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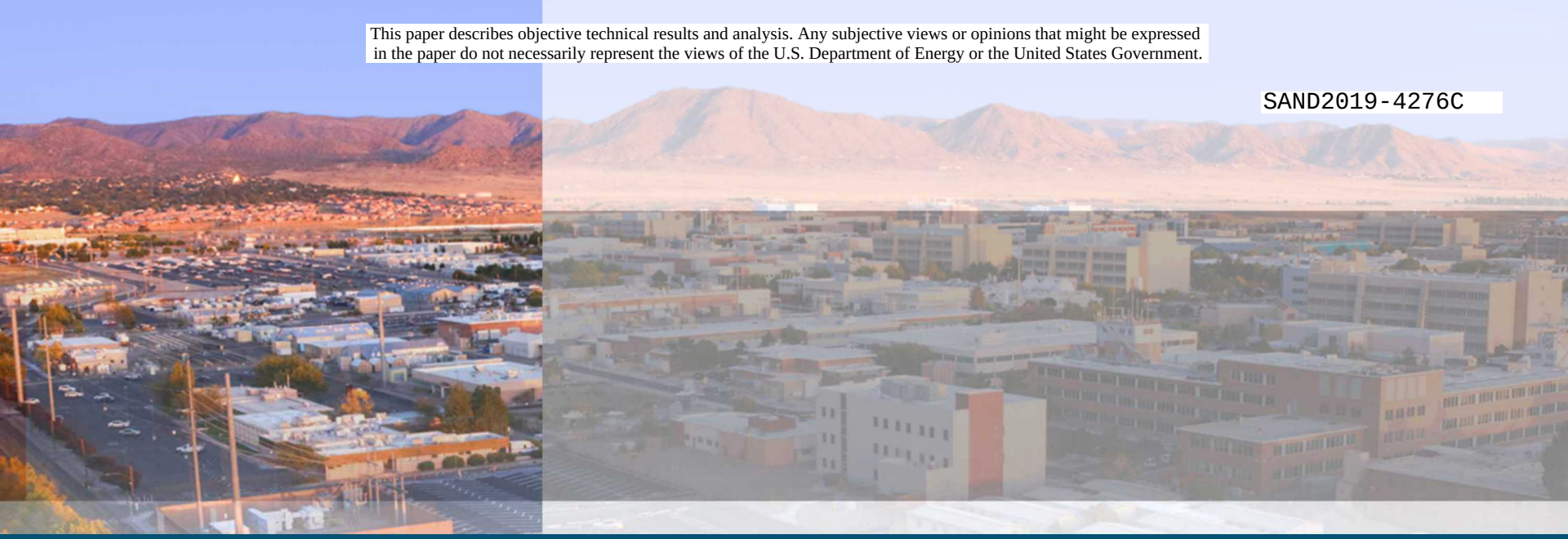

Using lanthanides to probe the interfacial chemistry of nano-scale pores

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Sandia National Laboratories

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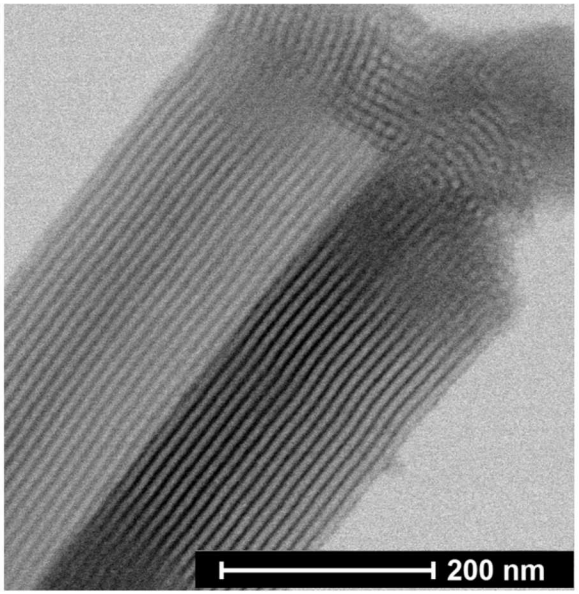
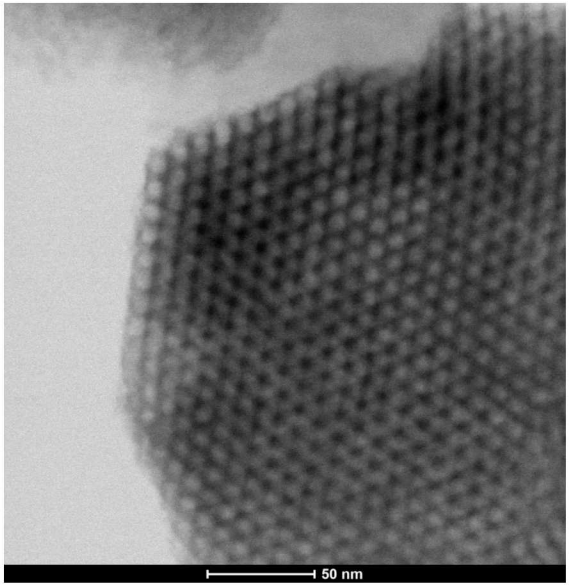
Interfacial chemistry under nano-scale confinement

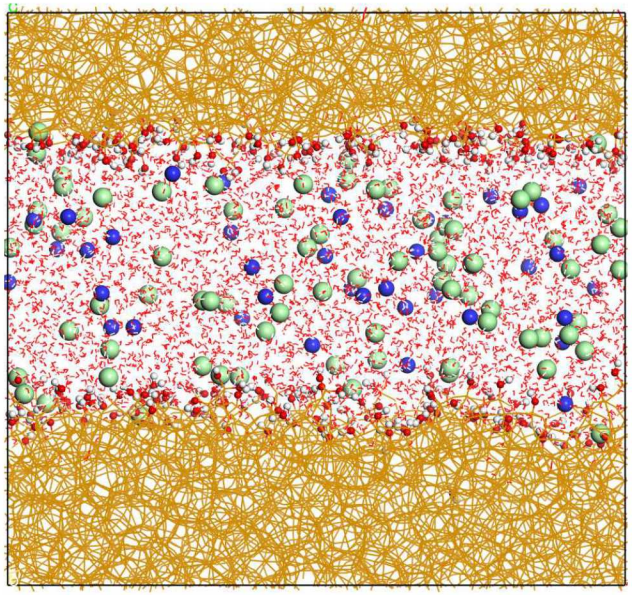
Emergent chemical behavior due to nano-scale confinement:

