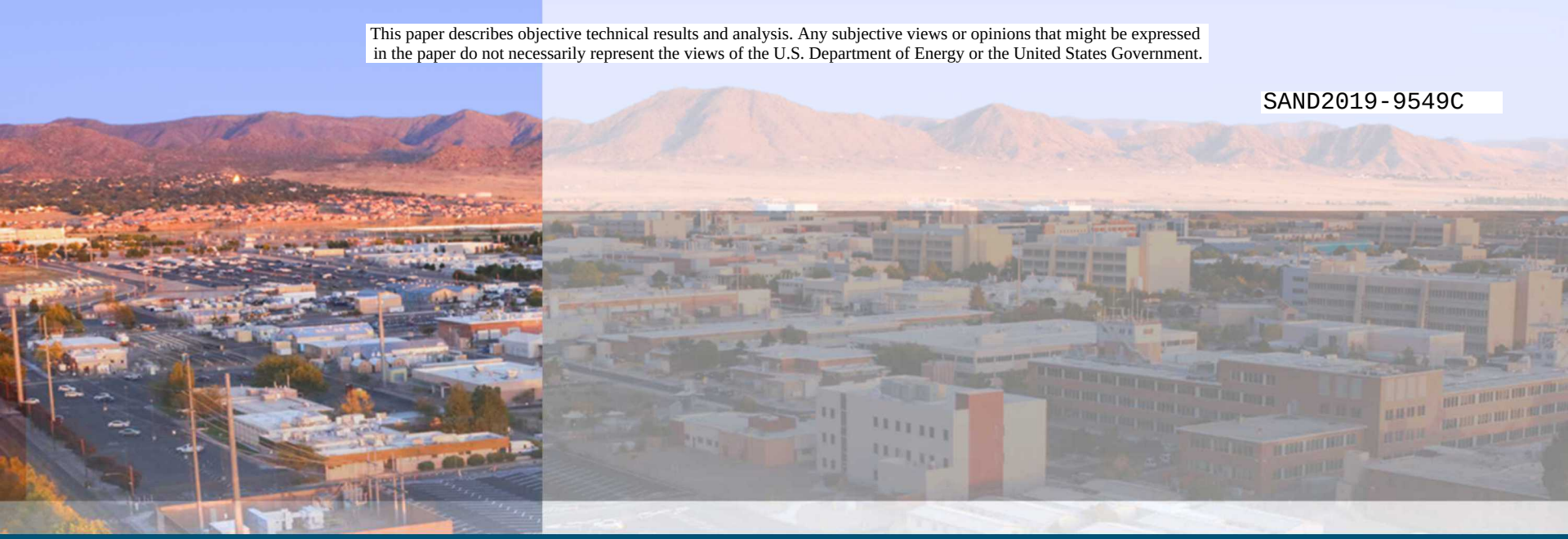
SAND2019-9549C



Interfacial chemistry of lanthanides under nano-scale confinement

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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.

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Nadine Kabengi, Georgia State University

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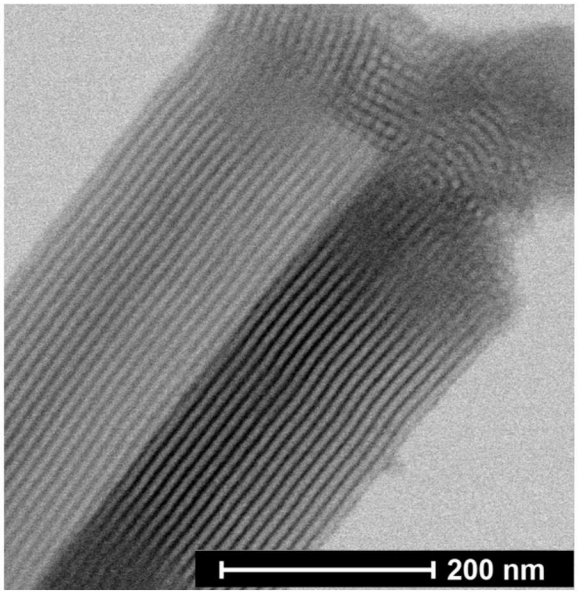
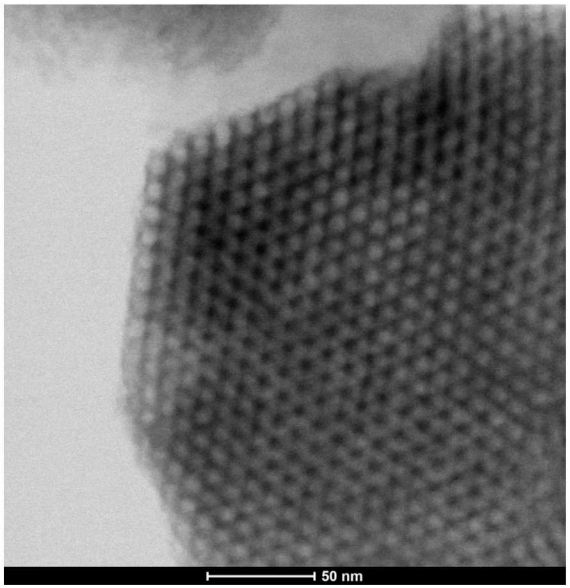
Interfacial chemistry under nano-scale confinement

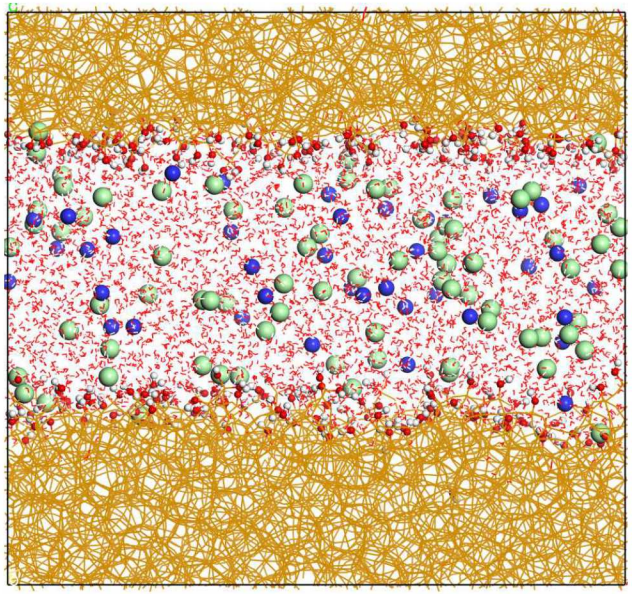
Emergent chemical behavior due to nano-scale confinement:

- **Decreased dielectric constant[1-2], surface tension[3], and density of water.[3]**
- **Decreased solvation energies of metal cations.[4]**
- **Increased inner sphere coordination of metal cations.[4]**
- **Enhanced metal adsorption[5-6], modified redox[7] and diffusion properties.[8,9]**





TEM images, P. Lu



MD model, J. Greathouse

[1]Marti et al., *J. Phys. Chem. B* (2006)
[2]Senapati et al., *J. Phys. Chem. B* (2001)
[3]Takei et al., *Colliod Polym. Sci.* (2000)
[4]Kalluri et al., *J. Phys. Chem. C* (2011)
[5]Wang et al., *Geology* (2003)
[6]Zimmerman et al., *Environ. Sci. Techol.* (2004)
[7]Mattia and Calabro, *Microfliud Nanofluid* (2012)
[8]Samsom and Biggin, *Nature* (2001)
[8]Ma et al., *JACS* (2019)

