

FIRST PRINCIPLES STUDIES OF MINERAL CARBONATION REACTION PROCESSES IN SERPENTINE MINERALS

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INTRODUCTION

The potential environmental effects of increasing atmospheric CO₂ levels are of major worldwide concern. One alternative for managing CO₂ emissions is carbon sequestration: the capture and secure confinement of CO₂ before it is emitted to the atmosphere. Successful technologies must be environmentally benign, permanent, economically viable, safe and effective. As a result, their timely development represents a significant challenge.

Unlike many other proposed CO₂ sequestration technologies, which provide storage, CO₂ mineral sequestration provides permanent disposal via geologically stable mineral carbonates (e.g., MgCO₃). As such, mineral sequestration provides permanent containment and avoids many adverse environmental consequences and the cost of continuous site monitoring. The major remaining challenge for CO₂ mineral sequestration is economically viable process development. This is the focus of the CO₂ Mineral Sequestration Working Group managed by DOE Fossil Energy, which includes members from the Albany

Research Center (ARC), Arizona State University (ASU), Los Alamos National Laboratory, the National Energy Technology Laboratory, Pennsylvania State University, University of Utah and Science Applications International Corporation.

Mg-rich lamellar hydroxide minerals, such as serpentines, represent a promising class of feedstock materials, with good potential for economically viable process development. The key reaction for serpentine is:



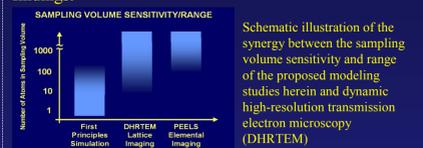
The carbonation of unpretreated serpentine is found to be significantly slower than that observed for olivine, another Mg-rich feedstock mineral currently being actively explored. However, serpentine is much more plentiful in readily mineable deposits worldwide, making it the CO₂ sequestration feedstock material of choice if its carbonation reactivity can be further enhanced. When serpentine is heat pretreated for an hour or more at over 600°C, its carbonation rate has been found to increase dramatically (see below). 70-85% carbonate conversion

has been achieved in under an hour (~150°C and 115-185 atm CO₂) using an aqueous reaction process developed at the U.S. DOE Albany Research Center! Unfortunately, heat pretreatment is energy intensive and costly. *An atomic-level understanding of the mechanism(s) by which heat pretreatment enhances serpentine carbonation reactivity is therefore crucial to being able to engineer more cost-effective pretreatment processes.* Many important factors that govern serpentine heat-activation via dehydroxylation are only observable at the atomic level.

OBJECTIVE

The objective of this project is to use advanced first-principles simulation techniques in concert with experimental observations to develop a detailed, quantitative, atomic-level understanding of aqueous-solution serpentine carbonation mechanisms. The goal is to develop the necessary atomic-level understanding to facilitate the engineering of improved carbonation feedstock materials and reaction processes for CO₂ sequestration. Scientific productivity is optimized by

closely integrating our studies with those being simultaneously performed at the Albany Research Center, and in a joint ASU-Argonne National Laboratory (ANL) study that focuses on *in situ* investigations of aqueous-solution serpentine carbonation reaction mechanisms. Key focal points of our multi-year project include: (i) simulation of the structural/compositional changes associated with serpentine heat-activation to understand their role in enhancing carbonation reactivity, (ii) development of a non-empirical site reactivity model for CO₂ with serpentine, (iii) detailed investigation of mineral surface dissolution mechanisms that govern carbonation kinetics, and (iv) simulation of Infrared/Raman, EELS, XPD, and XANES spectra to help interpret experimental findings.



SIMULATION AND MODELING GOALS

- Understanding the enhanced carbonation reactivity of heat pretreated serpentine: What is the dehydroxylation mechanism? Can first-principles modeling help interpret XPD and IR spectra?
- Fundamental simulations of mineral surface reconstructions during dehydroxylation → impact on dissolution rates, and near-surface mineral carbonation mechanisms.
- The role of substitutional impurities (e.g., Al, Fe): Impact on carbonation?
- Simulations of carbonation processes and speciation of carbon-bearing species in aqueous solutions.
- Ab initio* simulations of electron energy loss spectra (EELS), x-ray powder diffraction spectra and vibrational spectra.

