



- 1 New observations of the distribution, morphology, and dissolution dynamics of
- 2 cryogenic gypsum in the Arctic Ocean

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Abstract

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13 To date observations on a single location indicate that cryogenic gypsum (Ca[SO₄]·2H₂O) may 14 constitute an efficient but hitherto overlooked ballasting mineral enhancing the efficiency of 15 the biological carbon pump in the Arctic Ocean. In June-July 2017 we sampled cryogenic gypsum under pack-ice in the Nansen Basin north of Svalbard using a plankton net mounted 16 on a Remotely Operated Vehicle (ROVnet). Cryogenic gypsum crystals were present at all 17 18 sampled stations, which suggested a persisting cryogenic gypsum release from melting sea ice 19 throughout the investigated area. This was supported by a sea ice backtracking model that 20 indicated that gypsum release was not related to a specific region of sea ice formation. The 21 observed cryogenic gypsum crystals exhibited a large variability in morphology and size, with 22 the largest crystals exceeding a length of 1 cm. Preservation, temperature and pressure 23 laboratory studies revealed that gypsum dissolution rates accelerated with increasing 24 temperature and pressure, ranging from 6% d1 by mass in Polar Surface Water (-0.5 °C) to 81% d¹ by mass in Atlantic Water (2.5 °C at 65 bar). When testing the preservation of gypsum 25 26 in Formaldehyde-fixed samples we observed immediate dissolution. Dissolution at warmer 27 temperatures and through inappropriate preservation media may thus explain why cryogenic 28 gypsum was not observed in scientific samples previously. Direct measurements of gypsum 29 crystal sinking velocities ranged between 200 and 7000 m d-indicated that gypsum-loaded 30 marine aggregates could rapidly sink from the surface to abyssal depths, supporting the 31 hypothesised potential as a ballasting mineral in the Arctic Ocean.

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Keywords:

34 Cryogenic gypsum, Arctic Ocean, mineral ballasting. biological carbon pump, sea ice.





36 1 Introduction

37	Climate change in the Arctic Ocean has led to a drastic reduction of summer sea ice extent as
38	well as to a significant thinning of the sea ice (Kwok, 2018; Kwok and Rothrock, 2009). Sea
39	ice strength has reduced, and increased deformation and fractionation result in a progressively
40	increasing sea ice drift speed (Docquier et al., 2017) and sea ice export. Over the past decades
41	the ice export via the Fram Strait alone has increased by 6% and 11% per decade as annual
42	mean, and during the productive spring and summer period, respectively (Smedsrud et al.,
43	2017). An increasing amount of sea ice produced in the East Siberian and Laptev Sea melts
44	over the adjacent continental slopes or in the central Arctic Ocean (Krumpen et al., 2019).
45	Overall, the Arctic Ocean sea ice cover has shifted to a predominantly seasonal ice cover.
46	However, although the majority of sea ice diminishes during late summer, the amount of sea
47	ice produced in autumn to winter progressively increases (Kwok, 2018).
48	Large-scale transformations in the seasonal sea ice cover impact the physical, chemical and
49	biological dynamics of the sea ice-ocean system. However, especially the interactions of
50	physical-chemical processes within the sea ice and pelagic to benthic biological processes
51	have only received little attention. Of particular importance are poorly soluble minerals
52	precipitated within the brine channels of sea ice which, once released, may ballast organic
53	material sinking to the sea-floor. The changing icescape with more leads and the thinner
54	Arctic sea ice allows increasing light penetration into the under-ice surface water (Katlein et
55	al., 2015; Nicolaus et al., 2013; Nicolaus et al., 2012), supporting fast-growing and often
56	massive under-ice phytoplankton blooms (Arrigo et al., 2012; Arrigo et al., 2014; Assmy et
57	al., 2017). A recent study reported on a sudden export event of an under-ice bloom of the
58	'unsinkable alga' Phaeocystis, caused by the ballasting effect of cryogenic gypsum released
59	from melting sea ice (Wollenburg et al., 2018a). This single event was the first and only
60	report of cryogenic gypsum release in the Arctic Ocean. Moreover, this sea ice precipitation
61	of cryogenic gypsum has never been recorded in Arctic sediments, sediment traps or other
62	field studies.
63	When sea ice forms, the concentrations of dissolved ions in brine increase, and depending on
64	the temperature of sea ice, a series of minerals (ikaite, mirabilite, hydrohalite, gypsum,
65	$hydrohalite, sylvite, MgCl_{:}, Antarcticite)\ precipitate\ (Butler, 2016;\ Butler\ and\ Kennedy, 2015;$
66	Geilfus et al., 2013; Golden et al., 1998; Wollenburg et al., 2018a). Once released into the

ocean, gypsum seems to be the most stable of the cryogenic precipitates (Butler et al., 2017;





69 et al. (Geilfus et al., 2013), in a comprehensive work on the chemical, physical, and 70 mineralogical aspects of its precipitation in experimental and natural sea ice off Greenland. 71 According to FREZCHEM, a chemical-thermodynamic model that was developed to quantify 72 aqueous electrolyte properties at sub-zero temperatures, cryogenic gypsum can precipitate at 73 temperatures below -18 °C, and within a small temperature window between -6.5 and -8.574 °C (Geilfus et al., 2013; Marion et al., 2010; Wollenburg et al., 2018a). However, 75 measurements on the stoichiometric solubility products showed that gypsum dynamics in ice-76 brine equilibrium systems strongly depend on the solubility and precipitation of hydrohalite 77 and mirabilite (Butler, 2016; Butler et al., 2017). So far gypsum precipitation in experimental 78 setups were only observed at temperatures between -7.1 and -8.2 °C, and not in the lower 79 temperature range (Butler, 2016; Butler et al., 2017). Moreover, as Arctic sea ice rarely 80 reaches temperatures lower than -18 °C, cryogenic gypsum is more likely precipitated within 81 the higher temperature window in the Arctic Ocean (Wollenburg et al., 2018a). 82 A model applied to understand the gypsum release event of 2015 showed that the ice flow 83 was to warm when it started to form and identified December to February as the most likely 84 time span for gypsum precipitation (Wollenburg et al., 2018a). Due to the absence of a 85 downward brine flux in this advanced phase of sea ice formation, gypsum crystals likely 86 remain trapped in the ice until spring. In the absence of sufficient field observations gypsum release from sea ice is expected to peak at the beginning of the melting season, when sea ice 87 warms to temperatures above -5 °C. This temperature marks the transition in the fluid 88 89 transport capacities of sea ice allowing brine water and included crystals to be released into 90 the water column (Golden et al., 1998). However, in lack of any extensive, best year-round 91 field studies our knowledge depends on models, kinetics and two single field observations 92 (Geilfus et al., 2013; Wollenburg et al., 2018a). There are no studies on sea ice-derived 93 cryogenic gypsum crystal morphologies and its stability in seawater. It is unclear whether 94 gypsum just precipitates during the assumed peak in December to February or whether it continues to grow from remaining brines during sea ice drift. We therefore need more studies 95 96 on the formation and release of cryogenic gypsum to assess its impact on biogeochemistry in 97 the Arctic and sub-Arctic. 98 In this study, we systematically investigated the occurrence of cryogenic gypsum release from 99 sea ice in spring 2017 with special emphasis on the overall appearance of the crystals. 100 Varieties of cryogenic gypsum crystal morphologies are described and illustrated. The

