-Serrano H. and Pierrot D. (2006) Dissociation  
737 constants of carbonic acid in seawater as a function of salinity and temperature. *Mar. Chem.*  
738 **100**, 80-94.
- 739 Millero F. J., Feistel R., Wright D. G. and McDougall T. J. (2008) The composition of standard  
740 seawater and the definition of the reference-composition salinity. *Deep-Sea Res Part I* **55**, 50-  
741 72.
- 742 Mohica-Prieto F. J. and Millero F. J. (2002) The values of  $pK_1 + pK_2$  for the dissociation of  
743 carbonic acid in seawater. *Geochim. Cosmochim. Acta* **66**, 2529–2540.
- 744 Munro D. R., Dunbar R. B., Mucciarone D. A., Arrigo K. R. and Long M. C. (2010) Stable  
745 isotopic composition of dissolved inorganic carbon and particulate organic carbon in sea ice  
746 from the Ross Sea, Antarctica. *J. Geophys. Res.* **115**, C09005, doi:10.1029/2009JC005661.
- 747 Papadimitriou S., Kennedy H., Kattner G., Dieckmann G. S. and Thomas D. N. (2004)  
748 Experimental evidence for carbonate precipitation and CO<sub>2</sub> degassing during sea ice  
749 formation. *Geochim. Cosmochim. Acta* **68**, 1749-1761.

- 750 Papadimitriou S., Thomas D. N., Kennedy H., Haas C., Kuosa H., Krell H. and Dieckmann D. S.  
751 (2007) Biogeochemical composition of natural sea ice brines from the Weddell Sea during  
752 early austral summer. *Limnol. Oceanogr.* **52**, 1809-1823.
- 753 Papadimitriou S., Kennedy H., Norman L., Kennedy D. P. and Thomas D. N. (2012) The effect  
754 of biological activity, CaCO<sub>3</sub> mineral dynamics, and CO<sub>2</sub> degassing in the inorganic carbon  
755 cycle in sea ice in late winter-early spring in the Weddell Sea, Antarctica. *J. Geophys. Res.*  
756 **117**, C08011, doi: 10.1029/2012JC008058.
- 757 Papadimitriou S., Kennedy H., Kennedy P. and Thomas D. N. (2013) Ikaite solubility in  
758 seawater-derived brines at 1 atm and sub-zero temperatures to 265 K. *Geochim. Cosmochim.*  
759 *Acta* **109**, 241-253, doi:10.1016/j.gca.2013.01.044.
- 760 Papadimitriou S., Kennedy H., Kennedy P. and Thomas D. N. (2014) Kinetics of ikaite  
761 precipitation and dissolution in seawater-derived brines at subzero temperatures to 265 K.  
762 *Geochim. Cosmochim. Acta* **140**, 199-211, doi: 10.1016/j.gca.2014.05.031.
- 763 Papadimitriou S., Loucaides S., Rérolle V. M. C., Achterberg E. P., Dickson A. G., Mowlem M.  
764 C. and Kennedy H. (2016) The measurement of pH in saline and hypersaline media at sub-  
765 zero temperatures: Characterization of Tris buffers. *Mar. Chem.* **184**, 11-20.
- 766 Pierrot D., Neill C., Sullivan K., Castle R., Wanninkhof R., Lüge H., Johannessen T., Olsen A.,  
767 Feely R. A. and Cosca C. E. (2009) Recommendations for autonomous underway pCO<sub>2</sub>  
768 measuring systems and data reduction techniques. *Deep-Sea Res Part II* **56**, 512-522.
- 769 Pitzer K. S. (1973) Thermodynamics of electrolytes. I. Theoretical basis and general equations. *J.*  
770 *Phys. Chem.* **77**, 268–277.
- 771 Plummer N. L. and Busenberg E. (1982) The solubility of calcite, aragonite, and vaterite in CO<sub>2</sub>-  
772 water solutions between 0 – 90 °C and an evaluation of the aqueous model for the system  
773 CO<sub>2</sub>-H<sub>2</sub>O-CaCO<sub>3</sub>. *Geochim. Cosmochim. Acta* **46**, 1011-1040.
- 774 Pytkowicz R. M. and Kester D. R. (1969) Harned's rule behaviour of NaCl–Na<sub>2</sub>SO<sub>4</sub> solutions  
775 explained by an ion association model. *Am. J. Sci.* **267**, 217–229.
- 776 Rérolle V. M. C., Floquet C. F. A., Harris A. J. K., Mowlem M. C., Bellerby R. R. G. J. and  
777 Achterberg E. P. (2013) Development of a colorimetric microfluidic pH sensor for  
778 autonomous seawater measurements. *Anal. Chim. Acta* **786**, 124-131.

