

## **LOW TEMPERATURE X-RAY DIFFRACTION STUDIES OF NATURAL GAS HYDRATE SAMPLES FROM THE GULF OF MEXICO**

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### **ABSTRACT**

Clathrate hydrates of methane and other small alkanes occur widespread terrestrially in marine sediments of the continental margins and in permafrost sediments of the arctic. Quantitative study of natural clathrate hydrates is hampered by the difficulty in obtaining pristine samples, particularly from submarine environments. Bringing samples of clathrate hydrate from the seafloor at depths without compromising their integrity is not trivial. Most physical property measurements are based on studies of laboratory-synthesized samples. Here we report X-ray powder diffraction measurements of a natural gas hydrate sample from the Green Canyon, Gulf of Mexico. The first data were collected in 2002 and revealed ice and structure II gas hydrate. In the subsequent time the sample has been stored in liquid nitrogen. More recent X-ray powder diffraction data have been collected as functions of temperature and time. This new data indicates that the larger sample is heterogeneous in ice content and shows that the amount of sII hydrate decreases with increasing temperature and time as expected. However, the dissociation rate is higher at lower temperatures and earlier in the experiment.

*Keywords:* natural gas hydrates, X-ray powder diffraction, thermal expansion

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## INTRODUCTION

Clathrate hydrates of methane and other small alkanes occur widespread terrestrially in marine sediments of the continental margins and in permafrost sediments of the arctic [1,2]. Quantitative study of natural clathrate hydrates is hampered by the difficulty in obtaining pristine samples, particularly from submarine environments. Bringing samples of clathrate hydrate from the seafloor at depths greater than 500 m without compromising their integrity is not trivial [3]. Most physical property measurements are based on studies of laboratory-synthesized samples. Here we report the quantitative phase fractions of ice and sII hydrate from the Green Canyon, Gulf of Mexico, at various temperatures and the thermal expansion of the sII hydrate determined from X-ray powder diffraction data.

## EXPERIMENTAL

### Samples

The natural hydrate sample (GC-234) was recovered from the Green Canyon in the Gulf of Mexico by a research submersible at a depth of 540 m, and the sample was free of obvious sediment. After recovery the sample was stored at liquid nitrogen temperature, and shipped in a liquid nitrogen dry shipper.

### X-ray diffraction

For initial phase identification a Scintag X-ray diffractometer with a theta-theta goniometer modified with a closed-cycle He refrigerator, vacuum pumping station, and temperature controller was used. A deep-well sample holder was fabricated from Cu. The diffraction patterns were collected using  $\text{CuK}_\alpha$  radiation (45 kV and 40 mA) and step scans with a step size of  $0.02^\circ 2\theta$  and a rate of  $1^\circ 2\theta/\text{min}$ . The sample was loaded onto the pre-cooled sample holder enclosed in a flowing He glove bag to prevent frosting. The maximum temperature during sample loading was easily kept below the decomposition temperature of the hydrate. The X-ray patterns were suitable for phase identification. After decomposition, the solid residue remaining was also examined by X-ray diffraction.

Additional X-ray powder diffraction data were collected on a PANalytical X'Pert PRO MPD  $\theta - \theta$  diffractometer with an Anton Paar TTK 450 low temperature chamber. The

diffractometer was equipped with an X'celerator detector that allows fast data collection. The sample was removed from liquid nitrogen storage and ground in a pre-cooled agate mortar and pestle under liquid nitrogen and then was transferred quickly to the Ni-plated Cu sample stage that was pre-cooled to liquid nitrogen temperature. Due to thermal gradients, the temperature of the sample may be less accurately known than the  $\pm 0.5$  K reported by the temperature controller. The data were collected using  $\text{Cu K}_\alpha$  radiation at 45 kV and 40 mA. Data were collected between  $10$ - $120^\circ 2\theta$ .

