Investigation of heterogeneously composed Gas Hydrates via Raman Mapping

Manja Luzi-Helbing1,*, J. Prinz2, I. Bald3, J. M. Schicks1
1Helmholtz Centre Potsdam GFZ German Research Centre for Geosciences, Germany; 2University of Potsdam, Germany; 3BAM Federal Institute for Materials Research and Testing, Germany
*Corresponding author: mluzi@gfz-potsdam.de

Abstract

Hydrates of mixed composition and structure have been identified at various sites such as the Gulf of Mexico, Lake Baikal, Caspian Sea, the southern summit of the Hydrate Ridge, the northern Cascadia margin, the Sea of Japan or the Qilian mountains permafrost region. These hydrates may contain C1-C6 hydrocarbons as well as CO2, H2S and N2 resulting in different hydrate crystal structures. The cubic gas hydrate structures I and II and the hexagonal structure H have been identified in natural gas hydrate; noteworthy, all three gas hydrate structures have been also found as part of coexisting hydrates. Possible formation scenarios for heterogeneous hydrates at different sites have been discussed in the literature; however, the fundamental formation mechanism is still unclear. In order to understand the heterogeneous nature of gas hydrates an analytical tool with a high spatial resolution is required. In recent years Raman mapping is emerging as a powerful tool to study heterogeneities regarding structure and composition of hydrate crystals. As a first step this work aims to broaden the knowledge about the heterogeneous character of natural gas hydrates. Therefore, samples originating from the Indian Ocean, offshore New Zealand and from Cascadia margin were analyzed with Raman mapping.

Experimental setup

Macroscopically homogeneous hydrate crystals from natural samples were chosen and placed at ambient pressure and 150 K into a Linkam cooling stage under the microscope. Single Raman spectra and Raman maps were recorded using a confocal Raman microscope (WITec alpha300) equipped with an upright optical microscope. Herein, the incident laser light (λexc. = 532 nm) was coupled into a single-mode optical fibre and focussed through a 20x objective (Olympus SLMPlan) to a diffraction-limited spot on the sample. The scattered light was then coupled into a multi-mode optical fibre, passed to the spectrometer and finally focussed on the CCD camera. Within the spectrometer unit the grating was either set to 600 gr/mm for measuring large spectral ranges or to 1800 gr/mm for higher resolution measurements. For all measurements a laser power of 14 mW was applied. Single Raman spectra were recorded by accumulation of five spectra with an integration time of 5 s per spectrum. For Raman maps areas of 5 µm x 5 µm or 10 µm x 10 µm including crystals with planar surfaces were chosen. Within this area 10 x 10 spectra were recorded with an integration time of 5 s per spectrum.

Samples from the Indian Ocean

At first a natural gas hydrate sample recovered during the Indian National Gas Hydrate Program (NGHP) Expedition 01 in 2006 (Sample Code: HYD 13) showing nodular areas of white crystals within the surrounding sediment was chosen. The sample appeared to be microcrystalline under the microscope, therefore a 5 µm x 5 µm area including crystals with a planar surface was selected for mapping. Within this area 10x10 spectra were recorded. The Raman spectra showed prominent bands of CH4 at 2903 cm-1 (CH4 in 51262 cavities of sl) and 2914 cm-1 (CH4 in 514 cavities of sl). Although the sample only consists of sl CH4 hydrate it became obvious that the CH4 content in the different cavity types of the hydrate structure differs over the probed area. The ratio of CH4 encased in the 512 and 51262 cavities varied between 4.1:1 and 3.3:1 revealing an inhomogeneous CH4 distribution within the hydrate in a micrometer range.

Samples from offshore New Zealand

Secondly, a gas hydrate sample from the SONNE expedition 191-3 in 2007 from the Wairarapa South Tower area offshore New Zealand (Sample Code: SO 191 304 GC 43) was chosen. Under the microscope the sample showed little veins of white crystals within the sediment. Within one of these veins a planar area of 10 µm x 10 µm was mapped resulting in 10 x 10 spectra. The Raman spectra showed two prominent bands arising from CH4 in the 51262 (2903 cm-1) and in the 512 cavities (2914 cm-1) of sl. Also for this sample it became obvious that the CH4 content in the 51262 and 512 cavities varies over the probed area. It turned out that the ratio of CH4 encased in the 512 and 51262 cavities lies between 4.5:1 and 2.8:1 also displaying an inhomogeneous CH4 distribution within the hydrate in a micrometer range.
Samples from Cascadia Margin

The gas hydrate sample chosen for this analysis was recovered in 2002 from gas hydrate outcrops on the seafloor in Barkley Canyon (northern Cascadia margin) during a survey with the Canadian remotely operated submersible ROPOS (Remotely Operated Platform for Ocean Science), about 80 km off the west coast of Vancouver Island. The sample (Sample Code: C1) was completely white exhausting an oily smell. Single Raman spectra giving an overview of the spectral range showed multiple signals at 800 – 1000 cm\(^{-1}\) assigned to C-C stretching vibrations, and at 2800 – 3000 cm\(^{-1}\) assigned to C-H stretching vibrations. The Raman spectrum of the CC vibrational area included signals arising from C\(_2\)H\(_6\) (876 cm\(^{-1}\)) and C\(_3\)H\(_8\) (991 cm\(^{-1}\)) trapped in the 5\(^{12}\)6\(^{4}\) cavities of sII. The Raman spectrum of the CH vibrational area showed partly overlapping signals arising from C\(_3\)H\(_8\) (2871 cm\(^{-1}\) and 2940 cm\(^{-1}\)), C\(_2\)H\(_6\) (2886 cm\(^{-1}\) and 2940 cm\(^{-1}\)) in the 5\(^{12}\)6\(^{4}\) cavities of sII and CH\(_4\) in the 5\(^{12}\) (2913 cm\(^{-1}\)) and 5\(^{12}\)6\(^{4}\) (2902 cm\(^{-1}\)) cavities of sII. The map scan of an area of 10 µm x 10 µm in the spectral region between 2800 cm\(^{-1}\) and 3000 cm\(^{-1}\) revealed an inhomogeneous distribution of the guest molecules within the scanned area.

Conclusion

The analysis of gas hydrate samples from three different locations yielded two samples containing sI CH\(_4\) hydrate and one sII hydrate sample containing different guest molecules such as CH\(_4\), C\(_2\)H\(_6\), and C\(_3\)H\(_8\). Although the scanned area of all samples appeared to be macroscopically homogeneous Raman mapping revealed a varying guest molecule ratio in the cavities for the sI CH\(_4\) hydrates and a heterogeneous guest molecule composition for the sII hydrate on a high spatial resolution. This leads to the assumption that hydrate formation processes do not proceed constantly. The extent of constant and varying formation conditions on the composition and structure of gas hydrates will be subject of further investigations.