- **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

Cu^{2+} adsorption isotherms

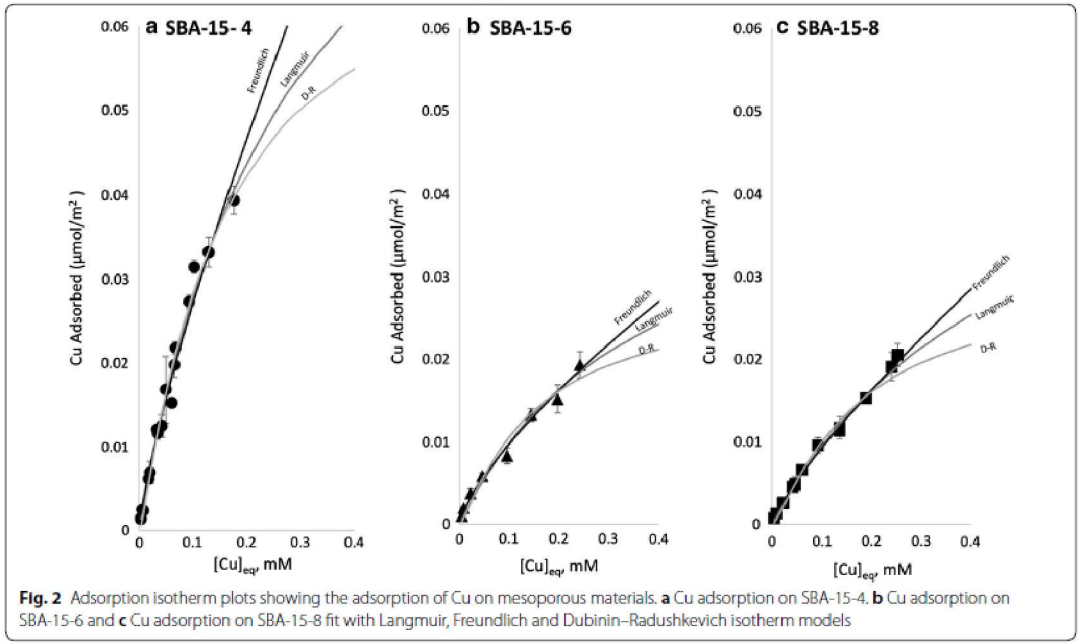


Fig. 2 Adsorption isotherm plots showing the adsorption of Cu on mesoporous materials. **a** Cu adsorption on SBA-15-4. **b** Cu adsorption on SBA-15-6 and **c** Cu adsorption on SBA-15-8 fit with Langmuir, Freundlich and Dubinin–Radushkevich isotherm models

Cu^{2+} adsorption kinetics

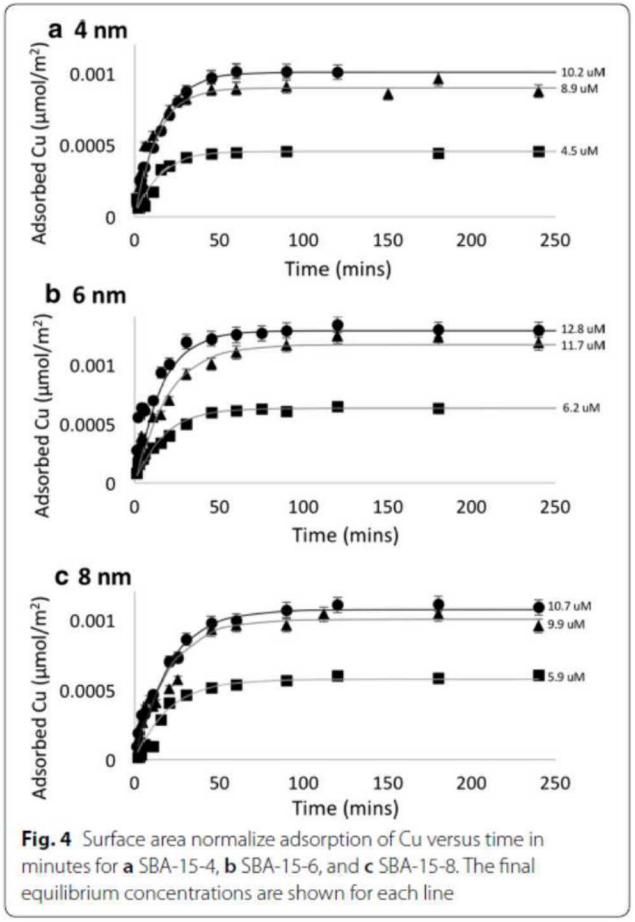


Fig. 4 Surface area normalize adsorption of Cu versus time in minutes for **a** SBA-15-4, **b** SBA-15-6, and **c** SBA-15-8. The final equilibrium concentrations are shown for each line

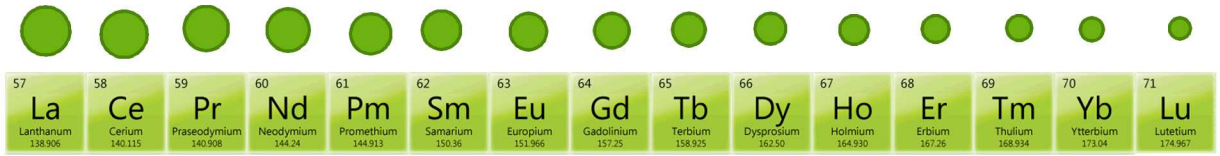
- Nano-scale confinement enhances both the adsorption maximum, and Cu^{2+} adsorption reaction rate.
- The pseudo-first-order reaction rate constant increased with decreasing pore size.
- External mass transfer diffusion constant increases with decreasing pore size: this rapid film diffusion in 4 nm pores is responsible for the observed increase in adsorption rate.

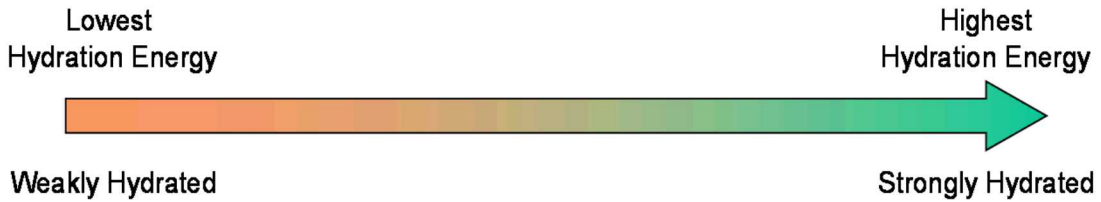
Knight, et al., 2018
Geochemical Transactions 19, 13-26

