



Gypsum and hydrohalite dynamics in sea ice brines

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Received 22 March 2017; accepted in revised form 15 June 2017; Available online 21 June 2017

Abstract

Mineral authigenesis from their dissolved sea salt matrix is an emergent feature of sea ice brines, fuelled by dramatic equilibrium solubility changes in the large sub-zero temperature range of this cryospheric system on the surface of high latitude oceans. The multi-electrolyte composition of seawater results in the potential for several minerals to precipitate in sea ice, each affecting the in-situ geochemical properties of the sea ice brine system, the habitat of sympagic biota. The solubility of two of these minerals, gypsum ($\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$) and hydrohalite ($\text{NaCl} \cdot 2\text{H}_2\text{O}$), was investigated in high ionic strength multi-electrolyte solutions at below-zero temperatures to examine their dissolution–precipitation dynamics in the sea ice brine system. The gypsum dynamics in sea ice were found to be highly dependent on the solubilities of mirabilite and hydrohalite between 0.2 and -25.0 °C. The hydrohalite solubility between -14.3 and -25.0 °C exhibits a sharp change between undersaturated and supersaturated conditions, and, thus, distinct temperature fields of precipitation and dissolution in sea ice, with saturation occurring at -22.9 °C. The sharp changes in hydrohalite solubility at temperatures ≤ -22.9 °C result from the formation of an ice–hydrohalite aggregate, which alters the structural properties of brine inclusions in cold sea ice. Favourable conditions for gypsum precipitation in sea ice were determined to occur in the region of hydrohalite precipitation below -22.9 °C and in conditions of metastable mirabilite supersaturation above -22.9 °C (investigated at -7.1 and -8.2 °C here) but gypsum is unlikely to persist once mirabilite forms at these warmer (> -22.9 °C) temperatures. The dynamics of hydrohalite in sea ice brines based on its experimental solubility were consistent with that derived from thermodynamic modelling (FREZCHEM code) but the gypsum dynamics derived from the code were inconsistent with that indicated by its experimental solubility in this system. Incorporation of hydrohalite solubility into a 1D thermodynamic model of the growth of first-year Arctic sea ice showed its precipitation to initiate once the incoming shortwave radiation dropped to 0 W m^{-2} , and that it can reach concentrations of 9.9 g kg^{-1} within the upper and coldest layers of the ice pack. This suggests a limited effect of hydrohalite on the albedo of sea ice. The insights provided by the solubility measurements into the behaviour of gypsum and hydrohalite in the ice–brine system cannot be gleaned from field investigations at present.

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Keywords: Gypsum; Hydrohalite; Solubility; Sea ice; FREZCHEM

1. INTRODUCTION

When sea ice forms in high latitude environments, seawater solutes are expelled from the ice crystal matrix and a concentrated brine forms which becomes trapped as inclusions in the sea ice microstructure (Petrich and Eicken, 2010). At ice–brine equilibrium, the brine inclusions have

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a temperature-dependent size and composition with respect to major seawater ions, the latter further governed by the solubility of their related salts (Marion, 2001). The Na–K–Mg–Ca–SO₄–Cl–H₂O system contains 99.4% of the total dissolved ions in Standard Seawater by mass (Millero et al., 2008), and, as sea ice temperature changes, solid–solution reactions of the brine with the predominantly hydrated salts of these major ions dominate the geochemistry of the system (Gitterman, 1937; Nelson and Thompson, 1954). The combined effect of changing temperature, solute concentration, and mineral (sea salt) solubility in the sea ice brine is that, as sea ice cools, the brines become sequentially supersaturated with respect to a suite of minerals. Each mineral in the sequence has a distinct solubility–temperature relationship and, hence, a distinct equilibrium onset temperature of precipitation from the brines between the freezing point of seawater and its eutectic (Gitterman, 1937; Nelson and Thompson, 1954; Marion et al., 1999). These authigenic minerals become part of the heterogeneous sea ice matrix (Light et al., 2003; Dieckmann et al., 2008; Geilfus et al., 2013), contributing to its optical, mechanical, thermal, and structural properties (Assur, 1960; Light et al., 2004; Carns et al., 2015). Precipitation of sea ice minerals also modifies the physico-chemical properties of the brine inclusions, including salinity (Butler et al., 2016a) and the inter-ionic ratios of dissolved constituents, thus contributing to the physiological challenges for ice-associated micro-organisms (Thomas and Dieckmann, 2002). Further, mineral precipitation features in the salt mass balance of saline cryogenic systems in past and present polar environments on Earth (Assur, 1960; Light et al., 2009) and other water-bearing planetary bodies (Marion and Kargel, 2008).

