**ENHANCING THE ATOMIC-LEVEL UNDERSTANDING
OF
CO₂ MINERAL SEQUESTRATION MECHANISMS
VIA
ADVANCED COMPUTATIONAL MODELING**

Type of Report:	Final Project Report
Reporting Period Start Date:	9/20/01
Reporting Period End Date:	9/20/05
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Date Report Issued:	March, 2006
DOE Award Number:	DE-FG26-01NT41295
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ABSTRACT

Fossil fuels currently provide 85% of the world's energy needs, with the majority coming from coal, due to its low cost, wide availability, and high energy content. The extensive use of coal-fired power assumes that the resulting CO₂ emissions can be vented to the atmosphere. However, exponentially increasing atmospheric CO₂ levels have brought this assumption under critical review. Over the last decade, this discussion has evolved from whether exponentially increasing anthropogenic CO₂ emissions will adversely affect the global environment, to the timing and magnitude of their impact. A variety of sequestration technologies are being explored to mitigate CO₂ emissions. These technologies must be both environmentally benign and economically viable. Mineral carbonation is an attractive candidate technology as it disposes of CO₂ as geologically stable, environmentally benign mineral carbonates, clearly satisfying the first criteria. The primary challenge for mineral carbonation is cost-competitive process development.

CO₂ mineral sequestration – the conversion of stationary-source CO₂ emissions into mineral carbonates (*e.g.*, magnesium and calcium carbonate, MgCO₃ and CaCO₃) – has recently emerged as one of the most promising sequestration options, providing *permanent* CO₂ disposal, rather than storage. In this approach a magnesium-bearing feedstock mineral (typically serpentine or olivine; available in vast quantities globally) is specially processed and allowed to react with CO₂ under controlled conditions. This produces a mineral carbonate which (i) is environmentally benign, (ii) already exists in nature in quantities far exceeding those that could result from carbonating the world's known fossil fuel reserves, and (iii) is stable on a geological time scale. Minimizing the process cost *via* optimization of the reaction rate and degree of completion is the remaining challenge.

As members of the DOE/NETL managed National Mineral Sequestration Working Group we have already significantly improved our understanding of mineral carbonation. Group members at the Albany Research Center have recently shown that carbonation of olivine and serpentine, which naturally occurs over geological time (*i.e.*, 100,000s of years), can be accelerated to near completion in hours. Further process refinement will require a synergetic science/engineering approach that emphasizes simultaneous investigation of both thermodynamic processes and the detailed microscopic, atomic-level mechanisms that govern carbonation kinetics.

Our previously funded Phase I Innovative Concepts project demonstrated the value of advanced quantum-mechanical modeling as a complementary tool in bridging important gaps in our understanding of the atomic/molecular structure and reaction mechanisms that govern CO₂ mineral sequestration reaction processes for the model Mg-rich lamellar hydroxide feedstock material Mg(OH)₂. In the present simulation project, improved techniques and more efficient computational schemes have allowed us to expand and augment these capabilities and explore more complex Mg-rich, lamellar hydroxide-based feedstock materials, including the serpentine-based minerals. These feedstock materials are being actively investigated due to their wide availability, and low-cost CO₂ mineral sequestration potential.

Cutting-edge first principles quantum chemical, computational solid-state and materials simulation methodology studies proposed herein, have been strategically integrated with our new DOE supported (ASU-Argonne National Laboratory) project to investigate the mechanisms that govern mineral feedstock heat-treatment and aqueous/fluid-phase serpentine mineral carbonation *in situ*. This unified, synergetic theoretical and experimental approach has provided a deeper

understanding of the key reaction mechanisms than either individual approach can alone. We used *ab initio* techniques to significantly advance our understanding of atomic-level processes at the solid/solution interface by elucidating the origin of vibrational, electronic, x-ray and electron energy loss spectra observed experimentally.

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EXECUTIVE SUMMARY

OBJECTIVES

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 will be 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 project originally included (i) simulation of the morphological changes associated with serpentine heat-activation to understand its role in enhancing carbonation reactivity, (ii) development of a non-empirical site reactivity model for CO₂ with serpentine, and (iii) detailed investigation of the serpentine surface dissolution mechanisms that govern carbonation kinetics, and (iv) the use of first-principles methods to provide deeper atomic-level insight into the mechanistic experimental observations in the partner ASU/ANL studies (*e.g.*, *in situ* studies of reaction intermediate formation).

It should be noted that a critical development during the award performance period was a shift in effort distribution among the focal points listed above, including a significant additional focus on the study of carbonation of olivine-based feedstock minerals. Accordingly a significant fraction of the modeling and simulation support and thrust during the last 16 months of the project was devoted to understanding forsterite/olivine dissolution, the speciation and equilibrium properties of our reactant solution (ARC aqueous process). Beginning in August of 2004 we initiated a special thrust aimed at developing fundamental understanding of the negative effect of passivating layer formation on feedstock particles in the aqueous carbonation process. The elimination of the passivation layer is currently (March, 2006) viewed as a critical problem in the development of an efficient and cost-effective mineral carbonation process.

ACCOMPLISHMENTS

Fossil fuels, especially coal, can support the energy demands of the world for centuries to come, if the environmental problems associated with CO₂ emissions can be overcome[1,2]. Mineralization of stationary-source CO₂ emissions as carbonates can provide safe capture and long-term sequestration[3,4]. Carbonation of Mg-rich minerals (*e.g.*, the model Mg(OH)₂ system, olivine and serpentine based minerals) is a leading process candidate, which generates the stable, naturally-occurring mineral magnesite (MgCO₃). Optimizing the carbonation reaction rate and its degree of completion are key to process cost and viability.

This current project is based on the simulation of gaseous, liquid and solid properties, and carbonation reaction processes in Mg-bearing minerals at the atomic level. Carbonation and treatment processes in both olivine and serpentine feedstock minerals are also a relevant point of contact as they pertain to the research being carried out by the Mineral Sequestration Working

Group managed by NETL. Thus, the scope of the simulation studies undertaken under the auspices of the current project often overlap with the research activities of other members (other than ASU) of the working group. In all cases, the project objective is to provide mechanistic understanding which can accelerate the engineering development of improved carbonation materials and processes for carbon dioxide disposal. Specifically, the simulation and modeling thrust described in this report is synergistically integrated with a number of other mineral sequestration projects sponsored by Fossil Energy including: NETL/ANL Contract 1F-01262 and UCR Awards DE-FG26-98FT40112 and DE-FG26-01NT41282. The lead author of the present report (Chizmeshya) is a member of the Working Group on Mineral Sequestration managed by the National Energy Technology Laboratory. Some outstanding research highlights of the present project include:

- YEAR 1: Dehydroxylation of lizardite is an extremely complex process involving the loss of hydroxyl groups in the form of H_2O . State-of-the-art quantum mechanical simulation of the low temperature heat activation process has revealed a staging reaction in which hydroxyl concentrations in alternating lizardite lamella are preferentially reduced, leading to the appearance of characteristic low angle x-ray features observed experimentally. The reaction is endothermic with typical removal energy of $\Delta U \sim 46$ kcal/mol per hydroxyl. This was used to explain the unusual progression of x-ray diffraction patterns observed in association with the heat treatment of serpentine feed stock minerals. Studies were undertaken to elucidate the origin of dehydroxylation mechanisms via simulation of early stage decomposition (%OH loss in the 0-15% range).
- YEAR 1: First principles simulation of the subtle structural changes associated with initial dehydroxylation led a new method for analyzing x-ray data – Differential Diffraction Analysis – in which small, systematic XRD spectral changes are simulated and compared with experiment directly. By separating the effect of chemical modification from bonding/coordination changes the method provides new insight into structure modification. The technique may be of broad utility whenever chemical changes of interest in a solid produce minimal changes in X-ray scattering.
- YEAR 2 & 3: Very large scale molecular dynamics simulations (10,000-15,000 atoms) were developed to study the structure and properties of the silica-rich passivating layer (PL) which forms on reacting olivine surfaces. Density profiles of the PL indicate inhomogeneity with a reduction of density near the free surface, and that the bulk density of the PL (~ 2.20 g/cc) is similar to that of simulated vitreous SiO_2 (~ 2.30 g/cc). Simulations of the strain state of the PL as grown on the forsterite indicate that it is *tensile* (simulation predicts a 5% shrinkage parallel to the interface plane). However, while the internal structure of the PL material is glass-like (4-coordinate tetrahedral), it exhibits nano-porosity. The “occupiable volume” in both strained and relaxed PL’s is greater than that of thermal glass. The easiest diffusion is through strained PL material (H^+ , Mg^{2+} , ..). The extensive structure of “void” channels within the PL structure may provide effective pathways for ion transport as well a low free-energy locations for the formation of carbonate within the passivating layer matrix (observed experimentally).

- YEAR 3: Integrated simulation, X-ray and nuclear magnetic resonance (NMR) studies were carried out on a series of meta-lizardite (heat-treated) materials to elucidate the micro-structural evolution of the materials. This led us to develop a novel reaction model which directly links the structural correlations of the silica (SiO_4) units to the dehydroxylation extent of the decomposing lizardite mineral. The studies reveal that the most reactive meta-lizardite material is comprised of loosely coherent, remnant, sheet-like structures containing a significant density of silica dimers. Furthermore, the “open” structure associated with this microstructural morphology is likely responsible for the very rapid dissolution and concomitant increase in reactivity observed experimentally.

INTRODUCTION

The atomic level simulation studies of the type performed under the present award are extremely demanding since the systems of interest exhibit all phases of matter (solid, liquid and gas), often in combination. But even more importantly, the deviations from ideality continue to provide daunting challenges. To address this issue we have expanded our project resources at no cost to the original project by securing supercomputer resources through the (SC)² program managed by NETL. In addition we acquired a range of new modeling/simulation capabilities, such as the FEFF code, and developed original computer codes for optimizing classical potentials for large scale molecular dynamics studies. Advances in fundamental understanding are absolutely essential to the accelerated development of viable CO_2 sequestration technology, and the atomic level simulation of structure-energy relationships, reaction energetics and dynamical simulations including vibrational spectroscopy and molecular dynamics are indispensable when viewed as analytical tools. The synergy inherent in the intimate combination of advanced modeling/simulation and experiment has led to scientific insights that would have been difficult to achieve independently, and this benefit cannot be overstated.

RESULTS AND DISCUSSION

In YEAR 1 (see Appendix 2) of the present Innovative Concepts II award, DE-FG26-01NT41295, we focused on (i) the first principles simulation of fundamental reactant and products properties such as atomic structure, formation energy, vibrational structure and electronic spectral signatures (ii) the effects of heat treatment on the structure and composition of lizardite, the prototypical lamellar magnesium magnesium-hydroxy-silicate feedstock material, (iii) the preliminary steps associated with carbonation of defective (heat-treated) lizardite based on predicted *ab initio* atomic structures. The synergistic interaction of these initial studies with laboratory work has illuminated the origin of a number of observed phenomena including the critical assignment of the so-called “inner” and “outer” hydroxyl vibrational bands. These can/will be used as a fingerprint to diagnose the evolution of the departing structural hydroxyls in dehydroxylation experiments on lizardite, and eventually chrysotile and antigorite. Our simulations predicted the existence of a novel, metastable, meta-serpentine material in which order and disorder coexist. This was used to explain the unusual progression of x-ray diffraction patterns upon dehydroxylation. We also modeled the MIE-like particle scattering features at low-angle in the XRD spectrum in the 640°C heat treated sample (see report 41295R01). We also initiated supercomputer-based quantum molecular dynamics studies of the temperature

dependence of the dehydroxylation process to study the water formation rate and diffusivities of mineral (and product) components (Mg, Si, OH, H₂O and protons). These are described in section 3.0 below as a part of the last year's performance period but within the present report since the grant has a September start date.

. During YEAR 1 (see Appendix 2) state-of-the-art quantum mechanical simulation methods were used to predict the existence of a novel, metastable, meta-serpentine material in which order and disorder coexist. This was used to explain the unusual progression of x-ray diffraction patterns observed in association with the heat treatment of serpentine feed stock minerals. Studies were undertaken to elucidate the origin of dehydroxylation mechanisms via simulation of early stage decomposition (%OH loss in the 0-15% range). First principles simulation of the subtle structural changes associated with initial dehydroxylation led a new method for analyzing x-ray data – Differential Diffraction Analysis – in which small, systematic XRD spectral changes are simulated and compared with experiment directly. By separating the effect of chemical modification from bonding/coordination changes the method provides new insight into structure modification. The equation of state of the solid phases: 1T-Lizardite (Mg₃Si₂O₅(OH)₄), MgO, Mg(OH)₂, SiO₂ α-quartz, and MgCO₃ were simulated with purpose of generating data needed for end-member/product-phase reaction enthalpies. Minimum energy structural models based on these simulations are necessary as input for subsequent modeling studies, such as molecular dynamics simulations. A brief modeling study to elucidate the structure of x-ray spectra collected under target conditions (2300 psi/180°C) at the Advanced Photon Source (Argonne National Laboratory) in the 640°C heat treated sample was also undertaken. The modeling focused on the origin of MIE-like particle scattering features observed at low-angle in the XRD spectrum. First principles simulations were also used to predict the frequencies of infrared absorption bands in the baseline feedstock minerals. Our work provided the first unambiguous assignment of hydroxyl band features in lizardite: silica-cage vibrations are higher in frequency than their brucite-layer counterparts. These simulations were used to correlate shifts in frequency observed experimentally with changes local structure changes during feedstock pre-treatment and carbonation. Supercomputer-based quantum molecular dynamics studies of the temperature dependence of the dehydroxylation process were also initiated using the (SC)² resources through NETL. These studies were aimed at understanding the behavior of thermally activated diffusion of mineral (and product) constituents (Mg, Si, OH, H₂O and protons) during lizardite heat-treatment.

During YEAR 2 (see Appendix 2) further extensive quantum molecular dynamics simulations were performed on the lizardite system. The studies indicated that dehydroxylation is extremely complex. Stable structures exhibiting staging behavior were predicted. The silica-rich sheets in serpentine minerals exhibit stability at high temperatures. We showed that significant proton diffusion takes place over a broad temperature range implying many paths to dehydroxylation. During the second performance year we also briefly explored the conductor-like screening model for real systems (COSMO-RS). We used it to compute excess thermodynamic properties of CO₂-H₂O solution systems. Using quantum mechanical simulations of the solute and solvent we were able to reproduce the exsolution behavior of H₂O-CO₂ into CO₂-rich and H₂O-rich fluid phases. Work to extend and validate the approach to 3- and 4- component fluids was attempted but not pursued further since it was discovered that the COSMO simulations were not sufficiently quantitative in the supercritical regime relevant to our experiments. However, solvent effects on structural and vibrational properties of carbon-bearing solutes including CO₂(aq), CO₃²⁻, HCO₃⁻ H₂CO₃ as well as OH⁻ and H₂O itself, were found to be

reasonably well predicted by the COSMO-RS method. In addition to the structural modifications induced by solvation we calculated the shifts associated with key vibrational bands in these molecules providing important guidance for our FTIR spectroscopy studies. We also studied the structure and stability of forsterite surfaces in YEAR 2. The minimum dipole forsterite surface was predicted to be (010) while large structural reconstruction are predicted for the (100) and (001) surfaces (in agreement with the surface stabilities observed experimentally, e.g., in dissolution studies). The proton exchange reaction (dissolution on (010) surface) was studied using first principles methods and predicted to be exothermic by ~ 75 kcal/mol. An analogous study of iron extraction yielded a corresponding value of ~ 55 kcal/mol suggesting that leaching should tend to increase the surface concentration of iron, barring unforeseen complexation reactions in the hydration layer of the reacting mineral (not taken into account in our study). Finally, very large scale molecular dynamics simulations were developed to study the structure and properties of the silica-rich passivating layer which forms on reacting olivine surfaces. The simulations predict a low-density glass like network and extensive “void” channels suggesting an efficient ion transport mechanisms as well as a low free-energy mechanisms for the formation of carbonate within the passivating layer matrix.

In YEAR 3 (see Appendix 2) we expanded our molecular dynamics studies of the properties of the silica-rich passivating layer (PL) which forms on reacting olivine surfaces (see Figure 1 below). Structural relaxation of the PL, when decoupled from the olivine matrix,

Figure 1: High-quality 3D rendering of the simulated passivation layer (PL) that forms on olivine feedstock particles during dissolution and carbonation reaction. The figure shows the transition from bulk crystalline Mg_2SiO_4 (far left) through a transition zone (middle) and into the bulk silica-like passivating layer (far right). The green spheres represent the magnesium ions, while the red and grey sticks label oxygen and silicon, respectively.

produces a biaxial lateral contraction of approximately 5% indicating that even thin PLs ($< 8\text{nm}$) are in a state of tension. A detailed study of the internal structure of the simulated PLs was also undertaken. Both the occupiable and accessible internal volumes were calculated as a function of probe particle dimensions for the strained and relaxed PL structures, and these results were

compared with the results for a typical silica glass. One of our main findings is that the strained PL material possesses a greater internal occupiable volume than the fully relaxed material, suggesting that the permeability to reactive species is greater at the onset of the surface reaction. Another significant finding is that the accessible volume within the layer can accommodate carbonate ions (CO_3^{2-}), as well as Mg^{2+} and protons, which supports the notion that the layers are permeable to key reactant species in their hydrated state. Finally, integrated simulation, X-ray and nuclear magnetic resonance (NMR) studies were performed on a series of meta-lizardite (heat-treated) materials to elucidate in much greater detail the micro-structural evolution of the materials. This led to a novel reaction model which directly links the structural correlations of the silica (SiO_4) units to the dehydroxylation extent. The studies reveal that the most reactive meta-lizardite material is comprised of loosely coherent, remnant, sheet-like structures containing a significant density of silica dimers. The simulation of EELS spectra was significantly expanded to aid in the interpretation of the experimental characterization using this technique. The specific focus was on a detailed comparative study of known approximation techniques for calculating the energy loss cross-sections. Our research reveals the highest fidelity approximation (“relaxed core hole”) provides an excellent account of the observed spectra, and that this computationally intensive treatment is reasonably well reproduced by the much less demanding Z+1 approximation.

Work performed during the no-cost extension:

During our no-cost extension period we completed publications and disseminated our research results at conferences and other academic venues. We also pursued some basic modeling in support of the related DOE Field Work project at Argonne National Lab (jointly with ASU):

Interpretation of Synchrotron Scattering Profiles: One of the ongoing challenges associated with our synchrotron experiments is the interpretation of the detailed structure of the x-ray scattering structure. As discussed in prior reports and meetings the dominant contribution in the x-ray scattering is from the $\text{CO}_2\text{-H}_2\text{O-NaCl-NaHCO}_3$ solution, which constitutes most of the beam interaction volume in our experiments. The carbonate signatures which we seek are observed as small features above this prominent fluid scattering background as shown in the typical scattering profile in Figure 2. Note the magnitude of the magnesite peaks in relation to

Figure 2: Typical raw scattering profile of a reacted sample of Philips 3 “730°C heat treated” lizardite taken at $P_{\text{CO}_2} \sim 2,200$ psi and $T \sim 120^\circ\text{C}$.

the background scattering structure, which varies rather smoothly on the scale of the 2θ range ($\sim 2\text{-}16^\circ$). A systematic analysis of the magnesite nucleation and growth requires careful subtraction of the fluid scattering background which itself varies systematically with changes in pressure and temperature. Variations in the fluid scattering background in turn reflect changes in density and internal structure (composition) of the reactant solution. In principal, the equilibrium behavior of the solution can be used to determine the speciation of reacting species within the fluid at various (P,T) and molecular modeling can then be used to simulate the x-ray scattering from the internal molecular structure

of the system. Here we describe our progress in pursuing such an approach.

As a starting point we modeled the equation of state and structure of water using the so-called TIP4P force field[5], which has been extensively used in the literature. In real diffraction experiments the x-ray scattering represents an average over the entire irradiated volume of a macroscopic sample. Thus, the molecular models employed must be large enough to ensure that the diffraction simulations

Figure 4: Scattering geometry and definition of the scattering vector Q (difference between the incoming and scattered wave vectors). Magnitude of Q depends on wavelength λ and scattering angle θ .

are representative of the bulk material. In our simulations we used between 500-1000 atoms. The volume per H_2O molecule at STP (liquid state) is about $30 \text{ \AA}^3$, which yields computational cells with a typical edge length of 25-30 $\text{\AA}$. A snapshot of a typical H_2O computational cell containing 768 atoms is illustrated in Figure 3. As we will show below, this

Figure 3: Molecular model of liquid water obtained from the TIP4P force field (768 atoms).

spatial range is sufficient to capture most of the essential scattering structure of the liquid water.

We carried out simulations on liquid water using the MOLDY molecular dynamics program [6] using time steps of 0.5 fs and the Raman-Parrinello constant pressure algorithm, and full velocity rescaling for the first 5,000 steps. After 20,000 equilibration time steps average thermodynamic properties were computed during a subsequent 10,000 steps. Several representative equilibrium molecular structures were then extracted from the final sequence for analysis. We calculated the total (isotropic) scattering intensity of x-rays from the fluid specimen using the Debye formula (also known as the Wierl formula):

$$I(Q) = \sum_k \sum_j \frac{f_j(Q) f_k(Q) \sin(QR_{jk})}{QR_{jk}}$$

where Q is the magnitude of the scattering vector (see Figure 4), f_j and f_k is the scattering factors for atom j , and k , and R_{jk} is the distance between atoms j and k . As a preliminary test of the simulation method we calculated the isotropic scattering from pure water, which is an approximation to the actual reactant solution (1 M NaCl + 0.66 M NaHCO_3) prior to CO_2 pressurization. The outcome of the calculation is shown in Figure 5. The blue trace is the integrated scattering intensity obtained experimentally for the H_2O -NaCl- NaHCO_3 solution at STP, prior to any CO_2 injection. The orange trace is the simulated scattering intensity. The general agreement with the observed behavior is gratifying considering that very little experimental input was used in the simulation. The result confirms that the x-ray scattering behavior is dominated by water with maxima at $2\theta \sim 6.5^\circ$ and 8.8° corresponding to mean oxygen-oxygen (2.9 $\text{\AA}$) and hydrogen-hydrogen (2.16 $\text{\AA}$) length scales, respectively. The oscillatory features present in the simulated curve at low angle are an artifact of the spatial cutoff

employed in the Debye formula summation, which was limited to about 15 Å in the present simulation. The origin of the higher angle features observed in the blue trace around 12.2° and 14.3° is not yet known, but we suspect that these features will be accounted for by the new spatial (length-scale) correlations introduced by the hydration shells of Na⁺ and carbonatous ions. We also re-calculated the scattering profile of water at 200°C and 100 atm and found a systematic 5-10% decrease in the scattering profile magnitude (compared to that at STP shown in Figure 5). We will be performing routine simulations of this kind for the more complex CO₂-H₂O-NaCl-NaHCO₃ system in the near future in order to aid in the interpretation of synchrotron x-ray scattering data.

Figure 5: Observed and calculated fluid scattering profiles for synchrotron x-rays of wavelength $\lambda=0.3311$ Å prior to reaction (STP) of the PH3-730 sample (no CO₂) in H₂O-NaCl-NaHCO₃.

CONCLUSIONS

We believe that the Innovative Concepts program support of the current simulation and modeling effort DE-FG26-01NT41295, had a significant and tangible impact on the progress achieved within the mineral sequestration research area. Our work has demonstrated that atomic level modeling, when integrated synergistically with active experimental inquiry can accelerate the process of discovery. We have elucidated important aspects of the solid reactant response to decomposition, along the path to carbonation in an aqueous environment. For example, in the case of lizardite we have developed a comprehensive picture of the modifications to the feedstock mineral due to dehydroxylation induced by heat treatment. This is an expensive step in the overall process and the knowledge generated provides a framework for developing methods to improve the reactivity. The identification of specific micro-morphological features associated with dehydroxylation can be used in the future to interpret the effect of, e.g., heating rate on the reactivity of the meta-lizardite. In a related preliminary study we have already discovered that meta-serpentines with a specific (chosen) hydroxyl content can be synthesized using different thermal pathways, yielding significantly different reactivity. This underscores the need for a deeper understanding and future work in this area.

With the advent of more powerful supercomputers, and more efficient simulation codes even more will be achieved in the future. A systematic first principles simulation effort devoted primarily to the properties of supercritical fluid mixtures would be very relevant to sequestration technology development in the future. This is particularly true for complex (synthetic) buffered H₂O-CO₂ solutions and natural brines in which supercritical CO₂ has been added, whether the target process is above- or below-ground (e.g., geological sequestration). It is well known that the behavior of supercritical fluids in this (P,T) regime is poorly understood experimentally; the knowledge base for diffusivity of the solvated carbon bearing species is very scant. In view of the constantly improving predictive capability of first principles methods future funding focused on this area would deliver a guaranteed impact.

Numerous discussions with this project's CORs, National Mineral Sequestration Working Group Members and NETL program coordinators are gratefully acknowledged.

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APPENDIX 1 : ARTICLES, PRESENTATIONS, AND STUDENT SUPPORT

Publications

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“In-situ Observation of CO₂ Sequestration Reactions using a Novel Microreaction System”, G. H. Wolf, A.V.G. Chizmeshya, J.R. Diefenbacher and M.J. McKelvy, *Environmental Science and Technology* (In press, December 2003).

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Students Supported under this Grant

Deirdre Gormley: Doctoral candidate in the Science and Engineering Materials Ph.D. Program at Arizona State University from 2001-2005 (Ph.D. awarded Dec 2005).

Michael Kocher: Undergraduate research assistant jointly enrolled in the Physics and Chemistry programs at Arizona State University.

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Youngechul Kim: Doctoral candidate in the Science and Engineering Materials Ph.D. Program at Arizona State University.

