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# Pore-Scale Visualization of CH<sub>4</sub> Gas Hydrate Dissociation under Permafrost Temperature Conditions

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# 9 ABSTRACT

In this study, we demonstrate the effectiveness of combined production technique involving depressurization and thermal stimulation for gas production from CH<sub>4</sub> gas hydrates in subzero temperature range between  $-3^{\circ}$ C to  $0^{\circ}$ C. CH<sub>4</sub> gas hydrate phase transitions during formation, depressurization, re-formation, self-preservation, thermal stimulation stage were visualized using a high-pressure, water-wet, silicon-wafer micromodel with pore network of actual sandstone rock. A set of eight experiments were performed in which CH<sub>4</sub> gas hydrate was formed at a constant pressure between 60 – 85 bar and constant temperature between 0 °C – 4°C. CH<sub>4</sub> gas hydrate was

then dissociated at constant system temperature between -3 °C to - 2 °C by pressure depletion to 17 18 study the effect of hydrate and fluid saturation on dissociation rate, self-preservation, and risk of 19 ice formation. The dissociation rate and behaviour were heavily affected by the total hydrate 20 saturation and initial hydrate distribution in the pore space. Additionally, the amount of produced 21 CH<sub>4</sub> gas was limited below 0 °C due to the rapid formation of ice from the liquid water that was 22 liberated from the initial hydrate dissociation. The liberated CH<sub>4</sub> gas was therefore immobilized 23 and trapped by the formed ice and could not be produced without thermal stimulation. Thermal 24 stimulation removed the blockage of pore space caused by ice and secondary hydrate formation 25 and enhanced gas production. Visual observation showed self-preserved hydrates in metastable 26 state dissociated before ice below subzero temperature providing experimental evidence of 27 recently discovered methane leaking from gas hydrate deposits due to global warming. The results 28 highlight the influence of heterogeneity in hydrate distribution and total saturation on the hydrate 29 dissociation behaviour below 0 °C temperature. Micromodel observation provides direct insights 30 into hydrate dissociation, self-preservation, fluid migration, gas coalescence, ice and secondary 31 hydrate formation at pore scale below subzero temperature.

# 32 **1. Introduction**

Experimental modelling of methane (CH<sub>4</sub>) gas hydrate formation, dissociation, and phase stability in permafrost sediments are essentially related to global warming and in schemes for CH<sub>4</sub> recovery and/or carbon dioxide (CO<sub>2</sub>) storage. CH<sub>4</sub> gas hydrate is an ice-like crystalline substance formed by CH<sub>4</sub> gas and water at moderate-to-high pressure and low-temperature conditions <sup>1</sup>. CH<sub>4</sub> gas hydrate in sediments is of particular interest due to the vast amount of gas hydrate reserves discovered in shallow permafrost sediments and on continental margins in the marine environment <sup>2</sup>. These deposits may provide large volumes of Natural Gas in the future; therefore, gas production via dissociation of sedimentary CH<sub>4</sub> gas hydrate is a topic of intense research. Hydrate dissociation via depressurization is a well-studied phenomenon both at lab-scale as well as through field trials and is considered as the most cost-effective and well-understood production technique to be implemented at commercial scale <sup>3</sup>. Still, there are challenges associated with hydrate dissociation such as changes in physical properties <sup>4</sup>, risk of hydrate re-formation, sand and water production, and discontinued gas production <sup>5</sup>.

46 Permafrost environment, including ice containing frozen soil, rock or sediments at or below 0°C 47 provides favorable thermodynamic conditions for gas hydrate occurrence. A hydrate stability zone 48 within permafrost and below permafrost and its thickness is controlled by permafrost layer 49 temperature, the geothermal gradient of sediments in permafrost and below the permafrost, pore 50 fluid salinity, gas chemistry, gas and water saturation, formation pore pressure and the difference between pore pressure and hydrostatic pressure <sup>6</sup>. Permafrost temperature varies according to 51 52 longitude/latitude and altitude. For example, it is reported that the annual average geothermal 53 temperature in the permafrost layer in Qinghai- Tibet plateau is between -4°C to 0°C<sup>7</sup>. Permafrost 54 based hydrate deposits are characteristically different from oceanic hydrates due to relatively low 55 concentration of salts in permafrost lead to lower and delayed gas production from permafrost, 56 shallow depth cause lower sensible heat of reservoir thus controlling rate of fluid withdrawal and a higher level of hydrate saturation presence in permafrost <sup>8</sup>. It is reported that gas hydrates in 57 58 permafrost sediments are usually located at 200-250 m within the permafrost zone and/or 800-1500 m below the permafrost regions <sup>9</sup>. Hydrates within frozen rocks found in the Bovanekovo 59 60 Gas Field in West Siberia permafrost have an ice saturation (25%-85%) and unfrozen water saturation (2%-20%), varying with depth <sup>10</sup>. Unfrozen pore water is defined as the amount of pore 61

liquid water in equilibrium with gas hydrate and ice at elevated pressure at a subzero temperature in sediments. Hydrate deposits have also been found in shallow depths of 50-70 m in the Mackenzie Delta, Canada, suggesting the presence of preserved pore hydrate outside the thermodynamic stability zone <sup>9</sup>. These metastable hydrates have very low dissociation rates due to the self-preservation behaviour associated with subzero temperatures. Here, gas hydrates and ice coexist, and the gas hydrates are covered with thin ice sheets that delay hydrate dissociation <sup>11–17</sup>.

Several theories have been proposed to explain the self-preservation effect. Zhong et al. <sup>18</sup> studied 68 69 the self-preservation effect on the dissociation of CH<sub>4</sub> gas hydrate below 0 °C using Raman 70 spectroscopy and confirmed the role of the guest molecule on hydrate self-preservation nature. Takeya et al.<sup>19</sup> proposed it to be due to the interaction between guest and water molecules. 71 According to Giavarini et al.<sup>20</sup>, high hydrate saturation shows weaker self-preservation effect due 72 73 to less entrapped water or ice. The decrease in temperature below 0 °C, would improve self-74 preservation and reduce dissociation rate. Studies also show that below subzero temperatures, pressure increase improves self-preservation <sup>14,21,22</sup> due to collapse of pore space by sintered ice 75 <sup>23</sup> and an increase in dissociation temperature <sup>24</sup>. During the pressurization, unfrozen residual pore 76 77 water present in frozen sediments could convert into pore ice and enhance self-preservation during dissociation due to subsequent annealing of the surrounded ice coating <sup>25,26</sup>. 78

Two-dimensional micromodels offer a unique opportunity to perform pore-scale visualization during the formation and dissociation of hydrate at high resolution using artificial sedimentary rock <sup>27</sup>. Current micromodels are fabricated to work in the high-pressure environment, equipped with actual geological, topographical properties and pore-scale geometry of real rocks. Micromodels offer a non-destructive, low-cost solution and shorter experiments compared to other pore-scale techniques, such as x-ray computer tomography (CT) scanning and magnetic resonance

85 imaging. The micromodels have previously been used to visualize hydrate formation in the 86 presence of water-soluble tetrahydrofuran (THF) at atmospheric pressure and with CH<sub>4</sub>/CO<sub>2</sub> saturated water at high pressure <sup>28</sup>. Direct visualization showed hydrate formation from the vapor 87 88 saturated liquid phase, the formation of hydrate in the centre of pore space in water wet 89 micromodels, isolated gas bubble conversion into hydrates, and redistribution of gas hydrate with time. Katsuki et al. <sup>29</sup> used a glass micromodel to study the subcooling effect on hydrate growth 90 91 kinetics. Direct visualization showed the conversion of dendritic hydrate into particulate hydrate system at higher subcooling temperature (greater than 12 K). Hauge et al. <sup>30</sup> discussed the 92 93 formation of CH<sub>4</sub> and CO<sub>2</sub> hydrate using high-pressure silicon micromodels and concluded that 94 growth pattern is dependent on fluid connectivity and local fluid distribution. Almenningen et al. 95 <sup>31</sup> discussed the experimental protocol to calculate the thermodynamics of hydrate formation and 96 dissociation using high-pressure micromodel. Almenningen et al. also studied the salinity effect on hydrate dissociation <sup>32</sup> and CO<sub>2</sub> hydrate formation in the porous medium <sup>33</sup> using high-pressure 97 micromodels. So far, the dissociation behaviour of CH<sub>4</sub> gas hydrate using micromodels <sup>31,32</sup> is 98 99 studied above 0°C. CH<sub>4</sub> gas hydrate dissociation is dependent on initial hydrate saturation, hydrate 100 morphology, and the mobility of the fluid phases; however, hydrate dissociation below subzero 101 temperature is not well understood. Thus, a fundamental understanding of CH<sub>4</sub> gas hydrate 102 distribution, dissociation mechanism, and self-preservation in sediments at the pore-scale level are 103 essential to optimize the CH<sub>4</sub> gas production method from permafrost-affected hydrate reservoirs. 104 Recent work has focused on hydrate formation in frozen rocks and ice-to-hydrate conversion in 105 free space or pore space, but few studies have been subject to dissociation and self-preservation of hydrate in pore space in permafrost <sup>9</sup>. 106

107 This study provides a quantitative analysis of CH<sub>4</sub> gas hydrate dissociation below 0 °C using a 108 high-pressure micromodel network replicating a cross-section of porous sandstone rock. Direct 109 optical visualization of dissociation behaviour at pore-scale provides a fundamental understanding 110 of the effect of various parameters, including temperature, hydrate saturation, and free gas in the 111 pore space on the dissociation behaviour in coarse-grained sediments. Optical access to pore-scale 112 visualization offers identification of different mechanisms activated below 0°C, including self-113 preservation, hydrate re-formation, and gas trapping.