The first data collected were at 133 K and after that a data collection routine was carried out where data were collected at 143 K and then the temperature was increased in steps of 15 K up to the final temperature of 163 K. Each data set took approximately 10 min to collect. The second data collection routine was designed so the sample would sit at the target temperature for approximately 2 h during which consecutive scans taking approximately 10 min each would be collected. The base temperature for this experiment was 188 K and the temperature was increased in 5 K steps to 213 K. Based on the results of this temperature/time dependent experiment a third data collection regiment was designed so that data were collected at 193 K every 10 min over a 6 h period. At the end of the 6 h the temperature was increased to 213 K where two 10 min data sets were collected. The temperature was then decreased back to 193 K where 6 additional 10 min scans were collected.

The data were analyzed by the Rietveld method using the EXPGUI graphical interface [4] for the General Structure Analysis System (GSAS) [5]. Sample surface displacement, a variable highly correlated with the lattice parameters, was included in the refinements.

## RESULTS AND DISCUSSION

Samples were received from Texas A&M University in November of 2002 and X-ray powder diffraction data collected immediately after the samples were received showed sII gas hydrate and ice present. Data were collected at various temperatures, however, the quality of the data was not sufficient to obtain the refined lattice parameters needed to calculate the thermal expansion or phase fractions of the hydrate and

ice. After the sample decomposed some residue remained in the holder and the phases that could be identified after drying included aragonite, quartz, and halite. The former is probably from shell matter, and the latter from the seawater.

The samples were stored in liquid nitrogen until additional X-ray diffraction experiments were conducted in October 2007. Rietveld refinements on the data set collected at 133 K showed 50 wt% sII hydrate present and as the temperature was increased up to 188 K the amount of wt% sII hydrate remained approximately 50 wt% as shown in Figure 1. At 188 K decomposition began, and between 188 and 233 K the amount of sII hydrate decreased rapidly with only approximately 11 wt% sII hydrate remaining at 233 K. Between 233 and 263 K the amount of remaining sII hydrate decreased less rapidly than in the previous temperature range and at 263 K only 6 wt% sII hydrate was present. These results suggest that dissociation of the sII hydrate obtained from samples harvested from the Green Canyon, Gulf of Mexico is around 188 K.

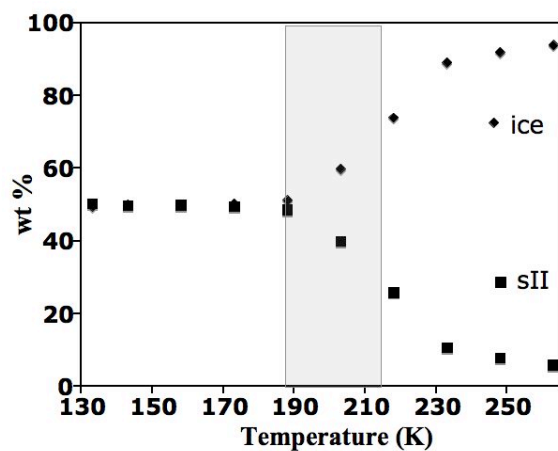


Figure 1. Refined phase fractions for ice and sII gas hydrate as a function of temperature. The shaded region is the temperature interval studied in more detail subsequently.

Lattice parameters were refined from the data and are plotted against temperature in Figure 2. The error bars are  $3\sigma$  and at lower temperatures are smaller than the symbol size, however, as the temperature increases and the amount of hydrate decreases, the lattice parameter error increases. For data collected at 188 K  $a = 17.243(2)$  Å was obtained. Hester et al. [6] synthesized a sample with a natural gas mixture obtained from the

Green Canyon, Gulf of Mexico and reported  $a = 17.211$  Å for 184 K. There are many factors that could contribute to the difference between the two reported lattice parameters, however, the one most likely is variation in the exact gas composition. Hester et al. [6] did a rigorous study evaluating the thermal expansivity of sI and sII gas hydrates by using a third order polynomial to describe the thermal expansion coefficient. For their analysis  $T_0 = 298.15$  K and  $a_0$  is the lattice parameter at 298.15 K. Here a more simplistic evaluation is used by plotting  $(a - a_0)/a_0$  or  $\Delta a/a_0$  versus temperature and using the slope of a linear fit to determine the thermal expansion coefficient  $\alpha$ . The lattice parameter refined from the data collected at 188 K, corresponding to temperature before dissociation was observed, was chosen as  $a_0$  and only the refined lattice parameters from the data collected below 188 K were used for evaluation of  $\alpha$ . Using this method  $\alpha = 53.1 \times 10^{-6}$  deg<sup>-1</sup> was obtained.