APPENDIX 2 : Technical Progress Reports for Years 1, 2 and 3

**ENHANCING THE ATOMIC-LEVEL UNDERSTANDING
OF
CO₂ MINERAL SEQUESTRATION MECHANISMS
VIA
ADVANCED COMPUTATIONAL MODELING**

Type of Report: Year 1 Technical Progress

Reporting Period Start Date: 9/20/01

Reporting Period End Date: 9/20/02

Principal Author: A.V.G. Chizmeshya*

Co-Investigators: M.J. McKelvy and O.F. Sankey

Date Report Issued: December 19, 2002

DOE Award Number: DE-FG26-01NT41295

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ABSTRACT

Fossil fuels currently provide 85% of the world's energy needs, with the majority coming from coal, due to its low cost, wide availability, and high energy content. The extensive use of coal-fired power assumes that the resulting CO₂ emissions can be vented to the atmosphere. However, exponentially increasing atmospheric CO₂ levels have brought this assumption under critical review. Over the last decade, this discussion has evolved from whether exponentially increasing anthropogenic CO₂ emissions will adversely affect the global environment, to the timing and magnitude of their impact. A variety of sequestration technologies are being explored to mitigate CO₂ emissions. These technologies must be both environmentally benign and economically viable. Mineral carbonation is an attractive candidate technology as it disposes of CO₂ as geologically stable, environmentally benign mineral carbonates, clearly satisfying the first criteria. The primary challenge for mineral carbonation is cost-competitive process development.

CO₂ mineral sequestration – the conversion of stationary-source CO₂ emissions into mineral carbonates (*e.g.*, magnesium and calcium carbonate, MgCO₃ and CaCO₃) – has recently emerged as one of the most promising sequestration options, providing *permanent* CO₂ disposal, rather than storage. In this approach a magnesium-bearing feedstock mineral (typically serpentine or olivine; available in vast quantities globally) is specially processed and allowed to react with CO₂ under controlled conditions. This produces a mineral carbonate which (i) is environmentally benign, (ii) already exists in nature in quantities far exceeding those that could result from carbonating the world's known fossil fuel reserves, and (iii) is stable on a geological time scale. Minimizing the process cost *via* optimization of the reaction rate and degree of completion is the remaining challenge.

As members of the DOE/NETL managed National Mineral Sequestration Working Group we have already significantly improved our understanding of mineral carbonation. Group members at the Albany Research Center have recently shown that carbonation of olivine and serpentine, which naturally occurs over geological time (*i.e.*, 100,000s of years), can be accelerated to near completion in hours. Further process refinement will require a synergetic science/engineering approach that emphasizes simultaneous investigation of both thermodynamic processes and the detailed microscopic, atomic-level mechanisms that govern carbonation kinetics.

Our previously funded Phase I Innovative Concepts project demonstrated the value of advanced quantum-mechanical modeling as a complementary tool in bridging important gaps in our understanding of the atomic/molecular structure and reaction mechanisms that govern CO₂ mineral sequestration reaction processes for the model Mg-rich lamellar hydroxide feedstock material Mg(OH)₂. In the present simulation project, improved techniques and more efficient computational schemes have allowed us to expand and augment these capabilities and explore more complex Mg-rich, lamellar hydroxide-based feedstock materials, including the serpentine-based minerals. These feedstock materials are being actively investigated due to their wide availability, and low-cost CO₂ mineral sequestration potential.

Cutting-edge first principles quantum chemical, computational solid-state and materials simulation methodology studies proposed herein, have been strategically integrated with our new DOE supported (ASU-Argonne National Laboratory) project to investigate the mechanisms that govern mineral feedstock heat-treatment and aqueous/fluid-phase serpentine mineral carbonation *in situ*. This unified, synergetic theoretical and experimental approach will provide a deeper understanding of the key reaction mechanisms than either individual approach can alone. *Ab initio*

techniques will also significantly advance our understanding of atomic-level processes at the solid/solution interface by elucidating the origin of vibrational, electronic, x-ray and electron energy loss spectra observed experimentally.

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1. INTRODUCTION

The main focal point of the modeling effort in YEAR 1 of the present Innovative Concepts II award, DE-FG26-01NT41295, has been to explain and elucidate the microscopic origin of structural modifications in lizardite due to heat induced dehydroxylation. Robust, quantitative structural models of the modified mineral are a necessary prerequisite for the subsequent study of carbonation in these materials (see work plan for year 2-3 of the current award performance period, reproduced from the Original proposal in Appendix 2 of the present document). A preliminary account of the first accomplishment has been published in a conference proceeding. Archival journal articles describing both accomplishments are soon to be submitted for publication. The following Technical Progress Report describes research achievements during the first year of performance.

2. EXECUTIVE SUMMARY

2.1 OBJECTIVES

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 will be 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 project will include (i) simulation of the morphological changes associated with serpentine heat-activation to understand its role in enhancing carbonation reactivity, (ii) development of a non-empirical site reactivity model for CO₂ with serpentine, and (iii) detailed investigation of the serpentine surface dissolution mechanisms that govern carbonation kinetics, and (iv) the use of first-principles methods to provide deeper atomic-level insight into the mechanistic experimental observations in the partner ASU/ANL studies (*e.g.*, *in situ* studies of reaction intermediate formation).

2.2 ACCOMPLISHMENTS TO DATE

Personnel: Shortly after the establishment of the financial accounting we circulated advertisements for a graduate research assistant (GRA) and for an undergraduate research assistant (URA). In early December we interviewed a number of candidates and subsequently hired two very promising students. The graduate researcher is Ms. Deirdre Gormley, a Science and Engineering of Materials program doctoral candidate. She was selected because of her strong quantum mechanics and previous modeling and computation background. Her start date is January 1, 2002. The URA position has been filled by Mr. Michael Kocher, a senior undergraduate completing a joint Physics-Chemistry bachelor's degree program. Michael has an excellent background in computing and programming and will assist in retrieval, organization and analysis of numerical data generated by our simulation programs.

Equipment and Software: The DMol³ computer program (Accelrys Inc.) was purchased on schedule, and installed on one of our Facility SGI Workstation/Servers in mid-October. Benchmark calculations on simple oxides (MgO, Mg(OH)₂) and gas phase systems (H₂O, CO₂) were performed within the first month of the award period by the principal author. The dedicated dual-processor computational workstation intended for production runs, which was ordered in October, did not arrive until 11/10/01. In the interim, *ab initio* modeling was carried out on a comparable set of machines owned by co-PI Prof. O.F. Sankey, as well as on other shared ASU resources (listed in the award proposal). The dedicated project workstation, together with the software required to execute the proposed research, was fully tested and operational on 11/19/01.

Technical Highlights:

- State-of-the-art quantum mechanical simulation methods were used to predict the existence of a novel, metastable, meta-serpentine material in which order and disorder coexist. This was used to explain the unusual progression of x-ray diffraction patterns observed in association with the heat treatment of serpentine feed stock minerals. Studies were undertaken to elucidate the origin of dehydroxylation mechanisms via simulation of early stage decomposition (%OH loss in the 0-15% range).
- First principles simulation of the subtle structural changes associated with initial dehydroxylation led a new method for analyzing x-ray data – Differential Diffraction Analysis – in which small, systematic XRD spectral changes are simulated and compared with experiment directly. By separating the effect of chemical modification from bonding/coordination changes the method provides new insight into structure modification.
- Modeling and Simulation research results presented at the 27th International Coal Utilization and Fuel Systems conference in Tampa, Florida at the beginning of March 2002.
- Equation of state properties: Completed benchmark simulation of solid phases of 1T-Lizardite (Mg₃Si₂O₅(OH)₄), MgO, Mg(OH)₂, SiO₂ α-quartz, MgCO₃, and gas phase CO₂, and H₂O. The purpose is to generate data needed for end-member/product-phase vertical reaction enthalpies. Structural models based on these simulations are necessary as input for subsequent modeling studies.
- Request for supercomputer resources at the National Energy Research Supercomputer Center (NERSC), and at the Pittsburgh Supercomputing Center (PSC). An initial startup grant was awarded by the PSC on April 24, 2002 providing the theory group at ASU with 50 units on a CRAY platform. This allocation will be used to initiate the serpentine-mineral-surface/aqueous-interface study aimed at elucidating the dissolution and surface chemistry processes under target experimental solution conditions. We anticipate additional allocation awards in connection with the planned aqueous mineral reaction investigations in YEAR 2.
- Modeling of x-ray spectra collected under target conditions (2300 psi/180°C) at the Advanced Photon Source (Argonne National Laboratory) in the 640°C heat treated sample. Focus on MIE-like particle scattering features at low-angle in the XRD spectrum.

- First principles simulations were used to predict the frequencies of infrared absorption bands in the baseline feedstock mineral. Our work provides the first unambiguous assignment of hydroxyl band features in lizardite: silica-cage vibrations are higher in frequency than their brucite-layer counterparts. Simulations will be used to correlate shifts in frequency with changes in local structure during feedstock pre-treatment and carbonation.
- Supercomputer-based quantum molecular dynamics studies of the temperature dependence of the dehydroxylation process have been initiated. This involves the calculation of water formation rate and diffusivities of mineral (and product) components (Mg, Si, OH, H₂O and protons).

2.3 SIGNIFICANCE TO FOSSIL ENERGY PROGRAMS

Fossil fuels, especially coal, can support the energy demands of the world for centuries to come, if the environmental problems associated with CO₂ emissions can be overcome¹⁻². Mineralization of stationary-source CO₂ emissions as carbonates can provide safe capture and long-term sequestration³⁻⁴. Carbonation of Mg-rich lamellar-hydroxide-based minerals (*e.g.*, the model Mg(OH)₂ system and serpentine based minerals) is a leading process candidate, which generates the stable, naturally-occurring mineral magnesite (MgCO₃). Optimizing the carbonation reaction rate and its degree of completion are key to process cost and viability. This project focuses primarily (but not exclusively) on the carbonation reaction process mechanisms in serpentine minerals at the atomic level. Carbonation and treatment processes in the olivine class of feedstock minerals will also be briefly studied in support of the research being carried out by the National Mineral Sequestration Working Group managed by NETL. In both cases, the objective is to provide the mechanistic understanding to accelerate the engineering development of improved carbonation materials and processes for carbon dioxide disposal.

3. KEY RESULTS AND DISCUSSION

3.1 Feedstock Pre-processing and the Effects of Heat Treatment: Background

Mg-rich minerals, such as brucite (Mg(OH)₂), olivine (*e.g.*, forsterite: Mg₂SiO₄), and serpentine (Mg₃Si₂O₅(OH)₄), represent a related class of materials that are particularly well suited for this application. Among these, both serpentine and olivine deposits are common throughout the world. Serpentine-based CO₂ mineral sequestration is particularly appealing, as global serpentine deposits can be mined at low cost and in vast. Enhancing the carbonation reaction rate is the key to lowering process cost, as longer reaction times dramatically increase cost.⁵⁻⁷ This is the primary focus of the CO₂ Mineral Sequestration Working Group managed by the U.S. Department of Energy, consisting of members from the Albany Research Center, Arizona State University, Los Alamos National Laboratory, the National Energy Technology Laboratory, and Science Applications International Corporation. The low-cost potential offered by serpentine CO₂ mineral sequestration has been recognized by the Zero Emission Coal Alliance (ZECA); an organization of researchers from Los Alamos National Laboratory and U.S. and Canadian coal suppliers and

utilities. Again, the key is increasing the serpentine carbonation reaction rate enough to allow economically viable CO₂ sequestration process development.

Recently our working group colleagues at the Albany Research Center have made exciting breakthroughs by showing that aqueous-solution CO₂ mineral carbonation reactions can accelerate Mg-rich mineral carbonation from the naturally occurring geological time scale (100,000's years) to less than an hour under moderate temperature and CO₂ pressure conditions⁶. The key reactions for serpentine and olivine/forsterite, respectively, are as follows:

The carbonation of untreated serpentine is found to be significantly slower than that observed for olivine.⁸ 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 several hours at over 600°C, its carbonation rate has been found to increase dramatically. 70-85% carbonate conversion has been

Figure 1: XPD patterns and IR spectra for heat treated Globe lizardite (see preceding companion article for additional details). Black traces: Reference lizardite material under ambient conditions; blue traces: meta-serpentine (heated to 600°C) containing 50% residual hydroxyl, red traces: meta-serpentine (heated to 680°C) containing ~10% residual hydroxyl. Orange arrow in (a) indicates a new low-angle feature in the XPD pattern; asterisks in (b) indicate new vibrational features in the IR data (see preceding companion article for data sequence).

achieved in ~ 1hr (~150°C and 115-185 atm CO₂), exceeding the 1hr conversion rate observed for olivine by an order of magnitude. Unfortunately, heat pretreatment is energy intensive and cost prohibitive. As discussed in the preceding article, an atomic-level understanding of the mechanism(s) by which heat pretreatment enhances serpentine carbonation reactivity is crucial to being able to engineer more cost-effective pretreatment processes. However, many of the important

factors that govern serpentine heat-activation *via* dehydroxylation are only observable at the atomic level.

The infrared (IR) and x-ray powder diffraction (XPD) data for Globe A lizardite, collected as a function of % hydroxyl content, point to a complex relationship between the structural evolution of the system, its extent of dehydroxylation, and ultimately its reactivity with CO_2 . We have reproduced a portion of the IR and XPD data sequence in Figure 2, above. The corresponding XPD spectra evolve from that of the baseline lizardite (black trace) to an intermediate meta-serpentine material (red trace), with what appears to be a doubled c lattice parameter (a stage-2 lamellar meta-serpentine intermediate material), as evidenced by the new low-angle reflection near $2\theta \sim 6^\circ$. The corresponding vibrational spectra (shown in the right panel of the figure) reveal a concomitant shift in the hydroxyl band frequencies accompanying the formation of the meta-serpentine. Further heating leads to amorphization, and upon complete dehydroxylation, by the condensation into an assemblage of Mg_2SiO_4 (forsterite) and MgSiO_3 (enstatite). Clearly the detailed interpretation of the IR and XPD behavior with respect to variation in hydroxyl content requires a structural model. This is the focus of our recent modeling activity. The goal is to relate the observed spectroscopic observations to an atom-level description of the heat-activated lizardite.

Our general approach to modeling these systems is to first generate model structures which correspond *precisely* the stoichiometry of the observed meta-serpentine. Relaxation of the volume and atomic positions using accurate quantum mechanical forces and total energy is then expected to provide plausible meta-serpentine representations which can then be subsequently used in the simulation of vibrational, electronic and elastic behavior. We use two schemes to generate hypothetical structures: (i) beginning with an appropriate supercell of lizardite we remove a stoichiometric amount of water to produce meta-serpentine, and (ii) we start with an assemblage of MgSiO_3 and Mg_2SiO_4 and add water to achieve the target stoichiometry. In the present work we adopt the first approach, and focus on the interpretation of XPD and IR spectra discussed in the preceding article on heat-activated lizardite.

3.1.1 Static Ground State Crystalline Simulations

As a preliminary step to simulating lizardite, and “meta-lizardite” we computed the ground state properties and compression equation of state of a number of related oxide materials: MgO , $\text{Mg}(\text{OH})_2$, MgSiO_3 . In addition to providing a necessary check on the numerical procedure, valuable structural, electronic and elastic information is also generated in the process.

Our calculations were performed using the first-principles total-energy VASP code⁹, which employs a plane-wave basis and ultrasoft pseudopotentials within density functional theory. The exchange-correlation effects are treated with the local density ap-approximation¹⁰ (LDA) using the Ceperley-Alder functional¹¹, or with the generalized gradient approximation¹⁰

Figure 2: Model representation of the 1T-Lizardite polymorph of serpentine mineral feedstock showing approximately 48 unit cells (16 per layer).

(GGA). The compression equation of state was computed by optimizing the crystalline structures (cell parameters as well as internal parameters) for a series of volumes spanning a range of about -15% to $+40\%$ about the experimentally observed ambient pressure volume. We used an energy cutoff of 600 eV for the plane wave basis to ensure good convergence of the state properties. Several dozen special k -points were used for the dense systems, whereas Γ -point sampling was sufficient for systems like lizardite. However, as we shall show below, a reliable prediction of the internal crystalline structure of lizardite requires a denser (more computationally expensive) k -point integration grid.

A conjugate-gradient technique was used to drive the fixed volume structures to a minimum force configuration.

System	E_0 (eV/atom)	V_0 ($\text{\AA}^3/\text{atom}$)	K (GPa)	K'
MgO (Periclase)	-5.827	9.10 (9.35)	172 (160)	4.0 (4.0)
Mg(OH) ₂ (Brucite)	-4.879	7.33 (8.02)	65 (45)	5.2 (5.7)
MgSiO ₃ (Enstatite)	-6.803	10.45 (10.48)	125 (121)	3.1 (3.8)
Mg ₃ Si ₂ O ₅ (OH) ₄ (1T-Lizardite)	-5.844	9.38 (9.91)	78 (*)	7.3 (*)

Table 1. Experimental and theoretical parameters of the Birch-Murnaghan equations of state for MgO ($Fm\bar{3}m$ symmetry), Mg(OH)₂ ($P\bar{3}m1$), MgSiO₃ ($Pbcn$) and Mg₃Si₂O₅(OH)₄ ($P31m$). The tabulated values for the binding energy (E_0), equilibrium volume (V_0), zero-pressure bulk modulus (K) and $P=0$ bulk modulus pressure derivative (K') were obtained by fitting our energy vs. volume data to a third-order Birch-Murnaghan equation of state. Experimental data shown in bold face from Ref.[12]. An asterisk indicates that the value has not yet been measured and/or reported.

The LDA results are summarized in Table 1 and indicate that the simulations generally give a very good account of experimental trends. The binding energies represent the difference between the crystalline energy and neutral atoms, divided by the total number of atoms per unit cell. The predicted internal unit cell parameters and lattice constants for brucite, enstatite and lizardite (not shown) are found to agree with experiment to better than 1%, except for in the case of brucite and lizardite, where the interlayer binding is overestimated by the LDA. This results in the c -parameter being slightly underestimated compared with experiment. The tendency of the LDA to underestimate bond lengths (and therefore volume) is well known. As can be seen from the table, this effect leads to a concomitant increase in the bulk moduli relative to experiment.

In carrying out the fixed volume internal structure optimizations described above no shape constraint was imposed upon the computational cells. The associated stress tensor exhibited negligible anisotropy indicating no departure from hexagonal symmetry. After each complete equation of state determination we also performed a highly accurate full stress relaxation starting with a volume and lattice configuration close to equilibrium, and obtained the same equilibrium volume as determined from a energy-volume fit. This procedure also yields the detailed internal atomic structure of the mineral. A plane wave basis cutoff of 1000eV (using projected-augmented

wave (PAW) type ultrasoft pseudopotentials⁹⁾ was used to ensure a high level of convergence of the energy and atomic forces within the system. The k -space integrations were carried out using 1x1x1 and 2x2x1 Monkhorst-Pack grids and Gamma point centering. The results for the 1x1x1 and 2x2x1 calculations are presented in Tables 2 and 3, respectively, where they are compared with the experimental structural data of Guggenheim and Zhan¹³.

<i>Atom</i>	LDA			GGA			Experiment		
<i>a</i> (Å)	5.1524			5.2750			5.3267		
<i>c</i> (Å)	7.1101			7.4037			7.2881		
	x	y	z	x	y	z	x	y	z
<i>Mg</i>	0.331	0	0.454	0.331	0	0.451	0.332	0	0.455
<i>Si</i>	1/3	2/3	0.064	1/3	2/3	0.070	1/3	2/3	0.074
<i>O1</i>	1/3	2/3	0.286	1/3	2/3	0.287	1/3	2/3	0.291
<i>O2</i>	0.602	0	-0.014	0.592	0	-0.005	0.507	0	-0.008
<i>O3</i>	0.664	0	0.592	0.664	0	0.586	0.664	0	0.588
<i>O4</i>	0	0	0.296	0	0	0.303	0	0	0.304
<i>H1</i>	0.660	0	0.729	0.658	0	0.717	0.583	0	0.732
<i>H2</i>	0	0	0.159	0	0	0.172	0	0	0.197

Table 2: LDA and GGA calculations of the internal structure (in fractional coordinates) and unit cell parameters (in Angstroms) of 1T-Lizardite. Single k -point ($k=0$) sampling was used in the reciprocal space integrations.

From an examination of these tables it is clear that the GGA slightly overestimates the lattice parameters while the LDA yields a slight underestimate relative to experimental observation. However, the overall predictive ability of density functional theory is remarkable. The internal positions of all the heavy atoms are extremely well reproduced, especially using the 2x2x1

<i>Atom</i>	LDA			GGA			Experiment		
<i>a</i> (Å)	5.2653			5.3633			5.3267		
<i>c</i> (Å)	7.0904			7.4167			7.2881		
	x	y	z	x	y	z	x	y	z
<i>Mg</i>	0.331	0	0.456	0.331	0	0.453	0.332	0	0.455
<i>Si</i>	1/3	2/3	0.067	1/3	2/3	0.074	1/3	2/3	0.074
<i>O1</i>	1/3	2/3	0.290	1/3	2/3	0.291	1/3	2/3	0.291
<i>O2</i>	0.531	0	-0.020	0.514	0	-0.008	0.507	0	-0.008
<i>O3</i>	0.664	0	0.591	0.664	0	0.585	0.664	0	0.588
<i>O4</i>	0	0	0.298	0	0	0.303	0	0	0.304
<i>H1</i>	0.660	0	0.729	0.650	0	0.715	0.583	0	0.732
<i>H2</i>	0	0	0.159	0	0	0.173	0	0	0.197

Table 3: As for Table 2 but with reciprocal space integrations evaluated using a 2x2x1 Monkhorst-Pack grid.

integration grid and GGA (Table 3). The only minor discrepancy is found in the prediction of the hydroxyl bond lengths which are estimated to be 0.02-0.06 Å too long. It is also noteworthy that the GGA also overestimates the c-axis cell parameter by about 0.13 Å (for the 2x2x1 GGA case). This is not surprising since it is well known that non-local correlation effects, *e.g.*, van der Waals bonding, are not included at this level of theory. In spite of this the agreement is excellent and more than sufficient in terms of predictive accuracy for all of our subsequent modeling studies.

3.1.1(a) Initial stages of Dehydroxylation

Combined thermogravimetric and x-ray diffraction analysis indicates that the dehydroxylation induced by heat-treatment produces a gradual change in the structure and composition of the lizardite. An understanding of the structural origin of carbonation reactivity enhancement in heat-treated lizardite seems to be related to the microscopic structure, *e.g.*, the access to reactive sites such as under-coordinates oxygen ions, etc. In order to systematically

Figure 3: Simplified conceptual models of the dehydroxylation process in lizardite. Green triangles represent the silica sheet tetrahedral; black filled circles: Mg; yellow rectangles: hydroxyls and hollow and semi-hollow rectangles: hydroxyl and proton vacancies, respectively.

explore the effect of heat-treatment and water loss on the solid-state structure of the mineral we undertook the study of 12.5% dehydroxylated materials. This corresponding to one out of every eight hydroxyls being removed from the system. To model this system we adopted a large periodic supercell representation of the mineral with sufficient extent to ensure that individual defects (missing protons and hydroxyls) do not significantly interact with their periodic images in neighboring cells.

Ab initio simulation methods (*e.g.*, the

VASP code) were used to elucidate the dehydroxylation reaction, including water formation, in the early stages of heat-treatment in serpentine. Very precise comparisons of the structural trends in going from the baseline (untreated) material to a slightly dehydroxylated sample can be obtained in this way. The main focus is on the initial modifications of the “lizardite” system due to the water loss, and in particular on the implications for the XRD spectra. Figure 3 illustrates schematically two specific water loss/de-hydroxylation scenarios labeled as heteroplanar, involving neighboring planes separated by the inter-lamellar gallery, and homoplanar, in which water is formed from neighboring hydroxyls and protons from within the same “brucite”-like layer.

For stoichiometric 1T-lizardite we have identified four candidate dehydroxylation paths involving various combinations of “brucite-like” and “cage” hydroxyls and protons. Typical configurations are illustrated schematically in Figure 4. The configurations are labeled by two consecutive letters: “B” and/or “C” denoting “brucite”-layer and “cage”-layer protons and/or hydroxyl species. Thus, the configuration CB (not shown in the figure) designates water formation from a cage hydroxyl and a brucite-layer proton while “BB” represents the homoplanar mechanism shown in the right panel of Figure 3. These choices for the configurations assume that the most

energetically accessible water formation routes involve nearest neighbor proton-hydroxyl combinations. However, both homo-planar and hetero-planar situations are considered.

All of the defective (dehydroxylated) unit cells (BB,BC,CB and CC) were derived from an structurally optimized stoichiometric lizardite cell of composition $\text{Mg}_3\text{Si}_2\text{O}_5(\text{OH})_4$ (s) by simple removal of the desired hydroxyl/proton pair according to the procedure described above. We calculated the vertical reaction energy, ΔE , for endothermic formation of the 12.5 % dehydroxylated material according to:

The static ground state energy of a gas-phase water was estimated by placing a single molecule into a large cubic supercell of edge length $\sim 8 \text{ \AA}$. Convergence was obtained by varying the plane-wave cutoff and the cell size until changes of less than $\sim 0.01 \text{ eV}$ in the total energy were observed. After 41 steps, the defective structure reached its ground state. All calculations were carried out on a Pentium IV dual processor workstation using the highly efficient *ab initio* VASP code. For each case considered the equilibrium structure (ground state) of the defective lizardite was obtained by minimizing the quantum mechanical forces on all of the atoms/ions. The unit cell parameters (cell length edges and inter-axial angles) were also determined by simultaneously minimizing the external stress tensor. Full details of our calculations and results are being written up as an archival journal article (see Appendix 1).

Figure 4: (a) Atomic positions of the relaxed lizardite reference structure prior to dehydroxylation reaction , (b) schematic legend indicating the location of: “brucite”-layer (B) and silica cage (C) defect sites. (c) the least metastable BC configuration in which a hydroxyl group is removed from a B site and a proton vacates a C site; (d) most metastable (least favorable) BB configuration, water formation from within a brucite layer.

