	Experiment title: Structural investigations of natural clathrate hydrates	Experiment number: CH-1880
	Beam line: ID31	Date of experiment: from: 07.05.05 to: 10.05.05
	Shifts: 9	Local contact(s): Dr. M. Brunelli
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Report:

Natural gas hydrates (clathrates) are formed by the inclusion of gas molecules into the cavities of a crystalline network composed of H-bonded water molecules. Methane is the most abundant natural gas present in these samples that occur naturally in permafrost or sediments of many continental margins. The properties of naturally formed natural gas hydrates are not well understood due to the difficulty to recover intact hydrates in sediment. Knowledge of the structure and thermal properties (expansivity) is of practical importance for a better understanding of well logging data. It is also important to better characterize the intermolecular interactions between gas-water and gas-gas molecules. For example, an increase in the expansivity relative to ice can be attributed to a greater anharmonicity in the crystal (Tse, 1987). Gas-water interactions may be responsible for a greater thermal expansivity in the hydrates.

Three different geological sites have been investigated where hydrates can be recovered: Norwegian margin, Nigerian margin, Congo-Angola basin. These localizations are characterized by a high spatial variability in the growth environment that may reflect the occlusion of various chemical species. However, the diffraction data reveals that the preservation state of the different specimens is not equivalent.

The natural samples are inserted at low temperature in quartz capillary tubes suitable for adaptation onto the ID31 diffractometer and maintained at ~ 90 K by the cold nitrogen gas blower. They were mounted horizontally with a spin speed set to ~ 1 Hz. The experiments were conducted at wavelength $\lambda = 0.8002$ Å, in the $1^\circ < 2\theta < 80^\circ$ range, with a $\Delta(2\theta)$ step set to 0.005° . The collected diffraction patterns are analyzed using a Least-square fitting procedure with GSAS. Figure 1 shows a typical diffraction pattern collected at ~ 90 K and atmospheric pressure for the Congo-Angola specimen. All the 768 reflections are indexed in the full-pattern structure refinement, with two independent phases: type I clathrate and ice Ih. The hexagonal structure of ice Ih with space group $P6_3/mmc$, yields a lattice constant of $a = 4.500831(7)$ Å, and $c = 7.328262(13)$ Å. The refinement of lattice parameters of the type I structure gives $a = 11.869522(23)$ Å. This result may be compared with that obtained on a natural gas hydrate collected in the Cascadia margin (Yousuf et al., 2004) with a lattice constant $a = 11.8875(75)$ Å obtained at 85 K and 56 MPa N_2 gas (Other reported lattice constants in Yusuf et al., 2004 being less accurate). In our samples, ice is found to be present in relatively large quantity as the refined weighted phase fraction indicates $\sim 27\%$ and $\sim 73\%$ for the type I and the ice respectively (ZaiAngo). The ice present may originate from hydrate dissociation during core recovery and interstitial frozen sea water. It also reflects the need for preservation at 77 K (which was not the case of the Norwegian specimens: 190 K).

