

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).

Keywords: water, high pressure, structure

MS.75.3

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Stability of hydrocarbons at deep Earth pressures and temperatures

Leonardo Spanu,^a Davide Donadio,^b Detlef Hohl,^c Eric Schwegler,^d Giulia Gallia,^{a,c} ^a*Department of Chemistry, University of California at Davis, Davis, 95616 CA (USA)*. ^b*MPI for Polymer Research Ackermannweg 10 55128 Mainz – (Germany)*. ^c*Shell Global Solutions Inc. 3737 Bellaire Blvd. Houston, TX 77025 (USA)*. ^d*Lawrence Livermore, National Laboratory, Livermore, CA 94551 (USA)*. ^e*Department of Physics, University of California at Davis, Davis, 95616 CA (USA)*. E-mail: lspanu@ucdavis.edu

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

Chris A. Tulk,^a Dennis D. Klug,^b Antonio Moreira dos Santos,^a Jamie J. Molaison,^a ^a*Neutron Scattering Sciences Division, Oak Ridge National Laboratory, Oak Ridge TN (USA)*. ^b*Steeacie Institute for Molecular Sciences, National Research Council of (Canada), Ottawa ON, (Canada)*. E-mail: tulkca@ornl.gov

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

S.Petitgirard,^a M. Borchert,^b D. Andrault,^c K. Appel,^b H.P. Liermann,^b M. Mezouar,^a ^a*European Synchrotron Radiation Facility (ESRF), Grenoble, (France)*. ^b*Deutsches Elektronen-Synchrotron (DESY), Hamburg, (Germany)*. ^c*Universite Blaise Pascal, Laboratoire des Magmas & Volcans, Clermont-Ferrand, (France)*. E-mail: petitgir@esrf.fr

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

this phenomenon has been a long-lasting enigma in the interpretation of geochemical signatures of the Earth's mantle and the geochemistry of core-mantle differentiation. This inconsistency has been explained either by a differentiation model with a chemical equilibrium at the bottom of a silicate magma ocean while a metallic core forms at a depth of 1100 km [2] or by the so called 'late veneer' hypothesis. The later postulates an enrichment of HSE in the Earth's mantle by an intensive meteorite bombardment 100±50 My after the Earth's accretion [3].

So far, all the metal-silicate partitioning studies make use of 'classical' HP-HT techniques, e.g., multi-anvil press, and therefore are limited to PT conditions of the Earth's mantle (max. 15-20 GPa/2200°C). There is urgent needs for experiments at much higher pressures and temperatures (e.g., to simulate conditions of core-mantle boundary) because it remains unclear if determined metal-silicate partition coefficients of HSE can simply be extrapolated to much higher pressures and temperatures. In the case of Pd, it has recently been shown that the partition coefficient decreases with increasing pressure (1.5 to 15 GPa) and temperature (1400 to 2200 °C) [2]. Here, we present first preliminary data on metal-silicate trace element partitioning from a new experimental approach to obtain *in-situ* information at high pressures and temperatures up to 50 GPa and 4400 K which were performed at beamline ID27 (ESRF, Grenoble, France) using double-side laser-heated diamond-anvil cells (DAC). Samples are analysed before, during and after laser heating by mean of XRF and XRD. The sample chamber was loaded with a trace element (HSE: Pd, Ru; Zr (metal incompatible)) doped chondrite glass chip placed next to a trace element free metal foil (Fe₉₀Ni₁₀) very close to early earth composition. Laser heating was performed at the interface of chondrite glass - metal foil and in situ XRF spectra and XRD pattern were recorded at the same time. Fluorescence analysis is used to quantify trace element concentration evolution in the melt induced by the laser heating and Diffraction patterns give information on melting stage and appearance of high pressure phases at the same time in the laser spot. First qualitative analysis verify existing data and show a strong partitioning of HSE (Pd, Ru) into the metal liquid with increasing temperature whereas Zr prefers the silicate melt. Quantitative data analyses are currently in progress.

