Experimental report

04/01/2022

Proposal: **7-05-548**

Council: 4/2021

Title: Investigating natural methane hydrate from the Black Sea.

Research area: Materials

This proposal is a continuation of 7-05-528

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Samples: CH4 / H2O / sand / clay

Instrument	Requested days	Allocated days	From	To
IN1	5	4	07/10/2021	11/10/2021

Abstract:

Natural gas hydrates (NGH) are crystalline materials in which water molecules form networks where gas molecules are trapped. These NGH have very large gas storage capacity and methane NGH are found worldwide in marine sediments on continental margins. Their formation mechanisms in such complex porous medium are still poorly known. In the case of clay-rich sediment like those encountered in the Black Sea, the question of the accumulation of hydrate in the interlayer remains elusive. Only few studies have been devoted to the plausible formation of NGH in sediment nanopores (natural or synthetic). Recent IN1 experiments (8-12 feb. 2021) showed different inelastic spectral signatures for the various synthetic clay/silica matrix sediments at various salt concentrations. In September 2021, an IFREMER oceanic cruise, GHASS 2, is scheduled with the aim to collect natural hydrate-bearing sediments from the deep-sea floor of the Black Sea. The goal of this continuation experiment is to acquire inelastic spectra of these natural gas hydrates in order to evaluate the validity of the ¿lab-made hydrate bearing¿ as model systems reproducing the geo- and physical- chemistry properties of NGH.

Investigating natural methane hydrate from the Black Sea.

IN1 - Proposal 7-05-548

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Objectives of the proposal The present proposal aims at completing the ongoing investigation on the effect of clay matrix and ionic strength on the formation of gas hydrates in sediment matrix surrogates made of silica sands and clays, through the analysis of their inelastic neutron scattering signatures. In the first IN1 experiment [7-05-728], the allocated beam time has permitted to investigate both montmorilonite and illite clay-based samples. These results needed to be completed with measurements of methane hydrates synthesized in kaolinite, and in the natural sediments from Black Sea collected during the GHASS cruise in 2015 (made of sand and various clays including illite, montmorillonite and kaolinite). In addition, the requested beam time has provided a unique opportunity to investigate natural-gas hydrate samples recovered from the Black sea during the GHASS-2 cruise (September 2021). Combining previous IN1 results with those of the present continuation were required to validate the use of “lab-made” sedimentary matrixes as surrogates for natural gas hydrate bearing. The results will contribute to the progress of Charlène Guimpier’s and Constant Agnissan’s PhDs research at the frontier between physical-chemistry and geochemistry.

Work carried out during the experiment and main results obtained. During the experiment, the allocated beam time has permitted to investigate both lab-made and natural samples from the Black Sea collected in September 2021. 21 samples were investigated thanks to the automatic ILL sample changer. The lab-made methane hydrate bearing sediments were prepared before the experiment. Two different matrices were used. First, the samples with kaolinite were prepared with a mixture of silica beads (so-called “Fontainebleau” sand as geoscience reference) and kaolinite clay with a 40:60 ratio (in agreement with the geochemistry data). Then, hydrates samples were made using natural sediments collected during GHASS cruise (natural composition – 60% clay). Each mixture hydrated at 75% with H_2O and salty H_2O and pressurized with CH_4 at 200 bar during 15 days at constant temperature 282K. The samples were cold-transferred to the sample changer to be analyzed at 10K – 1bar (in the P-T stability region of the methane hydrate). The inelastic spectra were collected for all the sample between 4.5 meV and 150 meV with three monochromators (Si111, Si311, Cu220). The collected signals were then compared to the pure methane hydrate, pure salty methane hydrate, hexagonal ice and salty ice and to the reference matrices dry and wet.

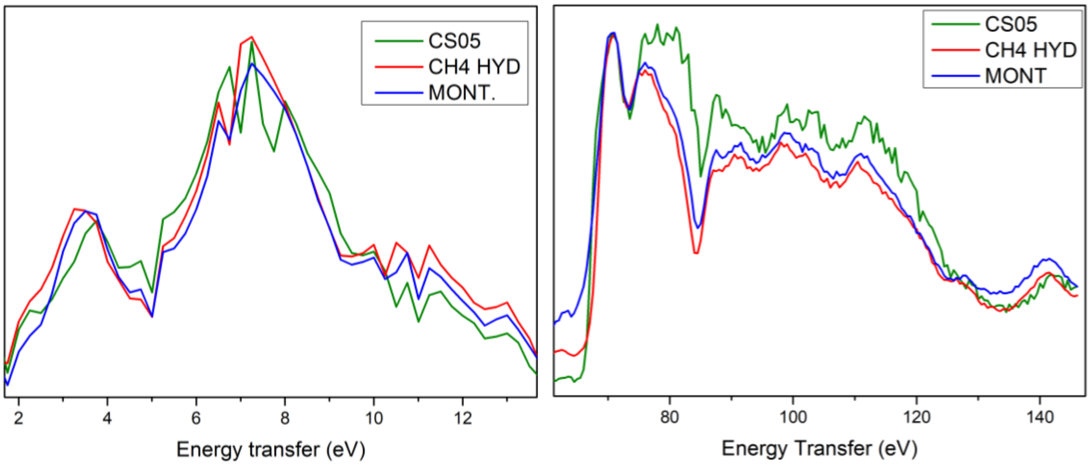

Figure 1. Left: rotational spectra of encapsulated methane molecules in the sediment-free methane hydrate, in the Montmorillonite/sand methane hydrate and in natural hydrate. **Right:** librational spectra of water molecules forming the hydrate cage. All spectra correspond to raw data (no corrections applied).

The inelastic signal of the lab-made samples revealed the presence of two peaks at 2.3meV and 3.3meV, which are attributed to the rotational bands of encapsulated methane molecules in the hydrate cages adopting the so-called structure I (Figure 1.left). The observation of these inelastic quantum rotational bands is the first direct evidence of the methane hydrate formation in the sedimentary matrix. The rotational bands are also observed in the natural methane hydrate, with a slight energy shift. Another evidence of the presence of methane hydrate in this matrix is the modification of the inelastic signal at higher energies corresponding to the librational bands of water molecules. A shoulder is observed at about 70meV for Montmorillonite/sand methane hydrate, that is not observed in the case of sediment-free methane hydrate. And a different signal at about 70meV, is also observe for the natural hydrate sample (Figure 1.Right). It may involve a specific organization of the water molecules.

The collected results during the experiment offer us new information on the presence and formation of methane hydrate in clay/sand matrix by analyzing the inelastic quantum rotational signal of methane and the librational band of water in the various samples. We have the evidence of the presence of hydrate in all the samples and we can now compare them with the previous results from the experiment 7-05-528.

Pursue of the project and future work. In the first IN1 experiment (7-05-528), the allocated beam time permitted to investigate both montmorilonite and illite clays. These results were completed with this experiment with the study of lab-made methane hydrates in kaolinite and natural sediments from the Black Sea. But also, we acquired original data on **natural-gas hydrate samples recovered from the GHASS-2 cruise.** Combining previous IN1 results with the present ones is needed to validate the use of "lab-made" sedimentary matrixes as surrogates for natural gas hydrate bearing. It should thus offer the opportunity to evaluate the implication of gas hydrates in geo-hazards. Indeed, it should provide novel information on methane storage capacity in ocean floors and thus, on the volume of greenhouse gas that could be released into the water column, and potentially reach the atmosphere.