COMPUTATIONAL METHODS

Most of our simulations employ an efficient quantum mechanical description based on density functional theory (DFT), which provides access to all the measurable quantities derivable from the knowledge of the ground state wave function of a system, including the electronic and vibrational spectrum of the subject material, and its compressibility/elasticity. In addition, microscopic quantities not normally accessible in the laboratory are available including atomic forces, local electric potentials and fields – useful fictitious constraints may also be imposed (artificial masses, artificial charges, stationary ions). In addition to our own computer codes, we make use of the WIEN2K and CRYSTAL98 packages for all-electron calculations, and the VASP and DMol³ codes for molecular dynamic and thermodynamic calculations of the gas, crystalline and liquid states. We also make use of approximate methods to treat systems too large or complex to be tractable using *ab initio* methods. Examples of such tools also include semiempirical quantum-mechanical methods such as PM3 and AM1 (as imple-

mented within the GAMESS package), and the non-empirical VIB DFT method.

CONCLUSIONS

We have shown that modern first-principles electronic structure simulations are able to accurately describe the structural, elastic and vibrational properties of magnesium bearing feedstock minerals. Using these same methods, simulations of the initial stages of 1T-Lizardite dehydroxylation reveal that the process involving a brucite-layer hydroxyl, and a cage proton from an adjacent layer, represents the lowest energy reaction path². Simulations of moderately dehydroxylated systems containing 50% residual hydroxyl, corresponding to Mg₃Si₂O₅(OH)₂, show that experimentally observed x-ray features are due to H₂O being preferentially removed from alternating lizardite layers with a ratio of 4:1, or greater. This results in an open structure, with potentially enhanced dissolution potential and higher carbonation reactivity, as observed experimentally.

Large scale molecular dynamics simulations of micron scale systems is prohibitive. To circumvent this limitation

we have undertaken simulations of both the bulk and near-surface regions. In the latter case, 720°C simulations reveal that “silica-layer” hydroxyl protons have very high diffusivities, but kinetics limit the formation of water. Instead, meta-stable water is observed to form in the “brucite-like” layers within the bulk crystal. This is likely a key step in the initial dehydroxylation process associated with heat activation. In both surface and bulk regions, the silica layers exhibit long-term dynamic stability and may be implicated in the stability of the highly reactive amorphous meta-serpentine. Dynamical simulations of bulk H₂O-CO₂ solutions were also found to be accurate. Future work will focus on the mineral solution interface.

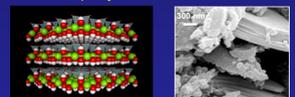
ACKNOWLEDGEMENTS

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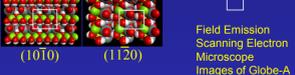
BASIC REACTANT/PRODUCT PROPERTIES:

Serpentine Minerals with Ideal Composition Mg₃Si₂O₅(OH)₄

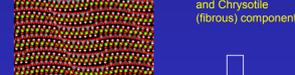
Lizardite → platy



Antigorite → modulated

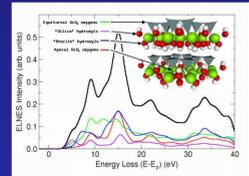


Chrysotile → coiled



“Fingerprinting” via Electron Energy Loss Spectra (EELS): Local probe of oxygen environment → interpretation of structural/chemical alteration of feedstock during processing

1T-lizardite:

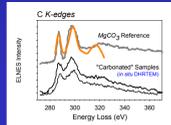


Energy Loss Near Edge Spectra obtained using the FFLAPW method within the generalized gradient approximation (GGA). Full dynamic form factors were computed using crystalline Bloch states. A broadening of ~2eV was applied to the raw spectra to simulate experimental data.

