1   **The stoichiometric dissociation constants of carbonic acid in seawater brines from 298 to**

2   **267 K**

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Abstract

The stoichiometric dissociation constants of carbonic acid (K^*_{1C} and K^*_{2C}) were determined by measurement of all four measurable parameters of the carbonate system (total alkalinity, total dissolved inorganic carbon, pH on the total proton scale, and CO_2 fugacity) in natural seawater and seawater-derived brines, with a major ion composition equivalent to that Reference Seawater, to practical salinity (S_P) 100 and from 25 °C to the freezing point of these solutions and –6 °C temperature minimum. These values, reported in the total proton scale, provide the first such determinations at below-zero temperatures and for $S_P > 50$. The temperature (T, in Kelvin) and S_P dependence of the current pK^*_{1C} and pK^*_{2C} (as negative common logarithms) within the salinity and temperature ranges of this study ($33 \leq S_P \leq 100$, -6 °C $\leq t \leq 25$ °C) is described by the following best-fit equations: $pK^*_{1C} = -176.48 + 6.14528\ S_P^{0.5} - 0.127714\ S_P + 7.396\times10^{-5}\ S_P^2 + (9914.37 - 622.886\ S_P^{0.5} + 29.714\ S_P)\ T^{-1} + (26.05129 - 0.666812\ S_P^{0.5})\ \ln T$ ($\sigma = 0.011$, $n = 62$), and $pK^*_{2C} = -323.52692 + 27.557655\ S_P^{0.5} + 0.154922\ S_P - 2.48396\times10^{-4}\ S_P^2 + (14763.287 - 1014.819\ S_P^{0.5} - 14.35223\ S_P)\ T^{-1} + (50.385807 - 4.4630415\ S_P^{0.5})\ \ln T$ ($\sigma = 0.020$, $n = 62$). These functions are suitable for application to investigations of the carbonate system of internal sea ice brines with a conservative major ion composition relative to that of Reference Seawater and within the temperature and salinity ranges of this study.

1. Introduction

The investigation of the carbonate system in aquatic environments is essential in the understanding and monitoring of the carbon cycle in the hydrosphere. Such investigations have intensified in the marine environment because of the crucial role the ocean plays in the absorption and storage of the anthropogenic CO_2 emitted to the atmosphere during the Industrial era (Takahashi et al., 1997; Sabine et al., 2004). Through this process, the ocean is a major repository of anthropogenic CO_2 (Takahashi, 2004), with consequent chemical and ecosystem functioning effects from the acidification of surface oceanic waters (decreased oceanic pH relative to pre-industrial era values) (Caldeira and Wickett, 2003; Feely et al., 2004; Takahashi et al., 2014; Gattuso et al., 2015). The acidification effect on the oceanic carbonate system by atmospheric CO_2 absorption (Takahashi, 2004; Sabine et al., 2004) has been observed in surface coastal and pelagic waters (Takahashi et al., 2014), including large areas of the Arctic Ocean (Feely et al., 2008; Yamamoto-Kawai et al., 2009; Cai et al., 2010; Semiletov et al., 2016).

One of the challenges that remain in the high latitude (polar) oceans of the Earth's cryosphere is reliable determination of the carbonate system in the brine-ice system in the extensive seasonal sea ice cover of these environments (Brown et al., 2014; Miller et al., 2015; Papadimitriou et al., 2016). Early investigations in the composition and activity of the ice-associated (sympagic) microbial community in sea ice have uncovered the role of this multi-phase system on the surface of high latitude oceans as a habitat akin to other large-scale biomes, such as the desserts and tundra (Fritsen et al., 1994; Gleitz et al., 1995; Arrigo et al., 1997; Thomas and Dieckmann, 2002; Kennedy et al., 2002). Subsequent investigations have revealed a complex internal carbon cycle driven not only by the sympagic autotrophic and heterotrophic microbial communities, but also by two other major chemical reactions in the surface ocean, CO_2 gas exchange and hydrated $CaCO_3$ authigenesis (Papadimitriou et al., 2004; Delille et al., 2007; Dieckmann et al., 2008; Munro et al., 2010; Papadimitriou et al., 2012; Fischer et al., 2013). The internal carbon cycling in sea ice is complemented by measurable CO_2 fluxes to and from the atmosphere as a function of ice temperature (Delille et al., 2014) and to the underlying ocean by gravity drainage of the internal brines (Rysgaard et al., 2007; Rysgaard et al., 2011). These past investigations have culminated in a keen interest in the carbonate system of sea ice brines (Brown et al., 2014; Miller et al., 2015), the residual internal solution where all biogeochemical reactions occur either in 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 °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 °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 (fCO_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 °C, S_P > 50) (Brown et al., 2014). Direct in-situ measurements of fCO_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 $$K_{1C}^* = [H^+]_T \frac{2C_T - A_C - 2[CO_2^*]}{[CO_2^*]}, \qquad (1)$$

