7 High Pressure Science

7-1 High-pressure Structures of Methane Hydrates up to 86 GPa

Methane hydrate, called as “fiery ice”, is expected an useful natural resource, while methane is an effective greenhouse gas causing global warming. The gas hydrates consist of hydrogen-bonded host water molecules forming cages and of included guest molecules or atoms in these cages. An outline of the structural changes depending of guest size and pressure has been reported by the present authors (Fig.1) [1]. The initial cubic structure (sI) of methane hydrate transforms to a hexagonal structure (sH) at about 1 GPa, and it further transforms to a filled-ice-Ih*) structure (FIIhS) at about 2 GPa (Fig. 2) [e.g. 2-4]. The FIIhS of methane hydrate survives at least to 40 GPa [1,5], while the FIIhSs of other gas hydrates decompose at various pressure below 6.5 GPa [e.g. 6]. A theoretical study using the first principle calculation predicted the retention of the FIIhS of methane hydrate until 100 GPa [7]. Here, interesting point arises whether the FIIhS of methane hydrate survives above 40 GPa or a certain post filled-ice-Ih structure (post-FIIhS) exists.

In situ X-ray diffraction(XRD) studies were performed at BL-18C and BL-13A in the pressure range from 0.2 GPa to 86 GPa. Pressure measurements were made by the ruby fluorescence method. The initial material of methane hydrate powder was prepared using a conventional ice-gas interaction method. In the XRD patterns, the typical diffraction lines of the FIIhS were observed below 40 GPa, although the patterns became somewhat broad. At 40 GPa, new peaks began to appear (Fig. 3). The relative intensities of these peaks became stronger above 40 GPa. Instead, the remaining peaks weakened above 40 GPa and completely disappeared at 60GPa. At above 60 GPa, only the four peaks were observed with strong intensities. The XRD patterns characterized by the four peaks continued at least until to 86 GPa. With decreasing pressure, the patterns reverted at 40 to 35 GPa. The XRD patterns above 60 GPa were different from those of solid methane. Thus, the observed XRD patterns were intrinsic for a new high-pressure structure, post-FIIhS, of methane hydrate.

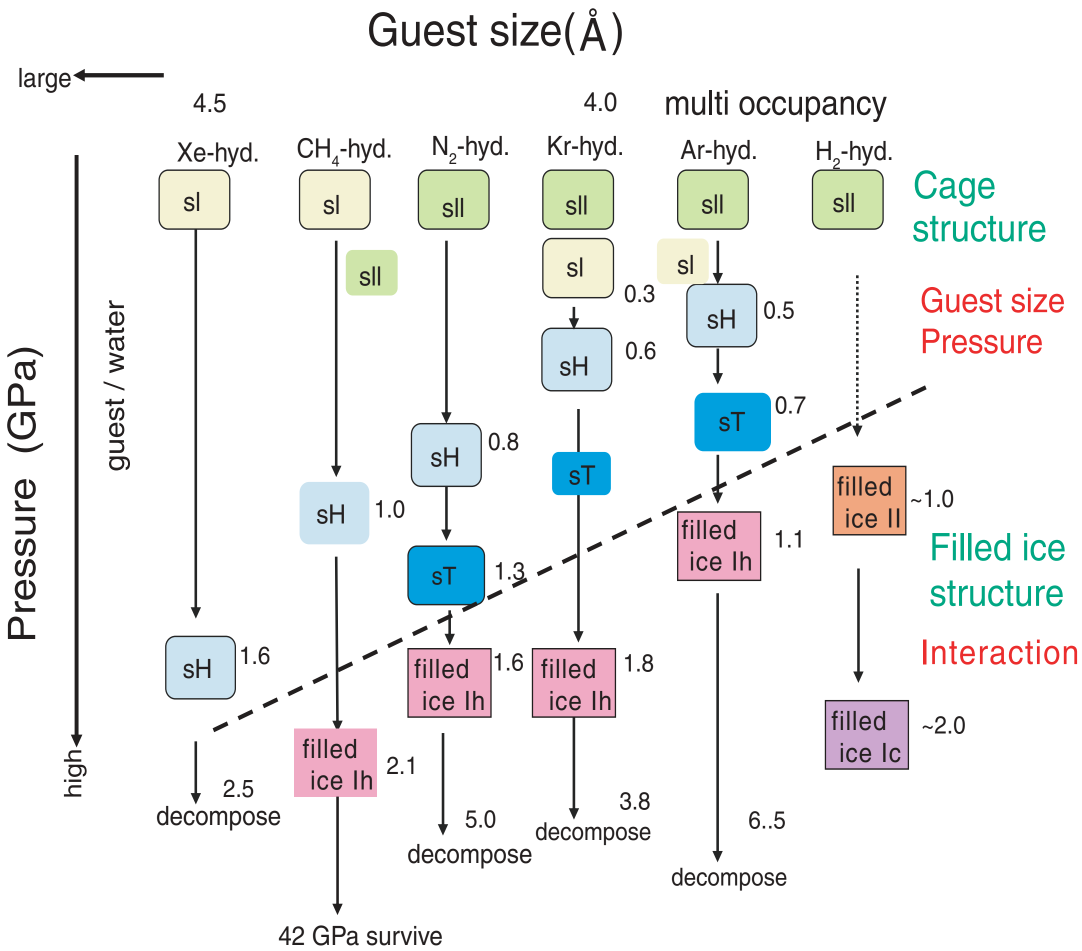

Figure 1
Structural changes of gas hydrates in terms of pressure and guest size at room temperature. The Arabic numbers indicate transition pressures.

