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NERSC Future Challenges Workshop

Case Study: Computational Studies in Molecular Geochemistry

Andrew R. Felmy
Eric J. Bylaska
Sebastien Kerisit
Anne Chaka

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U.S. DEPARTMENT OF ENERGY | Office of Science | Basic Energy Sciences

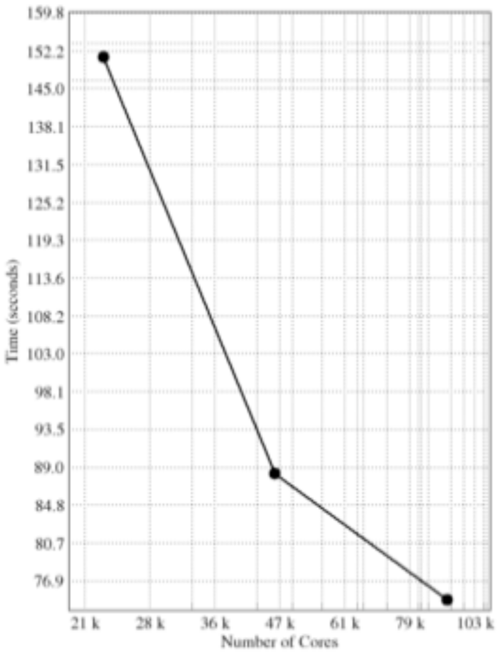
Computational Studies in Molecular Geochemistry

Supports Project 56674 : “Molecular Mechanisms of Interfacial Reactivity in Near Surface and Extreme Geochemical Environments”

- Project composed of three main theme areas
  - Electron Conduction/Transfer in Minerals
    - **Rosso**, Ilton (**Bagus**), Zachara
  - Mineral/water film nucleation and growth
    - **Felmy (Dixon)**, **Kerisit**, De Yoreo
  - Theory and Model Development
    - **Bylaska, Chaka, Weare**
  - **Large programmatic investment in computation**
    - **Unique Capability for the Development of new algorithms and code**

Development of New Simulation Tools (Strategy)

Develop Algorithms that scale to +100K CPUs (Address new science)

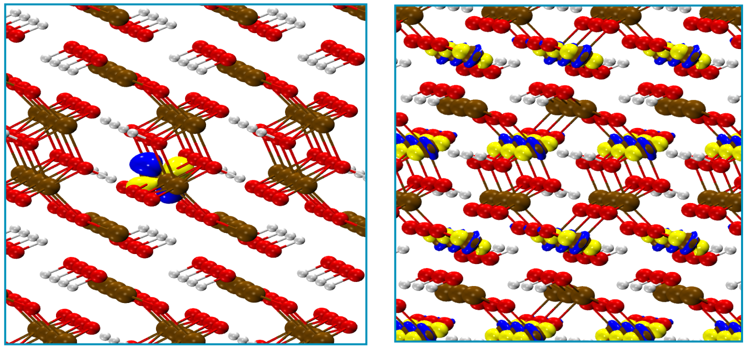


Bylaska, Eric J., Kiril Tsemekhman, Scott B. Baden, John H. Weare, and Hannes Jonsson. "Parallel implementation of γ-point pseudopotential plane-wave DFT with exact exchange." Journal of Computational Chemistry 32, no. 1 (2011): 54-69.

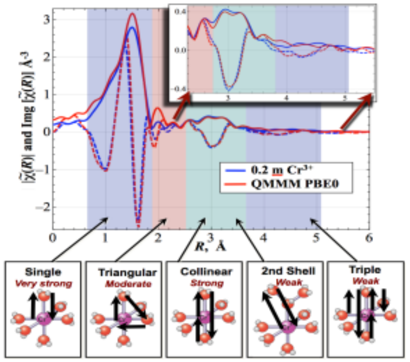
Bylaska, Eric., Kiril Tsemekhman, Niranjan. Govind, and Marat Valiev. "Large-scale plane-wave-based density-functional theory: formalism, parallelization, and applications." *Computational methods for large systems: electronic structure approaches for biotechnology and nanotechnology. Wiley, Hoboken* (2011): 77-116.

Develop models that are more physically realistic

Electron localization on iron oxides



Improved understanding of experimental measurements at unprecedented levels of detail



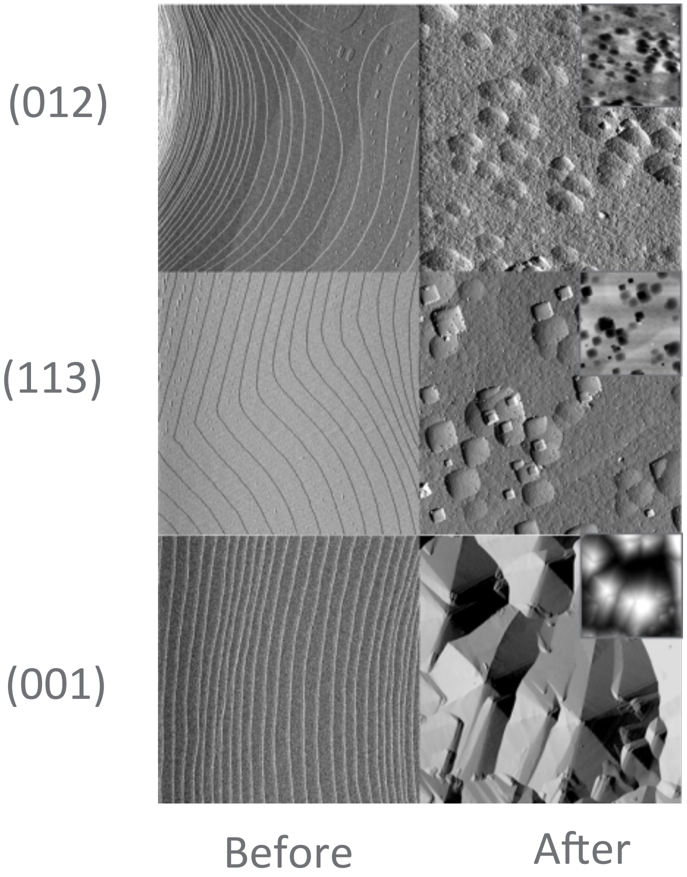
The close agreement between the Hybrid DFT simulation of observed XAFS spectra for the Cr^{3+} ion