#### 114 **2. Materials and Methods**

#### 115 2.1 Experimental Setup

116 The micromodel setup (Figure 1) included four key elements. The micro model, visualization 117 assembly, the high-pressure/low-flow rate pumps, and the cooling system. Micromodel assembly 118 includes high-pressure micromodel with stand placed inside dual-chamber filled with 119 water/glycol. A dual-chamber design facilitates temperature control and pore space visualization. 120 The micromodel was made of a silicon wafer that was anodically bonded to a borosilicate glass 121 wafer. The rectangular micromodel was 2.8 cm long and 2.2 cm wide. The realistic two-122 dimensional pore network of Berea sandstone was etched into the silicon wafer with the deep 123 reactive ionic etching (DRIE) technique that developed a two-dimensional vertical profile with 124 constant height throughout the cross-section. Anodic bonding was performed to isolate the flow 125 path under a high-pressure environment to facilitate direct visual observation. Due to the high 126 aspect ratio and large coordination number, the model carried realistic capillary forces of similar scale found in actual rock <sup>31</sup>. The micromodel was water wet in nature, and wettability was 127 128 uniform. The solid grains were thus coated with thin water films, and the pores were filled with 129 water, gas or hydrate. The water-wet nature of solid grains induced a curved interface between 130 liquid and gas and allowed for visual differentiation between fluid phases. The model consisted of 131 average pore diameter of 100 µm and a constant vertical height of 25 µm.



Figure 1 A layout of the experimental setup (subfigure A and B) and field of view (FOV) cross-section of the micromodel (Sub figure C). For better visualization, images are segmented, and phases are highlighted in different colours. The solid grain is shown in brown, gas in red and water in blue. Spatial scale of the images used in this study is 1100 x 800 pixel.

132

136 The micromodel had four nano ports with nano-tubing guiders and rubber packing 137 (Upchurch/IDEX), connected to high-pressure pumps using a combination of 1/16" PEEK tubing 138 and 1/8" steel tubing. Ports were used for injection/production of liquid/gas. It was placed between 139 two steel casings to ensure it remained still during the experiment. The micromodel was carefully 140 placed on the stand and lowered into the inner cooling chamber. Due to steel-casing, the 141 micromodel was able to withstand pressures up to 150 bar. A high-pressure (HP) pump controls 142 the pore pressure, and flow of water (port 1) and CH4 (port 3) situated diagonal opposite. CH4 143 pressure inside the micromodel was controlled by a dual-piston high-pressure pump (Chandler 144 Engineering, Quizix Q5200). FOV of pore space inside micromodel generated as a Top view from

145 Stereomicroscope. FOV is partially saturated with gaseous CH4 and liquid water. The gaseous 146 phase and liquid phase are differentiate based on the contrast difference between the liquid and 147 gas phase. Gas-phase being brighter than the liquid phase and separated by a sharp interface and a 148 curvature towards the hydrophilic grains. Images are segmented to enhance the visualization. Gas-149 phase is represented in red colour while grains are coloured as brown. Later, the water phase is 150 represented in blue colours. Valves at port 2 and port 4 were used for venting. The micromodel 151 was placed on the holder, fully submerged into glycol in the inner chamber of the custom-designed, 152 dual-chamber water bath. Glycol was used to achieve a temperature below 0°C without freezing. 153 The outer chamber was insulated to reduce heat loss and to have better temperature control. The 154 outer chamber and inner chamber were separated by aluminium walls, which allowed rapid heat 155 exchange between the inner and outer chamber. Cooling fluid (water mixed with antifreeze) was 156 circulated between the inner and outer chamber using the cooling bath to achieve the desired 157 temperature. The temperature was measured by a thermocouple (HH506RA Omega Multi-logger, 158 Type K), placed directly beneath the micromodel. The dual-chamber was placed above the anti-159 vibration platform. A stereomicroscope (Nikon SMZ1500) with DSLR camera (NikonD7100) was 160 used for visualization and recording. The working distance was 54 mm, and field of view (FOV) was of the order of 2 mm using 1X objective lenses and 110X magnification. A light source 161 162 (Photonic LED F1, cold light 5500K) was installed to record clear images, and the camera was 163 connected to a monitor for improved image interpretation.

Phase saturation was calculated using the image processing software Paint.net. Different phases were segmented whenever it was necessary, and two-dimensional fluid saturation was estimated using the pixel count method. In this method, each colour cover specific image area expressed in the number of pixels. The two-dimensional fluid saturation for the phase "i" (S<sub>i</sub>) were estimated
using the following formula.

169 
$$S_i = \frac{A_i}{A_v} = \frac{N_i}{N_v} = \frac{N_i}{N_{tot} - N_{grains}}$$
(1)

170 Where A<sub>i</sub> is the area of the phase (Gas, water or hydrate) in the given image after segmentation. N<sub>i</sub> 171 is the number of pixels for phase (gas, liquid or water). Nv, Ntot, Ngrains are the number of void 172 pixels, total number of pixels in the image and number of pixels corresponding to grains 173 respectively. Both porous hydrates (grey colour) and non-porous hydrates (transparent-crystalline) 174 were considered to calculate two-dimensional hydrate saturation. This method has a few 175 limitations. Phase saturation was obtained locally (approx. 1% of the total micromodel area) within 176 FOV, which could be different from saturation in the entire micromodel. The phase saturation 177 calculation was based on the assumption that pore space was saturated with single fluid; however, 178 it may be possible that based on hydrate morphology, multiple phases coexisted within the pore 179 depth of 25 µm.

# 180 2.2 Experimental procedure and data processing

The micromodel was flushed with water to remove residual air, followed by distilled water injection into the pore space via port 1 (Figure 1). The entire pore space of the micromodel was thoroughly studied to ensure 100% water saturation. The water pore pressure was increased to 60 bar by injection water while keeping the remaining ports closed. The methane pump pressure was increased to 61 bar and subsequently, a valve at port 3, was opened to make a connection between CH<sub>4</sub> gas and water inside micromodel. After that, the water pore pressure was reduced to 59 bar to allow CH<sub>4</sub> gas to enter into micromodel and appear in FOV. Thereafter, the valve at port 1 was

188 closed, and the methane pump was kept at a constant pressure operating mode. The methane pump 189 pressure kept constant for 24 hours to allow CH<sub>4</sub> gas to dissolve into the water and to check the 190 high-pressure system for leaks. Once the water was thoroughly saturated with methane, the 191 temperature was brought down within the hydrate formation zone to trigger hydrate formation. 192 During the cooling down, additional gas dissolved in the water due to the increase in gas solubility 193 at a lower temperature, and some of the gas bubbles within the FOV disappeared. In those case, 194 when hydrate formation was not triggered within a couple of hours after the temperature had 195 stabilized, the sudden and temporary turbulence was created within the pore space by venting gas through port 4 by quick opening/closing of the valve <sup>32</sup>. After the system returned to static 196 197 conditions (constant pressure, no flow), hydrate nucleation usually followed within minutes. 198 Pressure differential (Difference in pressure between micromodel and atmospheric pressure due to 199 port opening) developed during agitation, caused dissolved gas liberation from water, and gas-200 water contact was surface-enhanced, and nucleation was initiated. The growth pattern was then 201 monitored and recorded until there were no further phase changes occurring (usually 24 hours). 202 The temperature was reduced below  $0^{\circ}$ C in the interval between  $-3^{\circ}$ C to  $-0.1^{\circ}$ C to achieve 203 permafrost temperature conditions. To prepare for hydrate dissociation, the valve at port 1 was 204 reopened to establish a connection between the water pump and micromodel. Afterwards,  $CH_4$ 205 pump was retracted via port 3 at a constant rate of 30-60 ml/hour until the pressure reached CH<sub>4</sub> 206 gas hydrate equilibrium pressure ( $P_{eq}$ ) at the given temperature ( $P_{eq}=32$  bar for CH<sub>4</sub> gas hydrate at 1.5 °C using CSMGem). From Peq and below, the pump was retracted at 10 ml/hour to observe 207 208 dissociation. During retraction, the water pump pressure was reduced gradually to 35 bar to 209 maintain a manageable pressure difference between the water pump (port 1) and gas pump (port 210 3). Subsequently, the water pump was shut down, but the valve (port 1) remained open to allow

211 recording of differential pressure during dissociation. The retraction was continued until full
212 dissociation was observed except for some experiments where hydrates did not dissociate even at
213 atmospheric pressure. Thermal stimulation was then needed to finalize hydrate dissociation.

