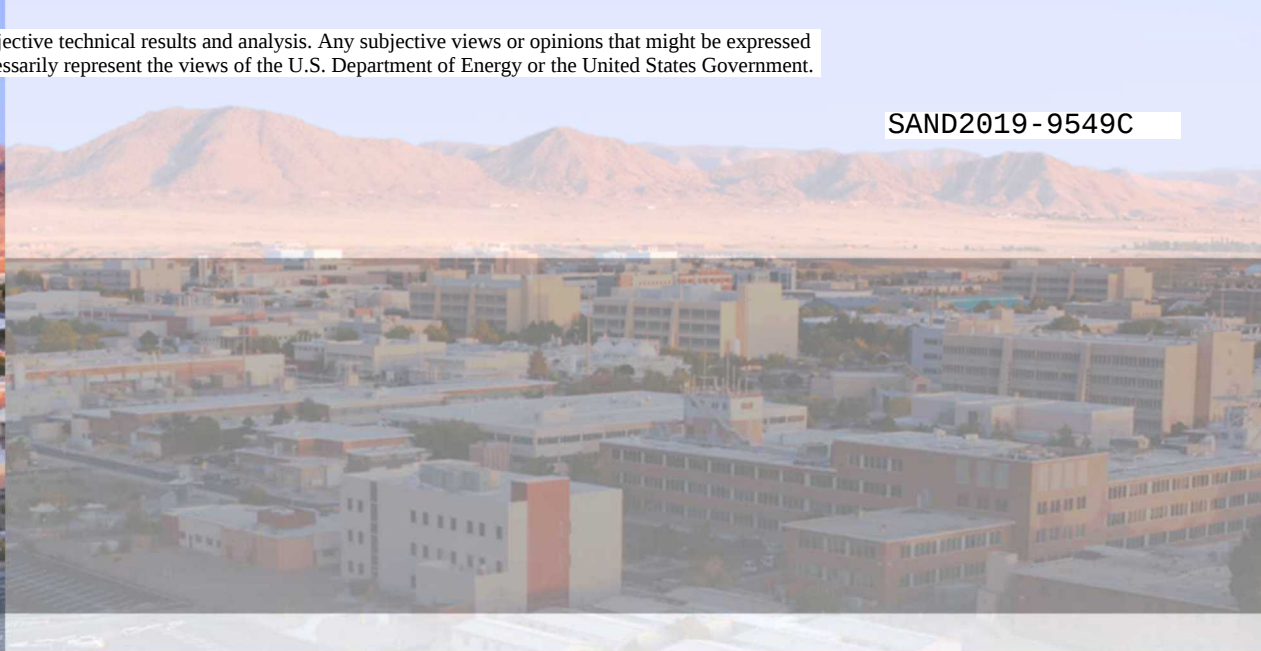




Interfacial chemistry of lanthanides under nano-scale confinement

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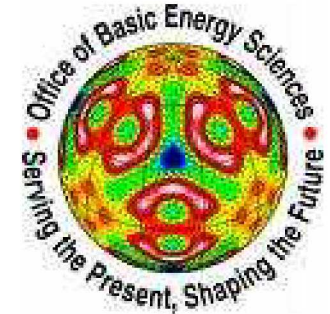


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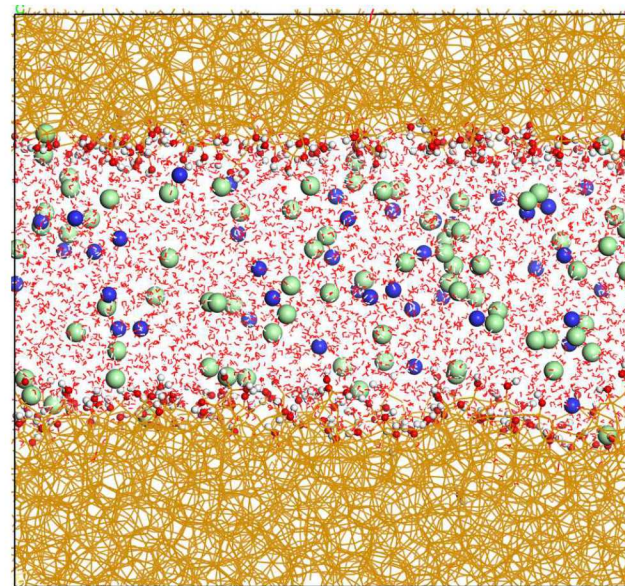
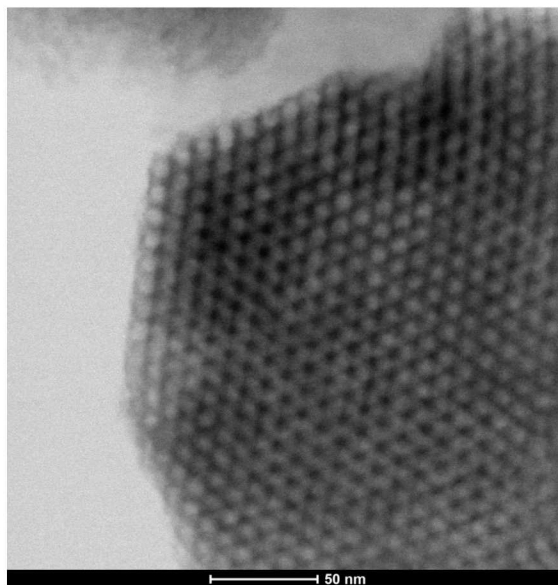
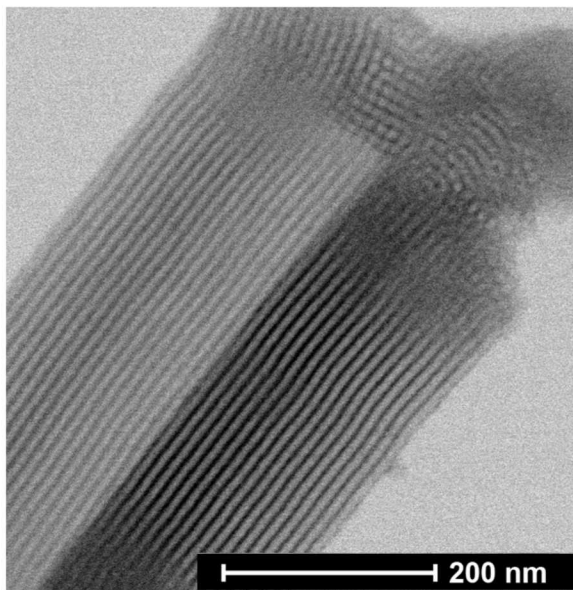
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Interfacial chemistry under nano-scale confinement

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)