To summarize, our simulations predict a systematic dilation of Mg-Mg bonds in the vicinity of hydroxyl vacancies, leading to a decoherence in x-ray scattering intensity for reflections originating from these planes. Furthermore, a systematic *decrease* is predicted for the c-axis in the defective structures. Perhaps surprisingly, the least *metastable* structure is BC involving the formation of water from a “brucite”-layer hydroxyl and an abstracted proton from a silica-cage site. The defect formation energies for BB, CB and CC are also positive and range in value from 3.5 to 4.5 eV per H₂O desorbed (*e.g.*, 338 to 435 kJ/mol). It is significant that the spread in defect formation energies is small. This suggests that all of the candidate mechanisms considered may be thermodynamically important in the dehydroxylating mineral. Accordingly, the actual XRD pattern of the meta-lizardite may best be modeled by averaging of the individual XRD patterns for BB, BC, CB and CC configurations according to their Boltzmann weighted energies relative to the lowest energy configuration, BC, at finite temperature.

Differential XRD Analysis: A powerful bridge between Experiment and Theory

The point of contact with experiment is made by comparing the x-ray patterns measured in the laboratory with the synthetic patterns obtained from our predicted structural models. The model x-ray scattering intensities (synthetic powder patterns) were calculated using the *Cerius*² package (Accelrys Inc.) using a preferred orientation along (001), which is consistent with the experimental data, and a March-Dollase function parameter of $R_0=0.7$. The numerical difference between two integrated x-ray diffraction spectra (2θ plots) is exploited in the structural refinement procedure used to derive crystal structures from x-ray data, where it represents the objective function to be minimized. Typically, a synthetic pattern based on an assumed structure is subtracted from the experimental trace and a weighted average of the difference is numerically minimized with respect to the structural parameters in the model to obtain a “best fit” structure. In our case, we seek to interpret the origin of the features in the differential spectrum between two similar materials. The latter pair could be the reference lizardite and a slightly dehydroxylated meta-lizardite, or two neighboring meta-serpentine with similar composition. For small changes in stoichiometry the diffraction patterns of the reference and altered materials are nearly identical, hampering interpretation. However, when the differential spectrum (numerical difference between the two spectra) is examined characteristic features are evident. These are illustrated in left panel of Figure 5, where the effects of structural and chemical change are shown. For examples, a substitutional impurity ($\text{Mg} \leftrightarrow \text{Fe}$) may induce a slight structural change (no shift in peak position) but a significant reduction/increase in peak intensity (top two cases). Alternatively, a systematic trend in the local environment of a given scatterer can lead to a shift in peak position with negligible effect in the intensity. The most general case involves simultaneous combinations of all of these effects.

In the right panel of Figure 5 we illustrate the usefulness of this direct approach by comparing the measured differential patterns for two heat treated samples with the predictions obtained above for the 12.5% meta-lizardite. The most intense reflections in the lizardite system are related to the characteristic length scales of the unit cell. In Table 4 we list the optimized cell parameters for the reference lizardite (designated 100% OH) and the BC 12.5% dehydroxylated model (designated 87.5% OH). The magnitude of the changes in the cell parameters is quite small ($\sim 0.2\%$), but the structural coherence of the internal structure is preserved in the defective meta-lizardite. These and related details will be discussed in an upcoming paper (see Appendix 1). These converged (zero-force) structures were used to generate synthetic XRD patterns, and these were

numerically subtracted to yield the black trace in the right panel of Figure 5. The corresponding differential spectrum for the 550°C Philips sample is shown as the green curve while that corresponding to Globe A 580°C/20°C samples is shown in orange. While the experimental traces share some common features it is clear from a comparison with the theoretical trace that the Philips sample is closer to the ideal 1T-lizardite, and its dehydrolyte than the Globe A sample.

Figure 5: Left panels: Concept schematic illustrating the origin of differential signatures (black curves). Blue curves represent a spectral feature in the reference structure while the red curves denote the corresponding feature in the chemically or structurally altered structure. Right panel: Representative results and comparisons for Philips and Globe A lizardite. The green curve is the differential XRD pattern corresponding to the 550°C Philips sample relative to 20°C spectrum; orange curve: corresponding difference spectrum for Globe A 580°C/20°C samples. Black curve: Theoretical results obtained from first principles simulation.

	$a=2a_L$	$b=\sqrt{3}a_L/2$	$c=c_L$
100% OH	10.780	9.359	7.253
87.5% OH	10.787	9.378	7.238
	0.0 %	+0.2%	-0.2%

Table 4: Change in cell lattice constants of the 12.5% dehydroxylated lizardite model. Here a_L and c_L refer to the 1T lizardite unit cell parameters (in Angstroms).

3.1.1(b) Structural model for 50% weight loss Meta-Lizardite

Since the initial and strongest appearance of the low-angle meta-serpentine intermediate occurs at 50% dehydroxylation (blue IR and XPD traces in Figure 1), we have initiated our studies based on this as a target composition. Figure 6 illustrates the example of 50% dehydroxylated $Mg_3Si_2O_5(OH)_4$ (lizardite) obtained via scheme (i) described on p.10, Section 3.1. Several dozen

model structures were constructed from a 144-atom ($Z=8$) supercell of 1T-lizardite by removal of H_2O corresponding to 50% dehydroxylation. These corresponding supercells have stoichiometry $8 \cdot \text{Mg}_3\text{Si}_2\text{O}_5(\text{OH})_4 - 8 \cdot \text{H}_2\text{O}$ and contain 120 atoms. By experimenting with different strategies for removing the requisite number of OH and H's from the reference cell, we ascertained that the low angle feature near $2\theta \sim 6^\circ$ can only be reproduced when H_2O is preferentially removed from alternating layers with a ratio of 4:1 or greater. A unit cell corresponding to a 13:3 model is shown in Figure 6(b). It also follows that stage-2 behavior (every other lizardite lamella having different oxide/hydroxide compositions) is optimally found for half of the full hydroxide concentration, in analogy with lamellar de-intercalation reaction mechanisms. Note that the meta-serpentine structures represented in Figure 6 are empirical at this stage, namely, they are based on experimental lattice parameters and internal coordinates. Thus, the simulated XPD patterns do not account for ionic relaxation. Nevertheless, these simple structural models demonstrate that uniform dehydroxylation cannot account for the appearance of the low angle features observed, but non-uniform dehydroxylation can.

Figure 6: (a) Synthetic XPD pattern for reference material (1T-Lizardite), (b) Meta-serpentine (50% dehydroxylated) obtained by randomly removing OH and H from the reference lizardite in (a) using a target ratio of $\sim 1:4$ between alternate layers (Legend: H=white, Mg=green, O=red, SiO_4 =grey). Horizontal axes: 2θ (degrees).

Using the 50% dehydroxylated meta-serpentine model structure shown in Figure 6(b) above as a starting point we subsequently carried out full structural relaxation calculation for a 120-atom supercell. A high-quality plane-wave basis set with a cutoff of 600 eV was used together with an

System	Cell Parameters (lengths in Å, angles in degrees)		Energy/atom (eV)	Volume/atom (Å ³ /atom)	Energy/Formula (eV)
$8 \cdot \text{Mg}_3\text{Si}_2\text{O}_5(\text{OH})_4$	$a = 10.484$	$\alpha = 90^\circ$	-5.838	9.364	-105.084
	$b = 9.106$	$\beta = 90^\circ$			
	$c = 14.124$	$\gamma = 90^\circ$			
$8 \cdot \text{Mg}_3\text{Si}_2\text{O}_6(\text{OH})_2$	$a = 10.486$	$\alpha = 90^\circ$	-5.982	11.165	-89.73
	$b = 9.137$	$\beta = 91.45^\circ$			
	$c = 13.987$	$\gamma = 90^\circ$			

Table 5: Structural relaxation results for the 1T-lizardite supercell and for the 50% dehydroxylated serpentine (meta-serpentine) model.

increased tolerance criterion for the calculation of unit cell stress. Identical computational parameters were also used to optimize a 144-atom supercell of stoichiometric lizardite, so that an accurate energy difference for the dehydroxylation reaction could be determined. Simultaneous optimization of the cell shape and volume as well as the internal positions of the atoms required a very accurate calculation of forces and stresses within the unit cell, and demanded several weeks of continuous computation on a modern dual-processor workstation. Symmetry constraints were not imposed upon the atomic positions within the cell. The results are summarized in Table 5, which lists the relaxed cell parameters, as well as the binding energies. The lizardite results listed here can be directly compared with those listed in Table 1. Small differences arise because slightly less stringent computational conditions were employed for the larger cells. The removal of water to form meta-serpentine, $\text{Mg}_3\text{Si}_2\text{O}_6(\text{OH})_2$, induces a slight monoclinic distortion in the crystalline structure and an increase in the volume per atom. This result suggests that staged dehydroxylation is not correlated with a dramatic volume collapse. From the parameters listed above the unit cell volume decrease amounts to about 1%, but because water was removed the density also is found to decrease from ~ 2.73 g/cc in the simulated lizardite to ~ 2.57 g/cc in the simulated meta-serpentine. Using the energies given in Tables 1 and 5 it is possible to compute the binding energy difference associated with dehydration, *e.g.*,

The binding energy of H_2O is computed to be -11.93 eV¹⁴. This yields a formation enthalpy of 18.7 kcal/mol for reaction (3) which compares well with the observed value of 19.4 kcal/mol¹⁵, while for reaction (4) we obtain a substantially larger value of 79.0 kcal/mol. This large value may be associated with the larger binding energy of the silica sheet hydroxyls compared with their “brucite”-like analogs.

The implications of these calculations for the XPD are illustrated in Figure 7, which shows that the low angle feature is preserved even after relaxation and that the primary reflection near $2\theta \sim 12^\circ$ (now indexed as 002) is slightly shifted but not significantly attenuated. The slight disordering of the basal plane symmetry in every alternate layer apparently leads to blunting of the reflections in the range $2\theta \sim 40$ - 80° , which is also consistent with the observed XPD pattern. The simulations indicate that dehydroxylation induces comparatively small distortion in the tetrahedral silica layer in spite of the rather significant disordering of the Mg and O sublattices. Preliminary analysis of the bonding within the dehydroxylated layer indicates the presence of several low-coordination oxygen sites which have been experimentally identified as preferred CO_2 adsorption sites in oxide surfaces¹⁶. Our simulations indicate that the residual hydroxyls within the heavily dehydroxylated bottom layer (figure 4(a)) retain their functionality as pillars and serve to maintain the ~ 7 Å spacing between silica sheets. The stage-2 behavior alluded to above is very common in graphite and transition-metal dichalcogenide deintercalation processes. This suggests that a somewhat similar process may be occurring in the early stages of meta-serpentine formation. The rumpling of the Mg and O sublattice that accompanies stage-2 compound formation is also particularly intriguing, as this may well be related to the enhanced Mg solubility and carbonation reactivity observed for meta serpentine.

Figure 7: Effects of structural relaxation on the XPD pattern. (a) 50% residual hydroxyl meta-serpentine, (b) initial lizardite structure. Left panel: simulated XPD; black trace: initial lizardite structure, red trace: relaxed meta-lizardite structure. (Legend: H=white, Mg=green, O=red, SiO₄=grey)

The above results are based on a statistical description of plausible defective crystalline configurations for 50% water removal were presented at the 2002 Clearwater conference. Our detailed modeling of the 50% dehydroxylated material has nicely explained the origin of a number of observed spectroscopic features. However, the precise thermal dehydroxylation mechanism, *e.g.*, diffusion path of OH and H₂O within the decomposing material is has still not been identified. However, this information may be obtained from a full first principles quantum molecular dynamics simulation at finite temperature and pressure. Our work in this area has already been initiated (October of 2002) and preliminary results will be discussed at the 2003 Clearwater conference. A complete detailed summary will be provided in next years Technical Progress Report.

3.1.1(c) Carbonation in 50% weight loss Meta-Lizardite

The natural question arising from the results of the previous section is: Why does the 50% meta-lizardite carbonate more readily? A partial answer is suggested by the modeling study just discussed: The removal of half significant water from the mineral does not necessarily lead to imminent collapse of the structure. Instead, a staging type of behavior is adopted as a low energy state. The open “pillared” configuration of this meta-lizardite may promote rapid diffusion of water and CO₂ under the supercritical conditions observed experimentally. To obtain a preliminary picture of the interaction of CO₂ with meta-lizardite we have carried out a quantum molecular dynamics study using a previously converged 50% model (see 3.1.1(b) above), in which the lattice parameters are $a=10.5311 \text{ \AA}$, $b=9.1732 \text{ \AA}$ and $c=14.0226 \text{ \AA}$. The latter values are slightly larger than those reported in Table 5, above, due to thermal expansion. A somewhat large time step of 1.0 fs was used to integrate the equations of motion under constant temperature rescaling conditions and $T=450\text{K}$ (*e.g.*, $\sim 177^\circ\text{C}$). The meta-serpentine lattice was initially prepared by running the

dynamics for about 2.0 ps. The instantaneous velocities were stored and used to initiate a new simulation in which the CO₂ molecule was introduced into the void-like gallery between heavily/lightly dehydroxylated layers in the meta-lizardite. Using the same computational conditions the dynamics was then re-initiated. Minimal drift in the total energy was observed until 0.82 ps into the simulation when the CO₂ molecule was observed to bind to an oxygen site. Analysis of the E(t) reveals a mean binding energy of ~ 2.82 eV (272 kJ/mol) for the CO₂. The resulting configuration is shown in Figure 8, and consists of a CO₃ type propeller structure characteristic of carbonate (MgCO₃). Several other runs, initiated under similar starting conditions, led to the same final structure, but involving other (similar) low-coordination oxygen sites.

Our simulation results strongly suggest that once access to low-coordination oxygen sites is available, the mechanism for precursor formation proceeds quite readily. Conversely, a stoichiometric lizardite structure may only allow CO₂ to permeate the gallery between layers (with ~ 2 Å clearance). The conformational restriction on CO₂ together with its interaction with essentially saturated oxide and hydroxyl sites, means that carbonate formation should be strongly precluded. It is in fact not observed, as confirmed by a recent synchrotron study which we undertook to establish that untreated lizardite feedstock does not readily carbonate, even when

Figure 8: Quantum molecular dynamics simulation of a CO₂ molecule interacting with meta-lizardite. The yellow arrows indicate the position of the CO₂ molecule. Left frame: initial configuration, as described in the test. Right frame: Stable binding configuration of CO₂ in the bulk defective mineral. Note the minimal structural perturbation to the top lizardite-like layer. The carbonate precursor is seen as the propeller structure formed from the CO₂ and an under-coordinated oxygen atom in the right panel. (Legend: H=white, Mg=green, O=red, SiO₄=grey)

subjected to high temperatures and CO₂ pressures. Another intriguing formation mechanism could occur near the free surface of the meta-lizardite. Namely, the newly formed MgCO₃ precursor formed in the near-surface region of the mineral may subsequently diffuse out into the solution and provide a nucleation site for further carbonate growth in solution. Because of its potential importance to the overall reactions being studied, we plan on exploring this idea in more detail in

YEAR 2 studies which will focus on the mineral-solution interface and the aqueous carbonation of meta-lizardite.

3.1.2 SPECTROSCOPIC CHARACTERIZATION

3.1.2(a) Vibrational Spectra: Phonons

The Γ -point vibrational spectrum of lizardite was computed using a frozen phonon approach. An 18-atom unit cell of 1T-lizardite was first structurally optimized to obtain a minimum energy configuration. The DMol³ code¹⁷ with the Perdew-Wang local exchange-correlation functional¹⁸, and an accurate double numerical basis set with polarization (DNP¹⁹) was used to compute the dynamical matrix using a five-point finite difference scheme 0.01Å atomic displacements. The mass-weighted Hessian was then diagonalized to yield 54 normal modes. The full spectrum will be discussed in detail in a subsequent publication. Here, for the purpose of elucidating the dehydroxylation behavior of lizardite in the context of heat-treatment, we focus on the hydroxyl bands.

The results are summarized in Figure 9 below, where it is seen that the manifold consists of two non-degenerate modes of frequency 3683 and 3642 cm⁻¹, and a pair of degenerate modes at 3614 cm⁻¹. In order to facilitate the discussion we have inset a structural model of the unit cell, with the silica “cage” hydroxyls denoted by the subscript “C”, and the “brucite”-like hydroxyls indicated by a subscript “B”. With respect to the space group symmetry of the unit cell, *P3m1*, the latter reside on (3c) sites having *C*₃ symmetry, while the “cage” hydroxyls occupy (1a) sites possessing *C*_{3v} symmetry. From factor group analysis it follows that the stretching hydroxyl modes are active in both the Raman and IR. The hydroxyl band portion of a Raman spectrum collected in our laboratory is shown in Figure 9(b) and confirms that the primary OH vibrational bands are common to both spectra. In our preliminary work we did not compute the intensities, but from the displacement patterns indicated by the eigenvectors in the figure we expect the two non-degenerate modes at 3642 and 3683 cm⁻¹ to be dominant. In the literature on FTIR spectroscopy of serpentine minerals, reference is frequently made to bands associated with “inner” and “outer” hydroxyl motion. Our calculated eigenvectors indicate that the highest frequency band is due to the motion of the hydroxyls located within the silica cages, while the 3642 cm⁻¹ band is associated with “brucite”-like hydroxyls denoted by “B” subscripts in the figure inset.

To address the possible effects due to impurities such as iron on the hydroxyl band frequencies, we repeated the calculations using the above procedure, but for the hypothetical phase Mg₂FeSi₂O₅(OH)₄. The resultant eigenvectors were found to be almost identical to those reported in Figure 5 while the OH bands are slightly shifted to lower frequencies (3668, 3626, 3601, 3601 cm⁻¹). Recent by studies by other groups²⁰ have also shown that a detailed analysis of the OH stretching bands between 3500-3700 cm⁻¹ can be used to distinguish between different serpentine polymorphs even when other natural or synthetic minerals are present within the samples. The interlayer OH frequencies generally shift downwards in going from chrysotile to lizardite to antigorite. Such information can be used to accelerate the development of a practical carbonation reactivity matrix for serpentine feedstock materials by providing a efficient, low-cost screening/characterization technique for use in the field separation of serpentine feedstock materials.

Figure 9: Summary of hydroxyl band vibrational analysis: (a) Observed OH-band infrared spectrum of Globe A Lizardite, (b) observed OH-band Raman spectrum of Globe A Lizardite, (c) Schematic of the unit cell of Lizardite indicating the species labeling. The accompanying table lists the computed frequencies and mass-weighted eigenvectors describing the atomic displacement patterns corresponding to each mode. (Legend: H=white, Mg=green, O=red, SiO₄=gray.)

3.1.5 Energy Loss Near Edge Spectra (ELNES) of Lizardite

Electron Energy Loss Spectra (EELS) and vibrational spectra (IR/Raman) can be used to help characterize, or “fingerprint”, hitherto unknown intermediate materials formed during dehydroxylation/carbonation by providing an interpretation of the corresponding observed spectra in actual experiments. In principle, this provides an important bridge between the atomic level structure of the material and the energy loss spectrum at various energies. We have used state-of-the-art first principles simulations to generate very detailed information about the source of EELS spectral features. The near edge structure is approximately related to the conduction band density of states, and variations in magnitude as a function of energy loss are related to differences in the chemical environment for each constituent (*e.g.*, oxygen, carbon). We employed the full potential linearized augmented plane wave (FPLAPW) method as implemented in the WIEN2k program²¹ to compute the Energy Loss Near Edge Spectra (ELNES) within the generalized gradient approximation (GGA). Full dynamic form factors were computed using crystalline Bloch states²². The latter were generated using the well-converged structures obtained earlier (as described in section 3.1 above). A broadening function of $\sim 2\text{eV}$ was applied to the raw spectra to simulate experimental conditions.

The symmetry of the lizardite unit cell suggests oxygen K-edges should be a very sensitive probe of local bonding and structure. This is because oxygens are present in the tetrahedral framework, the magnesium layer and in the hydroxyl layer. This is less true for Magnesium and Silicon L_{23} edges, which are expected to be less rich in structure due to their simpler range of coordination within the crystalline environment. For the oxygen K-edge, differences in bonding character for chemically distinct oxygen sites within the crystal yield individual weighted contributions to the total cross-section, as shown in Figure 10, above. Thus, with reference to the total curve (black) and the violet curve, the shoulder feature at edge onset near 5 eV can be seen to be due to silica cage hydroxyl oxygen. The prominent feature at 15 eV is due to Mg near neighbor oxygens *e.g.*, apical tetrahedral oxygens and “brucite-like” hydroxyl oxygens denoted by the red and blue curves, respectively. Apical oxygens are also clearly responsible for the main feature near 22 eV (enhancement in energy loss coming from the red curve). Similarly, the 34 eV feature is mainly related to brucite hydroxyl oxygens.

Figure 10: Composite figure containing a schematic representation of the 1T lizardite structure (inset) as well as the predicted oxygen K-edge electron energy loss structure (black curve). The individual colored curves represent the contributions to the full spectrum arising from different oxygen sites within the crystal (see explanation in text). Legend: H=white, Mg=green, O=red, SiO₄=gray.

Experimental EELS analysis of the baseline lizardite as well as a series of meta-serpentine prior to and after carbonation, are planned in the coming year. Predictive calculations of the energy loss spectrum similar to those described here, will be used in conjunction with the baseline spectrum of the unaltered lizardite to interpret the structural changes induced by heating, leaching and carbonation.

3.2 SIMULATIONS OF THE CARBONATE PRODUCT

3.2.1 Origin of Low-angle MIES Scattering in Synchrotron Data

Figure 11: Integrated synchrotron diffraction data of the 640°C meta-serpentine sample in a NaCl/Na₂CO₃ solution after introduction of CO₂ at 1250 psi. Carbonate formation onset occurs upon heating to ~150°C. Left panel: “Amorphous” signature of the partially decomposed lizardite prior to carbonate formation. Right panel: Spectrum taken at 180°C showing carbonate peaks (2θ ~6-12 degrees) and large low-angle feature with an onset near 0.5 degrees.

Particle Scattering Effects in the small-angle XRD spectrum of 640oC heat-treated sample after carbonation: The objective of this study is to try to provide an explanation for the large intensity scattering signal found in the 640°C sample at reaction conditions (e.g., upon carbonation). As

Figure 12: Figure illustrating the construction of a simple particle-scattering model. In this case carbonate “chunks” of diameter d are placed in a large cell of edge length D . In the example above D is approximately equal to the inter-particle distance.

shown in Figure 12 the relevant spectral feature spans the small-angle region in the vicinity of $2\theta \sim 2^\circ$. We used the Cerius² simulation package to investigate the relationship between inter-particle distance, wavelength and particle size. In our straightforward approach we placed small (~ 1 - 10 nm) “carbonate” particles with definite internal crystalline structure on a large supercell (grid) of size D (~ 1 - 10 nm) as shown in Figure 12 below. Figure 13 shows the relationship between d , D . The incident radiation wavelength was taken to be 0.3311 Å as in the synchrotron experiments. Many of these simulations require several hours on a typical SGI workstation because effectively millions of reflections must be computed to produce a spectrum. Our largest carbonate “chunklette” ($d \sim 32$ Å) contains about 1600 atoms.

Figure 13: Representative simulation results of particle scattering effect. The top panels display the low-angle behavior while the bottom panels show the emergence of crystalline signatures at higher angles. In this example the broadened peaks reflect the position of carbonate features. The latter are shown (for a carbonate powder of particle size ~ 500 Å) as a gray XPD spectrum.

The simulated trends indicate that the onset of particle scattering for fixed particle size occurs at larger angles in proportion to the inter-particle distance (see d vs. D plots below). A surprising amount of structure is observed for fixed inter-particle distance as the particle size is varied. In particular, we find that for small d/D ratios, the low-angle spectrum is the most diffuse. Preliminary results for d/D in the large D limit show that onset of the particle scattering effects can be shifted to larger and larger 2θ values. Note that the simulations were carried out for carbonate particles in an otherwise empty cell. It is likely that the residual silica matrix may provide the dominant particle scattering contribution, but we have shown that the main effect on the low-angle structure of the XPD is mostly independent of the precise nature of the particles. Further studies to validate this concept are currently underway under the pretext of spectroscopic modeling in support of experimental understanding, which extends into the YEAR 2 performance period.

4. CONCLUSIONS

Simulations are most useful when they are carefully designed to answer questions relevant to a specific experimental investigation or technical problem. Close integration of theoretical modeling/simulation with experiment has led to scientific insight that is difficult to achieve independently – a powerful synergy. These notions exemplify the strategy in the present Innovative Concepts Award and we shall continue to integrate advanced quantum mechanical modeling with Dynamic High Resolution Transmission Electron Microscopy (DHRTEM), Electron Energy Loss Spectroscopy (EELS) and infrared (IR) and Raman spectroscopy. The objective is to develop a detailed understanding of carbonation for the model Mg-rich lamellar hydroxide based minerals including lizardite, chrysotile and antigorite which ultimately will lead to the optimization of the relevant CO_2 mineral sequestration reaction processes, and a reduction in process cost. Such advances in fundamental understanding are absolutely essential to the accelerated development of viable CO_2 sequestration technology.

To our knowledge the work presented here represents the first *ab initio* investigation into the combined structural, electronic and vibrational properties of serpentine minerals. It is important to emphasize the role of *ab initio* modeling in the investigation of complex geochemical systems. Our calculations demonstrate that significant insight into the atom-level processes can be obtained from a predictive modeling approach.

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6. APPENDIX 1 : ARTICLES, PRESENTATIONS, AND STUDENT SUPPORT

(i) Publications (in preparation)

“*Ab Initio* investigations of Dehydroxylation Reactions in 1T-Lizardite”, Andrew V.G. Chizmeshya, Deirdre Gormley, Otto F. Sankey and Michael J. McKelvy, *to be submitted*.

“Infrared and Raman Spectroscopic Interpretation of the Dehydroxylation of Lizardite: An Experimental and Theoretical Study”, Jason R. Diefenbacher, Andrew V.G. Chizmeshya, George H. Wolf and Michael J. McKelvy *to be submitted*.

(ii) Publications (in print)

“Developing a Mechanistic Understanding of Serpentine CO₂ Mineral Carbonation Reaction Processes”, Michael J. McKelvy, R. Sharma, R.W. Carpenter, George Wolf, Andrew V.G. Chizmeshya, Hamdallah Bearat and Jason Diefenbacher, *Proc. 27th Int. Tech. Conf. On Coal Util. And Fuel Syst*, Vol.1, 791-802 (2002).