Temperature variation during the experiment would affect dissociation pressure. The uncertainty associated with a thermometer is in the range  $\pm 0.1$ °C and temperature had the uncertainty of  $\pm 0.2$ °C. The methane gas volume injected/retracted from the pump is an important parameter for calculating hydrate saturation. The fluctuation in room temperature may cause a change in gas volume in the range of  $\pm 0.7$  ml at 83 bar under ideal gas law.

Table 1 summarizes the P-T conditions and dissociation techniques used for each experiment. The experiments were divided into three different groups based on the dissociation temperature that was used. For experiments 1-3, the dissociation temperature was above 0°C. For experiments 4 and 5, the dissociation temperature was close to 0°C. For experiment 6-8, the dissociation temperature was below 0°C. If depressurization (DP) was insufficient to complete hydrate dissociation within 24 hours, thermal stimulation (TS) was additionally used.

Table 1 Experimental summary of P, T conditions during hydrate formation and dissociation. DP = Depressurization, TS =
 Thermal stimulation.

Exp.	H	lydrate forma	ition	Hydrate dissociation				
	P (bars)	T (°C)	Method	Peq (bars	T (°C)	Method		
1	85	0.9	Agitation	28.4	0.9	DP		
2	80	0.8	Agitation	28.1	0.8	DP		
3	60	1.0	Memory	28.7	1.0	DP		
4	79	1.4	Agitation	25.0	-0.5	DP		
5	71	1.5	Agitation	25.4	-0.1	DP+TS		
6	80	1.7	Agitation	23.3	-3.0	DP+TS		
7	55	1.9	Memory	23.4	-2.6	DP		
8	80	2.0	Agitation	23.4	-2.7	DP+TS		

For all experiments excluding 3 and 7, agitation was used to initiate hydrate nucleation effectively.
During experiments 3 and 7, hydrate nucleation occurred quickly without any agitation due to the
memory effect of water, which had pressure and temperature history from previous experiments.

**3. Results and Discussion** 

Micromodel experiments were carried out to visualize the dissociation behaviour at different dissociation temperatures both below and above 0 °C to discuss the methane hydrate phase change during depressurization, self-preservation and re-formation stage. The qualitative study was performed to study the gas production behaviour from methane hydrate reservoir under different hydrate saturation and arrangement within pore space under subzero temperature conditions.

# 237 3.1. Hydrate formation at constant P and $T > 0^{\circ}C$

238 Direct visualization confirmed that hydrate nucleation and subsequent growth is a rapid process 239 described as a heterogeneous front movement along with fluid interfaces. The hydrate formation started at the gas and water interface <sup>28,29,34</sup> and encapsulated the gas phase by hydrate films (HF). 240 241 Initial water and gas saturation and mass transfer of gas/water molecules across the hydrate film controlled the hydrate film vertical thickness <sup>35</sup>. The thickness of the hydrate film between the gas-242 liquid interface has previously been estimated to be  $10-20\mu m^{27,36,37}$ . The gas bubbles were usually 243 244 fully consumed in areas with low gas saturation, whereas gas remained coated by hydrate films in 245 areas with high gas saturation and limited availability of water [23]. Hydrate formation in the water 246 phase was also observed when liquid water was saturated with dissolved methane <sup>29,38</sup>. 247 Crystallization of hydrates in the water phase led to transparent hydrate crystals (HC) that were 248 easily distinguishable from the dark-grey coloured hydrate films because of the difference in 249 refractive indexes between gas, water, and hydrates (Gas hydrate = 1.35, Water = 1.33, gas = 1)<sup>39</sup>.

Laboratory studies deal with the oversupply of gas, whereas in nature, hydrate formation is controlled by limited gas supply that leads to crystalline hydrates as pore water is over-saturated with gas. Table 2 provides the information regarding hydrate formation pressure, temperature, subcooling temperature, observed hydrate morphology and change in different phase saturations before and after hydrate formation and hydrate distribution. The fluid saturations were quantified based on image analysis and provide an estimation of the 2D fluid saturations.

256 Table 2 Experimental summary of P, T conditions and fluid saturations during hydrate formation. HF = Hydrate films, HC=

	Consta	nt P, T		Before for	After				
Exp.	P(bars)	T(°C)	T <sub>eq</sub> -T	S <sub>iw</sub>	Sig	$S_{W}$	Sg	$S_{\mathrm{H}}$	HM
1	85	0.9	10.6	10 %	90 %	1 %	6 %	93 %	HF
2	76	0.8	9.7	93 %	7 %	92 %	0 %	8 %	HC
3	60	1.0	7.2	61 %	39 %	8%	4%	88 %	HF, HC
4	79	1.4	9.4	57 %	43 %	1 %	5 %	95 %	HF
5	71	1.5	8.3	56 %	44 %	16 %	0 %	84 %	HC
6	80	1.7	9.2	50 %	50 %	7 %	2 %	91 %	HF, HC
7	55	1.9	5.5	53 %	47 %	12 %	1 %	87 %	HF
8	80	2.0	8.9	87 %	13 %	74 %	1 %	25 %	HF, HC

257 *Hydrate crystals, Teq-T = Subcooling. Teq was calculated using CSMGem, HM = Hydrate morphology* 

258

In general, hydrate morphology in pore space could be grain cementing or pore-filling. For  $S_{iw}$  = 259 0.35, or above, hydrate formed are pore filling <sup>40,41</sup>. Ohmura et al. <sup>42</sup> studied the methane hydrate 260 261 morphology experimentally and found that system pressure does not influence the formation 262 mechanism. Methane hydrate formed at gas-liquid interface and later hydrate grew into liquid 263 water due to methane solubility. Many morphology-based studies suggest that hydrate crystals 264 morphology depends on the applied driving force. Several morphologies studies suggest that 265 Hydrate crystals morphology depends on applied driving force such that at higher driving force, crystal growth would become more random due to faster nucleation at different locations <sup>43</sup>. 266

267 Figure 2 summarizes the hydrate morphologies observed after hydrate formation at constant T 268 above 0°C. The field of view includes porous HF, non-porous HC, pore water, and gaseous CH<sub>4</sub>. 269 Figure Exp.3a, 5.a and 7.a show initial gas and liquid saturation and distribution before hydrate 270 formation starts. The difference in initial conditions leads to heterogeneity defined by the 271 difference in hydrate saturation and distribution, as shown in Figure Exp.3c, 5.c and 7.c. It is 272 common practice to modelled hydrate systems as homogenous systems and constant hydrate saturation at pore scale during the gas production modelling <sup>4445</sup> however natural hydrate system 273 274 is complex, and hydrate distribution is heterogeneous <sup>46</sup>. Heterogeneity would cause the 275 development of a preferential pathway for fluid migration during the depressurization.



Figure 2. Overview of three different hydrate distribution patterns (Exp. 3, 5, and 7) in the pore space at  $T > 0^{\circ}C$ . The silicon grains, liquid water, and gaseous  $CH_4$  are coloured brown, blue, and red, respectively when required. The  $CH_4$  gas hydrate phase

278 is not segmented, and porous hydrate films (HF) are observed in dark grey and non-porous crystalline hydrate (HC) in transparent 279 white. Figure Exp.3c, Exp.5c and Exp.7c show three different hydrate morphology at the end of the formation. Field of view in 280 Figure Exp.3a shows equal water and methane gas saturation. During hydrate formation, gas dissolved into water and hydrate 281 film encapsulating the gas phase as shown in figure Exp.3b. Figure Exp.3c displays both porous and non-porous hydrates along 282 with unconsumed liquid water and CH<sub>4</sub> gas. Shows hydrate morphology distribution, including hydrate crystals and hydrate film. 283 Field of view in figure Exp.5a shows high Siw and low Sig before the start of hydrate formation. During hydrate formation, methane 284 gas saturated water crystalized first, as shown in figure Exp.5b. Field of view after 60 minutes in figure Exp.5c displays non-porous 285 and liquid water. All gas consumed during hydrate growth. Figure Exp.7a illustrates high Sig and low Siw. Figure Exp.7b displays 286 HF encapsulating CH<sub>4</sub> Gas in the middle of the pores as well as some HC. Figure Exp.7c displays both porous hydrates and 287 unconsumed liquid water and CH<sub>4</sub> gas.

The figure 2 above confirms that hydrate distribution within pore space is characterized as heterogeneous due to different initial conditions, including pressure and temperature, initial fluid saturations and distribution. Pore-scale heterogeneity in hydrate saturation would create uncertainty in gas production behaviour, and production rate can vary up to  $\pm 25\%$  <sup>47</sup>. Lab-scale experiments using different formation techniques also confirm heterogeneous methane hydrate formation in pore space <sup>48</sup>.

Experiment 1 started with high gas saturation,  $S_{ig}=90\%$ , and HF formed and encapsulated the gas phase. Experiment 2 had high initial water saturation,  $S_{iw} = 93\%$ , and HC were formed, and the gas was fully consumed. Experiment 3 has initial water and gas saturation equal to 61% and 39% respectively, and hydrate distribution included HC and HF. Subcooling temperature ( $T_{eq}$ -T) varied between 5.5 to 10.6 °C however, no correlation between subcooling and hydrate morphology was observed. Additionally, the growth pattern during hydrate formation also depends on pore size distribution, pore throats, and capillary forces that control initial water and gas distribution.

