Experimental report

15/02/2021

Proposal: **5-22-786**

Council: 4/2020

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

Research area: Materials

This proposal is a new proposal

Main proposer: **Charlene GUIMPIER**

Experimental team: Charlene GUIMPIER
Arnaud DESMEDT

Local contacts: Thomas HANSEN

Samples: methane-water-silica-clay

Instrument	Requested days	Allocated days	From	To
D20	5	4	04/02/2021	08/02/2021

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 kinetics of NGH formation comparing natural sediments present in deep-ocean (Black sea) and geological materials mimicking the natural ones. NGH formation kinetics are required information for understanding the formation history and formation mechanism of NGH - crucial to prevent their destabilization (potential climate change contributor). The present proposal aims at investigating the NGH formation within sediments (artificial and natural clay/silica matrix) at various salt concentrations. This in-situ neutron diffraction experiment will help us to study the influence, in presence of salt, of the spatial organization and the confinement effect of the porous matrix onto the thermodynamic stability and formation kinetics of NGH, under conditions reproducing their Black Sea natural environment.

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

D20 - Proposal 7-22-786

Proposer: Charlène Guimpier

Co-proposers: Art Clarie Constant Agnissan, Laurent Michot, Livio Ruffine, Arnaud Desmedt

Experimental team: Charlène Guimpier, Arnaud Desmedt, Thomas Hansen

Objectives of the proposal. This *in-situ* neutron diffraction experiment aimed at investigating the influence, in presence of salt, of the spatial organization and of the confinement effect of the porous matrix onto the thermodynamic stability and formation kinetics of methane hydrate, under conditions reproducing their Black Sea natural environment. 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. During the experiment, 13 samples were investigated according to two different formation process. A first set of hydrate bearing sediments sample was synthesized in-situ within a high-pressure aluminum cell – mixing the various sedimentary matrix with liquid D_2O or with salted D_2O; the hydrate formation kinetics was monitored by in-situ diffraction (recording 1 min data as a function of time) in the thermodynamic conditions of the Black Sea after pressurization with CH_4 (70 bar – 282K). Once formed, the diffractogram of the samples were collected at 150K and 1 bar (i.e. in the stability zone of the gas hydrate). The kinetic of decomposition of methane hydrate was then monitored from 150K to 300K. The second set of hydrate bearing sediments samples was synthesized at the laboratory (pressurized with CH_4 at 200 bar during 15 days at constant temperature) and then stored in liquid nitrogen until analyses (so-called ex-situ samples in the following). The diffractograms of these samples were collected and the kinetic of decomposition of methane hydrate was recorded from 150 K to 300K.

The samples were prepared 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: kaolinite, illite and smectite and natural sediments collected in Black Sea (which correspond to a mixture of these three clays).

Main results obtained. The collected results during the experiment offer us new information on the formation kinetic and on the decomposition mechanism of the methane hydrate in clay/sand matrix by analyzing the evolution of characteristic Bragg peak intensity as a function of time (formation) and of temperature (decomposition). Formation occurs on timescale ranging from less than an hour to several days depending on the structural characteristics of the clay and on the presence of salt. On the example showed in the figure below, one can clearly see that methane hydrate is formed in less than 1 hr when considering the Montmorillonite sediment, while after 6 hrs of pressurization, the illite sediment did not allow to observe the formation of methane hydrate. It should be noted that a small fraction of the water confined in illite and expose to methane pressure for 15 days (pre-made sample at the lab prior to the D20 experiment) is transformed into methane hydrate, as revealed by the experiment on the ex-situ sample. Moreover, complex decomposition processes have been measured and the acquired diffractograms while heating the samples from 150K to 300K (with a heating rate of 1K/min) at 1 bar reveal the importance of the clay nature and of the salinity on the thermodynamics stability of synthetic methane hydrate sediment bearing.

