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

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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

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

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).

and refined by Klamt [15] to include a self-consistent treatment of the screening charge interactions between solvents and solutes, thereby putting them on the same footing. The method is commonly referred to as the conductor-like screening model for real systems (COSMO-RS). Accurate density functional theory methods are used to obtain the self-consistent charge densities and electrostatic and exchange-correlation potentials for any molecule

(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)			sym str asym str.
		freq (cm ⁻¹)		
	617.4	-8.8	626.2	
	618.3	-7.9	626.2	
	1335.5	-14.4	1321.1	
bond l.			1.172	1.175
angle			180	180
H ₂ O(aq)			bend sym str. asym str
		freq (cm ⁻¹)		
	1593.3	-5.9	1599.2	
	3698.6	-14.1	3712.7	
	3802.8	-27.1	3829.9	
bond l.			0.972	0.97
angle			104	104
OH ⁻ (aq)			
		freq (cm ⁻¹)		
	3720.9	120.5	3600.4	
bond l.			0.973	0.978
CO ₃ ²⁻ (aq)			sym stretch stretches along bond direction
		freq (cm ⁻¹)		
	661.9	11.1	650.8	
	666.6	14.9	651.7	
	866.4	8.6	857.8	
bond l.			1.297	1.308
angle			120	120
HCO ₃ ⁻ (aq)			OH wag CO stretch (CO(H) bond) COH bend CO stretch (CO(H) bond) sym CO stretch
		freq (cm ⁻¹)		
	533.6	9.7	523.9	
	541.8	-40.8	582.6	
	629.3	38.6	590.7	
bond l.			1.171	1.167
angle			115.8	113
H ₂ CO ₃ (aq)			HO-C-OH bend asym. OH wag asym. CO stretch OH wag
		freq (cm ⁻¹)		
	507.6	-6.3	513.9	
	548.4	12.5	535.9	
	574	-3.1	577.1	
bond l.			1.22	1.215
angle			107.8	105.5

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 ($1 \text{ \AA} = 10^{-10} \text{ m}$), picoseconds ($1 \text{ ps} = 10^{-12} \text{ s}$) and molecules ($1 \text{ molecule} \sim 10^{-24} \text{ mol}$) so that $1 \text{ mol/cm}^2/\text{s}$ corresponds to $\sim 10^{-4}$ molecules/ $\text{\AA}^2/\text{ps}$. The present example (Mg dissolution at $R \sim 10^{-11} \text{ mol/cm}^2/\text{s}$) then implies one Mg ion leaving a $100\text{\AA} \times 100\text{\AA}$ 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 carbonatious 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.

5. REFERENCES

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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.”