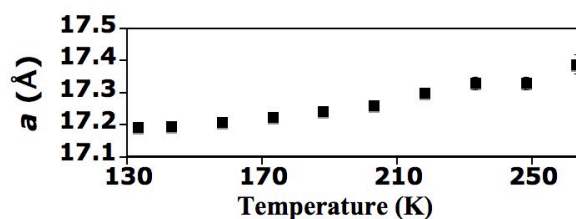


Figure 2. Refined lattice parameter for the cubic sII sample plotted as a function of the temperature.

The temperature range for the subsequent experiment was based on these results. The next experiment was designed to explore the effect of time, over the temperature range where initial decomposition was observed (between 188 and 213 K at 5 K increments). These experiments are destructive to the sample so a new sample is needed and a small amount was taken from the larger sample. For this sample at 188 K the initial amount of sII hydrate present was approximately 28 wt%, which indicates the larger sample is heterogeneous in ice content. Figure 3 shows that the amount of sII hydrate decreases with increasing temperature and time, however, this decrease with time is more pronounced at the lower temperatures where the amount of sII hydrate is greater than at higher temperatures. These results support the possibility of anomalous or “self” preservation similar to that previously reported for some sI gas hydrates [7-9]. However,

Stern et al. [8] studied two sII methane-ethane hydrate samples and did not find any evidence of anomalous preservation. The final amount of sII hydrate present at 213 and after 13.3 hours of data collection was approximately 3 wt%.

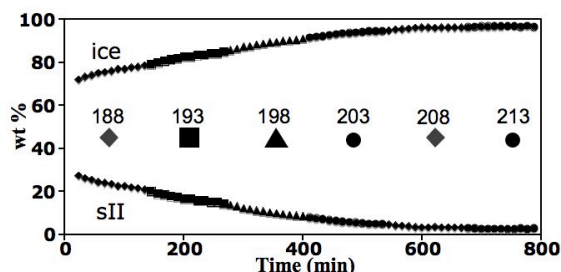


Figure 3. The amount of sII hydrate decreases with increasing temperature and time, however, this decrease with time is more pronounced at the lower temperatures where the amount of sII hydrate is greater than at higher temperatures.

Figure 4 shows the lattice parameters for sII hydrate refined from data collected at the target temperatures plotted against time. The lattice parameter refined from the first data collected at 188 K was  $a = 17.263(1) \text{ \AA}$ , slightly higher than that obtained for the previous sample, and was found to increase with time. At 193 K the lattice parameter slightly increased with time while at 198 K the lattice parameter stayed fairly constant with time and then slightly decreased over time at 203 K and then remained fairly constant over time with increased scatter at 208 and 213 K. The lattice parameters refined from data collected at these latter two temperatures are approximately the same as that from the data collected at 188 K.

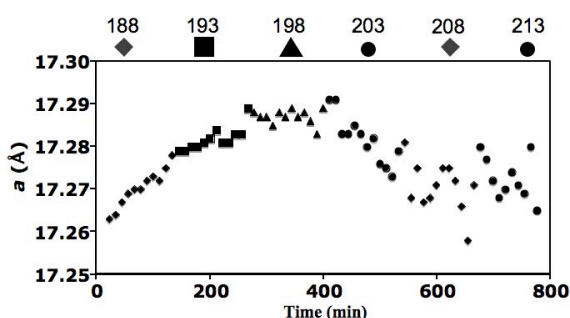


Figure 4. The lattice parameter of sII hydrate at the target temperatures indicated versus time.