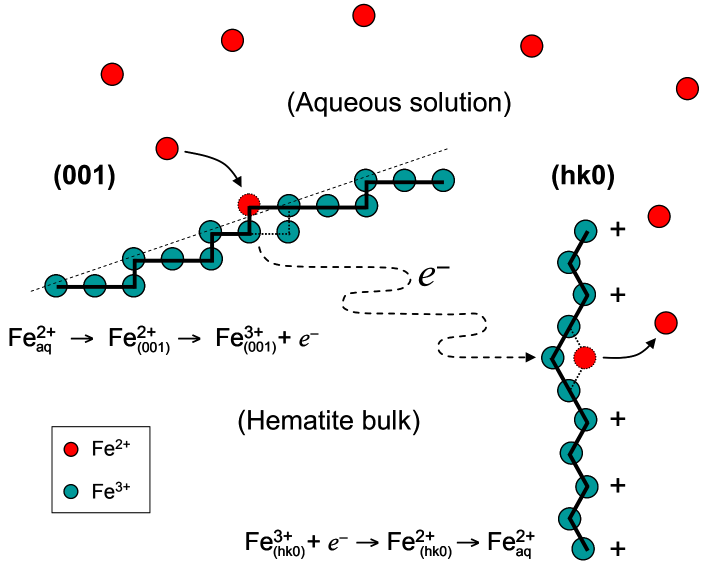
Fulton, John L., Eric J. Bylaska, Stuart Bogatko, Mahalingam Balasubramanian, Emilie Cauët, Gregory K. Schenter, and John H. Weare. "Near-Quantitative Agreement of Model-Free DFT-MD Predictions with XAFS Observations of the Hydration Structure of Highly Charged Transition-Metal Ions." *The Journal of Physical Chemistry Letters* 3, no. 18 (2012): 2588-2593.

Electron Conduction/Transfer

(Need for highly accurate models to interpret experiments)

Hematite (001) Reductive Dissolution by Fe(II) + Oxalate





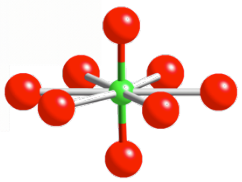
Reductive dissolution of hematite in 1mM $FeCl_2$ + 10mM oxalic acid for 12 hrs at 75ºC. Each image is 10×10 μm^2

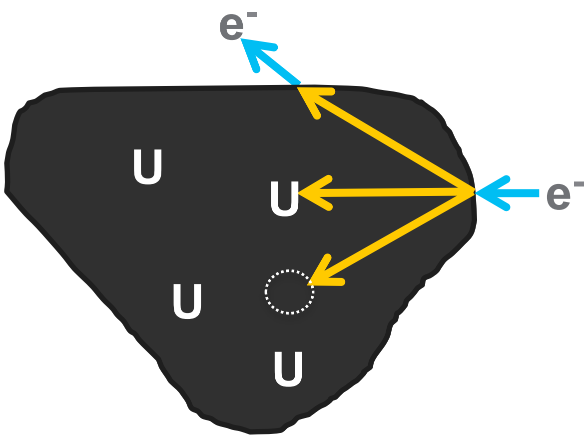
Yanina and Rosso (2008) Science

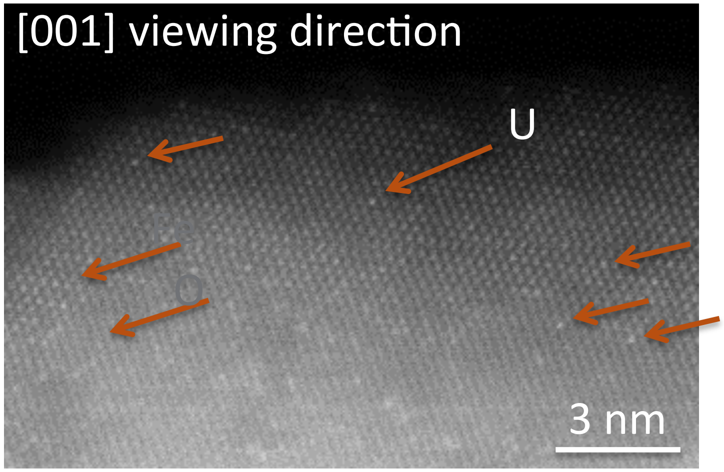
Key Question: How does electron conduction impact the oxidation/reduction of substituted ions?

U Reduction in Iron Oxides

- **Previous calculations indicate that electron conduction is rapid**
- **Rate limiting steps are related to structural re-arrangement of the incorporated redox active component and/or charge compensation mechanisms**
  - Ex:U(VI)→U(V)→U(IV)
    - U(VI) and U(V) uranyl bond
  - Reduction of U^{VI} to U^{IV} can be inhibited or slowed, and “hang up” at U^{V} by incorporation of U in different coordination environments
- **Computational Challenges:**
  - Many possible structural environments and many possible charge compensation mechanisms
    - Ex: $U^{6+} \rightarrow Fe^{3+} + 3H^{+}$







TEM image of U incorporated into hematite

Plane-wave DFT Calculations

Sebastien Kerisit and Eric Bylaska

Energy minimizations and Car-Parrinello AIMD simulations.

GGA-PBE and PBE0 exchange-correlation potentials.

Generalized norm-conserving pseudo-potentials.

Plane-wave cutoff energy = 50 Ry

Car-Parrinello AIMD

Temperature = 300 K (Nosé-Hoover)

Integration time step = 0.12 fs

Electronic fictitious mass = 750 a.u.

