

Over-determination of the carbonate system in natural sea-ice brine and assessment of carbonic acid dissociation constants under low temperature, high salinity conditions

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ABSTRACT

By over-determining the carbonate system in natural sea-ice brine samples, we have confirmed that stoichiometric equilibrium constants for the dissociation of carbonic acid in seawater (K_1^* , K_2^*) derived for general oceanic conditions may not be readily extrapolated to sea-ice brine systems. Dissolved inorganic carbon, total alkalinity, pH, and $p\text{CO}_2$ measurements in sea-ice brine have allowed us to rigorously examine the validity of K_1^* and K_2^* at salinities as high as 82 and in-situ temperatures as low as $-4.8\text{ }^\circ\text{C}$. The use of seawater-derived constants yields average offsets between calculated and measured values ranging from 10% to 43% for brine salinities of 38–82. Future high-accuracy determination of sea-ice brine carbonate system components will require the specific determination of carbonate system equilibrium constants under appropriate temperature and salinity conditions. Furthermore, the community is in need of a means to evaluate the accuracy of carbonate system measurements in natural, high-salinity brine samples using the presently available analytical methods.

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1. Introduction

The polar oceans play a pivotal role in the global carbon cycle as sites of significant deep-water formation and atmospheric CO_2 sequestration. Recent reduced summer sea-ice extent and polar warming have stimulated increased effort to understand the role of sea ice in the transfer of carbon between the atmosphere and the ocean (e.g., Barber et al., 2012; Loose et al., 2011; Parmentier et al., 2013; Rysgaard et al., 2011). High-salinity brine contained within the sea-ice matrix is of particular interest in the polar carbon cycle, as the brine acts as both a seasonal repository of inorganic carbon (e.g., Delille et al., 2007; Geilfus et al., 2012; Miller et al., 2011a,b; Papadimitriou et al., 2012) and as an important ecological province conducive to high primary productivity (e.g., Arrigo et al., 2010; Boetius et al., 2013; Kirst and Wiench, 1995; Niemi et al., 2011; Welch and Bergmann, 1989). Furthermore, export of high-salinity brine into the underlying surface waters can transport dissolved inorganic carbon from sea ice into, and below, the mixed

layer (e.g., Miller et al., 2011b; Omar et al., 2005; Rysgaard et al., 2011, 2009, 2007), potentially contributing to the sequestration of carbon on timescales longer than the seasonal cycle of sea-ice formation-growth-melt.

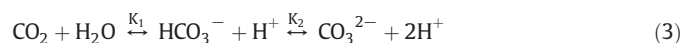
Understanding the role of sea ice in the polar ocean carbon cycle rests on an accurate characterization of the thermodynamic equilibria that govern the inorganic carbon system in sea ice. In ice-free, open ocean systems, the thermodynamic equations governing inorganic carbon speciation have been studied extensively (see Millero, 1995 and Millero et al., 2006, 2002, for comprehensive reviews), resulting in robust equations to calculate the first and second dissociation constants of carbonic acid (K_1 and K_2 , respectively) over the relatively narrow range of oceanographic temperature and salinity conditions. Empirically-derived stoichiometric equilibrium constants (K_1^* , K_2^*) describe the system as a function of oceanic salinity, temperature, and pressure (as in Eqs. (1) and (2)), where brackets refer to total stoichiometric concentrations in mol kg^{-1} of seawater). These constants represent the equilibrium concentrations of dissolved CO_2 ($\text{CO}_2 = \text{CO}_2(\text{aq}) + \text{H}_2\text{CO}_3$), bicarbonate (HCO_3^-), and carbonate (CO_3^{2-}), according to their equilibrium speciation in the ocean (Eq. (3)).

$$K_1^* = \frac{[\text{HCO}_3^-][\text{H}^+]}{[\text{CO}_2]} \quad (1)$$

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$$K_2^* = \frac{[\text{CO}_3^{2-}][\text{H}^+]}{[\text{HCO}_3^-]} \quad (2)$$



