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.

SAND2020-5722C

Ab initio Molecular Dynamics Simulations of Rare Earth (III) Ions Desorption from Silica Surfaces

Kevin Leung and Anastasia Ilgen

Sandia National Laboratories

Thanks (or coauthors): Louise Criscenti, Jeffery Greathouse, Tuan Ho

TSRC Workshop on Interfacial Molecular and Electronic Structure & Dynamics
June 15-20, 2020 (Virtual Conference)

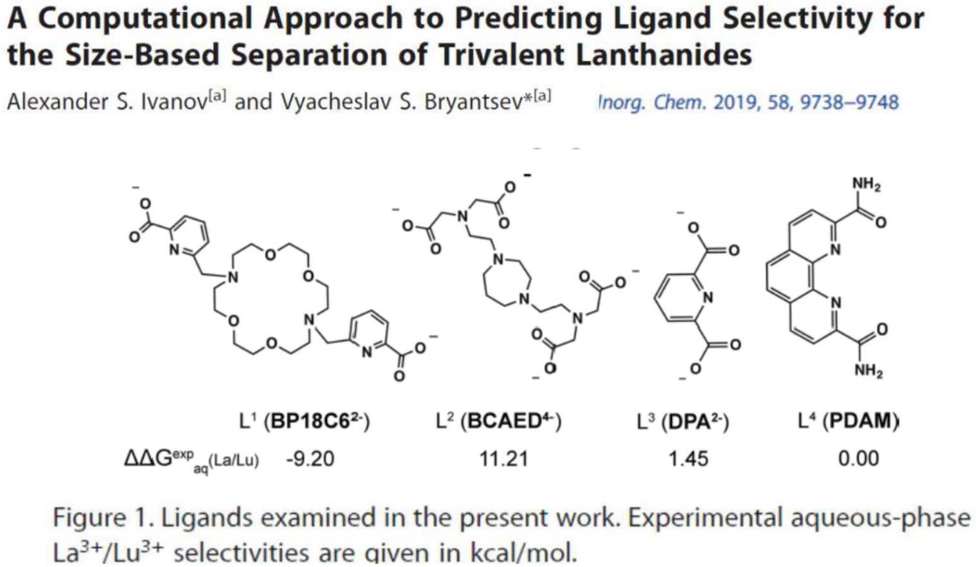
Sandia National Laboratories is a multimission laboratory managed and operated by National Technology and Engineering Solutions of Sandia, LLC, a wholly owned subsidiary of Honeywell International, Inc., for the U.S. Department of Energys National Nuclear Security Administration under contract DE-NA0003525. We acknowledge support from the U.S. DOE Office of Basic Energy Sciences, Division of Chemical Sciences, Geosciences, and Biosciences.

Sandia National Laboratories

Office of Basic Energy Sciences

Motivations

- Basic Science understanding to advance rare earth extraction, mining, separation techniques
- Rare earth (RE) elements critical for renewable energies and other technologies of interest to Department of Energy, due to unique magnetic properties
- Hard to separate RE (III+) in solution
- Much computational work done, e.g. on Re(III) solvation free energy
- but not with inorganic substrates



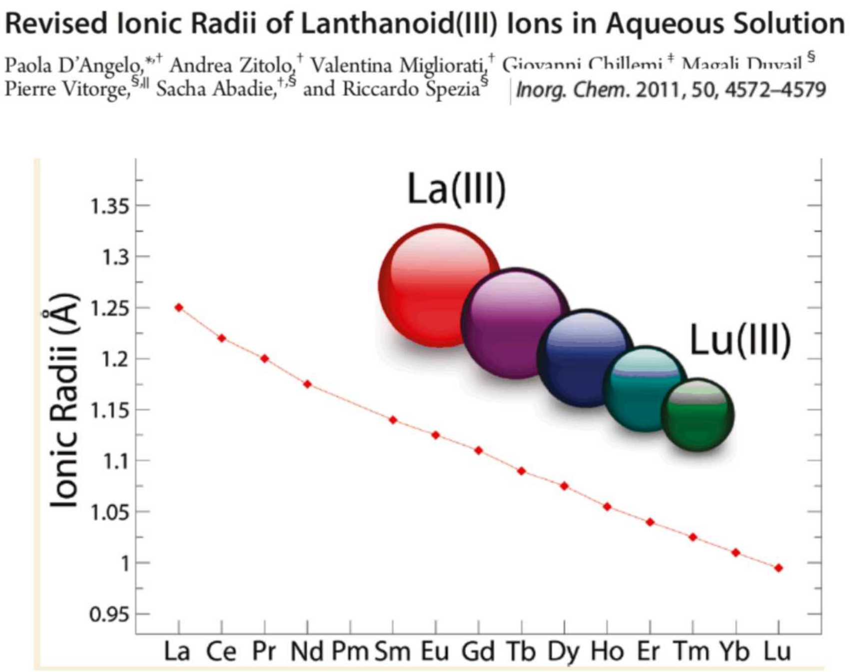
A Computational Approach to Predicting Ligand Selectivity for the Size-Based Separation of Trivalent Lanthanides

Alexander S. Ivanov[a] and Vyacheslav S. Bryantsev*[a] *Inorg. Chem.* 2019, 58, 9738–9748

	L^1 (**BP18C6^{2-}**)	L^2 (**BCAED^{4-}**)	L^3 (**DPA^{2-}**)	L^4 (**PDAM**)
$\Delta\Delta G^{exp}_{aq}$(La/Lu)	-9.20	11.21	1.45	0.00

Figure 1. Ligands examined in the present work. Experimental aqueous-phase La^{3+}/Lu^{3+} selectivities are given in kcal/mol.

