

結晶構造I型のメタン・エタン混合ガスハイドレート解離時における結晶構造II型の結晶二次生成  
Formation of sII gas hydrate during dissociation of sI mixed-gas hydrate composed of methane and ethane

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Double structure gas hydrate, composed of the cubic structure I and II, has been discovered in a same sediment core retrieved from the Kukuy K-2 mud volcano at Lake Baikal (e.g., Kida *et al.*, 2006). The structure II gas hydrate contained 13-15% of ethane, on the contrary, the structure I has only several % of ethane. It has been reported that a structure II gas hydrate appears in appropriate gas composition of methane and ethane (Subramanian *et al.*, 2000a; 2000b). Some models tried to explain how the double structure formed (Hachikubo *et al.*, 2009; Manakov *et al.*, 2013), however, which structure first formed has been still unknown.

Synthetic mixed-gas (methane and ethane) gas hydrates were formed and their dissociation process was investigated by using a calorimeter (Hachikubo *et al.*, 2008). In most cases, two peaks of heat flow appeared and the dissociation process was divided into two parts. This can be understood in the following explanation that (1) the sample contained both crystal structures (I and II), and/or (2) ethane-rich gas hydrate formed simultaneously from dissociated gas and showed the second peak of heat flow. However, Raman spectra of these samples showed that the crystallographic structure of the samples was originally unique in most cases. In this study we tried to check the latter process, namely a secondary formation of ethane-rich gas hydrate.

We made a methane and ethane mixed-gas hydrate (3.62% C<sub>2</sub>) in a pressure chamber (volume: 20mL), and stored in liquid nitrogen. A part of the sample was put into a calorimeter (Setaram BT2.15) and dissociated under the temperature gradient of 0.15 K min<sup>-1</sup>. We observed double peaks in the thermograph, indicating that a new gas hydrate formed from the dissociation gas of the original hydrate, concentrated ethane, and then dissociated. In the next experiment, we put the rest of the sample into the calorimeter, heated in the same condition, and recovered the sample at the end of the first peak of dissociation. The raman spectra of the sample revealed that a structure II ethane-concentrated gas hydrate formed secondarily in the sample. The composition of ethane was 23.4%, corresponded to the field of structure II (Subramanian *et al.*, 2000a; 2000b). Stable isotopes ( $\delta^{13}\text{C}$  and  $\delta\text{D}$ ) of methane and ethane were also measured, and confirmed the existence of several ‰ difference in ethane  $\delta\text{D}$  between the first and second peaks, corresponded to the field data of the double structure observed at the Kukuy K-2 mud volcano (Hachikubo *et al.*, 2009).

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キーワード: ガスハイドレート, メタン, エタン, バイカル湖

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MIS24-P11

会場:コンベンションホール

時間:5月27日 18:15-19:30

Keywords: gas hydrate, methane, ethane, Lake Baikal