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Geochimica et Cosmochimica Acta

DOI:

[10.1016/j.gca.2017.06.020](https://doi.org/10.1016/j.gca.2017.06.020)

Published: 01/09/2017

Peer reviewed version

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

Dyfyniad o'r fersiwn a gyhoeddwyd / Citation for published version (APA):

Butler, B., Papadimitriou, S., Day, S. J., & Kennedy, H. (2017). Gypsum and hydrohalite dynamics in sea ice brines. *Geochimica et Cosmochimica Acta*, 17-34.
<https://doi.org/10.1016/j.gca.2017.06.020>

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Gypsum and hydrohalite dynamics in sea ice brines

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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 $-22.9\text{ }^{\circ}\text{C}$ (investigated at -7.1 and $-8.2\text{ }^{\circ}\text{C}$ here) but gypsum is unlikely to persist once mirabilite forms at these warmer ($> -22.9\text{ }^{\circ}\text{C}$) 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.

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 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

15 sequentially supersaturated with respect to a suite of minerals. Each min-
 16 eral in the sequence has a distinct solubility–temperature relationship and,
 17 hence, a distinct equilibrium onset temperature of precipitation from the
 18 brines between the freezing point of seawater and its eutectic (Gitterman,
 19 1937; Nelson and Thompson, 1954; Marion et al., 1999). These authigenic
 20 minerals become part of the heterogeneous sea ice matrix (Light et al., 2003;
 21 Dieckmann et al., 2008; Geilfus et al., 2013), contributing to its optical, me-
 22 chanical, thermal, and structural properties (Assur, 1960; Light et al., 2004;
 23 Carns et al., 2015). Precipitation of sea ice minerals also modifies the physico-
 24 chemical properties of the brine inclusions, including salinity (Butler et al.,
 25 2016a) and the inter-ionic ratios of dissolved constituents, thus contributing
 26 to the physiological challenges for ice-associated micro-organisms (Thomas
 27 and Dieckmann, 2002). Further, mineral precipitation features in the salt
 28 mass balance of saline cryogenic systems in past and present polar environ-
 29 ments on Earth (Assur, 1960; Light et al., 2009) and other water-bearing
 30 planetary bodies (Marion and Kargel, 2008).

31 In absence of metastable supersaturated conditions (see section 2.3), the
 32 suite of minerals that can precipitate within sea ice includes ikaite ($\text{CaCO}_3 \cdot$
 33 $6\text{H}_2\text{O}$), mirabilite ($\text{Na}_2\text{SO}_4 \cdot 10\text{H}_2\text{O}$), hydrohalite ($\text{NaCl} \cdot 2\text{H}_2\text{O}$), gypsum ($\text{CaSO}_4 \cdot$
 34 $2\text{H}_2\text{O}$), sylvite (KCl), $\text{MgCl}_2 \cdot 12\text{H}_2\text{O}$, and antarcticite ($\text{CaCl}_2 \cdot 6\text{H}_2\text{O}$) at
 35 progressively decreasing temperatures. Depending on the exact sequence of
 36 mineral precipitates, the eutectic temperature of sea ice can be -36°C (in
 37 association with $\text{MgCl}_2 \cdot 12\text{H}_2\text{O}$; Gitterman, 1937) or -54°C (in association
 38 with antarcticite; Nelson and Thompson, 1954).

39 Ikaite has been identified in natural and experimental sea ice (Dieckmann
 40 et al., 2008; Geilfus et al., 2013; Fischer et al., 2013). The solubility of ikaite
 41 in sea ice brines has been investigated to -7.5°C , and this CaCO_3 polymorph
 42 can precipitate below -2°C depending on the brine $p\text{CO}_2$ (Papadimitriou
 43 et al., 2013). Mirabilite solubility in sea ice brines has been investigated
 44 to -20.6°C (Butler et al., 2016b). Sea ice brines become supersaturated

45 with respect to mirabilite at temperatures ≤ -6.4 °C, and its consequent
 46 precipitation causes this mineral to become the main sink of SO_4^{2-} in sea ice
 47 brines (Marion et al., 1999; Butler et al., 2016b). Gypsum has long been
 48 predicted to precipitate from frozen seawater but information on its stabil-
 49 ity in sea ice brines is less precise than for ikaite and mirabilite. From the
 50 major ion composition of residual brine during the freezing of synthetic sea-
 51 water to its eutectic, Gitterman (1937) inferred that gypsum precipitation
 52 should occur at temperatures below -15 °C. In these experiments, all po-
 53 tential authigenic minerals were allowed to interact with the residual brine
 54 to solid-solution equilibrium. More recently, Marion et al. (1999) combined
 55 thermodynamic model predictions (FREZCHEM) with experimental analy-
 56 sis of seawater brines seeded with gypsum at -15 , -20 and -26 °C, and
 57 proposed that gypsum in brines becomes supersaturated at -22.2 °C but
 58 its precipitation is enhanced below -22.9 °C as a result of brine-mirabilite-
 59 hydrohalite interaction. Specifically, initial removal of Na^+ and SO_4^{2-} from
 60 the brine via mirabilite precipitation between -6.4 and -22.9 °C is followed
 61 by additional removal of Na^+ from the brine through hydrohalite precipita-
 62 tion upon further cooling. The large Na^+ change via hydrohalite precipitation
 63 results in brine undersaturation with respect to mirabilite, which dissolves
 64 when in contact with the brine. The liberated SO_4^{2-} from mirabilite disso-
 65 lution enhances the degree of gypsum supersaturation of the brine, resulting
 66 in enhanced gypsum precipitation (Gitterman, 1937; Marion et al., 1999).
 67 In contrast, the effects of gypsum precipitation on brine composition during
 68 seawater freezing were not observed by Nelson and Thompson (1954) due to
 69 their experimental protocol, in which the minerals were removed from the
 70 natural seawater-derived brine as they formed. The sea ice brine systems rep-
 71 resented by the experimental protocols of Gitterman (1937) and Nelson and
 72 Thompson (1954) are considered to be representative of the equilibrium crys-
 73 tallisation (hereafter full crystallisation) pathway and the fractional crystalli-
 74 sation pathway, respectively (Marion et al., 1999; Marion and Kargel, 2008;

75 Butler and Kennedy, 2015). In an experimental approach representative of
76 the full crystallisation pathway, the brine–mirabilite–hydrohalite interaction
77 was observed during cooling and warming of frozen seawater brines but gyp-
78 sum was not identified Butler and Kennedy (2015).

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

87 Here, we investigated the characteristics of the gypsum–brine reaction in
88 sea ice via measurements of the concentration-based (stoichiometric) solubil-
89 ity of this mineral in relevant brines at below-zero temperatures. We sought
90 to identify the conditions that can lead to internal gypsum authigenesis and
91 stability in the large below-zero temperature and salinity ranges of sea ice
92 brines. Knowledge of the hydrohalite dynamics in the sea ice system is es-
93 sential for this purpose given the common ion effect on mineral stability of
94 the brine–gypsum–mirabilite–hydrohalite interaction outlined earlier and the
95 available information about mirabilite solubility in the sea ice system in our
96 previous work (Butler et al., 2016b). Thermodynamic modelling (Marion
97 et al., 1999) and experimental observations from the Gitterman (1937) and
98 Nelson and Thompson (1954) experiments predict that hydrohalite precipi-
99 tates in sea ice below -22.9 °C. Its presence has been identified in laboratory
100 experiments on frozen seawater brines (Butler and Kennedy, 2015) and in
101 sea ice (Light et al., 2003), and affects the optical, mechanical, and frictional
102 properties of sea ice (Light et al., 2004; Carns et al., 2015). From the onset,
103 hydrohalite precipitation is rapid and by -30 °C, 87 % of dissolved NaCl is
104 removed from the brine as a result (Richardson, 1976). In frozen seawater

105 from a starting absolute salinity of $35 \text{ g kg}_{\text{solution}}^{-1}$ (in the absence of brine
 106 drainage), hydrohalite concentrations can approach 4 % by mass by $-40 \text{ }^{\circ}\text{C}$
 107 (Richardson, 1976; Light et al., 2003). Precipitation of hydrohalite has been
 108 shown to be closely associated with enhanced ice formation, which substan-
 109 tially reduces the volume of brine remaining in the ice (Richardson, 1976;
 110 Butler and Kennedy, 2015).

111 The current investigation expands upon recent work on mirabilite solu-
 112 bility in similar conditions (Butler et al., 2016b). The solubility of both gyp-
 113 sum and hydrohalite was measured to a minimum temperature of $-25.0 \text{ }^{\circ}\text{C}$.
 114 Because of the large increase in hydrohalite solubility with increasing tem-
 115 perature, the maximum experimental temperature was $-14.3 \text{ }^{\circ}\text{C}$ while that
 116 for gypsum solubility was $0.2 \text{ }^{\circ}\text{C}$, with experiments designed to investigate
 117 the behaviour of gypsum under conditions equivalent to fractional and full
 118 crystallisation pathways. Finally, given the dominance of hydrohalite as a
 119 mineral precipitate in cold sea ice, its solubility data set was incorporated
 120 into a 1D model of the growth of snow-free first-year sea ice to allow eval-
 121 uation of its depth distribution and temporal dynamics. The dynamics of
 122 gypsum are shown here to be too complex in its dependence on mirabilite
 123 and hydrohalite dynamics for this modelling approach.

124 2. Methods

125 2.1. Synthetic mineral preparation and synchrotron X-ray powder diffraction

126 Synthetic gypsum, hydrohalite, and mirabilite were used for seeding the
 127 solid–solution equilibrium reaction and were prepared based on the methods
 128 described in Wang et al. (2012), Light et al. (2009), and Butler et al. (2016b),
 129 respectively. All synthetic solids were stored in screw-capped bottles; gypsum
 130 was stored at room temperature, while hydrohalite and mirabilite were stored
 131 at $-20 \text{ }^{\circ}\text{C}$.

