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# Heterogeneous molecular composition of Lake Baikal gas hydrate revealed by a calorimetric measurement

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We got methane and ethane mixed-gas hydrates at southern and central basins of Lake Baikal (Kida et al., 2006; 2009; Hachikubo et al., 2009; 2010). Their ethane composition reached to 15%, suggested crystallographic structure II. NMR and Raman spectroscopic methods revealed the both existence of sI and sII in the same sediment cores, respectively (Kida et al., 2006; Hachikubo et al., 2009). Kida et al. (2006) showed sI and sII mixed samples in the scale of the cell for the NMR device. However, it has been still unknown how the above different crystallographic structures and/or gas hydrates of different gas composition are mixed. It is both possible that macroscopic (scale of nodules, from submillimeter to centimeter order) and microscopic (scale of the molecules) mixtures. In this study, we focused on ethane composition and heterogeneous molecular composition of hydrate-bound gas was investigated by using a calorimeter.
The samples were retrieved at Lake Baikal from 2005-2008 and stored in the temperature of liquid nitrogen. Ethane compositions of gas hydrate samples retrieved at Goloustnoye G-1 were about 0.5-1.5%, whereas those at Kukuy K-2 mud volcano were about 14% for sII and sI+sII mixed type. About 1g of gas hydrate sample was ground up well in liquid nitrogen and put into a small pressure cell for the calorimeter (Setaram BT2.15). The cell was set into the calorimeter at 93K and then heated from 93K to 298K at a rate of 0.15 (K $min^{-1}$). Gas flow system flushed inside the cell by pure $N_2$or He at a rate of 1 [mL $min^{-1}$] to avoid recrystallization of ethane-rich gas hydrate in the cell. Dissociation gas was sampled every 15 minutes by a gas-tight microsyringe and measured the gas composition by a gas chromatograph (Shimadzu GC-14B).
Preliminary results indicated that the ethane composition increased as temperature in the dissociation processes. The change of gas composition was relatively small in the case of Goloustnoye G-1 (sI), whereas that of Kukuy K-2 (sI+sII) increased drastically from several % to 18%. Bulk gas composition of this sample was reported about 15% by Kida et al. (2006), however, real gas composition of sII part seemed to be more ethane rich. The ethane composition of sII part was almost constant. These results supported the hypothesis of double structure gas hydrate (Hachikubo et al., 2009). On the other hand, we also checked the heterogeneity by using Raman spectrometer (RMP-210, JASCO Corp.) because the device can provide a small laser spot (about 5 0um in diameter) to the sample surface. We obtained Raman spectra several times from the same hydrate nodule and found large differences in crystallographic structure and ethane composition even in the same sample.

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