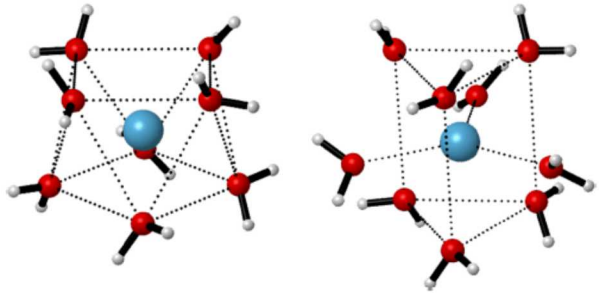
Research Goals

Chemistry under Nano-scale Confinement

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





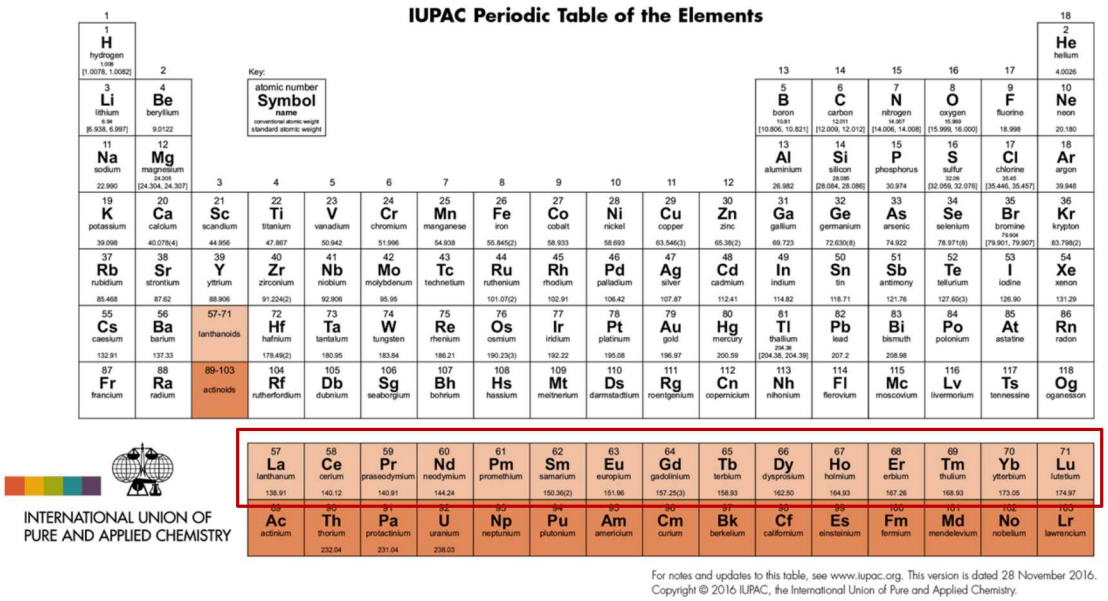


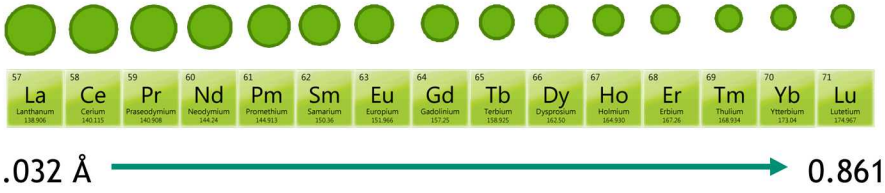
Research goal

- 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

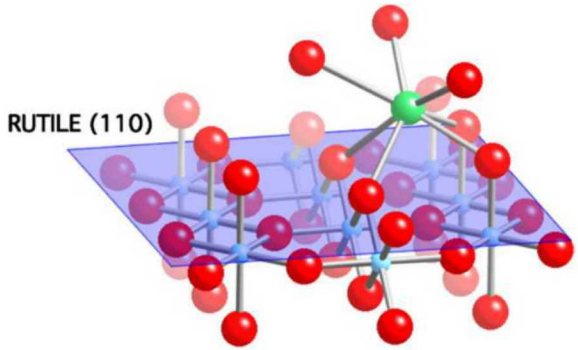




Lanthanides

- 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.



Piasecki and Sverjensky, 20

Geochimica et Cosmochimica Acta 72, 3964-3979

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.

[1] Huang (2011)

Methods

Batch experiments

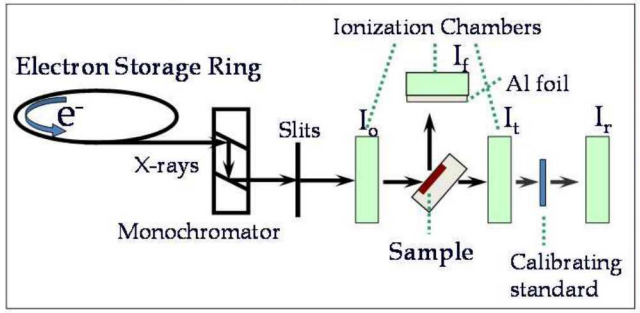
ICP-MS

Ab initio DFT

Red Sky supercomputer, www.sandia.gov

X-ray Absorption Spectroscopy (XAS)