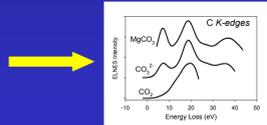
Interpretation:

- Shoulder feature at edge onset ~ 5 eV due to silica cage hydroxyl oxygen.
- Prominent feature at 15 eV due to Mg near neighbor oxygens (Apeal tetrahedral oxygens and “brucite-like” hydroxyl oxygens).
- Main contribution to feature at ~22 eV due to apeal tetrahedral oxygen.
- 34 eV feature mainly related to brucite layer hydroxyls.

Carbonate product:



→ evolution of carbon K-edge



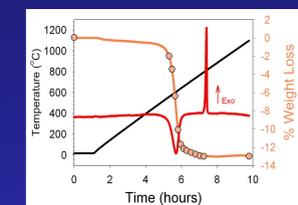
Comparison of simulated structure properties with experiment: Validation of predictive capability

Solid Reactants: Forsterite, Olivine, Lizardite, Meta-lizardite
Solid Products: Magnetite, “carbonate” (Mg, Fe)₃CO₃, silica, others?

Atom	LDA	GGA	Experiment
r(A)	2.3603	2.3533	2.3267
σ(A)	7.6964	7.4187	7.2981
Mg	x	y	z
Si	0.331	0.249	0.403
O1	0.15	0.167	0.15
O2	0.053	0.020	0.044
O3	0.064	0.051	0.064
O4	0.080	0.056	0.060
O5	0.080	0.056	0.060
O6	0.080	0.056	0.060
O7	0.080	0.056	0.060
O8	0.080	0.056	0.060
O9	0.080	0.056	0.060
O10	0.080	0.056	0.060
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O98	0.080	0.056	0.060
O99	0.080	0.056	0.060
O100	0.080	0.056	0.060

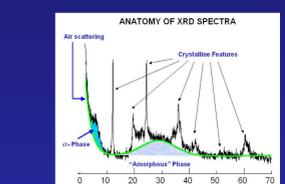
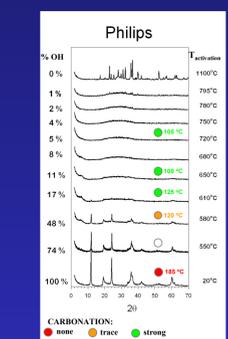
EFFECTS OF HEAT-TREATMENT:

Controlled Intermediate Formation -- Enhanced Carbonation

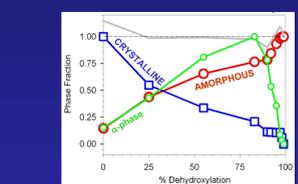


Above: “Philips mine” lizardite is heat-treated in a TGA and quenched at the temperatures indicated by dots to produce a range of reactant materials (meta-serpentines) with varying OH content.

Right: Progression of XPD spectra illustrating the evolution of structure over the composition range shown in the left margin. The colored dots indicate the degree of carbonation achieved at the temperatures shown.

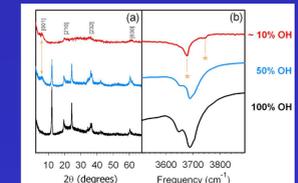


A visual guide to the characteristic features exhibited by meta-serpentines. The low angle feature (2θ~6°) is labeled as α-phase and is shown as distinct in the phase analysis shown at right. The broad “glassy” feature centered around 2θ~30°, which grows in for residual hydroxyl contents < 50%, is associated with enhanced carbonation (left).

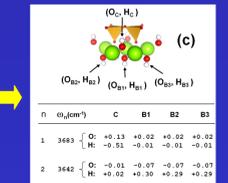


Results of a multi-phase analysis of the XPD spectra as a function of degree of dehydroxylation. Note the coincidence of the phase fractions of amorphous and α-phase below 25%. The most efficient carbonation is observed near the point where the green and red curves cross (~ 11% residual hydroxyl).

Correlation between Infrared spectroscopic features and character of XPD.