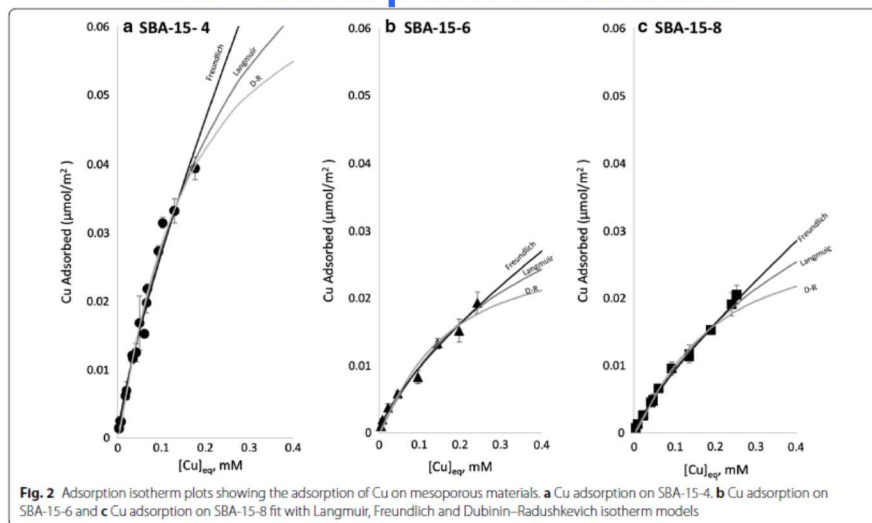
⁷Mattia and Calabro, *Microfluid Nanofluid* (2012)

⁸Samsom and Biggin, *Nature* (2001)

⁹Ma et al., *JACS* (2019)

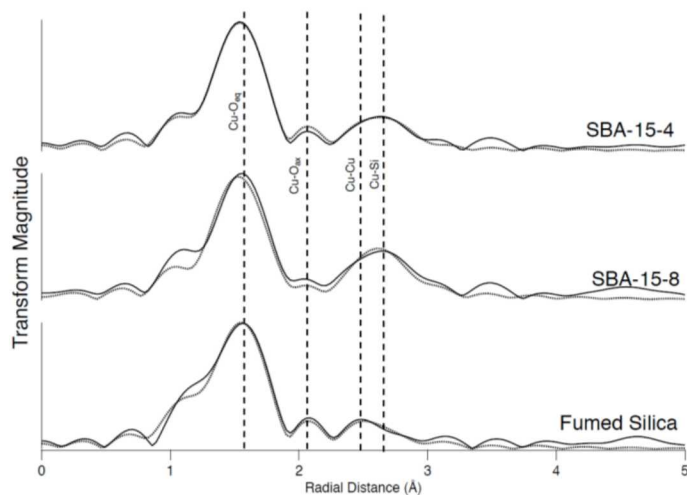
Adsorption of Cu^{2+} on Mesoporous Silica

Cu^{2+} adsorption isotherms

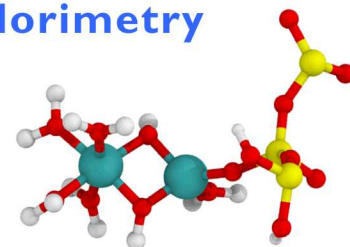
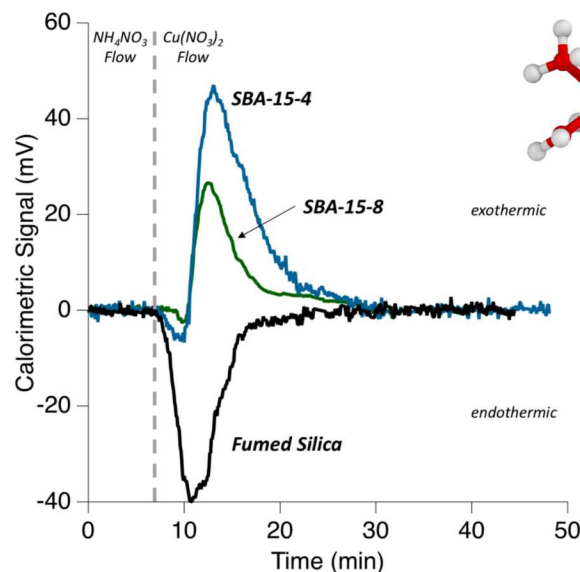


- Enhanced Cu^{2+} adsorption under nano-scale confinement;
- More distorted coordination complexes ($\text{Cu-Oax} \gg \text{Cu-Oeq}$);
- Increase in Cu^{2+} dimerization inside nano-scale pores;
- Weak endothermic signal followed by a strong exothermic signal: Cu^{2+} undergoes dehydration during the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

Cu^{2+} adsorption complexes



Cu^{2+} flow microcalorimetry

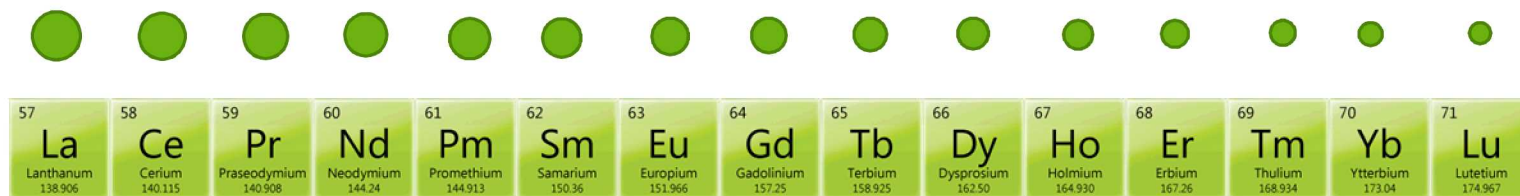


Research Goals

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

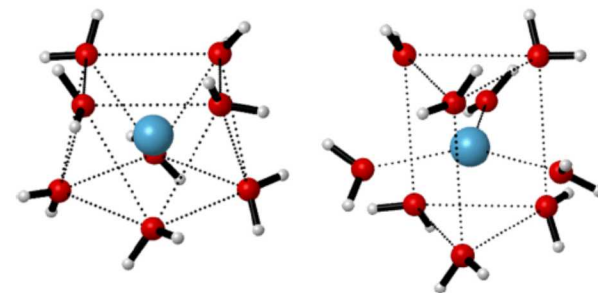


Lowest hydration energy

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.



Chemistry of lanthanides

1

H

hydrogen

1.0078, 1.0062

2

He

helium

4.0026

3

Li

lithium

6.938, 6.997

4

Be

beryllium

9.0122

11

Na

sodium

22.990

12

Mg

magnesium

24.304, 24.3037

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

36

Kr

krypton

83.798(2)

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

cesium

132.91

56

Ba

barium

137.33

57-71

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(3)

77

Ir

iridium

192.22

78

Pt

platinum

195.08

79

Au

gold

196.967

80

Hg

mercury

200.59

81

Tl

thallium

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

actinoids

104

Rf

rutherfordium

105

Db

dbium

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

Key:

atomic number

Symbol

name

conventional atomic weight

standard atomic weight

IUPAC Periodic Table of the Elements

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 227.03	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. Copyright © 2016 IUPAC, the International Union of Pure and Applied Chemistry.



