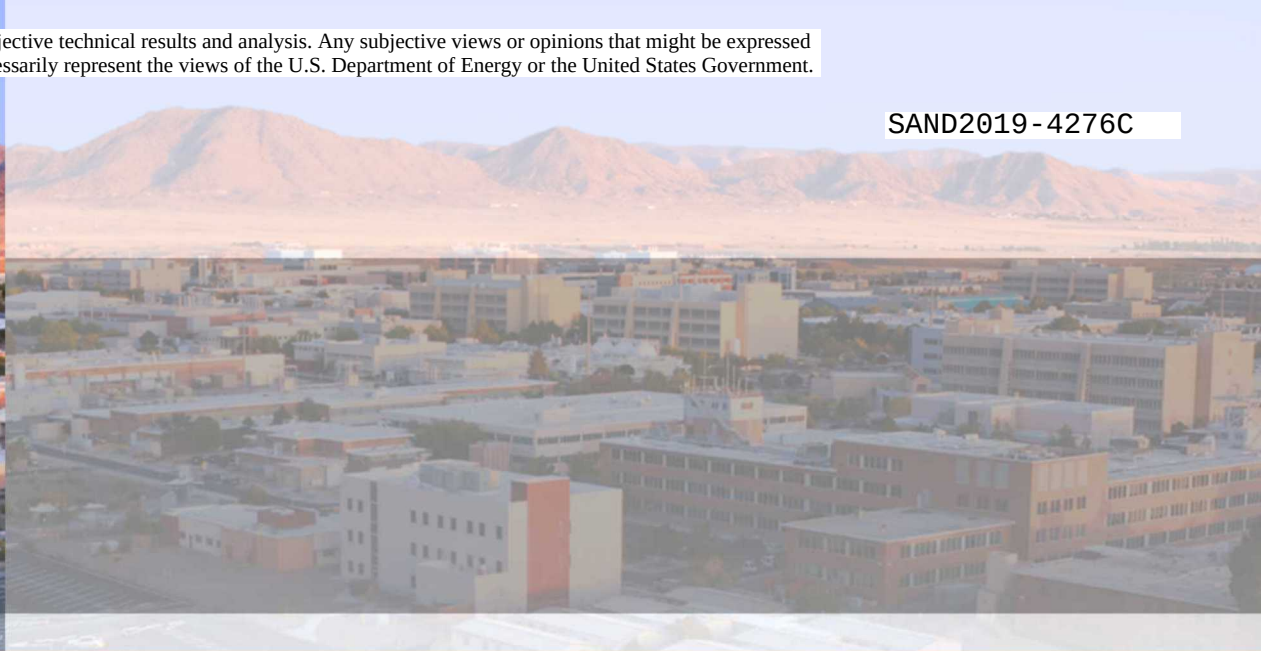




Using lanthanides to probe the interfacial chemistry of nano-scale pores

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Andrew W. Knight², and Kevin Leung¹

1.Geochemistry Department; 2.Storage and Transportation Department
Sandia National Laboratories

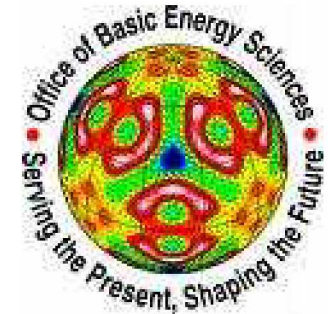


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Nikolai Kalugin, NM Tech
Nadine Kabengi, Georgia State University



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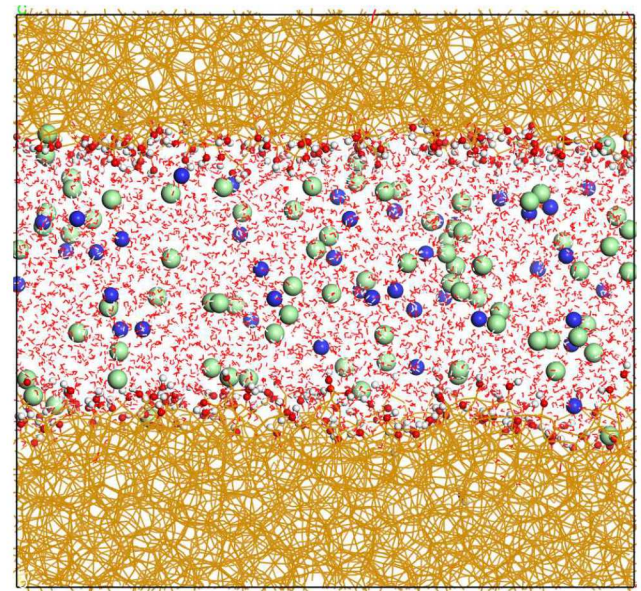
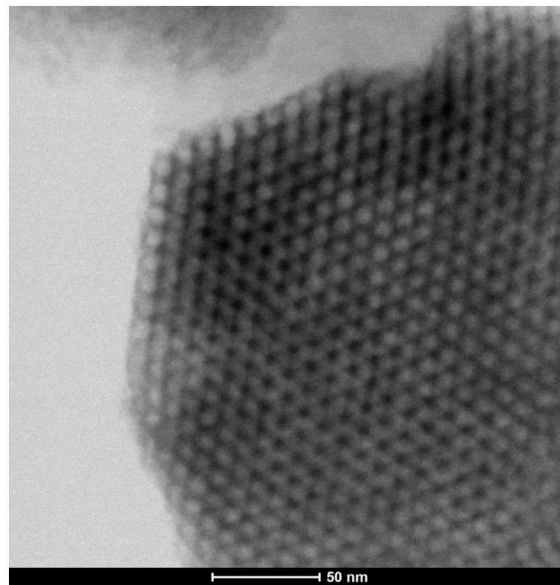
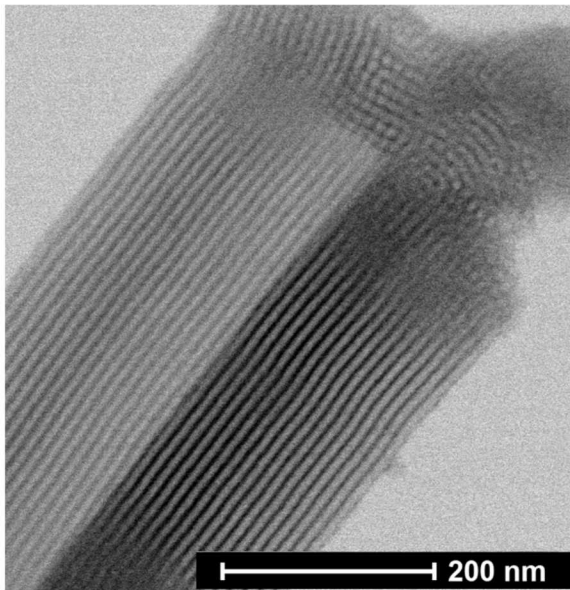
This research used resources of the Advanced Photon Source, a U.S. Department of Energy (DOE) Office of Science User Facility operated for the DOE Office of Science by Argonne National Laboratory under Contract No. DE-AC02-06CH11357.