132 The mineralogy of the synthetic solids and of some of the mineral aggre-
 133 gates recovered following solid–solution reaction was characterised at $-30 \text{ }^{\circ}\text{C}$

134 using synchrotron X-ray powder diffraction (XRPD) on Beamline I11 at
135 Diamond Light Source (Harwell Science and Innovation Campus, Oxford-
136 shire, UK). Published cell parameters for hydrohalite (Klewe and Pederson,
137 1974), gypsum (Boeyens and Ichharam, 2002), and mirabilite (Brand et al.,
138 2009) were used as an initial starting point for LeBail (Le Bail et al., 1988)
139 and Rietveld (Rietveld, 1969) refinements in TOPAS-Academic V6 software
140 (Coelho, 2012). Based on the semi-quantitative (Hillier, 2003) Rietveld re-
141 finements, it was established that all batches of synthetic mineral seeds dis-
142 played ≥ 99 % purity.

143 2.2. Closed bottle incubations and brine analysis

144 Mineral solubility was determined with closed bottle incubations of nat-
145 ural or synthetic seawater and brines with synthetic solids to solid–solution
146 equilibrium as previously used for this purpose (Mucci, 1983; Papadimitriou
147 et al., 2013; Butler et al., 2016b). The time to solid–solution equilibrium
148 was determined by monitoring the change in Ca^{2+} with time for gypsum
149 and in Cl^- for hydrohalite during incubation (protocols described in sec-
150 tion 2.4). Changes sustained within the analytical uncertainty over 1 week
151 were taken to indicate attainment of solid–solution equilibrium. Using this
152 approach the gypsum experiments were incubated for between 41 and 90
153 days, and hydrohalite experiments incubated for between 24 and 36 days.
154 All incubation experiments were conducted in triplicate, with bottles fully
155 submersed in constant temperature circulating chillers and shaken by hand
156 daily to facilitate exposure of the mineral seed to the bulk solution. Incu-
157 bation temperatures were controlled by Grant RC 1400G recirculating baths
158 and Grant TX120/TX150 circulators coupled with Grant R2/R3 refrigera-
159 tion units. Chiller temperatures were monitored at thirty-minute intervals
160 using data loggers (Tinytag aquatic 2 TG4100).

161 Detailed preparation protocols for the natural and synthetic seawater
162 brines can be found in Butler et al. (2016b). The synthetic seawater and
163 brines were prepared with their major ionic composition (NaCl , Na_2SO_4 ,

164 CaCl_2 , MgCl_2 , KCl) a linear function of salinity relative to the recipe of
 165 salinity 35 synthetic seawater in Papadimitriou et al. (2016). Natural brines
 166 were prepared from local seawater (Menai Strait, 53.1806°N, 4.2333°W) by
 167 freezing. The major ion composition (as total ion concentrations) of natural
 168 and synthetic experimental solutions was fully quantified before incubation
 169 to determine their initial saturation state with respect to the investigated
 170 minerals, and after incubation for the determination of the relevant mineral
 171 solubility.

172 The major ion composition of the samples was determined within 4 weeks
 173 from sampling, with refrigerated storage before analysis. To eliminate the
 174 risk of mineral precipitation during storage, all samples were immediately
 175 diluted gravimetrically to a practical salinity of 35 with deionised water.
 176 The Na^+ and K^+ concentrations were determined by ion chromatography
 177 on a Dionex Ion Exchange Chromatograph ICS 2100. The Mg^{2+} and Ca^{2+}
 178 concentrations were determined by potentiometric titration as described by
 179 Papadimitriou et al. (2013). The Cl^- concentration was determined by gravi-
 180 metric Mohr titration with 0.3 M AgNO_3 standardised against NaCl purified
 181 by recrystallisation. The SO_4^{2-} concentration was determined by precipita-
 182 tion as BaSO_4 in ethylenediaminetetraacetic acid (EDTA) followed by gravi-
 183 metric titration with MgCl_2 (Howarth, 1978). Repeat measurements of the
 184 major ion composition of local seawater were used as an internal standard
 185 relative to the composition of Standard Seawater (Millero et al., 2008). This
 186 comparison provided an estimate of measurement accuracy and precision rel-
 187 ative to Standard Seawater, summarised in Table 1.

188 2.3. Determination of saturation state and stoichiometric solubility products

189 Mineral solubility is defined here as the equilibrium concentration-based
 190 (stoichiometric) solubility product at mineral–solution equilibrium, $K_{\text{sp,gypsum}}^* =$
 191 $[\text{Ca}^{2+}]_{\text{eqm}}[\text{SO}_4^{2-}]_{\text{eqm}}$ and $K_{\text{sp,hydrohalite}}^* = [\text{Na}^+]_{\text{eqm}}[\text{Cl}^-]_{\text{eqm}}$, with brackets de-
 192 noting total ion concentrations and ‘eqm’ subscripts denoting equilibrium
 193 conditions. The K_{sp}^* is a function of temperature, ionic strength (salinity),

Table 1: The accuracy and precision of brine analyses estimated using repeat measurements of local seawater (normalised to practical salinity = 35) as an internal standard relative to the composition of Standard Seawater (Millero et al., 2008).

	Standard Seawater	Measurements $\pm \sigma$	$\Delta \pm \sigma$
		mmol kg _{sol} ⁻¹	%
Na ⁺	468.97	470.53 $\pm$ 7.97 ($n = 29$)	0.33 $\pm$ 1.70
K ⁺	10.21	10.11 $\pm$ 0.05 ($n = 9$)	-0.97 $\pm$ 0.49
Mg ²⁺	52.82	52.63 $\pm$ 0.54 ($n = 82$)	-0.36 $\pm$ 1.02
Ca ²⁺	10.28	10.24 $\pm$ 0.14 ($n = 82$)	-0.39 $\pm$ 1.36
Cl ⁻	545.87	548.48 $\pm$ 6.90 ($n = 38$)	0.48 $\pm$ 1.26
SO ₄ ²⁻	28.24	28.34 $\pm$ 0.41 ($n = 35$)	0.35 $\pm$ 1.45

194 and solution composition (Papadimitriou et al., 2013; Butler et al., 2016b),
195 and is hereafter reported as the negative common logarithm (pK_{sp}^*) on the
196 per kg_{solution} basis of the concentration measurements. The pK_{sp}^* values of
197 each mineral were fitted to non-linear functions of temperature (T , in K;
198 eq. 1), using Regression in the Data Analysis ToolPak of Microsoft Excel,
199 with the fitted regression coefficients A to D given in Table 2.

$$pK_{\text{sp}}^*(T) = A + BT + CT^2 + DT^3, \quad (1)$$

200 The saturation state of samples was determined as $\Omega = \text{ICP}/K_{\text{sp}}^*$ (Berner,
201 1980), with ICP = total ion concentration product prior to seeding (i.e.
202 $[\text{Ca}^{2+}][\text{SO}_4^{2-}]$ for gypsum, and $[\text{Na}^+][\text{Cl}^-]$ for hydrohalite) and K_{sp}^* as above.
203 When $\Omega < 1$ the initial solution is undersaturated with respect to the min-
204 eral. When $\Omega > 1$ the initial solution is supersaturated with respect to the
205 mineral. Supersaturation is a metastable state that results in mineral pre-
206 cipitation if suitable nucleation sites are provided. The Ω values were fitted
207 to non-linear functions of temperature (T , in K; eq. 1), with fitted regression
208 coefficients also given in Table 2. Each solid-solution equilibrium system
209 was defined by the solid phases (including ice, if present) in contact with the
210 brine at equilibrium. For example, a brine attaining equilibrium in contact

211 with mirabilite and gypsum will be defined as a brine–mirabilite–gypsum
212 equilibrium system.

213 The solubility of gypsum was determined in both natural and synthetic
214 brines between 0.2 and -5.0 °C to investigate potential matrix effects on the
215 $K_{\text{sp,gypsum}}^*$. The differences between $pK_{\text{sp,gypsum}}^*$ in natural and synthetic brine
216 experiments over this temperature range were generally within the analytical
217 uncertainty (Figure 1; Table 3) and, therefore, only synthetic brines were
218 used at temperatures below -5.0 °C. Given the dominance of Na^+ and Cl^-
219 in the composition of seawater and their tendency to remain as free ions in
220 solution (Millero et al., 2008; Marion and Kargel, 2008), the determination of
221 $K_{\text{sp,hydrohalite}}^*$ only in synthetic brines, as done here, was considered to provide
222 values representative of those in natural seawater-derived brines.

223 2.4. Incubation protocols

224 Due to the large investigated temperature range and the sequential pre-
225 cipitation of minerals from the brine at various points in this range, three
226 different protocols were employed for the bottle incubations.

227 *Protocol-1: Gypsum solubility.* Between 0 and -6 °C, major ions in
228 seawater and its brines during freezing (absolute salinity, $S_A = 35$ to 100 g
229 $\text{kg}_{\text{solution}}^{-1}$; hereafter, g kg^{-1}) behave conservatively, and so, synthetic solutions
230 were prepared at room temperature with Standard Seawater major ionic ra-
231 tios and composition (Millero et al., 2008) and were seeded with gypsum.
232 Solutions of $S_A \geq 35$ g kg^{-1} were incubated within 0.3 °C of their freez-
233 ing point, which was estimated using the equation from Millero and Leung
234 (1976).

235 *Protocol-2: Gypsum and hydrohalite solubilities.* Protocol-2 was used for
236 incubations between -6 and -22 °C to take into account the ice–brine–
237 mirabilite reaction, which is documented in this temperature range (Butler
238 et al., 2016b). Conservative seawater brines were prepared ($S_A = 75$ to 225
239 g kg^{-1}), cooled to at least 2 °C colder than their freezing point, and were
240 incubated with mirabilite seed until attainment of ice–brine–mirabilite equi-

Table 2: Coefficients for use with equation 1 describing the change in pK_{sp}^* and Ω for gypsum and hydrohalite, and the mass of hydrohalite to precipitate from frozen seawater ($S_A = 35 \text{ g kg}^{-1}$), all as functions of temperature (K).