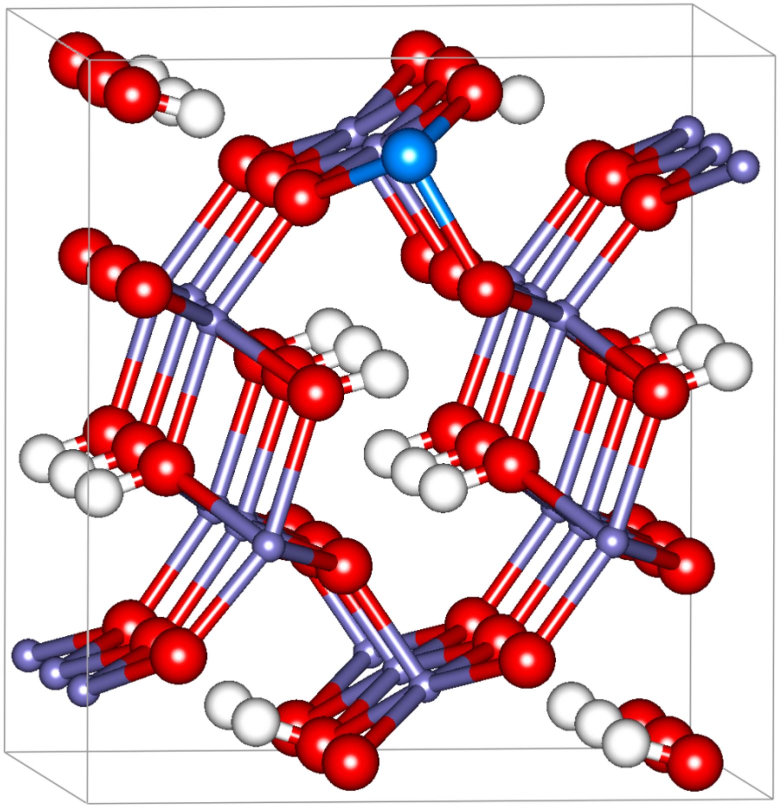
U incorporation in goethite (α-FeOOH)

U(IV), U(V), U(VI) substituted for Fe(III)

Supercell: 24 FeOOH units ~ 4 mol% U

Charge compensation schemes (CCS)

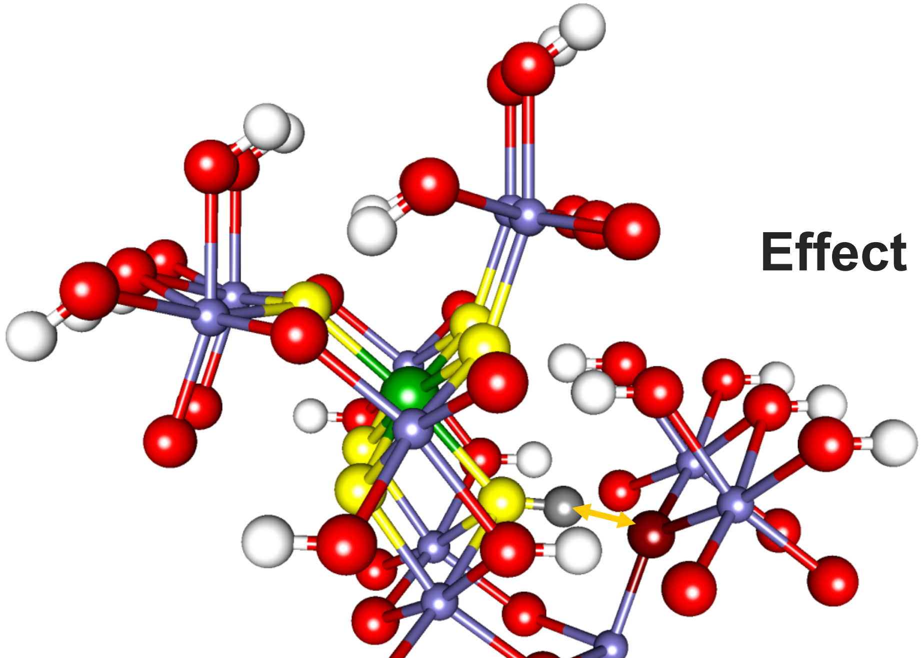
U	Electrons (=insertion as neutral U atom)
V	Creation of iron vacancies
H	Deprotonation of hydroxyl groups



U(VI)-3H incorporation in goethite

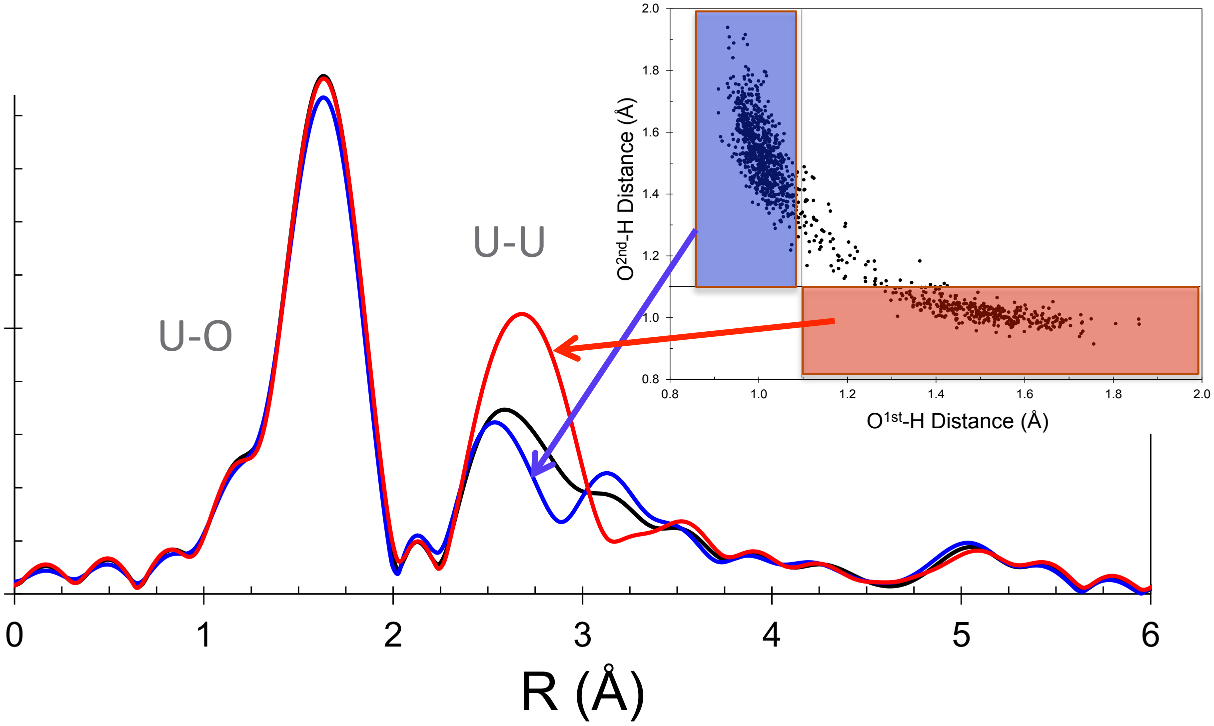
U – large blue
Fe – small purple
O -red

Effect of proton shuttling on FT magnitudes



Experimental measurements are becoming increasingly sensitive to the molecular level structure.