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Emergent chemical behavior due to nano-scale confinement:

- Decreased dielectric constant¹⁻², surface tension³, and density of water.³
- Decreased solvation energies of metal cations.⁴
- Increased inner sphere coordination of metal cations.⁴
- Enhanced metal adsorption⁵⁻⁶, modified redox⁷ and diffusion properties.^{8,9}



TEM images, P. Lu

MD model, J. Greathouse

¹Marti et al., *J. Phys. Chem. B* (2006)

²Senapati et al., *J. Phys. Chem. B* (2001)

³Takei et al., *Colloid Polym. Sci.* (2000)

⁴Kalluri et al., *J. Phys. Chem. C* (2011)

⁵Wang et al., *Geology* (2003)

⁶Zimmerman et al., *Environ. Sci. Technol.* (2004)

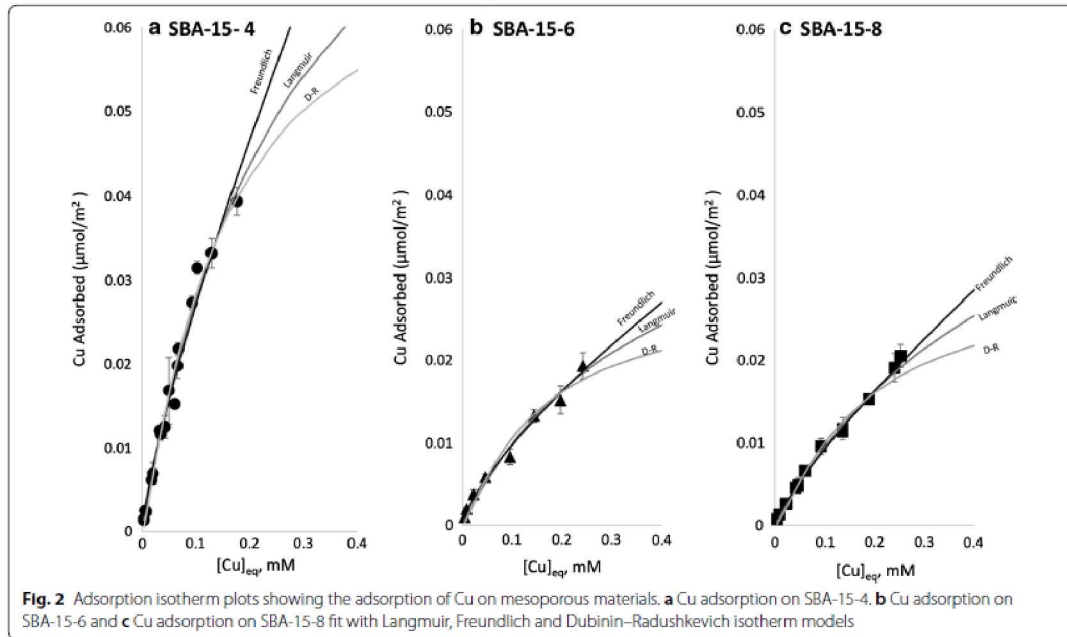
⁷Mattia and Calabro, *Microfluid Nanofluid* (2012)

⁸Samsom and Biggin, *Nature* (2001)

⁹Ma et al., *JACS* (2019)

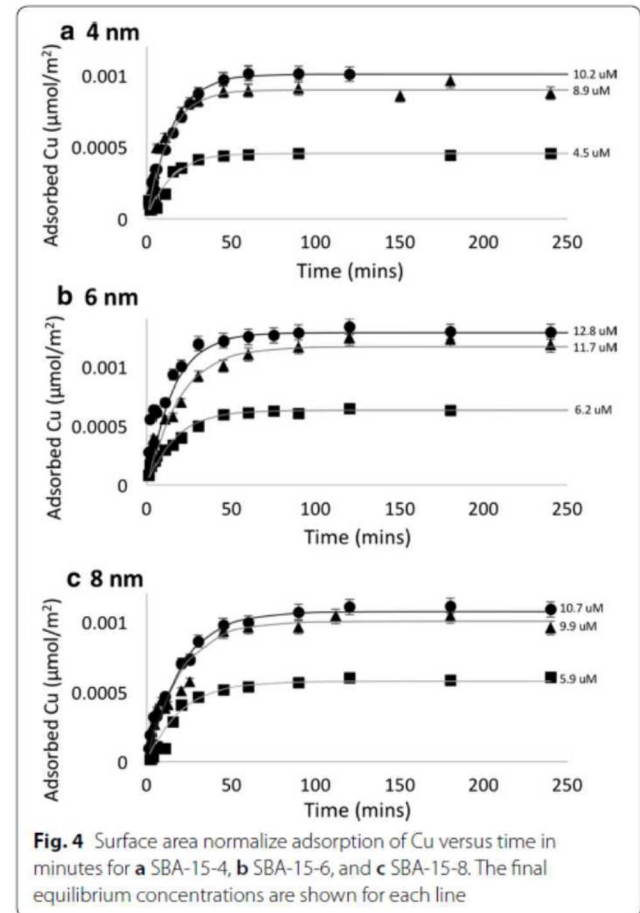
Adsorption of Cu^{2+} on Mesoporous Silica

Cu^{2+} adsorption isotherms



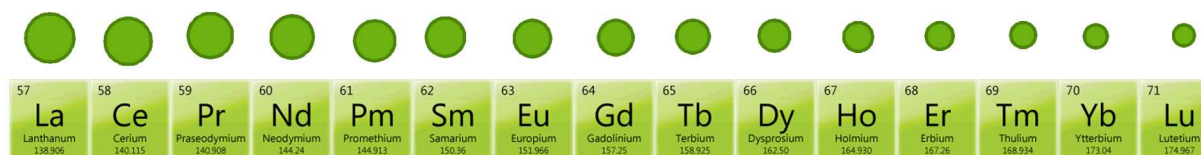
- Nano-scale confinement enhances both the adsorption maximum, and Cu^{2+} adsorption reaction rate.
- The pseudo-first-order reaction rate constant increased with decreasing pore size.
- External mass transfer diffusion constant increases with decreasing pore size: this rapid film diffusion in 4 nm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

Cu^{2+} adsorption kinetics



Chemistry under Nano-scale Confinement

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



57	58	59	60	61	62	63	64	65	66	67	68	69	70	71
La	Ce	Pr	Nd	Pm	Sm	Eu	Gd	Tb	Dy	Ho	Er	Tm	Yb	Lu
Lanthanum	Cerium	Praseodymium	Neodymium	Promethium	Samarium	Europium	Gadolinium	Terbium	Dysprosium	Holmium	Erbium	Thulium	Ytterbium	Lutetium
138.906	140.115	140.908	144.24	144.913	150.36	151.966	157.25	158.925	162.50	164.930	167.26	168.934	173.04	174.967