301

# 302 3.2. Phase transitions during cooling to T < 0 °C at constant P

The change in water, gas and hydrate saturations were recorded and quantified during cooling of 303 304 the micromodel from  $T > 0^{\circ}C$  to  $T < 0^{\circ}C$  at constant pressure (Table 3). However, the similar 305 texture and refractive index between CH<sub>4</sub> hydrates and ice made it difficult to distinguish the two 306 phases from one another. Thin layers of ice formed close to the grain surface could neither be 307 identified due to limitations of the magnification power. Additionally, metastable unfrozen pore water was always present after cooling to subzero temperature <sup>49</sup>. Some of the pore water in 308 309 permafrost does not convert into ice because of the freezing temperature of the water is depressed 310 below 0°C due to confining pressure, dissolved salts and capillary forces.

311 Table 3 Change in fluid saturation during cooling below 0 °C. HF = Hydrate films, HC= Hydrate Crystals, (Tf= Formation

312 Temperature above 0 °C, Tf1=formation temperature below 0 °C) Sfw = Final water saturation below 0 °C, Sfg = final gas

313 saturation below 0°C. HM = Hydrate Morphology

	Cooli	ng	Above 0°C			Belo			
Exp	T <sub>f</sub> (°C)	T <sub>f1</sub> (°C)	Siw	Sig	S <sub>H</sub>	Sfw	S <sub>fg</sub>	S <sub>H</sub> /S <sub>ice</sub>	HM
4	1.4	-0.5	1 %	5%	95%	1%	6%	93%	HF
5	1.5	-0.1	16 %	0%	84%	10%	0%	90%	HC
6	1.7	-3.0	7 %	2%	91%	4%	4%	92%	HF, HC
7	1.9	-2.6	12 %	1%	87%	9%	4%	87%	HF
8	2.0	-2.7	74 %	1%	25%	74%	2%	24%	HF, HC

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During cooling to below 0°C, there was a general trend that the unfrozen pore water content decreased as the ice was formed, and the gas saturation slightly increased (Figure 3). During cooling below 0°C, not all pore water converted into ice. The amount of unfrozen pore water is dependent on temperature, sediment type, hydrate forming Gas and Gas pressure<sup>50</sup>. As temperature decrease from 0°C to  $-3^{\circ}$ C, amount of unfrozen water content decreased<sup>5051</sup>. The gas saturation increased from 2% to 4% in Experiment 6 and from 1% to 4% in Experiment 7. These new gas pockets were generated either due to the release of CH<sub>4</sub> from CH<sub>4</sub> saturated water as it crystallized

322 into ice or from liberated CH4 when porous HF was destabilized and converted into ice. The CH4 323 gas solubility in water decreases with decreasing temperature in the hydrate stability region <sup>5253</sup>. 324 The cooling process could therefore trigger additional hydrate formation from dissolved CH<sub>4</sub> in 325 the water phase. However, the increase in CH<sub>4</sub> gas saturation during cooling, suggests that the 326 formation of ice was preferred over the formation of additional hydrates. Mechanisms such as the 327 expulsion of gas during water crystallization, trapped gas in low permeable rock, conversion into 328 hydrate, and extent of the hydrate stability zone due to loading by an ice sheet may cause pore gas hydrate formation in permafrost <sup>54</sup>. Likelihood of methane gas presence in permafrost is higher <sup>55</sup>, 329 and the presence of free methane in near-surface permafrost is reported previously <sup>56</sup>. 330



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Figure 3 Temperature-induced gas pocket development in Exp. 6 and 7 during cooling below 0°C. The silicon grains, liquid water, and gaseous CH<sub>4</sub> are coloured brown, blue, and red, respectively. The CH<sub>4</sub> gas hydrate phase is not segmented, and porous hydrate films (HF) are observed in dark grey and non-porous crystalline hydrates (HC) in transparent white. During cooling, new gas pockets (red) appeared, and the water saturation (blue) decreased. The amount of ice that formed during the cooling could not be inferred from the images.

# 337 3.3. Effect of temperature on hydrate dissociation by pressure depletion

Hydrate dissociation during depressurization within porous media is influenced by heat transfer,
 mass transfer and intrinsic kinetics <sup>57–59</sup>. At the laboratory scale, kinetics and heat transfer

influence the dissociation behaviour whereas, at the field scale, the mass transfer via gas/water flow away from the hydrate dissociation front also influence the dissociation <sup>59</sup>. Overall, hydrate dissociation is characterized as endothermic process predominantly influenced by heat transfer due to the development of temperature gradient within the hydrate region during the dissociation <sup>57</sup>.

#### 344 **3.3.1** Hydrate dissociation at constant T > 0°C

In this section, we have discussed the effect of hydrate morphology and its distribution within micromodel on the gas production behaviour during the dissociation at constant T >0°C. Dissociation through pressure depletion was conducted for three different hydrate saturation and distributions (Table 4).

**Table 4** includes experimental conditions for hydrate dissociation at constant T > 0°C. Pi denotes the pressure at the start of the dissociation. P1 denotes the pressure value at which dissociation/phase changes first occurred, and P2 is the pressure value at which the hydrate completely dissociate within FOV. Peq is calculated using CSMGem software for pure CH<sub>4</sub> gas hydrate at the given temperature. PM = Production method, DP = Depressurization, HM = Hydrate Morphology

Exp	T (°C)	Before dissociation			HM	Pressure response (bars)				$\Delta t (min)$	PM
		Sw	Sg	S <sub>H</sub>		P (bar)	Peq	<b>P</b> <sub>1</sub>	P <sub>2</sub>		
1	0.9	1%	6%	93%	HF	85	28.4	27.58	22.75	46	DP
2	0.8	92%	0%	8 %	HC	76	28.1	19.50	14.12	135	DP
3	1.0	8%	3%	89%	HF, HC	60	28.7	18.30	15.98	61	DP

353

Experiment 1 had high hydrate saturation,  $S_H=93\%$ , and contained HF and free gas. Experiment 2 had low hydrate saturation,  $S_H=8\%$ , and contained HC and pore water, while experiment 3 had high hydrate saturation,  $S_H=88\%$ , and contained HF, HC, and pore water within FOV. During pressure depletion, in each experiment, dissociation was observed at different pressures below the equilibrium pressure ( $P_{eq} \sim 28$  bar).



360 Figure 4 Overview of the dissociation behaviour in Experiment 1. Dissociation temperature was 0.9°C, and the starting pressure 361 was P = 85 bar. Dissociation was carried out at a constant flow rate of 10 ml/hours. Methane hydrate stability pressure is P =362 28.4 bar at T = 0.9 °C. Figure Exp. 1a shows initial water and gas saturation before hydrate formation starts. FOV can be defined 363 as low water and high gas saturation containing system. Figure Exp. 1b displays the hydrate distribution and saturation at the start 364 of the dissociation experiment. FOV displays high hydrate saturation containing HF and free gas saturation. Figure Exp.1c 365 displays the segmented field of view, where red indicates the gas pockets. Figure Exp. 1d is the status within the field of view (FOV) 366 when pressure was reduced to 28.21 bar, after 35 minutes. No change in the field of view was observed. Figure Exp.1e shows the 367 first dissociation point at P = 27.58 bar at t = 36 min shows HF melting. Figure Exp. If shows complete dissociation at t = 46 minutes 368 at P=22.75 bar.

369 Figure 4 illustrates the dissociation behaviour in experiment 1. FOV contains high hydrate 370 saturation consists of HF ( $S_H$ = 93%) and free gas (6%). In experiment 1, HF started to dissociate 371 immediately at P = 28.21 bar (refer to Figure Exp.1d) below  $P_{eq}$  (CH4) = 28.4 bar due to porous 372 nature and liberated Gas mobilized through the connected gas phase, leaving the hydrate film in 373 contact with water. HF dissociated rapidly and from the centre of pore space towards pore walls 374 and created a preferential pathway for fluid migration within hydrate distribution. Porous hydrates 375 in excess gas environment experienced pressure response via connected gas phase, and the 376 liberated CH<sub>4</sub> gas escaped the dissociation front via advective gas flow. Dissociation of HF formed

in narrow pore throats or in contact with water stopped temporarily, until gas invaded or expanded into pore throats from other parts of the micromodel, and contacted the hydrate (refer to Figure Exp.1e). Hydrate in FOV fully dissociated at P = 22.75 bar, approx. 6 bar below the hydrate stability pressure ((refer to Figure Exp.1f).

