

MS.74.5

Acta Cryst. (2011) A67, C167**Powder X-ray diffraction combined with solid state and ^{129}Xe NMR to study supramolecular crystalline materials**

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The study of crystalline architectures showing permanent porosity that can absorb molecules from the gas phase or include selectively target polymer segments in the nanochannels will be addressed [1]. The porous crystalline matrices span from dipeptide crystals and molecular zeolites to metal-organic frameworks and crystalline hybrid organosilicas [2], [3]. The open pore structure of the nanochannels and the diffusion rates of the gases was established by hyperpolarized Xenon NMR whilst gases such as carbon dioxide and methane were observed directly by ^1H and ^{13}C NMR spectroscopy after gas diffusion into the cavities. We recognized, for the first time, the presence of parallel and aligned molecular rotors in the crystalline pore walls of nanoporous hybrid materials, yielding an unusual anisotropic arrangement of surface-exposed molecular rotors in a 3D framework [4]. The entrapment of molecules inside the channels could successfully regulate the fast molecular rotor dynamics.

The spontaneous formation of the supramolecular architectures were realized by a solvent-free mechanochemical approach or by thermal treatment of a host molecule and block copolymers, as demonstrated by *in situ* synchrotron X-ray diffraction. The driving force for the fabrication of crystalline inclusion compounds with target segments of copolymers was based on the establishment of cooperative noncovalent intermolecular interactions, while steric effects prevented the formation of the inclusion-crystals with the remaining blocks. The 2D ^1H - ^{13}C solid state and fast- ^1H MAS NMR provided direct evidence of the intimate interactions between the host and selected block. The large magnetic susceptibility generated by the aromatic host groups surrounding the included segments could be described by *ab initio* calculations that enabled the evaluation of short intermolecular distances between the host and the target block, demonstrating the existence of a diffuse network of multiple $\text{CH}\cdots\pi$ host-guest interactions. The partitioning of the copolymer blocks in inclusion crystals regularly alternated by amorphous nanophases could fabricate architectures on molecular and nanometric hierarchical scales, as demonstrated by high resolution SEM images.

By a similar strategy, a flexible homopolymer was transformed into a semicrystalline polymer through the partial inclusion of chain segments within the cavities of a crystalline host [5]. The self-assembly process was realized by simple co-grinding of minor amounts of host molecules and the polymer bulk. This assembly led to the formation of innovative nanocrystalline adducts which behaved as cross-linking nanodomains. A multitechnique approach comprising powder XRD and fast- ^1H solid state NMR enabled the identification of the unusual phase architecture in the material.

[1] S. Bracco, A. Comotti, L. Ferretti, P. Sozzani *J. Am. Chem. Soc.* **2011**, *in press*.

[2] A. Comotti, S. Bracco, P. Sozzani, S. Horike, S. Kitagawa *J. Am. Chem. Soc.* **2008**, *130*, 13664-13672. [3] A. Comotti, S. Bracco, G. Distefano, P. Sozzani *Chem. Commun.* **2009**, 284-286. [4] A. Comotti, S. Bracco, M. Beretta, P. Valsesia, P. Sozzani *Angew. Chemie Int. Ed.* **2010**, *49*, 1760-1764. [5] S. Bracco, A. Comotti, P. Valsesia, M. Beretta, P. Sozzani *Cryst. Eng. Commun.* **2010**, *12*, 2318-2321.

Keywords: NMR, inclusion, dynamics

MS.75.1

Acta Cryst. (2011) A67, C167**Structure of silicate liquids in the deep Earth**

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The structure of silicate liquids undergoes major change over the pressure regime of Earth's mantle. This structural evolution affects thermodynamic and transport properties in ways that have profound significance for the origin and long term thermal evolution of Earth's interior. Conclusions are drawn from our first principles molecular dynamics simulations based on density functional theory. The simulations are predictive (parameter-free and independent of experiment) and accurate (results agree well with extant experimental data) and have been used to explore a wide range of compositions in the SiO_2 -MgO-CaO-FeO- H_2O system.

A unifying theme is the change in the Si-O coordination number on compression (mean number of O bonded to Si). The Si-O coordination number increases smoothly and nearly linearly on compression from 4-fold near zero pressure to 6-fold on two-fold compression where the pressure is similar to that at the base of the mantle. Among the important implications of the large change in structure are: 1) the density of the liquid surpasses that of coexisting crystals deep in the mantle, permitting the survival of deep melt layers and 2) the Grüneisen parameter in the liquid increases on compression, making deep magma oceans much hotter than previously thought.

Liquid structure differs fundamentally from crystalline structure and does not represent a disordered form of any crystal. For example, at intermediate compressions, we find that 5-fold Si-O coordination is the most abundant in contrast to crystalline silicates in which 5-fold coordination is rare. The abundance of five-fold coordination explains minimum values of the viscosity on compression.

Fe and H behave differently from other cations. Fe undergoes a gradual transition from a high-spin state to a low-spin state on compression. The decrease in spin tends to increase the density by shrinking coordination environments. H occurs primarily as molecules in silicate liquids at low pressure (OH and H_2O), but this picture rapidly changes on compression. More extended structures ($-\text{O}-\text{H}-\text{O}-\text{H}-$) rapidly form on compression, integrating the H_2O component with the silicate network. The change in H-speciation explains the approach towards ideal behavior on compression: the partial molar volume of water in silicate liquids, small at low pressure, converges to the volume of pure water at mid-mantle pressures, implying unlimited solubility of water in silicate liquids over most of the mantle regime. H remains highly mobile in silicate liquids on compression even under conditions where the silicate network is essentially static, a state resembling a superionic conductor, and allowing connections to deep electromagnetic sounding of the mantle.

Keywords: liquid, silicate, pressure

MS.75.2

Acta Cryst. (2011) A67, C167-C168**Structure of water under high temperature and pressure**

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Liquid water at ambient pressure shows unique properties and

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. Maillat, M. Mezouar, M. Hanfland, *Phys. Rev. B* **2009**, *80*, 180202(R).

Keywords: water, high pressure, structure

MS.75.3

Acta Cryst. (2011) A67, C168

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.

Keywords: carbon cycle, earth interior, numerical simulation

MS.75.4

Acta Cryst. (2011) A67, C168

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

MS.75.5

Acta Cryst. (2011) A67, C168-C169

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