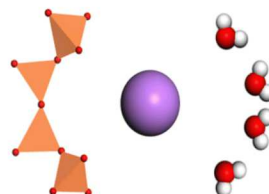
Lowest
Hydration Energy

Highest
Hydration Energy

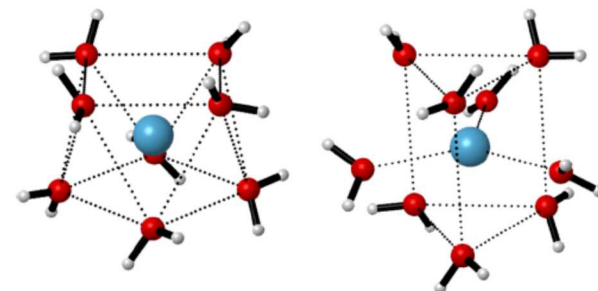
Weakly Hydrated

Strongly Hydrated

Mineral-Ion
Interactions Dominate



Water-Ion
Interactions Dominate



Research goal

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

6 Chemistry of lanthanides

IUPAC Periodic Table of the Elements

1 H hydrogen 1.0078, 1.0082																	18 He helium 4.0026																		
3 Li lithium 6.938, 6.997	2 Be beryllium 9.0122																	19 K potassium 39.098	20 Ca calcium 40.078(4)	21 Sc scandium 44.956	22 Ti titanium 47.867	23 V vanadium 50.942	24 Cr chromium 51.996	25 Mn manganese 54.938	26 Fe iron 55.845(2)	27 Co cobalt 58.933	28 Ni nickel 58.693	29 Cu copper 63.546(3)	30 Zn zinc 65.38(2)	31 Ga gallium 69.723	32 Ge germanium 72.630(8)	33 As arsenic 74.922	34 Se selenium 78.971(8)	35 Br bromine 79.904 (79.901, 79.907)	36 Kr krypton 83.798(2)
11 Na sodium 22.990	12 Mg magnesium 24.305 (24.304, 24.307)																	37 Rb rubidium 85.468	38 Sr strontium 87.62	39 Y yttrium 88.906	40 Zr zirconium 91.224(2)	41 Nb niobium 92.906	42 Mo molybdenum 95.94	43 Tc technetium	44 Ru ruthenium 101.07(2)	45 Rh rhodium 102.91	46 Pd palladium 106.42	47 Ag silver 107.87	48 Cd cadmium 112.41	49 In indium 114.82	50 Sn tin 118.71	51 Sb antimony 121.76	52 Te tellurium 127.6(3)	53 I iodine 126.90	54 Xe xenon 131.29
55 Cs caesium 132.91	56 Ba barium 137.33																	57-71 La lanthanoids	72 Hf hafnium 178.49(2)	73 Ta tantalum 180.95	74 W tungsten 183.84	75 Re rhenium 186.21	76 Os osmium 190.23	77 Ir iridium 192.22	78 Pt platinum 195.08	79 Au gold 196.97	80 Hg mercury 200.59	81 Tl thallium 204.38 (204.38, 204.39)	82 Pb lead 207.2	83 Bi bismuth 208.98	84 Po polonium	85 At astatine	86 Rn radon		
87 Fr francium	88 Ra radium																	89-103 Ac actinoids	104 Rf rutherfordium	105 Db dubnium	106 Sg seaborgium	107 Bh bohrium	108 Hs hassium	109 Mt meitnerium	110 Ds darmstadtium	111 Rg roentgenium	112 Cn copernicium	113 Nh nihonium	114 Fl flerovium	115 Mc moscovium	116 Lv livermorium	117 Ts tennessine	118 Og oganesson		

57 La lanthanum 138.91	58 Ce cerium 140.12	59 Pr praseodymium 140.91	60 Nd neodymium 144.24	61 Pm promethium	62 Sm samarium 150.36(2)	63 Eu europium 151.96	64 Gd gadolinium 157.25(3)	65 Tb terbium 158.93	66 Dy dysprosium 162.50	67 Ho holmium 164.93	68 Er erbium 167.26	69 Tm thulium 168.93	70 Yb ytterbium 173.05	71 Lu lutetium 174.97
89 Ac actinium 227.04	90 Th thorium 232.04	91 Pa protactinium 231.04	92 U uranium 238.03	93 Np neptunium	94 Pu plutonium	95 Am americium	96 Cm curium	97 Bk berkelium	98 Cf californium	99 Es einsteinium	100 Fm fermium	101 Md mendelevium	102 No nobelium	103 Lr lawrencium

For notes and updates to this table, see www.iupac.org. This version is dated 28 November 2016.
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1.032 Å → 0.861 Å

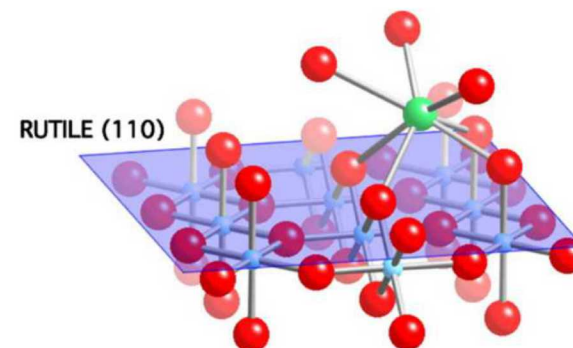
Approach

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

Lanthanides

- Have large and variable coordination numbers (CN)¹.
- Coordination number vary from 3 to 12, the most common CN=8¹.
- Crystal structures differ for light (Z=57-63) and heavy (Z=64-71) elements¹.

Y³⁺ adsorbed to the rutile (110) surface and forms a tetranuclear surface complex.



Piasecki and Sverjensky, 2001
Geochimica et Cosmochimica Acta 72, 3964-3979

¹ Huang (2011)

Batch experiments



ICP-MS



Ab initio DFT

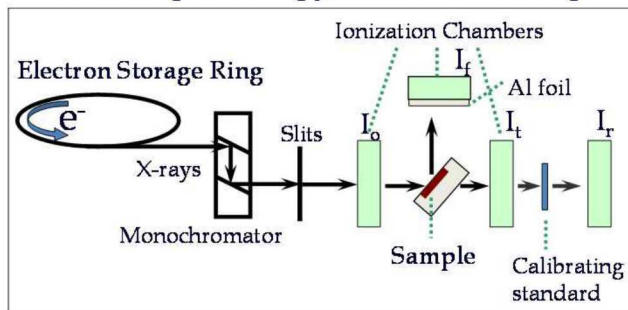


Red Sky supercomputer, www.sandia.gov

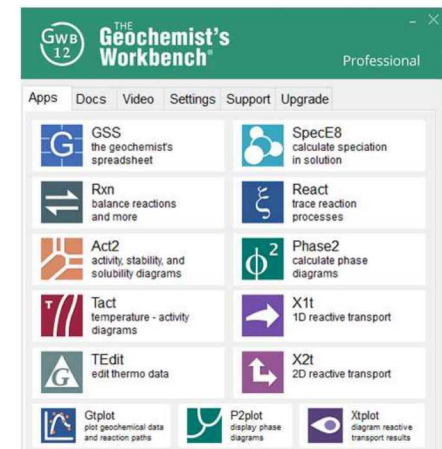
X-ray Absorption Spectroscopy (XAS)

EXAFS spectroscopy instrumental setup

APS, Argonne National Lab.

