ABSTRACT
Gas hydrates pose a major risk of disruption to the marine pipelines of the oil and gas industry. At the temperatures and pressures in these pipelines gas hydrates can form large solid plugs. A clearer understanding of these processes would allow implementation of effective strategies to avoid production losses in gas pipelines. In-situ neutron powder diffraction was used to study hydrate growth and dissociation for 10% propane-methane gas and D$_2$O ice and liquid water in the temperature and pressure range of 263 – 288 K and 3.0 – 4.8 MPa. Of our three samples one formed a mixed sI and sII hydrate while the other two formed single sII hydrate. Thermodynamic stability calculations could not accurately predict if a mixed hydrate would be formed. Our hydrate dissociation experiments question the relevance of anomalous hydrate preservation in our particular case. Furthermore these experiments elucidate the importance of the heat flow of the reaction processes and the role of a free liquid-gas interface.

*Keywords:* methane-propane hydrates, transformation kinetic, hydrate dissociation, neutron scattering

INTRODUCTION
Gas hydrates form readily under the high pressures and low temperatures typical of deep-sea oil and gas pipelines. They form large solid plugs that can block and damage pipelines, disrupting production. As a production field matures the proportion of water in the gas flow increases. The quantity of chemical inhibitors must therefore increase resulting in additional production costs. The ability to understand the processes associated with hydrate formation would allow design engineers and operators to work to tighter margins at considerable cost savings.

Gas hydrates (or clathrate hydrates) are inclusion compounds, which form from the action of water molecules encapsulating gases. Three main
distinct crystal structures are known as sI, sII and sH. The sI structure contains two pentagonal dodecahedron ($5^{12}$) and six tetrakaidecahedron ($5^{12}6^4$) cavities, sII contains sixteen $5^{12}$ and eight $5^{12}6^4$ cavities, and sH contains three types of cavities, $5^{12}$, $4^35^6$, and $5^{12}6^4$[1]. The stability of the hydrate structure depends on temperature and pressure, the size and shape of the guest gas molecules, and for mixed guest molecules the relative proportions of the molecules.

Typically natural gas consists of eight sI and sII formers (methane, ethane, propane butane (i-, n-), carbon dioxide, nitrogen and hydrogen sulfide, which cause an infinite number of mixture hydrate possibilities. In this work we are focused on methane-propane hydrates formed from an initial gas mixture of 10 vol % propane in methane. Experimental studies on the phase equilibrium of methane-propane double hydrates have been available since 1946 [3-6]. It was predicted that at pressures slightly above the hydrate formation conditions a small amount of propane (0.0005 mole fraction) added to a methane-water mixture will form sII hydrates [1] with the propane molecules occupying the large $5^{12}6^4$ cages. In contrast, pure methane gas forms sI and pure propane forms sII hydrates.

The formation from mixtures differs from the formation from single gases not only because of the different sizes and shapes of the gas molecules but also due to their different solubility and diffusion constants in water. The formation of both sI and sII hydrates in a methane propane system has been observed by several authors [7, 8, 9]. A two stage formation process was found in a batch-type reactor, where sII was formed first and was accompanied by a depletion of propane component of the gas mixture. In the second stage sI was formed [7]. The coexistence of sI and sII phases was confirmed by Raman spectroscopy and X-ray diffraction [8]. Kinetic studies using NMR measurements on the methane-propane sII hydrate from ice showed that the $5^{12}6^4$ cavities occupied by propane were formed faster than the $5^{12}$ cavities by methane, although the ratio between the cavities is 0.5 in a unit cell [9]. Alternatively, a more rapid filling of the $5^{12}$ cavities in the sII methane-propane hydrate has been reported [10]. This discrepancy may be due to different gas mixtures or the difference between experiments growing hydrates from ice or liquid water. The depletion of heavy hydrocarbon in the vapor phase of natural gas containing methane, ethane, propane and iso-butane during the formation of sII mixed hydrates and the resulting formation and coexistence of sI methane hydrate has also been reported [13].

More recently methane-propane sII double hydrate has been studied as an effective method of storing/transporting natural (methane) gas [11, 12]. At temperatures and pressures conveniently close to ambient conditions 1 m$^3$ of hydrate can contain as much as 180 m$^3$ of gas. The fractionation effect during the methane-propane sII hydrate formation was experimentally confirmed using a semi-batch stirred reactor (fixed amount of water and a continuous supply of gas at constant pressure) [12].