EXAFS spectroscopy instrumental setup

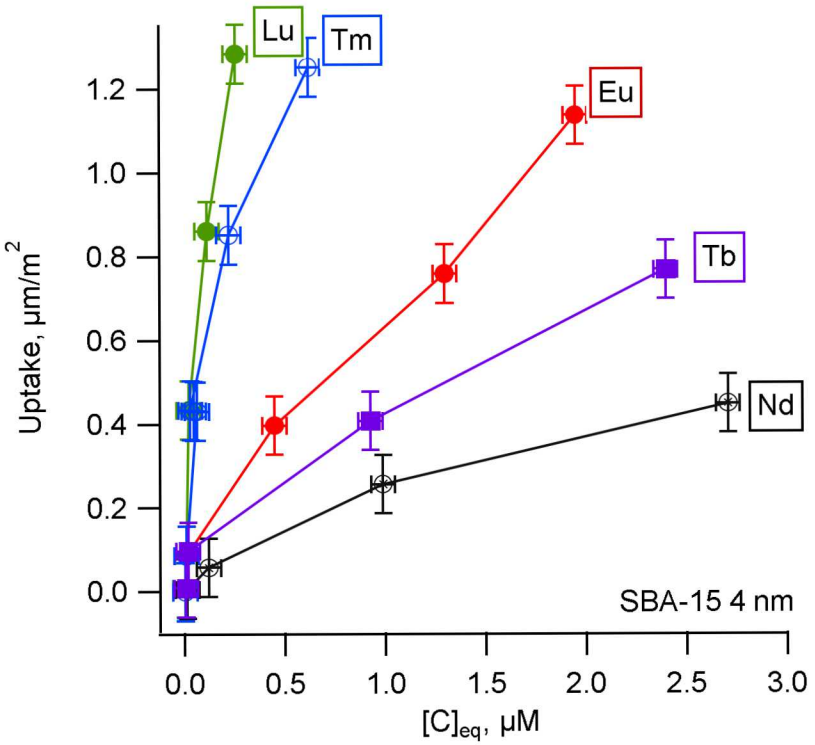


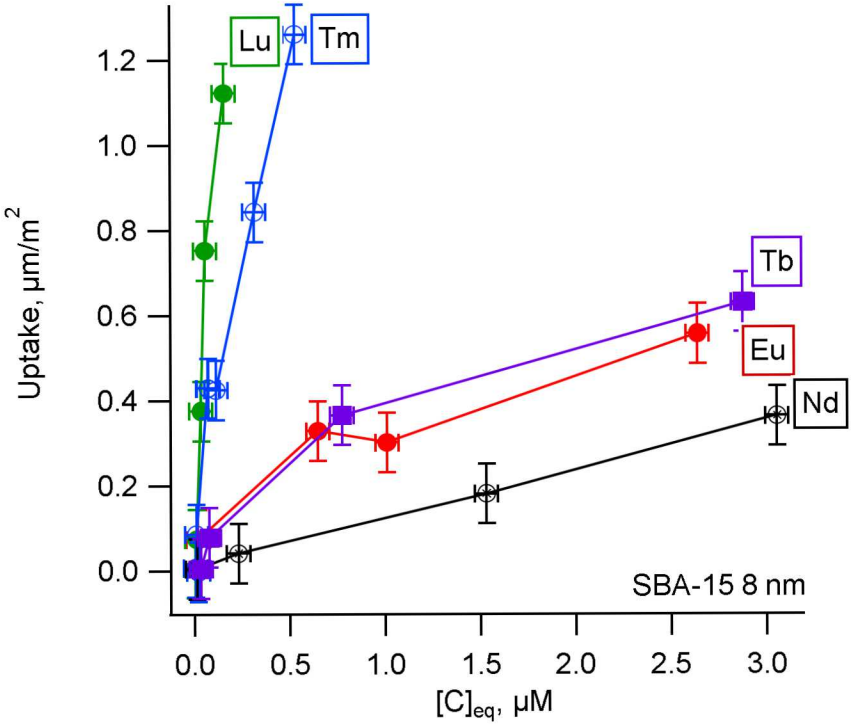
APS, Argonne National Lab.

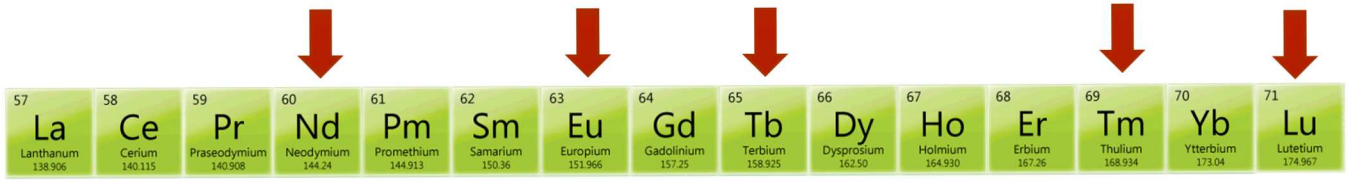
GWB

Results: adsorption isotherms

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



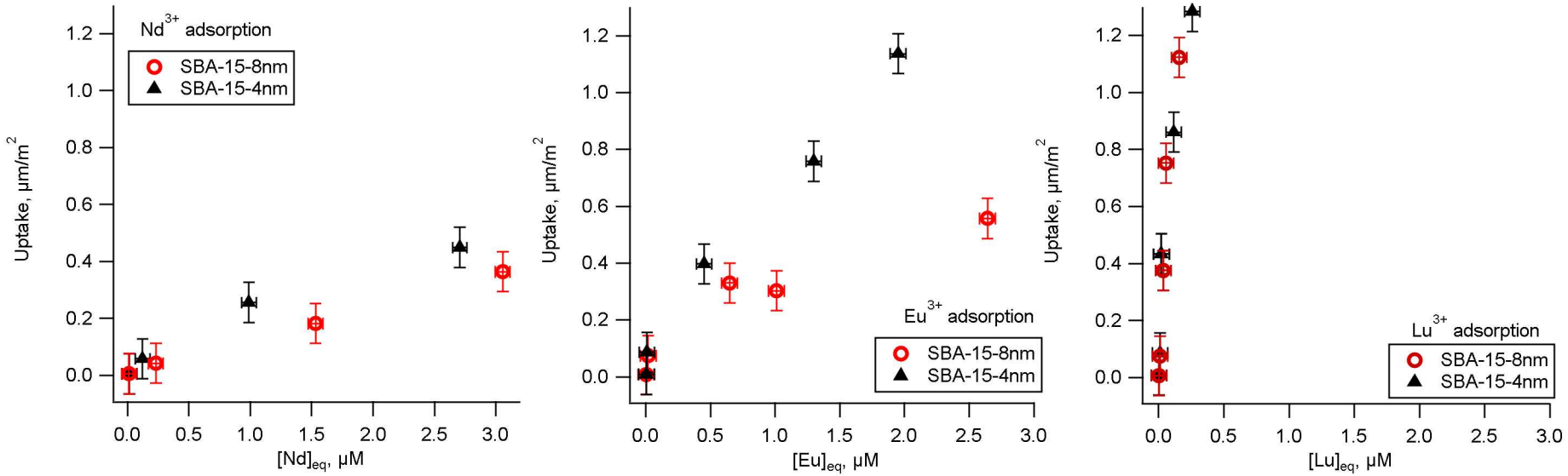


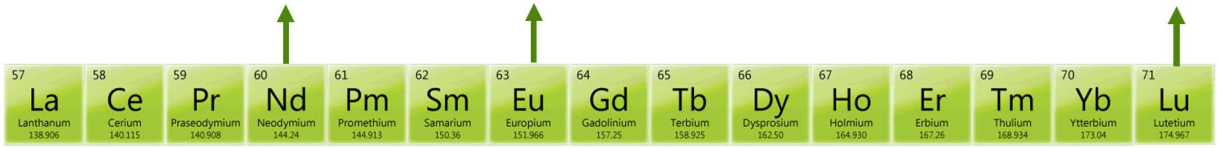


Ilgen, et al.
In prep.

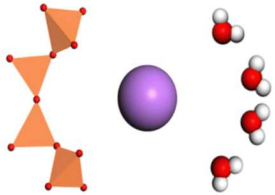
Results: Pore-size (in)dependence

- 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.