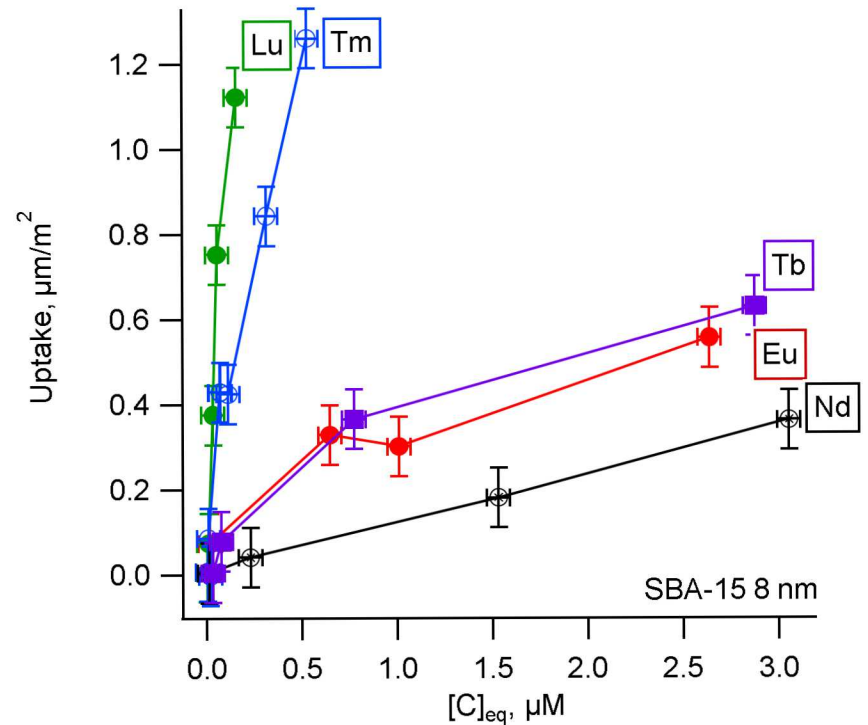
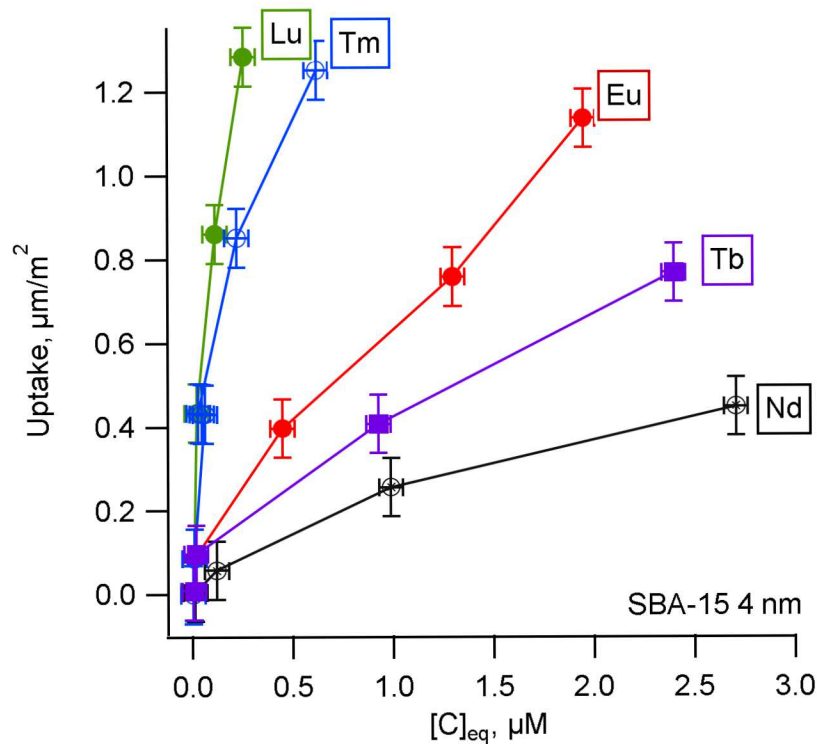


GWB



Results: adsorption isotherms

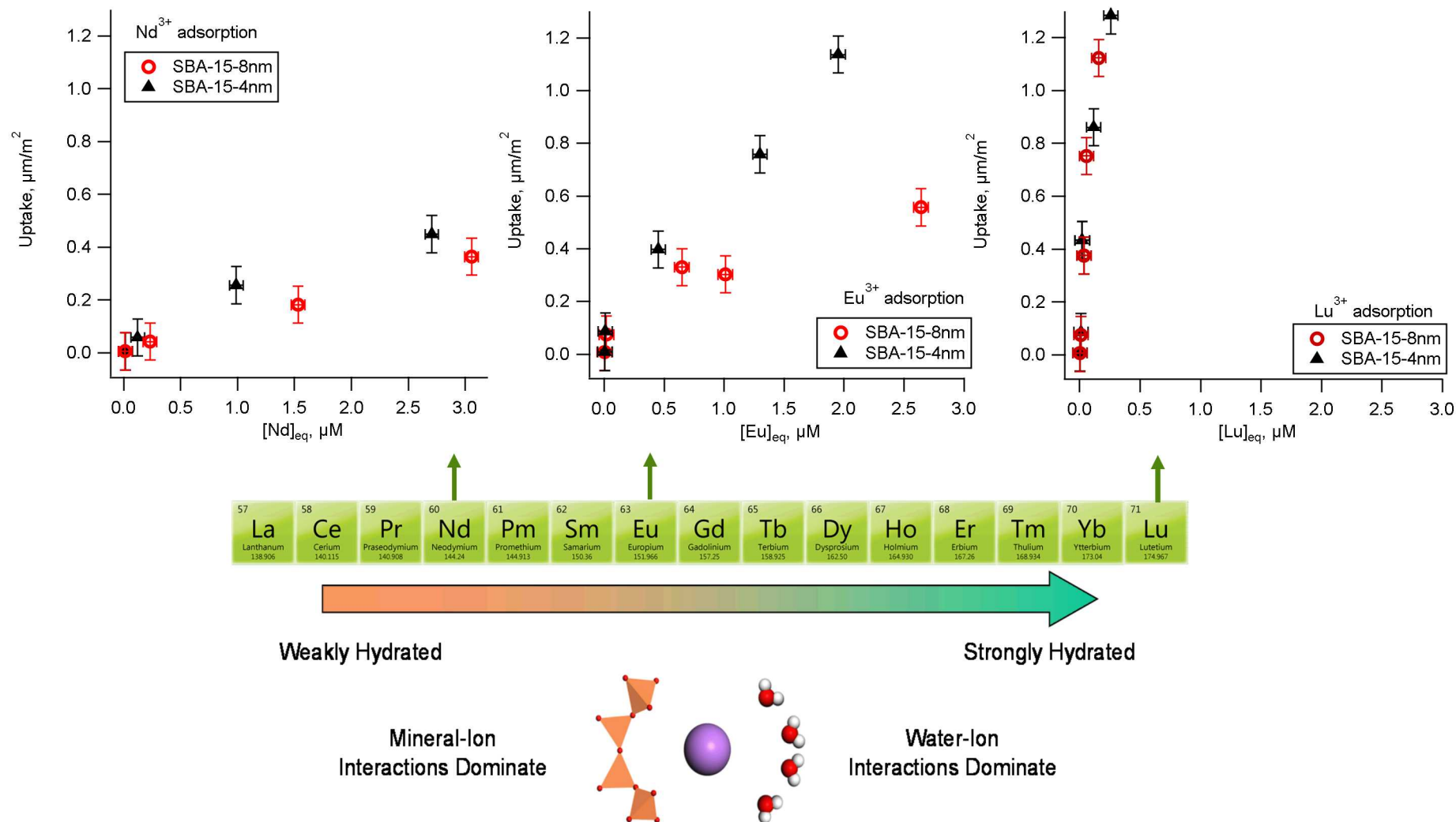
- For both SBA-15-4 nm and SBA-15-8 nm with increasing Z uptake increased.



