Experimental report

15/02/2021

Proposal: 7-05-528 **Council:** 4/2020

Title: Methane hydrate formation in BlackSea sediments: ionic strength and confinement effect.

Research area: Materials

This proposal is a new proposal

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Samples: methane-water-silica-clay

Instrument	Requested days	Allocated days	From	To
IN1 LAG	5	3	09/02/2021	12/02/2021

Abstract:

Natural gas hydrates (NGH) are crystalline materials in which water molecules form networks where gas molecules are trapped. These NGH have a very large gas storage capacity and have been studied for many years in various fields, both in geosciences and astrophysics and in process engineering. Methane NGH are found in marine sediments on continental margins. Only few studies focus on the plausible formation of NGH in sediment nanopores, especially by considering natural sediments present in deep-ocean (Black sea) and geological materials mimicking the natural ones. Hydrate formation in confined spaces is a required knowledge for understanding the formation history and formation mechanism of NGH, crucial to evaluate NGH destabilization and potential impact on climate change. This proposal aims at investigating the methane hydrate formation within sediments (artificial and natural clay/silica matrix) at various salt concentrations. The effect of ionic strength (salinity) and confinement properties (multiscale pores distribution in sediments) on methane hydrates formation will be explored via inelastic neutron scattering under conditions reproducing their Black Sea natural environment

Methane hydrate formation in Black Sea sediments: ionic strength and confinement effect.

IN1 - Proposal 7-05-528

Proposer: Charlène Guimpier
Co-proposers: Art Clarie Constant Agnissan, Laurent Michot, Livio Ruffine, Arnaud Desmedt
Experimental team: Charlène Guimpier, Arnaud Desmedt, Monica Jimenez

Objectives of the proposal Inelastic neutron scattering was used to investigate the methane hydrate within sediments (clay/silica matrix) at various salt concentrations. The effect of ionic strength (salinity) and confinement properties (multiscale pores distribution in sediments) on methane hydrates formation was investigated on samples reproducing the Black Sea natural environment. Hydrate formation in confined spaces is a required knowledge for understanding the formation history and formation mechanism of natural gas hydrate (NGH), crucial to evaluate NGH destabilization and potential impact on climate change. The present experiment is enrolled in a larger project to evaluate the implication of gas hydrates in geo-hazards and to complete our knowledge on methane storage capacity in ocean floor. The results will contribute to the progress of Charlène Guimpier's and Constant Agnissan's PhD 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 montmorilonite and illite clays. 14 samples were investigated. The lab-made methane hydrate bearing sediments were prepared before the experiment with mixtures of silica beads (so-called "Fontainebleau" sand as geoscience reference) and clay with a 35:65 ratio (thanks to the geochemistry data). For each mixture, one type of clay has been used: illite and montmorillonite. The various mixtures were 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, hexagonal ice and to the reference matrices dry and wet.

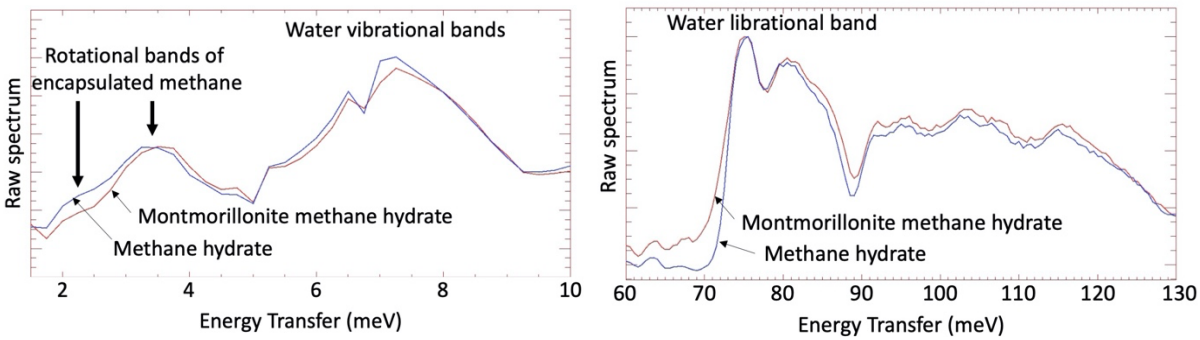

Figure 1. Left: rotational spectra of encapsulated methane molecules in the sediment-free methane hydrate and in the Montmorillonite/sand methane hydrate. **Right:** librational spectra of water molecules forming the hydrate cage. All spectra correspond to raw data (no corrections applied).

The inelastic signal of the samples made of a mixture of montmorillonite and Fontainebleau sand, revealed the presence of two peaks at 2.3meV and 3.5meV 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 pure methane hydrate, with a slight energy shift (Figure 1.Left). 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 (Figure 1.Right). It may involve a different special organization of water molecules, observed only for the swelling clay able to offer large interlayer spaces (Montmorillonite).

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 the monmorillonite/sand matrix whereas the hydrate signals with the illite/sand matrix were weak. Moreover, preliminary results suggest that the salt has negligible impact on the inelastic spectra of the formed methane hydrate, confirming that salts do not include within the clathrate structure.

Pursue of the project and future work. A continuation proposal is required to complete the study on the effect of clay matrix and ionic strength on the formation of gas hydrates in sediment matrix surrogates made of silica sands and clay, through the analysis of their inelastic neutron scattering signatures. This first IN1 experiment, the allocated beam time has permitted to investigate both montmorilonite and illite clays. These results need to be completed with measurements with non-swelling clays (kaolinite) and with the natural GHASS1 sediment (made of sand and various clays including illite, montmorillonite and kaolinite). In addition, the requested beam time will provide a **unique opportunity to investigate natural-gas hydrate samples recovered from the GHASS-2 cruise**. Combining previous IN1 results with those of a continuation 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.