Strunz and Nickel, 2001). Sea ice derived cryogenic gypsum was firstly described by Geilfus



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sampled gypsum crystals were further subjected to various laboratory experiments. Hereby, the dissolution behaviour over typical depth- and temperature ranges of the Arctic water column, in Formaldehyde solution typically used in biological sampling were investigated and the sinking speed of gypsum crystal measured. These experiments were conducted to answer the question, why cryogenic gypsum has not previously been observed in field studies and if it qualifies as ballast mineral. 2 **Material and Methods** 2.1 Gypsum sampling with the ROVnet and on-board treatment RV Polarstern expedition PS 106 (June-July 2017) in the early melting season gave the opportunity to systematically study the occurrence of cryogenic gypsum release and the overall appearance of crystals in the area north of the Svalbard and on the Barents Sea shelf (Fig. 1A; Table 1). Cryogenic gypsum was sampled from the upper 10 m of the under-ice water at four stations distributed throughout the expedition area (Fig. 1A; Table 1). The first part of the expedition (PS106/1) consisted of a drift study to the north of Svalbard, during which the vessel was anchored to an ice floe (station 32). This ice floe was revisited 6 weeks later at the end of the expedition (PS106/2) (station 80). During the second part of the expedition (PS106/2), cryogenic gypsum was collected over the western Barents Sea (station 45) and in the Nansen Basin to the north-east of Svalbard (station 66). Gypsum crystals were sampled with a plankton net mounted on a remotely operated vehicle (ROVnet). The ROVnet consists of a Polycarbonate frame with an opening of 40 cm by 60 cm, to which a zooplankton net with a mesh size of 500 µm was attached (Flores, 2018). For gypsum sampling, a handmade nylon net with an opening of 10 cm by 15 cm and a mesh size of 30 μ m was mounted in the zooplankton net opening. The concentrated particulate material of the small nylon net was collected in a 2 L polyethylene bottle attached to the cod end of the net. A gauze-covered window in the cod-end bottle allowed seawater to drain off. Both nets were mounted on the aft end of a M500 (Ocean Modules, Sweden) observation class ROV carrying an extensive

sensor suite described in Katlein et al. (Katlein et al., 2017). After each ROVnet deployment,





131 the nets were rinsed with ambient sea-water to concentrate the sample in the cod end of the 132 net. The ROVnet sampled horizontal profiles in the water directly below the sea ice. Standard 133 ROVnet profiles were conducted at the ice-water interface, at 5 m and at 10 m depth. The 134 distance covered by each profile ranged between 300 and 600 m. At station 32, the 10 m profile was aborted due to technical failure, and at station 80 no 5 m profile was sampled due 135 136 to time constraints, and the subsurface sample was discarded due to handling failure (Table 137 1). 138 The concentrated particulate material collected in the cod-end bottle of the gypsum sampling net was mixed with a sample equivalent volume of 98% ethanol, and stored at 4 °C until 139 140 further analyses (Wollenburg et al., 2018a). 141 At ROVnet sampling stations, ice thickness was estimated through thickness drill holes with a 142 tape measure. To characterize the properties of the ice floes sampled on the floe-wide scale, ice thickness surveys were conducted at each sampling station with a GEM2 (Geophex) 143 144 electromagnetic induction ice-thickness sensor (Katlein et al., 2018). 145 2.2 **Initial analyses of ROVnet samples** 146 In the home laboratory the samples were rinsed onto a 32 μ m mesh using fresh water. The samples were then oven-dried at 50°C for 20 hours. The remaining crystals were transferred 147 148 into pre-weighed micropaleontological slides, and their weight was determined with a highprecision Sartorius SE2 ultra-microbalance. Under a Zeiss Axio Zoom V16 microscope, 149 150 pictures were taken with an Axiocam 506 colour camera. We made both overview images of the whole sample and detailed images of individual crystals. From all samples and crystal 151 152 morphologies, individual crystals were analysed using Raman microscopy, which confirmed 153 that the crystals were gypsum (Wollenburg et al., 2018a). As in some samples both, very large 154 and very small crystals (Figs. S3-S4) were observed, the >32 μ m samples were dry-sieved 155 over a 63 μ m analysis sieve. The length and width of the cryogenic gypsum crystals in the 156 size fractions $>32<63 \mu m$ and $>63 \mu m$ was determined with the software application ImageJ on 50 crystals in each sample and size fraction (Schneider et al., 2012) (Tab. 2). 157 158 2.3 Initial analyses of ice cores 159 At all ice stations, sea ice cores for archive purposes and for further measurement of bottom 160 communities were drilled with a 9 cm diameter ice corer (Kovacs Enterprise) and stored at -





162 cores from station 45 were studied to investigate the gypsum crystal morphologies within sea 163 ice. Each section was transferred into a measuring jug with lukewarm tap water for approx. 164 two seconds, and then the jug was emptied over a 32 μ m analysis sieve, and repeatedly 165 refilled. This process was continued until all ice was melted. With the aid of a hand shower and a wash bottle the residue on the sieve was rinsed and transferred into a 30 μ m mesh-166 167 covered funnel, dried and transferred into a micropaleontological picking tray for inspection and documentation. For storage, the residue was transferred into pre-weighed labelled 168 169 micropaleontological slides. 170 2.4 **Dissolution experiments** 171 The aim of our dissolution experiments was to investigate the persistence of gypsum crystals 172 against dissolution in the Arctic water column (water mass trials) and under common biological sample treatment (Formaldehyde trial). 173 174 Dissolution experiments were carried out on individual gypsum crystals collected from 175 ROVnet samples. Hereby, 5 cryogenic gypsum crystals with different crystal morphologies, 176 and from both size fractions were used in each reaction chamber. Before the start and after the 177 termination of each experiment, pictures of the cryogenic gypsum crystals used were taken 178 with an Axiocam 506 colour camera under a Zeiss Axio Zoom V16 microscope. The weight 179 of the crystals before and after each treatment was determined with a high-precision Sartorius 180 SE2 ultra-microbalance after they had been transferred into a pre-weighted silver boat. The experimental running time of each experiment was 24 hours. 181 182 2.4.1 Water mass trials 183 The experiments to simulate dissolution within the different water masses and hydrostatic 184 pressure regimes of the Arctic Ocean were carried out with high-pressure chambers installed in a cooling table (Wollenburg et al., 2018b). With a high-pressure pump (ProStar218 Agilent 185 186 Technologies), peak tubing, and multiple titanium valves a continuous isobaric and isocratic 187 one-way seawater flow of 0.3 ml/min was directed through a set of four serially arranged 188 high-pressure chambers each with an internal volume of 0.258 ml (Wollenburg et al., 2018b). 189 This setup allowed for dissolution experiments at defined pressures and temperatures 190 (Wollenburg et al., 2018b). For the experiments, we used sterile-filtered (0.2 µm mesh) North 191 Sea water that was adjusted to a salinity of 34.98 by addition of 1 g Instant Ocean® sea salt