	Range		A	B	C	D	R^2	σ
	$^{\circ}\text{C}$	K						
$pK_{sp, \text{gypsum}}^*$	0.2 to -1.8	273.35 to 271.35	7.8871287e2	-5.7598725	1.0554382e-2		0.868	0.005
	-1.8 to -5.0	271.35 to 268.15	2.1151892e3	-1.5748129e1	2.9348641e-2		0.999	0.005
	-5.0 to -22.2 ^a	268.15 to 250.95	-1.8167179e3	2.1378285e1	-8.3629854e-2	1.0892019e-4	0.993	0.008
Ω_{gypsum}	0.2 to -1.8	273.35 to 271.35	9.4425558e2	-6.9204629	1.2682971e-2		0.949	0.003
	-1.8 to -6.8	271.35 to 266.35	-1.4732875e5	1.6448060e3	-6.1202247	7.5900980e-3	0.999	0.010
	-6.8 to -22.2 ^a	266.35 to 250.95	3.3343577e3	-3.8584742e1	1.4835926e-1	-1.9001908e-4	0.990	0.010
$pK_{sp, \text{hydrohalite}}^*$	-14 to -22.8	259.15 to 250.35	1.2839471	-9.4961523e-3			1.000	0.000
	-22.8 to -26.0	250.35 to 247.15	-1.2285077e2	1.0287111	-2.1664221e-3		1.000	0.001
$\Omega_{\text{hydrohalite}}$	-14 to -22.8	259.15 to 250.35	7.8679083e1	-5.50716264e-1	9.6040378e-4		1.000	0.000
	-22.8 to -26.0	250.35 to 247.15	2.0188738e3	-1.4909085e1	2.7357085e-2		1.000	0.001
Hydrohalite (g kg^{-1})	-22.9 to -25.0	250.25 to 248.15	292.1993911e5	-3.5284595e5	1.4202904e3	-1.9057022	1.000	0.168
	-25.0 to -36.0	248.15 to 237.15	2.1156841e5	-2.6436200e3	11.0142323	-1.529829e-2	0.998	0.153

^a Extrapolated to -22.8 $^{\circ}\text{C}$ in figures 1 and 2

241 librium. The brine was then extracted by in-situ filtration using WHATMAN
 242 0.2 μm syringe filters in line with Teflon tubing extensions. The filtrate was
 243 transferred to triplicate 25 ml bottles and was returned to the circulating
 244 chiller seeded with either gypsum or hydrohalite until equilibrium had been
 245 attained. It is worth emphasising that hydrohalite and ice cannot co-exist
 246 above $-22.9\text{ }^{\circ}\text{C}$ (Marion et al., 1999; Marion and Kargel, 2008), therefore
 247 all hydrohalite solubility experiments carried out using protocol-2 represent
 248 the extent to which hydrohalite would dissolve (i.e. the degree of undersat-
 249 uration) in the solutions extracted from an ice–brine–mirabilite equilibrium
 250 system.

251 *Protocol-3: Gypsum and Hydrohalite solubilities.* Protocol-3 was followed
 252 at the coldest experimental temperatures (-23.7 and $-25.0\text{ }^{\circ}\text{C}$) to circum-
 253 vent the substantial reduction in brine volume following hydrohalite precipi-
 254 tation. Conservative seawater brines were prepared to $S_A \sim 225\text{ g kg}^{-1}$ in 500
 255 ml bottles and were cooled to $-21\text{ }^{\circ}\text{C}$ when mirabilite seed was added, with
 256 ice formation and mirabilite precipitation ensuing. At this stage, the exper-
 257 imental medium included an ice layer at the brine surface and a mirabilite
 258 layer at the bottom of the bottle. The ice–brine–mirabilite system was then
 259 cooled to either -23.7 or $-25.0\text{ }^{\circ}\text{C}$. On these occasions, buoyant, irregular,
 260 mottled bright white crystal flocs formed during cooling to target tempera-
 261 ture and filled the bottle at thermal equilibrium, consistent with reports of
 262 ice–hydrohalite aggregates (Nelson and Thompson, 1954; Assur, 1960; Mc-
 263 Carthy et al., 2007; Light et al., 2009). The residual brine was trapped
 264 within the aggregate and was extracted by drainage into a hole bored into
 265 the aggregate with a steel rod. The extracted brine was considered rep-
 266 resentative of the fractional crystallisation pathway (section 1) because the
 267 mirabilite precipitate at the bottom of the bottle was isolated from further re-
 268 action with the emergent ice–hydrohalite aggregate and its interstitial brine
 269 (previously at equilibrium with the mirabilite). The extracted brine pro-
 270 vided the measurements for the determination of $K_{\text{sp,hydrohalite}}^*$ at -23.7 and

271 $-25.0\text{ }^{\circ}\text{C}$, as well as aliquots for further incubations and the determination of
 272 the $K_{\text{sp,gypsum}}^*$ at these temperatures. To this end, the extracted brines were
 273 incubated with gypsum seed with and without mirabilite seed. Gypsum sol-
 274 ubility was therefore determined under two different conditions at -23.7 and
 275 $-25.0\text{ }^{\circ}\text{C}$: (i) in the absence of mirabilite seed, representative of the fractional
 276 crystallisation pathway of restricted brine–mirabilite interaction limited by
 277 the ice–hydrohalite aggregate; and (ii) in the presence of mirabilite seed, rep-
 278 resentative of the full crystallisation pathway of unrestricted brine–mirabilite
 279 interaction.

280 *Additional protocol: Gypsum solubility.* Although seawater brines be-
 281 come supersaturated with respect to mirabilite at $T \leq -6.4\text{ }^{\circ}\text{C}$, persistence
 282 of metastable mirabilite supersaturation has been observed between -7 and
 283 $-8\text{ }^{\circ}\text{C}$ in the absence of mirabilite seed (Butler et al., 2016b). To examine
 284 the potential for gypsum precipitation in this narrow temperature window of
 285 metastable mirabilite supersaturation in sea ice brines, bottle incubations of
 286 conservative solutions were undertaken at $-7.1\text{ }^{\circ}\text{C}$ ($S_{\text{A}} = 113.9\text{ g kg}^{-1}$) and
 287 $-8.2\text{ }^{\circ}\text{C}$ ($S_{\text{A}} = 125.1\text{ g kg}^{-1}$) in an adaptation of protocol-2 that omitted
 288 the addition of mirabilite seed. At these temperatures, the solutions were
 289 supersaturated with respect to mirabilite and their ionic composition repre-
 290 sented that at ice–brine equilibrium. The solutions were seeded with gypsum,
 291 the $K_{\text{sp,gypsum}}^*$ was determined at brine–gypsum equilibrium, and mirabilite
 292 seed was added to the incubations, resulting in mirabilite precipitation and
 293 dissolution of the gypsum precipitate/seed, which remained in excess. The
 294 system was then allowed to attain brine–mirabilite–gypsum equilibrium, i.e.,
 295 the same system investigated using the original protocol-2, but with reversed
 296 seeding, from which the $K_{\text{sp,gypsum}}^*$ was again determined.

297 2.5. *FREZCHEM modelling of gypsum and hydrohalite solubilities*

298 As a means of relating the experimental $K_{\text{sp,gypsum}}^*$ and $K_{\text{sp,hydrohalite}}^*$ with
 299 their thermodynamic counterparts at infinite dilution in pure water, their val-
 300 ues were compared with those calculated from the thermodynamic database

Table 3: The absolute salinity (S_A) of incubated brines prior to seeding with gypsum, incubation temperature at point of sampling, Ca^{2+} and SO_4^{2-} concentrations at equilibrium, the resulting measured $pK_{\text{sp,gypsum}}^*$ and Ω_{gypsum} , and the ΔCa^{2+} observed over the course of each experiment included as a measure of reaction direction ($\Delta\text{Ca}^{2+} = \text{Ca}_{\text{eqm}}^{2+} - \text{Ca}_{\text{initial}}^{2+}$). The S_A measured between 0.2 and -6.0 °C are at ice–brine equilibrium, while those at -6.8 °C and below were measured at ice–brine–mirabilite equilibrium. In each case, equilibrium was attained by gypsum dissolution, evidenced by positive ΔCa^{2+} values. Tabulated errors are calculated as the standard deviation of measurements from triplicate experiments.

Exp. #	S_A	T	Ca^{2+}	SO_4^{2-}	$pK_{\text{sp,gypsum}}^*$	Ω_{gypsum}	ΔCa^{2+}
	$\text{g kg}_{\text{sol}}^{-1}$	°C	mmol $\text{kg}_{\text{sol}}^{-1}$	$\text{mmol kg}_{\text{sol}}^{-1}$			mmol $\text{kg}_{\text{sol}}^{-1}$
NG-0	35.1	0.2	27.8±0.2	48.3±0.1	2.872±0.002	0.219±0.003	17.6
SG-0	35.3	0.2	27.8±0.2	47.1±0.7	2.883±0.005	0.224±0.007	17.4
NG-1	35.3	-1.1	28.1±0.4	46.4±0.4	2.884±0.009	0.228±0.004	17.7
SG-1	35.3	-1.1	28.4±0.2	46.4±0.2	2.880±0.005	0.223±0.007	18.1
NG-2	35.2	-1.8	28.2±0.1	44.9±1.0	2.897±0.011	0.247±0.008	17.7
SG-2	35.2	-1.8	28.1±0.2	44.6±0.3	2.902±0.005	0.244±0.004	17.4
NG-3	53.2	-2.9	31.7±0.5	58.7±0.5	2.730±0.011	0.357±0.012	16.1
SG-3	53.0	-2.9	31.0±0.4	58.5±1.3	2.742±0.014	0.362±0.004	15.7
NG-4	70.3	-3.9	32.6±0.1	68.9±1.1	2.648±0.005	0.539±0.001	12.1
SG-4	70.4	-3.9	32.1±0.3	68.6±0.4	2.658±0.006	0.512±0.005	11.3
NG-5	85.2	-5.0	30.9±0.2	76.8±1.7	2.625±0.013	0.740±0.022	6.0
SG-5	85.0	-5.0	30.2±0.1	78.5±0.5	2.625±0.004	0.733±0.018	5.4
SG-6	99.7	-6.0	31.8±0.1	81.5±1.3	2.587±0.008	0.912±0.010	7.1
SG-7	111.1	-6.8	34.6±0.2	73.5±0.4	2.595±0.004	0.979±0.005	0.4
SG-8	120.6	-7.9	38.9±0.5	65.6±0.3	2.593±0.005	0.965±0.005	1.0
SG-9	131.6	-8.9	42.1±0.2	61.6±0.5	2.587±0.002	0.964±0.005	1.1
SG-10	140.6	-10.1	46.1±0.1	55.2±0.1	2.595±0.001	0.916±0.007	1.8
SG-12	156.9	-11.8	53.0±0.3	45.8±0.6	2.615±0.007	0.898±0.010	2.8
SG-13	165.2	-12.8	61.6±0.3	39.1±0.2	2.618±0.001	0.876±0.006	7.3
SG-14	173.8	-14.3	65.3±0.7	32.4±0.5	2.674±0.007	0.818±0.007	9.4
SG-15	180.7	-15.1	69.1±0.3	30.1±0.4	2.683±0.003	0.795±0.023	11.2
SG-18	200.2	-17.5	76.1±0.7	23.7±0.4	2.745±0.006	0.764±0.042	11.7
SG-21	218.7	-20.6	88.5±1.0	17.3±0.2	2.815±0.003	0.750±0.011	17.1
SG-22	225.3	-22.2	92.3±0.4	15.2±0.4	2.852±0.009	0.767±0.056	17.2

