Thermal stability of methyl radicals at high pressure in gamma-irradiated methane hydrate

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Methane hydrate found beneath the deep sea and in permafrost region is a clathrate hydrate composed of methane and water molecules. As natural methane hydrate should be exposed to ,  and -rays emitted from radioisotopes in sediments, free radicals can be formed in methane hydrate. Takeya et al. (2004) showed that the freely rotating methyl radical was observed in synthetic methane hydrate irradiated by -rays at 77 K and decayed around 200 K where methane hydrate becomes unstable. They proposed the decay model that the methyl radical reacted with each other under dissociation of methane hydrate. If the methyl radical is stable and accumulated in methane hydrate under the temperature and the pressure where natural methane hydrate exists, we could estimate the formation age of methane hydrate by conventional electron spin resonance (ESR) dating method. In this work, we investigated thermal stability of the methyl radical in -ray irradiated synthetic methane hydrate under high pressure by ESR.

Samples were synthesized by mixing methane gas and ultrapure water at 277 K and measured at 120 K using the ESR spectrometer (JEOL RE-1X) after -ray irradiation at 77 K under atmospheric pressure. In the isochronal and isothermal annealing experiments under high pressure of 1, 7, 10 MPa, the stainless high-pressure cell were immersed in liquid coolant of ethanol for 30 min. The annealing temperature was controlled using a Nichrome wire heater and dry ice. For the comparison, annealing experiments at atmospheric pressure were performed using temperature controller unit (JEOL ES-DVT2).

Although the methyl radical was thermally more stable under higher pressure, it decreased by half in an hour at 210 K even under 10 MPa. The radical may not be accumulated in natural methane hydrate. In addition, the decay of the radical under high pressure may not have correlation with dissociation of the hydrate. We still consider that the methyl radical may react with each other because the other radicals like OH and atomic hydrogen have already disappeared at 120 K under 0.1 MPa (the first ESR measurement condition). The migration of the radical might be occurred in methane hydrate over 200 K under high pressure.