



Water and methane stay together at extreme pressures

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Large lakes of liquid methane nestle between mountain ranges of solid water ice in the polar regions of Jupiter's moon Titan (1, 2). This strange world illustrates in a quite dramatic fashion that the isoelectronic CH₄ and H₂O molecules display profoundly different physical properties including a 182 °C difference in their melting points at ambient pressure. Unlike methane, water molecules form strong hydrogen bonds with up to 4 neighbors, which explains the high melting point of ice compared to that of solid methane. Rearrangements of those hydrogen bonds, which take place as temperature and pressure are varied, give rise to a large family of complex network structures beyond the "ordinary" hexagonal form of ice, ice *Ih* (3). However, the structural diversity of H₂O does not end with the pure phases of ice. Water molecules can form cages around hydrophobic species such as methane to form clathrate hydrates (4, 5). These important inclusion compounds have been suggested as model systems for studying hydrophobic interactions (4), and they are also relevant for a wide range of industrial, geological, atmospheric, and cosmological settings (6, 7). Methane clathrate hydrate (MH) is one of the most thoroughly studied materials in this context with 3 distinct structural forms identified so far experimentally at different pressures (5). Schaack et al. (8) now report in PNAS the existence of a fourth hydrate of methane (MH-IV) that forms above ~40 GPa and remains stable up to at least 150 GPa. Intriguingly, the water network of MH-IV takes on a very familiar form, that of ice *Ih*, but it is densely packed with methane molecules at a 2:1 H₂O:CH₄ ratio.

Fig. 1 shows the up-to-date sequence of phase transitions observed upon compression of ice/methane mixtures together with the crystal structures of the various MHs. The low-pressure phase (MH-I) is the well-known cubic structure I clathrate hydrate which can be found on the seafloors of Earth (6). Compression above 0.9 GPa leads to the formation of the hexagonal MH-II clathrate hydrate (9) with its almost "baroque" crystal structure that includes large, barrel-shaped cages (10). This type of cage, highlighted in green in

Fig. 1, is the largest identified so far experimentally in the clathrate hydrates and it can host several guest species (4, 5, 9).

Upon further compression, the realm of the clathrate hydrates ends and a so-called filled ice structure is encountered in the form of MH-III (9). It needs to be emphasized that the water network of MH-III does not correspond to any of the known phases of ice (3). As can be seen in Fig. 1, MH-III contains an unusual combination of 4-, 6-, and 8-membered rings of hydrogen-bonded water molecules that confine the methane guest molecules. An interesting aspect of the compression sequence so far is that the H₂O:CH₄ molecular ratio decreases from 5.75:1 for MH-I to 2:1 for MH-III, which means that pure high-pressure ices form as side products as the high-pressure MHs appear (9).

MH-III itself undergoes a subtle structural change as the pressure increases: Above 30 GPa, the O–H...O hydrogen bonds become symmetrical, a process that has also been observed for pure ice X (11). However, this is not where the story ends. Pushing toward even higher pressures, Schaack et al. (8) now report that yet another methane-filled ice structure, which they name MH-IV, exists above 40 GPa. In contrast to MH-III, the water network of MH-IV is simple, containing only 6-membered rings in a structure that is very similar to the "ordinary" ice *Ih* as shown in Fig. 1. It is highly intriguing that a structure that is only stable at very low pressures in the case of pure ice reappears at extreme pressures in the presence of methane.

The evidence for these discoveries is based on Raman spectroscopy carried out in a diamond anvil cell and supported by high-level computational calculations. Schaack et al. (8) also show that their proposed structure for MH-IV is consistent with previously unresolved X-ray diffraction data reported by Tanaka et al. (12). The mechanism of the MH-III to MH-IV phase transition is quite subtle and requires the reorganization of only a few hydrogen bonds, which explains why the H₂O:CH₄ ratio can remain constant at 2:1 during the phase transition. Just as for MH-III (11), Schaack et al. report that MH-IV eventually undergoes hydrogen-bond