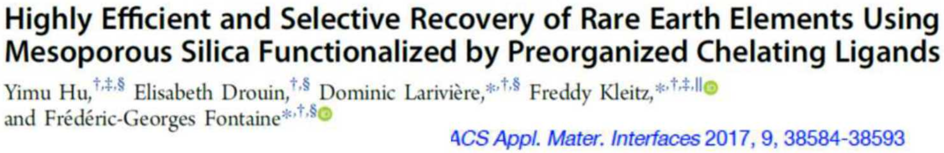
… modeling organic ligand-assisted separation



Revised Ionic Radii of Lanthanoid(III) Ions in Aqueous Solution

Paola D'Angelo,*† Andrea Zitolo,† Valentina Migliorati,† Giovanni Chillemi,‡ Magali Duvail,§ Pierre Vitorge,§,∥ Sacha Abadie,†,§ and Riccardo Spezia§ *Inorg. Chem.* 2011, 50, 4572–4579

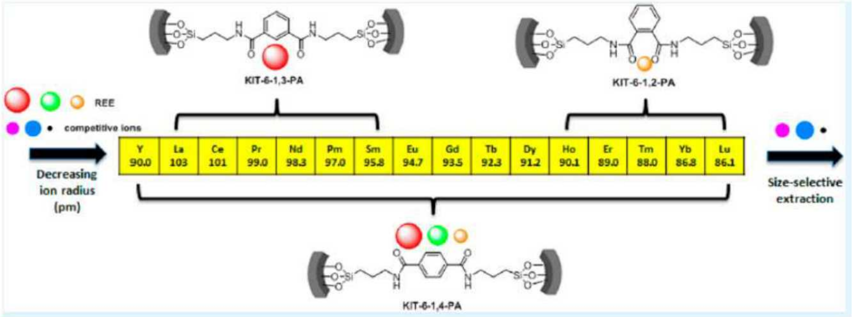
REE separation in silica pores/on silica surfaces



Highly Efficient and Selective Recovery of Rare Earth Elements Using Mesoporous Silica Functionalized by Preorganized Chelating Ligands

Yimu Hu,[†,‡,§] Elisabeth Drouin,[†,§] Dominic Larivière,[*,†,§] Freddy Kleitz,[*,†,‡,∥] and Frédéric-Georges Fontaine[*,†,§]

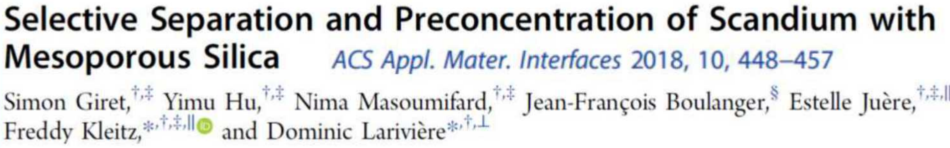
ACS Appl. Mater. Interfaces 2017, 9, 38584-38593



Y	La	Ce	Pr	Nd	Pm	Sm	Eu	Gd	Tb	Dy	Ho	Er	Tm	Yb	Lu
90.0	103	101	99.0	98.3	97.0	95.8	94.7	93.5	92.3	91.2	90.1	89.0	88.0	86.8	86.1

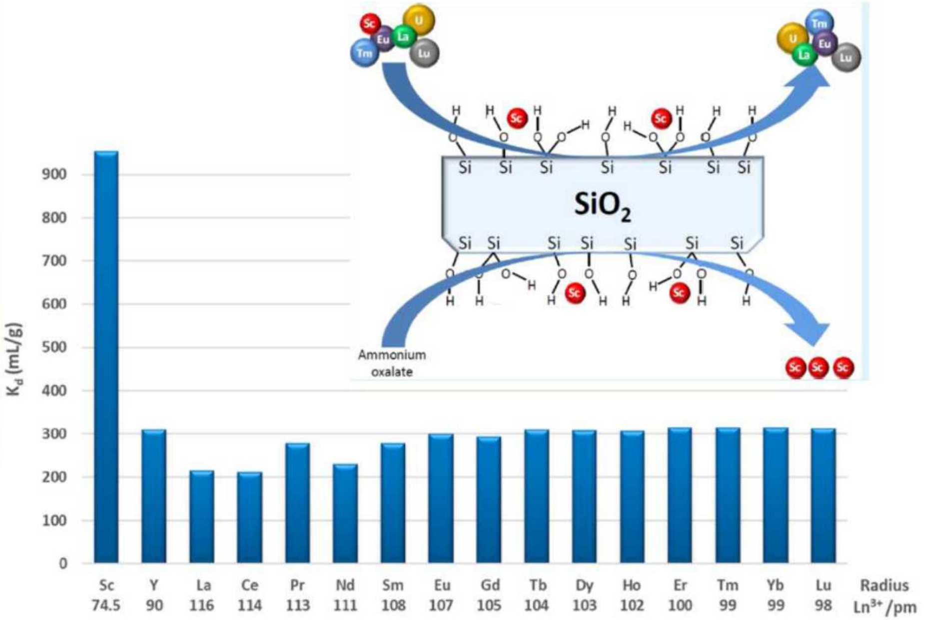
Silica pores functionalized with organic ligands