[1] Ertel et al. *Geochemica and Cosmochimica Acta* **1999**, *63*, 2439-2449. [2] Righter et al. *Nature Geoscience* **2008**, *1*, 321-323. [3] Holzheid et al. *Nature* **2000**, *406*, 396-399. [4] Zerr et al *Nature*, **1994**, *371*, 506-508.

Keywords: in situ, partitioning, siderophile elements

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Structure and electronic properties of free, supported and protected clusters

Michael Walter, *Material research center and dep. of Physics, University of Freiburg (Germany)*. E-mail: Michael.Walter@mf.uni-freiburg.de

Clusters can be viewed as small representations of the crystals formed by metal. Due to finite size effects caused by their special electronic and/or ionic configurations, the properties of clusters can be substantially different from the bulk however. One example is the well known catalytic activity of small gold particles in sharp contrast to the inertness of bulk gold.

In our work, we explore the world of small metal clusters with the help of density functional theory. In particular small gold clusters are governed by strong electronic confinement effects that can be understood in a simple jellium picture. The corresponding shell closings give a unified explanation of the magic stability in ligand protect clusters [1]. This includes an alternative model for the well known Schmid "Au₅₅" cluster different from the models used in the literature. Electronic

effects explain STM signatures of supported clusters and even give the possibility to determine the cluster's charge directly (see the figure) [2]. The work is extended to mixed clusters and clusters of other metals.

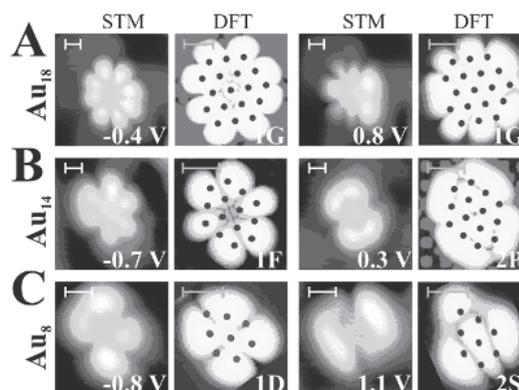


Figure: Experimental and simulated STM signatures for MgO supported gold clusters [2].

[1] M. Walter, J. Akola, O. Lopez-Acevedo, P.D. Jadzinsky, G. Calero, Ch.J. Ackerson, R.L. Whetten, H. Grönbeck, H. Häkkinen *PNAS* **2008**, *105*, 9157-9162. [2] X. Lin, N. Nilius, H.-J. Freund, M. Walter, P. Frondelius, K. Honkala, H. Häkkinen *Phys. Rev. Lett.* **2009**, *102*, 206801.

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Pushing all-electron DFT past old limits for structure of surfaces and molecules

Volker Blum, *Fritz Haber Institute of the Max Planck Society, D-14195 Berlin, (Germany)*. E-mail: blum@fhi-berlin.mpg.de

The prediction and our understanding of structural and chemical processes of matter benefit tremendously from the strength of today's first-principles total-energy methods. The obvious and ongoing limitations of these methods are:

- the affordability and accuracy of the physical approximations [in density functional theory (DFT), primarily the exchange-correlation functional]
- but in addition, the affordability and accuracy of all other numerical approximations that lead to a total energy for a given structure.

For few-atom structures, serial structure screening, exhaustive structure predictions and meaningful time scales in molecular dynamics are now routinely possible, but the challenge still grows immensely for larger system sizes. The present work describes some recent efforts to push out these limits further, using all-electron density functional theory as implemented in the numeric atom-centered orbital based code package FHI-aims [1]. We show how accurately the classic large-scale surface reconstruction of Au(100) and Pt(100) are captured in terms of structure and energetics by current all-electron DFT - if large enough structure approximants (up to ~1000 atoms in a slab model) are considered [2]. We then comment on the additional challenges encountered for the structure and dynamics of biochemical molecules at the other end of the periodic table, addressing both the structure and high-temperature stability of a series of polyaniline-based peptide molecules (up to 180 atoms) in the gas phase. In particular, we find that van der Waals interactions are of unexpectedly large relevance to stabilize specifically the "classic" α -helical structure over competing conformations (even in the gas phase) [3]. Our results are directly verified by comparing theoretical infrared spectra from basis-set