

Phase changes and cage-occupancy changes of methane-ethane mixed hydrates under high pressure

Naoya Takahara[1]; Hisako Hirai[2]; Taro Kawamura[1]; Yoshitaka Yamamoto[1]; Takehiko Yagi[3]

[1] MH Lab., AIST; [2] Geoscience, Tsukuba Univ.; [3] Inst. Solid State Phys, Univ. Tokyo

High-pressure experiments on methane-ethane mixed hydrates with compositions of 22%, 30%, 34%, 53%, 73% and 100% of ethane were performed in the pressure range of 0.1 to 10.3 GPa using diamond-anvil cell. Phase changes and cage-occupancy changes of these hydrates were analyzed by in-situ X-ray diffraction study and Raman spectroscopy. Methane-ethane mixed hydrates (MEH) were found to have phase changes depending on pressure and their compositions. Ethane-rich MEH samples with 53, 73 and 100% retained structure I up to about 2 GPa, but methane-rich MEH ones with 22% formed structure II under lower pressure and structure H under higher pressure, respectively coexisting with structure I. Above about 2 GPa, all of MEH decomposed into fluid (methane, ethane) and ice VII, did not form Filled-ice structure. For all of compositions, MEH released water from hydrate structure with increasing pressure, indicating the increase of the total occupancy of the hydrate structure. In the compositions of 53, 73 and 100%, relative cage occupancy between large cage to small cage by methane and ethane in structure I were changed with increasing pressure. And the slope of relative occupancy with pressure changed at about 1 GPa. This indicates the change of the mechanism for stabilizing the structure I under between lower and higher pressure regions. The mechanism for stabilizing the structure I is thought to be controlled by releasing water and guest movements between large cages to small ones. Changing the mechanism for stabilizing reflected the change of the compressibility for structure I.