My Sandia colleague Dr. Anastasia Ilgen observes selectivity in bare silica pores at higher pH (patent filed, next slide)



Selective Separation and Preconcentration of Scandium with Mesoporous Silica *ACS Appl. Mater. Interfaces* 2018, 10, 448–457

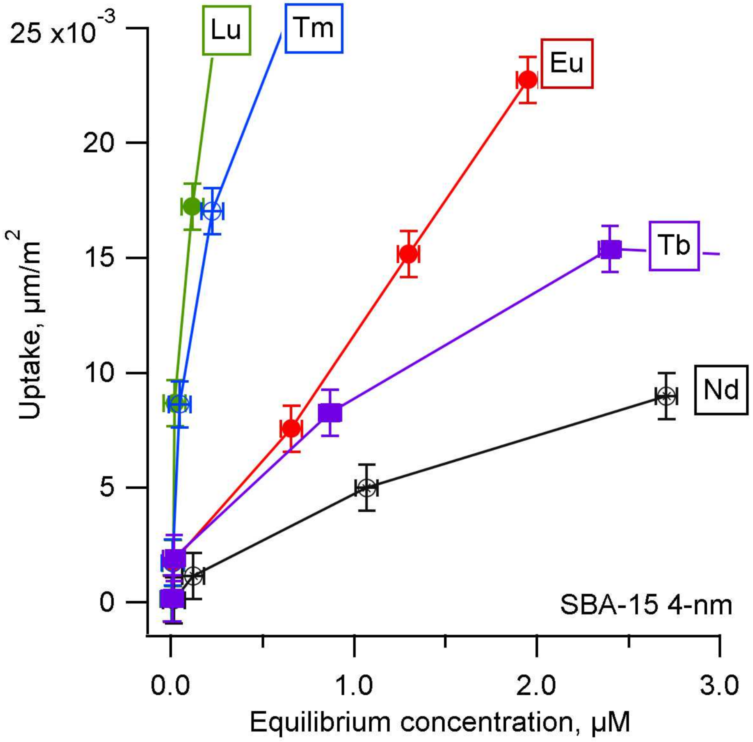
Simon Giret,[†,‡] Yimu Hu,[†,‡] Nima Masoumifard,[†,‡] Jean-François Boulanger,[§] Estelle Juère,[†,‡,∥] Freddy Kleitz,[*,†,‡,∥] and Dominic Larivière[*,†,⊥]

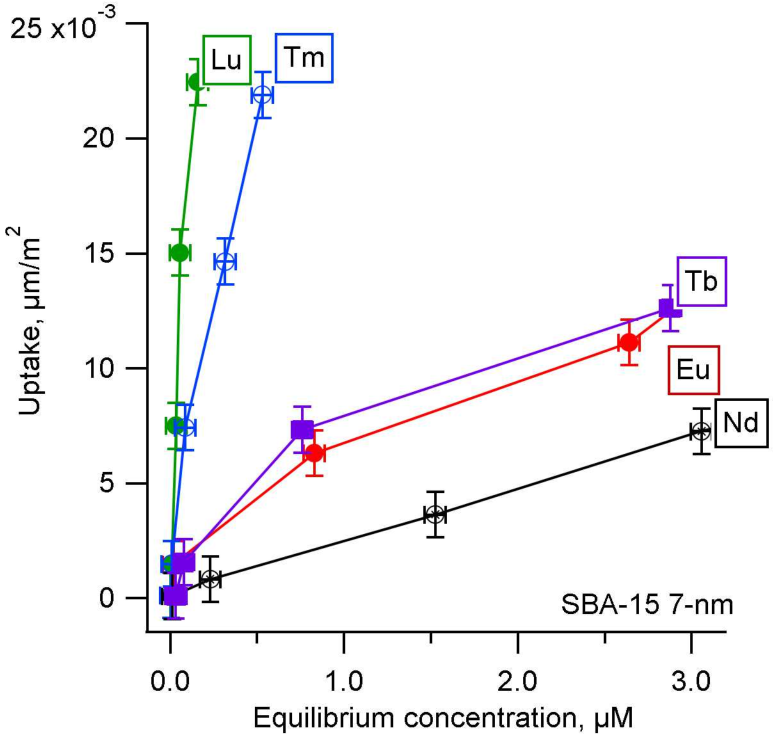


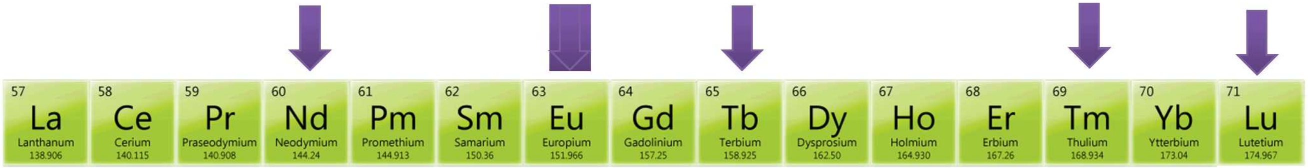
not functionalized: REE not much selectivity -- but this is at pH~4

