

## THE CHARACTERISTICS OF GAS HYDRATES FORMED FROM H<sub>2</sub>S AND CH<sub>4</sub> UNDER VARIOUS CONDITIONS

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### ABSTRACT

Shallow marine gas hydrates occurring above the Sulfate-Methane-Interface (SMI) often contain small amounts of H<sub>2</sub>S beside methane and other hydrocarbons, but the distribution of H<sub>2</sub>S in these natural samples is not always homogeneous. To learn more about the formation of H<sub>2</sub>S-containing hydrates, gas hydrates with different ratios of H<sub>2</sub>S/CH<sub>4</sub> were synthesized under various conditions. The samples were synthesized from ice and water phases, with constant feed gas compositions or controlled changes in feed gas compositions. It turns out that the detailed nature of the synthetic hydrate samples depends on the method of sample preparation. The sample prepared with gas containing small amounts of H<sub>2</sub>S (1% H<sub>2</sub>S and 99% CH<sub>4</sub>) appeared homogeneous in composition, while that prepared in a water-H<sub>2</sub>S-CH<sub>4</sub> system with higher H<sub>2</sub>S contents was heterogeneous. The samples were analysed with Raman spectroscopy, and differential scanning calorimetry (DSC).

Keywords: H<sub>2</sub>S-CH<sub>4</sub>-hydrates, differential scanning calorimetry, Raman spectroscopy

### INTRODUCTION

Recent investigations on shallow marine gas hydrates recovered from IODP Expedition 311 provide data regarding the distribution of H<sub>2</sub>S and methane in these natural samples. It turned out, that even in hydrate pieces that appeared as large, homogeneous and transparent crystals, the spatial distribution of composition varied [1]. The heterogeneous compositions of these natural samples may be the result of a hydrate formation process in an environment with fluctuating composition of H<sub>2</sub>S and CH<sub>4</sub> in the feed gas over a temporal and/or spatial scale. In shallow marine sediments, H<sub>2</sub>S is locally produced by the reduction of sulphate via anaerobic methane oxidation (AMO) as a result of a complex interaction between microbes – a syntrophic consortium of methanotrophic archaea and

sulphate reduction bacteria - which uses the sulphate to oxidize the methane anaerobically [2,3,4,5]. The methane is in general from deeper sediment sections, either originally biogenic or thermogenic. Both gases in hydrate are related to the hydrocarbon flux, and the ratio between them might change over time. The hydrate formation and growth is supported by the dissolved gases in the surrounding pore water. Therefore, the hydrate will only incorporate gases into its structure which are available in the pore water. But it is questionable if the composition of the hydrate changes or homogenization will happen for the resulting hydrate when the composition of gas available from pore water changes.

Experimental data about formation and growth processes for hydrates containing H<sub>2</sub>S beside CH<sub>4</sub> are rare. Noaker and Katz studied the conditions

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for hydrate formation with hydrogen sulphide and methane-water mixtures but they did not investigate the compositions of the resulting hydrate phases [6]. Others, such as Selleck et al. or Carroll and Mather investigated the behaviour of hydrogen sulphide–water mixtures and in this context the H<sub>2</sub>S-hydrate formation conditions [7,8]. Robinson and Hutton reported hydrate formation in the systems containing CH<sub>4</sub>, H<sub>2</sub>S and CO<sub>2</sub> [9]. However, it is very likely that the phase behaviour and hydrate formation in those systems containing three gas components beside water will differ from a system containing CH<sub>4</sub>, H<sub>2</sub>S and H<sub>2</sub>O. To learn more about the formation of H<sub>2</sub>S-CH<sub>4</sub>-hydrates and the complex interactions mentioned before, we performed experiments with gas hydrates which were synthesized from water or ice and different H<sub>2</sub>S-CH<sub>4</sub>-compositions.

## EXPERIMENTAL METHODS

Gas hydrates were synthesized from water or ice and gas mixtures containing H<sub>2</sub>S and CH<sub>4</sub> in various concentrations with different synthesis routes and were characterized with Raman spectroscopy or Differential Scanning Calorimetry (DSC).

### In situ Raman spectroscopic measurements:

For Raman spectroscopic measurements the gas hydrates were synthesized in a pressure cell which has been described in detail elsewhere [10]. The pressure cell can be used in a temperature range between 245 K and 350 K. The temperature of the sample cell is controlled by a thermostat and the temperature is determined with a precision of  $\pm 0.1$  K. The applicable pressure range is between 0.1 and 10.0 MPa. A pressure controller adjusts the pressure with a precision of 2% relative.