Need accurate computational models to interpret



300 K AIMD: Combining U(V) and U(VI)

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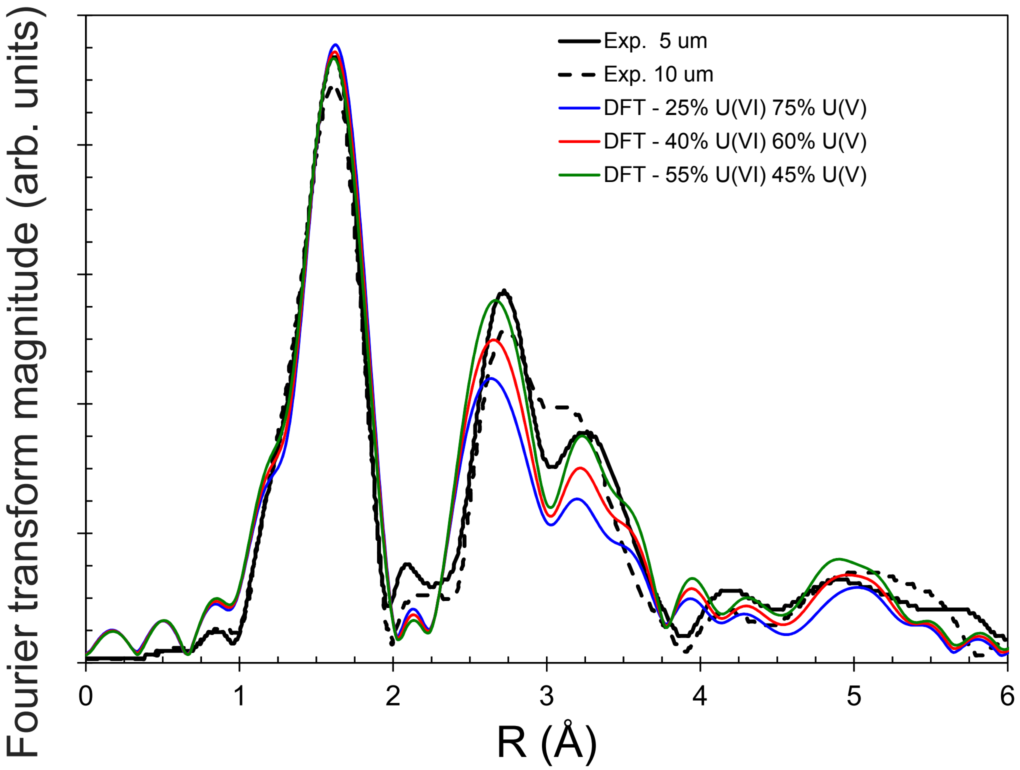
- U(V) + U(VI) with deprotonation CCS
  - ~50% U(VI) and 50% U (V).
  - Good agreement with XPS
- **First use of EXAFS to determine U(V) oxidation state**
  - **Increased sensitivity allows determination of U oxidation states at geochemically important concentrations**
- Requires accurate computational models



Future Challenges

Simulation of Reaction Paths

Ex: Mineral/Water Film Nucleation and Growth
(Need for large scale simulations)

Mineral/Water Film Nucleation and Growth

- Originated from studies of carbon dioxide sequestration in geochemical systems

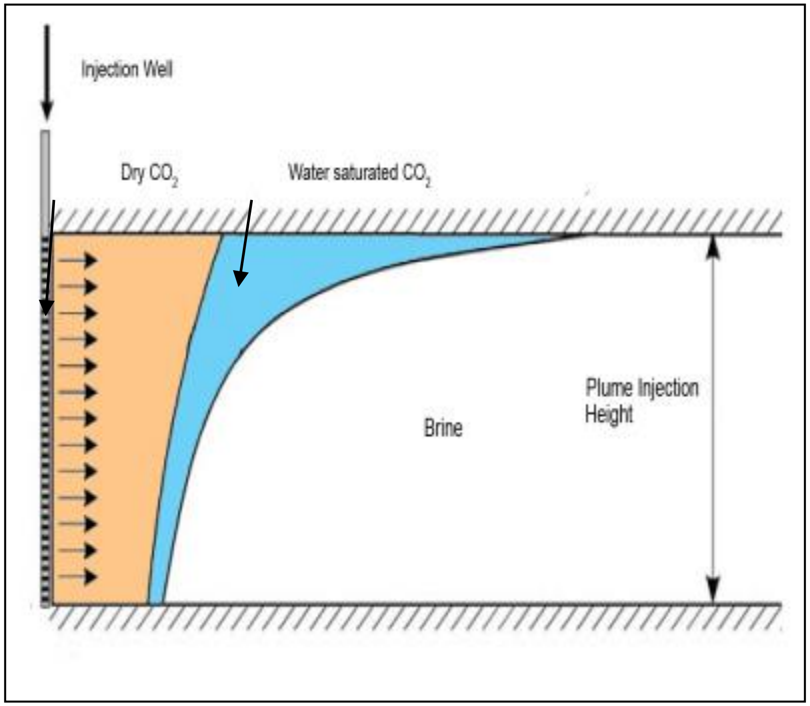
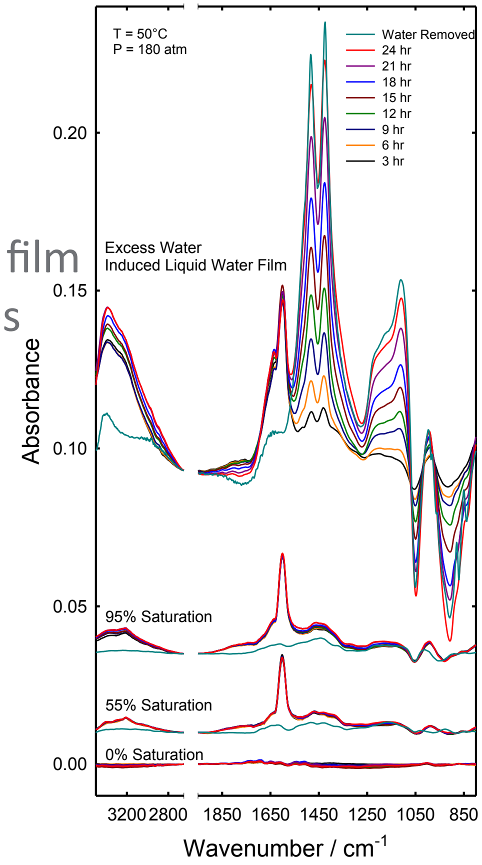


Figure 1. Diagram showing a typical plume of injection dry CO_2. Adapted from Nordbotten and Celia (2006).