Adsorption of Cu^{2+} on Mesoporous Silica

Knight, et al., 2018
Geochemical Transactions 19, 13-26

Cu^{2+} adsorption isotherms

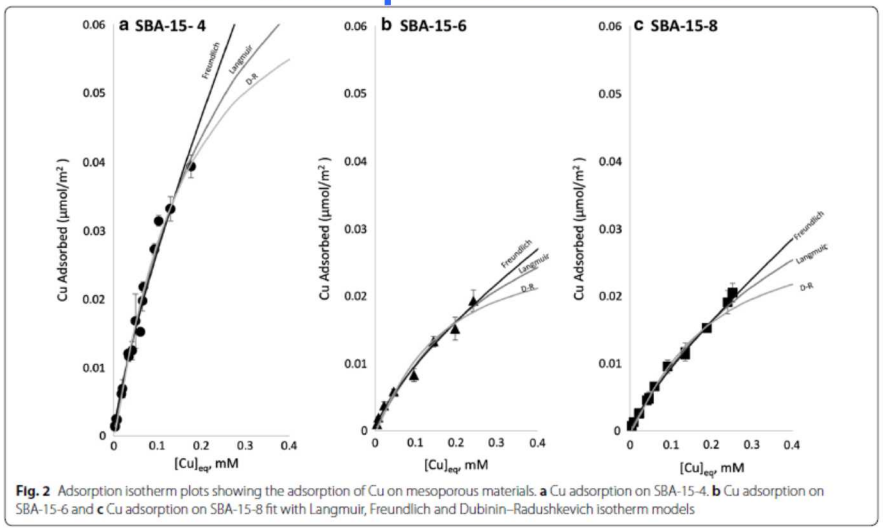
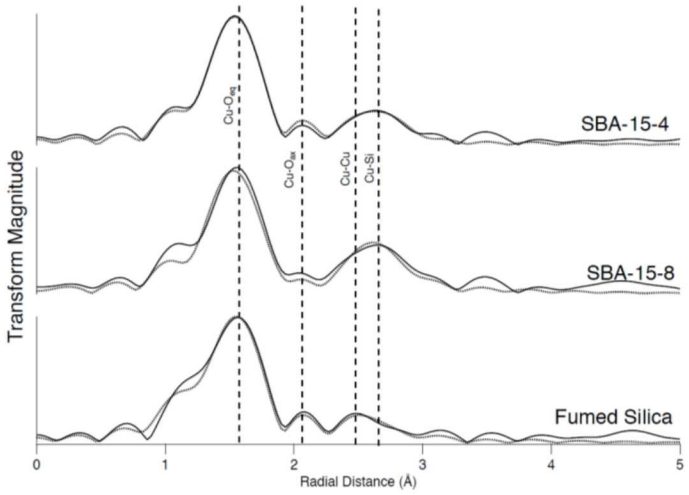


Fig. 2 Adsorption isotherm plots showing the adsorption of Cu on mesoporous materials. **a** Cu adsorption on SBA-15-4. **b** Cu adsorption on SBA-15-6 and **c** Cu adsorption on SBA-15-8 fit with Langmuir, Freundlich and Dubinin–Radushkevich isotherm models

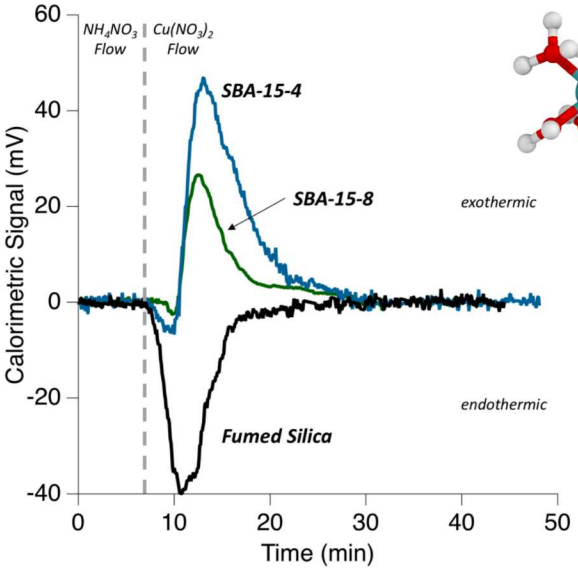
- Enhanced Cu^{2+} adsorption under nano-scale confinement;
- More distorted coordination complexes (Cu-Oax >> Cu-Oeq);
- Increase in Cu^{2+} dimerization inside nano-scale pores;
- Weak endothermic signal followed by a strong exothermic signal: Cu^{2+} undergoes dehydration during the dimerization process.

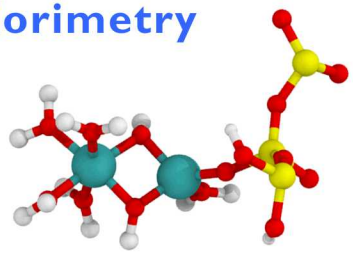
Knight, et al.
Submitted to Environmental Science Nano

Cu^{2+} adsorption complexes



Cu^{2+} flow microcalorimetry



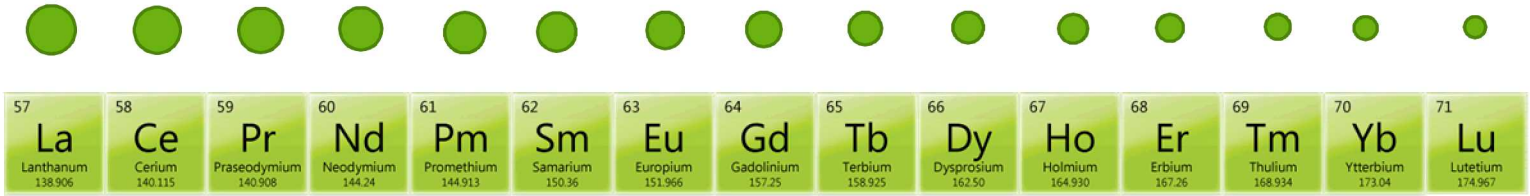


Research Goals

Chemistry under Nano-scale Confinement

- **Effect of pore size on adsorption and coordination of adsorbed species.**
- **Effect of confinement on water properties.**

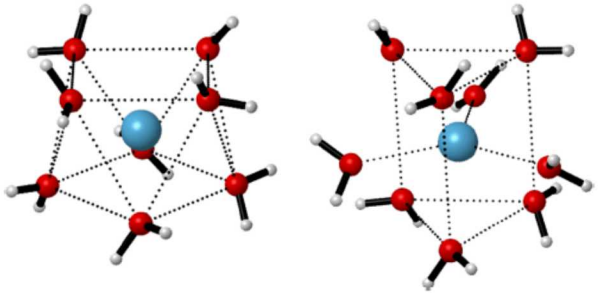
Size decreases across the series



Lowest hydration energy — Highest hydration energy

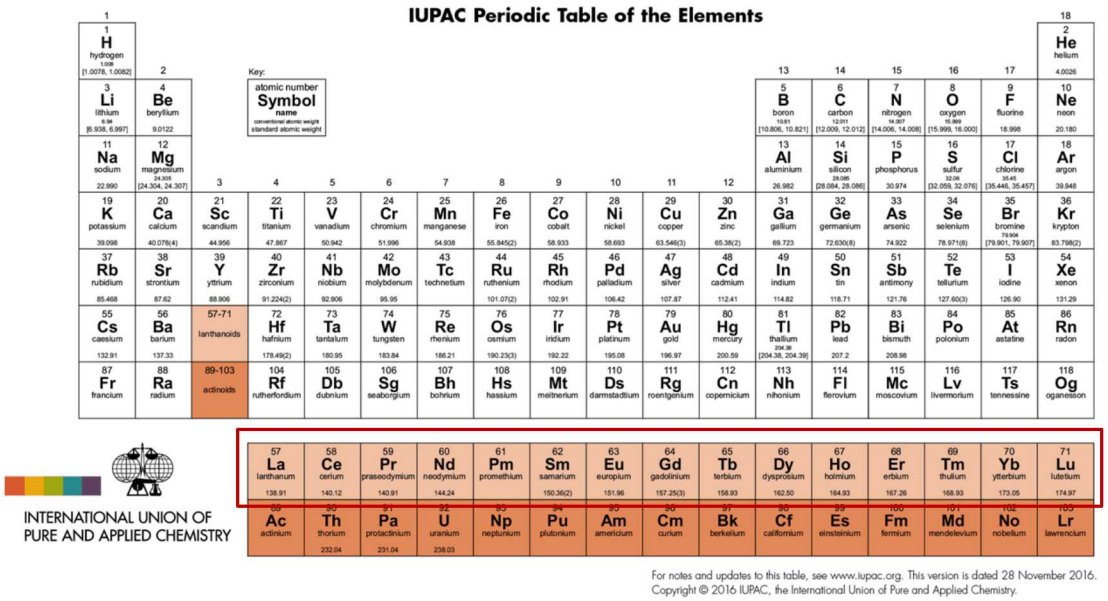
Research goal

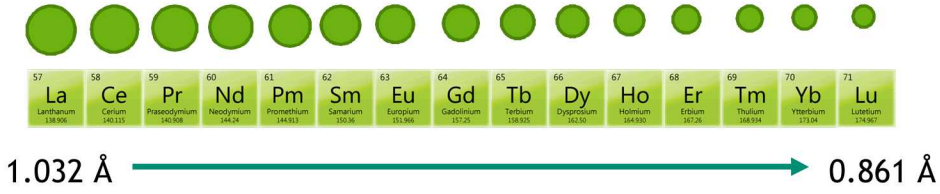
- **Quantify the impact of ionic radii and hydration energies on ion adsorption and ion coordination chemistry under nano-scale confinement.**



