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New hydrates in the Ne-, He- and D₂-water system via a high-pressure route

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Formation of gas hydrates from ice is generally a slow process due to the intrinsically sluggish solid-state mass transfer (Salamatin et al. 2015). Small size Ne, H₂ and He are an exception to this rule by being able to penetrate into the lattice of the ordinary ice I_h with ease. Upon further compression ice I_h presaturated with He-gas was found to transform rapidly into gas-filled ice II. Interestingly, H₂ and Ne were found also to form a cubic sII clathrate hydrate at intermediate pressures. In planetary science, such ices filled with Ne, H₂ and He are seen as potent materials selectively trapping and fractionating these primordial gases. Moreover, in the context of fundamental clathrate research Ne- and H₂-hydrates have played the unorthodox role as starting point for the formation of ice XVI, the empty clathrate structure sII (Falenty et al. 2014).

Here we report on the gas loading into ice I_h spheres. The pressure in the system was increased stepwise to 320MPa for D₂ and 400MPa for He and Ne. All guest types were found to rapidly penetrate into ice yet with marked differences. Pressurization of ice with deuterium lead to a rapid formation of sII D₂-hydrate initiated already at 110 MPa. The sII structure remained stable at least up to 320MPa. Ice loaded with Ne remained stable up to 210MPa, i.e. to approximately the stability boundary between pure I_h and unfilled ice II. After crossing this threshold, the sample adopted the sII Ne-hydrate structure and remains stable at least up to 350MPa. Further compression up to ~400MPa resulted in a new Ne-hydrate, topologically similar to the H₂-filled chiral C₀-structure and the recently discovered C₀ structure of CO₂ (Amos et al. 2017). Upon decompression to 350MPa C₀ structure reverted back to sII Ne-hydrate. Upon recovery at liq. N₂ temperature to ambient pressure, cage occupancies in Ne- and D₂-hydrates rapidly readjust by decreasing the number of guests in all cages. A similar pattern can be seen upon guest-removal under vacuum where larger cages empty much faster than the smaller ones; curiously D₂ molecules at comparable conditions seems to leave the sII structure slower than the larger Ne atoms. Smaller cavities seem to be much more difficult to empty and may require the presence of water vacancies for the cage-to-cage hopping.

The He-water system has proven to be the most peculiar one as the compression up to 300MPa did not yield any structural change. He-loaded ice I_h remained stable in the whole investigated pressure range. Still, for the first time we succeeded to form unequivocally sII He-clathrate by filling ice XVI at 120K with 150MPa of He gas; both, the crystal structure and the He-uptake and release, was studied as a function of pressure.

Amos et al.(2017) J.Phys.Chem.Lett. 8, 4295-4299

Falenty, Hansen & Kuhs (2014) Nature 516, 231-233

Salamatin, Falenty, Hansen & Kuhs (2015) Energy & Fuels 29, 5681-5691

Significance statement

We represent two new high pressure phases in small gas - water systems: A Ne-hydrate with a chiral water structure and the long-searched Helium form of sII clathrate hydrate. These new structural forms are manifestations of the importance of van der Waals interactions between water and small gas molecules.

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Track Classification: Amorphous Ice