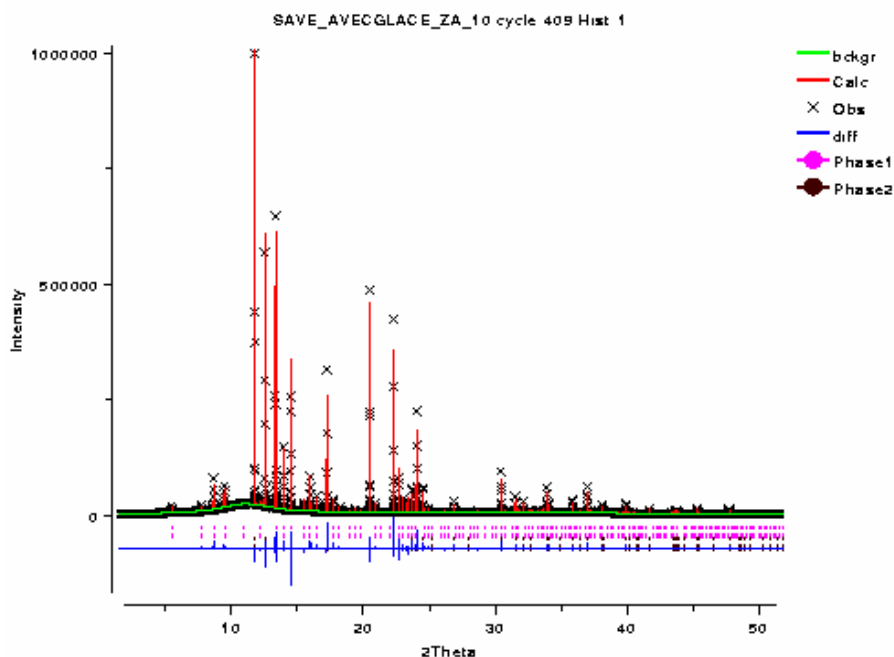


Figure 1. Diffraction pattern analyzed by GSAS of a natural gas hydrate (ZaiAngo specimen)

The resulting lattice constant of ice are shown to be up-shifted in comparison with literature values. The situation can be only slightly improved by applying a temperature correction due to a temperature gradient in the capillaries. Other effects like the presence of an inhomogeneous distribution in size of crystallites may also occur.

When the ice lattice parameters are fixed at literature values, the lattice constant of the clathrate do not show significant changes. Therefore, the ice lattice was freely refined in the following analysis. The lattice constant of the type I clathrate shows some dispersion at 90 K depending on the specimen studied. However, the values obtained are intermediate between the values found for the natural hydrate from Cascadia margin in Pacific (Yousuf et al., 2004) and synthetic CH_4 -hydrate (powder data and single crystal data). It is to notice that discrepancies exist in the literature concerning the lattice parameters of synthetic CH_4 -hydrate without any rational explanation.

Our reported lattice constants are comparatively slightly higher than those found in artificial CH_4 -hydrate. This can be explained by a difference in the gas composition. Other gases like CO_2 , H_2S present in small quantities in the ZaiAngo specimens (99.1% CH_4) are also co-clathrated. They are present to a lesser extent in the NerisII samples. Their presences are thought to alter the lattice parameters. The value reported by Yousuf et al., 2004 indicate that the lattice constant of their specimens are affected by the presence of small quantity of H_2S and traces like CO_2 , C_2H_6 , C_3H_8 . Furthermore, the NerisII specimens proves to have a higher methane purity compared to the ZaiAngo specimens. This result in a lattice constant comparatively smaller (Figure 2).

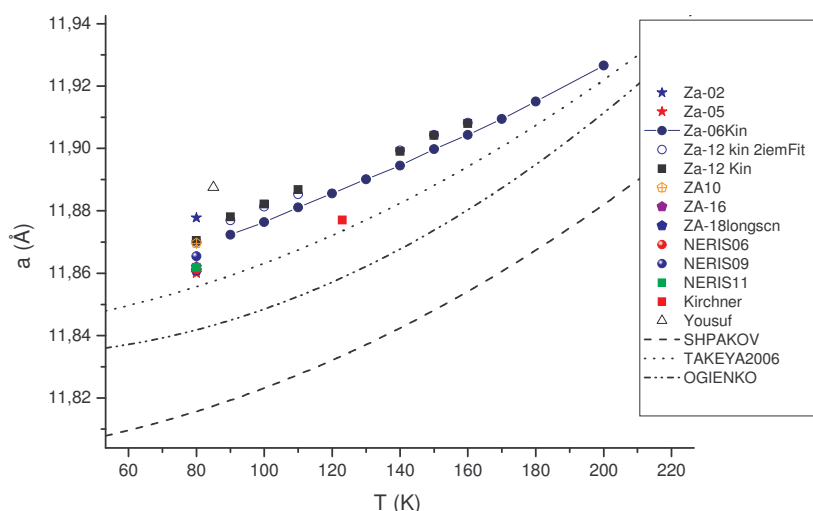


Figure 2. Lattice parameters of natural gas hydrates (Za = ZaiAngo, NerisII, lit. data)

References:

Tse, J; Journal de Physique, C1-143, 48 (1987)
Yousuf et al., Appl. Phys. A 78, 925 (2004)