Zhang, et al., 2014
Inorganic Chemistry 53, 7700-770

Chemistry of lanthanides

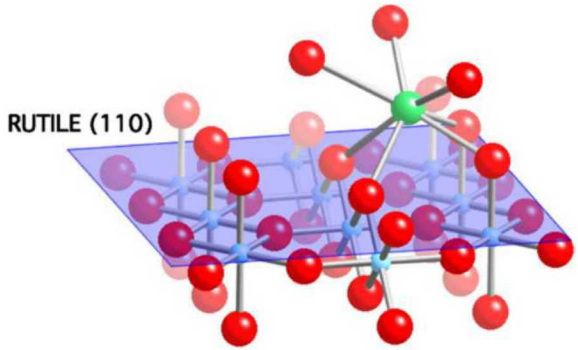




Lanthanides

- Have large and variable coordination numbers (CN)[1].
- Coordination number vary from 3 to 12, the most common CN=8[1].
- Crystal structures differ for light (Z=57-63) and heavy (Z=64-71) elements[1].

Y^{3+} adsorbed to the rutile (110) surface and forms a tetranuclear surface complex.



Approach

- Single lanthanide adsorption kinetics and isotherms.
- Mixed lanthanide system - competitive adsorption.
- XAS for assessing coordination chemistry of lanthanides.
- *Ab initio* MD for mechanistic insight.

Piasecki and Sverjensky, 20

Geochimica et Cosmochimica Acta 72, 3964-3979

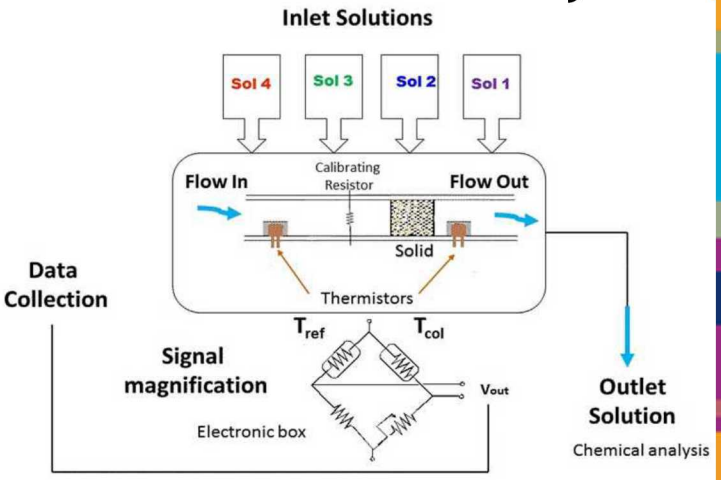
[1] Huang (2011)

Methods

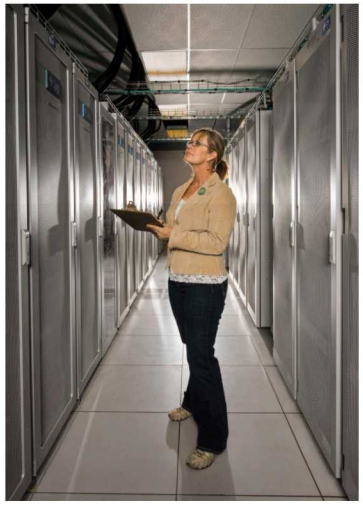
Batch experiments

ICP-MS

Flow microcalorimetry

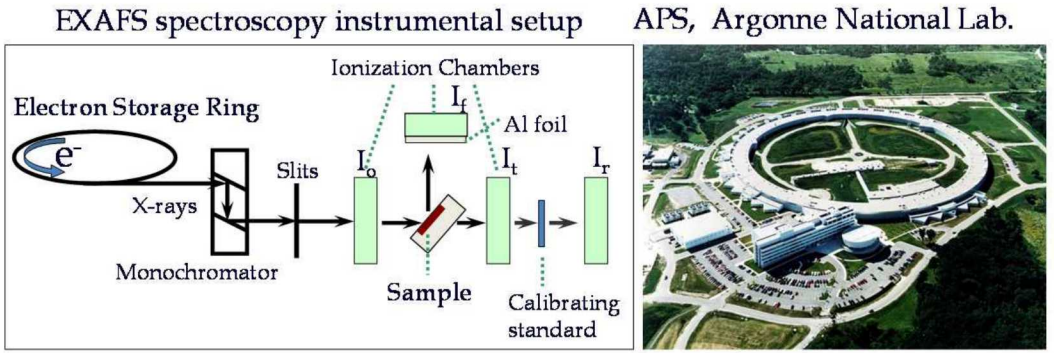


Ab initio DFT



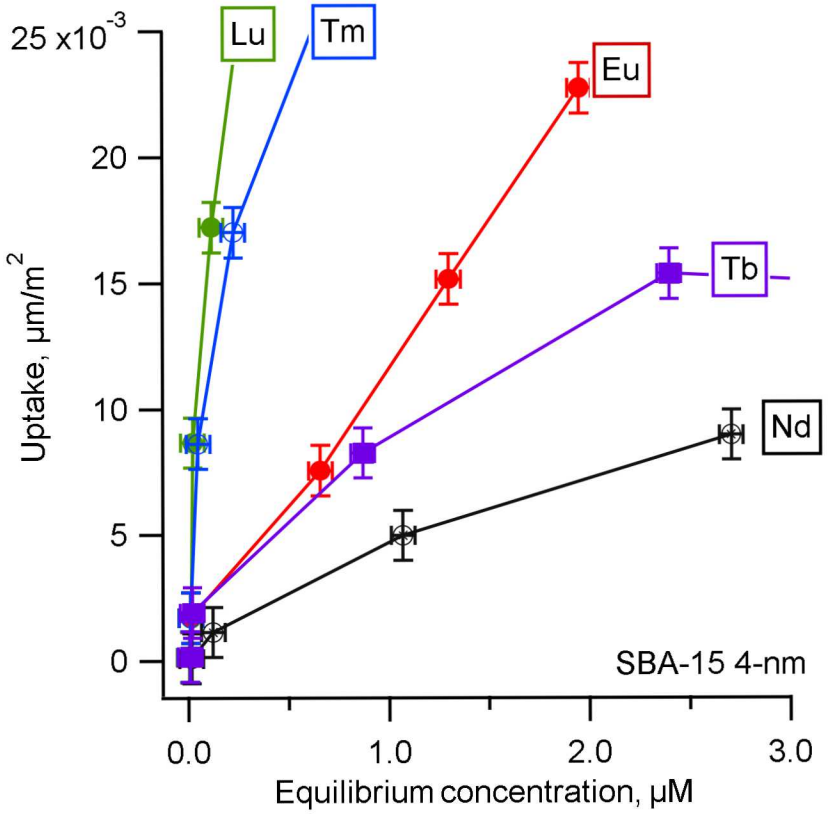
Red Sky supercomputer, www.sandia.gov

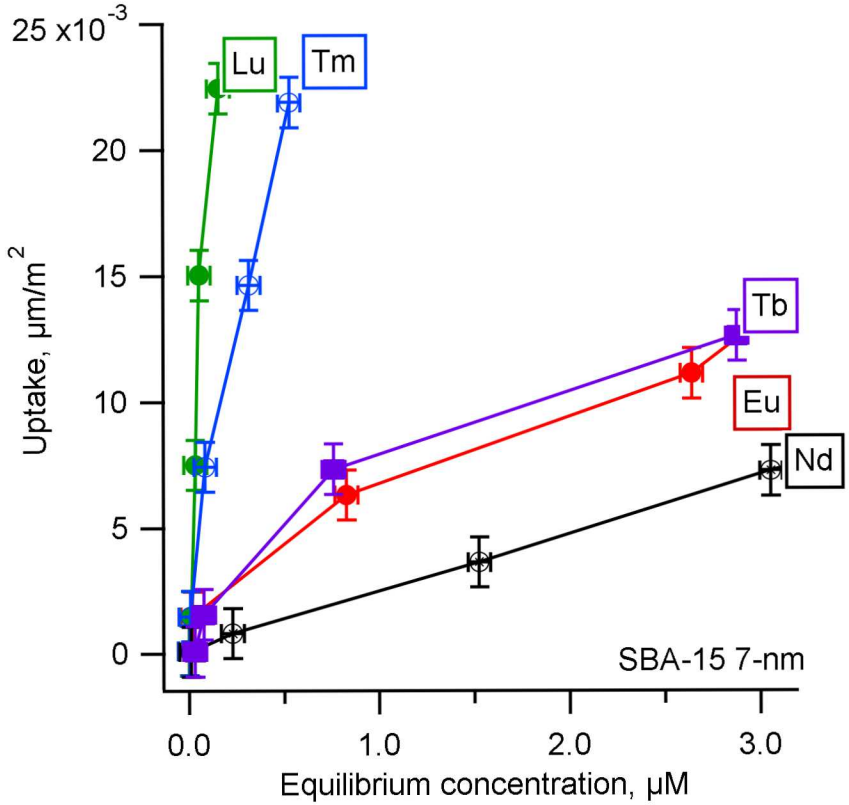
X-ray Absorption Spectroscopy (XAS)