The experiments were performed with a continuous gas flow to avoid changes in the gas composition. With a gas flow of 1 ml/min, it takes 17 sec for the incoming gas to pass the cold cell body and to enter the cell void space; this time is sufficient to allow the gas flow to attain the cell temperature. Therefore the sample in the cell is cooled from cell body below and the gas phase above. Please note, that the small sample volume (393  $\mu$ l) and the above mentioned all-around cooling of the sample prevent the possibility of establishing a temperature gradient. A quartz window permits the analysis of the phases by Raman Spectroscopy as well as visual observation and the recording of microscopic

photo-documentation of formation and decomposition processes.

The experiments were carried out using the following procedure. First, 150  $\mu$ l pure and degassed water or 100  $\mu$ g ice were placed in the sample cell. In case of hydrate synthesis from the liquid water phase, the cell was carefully sealed and flushed with the appropriate gas before pressurization (1% H<sub>2</sub>S and 99% CH<sub>4</sub>). Thereafter, the system was cooled down as rapidly as possible until hydrates were formed. After that, the system was warmed at constant pressure in order to melt most of the hydrate. When only a few crystals were left, the temperature was lowered by 0.5 K and the euhedral crystals of gas hydrate grew under steady state conditions.

In case of hydrate synthesis from the ice phase, the ice was placed into the sample cell at a temperature of 272 K and slowly pressurized.

The Raman spectra were taken with a confocal Raman spectrometer (LABRAM, HORIBA JOBIN YVON), which allowed the laser beam to be focused on an exact point, e.g. the surface of a hydrate crystal, thus assuring that only the selected phase was analyzed.

### Hydrate sample preparation for Differential Scanning Calorimetry (DSC) and Raman Spectroscopy after hydrate formation from ice-H<sub>2</sub>S-CH<sub>4</sub> or water-H<sub>2</sub>S-CH<sub>4</sub>

The CH<sub>4</sub>-H<sub>2</sub>S-hydrates were synthesized from powdered ice with gas composition of 1% H<sub>2</sub>S and 99% CH<sub>4</sub>. 5 g powdered ice was filled into a pressure vessel at 263 K. The vessel itself contained a volume of approximately 1.1 L. The vessel was carefully sealed and pressurized (9 MPa). The pressure vessel was placed into a cooling box at 263 K for several weeks until no more changes in pressure were observed. The samples were recovered from the accumulators and stored immediately in liquid nitrogen. Before analyses, the gas hydrate samples were handled in liquid nitrogen inside a nitrogen-flooded cooled glovebox.

To examine whether composition homogenization happens or not after initial hydrate formation, a H<sub>2</sub>S-CH<sub>4</sub> hydrate sample was also prepared from a water-H<sub>2</sub>S-CH<sub>4</sub> system. For the synthesis 7 cm<sup>3</sup> of pure water was added to a 125 cm<sup>3</sup> pressure cell. After evacuation of the pressure cell for 20 minutes H<sub>2</sub>S and CH<sub>4</sub> gases were charged into the cell at a ratio of 1:2 (v:v) to 6 MPa. Thereafter the cell was put into a 276.15 K water path to let the gas react with water. When no obvious change in pressure was

observed, the sample prepared was ready for recovery. For sample recovery, the pressure cell was first cooled in dry ice, and then the gas was released. Finally the sample was recovered while the cell sat in a liquid nitrogen bath. The sample recovered was stored in a liquid nitrogen dewar for characterization.

## RESULTS AND DISCUSSION

### In-situ Raman spectroscopic measurements:

One series of experiments have been performed to investigate the formation and growth processes of  $\text{H}_2\text{S}$ - $\text{CH}_4$ -hydrates regarding the formation kinetics, cage occupancy, composition of the resulting hydrate phase and its stability fields. The Raman spectroscopic measurements have been performed in-situ during the hydrate formation from liquid water and the gas phase. It turned out that, compared to pure methane hydrate, the formation of a solid phase was much faster, but the resulting crystals did not show the expected Raman spectra of a structure I hydrate phase. Representative spectra from this early formation of crystals are shown in Figure 1.