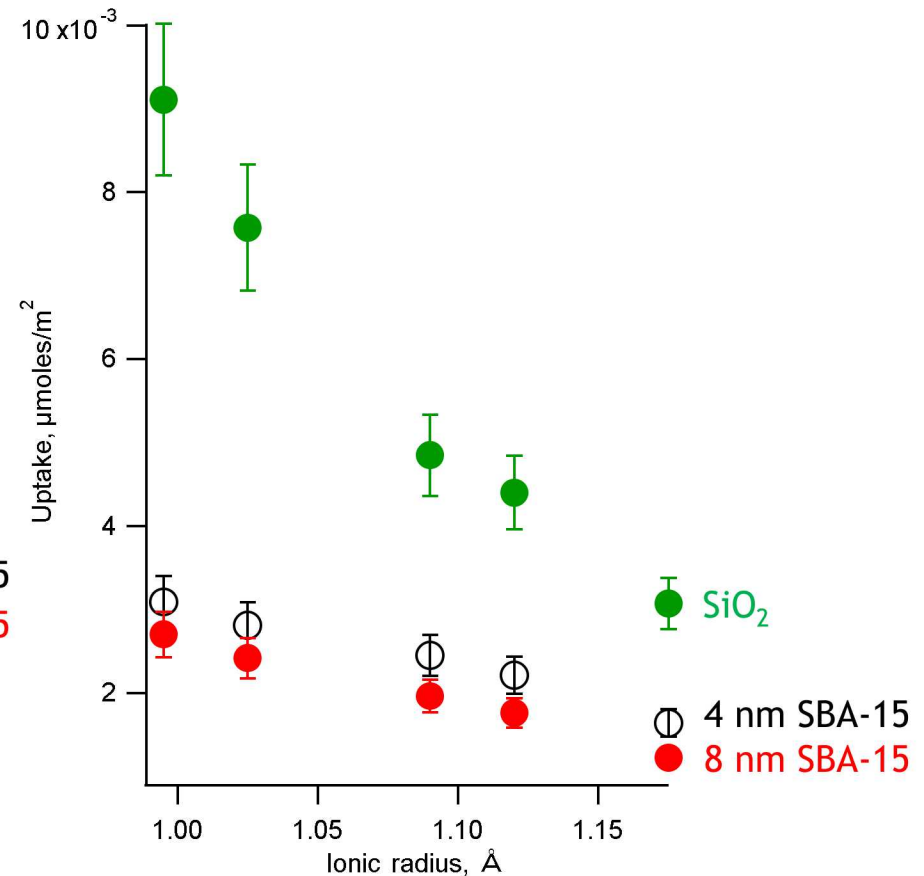
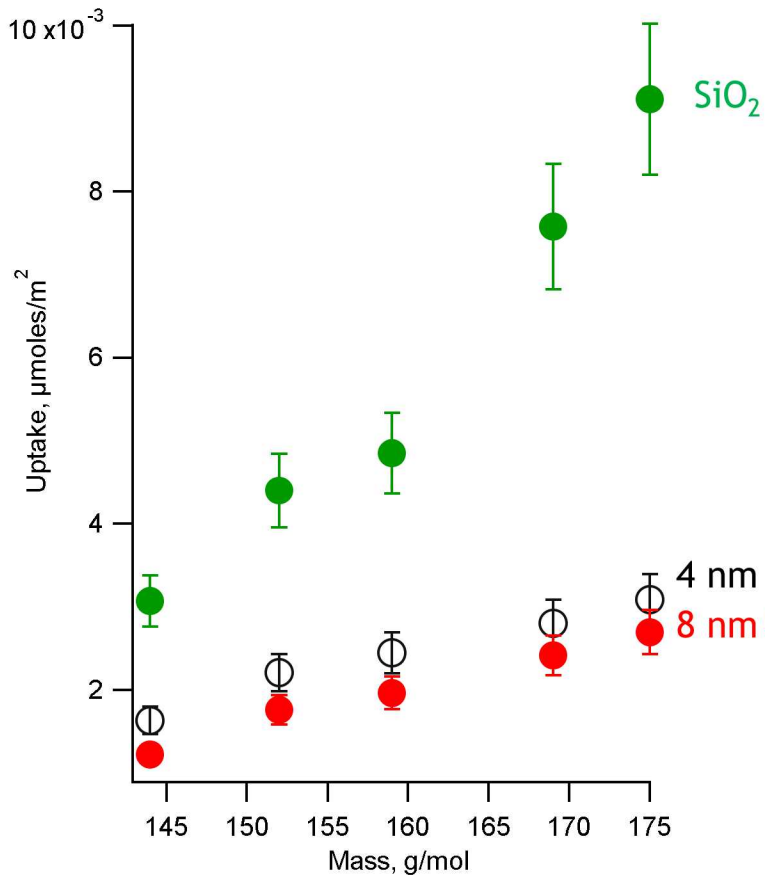
57	58	59	60	61	62	63	64	65	66	67	68	69	70	71
La	Ce	Pr	Nd	Pm	Sm	Eu	Gd	Tb	Dy	Ho	Er	Tm	Yb	Lu
Lanthanum	Cerium	Praseodymium	Neodymium	Promethium	Samarium	Europium	Gadolinium	Terbium	Dysprosium	Holmium	Erbium	Thulium	Ytterbium	Lutetium
138.906	140.115	140.908	144.24	144.913	150.36	151.966	157.25	158.925	162.50	164.930	167.26	168.934	173.04	174.967

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.

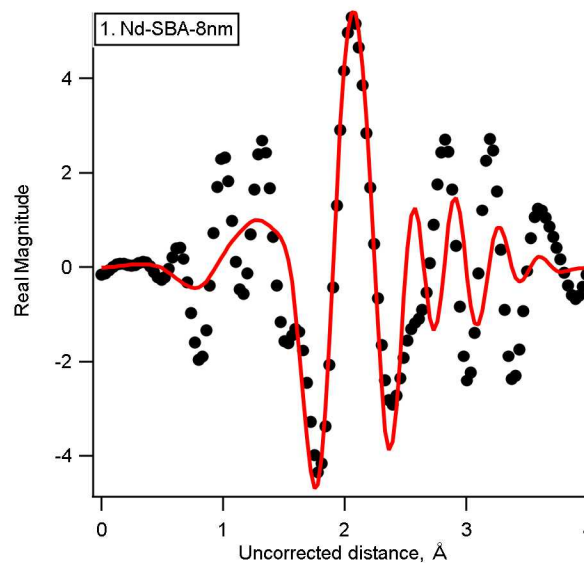
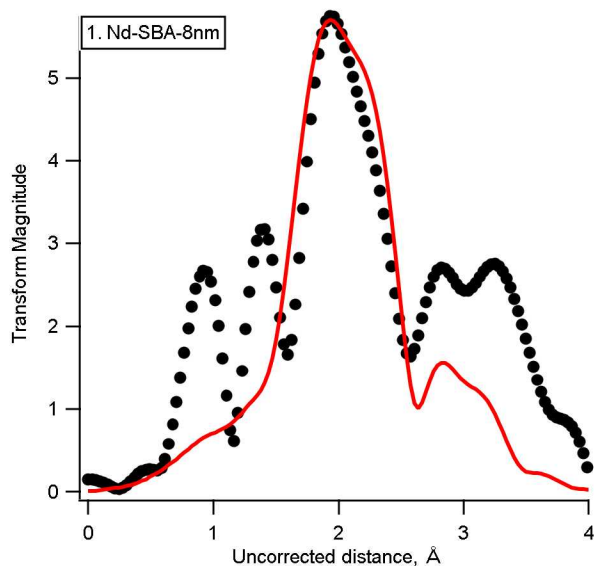