“Atomic-level Understanding of CO₂ Mineral Carbonation Mechanisms from Advanced Computational Modeling”, Andrew V.G. Chizmeshya, Otto F. Sankey, Michael J. McKelvy, R. Sharma, R.W. Carpenter, George Wolf, Hamdallah Bearat and Jason Diefenbacher, *Proc. 27th Int. Tech. Conf. On Coal Util. And Fuel Syst*, Vol.1, 803-814 (2002).

(iii) Conference Presentations

“CO₂ Mineral Sequestration: An Opportunity for Materials Science in Greenhouse Gas Mitigation Technology”, A.V.G. Chizmeshya, Department of Physics and Astronomy, November 7, Tempe, Arizona (2002).

“Fundamental modeling of pre-carbonation treatment effects on serpentine and olivine feedstock”, A.V.G. Chizmeshya, National Mineral Carbonation Working Group Meeting, Sept 9-10, U.S. Department of Energy, Office of Fossil Energy, Albany Research Center, Albany, Oregon (2002).

“Application of First principles Simulation to CO₂ Mineral Sequestration”, A.V.G. Chizmeshya, 17th International Coal Conference, March 11-14, Clearwater, Florida (2002).

(iv) Students Supported under this Grant

Michael Kocher: Undergraduate research assistant, jointly enrolled in the Physics and Chemistry programs at Arizona State University.

Deirdre Gormley: Doctoral candidate in the Science and Engineering Materials Ph.D. Program at Arizona State University.

APPENDIX 2 : WORK PLAN

Work Plan Guide reproduced from the original Proposal:

“The timeline for the proposed work will closely parallel that of the joint ASU/ANL study in order to maximize the impact of the modeling/simulation results, and support the overarching need to efficiently explore ways to optimize serpentine carbonation. Key activities are summarized in the table below. The major focus areas, (i) surface reconstruction/heat-activation

ACTIVITY	YEAR 1	YEAR 2	YEAR 3
Computer Hardware and Software Installation, Configuration and Benchmarking			
Heat-activation (dehydroxylation) Studies of surface reconstruction			
Fluid phase carbonation mechanisms & reaction rate modeling			
EELS, XRD and Vibrational Spectroscopic Simulation			
Modeling defects/impurities and their effect on reactivity			
Technical Progress Reports			
Contractors Annual Review Meeting			
Final Year Peer Review Meeting			

effects, (ii) fluid-phase carbonation mechanism modeling, and (iii) modeling of impurity/defect effects on carbonation, are timed to optimize the overlap with anticipated within the parallel experimental study. The calculation of electron energy-loss spectra, vibrational (IR and Raman) and XRD patterns derived from structural modeling will be ongoing throughout the performance period of the project. Specific studies will complement, and be guided by, the ASU-ANL serpentine carbonation experiments.”

**ENHANCING THE ATOMIC-LEVEL UNDERSTANDING
OF
CO₂ MINERAL SEQUESTRATION MECHANISMS
VIA
ADVANCED COMPUTATIONAL MODELING**

Type of Report:	Year 2 Technical Progress
Reporting Period Start Date:	9/20/02
Reporting Period End Date:	9/20/03
Principal Author:	A.V.G. Chizmeshya*
Collaborators:	M.J. McKelvy, G.H. Wolf, R.W. Carpenter and D.A. Gormley
Date Report Issued:	December 19, 2003
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ABSTRACT

Fossil fuels currently provide 85% of the world's energy needs, with the majority coming from coal, due to its low cost, wide availability, and high energy content. The extensive use of coal-fired power assumes that the resulting CO₂ emissions can be vented to the atmosphere. However, exponentially increasing atmospheric CO₂ levels have brought this assumption under critical review. Over the last decade, this discussion has evolved from whether exponentially increasing anthropogenic CO₂ emissions will adversely affect the global environment, to the timing and magnitude of their impact. A variety of sequestration technologies are being explored to mitigate CO₂ emissions. These technologies must be both environmentally benign and economically viable. Mineral carbonation is an attractive candidate technology as it disposes of CO₂ as geologically stable, environmentally benign mineral carbonates, clearly satisfying the first criteria. The primary challenge for mineral carbonation is cost-competitive process development. CO₂ mineral sequestration – the conversion of stationary-source CO₂ emissions into mineral carbonates (*e.g.*, magnesium and calcium carbonate, MgCO₃ and CaCO₃) – has recently emerged as one of the most promising sequestration options, providing *permanent* CO₂ disposal, rather than storage. In this approach a magnesium-bearing feedstock mineral (typically serpentine or olivine; available in vast quantities globally) is specially processed and allowed to react with CO₂ under controlled conditions. This produces a mineral carbonate which (i) is environmentally benign, (ii) already exists in nature in quantities far exceeding those that could result from carbonating the world's known fossil fuel reserves, and (iii) is stable on a geological time scale. Minimizing the process cost *via* optimization of the reaction rate and degree of completion is the remaining challenge.

As members of the DOE/NETL managed National Mineral Sequestration Working Group we have already significantly improved our understanding of mineral carbonation. Group members at the Albany Research Center have recently shown that carbonation of olivine and serpentine, which naturally occurs over geological time (*i.e.*, 100,000s of years), can be accelerated to near completion in hours. Further process refinement will require a synergetic science/engineering approach that emphasizes simultaneous investigation of both thermodynamic processes and the detailed microscopic, atomic-level mechanisms that govern carbonation kinetics.

Our previously funded Phase I Innovative Concepts project demonstrated the value of advanced quantum-mechanical modeling as a complementary tool in bridging important gaps in our understanding of the atomic/molecular structure and reaction mechanisms that govern CO₂ mineral sequestration reaction processes for the model Mg-rich lamellar hydroxide feedstock material Mg(OH)₂. In the present simulation project, improved techniques and more efficient computational schemes have allowed us to expand and augment these capabilities and explore more complex Mg-rich, lamellar hydroxide-based feedstock materials, including the serpentine-based minerals. These feedstock materials are being actively investigated due to their wide availability, and low-cost CO₂ mineral sequestration potential.

Cutting-edge first principles quantum chemical, computational solid-state and materials simulation methodology studies proposed herein, have been strategically integrated with our new DOE supported (ASU-Argonne National Laboratory) project to investigate the mechanisms that govern mineral feedstock heat-treatment and aqueous/fluid-phase serpentine mineral carbonation *in situ*. This unified, synergetic theoretical and experimental approach will provide a deeper

understanding of the key reaction mechanisms than either individual approach can alone. *Ab initio* techniques will also significantly advance our understanding of atomic-level processes at the solid/solution interface by elucidating the origin of vibrational, electronic, x-ray and electron energy loss spectra observed experimentally.

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1. INTRODUCTION

In YEAR 1 of the present Innovative Concepts II award, DE-FG26-01NT41295, we focused on (i) the first principles simulation of fundamental reactant and products properties such as atomic structure, formation energy, vibrational structure and electronic spectral signatures (ii) the effects of heat treatment on the structure and composition of lizardite, the prototypical lamellar magnesium magnesium-hydroxy-silicate feedstock material, (iii) the preliminary steps associated with carbonation of defective (heat-treated) lizardite based on predicted *ab initio* atomic structures. The synergistic interaction of these initial studies with laboratory work has illuminated the origin of a number of observed phenomena including the critical assignment of the so-called “inner” and “outer” hydroxyl vibrational bands. These can/will be used as a fingerprint to diagnose the evolution of the departing structural hydroxyls in dehydroxylation experiments on lizardite, and eventually crysotile and antigorite. Our simulations predicted the existence of a novel, metastable, meta-serpentine material in which order and disorder coexist. This was used to explain the unusual progression of x-ray diffraction patterns upon dehydroxylation. We also modeled the MIE-like particle scattering features at low-angle in the XRD spectrum in the 640°C heat treated sample (see report 41295R01). We also initiated supercomputer-based quantum molecular dynamics studies of the temperature dependence of the dehydroxylation process to study the water formation rate and diffusivities of mineral (and product) components (Mg, Si, OH, H₂O and protons). These are described in section 3.0 below as a part of the last year’s performance period but within the present report since the grant has a September start date.

The work plan (Appendix 2) for YEAR 2 focuses primarily on understanding the fluid phase and carbonation mechanisms associated with the fluid phase, as outlined in the accomplishments section below and as described in some detail in sections 3.1-3.3 herein. Electron energy loss spectroscopy (EELS), XRD and vibrational spectroscopy simulations were undertaken at various junctures throughout the year to elucidate and complement the corresponding experimental studies.

2. EXECUTIVE SUMMARY

2.1 OBJECTIVES

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 will be 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 project will include (i) simulation of the morphological changes associated with serpentine heat-activation to understand its role in enhancing carbonation reactivity, (ii) development of a non-empirical site reactivity model for CO₂ with serpentine, and (iii) detailed investigation of the serpentine surface dissolution mechanisms that govern carbonation kinetics,

and (iv) the use of first-principles methods to provide deeper atomic-level insight into the mechanistic experimental observations in the partner ASU/ANL studies (*e.g.*, *in situ* studies of reaction intermediate formation).

A critical development during this performance period is the increased effort being devoted by all members of the National Working Group on Mineral Sequestration to the study of carbonation in the olivine-based feedstock minerals. Accordingly a significant fraction of the modeling and simulation support and thrust this year was/is devoted to understanding forsterite/olivine dissolution, the speciation and equilibrium properties of our reactant solution (ARC aqueous process), and developing an understanding of the negative effect of passivating layer formation on the carbonation process. The elimination of the passivation layer is currently viewed as a critical problem in the development of an efficient and cost-effective conversion process.

2.2 ACCOMPLISHMENTS TO DATE

Personel: The computational research is carried out primarily by Chizmeshya (PI) and by two students, Deirdre Gormley and Michael Kocher:

Graduate researcher Deirdre Gormley, a Science and Engineering of Materials (SEM) program doctoral candidate, continues to be supported under the current award. Much of the YEAR 1 & 2 research will form a significant portion of her doctoral dissertation research. Deirdre has contributed significantly to the day-to-day execution of simulation tasks including (but not limited to) running the VASP[1] and DMOI³[2] computer codes on various problems as described below. Maintenance of a database of results related to the dehydroxylation studies, including tabulation and correlation of experimental thermodynamic data (formation enthalpies, etc.) with the results of modeling studies. She is also the lead on the first principles calculation of EELS spectra and has participated and participated in our synchrotron studies carried out at Argonne National Laboratory as a research assistant.

Mr. Michael Kocher, a senior undergraduate research assistant supported on this project, has not only assisted in retrieval, organization and analysis of numerical data generated by our simulation programs but has also carried out the computational studies on forsterite surface reactivity. Michael has also initiated quantum chemical studies of Mg²⁺ binding and reactivity in citrate, and mineral surfaces. These are delicate computational problems and two concurrent methods are being employed to quantify the strength of the binding sites on the molecule and mineral surface. The first method employs a standard quantum chemical code which allows the treatment of free ions and molecular ions, but which require significant computational effort to achieve chemical accuracy. As more efficient alternative, Michael has been repeating some of the calculations using a periodic supercell code which uses a plane-wave basis to accelerate the simulations. However, only neutral molecular assemblages can be treated, necessitating the inclusion of distant neutralizing species within the cell. In this report we discuss the preliminary outcome of these studies. Final results will be discussed in next year's report.

Equipment and Software: The dedicated project workstation, together with the software required to execute the proposed research, was has been fully operational since 11/06/01, and continues to

be heavily used exclusively for project work. In addition, we recently applied for and were granted access to supercomputer resources (see bullet below) to accelerate some of the large-scale research to be described below (large scale molecular dynamics Section 3.2.1).

Research Highlights:

- Our most recent quantum molecular dynamics simulations indicate that dehydroxylation is extremely complex. Stable structures exhibiting staging behavior were predicted. The silica-rich sheets in serpentine minerals exhibit stability at high temperatures. We showed that significant proton diffusion takes place over a broad temperature range implying many paths to dehydroxylation.
- The conductor-like screening model for real systems (COSMO-RS) has been used to compute excess thermodynamic properties of CO₂-H₂O solution systems. Using quantum mechanical simulations of the solute and solvent we were able to reproduce the exsolution behavior of H₂O-CO₂ into CO₂-rich and H₂O-rich fluid phases. Work to extend and validate the approach to 3- and 4- component fluids is ongoing.
- Solvent effects on structural and vibrational properties of carbon-bearing solutes including CO₂(aq), CO₃²⁻, HCO₃⁻, H₂CO₃ as well as OH⁻ and H₂O itself, are reasonably well predicted by the COSMO-RS method. In addition to the structural modifications induced by solvation we calculated the shifts associated with key vibrational bands in these molecules providing important guidance for our FTIR spectroscopy studies.
- We studied the structure and stability of forsterite surfaces. The minimum dipole forsterite surface is predicted to be (010) while large structural reconstruction are predicted for the (100) and (001) surfaces.
- The proton exchange reaction (dissolution on (010) surface) was studied using first principles methods and predicted to be exothermic by ~ 75 kcal/mol. An analogous study of iron extraction yielded a corresponding value of ~ 55 kcal/mol suggesting that leaching leads should tend to increase the surface concentration of iron, barring unforeseen complexation reactions in the hydration layer of the reacting mineral (not taken into account in our study).
- Very large scale molecular dynamics simulations were developed to study the structure and properties of the silica-rich passivating layer which forms on reacting olivine surfaces. The simulations predict a low-density glass like network with a mean density of ~ 1.2 g/cc. Furthermore, extensive “void” channels are predicted in the structure suggesting an efficient ion transport mechanisms as well a low free-energy mechanisms for the formation of carbonate within the passivating layer matrix.
- Modeling and Simulation research results presented at three conferences: (i) The 28th International Coal Utilization and Fuel Systems (CUFS) Conference in Tampa, Florida in March 2003 (speaker: A. Chizmeshya), (ii) the Second Annual Carbon Sequestration

Conference in Alexandria, Virginia in May (presenter: A. Chizmeshya) and (iii) the Four-corners American Physical Society Meeting in Tempe, Arizona on October 24, 2003 (presenter: D. Gormley). In addition, (PI) Andrew Chizmeshya presented a one hour invited talk at the Departmental Colloquium in the Department of Physics and Astronomy at Arizona State University in November 2003.

- Our request for supercomputer resources at the Pittsburgh Supercomputing Center (PSC) was granted (*PSC-USDOE (SC)² Program*, A.V.G. Chizmeshya (PI), Grant # MP3020002P – 32,000 SU 5/31/03-6/1/04). This allocation was used to study serpentine-mineral-surface modification on dehydroxylation (activation) and the surface structure in order to elucidate these processes under target experimental solution conditions. We anticipate additional allocation awards in connection with the planned aqueous mineral reaction investigations in YEAR 3.

2.3 SIGNIFICANCE TO FOSSIL ENERGY PROGRAMS

Fossil fuels, especially coal, can support the energy demands of the world for centuries to come, if the environmental problems associated with CO₂ emissions can be overcome[3,4]. Mineralization of stationary-source CO₂ emissions as carbonates can provide safe capture and long-term sequestration[5,6]. Carbonation of Mg-rich lamellar-hydroxide-based minerals (*e.g.*, the model Mg(OH)₂ system and serpentine based minerals) is a leading process candidate, which generates the stable, naturally-occurring mineral magnesite (MgCO₃). Optimizing the carbonation reaction rate and its degree of completion are key to process cost and viability. This project focuses primarily (but not exclusively) on the carbonation reaction process mechanisms in serpentine minerals at the atomic level. Carbonation and treatment processes in the olivine class of feedstock minerals will also be briefly studied in support of the research being carried out by the National Mineral Sequestration Working Group managed by NETL. In both cases, the objective is to provide the mechanistic understanding to accelerate the engineering development of improved carbonation materials and processes for carbon dioxide disposal.

The simulation and modeling thrust described in this report is synergistically integrated with a number of other mineral sequestration projects sponsored by Fossil Energy including: NETL/ANL Contract 1F-01262 and UCR Awards DE-FG26-98FT40112 and DE-FG26-01NT41282. The author of the present report (Chizmeshya) is a member of the National Working Group on Mineral Sequestration managed by the National Energy Technology Laboratory.

3. KEY RESULTS AND DISCUSSION

Section 3.0 briefly describes portions of YEAR 1 research that was completed during the beginning of the current reporting period. The bulk of the YEAR 2 research results are described and reported in sections 3.1-3.3.

3.0 DEHYDROXYLATION VIA MOLECULAR DYNAMICS

By directly comparing last year's simulation results with experiment 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 revealed that the process involving a brucite-layer hydroxyl, and a cage proton from an adjacent layer, represents the lowest energy reaction path (see report 41295R01). Simulations of moderately dehydroxylated systems containing 50% residual hydroxyl, corresponding to $\text{Mg}_3\text{Si}_2\text{O}_6(\text{OH})_2$, show that experimentally observed x-ray features are due to H_2O 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. As we shall discuss below (Section 3.1.2) large scale molecular dynamics simulations of micron scale systems are currently prohibitive. To circumvent this limitation we therefore undertook simulations of both the bulk and near-surface regions, which can be treated efficiently using bulk supercells and slab supercells, respectively. The molecular dynamics simulations were carried out using the VASP code, which uses a plane wave basis, ultrasoft pseudopotentials and density functional theory[7] within the local density approximation[8] to calculate energies and forces from first principles. The bulk supercells contained 72 atoms while the surface slab supercells contained 144 atoms. The latter were constructed with free (1120) surface planes. In both cases a plane wave cutoff of about 350 eV was used with a $2 \times 2 \times m$ Monkhorst-Pack k -point grid, with $m=1$ and 2 for the slab and bulk calculations, respectively. The diffusivity, D_m , of species m is computed from positional correlations according to the formula

$$\left\langle \left| \vec{r}_m(t) - \vec{r}_m(0) \right|^2 \right\rangle_N = 6D_m t \quad (1)$$

where the angular brackets represent an ensemble average over like species within the supercell. The time-dependence of the positions is obtained directly from quantum molecular dynamics calculations carried out in a microcanonical setting with finite temperature scaling at each 0.5 fs timestep. This short timestep was chosen in order to accurately capture the proton dynamics.

For each case considered, several picoseconds of evolution were simulated on a Cray T3E supercomputer. Table 1 listed the calculated diffusivities for Mg, Si and the various “kinds” of protons and oxygen ions at 1000°K (~700°C). The most dramatic surface enhancements to the diffusivity in the surface layer occur for “cage” oxygens and Mg ions. For Mg ions this enhancement may be implicated in the temperature dependence of the dissolution process, which is still not well understood and is currently being experimentally investigated.

Species	Bulk Diffusivity	(1120) Surface Region Diffusivity	Enhancement Factor
“Brucite” protons	10.2	22.8	2
“Cage” protons	10.3	20.3	2
Magnesium	0.07	0.30	4
Silicon	0.05	0.10	2
“Cage” oxygens	0.06	0.97	16
Other oxygens	0.06	0.19	3

Table 1: Calculated diffusivities, D ($\times 10^{-5} \text{ cm}^2/\text{s}$) for various species in lizardite at $\sim 700^\circ\text{C}$. The enhancement factor is the (rounded) ratio of surface to bulk diffusivity.

At room temperature the simulations reveal a stable lattice with the exception of the cage protons which exhibit a diffusivity of nearly $10^{-5} \text{ cm}^2/\text{s}$, while their brucite-layer counterparts, coordinated in a more close-packed fashion, have a diffusivity of about 20% of this value. One noteworthy phenomenon predicted by our simulations is a hydroxyl “flipping” mechanism present at room temperature in which a *brucite-layer* hydroxyl spontaneously flips over with the

proton pointing into the Mg-layer (see Figure 1). Static lattice calculations based on this new structure reveal that it is thermally accessible at room temperature, confirming the molecular dynamics result. The frequency spectrum of this new ground state structure exhibits new weak hydroxyl bands distributed throughout the several hundred cm^{-1} range just below the primary 3600 cm^{-1} hydroxyl bands. We are preparing an archival journal article based on this work.

Figure 1: A snapshot of a portion of a 72-atom lizardite molecular dynamics simulation showing a “flipped” hydroxyl. “B” and “C” denote the so-called “brucite” and “cage” hydroxyls. Colored spheres are: Mg (green), Si (grey), O (red) and H (white).

layers exhibit long-term dynamic stability and may be implicated in the stability of the highly reactive amorphous meta-serpentine. A complete detailed account of these studies is currently being summarized in a journal article in preparation.

3.1 FLUID PHASE MODELING

3.1.1 Quantum Molecular Dynamics Calculations of Aqueous Systems

Our initial investigations of the bulk aqueous solution focus on the simulation of water, which has been well investigated using classical molecular dynamics methods, but not in as much detail within the first-principles context. Hydrogen bonding is a hallmark of liquid water’s bonding behavior and

generating the expected behavior using density functional theory has been one of our simulation goals. We constructed periodic supercells containing between 12 and 48 water molecules at several different densities near 1 g/cc and then initiated molecular dynamics runs at $T=300 \text{ }^\circ\text{K}$

Figure 3: Initial (a) and final (b) configuration snapshots of a 12-water molecule representation of simulated liquid water. Dashed lines denote hydrogen bonds. (c) Total radial distribution function (2 ps run) showing first peak in the vicinity of $1 \text{ }^\circ\text{Å}$ corresponds to OH and a liquid-like structure beyond $R \sim 3.5\text{-}4.0 \text{ }^\circ\text{Å}$.

Simulations were also carried out at 750, 875 and $1000 \text{ }^\circ\text{K}$. The 1000°K simulations reveal that “silica-layer” hydroxyl protons have very high diffusivities, but perhaps surprisingly the kinetics limit the formation of water in the near-surface region. Instead, meta-stable water is observed to form in the “brucite-like” layers within the bulk crystal. To quantify this behavior we calculated the activation energy of “cage” hydroxyls by plotting their diffusivities as a function of $1/T$ as shown in Figure 2. This yields a value of $\sim 10 \text{ kJ/mol}$, which is compatible with observation. This is likely a key step in the initial dehydroxylation process associated with heat activation. In both surface and bulk regions, the silica

Figure 2: Calculation of the activation energy for “cage” hydroxyls in bulk lizardite. The slope yields $\Delta E_a \sim 10 \text{ kJ/mol}$.

(room temperature) for a duration of typically several picoseconds (thousands of OH vibrational periods). Correlation functions describing the structural state of the liquid were then computed. The results shown in Figure 3 illustrate that the generalized density approximation (GGA) employed in our *ab initio* simulations correctly describes the hydrogen bonding behavior in water and yields a total pair correlation function very similar to the experimentally observed one. The most significant shortcoming of this approach is the slight (10-15%) underestimation of the hydrogen-bond (inter-molecular O-OH) length. We then attempted to validate the application of the above approach to a simple 1.5 M NaCl solution. Unfortunately, the target system representing NaCl/NaHCO₃ concentrations representative of the aqueous mineral carbonation process is too computationally demanding, involving time-scales much larger than the inverse of the typical reaction rates of interest (see discussion in Section 3.2.1, below). We therefore explored several alternatives in keeping with the research plan for YEAR 2 (see Appendix 2).

3.1.2 Classical Thermodynamic Modeling of the H₂O-CO₂-NaCl System

The aqueous reaction of ground magnesium-bearing feedstock minerals with supercritical CO₂ takes place in a sodium buffered H₂O-CO₂ mixture with 1 M NaCl and 0.6 M Na₂CO₃ [9]. Although these particular concentrations appear to produce the most stable and efficient reactions and minimal pH swings the precise mechanisms responsible for the carbonation are still not well understood. To promote new fundamental understanding our group at ASU recently designed a special externally controlled chemical microreactor for reaction investigations under supercritical conditions [10]. The device is fitted with transparent moissanite windows that allow direct probes (such as laser, x-ray beams etc) to interact directly with the mineral carbonation reactants and products *in situ*. Unfortunately there is very little reliable data on the equation of state of our reactant solution in the temperature and pressure range near 200°C and 200 atm of CO₂. As discussed in the previous section, brute force quantum molecular dynamics simulations of simple H₂O and CO₂ mixtures is feasible and predictive, but very computationally expensive. Once the buffer constituents are added, however, the problem becomes intractable since even small concentrations (1M NaCl) requires on the order of a thousand atoms.

To better understand the effect of microreactor control parameters on fluid speciation and its impact on carbonation reactivity, a detailed thermodynamic understanding of the supercritical CO₂-H₂O system is needed. We therefore investigated the effect of pressure and temperature on the concentrations of various fluid-phase species by analyzing the solution equilibrium equations for a Na⁺ buffered H₂O-CO₂ system. The pressure and [Na⁺] dependence of the concentration of aqueous dissolved CO₂(aq) under typical mineral carbonation conditions is described by the following equilibrium equations:

The last equation expresses charge neutrality. The temperature dependence of the relevant equilibrium constants was obtained from Stumm and Morgan [11], except for K_W(T), which was

taken from Harned and Owen [12]. Accurate temperature dependence for the Henry's law constant was obtained from a recent reparametrization of the equation of state of pure CO₂ appropriate for the temperature and pressure range of interest [13]. This improves upon an earlier form valid at higher temperatures and pressures [14]. The Na⁺ concentration is that used in the reactant solution (0.64M NaHCO₃ + 1.0 M NaCl), although ionic strength effects, including the activity of Cl⁻, are not yet explicitly taken into account.

Figure 4: Equilibrium speciation in a Na⁺ buffered CO₂-H₂O system as a function of CO₂ partial pressure at 50 °C (left panel) and 180 °C (right panel). The curves are color coded as follows: pH (black), OH⁻ (blue), CO₂(aq) (green), CO₃²⁻ (red), and HCO₃⁻ (orange).

At lower CO₂ pressures the bicarbonate concentration dominates. A crossover occurs at ~ 5 -8 MPa, with the CO₂(aq) concentration dominating at higher pressures, followed by the bicarbonate ion concentration. On the basis of this model, we expect similar variations in speciation over the range of reaction conditions observed in our experiments, namely, 15 MPa CO₂ from 20 to 180 °C.

