Effect of ammonia on the stability of methane hydrate under high-pressure and high-temperature

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Methane hydrate may be present in significant amounts in the interior of Titan and other icy moons and is thought to be a candidate for a source of their atmospheric methane [e.g., Loveday *et al.* (2001); Choukroun *et al.* (2010)]. The icy mantles of these moons mainly consist of water, methane and ammonia, but the stability of methane hydrate coexisting with these components under high-pressure and high-temperature have been still unknown. 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. X-ray diffraction studies revealed that methane hydrate in water-methane-ammonia system transforms from sI cage structure into sH cage structure at approximately 0.8 GPa at room temperature, and further transforms into a filled-ice Ih structure at approximately 1.8 GPa without decomposition into water ice and solid methane. These transition pressures at room temperature were same as those reported for pure methane hydrate [Hirai *et al.* (2001); Loveday *et al.* (2001); Shimizu *et al.* (2002)]. At higher temperature, the melting temperatures for the sI and sH cage structures below 1.8 GPa determined by in situ Raman spectroscopy were good agreement with those of pure methane hydrate reported by previous studies [Dyadin *et al.* (1997); Bezacier *et al.* (2014)]. 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). 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.

Keywords: icy satellite, Titan, methane hydrate, diamond anvil cell, high-pressure experiment