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

139

140 In the above equations, A_C = 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, $[B_T] = 0.000432578$ mol $kg_{solution}^{-1}$ (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 ($t \geq 0$ °C, $S_P < 50$; Dickson,

159 1990; Millero, 1995) when the experimental conditions extended beyond them ($t \leq 0$ °C, $S_P >$

160 50). Locally sourced seawater (Menai Strait; 53.1806N 4.2333W), UV-sterilized and filtered

161 through a 0.2 μm 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 MΩ·cm) Milli-Q™ water. The brines were filtered

164   through pre-combusted (500 °C, 3 hrs) GF/F filters (0.7 μm, 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 (fCO$_2$ and pH$_T$) at the experimental temperature

188   and the sample collection for the remainder of analyses. First, the fCO$_2$ 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, $Si(OH)_4$] were removed and the remaining

195   sample was used for replicate A_T determinations.

196

197   **2.1 fCO$_2$ measurement**

198   The fCO$_2$ was determined from the CO$_2$ mole fraction (x_{CO_2}) measured on a LICOR 840A

199   CO$_2$/H$_2$O analyzer of the dry gas generated in a closed loop by exchange with the sample via a

200   0.5×1 MicroModule^{TM} 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 fCO$_2$ 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_{CO_2} < 1000 ppm and within 3 ppm for x_{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   ≤ 5%, BOC, boc.com). The calibrations were conducted between two consecutive experiments.

213   The sample fCO$_2$ 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 fCO$_2$ 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   fCO$_2$ 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_2 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 fCO$_2$ 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 fCO$_2$ differed by (mean ± 1σ) –9 ±

231   10 µatm ($n = 12$). This estimated uncertainty is equivalent to –2 ± 3% relative to the computed

232   fCO$_2$ 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 fCO$_2$ 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   fCO$_2$. The measured fCO$_2$ differed by –85 µatm at CRM fCO$_2$ = 1062 µatm at 18.06 °C for batch

241   #125, equivalent to –8% relative to the computed fCO$_2$. In contrast, in the assessment of Lueker

242   et al. (2000), the measured fCO$_2$ was systematically higher by +3.35 ± 1.22% than the computed

243   fCO$_2$ at fCO$_2$ > 500 µatm. In comparison, the uncertainty based on the single high-fCO$_2$ CRM

244   measurement (batch #125) available during this study suggests an increased negative bias at high

245   fCO$_2$ (~ 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 fCO_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 fCO_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 fCO_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 fCO_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 ± 1σ) –0.013 ± 0.011 pH unit ($n = 21$). For the high-fCO_2 CRM batch #125

271   (CRM 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 μmol kg^{-1} for both A_T and C_T; Bockmon and Dickson,

274   2015) and in the pK_{1C}^* and pK_{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 pH < 3.5 (Gleitz et al., 1995; Papadimitriou et al., 2013) with a

285   Metrohm Titrando 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_2 (400 ppm CO_2)

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 µmol 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 ± 1.7 µmol 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 ± 2.8 µmol 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 ± 39 µmol kg^{-1} (n = 10),

303   while the local seawater had a two-year (2014-2015) average $A_{T,35}$ = 2398 ± 22 µmol 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_2 generated and extracted in vacuo in a glass manifold following reaction

307   of a weighed sample aliquot with H_3PO_4 and cryogenic CO_2 gas distillation in successive cold (–

308   95 ºC) 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 µmol 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 ± 1σ) +0.7 ± 8.8 µmol kg^{-1} (n = 111).

313

314   **2.4 Other measurements**

315   The salinity of the experimental solutions was measured at laboratory temperature (~20 ℃)

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 Ca^{2+} and Mg^{2+} 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} $AgNO_3$

324   standardized against NaCl purified by re-crystallization (Dickson, 1990; Millero et al., 1993), and

325   (iv) for SO_4^{2-}, precipitation as $BaSO_4$ in EDTA followed by titration with $MgCl_2$ (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 $\sigma_{K_{iC}^*}^2 = \sum[(dK_{iC}^*/dX)\,\sigma_X]^2$

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 $fCO_2 < 1000$ µatm, 90 µatm for $fCO_2 > 1000$ µatm, 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 $fCO_2 > 250$ µatm to 0.050 pK unit at fCO_2