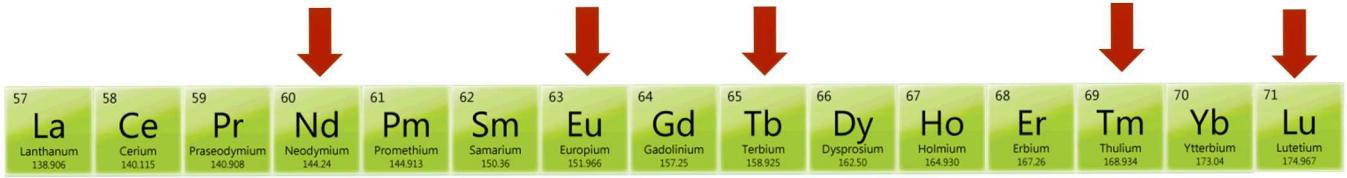


Results: adsorption isotherms

- For both SBA-15-4 nm and SBA-15-8 nm with increasing Z uptake increased.





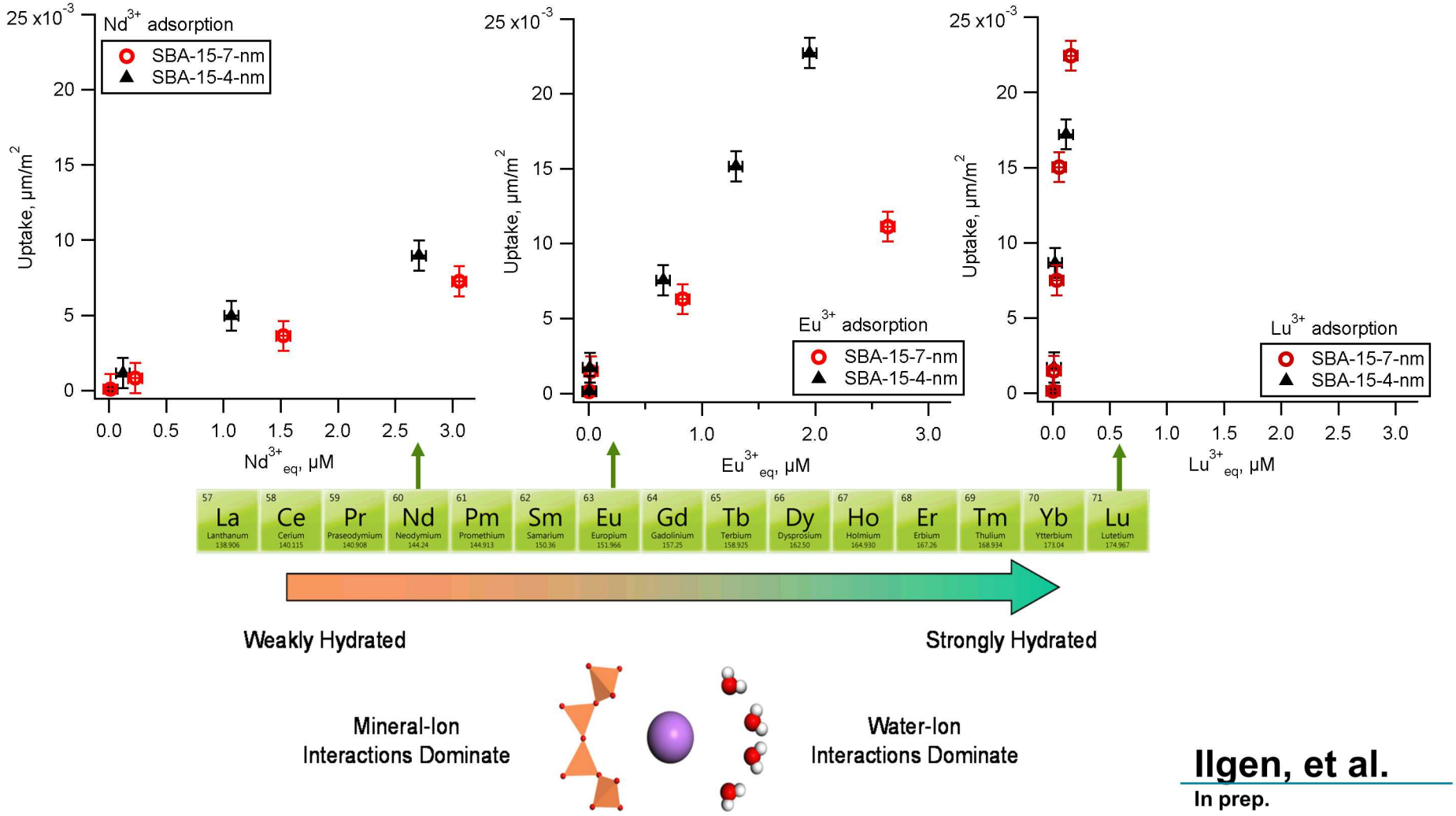


Ilgen, et al.

In prep.