1.032 Å $\longrightarrow$ 0.861 Å

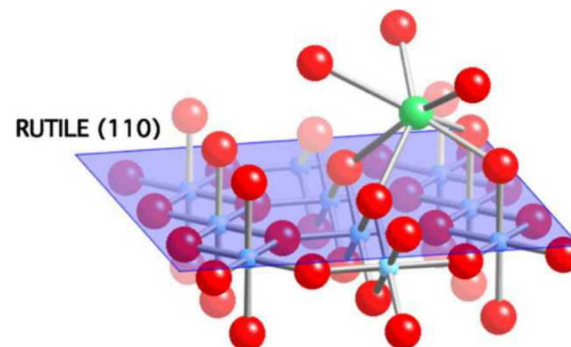
Approach

- 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, 2000
Geochimica et Cosmochimica Acta 72, 3964-3979

¹ Huang (2011)

Methods

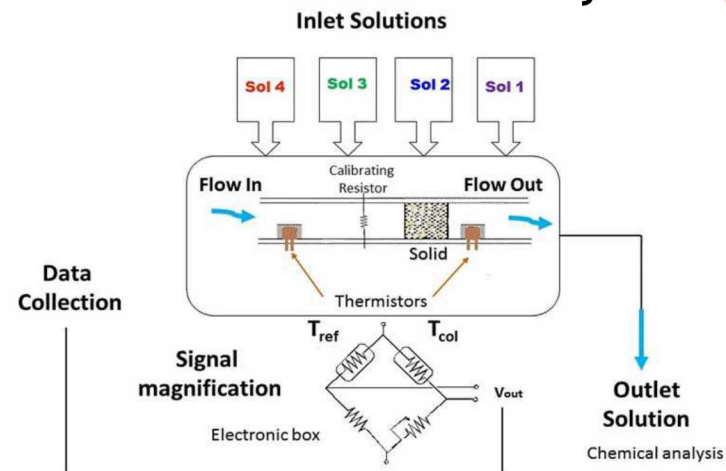
Batch experiments



ICP-MS



Flow microcalorimetry



Ab initio DFT

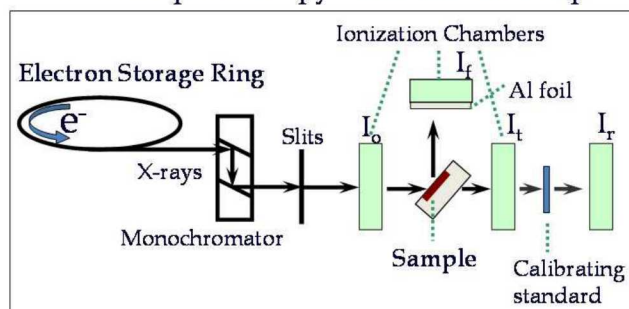


Red Sky supercomputer, www.sandia.gov

X-ray Absorption Spectroscopy (XAS)

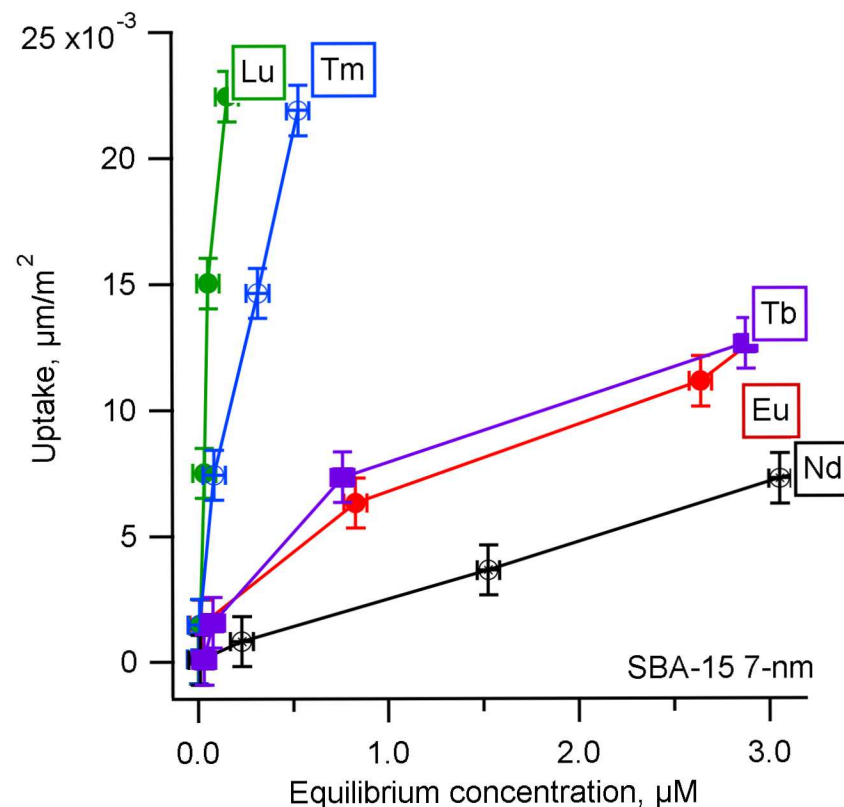
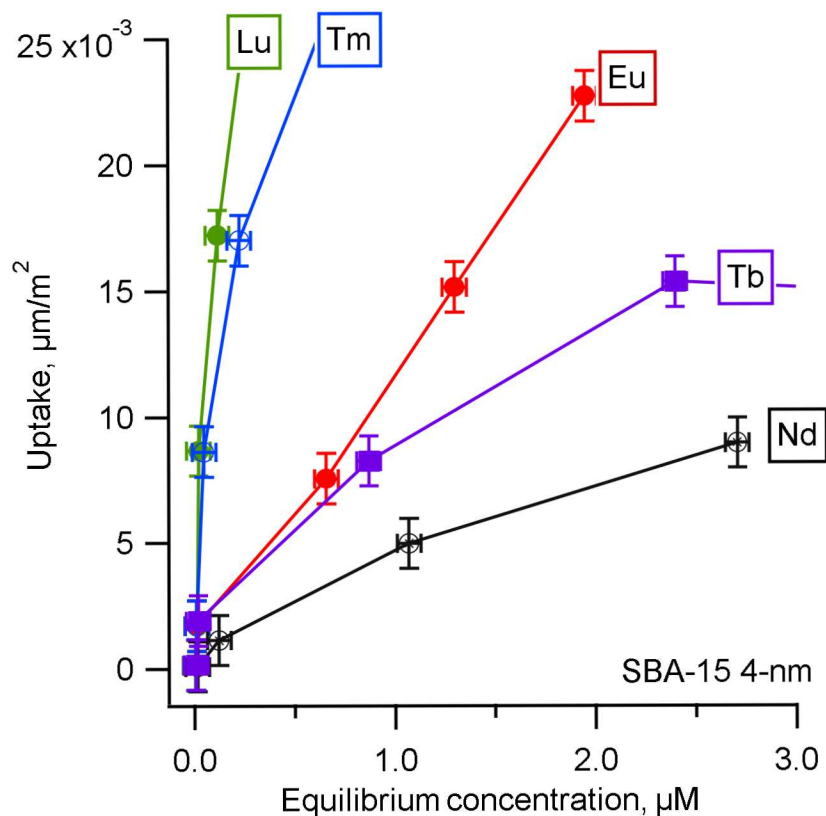
EXAFS spectroscopy instrumental setup

APS, Argonne National Lab.



