

poster

## **Heterogeneous molecular composition of hydrate-bound gas in subsurface sediments from offshore Sakhalin Island, Sea of Okhotsk**

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Gas hydrates are crystalline clathrate compounds composed of water and gas molecules that are stable at low temperature, high partial pressure of each gas component, and high gas concentration. Natural gas hydrates retrieved off Sakhalin Island, the Sea of Okhotsk contain not only methane but also small amounts of other higher hydrocarbons (ethane, propane, etc.), CO<sub>2</sub>, and H<sub>2</sub>S. Gas chromatography reveals molecular composition of hydrate-bound gas by a dissociation of some amount of the sample; however, the sample size may affect the result of gas analysis due to the mixing scale of guest gases in the hydrate phase. In this work, heterogeneous molecular composition of hydrate-bound gas was investigated. The samples were retrieved off Sakhalin Island, the Sea of Okhotsk within the framework of the CHAOS (hydroCarbon Hydrate Accumulations in the Okhotsk Sea) and the SSGH (Sakhalin Slope Gas Hydrate) projects from 2003 to 2009. Our Raman spectrometer (RMP-210, JASCO) can provide small laser spot (about 50µm in diameter) and we can check such heterogeneity at this scale. We found some differences in H<sub>2</sub>S composition in the hydrate samples of the Sea of Okhotsk. Besides this, a ratio of cage occupancies of H<sub>2</sub>S molecules between large and small cages was also estimated from their Raman spectra. These results indicated that H<sub>2</sub>S molecules are rather encaged in the small cages in contrast to methane molecules. Calorimetric study by using a heat-flow calorimeter (BT2.15, Setaram) showed that the gas composition changed with the process of dissociation. We propose that H<sub>2</sub>S molecules formed by AOM (anaerobic oxidation of methane) process intruded secondary into the hydrate phase.