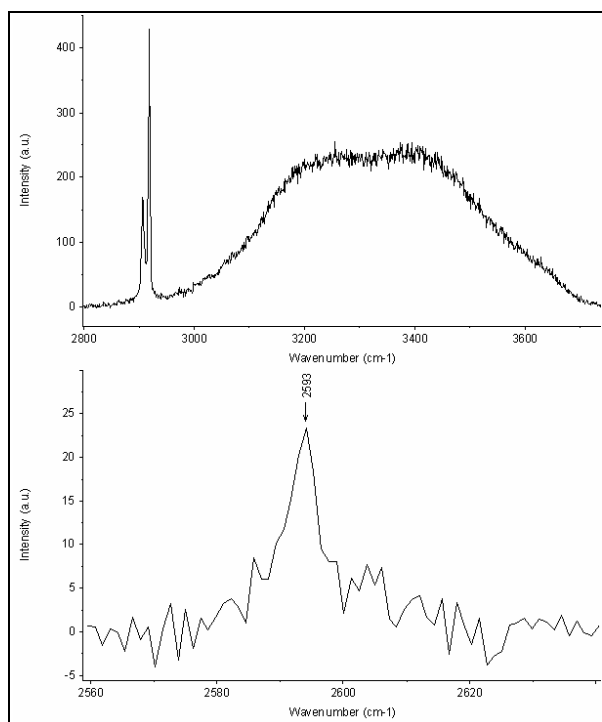


Figure 1 Raman spectra of preliminary hydrate crystals formed from water and gas phase. At the top: C-H stretching bands at  $2903\text{ cm}^{-1}$  and  $2815\text{ cm}^{-1}$  and O-H stretching bands. At the bottom: S-H stretching band at  $2593\text{ cm}^{-1}$ .

Two bands at  $2903\text{ cm}^{-1}$  and  $2915\text{ cm}^{-1}$  were detected and assigned to C-H  $\nu_1$  stretching modes for  $\text{CH}_4$  in large  $5^{12}6^2$  and small  $5^{12}$  cavities, respectively. Also, typical O-H

stretching bands were detected in the range between  $3000\text{ cm}^{-1}$  and  $3600\text{ cm}^{-1}$ . In addition, one band at  $2593\text{ cm}^{-1}$  was detected and assigned to S-H  $\nu_1$  stretching mode for  $\text{H}_2\text{S}$  in large  $5^{12}6^2$  cavities of structure I hydrate, whereas there was no obvious indication for  $\text{H}_2\text{S}$  in small cavities of structure I hydrates from the Raman spectra at this point of time.

With time, these crystals transformed and exhibited the typical Raman spectra for structure I hydrate after approximately 48 h. These Raman spectra are shown in Figure 2. This transformation from crystals with unclear structure to those with structure I character proceeded without obvious changes regarding the appearance of the crystals. All detected bands are listed in Table 2.