Experimental Results: adsorption isotherms for porous silica

- **For both SBA-15 4-nm and SBA-15 7-nm with increasing Z uptake increased.**



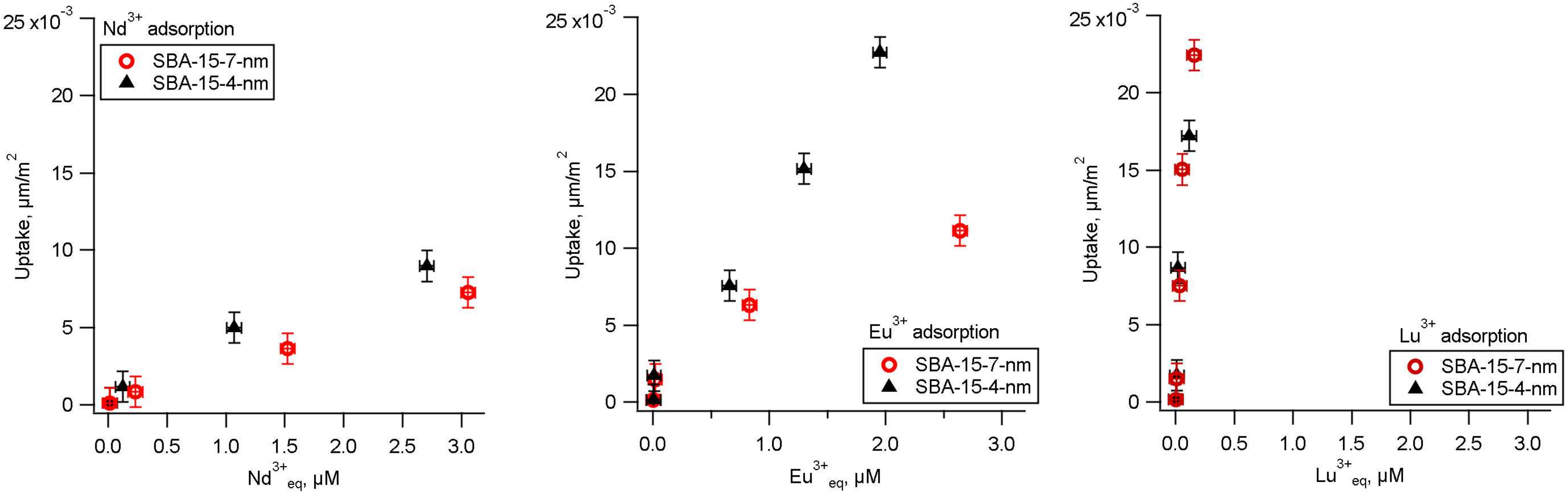


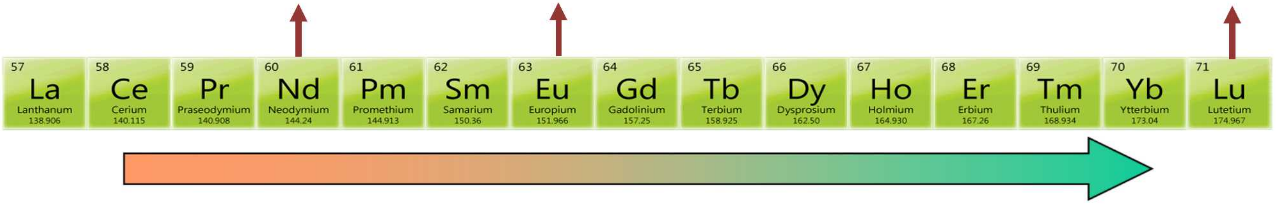


Ilgen, et al.
In prep.

Experimental Results: Pore-size (in)dependence

- Eu^{3+} uptake is consistent with Cu^{2+} results: higher uptake on 4-nm, compared to 7-nm pores.
- Tm^{3+} and Lu^{3+} uptake appears independent of pore size.

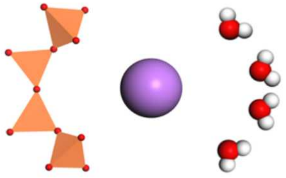




Weakly Hydrated

Strongly Hydrated

Mineral-Ion
Interactions Dominate

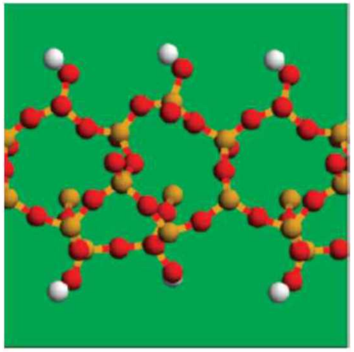


Water-Ion
Interactions Dominate

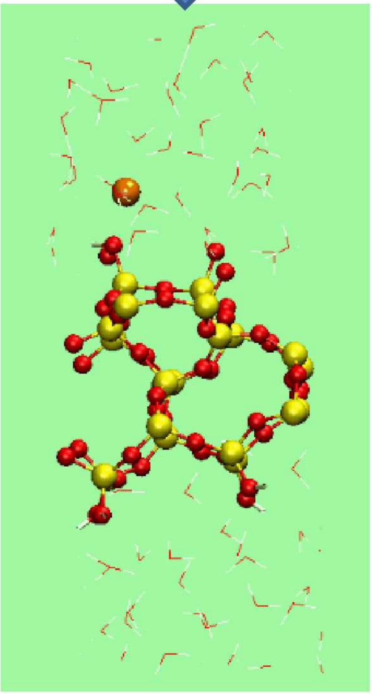
Ilgen, et al.
In prep.