The theoretical study reported that the FIIhS will be held up to 100 GPa [7]. However, in the present study, the change in the XRD patterns was clearly observed above 40 GPa, thus the retention of the FIIhS can be said to be limited up to 40 GPa. We attempted to examine the post-FIIhS using the four new diffraction lines, in spite of the small number of diffraction lines. Two possible ways of indexing were suggested. One indexing was as an orthorhombic symmetry with the lattice parameters of a=0.4069 nm, b=0.6890 nm, c=0.5976 nm at 50.6 GPa. These lattice parameters were almost same as those calculated as the FIIhS by the theoretical study [7], so the volume was almost same. But the extinction rule of diffraction was completely different. The second indexing was as another orthorhombic symmetry with the lattice parameters of a=0.3344 nm, b=0.7554 nm, c=0.6671 nm at 50.6 GPa. In this case, two times of the length of a-axis became almost that of c-axis, indicating pseudo-tetragonal symmetry. In any case, the volume change was very small. And, the relative intensity-ratio of the post-FIIhS to the coexisting ice VII were almost same for that of FIIhS to ice VII. Thus, the molecular ratio of methane to water is suggested to be unchanged between both structures. Considering the unchanged molecular ratio and the small volume change, the fundamental structure of the post-FIIhS might be not largely different from that of the FIIhS. The true symmetry of the post-FIIhS can not be determined at present because of the limited diffraction lines.

*) The name "filled-ice" was named in order to make contrast with the ice having a open structure.

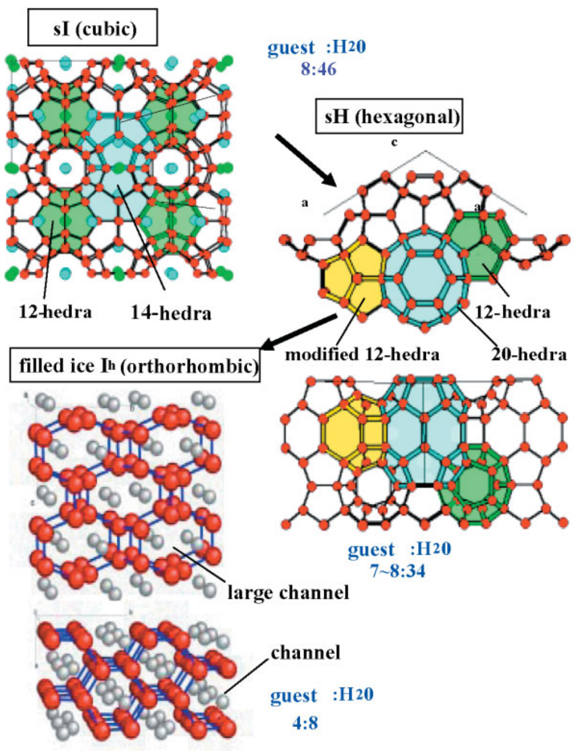

Figure 2
Structure models of methane hydrate; sI, sH, and filled ice-Ih structure.

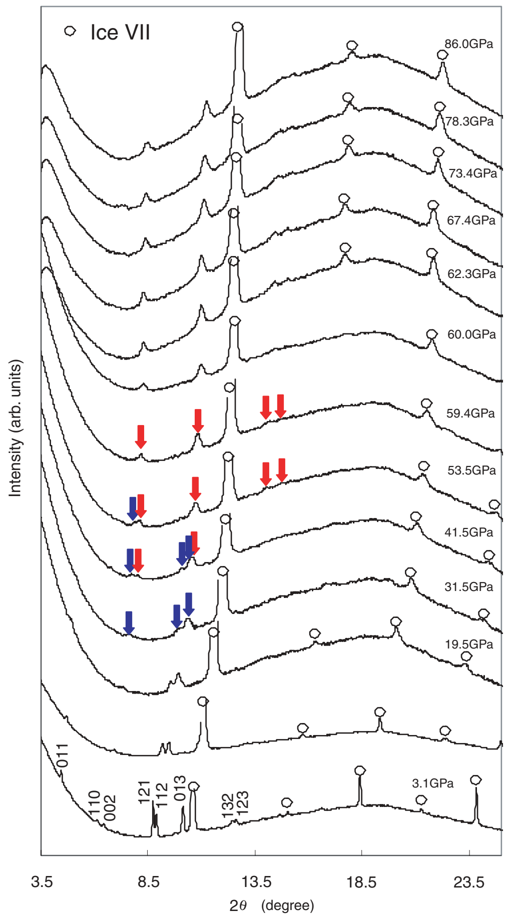

Figure 3
Representative X-ray diffraction patterns with pressure change. At 40 GPa, new peaks (marked by red arrows) began to appear. The relative intensities of the new peaks became stronger, instead, the remaining peaks (marked by blue arrows) weakened above 40 GPa.

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References

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