- 779 Roy R. N., Roy L. N., Lawson M., Vogel K. M., Porter-Moore C., Davis W., Millero F. J. and  
780 Campbell D. M. (1993) The dissociation constants of carbonic acid in seawater at salinities 5  
781 to 45 and temperatures 0 to 45 °C. *Mar. Chem.* **44**, 249-259.
- 782 Rysgaard S., Glud R. N., Sejr M. K., Bendtsen J. and Christensen P. B. (2007) Inorganic carbon  
783 transport during sea ice growth and decay: A carbon pump in polar seas. *J. Geophys. Res.*  
784 *Oceans* **112**, C03016, doi: 10.1029/2006JC003572.
- 785 Rysgaard S., Bendtsen J., Delille B., Dieckmann G. S., Glud R. N., Kennedy H., Mortensen J.,  
786 Papadimitriou S., Thomas D. N. and Tison J.-L. (2011) Sea ice contribution to the air–sea CO<sub>2</sub>  
787 exchange in the Arctic and Southern Oceans. *Tellus B* **63**, 823-830.
- 788 Sabine C. L., Feely R. A., Gruber N., Key R. M., Lee K., Bullister J. L., Wanninkhof R., Wong  
789 C. S., Wallace D. W. R., Tilbrook B., Millero F. J., Peng T.-H., Kozyr A., Ono T., Rios A. F.  
790 (2004) The oceanic sink for anthropogenic CO<sub>2</sub>. *Science* **305**, 367-371.
- 791 Semiletov I., Pipko I., Gustafsson Ö., Anderson L. G., Sergienko V., Pugach S., Dudarev O.,  
792 Charkin A., Gukov A., Bröder L., Andersson A., Spivak E. and Shakhova N. (2016)  
793 Acidification of East Siberian Arctic Shelf waters through addition of freshwater and  
794 terrestrial carbon. *Nat. Geosci.* **9**, 361-365.
- 795 Takahashi T. (2004) The fate of industrial carbon dioxide. *Science* **305**, 352-353.
- 796 Takahashi T., Sutherland S. C., Chipman D. W., Goddard J. G., Ho C., Newberger T., Sweeney  
797 C. and Munro D. R. (2014) Climatological distributions of pH, pCO<sub>2</sub>, total CO<sub>2</sub>, alkalinity,  
798 and CaCO<sub>3</sub> saturation in the global surface ocean, and temporal changes at selected locations.  
799 *Mar. Chem.* **164**, 95-125.
- 800 Takahashi T., Feely R. A., Weiss R. F., Wanninkhof R. H., Chipman D. W., Sutherland S. C. and  
801 Takahashi T. T. (1997) Global air-sea flux of CO<sub>2</sub>: An estimate based on measurements of  
802 sea-air pCO<sub>2</sub> difference. *Proc. Natl.Acad. Sci. USA* **94**, 8292-8299.
- 803 Thomas D. N. and Dieckmann G. S. (2002) Sea ice – A habitat for extremophiles. *Science* **295**,  
804 641-644.
- 805 Turner D. R., Achterberg E. P., Chen C.-T. A., Clegg S. L., Hatje V., Maldonado M., Sander S.  
806 G., van den Berg C. M. G. and Wells M. (2016) Toward a quality-controlled and accessible  
807 Pitzer model for seawater and related systems. *Front. Mar. Sci.* **3**, 139,  
808 doi:10.3389/fmars.2016.00139.