20°C (Peeken, 2018). One ice-core from station 80 and four bottom slices (10 cm) of ice-



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192 per L and psu-offset. The natural pH of 8.1 after equilibration to the refrigerator's atmosphere 193 (at 2.5 °C and at atmospheric pressure), lowers to pH 8.05 at 2.5 °C at 150 bar (Culberson and 194 Pytkowicx, 1968). Five experiments, with 4 high-pressure chambers were carried out. The 195 Polar Surface (PSW) water corresponding experimental trial was running at -0.5 °C and 3 bar, the experimental Atlantic Water (AW) trial at +2.5 °C and 65 bar, and three experimental 196 197 Deep Water trials were conducted at -1 °C and 100, 120 and 150 bar, respectively. 198 2.4.2 Formaldehyde trial 199 To study the effect of Formaldehyde treatment on cryogenic gypsum, the crystals were 200 subjected to a Formaldehyde solution of 4% in seawater, which is commonly used to preserve 201 biological samples. The stock solution consisted of 500 ml Formaldehyde concentration of 202 40%, 500 ml aqua dest. and 100 g hexamethylenetetramine, adjusted to a pH of 7.3-7.9. 203 Aliquots of the 20% stock solution were added to the four-fold volume of artificial Arctic 204 Ocean sea water to obtain a final concentration of 4%. 205 The Gypsum crystals were transferred into Falcon Tubes, and the 4% Formaldehyde solution 206 was added. The Falcon tubes were then either stored at 3 °C, or at room temperature. After 207 the experiments, the gypsum crystal-Formaldehyde suspension was washed with deionized 208 water over a 10 μ m mesh using a wash bottle, and dried on gauze. As in all formaldehyde 209 trials all gypsum dissolved, no post-experimental weight was determined. 210 211 2.5 Size-specific settling velocities of gypsum 212 213 The size-specific sinking velocity of cryogenic gypsum was measured in a settling cylinder 214 (Ploug et al., 2008). The cylinder (30 cm high and 5 cm in diameter) was filled with filtered 215 seawater (salinity 32) and surrounded by a water jacket for thermal stabilization at 2 °C. The 216 settling cylinder was closed at both ends, only allowing insertion of a wide-bore pipette at the 217 top. Immediately before measurement, the gypsum was submerged into seawater with a 218 salinity of 32 and a temperature of 2 °C, and then transferred to the settling cylinder with a 219 wide-bore pipette. The gypsum crystals were allowed to sink out of the wide-bore pipette, 220 which was centered in the cylinder. The descent of the pellets was recorded by a Basler 4 221 MPixel Ethernet camera equipped with a 25 mm fixed focal lens (Edmund Optics). The 222 settling column was illuminated from the sides by a custom-made LED light source. The 223 camera recorded 7 images per second as the gypsum crystals sank through the settling

column. The setup was calibrated by recording a length scale before sinking velocity

measurements. The size and settling of the individual gypsum crystals was determined with





the image analysis software ImageJ. This was done by using the projected area of the crystals

227 to calculate the equivalent spherical diameter and the distance traveled between the

228 subsequent images to determine the sinking velocity of the individual crystals (Iversen et al.,

229 2010)

230 We calculated the excess density $(\Delta \varrho)$ ($\Delta \varrho$ = gypsum density – water density) of the crystal

231 from the Stokes drag equation:

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$$\Delta \rho = \frac{c_D \rho_w S V^2}{\frac{4}{3} g E S D} \tag{1}$$

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where $C_{\scriptscriptstyle D}$ is the dimensionless drag force (equation 2), $\varrho_{\scriptscriptstyle W}$ is the density of seawater (1.0256 g

236 cm³, for a salinity of 32 at 2 °C), SV is the measured sinking velocity in cm s³, g is the

gravitational acceleration of 981 cm s², and ESD is the equivalent spherical diameter in cm.

We calculated C_p using the drag equation for low Reynolds numbers (White, 1974):

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$$C_D = \left(\frac{24}{Re}\right) + \left(\frac{6}{1 + Re^{0.5}}\right) + 0.4 \tag{2}$$

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where the Reynolds number (Re) was defined as

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$$Re = SV ESD \frac{\rho_w}{\eta}$$
 (3)

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where η is the dynamic viscosity (1.7545 × 10° g cm° s° for a salinity of 32 at 2 °C). Equation

247 2 is valid up to a Reynolds number of 2x10⁵ (Vogel and Beety, 1994). The gypsum crystals

248 had Reynolds numbers ranging from 0.77 to 128.

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2.6 Backtracking the sampled ice flows under which cryogenic gypsum was sampled

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252 To determine sea ice drift trajectories of sampled sea ice we used a Lagrangian approach

253 (IceTrack) that traces sea ice backward or forward in time using a combination of satellite-

derived low resolution drift products. So far, IceTrack has been used in a number of

255 publications to examine sea ice sources, pathways, thickness changes and atmospheric

processes acting on the ice cover (Damm et al., 2018 {Peeken, 2018 #13678; Krumpen et al.,

257 2016; Peeken et al., 2018). A detailed description is provided in Krumpen et al. (Krumpen et

258 al., 2019).