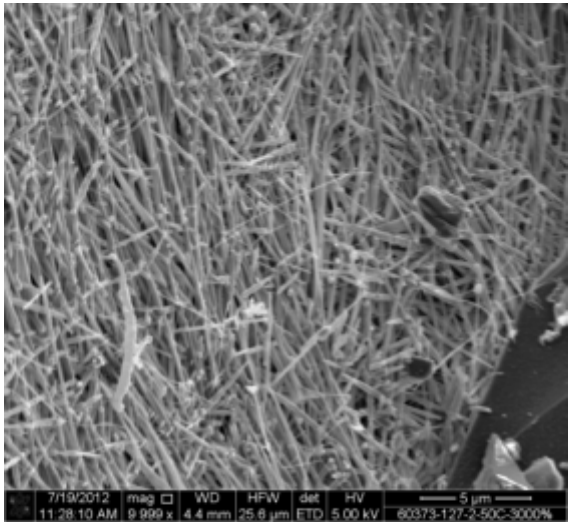
Water saturated CO_2 forms a water film on mineral surfaces



Loring et al. 2010

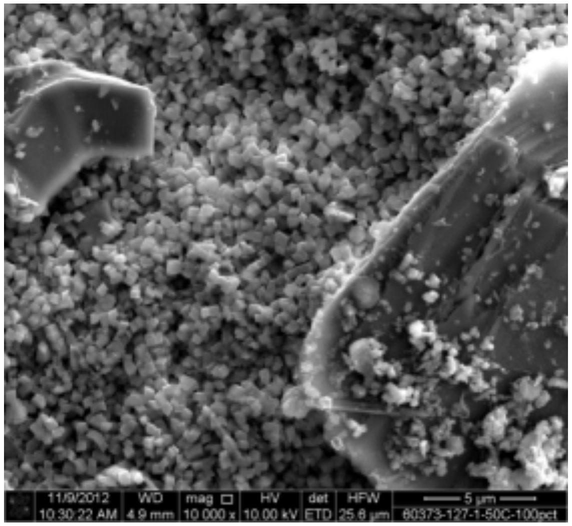
Unique Reactivity

Ex: Forsterite reactivity in supercritical CO_2 at 90 atm and 50°C



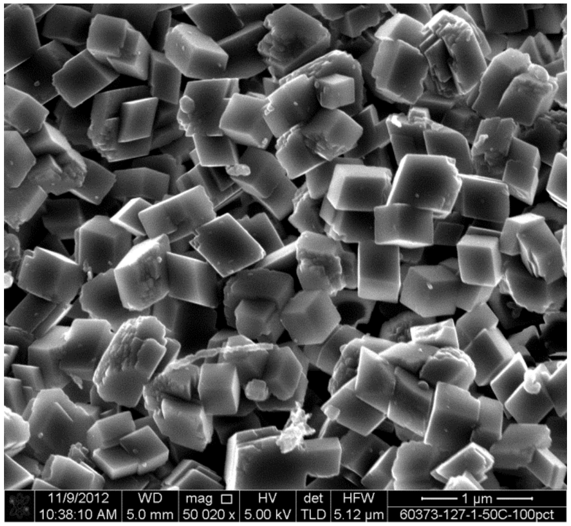
56 days liquid water
(nesquehonite $MgCO_3{\cdot}3H_2O$)

Liquid water placed in contact with forsterite



56 days H_2O-saturated 5µm image
(magnesite)