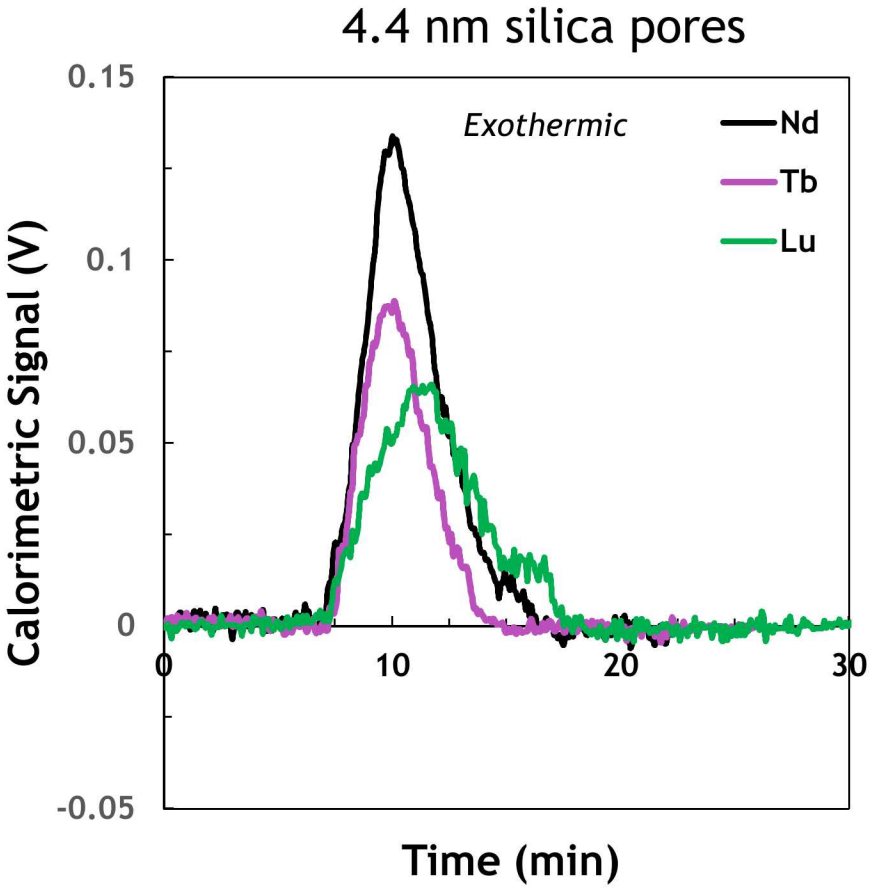
Results: Pore-size (in)dependence

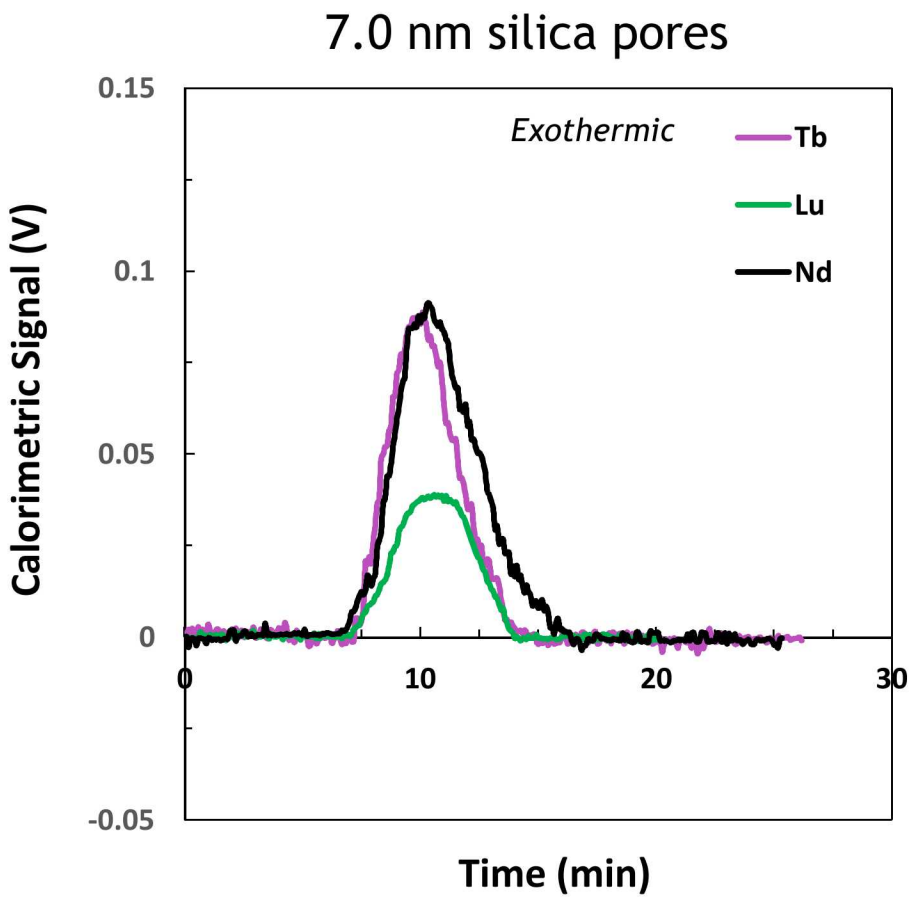
- Eu^{3+} uptake is consistent with Cu^{2+} results: higher uptake on 4nm, compared to 8nm pores.
- Tm^{3+} and Lu^{3+} uptake appears independent of pore size.



Ilgen, et al.
In prep.

Results: flow microcalorimetry

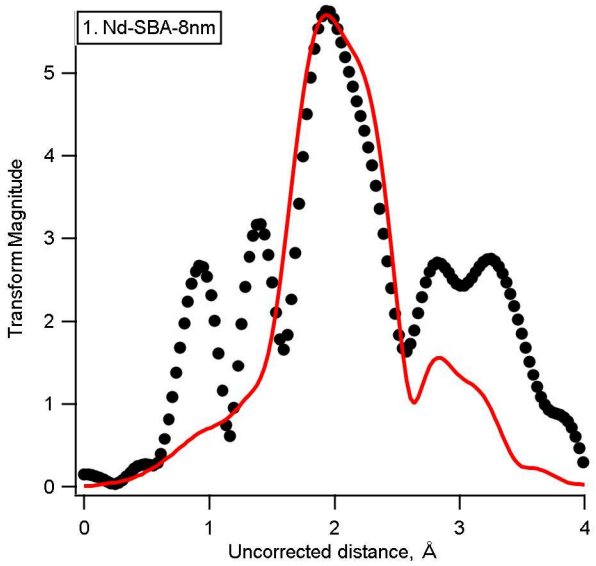


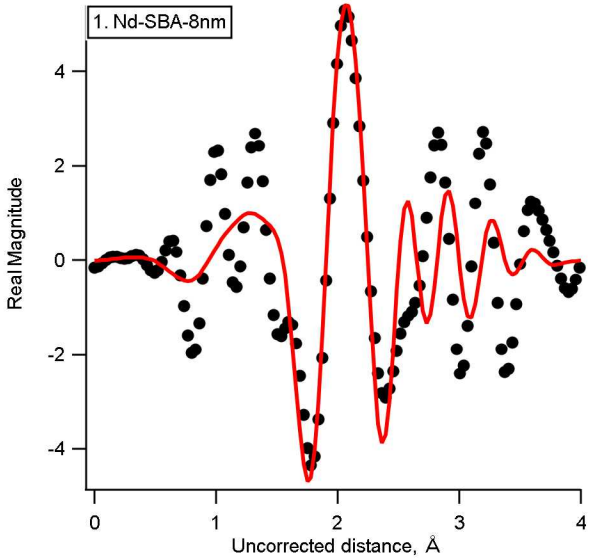


- Nd^{3+}, Tb^{3+}, and Lu^{3+} adsorption is exothermic on silica with 4nm and 7nm pores.
- Heat of adsorption depends on pore size.

			4nm Silica	8 nm Silica	Non-porous silica
	Mass (g/mol)	Radius (A°)	Heat (mJ/mg $_{solid}$)		
Lu	174.908	0.848	-0.140	-0.075	-
Tb	158.925	0.923	-0.157	-0.177	-
Nd	144.242	0.995	-0.225	-0.184	-

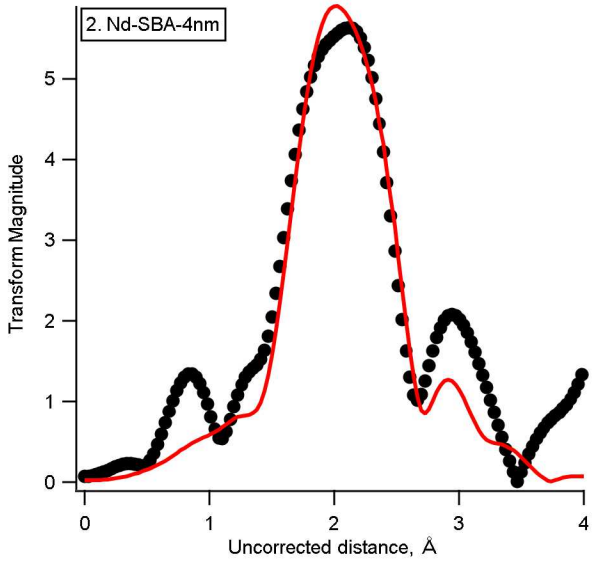
XAFS: preliminary results for neodymium

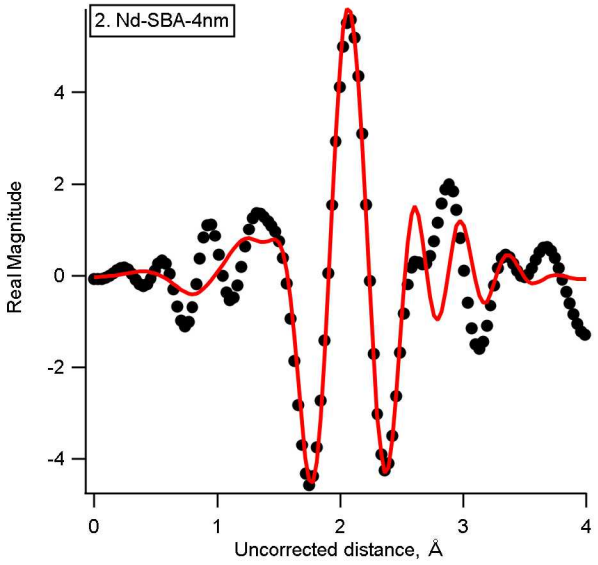




- 1st shell fit with two Nd-O distances;
- Nd–O bond length:

SiO_2 < 8nm SBA < 4nm SBA.