3.2

The morphology of cryogenic gypsum



259	Sea ice motion information was provided by different institutions, obtained from different
260	sensors, and for different time intervals. In this study we applied a combination of three
261	different products: (i) motion estimates based on a combination of scatterometer and
262	radiometer data provided by the Center for Satellite Exploitation and Research (CERSAT
263	(Girard-Ardhuin and Ezraty, 2012), (ii) the OSI-405-c motion product from the Ocean and
264	Sea Ice Satellite Application Facility (OSISAF (Lavergne, 2016), and (iii) Polar Pathfinder
265	Daily Motion Vectors from the National Snow and Ice Data Center (NSIDC (Tschudi et al.,
266	2016).
267	The tracking approach works as follows: An ice parcel is traced backward or forward in time
268	on a daily basis. Tracking is stopped if a) ice hits the coastline or fast ice edge, or b) ice
269	concentration at a specific location drops below 50% and we assume the ice to be formed.
270	The applied sea ice concentration product was provided by CERSAT and was based on
271	85 GHz SSM/I brightness temperatures, using the ARTIST Sea Ice (ASI) algorithm.
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273	3 Results
274	3.1 Presence and distribution of cryogenic gypsum under the investigated ice-floes
275	Based on backtracking (Krumpen, 2018) and sea ice observations, the sampled ice-floes had
276	an age of 1 to 3 years (Fig. 1B) and were originating from the Siberian Sea (station 32/80), the
277	Laptev Sea (station 45), and were more locally grown in the Nansen Basin (station 66).
278	Whereas the mean sea ice thickness at the ROV survey stations ranged between 94 and 156
279	cm, the mean sea ice thickness of the investigated ice-floes estimated by an ice-thickness
280	sensor surveys (Katlein et al., 2018) was 1.90 m for station 32, 1.00 m for station 45, and 1.80
281	m for stations 66 and 80 (Fig. 1A, Table 1). Despite the different origins and thicknesses of
282	sea ice, cryogenic gypsum crystals were found at all stations and in all depth layers sampled
283	with the ROVnet (Figs. 1A, B, Tab. 1). At all stations and sampling depths the samples were
284	dominated by cryogenic gypsum, with a proportional dry weight of >96.5% in the 5 m-sample
285	at station 32, and with >99% in all other samples (Figs. 2, Figs. S1-S4). Other lithogenic
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288	The samples collected at station 32 were dominated by rounded, matte, solid cryogenic
289	gypsum crystals with a mean length-width ratio of 1.40-1.76 (Tab. 2, S1). The proportional
290	mass contribution of the smaller-sized crystals of the >30<63 μ m size fraction increased with
291	depth and outweighed the contribution of the >63 μm size fraction with 56.30%, and 66.28%
292	for the 0 and 5 m water depth sample, respectively (Fig. 3). At 0 m, the mean length of the
293	crystals was 68.46 μ m in the >63 μ m size fraction and 44.27 μ m in the >30<63 μ m fraction.
294	At 5 m depth, crystal dimensions were similar, ranging at mean crystal lengths of 63.28 μ m in
295	the >63 μ m, and 35.90 μ m in the >30<63 μ m size fraction, respectively.
296	At station 45, the crystals were mostly solid and for most part hyaline, rather than matte
297	crystals as at station 32 (Figs. 2C-D, 6, S2). With decreasing weight proportion, the >63 μ m
298	size clearly dominated the 0, 5, and 10 m samples with 79.90, 73.39, and 66.14%,
299	respectively. In the 0 m layer samples, mean crystal lengths were 114.18 μ m in the >63 μ m
300	size fraction and 58.74 μ m in the >30<63 μ m size fraction (Tab. 2). At 5 m depth, we
301	observed mean crystal lengths of 111 μ m in the >63 μ m size fractions, and 56.73 μ m in the
302	>30<63 μ m fraction. The mean crystal lengths in the 10 m sample was 92.83 and 50.32 μ m
303	for the >63 and >30<63 μ m size fraction, respectively. At station 45 the crystal length-width
304	ratio varied between 1.37 and 1.98, measured in the >30<63 μ m size fraction of the surface
305	sample, and the >63 μ m size fraction of the 10 m sample. The cryogenic gypsum crystals
306	retrieved from the melted ice core drilled at this station were solid and hyaline. In size and
307	shape they resembled the crystals of the 10 m layer at this station, with a mean crystal length
308	of 114.2 μ m, mean width of 57.2 μ m, and a length-width ratio of 2 (Fig. 4).
309	At station 66, the crystals from 0 m water depth were dominated by large, pencil-like, hyaline
310	and solid crystals with a mean crystal length of 1,355 μ m and mean width of 415 μ m in the
311	dominating >63 μ m fraction (99.25% mass) (Fig. 2B, S3, Tab. 2). These crystals with an
312	average length-width ratio of 3.27 were found as isolated crystals, but very often also as inter-
313	grown crystal rosettes with two to more than 10 individual crystals involved (Fig. S3; Tab. 2).
314	The >30<63 μ m size fraction (0.75% mass) was dominated by matte, whitish, rounded
315	gypsum particles and tiny gypsum needles with a mean crystal length of 56.67 μ m (Fig. S3,
316	Tab. 2.). As at the other stations the weight proportion of the >63 μ m size fraction
317	significantly decreased from 99.25 in the 0 m, to 75.23 at 5 m, and 61.18% in the 10 m
318	sample (Fig. 2). The size of cryogenic gypsum crystals collected from the 5 and 10 m layers
319	was significantly smaller and predominantly composed of isolated small hyaline and euhedral
320	gypsum needles. The length-width ratio ranged between 5.60 (5 m) and 4.37 (10 m) (Figs.





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323	mean crystal length of 101.40 μ m in the >63, and 30.71 μ m in the >30<63 μ m size fraction								
324	(Tab. 2).								
325	In the 10 m layer sample of station 80, large tabular gypsum crystals measuring up to 1 cm in								
326	length (mean length: 3,078 μ m, mean width: 1,830 μ m) dominated the >63 μ m size fraction.								
327	Their average length-width ratio was 1.7. This size fraction contributed 89.1% of the gypsum								
328	mass (Figs. 5, S4, Tab. 2). The >30<63 μ m size fraction was composed of fragments of these								
329	large crystals and few small gypsum needles. These often intergrown columnar crystals								
330	looked bladed, for most part also dented and with numerous cracks. Their mean length was								
331	71.8 μ m. The ice core retrieved from this station was very porous and broke into pieces of 9								
332	to 11 cm. Cryogenic gypsum was retrieved from all these ice core sections and revealed a								
333	dominance of extraordinary large crystals (Figs. 5, S4), resembling the ROVnet samples from								
334	this station. The largest cryogenic gypsum crystals >6,000 μ m (mean crystal length: 2,821								
335	μ m, mean width: 1,689 m) were retrieved from the top-most 8 cm ice core section, whereas,								
336	the maximum crystal size gradually decreased downcore (Fig. S4). The crystals themselves								
337	lacked sharp corners, and the large crystals had cavities inside, indicating an advanced stage								
338	of dissolution (Figs. 5C-D; S4).								
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340	3.3 Dissolution experiments								
341	3.3.1 Experiments to simulate cryogenic gypsum dissolution within the Arctic water								
342	column								
343	Our study area was characterized by the presence of three main water masses (Nikolopoulos								
344	et al., 2018; Rudels, 2015): 1) The Polar Surface Water (PSW) including the halocline, with a								
345	variable mean salinity of 32 and a temperature range of -1.8 to 0.0 $^{\circ}$ C, extended from the								
346	surface to maximum 100 m water depth (Nikolopoulos et al., 2018). 2) The Atlantic Water								
347	(AW) with a mean salinity of 34.4 to 34.7 and variable temperature of 0.0 to 4.7 °C in the								
348	study area extended from below the PSW to 600-800 m water depth (Nikolopoulos et al.,								
349	2018). 3) The Eurasian Arctic Deep Water (EADW) fills the deep Eurasian Basin below the								
350	AW with a temperature range of <0 to -0.94 $^{\circ}$ C and a salinity of about 34.9 (Nikolopoulos et								
351	al., 2018).								
	1:								

2A, S3, Tab. 2). In the 5 m layer sample, the mean crystal length was $411.42 \mu m$ in the >63

 μ m size fraction, and 62.03 μ m in the >30<63 μ m size fraction. The 10 m samples showed a