381 In contrast, in experiments 2 and 3, the first dissociation was observed at 19.5 bar and 18.3 bar, 382 respectively, which is 9 bar and 10.4 bar below the equilibrium pressure. Figure 5 displays the 383 dissociation behaviour observed in experiment 2. The hydrate morphology was dominated by HC. 384 FOV contained HC ( $S_H=8\%$ ) and pore water ( $S_w=92\%$ ) (refer to Figure Exp.2b). Hydrate stability 385 pressure  $P_{CH4} = 28.1$  bar at T = 0.8 °C. No change in FOV was observed when the pressure reached 386 at P = 19.53 bar (refer to Figure Exp.2d). HC experienced pressure response via the water phase, 387 and initial liberated CH<sub>4</sub> gas was trapped as immobile gas bubbles (figure Exp.2e and figure 388 Exp.2f). The trapped gas bubbles started to mobilize when they achieved a critical size through 389 coalescence with other nearby gas bubbles. A low hydrate saturation and the presence of free gas in the pores could accelerate the coalescence of the gas bubbles <sup>32,33</sup>. During pressure reduction, 390 391 liberate gas from dissociation in adjacent pores invaded the field of view, displaced water from 392 pore space and accelerated coalescence of isolated gas bubbles (refer to figure Exp.2f). In case of 393 high hydrate saturations dominated by HC, the coalescence of gas bubbles would be slow due to 394 shielding by non-porous hydrates. The dissociation front advanced through the pores dissociating 395 HC in larger pore space while hydrate filled pores with narrow pore throats remained un-396 dissociated due to higher entry capillary pressure as the pressure response propagated to the next 397 pore (refer to figure Exp.2h). Dissociation of HC in small pore throats occurred via methane gas 398 molecule diffusion through the water phase. It is proposed that gas molecules from hydrate crystals 399 diffuse through the water phase to the free gas phase in adjacent pore due to the methane

400 concentration gradient in water phase between free gas-water interface and water-hydrate 401 interface. This gradient was caused by the difference in methane solubility in water phase due to 402 the difference in temperature at two interface caused by endothermic hydrate dissociation <sup>29</sup>.



404 Figure 5 Overview of the dissociation behaviour in experiment 2. Dissociation temperature was 0.8°C, and the starting pressure 405 was P = 76 bar. Dissociation was carried out at a constant flow rate of 10 ml/hours. Figure Exp.2a display initial liquid water (W) 406 and gas (G) saturation before hydrate formation. Figure Exp.2b display hydrate distribution before dissociation starts. Field of 407 view includes crystalline hydrates (HC), water (W) and grains. Figure Exp.2c show segmented image. Blue colour indicates the 408 presence of water and brown colour shows grains. HC are shown within the circle. No gas pocket was observed in the field of view. 409 The starting saturation state is characterized as low hydrate saturation having HC surrounded by water in pore space. Figure 410 Exp.2d is the status within the field of view (FOV) when pressure was reduced to 19.53 bar, after 48 minutes. No change in the 411 field of view was observed. Figure Exp.2e shows the first dissociation point at P=19.23 bar when the gas bubble appeared at t =412 49 minutes. Figure Exp.2f shows the gas invasion from adjacent pores into the field of view displacing the water in pore space at 413 P=18.7 bar, t=53 minutes. Figure Exp.2g shows the gas dissolve back into water reflected by a decrease in gas saturation at t=

414 55 minutes. Figure Exp.2h display invaded Gas-assisted HC dissociation at large pore space and stabilized HC in small pore 415 throats, and free gas does not enter these pore throats. Figure Exp.2i shows the full dissociation at t=135 minutes at P=14.12 bar.

Due to endothermic cooling and Joule Thomson effect <sup>60</sup>, immobile trapped gas bubbles could 416 417 participate in secondary hydrate formation that would enhance the hydrate saturation within the pore space and reduce the relative permeability of the gas <sup>61,62</sup>. This could lead to gas pockets being 418 419 temporarily trapped and surrounded by secondary hydrates. Delayed hydrate dissociation above 420 0°C due to extent and type of hydrate morphology can be described as hydrate self-preservation effect above 0°C. Makogon and Ghassemi<sup>63</sup> studied self-preservation for methane hydrate formed 421 422 in freshwater above 0°C and suggested that self-preservation is caused by a change in pore space 423 structure and size due to hydrate accumulation. Change in pore space geometry in the presence of 424 hydrates increased the capillary pressure in pore space and reduced the water vapour pressure. In 425 such cases, the gas production rate was a low, discontinuous and higher amount of energy needed 426 to dissociate the hydrates in pore space. The pressure was depleted far below the equilibrium 427 pressure before all the hydrates dissociated in the FOV.

428 **Figure 6** below demonstrate the dissociation behaviour of hydrate system in experiment 3 having 429 both HC and HF present within the field of view. FOV included high hydrate saturation (SH = 430 containing HC, HF, pore water and CH<sub>4</sub> gas. Dissociation was carried out at constant temperature T = 1°C. When pressure arrived P = 18.3 bar, 10 bar below the hydrate stability pressure ( $P_{eq}$  = 431 432 28.7 bar), HF encapsulating the gas phase dissociated (refer to Figure Exp.3d). Hydrate film in all 433 pores dissociated uniformly, and dissociation started from the middle of pore space. Heterogeneity 434 in hydrate distribution and HF melting had created a preferential pathway within FOV for gas 435 migration. HC in large pore space dissociated but gas remained trapped encapsulated by HF 436 indicated by grey colour (refer to Figure Exp.3e). Dark-grey HF began to dissociate in pores when 437 in contact with the gas phase or when the size of gas inside these dark film achieve critical size 438 (refer to Figure Exp.3f). Increase in gas saturation due to dissociation leads to invasion of gas into 439 narrow pore throats against high capillary pressure and dissociate remained HC and HF. Hydrate 440 in narrow pore throats was last to dissociate through the invasion of gas into pores and /or methane 441 diffusion via connected liquid phase. (refer to Figure Exp.3j, Exp.3i)





Figure 6 Overview of the dissociation behaviour in experiment 3. Dissociation temperature was 1.0°C, and the starting pressure
was P = 60 bar. Dissociation was carried out at a constant flow rate of 10 ml/hours—figure Exp.3a display initial liquid water
(W) and gas (G) saturation before hydrate formation. Figure Exp.3b display hydrate distribution before dissociation starts. Field
of view includes crystalline hydrates (HC), hydrae films (HF), water (W), Gas (G) and grains. HC and HF are identified within
the circle. Figure Exp.3c show segmented image. Blue colour indicates the presence of water, red colour shows gas and brown
colour shows grains. The starting saturation state is characterized as high hydrate saturation having HC, and HF surrounded by

water and gas in the pore space. Figure Exp.3d showed hydrate film dissociation when pressure was reduced to 18.3 bar, after 50 minutes. Dissociation initiate at the centre of the pores. Figure Exp.3e shows complete dissociation of hydrate films, and liberated gas mobilized within pore space. Dissociation of HC adjacent to HF initiated. Figure Exp.3f shows the black colour hydrate films encapsulating liberated Gas from HC dissociation. Figure Exp.3g shows the liberated gas from black hydrate film dissociation expand to nearby HC present in narrow pore throats. Figure Exp.3h shows un-dissociated HC in pore throats dissociated by free gas or via methane gas diffusion through the water phase. Figure Exp.3i shows the full dissociation at t=61 minutes at P=15.98 bar.

The observations during this study reconfirm that porous hydrate and non-porous hydrate have 456 distinctive dissociation behaviour that affects production rates of CH4 Gas <sup>32,64</sup>. The hydrate phase 457 458 present in small pore throats is last to dissociate due to high capillary pressure. Hydrate 459 dissociation is also accelerated in the presence of mobile free gas due to increased mass transfer 460 and added convective heat flow to the overall heat transfer <sup>27</sup>. Endothermic nature of dissociation 461 makes the mobility of gas phase in pore space an essential factor as immobile free gas act as heat 462 insulator compare to water and restrict the heat transfer to the gas hydrate dissociation front thus 463 lead to low dissociation rate. Heterogeneous hydrate saturation influence gas production rate such 464 that gas recovery is slower for high hydrate saturation, and total gas produced is dependent on overall saturation <sup>6547</sup>. Simulation studies have also confirmed that gas production enhanced in 465 the presence of free gas <sup>66</sup>. Therefore hydrate distribution with free gas presence would be an 466 attractive target for gas production by pressure depletion. Recently, experimental studies show that 467 468 hydrate specific surface area also control hydrate dissociation kinetics <sup>67</sup> such that surface coating hydrate dissociates faster than pore filling hydrates due to the higher specific surface area <sup>68</sup>. It is 469 suggested that the hydrate surface area is a linear approximation of  $(hydrate volume)^2$  during 470 471 depressurization and (hydrate volume)<sup>3</sup> during thermal stimulation. Hydrate surface area is also proposed as a linear relationship of (hydrate volume) $^{2/3}$  for given hydrate saturation threshold  $^{67}$ . 472

473 **3.3.2** Hydrate dissociation via depressurization at constant T < 0°C

- 474 In this section, we have discussed hydrate phase change during the pressure depletion at constant
- 475 temperature T  $<0^{\circ}$ C and the effect of heterogeneity in hydrate saturation within micromodel and
- 476 dissociation temperature on the production rate and total production yield. (refer to table 4).