301 of the FREZCHEM (version 15.1) with ice, mirabilite, gypsum, and hydro-
302 halite the only solids enabled in the mineral database. The FREZCHEM code
303 is frequently used to investigate geochemical reactions in the cryosphere. It is
304 based on the Pitzer formalism of ionic interactions in concentrated electrolyte
305 solutions and includes ion pairs (CaCO_3^0 , MgCO_3^0 , MgOH^+) with high for-

306 mation constants (He and Morse, 1993), while it also accounts for the SO_4^{2-} –
 307 HSO_4^- equilibrium (Marion and Grant, 1994; Marion and Farren, 1999). The
 308 code runs replicated the experimental starting solution compositions (i.e.
 309 prior to seeding) studied in the protocols outlined in section 2.4. Because
 310 the code is predominately designed to simulate mineral–solution equilib-
 311 rium from precipitation, excess gypsum or hydrohalite were added to the
 312 FREZCHEM input files when the brine–gypsum and brine–hydrohalite equi-
 313 librium was simulated for undersaturated experimental brines. The deriva-
 314 tion of $K_{\text{sp,gypsum}}^*$ and $K_{\text{sp,hydrohalite}}^*$ from the code output was based on that
 315 used for ikaite (Papadimitriou et al., 2013) and mirabilite (Butler et al.,
 316 2016b) solubilities in sea ice brines.

317 *2.6. First-year sea ice modelling*

318 The FREZCHEM code was also run to simulate freezing of Standard
 319 Seawater (Millero et al., 2008) in order to determine the mass of hydrohalite
 320 precipitate as a function of temperature between -22.9°C and -36.0°C , i.e.,
 321 the temperature field between the onset of hydrohalite precipitation and the
 322 seawater eutectic in the presence of gypsum and mirabilite. The fractional
 323 crystallisation pathway (section 1) was used for this computation, which does
 324 not allow further brine–mirabilite reaction during hydrohalite precipitation,
 325 and so, it reflected the hydrohalite solubility experiments carried out using
 326 protocol-3 (section 2.4). As will be shown, the FREZCHEM code accurately
 327 computes hydrohalite equilibria in sea ice brines (section 3.4), thus justi-
 328 fying its use here. The mass of hydrohalite precipitate extracted from the
 329 FREZCHEM output at 0.25°C cooling steps was incorporated into a 1D
 330 numerical model of first-year sea ice (Cox and Weeks, 1988) as described for
 331 mirabilite in Butler et al. (2016b). The 1D model calculated the thickness
 332 and bulk S_A depth profile of the ice pack as it grows in autumn–winter, and
 333 accounts for brine drainage in permeable sea ice ($T > -5^\circ\text{C}$) and the effect
 334 of hydrohalite precipitation on brine salinity ($T < -22.9^\circ\text{C}$). The model was
 335 used to estimate the hydrohalite mass per unit mass of sea ice (0.5 cm depth

336 increments) at temperature $T[H_i(T)$, in g kg^{-1} sea ice] after desalination by

$$H_i(T) = H(T) \frac{S_i}{S_{\text{sw}}} \quad (2)$$

337 where $H(T)$ is the hydrohalite mass at temperature T that would precip-
 338 itate from 1 kg of Standard Seawater ($S_A = 35.165 \text{ g kg}^{-1}$) based on the
 339 FREZCHEM model output, S_i is the bulk S_A of the ice as calculated by the
 340 1D model, and S_{sw} is the S_A of Standard Seawater. The incorporation of
 341 hydrohalite precipitation dynamics into the sea ice model allowed evaluation
 342 of its temporal depth distribution in sea ice as the modelled ice pack grows
 343 throughout an Arctic winter.

344 3. Results

345 3.1. Gypsum solubility and saturation state between 0.2 and -22.2°C

346 The positive ΔCa^{2+} values during protocol-1 and protocol-2 experiments
 347 (Table 3) indicate that the brine–gypsum equilibrium was attained by disso-
 348 lution of the gypsum seed throughout the 0.2 to -22.2°C temperature range,
 349 and so the $pK_{\text{sp,gypsum}}^*$ was determined from undersaturation. This becomes
 350 evident in Ω_{gypsum} remaining below 1 throughout this temperature range,
 351 approaching, but not exceeding, saturation ($\Omega = 1$) only at -6.8°C (Fig-
 352 ure 2; Table 3). The $pK_{\text{sp,gypsum}}^*$ increased from 2.878 to 2.900 between 0.2
 353 and -1.8°C , which represents a slight reduction in gypsum solubility with
 354 decreasing temperature at constant salinity in seawater (Figure 1; Table 3).
 355 Between -1.8 and -6.0°C , the $pK_{\text{sp,gypsum}}^*$ decreased from 2.900 to 2.587
 356 with decreasing temperature in brines representative of conservative physi-
 357 cal solute concentration. The $pK_{\text{sp,gypsum}}^*$ was relatively stable (2.591 ± 0.004 ,
 358 $n = 5$) between -6.8 and -10.1°C , and then increased measurably and
 359 monotonically to 2.852 between -10.1 and -22.2°C in conditions of decreas-
 360 ing temperature, increasing ionic strength, and increasingly reduced SO_4^{2-}
 361 via mirabilite precipitation from the brine before and during the gypsum

Figure 1: Measured $pK_{\text{sp,gyypsum}}^*$ in equilibrium sea ice brines plotted alongside output from the FREZCHEM model both for the seawater (0 to -1.8 °C), ice–brine (-1.8 to -6.4 °C), and ice–brine–mirabilite (-6.4 to -22.2 °C) equilibrium systems. Also plotted are the $pK_{\text{sp,gyypsum}}^*$ measurements in full and equilibrium crystallisation conditions at -23.7 and -25.0 °C (see sections 2.4 and 3.3). The vertical line at -1.8 °C marks the point of which the solubility product begins to become affected by coupled changes in salinity and temperature as a result of freezing. The fitted line is based only on measurements from synthetic and natural brines (square and circle markers) between 0.2 and -22.2 °C. B = Brine, G = Gypsum, M = Mirabilite.

solubility experiments (Figure 1; Table 3). Mirabilite seed was not present during the gypsum solubility experiments in this temperature range, but the initial brine equilibrated with mirabilite before the gypsum solubility experiments (protocol-2) and, also, during the experiments. The SO_4^{2-} addition to the mirabilite-equilibrated brine via gypsum seed dissolution resulted in mirabilite supersaturation and further mirabilite precipitation from this brine. Mirabilite as a result of this gypsum dissolution reaction was identified by XRPD analysis of the solids recovered at the end of these experiments (section 2.1. The $K_{\text{sp,gyypsum}}^*$ between -6.8 and -22.2 °C therefore represents

371 the brine–mirabilite–gypsum equilibrium.

372 3.2. Gypsum dynamics in conditions of metastable mirabilite supersaturation

373 In the experiments carried out under metastable conditions of mirabilite
374 supersaturation at -7.1 and -8.2 °C, the initial brines had a composition
375 equivalent to that resulting from physical solute concentration at ice–brine
376 equilibrium. Mirabilite would almost certainly not precipitate by homoge-
377 neous nucleation in these conditions, and so, these brines had $\Omega_{\text{mirabilite}} =$
378 1.252 and 1.717 at -7.1 and -8.2 °C, respectively, calculated from the
379 $\Omega_{\text{mirabilite}} - T$ relationship in Butler et al. (2016b). Seeding these brines with
380 gypsum resulted in a decrease in Ca^{2+} and SO_4^{2-} , with a $\Delta\text{Ca}^{2+}:\Delta\text{SO}_4^{2-} =$
381 0.90 ± 0.05 (Table 4), indicating gypsum precipitation. Based on the pK_{gypsum}^*
382 determined at the brine–gypsum equilibrium of these experiments (Table 4),
383 the saturation state of the initial ice–brine equilibrium condition was $\Omega_{\text{gypsum}} =$
384 1.173 at -7.1 °C and 1.379 at -8.2 °C. The measured ΔCa^{2+} indicates that
385 the amount of gypsum precipitate at brine–gypsum equilibrium was 3.8 mmol
386 kg^{-1} at -7.1 °C and 7.5 mmol kg^{-1} at -8.2 °C.