- 809 UNESCO (1983). Algorithms for computation of fundamental properties of seawater. UNESCO  
810 Technical Papers in Marine Science 44, 53 pp.
- 811 Weiss R. S. (1974) Carbon dioxide in water and seawater: The solubility of a non-ideal gas. *Mar.*  
812 *Chem.* **2**, 203-215.
- 813 Yamamoto-Kawai M., McLaughlin F. A., Carmack E. C., Nishino S. and Shimada K. (2009)  
814 Aragonite undersaturation in the Arctic Ocean: Effects of ocean acidification and sea ice melt.  
815 *Science* **326**, 1098-1100.
- 816
- 817
- 818

819 **List of Figures**

820 **Figure 1.** The stoichiometric equilibrium first and second dissociation constants of carbonic acid  
 821 as negative common logarithm versus temperature (open circles) in natural seawater ( $S_P = 33 -$   
 822  $34$ ). The curves were derived from the salinity-temperature functions in Lueker et al. (2000)  
 823 based on the measurements of Mehrbach et al. (1973) (dashed line) and from the measurements  
 824 on the seawater proton scale of Millero et al. (2006), converted to the total proton scale as in  
 825 Millero (1995) and re-fitted here (solid line). Note the difference in the scale of the y-axis in the  
 826  $pK_{1C}^*$  and  $pK_{2C}^*$  panels.

827 **Figure 2.** The stoichiometric equilibrium first and second dissociation constants of carbonic acid  
 828 as negative common logarithm versus salinity from this study (open circles) and from Millero et  
 829 al. (2006) (crosses) when available at  $20\text{ }^\circ\text{C}$  [panels (a) and (b)],  $5\text{ }^\circ\text{C}$  [panels (c) and (d)],  $0\text{ }^\circ\text{C}$   
 830 [panels (e) and (f)], and the freezing point [panels (g) and (h)]. The dashed curve represents the  
 831 salinity-temperature functions in Lueker et al. (2000) based on the measurements of Mehrbach et  
 832 al. (1973), extrapolated outside their empirical range of  $S_P = 19 - 43$  and for  $t < 2.0\text{ }^\circ\text{C}$ . The solid  
 833 curve represents the salinity-temperature functions based on the measurements on the seawater  
 834 proton scale of Millero et al. (2006), converted to the total proton scale and re-fitted here, and  
 835 extrapolated outside their empirical range for  $S_P > 51$  and for  $t < 1.0\text{ }^\circ\text{C}$ . Note the difference in  
 836 the scale of the y-axis in the  $pK_{1C}^*$  and  $pK_{2C}^*$  panels.

837 **Figure 3.** The stoichiometric equilibrium first and second dissociation constants of carbonic acid  
 838 as negative common logarithm versus temperature in panels (a) and (b), and versus salinity in  
 839 panels (c) and (d), respectively, at the freezing point of seawater and seawater-derived brine from  
 840 this study (open circles) and from the output of the thermodynamic code FREZCHEM v15.1  
 841 (dashed line). Note the equivalent scale of the y-axis in the  $pK_{1C}^*$  and  $pK_{2C}^*$  panels.

842 **Figure 4.** Difference between observed and fitted values of the stoichiometric equilibrium first  
 843 and second dissociation constants of carbonic acid as negative common logarithm in seawater  
 844 and brines as a function of salinity [panels (a) and (b)] and temperature [panels (c) and (d)].

