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

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

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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 CO₂ 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 CO₂ 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 CO₂ (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 CO₂ 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, CO₂ gas exchange and hydrated
63 CaCO₃ 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 CO₂ 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 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 $p(K_{2e2})$ 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 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 Ω -cm) Milli-QTM water. The brines were filtered
164 through pre-combusted (500 °C, 3 hrs) GF/F filters (0.7 μ m, WHATMAN); they were then
165 sampled for the determination of major ion concentrations (Na^+ , K^+ , Ca^{2+} , Mg^{2+} , Cl^- and Br^- ,
166 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⁻¹) 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 ± 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 ~ 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 pH_T) at the experimental temperature
188 and the sample collection for the remainder of analyses. First, the $f\text{CO}_2$ and 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 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 CO_2 mole fraction (x_{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 0.5×1 MicroModule™ Membrane Contactor (Liqui-Cell; 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 mL min^{-1}
202 through a custom-made DRIERITE desiccant column (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 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_{CO_2} was
208 achieved in 50 min, and the x_{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 CO_2/N_2 mixtures with a certified x_{CO_2} (0, 20, 100, 400, 1000, and 2000 ppm; uncertainty
212 $\leq 5\%$, BOC, boc.com). The calibrations were conducted between two consecutive experiments.
213 The sample $f\text{CO}_2$ was computed from the measured x_{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 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 CO₂ in seawater, and the B_T 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*CO₂ 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*CO₂ differed by (mean ± 1σ) -9 ±
231 10 μatm (*n* = 12). This estimated uncertainty is equivalent to -2 ± 3% relative to the computed
232 *f*CO₂ 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_{1C}^{*}
235 and pK_{2C}^{*} (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*CO₂ uncertainty has been estimated to be
237 1.6% for the uncertainty in the certified A_T and C_T concentrations (3 μmol kg⁻¹ for both A_T and
238 C_T; 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*CO₂. The measured *f*CO₂ differed by -85 μatm at CRM *f*CO₂ = 1062 μatm at 18.06 °C for batch
241 #125, equivalent to -8% relative to the computed *f*CO₂. In contrast, in the assessment of Lueker
242 et al. (2000), the measured *f*CO₂ was systematically higher by +3.35 ± 1.22% than the computed
243 *f*CO₂ at *f*CO₂ > 500 μatm. In comparison, the uncertainty based on the single high-*f*CO₂ CRM
244 measurement (batch #125) available during this study suggests an increased negative bias at high
245 *f*CO₂ (~ 1,000 μatm, or higher) with the current methodology.

246

247 2.2 pH measurement

248 The pH_T (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 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 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 1σ). The uncertainty associated with the pH_T
263 measurement protocol was assessed against the 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 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 pH_T
270 differed by (mean $\pm 1\sigma$) -0.013 ± 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 pH_T differed by +0.015 pH unit. Numerical
272 evaluation yielded a computational uncertainty of ± 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 pH_T . This suggests that about half of the overall uncertainty
276 evaluated on the CRM pH_T determinations (~ 0.020 pH unit as 2σ) can be attributable to
277 computational uncertainty. A similar uncertainty of 0.010 – 0.020 pH unit was evaluated for the
278 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 pCO₂ (400 ppm CO₂)
289 provided at a controlled rate (200 mL min⁻¹) 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⁻¹, ~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 CO₂ generated and extracted in vacuo in a glass manifold following reaction
307 of a weighed sample aliquot with H₃PO₄ and cryogenic CO₂ 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 (~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 ~8.5 for Ca²⁺ and Mg²⁺ as described in Papadimitriou et al. (2012), (ii) ion chromatography
 321 on a Dionex Ion Exchange Chromatograph ICS 2100 for Na⁺ and K⁺, (iii) gravimetric Mohr
 322 titration for total halides (except F⁻, but mostly Cl⁻, with comparatively small contributions from
 323 bromide and smaller by iodine; hereafter termed: [Cl⁻] + [Br⁻]) with 0.3 mol kg⁻¹ AgNO₃
 324 standardized against NaCl purified by re-crystallization (Dickson, 1990; Millero et al., 1993), and
 325 (iv) for SO₄²⁻, precipitation as BaSO₄ in EDTA followed by titration with MgCl₂ (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 $X = H^+$, C_T , A_C , $CO_2(aq)$ (all in mol kg⁻¹). The maximum measurement
 334 uncertainty (σ_X) was 0.020 pH unit for the pH measurements, 0.4% for the C_T determinations, 20
 335 μatm for $fCO_2 < 1000 \mu\text{atm}$, 90 μatm for $fCO_2 > 1000 \mu\text{atm}$, 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 pH_T , C_T , fCO_2 , and A_C determinations indicated that K_{1C}^* is most
 339 sensitive to uncertainties in the pH and fCO_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 $fCO_2 > 250 \mu\text{atm}$ to 0.050 pK unit at fCO_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 ± 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, α_{H_2O} =
 382 activity of water, γ_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 α_{H_2O} , and γ_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 20th 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 μatm (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 $\text{mol kg}_{\text{H}_2\text{O}}^{-1}$) 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 $\alpha_{\text{H}_2\text{O}}$, γ_{CO_2} , and the single ion activity coefficients of HCO_3^- and
 405 CO_3^{2-} from the Pitzer equations (Pitzer, 1973) and relevant Pitzer parameters. All ion pairs for
 406 HCO_3^- are considered adequately represented in the Pitzer computation (He and Morse, 1993)
 407 and so, the single ion activity coefficient of 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 CO_3^{2-} in the form of
 409 CaCO_3^0 and 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 CO_3^{2-} as a single ion in the
 411 code output to compute the total activity coefficient of 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 γ_{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 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, 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 SO_4^{2-} and 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 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 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 CO_2 molar ratio
436 (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 K^+ ,
444 which was less by 1 mmol kg^{-1} on average, likely as a result of shading of the K^+ peak by the
445 much greater 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 CaCO_3 , CaSO_4 , or Na_2SO_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, pK_{1C}^* and pK_{2C}^*) are given in Table
453 2, with pK_{1C}^* and 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°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 ΔpK_{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 , γ_{CO_2} , $\gamma_{\text{HCO}_3^-}$, γ_{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 , γ_{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), γ_{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_{C} estimated from
492 the measured pH_{T} and A_{T} , and are, therefore, affected by the (unknown) extrapolation error for
493 the estimates of the non-carbonate A_{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 CO_3^{2-} , or both, at below-zero
498 temperatures. The total activity coefficient of CO_3^{2-} depends strongly on the extent of ion pair
499 formation in solution. Its ion pairs with Ca^{2+} and 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 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 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 C_{T} species
507 to below-zero temperatures may reconcile such differences as that seen here with respect to
508 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-SO₄-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 μatm 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