342   < 250 µatm. 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    $pK_{iC}^{*} = pK_{iC}^{o} + A_i + B_i/T + C_i \ln T$ (i = 1, 2),   (3)

357

358   In the above equation, T = temperature (in Kelvin), $A_i = a_o S_P^{0.5} + a_1 S_P + a_2 S_P^{2}$, $B_i = a_3 S_P^{0.5} + a_4 S_P$,

359    $C_i = a_5 S_P^{0.5}$, and $pK_{iC}^{o} = b_o + b_1/T + b_2 \ln T$ = thermodynamic equilibrium dissociation constant,

360   with a_o, 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_o, b_1, and b_3 are from Millero et al. (2006). The standard

362   error of the fit was the same as in the original study ($\sigma_{pK_{1C}^{*}} = 0.006$ and $\sigma_{pK_{2C}^{*}} = 0.011$).

363   The current pK_{1C}^{*} and pK_{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 $\Delta pK_{1C}^{*} = -0.009 \pm 0.016$ and

367    $\Delta pK_{2C}^{*} = +0.002 \pm 0.018$ relative to the Mehrbach et al. (1973) data set, and $\Delta pK_{1C}^{*} = -0.014 \pm$

368   0.016 and $\Delta pK_{2C}^{*} = -0.003 \pm 0.022$ 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     $$K_{1C}^* = K_{1C}^o \, \frac{\gamma_{CO_2} \alpha_{H_2O}}{\gamma_{H^+} \gamma_{HCO_3^-}} \Theta, \qquad\qquad (4)$$

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

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, CaCO₃-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 pCO₂ 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, $\gamma_{H^+} = \gamma_{H^+,free} \; m_{H^+,free} \, / \, (m_{H^+,free} + m_{HSO_4^-})$ (Millero, 1995), with m

401 = molality (in mol $kg_{H_2O}^{-1}$) 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 α_{H_2O}, 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 $\gamma_{HCO_3^-}$ in

408 eqs. (3) and (4). The code takes into account explicitly ion pair formation for CO_3^{2-} in the form of

409 $CaCO_3^{\circ}$ and $MgCO_3^{\circ}$ (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-} ($\gamma_{CO_3^{2-}}$) 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 fCO$_2$ 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 fCO_2 and A_T, yielding C_T and its speciation. In this

434 case, the fCO_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°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 °C to near their freezing point

461 (from –2.1 °C at $S_P = 40$ to –6.0 °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}^o, γ_{CO_2}, $\gamma_{HCO_3^-}$, γ_{H^+} and α_{H_2O}) 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}^o, γ_{CO_2}, and $\gamma_{HCO_3^-}$ 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 α_{H_2O} from the

487 Pitzer parameterization of the osmotic coefficient. This was not the case, however, for pK_{2C}^*,

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 pK_{2C}^* 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 pK_{2C}^* determinations and the FREZCHEM-derived

496 values. Based on eqs. (4) and (5), the disagreement in pK_{2C}^* with the thermodynamic code

497 suggests uncertainty in K_{2C}^o 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 pK_{1C}^* and pK_{2C}^* 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 $\sigma_{pK_{1C}^*} = 0.011$ and $\sigma_{pK_{2C}^*} = 0.020$, 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 °C $\leq t \leq$ 25 °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$_4$-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 °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 °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 µmol 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 °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 µmol 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: $–0.2 \pm 3.8$ µmol 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 $–6000$ µatm fCO_2 in the conservative brine C_T scenario (Figs. 5a-c), as

557   well as up to $–1300$ µmol CO_3^{2-} 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 $f\mathrm{CO_2}$ 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 $f\mathrm{CO_2}$ and pH in sea ice from direct measurements
576   of $\mathrm{A_T}$ and $\mathrm{C_T}$ 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

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

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818

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_2 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   [a]mean concentration of brines normalized to salinity 35

874   [b]composition 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 [$Si(OH)_4$]
877 (in µmol kg^{-1}), the measured parameters of the carbonate system in seawater and seawater-
878 derived brines [C_T (in µmol kg^{-1}), A_T and derived carbonate alkalinity (A_C) (in µmol kg^{-1}), fCO_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	$Si(OH)_4$	t	C_T	A_T	A_C	fCO_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
			25.05	2977	3446	3323	807	7.895	5.807	8.743
60.28	0.4	15.3	−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

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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.

| | | data set | | | |
| | | Millero et al. (2006) | | this study | |
Parameter	Coefficient	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 $S_P = 35$, $T = 273.15$ K		6.1184	9.3827	6.1267	9.3940

890 [a] from Millero et al. (2006)

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