Results: Competitive adsorption

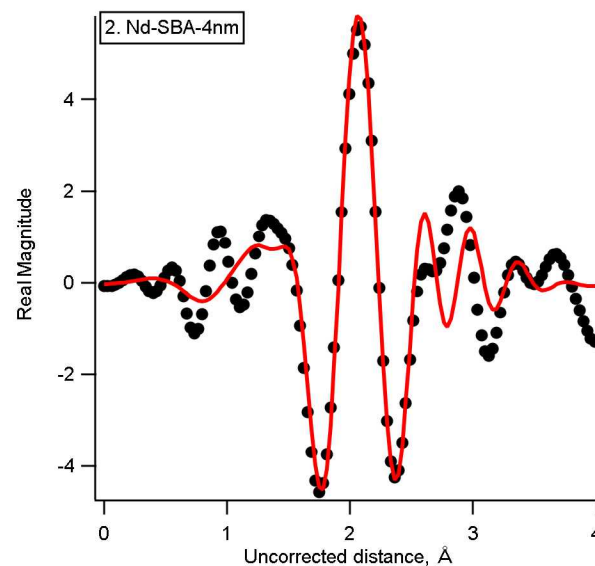
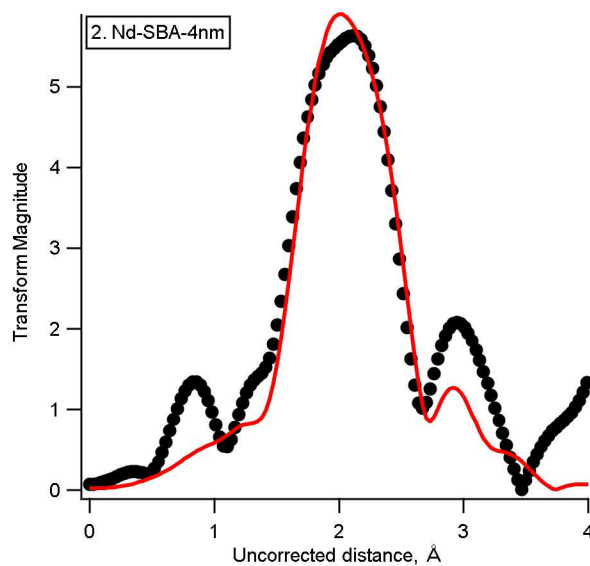


- Increased uptake with increasing Z and decreasing ionic radii.
- Higher uptake on 4 nm- vs 8 nm-silica, but below non-porous SiO_2 .

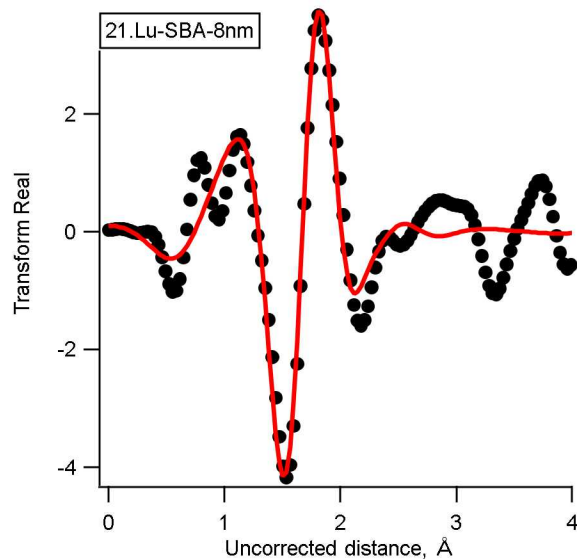
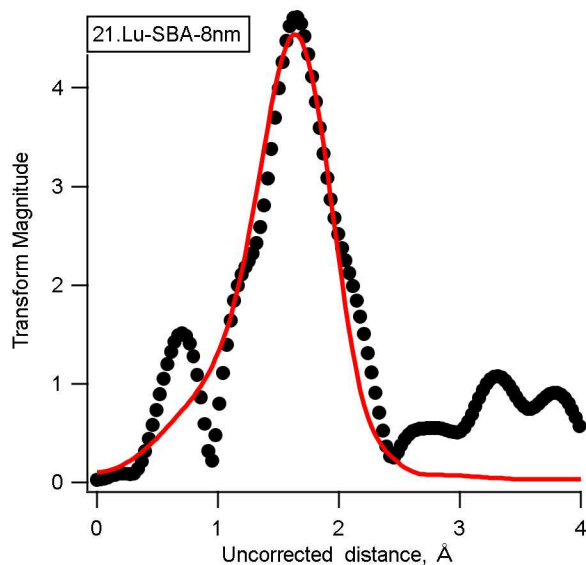
XAFS: preliminary results for neodymium



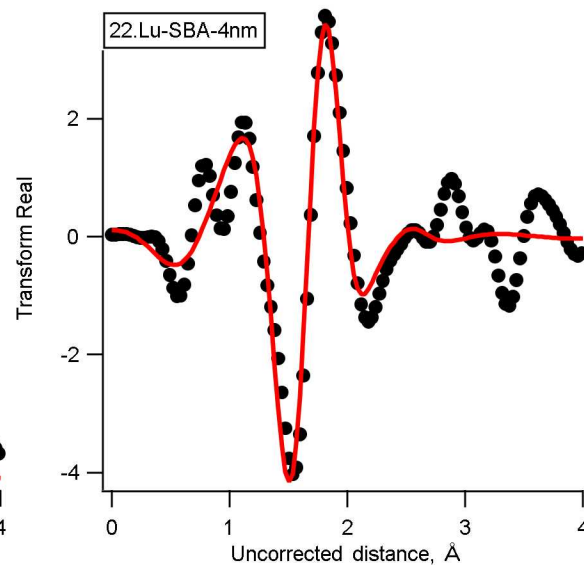
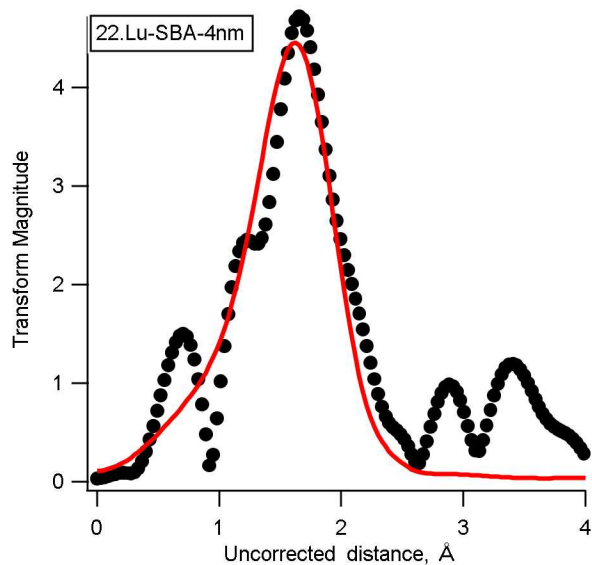
- 1st shell fit with two Nd-O distances;
- Nd-O bond length:
 $\text{SiO}_2 < 8\text{nm SBA} < 4\text{nm SBA}.$