Results: adsorption isotherms

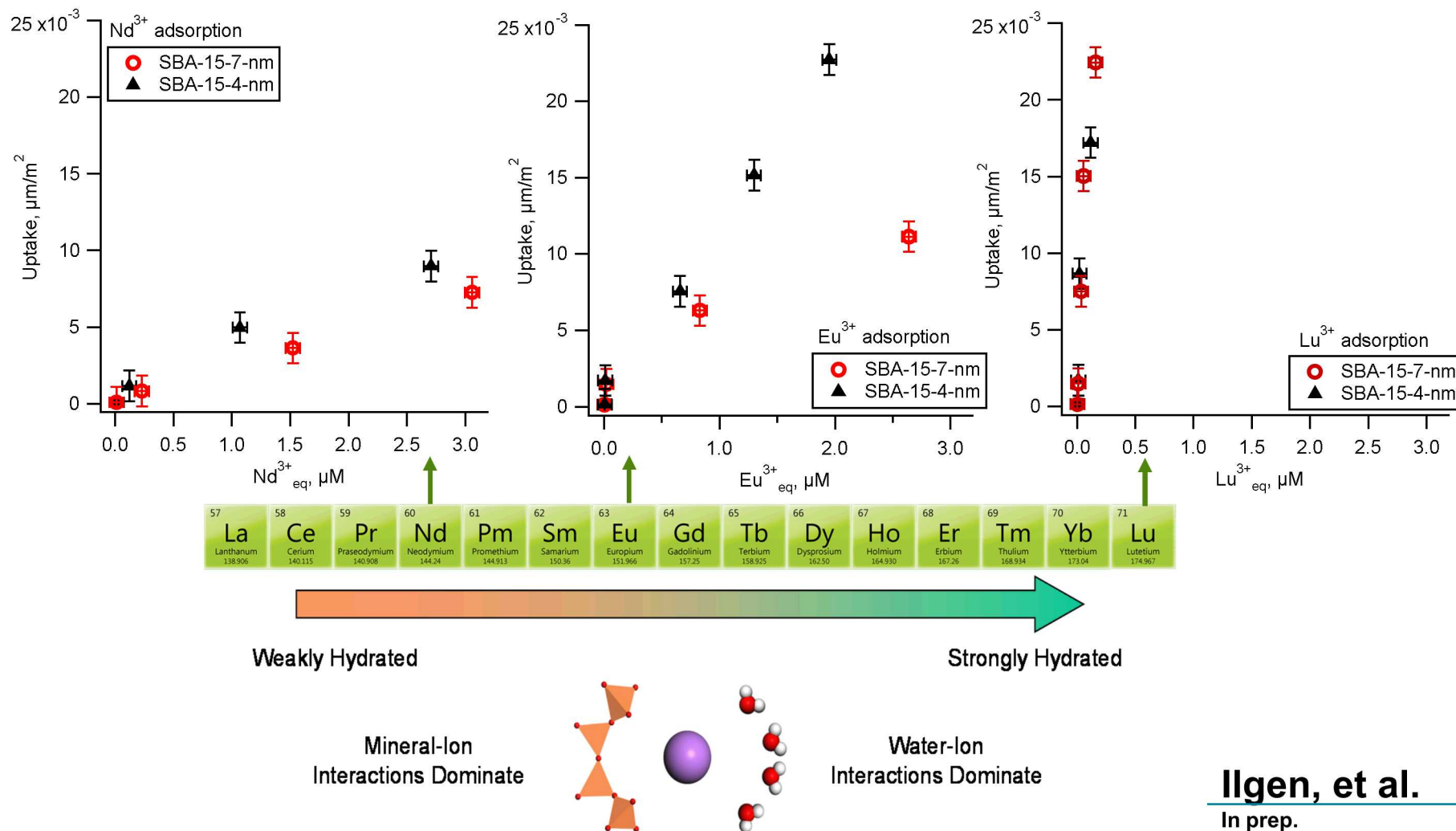
- For both SBA-15-4 nm and SBA-15-8 nm with increasing Z uptake increased.



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

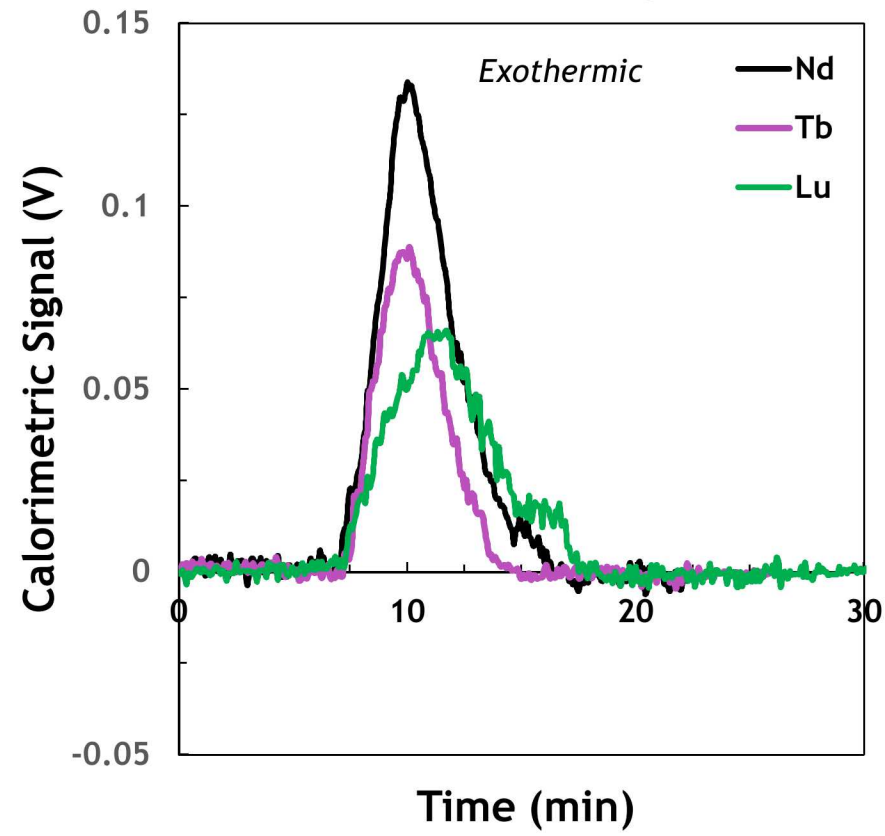
Results: Pore-size (in)dependence

- 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.

