Experimental study on the stability of methane hydrate under high pressure and high temperature

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Abstract

Methane hydrate (MH) is thought to be an important constituent of icy planets and their satellites, such as Neptune, Uranus and Titan. It is a clathrate compound composed of hydrogen-bonded water cages and methane molecules included in the cages. MH has an sI cage structure composed of two 12-hedral and six 14-hedral components in a unit cell at low ($<$ 0.8 GPa) pressures and room temperature. It transforms to an sH cage structure composed of three 12-hedra, two modified 12-hedra, and a 20-hedra at approximately 0.8 GPa, which further transforms to a filled-ice Ih structure at approximately 1.8 GPa (Loveday et al., 2001). The Ih structure consists of an ice framework similar to ice Ih and voids that are filled with methane molecules. Although the sequence of the phase transitions with pressure have been studied well at room temperature, there are only a few studies that addressed the stability of MH under high pressure and high temperature. A recent work by Bezacier et al. (2014) studied the decomposition temperatures of MH at pressures between 1.5 and 5 GPa. They demonstrated that it decomposes into solid methane and liquid water at temperatures close to the melting curves of ices, which is, however, not consistent with an earlier report by Kurnosov et al. (2006). In addition, the pressure range of these previous studies is only limited to $<$ 5 GPa. Therefore, a further investigation is needed to understand the stability and physicochemical behavior of MH under extreme conditions corresponding to the mantle of giant icy planets. In this study, we carefully investigated the stability of MH under 2-51 GPa and 298-653 K using in-situ Raman spectroscopy and X-ray diffraction. Prior to in-situ high P-T experiments, the typical C-H vibration modes and their pressure dependence of MH were measured at room temperature using Raman spectroscopy to distinguish MH from solid methane which would appear through the decomposition of MH into solid methane and ice VII. The results of high P-T experiments showed that MH decomposes into solid methane and ice VII at temperatures considerably lower than the melting curves of solid methane and ice VII in the pressure range of 2-51 GPa. This suggests that MH is unlikely to be stable in the mantle of giant icy planets such as Neptune and Uranus.

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