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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 (CO₂, O₂,
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 CO₂ 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 CO₂ 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 CO₂ on the CaCO₃ 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 CO₂
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 pCO₂ and related air-ice CO₂ 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 CO₂ 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-SO₄ 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 pCO₂ calculated from dissolved
706 inorganic carbon, alkalinity, and equations for K₁ and K₂: validation based on laboratory
707 measurements of CO₂ 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 SO₄-OH-HCO₃-CO₃-CO₂-H₂O 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⁻¹)
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 pK₁ + pK₂ 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 CO₂ 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, CaCO₃ mineral dynamics, and CO₂ 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 pCO₂
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 CO₂-
772 water solutions between 0 – 90 °C and an evaluation of the aqueous model for the system
773 CO₂-H₂O-CaCO₃. *Geochim. Cosmochim. Acta* **46**, 1011-1040.
- 774 Pytkowicz R. M. and Kester D. R. (1969) Harned's rule behaviour of NaCl–Na₂SO₄ 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 CO₂
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 CO₂. *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, pCO₂, total CO₂, alkalinity,
798 and CaCO₃ 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 CO₂: An estimate based on measurements of
802 sea-air pCO₂ 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.
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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)], 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 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 CO₂ 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 [ΔfCO_2 : panels (a) and (b)] and pH on the total proton scale [ΔpH_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 ΔfCO_2 and ΔpH_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).

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871

872 **Table 1.** Major ion composition of brines (in mmol kg⁻¹).

Salinity	[Na ⁺]	[Mg ²⁺]	[Ca ²⁺]	[K ⁺]	[Cl ⁻]+[Br ⁻]	[SO ₄ ²⁻]
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
^a 35	470±2	52.60±0.45	10.29±0.10	9.27±0.23	550±2	27.82±0.54
^b 35	469	52.82	10.28	10.21	547	28.24

873 ^amean concentration of brines normalized to salinity 35874 ^bcomposition of Reference Seawater of salinity 35 (Millero et al., 2008)

875

876 **Table 2.** Practical salinity (S_P), temperature (t , in °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 μatm), and pH_T (total proton scale; in mol kg^{-1})], and the stoichiometric equilibrium first and
 880 second dissociation constants of carbonic acid (in mol kg^{-1} , total proton scale) as negative
 881 common logarithms (pK_{1C}^* and pK_{2C}^*).

S_P	SRP	$\text{Si}(\text{OH})_4$	t	C_T	A_T	A_C	$f\text{CO}_2$	pH_T	pK_{1C}^*	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

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884 **Table 2** (continued)

S_P	SRP	Si(OH) ₄	t	C_T	A_T	A_C	fCO_2	pH _T	pK _{1C} *	pK _{2C} *
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
60.30	1.2	26.9	25.02	3627	4116	3987	1183	7.802	5.765	8.718
			-3.37	3641	4180	4012	302	8.340	6.101	9.259
			-2.40	3652	4180	4016	308	8.310	6.060	9.240
61.54	0.4	0.5	-2.37	3661	4180	4016	318	8.308	6.069	9.250
			20.29	3649	4180	4035	864	7.925	5.802	8.819
			-3.46	3707	4228	4060	328	8.331	6.115	9.279
84.62	1.0	18.0	-0.11	3705	4228	4062	370	8.276	6.056	9.219
			-4.97	4863	5811	5562	371	8.409	6.118	9.167
98.69	1.4	22.6	-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
			-6.00	5457	6795	6486	392	8.509	6.196	9.130
100.52	2.0	20.7	-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

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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	-5.534×10^{-5}	-3.68×10^{-4}	7.396×10^{-5}	-2.48396×10^{-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	^a -126.34048	^a -90.18333	-176.48	-323.52692
$1/T$	b_1	^a 6320.813	^a 5143.692	9914.37	14763.287
$\ln T$	b_2	^a 19.568224	^a 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 ^a from Millero et al. (2006)

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