The equilibrium reaction equations (2) – (6) were solved for the concentrations of [CO₂(aq)], [OH⁻], [HCO₃⁻], [CO₃²⁻], and [H⁺]. The results, shown in Figure 4, reveal that temperature and pressure variations over the range of reaction conditions of interest lead to significant variations in speciation. The left and right panels of the figure show the results for T=50 °C and T=180 °C, respectively. According to our model, the largest variations in speciation are expected in the pressure range from 0 to 7 MPa P(CO₂), i.e., below the critical pressure of CO₂.

Figure 5: Pressure-volume equation of state for H₂O-rich fluid in H₂O-CO₂-NaCl as calculated according to the Duan parameterization, for a range of temperatures spanning the critical regime for CO₂.

3.1.3 Continuum Solvation Models based on Quantum Mechanics

Recently, the traditional continuum solvation model of quantum chemistry has been extended

Figure 6: Schematic illustration of space-filling solvent (H₂O) and solute (CO₂) shells (left panel). The self-consistently determined shell charges on give rise to a “contact” interaction (right panel).

(solute or solvent) with little more effort than a free molecule calculation. We have applied this

method, as implemented in the DMol³ code [2] described in the original proposal, to the CO₂-H₂O system. A schematic of the computational scheme is presented in Figure 6, where each molecule is shown within a conforming cavity, and the contact interactions between the screening charges of the solutes/solvents are illustrated. The ensemble of screened molecules is compressed to a desired density (obtained from the equilibrium thermodynamic state data of Section 3.1.2, above for example) and the pertinent excess free energy is calculated as a function of concentration. Illustrative results for the H₂O-CO₂ system are shown in Figure 7 corresponding to 100 bar of pressure and two temperatures (near room temperature and ~ 180°C). As can be seen, the COSMO-RS method correctly predicts a speciation of the system into H₂O-rich and CO₂-rich components, in accord with observation. Professor George H. Wolf (a member of our CO₂ sequestration research group at ASU) is currently developing a new equation of state code using the most recent H₂O-CO₂ data available, in order to improve the interpretation of our supercritical CO₂ experiments. This will also provide benchmarks for the DMol³ COSMO-RS calculations. Our goal is to develop a systematic and reliable understanding of the H₂O-CO₂ equation of state at high temperatures and pressures, and ultimately to incorporate the effects of buffers using DMol³ *ab initio* calculations as well as quantum molecular dynamics.

Figure 7: Excess free energy calculated at 27 and 100°C and 100 atm showing exsolution behavior.

3.1.4 Solvation Effects on the Vibrational Spectra of Carbonatious Species

Another application of the COMSO-RS approach with immediate implications for our ongoing sequestration research is the prediction of vibrational spectrum changes induced by solvation. This is crucial for interpreting the speciation of carbonatious species in reaction experiments. One of the principal collective goals of our mineral sequestration research is to discover which carbon bearing molecular species are responsible for the carbonation reaction in forming magnesite (MgCO₃). For examples, which species is being consumed by the reaction? Experimental understanding is currently quite limited. In Table 2 below we show some results of our simulation studies aimed at learning whether infrared spectroscopy may be useful in fingerprinting the reaction constituents under reaction conditions. As a first step we systematically computed the vibrational spectra of a H₂O, CO₂, and HCO₃⁻ in the gas phase as well as in a solvation shell corresponding to water at STP. The results are compatible with experiment: for water we find a downward shift of ~ 30cm⁻¹ in the asymmetric stretch mode, while for CO₂ we find that solvation induces a splitting in the degenerate symmetric bend mode, just as observed experimentally[16]. For species like HCO₃⁻ the situation is more complicated, and our calculations predict that solvation induced shifts can be both positive and negative. Here the largest shift (~ 80 cm⁻¹) occurs in the O-C-O asymmetric stretch. Experiments are underway to verify this latter observation and provide validation for the theoretical studies. The value of this type of synergetic interaction between experiment and theory cannot be understated. A key to understanding the reaction mechanisms clearly lies in the interpretation of spectroscopic data that signals important changes in the reactant/product speciation. One concern is that CO₂ pressure

induced density changes in the fluid phase may squelch the weak FTIR signal intensity, and the absorption bands of interest.

CO ₂ (aq)	left-right	CO ₂ (g)
617.4	-8.8	626.2
618.3	-7.9	626.2
1335.5	-14.4	1321.1
2328.8	-20.3	2349.1
sym str		
asym str.		
bond l.	1.172	1.175
angle	180	180

H ₂ O(aq)	left-right	H ₂ O(g)
1593.3	-5.9	1599.2
3698.6	-14.1	3712.7
3802.8	-27.1	3829.9
bend		
sym str.		
asym str		
bond l.	0.972	0.97
angle	104	104

OH ⁻ (aq)	left-right	OH ⁻ (g)
3720.9	120.5	3600.4
bond l.	0.973	-0.005
		0.978

CO ₃ ²⁻ (aq)	left-right	CO ₃ ²⁻ (g)
661.9	11.1	650.8
666.6	14.9	651.7
866.4	8.6	857.8
1047.6	33.3	1014.3
1423.7	4.7	1419
1428.2	7.3	1420.9
sym stretch		
stretches along		
bond direction		
bond l.	1.297	1.308
angle	120	120

HCO ₃ ⁻ (aq)	left-right	HCO ₃ ⁻ (g)
533.6	9.7	523.9
541.8	-40.8	582.6
629.3	38.6	590.7
792.6	13.6	779
862.5	43.5	819
1171.1	4	1167.1
1276.9	5.3	1271.6
1663.2	-86.4	1749.6
3673.8	2.9	3670.9
OH wag		
CO stretch (CO(H) bond)		
COH bend		
CO stretch (CO(H) bond)		
sym CO stretch		
COH	CO	1.423
	OH	0.975
CO	CO	1.26
	CO	1.254
angles	COH	105.6
	OCO	115.8
	OCO	130.2
		1.471
		0.973
		1.261
		1.245
		99.7
		113
		132.9

H ₂ CO ₃ (aq)	left-right	H ₂ CO ₃ (g)
507.6	-6.3	513.9
548.4	12.5	535.9
574	-3.1	577.1
594.9	-7.9	602.8
769.7	3.4	766.3
957.1	7.1	950
1097.6	-24.3	1121.9
1250	-18.5	1268.5
1408.6	-19	1427.6
1732.4	-67.6	1800
3654.1	-31.6	3685.7
3668.9	-31.8	3690.7
HO-C-OH bend		
asym. OH wag		
asym. CO stretch		
CO stretch		
OH wag		
COH	CO	1.343
	OH	0.978
CO	CO	1.22
angles	COH	107.9
	COH	107.8
	OCO	125.8
		1.35
		0.975
		1.215
		105.5
		105.5
		125.8

Table 2: Composite table containing a complete listing of free-ion/atom and solvated (H₂O at STP) vibrational frequencies, bond lengths and bond angles for six key aqueous molecular species.

To circumvent this potential problem and provide a complementary set of observations a special NMR cell is currently being developed in our group. In this case the intensities of the chemical shifts are directly proportional to the number density of each species. Density changes in the fluid will not affect the NMR signal. Calculations of the shielding factors and chemical shifts associated with all of the species of interest can be readily performed using our various quantum codes. A detailed account of our present study will be published and presented at an upcoming conference in 2004.

3.2 DISSOLUTION AND PASSIVATION OF FEEDSTOCK MINERALS

3.2.1 Growth and Reaction Concepts: Olivine Carbonation

Initial investigations of the carbonation of single crystal olivine reveal the presence crystallites of ranging size within the near surface region of the olivine reaction matrix, e.g., the solid product recovered from the reactor. Electron microscopy observations strongly suggest the possibility of a product morphology consistent with magnesite/olivine intergrowth, although dissolution/precipitation is still likely the dominant process.

Little is known about the dynamic nanoscale processes (kinetics) occurring within the near surface region of the solid/liquid interface during carbonation. However, a recent detailed analysis of titration measurements[17] for forsterite dissolution in solutions of varying pH (but without CO_2) has been used to tentatively identify various proton exchange reactions associated with: (a) stoichiometric dissolution of the bulk solid releasing Mg and Si to the solution, (b) exchange of two protons for a Mg dissolved into solution and (c) simultaneous absorption of hydroxide and protons into the surface region leading to an expansion of molar volume of the crystalline constituents and encouraging processes such as (a) and (b). For $pH < 9$ these studies concluded that the dominant dissolution mechanism is associated with the second process, (b). Surface XPS analyses further confirm a depletion of Mg within the first ~ 20 Å of the forsterite surface.

Many of the existing studies on forsterite dissolution are designed to simulate natural weathering processes and are typically carried out under low temperature and pressure conditions, and without the effects of stirring found in our experiments. The apparent intergrowth phenomena observed in our recent olivine carbonation studies is difficult to explain using the conventional dissolution/precipitation model. This suggests that other modes of nucleation and growth could also include, and may not be limited to: (a) solid state reactions between the aqueous carbon-bearing phases and the abraded olivine surface, (b) nucleation and growth involving preferential diffusion of dissolved aqueous CO_2 . Under the pressure and temperatures considered in our experiments supercritical CO_2 exhibits the diffusivity of a gas and the viscosity of a liquid. However the diffusivity is also known to generally decrease with increasing pressure. The relative diffusivity of various dissolved species ($CO_2(aq)$, CO_3^{2-} , OH^- , HCO_3^- , H_2CO_3) is

Figure 8: Left panel: Schematic representation of a diffusion mediated growth mode involving an expanding reaction zone (dark gray), surface promotion of a silica-like product, and diffusion of reactant species. Right panel: FESEM image of the magnesite crystals (yellow arrows) that are observed intergrown with the olivine matrix.

usually not considered in the description of near surface reactions and bulk estimates, even if known, are likely not valid within the hydration layer of the mineral. Nevertheless, the relative diffusion may become important under certain conditions. Figure 8 depicts a schematic of a growth model involving a hypothetical surface nucleation of carbonate in which aqueous constituents

are assumed to diffuse with the expanded volume of the growth zone. In this scenario the nucleation process can be initiated by a surface defect or by the precipitation of carbonate grain onto a dissolving olivine surface. Large scale mass transport (e.g., dissolution and re-precipitation) of Mg ions may not be required for magnesite growth if a sufficiently high concentration of dissolved $CO_2(aq)$ is present with sufficiently high diffusivity to deliver reactant species into the reaction zone (dark grey region in Figure 8). There is also some evidence (from experiments performed at ASU, ARC and LANL) that the silica-like product does not readily

dissolve into solution, with substantial silica exhibiting significant surface mobility together with the olivine matrix.

3.2.2 Surface Properties of Olivine from Simulation

In attempting to explain these complex phenomena one of our first objectives was to explore relationship between surface structure and dissolution. Is there a face dependence? How do different surfaces reconstruct/relax? These kinds of studies can also help interpret complementary face dependence studies being carried out in the laboratory. To investigate these effects we again used the VASP code [1] to compute the ground state energies, forces and structural relaxations for various olivine surfaces. In all cases ultrasoft pseudopotentials were used within the local density approximation (LDA)[8] with a cutoff of 400 eV. We built symmetrical multi-layer slabs from unit cells using bulk lateral slab dimensions and 3-, 5-, and 7-Mg layers for the (100), (010) and (001) surfaces. Forces on all atoms minimized using accurate quantum mechanical approach (VASP code [1]) to an accuracy of about 0.01 eV/Å.

In all cases the relaxations observed involve opposing displacements of both the Mg ions and the SiO_4 units, and rotations of the latter. Large scale reconstruction is found for the (100) surface while minimal reconstructions were observed for both the (010) and (001) surfaces. In the case of the (100) surface, non-negligible atomic displacements were observed three layers from the outer surface (symmetrical 7-layer model). For the (010) and (001) surfaces, a five-layer slab representation was found to be sufficient. For the (001) surface our calculations predict row doubling reconstruction perpendicular to surface normal involving SiO_4 units and Mg ions moving out of phase. This exposes magnesium ion rows within the surface layer, implying facile dissolution. However, the subsequent layer would require incongruent removal of magnesium, leading to a higher energy state. The minimum dipole is found for the (010) surface, which also possesses stoichiometric layers parallel to the surface normal. This is also the most common stable surface observed experimentally.

Figure 9: Figure showing the final configuration of the magnesium proton exchange reaction on the (010) surface of forsterite. The hydroxylated tetrahedral tilt toward one another as indicated by the white arrows.

In order to elucidate the dissolution mechanisms in olivine, we used the (010) surface model as a basis for preliminary studies of the proton exchange dissolution mechanism mentioned in the previous section. To obtain detailed information of the reaction mechanisms we used a supercell containing a 5-layer model doubled (2x2) in extent in the basal dimension. Four hydrogen atoms separated by ~ 6 Å were placed in pairs at equidistant ~ 15 Å (symmetrical) intervals in the vacuum space between the forsterite slabs. We verified that the presence of the distant hydrogen atoms did not alter the reconstructed (010) surface structure in this

configuration. The lateral cell doubling was imposed in order to minimize the artificial interactions between the protons and the surface defects introduced by the removal of a magnesium ion. A reference energy was first calculated for the separated protons and the relaxed

(010) slab, and then a magnesium was removed from the surface (on each side of the slab) and placed in the vacuum region while the hydrogen atoms were brought into close proximity of the surface defect (an M2 type Magnesium site on the (010) surface). This step alone yields an endothermic energy change of approximately 30 kcal/mol Mg. But this value varies by about 10 kcal/mol depending on the initial positions of the protons above the M2 vacancy. Relaxation of all atomic forces for the defective surface leads to a dramatic energy lowering and an exothermic reaction with $\Delta E \sim 75$ kcal/mol per removed Mg. This value is reproducible, stable and independent of the starting positions of the protons. The final configuration of the surface defect is shown in Figure 9.

In the above simulations forsterite is used as an approximation to olivine in which iron occupies a number of magnesium sites. The incorporation of iron is a very complex problem, and one could re-examine the proton exchange process for a large variety of configurations involving only a single iron ion. We therefore pursued the simplest analogue involving the removal of an iron ion from the surface layer. We first replaced a surface Mg ion by Fe and re-relaxed the surface structure. This yielded a slight $< 0.2\%$ dilation in the basal dimension due to expanded Fe-O bonding. We then followed an identical procedure to that of the Mg-proton exchange and obtained a final exothermic reaction of $\Delta E \sim 55$ kcal/mol per removed Fe at an M2 site.

We are continuing work in this area with the goal of calculating the reactant-product transition state using the nudged elastic band (NEB) method. The reaction rate pre-factor for various pH levels in the solution can be estimate from thermodynamics and known surface areas, and quantum mechanical calculations of the kind just described will be used to estimate the exponent, yielding estimates of the reaction rates. All of the calculations described so far pertain to the proton-exchange Mg dissolution mechanism which is likely at play in the early stages of dissolution. A detailed understanding of dissolution on the nanoscale will require knowledge of dynamical properties such as diffusivities which in turn require a model of the leached silicate layer on the nanometer scale. We discuss the development and implications of such a model below.

3.2.3 Large scale Semi-classical and classical molecular dynamics simulations

Most of the atomistic modeling and simulation carried out by our group to date has been based on first principles simulation methods. As shown in our talks (see Appendix 1), these methods yield excellent predictions of the electronic, structural and vibrational properties of the baseline mineral, liquid and gaseous systems of interest in mineral carbonation. The success of these simulations is achieved without adjustable parameters of any kind -- only fundamental constants and initial structural guesses are required. But this predictive capability comes at a cost: the simulations are very computationally demanding, often requiring days of continuous supercomputer use to deliver the detailed atomic-level behavior of systems containing only several hundred atoms.

It is instructive to estimate pertinent time-scales and length-scales associated with key reaction processes. Consider a typical Mg dissolution rate of $\sim 10^{-11}$ mol/cm²/s [17]. The natural units in atomic level simulations are Angstroms (1 Å = 10^{-10} m), picoseconds (1 ps = 10^{-12} s) and molecules (1 molecule $\sim 10^{-24}$ mol) so that 1 mol/cm²/s corresponds to $\sim 10^{-4}$ molecules/Å²/ps. The present example (Mg dissolution at $R \sim 10^{-11}$ mol/cm²/s) then implies one Mg ion leaving a $100\text{Å} \times 100\text{Å}$ surface region every 0.1 seconds. Equivalently, this corresponds

to one molecule/ion leaving a $1\text{ nm} \times 1\text{ nm}$ surface region every 10 ps. As discussed earlier, first principles simulations are currently limited to several hundred atoms (surface areas of $\sim 20\text{ \AA} \times 20\text{ \AA}$) and 10-100 ps timescales, but for many of the questions we want to answer the exquisite detail provided by this sophisticated level of simulation may not be necessary.

To address these limitations we have adopted a semi-classical simulation approach capable of treating the dynamics of 10,000-20,000 atom systems within a reasonable time scale. Accurate quantum simulations, such as those we have carried out to date, represent a source of “configuration-energy” data. In other words, first principles methods are used to generate an accurate energy-structure relationship for a broad range of equilibrium and non-equilibrium geometries in solids, liquids and solid-liquid systems. The properties of the reference system is first simulated using “classical” pair-pair interaction potentials involving about seven parameters per chemically distinct atom/ion. Optimized parameters are then subsequently used to simulate much larger systems involving the same chemical constituents.

Accordingly, we have developed a number of force field models to accurately describe the mineral-solution interface at various pressure and temperatures. We have already validated this approach for forsterite, silica and water with the goal of studying the nature of hydration layer on defective (imperfect) olivine surfaces next. This is a key step in understanding the function of chelating molecules whose reaction with metal ions is dictated by their local chemical environment. Thus, extensive and sophisticated models will be needed to study the properties of the silica-rich passivating film in order to understand its structure as well as the influence of the solution chemistry on its structural stability.

The results of the classical and semi-classical modeling studies will in turn be used to target salient high-level simulations at the quantum level. For instance, once the structure of the hydration layer near the mineral-solution interface is well understood specific local chemical reactions can be more accurately explored using the quantum methods. A detailed understanding of the structure of the mineral-solution interface, particularly in the presence of various molecular complexes, is currently lacking although fairly sophisticated force-fields have been

devised to study hydrated clay minerals. What is required for mineral carbonation simulation, however, is a comprehensive molecular model involving all of the solution species, together with a reliable model of the mineral component. Work to develop this simulation framework is ongoing.

Figure 10: (a) Schematic illustration of the silica-rich passivating layer found on reacted olivine mineral grains. Solid dark gray: olivine mineral, light gray: silica matrix, textured gray pieces: carbonate nanocrystals, light blue: solution.

3.2.4 Conceptual models of the passivation layers in Olivine carbonation

As mentioned earlier in this report, quantitative nanoscale observations indicate the presence of magnesite nanocrystals within the silica rich matrix found on reacted

olivine particles. As magnesium is leached from the mineral the reaction front recedes inwards from the original mineral surface position. The formation of carbonate within the leached layer implies that CO₂ must diffuse inwards, as shown schematically in Figure 10. High-resolution electron microscopy analysis shows that the carbonate nanocrystals comprise 13% of layer volume with SiO₂ occupying the other 87%. We have also confirmed that the amorphous matrix is “SiO₂” at the nanoscale (to be published). Simple theoretical calculations (see Table 3 below)

% MgCO ₃ free	% MgCO ₃ in PL	Molar vol of MgCO ₃ in film (x2)	Molar volume glass	Molar volume of film	Molar volume Olivine	RATIO of V(products)/ V(reactants)	Stress State	MgCO ₃ Volume % in PL
0%	100%	93.17	45.10	138.27	72.58	1.91	compression	67%
10%	90%	83.86	45.10	128.95	72.58	1.78	compression	65%
20%	80%	74.54	45.10	119.63	72.58	1.65	compression	62%
30%	70%	65.22	45.10	110.32	72.58	1.52	compression	59%
40%	60%	55.90	45.10	101.00	72.58	1.39	compression	55%
50%	50%	46.59	45.10	91.68	72.58	1.26	compression	51%
60%	40%	37.27	45.10	82.36	72.58	1.13	compression	45%
70%	30%	27.95	45.10	73.05	72.58	1.01	compression	38%
80%	20%	18.63	45.10	63.73	72.58	0.88	tension	29%
90%	10%	9.32	45.10	54.41	72.58	0.75	tension	17%
100%	0%	0.00	45.10	45.10	72.58	0.62	tension	0%

Table 3: Molar volume trends for the passivating layer as a function of composition (Silica + Carbonate). The molar volumes of forsterite, magnesium carbonate and silica are 72.58, 46.59 and 45.10 Å³, respectively.

show that MgCO₃ would comprise 67% of passivating layer volume if all the carbonate and silica that form were retained. Thus, most of the carbonate forms outside of the passivating layer. Table 3 also shows that if carbonate occupies more than ~ 30% of the films molar volume, a compressive state would ensue. Homogeneous tension is generally expected to lead to cracking, but almost nothing is known about the elastic response of the (film + olivine) system. Under certain conditions, compressive forces may also lead to a destabilization of the silica-rich film.

The quasi-steady state diffusion of ions through a leached shell surrounding the mineral is consistent with the parabolic exchange kinetics model proposed by Luce, Bartlett and Parks [18] some twenty years ago following their study of magnesium silicate dissolution kinetics. Parabolic exchange kinetics, in which the amount of extracted Mg is proportional to $t^{1/2}$, are also consistent with non-steady state diffusion of ions within the mineral, with Mg diffusion coefficients being greater than those for silicon. This implies incongruent dissolution over moderate time frames. One mechanism consistent with this picture involves the exchange of surface Mg's for protons, even at the reaction interface within the mineral. In this case the absorbed protons likely bind to the oxygen sites forming Si-OH groups, resulting in a glassy product that is less dense than a fully networked silica glass. A careful vibrational analysis of *dehydrated* reaction products should reveal hydroxyl signatures consistent with this hypothesis.

3.2.5 Modeling and Simulation of the Glassy Passivation Layer:

Classical molecular dynamics simulations were used to study the chemical and structural character of the passivating layer. The MOLDY computer program [19], which provides an efficient means of tuning the required rigid-ion pair potentials, also employs a highly efficient algorithm for advancing the dynamics of complex multi-component systems. Beginning with the

Pair	A_{ij} ($\times 10^{-3}$) (eV)	b_{ij} ($\text{\AA}^{-1}$)	C_{ij} ($\text{eV \AA}^6$)
O-O	1.622	3.333	30.22
O-Mg	8.038	4.951	0.0
O-Si	7.367	5.263	0.0
Mg-Mg	1310.1	9.615	0.0
Mg-Si	2329.2	10.870	0.0
Si-Si	5008.1	12.501	0.0

Table 4: Born-Mayer potential parameters for the forsterite simulations. Ionic charges for O, Mg and Si ions are -1.365 , 1.365 and $2.730 e$ respectively.

phases were carried out in a supercell built from $N \times N \times N$ replicas of the respective unit cells, containing $\sim 10^2$ - 10^3 atoms.

The experimentally observed leaching process involves timescales (hours) beyond the reach of modern simulation methods (picosecond timescales). Passivating layers ranging in thickness from $100 \text{ \AA}$ to $1000 \text{ \AA}$ are observed, depending on reaction time – a typical HRTEM image of the passivating layer is shown in Figure 11. The fringes associated with a well-ordered crystalline olivine substrate can be clearly seen. Also seen is the passivating layer and the reaction front across which we have inscribed a small rectangle indicating the region of the simulations described below.

Figure 12: Simulation of the forsterite-passivation-layer reaction interface. Top panel shows the ~ 9000 atom model in which Mg, O and Si atoms are represented by green spheres, red sticks and gray sticks, respectively. Bottom panel shows the speciation (chemical profiles) indicating that the transition layer from Mg_2SiO_4 to “ SiO_2 ” is predicted to be about 20 - $30 \text{ \AA}$ thick.

van Beest pair potentials for silica [20] and our own pair potential parameters for oxygen, we first averaged the oxygen charges between the two models and then adjusted the Mg charge to preserve charge neutrality while re-adjusting the repulsion amplitudes in a Born-Mayer potential to simultaneously reproduce the $\alpha\text{-SiO}_2$ and forsterite ground state structures. The optimized pair-potential parameters are provided in Table 4 along with the effective ionic charges. The simulations of the basic crystalline

Figure 11: HRTEM image of the passivating layer (PL) which develops on a single-crystal grain of forsterite (Fo). The yellow rectangle denotes the region represented by the molecular model.

Because the formation rates of the passivation layer are beyond the reach of our simulation times we approximated this step in the process by explicitly removing Mg and O from a structurally converged forsterite model, $10 \text{ \AA}$ at a time, followed by an annealing (relaxation step) using molecular dynamics. This was continued until an initial forsterite layer of $80 \text{ \AA}$ thickness collapsed to a $\sim 50 \text{ \AA}$ passivation layer of nominally SiO_2 stoichiometry. The top panel of Figure 12 shows

a typical atomic arrangement obtained after numerous structural annealing steps. The bottom panel shows the chemical profiles obtained from the simulation, which indicate that the passivation layer consists of a glass-like SiO_2 network very similar to thermal SiO_2 glass, albeit with a lower density of 1.1-1.3 g/cc. The simulations also reveal the presence of stable nano-sized voids (7-12 Å diameter) within the passivation layer. These structures may provide the low free-energy nucleation sites for the MgCO_3 nanoparticle growth discussed in the previous section.

Another fundamental reason for undertaking these simulations is to obtain a plausible structural model of the passivating layer for subsequent detailed modeling of the electron energy loss spectra (EELS). Other physico-chemical aspects of the passivating layer which we are currently investigating include:

- Thermal stability of the passivating layer
- Diffusion of reactants in the layer
- Correlation of the distribution of voids with observed carbonate “pockets”
- Structural analysis of the coordination distribution of silicon for direct comparison with the results of ^{29}Si NMR analysis.
- Studies to elucidate the response of the passivating layers to mechanical strain, chemical impurities and combinations of these two effects.