352 The dissolution experiments carried out to simulate dissolution in the PSW were set to 3 bar, 353 -0.5 °C. Over the 24 hours lasting PSW-simulating dissolution experiment, about 6% of the 354 gypsum dissolved (Figs. 6, S5A, Tab. 3). In the AW experiment, the combination of positive 355 temperatures (2.5 °C) and a pressure of 65 bar impacted the dissolution on the cryogenic 356 gypsum crystals more than in any other seawater trial. More than 80% of the cryogenic 357 gypsum crystals dissolved during the 24-hours experiment (Figs. 6, S5B, Tab. 3). Moreover, 358 as dissolution mainly affects the crystal's surface, smaller gypsums crystals and those with increased surface roughness were preferentially impacted by dissolution, whereas larger and 359 360 solid crystals with smooth surface showed the lowest dissolution (Fig. S5B). The EADW-361 simulating dissolution experiments set to a temperature of -0.5 °C showed a progressive 362 cryogenic gypsum dissolution of 26, 58, and 62% with increasing pressure for the 100, 120 363 and 150 bar experiments, respectively (Figs. 6, S6, Tab. 3). 364 3.3.2 Experiments to simulate cryogenic gypsum dissolution within Formaldehyde-365 treated biological samples 366 In the Formaldehyde experiments we exposed our set of cryogenic gypsum crystals to a Formaldehyde solution of 4%, which is commonly used to store pelagic samples from the 367 Polar Oceans (Edler, 1979). Irrespective of the temperature at which the sample was stored, 368 369 all gypsum dissolved within 24 hours. 370 3.4 Sinking velocities of gypsum crystals 371 372 The sinking velocity (SV) of the gypsum crystals increased with crystal size (Fig. 7A). Small 373 crystals with an equivalent spherical diameter (ESD) of 200 µm sank with 300 m d⁻¹ while 374 large gypsum crystals with ESDs of 2,000 to 2,500 μ m sank with velocities of 5,000 to 7,000 m d \cdot . The size to settling relationship was best described by a power function (SV = 4239.9 375 $ESD^{0.839}$, $R^2 = 0.84$). As the power function suggests, the settling velocity levelled off for the 376 377 largest gypsum crystals (Fig. 7A). The observed excess density of all crystals was smaller 378 than is expected from the density of gypsum (2310 kg/m²). For the visually non porous 379 smaller crystals drag, the deviation of gypsum crystals from round particles, and dissolution 380 may be the main reason for the calculated lower density. 381 However, plotting the excess density as a function of size (Fig. 7B) also showed that the 382 excess density of the gypsum decreased with increasing crystal size. The microscopic images 383 show that large crystals were more porous and had more complex shapes (Fig. S8 A-C)





compared to the small crystals that were more spherical and less porous (Figs. 2, 4-5, S8 D).

Hence, the flat settling to size relationship for large gypsum crystals (Fig. 7A), was essentially
due to a combination of increased porosity causing decreasing excess density and increased
drag due to the complex shapes of the large crystals.

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4 Discussion

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4.1 Distribution and morphology of cryogenic gypsum crystals

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414 415 fraction of particles $> 30 \,\mu \text{m}$ in Eurasian Basin surface waters, indicating a continuous cryogenic gypsum flux from warming sea ice over a period of six weeks. When designing the ROVnet for cryogenic gypsum sampling, we opted for the coarser $>30 \mu m$ mesh to prohibit an overflow of the sampling container when running into a phytoplankton bloom. However, as Geilfus et al. (Geilfus et al., 2013) had observed gypsum crystals as small as 10 μ m, we probably lost an unknown proportion of smaller gypsum crystals by the chosen sampling strategy. The gypsum crystals described from sea ice so far retrieved from only 3days-old experimental and 30 cm thick natural sea ice off Greenland were small (crystal length max. 100 µm), planar euhedral gypsum crystals often intergrown or as rosettes (Geilfus et al., 2013). Similar, but larger (crystal length up to 1 mm), gypsum crystals were observed within Phaeocystis aggregates collected in the region of the present study (Wollenburg et al., 2018a). However, here we show that gypsum crystals exhibit a strong variability in size and morphology. Particularly large crystals were characterised by more complex shapes (Fig. 2, 5, S3-4) and increased porosity (Figs. S6A-C), compared to the small planar euhedral (Fig. 2A) and more spherical crystals (Fig. S6D). Euhedral crystal needles larger but otherwise similar to those described by Geilfus et al. (Geilfus et al., 2013) and Wollenburg et al. (Wollenburg et al., 2018a) dominated the $>63 \mu m$ fraction collected at 5 and 10 m depths at station 66, and smaller crystals contributed especially to the $>30<63 \mu m$ size fraction of the station's subsurface samples.

As cryogenic gypsum forms in sea ice brine pockets or channels, the size and morphology

especially of large crystals is likely determined by sea ice texture and porosity during gypsum

This study shows for the first time the wide-spread presence of cryogenic gypsum under melting Arctic sea ice of different origin. At all stations cryogenic gypsum dominated the sample





417 0 m layer at station 66, and the 10 m layer and ice-core at station 80, formed in highly 418 branched granular sea ice (Lieb-Lappen et al., 2017; Weissenberger et al., 1992). In contrast, 419 the small cryogenic gypsum needles reported by Geilfus et al. (Geilfus et al., 2013) and 420 Wollenburg et al. (Wollenburg et al., 2018a), may have preferentially formed in columnar sea 421 ice. Even sampling the same ice-floe (station 32 and 80), the appearance of the crystals 422 changed. Possibly, a widening of the brine channels during the elapsed time (6 weeks) 423 allowed a release of larger crystals at station 80 when compared to station 32. However, 424 crystal growth during this elapsed period or lateral advection of large crystals cannot be 425 excluded. Thus, detailed texture analyses on sea ice cores prior to sampling are needed to 426 validate or reject hypotheses on a link between sea ice porosity and cryogenic gypsum crystal 427 size and morphology and should be considered in future studies. 428 The sea ice microstructure dictating the formation of gypsum crystals in the brine matrix 429 likely varied among ice-floes due to different ages, origins and drift trajectories (Fig. 1B). For 430 example, station 66 was the only station where the sea ice likely formed over the central 431 Nansen Basin only months before our study (Fig. 1B). The surface sample of station 66 had 432 large intergrown hyaline star-shaped gypsum crystals that were observed at no other station. 433 They also showed a considerably higher length-width ratio than crystals from second-year ice 434 of stations 32/80 and 45 (Fig. 1B; Fig. 2). Accordingly, a close relationship between local sea 435 ice properties and gypsum crystal morphology in the underlying water was evident from the 436 comparison of gypsum crystals collected with the ROVnet with those retrieved from ice cores 437 collected at two stations. The ice-core samples revealed cryogenic gypsum crystals that 438 basically resembled the crystal morphologies collected from the water column at these 439 stations, indicating that the gypsum morphologies observed in the water column likely reflect 440 the gypsum precipitation conditions and brine-channel structure of local ice-floes. The current 441 understanding of mineral precipitation in supersaturated brines relies on ice-core analyses, sea 442 ice brine- and experimental studies, and on mathematical modelling of the temperature 443 window in which each mineral is likely to form (Butler et al., 2017; Marion et al., 2010). 444 There are still many uncertainties regarding the precipitation and dissolution of gypsum 445 within natural sea ice and during ice-core storage. Although the FREZCHEM model and Gitterman Pathway predict gypsum precipitation under defined conditions, only Geilfus et al. 446 (Geilfus et al., 2013) and Butler et al. (Butler et al., 2017) succeeded in retrieving gypsum 447 448 under such conditions, whereas others failed (Butler and Kennedy, 2015). According to the FREZCHEM model, cryogenic gypsum precipitates at temperatures of -6.2 to -8.5 °C and at 449

precipitation. Pursuing this hypothesis, the large and intergrown crystals collected from the