The formation of double or mixed gas hydrates is a complex process influenced by many parameters and therefore a large variety of techniques at the macroscopic (e.g visual microscopy, gas-uptake method) and molecular or atomic level (x-ray diffraction, spectroscopy and chromatography) are used to study these processes. These techniques have limitations, either in situ measurements are impossible or difficult, or the technique lacks sensitivity to distinguish the various phases present. Our studies use neutron scattering to simultaneously observe the transformation kinetics and structural information such as hydrate structure, phase fraction and cage occupancy. This enables us to study in-situ the hydrate formation in a multiphase system (sI, sII, ice, water) at various pressure and temperature conditions close to those of sub-sea pipelines.

Though gas hydrate forms readily at the liquid-gas interface [1] further growth is slowed by the formation of a hydrate crust [15–20]. Consequently, the simple growth of gas hydrate from bulk water and gas does not result in adequate quantities of hydrate within the time scales suitable for our experimental method of neutron diffraction. We present an alternative experimental approach where ice particles are first reacted with gas to form a thin hydrate layer. The ice within the particles was then rapidly melted so to observe the formation of hydrates from the liquid water phase. Finally, the hydrate decomposition process was studied by a rapid gas pressure reduction at constant temperature.
EXPERIMENTAL METHOD

Finely ground deuterated ice (D$_2$O) powder, with particles no greater than 30 µm in size, was inserted into a cooled aluminum pressure cell. The cell was mounted in an aluminum cell holder designed with access ports suitable for a neutron powder diffraction experiment. Details of the sample preparation, pressure cell and cell holder are given in Reference 2. The sample temperature was controlled using a re-circulating glycol-water mixture from a Julabo LH45 water bath. All sample temperatures refer to the temperature measured at the top of the cell holder using a PT 100 resistor calibrated to an ice-water bath. The cell holder and pressure cell were designed to minimize temperature differentials across the cell. The cell holder was surrounded by dry nitrogen gas to prevent condensation forming on the cooled surfaces of the cell and holder.

Once the desired sample temperature was reached a gas mixture of 10 vol% propane in methane (CH$_4$-C$_3$H$_8$ gas mixture) (BOC Scientific Support Centre, gas purity 99.995%) was added to the cell and maintained at the desired pressure using the mechanical regulator of the gas cylinder. The pressure was electronically logged using a 70 MPa Quartzdyn pressure sensor.

DATA COLLECTION AND ANALYSIS

The neutron powder diffraction experiments were performed using the Wombat high intensity diffractometer at the OPAL research reactor (ANSTO, Australia). Wombat was operated at a wavelength of 2.41 Å using an oscillating tertiary collimator with a 60 second data collection time and no appreciable delay between consecutive measurements. Diffraction data were collected as 2D images from the continuous detector bank of 120° with 0.125° wire spacing [21].

The data were corrected for detector efficiency and integrated to create conventional powder diffraction patterns. The color maps of the powder patterns in Figure 1 illustrate the in-situ formation of methane-propane hydrate at sample conditions; starting from ice powder, the transformation to gas hydrate, melting of the ice phase and further transformation to hydrate, and the subsequent decomposition process due to depressurization.

Diffraction data was analyzed using single peak fits from an automated profile refinement of the software LAMP [14]. The (321), (531) and (002) peaks were chosen for the sI, sII hydrate and hexagonal ice (ice Ih) phases, respectively, to ensure no overlap from neighboring peaks. Hydrogen atoms strongly scatter neutrons due to their large incoherent scattering cross-section. This effect increases the background level, and reduces the diffraction peak intensities due to increased attenuation of the neutron beam. The amount of attenuation varies during our experiment as the amount of hydrogen in the system changed. The dramatic change in background from blue to orange in Figure 1 illustrates this variation. The peak intensities were corrected for this effect using the fitted background under the peaks as a measure of the amount of incoherent scattering in the experiment.

Quantitative phase analysis (QPA) of the ice and hydrate components was obtained as a function of time to provide a rate of transformation from ice and liquid water phases to gas hydrate. The liquid water component was calculated assuming the summed phase fractions equals 1. The QPA relies
on the theoretical ratio of 0.9 for the scattering intensity of sII and sI. The ratio was calculated using fully occupied crystallographic models of sI and sII methane hydrate.