In absence of metastable supersaturated conditions (see Section 2.3), the suite of minerals that can precipitate within sea ice includes ikaite (CaCO₃ · 6H₂O), mirabilite (Na₂SO₄ · 10H₂O), hydrohalite (NaCl · 2H₂O), gypsum (CaSO₄ · 2H₂O), sylvite (KCl), MgCl₂ · 12H₂O, and antarcticite (CaCl₂ · 6H₂O) at progressively decreasing temperatures. Depending on the exact sequence of mineral precipitates, the eutectic temperature of sea ice can be –36 °C (in association with MgCl₂ · 12H₂O; Gitterman, 1937) or –54 °C (in association with antarcticite; Nelson and Thompson, 1954).

Ikaite has been identified in natural and experimental sea ice (Dieckmann et al., 2008; Fischer et al., 2013; Geilfus et al., 2013). The solubility of ikaite in sea ice brines has been investigated to –7.5 °C, and this CaCO₃ polymorph can precipitate below –2 °C depending on the brine pCO₂ (Papadimitriou et al., 2013). Mirabilite solubility in sea ice brines has been investigated to –20.6 °C (Butler et al., 2016b). Sea ice brines become supersaturated with respect to mirabilite at temperatures ≤ –6.4 °C, and its consequent precipitation causes this mineral to become the main sink of SO₄^{2–} in sea ice brines (Marion et al., 1999; Butler et al., 2016b). Gypsum has long been predicted to precipitate from frozen seawater but information on its stability in sea ice brines is less precise than for ikaite and mirabilite. From the major ion composition of residual brine during the freezing of synthetic seawater to its eutectic, Gitterman (1937) inferred that gypsum precipitation

should occur at temperatures below –15 °C. In these experiments, all potential authigenic minerals were allowed to interact with the residual brine to solid–solution equilibrium. More recently, Marion et al. (1999) combined thermodynamic model predictions (FREZCHEM) with experimental analysis of seawater brines seeded with gypsum at –15, –20 and –26 °C, and proposed that gypsum in brines becomes supersaturated at –22.2 °C but its precipitation is enhanced below –22.9 °C as a result of brine e–mirabilite–hydrohalite interaction. Specifically, initial removal of Na⁺ and SO₄^{2–} from the brine via mirabilite precipitation between –6.4 and –22.9 °C is followed by additional removal of Na⁺ from the brine through hydrohalite precipitation upon further cooling. The large Na⁺ change via hydrohalite precipitation results in brine undersaturation with respect to mirabilite, which dissolves when in contact with the brine. The liberated SO₄^{2–} from mirabilite dissolution enhances the degree of gypsum supersaturation of the brine, resulting in enhanced gypsum precipitation (Gitterman, 1937; Marion et al., 1999). In contrast, the effects of gypsum precipitation on brine composition during seawater freezing were not observed by Nelson and Thompson (1954) due to their experimental protocol, in which the minerals were removed from the natural seawater-derived brine as they formed. The sea ice brine systems represented by the experimental protocols of Gitterman (1937) and Nelson and Thompson (1954) are considered to be representative of the equilibrium crystallisation (hereafter full crystallisation) pathway and the fractional crystallisation pathway, respectively (Marion et al., 1999; Marion and Kargel, 2008; Butler and Kennedy, 2015). In an experimental approach representative of the full crystallisation pathway, the brine–mirabilite–hydrohalite interaction was observed during cooling and warming of frozen seawater brines but gypsum was not identified (Butler and Kennedy, 2015).

Gypsum has recently been identified in experimental and natural sea ice at temperatures between –2 and –10 °C, and, in view of this, has been proposed as a potential marine deposit in polar seas (Geilfus et al., 2013). This suggests more complex gypsum dynamics in the sea ice system than construed from the available information about the sub-zero temperature field of gypsum stability in seawater brines outlined above. This issue can be elucidated from a more detailed knowledge of the equilibrium gypsum solubility in sea ice conditions.

Here, we investigated the characteristics of the gypsum–brine reaction in sea ice via measurements of the concentration-based (stoichiometric) solubility of this mineral in relevant brines at below-zero temperatures. We sought to identify the conditions that can lead to internal gypsum authigenesis and stability in the large below-zero temperature and salinity ranges of sea ice brines. Knowledge of the hydrohalite dynamics in the sea ice system is essential for this purpose given the common ion effect on mineral stability of the brine–gypsum–mirabilite–hydrohalite interaction outlined earlier and the available information about mirabilite solubility in the sea ice system in our previous work (Butler et al., 2016b). Thermodynamic modelling (Marion et al., 1999) and experimental

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