This paper describes objective technical results and analysis. Any subjective views or opinions that might be expressed in the paper do not necessarily represent the views of the U.S. Department of Energy or the United States Government.

SAND2018-7481C

Interfacial Geochemistry of Nanopores: Molecular Behavior in Subsurface Environments

Anastasia G. Ilgen[1], Louise J. Criscenti[1], Jeffery A. Greathouse[1], Kevin Leung[2], Andrew W. Knight[1], Tuan A. Ho[1], Jacob Harvey[1], Austen B. Tigges[1], and Lourdes Loera[1]

[1]Geochemistry Department and [2]Nanostructure Physics Department
Sandia National Laboratories, Albuquerque, New Mexico 87185

Our goal is to develop a molecular-level understanding of interfacial chemistry inside nano-scale pores. We use experimental and model systems relevant to geological environments to address two research tasks: *Chemistry under Nano-Scale Confinement*, and *Upscaling from the Nano- to the Meso-Scale*. This presentation will highlight our recent results from nano-scale confinement studies. Specifically, we will discuss how nano-scale confinement leads to unique chemical behavior of water and other species inside nano-scale domains.

We measured the thermodynamic, vibrational, and physical properties of water residing inside silica pores. In our laboratory systems we use mesoporous silica, with a narrow pore size distribution, with mean pore diameters ranging from 2 nm to 8 nm. We quantified the kinetics of adsorption and uptake of the trace metal copper (Cu^{2+}) and the lanthanides europium (Eu^{3+}) and lutetium (Lu^{3+}), as well as mixtures of lanthanides. We found that when water is confined within the mesoporous silicas, its melting temperature decreases with decreasing pore size from -11.3 °C in the 8 nm pore to -16.5 °C in the 4 nm pore. No melting point was observed for the smallest (2.2 nm) pore, indicating that pore water remained in a liquid-like state over the temperature range of our measurements (from 20 °C to -160 °C). This deviation from bulk water behavior is due to re-structuring of the H-bonding networks. Vibrational spectroscopy was used to quantify the variations in the molecular populations of water. We observed a systematic blue shift in the peak locations of water populations with different degrees of H-bonding under nano-scale confinement (Figure 1). These include highly H-bonded water molecules, referred to as network water (NW), intermediate water (IW), and multimer water (MW).

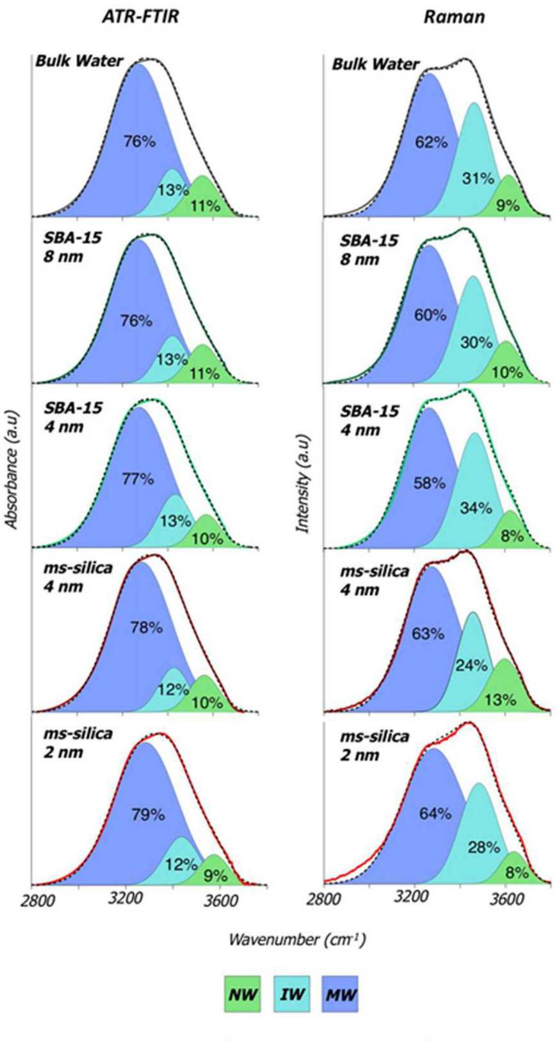

Figure 1. *Systematic changes in reactivity due to nano-scale confinement in mesoporous silica: H-bonding networks in water.*

These observed deviations in the properties of water inside silica pores are also manifested in

Sandia National Laboratories is a multimission laboratory managed and operated by National Technology & Engineering Solutions of Sandia, LLC, a wholly owned subsidiary of Honeywell International Inc., for the U.S. Department of Energy's National Nuclear Security Administration under contract DE-NA0003525.