Computational Model and method

reconstructed (001)



add water, cation



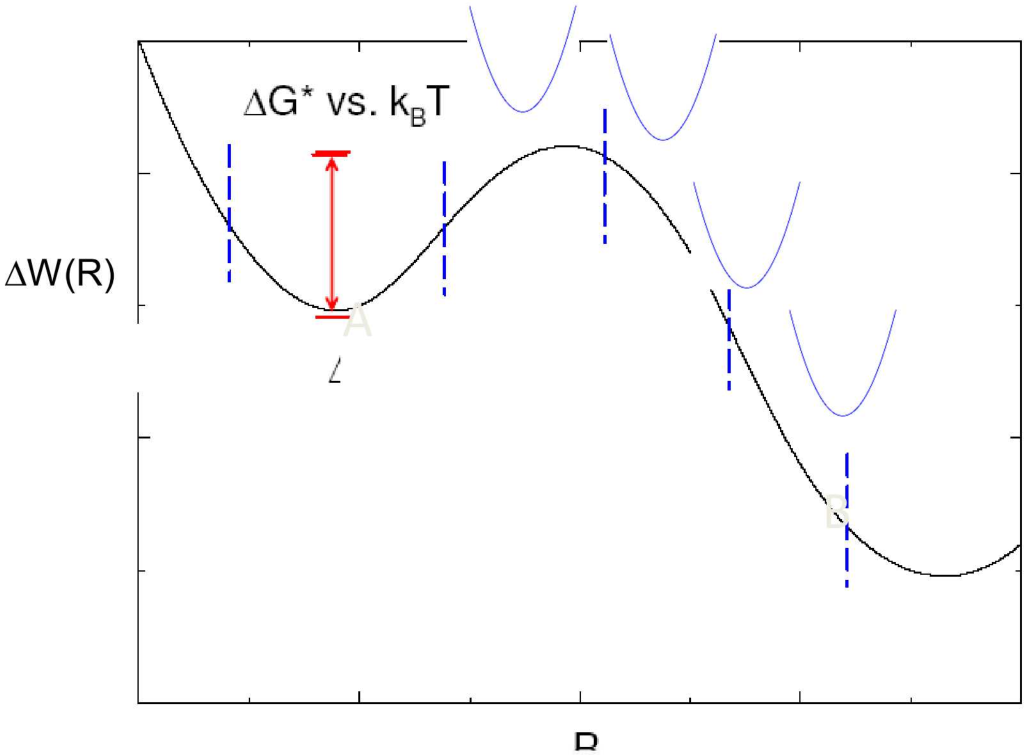
- focus on silica, use model with single binding site as benchmark
- use previous reconstructed β-cristobalite (001), pKa = 7.0 – 8.1
- ~4 SiOH groups per nm^2, agree with measurements
- DFT/PBE, 14x14x26 A^3 simulation cell, Γ-point sampling

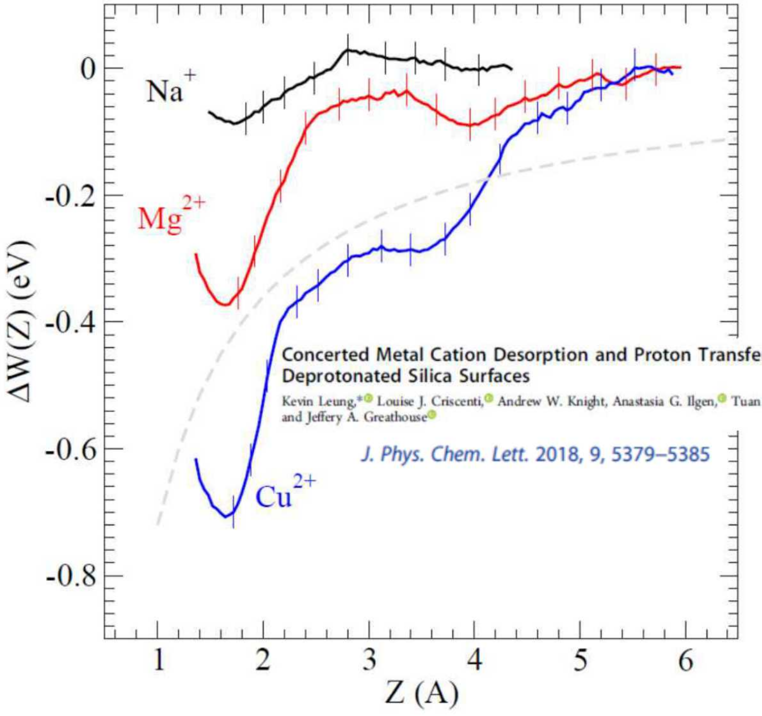
  (larger cell than in Leung et al, 2009) *J. Am. Chem. Soc.*, **2009**, *131*, 18358
- T=400 K, umbrella sampling
- One REE^{3+} in each simulation cell, ~350 ps total each
- 3 SiO$^-$ group to keep charge neutrality
- Qualitatively compare with measurements