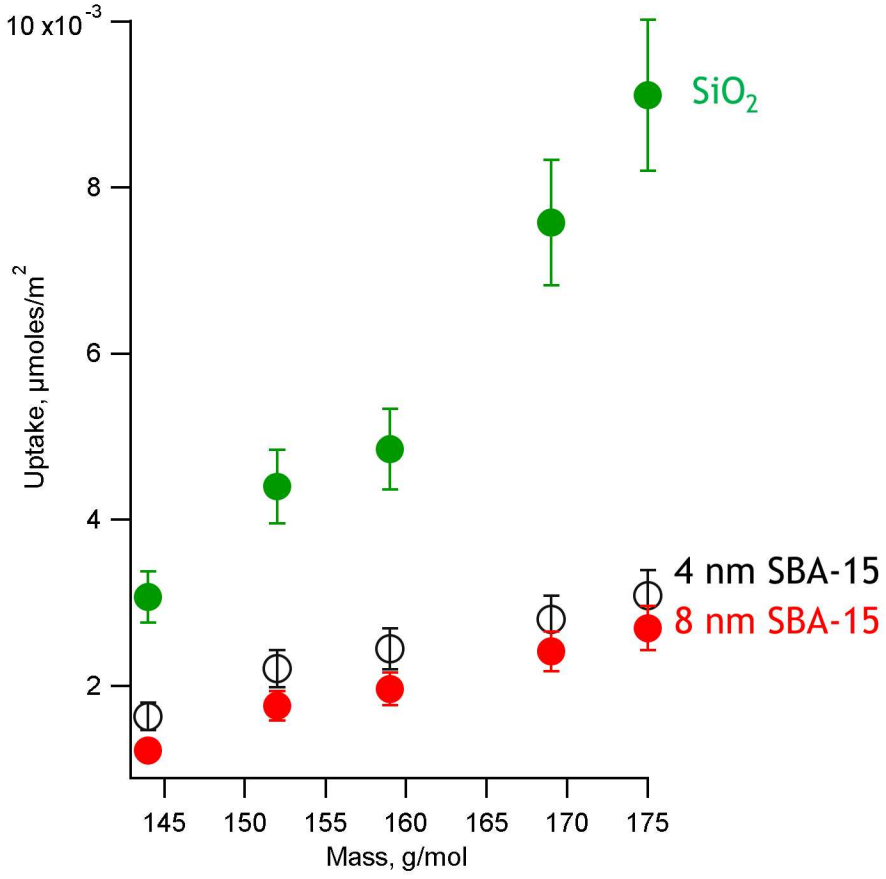
Weakly Hydrated — Strongly Hydrated

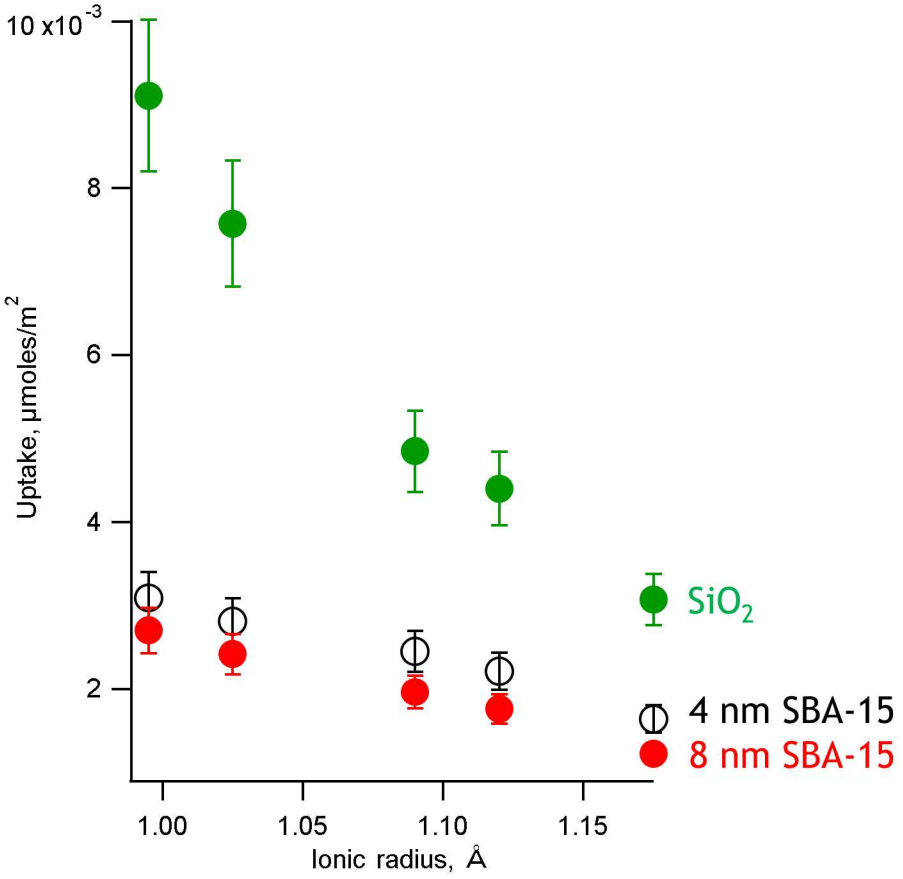


Mineral-Ion Interactions Dominate

Water-Ion Interactions Dominate

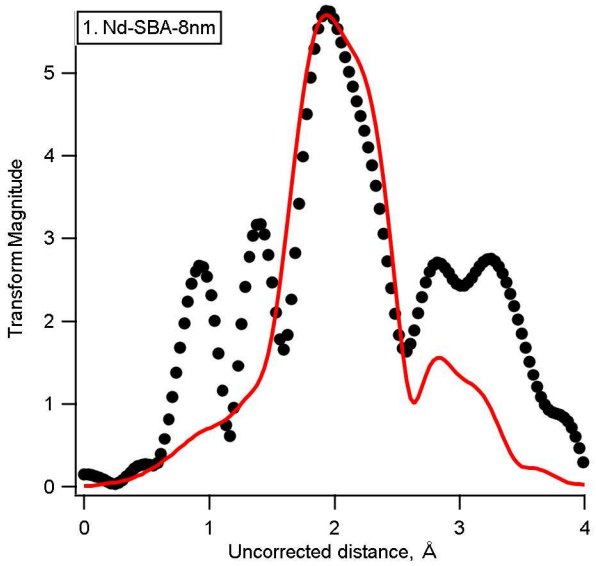
Results: Competitive adsorption

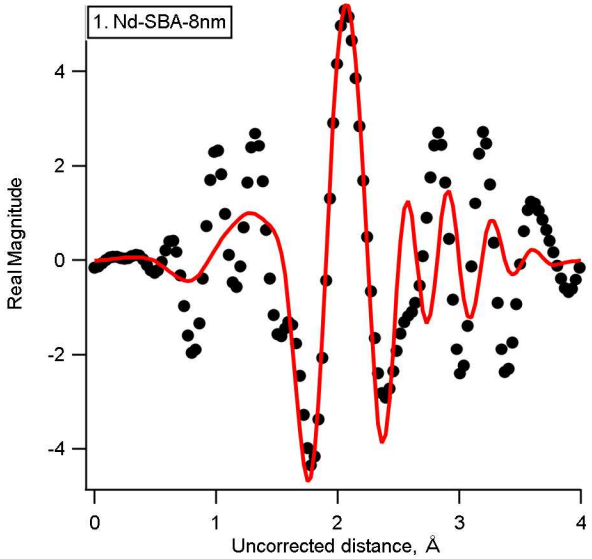




- Increased uptake with increasing Z and decreasing ionic radii.
- Higher uptake on 4 nm- vs 8 nm-silica, but below non-porous SiO_2.