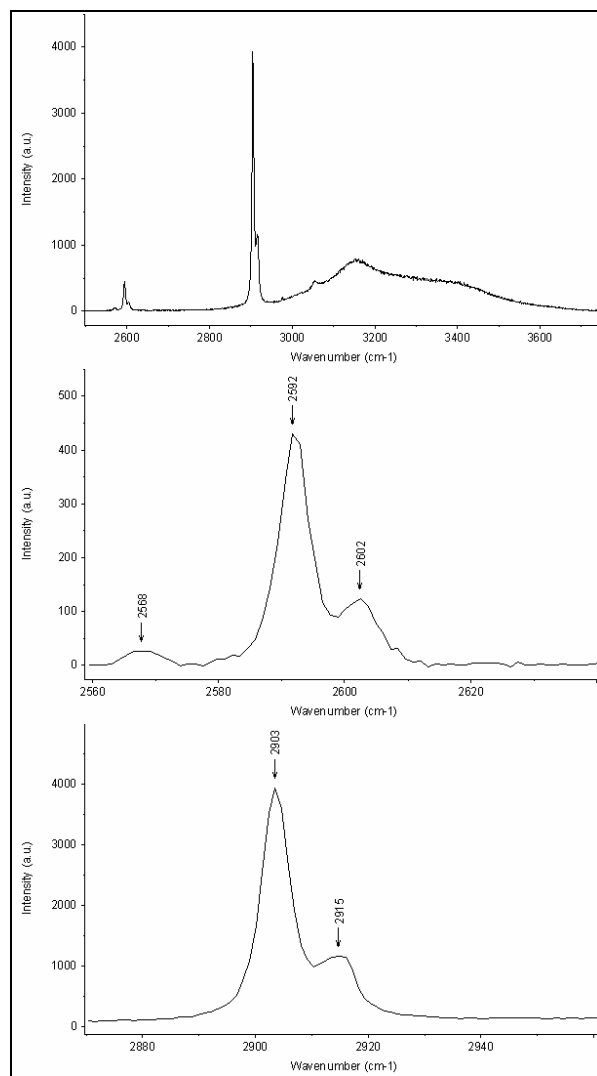


Figure 2 Raman spectra of the hydrate phase after 48 h. At the top: complete spectra. Middle: S-H stretching band at  $2593\text{ cm}^{-1}$  and  $2602\text{ cm}^{-1}$  and  $\text{CH}_4$  bending ( $2568\text{ cm}^{-1}$ ). At the bottom: C-H stretching bands at  $2903\text{ cm}^{-1}$  and  $2915\text{ cm}^{-1}$ .

Table 2. Detected bands and assignment.

Band position [cm <sup>-1</sup> ]	Component	Band assignment
2568	CH <sub>4</sub>	2v <sub>4</sub> (bending)
2593	H <sub>2</sub> S	v <sub>1</sub> (S-H )
2602	H <sub>2</sub> S	v <sub>1</sub> (S-H )
2903	CH <sub>4</sub>	v <sub>1</sub> (C-H )
2915	CH <sub>4</sub>	v <sub>1</sub> (C-H)

\*: the band position may vary for 1 cm<sup>-1</sup>

It turned out that the composition of the hydrate phase differs significantly from that of the feed gas. The resulting hydrate phase was almost homogeneous. The average composition of the gas in the hydrate phase was 12% H<sub>2</sub>S and 88% CH<sub>4</sub>, whereas the composition of the feed gas was 1% H<sub>2</sub>S and 99% CH<sub>4</sub>. The stability of these hydrogen sulphide containing hydrates was shifted to slightly higher temperatures or lower pressures compared to pure methane hydrate as shown in Figure 3.

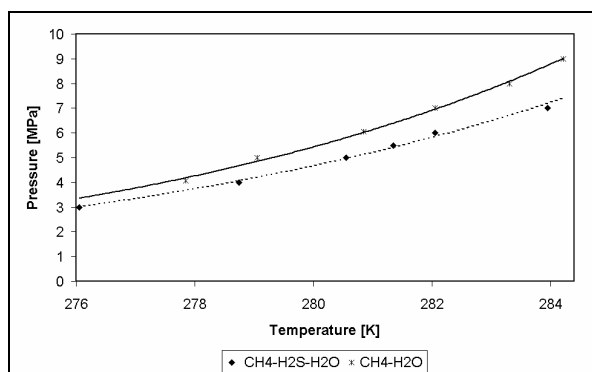


Figure 3 Decomposition line for CH<sub>4</sub>-hydrate and H<sub>2</sub>S-CH<sub>4</sub>-hydrate.

Based on this observation the question arose if the preferred incorporation of H<sub>2</sub>S into the large 5<sup>12</sup>6<sup>2</sup> cavities of structure I hydrate at the initial stage was typical of the formation and growth process for H<sub>2</sub>S-containing hydrates or if this observation was a result of the spontaneous formation of ice and hydrate crystals during the first cooling period due to the fact that no hydrate formation was observed from water and gas without sub-cooling the system until spontaneous hydrate and ice formation occurred. To clarify this, another run of experiments was performed: the time-depending observation of hydrate formation and growth from ice and a gas phase. These experiments were performed at 272 K and 2.1 MPa. 15 min after pressurisation of the sample cell filled with powdered ice the formation of a gas hydrate layer at the surface of the ice crystal was observed. The formation and

growth processes were documented during the following six hours. Raman spectra were taken every 15 min. The results are presented in Figure 4 and Figure 5.

Figure 4 shows the development of the Raman spectra regarding the v<sub>1</sub> stretching mode of CH<sub>4</sub> for methane encased in large 5<sup>12</sup>6<sup>2</sup> and small 5<sup>12</sup> cavities of structure I. At the beginning of the experiment, only one band at 2915cm<sup>-1</sup> was detected and assigned to CH<sub>4</sub> encased in the small 5<sup>12</sup> cavities. After 45 min a second band at 2903 cm<sup>-1</sup> was detected, indicating CH<sub>4</sub> encased in the large hydrate cavities. The intensity of this band increased with time indicating an increasing incorporation of CH<sub>4</sub> into the large 5<sup>12</sup>6<sup>2</sup> cavities and thus the transformation of the preliminary structure into structure I with time.