387 The subsequent seeding of the brine–gypsum equilibrium solutions with
388 mirabilite in the presence of the gypsum seed/precipitate resulted in an in-
389 crease in Ca^{2+} and further reduction of SO_4^{2-} (Table 4), implying concurrent
390 gypsum dissolution and mirabilite precipitation by heterogeneous nucleation,
391 respectively. This suggests that, despite the SO_4^{2-} removal from solution as
392 gypsum, the brines at brine–gypsum equilibrium remained in a metastable
393 supersaturated state with respect to mirabilite. It is also apparent that the
394 consequent SO_4^{2-} removal to mirabilite resulted in $\Omega_{\text{gypsum}} < 1$, facilitat-
395 ing gypsum dissolution. Based on the Ca^{2+} difference between the brine–
396 gypsum and brine–gypsum–mirabilite equilibrium (Table 4), the amount of
397 gypsum that dissolved in the presence of mirabilite seed was 4.7 and 9.1
398 mmol kg^{-1} at -7.1 and -8.2 °C, respectively. This amount of gypsum disso-
399 lution exceeds the amount of gypsum precipitation at sustained metastable
400 mirabilite supersaturation and brine–gypsum equilibrium (computed in the

Figure 2: The measured Ω_{gypsum} in equilibrium sea ice brines between 0.2 and -22.2 °C plotted alongside the output from the FREZCHEM model. The vertical line at -1.8 °C marks the point of which the saturation state begins to become affected by coupled changes in salinity and temperature as a result of freezing, while that at -6.4 °C marks the onset of mirabilite precipitation. The horizontal line at $\Omega_{\text{gypsum}} = 1$ is used to highlight the transition between undersaturation ($\Omega_{\text{gypsum}} < 1$) and supersaturation ($\Omega_{\text{gypsum}} > 1$).

previous paragraph). This then indicates that gypsum should be unstable once mirabilite begins to form. The $pK_{\text{sp,gypsum}}^*$ at brine–mirabilite–gypsum equilibrium obtained from these experiments was in close agreement with the $pK_{\text{sp,gypsum}}^* - T$ relationship outlined in section 3.1 (Figure 1; Tables 3 and 4). This indicates that identical chemical equilibrium conditions can be attained independently of the order of mineral seeding/nucleation.

3.3. Gypsum solubility in the fractional and full crystallisation pathways

The brines used for the gypsum solubility measurements in conditions representative of fractional and full crystallisation pathways at -23.7 and -25.0 °C were extracted from the ice–hydrohalite aggregate in protocol-3

Table 4: Equilibrium measurements of Ca^{2+} and SO_4^{2-} concentrations from experiments that investigated gypsum solubility in conditions of metastable mirabilite supersaturation at -7.1 and -8.2 °C. * denotes solutions that were supersaturated with respect to mirabilite at the point of measurement. Tabulated errors are calculated as the standard deviation of measurements from triplicate experiments.

System	T °C	Ca^{2+}	SO_4^{2-}	$pK_{\text{sp,gypsum}}^*$
		mmol $\text{kg}_{\text{sol}}^{-1}$	mmol $\text{kg}_{\text{sol}}^{-1}$	
Ice–brine*	-7.1	33.8 ± 0.1	91.9 ± 0.6	
Brine–gypsum*	-7.1	30.0 ± 0.1	88.0 ± 0.6	2.578 ± 0.002
Brine–gypsum–mirabilite	-7.1	34.7 ± 0.1	73.2 ± 0.2	2.595 ± 0.001
Ice–brine*	-8.2	37.1 ± 0.4	100.7 ± 0.2	
Brine–gypsum*	-8.2	29.6 ± 0.5	91.6 ± 1.0	2.567 ± 0.011
Brine–gypsum–mirabilite	-8.2	38.7 ± 0.4	65.3 ± 0.3	2.597 ± 0.006

experiments (section 2.4). These brines were at equilibrium with ice and hydrohalite but supersaturated with respect to gypsum because, when incubated only with gypsum seed (representative of the fractional crystallisation pathway), a negative ΔCa^{2+} was observed, implying 6.8 and 9.3 mmol kg^{-1} of gypsum precipitate at -23.7 and -25.0 °C, respectively (Table 5). This corresponds to $\Omega_{\text{gypsum}} = 1.064$ and 1.069 in the brines of the ice–hydrohalite aggregate at -23.7 and -25.0 °C, respectively (Table 5). When these brines were seeded with both gypsum and mirabilite (representative of the full crystallisation pathway), the ΔCa^{2+} was more negative and the ΔSO_4^{2-} less so than in the absence of mirabilite in the fractional crystallisation pathway at both temperatures (Table 5). The ΔCa^{2+} in these experiments is equivalent to 23.2 mmol kg^{-1} and 80.9 mmol kg^{-1} of gypsum precipitate at -23.7 °C (corresponding to $\Omega_{\text{gypsum}} = 1.257$ in the initial brine) and -25.0 °C (corresponding to $\Omega_{\text{gypsum}} = 2.276$ in the initial brine), respectively (Table 5). Collectively, these observations indicate enhanced gypsum precipitation in the presence of mirabilite, with the additional source of SO_4^{2-} provided by mirabilite dissolution.

The pK_{gypsum}^* determined at brine–hydrohalite–gypsum equilibrium (frac-

tional crystallisation pathway) was in close agreement with the values determined at brine–mirabilite–hydrohalite–gypsum equilibrium (full crystallisation pathway) at -25.0 °C and within experimental uncertainty at -23.7 °C, despite differing equilibrium brine composition and inter-ionic ratios of Ca^{2+} and SO_4^{2-} (Table 5; Figure 1). This suggests that, within experimental error at the two coldest temperatures of this investigation, the pK_{gypsum}^* is not measurably influenced by differences in the equilibrium ionic composition of the brine resulting from the fractional and full crystallisation pathways.

Table 5: Equilibrium measurements of gypsum solubility at -23.7 and -25.0 °C in experiments considered representative of fractional and full crystallisation. The Ω_{gypsum} values presented here were based exclusively on the ΔCa^{2+} , since the SO_4^{2-} is affected by mirabilite dissolution. $\Delta\text{Ca}^{2+} = \text{Ca}_{\text{eqm}}^{2+} - \text{Ca}_{\text{initial}}^{2+}$. $\Delta\text{SO}_4^{2-} = \text{SO}_{4\text{eqm}}^{2-} - \text{SO}_{4\text{initial}}^{2-}$. Tabulated errors are calculated as the standard deviation of measurements from triplicate experiments.

Type	T °C	Ca^{2+}	SO_4^{2-}	$pK_{\text{sp,gypsum}}^*$	Ω_{gypsum}	ΔCa^{2+}	ΔSO_4^{2-}
		mmol $\text{kg}_{\text{sol}}^{-1}$	mmol $\text{kg}_{\text{sol}}^{-1}$			mmol $\text{kg}_{\text{sol}}^{-1}$	mmol $\text{kg}_{\text{sol}}^{-1}$
Fractional	-23.7	107.0 ± 1.0	12.2 ± 0.4	2.883 ± 0.011	1.064 ± 0.027	-6.8	-6.6
Full	-23.7	90.7 ± 3.9	16.5 ± 2.4	2.830 ± 0.055	1.257 ± 0.052	-23.2	-2.4
Fractional	-25.0	135.3 ± 0.4	9.7 ± 1.9	2.885 ± 0.038	1.069 ± 0.003	-9.3	-13.3
Full	-25.0	63.7 ± 3.8	20.6 ± 2.1	2.883 ± 0.027	2.276 ± 0.139	-80.9	-2.1

3.4. Hydrohalite solubility and saturation state

The brine–hydrohalite equilibrium was attained by dissolution between -14.3 and -22.0 °C in protocol-2 experiments (section 2.4), as evidenced by positive ΔCl^- (Table 6). In this temperature range, the $pK_{\text{sp,hydrohalite}}^*$ (Figure 3) and $\Omega_{\text{hydrohalite}}$ (Figure 4) increased from -1.175 to -1.107 and from 0.465 to 0.953 (Table 6), respectively, indicating a decrease in hydrohalite solubility with decreasing temperature at brine–hydrohalite equilibrium. During the protocol-3 experiments (section 2.4) at -23.7 and -25.0 °C, the ice–brine–hydrohalite equilibrium was attained by precipitation as evidenced by negative ΔCl^- values (estimated using FREZCHEM; see below and Table 6). The $pK_{\text{sp,hydrohalite}}^*$ increased sharply to -0.976 at -25.0 °C, representing a

dramatic decrease in hydrohalite solubility at $T \leq -22.9$ °C (Figure 3) in the fractional crystallisation pathway.

Because it was not possible to determine $\Omega_{\text{hydrohalite}}$ experimentally at -23.7 and -25.0 °C, the FREZCHEM code was used to compute the solution composition at ice–brine–mirabilite equilibrium at these temperatures by excluding hydrohalite and gypsum from the mineral database. At $T \leq -22.9$ °C, the $\Omega_{\text{hydrohalite}}$ increased steeply to 3.848 at -25.0 °C (Figure 4). Because the $pK_{\text{sp,hydrohalite}}^*$ from the experiments between -14.3 and -25.0 °C was in excellent agreement with that of the FREZCHEM model (Figure 3), the experimental values were combined with the FREZCHEM model output to derive the $pK_{\text{sp,hydrohalite}}^* - T$ relationship (eq. 1; Table 2).

4. Discussion

This section will associate the laboratory measurements of gypsum and hydrohalite solubilities to their dynamics within the natural sea ice environment. Discussing hydrohalite dynamics in this context highlights its role within the sea ice system as a mediator of physical sea ice properties, and its contribution to geochemical changes that add to physiological challenges imposed upon sympagic biota. Discussing gypsum dynamics in this context aids in elucidating the conditions in which it can precipitate and persist in sea ice, and allows evaluation of its potential as a marine deposit.