Simple Avrami kinetics equations were fitted to the observed QPA (using the least-squares method) to describe the kinetics in various multiphase mixtures of methane-propane hydrate, ice and liquid water. The Avrami equation [22] for transformed phase fraction at time \( t \) is given by

\[
f(t) = 1 - \exp\left(-kt^n\right)
\]

where \( k \) is the reaction rate constant and \( n \) is the order of the reaction. This equation provides a general description of chemical reaction kinetics and is often used to determine the dimensionality (through the order term) and reaction rate in phase transformations.

We use two Avrami terms to describe the transformation from ice and water separately. Initially one equation was fitted to the data of hydrate transformation from ice. For the second stage of reaction, while the ice is melting and hydrate begins to form from liquid water, the mathematical combination of two Avrami fits were used. One is based on the formation from the remaining ice and a second one originates from the available dispersed liquid water. These two Avrami terms are combined with phase fraction weighting. The constraint that the summed phase fractions of ice, gas hydrate and respectively water equals 1 was used. The average error for the fitted Avrami terms is 1%.

### EXPERIMENTAL RESULTS

Three different methane-propane hydrate samples (10 vol% propane in methane) were studied at two pressures (4.8 MPa, 3.0 MPa) and temperatures of 263 to 288 K as listed in Table 1. Note that the formation temperature of CH₄-D₂O hydrate is ~2 K higher than for CH₄-H₂O hydrate [23] while the melting point of D₂O is 3.8 K higher than H₂O.

Diffraction data was measured continuously starting at the initial experimental conditions. The gas pressure was then increased within 10 to 30 minutes to initiate ice to hydrate formation. After 1 to 2 hours the temperature was increased to melt the ice and initiate water to hydrate formation. The observed rate of temperature change on the outside of the cell was 2 K per minute. The final stage involved a pressure release resulting in total decomposition of the hydrate to liquid water. The variation in phase fraction for the three samples is shown in Figures 2, 3 and 4 along with fits of Avrami kinetics to the data (solid lines).

<table>
<thead>
<tr>
<th></th>
<th>Initial</th>
<th>Ice ( \rightarrow ) hydrate</th>
<th>Water ( \rightarrow ) hydrate</th>
<th>Final</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>263 K</td>
<td>263 K</td>
<td>282 ( \rightarrow ) 288 K</td>
<td>288 K</td>
</tr>
<tr>
<td></td>
<td>0.1 MPa</td>
<td>4.8 MPa</td>
<td>4.8 MPa</td>
<td>1 MPa</td>
</tr>
<tr>
<td>2</td>
<td>276 K</td>
<td>275.7 K</td>
<td>277.7 K</td>
<td>277.7 K</td>
</tr>
<tr>
<td></td>
<td>0.1 MPa</td>
<td>4.8 MPa</td>
<td>4.8 MPa</td>
<td>1.25 MPa</td>
</tr>
<tr>
<td>3</td>
<td>276 K</td>
<td>275.3 K</td>
<td>277.3 K</td>
<td>277.3 K</td>
</tr>
<tr>
<td></td>
<td>0.1 MPa</td>
<td>3.0 MPa</td>
<td>3.0 MPa</td>
<td>0.1 MPa</td>
</tr>
</tbody>
</table>

Table 1 Experimental conditions for the three diffraction samples during the four stages of the experiment. The final stage was used to study the decomposition of the hydrate.

On gas pressure increase hydrate formation started immediately for all three samples. For sample 2 both sII and sI hydrate was formed, whereas in samples 1 and 3 only sII hydrate was detected. Sample 1 forms sII hydrate at a constant transformation, reaching 31% at 110 minutes after pressure increase (Figure 2). Samples 2 and 3, measured at temperatures close to the D₂O ice point, show an immediate formation of sII on pressure increase (within the 1 minute time resolution of our experiment) followed by a continuing rapid transformation within the first few minutes (Figures 3 & 4). The transformation rate then decreases to a much lower rate that slowly decreases with time. After 120 minutes sample 2 had transformed to 18% sII and 7% sI, while sample 3 had transformed to 21% sII after 63 minutes.