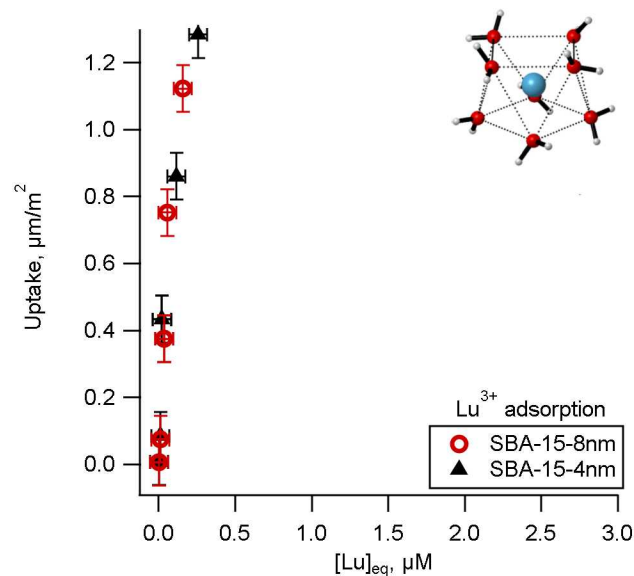
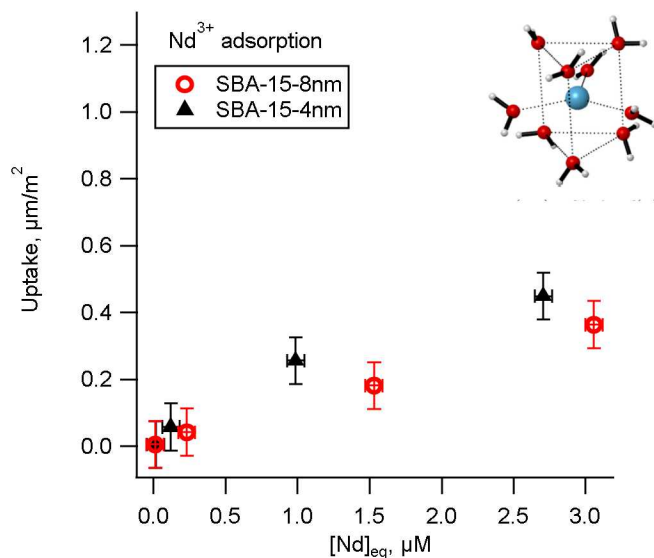
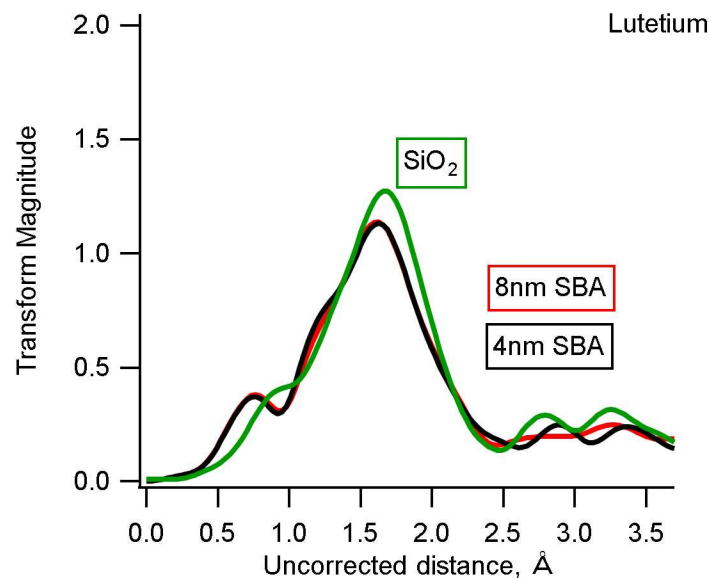
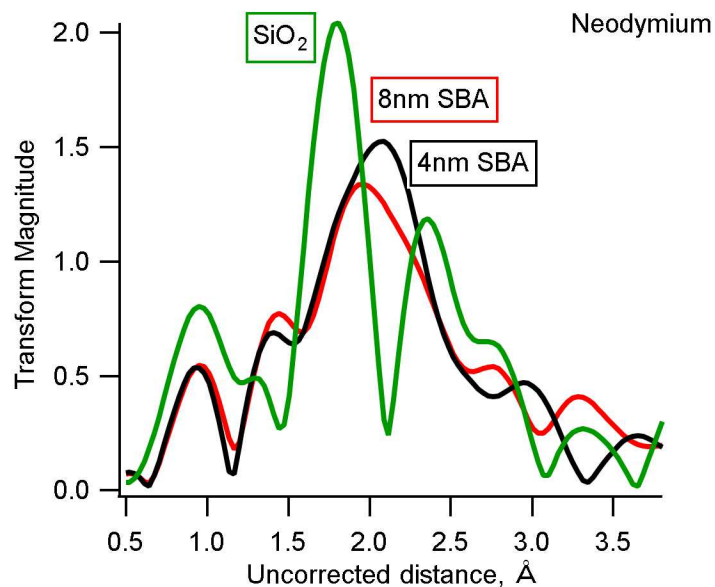
XAFS: preliminary results for lutetium