*important to have only one unique binding site; most mineral surfaces have cation multiple binding sites, hard to get clean results, e.g., Leung & Criscsenti, J. Phys. Condens. Matter 29, 365101 (2017)

Potential of Mean Force is the way to calculate barriers/exothermicity in liquids

$\Delta W(R) \sim -k_BT \ln [P(R)]$

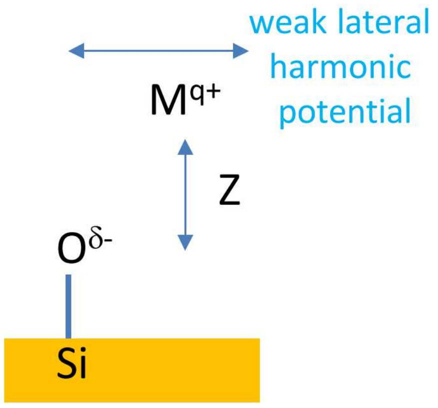




Concerted Metal Cation Desorption and Proton Transfer on Deprotonated Silica Surfaces

Kevin Leung,* Louise J. Criscenti, Andrew W. Knight, Anastasia G. Ilgen, Tuan A. Ho, and Jeffery A. Greathouse

J. Phys. Chem. Lett. 2018, 9, 5379–5385

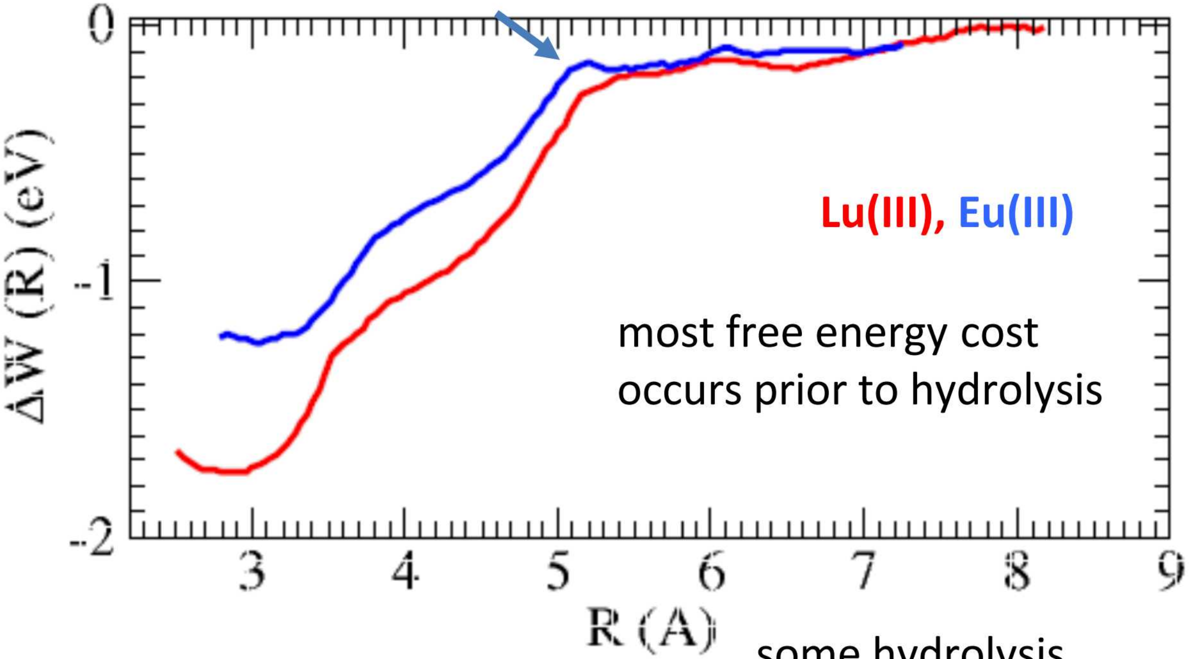


desorption free energy: $\Delta G_{\rm ads}/k_{\rm B}T = -\log\{\int_\Omega d\Omega \exp[-\Delta W(Z)/k_{\rm B}T]/(V_o)\}$

Na$^+$: +0.13 +/- 0.03 eV (unbound)
Mg^{2+}: -0.14 +/- 0.05 eV
Cu^{2+}: -0.47 +/- 0.07 eV