At 110, 120, and 63 minutes after the initial pressure increase the temperature was raised to melt any remaining ice in samples 1, 2, and 3 respectively. An increase in transformation rate was observed until an apparent saturation concentration of hydrate was reached. This occurred for all samples despite the difference in temperature change, 19 degrees for sample 1 but only 2 degrees for samples 2 and 3. The complete melting of the ice component was observed at 13, 33, and 128 minutes after the temperature increase.
for samples 1, 2, and 3 respectively. In sample 1 a hydrate saturation concentration of 55 % was reached 40 minutes after the temperature increase, for sample 3 the values are 33 % after 65 minutes. Sample 2 reached a saturation concentration after 150 minutes of 36 % sII and 25 % sI.

The decomposition process was initiated by a rapid pressure release, and in the case of sample 1 a temperature increase, to the values given in Table 1. For sample 2 the pressure was reduced in stages to slow down the decomposition process, first 10 minutes at 1.25 MPa and then a reduction to 0.1 MPa. Complete decomposition of the gas hydrate was observed at 41, 28, and 7 minutes for samples 1, 2 and 3 respectively. A direct comparison of these times is complicated by the different pressures and temperatures used for decomposition. On pressure reduction we observed the immediate formation of a three phase mixture of liquid water, ice and hydrate for samples 2 & 3. For sample 1, which was decomposed at the higher temperature of 288 K, only two phases were involved, no ice was observed. The maximum proportion of ice occurred in samples 2 and 3 at 15 and 2 minutes after pressure release, respectively.

**DISCUSSION**

**Hydrate formation from solid ice particles**

The initial (within a few minutes) very rapid transformation at temperatures close to the D$_2$O ice point (samples 2 and 3) are comparable to our findings for pure methane hydrate [2]. The effect results from melting of ice particles due to localised heating from a combination of adiabatic heating of the gas and the exothermic reaction of the hydrate formation [2, 24]. For sample 1 the initial temperature is 13 degrees below the D$_2$O melting point, much lower than for samples 2 and 3. The lower temperature appears to prevent melting of the ice and so the initial enhanced hydrate formation does not occur for sample 1.

Hydrate formation beyond the first few minutes slow downs, apparently due to diffusion limitations, for samples 2 and 3 but not sample 1.
Sample 1 is at the coldest temperatures and a high gas pressure resulting in a higher driving force and a reaction which is less inhibited by diffusion processes. The Avrami parameters (see Table 1) for sample 1 show the highest order and the smallest rate constant, which supports this suggestion. Sample 2 was prepared at the same pressure but at higher temperatures, which means less driving force, and a slower reaction rate. This is also demonstrated by the Avrami parameters with a higher rate constant and a lower order parameter.

<table>
<thead>
<tr>
<th>Transformation</th>
<th>Ice (\rightarrow) gas hydrate</th>
<th>Water (\rightarrow) gas hydrate</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Rate constant (k, \text{sec}^{-n})</td>
<td>Order (n)</td>
</tr>
<tr>
<td>1 sII</td>
<td>5.05 x 10^{-5}</td>
<td>1.95</td>
</tr>
<tr>
<td>2 sII sI</td>
<td>3.5 x 10^{-2}</td>
<td>0.37</td>
</tr>
<tr>
<td>3 sII sl</td>
<td>7.85 x 10^{-2}</td>
<td>0.26</td>
</tr>
</tbody>
</table>

Table 2 Fitted Avrami coefficients.

The fitted Avrami parameters \(k\) and \(n\) are similar for samples 2 and 3, but very different for sample 1. The experiments for samples 2 and 3 were run at similar temperatures but different pressures. Sample 3 used a lower pressure and thus has a lower driving force, consistent with a smaller order parameter and higher rate constant. This indicates for sample 3 the slowest sII hydrate formation at a low driving force which is limited by diffusion.

**Hydrate growth from melting ice particles**

While heating above the ice point a three phase mixture of gas hydrate, ice and liquid water appears. The appearance of liquid water coincides with a large increase in the transformation rate. The exposure of a large surface area of liquid-gas interface is then responsible for the increased transformation rate [2, 24]. Later on the transformation slows to a negligible rate, though we continue to observe a significant component of liquid water in the sample. This may occur for several reasons. In terms of the shrinking core model, the thickening of the hydrate crust dramatically slows down the diffusion of gas and water molecules through the crust [15-19]. Alternatively, the appearance of closed pores can result in liquid water with no connectivity to the bulk gas and therefore cannot contribute to hydrate growth [19, 20].