450 temperatures <-18 °C (Geilfus et al., 2013; Wollenburg et al., 2018a). Accordingly, a storage 451 temperature of -20 °C would allow the post-coring precipitation of gypsum from contained 452 brines. However, in field and experimental studies cryogenic gypsum was so far only observed to precipitate in the -6.2 to -8.5 °C temperature window, even when treatments were 453 conducted below -20 °C (Butler et al., 2017; Geilfus et al., 2013). Furthermore, the observed 454 455 signs of dissolution on the large cryogenic gypsum crystals from the ice-core when compared 456 to the sharp-edged crystals retrieved from the water column at station 80 indicate that significant new precipitation of gypsum during storage did not occur, rather the opposite. 457 458 Apart from the growing conditions of gypsum crystals within sea ice, the size spectrum of 459 crystals retrieved from different depths in the water column likely was essentially altered by 460 the size-dependent sinking velocity of the crystals. Because the sinking velocity of large cryogenic gypsum crystals is high the chance to catch large crystals with horizontal transects 461 directly under the ice should be lower compared to small crystals (Fig. 7A). Accordingly, 462 463 significant amounts of large cryogenic gypsum crystals were mainly sampled from the 0 m 464 layer where they could be scraped off the underside of the ice (see station 66, Tab. 2). In 465 contrast, smaller cryogenic gypsum crystals sink at lower velocities (Fig. 7A). Hence, the large quantity of small-sized crystals retrieved in the deeper layers of station 66, and all layers 466 of station 32 and 45 likely were influenced by the accumulated gypsum release in this size-467 468 fraction, whereas the rarer large crystals indicated the momentary release at these stations. 469 The extremely large crystals sampled at station 80 at 10 m depth probably indicated an on-470 going flux event during rapid melting. According to our dissolution experiments, gypsum 471 dissolution within Arctic surface waters should only have a minor impact on the size 472 distribution of cryogenic gypsum crystals within the surface water. Besides vertical flux, 473 advection of gypsum crystals with surface currents may also have influenced the size-474 distribution of gypsum crystals sampled in the water column.

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4.2 Reasons why cryogenic gypsum was rarely observed in past studies

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481 482 The small temperature range of the -6.2 to -8.5 °C window, which is also the only gypsum precipitation temperature spectrum applicable in the Arctic Ocean, has been considered one reason why gypsum was not detected in other studies (Butler and Kennedy, 2015; Wollenburg et al., 2018a). Furthermore, the kinetics of gypsum precipitation was considered as too slow for detection during experimental studies, and the amount of gypsum hard to verify versus





483 other sea ice precipitates that are quantitatively much more abundant, leading the focus 484 towards other sea ice precipitates (Butler and Kennedy, 2015; Geilfus et al., 2013). Although 485 cryogenic mirabilite and hydrohalite are three and twenty-two times more abundant than 486 gypsum, respectively (Butler and Kennedy, 2015), gypsum is the only sea ice precipitate that 487 survives for one to several days within the Arctic water column. Cryogenic gypsum 488 dissolution increases with increasing hydrostatic pressure and increasing temperatures (Fig. 489 6). However, well preserved cryogenic gypsum crystals were retrieved from algae aggregates collected from 2,146 m water depth, suggesting that either the transport from the surface to 490 491 this depth was very rapid or that dissolution was decreased and/or prevented once gypsum 492 crystals were included within the matrix of organosulfur compound-rich aggregates 493 (Wollenburg et al., 2018a). Yet, as seawater is usually undersaturated with respect to gypsum 494 (Briskin and Schreiber, 1978a; Briskin and Schreiber, 1978b) and is shown by our dissolution 495 experiments, disaggregation of organic aggregates would expose the gypsum to the seawater 496 and dissolve any crystals making it to the deep ocean or seafloor likely within a few days. The 497 same dissolution would occur within the sampling cups of sediment traps, explaining why 498 gypsum has not been observed in those type of samples. 499 Our dissolution experiments showed that cryogenic gypsum can persist long enough in the 500 cold polar surface water to be collected in measurable concentrations. The missing evidence 501 of gypsum from past studies was likely due to the quick dissolution of gypsum crystals at 502 higher temperatures and pressure dependence of dissolution kinetics, impeding the discovery 503 of gypsum in sediment trap samples and on the sea-floor. In addition, Formaldehyde 504 preservation leads to the immediate dissolution of gypsum, too, destroying any evidence of 505 cryogenic gypsum in all kinds of biological samples including water column and net samples.

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4.3 Potential of cryogenic gypsum as a ballast of algae blooms

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We found less than 6% dissolution of individual crystals in Polar Surface Water (PSW) per day. Thus, at depths immediately below the fluorescence maximum where a significant part of organic aggregates are formed (Iversen et al. 2010), the gypsum scavenging and ballasting of aggregates (Turner, 2015) is little affected by gypsum dissolution (Olli et al., 2007) (Fig. 6, Tab. 3). Incorporation of dense minerals into settling organic aggregates will increase their density and, therefore, the size-specific sinking velocities of the aggregates (Iversen and Ploug, 2010; Iversen and Robert, 2015; van der Jagt et al., 2018). The high sinking velocity of large gypsum crystals >1 mm (5,000-7,000 m d⁺ (Fig. 7A)) could create strong hydrodynamic





517 shear that might cause disaggregation of fragile algae aggregates (Olli et al., 2007). This 518 supports previous suggestions of gypsum as an important ballast mineral of organic 519 aggregates, such as *Phaeocystis* (Wollenburg et al., 2018a) by rather small crystals. 520 As chlorophyll concentrations in the surface water were mostly low (< 1 mg m³, H.F. 521 unpublished data), a massive gypsum-mediated export of phytoplankton was unlikely during 522 expedition PS106. However, especially at the ice floe of station 32/80, we observed a high 523 coverage of the ice underside by the filamentous algae *Melosira arctica*, and gypsum crystals were found in M. arctica filaments collected nearby (Figs. 2D, 8). This indicates a potential 524 525 for rapid M. arctica downfall mediated by cryogenic gypsum, as soon as the algal filaments 526 were released from the melting sea ice. Hence, ballasting by cryogenic gypsum may also have 527 contributed to the mass export of Melosira arctica aggregates observed in 2012 (Boetius et al. 528 2013). 529 530 531 5 **Conclusions** 532 This study shows for the first time that gypsum released to the water at the onset of melt 533 season in the Arctic Ocean causes a constant flux of gypsum over wide spread areas and over a long period of time (> six weeks). The morphological diversity of gypsum crystals retrieved 534 535 from Arctic surface waters and ice-cores indicated a complex variety of precipitation and 536 release processes as well as modifications during sea ice formation, the melt phase, and in the water column. In the fresh and cold Polar surface water, gypsum crystals persist long enough 537 538 to act as an effective ballast on organic matter, such as phytoplankton filaments and marine 539 snow. 540 541 **References:** 542 Arrigo, K. R., Perovich, D. K., Pickart, R. S., Brown, Z. W., van Dijken, G. L., Lowry, K. E., Mills, 543 M. M., Palmer, M. A., Balch, W. M., Bahr, F., Bates, N. R., Benitez-Nelson, C., Bowler, B., 544 Brownlee, E., Ehn, J. K., Frey, K. E., Garley, R., Laney, S. R., Lubelczyk, L., Mathis, J., Matsuoka, 545 A., Mitchell, B. G., Moore, G. W. K., Ortega-Retuerta, E., Pal, S., Polashenski, C. M., Reynolds, 546 R. A., Schieber, B., Sosik, H. M., Stephens, M., and Swift, J. H.: Massive Phytoplankton 547 Blooms Under Arctic Sea Ice, Science, 336, 1408, 2012. 548 549 Arrigo, K. R., Perovich, D. K., Pickart, R. S., Brown, Z. W., van Dijken, G. L., Lowry, K. E., Mills, 550 M. M., Palmer, M. A., Balch, W. M., Bates, N. R., Benitez-Nelson, C. R., Brownlee, E., Frey, K. 551 E., Laney, S. R., Mathis, J., Matsuoka, A., Greg Mitchell, B., Moore, G. W. K., Reynolds, R. A., 552 Sosik, H. M., and Swift, J. H.: Phytoplankton blooms beneath the sea ice in the Chukchi sea, 553 Deep Sea Research Part II: Topical Studies in Oceanography, 105, 1-16, 2014.