In contrast to the large body of carbonate system data in seawater, relatively few published studies have successfully collected and analyzed brine carbonate system samples from the field (Delille et al., 2007; Fransson et al., 2011; Geilfus et al., 2012; Gleitz et al., 1995; Miller et al., 2011a; Nomura et al., 2013b, 2010; Papadimitriou et al., 2012, 2007). Standard operating procedures for carbonate system measurements developed for open ocean and estuarine conditions (such as Dickson et al., 2007) are often impractical in the polar regions, as freezing conditions and difficult access to sampling sites complicate routine sampling and analyses (e.g., Loose et al., 2011; Miller et al., 2011a,b). Moreover, inconsistency between pH measurement methods (e.g., spectrophotometric vs. potentiometric) and scales (e.g., pH_F , Miller et al., 2011a; pH_T , Delille et al., 2007; pH_{SWS} , Gleitz et al., 1995) are particularly problematic in sea-ice brine. As a result of these limitations, only a handful of studies have presented field measurements of two or more components of the sea-ice brine carbonate system (Table 1).

Beyond the difficulty associated with actual measurements of carbonate system parameters in sea-ice brine, there is a fundamental lack of information on the thermodynamic constants governing the equilibrium among different carbonate species in these environments. Rigorous determination of K_1^* and K_2^* in natural and artificial seawater has only been carried out at temperatures above -1°C and salinities less than 50 (Table 2), conditions at the warm, fresh extreme of sea-ice brine systems (Petrich and Eicken, 2010). Straightforward extrapolation to high-salinity, low-temperature conditions found in natural sea-ice brine is tenuous given the non-linear nature of the governing equations. Even so, the difficulty in accurately measuring brine carbonate system components in the field (particularly pH and pCO_2) has led investigators of sea-ice environments to generously apply these constants outside of their experimental ranges (e.g., see discussions in Delille et al., 2007, and Miller et al., 2011a). Furthermore, validation of these extrapolations has been elusive, as few studies have reported independent measurement of a third component of the carbonate

system in sea-ice brine (Delille et al., 2007; Geilfus et al., 2012; Miller et al., 2011a; Table 1). With appropriate equilibrium constants, the full carbonate system can be resolved from measurements of any two parameters. As a result, the measurement of a third parameter provides an 'over-determination' that can be used to directly validate computed values against measurements. Such an over-determination is critical to evaluate the robustness of extrapolated carbonate system equilibrium constants to sea-ice brine systems.

Our goal with this study was to over-determine the carbonate system in natural sea-ice brine samples and address the question of how applicable seawater-derived carbonic acid dissociation constants are to sea-ice brine. We collected brine samples from sackholes in spring sea ice during two field campaigns in the Canadian Arctic Archipelago, during the spring seasons of 2010 (Resolute Passage) and 2011 (Allan Bay), and analyzed the samples for DIC, TA, pCO_2 , and pH. With these results, we determined the utility of seawater carbonic acid dissociation constant parameterizations in reproducing the measured values using CO2SYS XLS v. 2.1 (Pierrot et al., 2006). Our findings indicate that agreement between measured and calculated parameters can be poor, and that a more rigorous, laboratory-based study to define the carbonic acid dissociation constants (K_1^* , K_2^*) at low-temperature and high-salinity conditions is warranted.

2. Methods

Sackhole brine samples were collected over two spring seasons as part of the Arctic-ICE (Arctic - Ice Covered Ecosystem) program, based out of the Polar Continental Shelf Program (PCSP) in Resolute Bay, Nunavut, Canada. The 2010 program was carried out from May 8th to June 19th in land-fast, first-year sea ice in Resolute Passage (74.708 N, 95.250 W), whereas the 2011 program was conducted from April 16th to July 9th, under similar land-fast sea-ice conditions in Allan Bay (74.716 N, 95.15 W). In both years, brine samples were collected from smooth, land-fast, first-year sea ice with a relatively uniform thickness of 140 ± 2 cm and 144 ± 7 cm in 2010 and 2011, respectively. Sampling was conducted in the early spring season, when warm air temperatures ($-7.6 \pm 3.1^\circ\text{C}$ and $-2.5 \pm 2.5^\circ\text{C}$, for the 2010 and 2011 sampling dates, respectively, listed in Table 3; Environment Canada, 2013) had begun to melt the surface snow pack (16 ± 11 cm and 16 ± 4 cm over the 2010 and 2011 sampling dates, respectively).