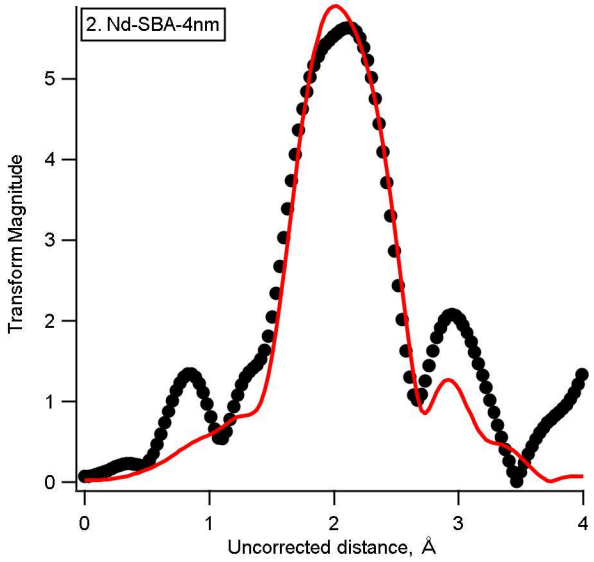
XAFS: preliminary results for neodymium

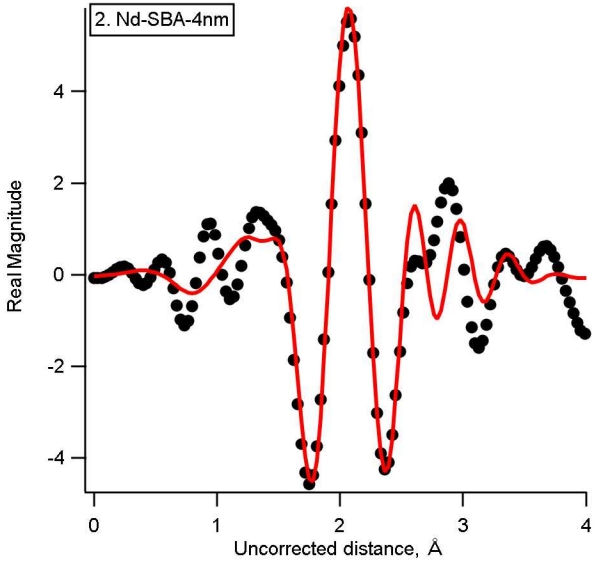




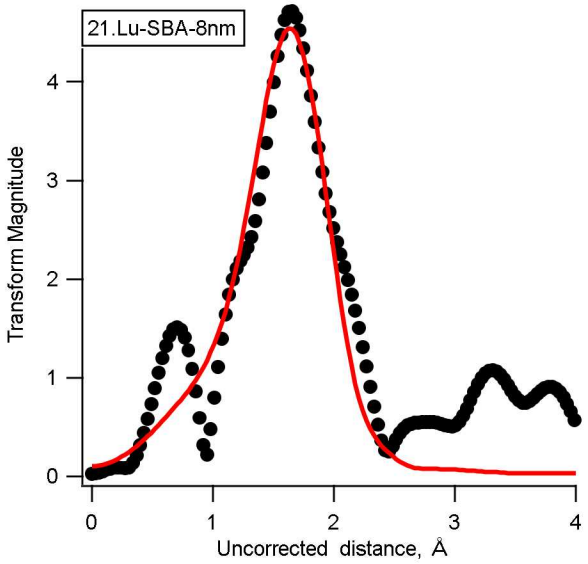
- 1st shell fit with two Nd-O distances;
- Nd–O bond length:

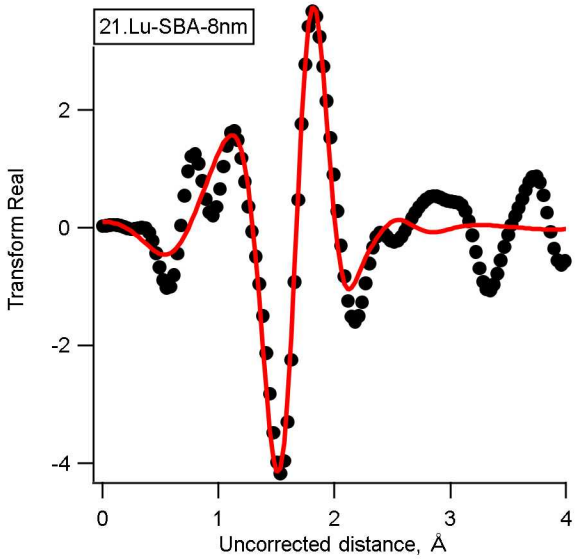
SiO_2 < 8nm SBA < 4nm SBA.