4.1. Gypsum solubility in seawater and sea ice brines between 0.2 and -22.2 °C

The consistency in $pK_{\text{sp,gypsum}}^*$ determined in both natural and synthetic sea ice brines between 0.2 and -5.0 °C (Figure 1 ; Table 3) indicates that, as with mirabilite solubility (Butler et al., 2016b), gypsum solubility is unaffected by parameters such as pH, carbonate and borate alkalinity, and trace metals within the measurement uncertainty. By considering solutions either at equilibrium, or supersaturated, or undersaturated with respect to mirabilite, gypsum solubility was measured mostly via dissolution, with measurements via precipitation possible on a few occasions, in a range of scenarios

Table 6: The absolute salinity (S_A) of incubated brines prior to seeding with hydrohalite (see footnote for exceptions), incubation temperature at point of sampling, Na^+ and Cl^- concentrations from each of the bottle incubations at equilibrium, the resulting measured $pK_{\text{sp,hydrohalite}}^*$ and $\Omega_{\text{hydrohalite}}$, and the change in Cl^- observed over the course of each experiment, included as a measure of reaction direction ($\Delta\text{Cl}^- = \text{Cl}_{\text{eqm}}^- - \text{Cl}_{\text{initial}}^-$). All data above -22.9°C are derived from dissolution of hydrohalite in solutions extracted from an ice–brine–mirabilite equilibrium system (see protocol-2, section 2.4). D = dissolution, P = precipitation. Tabulated errors are calculated as the standard deviation of measurements from triplicate experiments.

Exp. #	Reaction	S_A	T	Na^+		Cl^-		ΔCl^-
		$\text{g kg}_{\text{sol}}^{-1}$	$^{\circ}\text{C}$	mmol		$\text{kg}_{\text{sol}}^{-1}$	$pK_{\text{sp,hydrohalite}}^*$	$\Omega_{\text{hydrohalite}}$
H-14	D	173.8 ^a	-14.3	3596±26	4164±5	-1.175±0.003	0.465±0.003	1170
H-15	D	180.7 ^a	-15.1	3591±18	4159±8	-1.174±0.002	0.508±0.001	1022
H-16	D	187.8 ^a	-15.9	3503±20	4130±3	-1.160±0.003	0.568±0.004	857
H-17	D	200.2 ^a	-17.5	3403±33	4120±12	-1.147±0.003	0.672±0.006	632
H-18	D	201.3 ^a	-18.0	3398±35	4102±11	-1.144±0.004	0.693±0.004	579
H-21	D	218.7 ^a	-20.6	3181±28	4053±4	-1.110±0.002	0.886±0.003	189
H-22	D	225.9 ^a	-22.0	3173±40	4031±7	-1.107±0.003	0.953±0.001	87
H-24	P	225.3 ^{a,b}	-23.7	2720±36	4094±8	-1.047±0.004	2.037±0.001 ^c	-1359 ^c
H-25	P	225.3 ^{a,b}	-25.0	2274±22	4158±18	-0.976±0.005	3.848±0.011 ^c	-2747 ^c

^a S_A measured at brine–ice–mirabilite equilibrium.

^b Brine further cooled to target temperature, initiating ice and hydrohalite precipitation.

^c Estimated from brine–mirabilite equilibrium using FREZCHEM.

relevant to sea ice. It is noted that these incubations do not account for the effect of ikaite precipitation on the availability of Ca^{2+} within the sea ice brine system, but this effect is predicted to be relatively minor (Butler et al., 2016a).

The current measurements of the stoichiometric solubility product of gypsum (Figure 1) indicated that seawater and the ice–brine and ice–brine–mirabilite equilibrium systems between 0.2 and -22.2°C were all undersaturated with respect to gypsum, as reflected in the Ω_{gypsum} remaining below 1 (Figure 2). Exception to this trend is a narrow temperature range of metastable mirabilite supersaturation between -6.4°C and -8.2°C that concurs with gypsum supersaturation, which can lead to gypsum precipitation (see section 4.2 for further discussion).

The equilibrium Ca^{2+} as a function of temperature between -6.4 and

Figure 3: Measured $pK_{sp,hydrohalite}^*$ in equilibrium sea ice brines plotted alongside the output from the FREZCHEM model. The vertical line at -22.9 °C marks the point of which the solubility product begins to become affected by the precipitation of hydrohalite. All data above -22.9 °C are derived from dissolution of hydrohalite seed in solutions extracted from an ice–brine–mirabilite equilibrium system (see protocol-2, section 2.4).

490 -22.2 °C (Figure 5, top panel) reflects the increase by both physical con-
 491 centration of a cooling ice–brine system and the dissolution of the gypsum
 492 seed in the current experiments, the latter reaction leading to higher Ca^{2+}
 493 than in conservatively concentrated seawater-derived brine at each experi-
 494 mental temperature. In contrast, the decrease in equilibrium SO_4^{2-} between
 495 -6.4 and -22.2 °C reflects the imbalance between the processes that in-
 496 crease SO_4^{2-} , i.e., the physical concentration of the brine during cooling of
 497 the system and the dissolution of the gypsum seed during the experiments,
 498 and the removal of SO_4^{2-} from the brine before and during the solubility ex-
 499 periments via mirabilite precipitation (Figure 5, bottom panel). The Ca^{2+}
 500 at brine–mirabilite–gypsum equilibrium predicted by the FREZCHEM code

Figure 4: Measured $\Omega_{\text{hydrohalite}}$ in equilibrium sea ice brines plotted alongside the output from the FREZCHEM model. The vertical line at -22.9 °C marks the point of which the saturation state begins to become affected by precipitation of hydrohalite. The horizontal line at $\Omega_{\text{hydrohalite}} = 1$ is used to highlight the transition between undersaturation ($\Omega_{\text{hydrohalite}} < 1$) and supersaturation ($\Omega_{\text{hydrohalite}} > 1$). All data above -22.9 °C are derived from dissolution of hydrohalite in solutions extracted from an ice–brine–mirabilite equilibrium system (see protocol-2, section 2.4).

501 showed increasing deviation from the measured equilibrium concentrations
502 with decreasing temperature below -10 °C (Figure 5, top panel). This devia-
503 tion was not observed between the measured and modelled equilibrium SO_4^{2-}
504 (Figure 5, bottom panel). The close agreement between code output and ob-
505 servations as regards SO_4^{2-} reflects the mirabilite equilibrium ($\Omega_{\text{mirabilite}} = 1$)
506 via precipitation before and during the brine incubation with gypsum, the
507 latter fuelled by the excess SO_4^{2-} released into the brine via dissolution of the
508 gypsum seed and supported by synchrotron XRPD (sections 2.1 and 3.1).

509 Direct comparison of the measured $pK_{\text{sp,gypsum}}^*$ with values derived from
510 the FREZCHEM output (section 2.5; Figure 1) shows that the FREZCHEM-

511 derived values follow the same trend with temperature as the experimentally
 512 determined values, but the code overestimates the $pK_{\text{sp,gypsum}}^*$ by 0.069 ± 0.024
 513 throughout the investigated temperature range. Between 0.2 and -10.1 °C,
 514 FREZCHEM underestimated the equilibrium Ca^{2+} and SO_4^{2-} by 2.03 ± 0.98
 515 and 3.14 ± 3.05 mmol kg^{-1} , respectively (Figure 5). As mentioned above,
 516 between -10.1 and -22.2 °C, the FREZCHEM computation of the equilib-
 517 rium SO_4^{2-} was increasingly consistent with measurements, with deviations
 518 decreasing from 5.82 to 0.15 mmol kg^{-1} , as would be expected from the reli-
 519 able representation of measured mirabilite equilibria by the thermodynamic
 520 database of the code (Butler et al., 2016b). In contrast, the underestimation
 521 of equilibrium Ca^{2+} by the code increased from 1.54 to 25.33 mmol kg^{-1}
 522 between -10.1 and -22.2 °C. This discrepancy was also seen in the Ω_{gypsum}
 523 (Figure 2), with the FREZCHEM predictions consistently exceeding those
 524 based on the experimental values. Between 0.2 and -22.2 °C, the current
 525 experiments indicate that gypsum would not exceed saturation in the pres-
 526 ence of mirabilite in the sea ice brines but the FREZCHEM code shows two
 527 regions of gypsum supersaturation: first between -6.4 and -9.3 °C, and
 528 secondly at temperatures ≤ -17.3 °C (Figure 2).

529 Compared to its reliable computation of mirabilite (Butler et al., 2016b)
 530 and hydrohalite (Figures 3 and 4) dynamics in sea ice brines, the thermody-
 531 namic database of the FREZCHEM code yields gypsum dynamics in sea ice
 532 brines inconsistent with the dynamics determined here. The inconsistency is
 533 moreover particularly related to the modelled equilibrium Ca^{2+} between -10
 534 and -22.8 °C (Figure 5). To predict gypsum solubility in the sea ice brines
 535 presented here, FREZCHEM parameters have to be extrapolated into an
 536 experimentally unknown region since the majority of relevant experimental
 537 data has a minimum temperature of 0 °C (Marion and Farren, 1997; Mar-
 538 ion and Kargel, 2008; Raju and Atkinson, 1990; Marion et al., 2016). Such
 539 extrapolation is regularly applied at below-zero temperatures, and targeted
 540 experiments would help improve on the currently observed discrepancies with

541 respect to gypsum solubility at these temperatures.

542 4.2. Gypsum dynamics in metastable mirabilite supersaturation

543 The degree of gypsum supersaturation observed in brines that sustained
544 metastable supersaturation with respect to mirabilite ($\Omega_{\text{gypsum}} = 1.171$ at
545 -7.1 °C, and $\Omega_{\text{gypsum}} = 1.358$ at -8.2 °C) would be predicted by extrap-
546 olating the $\Omega_{\text{gypsum}} - T$ relationship observed at ice–brine equilibrium be-
547 tween -1.8 and -6.0 °C (Table 2, row 5) into this temperature region with
548 commensurate physical concentration of the brine (Figure 2, cross markers).
549 Thus, gypsum precipitation could occur in sea ice at temperatures below
550 -7 °C if nucleation and crystal growth conditions are more favourable for
551 this phase than for mirabilite. Even with gypsum precipitation under these
552 conditions, mirabilite will remain supersaturated. The further the tempera-
553 ture decreases below ~ -7.1 °C, the greater the tendency for mirabilite to
554 precipitate by homogeneous nucleation because its solubility in brines de-
555 creases sharply with decreasing temperature (Butler et al., 2016b) while that
556 of gypsum is essentially unchanging ($pK_{\text{sp,gypsum}}^* = 2.59$) between -6 and
557 -10 °C (Figure 1). Subsequent mirabilite nucleation and precipitation in
558 this temperature range will destabilize the gypsum completely. Therefore,
559 over the -6.4 °C to -22.2 °C temperature range, mirabilite precipitation
560 will dominate the compositional changes in the brine, with 92 % of SO_4^{2-}
561 removed from the brine as mirabilite by -20.6 °C (Butler et al., 2016b).