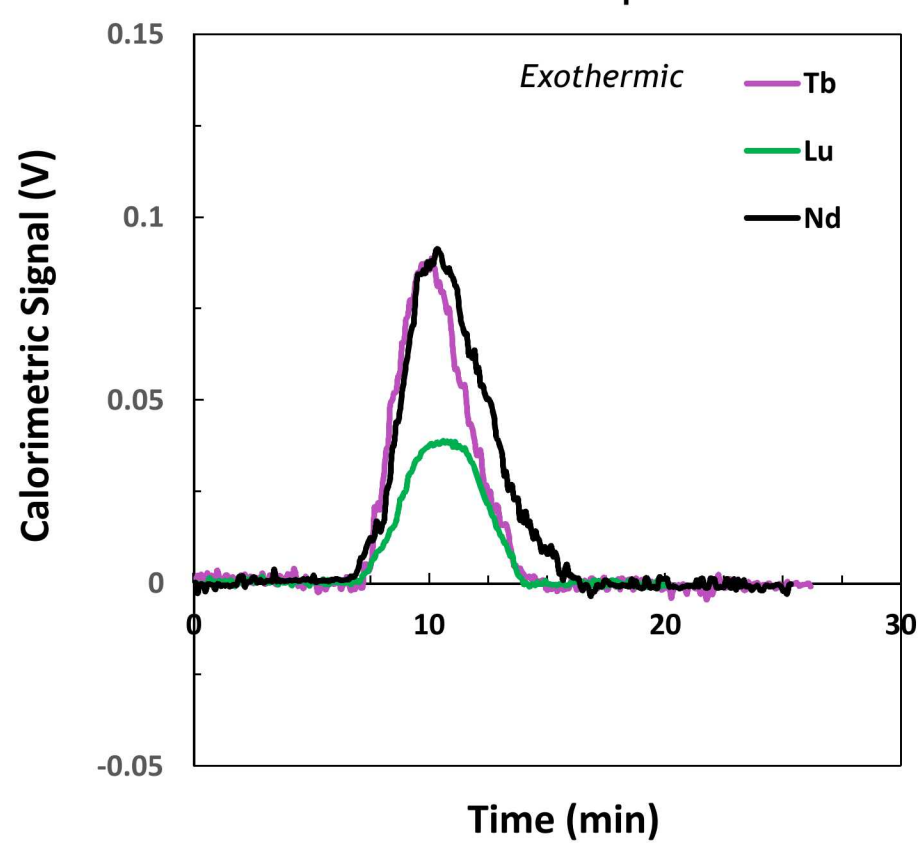


Results: flow microcalorimetry

4.4 nm silica pores



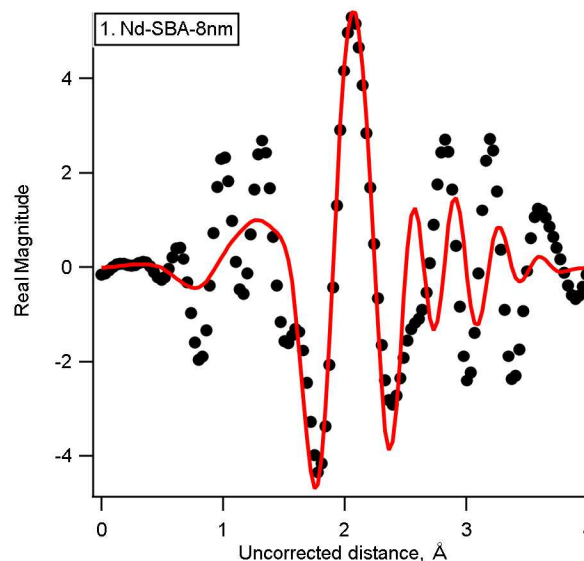
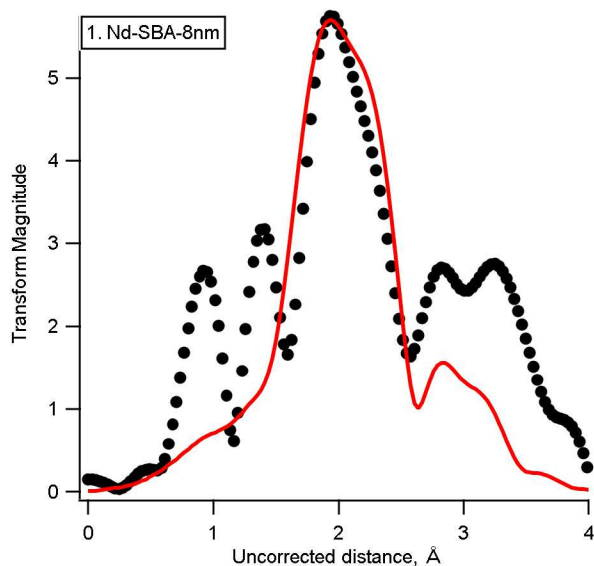
7.0 nm silica pores



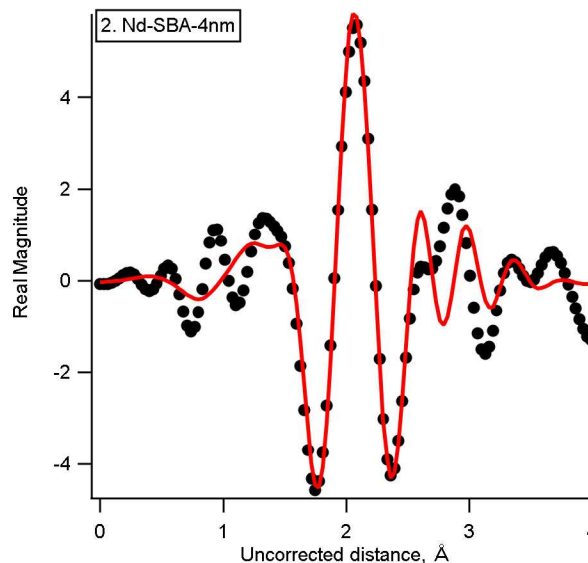
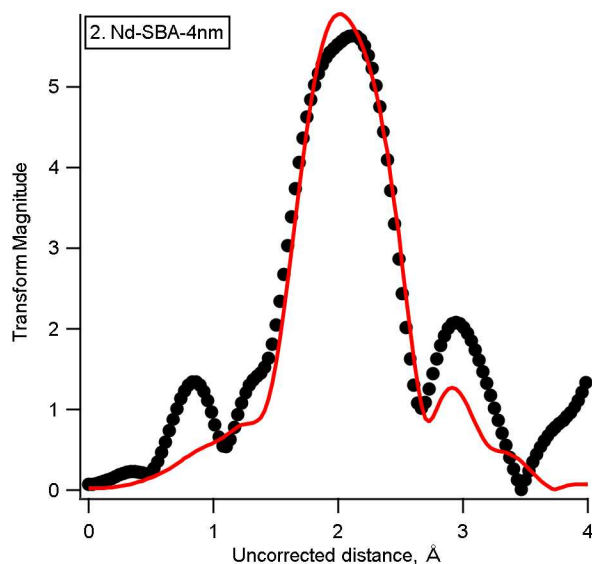
- Nd^{3+} , Tb^{3+} , and Lu^{3+} adsorption is exothermic on silica with 4nm and 7nm pores.
- Heat of adsorption depends on pore size.

			4nm Silica	8 nm Silica	Non- porous silica
	Mass (g/mol)	Radius (Å°)	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	-

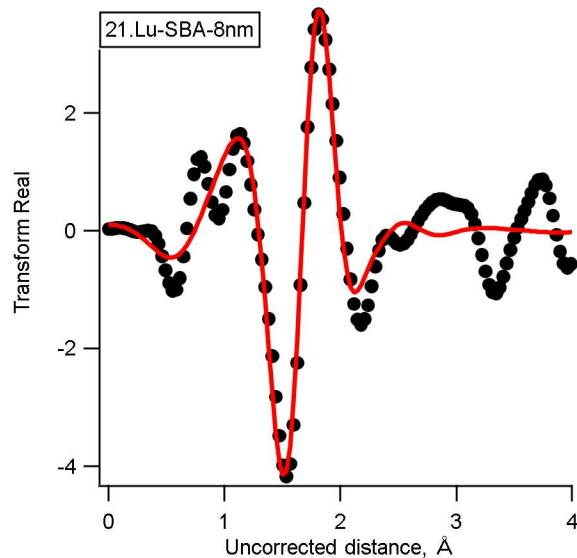
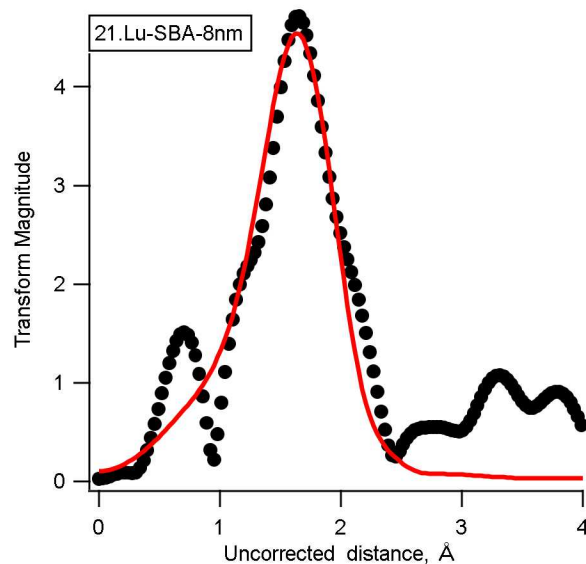
XAFS: preliminary results for neodymium



