

Study on formation efficiency of alcohols and aldehydes in gamma-irradiated methane and ethane hydrates

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Clathrate hydrate is a crystal compound of water molecules encaging guest molecules. Natural gas hydrate, whose guest molecule is mainly methane, is found under deep sea and in permafrost region. Estimation of formation age in natural gas hydrate has been attempted using the ¹²⁹I method (e.g. Fehn et al., 2003), which is an indirect age determination method. In contrast, we have investigated to establish a direct age determination method from hydrate crystal itself. Since natural gas hydrate is formed in sediment and irradiated by natural radiation due to natural radioisotopes like ⁴⁰K, U-series and Th-series, chemical reaction via radicals may occur in natural samples. In methane hydrate, methyl radicals are induced by gamma-rays (Takeya et al., 2004). However, they are unstable at the temperature and pressure of natural gas hydrate occurrence, and dimerize to ethane (Ishikawa et al., 2007). In another reaction, methanol and formaldehyde are also formed in gamma-irradiated methane hydrate (Tani et al., 2011). If the radiation-induced compounds in hydrate accumulate after hydrate formation, the amount may be related to a formation age of natural gas hydrate. The formation efficiency of the compounds should be determined for estimation of the formation age. Therefore, we have measured dissociated water of gamma-irradiated methane and ethane hydrates to analyze alcohols and aldehydes in the hydrates quantitatively by gas chromatography-mass spectrometry (GC-MS).

Methane and ethane hydrates were synthesized and irradiated by gamma-rays at 273 K under high pressure to avoid dissociation of the hydrates. Headspace gas of the dissociated water was analyzed by GC-MS. The formation efficiency of aldehydes is higher than that of alcohols. In addition, the formation efficiency of the compounds in ethane hydrate is higher than that in methane hydrate. These may be caused by the formation mechanism of the alcohols and aldehydes. We will discuss the possibility of dating natural gas hydrate based on these results.

Keywords: methane hydrate, ethane hydrate, radiation, GC-MS, alcohol, aldehyde