477 *Table 5* includes initial dissociation temperature (Td), initial hydrate/Ice saturation (SH/Sic), Initial starting pressure (P), Pressure

- 478 at which the first dissociation observed (P1) and pressure at which hydrate fully dissociated (P2), Peq (CH4) was calculated using
- 479 CSM gem software, the total time during depressurization (Δt), Description of hydrate morphology pattern within field of view
- 480 (FOV) and Dissociation method (DM). HM = Hydrate Morphology

Exp	T <sub>d</sub> (°C)	Before dissociation			HM	Pressure response (bars)				$\Delta t (min)$	DM
		Sfw	Sfg	SH/Sice		Р	Peq	<b>P</b> 1	<b>P</b> <sub>2</sub>		
4	-0.5	1 %	6 %	93 %	HF	79	25.0	22.9	20.1	42	DP
7	-2.6	9 %	4 %	87 %	HF	55	23.4	15.5	14.4	89	DP
5	-0.1	10 %	0 %	90 %	HC	71	25.4	-	-	2846	DP+TS
6	-3.0	4 %	4 %	92 %	HF+HC	80	23.3	17.8	5.0	1115	DP+TS
8	-2.7	74 %	2 %	24 %	HF+HC	80	23.4	14.2	13.0	1450	DP+TS

481

482 Kinetics of methane hydrate dissociation below 0°C can be divided into two steps due to ice 483 shielding mechanism.<sup>69</sup>. The first step includes melting of water lattice and desorption of methane 484 molecule from the surface of the hydrate particle; the second step includes methane gas molecule 485 migration towards the gas phase via diffusion through the ice sheet. The second step is the rate-486 determining step <sup>70</sup>. Table 5 describes the dissociation behaviour in experiments 4 and 7, carried 487 out in the subzero temperature range (0 °C to -3 °C). We have discussed dissociation behaviour in 488 Experiment 4 and experiment 7 together due to similar hydrate morphology at the start of hydrate 489 dissociation. Experiments 4 and 7 had high saturations,  $S_H=93\%$  in experiment 4 and  $S_H=87\%$  in 490 experiment 7. In both cases, the hydrate saturation and morphology were very similar. Porous 491 hydrates films HF were visible in FOV identified by their grey colour texture. FOV was also 492 saturated with unfrozen pore water and gaseous CH<sub>4</sub> gas.

493 Figure 6 illustrates the dissociation sequence in experiment 4 under pressure depletion. FOV 494 contained HF was surrounded by the free gas phase, and small pores contained hydrate crystals 495 (refer to figure Exp.4b). Hydrate stability pressure is  $P_{CH4} = 25$  bar at T = -0.5°C. At constant 496 production rate (10 mL/hour), the first instance of hydrate dissociation was observed at a pressure 497 of 22.9 bar indicated by uniform and rapid dissociation of HF which created preferential gas 498 migration pathway (refer to Figure exp.4e). The pressure at the first instance of dissociation was 2 499 bar below the dissociation pressure due to lower sensible heat availability from surrounding at T< 500  $0^{\circ}$ C. At the same time, hydrate crystals also dissociated indicated by a change in colour from 501 transparent to dark-grey. Liberate gas remained encapsulated in hydrate film (refer to Figure 502 exp.4f). As pressure further decreased, gas front arrived at HF, and Gas-assisted dissociation 503 happens due to enhance mass transfer caused by connecting the gas phase (refer to Figure exp.4g). 504 HF within narrow pore throats and smaller pore space were last to dissociate (refer to Figure 505 exp.4i) and hydrate fully dissociated at P = 20.1 bar after 42 minutes.





507 Figure 6 Overview of the dissociation behaviour of CH4 gas hydrate in experiment 4. Dissociation is carried out at -0.5°C in 508 experiment 4. Dissociation is carried out at a constant flow rate of 10 ml/hours. Figure Exp.4a display initial water and gas 509 saturation before hydrate formation. Figure Exp.4b show hydrate distribution and starting saturation state at P = 79 bar, T = -0.5510  $^{\circ}C$  before dissociation starts. Figure Exp.4c shows the segmented field of view displaying grey hydrate film and gas pockets in red 511 colour. Figure Exp.4d display partial melting of HC indicated by the change in colour from white to grey. Figure Exp.4e displays 512 the first instance of hydrate dissociation at P=22.9 bar. Figure Exp.4f displays hydrate melting initiation at different locations. 513 Figure Exp.4f to Figure Exp.4h displays hydrate melting, indicating continuous hydrate dissociation. Figure Exp.4i display full 514 hydrate dissociation within 42 minutes when pressure arrived at 20.1 bar. No hydrate and ice formation was observed

Figure 7 illustrates the dissociation behaviour in experiment 7. FOV included dark-grey HF, unfrozen pore water and trapped gas (refer to figure Exp.7b). Methane hydrate stability pressure  $P_{CH4}$  is 23.4 bar at T = -2.6°C. As pressure started to go below stability pressure, trapped gas in isolated pore space expanded with no distinctive dissociation until pressure arrived at P=15.5 bar

(refer to Figure Exp.7d and Exp.7e). Large pressure drop ( $\Delta P = 8$  bar) was required to dissociate HF due to low sensible heat availability in surrounding as the temperature was -2.6°C. HF dissociated rapidly and uniformly and created a preferential pathway for gas and liquid migration (refer to Figure Exp.7f). Hydrate formed within narrow pore throats were last to dissociate as gas was not able to invade into crystals due to high capillary pressure (refer to Figure Exp.7g). Complete dissociation was observed at P = 14.4 bar after 89 minutes.





**Figure** 7 Overview of the dissociation behaviour of CH4 gas hydrate in experiment 7. Dissociation is carried out at -2.6°C. Dissociation is carried out at a constant flow rate of 10 ml/hours. Figure Exp.7a display initial water and gas saturation within the field of view before hydrate formation. Figure Exp.7b show hydrate distribution and starting saturation state at P = 55 bar, T = -2.6 °C before dissociation starts. Figure Exp.7c shows the segmented field of view

displaying grey hydrate film and gas pockets in red colour and water pocket in blue colour. Figure Exp.7d and Figure Exp.7d display partial dissociation indicated by an increase in gas saturation. Figure Exp.7e and Figure Exp.7f display the first instance of hydrate film dissociation at P = 15.5 bar after t = 59 minutes. Figure Exp.7g displays undissociated hydrates which fully dissociated at P = 14.4 bar after t = 89 minutes, as shown in Figure Exp.7h. No hydrate and ice formation was observed

535 Dissociation behaviour in experiment 4 and experiment 7 illustrate that depressurization was 536 sufficient to completely dissociate the hydrate, and no heating was required. No secondary hydrate 537 formation was observed during the dissociation. Dissociation behaviour in experiments 4 and 7 538 can also be compared with experiment 1 due to similar hydrate morphology at the start of 539 dissociation. All three experiments, hydrate morphology HF and some amount of HC at narrow 540 pore throats. Presence of HF suggests high initial gas saturation and low initial water saturation. 541 Depressurization was found to be sufficient to dissociate completely without combining with other 542 techniques such as thermal stimulation. However, as dissociation temperature decreased from 543  $0.9^{\circ}$ C in experiment 1 to -2.6°C in experiment 7, a larger pressure drop was required below stability 544 pressure to initiate the hydrate dissociation. For example, in experiment 1, hydrate started to 545 dissociate at P = 27.58 bar, whereas in experiment 4, it started to dissociate at 22.9 bar and in 546 experiment 7, it started to dissociate at P = 15.5 bar. This was due to lower sensible heat available 547 in surrounding as temperature reduced.

Table 5 also provides information regarding the dissociation behaviour in experiments 5, 6 and 8. In experiment 5, dissociation was performed at -0.1 °C, whereas in experiments 6 and 8 dissociation experiments were performed at -3 °C approx. Hydrate distribution in experiments 5, 6 and 8 was different from experiments 4 and 7. In experiment 5, 6 and 8 hydrate saturation included a high volume of the non-porous and low volume of porous hydrate and had different hydrate distribution than experiments 4 and 7. Hydrate saturation before dissociation in experiment
5, 6 and 8 was 90%, 92% and 24% respectively. In experiments 6 and 8 hydrates were surrounded
by unfrozen pore water and trapped gas, whereas, in experiment 5, only unfrozen pore water was
visible in FOV.