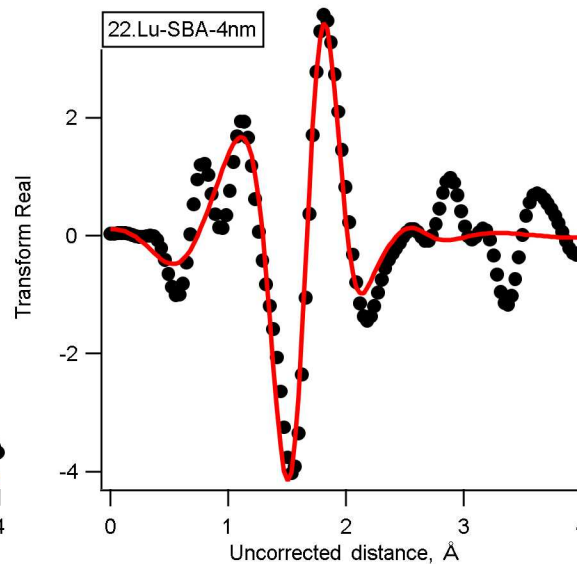
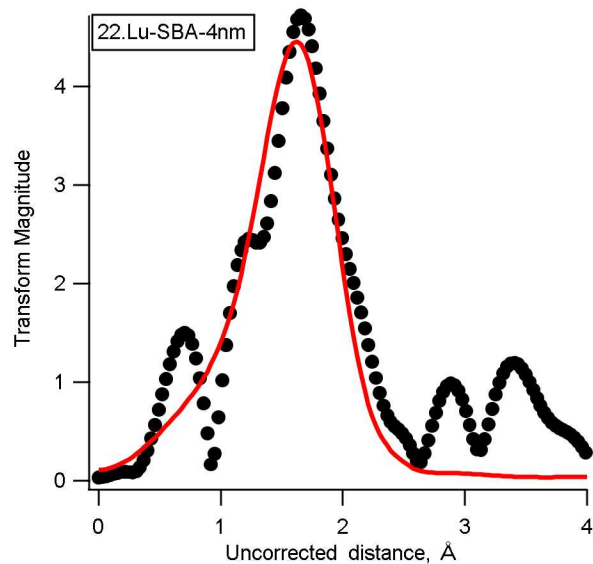
- 1st shell fit with two Nd-O distances;
- Nd-O bond length:
 $\text{SiO}_2 < 8\text{nm SBA} < 4\text{nm SBA}.$



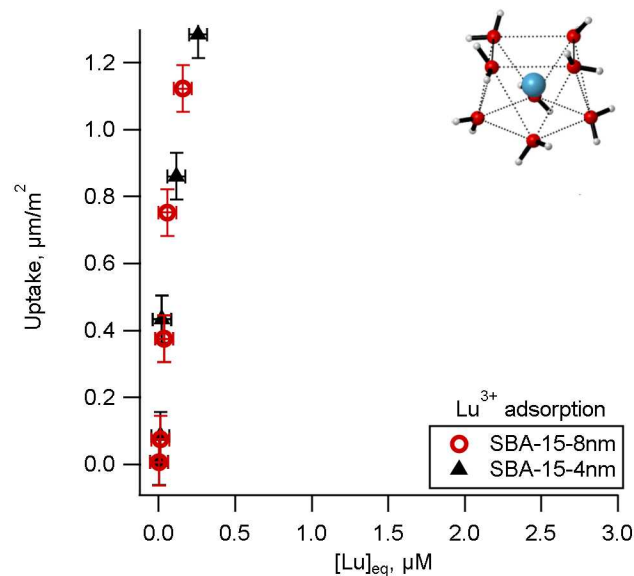
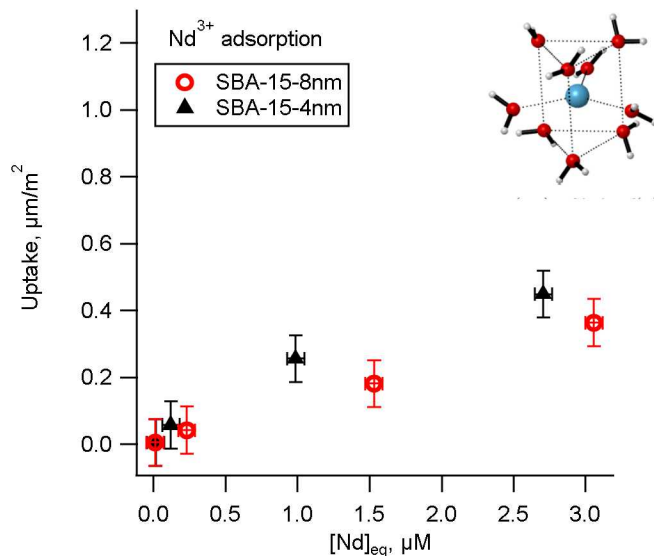
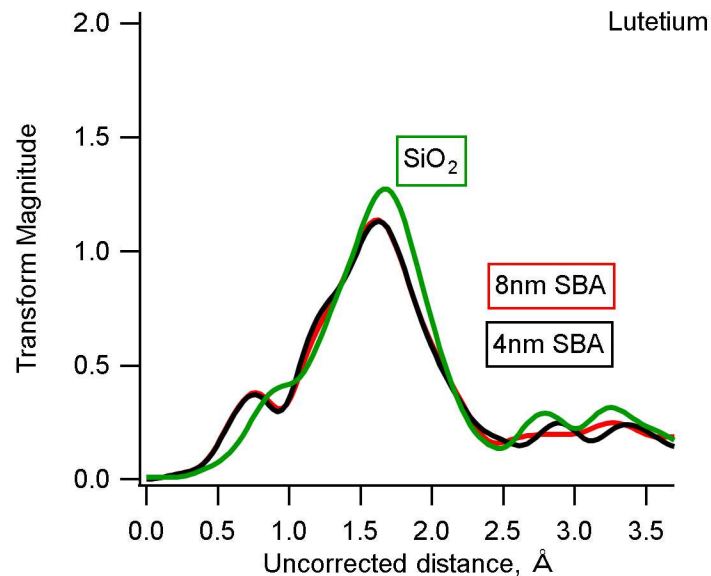
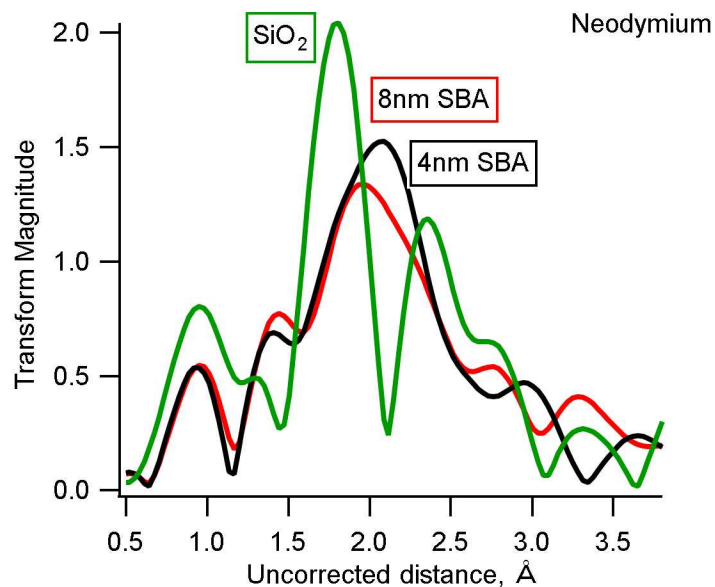
XAFS: preliminary results for lutetium