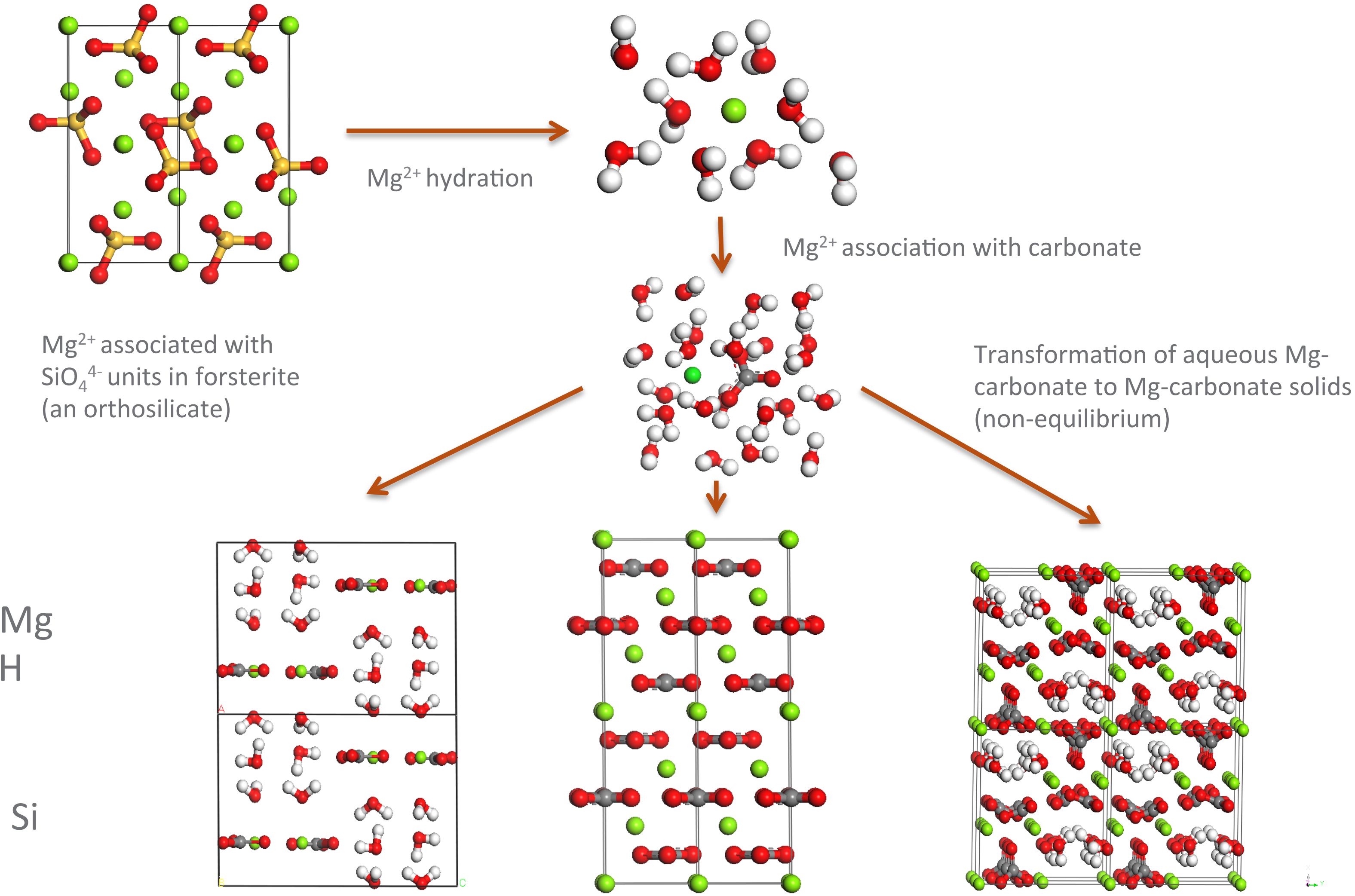
No liquid water on sample – water saturated $scCO_2$ forms a thin reactive film on forsterite



56 days H_2O-saturated 1µm image
(magnesite)

Concept: the thin water film in contact with the forsterite surface causes the Mg-carbonate clusters to follow a different reaction path that leads to unique phase formation

Unraveling Reaction Paths



Mg^{2+} associated with SiO_4^{4-} units in forsterite (an orthosilicate)

Mg^{2+} hydration

Mg^{2+} association with carbonate

Transformation of aqueous Mg-carbonate to Mg-carbonate solids (non-equilibrium)

Nesquehonite
($MgCO_3 \cdot 3H_2O$)

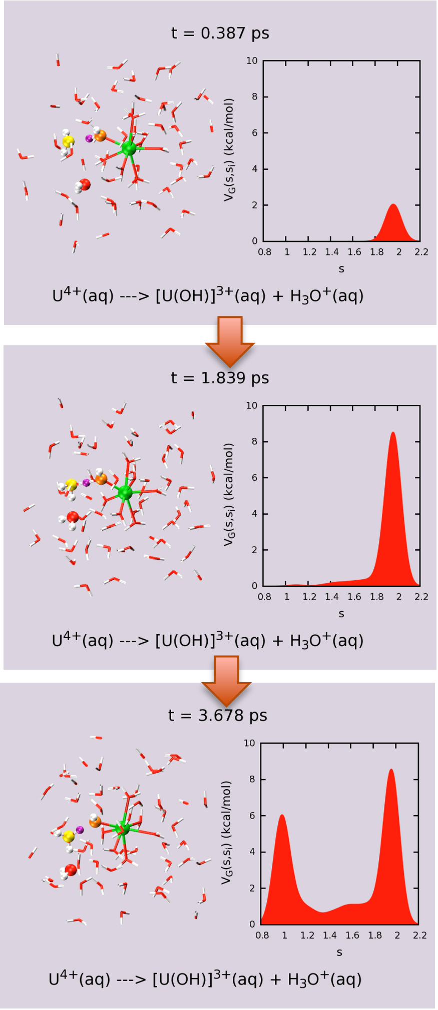
Magnesite
($MgCO_3$)

Hydromagnesite
($4MgCO_3 \cdot Mg(OH)_2 \cdot 4H_2O$)

Green – Mg
White – H
Red – O
Grey – C
Orange - Si

Simulation of Reaction Paths

Hydrolysis Reaction Path



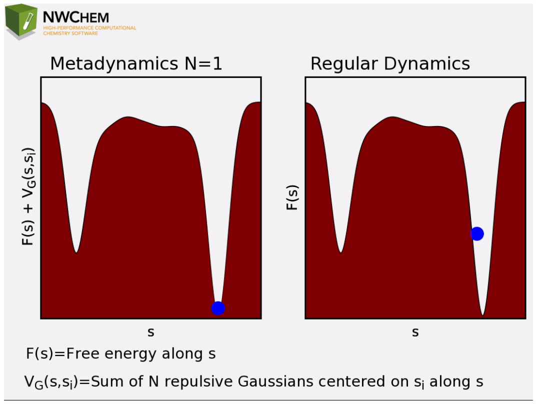
Need to calculate the free energy as a function of the reaction coordinates. This requires integration of the dynamics over all the particle coordinates for fixed reaction coordinates.

$$\Delta W_{AB} = -\frac{1}{\beta}\ln\left\langle e^{-\beta E(\mathbf{r}_B,\psi_B,\mathbf{R})} - e^{-\beta E(\mathbf{r}_A,\psi_A,\mathbf{R})}\right\rangle_{\mathbf{r}_A} .$$

We implemented Metadynamics and other free energy methods into our AIMD, AIMD/MM, and MD programs

Developing reaction coordinates (collective variables) designed to treat interface and microsolvation problems

> Reaction coordinates – combinations of bond distances or coordinates that can be used to follow reaction paths (phase transformations).



F(s)=Free energy along s

$V_G(s,s_i)$=Sum of N repulsive Gaussians centered on s_i along s

- **s** is the reaction coordinate
- Repulsive potentials (Gaussians) are continually injected along **s.**
- system is forced to explore high energy regions.
- Eventually (i.e. the large N limit), $\boldsymbol{V_G(s,s_i)} + \mathbf{F(s)} \approx 0$
- Hence $\mathbf{F(s)} \approx -\boldsymbol{V_G(s,s_i)}$

New Algorithms That Support the Parallel Implementation of High Level Quantum Chemistry Methods

- Some problems such as acid/base reactions and mineral growth in surface layers require high accuracy to identify chemical mechanisms.