Table 1
Field studies measuring two or more carbon system parameters in sea-ice brine.

| Sea-ice brine study | S | | DIC ($\mu\text{mol kg}^{-1}$) | | RU (\pm) | TA ($\mu\text{mol kg}^{-1}$) | | | pH_F^{pot} | | | pCO_2 (μatm) | | |
|-----------------------------|------|-------|---------------------------------|---------|--------------|--------------------------------|---------|--------------|-----------------------------|--------------------|--------------|------------------------------------|-------------------|--------------|
| | Min | Max | Min | Max | | Min | Max | RU (\pm) | Min | Max | RU (\pm) | Min | Max | RU (\pm) |
| Gleitz et al. (1995) | 21.0 | 107.8 | | | | 1728 | 7835 | n.r. | 7.830 ^a | 9.932 ^a | n.r. | | | |
| Papadimitriou et al. (2007) | 40 | 63 | 2091 | 3551 | $\pm 2\%$ | 2690 | 4620 | $\pm 2\%$ | n.r. | n.r. | ± 0.04 | | | |
| Delille et al. (2007) | ~20 | 90 | | | | n.v. | n.v. | ± 4 | 8.405 ^b | 9.457 ^b | ± 0.01 | ~30 ^c | ~420 ^c | n.r. |
| Nomura et al. (2010) | 23.3 | 33.2 | n.r. | n.r. | $\pm 0.1\%$ | n.r. | n.r. | $\pm 0.2\%$ | | | | | | |
| | | | | | | | | | $\text{pH}_F^{\text{spec}}$ | | | | | |
| Miller et al. (2011a) | 68 | 163 | 4000 | 9600 | ± 3 | n.r. | n.r. | ± 3 | 8.281 | 8.496 | ± 0.002 | | | |
| Fransson et al. (2011) | 33 | 43.3 | 1451 | 2191 | n.r. | 2201 | 2932 | n.r. | n.r. | n.r. | n.r. | | | |
| Geilfus et al. (2012) | 0 | 138 | 165 | 8254 | ± 2 | 173 | 8191 | ± 3 | | | | 0 | 1839 | n.r. |
| Papadimitriou et al. (2012) | 58 | 134 | 2839 | 8405 | $\pm 2\%$ | 3912 | 9054 | $\pm 2\%$ | | | | | | |
| This Study | 38 | 82 | 2491.38 | 4801.30 | ± 2.54 | 2625.57 | 5238.96 | ± 4.36 | 8.216 | 8.389 | ± 0.0064 | 278 | 656 | ± 15 |

RU refers to reported uncertainty.

pH_F^{pot} indicates potentiometric measurement with a glass probe, corrected to in-situ T & S.

$\text{pH}_F^{\text{spec}}$ indicates spectrophotometric pH measurements, corrected to in-situ T & S.

n.v. refers to only salinity normalized values reported.

n.r. refers to "not reported" values, although methods for collection and determination are listed.

^a Gleitz et al. (1995) pH_{SWS} data were converted to the Free Ion scale for this comparison following Zeebe and Wolf-Gladrow (2001).

^b Delille et al. (2007) pH_T data were converted to the Free Ion scale for this comparison following Zeebe and Wolfe-Gladrow (2001).

^c Only low pCO_2 ($< 150 \mu\text{atm}$) brine samples were independently measured using the modified equilibrator method of Delille (2006) (Fig. 2 in Delille et al., 2007), meaning the high end of this range includes pCO_2 values calculated from pH_T and TA measurements.

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