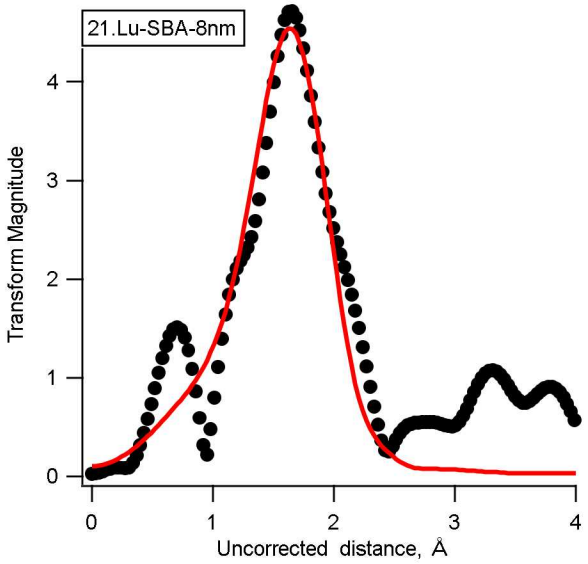


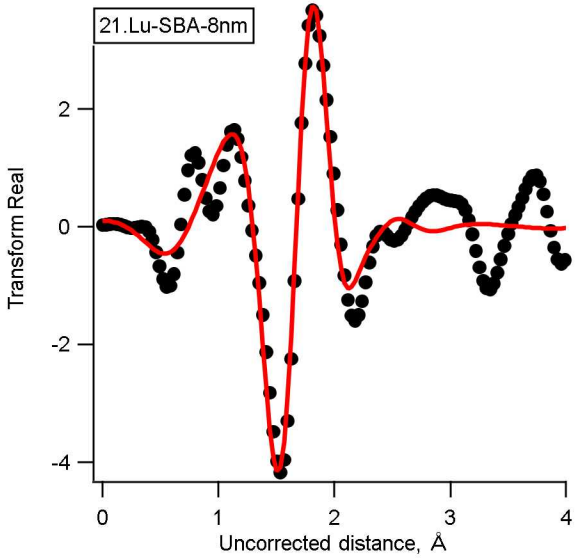


Ilgen, et al.

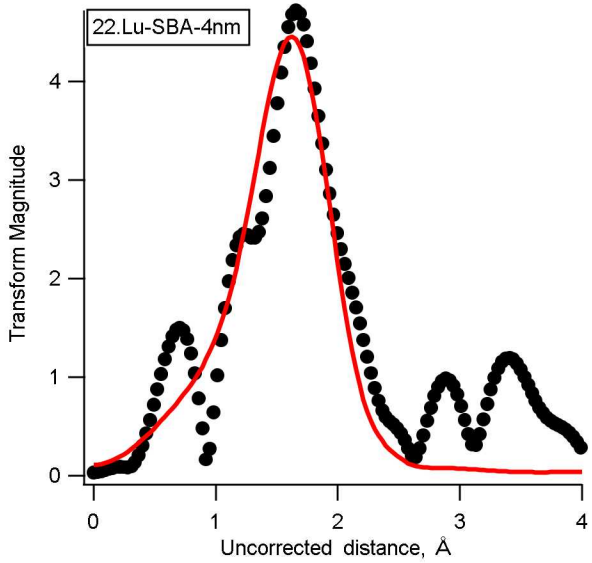
In prep.

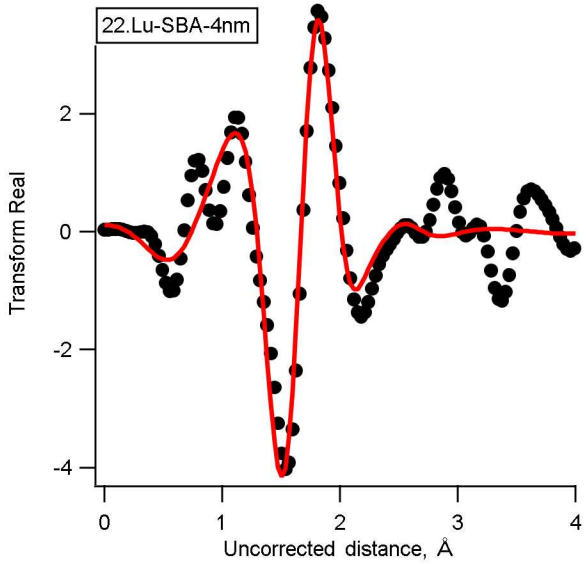
XAFS: preliminary results for lutetium





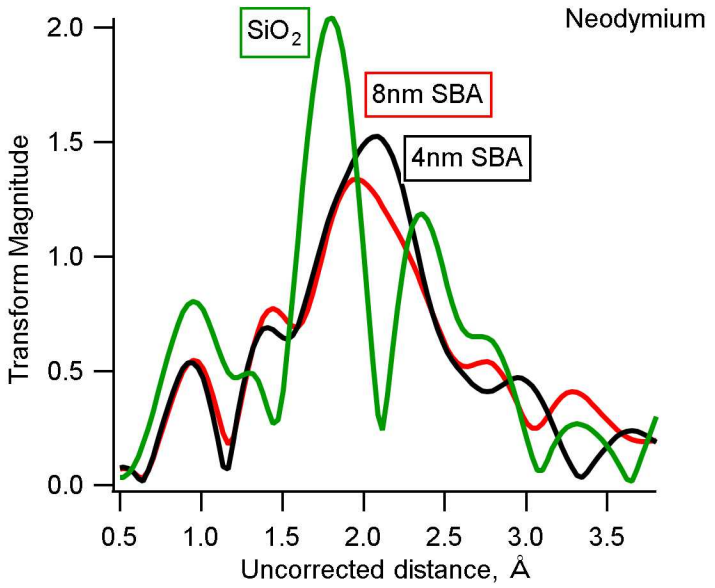
- 1st shell fit with one Lu-O distance;
- Same Lu–O bond length for non-porous SiO_2, and for SBA-15 with 4 nm and 8 nm pores.

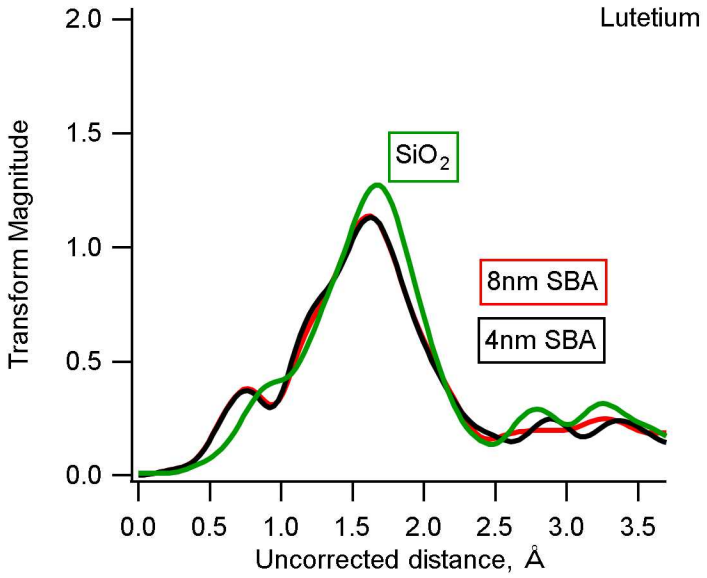


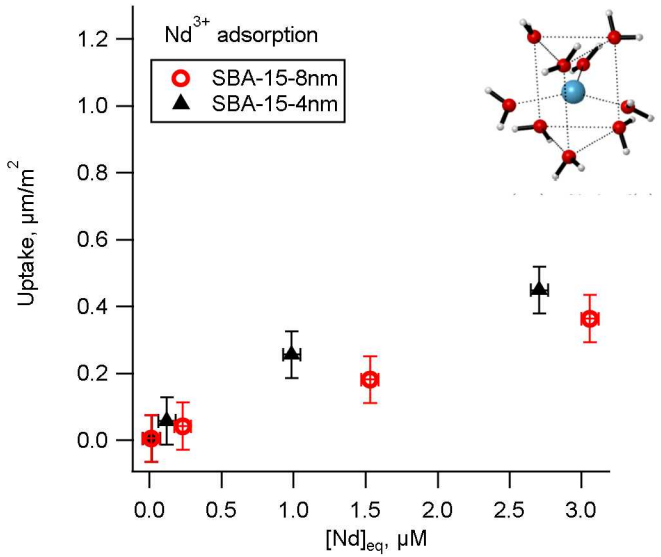


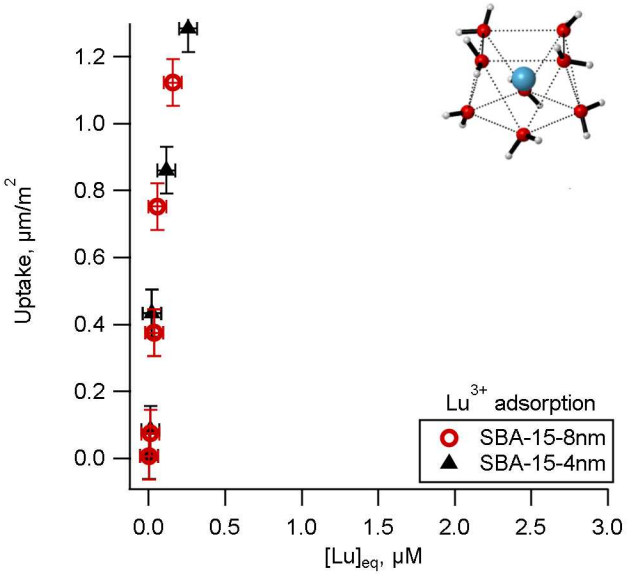
Ilgen, et al.
In prep.