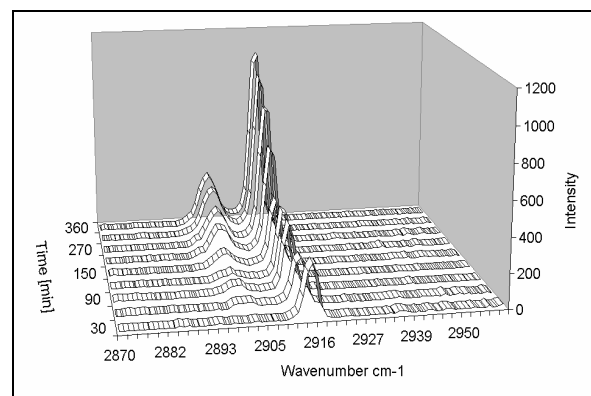


Figure 4: Real-time Raman spectra monitoring the incorporation of CH<sub>4</sub> in large 5<sup>12</sup>6<sup>2</sup> and small 5<sup>12</sup> cavities of structure I.

Figure 5 shows the development of the Raman spectra regarding the v<sub>1</sub> stretching modes of H<sub>2</sub>S encased in 5<sup>12</sup>6<sup>2</sup> and 5<sup>12</sup> cavities of structure I. At the beginning of the experiment no indication for H<sub>2</sub>S encased into the solid phase was given from the Raman spectra. After 60 min only one band at 2592 cm<sup>-1</sup> was detected, indicating H<sub>2</sub>S in 5<sup>12</sup>6<sup>2</sup> cavities of structure I. After 210 min the ratio of the integral intensities of the bands at 2592 cm<sup>-1</sup> to 2602 cm<sup>-1</sup> reached 3:1 which corresponds to the ratio of large 5<sup>12</sup>6<sup>2</sup> to small 5<sup>12</sup> cavities in structure I.

These experimental results lead to the conclusion that at the beginning of the hydrate formation and growth process the H<sub>2</sub>S is preferentially encased into the large cages whereas CH<sub>4</sub> is primarily encased into the small cages. With time the ratio of the integral intensities of the bands for both, H<sub>2</sub>S and CH<sub>4</sub> reached 3:1 which corresponds well to the ratio of large to small cavities in structure I. The resulting hydrate phase in the equilibrium state is a mixed H<sub>2</sub>S-CH<sub>4</sub>-hydrate with

homogeneous composition where both gas molecules occupy large  $5^{12}6^2$  and small  $5^{12}$  cavities of structure I.

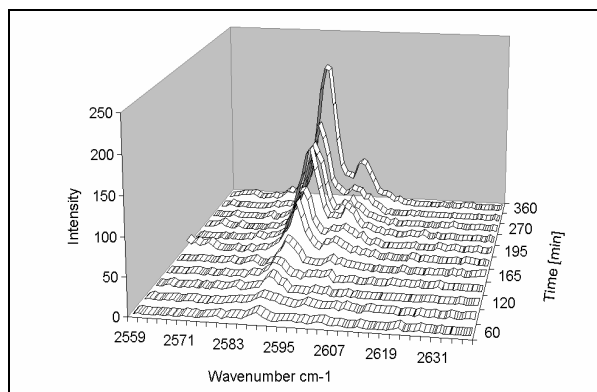


Figure 5: Real-time Raman spectra monitoring the incorporation of  $H_2S$  in large and small cavities.