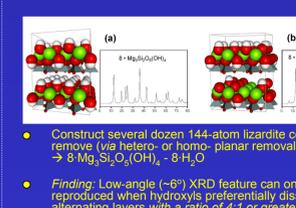


- 50% dehydroxylated material exhibits new feature at 2θ~6° while parent phase features are still present.
- Low angle feature still present in ~10% dehydroxylated material, but with remnants of primarily “in-plane” reflections remaining from the parent phase.
- The appearance of two new frequencies in the ~10% OH meta-serpentine suggests that the local hydroxide environment has changed.
- New vibrational signature near ~ 3740 cm⁻¹. How is it related to the structure of meta-serpentine? Simulations suggest the formation of siloxane intermediates (Si-OH groups) upon decomposition. Predicted frequencies are in the range 3700-3770 cm⁻¹ depending on Si termination.



Origin of lizardite vibrational bands in the hydroxyl stretch frequency range. Low frequency feature (~3640 cm⁻¹) is associated with brucite layer hydroxyl motion. Results obtained quantum lattice dynamics using a plane wave pseudopotential approach. Note the excellent agreement with experiment (left).

Microscopic model of 50% meta-lizardite from first principles:



Construct several dozen 144-atom lizardite cells and remove (via hetero- or homo- planar removal) 50% water → 5Mg₃Si₂O₅(OH)₂ + 8H₂O

Finding: Low-angle (~6°) XRD feature can only be reproduced when hydroxyls preferentially dissociate from alternating layers with a ratio of 4:1 or greater.

The meta-serpentine intermediates formed include a range of amorphous solid-solution and/or locally-ordered material(s) and a stage-2 phase with ~14.6 Å interatomic order. They form and transform on heating, retaining residual OH levels from ~ 12 to 1% after complete lizardite/serpentine decomposition.

The OH groups in meta-serpentine derived from lizardite with a minor chrysotile component (e.g., Globe-A mine feedstock) have a new structural environment unlike the parent serpentine or the lizardite derived meta-serpentine (see Infrared Spectroscopy panel). Such structure related frequency shifts are not observed in meta-serpentines derived from pure lizardite (e.g., Philips mine Serpentine feedstock).

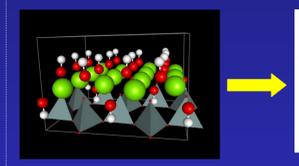
QUANTUM MOLECULAR DYNAMICS SIMULATIONS:

Mineral Reactant Decomposition: Bulk and Surface Stability

Objectives:

- Use state-of-the-art quantum simulation to study the dynamics of protons/hydroxyls as a function of temperature.
- Diffusion of H, OH, H₂O – stability of silica sheets.

- 72 to 144-atom cells (as in earlier dehydroxylation calculations).
- 1.5 femtosecond timestep integration using the Verlet algorithm
- Local density approximation (LDA)
- Ultra-soft pseudopotentials used to replace core electrons.
- Electronic structure computed (using the VASP code) at every time step + velocity rescaling.



Bulk lizardite @ 20°C

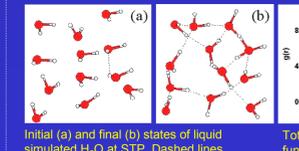
Room temperature Lizardite (~20°C): What is the real feedstock structure?

- New, slightly metastable (β) phase predicted at room temperature.
- Inverted hydroxyl within the brucite layer
- Origin for unexplained splittings and asymmetry of various in-plane features? e.g. (100) and (101)?
- Origin of the unexplained high frequency shoulder on the OH bands. Calculations in progress.

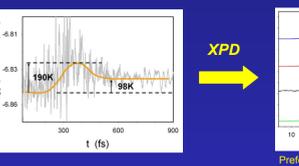
Aqueous System:

- Speciation and diffusivity information for aqueous species is very limited.
- The thermodynamics of the CO₂-H₂O system in the presence of solutes is complex (many key parameters unknown).

Validation of quantum molecular dynamics simulations for liquid phases:



Initial (a) and final (b) states of liquid simulated H₂O at STP. Dashed lines indicate hydrogen bonding.



High quality static lattice calculations → Primitive unit cell:

lizardite a = 5.265 Å c = 7.090 Å</