Sample 1 exhibits the largest increase in transformation rate after the temperature increase, but the shortest time to reach a saturation value. A possible explanation for this behaviour arises from the melting of the ice. We observe that the increased transformation rate occurs for sample 1 when the ice fraction is decreased most rapidly. This is also true for samples 2 & 3, though the increase in hydrate formation rate is much less pronounced as is the speed of the ice melting. During melting, liquid water is released from ice particles by rupture of the hydrate crust surrounding the ice cores or by direct melting of ice surfaces not completely covered by hydrate crust. As this water is obtained by melting of ice the temperature is just above freezing which will result in a larger driving force to form hydrate. The liquid will also be supported on a skeleton/matrix of existing hydrate that ensures the water is exposed to the gas over a large surface area. However, if the ice melts too quickly all of the released water may not be transformed to hydrate and some will pool at the bottom of the pressure cell. Once a hydrate crust has formed on the surface of this bulk water it will no longer contribute to hydrate formation.

Sample 3 exhibits an extremely slow melting of the ice component over a 2 hour period. This is a result of the nominal temperature being just 0.3 K above the melting point of \(D_2O\). We do not expect temperature accuracies better than 0.2 K, so the temperature could in fact be much closer to the melting point. Despite the very slow melting rate sample 3 exhibits an even lower hydrate saturation fraction than did sample 1. For sample 3 the explanation it most likely the low gas pressure resulting in a low driving force for the transformation instead of the pooling of water in the bottom of the pressure cell as occurred for sample 1.

Sample 2 exhibits an ice melting rate between that of samples 1 & 3. It exhibits by far the greatest hydrate saturation fraction, a total of 63%. It was
also the only sample where a combination of sI and sII hydrates was formed.

The fitted Avrami coefficients, given in Table 2, show larger rate constants $k$ but smaller order parameters $n$ for sII hydrate than sI hydrate, both before and after the temperature increase. We also see that the order parameter increases and the rate constant decreases after the temperature increase and the melting of the ice.

**Formation of mixed hydrates**

For sample 2, we observed sII hydrate forming immediately on pressure increase (within the 1 minute time resolution of our experiment). In contrast, sI formation began 6 minutes after the pressure increase by which time nearly 9% of sII hydrate had formed. The ratio of the sI/sII phase fractions is plotted in Figure 5 and shows four distinct stages. Stage 1 exists in the first 15 minutes where hydrate growth is dominated by the very rapid transformation to sII. In Stage 2 the ratio plateaus at ~1/3, until at 130 minutes Stage 3 begins when the temperature is raised and the ice component melts. During Stage 3 the transformation rates increase for both sI and sII hydrates until 260 minutes and the start of Stage 4 when the formation of both sI and sII hydrates dramatically slows down. Though the ratio of sI to sII increases significantly in Stages 3 and 4 the actual difference in phase fraction does not.

![Figure 5](image-url)

Figure 5 sI & sII phase fractions, and the ratio sI/sII versus time for sample 2. Symbols are: gas hydrate sII (▲), gas hydrate sI (∆) sI / sII ratio (●).

Careful investigation of Figure 5 shows the transformation rate for sII increases significantly above the rate for sI in the first 15 minutes of Stage 3. In the remainder of Stage 3 and Stage 4 the transformation rates is comparable though the sI rate is slightly higher. A similar effect was observed for samples 1 & 3, that is, an increased transformation rate while the ice is melting most rapidly. For sample 2 this effect is only apparent in the sII component with little or no effect on the sI component. This observation suggests that when a large surface area of liquid-gas interface is exposed through the melting of the ice it is the sII hydrate that is preferentially formed. This is most likely due to the higher driving force for that phase. Once the ice is completely melted the surface area of the liquid-gas interface is greatly reduced by the growth of hydrate crust over exposed liquid surfaces. In this diffusion dominated stage the methane gas has a higher diffusion rate than propane and so the sI rate should increase. As well, the formation of sII depletes the propane fraction which hinders the formation of further sII. Without further observations we are unable to determine which of these effects is dominant in explaining the increase in sI rate during Stage 3.

The occurrence of mixed or single sII hydrate can be partially explained by the thermodynamic stability limits for the hydrates. For sample 2 both sI and sII are predicted as stable, whereas for sample 3 only sII is predicted as stable by CMSHYD [1]. Sample 1 cannot be explained in this way, since it is predicted that both sI and sII should be stable at the condition prior to the melting of the ice (263 K & 4.8 MPa). The nominal temperature (282 K) after the ice is melted for sample 1 is just beyond the stability limit at 4.8 MPa (281 K), though while the ice is melting we would expect the free water to have a temperature closer to the ice point for D₂O (277 K). At this point we do not have any reasonable explanation as to why mixed hydrates did not form for sample 1.