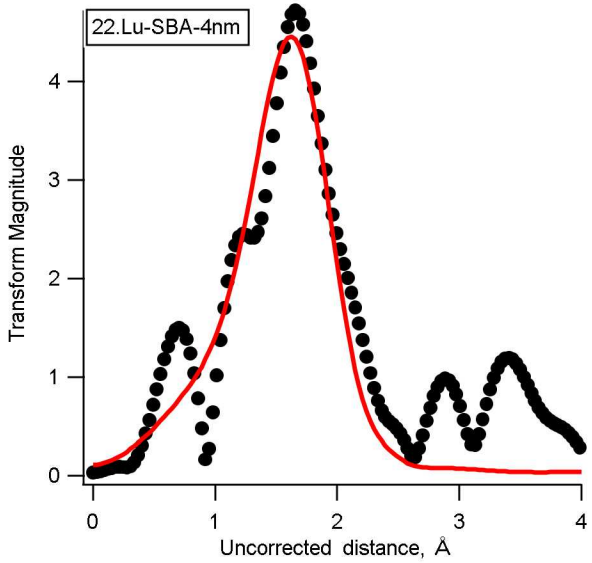


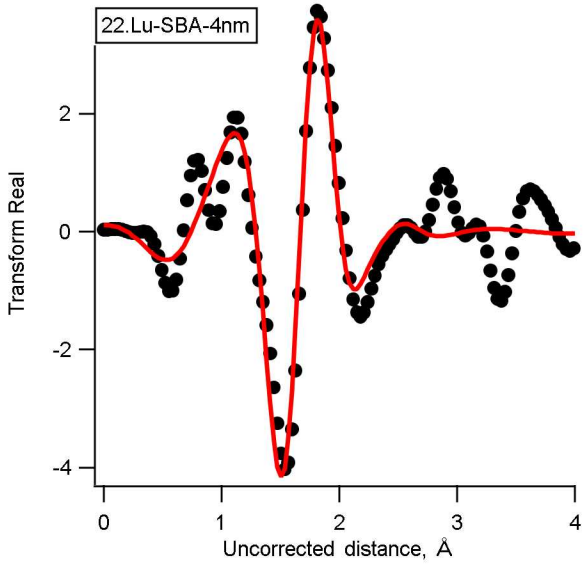
XAFS: preliminary results for lutetium



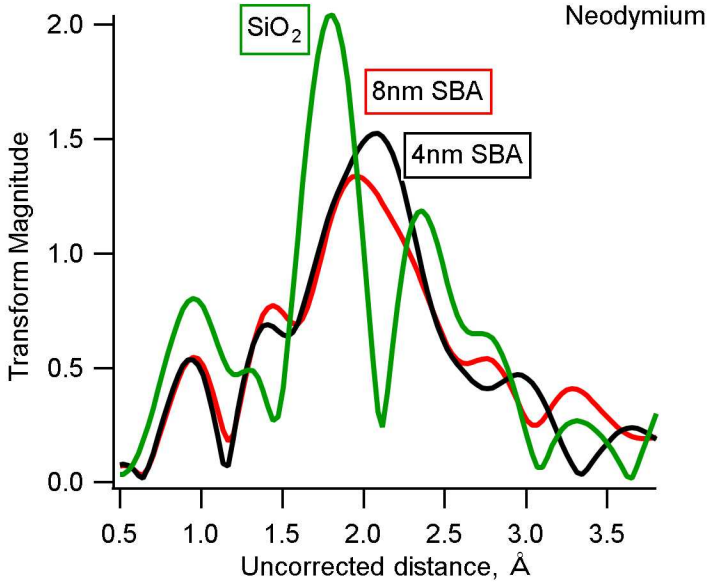


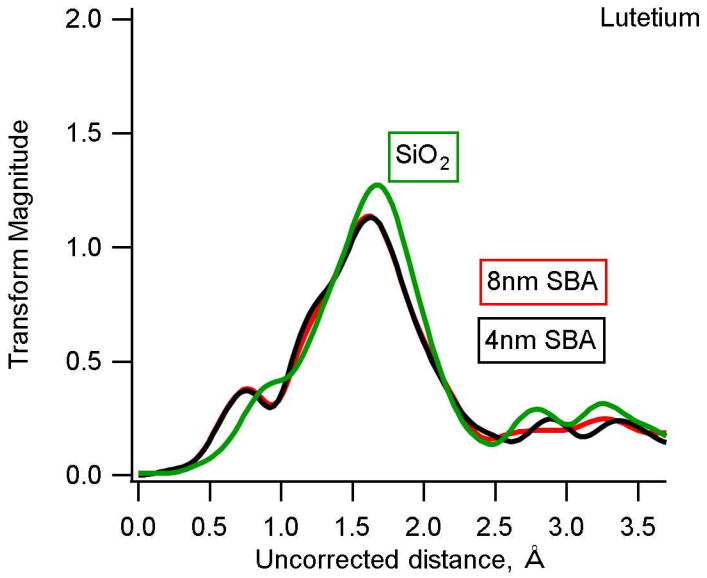
- 1st shell fit with one Lu-O distance;
- Same Lu–O bond length for non-porous SiO_2, and for SBA-15 with 4 nm and 8 nm pores.