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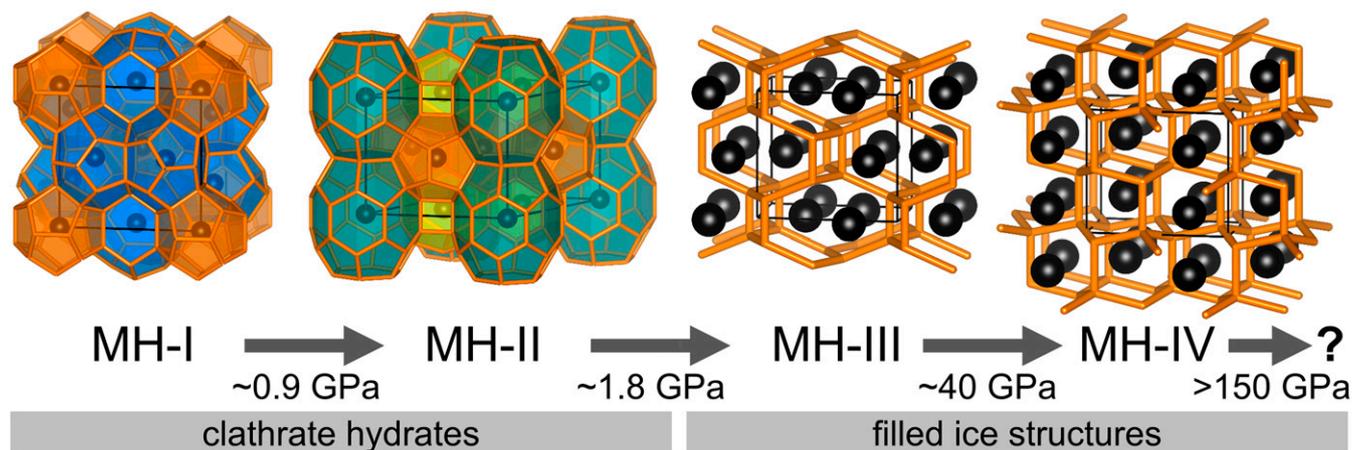


Fig. 1. Sequence of phase transitions of methane hydrates (MHs) upon compression at ambient temperature. MH-IV forms above 40 GPa and is stable up to at least 150 GPa (8). Orange lines indicate the hydrogen-bonded water networks. Black spheres are drawn using the van der Waals radius of methane (2.08 Å) (20) and highlight the central positions of the cages in the MH-I and MH-II clathrate hydrates and the locations of methane molecules in the MH-III and MH-IV hydrates. The various cages in MH-I and MH-II are highlighted in different colors including 5¹²6² (orange), 5¹²6³ (blue), 5¹²6⁸ (green), and 4³5⁶6³ (yellow) cages.

symmetrization upon compression. Overall, the MH-IV structure was found to be stable up to at least 150 GPa, the current limit of their experiments (8).

MH-IV now sets a pressure record for the existence of a gas hydrate. This is significant since it was originally suspected that MH decomposes into pure ice and methane at pressure as low as ~1 GPa (13). The remarkable pressure stability of MH-IV therefore opens up an exciting opportunity for studying the interactions between H₂O and CH₄ over a wide pressure window, and its existence is of course also highly relevant for understanding planetary processes involving water and methane, for example inside gas giants such as Uranus and Neptune (8).

The identification of MH-IV now also underpins the rule that clathrate hydrate structures with cages are favored at lower pressures whereas denser filled ice structures dominate the high-pressure domain (cf. Fig. 1). Upon decreasing the size of the guest species, this structural cross-over appears to shift toward lower pressures. For example, the tiny helium atom enters ice Ih and ice II at quite low pressures to form filled ice structures (14, 15). All attempts to form a helium clathrate hydrate directly have failed so far. However, it was shown recently that helium clathrate hydrate can be formed indirectly by first emptying neon clathrate hydrate to give ice XVI and then refilling the empty clathrate hydrate with helium at low temperatures (15). Other filled ice structures are the chiral C₀ hydrogen hydrate, which is called ice XVII in its empty form (16), and the hydrogen-filled cubic ice Ic (17). What is now clear is that all of the open, low-density phases of ice have corresponding filled counterparts if the size of the guest and the pressure are tuned appropriately. In this context, it is worth mentioning that the

fully cubic ice Ic appears to just have been made for the first time by carefully heating ice XVII (18).

Returning to the MHs, it is important to keep in mind that the composition of the H₂O/CH₄ mixture represents 1 degree of freedom in the phase diagram. The isoplethic trajectory shown in Fig. 1 is therefore strictly speaking only valid for the composition of the MH-I starting material. It is perfectly possible that a wholly different cascade of phase transitions could be observed if, for example, the methane content was increased at the beginning of the compression experiment. Ultimately, approaching pure methane, the phase transitions upon compression are of course expected to be related to the phase diagram of methane.

Other questions remain as well. What happens to MH-IV beyond 150 GPa? Does it ultimately decompose into pure ice and methane, or is there yet another, even denser, hydrate waiting to be found? Equally, the effect of temperature will need to be explored in future studies. Very recently, it has been proposed that pure ice undergoes a phase transition to a superionic phase, ice XVIII, above 100 GPa and 2,000 K (19). In this structure, the oxygen atoms are densely packed while the hydrogen atoms roam freely between them. At present, we can only begin to speculate about the sort of exotic chemistry that would take place if MHs, including MH-IV, were subjected to such extremes of pressure and temperature.

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