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740 Table captions:





Site	Date	Latitude (Deg N)	Longitud e (Deg E)	Ocean depth (m)	Sampling depth	Water temp. (°C)	Salinity	Mean ice thickness (m)	Filtered water volume (m3)
32	2017-06-	81.73	10.86	1608	under-	-1.94	34.27	1.90	2.2
	15				ice				
					5 m	n.a	n.a.	1.90	3.9
45	2017-06-	78.10	30.47	233	under-	-1.52	33.84	1.00	2.3
	25				ice				
					5 m	-1.47	34.11	1.00	4.5
					10 m	-1.68	34.29	1.00	2.5
66	2017-07-	81.66	32.34	1506	under-	-1.67	33.18	1.80	3.1
	02				ice				
					5 m	-1.71	33.76	1.80	2.7
					10 m	-1.73	33.78	1.80	3.1
80	2017-07- 12	81.37	17.13	1010	10 m	-1.37	32.87	1.80	1.7

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Tab. 1: Properties of sea ice stations and characteristics of ROVnet profiles.





	>63 µm fra	ction		>30<63 μn	n fraction			
Cruise, Site, mean water depth	Mean Mean		length/	Mean	Mean	length/	>63 μm	>30<63 μm
of the catch	length	width	width	length	width	width	fraction	fraction
	μm	μm	ratio	μm	μm	ratio	weight%	weight%
PS106.1, Stat. 32, 0 m	68.46	44.27	1.55	50.64	35.03	1.45	43.70	56.30
PS106.1, Stat. 32, 5 m	63.28	35.90	1.76	49.91	35.57	1.40	33.72	66.28
PS106.1, Stat. 32, mean (0-5 m)	65.87	40.09	1.64	50.28	35.30	1.42	38.71	61.29
PS106.2, Stat. 45, 0 m	114.18	65.93	1.73	58.74	42.84	1.37	79.90	20.10
PS106.2, Stat. 45, 5 m	110.98	64.84	1.71	56.73	38.89	1.46	73.39	26.61
PS106.2, Stat. 45 , 10 m	92.83	46.81	1.98	50.32	29.98	1.68	66.14	33.86
PS106.2, Stat. 45, mean (0-10 m)	85.49	44.45	1.92	77.93	24.28	3.21	73.14	26.86
PS106.2, Stat. 66, 0 m	1355.38	415.10	3.27	56.67	25.63	2.21	99.25	0.75
PS106.2, Stat. 66, 5 m	411.42	73.45	5.60	62.03	12.20	5.08	75.23	24.77
PS106.2, Stat. 66, 10 m	101.40	23.19	4.37	30.71	5.79	5.30	61.18	38.82
PS106.2, Stat. 66, mean (0-10 m)	599.17	164.78	3.64	59.96	12.61	4.76	58.16	41.84
PS106.2, Stat. 80, 10 m	3078.44	1830.00	1.68	71.78	30.76	2.33	89.05	10.95

Tab. 2: Size measurements and percentage of mass contribution of gypsum crystals from the $>63 \mu \text{m}$ size fraction and the $>30 < 63 \mu \text{m}$ size fraction

		Dissol	ution in wei	ght%		
Chamber (no.)/Water mass	PSW		AW	EADW (1)	EADW (2)	EADW (3)
1		11.34	76.22	47.52	57.08	74.92
2		1.33	86.23	26.09	71.03	53.77
3		8.29	82.93	21.05	47.15	57.43
4		2.99	78.57	10.91	58.56	
Mean		5.99	80.77	26.39	58.34	62.04

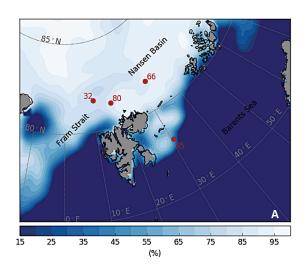
Tab. 3: Dissolution experiments on cryogenic gypsum crystals. 'Water mass' simulating experiments with 34.9% sterile filtered seawater. Each experiment was conducted in parallel in 3-4 separate pressure chambers.

Figure captions:



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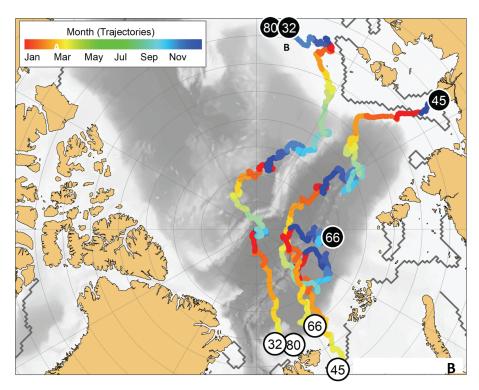


Fig. 1: Study area with sample locations. A: Sea ice coverage at the station and time of sampling in %. B) Trajectories of the sea ice from which the cryogenic gypsum was released. Each trajectory starts where sea ice formed (black circles), and shows its drift until the time





and place of sampling (white circles). The colour scale of the drift trajectories indicates the month in which the back-tracked sea ice was at any given position.