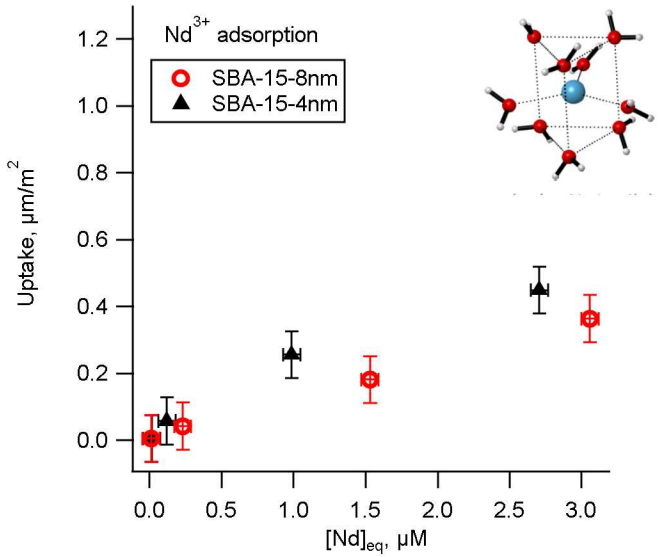


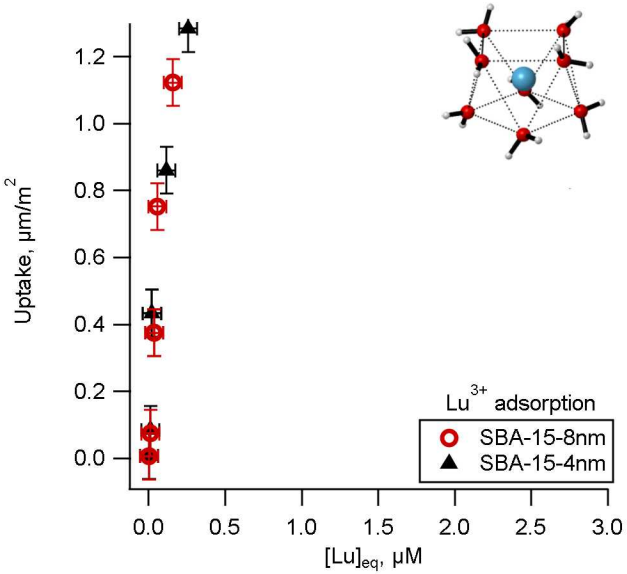


XAFS: difference between Nd and Lu

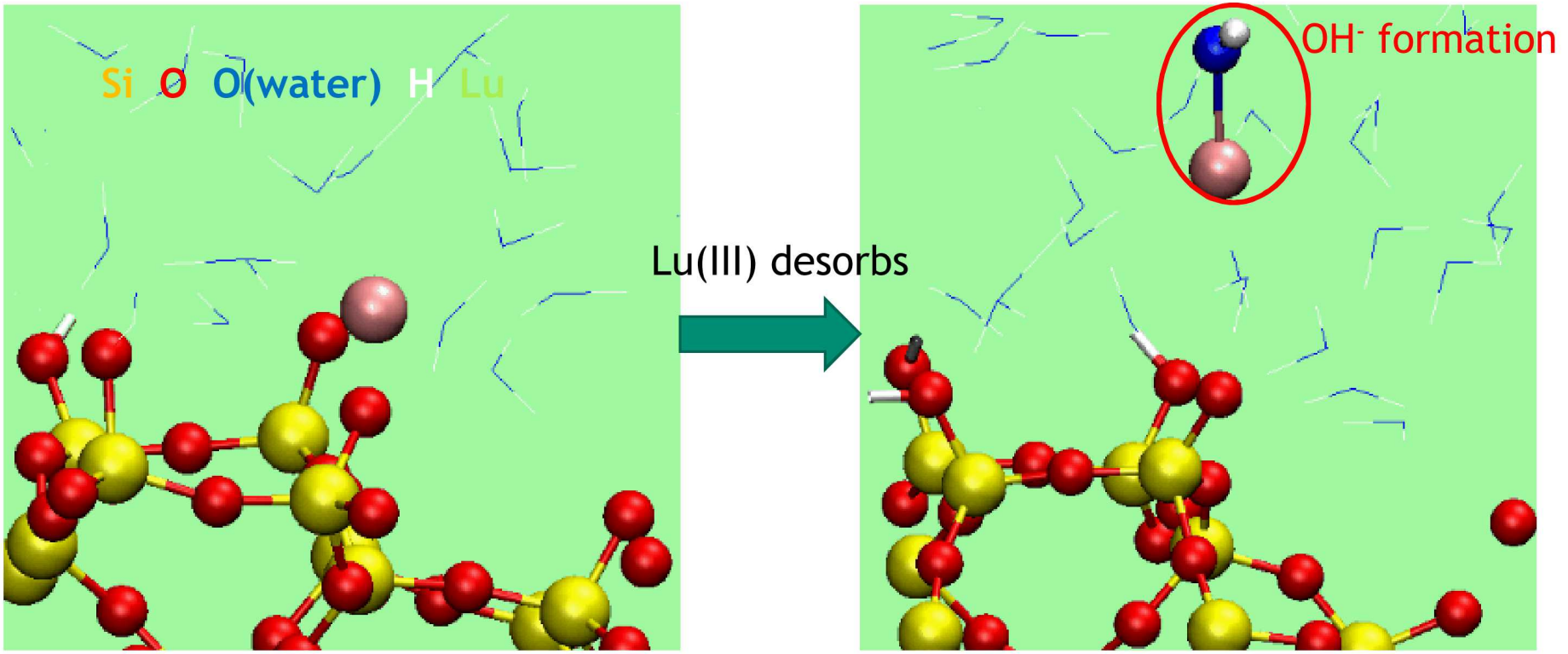








Hydrolysis of H_2O molecule as Lu(III) desorbs from silica surface



- *ab initio* molecular dynamics (AIMD) simulations + umbrella sampling to force desorption;
- Lu(III) desorption causes $H_2O + SiO^- \rightarrow OH^- + SiOH$;
- Previous AIMD simulations of this silica model predict pKa = 7 – 8.1;
- Combined with thermodynamic data Lu(IIII) hydrolysis of water is reasonable; need to check whether there are any system size effects;
- So far Eu(III) not observed to cause hydrolysis, but simulations at early stage.

Summary and future work

Adsorption of lanthanides onto 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.

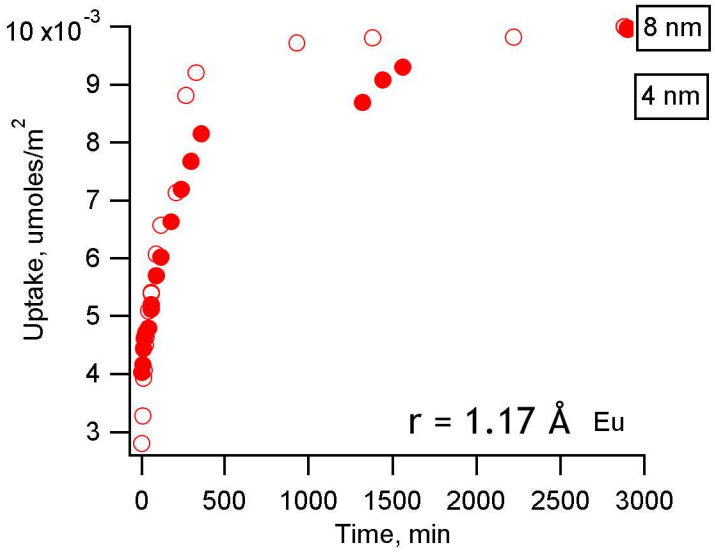
Work in progress

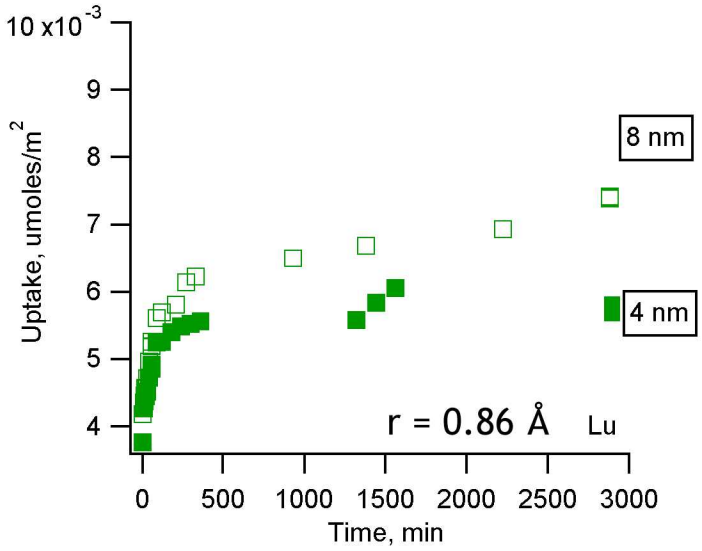
- Fitting XAS data.
- Examine other substrates, e.g. controlled-pore glass.
- Finalize *ab initio* models.

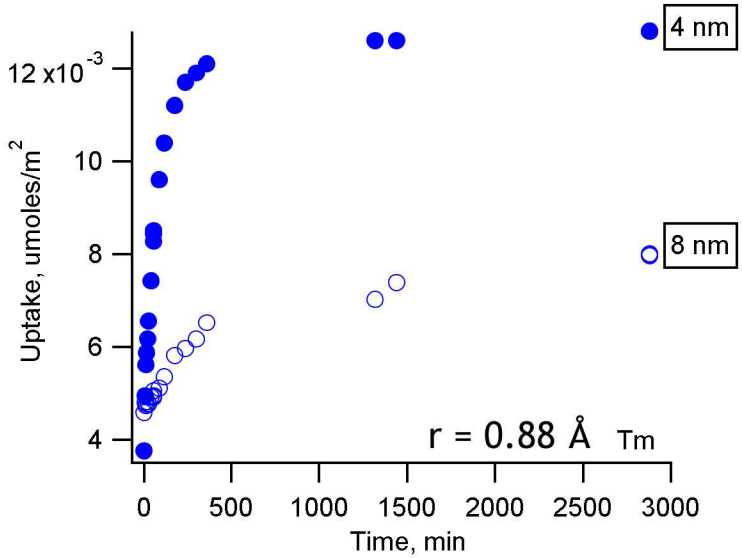
Thank you.

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.