- Quantum chemistry methods can provide such accuracy but highly parallel implementations of these methods are not available and force evaluations are far to long for meaningful sampling of reaction paths.

- **In this program we are developing new algorithms that will support the parallel implementation of these methods on petascale computers.**
  - These algorithms promise to reduce force evaluation times to levels that will allow calculation of free energies and interpretation of reaction mechanisms on these surfaces.

Computational Strategies (Approach)

- New types simulations will require multiple calculations running asynchronously to simulate particle aggregation and solid state transformation
  - Each calculation may require 100’s to 1000’s of cores
  - Increase simulations requirements (10x)
- Currently examining implementation of different possible methods for extended time and configuration space
  - Parallel in time integration (Bylaska et al. 2013)
  - Different free energy methods (e.g. temperature accelerated molecular dynamics (TAMD)) and minimum discrepancy free energy methods.)
- Development of higher levels of electronic structure methods to treat interfacial properties (e.g.DMFT)

HPC Resources Used Today

- **Codes and Algorithms**
  - Primarily NWChem
    - Nanostructures, quantum to classical, ground and excited states, relativistic properties, scales from one to thousands of processors
- **Computational Hours**
  - 2013 – 2M core hours on Hopper
- **Parallelism**
  - Typical simulation 240 – 1200 cores (AIMD in NWChem)
  - Codes demonstrated to scale to100K cores on NERSC
    - Core hours at NERSC limited
- **Scratch Data**
  - 1-10 GB per run
- **Shared Data**
  - No NERSC project directory
- **Archival Data Storage**
  - Up to 1Petabyte has been stored at NESC and EMSL

HPC Requirements in 2017

- Computational Hours
  - New free energy and parallel in time simulations
    - simulations will require multiple calculations (10-1000) run asynchronously
  - Possible factor of 10 increase
- Parallelism
  - Multiple calculations run asynchronously
  - Extend AIMD to 500K cores in 2017
- I/O
  - 1-50GB per run (Currently 1-10GB)

Needed Computational Resources

- Computational and Storage Requirements: Summary

	Current (2013)	In 2017
Computational Hours	~2M hours	~20M hours
Typical number of cores used in production runs	240-1200	10*(240-1200)
Maximum number of cores that could be used for production runs	100K	500K
Data read and written per run	1-10Gb	1-50Gb
Maximum I/O bandwidth		
Percent of runtime for I/O	<1%	<1%
Scratch File System space	<1Gb	<1Gb
Shared File system space	none	none
Archival Data	1Petabyte	10's of Petabytes
Memory per node	2GB	2-4GB
Aggregate Memory	1GB*ncores	1GB*ncores

Summary

- Significant investment in molecular simulation
    - Unique capabilities in algorithm and code development
- Experimental measurements increasingly sensitive
    - Must have computational capabilities to accurately interpret these measurements
- Difficult but important computational challenges remain
    - Move toward simulation of reaction paths in geochemical systems
- Require increased computational resources

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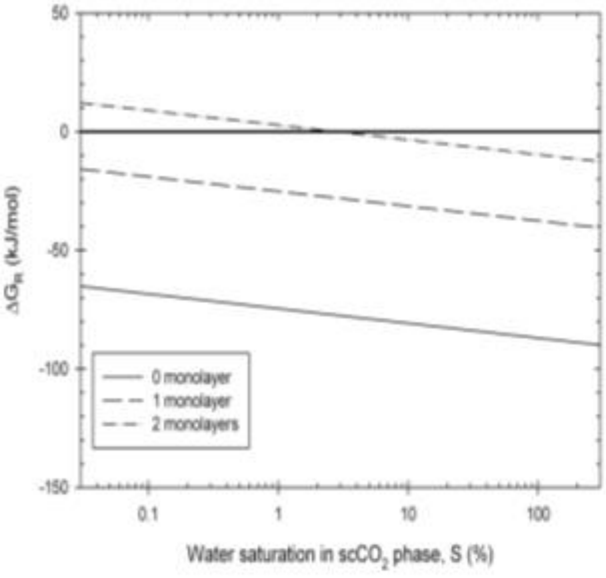
Questions?

Previous Studies

- Molecular dynamics simulations of growth of water films in CO_2/H_2O mixtures on minerals surfaces (forsterite)



Water strongly adsorbs to the surface forming a film at least 2-3 monolayers thick.

Kerisit S., Weare J. H., and Felmy A. R. (2012) Structure and dynamics of forsterite-$scCO_2/H_2O$ interfaces as a function of water content. *Geochimica et Cosmochimica Acta*, 84, 137-151.

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1/2

1

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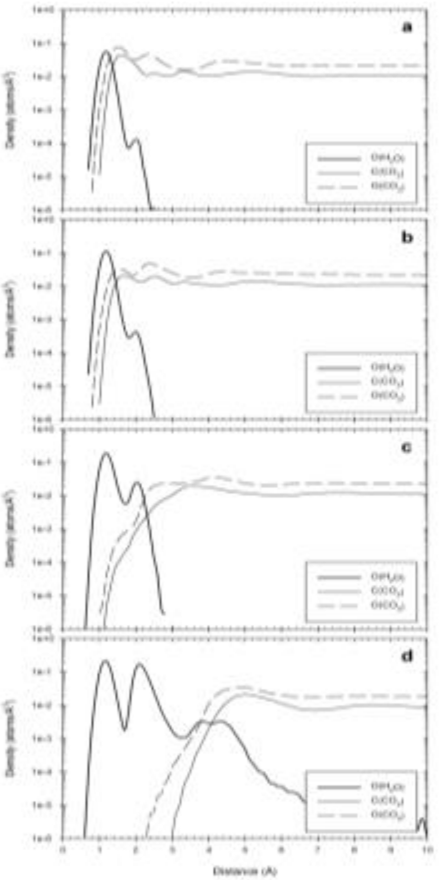
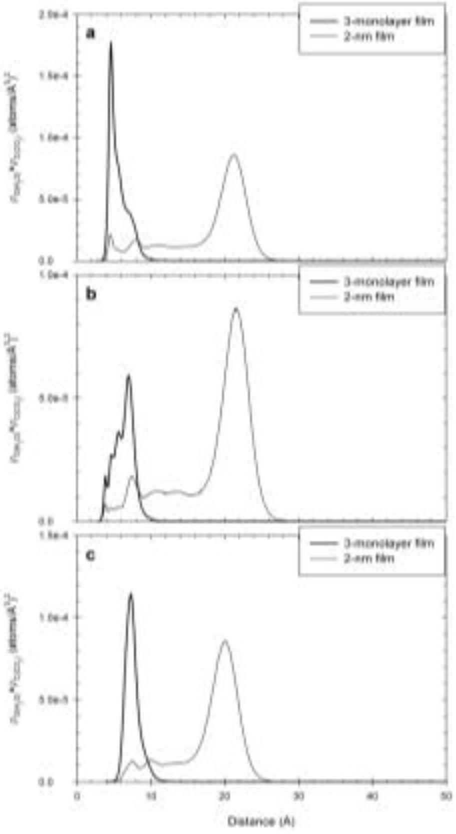