557 Figure 8 describes the hydrate dissociation behaviour in experiment 5. Dissociation was carried 558 out by depressurization, followed by heating. Hydrate morphology within FOV included 559 crystalline hydrates coexisting together with ice or unfrozen pore water. Due to the near similar 560 refractive index, it was hard to differentiate hydrate from unfrozen water. Hydrate saturation could 561 be described as high saturation ( $S_{H/Ice} = 90\%$ ) calculated using image analysis. No gas pockets 562 were visible within the field of view. During the pressure depletion at T = -0.1 °C, hydrate crystals 563 remained un-dissociated, and no partial dissociation or re-formation was observed when pressure 564 arrived and remained at 12 bar for 1260 minutes (refer to Figure exp.5d). The pressure further 565 reduced to 1 bar and remained stable at 1 bar for other 1620 minutes (refer to Figure exp.5e). 566 According to CSMGem based calculation, methane hydrate stability pressure is around 25 bar at 567 1°C. No change within FOV was observed when methane hydrate remained outside its stability 568 condition, confirming the strong self-preservation nature of pore-filling crystalline hydrate. Self-569 preservation was caused by crystalline hydrates reaching the metastable stage under subzero temperature in the presence of unfrozen pore water <sup>71</sup>. Another possibility could be ice formation 570 571 in the model which obstructed the arrival of pressure response from the pump into the FOV. Due 572 to the similar refractive index, unfrozen pore water and hydrate were not easily distinguished. Ice 573 formation outside FOV was also not ruled out. Heating was used to dissociate hydrates in 574 experiment 5 ultimately. During temperature increase, two major dissociation stage was observed 575 within FOV. The first dissociation was observed below 0 °C suggesting melting of hydrate due to

576 their metastable nature below their stability pressure. Hydrate melting was confirmed visually 577 based on the creation of gas pockets during heating (refer to Figure exp.5f). It was observed that 578 no intermediate hydrate film formed unlike during pressure depletion stage and hydrate melted 579 locally and rapidly creating liberated gas. As the heat was continued to supplied, gas volume 580 expanded within FOV and Gas in contact with hydrate crystals initiated dissociation of HC. Gas-581 assisted HC dissociation involved two steps. In the first step, liberated gas was encapsulated by 582 dark-grey HF and in the second step, full dissociation and gas liberation (refer to Figure exp.5f). 583 Hydrate continued to dissociate either due to heat supply from beneath due to high thermal 584 conductivity of silicon wafer or through Gas-assisted dissociation (refer to Figure exp.5g). Hydrate 585 in small pore space and narrow pore throats remained intact. Second rapid and uniform melting 586 was observed at 0.5°C (refer to Figure exp.5h). Remained hydrate in narrow pore throats 587 dissociated as the temperature reached T = 0.6 °C (refer to Figure exp.5i). No hydrate re-formation 588 was observed during the heating. Experimental study on the dissociation behaviour of frozen 589 hydrate-bearing sediments by temperature increase suggested that hydrate dissociates before the 590 pore ice melting and critical temperature sufficient for gas hydrate dissociation varies from -3°C 591 to -0.3°C and depends on particle size and salinity of the water <sup>71</sup>.



593 Figure 8 Overview of the dissociation behaviour in experiment 5. Dissociation temperature was -0.1°C, and the starting pressure 594 was P = 71 bar. Dissociation was carried out at a constant flow rate of 10 ml/hours. Figure Exp. 5a displays initial water and gas 595 saturation within the field of view before hydrate formation. Figure Exp.5b show hydrate morphology and distribution at P = 71596 bar, T = -0.6 °C at the start of dissociation. Figure Exp.5c shows the segmented field of view displaying transparent HC, Ice and 597 water pocket in blue colour. Figure Exp.5d and Exp.5e display the field of view (FOV) at P=12 bar after 1260 minutes and at P=12598 1 bar after 2820 minutes. No change in the field of view observed due to strong self-preservation below subzero temperature. 599 Figure Exp.5f to Figure Exp.5i display the dissociation behaviour during heating. Figure Exp.5f display the first instance of HC 600 dissociation at multiple places within FOV, 6 minutes after the heating started. HC dissociation was rapid and liberated gas 601 expanded and invaded into pore space, accelerated and assisted the HC dissociation in the vicinity due to connected gas phase as 602 shown in Exp.5g. As the temperature continues to increase and arrived above 0°C, Figure Exp.5h shows second hydrate 603 dissociation above 0 °C at T=0.5 °C. HC in narrow pore throats and small pore space dissociated in the end at T=0.6 °C.

604 Experiments 4 and 5, had a similar dissociation temperature but had different dissociation 605 behaviour. Initial FOV in during both experiments contained a similar amount of hydrate saturation ( $S_H=87\%-93\%$ ) but differ in hydrate morphology and hydrate distribution. Hydrate morphology in experiment 4 included HF and visible gas pockets, whereas hydrate morphology in experiment 5 included HC and unfrozen pore water. Pressure depletion was sufficient in experiment 4 but not in experiment 5 due to high self-preservation shown by HC in the presence of unfrozen pore water. Thus the difference in dissociation behaviour is attributed to the difference in hydrate morphology and the amount of unfrozen pore water.

612 Dissociation behaviour during experiments 6 and 8 had similar characteristic hence discussed 613 together. Experiments 6 and 8 both had similar hydrate morphology having both porous hydrate 614 film and non-porous crystalline hydrates within FOV at the start of the hydrate dissociation. 615 Experiments 6 and 8 also had near similar dissociation temperature at -3°C and -2.7°C respectively. 616 Figure 9 describes the dissociation behaviour in experiment 6. The pressure at the start of the 617 dissociation was 80 bar, and the temperature was -3°C. During the pressure depletion, when 618 pressure arrived below hydrate stability pressure (PeqCH4 equal to 23.1 bar) no change in the 619 hydrate morphology was observed when pressure reduced to 17.8 bar after 60 minutes (refer to 620 figure Exp.6d). As pressure depletion continued further, quick rearrangement within the field of 621 view was observed after 36 seconds (refer to figure Exp.6e). Rearrangement was identified by HF 622 colour change into a dark colour, suggesting a change in hydrate film thickness followed by 623 crystallization of unfrozen pore water identified by white colour (refer to figure Exp.6f). This 624 process was quick and finished within 1 minute at P = 17.3 bar. Further pressure depletion did not 625 lead to any significant redistribution within the field of view as pressure reduced to 13.7 bar (refer 626 to figure Exp.6g). As pressure continued to decrease and reached 5 bar, HF thickness reduced from 627 the centre of pore space towards pore wall and liberated gas remained trapped due to high 628 saturation and low permeability (refer to figure Exp.6i). When the pressure remained constant at 629 5 bar for next 840 minutes, we observed an increase in gas saturation. Increase in gas saturation 630 was caused due to enhanced ability of gas molecules to diffuse through hydrate film as hydrate 631 films were much thinner at lower pressure compared to a higher pressure (refer to figure Exp.6j). 632 Released gas remained trapped due to blocking of pore space caused by the presence of hydrates 633 and ice. Hydrates remained stable in narrow pore throats and FOV contained low hydrate 634 saturation and high hydrate saturation. To fully dissociate the hydrates, ambient heating was used. 635 Heat transported into micromodel from beneath and uniformly dissociated hydrate due to high 636 thermal conductivity of silicon wafer when the temperature reached to T=-0.9°C (refer to Figure 637 Exp.6k). Hydrate fully dissociated as shown at temperature T = -0.7 °C (refer to Figure Exp.6r). No 638 hydrate re-formation was observed during the heating and hydrate melted uniformly. All hydrate 639 dissociated much below 0°C indicating no presence of ice within FOV at the start of dissociation.



640

641 Figure 9 Overview of the dissociation behaviour in experiments 6.  $CH_4$  stability pressure (P) is equal to 23.3 bar at  $T = -3^{\circ}C$ 642 (CSMGem). Dissociation was carried out at a constant pump retraction at a flow rate of 10 ml/hours. Figure Exp.6a displays 643 initial water and gas saturation within the field of view before hydrate formation. Figure Exp.6b show hydrate morphology and 644 distribution at P = 80 bar, T = -3.0 °C at the start of dissociation. Figure Exp.6c segmented field of view displaying transparent 645 black-grey HF, unfrozen pore water in blue and isolated gas pockets in red. Figure Exp. 6d shows the field of view after 60 minutes 646 at P = 17.8 bar, Figure Exp.6e, Exp.6f displays phase change at constant pressure identified by crystallization of unfrozen pore 647 water into ice (circled in Exp.6f) and change in hydrate film thickness. Figure Exp.6g, Exp.6h and Exp.6i show trapped gas pocket 648 creation due to retarded melting of hydrae films at the centre of pores when pressure reduced from 13.7 bar to 5 bar. Trapped gas

remained immobile at P = 5 bar for next 840 minutes, as shown in figure Exp.6j. Field of view included low hydrate saturation and high gas saturation at  $T = -3^{\circ}$ C. Hydrate films remain stable at narrow pore throats and smaller pore space due to hydrate selfpreservation at  $-3^{\circ}$ C in the presence of ice. The ambient heating technique was used to dissociate hydrates. Heat transported into micromodel from beneath and uniformly dissociated hydrate due to high thermal conductivity of silicon wafer. Figure Exp.6j show melting of ice and hydrate dissociation at  $T = -0.9^{\circ}$ C. Hydrate fully dissociated, as shown in Figure Exp.6r at temperature  $T = -0.7^{\circ}$ C. No hydrate re-formation was observed during the heating and hydrate melted uniformly.