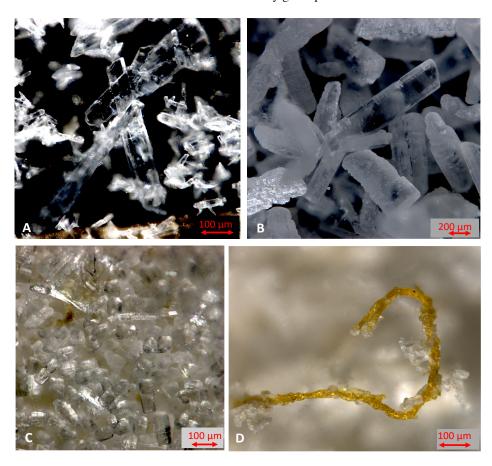


Fig. 2: Cryogenic gypsum crystals collected during Polarstern expedition PS106-1 from the upper water column. A) Crystals collected from station 66 at 5 m water depth. B) Crystals collected from station 66 at 0 m water depths. C) Crystals collected from station 45 at 10 m water depth. D) Crystals collected from station 45 at 10 m water depths entangled in an algae filament.





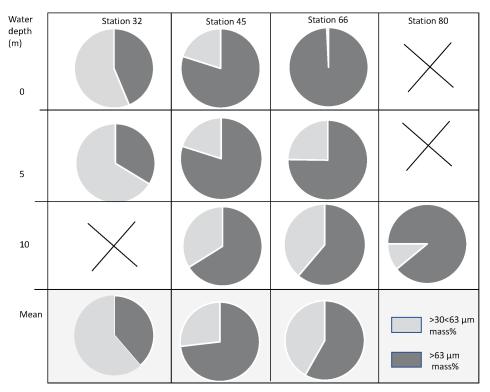


Fig. 3: Proportional mass (%) of cryogenic gypsum for the size fractions >30<63 μ m and >63 μ m for all ROV samples.





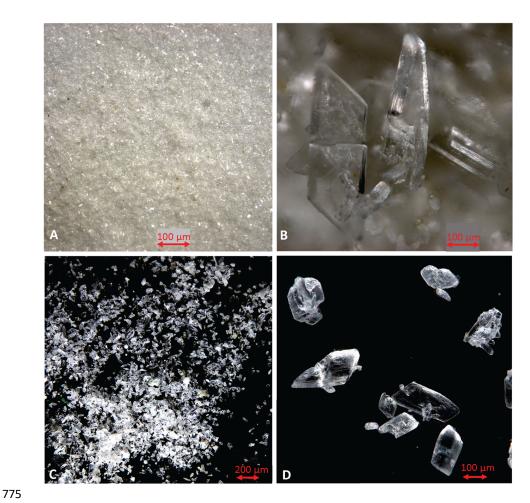


Fig. 4: Comparison of cryogenic gypsum crystals collected from the water column at station PS45 (10 m water depth) (A-B) with crystals retrieved from an ice-core collected above the ROVnet sampling area (C-D).

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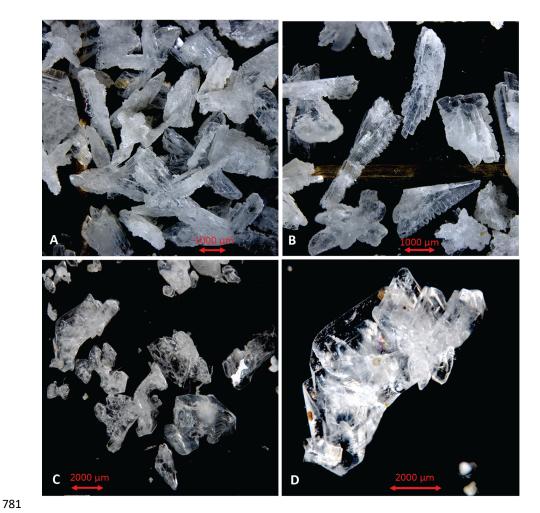


Fig. 5: Comparison of cryogenic gypsum crystals collected from the water column at station PS80-2 (10 m water depth) (A-B) with crystals retrieved from an ice-core collected above the ROVnet sampling area (C-D).

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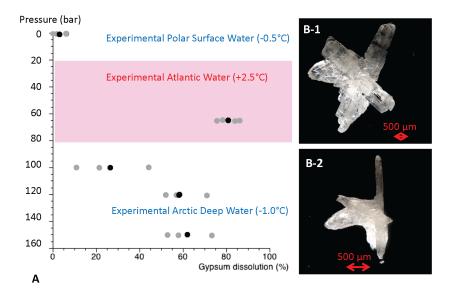
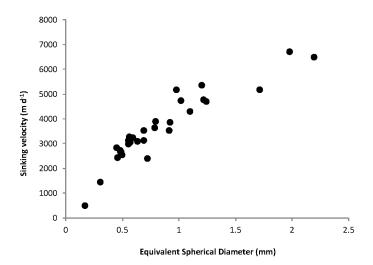


Figure 6: Results from cryogenic gypsum dissolution experiments. A) Graph showing the position of the simulated Arctic water masses in respect to pressure and temperature and how much gypsum (%) was dissolved on average over a 24-hours lasting exposure to such pressure and temperature conditions. Grey dots indicate the values from each aquarium, black dots the mean per experiment. B-1) Cryogenic gypsum crystal of the 120 bar-experiment before exposure. B-2) The same cryogenic gypsum crystal of the 120 bar-experiment after 24 hours.





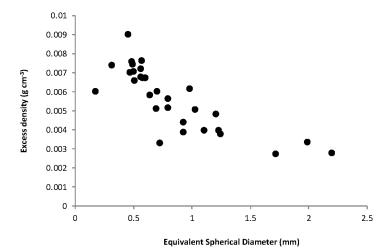


Fig. 7: (A) sinking velocity and (B) excess density (excess density = gypsum density – seawater density) of cryogenic gypsum crystals plotted against equivalent spherical diameter (ESD).

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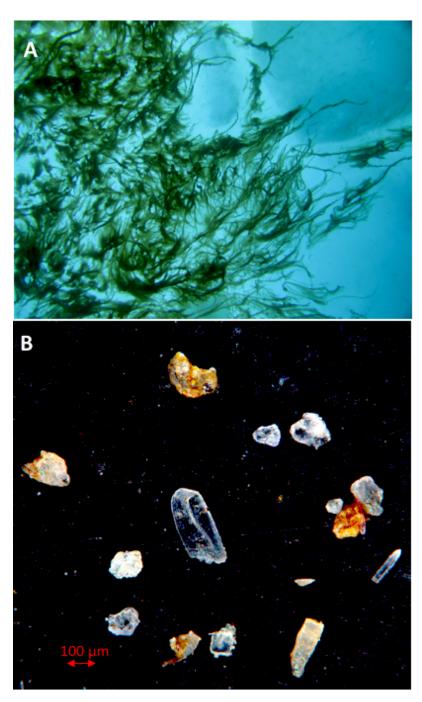
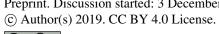


Fig. 8: Living *Melosira arctica* curtains hanging from ice flows during the PS106 expedition (photo taken by M. Nicolaus and C. Katlein). Cryogenic gypsum isolated from *Melosira arctica* (PS106-1, station 21(Peeken, 2018)).

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818	
819	Author Contributions:
820	J.W. lead the writing of this manuscript as well as gypsum sample preparation and analysis.
821	H.F., I.P., C.K., G.C., M.N. acquired ROVnet and ice samples in the field. M.I. measured
822	crystal settling velocities. T.K. performed the backtracking analysis. All authors contributed
823	to the writing and editing of the manuscript
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