Preliminary experimental findings obtained by our group suggest a similarity between PL and thermal SiO_2 glass. If this notion could be vindicated then the vast existing knowledge base for

Figure 13: Structure of thermal glass obtained from simulation. The edge length is approximately 21 Å. Left: Ball-stick model with silicon and oxygen indicated by grey and red balls, respectively. Right: Tetrahedral representation showing a corner-shared network of silica tetrahedral.

glass could perhaps be applied to understanding the passivating layer. This motivated us to make a direct comparison of the structural and thermo-mechanical properties of the simulated PL-Silica with those of thermal SiO_2 from a fundamental modeling perspective. The latter can be accurately calculated using the same ionic pair-potentials and molecular dynamics as described earlier. Using the parameters listed in Table 4 a structural model of silica glass was obtained by melting an 864-atom cell of quartz using classical molecular dynamics, and a slightly modified version of the van Beest pair potential. The structure was quenched from 3000°K by simulated annealing in nine 300°K cooling stages of 20,000 time steps (1 time step = 0.5 fs) each. The resulting structure exhibits all of the hallmarks of thermal glass including a fully connected corner-shared tetrahedral SiO_4 network, and a mean density of about 1.9 g/cc. This is shown in Figure 13 (left),

glass could perhaps be applied to understanding the passivating layer. This motivated us to make a direct comparison of the structural and thermo-mechanical properties of the simulated PL-Silica with those of thermal SiO_2 from a fundamental modeling perspective. The latter can be accurately calculated using the same ionic pair-potentials and molecular dynamics as described earlier. Using the

which illustrates the structure using both a conventional ball and stick representation, and the tetrahedral scheme. The structural model shown provides the starting point for subsequent analyses including the calculation of EELS spectra and equation of state calculation (stress-strain analysis). The model also provides an indispensable point of comparison for the PL silica structure, which is still not thoroughly understood. To quantify the bonding distribution of the simulated glass we computed the radial distribution function (RDF), which can be compared directly with the experimental counterpart obtained from neutron scattering studies[21] as shown in Figure 14. The simulated and observed RDFs are represented by black and green lines, respectively. The results are gratifying, and indicate that the simulation is able to capture all of the key features in the RDF. A

Figure 14: Comparison of calculated radial distribution functions for SiO₂ glass (black) and passivation layer silica (red) with data obtained from neutron scattering experiments (green)[20]. Simulations reveal that in spite of nanochannels (see below), the passivation layer exhibits strong glass-like characteristics.

notable exception is the underestimation of the second coordination shell feature at ~ 2.7 Å for which we have no simple explanation. Also shown as a red trace in the figure is the RDF calculated for the passivation layer model (extracted from the right hand side of the model shown in Figure 12). Close examination reveals a $\sim 4\%$ reduction in the average first and second

neighbor bond lengths (~ 0.05 Å) while the longer range correlations seem very similar those in silica glass. As mentioned above our analysis of the PL structural model yielded a density of ~ 1.2 g/cc, which is significantly less than that of our thermal glass model. This apparent contradiction (reduced bond-lengths, lower density) can be explained by the existence of void space in the PL structure leading to a diminished

Figure 15: Comparison of the intrinsic void volume in SiO₂ glass (from simulation) and that of the PL SiO₂. In the latter model, the tattered top surface is adjacent to the solution, while the bottom is next to the pure olivine/PL reaction front. In both cases the available volume is shown in blue. The glass network is represented by the yellow and orange stick-like structure (*c.f.*, Figure 13).

overall density and a slight densification of the networked portion of the structure. While the latter assumption is difficult to verify, the void space distribution can be mapped using the

Connolly algorithm. Here, a test particle of finite radius (1.7 Å in our case) is used to probe the interatomic regions in the structure. Contiguous over-lapping regions accessible to the particle are added and smoothed. The results can be readily visualized. Figure 15 shows a comparison of the *available* void volume for the SiO₂ glass and the passivation layer. We are also in the process of calculating the accessible void volume for both systems, which is the spatial sum of all contiguous *available* void volume regions. Even without this quantitative step, our figure clearly reveals that thermal glass model contains non-contiguous voids, while long channels are clearly present in the PL-SiO₂ model.

This type of structure has significant implications for the diffusion of carbonaceous species. As mentioned in last month's report we have experimentally confirmed the presence of carbonate particles within the glassy passivation layer matrix. The voids predicted by our simulations may explain the origin of this process in terms of an enhanced diffusivity of carbon bearing species (such as CO₃ ions, or aqueous CO₂) in the glassy matrix. Simulations of CO₃²⁻ and Mg²⁺ diffusion and subsequent reaction within the PL, are currently underway and will be reported soon. We are also pursuing the simulation of peak fracture stress of the PL in order to provide some insight into mechanically induced cracking and plan to report these and other results at the 2004 Clearwater conference.

3.3 SPECTROSCOPIC SIMULATION IN SUPPORT OF MINERAL SEQUESTRATION EXPERIMENTS

3.3.1 Simulated *EELS* Spectra

We have systematically calculated the Si *L*_{2,3}- and O *K*-edge electron energy loss structure (EELS) using the structural models derived for the silica glass, and the corresponding passivation layer (PL) material, described in the previous section. The objective is to correlate changes in the

Figure 16: Evolution of the Si *L*₂₃ edge features as the probe is moved from deep within the olivine (white) through the interface region (green) and into the amorphous passivation layer (blue).

EELS edge features with local structural variations predicted by the simulations and experiment. For the Si *L*_{2,3} edge the experimental spectra exhibit small changes in structure as one moves from the olivine region, through the reaction front and into the PL (see Figure 16). Thus, our findings so far are that the Si *L*_{2,3} edge is not very diagnostic of local structure.

Differences between “silica glass”, SiO₂ quartz and olivine Si *L*_{2,3} edges are subtle; the main features are primarily due to first neighbor bonding, which is tetrahedral (to oxygen), and common to all three materials. This is shown

Figure 17: Comparison of local structural environment surrounding a silicon atom in silica glass and crystalline quartz.

explicitly in Figure 17 in which the structural environment around a central silicon atom is displayed for both glass and crystalline quartz, as a function of distance from the central atom. The local structure for the amorphous glass is extracted from the model shown in the left panel of Figure 13 above. To elucidate the origin of this behavior we have explicitly calculated the near edge Si $L_{2,3}$ EELS spectrum for these models using the FEFF code [22] using clusters of radius $R=7$ Å, as illustrated in Figure 17. Based on our structural models the quantitative differences in the structure of the spectra are also found to be small, as shown in Figure 16 where the calculated spectra are compared with the PL Si $L_{2,3}$ spectrum acquired experimentally. Evidently, the glass model spectrum qualitatively reproduces the observed spectrum more accurately than the crystalline model. Apart from discrepancies in the intensities the glass spectrum exhibits the same fundamental peak positions as the observed PL spectrum (~ 0 , ~ 11 and ~ 21 - 23 eV). The calculated spectrum corresponding to the crystalline SiO₂ (a-quartz) has a distinctly different structure exhibiting an additional structure near 8 eV not found in the observed spectrum.

The results show that the spectral differences between the glass and the crystalline EELS spectra arise from the second and third neighbor atomic shells. An alternative is to focus on the oxygen K -edge spectra: in crystalline silica (quartz), oxygen sites are two-fold coordinated to silicon and have a fixed and narrow range of bond lengths and bond angles. In silica glass, the bond lengths and bond angles exhibit a broader distribution, and this is reflected in the EELS features. In olivine, the oxygen is coordinated to one silicon (short bond) and several magnesium ions (longer bonds), yielding a distinct EELS signature. We are continuing work to provide a definitive explanation of the EELS-“local structure” correlations based on a combination of first principles modeling and experimental observation. These preliminary results suggest local structure information may be more clearly manifested in the O K -edge spectra for the same systems.

Figure 18: Left panel: calculated Si $L_{2,3}$ near edge EELS spectrum of α -SiO₂ (black); right panel: corresponding calculated spectrum for the SiO_2 glass model (black). Observed passivation layer Si $L_{2,3}$ spectrum (blue trace).

4. CONCLUSIONS

The simulation studies performed under the present award are extremely challenging since the systems of interest exhibit all phases of matter (solid, liquid and gas), often in combination. But even more importantly, the deviations from ideality continue to provide daunting challenges. To surmount these difficulties we have expanded our resource base at no cost to the original project (e.g., successful request for supercomputer resources through the (SC)² program managed by NETL, acquisition of new modeling/simulation capabilities such as the FEFF code and development of original computer codes for optimizing classical potentials for large scale molecular dynamics studies). However, advances in fundamental understanding are absolutely essential to the accelerated development of viable CO₂ sequestration technology. The synergy inherent in the intimate combination of advanced modeling/simulation and experiment has led to

scientific insights that would have been difficult to achieve independently, and this benefit cannot be overstated.

In YEAR 2 of this award we have broken several conventional barriers to implementation by combining quantum level calculations with extremely ambitious classical level molecular dynamics simulations. This has allowed us to efficiently and meaningfully explore the structure and properties of complex large scale systems such as the passivating layer formed on olivine during carbonation. We have also exploited the middle-ground provided by novel integrated statistical mechanical methods such as the COSMO-RS approach. We shall continue to follow the original project activity chart (Appendix 2) by pursuing the development of fundamental fluid modeling in the high-P and high-T parameter space covered by our aqueous carbonation process experiments. This is not only worthwhile but essential as truly predictive capability in this regime currently does not exist. Furthermore, experimental information about the interaction of our reactants under conditions of high pressure (~ 200 atm) and high temperatures ($\sim 200^\circ\text{C}$) are also very limited. The simulation goal is ultimately to shine light on a path towards gentler reaction conditions (especially lower pressures). This may require a re-investigation of alternative solution buffers such as alkali carbonates and salts other than sodium.

An important caveat to the planned research is the re-focusing of the working group efforts on the olivine carbonation problem. While the principal thrust of the original proposed research was mainly aimed at understanding carbonation in the serpentine glass of feedstock minerals, it is clear that a proportional effort will need to be devoted to the study of corresponding reactions in the olivine mineral family. Fortunately, from the modeling/simulation perspective this “course correction” is easy to accommodate, as we have already demonstrated in this report. Numerous discussions with this project’s CORs, National Mineral Sequestration Working Group Members and NETL program coordinators are gratefully acknowledged.

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6. APPENDIX 1 : ARTICLES, PRESENTATIONS, AND STUDENT SUPPORT

Publications

“Quantum simulation studies of olivine mineral carbonation”. Chizmeshya, Andrew V. G.; McKelvy, Michael J.; Wolf, George H.; Kocher, Michael; Gormley, Deirdre. *Proceedings of the 28th International Technical Conference on Coal Utilization & Fuel Systems* **1**, 319-330 (2003).

“Investigations of the mechanisms that govern carbon dioxide sequestration via aqueous olivine mineral carbonation”. Bearat, Hamdallah; McKelvy, Michael J.; Chizmeshya, Andrew V. G.; Nunez, Ryan; Carpenter, R. W. *Proceedings of the 28th International Technical Conference on Coal Utilization & Fuel Systems*, **1**, 307-318 (2003).

“*In-situ* Observation of CO₂ Sequestration Reactions using a Novel Microreaction System”, G. H. Wolf, A.V.G. Chizmeshya, J.R. Diefenbacher and M.J. McKelvy, *Environmental Science and Technology* (In press, December 2003).

“*In Situ* Nanoscale Observations of Mg(OH)₂ Dehydroxylation and Rehydroxylation Mechanisms” Renu Sharma, Michael. J. McKelvy, Hamdallah Béarat, Andrew V.G. Chizmeshya, and R.W. Carpenter, *Philosophical Magazine* (In press, December 2003).

Conference and Professional Presentations

“Quantum simulation studies of olivine mineral carbonation”, A.V.G. Chizmeshya at the 28th International Technical Conference on Coal Utilization & Fuel Systems, March 10-13, Clearwater, Florida (2003).

“First Principles Simulation Studies of Mineral Carbonation Reaction Processes in Serpentine”, Andrew V. G. Chizmeshya, Michael J. McKelvy, George H. Wolf, Deirdre Gormley, *Second Annual Conference on Carbon Sequestration*, May 5-8, Alexandria, Virginia (2003)

“CO₂ Mineral Sequestration: An Opportunity for Materials Science in Greenhouse Gas Mitigation Technology”, A.V.G. Chizmeshya, *Departmental Colloquium*, Department of Physics and Astronomy, November 7, Tempe, Arizona (2002).

“A study of CO₂ mineral carbonation reactions in serpentine and olivine minerals using advanced computer modeling”, D. Gormley, A.V.G. Chizmeshya, M. McKelvy, G. Wolf and R.W. Carpenter, *Four-corners American Physical Society Meeting*, October 24, Tempe, Arizona (2002).

Students Supported under this Grant

Michael Kocher: Undergraduate research assistant jointly enrolled in the Physics and Chemistry programs at Arizona State University.

Deirdre Gormley: Doctoral candidate in the Science and Engineering Materials Ph.D. Program at Arizona State University.

APPENDIX 2 : WORK PLAN

Work Plan Guide reproduced from the original Proposal:

“The timeline for the proposed work will closely parallel that of the joint ASU/ANL study in order to maximize the impact of the modeling/simulation results, and support the overarching need to efficiently explore ways to optimize serpentine carbonation. Key activities are summarized in the table below. The major focus areas, (i) surface reconstruction/heat-activation

ACTIVITY	YEAR 1	YEAR 2	YEAR 3
Computer Hardware and Software Installation, Configuration and Benchmarking
Heat-activation (dehydroxylation) Studies of surface reconstruction
Fluid phase carbonation mechanisms & reaction rate modeling
EELS, XRD and Vibrational Spectroscopic Simulation
Modeling defects/impurities and their effect on reactivity
Technical Progress Reports
Contractors Annual Review Meeting
Final Year Peer Review Meeting

effects, (ii) fluid-phase carbonation mechanism modeling, and (iii) modeling of impurity/defect effects on carbonation, are timed to optimize the overlap with anticipated within the parallel experimental study. The calculation of electron energy-loss spectra, vibrational (IR and Raman) and XRD patterns derived from structural modeling will be ongoing throughout the performance period of the project. Specific studies will complement, and be guided by, the ASU-ANL serpentine carbonation experiments.”

**ENHANCING THE ATOMIC-LEVEL UNDERSTANDING
OF
CO₂ MINERAL SEQUESTRATION MECHANISMS
VIA
ADVANCED COMPUTATIONAL MODELING**

Type of Report:	Year 3 Technical Progress
Reporting Period Start Date:	9/20/03
Reporting Period End Date:	9/20/04
Principal Author:	A.V.G. Chizmeshya*, M.J. McKelvy, G.H. Wolf, R.W. Carpenter, D.A. Gormley and J.R. Diefenbacher, R. Marzke
Date Report Issued:	January 21, 2005
DOE Award Number:	DE-FG26-01NT41295
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ABSTRACT

Fossil fuels currently provide 85% of the world's energy needs, with the majority coming from coal, due to its low cost, wide availability, and high energy content. The extensive use of coal-fired power assumes that the resulting CO₂ emissions can be vented to the atmosphere. However, exponentially increasing atmospheric CO₂ levels have brought this assumption under critical review. Over the last decade, this discussion has evolved from whether exponentially increasing anthropogenic CO₂ emissions will adversely affect the global environment, to the timing and magnitude of their impact. A variety of sequestration technologies are being explored to mitigate CO₂ emissions. These technologies must be both environmentally benign and economically viable. Mineral carbonation is an attractive candidate technology as it disposes of CO₂ as geologically stable, environmentally benign mineral carbonates, clearly satisfying the first criteria. The primary challenge for mineral carbonation is cost-competitive process development.

CO₂ mineral sequestration – the conversion of stationary-source CO₂ emissions into mineral carbonates (*e.g.*, magnesium and calcium carbonate, MgCO₃ and CaCO₃) – has recently emerged as one of the most promising sequestration options, providing *permanent* CO₂ disposal, rather than storage. In this approach a magnesium-bearing feedstock mineral (typically serpentine or olivine; available in vast quantities globally) is specially processed and allowed to react with CO₂ under controlled conditions. This produces a mineral carbonate which (i) is environmentally benign, (ii) already exists in nature in quantities far exceeding those that could result from carbonating the world's known fossil fuel reserves, and (iii) is stable on a geological time scale. Minimizing the process cost *via* optimization of the reaction rate and degree of completion is the remaining challenge.

As members of the DOE/NETL managed National Mineral Sequestration Working Group we have already significantly improved our understanding of mineral carbonation. Group members at the Albany Research Center have recently shown that carbonation of olivine and serpentine, which naturally occurs over geological time (*i.e.*, 100,000s of years), can be accelerated to near completion in hours. Further process refinement will require a synergetic science/engineering approach that emphasizes simultaneous investigation of both thermodynamic processes and the detailed microscopic, atomic-level mechanisms that govern carbonation kinetics.

Our previously funded Phase I Innovative Concepts project demonstrated the value of advanced quantum-mechanical modeling as a complementary tool in bridging important gaps in our understanding of the atomic/molecular structure and reaction mechanisms that govern CO₂ mineral sequestration reaction processes for the model Mg-rich lamellar hydroxide feedstock material Mg(OH)₂. In the present simulation project, improved techniques and more efficient computational schemes have allowed us to expand and augment these capabilities and explore more complex Mg-rich, lamellar hydroxide-based feedstock materials, including the serpentine-based minerals. These feedstock materials are being actively investigated due to their wide availability, and low-cost CO₂ mineral sequestration potential.

Cutting-edge first principles quantum chemical, computational solid-state and materials simulation methodology studies proposed herein, have been strategically integrated with our new DOE supported (ASU-Argonne National Laboratory) project to investigate the mechanisms that govern mineral feedstock heat-treatment and aqueous/fluid-phase serpentine mineral carbonation *in situ*. This unified, synergetic theoretical and experimental approach will provide a deeper

understanding of the key reaction mechanisms than either individual approach can alone. *Ab initio* techniques will also significantly advance our understanding of atomic-level processes at the solid/solution interface by elucidating the origin of vibrational, electronic, x-ray and electron energy loss spectra observed experimentally.

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1. INTRODUCTION

In YEAR 1 of the present Innovative Concepts II award, DE-FG26-01NT41295, we focused on (i) the first principles simulation of fundamental reactant and products properties such as atomic structure, formation energy, vibrational structure and electronic spectral signatures (ii) the effects of heat treatment on the structure and composition of lizardite, the prototypical lamellar magnesium magnesium-hydroxy-silicate feedstock material, (iii) the preliminary steps associated with carbonation of defective (heat-treated) lizardite based on predicted *ab initio* atomic structures. The synergistic interaction of these initial studies with laboratory work has illuminated the origin of a number of observed phenomena including the critical assignment of the so-called “inner” and “outer” hydroxyl vibrational bands. These can/will be used as a fingerprint to diagnose the evolution of the departing structural hydroxyls in dehydroxylation experiments on lizardite, and eventually crysotile and antigorite. Our simulations predicted the existence of a novel, metastable, meta-serpentine material in which order and disorder coexist. This was used to explain the unusual progression of x-ray diffraction patterns upon dehydroxylation. We also modeled the MIE-like particle scattering features at low-angle in the XRD spectrum in the 640°C heat treated sample (see report 41295R01). We also initiated supercomputer-based quantum molecular dynamics studies of the temperature dependence of the dehydroxylation process to study the water formation rate and diffusivities of mineral (and product) components (Mg, Si, OH, H₂O and protons). These are described in section 3.0 below as a part of the last year’s performance period but within the present report since the grant has a September start date.

YEAR 2 focused primarily on understanding the fluid phase and carbonation mechanisms associated with the fluid phase. Possible reaction mechanisms associated with the dissolution were simulated. The minimum dipole forsterite surface was predicted to be (010) while large structural reconstruction are predicted for the (100) and (001) surfaces. The proton exchange reaction (dissolution on (010) surface) was studied using first principles methods and predicted to be exothermic by ~75 kcal/mol. An analogous study of iron extration yielded a corresponding value of ~55 kcal/mol suggesting that leaching leads should tend to increase the surface concentration of iron, barring unforeseen complexation reactions in the hydration layer of the reacting mineral (not taken into account in our study). Very large scale molecular dynamics simulations were also initiated in YEAR 2 to study the structure and properties of the silica-rich passivating layer which forms on reacting olivine surfaces by both the Albany DOE group and the ASU group. The simulations predict a low-density glass like network containing extensive “void” channels. Finally, electron energy loss spectroscopy (EELS), XRD and vibrational spectroscopy simulations were undertaken at various junctures throughout the year to elucidate and complement the corresponding experimental studies.

The simulation and modeling undertaken in YEAR 3 were targeted to maximize the synergism with ongoing parallel laboratory work. Considerable additional new focus was devoted to elucidation of the decomposition mechanism in lizardite, with a specific aim of indentifying the underlying atom structure responsible for the enhanced reactivity in heat treated feedstock (meta-lizardite). In the olivine area, our objective was to complete the molecular dynamics studies of the silica-rich passivation layers found experimentally to hinder the aqueous reaction (these are now believed to be rate-limiting). The structural configurations obtained from the latter simulation are used to generate clusters amenable to a more detailed and meaningful

simulations of the EELS and vibrational spectra of the reacted lizardite and olivine feedstock materials.

2. EXECUTIVE SUMMARY

2.1 OBJECTIVES

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 will be 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 project will include (i) simulation of the morphological changes associated with serpentine heat-activation to understand its role in enhancing carbonation reactivity, (ii) development of a non-empirical site reactivity model for CO₂ with serpentine, and (iii) detailed investigation of the olivine and serpentine surface dissolution mechanisms that govern carbonation kinetics, and (iv) the use of first-principles methods to provide deeper atomic-level insight into the mechanistic experimental observations in the partner ASU/ANL studies (*e.g.*, *in situ* studies of reaction intermediate formation). During the final project year critical development during this performance period is the increased effort being devoted by all members of the National Working Group on Mineral Sequestration to the study of carbonation in the olivine-based feedstock minerals. Accordingly a significant fraction of the modeling and simulation support and thrust this year was/is devoted to understanding forsterite/olivine dissolution, the speciation and equilibrium properties of our reactant solution (ARC aqueous process), and developing an understanding of the negative effect of passivating layer formation on the carbonation process. The elimination of the passivation layer is currently viewed as a critical problem in the development of an efficient and cost-effective conversion process.

2.2 ACCOMPLISHMENTS

- We expanded our molecular dynamics studies of the properties of the silica-rich passivating layer (PL) which forms on reacting olivine surfaces. Structural relaxation of the PL, when decoupled from the olivine matrix, exhibits a biaxial lateral contraction of approximately 5% indicating that even thin PLs (< 8nm) are in a state of tension.
- A detailed study of the internal structure of the simulated PLs was undertaken. Both the occupiable and accessible internal volumes were calculated as a function of probe particle dimensions for the strained and relaxed PL structures, and these results were compared with the results for a typical silica glass. We found that the strained PL material possesses a greater internal occupiable volume than the fully relaxed material, suggesting that the permeability to reactive species is greater at the onset of the surface reaction. A significant finding is that the accessible volume within the layer can accommodate carbonate ions (CO₃²⁻), as well as Mg²⁺ and protons, which supports the notion that the layers are permeable to key reactant species in their hydrated state.

- Integrated simulation, X-ray and nuclear magnetic resonance (NMR) studies were performed on a series of meta-lizardite (heat-treated) materials to elucidate in much greater detail the micro-structural evolution of the materials. This led to a novel reaction model which directly links the structural correlations of the silica (SiO_4) units to the dehydroxylation extent. The studies reveal that the most reactive meta-lizardite material is comprised of loosely coherent, remnant, sheet-like structures which are supposed to be prone to silica dimerization.
- The simulation of EELS spectra was significantly expanded to aid in the interpretation of the experimental characterization using this technique. The specific focus was on a detailed comparative study of known approximation techniques for calculating the energy loss cross-sections. Our research reveals the highest fidelity approximation (“relaxed core hole”) is reasonably well reproduced by a much less computationally intensive treatment (the $Z+1$ approximation).

2.3 SIGNIFICANCE TO FOSSIL ENERGY PROGRAMS

Fossil fuels, especially coal, can support the energy demands of the world for centuries to come, if the environmental problems associated with CO_2 emissions can be overcome[1,2]. Mineralization of stationary-source CO_2 emissions as carbonates can provide safe capture and long-term sequestration[3,4]. Carbonation of Mg-rich lamellar-hydroxide-based minerals (*e.g.*, the model $\text{Mg}(\text{OH})_2$ system and serpentine based minerals) is a leading process candidate, which generates the stable, naturally-occurring mineral magnesite (MgCO_3). Optimizing the carbonation reaction rate and its degree of completion are key to process cost and viability. This project focuses primarily (but not exclusively) on the carbonation reaction process mechanisms in serpentine minerals at the atomic level. Carbonation and treatment processes in the olivine class of feedstock minerals will also be studied in support of the research being carried out by the National Mineral Sequestration Working Group managed by NETL. In both cases, the objective is to provide the mechanistic understanding to accelerate the engineering development of improved carbonation materials and processes for carbon dioxide disposal. The simulation and modeling thrust described in this report is synergistically integrated with a number of other mineral sequestration projects sponsored by Fossil Energy including: NETL/ANL Contract 1F-01262 and UCR Awards DE-FG26-98FT40112 and DE-FG26-01NT41282. The author of the present report (Chizmeshya) is a member of the National Working Group on Mineral Sequestration managed by the National Energy Technology Laboratory.

3. KEY RESULTS AND DISCUSSION

3.0 STRUCTURAL ASPECTS OF THE DEHYDROXYLATION OF LIZARDITE

Background: The Mg-rich serpentine minerals (lizardite, antigorite and chrysotile) are of particular interest as mineral carbonation feedstock materials due to their wide availability and very large scale sequestration potential. Although the ideal formula for serpentine is

$\text{Mg}_3\text{Si}_2\text{O}_5(\text{OH})_4$, the minerals almost invariably contain significant amounts of other elements, such as iron and aluminum [5]. The lamellar structure of lizardite (Figure 1) is the simplest of the three serpentine mineral types, with antigorite and chrysotile possessing more complicated corrugated and spiral structures, respectively [6].