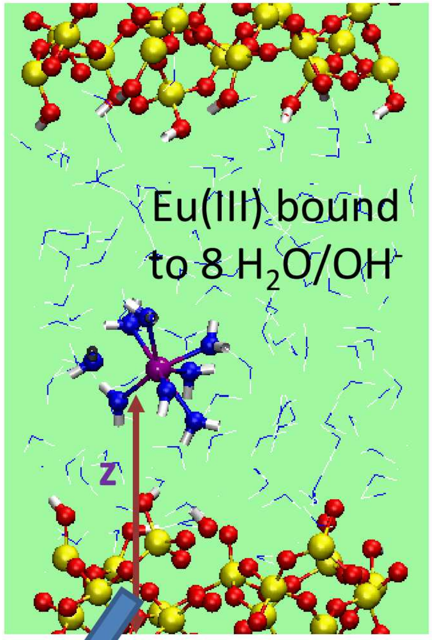
Free energy change as RE(III) desorbs

Not fully converged



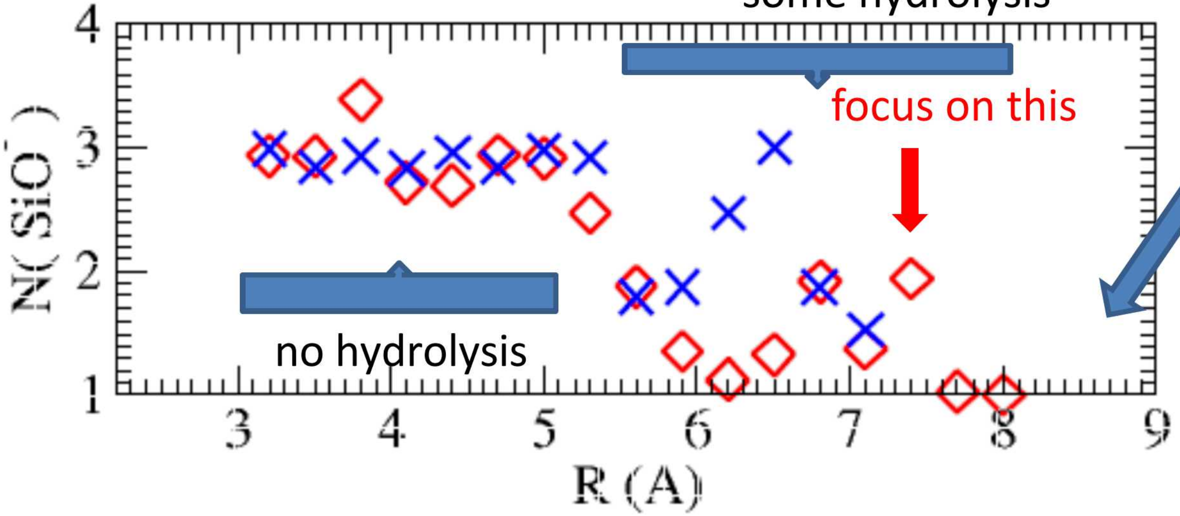
Lu(III), Eu(III)