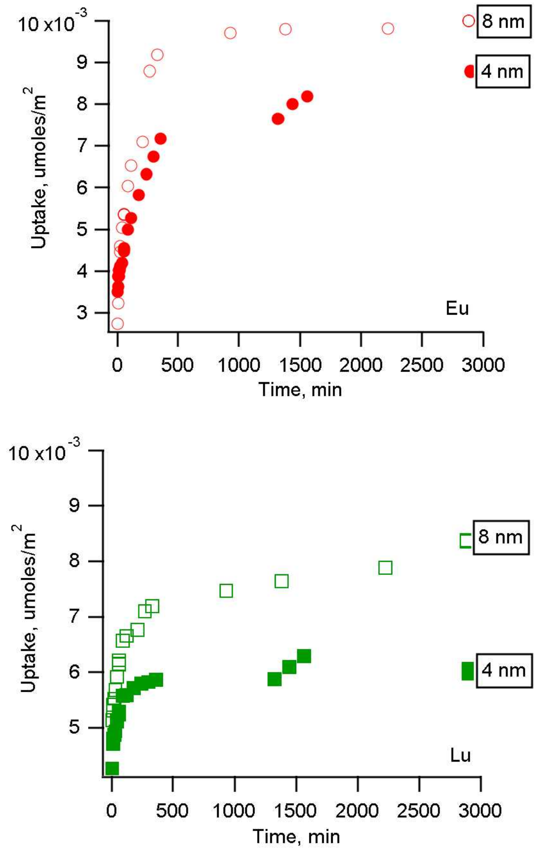

Figure 2. *Systematic changes in reactivity due to nano-scale confinement in mesoporous silica: adsorption of lanthanides Eu*$^{3+}$ *(top) and Lu*$^{3+}$ *(bottom).*

the ion adsorption behavior. With decreasing pore size, the maximum uptake of Cu^{2+} in mesoporous silica increases. The kinetics of Cu^{2+} adsorption is also faster for the 4 nm pores, compared to the 8 nm pores (Knight et al., 2018). Corresponding molecular modeling on an idealized silica surface provides additional insight into ion adsorption mechanisms. Molecular dynamics simulations at both quantum (density functional theory, DFT) and classical (ClayFF) levels of theory indicate strong adsorption of divalent Cu^{2+} and Mg^{2+} ions at a deprotonated (siloxide) surface site, while Na^{+} adsorption is only slightly favorable. Importantly, the quantum simulations show that a water molecule dissociates as Cu^{2+} desorbs, forming a $Cu[(OH)(H_2O)_3]^{+}$ complex. The speciation of adsorbed copper is being investigated now using X-ray absorption fine structure spectroscopy.

We use lanthanides to further probe the kinetics of adsorption and overall uptake as a function of pore size. The ionic radii of the lanthanides decrease with increasing atomic number; and we use this systematic variation to probe the adsorption properties of nano-scale confined surfaces. The uptake of individual lanthanides on mesoporous silicas varies as a function of atomic number, or ionic radii, as well as the pore diameter (Figure 2).

Reference

Knight A.W., Tigges A.B., Ilgen A.G. (2018) Adsorption of Copper on Mesoporous Silica: The Effect of Nano-scale Confinement. *Geochemical Transactions*, 19, 13.

Acknowledgements

This material is based upon work supported by the U.S. Department of Energy, Office of Basic Energy Sciences, Division of Chemical Sciences, Geosciences, and Biosciences. Sandia National Laboratories is a multimission laboratory managed and operated by National Technology and Engineering Solutions of Sandia, LLC., a wholly owned subsidiary of Honeywell International, Inc., for the U.S. Department of Energy's National Nuclear Security Administration under contract DE-NA-0003525.