It is by now well established that lizardite requires a heat pre-treatment step to promote reaction with CO_2 . X-ray powder diffraction indicates that the materials produced (often referred to as meta-lizardite) are a strong function of their activation temperature, as seen for the materials generated from lizardite in Figure 2. This step removes the existing water from the crystalline structure making dissolution of Mg^{2+} more facile. As lizardite initially decomposes, a broad, low intensity meta-serpentine X-ray feature develops at $2\theta \sim 6^\circ$, apparently associated with a doubling of the 7.34 Å interlamellar lizardite spacing (~ 14.7 Å observed at $2\theta \sim 6.0^\circ$). This “ α ” feature is due to the formation of a new meta-serpentine phase that coexists with the residual lizardite, as the feature is substantially broader than the residual interlamellar lizardite, as the feature is substantially broader than the residual interlamellar lizardite (001) and (002) reflections observed near 12 and 24° , respectively.

Figure 1: Sheet-like layered lizardite crystal structure. The outer layer “brucite” hydroxyls are drawn at the top of each layer, magnesium is represented by green spheres which are suspended above the rigid silica network drawn as tetrahedra and embedded “cage” hydroxyls.

Figure 2: X-ray spectroscopy results for each respective ^{29}Si Sample stacked vertically starting at the bottom.

Dehydroxylation induced doubling of the interlamellar lizardite distance suggests lamellar oxyhydroxide formation (*e.g.*, preferential dehydroxylation of alternate hydroxide lamella) occurs during serpentine heat activation, as previously seen during *in situ* observations of $\text{Mg}(\text{OH})_2$ heat activation [7,8]. Our first principles simulation studies (YEAR 1) are consistent with these observations, predicting the existence of a stable meta-serpentine material for 50% dehydroxylated lizardite. The ratio of neighboring layer hydroxide concentrations necessary for such α formation was found to be greater than 4:1 (see YEAR 1 Technical Progress Report). Only a 6% decrease in density was observed for the simulated material, along with a very slight monoclinic tilt and the structure exhibiting essentially the same interlamellar spacing as the parent lizardite, consistent with the doubling of the original lizardite spacing observed via XPD.

Phase analysis of the meta-serpentine materials that form during heat activation indicate two meta-serpentine components form during heat activation, the α component and an amorphous component [9]. These are associated with the broad diffraction peak

near 6° , as discussed above, and the diffuse intensity that is observed from ~ 18 to 38° , as seen during phase analysis of the X-ray data for the sample heat-activated at 580°C shown in Figure 3. α contributes a relatively minor component of the X-ray scattering observed, as the intensity observed for the feature near 6° varies from 0-7% of the total X-ray scattering observed, while the intensity of the amorphous component approaches 100% of the total X-ray scattering observed just before forsterite/enstatite formation. α increases in intensity, albeit to a much lesser degree, along with the amorphous component until 610°C , when 15% of the original hydroxide groups remain. Further heating results in the disappearance of the α component, while the amorphous component continues to grow in intensity until 795°C when its intensity decreases due to forsterite nucleation and growth. This suggests heat-activation/dehydroxylation initially results in the formation of an “ α ” meta-serpentine component with diffuse interlamellar ordering and intralamellar disorder, as predicted by the simulations from (Figure 7 of the YEAR 1 Technical Progress Report). The amorphous component is present as well at these lower temperatures, as the α component is relatively weak compared with the amorphous scatter observed (see Figure 4). As the activation temperature increases above 610°C , the scatter from the “ α ” component decreases, consistent with the loss of residual hydroxyl groups still present. At the same time, the amorphous scattering centered near 28° increases, eventually dominating, with an essentially pure amorphous meta-serpentine material forming by 780°C .

Figure 4: Variations in the relative amounts of the crystalline lizardite (blue), amorphous (red), and α (green) components throughout the heat-activated lizardite sample sequence. Their relative content is calculated as the ratio of each contribution to its maximum integrated value. The figure shows the emergence of the α and amorphous components is strongly correlated at higher OH contents. The low levels of the α and amorphous components suggested for lizardite are near the (10% analysis error limit and may or may not be present).

structural components of the mineral (e.g., silica groups, hydroxyl groups and magnesium octahedral). This prompted us to undertake a detailed study of the meta-lizardite materials based on NMR aimed at elucidating the local structural aspects of the decomposition process. As will be demonstrated below, the NMR analysis in combination with the first principles simulations

Figure 3: Phase analysis of the crystalline lizardite features and the α and amorphous meta-serpentine components that form during heat-activation.

As the activation temperature increases above 610°C , the scatter from the “ α ” component decreases, consistent with the loss of residual hydroxyl groups still present. At the same time, the amorphous scattering centered near 28° increases, eventually dominating, with an essentially pure amorphous meta-serpentine material forming by 780°C .

3.1.1 Structural Correlation Models based on NMR data

The results shown in Figure 4 suggest a complex structural decomposition mechanism involving the interplay between different

(YEAR 1 and 2) of structural disorder and X-ray analysis yield a systematic and comprehensive picture of the pathway to highly reactive materials.

Figure 5: From left to right are Q0, Q1, Q2, Q3 and Q4 silica species (circled). The oxygen atoms are the small red spheres while silicon atoms are located at the center of each grey tetrahedron.

The NMR analysis is based on a study of the local coordination of individual silica tetrahedral, and specifically, their linkage to other silica tetrahedral. This approach been used successfully in prior studies to identify the local silicon environment on the basis of ^{29}Si chemical shifts [10]. Depending on the degree of silica tetrahedral polymerization, the chemical shifts yield five possible assignments. These species are referred to as Q-species, ranging from Q-zero (or Q0) to Q-four (or Q4) as shown in Figure 5. A Q4 species, in the case of silicon, is a silica tetrahedron that is corner shared to four other silica tetrahedra. Similarly, a Q0 species is a silica tetrahedron that does not share any oxygen atoms with any other silica tetrahedral, e.g., as in the case of olivine which can be viewed as an ionic compound

composed of two Mg^{2+} ions and one SiO_4^{4-} ionic unit.

During YEAR 3 we developed a novel structural correlation model which links ^{29}Si chemical shifts directly to the degree of dehydroxylation in meta-lizardite. Below, we compare the dehydroxylation behavior derived from NMR with the results obtained from thermogravimetric analysis (TGA). To obtain a consistent comparison both X-ray and ^{29}Si NMR spectra were collected for 10 samples within the dehydroxylation series for lizardite obtained from the Philips site (referred to as “Ph1”-lizardite). Each peak within the measured ^{29}Si NMR spectrum is given a Q-assignment, and a peak fitting analysis is done for each sample. The X-ray results provide details about the gross crystallographic properties

Figure 6: Thermogravimetric analysis of Philips-1 lizardite sample heated from room temperature to 1100°C.

Sample temperature	% OH remaining
Ph1-Liz starting material	100
Liz-528	75
Liz-540	63
Liz-550	50
Liz-559	37
Liz-567	25
Liz-583	13
Liz-640	4
Liz-725	1
Liz-1100	0

Table 1: Amount OH remaining in heated Philips-1 lizardite samples used in NMR and X-ray studies.

of the material, whereas the NMR results elucidate the changes in the chemical environment on a scale smaller than the unit cell of the starting crystal.

Samples were prepared from the Phillips-1 lizardite feedstock, which was ground to sub 100 μ powder. The Phillips-1 feedstock material has been previously analyzed and found to be relatively phase pure, with a low concentration of impurities. The samples were dehydroxylated by heating to a given

temperature in a helium environment, using a Perkin Elmer Pyris 1 thermogravimetric analysis (TGA) instrument. Figure 6 illustrates the TGA curve of the Phillips-1 lizardite as it is heated to 1100°C. Ten points were selected along this curve and the corresponding samples were prepared. 100 g of starting material was used for each TGA run. Two batches were prepared for each sample, ensuring approximately 200g of material for the following NMR experiments. Each run began at room temperature and was heated at a rate of 2°C per minute, under helium gas. Once the maximum desired temperature was reached, the sample was held at temperature for 1 minute whereupon the power was cut and the sample allowed to cool to room temperature. Ten samples were prepared and used for further analysis. Table 1 illustrates the percent hydroxyl remaining in each sample. The sample identification values correspond to the temperature of heating. For example, Liz-528 was heated to 528°C and contains a residual of 75% hydroxyl (Table 1).

NMR Analysis: ^{29}Si NMR solid state MAS spectroscopy measurements were performed using a 300 MHz (7 Tesla) Varian CMX Infinity spectrometer. Conditions included 80,000 acquisitions with a pulse delay of 0.5 sec, an acquisition delay of 5 μsec and a receiver delay of 5 μsec for the first seven samples. Samples were spun at the magic angle at 7500 Hz. Due to the drastic change in structure and chemical composition of the final three structures, the instrumental conditions for

Q-assignment	peak positions (ppm)
Q_0	-64
Q_1	-73
Q_1'	-78
Q_2	-85
Q_3	-95
Q_3'	-99

Table 2. The following results depict the Q-assignments for the given peak positions. Q-assignments are based on earlier work [10]. The final peak positions for each fit are within ± 2 ppm of the tabulated values for all NMR chemical shifts.

sealed, airtight containers.

Figure 7: ^{29}Si NMR results of the dehydroxylation series data for Phillips-1 lizardite samples stacked vertically, based on percent dehydroxylation.

NMR collection were re-optimized. A new pulse delay of 1 sec, acquisition delay of 13 μsec and a receiver delay of 17 μsec were used.

^{29}Si NMR results are plotted and shown in the range of chemical shifts from 0 to (-150) ppm as a vertically stacked plot (Figure 7). The starting Philips-1 lizardite sample is shown at the base of the plot and has one major feature at -96 ppm. The uppermost plot is the Liz-1100 sample which was heated to 1100°C and contains no residual hydroxyl as verified in the TGA results above. It has two main features at -64 ppm and at -86 ppm. These two features belong to forsterite and enstatite respectively. It is unclear from NMR whether the material has completely recrystallized, but for the purpose of Q-assignment and the study of the dehydroxylation mechanism these results are adequate. The intermediate samples were found to be highly hygroscopic in the air and were stored in

Figure 8: ^{29}Si NMR spectrum liz-528 demonstrating the use of five Lorentzian curves centered at -64, -73, -78, -87 and -95 to model the chemical shift profile. Thick solid line -- experimental data; dotted blue line -- total fit; thin red curves -- individual contributions.

procedures including combinations of both Lorentzian and Gaussian curves. Where necessary, the spinning side bands were included in the integrations as part of a sum of the total integrated area for the corresponding peak. As a note, the spinning side bands are found 7500 Hz away from each peak in both directions, but are not always of great enough intensity to be seen. However, for those that were found to have considerable intensity, the integrations of the side bands were found to be an important contribution to the total integrated area for the peak of interest.

Once all of the Q-assignments were made, the integrated area under each individual curve was tabulated and organized

according to its corresponding chemical shift. Each fractional Q-contribution was taken as a sum and recorded as a fraction for the given sample, making the total fractional Q-contribution for each sample, unity. All final deconvolution results are summarized in Table 3. Several peak fitting methods were tested and compared to evaluate the sensitivity of the results to the deconvolution scheme. These results varied anywhere from 1 to 5% error, so that tabulated fractional values for each Q-species are considered to be within reasonable error.

It was found to be extremely important to have a flat baseline within the NMR data for the curve fitting procedure. In solid-state NMR, a baseline “rolling” can occur, but it can often be avoided by adjusting the instrumental parameters while collecting data. Testing was

Other peaks are identified throughout the dehydroxylation series and have been tracked and given a Q-assignment. Six chemical shift positions were chosen and kept constant. These peak positions were limited to a variance of ± 2 ppm for each chemical shift. By tracking the magnitude changes of specific peaks throughout the series of data, we developed new insight into the structures of the intermediate lizardite phases which helps to identify how they are changing with degree of dehydroxylation. The corresponding Q-assignments and chemical shifts are summarized in Table 2. All NMR spectra were carefully analyzed using a detailed curve fitting or deconvolution procedure as shown in Figure 8. Many of the peaks were fit to perfect Lorentzian curves whereas several features required more detailed fitting

Sample ID	% Dehydroxylation	Q_0	Q_1^T	Q_2	Q_3^T
Ph1-Liz	0	0.00	0.00	0.04	0.96
liz 528	25	0.00	0.15	0.05	0.80
liz 540	37	0.00	0.33	0.13	0.53
liz 550	50	0.00	0.43	0.21	0.36
liz 559	63	0.00	0.59	0.17	0.25
liz 567	75	0.00	0.54	0.16	0.30
liz 583	87	0.00	0.52	0.22	0.26
liz 640	96	0.00	0.76	0.15	0.08
liz 725	99	0.00	0.71	0.20	0.09
liz 1100	100	0.37	0.01	0.59	0.03

Table 3. Total fractional Q-contributions of individual Q-species calculated from the integrated area of each given chemical shift based on the peak assignments in Table 2. The final integrated peak areas for each Q-assignment are taken as the sum of each Q-species, shown as a superscript “T” in the table.

performed to minimize the instrumental “ring-down”, found at the beginning of the free induction decay (FID). The instrumental ring-down can be as large as 50 μ s at the NMR frequency of ^{29}Si and can mask parts of the desired data. One possible approach to avoiding this is to delete the first two or three free induction decay points. By deleting the initial data that is collected, instrumental noise is deleted, however part of the desired data is also deleted. This can have profound effects on the peak shapes and final intensities. By deleting too much of the initial data, it is possible to lose some of the signal from one of the peaks

and not from the others, resulting in an artificial change in peak ratios. However, by optimizing run conditions the amount of instrumental uncertainty due to ring down can be reduced. As the size of the initial ring-down is reduced, the amount of usable data is increased, and the background, baseline roll, is reduced. By reducing the amount of baseline roll, the curve fitting results were made more accurate and the deconvolution process became much simpler. Although considerable time was invested in initially optimizing the data run-parameters and fitting methods, the most important factor in this study was not to obtain perfectly accurate data but to analyze trends from one sample to another. The final methods and parameters gave the following results.

Figure 10: Expansion of Figure 9 from 95-100% dehydroxylation.

Figure 9: Q-species trends in dehydroxylated lizardite measured from ^{29}Si NMR characterization. This plot compares the relative contribution from each Q-species in each sample individually calculated from the integrated area for specific peak positions. The total fractional Q-contribution for each sample is normalized to unity. Sample regions are marked using solid vertical lines

The Q-contributions from Table 3 have been plotted and the trends can be seen in Figure 9. This figure identifies the trends in the local silicon environment for each given sample. The last two data points are close together and may be difficult to differentiate; therefore an expansion is shown in Figure 10.

In Figure 6, two of the most dramatic trends are those of Q3 and Q1. Q3 can be thought of as the crystalline phase that starts out as lizardite. Its presence steadily decreases throughout the series as the crystalline character of the material disappears. This can be verified

by referring to the X-ray spectroscopy results in Figure 2. It is apparent from the disappearance of the sharp features in the X-ray sequence shown in Figure 2, that all of the samples from Liz-528 to Liz-725 are gradually becoming amorphous. (see Figure 3).

The trends shown in the NMR Q-speciation in Figure 9 can now be directly compared with the phase analysis obtained from X-ray, shown in Figure 4. In the latter case the “crystallinity” is greatest in the first sample where its fractional contribution is equal to 1. Similarly, the 100% dehydroxylated sample is entirely crystalline (forsterite and enstatite) and the corresponding crystalline features are all present in the X-ray pattern in Figure 2. According to the NMR data in Figure 10, the final step from Liz-725 to Liz-1100 also results in a transformation or nucleation to two new crystalline phases. These phases are identified in the final NMR data in Figure 7 by signatures at -64 ppm (forsterite) and -86 ppm (enstatite) with the former being Q0 and the latter being Q2.

According to the X-ray data the “α” and “amorphous” components do not reach their maxima until much later in the dehydroxylation process. According to the NMR analysis the Q1 (silica dimmer) content steadily grows in while Q3 (sheet like silica) diminishes as the material loses water. From a reaction kinetics standpoint this regime can be identified with the formation of a metastable intermediate phase prior to nucleation. This phase grows in rapidly and disappears once all of the water is removed. It should be noted that the Q1 phase is not commonly observed in natural mineral structures. Clearly there is no evidence for this signature in either the starting material or in the final products. As noted above, the appearance of Q0 in the final dehydroxylate indicates that forsterite does not form until much later in the process. Q2, which is partially present in the starting structure as an impurity, grows to a level around 20

% and persists until onset of nucleation and growth of enstatite. In the final product, Q2 contributes slightly more than half of the total intensity. Another significant feature of interest in the X-ray results is the feature at 3° that appears in the Liz-528 sample and does not disappear until much later in the dehydroxylation process. This phase is connected with the decrease in Q3 and the increase of Q1. At the same time, the dimmer and sheet species (Q1 and Q2) grow and coexist with the parent crystalline material. Our results suggest that the metastable phase associated with Q1 is present in all of the intermediate meta-lizardites, but that it is absent in the starting material and in the final product.

In YEAR 1 of the this project we studied the initial stages of dehydroxylation in detail (see Section 3.1 in the YEAR 1 Technical Progress Report). There most energetically likely mechanism involved the reaction in which the removal of an H₂O molecule leaves a residual oxygen atom to react with the silica network. Our simulations elucidated the energetics of removing various “brucite” and “cage” hydroxyls. Thus, to form a Q3 unit from a Q4 species, $\frac{1}{2}$ of an oxygen atom must be added, as shown in Figure 11a. In Q4 silicon

Figure 11: Schematic illustration of inter-relationship between Q species: (a) conversion of Q4 to Q3 and (b) conversion of Q3 to Q2.

dioxide, all four oxygen atoms are bonded to other silicon tetrahedral thus Q3 is formed by breaking one of these bonds, with the simultaneous addition of one oxygen atom. Alternatively, two Q3 species are formed from two Q4 species by addition of one oxygen atom per cell. Similarly, the formation of a Q2 species from a Q3 unleashes one more oxygen atom from neighboring bonds while adding an oxygen atom to the silicon environment, as illustrated in Figure 11b. This oxygen atom could be taken from nearby hydroxyl groups, leaving an isolated proton. In turn, this proton can combine with another neighboring hydroxyl group to form water. In terms of the unit cell in Figure 11b, this involves the addition of one oxygen atom for transition from two Q3 species to two Q2 species. The resulting Q2 species is a chain-like structure. The progression can be trivially extended to the transformation from Q2 to Q1 (Figure 12a), and from Q1 to Q0 (Figure 12b). The Q1 species are pairs of tetrahedra while the Q0 species are isolated tetrahedra.

Using the above concepts we have developed a simple model to relate the silicon coordination to the degree of hydroxylation. The latter is assumed to be related to the amount of oxygen entering or leaving the system (e.g., the change in hydroxyl content). The associated stoichiometric reaction can be written as:

where x is the fractional dehydroxylation. The following well defined limits are described as follows: when $x=0$, the product becomes $\text{Mg}_3\text{Si}_2\text{O}_5(\text{OH})_4$, which is the starting lizardite material and $x=1$ corresponds to $\text{Mg}_3\text{Si}_2\text{O}_7 + 2\text{H}_2\text{O}$. Here $\text{Mg}_3\text{Si}_2\text{O}_7$ can be written as $\text{Mg}_2\text{SiO}_4 + \text{MgSiO}_3$, representing forsterite and enstatite respectively.

Sample ID	T(K)	%OH
Ph1-Liz	86	97.80 (100)
liz 528	528	82.46 (75)
liz 540	540	60.09 (63)
liz 550	550	46.37 (50)
liz 559	559	33.10 (37)
liz 567	567	37.99 (25)
liz 583	583	36.66 (13)
liz 640	640	16.24 (4)
liz 725	725	18.86 (1)
liz 1100	1100	14.38 (0)

Table 4: . % Hydroxyl remaining in each sample calculated using Equation 1 from NMR results found in Table 3. Experimental values are shown in brackets.

Figure 12: Schematic illustration of inter-relationship between Q species: (a) conversion of Q2 to Q1 and (b) conversion of Q1 to Q0.

Finally, when $x=0.5$, the product is: $\text{Mg}_3\text{Si}_2\text{O}_6(\text{OH})_2 + \text{H}_2\text{O}$. Thus, one may think of Si_2O_5 as being converted into $\text{Si}_2\text{O}_{5+2x}$, with x ranging from 0 to 1. Accordingly, from the oxygen stoichiometry and the reactions shown in Figures 11 and 12, the following assignments can be made: $\text{Q}_4 \Leftrightarrow \text{SiO}_2$, $\text{Q}_3 \Leftrightarrow \text{SiO}_{2.5}$, $\text{Q}_2 \Leftrightarrow \text{SiO}_3$, $\text{Q}_1 \Leftrightarrow \text{SiO}_{3.5}$, and $\text{Q}_0 \Leftrightarrow \text{SiO}_4$. The simplifying assumption that all of the oxygen reactions involve the silica framework imposes an additional stoichiometric constraint since there are $2x$ “silica” oxygens per mole of lizardite available to drive the conversion of the Q_n species. The remainder of the oxygen

leaves as H₂O or remains bound within the meta-lizardite. From the oxygen stoichiometry, the constraint can be expressed mathematically as:

$$2.5 + x = 2 \cdot N_4 + 2.5 \cdot N_3 + 3 \cdot N_2 + 3.5 \cdot N_1 + 4 \cdot N_0, \quad (2)$$

where N_n are the fractional contributions of each Q-species are obtained directly from the ²⁹Si chemical shift analysis (Table 3). The dehydroxylation fraction computed from this model, based on the ²⁹Si NMR data, is listed in Table 4. The values in brackets are the corresponding values from the TGA analysis. Figure 3 All values are plotted along the experimental TGA plot (Figure 15), and the values seem to agree very well up to about 50% dehydroxylation.

In order to explain the dehydroxylation process, one may visualize a sheet of the silica layer in the lizardite structure. If we assume that the inner layer, “cage” hydroxyls are more reactive than the outer layer “brucite” hydroxyls, then we can assume that this reaction initiates the dehydroxylation mechanism. As the cage hydroxyls react with the Q3 silica species, protons are liberated. These protons then react with outer layer “brucite” hydroxyls liberating water. The charged oxygen

Figure 13: Plot comparing experimental TGA data (solid red line), with calculated %OH (blue square points) as a function of temperature. The %OH remaining is calculated from ²⁹Si NMR results.

Figure 14: Figure of the silica tetrahedra within Lizardite as it “unzippers”. Q3

atom joins the silica network thereby tearing it or “unzipping” it into Q3’, Q2 and Q1 (Figure 14). We will refer to this initial reaction as “Mechanism I”. A possible structural relationship between Q1 and the new Q3’ species is shown schematically in Figure 14. As the layers come apart the original Q3 is destroyed forming a new Q3’, Q1 and a small amount of Q2 shown on the right side of Figure 14. The 6° feature identified in the X-ray spectra (Figure 2) may also therefore correspond to this “unzipped” Q3’ meta-lizardite structure that forms during reaction. In this case the Q-species conversion reactions involved may include $6 \text{ Q3} + 3 \text{ O}^* \rightarrow 3 \text{ Q3}' + 3 \text{ Q1} + 3 \text{ H}_2\text{O}$ as well as other reactions which produce Q2 species, such as $2 \text{ Q3} + \text{O}^* \rightarrow 2 \text{ Q2}$. Figure 15 is a plot of some of the previous work done by our group. It

shows the experimental IR spectra of the Philips and Globe A lizardite samples as a function of dehydroxylation. The “inner” hydroxyl label corresponds to the “cage” hydroxyls in our model,

Figure 15: A comparison of the OH IR modes for both the Globe A and the Philips lizardite samples during dehydroxylation.

and the “outer” hydroxyls at a lower IR frequency correspond to the “brucite” hydroxyls (see YEAR 1 Technical Progress Report, Figure 1). There are four hydroxyl sets in the primitive unit cell, 3 corresponding to brucite and 1 corresponding to the cage. This means that in the IR results, we should have four modes. In this case, there are two anti-symmetric stretches corresponding to the brucite hydroxyls, labeled “E” in Figure 15. The other two modes are located at higher frequency which corresponds to the symmetric stretches of the brucite hydroxyls, labeled A_{1b} and the symmetric stretch of the cage hydroxyls on the shoulder labeled A_{1c}. These A₁ stretches are doubly degenerate, so there may be some mixing of the modes. The trends in the IR intensity sequence suggest that, to some degree, the A_{1c} shoulder is disappearing as a function of % dehydroxylation, but further detailed studies are required to confirm quantify this notion.

According to the plot in Figure 13 the simple model defined by Eqn. (1) and (2) is quantitative up to approximately 50% dehydroxylation, and quantitative over full lizardite dehydroxylation range. It should be noted that the number of brucite hydroxyls far exceeds the number of cage hydroxyls. In fact, the ratio is approximately 3:1 respectively. Therefore, once all of the cage hydroxyls have been depleted, there are remaining brucite layer hydroxyls which must be removed via some other mechanism. Since the remaining protons and oxygen are in the brucite layer, these reaction must occur here. A brucite hydroxyl will react with another brucite hydroxyl by pulling a proton away leaving behind a negatively charged oxygen atom, as seen in the Mechanism I. However, this oxygen atom may also become trapped in the magnesium layer below (see Figure 1), which we now refer to as “Mechanism II”. In this case the magnesium ions may serve as a buffer for the highly charged oxygen atoms until nucleation and growth of forsterite and enstatite occurs. This notion is supported by our simulation studies of the initial

stages of lizardite dehydroxylation: In the lowest energy structure (referred to as BC in Figure 4 of the YEAR 1 Technical Progress Report) where we removed a hydroxyl from the brucite layer and a proton from the cage layer, we have evidence that the oxygen-magnesium bond distance decreases when its connecting proton is removed. The bond length from oxygen to magnesium in lizardite is $2.06\text{\AA}$, whereas in the defective structure the bond length is reduced to $1.87\text{\AA}$. This is further evidence that during Mechanism II the leftover oxygen atoms will migrate towards the magnesium layer for the remainder of the dehydroxylation mechanism.