most free energy cost occurs prior to hydrolysis



Eu(III) bound to 8 H_2O/OH^-

some hydrolysis

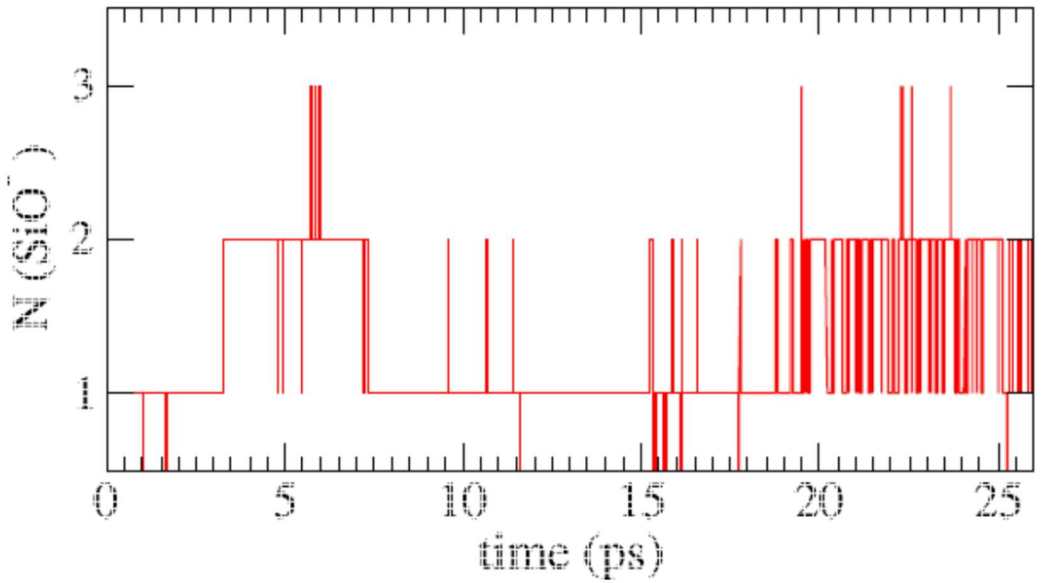


focus on this

no hydrolysis

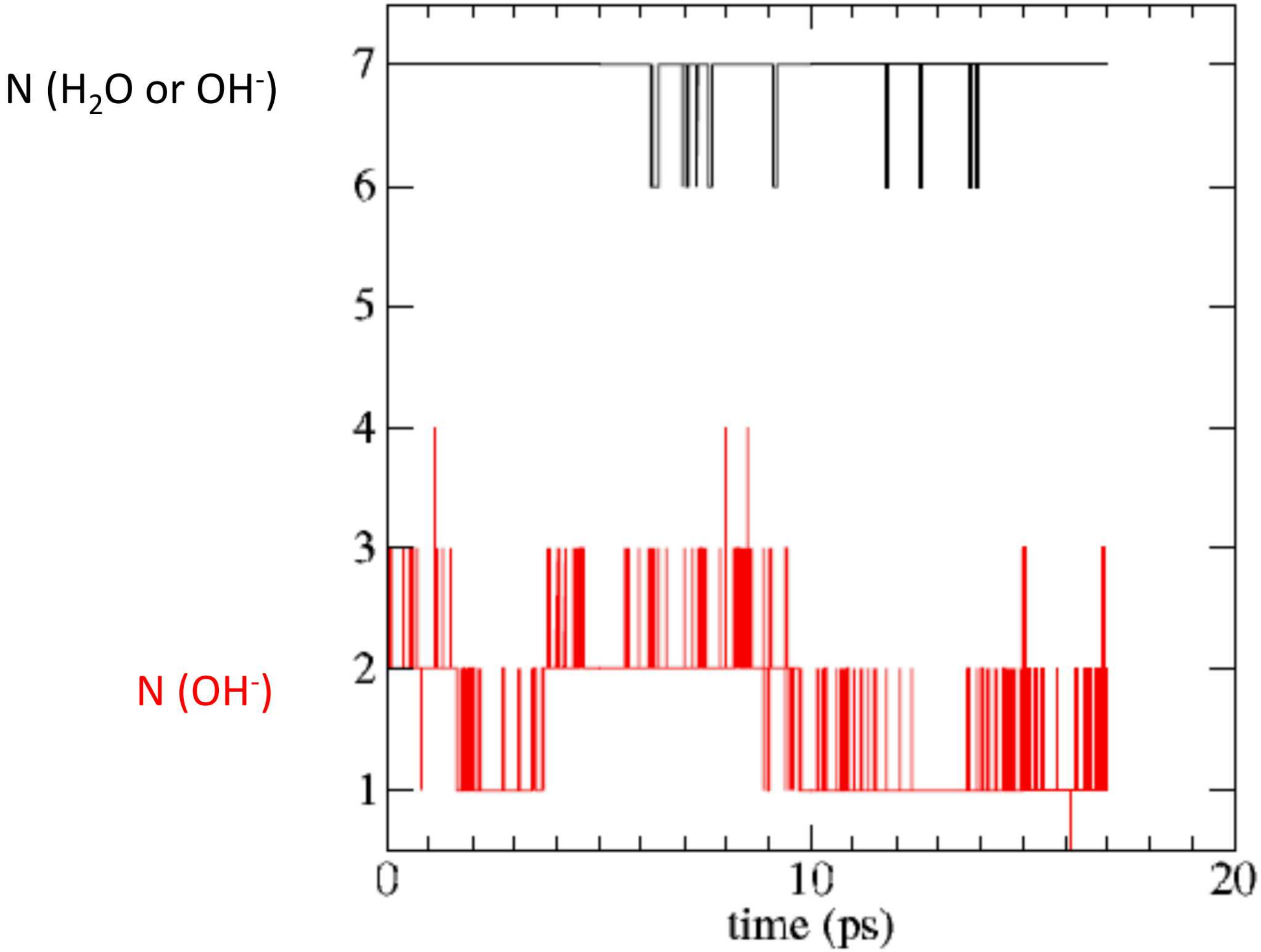
1-3 SiO^- group, meaning 2, 1, or 0 H_2O coordinated to Lu/Eu hydrolyzed

Protonation Dynamics in one sampling window



- Fast Grotthuss protonation/deprotonation on SiOH groups
- accompanied by hydrolysis of RE(III)$(H_2O)_n(OH^-)_m$
- Experimentally, counter ions (e.g., Cl^-) play some charge-neutrality role
- e.g., RE(III)$(H_2O)_n$ + Cl^- -> RE(III) $(H_2O)_n(Cl^-)$
- This is difficult to model on AIMD time scales because Cl^- moves slowly.
- pH of AIMD simulation cell not known precisely, but is > 7 (pKa of our SiOH model)

Water dynamics in one sampling window



- Total number of O atoms around Lu(III) (from water or hydroxides) is constant at 7
- Total number of deprotonated water (i.e., hydroxide anion) can vary

Conclusions

- Dr. Anastasia Ilgen’s work shows smaller REE cations selectively adsorbs in silica pores
- performed AIMD potential-of-mean-force of Re(III) cation desorption from …
- … simple but relevant, partly deprotonated silica surface model, pKa ~ 7-8.1 (but pH larger?)
- Predict selective adsorption of Lu(III) over larger Eu(III) cations
- Need larger simulation cell than previous AIMD simulations for Na^+, Cu^{2+}
- Onset of hydrolysis of H2O coordinated to RE(III) correlated energy cutoff
- Useful knowledge for future classical force fields MD (where no hydrolysis allowed)
- Protonation kinetics reasonably fast