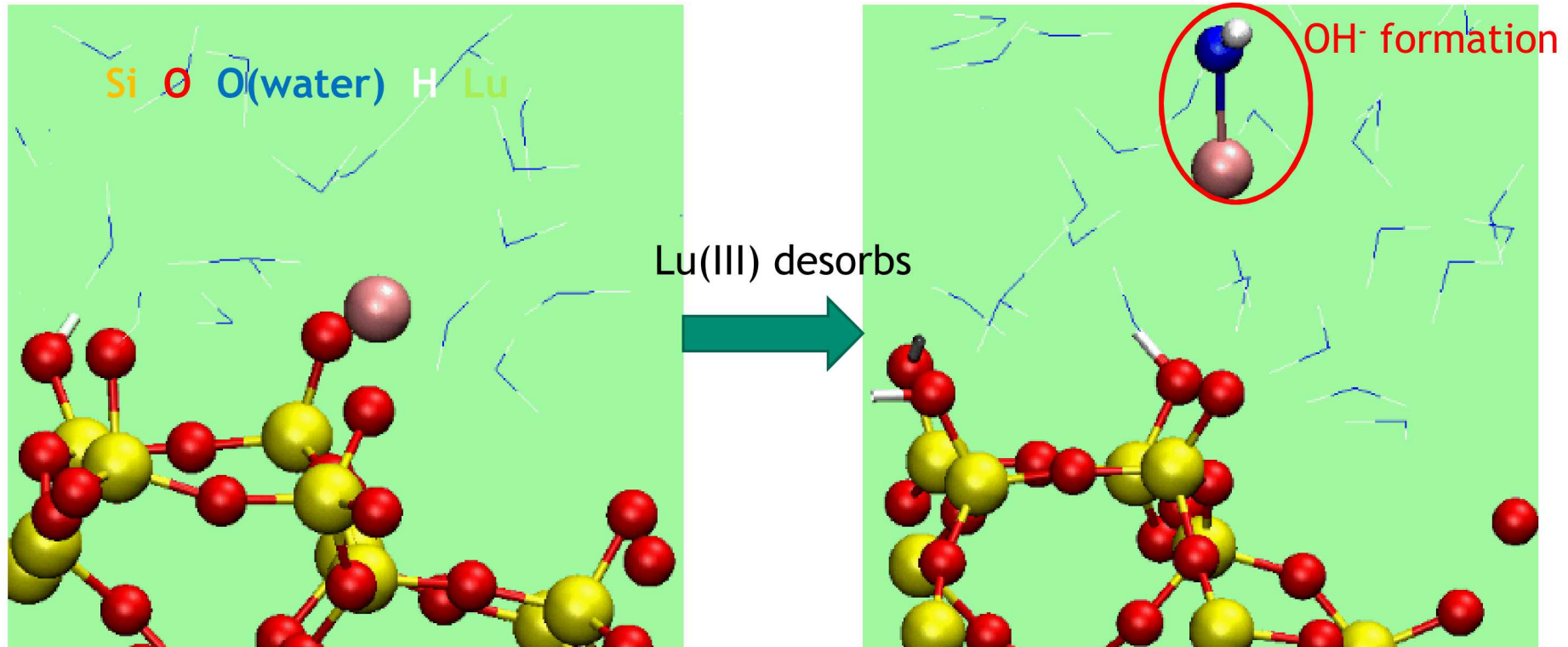
- 1st shell fit with one Lu-O distance;
- Same Lu-O bond length for non-porous SiO₂, and for SBA-15 with 4 nm and 8 nm pores.



XAFS: difference between Nd and Lu



Hydrolysis of H₂O molecule as Lu(III) desorbs from silica surface



- *ab initio* molecular dynamics (AIMD) simulations + umbrella sampling to force desorption;
- Lu(III) desorption causes $\text{H}_2\text{O} + \text{SiO}^- \rightarrow \text{OH}^- + \text{SiOH}$;
- Previous AIMD simulations of this silica model predict $\text{pK}_a = 7 - 8.1$;
- Combined with thermodynamic data Lu(III) 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:

$\text{Cu}^{2+} \Delta G_{\text{H}}$
-2130 kJ/mol

$\text{Nd}^{3+} \Delta G_{\text{H}}$
-3278 kJ/mol

$\text{Tm}^{3+} \Delta G_{\text{H}}$
-3509 kJ/mol

$\text{Lu}^{3+} \Delta G_{\text{H}}$
-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.

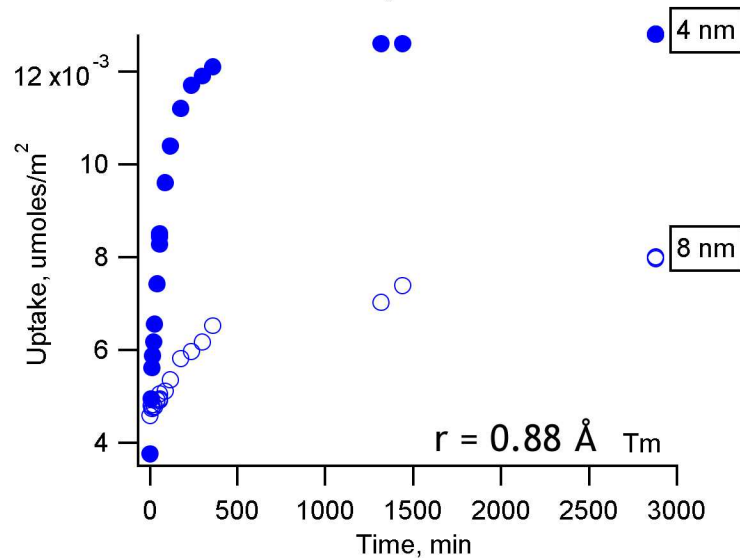
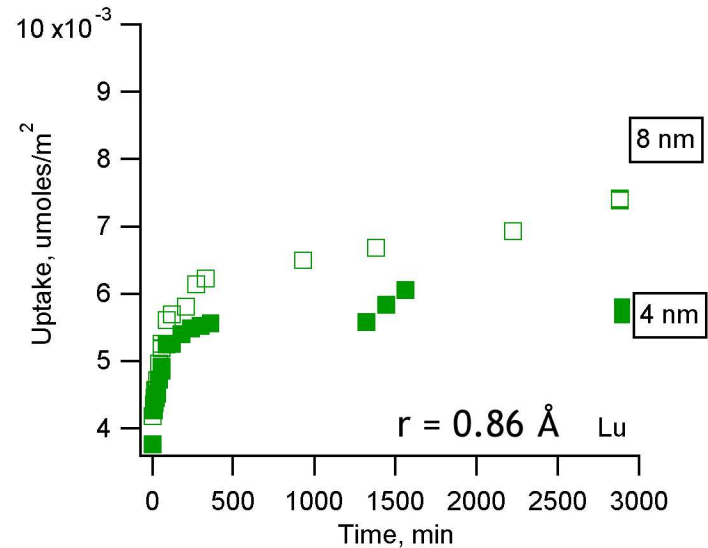
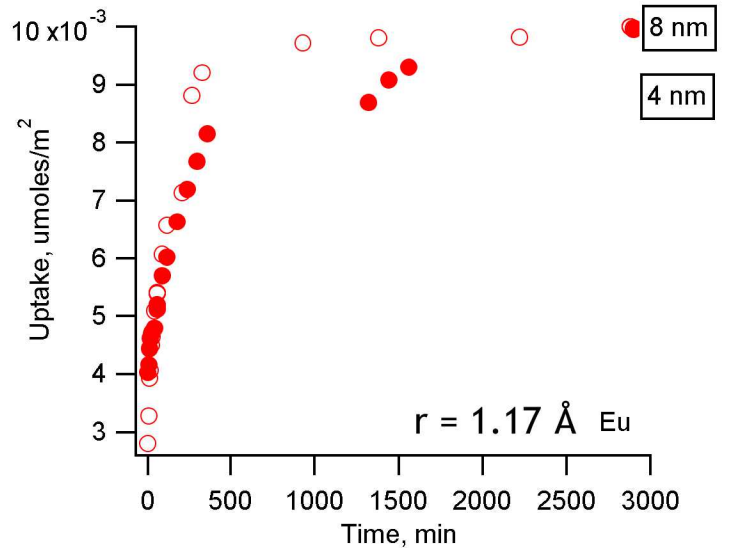
Work in progress

- 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 Eu³⁺ and Lu³⁺, on 8 nm pores adsorption is slightly more favorable and faster.
- For Tm³⁺ the trend is the same as for Cu²⁺: faster and more favorable adsorption onto 4 nm, compared to 8 nm pores.