XAFS: difference between Nd and Lu

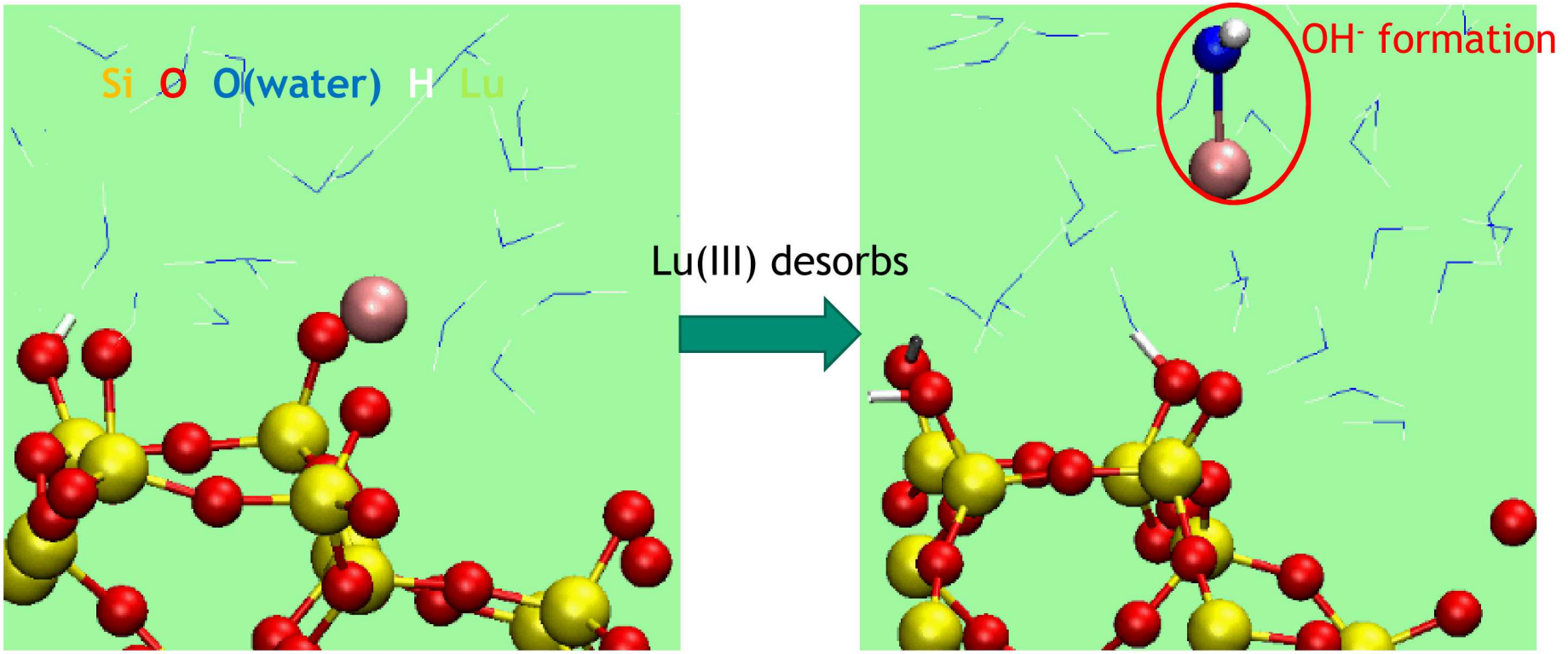








Hydrolysis of H_2O molecule by lanthanides



- *ab initio* molecular dynamics (AIMD) simulations + umbrella sampling to force desorption;
- Lu(III) and Eu(III) desorption causes $H_2O + SiO^- \rightarrow OH^- + SiOH$;
- Inner-sphere adsorption is observed, with each lanthanide hydrolyzing one water molecule upon adsorption onto cristobalite surface.

Leung, et al.
In prep.

Summary

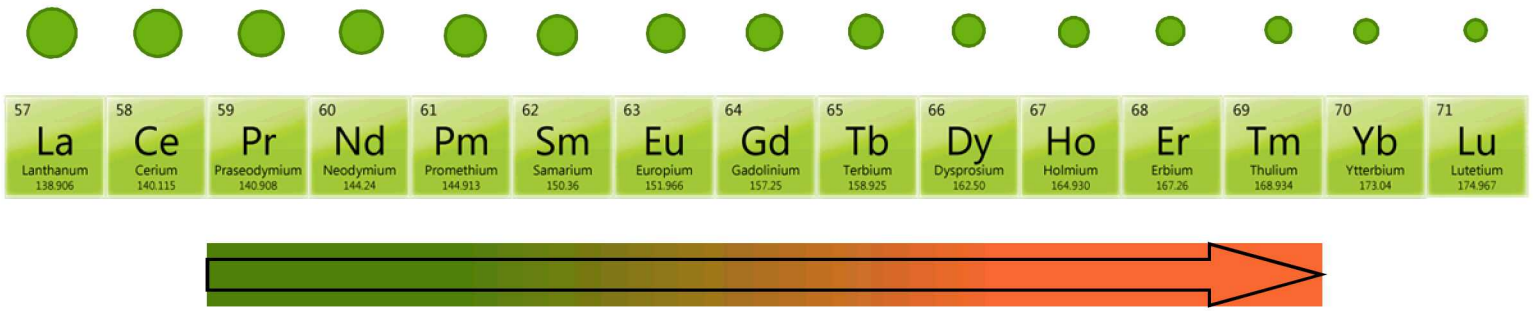
Adsorption of lanthanides onto spatially-confined surfaces

- Mass-dependent adsorption: with decreasing ionic radii, increased uptake.
- Pore-size dependency:

Cu^{2+} ΔG_H	Nd^{3+} ΔG_H	Tm^{3+} ΔG_H	Lu^{3+} ΔG_H
-2130 kJ/mol	-3278 kJ/mol	-3509 kJ/mol	-3556 kJ/mol

- Macroscopically, for heavier elements (Lu^{3+} and Tm^{3+}) uptake is independent of pore size, for lighter lanthanides SBA with 4 nm pores has higher uptake.
- XAS data supports macroscopic trends: differences in the local coordination environment for lighter lanthanides, and no differences for heavier lanthanides.