The changes in gas composition, such as propane depletion, changes the driving force and therefore the transformation kinetics of the two phases. The kinetics is further complicated by the possibility of local depletion of propane within the pressure vessel and at a microscopic level within the porous structure of the hydrate matrix. The kinetics of a mixed hydrate system is considerably more complex than for single hydrates, and with only
one mixed hydrate sample only limited interpretations is possible from our observations. Further experiments are planned using a variety of driving forces and methane-propane mixtures and these are expected to yield useful comparative information about the kinetics of such systems.

**Decomposition of hydrate particles**

On crossing the stability limit we observe the immediate start of decomposition of the hydrates and, for samples 2 & 3, a partial freezing of the liquid water component. For a pure methane gas it has been observed [2] that the sI hydrate and the ice components coexist during dissociation and simultaneously disappear. This is not the case for samples 2 & 3 where the hydrate is completely decomposed at least 20 minutes before the disappearance of the ice component.

Estimates of the decomposition rates calculated by the change in phase fraction and the time for total decomposition are 1.2, 1.3 & 4.7 % / minute for the sII phase of samples 1, 2 & 3, respectively. The sI phase of sample 2 has a higher decomposition rate of 2.1 % / minute compared to sII, which is expected as sI is further from its stability limits than sII. A comparison of the rates between the samples is complicated by the decompositions being performed at differing pressures. Sample 2 was held at 1.25 MPa for the first 10 minutes of decomposition which corresponds to 90% of the decomposition of the sI phase. If the decomposition had occurred at 0.1 MPa, as for sample 3, the decomposition rate for sI would probably be larger.

**CONCLUSIONS AND SUMMARY**

We have presented the methane-propane hydrate formation from ice and subsequent growth from water as the ice melts. In our neutron diffraction studies on Wombat, we have varied the temperature and pressure in a set of experiments using one mixture of methane-propane gas to facilitate a mapping of the dependencies of the chemical processes involved.

For ice samples at temperatures close to the D$_2$O ice point, we observed an initial very rapid hydrate formation associated with partial melting of the ice. On external heating of partially transformed ice samples all display a maximum in hydrate transformation rate when the ice is most rapidly melting. For a mixed sI/sII hydrate sample this increase in hydrate rate only appears to affect the sII phase.

The amount of hydrate formed prior to the melting of the ice is similar for all samples (22 to 31 %), while the amount formed after melting varies significantly (11 to 35 %). The samples with the highest and lowest driving forces had a lower hydrate formation from the liquid water than the sample with intermediate driving force. The fitted Avrami parameters also suggest greater similarity between the kinetics of the highest and lowest driving force samples. The reason for the lower hydrate formation is quite different; pooling of bulk water for the highest driving force, and depletion of propane for the lowest driving force. The intermediate driving force also was the only sample with mixed sI & sII hydrates. It is possible that the presence of mixed hydrates is related to large final amount of hydrate.

Towards the end of our experiments, when diffusion effects are dominant, we observed the transformation rate of sI exceeds that of sII. This effect may be due to the higher diffusion rate for methane compared to propane, or as a result of the local depletion of propane in the gas mixture, or both.

On pressure release below the stability limit we observe the immediate commencement of hydrate dissociation. For samples at a temperature slightly above the ice point we also observed the freezing of liquid water due to local cooling from the strongly endothermic hydrate dissociation. Unlike an earlier pure methane experiment [2] we did not see a concomitant hydrate dissociation and ice decomposition. Instead the sI hydrate component was the first to completely decompose, followed by the sII component, and then the ice component approximately 40 minutes later. It is not understood why the so called anomalous preservation effect [25], where ice encapsulation dramatically slows hydrate dissociation, does not appear to be significant in this case.

The Avrami fit on the quantitative phase fraction originating from a single peak fit of the diffraction data seems to be a useful tool to analyse the gas hydrate transformation kinetic in a multiphase system.
The complexity of hydrate formation using gas mixtures clearly indicates more observations are needed. Further experiments using neutron powder diffraction and small angle neutron scattering is planned to complement the results presented in this paper.

REFERENCES

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