Displacement of CO_2 from the 010 surface by increasing water coverage



010

010
Hydroxylated

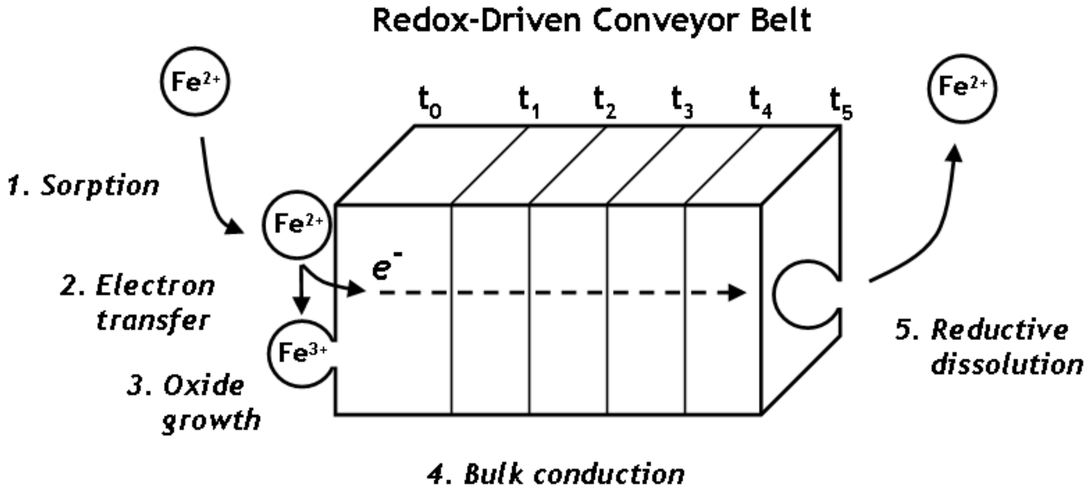
011

CO_2/H_2O mixing takes place some distance from the surface

Theme I: Electron Conduction/Transport in Redox Active Phases

Couples differences in surface energy with electron transport within a particle

Can result in complete phase transformation or conversion of amorphous to crystalline phases



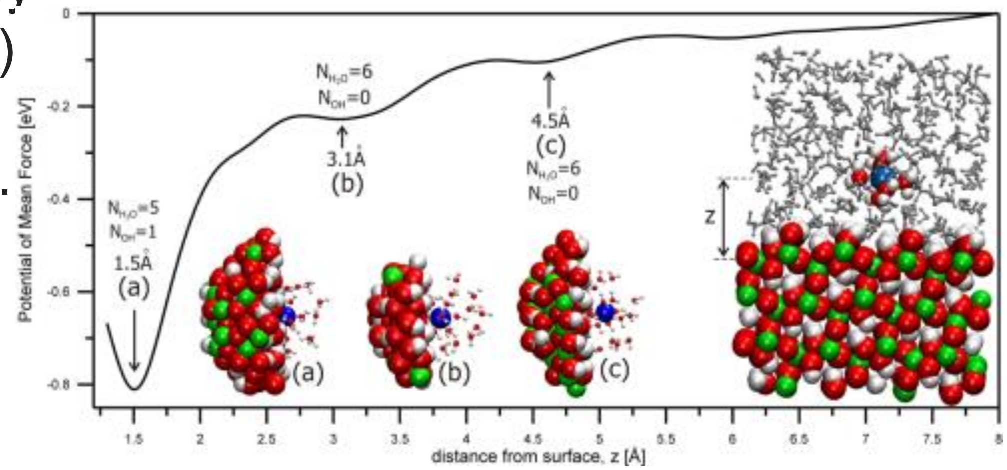
Handler et al. 2009

Previous Efforts

- Focused on unraveling the key steps (rate limiting processes) responsible for electron conduction in mineral phases.
  - Calculations of electron hopping dynamics in magnetite

    (Skomurski et al. 2010)
  - Intramolecular electron transfer in ferric-ferrous complexes

    (Zarycki et al. 2011)
  - Calculation of potential differences between different crystal faces of iron oxides (Chatman et al. 2013).



Key Results:

Electron Conduction can be driven by potential energy differences between surfaces.

Mineral structure (surface versus bulk) impacts electron conduction.

Electron transfer within semiconducting minerals is rapid.

Theme III:Theory and Model Development

- Development of new computational models of geochemical/chemical processes (E.J Bylaska, J.H. Weare)
  - Includes electronic structure, molecular dynamics and *ab inito* thermodynamics methods
  - Supports electron conduction and mineral/water film focus areas but also capabilities that assist other BES Laboratory and University programs
- Theory and Model Development Activities
  - Electron conduction/transfer (iron oxides)
    - Electrons in d band of iron oxides are highly correlated
      - Implementing methods to help treat electron-electron correlation
        - Exact exchange, dynamical mean-field theory (DMFT)
  - Mineral/water film focus area
    - Many body phase space (microsolvation/carbonation)
      - Implementing methods to expand the simulation size and the simulation time
        - Parallel in time molecular dynamics, metadynamics, Hill climbing