655 Figure 10 illustrates the dissociation behaviour in experiment 8. The pressure at the start of the 656 dissociation was 80 bar and temperature was -2.7 °C. Hydrate saturation was low and included 657 porous hydrate film HF in dark-grey colour and transparent HC. Most of FOV included unfrozen 658 pore water. The presence of ice within FOV could not be confirmed. During pressure depletion 659 under constant pump flow rate retraction (10 ml/h), the first instance of hydrate dissociation was 660 observed at P = 14.2 bar identified by uniform melting of HF (refer to figure Exp.8d). Hydrate 661 dissociation occurred 9 bar below the methane hydrate stability pressure P = 23.4 bar at T = -2.7 °C caused by low sensible heat availability below subzero temperature <sup>72</sup>. Thereafter, ice formation 662 663 and secondary hydrate formation was observed. Ice crystallized from unfrozen pore water and 664 identified in white colour and the second hydrate formed in smaller pore space and narrow pore 665 throats identified in dark-grey colour (refer to figure Exp.8g). Secondary hydrate stability in pore 666 space was driven by capillary pressure variation due to pore space geometry and local pressure 667 and temperature conditions in pore space. Secondary hydrate stability was further enhanced by 668 self-preservation effect in the presence of ice in the surrounding. Liberated gas from retarded 669 dissociation of hydrate film remain trapped and expanded the gas volume already present in pore 670 space at 5 bar pressure(refer to figure Exp.8i). Unfrozen pore water and liberated water from the 671 HF melting in pore space also participated in the ice formation and secondary hydrate formation, thus improved the self- preservation during the dissociation process <sup>7313</sup>. 672



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**Figure 10** Overview of the dissociation behaviour in experiment 8.  $CH_4$  hydrate stability pressure (P) is equal to 23.4 bar at T=- **675** 2.7°C (CSMGem). Figure Exp.8a displays initial water and gas saturation within the field of view before hydrate formation. Figure **676** Exp.8b show hydrate morphology and distribution at P= 80 bar, T= -2.7 °C at the start of dissociation. Figure Exp.8c shows the

677 segmented field of view displaying black-grey HF, transparent HC and unfrozen pore water in blue. Field of view is characterized 678 as low hydrate saturation having heterogeneous distribution and high saturation of unfrozen pore water. Figure Exp.8d and Exp.8e 679 shows the first instance of hydrate film melting followed by an invasion of Gas within FOV from surrounding pore space at 14 bar 680 pressure. Figure Exp.8f, Exp.8g shows re-formation process occurred at 13.2 bar. Field of view in figure Exp.8g included trapped 681 gas pockets, ice from unfrozen pore water crystallization and black-grey film. Figure Exp.8h shows the field of view after 122 682 minutes when P = 13 bar. Exp.8i shows the field of view at P = 5 bar after 1405 minutes. FOV included expanded gas volume 683 trapped in pore space due to pore space blocking caused by ice formation. Figure Exp.8j – Figure Exp.8o shows dissociation 684 behaviour under heating. Figure Exp.8j-Exp.8k shows the field of view at T = -0.3 °C. FOV shows homogenous ice melting within 685 pore space as ambient heat supplied from beneath the hydrate due to high thermal conductivity of silicon wafer. Figure Exp.8l-686 Exp.8n shows the hydrate re-formation and dissociation during the heating process above T > 0 °C and P=5 bar, which lasted for 687 10 minutes. During the hydrate re-formation, water in pore space encapsulated gas pocket as HF which converted into a crystalline 688 form. Exp.8n show HC in pore space which was unstable and quickly dissociated, as shown in Figure Exp.8o at  $T=0.6^{\circ}C$ .

689 Re-formation involving secondary hydrate formation and ice formation is characteristically different from hydrate formation due to its shorter induction time <sup>74</sup> and can be identified due to 690 691 large rearrangement within FOV within a short period. Risk of re-formation was higher in the 692 presence of unfrozen pore water in the vicinity. The sensible heat of hydrate, heat supply from the 693 sediment grains and pore fluid and heat transport from surrounding though conduction and 694 advection were not sufficient for the heat required for endothermic dissociation during depressurization <sup>75</sup>. The re-formation process further reduced the in situ permeability and obstruct 695 696 the gas migration as gas pockets were trapped and shielded by ice and hydrate. Secondary hydrate formation was also visually observed in other experimental studies <sup>60,76</sup>. Ice formation enhanced 697 698 self-preservation of hydrates and acted as a solid protective shield around hydrate to stop it from 699 further dissociation by reducing the heat transfer from the surrounding. Transport of liberated CH<sub>4</sub> 700 Gas from dissociation was limited to diffusion through the ice sheet. Reformation had made 701 depressurization ineffective, and FOV remained unchanged when the micromodel was kept at very 702 low pressures for more than 48 hours.

Experiments 6, 7 and 8 had near similar dissociation temperature and have depressurized under the same flow rate (10 ml/hour) however, no ice formation and secondary hydrate formation was observed in experiment 7. This could be due to the low amount of unfrozen pore water, and gas dominated hydrate saturation that had assisted in gas production and reduced the risk of secondary hydrate formation and ice formation. Risk of re-formation also increased as the temperature changed to -3°C as sensible heat supply decreased during the depressurization at the lower temperature.

710 The pressure drop required to initiate hydrate dissociation in experiments 5, 6 and 8 was much 711 higher than experiments 4 and 7. Non-porous hydrate crystals were more stable than porous 712 hydrates during the depressurization, and depressurization was not sufficient to dissociate 713 hydrates. During pressure depletion, the re-formation was observed, and hydrate remains un-714 dissociated due to self-preservation property. Experiments 5, 6 and 8, self-preserved, un-715 dissociated hydrates were dissociated using thermal stimulation. Thermal stimulation is considered 716 as an effective technique to address insufficient heat supply, avoid ice generation and formation 717 of the secondary hydrate. Thermal stimulation increase temperature and supply essential heat 718 during endothermic dissociation and cooling due to Joule Thomson Effect. In literature, different 719 heat supply methods have been proposed, including microwave stimulation, warm water injection, thermal huff and puff and heat transfer from overburden or underlying units <sup>77</sup>. 720

# 721 3.3.3 Self preserved hydrate dissociation via heating

Thermal stimulation via ambient heating was used to dissociate hydrate in experiment 5, 6 and 8
entirely. Hydrate dissociation during heating was uniform compared to pressure depletion. During
the heating, heat supplied distributed among hydrate dissociation, temperature increase and energy

change due to outflow to the pump. Hydrate dissociation and reformation is the function of
injection heat, heat transfer, mass transfer and hydrate saturation <sup>5</sup>.

727 Hydrate dissociated from beneath and uniformly due to the high thermal conductivity of the silicon 728 wafer. Simulation studies show that production performance correlate with deposit temperature 729 and increase in 1°C temperature of deposits could lead to 8 times increase in production rate due 730 to an increase in sensible heat available for dissociation. Thermal stimulation can provide 731 additional heat to compensate heat loss during the depressurization, remove unwanted ice and secondary hydrate formation leading to unblocking the pore space<sup>78</sup>. However, when this 732 technique is used, stand-alone, would require excessive energy and have low production rate <sup>79</sup>. 733 734 Studies show that warm water injection is preferred over ambient heating to achieve higher gas 735 production yield as injected water would displace the gas from pore space<sup>77</sup>.

736 During the heating in experiment 8, metastable secondary hydrate dissociated first at T  $<0^{\circ}$ C as 737 the heat was supplied into micromodel through the ambient heating method. Hydrate dissociation 738 identified by a decrease in black film area and increase in pore water (refer to figure Exp.8j) has 739 enabled gas migration within pore space. Not all secondary hydrate dissociated during heating 740 below 0°C suggest stability of secondary hydrate was driven by self-preservation as well as pore-741 scale factors such as capillary pressure, hydrate filled pore space geometry and local temperature. 742 As the heat was continued to supply, uniform ice melting was observed across pore space below 0 743 °C lead to gas and water migration within pore space (refer to figure Exp.8k). Some un dissociated 744 secondary hydrate dissociated as the temperature reached above 0°C. As Temperature continues 745 to increase, hydrate re-formation was observed at T = 0.3 °C (refer to figure Exp.81) due to thawing of porous ice that did not turn into hydrate <sup>80</sup>. Re-formation during heating included hydrate film 746 747 encapsulating the gas which later crystallized in the presence of pore water at T = 0.6 °C (refer to figure Exp.8n). Hydrate re-formation was temporary and hydrate dissociated uniformly and homogenously at T = 0.6 °C (refer to figure Exp.8o).

750 4. Conclusions

751 Permafrost gas hydrate sediments can be characterized as sediments containing non-uniformly 752 distributed gas pockets below the 0°C in equilibrium with unfrozen pore water, hydrate and ice. 753 Understanding of quantity and quality of initial hydrate saturation is very critical for the selection 754 of correct production techniques in the permafrost region as hydrate dissociation behaviour during 755 pressure depletion depends on heterogeneity in hydrate distribution (porous/non-porous hydrate), 756 temperature, and presence of unfrozen pore water. At subzero temperature, delayed hydrate 757 dissociation under pressure depletion was observed due to lower sensible heat and higher self-758 preservation in the presence of unfrozen pore water. Hydrate self-preservation was further 759 enhanced due to ice formation and/or secondary hydrate formation during pressure depletion 760 driven by the amount of unfrozen pore water. In the presence of free gas and the absence of 761 unfrozen pore water, the risk of re-formation reduced. Direct visualization suggests that 762 depressurization combined with thermal stimulation technique is an efficient technique for gas 763 production from high and low hydrate saturation reservoir in permafrost due to its ability to 764 unblock pores, melt secondary hydrate and improve permeability to enhance total gas yield and 765 gas production rate. Results suggest that initial information about hydrate saturation and free gas 766 availability is essential in selecting the correct production technique.

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