A third series of experiments has been performed to study the exchange reaction of  $H_2S$  with  $CH_4$  in case of a change in the composition of the gas phase. For these experiments 150  $\mu l$  pure water was placed into the sample cell. The cell was sealed and flushed with the pure methane gas (99.995 %  $CH_4$ ). Thereafter, the system was cooled down as rapidly as possible until hydrates (and ice) were formed. After that, the system was warmed at constant pressure in order to melt the ice and most of the hydrate. When only a few crystals were left, the temperature was lowered by 1 K and the euhedral crystals of methane hydrate grew under steady state conditions for one week. The resulting hydrate phase was analysed with Raman spectroscopy, showing the prominent bands at  $2903\text{ cm}^{-1}$  and  $2915\text{ cm}^{-1}$  indicating the incorporation of  $CH_4$  into large  $5^{12}6^2$  and small  $5^{12}$  cavities of structure I hydrate. The ratio of the integral intensities of the bands at  $2903\text{ cm}^{-1}$  and  $2915\text{ cm}^{-1}$  was approximately 3:1, corresponding to the ratio of large  $5^{12}6^2$  to small  $5^{12}$  cavities in structure I. At that point of time the composition of the gas phase was changed into 1%  $H_2S$  and 99%  $CH_4$  without changing the pressure or temperature conditions. Raman spectra were taken over the next seven days. No change in composition of the hydrate phase could be detected by Raman spectroscopy. This result implied that the methane hydrate has not been affected by  $H_2S$  after it was formed.

#### Differential Scanning Calorimetry (DSC) and Raman spectroscopy

The results from DSC measurements generally were not self consistent. It turned out that the hydrates, formed from ice and gas (1%  $H_2S$ -99%

$CH_4$ ) showed only one endothermic event (beside melting of ice at 273.15 K) with an onset temperature of  $T_0 = 236.7\text{ K} \pm 1.2\text{ K}$  indicating the dissociation of a  $H_2S$ - $CH_4$  mixed hydrate with a homogeneous composition into ice and gas. In contrast, as shown in Figure 6, the Raman spectroscopic analysis of the hydrate sample formed from water- $H_2S$ - $CH_4$  ( $H_2S:CH_4 = 1:2$ ) indicated an inhomogeneous composition, and the DSC thermogram showed a broad range of dissociation of  $H_2S$ - $CH_4$  hydrate with an onset-temperature of  $T_0 = 246\text{ K}$  (see also Figure 7). As a result the hydrate sample formed in the water- $H_2S$ - $CH_4$  system showed the coexistence of different hydrate phases with varying composition, similar to the phenomenon observed for natural gas hydrates [11]. The distribution of compositions in the heterogeneous sample might have resulted from the composition change due to the preferentially incorporating of  $H_2S$  into the hydrate phase throughout the reaction progress. Because the reaction in this system lasted 23 days, no significant composition homogenization was observed for the hydrate formed, consistent with the results of in situ observations.

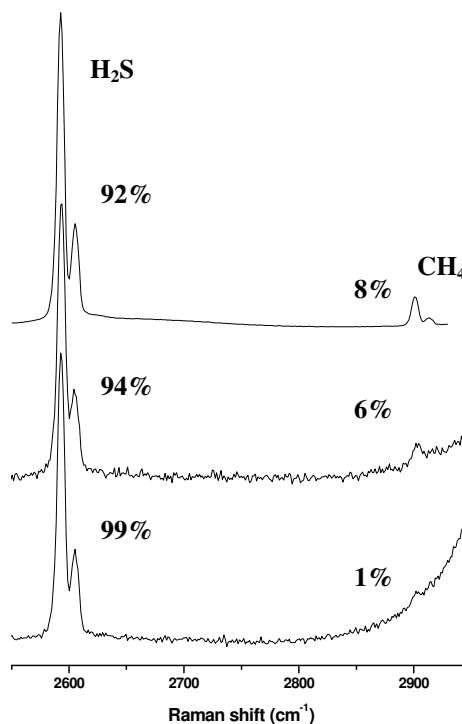


Figure 6: The Raman spectra of  $H_2S$ - $CH_4$  hydrates formed in Water- $H_2S$ - $CH_4$  system.

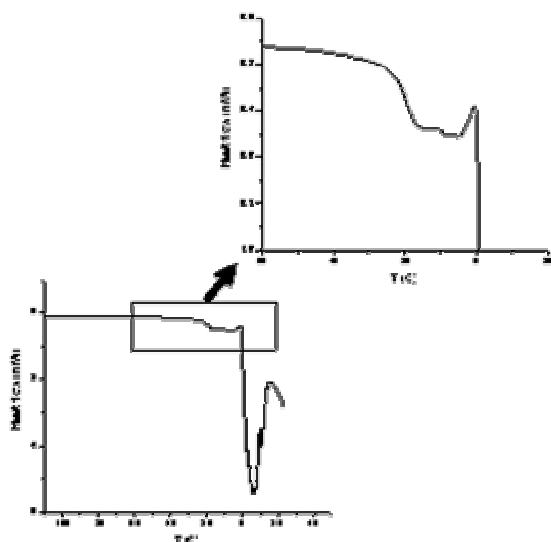


Figure 7: The DSC thermogram of H<sub>2</sub>S-CH<sub>4</sub> hydrate prepared in a water-H<sub>2</sub>S-CH<sub>4</sub> system.