3.3 DISSOLUTION AND PASSIVATION OF FEEDSTOCK MINERALS

3.3.1 Modeling of the Passivation Layer Strain State: During YEAR 2 we developed a series of structural models for silica-rich “passivating layer” (PL) structures found on reacted olivine particles. As pointed out in our YEAR 2 technical report the detailed modeling of the dissolution

Figure 16. (a) Initial bulk forsterite slab containing $\sim 11,000$ atoms prior to Mg+O removal. (b) Final simulated forsterite-passivation-layer reaction interface system containing ~ 9000 atoms. (c) The variation of Mg, O and Si atoms (chemical profile) throughout the structure are plotted in the frame below the model. Note that the apparent densification of Mg atoms near $-50\text{ \AA}$ is due to the projection employed, which emphasizes the departure from periodic crystalline order in the transition region (from $\sim -65\text{ \AA}$ to $-40\text{ \AA}$).

processes involve time scales which are prohibitive for atomic scale modeling (10^{-3} - 10^2 seconds). We have in fact modeled (using *ab initio* simulations on the picosecond timescale) the

Figure 17. Schematic representation of the procedure employed to compute the strain state of the passivation layer (PL). The boundary between the passivation layer and the underlying forsterite is taken as the peak in the derivative of the Mg chemical profile distribution ($\sim 80\text{\AA}$ from the free surface). (a) Strained PL layer on the forsterite substrate (PL – speckled region, Forsterite – black and white checkered region). (b) The PL layer is isolated and allowed to evolve to its zero stress state, as described in the text. A 5% contraction along both basal directions is obtained indicating that the PL bonded to forsterite is in a tensile state.

in the top panel for comparison. From this figure, the degree of contraction of the altered forsterite surface predicted by the model is clearly evident. The bottom panel shows the chemical profiles obtained from the simulation, which indicate that the passivation layer consists of a defective silica network very similar in stoichiometry to SiO_2 (e.g., O:Si ratio ~ 2 throughout the passivation layer). We have verified that these profiles remained essentially unchanged following several additional heating and cooling cycles from 300°K to 600°K .

As discussed in the YEAR 2 report, cracking is typically associated with the passivating layer material. Scanning electron microscopy reveals a “mud-crack” morphology consisting of lateral domains of a few tenths of a micron in size. This size, though small, exceeds the basal dimensions of our simulation cell making it impractical to model the process. To study the strain state of our structural PL layer model, we therefore employed the discretization procedure described schematically in Figure 17. The interface system consists of a continuous transition from bulk stoichiometric forsterite to a nominally SiO_2 stoichiometry glassy layer, as described in the previous section. As described earlier, the dimensions of the computational cell parallel to the surface normal are fixed to represent a thick, bulk forsterite substrate. Our simulations produced a strained silica-like layer consisting of almost completely corner-shared silica tetrahedral

exchange process of 2H^+ and Mg^{2+} , as well as the subsequent polymerization of SiO_4 units and release of H_2O in the near surface, under the auspices of another related research project. Our objective in the current project is to simulate the atomic level structure of the near surface region of the altered mineral, e.g., from bulk forsterite, through the reaction zone and into the magnesium-leached region (passivating layer). Although our simulated structure is initialized by the sequential “artificial” removal of Mg+O atoms (see YEAR 2 report), the final relaxed state is meant to provide a plausible representation of the anhydrous mineral surface whose detailed “ex situ” analysis is described in our paper. For clarity we reproduce one of the final PL models in panel (b) of Figure 16. In this new composite figure the crystalline starting structure of forsterite is provided

Figure 18: Cumulative and sectional density determinations for the PL material as a function of position in the structure. Color code as in Figure 16.

network including a nanochannel morphology using the same interaction potentials used to accurately describe thermal SiO₂ glass. Thus, because the PL layer and forsterite substrate are chemically bonded (coupled) it is not possible to deduce the strain state of the glass in this setting. In order to investigate the latter, we first examined the derivative of the chemical profile for Mg, Si and O in our system. The peak in the Mg distribution derivative occurring in the reaction zone between the PL and the underlying forsterite serves as our definition of PL/forsterite boundary. By slicing the model apart at this boundary and abstracting the residual Mg ions (along with a compensating number of O²⁻ ions), we arrived at a model for the isolated PL layer consisting of approximately 2600 atoms. Simultaneous minimization of the external stress and internal forces on this cell then yields an unstrained, stress-free PL material contracted by approximately 5% relative to the composite system (PL layer bonded to forsterite). The MOLDY code [11] was used to carry out the stress minimizations at 300°K using the same interaction potentials and computational parameters as for the full leached forsterite slab.

At this point we have in our possession detailed structural models of the passivation layer in both its bonded (strained) state, as well as in its relaxed stress-free state. The former is likely representative of the PL material during early stages of growth while the stress-free model provides a model for the outer portion of thick armoring layers far away from the forsterite reaction front. An interesting question is whether the relaxation process has led to densification of the silica-like structure. Examination of the chemical profiles provided in Figure 16(c) reveals that density fluctuations exist within our model PL material, even after a number of thermal “quenching” cycles. In addition, the density of the PL material falls off rapidly within the last ~ 10 Å of the structure (solution side). To estimate the density of the PL material we integrated through the sample in a step-wise fashion, as shown below in Figure 18. The lower portion of the model contains some artificial local structure associated with bonding to the forsterite substrate (now missing) while the region near the “free surface” possesses an anomalously low density (0.58 g/cc for strained PL and 0.92 g/cc for relaxed PL) due to the very open structure induced by the lack of hydroxylation in our model. The most reliable density estimates are those obtained from the central bulk-like structure yielding mean densities of ~ 2.2 g/cc for the relaxed PL material and ~2.0 g/cc for the strained one. This compares well with our thermal glass model for which the density was calculated to be ~ 2.3 g/cc, only about 5% higher than the observed value. Correcting our simulated PL material density by this amount yields a final predicted value of ~ 2.1 g/cc for the intrinsic density of the PL material.

Based on these simulated PL material structures, a series of additional calculations should be performed in the future including: (i) determination of the stiffness tensor, young’s modulus and Poisson ratio of the PL material and (ii) estimation of the critical fracture stress of the strained PL material (relevant to impact induced spalling).

3.2.2 Internal Structure of the Passivation Layer Material

The question of permeability is clearly implicated in the formation mechanisms of the layer, such as the leaching of Mg ions from the reaction front at the PL/forsterite interface to the solution and the diffusive processes possibly involved in the formation of carbonate within the PL matrix. A close examination of the simulated PL structure reveals the presence of stable nano-channels within the passivation layer. This feature may provide the diffusion pathways and low energy nucleation sites for the MgCO₃ nanoparticle growth observed experimentally, as discussed below. These features do not exist in our quenched thermal SiO₂ glass model, and are endemic to

the PL structures, which were obtained at low temperature through an artificial synthetic leaching procedure in our simulations. Nevertheless, as shown in YEAR 2 the radial distribution functions calculated for the simulated SiO₂ glass and passivation layer material are not profoundly different. This is mainly because the short-ranged structure of both materials is the same. To reveal the differences between the two structures we appeal to a “free volume” analysis module available in the *Cerius*² simulation software suite [12]. The available, occupiable and solvent volumes can be computed given an input structure: the van der Waals radii of the constituents and the radius of a probe particle. Here we focus on the occupiable volume, which is computed by overlaying grid points set at 0.5 Å intervals throughout the structure. A probe molecule is then placed at each grid point in sequence and the point is considered to be “occupiable” if there is no van der Waals contact with the PL structure in any of several hundred

Figure 19: Occupiable volume fraction (see text) as a function of probe particle diameter (see text) for strained PL, relaxed PL and thermal glass structures.

directions. Figure 19 shows the result of such calculations for the strained PL, relaxed PL and thermal glass structures obtained from our simulations. Nine probe particles with diameters ranging from 2 Å to 6 Å were used. As expected on the basis of visual inspection and density, the strained PL structure exhibits the largest fractional occupiable volume. This is followed by the relaxed PL structure and the thermal glass. The analysis suggests that the permeability should also decrease in going from the strained PL to the relaxed PL. However, note that the ratio of fractional occupiable volumes for the strained and relaxed PL structures do not scale with their corresponding densities. This is because the

fractional occupiable volume is sensitive to differences in network topology. It also represents a simplified measure of the excess entropy of insertion.

The distribution of “void” volumes and their connectivity is even more important to diffusion, but also more difficult to unambiguously quantify. Even in the absence of these distributions, the curves shown in Figure 19 indicate that about 4% of the occupiable volume of the strained PL material can accommodate CO₃²⁻ ions ($D_{\text{probe}} \sim 4.3$ Å) or CO₂ molecules ($D_{\text{probe}} \sim 3.9$ Å), while about half of this amount is available in the relaxed PL material (the occupiable volume in thermal glass is negligible, as expected). Protons and Mg²⁺ ions (mean diameter < 2.5 Å) see significant occupiable volume in both PL materials. While this does not account for the observed carbonate volume in the PL matrix, it is the correct trend. A definitive conclusion concerning the permeability of the PL to various species will emerge from molecular dynamics simulations, which are currently underway.

3.3 SPECTROSCOPIC SIMULATION IN SUPPORT OF MINERAL SEQUESTRATION EXPERIMENTS

3.3.1 Background: The ASU CO₂ Sequestration group routinely uses high resolution transmission electron microscope (HRTEM) analysis to study the chemical and morphological characteristics of the near surface region of reacted particles. The calculation of Electron Energy Loss Spectra (EELS) stems from the need to interpret the EELS spectra obtained experimentally for the silica-rich layers found on reacted olivine particles. The computational studies undertaken in YEAR 3 extend of the initial EELS studies described in YEAR 2 by adopting a more rigorous approach to the calculation of the energy loss cross sections. Initial work based on the FEFF code [13] was encouraging, but left open the question as the adequacy of a ground state calculation. Accordingly, in the final project period we carried out a series of calculations using the WIEN2K all-electron FPLAPW code [14], which can be used to carry out self-consistent calculations in the presence of a full core-hole. Below, we compare and contrast the results for SiO₂ quartz obtained using a fully self-consistent FPLAPW approach for the ground state, Z+1, non-self-consistent core hole, and fully relaxed self-consistent core-hole. The Z+1 approximation is a “ground state” –like calculation in which a target nucleus charge is increased by one unit charge to simulate the presence of a core-hole. This substitution breaks the symmetry of the unit-cell and increases the computational burden. In the “corehole” calculations, an electron is explicitly removed from the nucleus and promoted manually to a higher energy state. The electron states are then re-calculated with this electron configuration, e.g., one more non-self-consistent diagonalization – yielding the unrelaxed corehole approximation, or allowed to relax to a new minimum energy configuration relative to this newly introduced electron. In either case the manifold of Bloch states obtained is used to perform subsequent ELNES cross-section calculations. The calculation with the relaxation procedure is referred to as the “relaxed-corehole” calculation. If the states are left in their original ground state configuration after the

electron is promoted, the calculation is referred to as the “unrelaxed-corehole” calculation. It should be noted that the Z+1 approximation can be applied in both FEFF and WIEN2k, but the corehole calculation can only be done in WIEN2k.

Figure 20: Each unit represents different sized models used in amorphous SiO₂ XANES calculations. “R” represents the radius of the calculation from the central atom and “N” represents the number of atoms. Oxygen atoms are red and silicon are shown in grey. The oversized oxygen atoms at the center of each group represent the atom for which the near edge structure is calculated.

3.3.2 Simulation Approach: FEFF is an *ab initio* self-consistent real space multiple-scattering code for simultaneous calculations of x-ray absorption spectra and electronic structure [15]. Calculations are based on real space relativistic Green’s function formalism without symmetry requirements. This code is therefore well adapted to handle systems containing disordered. In EXAFS, only single scattering events are taken into account, but with the new methods derived based on Green functions, multiple scattering methods such as XAFS and XANES can also be included. These calculations rely on a muffin-tin

approximation in which a spherically averaged scattering potential is centered on each atom and the interstitials are given a constant value. Although the FEFF code allows the inclusion of

effects such as damping due to inelastic losses, self-energy corrections, and energy shifts at low energies based on systematic measurements, we employ default values provided by the code, which are based on prior calculations on similar systems. This code required that the atomic arrangement be thought of as a “cluster” with a central (excited) atom at the origin. The cluster is then “cut off” to include the desired number of atoms which must be compatible with the number of scattering paths specified in the input to the multiple scattering codes. With faster computers, we always choose more shells than we need to get the best results possible.

3.3.3 Results for Si-L23 edges in Silica and Silicon: The first study that will be discussed uses FEFF to do XANES calculations. In the near edge region, XANES features are very similar to ELNES. The first test compares the nearest neighbor effects in quartz and amorphous SiO_2 by varying the number of atoms in the calculation. Figure 20 shows representative clusters corresponding to amorphous SiO_2 taken from the central region of the “ SiO_2 ” passivating layer model. These models are used below to explore finite size effects associated with the inclusion of nearest neighbor shells. Our particular focus in the present study is the distinction between crystalline SiO_2 and amorphous silica, as described by differences in the near edge features. The large, oversized central atom represents in Figure 20 denotes the atom for which the near-edge is calculated. The extent of each cluster is characterized by a radius “R” and the number of atoms contained within the clusters is given by N. An identical procedure was used to generate quartz clusters.

The XANES results calculated using FEFF for the O-K edge of quartz are shown in Figure 21, which highlights the nearest neighbor effects. The result for the smallest ($3\text{\AA}$) model, plotted as the black curve in Figure 21, shares two common features with both the at $R=5\text{\AA}$ and $7\text{\AA}$ calculations. The first and most intense feature (below 540 eV) seen only in the $5\text{\AA}$ and $7\text{\AA}$ O-K near edge structure is therefore due to second and third nearest neighbor interactions whereas the shoulder corresponds to first nearest neighbor shell. The calculation is thus essentially converged for $R = 5\text{\AA}$.

We next examined the O-K edge in amorphous SiO_2 . It is slightly more complicated because it is not a periodic structure. Unlike quartz, the bonds around the central oxygen atom are not of equal length therefore every oxygen atom within the structure is different from the others. By examining the effects of the nearest neighbors around a single oxygen atom, we are only gaining insight into the environment of one oxygen atom. However, by comparing two different oxygen atoms we

Figure 21: Top panel: Quartz O-K edge calculated using a XANES setting in FEFF for three different sized models. Bottom panel: Amorphous SiO_2 XANES O-K edge for two different oxygen centers and three cluster radii, calculated using FEFF.

will gain further insight into how the amorphous nature of this structure affects the energy loss near-edge features. It would be better to do more, but the calculations are computationally intensive. Therefore, two central oxygen atoms were selected for three different radii; 3, 5 and 7 Å, as comparison. Figure 21 presents the results of these calculations. The calculation in this case is not converged until the sphere radii measures 7 Å. Although not shown, calculations of $R=12\text{Å}$ match the 7 Å calculations. The first nearest neighbor effects, or the effects of the silicon atoms around the central oxygen atom, can be seen in the black curve. Although there are some slight variations in the intensity, the general peak positions remain fixed. In the largest clusters, the change in the central oxygen atom is virtually undetectable. A similar study was described by Egerton [16] who compared the near edge fine structure of the O-K edge in MgO for different numbers of shells. The fine structure became more detailed as the number of shells was increased. In the case of SiO₂ and quartz, it is possible that these features cannot be seen in this type of calculation. If this procedure could be repeated using WIEN2K, further detail may emerge. At this point, simply understanding the limitations and convergence criteria for a FEFF calculation is an adequate result. In experimental results, studies of the passivating layer suggest that the structure is mainly composed of silicon and oxygen. The structural morphology is likely more complicated than the model proposed. HRTEM studies of the detailed structure of the

silica-rich layer are difficult since study since the sample is very susceptible to beam damage. It should be noted that beam damaged samples yield an SiO₂-glass-like EELS spectra.

In view of these sensitivities it is of significant interest to develop a corresponding understanding for crystalline systems containing more than one symmetrically unique oxygen atom per unit cell. In the case of forsterite, there are three symmetry unique oxygen in the periodic structure. A weighted average of the individual contributions is therefore proposed here in which the individual O-K edges for each type of oxygen atom are computed and the averaged based on their multiplicity in the structure. We designate the three forsterite oxygens as O1, O2 and O3, where O1 and O2 have multiplicity 1 and O3 has multiplicity 2. The oxygen K-edge for forsterite are shown in Figure 22 for each individual oxygen, as well as the final curve representing the average of the contributions from each type of oxygen.

Next we pursued a series of calculations aimed at comparing the performance of WIEN2K and FEFF in calculating Si L23 spectra in silicon bearing materials such as silica and silicon. We compare our calculations with experiment when the data is available.

Figure 22: Top panel: Forsterite oxygen K-edge calculated using three symmetry unique oxygen centers calculated using FEFF. Bottom panel: EELS ELNES Si-L23 edge for diamond cubic silicon calculated using WIEN2K using four different methods plotted against experimental data. The four methods are shown in the legend.

The first calculation is the well-known system of diamond cubic silicon. Four calculations were performed on this system: a regular eight atom silicon calculation, a Z+1 calculation, the unrelaxed-corehole calculation, and finally the relaxed corehole calculation. All four of these approximation can be applied using the WIEN2K as describe above. The main results are plotted with the experimental data in Figure 23. As described earlier, the Z+1 calculation and the corehole calculation are both used to model the presence of the corehole when the core electron is promoted to a higher energy state. The relaxed-corehole and the Z+1 curves both have similar fine structure, differing only slightly in intensity and in certain peak positions. All of the calculated EELS plots are horizontally aligned to match the experimental edge onset, as well as vertically scaled (using a global scale factor), to match the intensity. Although slight variations in the intensities of the spectra can be considered as contributing factors to the quality of the calculation [17], for the present purpose our empirical setting of the overall intensity and edge onset adequate.

Silicon is a useful example because of its distinctive L-edge structure (also seen in elemental K, Ca and Sc [16]). The threshold energy for silicon is at 100eV, but the maximum for this edge is not seen until about 25eV later. This edge effect is called “a delayed maximum due to centrifugal-barrier effects”. The sharp onset peak is due to the characteristic wavefunction of the d-states. Since the continuum 3d wavefunction is sufficiently compact to fit within the centrifugal barrier, the result is a strong overlap with the core-level 2p wavefunction and large oscillator strength at the threshold [16]. Figure 23 displays a summary of both the FEFF and WIEN2K results for the Si-L23 edge of diamond cubic silicon. The plot compares all of the approximation schemes for this system. The results indicate that in the FEFF calculation, the delayed maximum in the near edge structure is almost 10eV too low. The FEFF Z+1 calculation does not improve the results of calculation compared to the WIEN2K calculation (Figure 23), and has the effect of increasing the maximum peak height relative to the other two curves.

All of the WIEN2K LAPW calculations yielded good agreement for diamond cubic silicon. After a detailed examination of the relative peak heights within each calculation, there are points in each curve that are more consistent with experiment than the others. As described by Duscher et al [17], both the corehole and the Z+1 approximations are very reasonable estimates for the Si-L23 edges in diamond cubic silicon. Although it cannot be seen in this data, the overall intensity of the Z+1 calculation was actually significantly lower than that of the corehole approximation, therefore for this calculation, the corehole approximation may be most accurate. A summary of the best results is shown in Figure 24. One final calculation was

Figure 23: Top panel: A summary of both the ELNES (WIEN2K) and XANES (FEFF) calculations for the Si-L23 edge in diamond cubic silicon compared with experiment. Bottom panel: EELS EELS L23 edge for diamond cubic silicon calculated using the Z+1 approximation in both FEFF and WIEN2K compared with experiment.

performed to investigate the reliability of these calculations on α -quartz. The procedure here is similar to that of diamond cubic silicon above. Figure 24 illustrates the results from both FEFF and WIEN2K calculations. In WIEN2K, all three methods were tested including Z, Z+1, and relaxed corehole. Due to the results from silicon, the “unrelaxed-corehole” for WIEN2k and the “Z+1” calculation from FEFF were not included in this comparison. Once again, the corehole WIEN2k calculation gives excellent results.

4. CONCLUSIONS

We developed a novel method to analyze the chemical environment in heat-treated lizardite feestock (meta-lizardite). By studying the changes in the local silicon environment using stoichiometric analysis we developed a model which links the silica polymerization to the extent of dehydroxylation. All ^{29}Si NMR analysis was based exclusively on Q-species assignments. Corresponding X-ray spectra were collected and analyzed at the same compositions for consistency. Our analysis points to at least two mechanisms for dehydroxylation. The first mechanism involves a reaction between all available cage hydroxyls and the silica network below. The hydroxyls from the brucite layer take a proton from the cage layer to form water. Once all of the protons from the cage layer are removed, Mechanism II takes over. This mechanism is operative above 50% dehydroxylation and involves the conversion (and elimination) of the remaining brucite hydroxyls, and subsequent nucleation and growth of forsterite and enstatite.

The mechanisms described above suggest that silica sheets contained within the lizardite crystal “unzipper” as the material decomposes under heating. This produces several Q1, some Q2, and some new Q3’ species, while destroying the orderly Q3 rings. The low-angle X-ray feature near 6° is closely correlated to the meta-lizardite Q3’ feature. The NMR and model analysis also indicate that meta-lizardite maintains its rigidity while the structure and stoichiometry change rapidly. We have suggested that “Mechanism I” can be verified using FTIR analysis, by studying the order of disappearance of the “cage” and “brucite” hydroxyl bands. “Mechanism II” is completely consistent with simulated defective meta-lizardite structures obtained during YEAR 1 & 2, which predict that an oxygen (formerly a hydroxyl) moves towards the magnesium layer when its proton is removed.

Figure 24: Top panel: The best calculated results for the silicon L23 edge in diamond cubic silicon compared with experiment. The WIEN2K relaxed-corehole and Z+1 calculations are perhaps the most informative and accurate methods for this system. Bottom panel: ELNES Si L23 edge for α -Quartz calculated using FEFF and WIEN2K. The WIEN2K corehole calculation matches best with the curve shown the top panel.

Our studies suggest that future work should be devoted to a more detailed study of the crystallization process. This could easily be done by producing a series of meta-lizardite samples between the Liz-725 up to Liz-1300 (e.g., above 1100°C). The ASU team has also performed ^1H and ^{25}Mg NMR “TRAPDOR” experiments whose description is beyond the scope of this report. Ongoing work will give further insight into the highly disordered Liz-725 sample and may yield new details about nucleation and crystallization of the final products [18]. Although it cannot be confirmed that the material has completely recrystallized by 1100°C, it is evident that all of the hydroxyl has been removed, providing appropriate samples for mineral carbonation reactions.

We have also extended our preliminary YEAR 2 studies of the structure and composition of the silica-rich passivating layers that form on olivine feedstock grains during the mineral carbonation process. Dissolution mechanisms are discussed and several compatible atomic level processes are proposed to account for the observed formation of MgCO_3 nano-particles within the silica-rich passivating layer matrix. Atomic level simulations were used to elucidate the characteristics of the “glassy” matrix material. The simulations predict that a 50 Å thick passivation layer grown on a bulk Mg_2SiO_4 substrate experiences a tensile strain of 5%. The compression/tension state of the PL is a strong function of the volume of the magnesite that nucleates and grows in the layers, ranging from magnesite-free PLs that experience strong tension to magnesite-rich PLs that experience strong compression. The observed magnesite PL concentration is consistent with extensive tension cracking of the passivating layers, as observed experimentally. We also find that the internal structure and topology of the tetrahedral network in the passivation layer materials differs from that of dense thermal glass. Consequently, the density of the passivation layer material is reduced by 8-12% depending on its strain state. Detailed studies to further elucidate the thermoelastic, spectroscopic and diffusive properties of silica-rich passivating layers are currently underway to better understand the associated mechanisms and materials that can strongly impact olivine carbonation reactivity. The ability to control passivating layer formation/exfoliation may provide an intriguing low-cost path to enhance olivine carbonation reactivity, while avoiding the cost of pretreatment activation.

Finally, we expanded our spectroscopic EELS studies of disordered (amorphous) glassy silica materials to include multiple scattering XANES calculations using the FEFF code. The periodic all-electron FPLAPW WIEN2k code was then used to compute the Si-L23 EELS edges in α -quartz and silicon, using ground state, Z+1 and corehole approximations. We find that the corehole calculation is the most quantitative for both the Si-L23 edge in silicon and quartz.

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6. APPENDIX 1 : ARTICLES, PRESENTATIONS, AND STUDENT SUPPORT

Publications

“Exploration of the Role of Heat Activation in Enhancing Serpentine Carbon Sequestration Reactions”. McKelvy, M.J.; Chizmeshya, A.V.G.; Diefenbacher, J.; Bearat, H.; Wolf, G.H. *Environmental Science and Technology* , **38**(24), 6897-6903 (2004).

“In Situ Observation of CO₂ Sequestration Reactions Using a Novel Microreaction System”. Wolf, George H.; Chizmeshya, Andrew V. G.; Diefenbacher, Jason; McKelvy, Michael J. *Environmental Science and Technology*, **38**(3), 932-936 (2004).

“CO₂ Mineral Carbonation Processes in Olivine Feedstock: Insights from the Atomic Scale simulation”. Chizmeshya, A.V. G.; McKelvy, M.J.; Gormley, D.; Nunez, R.; Kim, Y.; Carpenter, R. *Proc. Int. Tech. Conf. Coal Utilization & Fuel Systems*, 29th(Vol. 1), 59-70 (2004).

Conference and Professional Presentations

“Enhancing the Atomic-Level Understanding of CO₂ Mineral Sequestration Mechanisms via Advanced Computational Modeling”, A.V.G. Chizmeshya , University Coal Research/ Historically Black Colleges and Universities Meeting, Pittsburgh, PA. Host: Dr. John Litinsky, July 17 (2004).

“Recent Advanced in CO₂ Sequestration by Mineral Carbonation: Experiments and Theory” A.V.G. Chizmeshya , Departmental Colloquium (Chemistry), Lehigh University, Bethlehem, PA. Host: Prof. K. Klier, November 10 (2004).

“CO₂ mineral carbonation processes in olivine feedstock: insights from the atomic scale simulation” Chizmeshya, Andrew V. G.; McKelvy, Michael J.; Gormley, Deirdre; Nunez, Ryan; Kim, Youngchul; Carpenter, Ray. 29th Coal Utilization and Fuel Systems Conference, Host: B. Sakkestad, Clearwater Florida, April 22 (2004).

Students Supported under this Grant

Deirdre Gormley: Doctoral candidate in the Science and Engineering Materials Ph.D. Program at Arizona State University.

Michael Kocher: Undergraduate research assistant jointly enrolled in the Physics and Chemistry programs at Arizona State University.