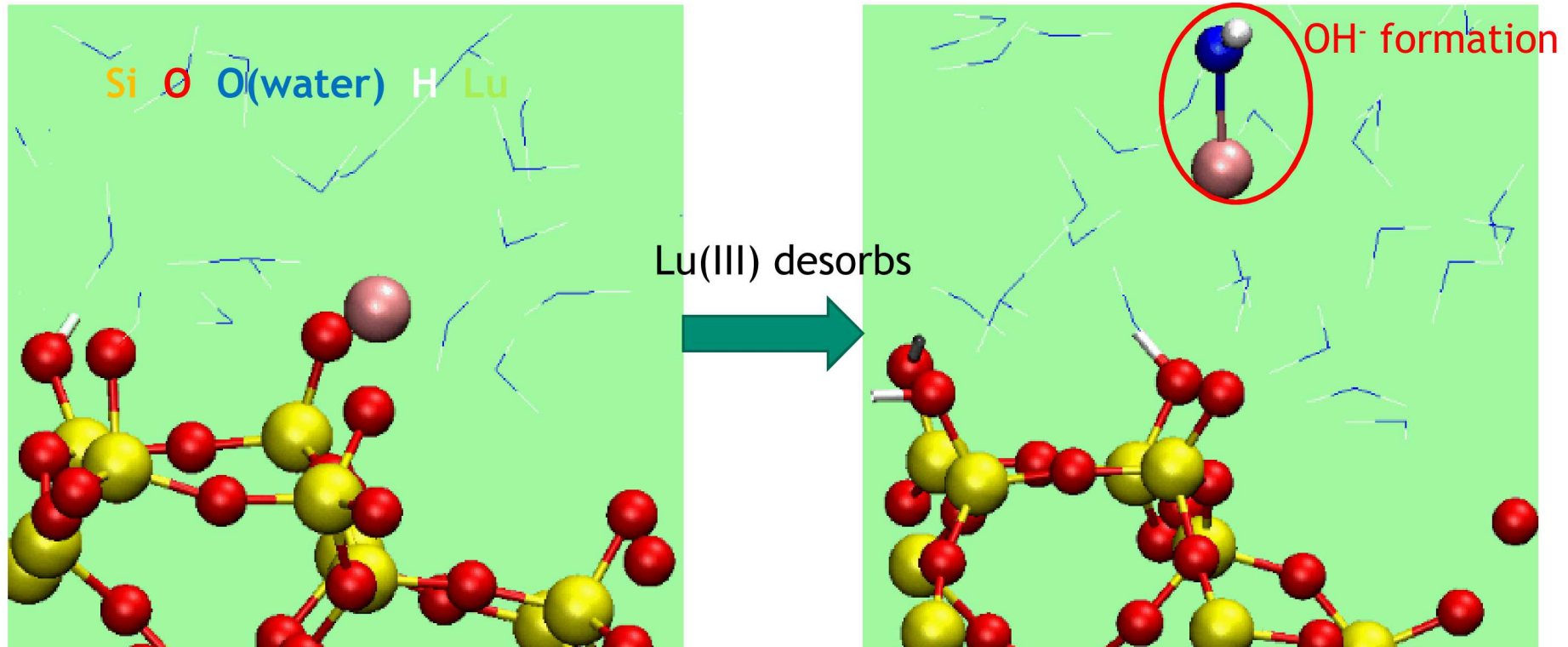
- 1st shell fit with one Lu-O distance;
- Same Lu-O bond length for non-porous SiO₂, and for SBA-15 with 4 nm and 8 nm pores.



XAFS: difference between Nd and Lu



Hydrolysis of H₂O molecule by lanthanides



- *ab initio* molecular dynamics (AIMD) simulations + umbrella sampling to force desorption;
- Lu(III) and Eu(III) desorption causes $\text{H}_2\text{O} + \text{SiO}^- \rightarrow \text{OH}^- + \text{SiOH}$;
- Inner-sphere adsorption is observed, with each lanthanide hydrolyzing one water molecule upon adsorption onto cristobalite surface.

Adsorption of lanthanides onto spatially-confined surfaces

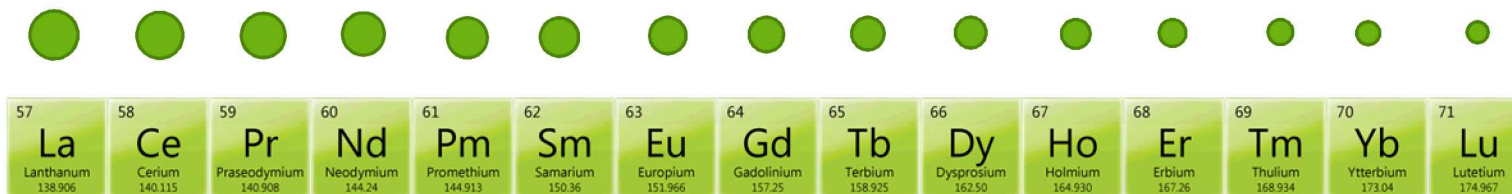
- Mass-dependent adsorption: with decreasing ionic radii, increased uptake.
- Pore-size dependency:

$\text{Cu}^{2+} \Delta G_{\text{H}}$ -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.