562 Collectively the current results do not support the results of Gitterman
563 (1937), who proposed gypsum to precipitate from synthetic seawater-derived
564 brines below approximately -15 °C. We instead propose that favourable
565 conditions for gypsum precipitation in sea ice between -7 and -22 °C are
566 entirely dependent on the occurrence of metastable mirabilite supersatura-
567 tion conditions, which are increasingly unlikely as the temperature decreases
568 within this range. The sea ice brine system will return to the ice–brine–
569 mirabilite equilibrium and become undersaturated with respect to gypsum
570 (Figure 2) once mirabilite authigenesis occurs. If gypsum precipitation oc-

571 curs via this mechanism in natural sea ice, its presence is therefore expected
572 to be transient in the presence of mirabilite.

573 *4.3. Fractional and full crystallisation pathways at -23.7 and -25.0 °C*

574 The more recent proposal for enhanced gypsum precipitation below -22.9 °C
575 (Marion et al., 1999) is relevant to the temperature region of hydrohalite pre-
576 cipitation, ice formation, and significant reduction in brine volume (Richard-
577 son, 1976; Butler and Kennedy, 2015), with consequent substantial shifts
578 in solution composition and inter-ionic ratios, particularly with respect to
579 Na^+ , K^+ , Mg^{2+} and Ca^{2+} (Table 7). The precipitation of gypsum in the
580 fractional and full crystallisation experiments was observed to occur over
581 weeks, in accord with the slow kinetics of sulphate minerals at cold temper-
582 atures (Kargel, 1991; Hogenboom et al., 1995; Marion and Kargel, 2008).
583 The gypsum solubility experiments at -23.7 and -25.0 °C considered rep-
584 resentative of the fractional crystallisation pathway (section 2.4), indicated
585 that this compositional change is sufficient for the brine to become slightly
586 supersaturated with respect to gypsum, resulting in its seeded precipitation
587 (Table 5 and section 3.3). And so, the sea ice system appears to sustain a
588 low gypsum supersaturation in the fractional crystallisation pathway within
589 the ice–hydrohalite aggregate. In the tandem experiments, considered repre-
590 sentative of the full crystallisation pathway, the presence of both mirabilite
591 and gypsum seed in the experimental brine yielded mirabilite dissolution
592 and gypsum precipitation in higher amounts than observed in the absence
593 of mirabilite (Table 5 and section 3.3). These observations collectively indi-
594 cate that, when all potential minerals are in contact with the brine in a sea
595 ice system (full crystallisation pathway) at these cold temperatures, a posi-
596 tive feedback will occur for gypsum precipitation via mirabilite dissolution in
597 the presence of hydrohalite, as was also observed by Gitterman (1937) and
598 Marion et al. (1999).

599 Combining the maximum amount of gypsum precipitation measured here
600 at -25.0 °C ($\Delta\text{Ca}^{2+} = 80.9$ mmol kg^{-1} during full crystallisation; Table 5)

Figure 5: The equilibrium Ca^{2+} and SO_4^{2-} concentrations in sea ice brines between 0.2 and -22.8 °C. Measured and modelled (FREZCHEM) values above -6.4 °C are at brine–gypsum equilibrium, and those below -6.4 °C are at brine–mirabilite–gypsum equilibrium. The vertical line at -1.8 °C marks the point at which coupled changes in salinity and temperature occur as a result of freezing, whilst that at -6.4 °C marks the onset of mirabilite precipitation. The dashed line represents the estimated concentration based on a conservatively concentrated solution at ice–brine equilibrium, computed using FREZCHEM with only ice enabled in the mineral database.

with the FREZCHEM estimate of the residual brine mass at this temperature in a closed sea ice system (no brine drainage) from a starting practical salinity of 35 g kg^{-1} (64.9 g of brine per kg frozen seawater), we estimate a maximum gypsum concentration in bulk sea ice of 0.9 g kg^{-1} at $-25.0 \text{ }^{\circ}\text{C}$. In comparison, the estimated concentrations of mirabilite and hydrohalite in undrained bulk sea ice at the same temperature and full crystallisation pathway are 6.7 and 28.6 g kg^{-1} , respectively.

4.4. *Hydrohalite solubility in sea ice brines*

The excellent agreement between the experimentally determined $pK_{\text{sp,hydrohalite}}^*$ and that computed by FREZCHEM reflects the abundance of experimental data for hydrohalite used to parameterise the model. All experimental (Gitterman, 1937; Nelson and Thompson, 1954; this study) and model (Marion et al., 1999; Marion and Kargel, 2008) evidence is in agreement that hydrohalite precipitates in sea ice at $T \leq -22.9 \text{ }^{\circ}\text{C}$, but its dynamics in undersaturated sea ice brines have never been investigated before. Between -14 and $-25 \text{ }^{\circ}\text{C}$, the solubility of hydrohalite (Figure 3) displays two distinct temperature fields corresponding with the undersaturated and supersaturated brines (Figure 4), with a sharp inflection at $\Omega_{\text{hydrohalite}} = 1$. This sharp change is reflected in the quantity of hydrohalite in a closed sea ice brine system (no brine drainage), which, by $-23.0 \text{ }^{\circ}\text{C}$, i.e., $0.1 \text{ }^{\circ}\text{C}$ into the temperature region in which its precipitation is viable in sea ice systems, amounts to 3.3 g kg^{-1} , and increases to 28.0 g kg^{-1} by $-26.0 \text{ }^{\circ}\text{C}$ (fractional crystallisation; Figure 6). Such quantities of hydrohalite are consistent with the formation of an ice–hydrohalite aggregate (Light et al., 2009; McCarthy et al., 2007; Butler and Kennedy, 2015).

Prior to the onset of hydrohalite precipitation, Na^+ and Cl^- comprise 91.7% of the total mass of dissolved ions in the brine (FREZCHEM computation, Table 7). Upon hydrohalite precipitation, the reduced ionic strength of the brine from the removal of Na^+ and Cl^- as hydrohalite promotes instantaneous ice formation to re-establish ice–brine equilibrium at these cold

Table 7: FREZCHEM predictions of the major brine composition before ($-22.8\text{ }^{\circ}\text{C}$) and after ($-26.0\text{ }^{\circ}\text{C}$) hydrohalite precipitation. Each ion is presented as its percentage contribution to the mass of total salt. The output at $-26.0\text{ }^{\circ}\text{C}$ is for fractional crystallisation, which retains the brine at undersaturation with respect to mirabilite. The displayed percentages are implicit of less concentrated ions that are also specified in the composition of Standard Seawater (Millero et al., 2008), which include HCO_3^- , CO_3^{2-} , NO_3^- , Br^- , $\text{B}(\text{OH})_4^-$, F^- and CO_2 . Ice, mirabilite and hydrohalite were the only solid phases enabled in the FREZCHEM database for this computation.

Ion	$-22.8\text{ }^{\circ}\text{C}$	$-26.0\text{ }^{\circ}\text{C}$
	$S_A = 230.82\text{ g kg}_{\text{sol}}^{-1}$	$S_A = 235.68\text{ g kg}_{\text{sol}}^{-1}$
% Na^+	29.89	20.00
% K^+	1.36	2.91
% Mg^{2+}	4.36	9.31
% Ca^{2+}	1.38	2.95
% Cl^-	61.77	64.59
% SO_4^{2-}	0.62	1.06

temperatures, which concentrates the brine and results in further hydrohalite precipitation. This cycle of both ice and hydrohalite formation in tandem continues until ice–brine–hydrohalite equilibrium is attained; in the process, the volume of remaining brine diminishes. Between -22.8 and $-26\text{ }^{\circ}\text{C}$ in a closed system modelled with FREZCHEM (1 kg of seawater, practical salinity = 35), the amount of ice increases from 857 g to 909 g, which decreases the amount of liquid water from 105 to 41 g (Figure 7). In sea ice, this would equate to a reduction in brine volume by more than 60 % within a $3\text{ }^{\circ}\text{C}$ drop in temperature.

If hydrohalite precipitation in sea ice results in the formation of an ice–hydrohalite aggregate, then the in-situ properties of this solid may be analogous to those studied in the $\text{NaCl-H}_2\text{O}$ system at its eutectic (McCarthy et al., 2007). The formation of an ice–hydrohalite aggregate may act as a hindrance for the hydrohalite–mirabilite–gypsum interaction with the residual brine of the full crystallisation pathway (Gitterman, 1937; Marion et al., 1999). Mirabilite crystals are understood to sink to the bottom of brine inclusions (Light et al., 2003); when hydrohalite forms as an aggregate with ice

with the residual brine trapped in it, it will fill the available pore space and can consequently restrict further brine–mirabilite interaction. The result is a microstructure with very limited mixing and surface area for brine–mineral interaction, acting to limit the dissolution of mirabilite and the consequently enhanced precipitation of gypsum. Although the hydrohalite–mirabilite feedback was observed by Butler and Kennedy (2015), their experimental protocol required continual spinning of the sample, which may have promoted mineral interaction with brine by mixing as the sample warmed and cooled. The determination of which crystallisation pathway occurs in the temperature field of hydrohalite precipitation in natural sea ice conditions requires further investigation, and would likely require in-situ measurements in controlled laboratory conditions that replicate those in sea ice.

4.5. *Hydrohalite modelling in first-year sea ice*

The dynamics of hydrohalite in first-year sea ice are outlined here based on the FREZCHEM output, confirmed by the current hydrohalite solubility data, and a 1D empirical model of sea ice growth and desalination. The FREZCHEM output of the mass of hydrohalite to precipitate in a 1 kg parcel of frozen seawater (Figure 6) was fitted to a stepwise polynomial function of temperature (Table 2, rows 11 and 12). This data was integrated (via equation 2) into a 1D model simulation of the vertical temperature and salinity profiles of snow-free first-year sea ice in the Arctic Basin as it grows over winter months, yielding hydrohalite concentration profiles within the ice pack at selected intervals (Figure 8). The temperature at the surface of the modelled ice pack drops below $-22.9\text{ }^{\circ}\text{C}$ after 1 month (early November) from the onset of freezing when the ice pack is 73.5 cm thick and the incoming shortwave radiation for the region is 0 W m^{-2} . Between early November and late February, the modelled ice pack thickens to 210 cm, while the surface temperature decreases to $-32.1\text{ }^{\circ}\text{C}$. Given the absence of sunlight and low temperatures, these conditions likely represent the most challenging and least studied aspects of Arctic sea ice dynamics.

