

they are related to the network structure formed by hydrogen bonds between water molecules. Due to the directional hydrogen bonds, the coordination number of the water molecules at ambient conditions is much smaller than that of simple liquid such as liquid metals and liquid rare gases. We have measured x-ray diffraction of liquid water under high-pressure and high-temperature conditions just above the melting line up to 9 GPa and 690 K using a cubic-type multi-anvil press at BL14B1 and up to 17 GPa and 850K using a Kawai-type press at BL04B1 in SPring-8 [1]. The coordination number of water molecules increased rapidly up to 4 GPa while maintaining the intermolecular distance. The local structure changed toward a simple liquid-like structure. Once a densely-packed, simple liquid-like structure was achieved, the volume was reduced through the decrease of the intermolecular distance on further compression. Measurements up to 20 GPa using sintered diamond anvils have confirmed this trend.

First-principles molecular dynamics simulations were performed for high-density water. The obtained oxygen-oxygen radial distribution functions were in excellent agreement with the experimental results. Results of the simulations in a wide temperature-pressure region revealed that temperature was more important factor for the crossover between the hydrogen-bonded and simple liquid-like liquids [2]. To verify this notion, we have performed in-situ high-pressure high-temperature x-ray diffraction measurements up to 4.1 GPa and 873K. The calculated oxygen-oxygen radial distribution functions were again consistent with our experimental results [2] and results of a recent x-ray diffraction study [3].

[1] Y. Katayama, T. Hattori, H. Saitoh, T. Ikeda, K. Aoki, H. Fukui, K. Funakoshi, *Phys. Rev. B* **2010**, *81*, 014109. [2] T. Ikeda, Y. Katayama, H. Saitoh, K. Aoki, *J. Chem. Phys.* **2010**, *132*, 121102. [3] G. Weck, J. Eggert, P. Loubeyre, N. Desbiens, E. Bourasseau, J.-B. Maillet, M. Mezouar, M. Hanfland, *Phys. Rev. B* **2009**, *80*, 180202(R).

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## MS.75.3

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### Stability of hydrocarbons at deep Earth pressures and temperatures

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Determining the thermochemical properties of hydrocarbons (Hcs) at high pressure and temperature is a key step toward understanding carbon reservoirs and fluxes in the deep Earth. The stability of carbon-hydrogen systems at depths greater than a few thousand meters is poorly understood and the extent of abiogenic HCs in the Earth mantle remains controversial. We report ab initio molecular dynamics simulations and free energy calculations aimed at investigating the formation of higher HCs from dissociation of pure methane, and in the presence of carbon surfaces and transition metals, for pressures of 2 to 30 GPa and temperatures of 800 to 4,000 K. We show that for  $T \geq 2,000$  K and  $P \geq 4$  GPa HCs higher than methane are energetically favored. Our results indicate that higher HCs become more stable between 1,000 and 2,000 K and  $P \geq 4$  GPa. The interaction of methane with a transition metal facilitates the formation of these HCs in a range of temperature where otherwise pure methane would be metastable. Our results provide a unified interpretation of several

recent experiments and a detailed microscopic model of methane dissociation and polymerization at high pressure and temperature [1].

[1] L. Spanu, D. Donadio, D. Hohl, E. Schwegler, G. Galli *PNAS* **2011**, *108*(17), 6843-6846.

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### High pressure amorphization processes in water – methane clathrates

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Clathrates are a class of inclusion compounds where a host lattice of cages are stabilized by inclusion of guest atoms or molecules. Water clathrate hydrates have been known for some time to contain the world's largest reservoir of natural gas. Pressurizing these open network structures has been known for some time to form either a high pressure crystalline polymorph or, at lower temperature, to result in structural collapse into a kinetically 'frozen' amorphous material, but until now the amorphous structure has remained largely unexplored. This process of amorphization likely is a result of the network collapse of the host with little disruption of the guest atom or molecule positions or structure. In this talk we will discuss recent *in situ* neutron diffraction (at the SNS-SNAP instrument) and molecular dynamics studies of water clathrate materials as they are compressed beyond the point of structural collapse. The MD calculations reproduce the measured scattering functions and allow for a higher level of understanding of the resulting amorphous material. The structural processes that occur just prior to, and at the point of collapse, will be covered and structural details of the amorphous structures will be discussed as the disordered materials are further compressed. Additionally, changes in the amorphous structures are followed upon pressure quench recovery and recrystallization.

**Keywords: high pressure, water, amorphous**

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### In-situ chemical partitioning of trace elements between silicate and iron rich liquids at extreme conditions

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From ambient pressure experimental data highly siderophile elements (HSE) should have sunk down with the iron in the Earth's core at the early stage of the Earth's formation, thanks to very high values of their partitioning with respect to the iron [1]. Consequently, the Earth's mantle (and crust) should be vanished of HSE and precious metals. On the contrary, these elements are found in excess in the Earth's upper mantle and crust (close to the chondrite abundance) and