Figure 5 shows the unit cell volume for ice  $I_h$  calculated from lattice parameters refined from

data collected at the target temperatures plotted against time. In contrast to the sII hydrate, both the  $a$  and  $c$  lattice parameters of the hexagonal ice structure show a steady increase with temperature.

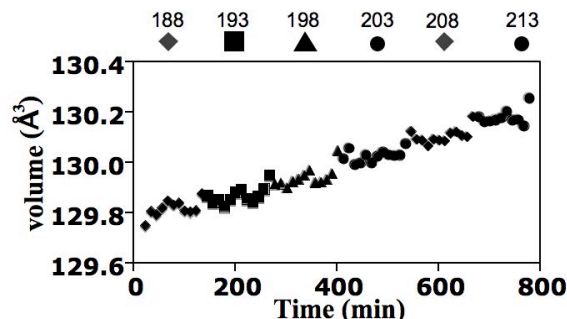


Figure 5. The unit cell volume of ice  $I_h$  refined from data collected at the target temperatures indicated versus time.

The steady increase of the ice  $I_h$  lattice parameters suggest that the unusual trend observed for the sII natural gas hydrates as seen in Figure 4 is genuine. One possible explanation could be ice-“shielding” where an ice layer forms around a gas hydrate core. This ice shield acts as barrier to the released gas and causes an increased isostatic pressure around the hydrate core compressing the planes of atoms and resulting in a small decrease of the lattice parameter. At 188 and 193 K the thermal expansion is dominant, at 203 K the isostatic pressure increase is slightly dominant, and for the other temperatures the two effects are balanced.

To further explore the previously observed behavior, data were collected on a third sample taken from the larger sample. During this data collection there was a 6 h dwell at 193 K and then the temperature was increased to 213 K for 20 min and then decreased back to 193 K for the remainder of the data collection. The amount of sII hydrate refined from the initial data set collected at 193 was 31.4(1) wt%, close to the 28 wt% observed for the second sample examined in this study, and the amount of sII hydrate refined from the data set collected at  $-80 \text{ }^\circ\text{C}$  after a 6 h dwell at that temperature was 19.2(1) wt%. Figure 6 shows that the amount of sII hydrate does decrease over time at 193 K, however, the rate of decrease is fairly low, especially compared to the rate of decrease observed when the temperature is increased to 213 K. The amount sII hydrate refined from the first data set collected at 213 K was

10.5(1) wt%, almost half of that refined from the previous data collected at 193 K. The amount sII hydrate refined from the second data set collected at 213 K was 7.3(1) wt%.

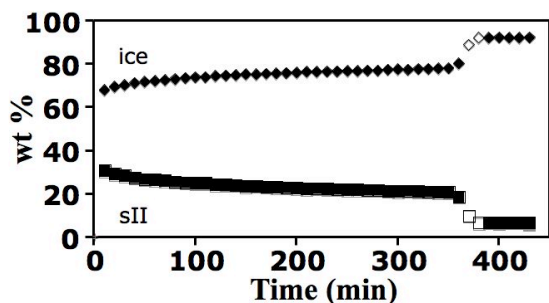


Figure 6. Change in the volume fraction of sII at constant temperature versus time. Solid symbols are for 193 K and open symbols are for 213 K.

These results are similar to those described by Takeya et al. [7] using time dependent energy-dispersive X-ray diffraction to study the dissociation rate of CH<sub>4</sub> hydrate. At both 168 and 89 K Takeya et al. [7] observed a faster rate of hydrate dissociation at the beginning of the experiment and after that the rate slowed.

## CONCLUSIONS

Laboratory X-ray powder diffraction is a useful tool to study gas hydrates recovered from natural setting. Data can be collected both as a function of temperature and time. The results reported here indicate large pieces of hydrate can be heterogeneous in ice content. The results reported here also show that the amount of sII hydrate decreases with increasing temperature and time however, this decrease with time is more pronounced at the lower temperatures where the amount of sII hydrate is greater than at higher temperatures. This behavior along with a unusual trend observed for the lattice parameter for sII natural gas hydrates could result from ice-“shielding”.

## ACKNOWLEDGMENTS

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