Size decreases across the series

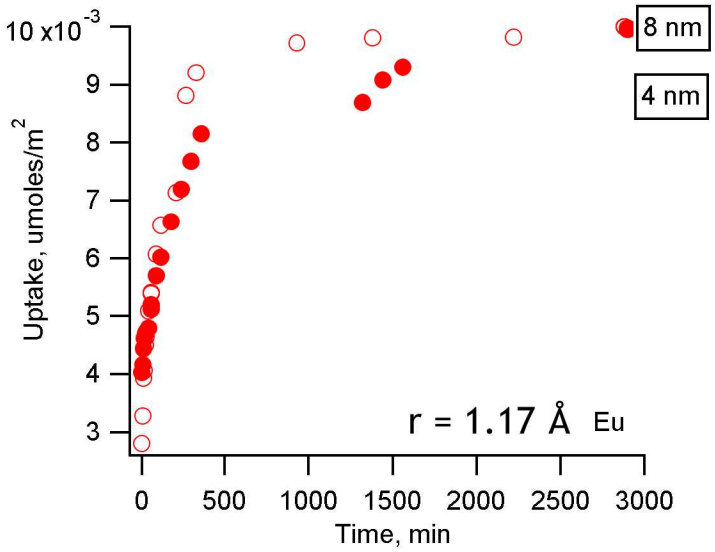


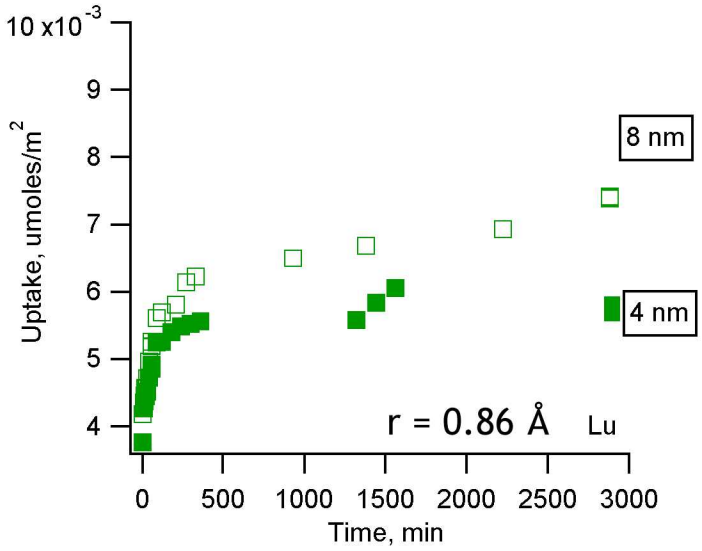
Lowest hydration energy — Highest hydration energy

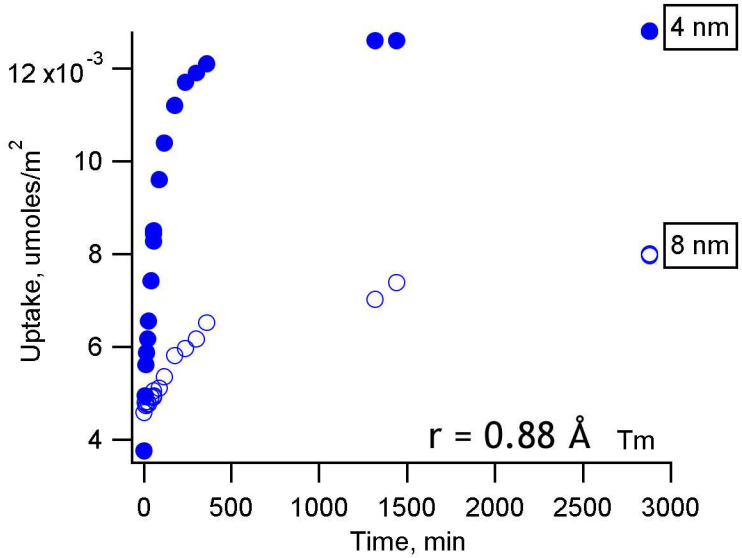
Thank you.

Extra slides

Results: Kinetics of adsorption



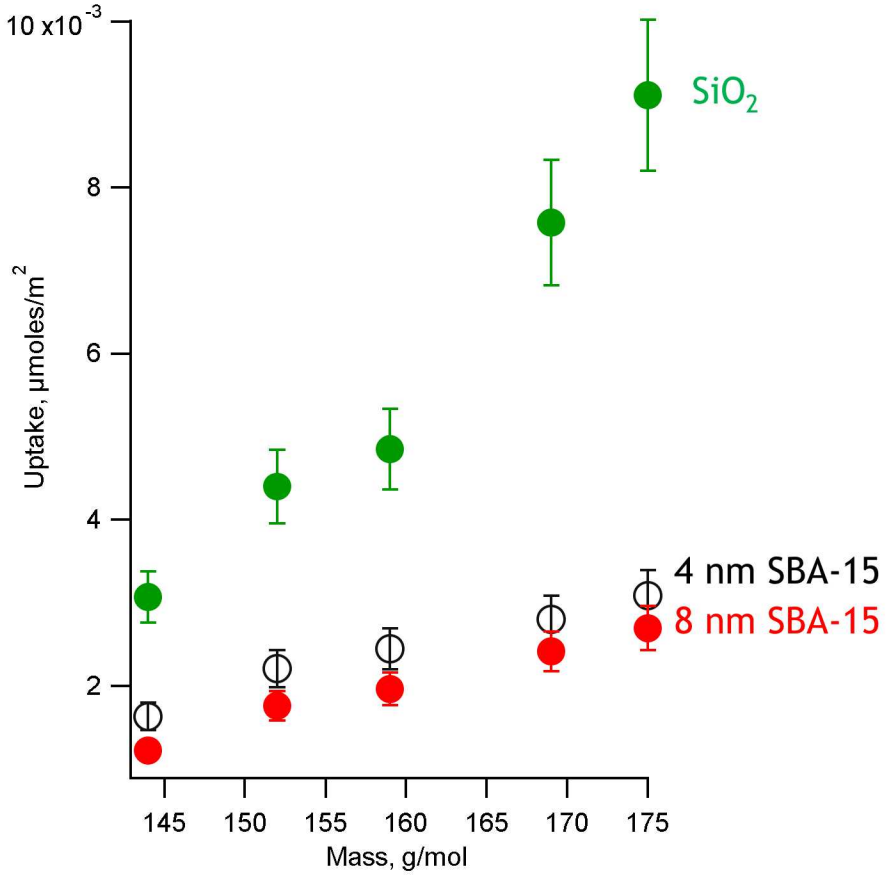


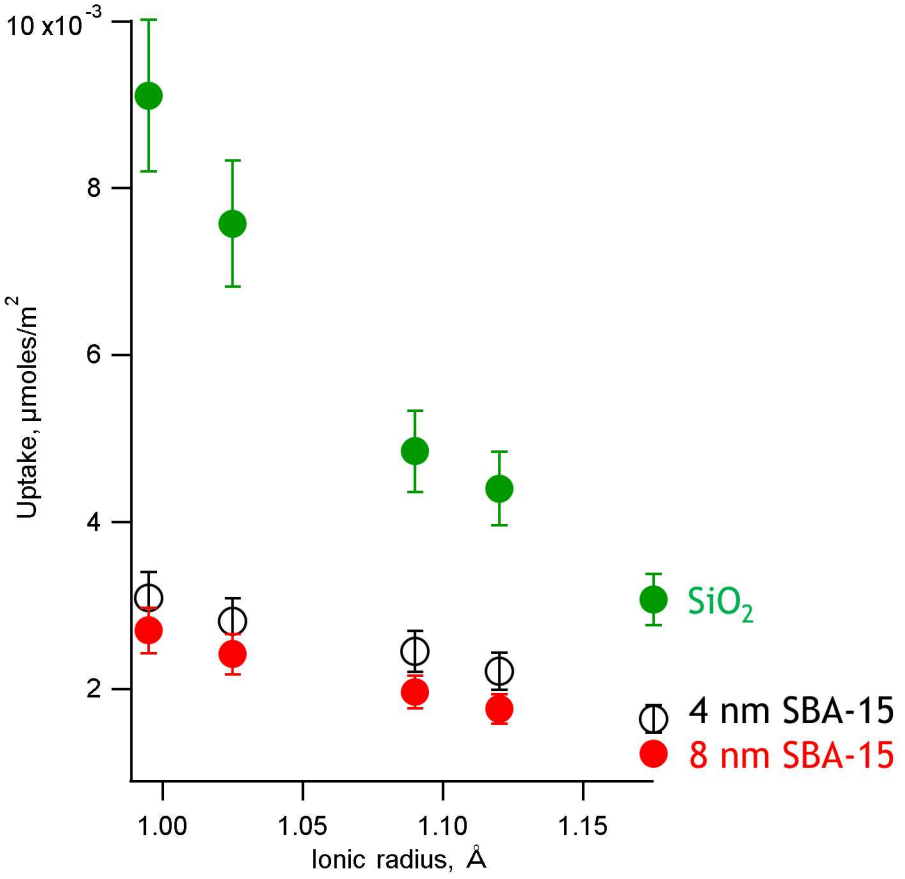


Preliminary results

- 2nd order reaction.
- For Eu^{3+} and Lu^{3+}, on 8 nm pores adsorption is slightly more favorable and faster.
- For Tm^{3+} the trend is the same as for Cu^{2+}: faster and more favorable adsorption onto 4 nm, compared to 8 nm pores.

Results: Competitive adsorption





- Increased uptake with increasing Z and decreasing ionic radii.
- Higher uptake on 4 nm- vs 8 nm-silica, but below non-porous SiO_2.