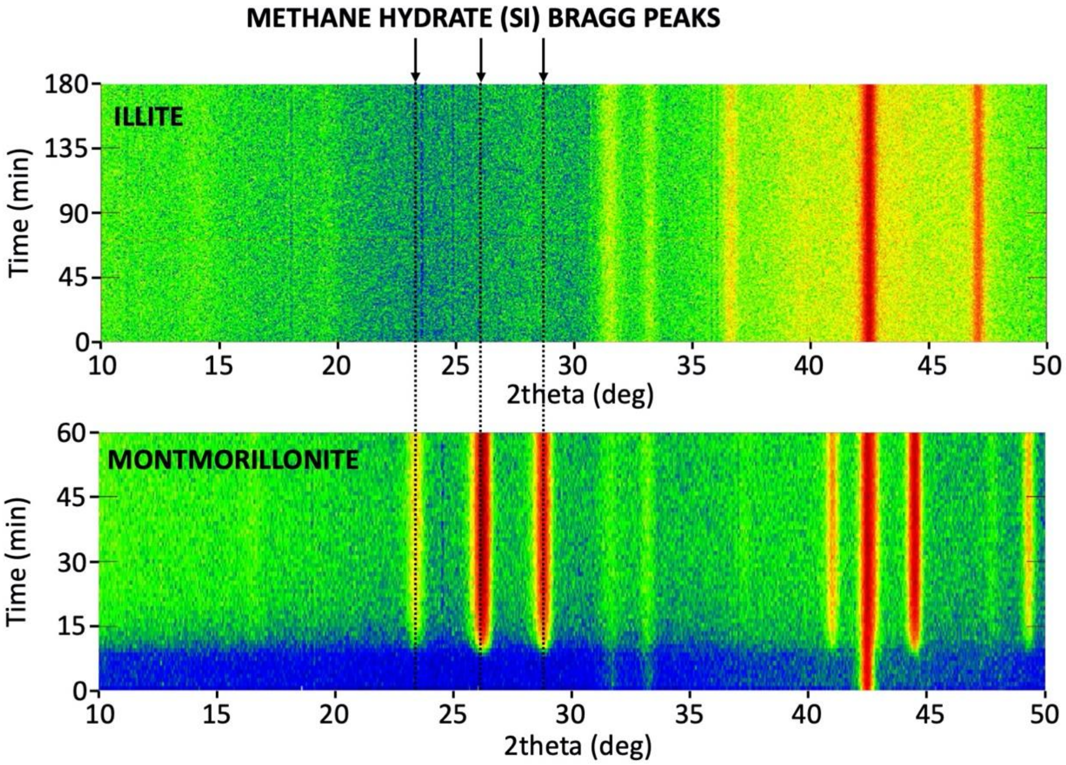

Figure. Top: *in-situ* D20 diffraction (at 2.41Å) recorded every minute on illite/sand sedimentary matrix at 282K and 70 bar – no hydrate formation is observed over 3 hrs. **Bottom:** *in-situ* D20 diffraction (at 2.41Å) recorded every minute on motmorillonite/sand sedimentary matrix at 282K and 70 bar – hydrate formation is observed after *ca.* 10 min of pressurization. On both figure, time *t = 0* corresponds to the start of CH_4 pressurization.

Future work and pursue of the project. Deeper analysis will be performed to quantify the cage occupancy for the various sedimentary matrix through Rietveld refinement and to investigate any variability of the hydrate cell parameters depending on the salinity and on the nature of the sedimentary matrix. This experiment provides unvaluable information on "artificial" hydrate bearing sediments. A deeper investigation on the structure of natural gas hydrates collected during the GHASS cruise in Black Sea (originally scheduled in July 2020 and postponed to September 2021) will be relevant to validate the results of the present experiment obtained on lab-made samples mimicking natural conditions (thermodynamics and sedimentology), kipping the same objective of having a better estimation of gas storage capacity in ocean floor.