845 **Figure 5.** Change in pH in the total proton scale [panels (a), (d)],  $\text{CO}_2$  fugacity [panels (b), (e)],  
 846 and the total concentration of the carbonate ion [panels (c), (f)] in sea ice brine inclusions at ice-  
 847 brine equilibrium (freezing point) as a function temperature in conservative seawater-derived  
 848 brines with respect to major ionic composition,  $A_T$ , and  $C_T$  (upper panels), and in conservative  
 849 brines at equilibrium with current atmospheric  $\text{CO}_2$  (non-conservative  $C_T$ ) (lower panels). The

850 values of the illustrated parameters were determined for equilibrium freezing of surface seawater  
 851 from the western Weddell Sea, Antarctica, in Papadimitriou et al. (2012) by solving the system of  
 852 equations that describe the chemical equilibria of the marine CO<sub>2</sub> system using the dissociation  
 853 constants of carbonic acid from this study (solid line), and as computed from the salinity-  
 854 temperature functions fitted to the measurements of Mehrbach et al. (1973) by Lueker et al.  
 855 (2000) (dashed line) and to the measurements of Millero et al. (2006) following conversion to the  
 856 total proton scale and re-fitting in this study (dotted line). Further details are given in *Section 2.7*.

857 **Figure 6.** The differences between the current data set and each of the two sets of extrapolated  
 858 oceanographic  $pK_{1C}^*$  and  $pK_{2C}^*$  equations (Lueker et al., 2000; Millero et al., 2006) in respect of  
 859  $fCO_2$  [ $\Delta fCO_2$ : panels (a) and (b)] and pH on the total proton scale [ $\Delta pH_T$ : panels (c) and (d)]  
 860 computed from  $A_T$  and  $C_T$  at the freezing point as a function of the  $C_T$  to  $A_T$  ratio ( $C_T/A_T$ ) of the  
 861 brine system. The  $\Delta fCO_2$  and  $\Delta pH_T$  are shown for  $S_P = 50$  (squares), 60 (diamonds), 85 (circles),  
 862 and 100 (triangles, crosses) for (i) the conservative brine  $A_T$  and  $C_T$  scenario (closed symbols;  
 863 also illustrated in Fig. 5a, b), (ii) between measured  $pH_T$  and  $fCO_2$  near the freezing point of  
 864 experimental brines and their values derived from the relevant  $A_T$  and  $C_T$  measurements (Table  
 865 2) as computed using each of the two sets of extrapolated oceanographic  $pK_{1C}^*$  and  $pK_{2C}^*$   
 866 equations (open symbols), and (iii) for illustration purposes, for  $C_T/A_T$  decreasing from the  
 867 conservative  $C_T/A_T$  scenario to lower values (conservative  $A_T$ , non-conservative  $C_T$ ) at a constant  
 868  $t_{FP} = -6.0$  °C and  $S_P = 100$  (crosses).

869

870

871

872 **Table 1.** Major ion composition of brines (in mmol kg<sup>-1</sup>).

Salinity	[Na <sup>+</sup> ]	[Mg <sup>2+</sup> ]	[Ca <sup>2+</sup> ]	[K <sup>+</sup> ]	[Cl <sup>-</sup> ]+[Br <sup>-</sup> ]	[SO <sub>4</sub> <sup>2-</sup> ]
100.52	1347	150.64	29.96	25.85	1566	77.21
98.69	1323	148.89	28.99	26.26	1554	77.47
84.62	1134	128.02	25.00	22.26	1327	66.97
61.54	825	92.66	18.18	16.23	968	50.48
60.30	808	91.34	17.87	15.40	946	47.25
60.28	808	91.25	17.84	16.11	944	47.93
50.24	681	74.20	14.54	13.57	795	39.79
50.15		75.15	14.55			40.37
48.90		72.65	14.30			38.80
40.20	539	60.84	11.83	11.09	632	32.77
<sup>a</sup> 35	470±2	52.60±0.45	10.29±0.10	9.27±0.23	550±2	27.82±0.54
<sup>b</sup> 35	469	52.82	10.28	10.21	547	28.24

873 <sup>a</sup>mean concentration of brines normalized to salinity 35874 <sup>b</sup>composition of Reference Seawater of salinity 35 (Millero et al., 2008)