## CONCLUSIONS

Raman spectroscopic measurements on H<sub>2</sub>S-CH<sub>4</sub>-hydrates formed from a gas phase and liquid water or ice showed that during the initial stages of hydrate formation H<sub>2</sub>S was preferentially incorporated into the large 5<sup>12</sup>6<sup>2</sup> cavities of structure I. In contrast, CH<sub>4</sub> was preferentially encased into the small 5<sup>12</sup> cavities of structure I during the initial stages of hydrate formation. The resulting hydrate phase showed the occupancy of large 5<sup>12</sup>6<sup>2</sup> and small 5<sup>12</sup> cavities of structure I with both guest molecules, H<sub>2</sub>S and CH<sub>4</sub> in the same ratio (3:1). This hydrate phase, formed from a gas mixture containing only 1% H<sub>2</sub>S beside CH<sub>4</sub> showed a homogeneous composition where H<sub>2</sub>S was strongly enriched into the hydrate phase. The resulting composition of the gas phase encased in the hydrate lattice was 12 % H<sub>2</sub>S and 88 % CH<sub>4</sub>.

In case of hydrate formation from a water-H<sub>2</sub>S-CH<sub>4</sub> with higher content of H<sub>2</sub>S in the feed gas both Raman and DSC measurements indicated the formation of multiple hydrate phases with different compositions.

## REFERENCES:

- [1] Schicks J.M., Ziemann M. A., Lu H., Ripmeester J.A. *Raman spectroscopic investigations on natural samples from IODP Expedition 311: indications for heterogeneous compositions in hydrate crystals* Geophysical research Letters, submitted
- [2] Barnes R.O., Goldberg E.D. *Methane production and consumption in anoxic marine sediments*. *Geology* 1976, 4: 297-300
- [3] Zehnder A.J.B., Brock T.D. *Methane formation and methane oxidation by methanogenic bacteria*. *J. Bacteriol.* 1979, 137: 420-432
- [4] Kastner M., Kvenvolden K. A., Lorenson T. D. *Chemistry, isotopic composition, and origin of a methane-hydrogen sulfide hydrate at the Cascadia subduction zone*. *Earth and Planetary Science Letters* 1998, 156: 173-183.
- [5] Boetius A., Ravensschlag K., Schubert C.J., Rickert D., Widdel F., Giesecke A., Amman R., Jørgensen B.B., Witte U., Pfannkuche O. *A marine microbial consortium apparently mediating anaerobic oxidation of methane*. *Nature* 2000, 407: 623-626
- [6] Noaker L.J., Katz D.L., *Gas Hydrates of Hydrogen Sulfide-Methane Mixtures*, *Petroleum Transactions, AIME* 1954, 201, 237-239
- [7] Selleck F.T., Carmichael L.T., Sage B.H. *Phase Behaviour in the Hydrogen Sulfide-Water System*. *Industrial and Engineering Chemistry* 1952, 2219-2226
- [8] Carroll J.J., Mather A.E. *Phase Equilibrium in the System Water-Hydrogen Sulphide: Hydrate-Forming Conditions*. *The Canadian Journal of Chemical Engineering* 1991, 69:1206-1212
- [9] Robinson D.B., Hutton J.M. *Hydrate Formation in Systems Containing Methane, Hydrogen Sulphide and Carbon Dioxide*. *The Journal of Canadian Petroleum Technology* 1967, January –March: 6-9
- [10] Schicks J.M., Ripmeester, J.A. *The coexistence of two different methane hydrate phases under moderate pressure and temperature conditions: kinetic vs thermodynamic products*. *Angewandte Chemie International Edition* 2004, 43:3310-3313.
- [11] Lu, H., Schicks, J.M., Moudrakovski, I.L., Udachin, K., Ripmeester, J.A., Zhang, M., Naumann, R., Dutrisac, R., Luzi, M., and Erzinger, J. Laboratory-based characterization of gas hydrate samples recovered from northern

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Cascadia by IODP Expedition 311. Journal of  
Geophysical Research, submitted.