Size decreases across the series



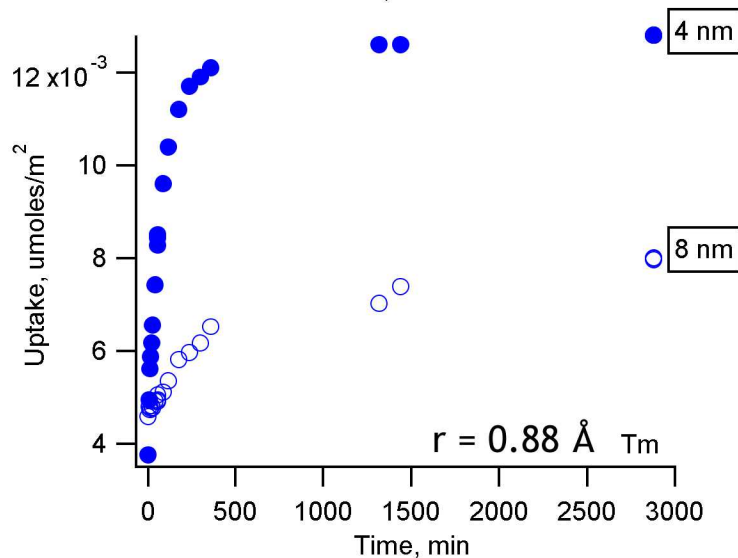
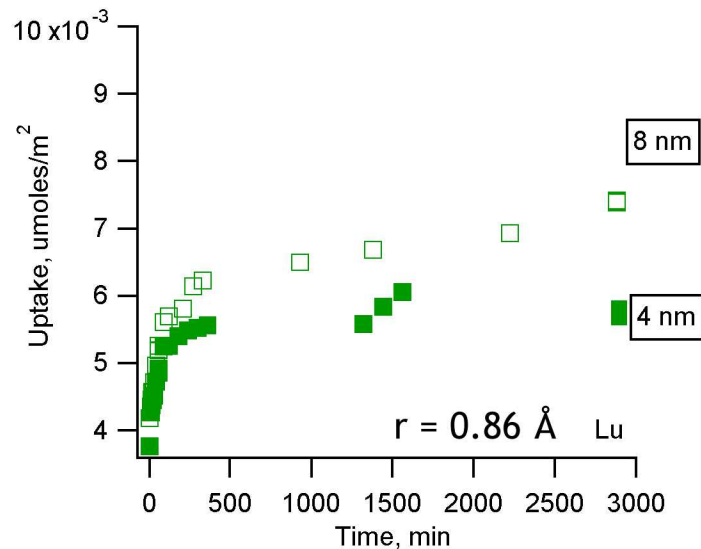
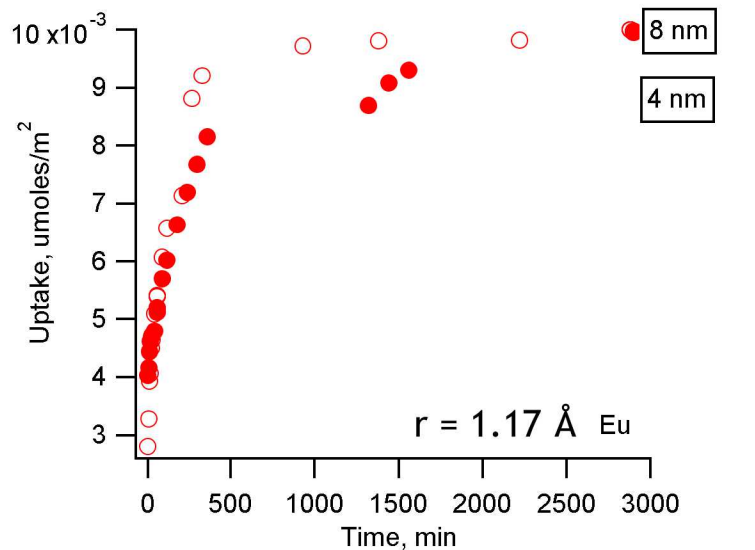
Lowest hydration energy

Highest hydration energy

Thank you.

Extra slides

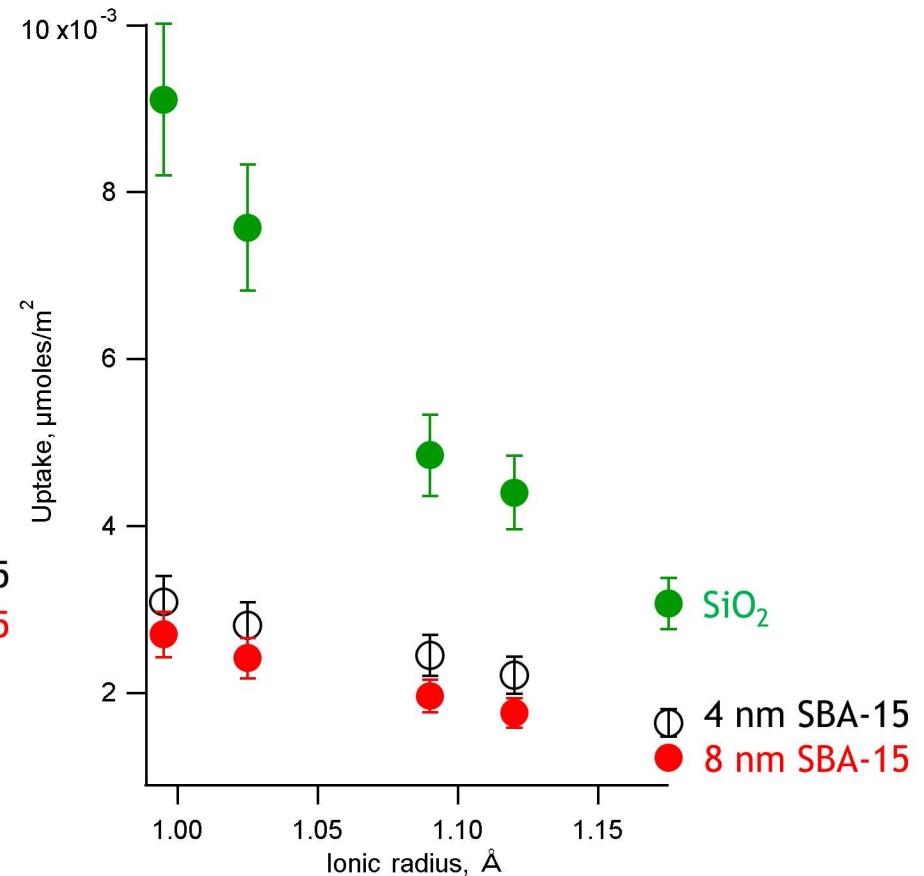
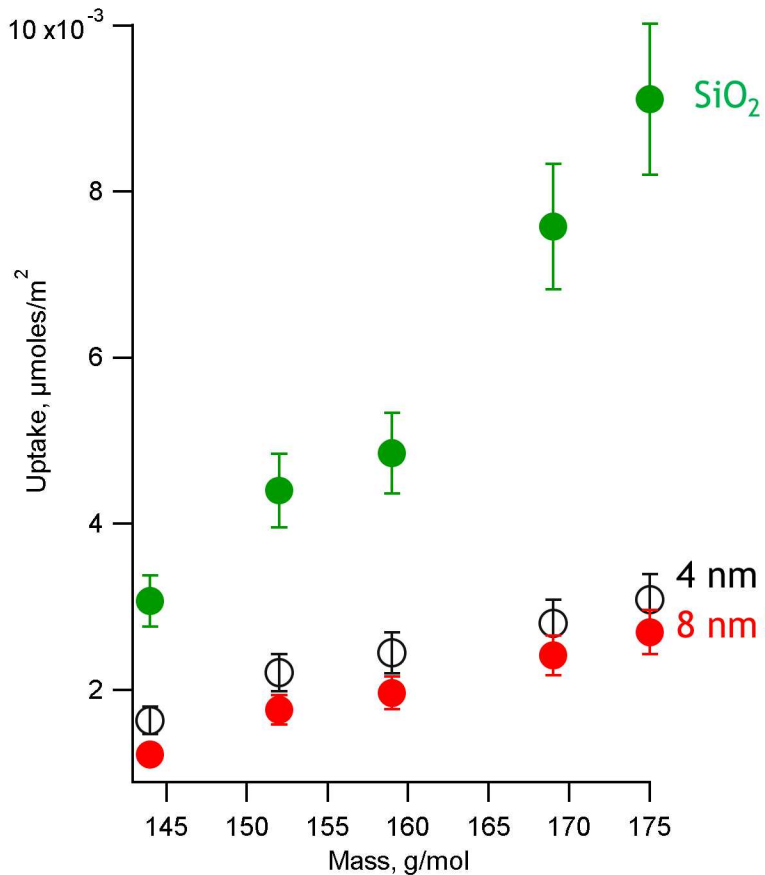
Results: Kinetics of adsorption



Preliminary results

- 2nd order reaction.
- For 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.

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 .