

High pressure and high temperature stability of methane hydrate in water-methane-ammonia system

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Methane hydrate is a clathrate compound consisting of host cages formed by hydrogen-bonded water molecules and guest molecules or atoms included in the cages [1]. Unlike methane, which is a greenhouse gas even more potent than carbon dioxide, methane hydrate (or “fiery ice”) has the potential to become an important energy resource in the future. Methane hydrate is also expected to be ubiquitous in space and an important constituent of outer icy planets such as Neptune and Uranus and their moons such as Titan and Europa [e.g., 2]. The internal structures of these icy bodies have been inferred by spacecraft probes, spectroscopic measurements, and theoretical calculations, but still remained unclear. The icy mantles of Neptune and Uranus are thought to consist of H₂O, CH₄, and NH₃ [3], and methane hydrate is a potential candidate for the major constituent of the mantle. Similarly, the recent high-pressure experimental studies suggested that the icy mantle of Titan is dominated by methane hydrate, which is likely an essential source of the methane-rich atmosphere at the surface [2, 4]. However, the behavior of methane hydrate under high-pressure and high-temperature conditions corresponding to those of the icy planetary interiors has not been understood.

In this study, we report a high-pressure and high-temperature investigation of the effect of ammonia on the stability of methane hydrate using X-ray diffraction and Raman spectroscopy combined with externally heated diamond anvil cell under 0.2-20 GPa and 298-413 K. Figure 1 shows the summary of the melting and decomposition conditions of methane hydrate (sI, sH, and filled-ice Ih) obtained by the present experiments. X-ray diffraction and Raman spectroscopy studies revealed that the melting temperatures for the sI and sH cage structures of methane hydrate below 1.8 GPa determined were good agreement with those of pure methane hydrate reported by previous studies [e.g., 5]. On the other hand, the decomposition temperatures of filled-ice Ih above 1.8 GPa were about 10-20 K lower than those of water-methane system reported by Kadobayashi *et al.* (2018) [6]. Our results suggest that ammonia has a potential to vary the stability of filled-ice Ih of methane hydrate in the interiors of icy moons. Finally, we briefly discuss the implications of our new results for the fate of methane hydrate in concerned with a source of atmospheric methane in Titan.

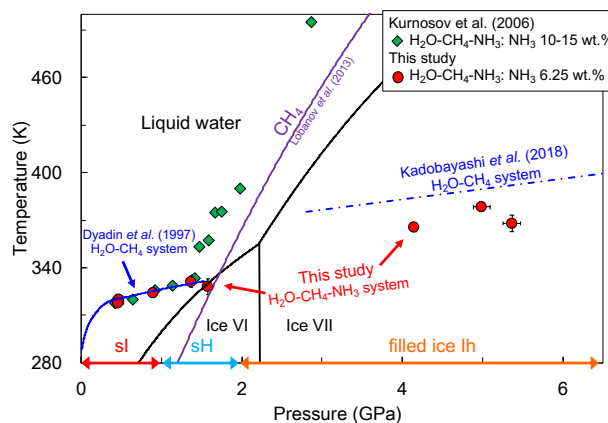


Figure 1. A summary of melting and decomposition conditions of methane hydrate. Black and purple solid curves indicate the melting curves of ice VI, ice VII, and solid methane, respectively. Blue solid and dashed curves indicate the melting and decomposition conditions of methane hydrate reported by Dyadin *et al.* (1997) and Kadobayashi *et al.* (2018). Solid red circles indicate the melting and decomposition conditions of methane hydrates (sI, sH, and filled-ice Ih) obtained by the present experiments. Solid green diamonds indicate the decomposition conditions of methane hydrate reported by Kurnosov *et al.* (2006).

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