875

876 **Table 2.** Practical salinity ( $S_P$ ), temperature ( $t$ , in  $^{\circ}\text{C}$ ), phosphate (SRP) and silicic acid [ $\text{Si}(\text{OH})_4$ ]  
 877 (in  $\mu\text{mol kg}^{-1}$ ), the measured parameters of the carbonate system in seawater and seawater-  
 878 derived brines [ $C_T$  (in  $\mu\text{mol kg}^{-1}$ ),  $A_T$  and derived carbonate alkalinity ( $A_C$ ) (in  $\mu\text{mol kg}^{-1}$ ),  $f\text{CO}_2$   
 879 (in  $\mu\text{atm}$ ), and  $\text{pH}_T$  (total proton scale; in  $\text{mol kg}^{-1}$ )], and the stoichiometric equilibrium first and  
 880 second dissociation constants of carbonic acid (in  $\text{mol kg}^{-1}$ , total proton scale) as negative  
 881 common logarithms ( $\text{pK}_{1C}^*$  and  $\text{pK}_{2C}^*$ ).

$S_P$	SRP	$\text{Si}(\text{OH})_4$	$t$	$C_T$	$A_T$	$A_C$	$f\text{CO}_2$	$\text{pH}_T$	$\text{pK}_{1C}^*$	$\text{pK}_{2C}^*$
33.14	0.1	2.9	-1.79	2047	2259	2177	184	8.345	6.167	9.468
33.54	0.0	8.1	17.98	2042	2282	2200	369	8.052	5.889	9.089
33.64	0.3	3.8	-1.53	2153	2287	2231	329	8.125	6.163	9.432
			-1.53	2157	2287	2231	329	8.122	6.158	9.448
			-1.53	2154	2287	2232	331	8.118	6.158	9.425
			22.01	2139	2287	2233	788	7.780	5.866	9.007
33.64	0.3	3.8	15.07	2114	2281	2221	520	7.934	5.932	9.126
			15.07	–	2281	2221	519	7.929	–	–
			15.11	2119	2281	2220	518	7.935	5.928	9.151
			25.01	2144	2281	2229	887	7.731	5.832	8.991
			25.02	2138	2281	2228	872	7.737	5.833	8.977
			25.06	2141	2281	2228	880	7.732	5.830	8.984
33.94	0.0	7.1	-1.17	2063	2278	2194	186	8.333	6.143	9.457
			-1.06	2073	2278	2199	206	8.298	6.148	9.436
			-1.06	–	2278	2199	203	8.298	–	–
			-0.03	2045	2278	2192	186	8.329	6.127	9.401
			0.04	2064	2278	2194	201	8.309	6.132	9.435
			0.04	2061	2278	2195	202	8.308	6.135	9.420
			0.04	2061	2278	2195	201	8.305	6.130	9.418
			5.03	2050	2278	2195	237	8.232	6.052	9.309
			9.94	2048	2278	2198	280	8.148	5.968	9.210
			20.04	2044	2278	2202	433	7.986	5.866	9.019
			24.96	2100	2278	2213	676	7.835	5.831	9.003
			24.99	2100	2278	2214	682	7.832	5.832	8.996
			25.04	2091	2278	2213	680	7.833	5.835	8.968
34.04	0.2	4.8	0.00	2053	2286	2199	191	8.327	6.134	9.403
			0.00	2054	2286	2199	190	8.324	6.128	9.403
			0.00	–	2286	2199	191	8.323	–	–
			0.06	2049	2286	2195	181	8.350	6.133	9.427
			20.03	2050	2286	2206	430	8.005	5.880	9.045
			20.03	2048	2286	2206	420	8.004	5.870	9.039
			20.03	2048	2286	2206	427	8.004	5.877	9.039

882

883

884 **Table 2** (continued)