Figure 6: The weight of hydrohalite predicted to precipitate from 1 kg of seawater (practical salinity = 35) between -22.9 and -36 °C (fractional crystallisation). Also plotted is the fitted relationship of hydrohalite concentration (g kg^{-1}) as a function of temperature (using equation 1) described by coefficients given in Table 2.

As the ice pack thickens and the surface temperature decreases, the modelled hydrohalite concentration increases (Figure 8). When the ice pack is 75 cm thick, hydrohalite is only present in the upper 1 cm but, as the winter progresses, the vertical distribution of hydrohalite extends well below the ice surface, and by mid-February, when the ice is over 2 m thick, hydrohalite is present within the upper 65 cm. The depth distribution of hydrohalite in the ice is governed by the bulk sea ice salinity and the temperature-related solubility changes leading to precipitation (Figure 6), while the sea ice temperature is assumed to have a linear depth distribution between the ice-air and ocean-ice interfaces (Cox and Weeks, 1988; Butler et al., 2016b). As a result of these two forcings, hydrohalite develops an S-shaped depth profile as the ice pack grows, reaching a maximum concentration below the ice-air

Figure 7: FREZCHEM predictions of the change in ice and water content in 1 kg of frozen seawater (practical salinity = 35) between -14 and -26 °C (fractional crystallisation). The vertical line at -22.9 °C marks the point of which the system begins to become affected by precipitation of an ice–hydrohalite aggregate.

690 interface of 9.9 g kg^{-1} .

691 Based on its solubility–temperature relationship (Figures 3, 4 and 6),
 692 the occurrence of hydrohalite in sea ice could display considerable daily
 693 or localised shifts between precipitation and dissolution in response to lo-
 694 cal weather patterns. Given that hydrohalite precipitation did not initiate
 695 within the modelled ice pack until incoming shortwave radiation had reduced
 696 to 0 W m^{-2} , its contribution to the albedo feedback mechanism (Light et al.,
 697 2004; Carns et al., 2015) in polar environments seems limited, and is likely to
 698 be more relevant to the energy balance of ‘Snowball Earth’ during the Neo-
 699 proterozoic (Light et al., 2009; Carns et al., 2015). Furthermore, the winter
 700 conditions in which hydrohalite precipitates likely hinder its identification
 701 and the examination of its dynamics in the sea ice system in the field.

Figure 8: Modelled hydrohalite concentrations during the formation of first-year snow-free sea ice in the Arctic Basin. The full depth of the ice pack is not displayed, but is instead annotated at each increment.

4.6. The occurrence of gypsum in sea ice

The available mirabilite (Butler et al., 2016b), gypsum, and hydrohalite solubility data (this study) can be used to evaluate the potential for occur-

705 rence of gypsum in sea ice. The tendency of gypsum formation is strongly
 706 constrained by SO_4^{2-} availability in the brine, first, due to mirabilite precip-
 707 itation at temperatures ≤ -6.4 °C and, subsequently, via mirabilite disso-
 708 lution at temperatures ≤ -22.9 °C. The recent identification of gypsum in
 709 experimental and natural sea ice at temperatures between -1.9 and -10 °C
 710 (Geilfus et al., 2013) is not consistent with the systematic gypsum undersat-
 711 uration observed here between 0.2 and -22.2 °C in the presence of mirabilite
 712 (section 4.1 and Figure 2). Furthermore, the gypsum crystals identified in
 713 the experimental sea ice formed during the freezing of synthetic seawater that
 714 was deficient in Ca^{2+} and SO_4^{2-} by 17 % and 40 %, respectively, relative to
 715 Standard Seawater (Geilfus et al., 2013). The deficiency of this solution with
 716 respect to the ionic constituents of gypsum would only act to impede this
 717 mineral from attaining saturation within the brine in the reported tempera-
 718 ture range that includes the temperature region of mirabilite precipitation.
 719 Our experiments showed that brines in metastable mirabilite supersatura-
 720 tion state can attain low gypsum supersaturation leading to precipitation of
 721 this CaSO_4 polymorph in small amounts, which will be likely transient in
 722 the presence of mirabilite given its dominant control on the availability of
 723 sulphate ions in the brine. It is possible that the brief storage (< 3 hours) of
 724 sea ice samples < -25 °C prior to analysis carried out by Geilfus et al. (2013)
 725 allowed gypsum precipitation, which could become enhanced if hydrohalite-
 726 mirabilite-gypsum interaction with brine is facilitated, but the quantity of
 727 gypsum formed in this way would be small ($< 0.3 \text{ g kg}_{\text{sea ice}}^{-1}$ at a bulk salinity
 728 of 12 g kg^{-1}) even if chemical equilibrium is attained.

729 Finally, the gypsum crystals that were observed in experimental and
 730 natural sea ice (Geilfus et al., 2013) may not have been authigenic but al-
 731 lochthonous. Though the gypsum crystals were identified as authigenic based
 732 on their grain morphology (Geilfus et al., 2013), gypsum is also a common
 733 mineral in aerosol particles (Prospero et al., 1981; Schütz and Seibert, 1987;
 734 Zimmermann et al., 2008) which are understood to be the source of its pres-

ence in ice cores taken from the Greenland Ice Sheet (Biscaye et al., 1997; Steffensen, 1997). Gypsum can persist in an ice sheet due to its sparing solubility in aqueous solutions (Steffensen, 1997). Therefore, gypsum may not occur authigenically in brine inclusions but in aerosols settling on, and encapsulated in, sea ice, and may be sufficiently stable kinetically to allow extraction and identification even when the conditions in the brine pockets are undersaturated with respect to gypsum. Given this generated understanding about gypsum dynamics in sea ice from solubility measurements, particularly with respect to its undersaturation in all conditions above -6.4 °C, its potential as a marine deposit in polar seas (Geilfus et al., 2013) seems limited.

5. Conclusions

The determination of gypsum and hydrohalite solubilities in seawater (gypsum) and seawater-derived brines (gypsum and hydrohalite) allowed investigation of the dynamics of each mineral within the sea ice system. Gypsum solubility changed substantially between 0.2 and -25.0 °C, displaying maximum solubility (i.e., minimum values for the stoichiometric equilibrium solubility product) in the temperature range from -6 °C to -10 °C, with decreasing solubility at warmer and colder temperatures. The precipitation of gypsum is affected by the precipitation of mirabilite at temperatures below -6.4 °C. When mirabilite is the dominant SO_4^{2-} sink in sea ice, the brines remain undersaturated with respect to gypsum to -22.2 °C. Gypsum is viable as a transient phase in conditions of metastable mirabilite supersaturation as observed in this study at -7.1 and -8.2 °C but potentially applicable to occurrences of increased metastable mirabilite supersaturation at colder temperatures. Upon the onset of hydrohalite precipitation at temperatures below -22.9 °C, gypsum can precipitate and, when the brine–mirabilite reaction is viable in these cold temperatures, mirabilite dissolution consequent on hydrohalite precipitation can enhance the amount of gypsum precipitate

764 to approximately 0.9 g kg^{-1} (closed seawater system) at $-25.0 \text{ }^{\circ}\text{C}$.

765 The solubility of hydrohalite in sea ice decreases with temperature, and
766 this decrease displays a sharp change at $-22.9 \text{ }^{\circ}\text{C}$, resulting in distinct tem-
767 perature fields of undersaturated and supersaturated brines. The sharp
768 change in hydrohalite solubility at temperatures below $-22.9 \text{ }^{\circ}\text{C}$ results from
769 the formation of an ice–hydrohalite aggregate. During this process, ice and
770 hydrohalite form cooperatively as an intergrowth, likely displaying similar
771 properties to the eutectic aggregates from binary $\text{NaCl-H}_2\text{O}$ systems (Mc-
772 Carthy et al., 2007). This heterogeneous mixture can fill the sea ice pores
773 and channels, and results in strong compositional changes in the little brine
774 that remains at these cold temperatures, affecting the microstructure of the
775 ice substantially.

776 The observed gypsum solubility is consistently underestimated by the
777 thermodynamic FREZCHEM code. This inconsistency was assessed here to
778 be associated with the discrepancy in the equilibrium Ca^{2+} concentration,
779 likely due to the model being extrapolated into an experimentally unknown
780 region. In contrast the measured and FREZCHEM-based hydrohalite sol-
781 ubilities display excellent agreement (within experimental error). Based on
782 the reliable FREZCHEM output of hydrohalite equilibria, a temperature
783 function of the hydrohalite mass in a closed sea ice system was incorporated
784 into a 1D model for the growth of Arctic sea ice. The model output of the
785 distribution of hydrohalite with time and depth in sea ice showed that hydro-
786 halite should be present in the upper layers of the ice pack once the incoming
787 shortwave radiation drops to 0 W m^{-2} , extending down to a depth of 65 cm
788 in the ice from a 9.9 g kg^{-1} surface concentration maximum at maximal
789 ice thickness. This suggests a critical role for hydrohalite in modifying the
790 physical and chemical properties of the sea ice brine inclusions but limited
791 hydrohalite effect on the albedo of sea ice.

792 Acknowledgements

793 The work was supported by a NERC Algorithm Studentship (NE/K501013),
794 beamtime awards EE-3897-1, EE-12301-01 and EE14575-1 from Diamond
795 Light Source Ltd., and a PhD Student Grant from the International Asso-
796 ciation of Geochemistry. We thank the two anonymous reviewers for their
797 constructive comments, which helped to improve this paper. All data pre-
798 sented here are freely available upon contacting the corresponding author.

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