$S_P$	SRP	Si(OH) <sub>4</sub>	$t$	$C_T$	$A_T$	$A_C$	$fCO_2$	pH <sub>T</sub>	pK <sub>1C</sub> *	pK <sub>2C</sub> *
40.20	0.1	46.9	-2.15	2512	2806	2703	216	8.327	6.123	9.375
			4.97	2584	2806	2729	426	8.071	6.025	9.229
48.90	0.0	259.4	-2.72	3177	3528	3411	347	8.247	6.134	9.300
			-0.09	3155	3528	3413	385	8.198	6.092	9.206
			20.05	3142	3528	3420	851	7.883	5.841	8.850
50.15	0.0	55.2	-2.74	3026	3481	3329	224	8.397	6.123	9.326
			-2.74	3038	3481	3337	248	8.366	6.134	9.300
50.24	0.0	38.3	-1.56	2947	3446	3296	232	8.373	6.114	9.223
			-0.06	2976	3446	3306	268	8.312	6.082	9.191
			4.88	2976	3446	3308	329	8.233	6.013	9.109
			10.00	2944	3446	3306	383	8.168	5.949	8.998
			15.00	2984	3446	3318	532	8.051	5.896	8.921
60.28	0.4	15.3	25.05	2977	3446	3323	807	7.895	5.807	8.743
			-3.36	3645	4116	3965	379	8.284	6.137	9.264
			-0.27	3643	4116	3968	419	8.229	6.073	9.202
			25.02	3627	4116	3987	1183	7.802	5.765	8.718
60.30	1.2	26.9	-3.37	3641	4180	4012	302	8.340	6.101	9.259
			-2.40	3652	4180	4016	308	8.310	6.060	9.240
			-2.37	3661	4180	4016	318	8.308	6.069	9.250
			20.29	3649	4180	4035	864	7.925	5.802	8.819
61.54	0.4	0.5	-3.46	3707	4228	4060	328	8.331	6.115	9.279
			-0.11	3705	4228	4062	370	8.276	6.056	9.219
84.62	1.0	18.0	-4.97	4863	5811	5562	371	8.409	6.118	9.167
			-4.93	4842	5811	5560	366	8.413	6.120	9.155
			0.04	4840	5811	5567	455	8.318	6.035	9.054
			5.02	4855	5811	5579	583	8.216	5.960	8.954
			20.33	4847	5811	5599	1088	7.953	5.773	8.668
98.69	1.4	22.6	-6.00	5457	6795	6486	392	8.509	6.196	9.130
			-5.93	5454	6795	6483	356	8.512	6.156	9.134
			0.03	5459	6795	6498	459	8.390	6.042	9.007
			4.87	5441	6795	6504	546	8.304	5.960	8.907
100.52	2.0	20.7	-5.98	5628	6901	6611	417	8.469	6.157	9.129
			20.30	5656	6901	6673	1308	7.946	5.755	8.587

885

886

887 **Table 3.** Best fit values for the coefficients of the salinity-temperature functions of the first and  
 888 second stoichiometric equilibrium dissociation constants of carbonic acid in seawater and  
 889 seawater-derived brines on the total proton scale.

Parameter	Coefficient	data set			
		Millero et al. (2006)		this study	
		$pK_{1C}^*$	$pK_{2C}^*$	$pK_{1C}^*$	$pK_{2C}^*$
$S_P^{0.5}$	$a_0$	13.47667	21.07076	6.14528	27.557655
$S_P$	$a_1$	0.032404	0.12322	-0.127714	0.154922
$S_P^2$	$a_2$	$-5.534 \times 10^{-5}$	$-3.68 \times 10^{-4}$	$7.396 \times 10^{-5}$	$-2.48396 \times 10^{-4}$
$S_P^{0.5}/T$	$a_3$	-535.036	-774.97	-622.886	-1014.819
$S_P/T$	$a_4$	-5.8655	-19.5835	29.714	-14.35223
$S_P^{0.5} \ln T$	$a_5$	-2.07643	-3.328487	-0.666812	-4.4630415
constant	$b_0$	<sup>a</sup> -126.34048	<sup>a</sup> -90.18333	-176.48	-323.52692
$1/T$	$b_1$	<sup>a</sup> 6320.813	<sup>a</sup> 5143.692	9914.37	14763.287
$\ln T$	$b_2$	<sup>a</sup> 19.568224	<sup>a</sup> 14.613358	26.05129	50.385807
user confirmation value $S_P = 35, T = 273.15 \text{ K}$		6.1184	9.3827	6.1267	9.3940

890 <sup>a</sup> from Millero et al. (2006)

891