TITLE: ENHANCING THE ATOMIC-LEVEL UNDERSTANDING OF CO_2 MINERAL SEQUESTRATION MECHANISMS VIA ADVANCED COMPUTATIONAL MODELING

PIs: Andrew V.G. Chizmeshya*, Michael J. McKelvy and Otto F. Sankey.

STUDENTS: Deirdre Gormley, Michael Kocher

INSTITUTION: Arizona State University
Center for Solid State Science
Tempe, AZ 85287-1704
* Phone: (480) 965-6072; FAX: (480) 965-9004; E-mail: chizmesh@asu.edu

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ABSTRACT

INTRODUCTION

CO_2 mineral sequestration – the conversion of stationary-source CO_2 emissions into mineral carbonates (e.g., magnesium carbonate, $MgCO_3$) – has recently emerged as one of the most promising sequestration options, providing *permanent* CO_2 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 CO_2 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. 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 less than an hour. 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.

The objective of this project is to combine advanced first-principles simulation techniques with experimental observations in order to develop new, 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 CO_2 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 CO_2 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).

ACCOMPLISHMENTS TO DATE

Our initial studies have focused on the integration of advanced modeling with the ongoing experimental research being undertaken as part of an ANL-ASU field-work project on serpentine-CO_2 reactivity. Infrared and XPD data for heat-activated Globe A lizardite, collected (at ASU) 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 first modeled the vibrational spectrum of the reference lizardite material using first principles density functional theory simulations. Our preliminary results indicate that the hydroxyl band features can be readily assigned to the motion of so-called "inner" and "outer" hydroxyls. Experiments have shown that a distinct shift in the hydroxyl band frequencies accompany the formation of meta-serpentine. The corresponding XPD spectra evolve from that of the baseline lizardite (crystalline) to an intermediate meta-serpentine material, 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 seen in Figure 1. This is followed by amorphization and upon complete dehydroxylation, by the condensation into an assemblage of $MgSiO_3$ (enstatite) and Mg_2SiO_4 (forsterite). 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.

Our basic approach has been to generate nominal initial structures for meta-serpentine corresponding to the desired stoichiometry (% hydroxyl content), and then to systematically relax the ionic and cell parameters using accurate quantum mechanical forces and total energy methods. We used two schemes to generate hypothetical structures: (i) beginning with an appropriate supercell of lizardite we removed a stoichiometric amount of water to produce meta-serpentine, and (ii) we started with an assemblage of $MgSiO_3$ and Mg_2SiO_4 and added H_2O to achieve the target stoichiometry. In both cases the volume, cell-shape and ionic configurations were optimized to produce candidate structures for a range of meta-serpentine materials. These initial structures were then used in turn to generate synthetic XPD and IR spectra for comparison with, and interpretation of, experimental spectra.

Since the initial and strongest appearance of the low-angle meta-serpentine intermediate occurs at 50% dehydroxylation, our initial studies are based on this as a target composition, using scheme (i) above. 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 deintercalation reaction mechanisms. Our simulations indicate that the low angle feature near $2\theta \sim 6^o$ (observed in experiment) only occurs for dehydroxylation ratios of 4:1 or greater, between adjacent layers. The model is based on Z=8 supercell with $8 \cdot Mg_3Si_2O_5(OH)_4$ - $8 \cdot H_2O$. The effect of structural relaxation (calculated using the VASP *ab initio* package) is significant. We find that dehydroxylation in the bottom layer leads to a structural decohesion of the Mg and O sublattice, but very little distortion of the tetrahedral silica layer. XPD simulations further show that the new low angle feature is preserved, and that the primary reflection associated with fully hydroxylated parent phase near $2\theta \sim 12^o$ (now indexed as 002) is slightly shifted and attenuated. The blunting of the basal plane reflections in the range $2\theta \sim 40\text{-}80^o$ is also more consistent with the observed XPD. This suggests a stage-2 behavior, which is very common during graphite and transition-metal dichalcogenide deintercalation processes, and that a similar mechanism may be involved in the early stages of meta-serpentine formation. The decohesion of the Mg and O sublattice that accompanies stage-2 compound formation is also relevant to the enhanced Mg solubility and carbonation reactivity observed for meta serpentine.

To explore this latter concept we carried out a preliminary series of carbonation reaction simulations based on the lowest energy structures deduced from the simulation of bulk-phase meta-serpentine (50% dehydroxylated lizardite). The latter have a morphology containing voids which may be accessible during the early stages of carbonation from the fluid phase. While carbonation is most likely to occur in the fluid phase *via* attack of dissolved Mg^{2+}, our simulations indicate that low coordination oxygen sites within the meta-serpentine also represent very favorable carbonation sites leading to the formation of "CO_3 propellers" structures bound to the disordered magnesium layers. Dissolution of such prototypical carbonate structures formed within the surface layers of the heat-activated lizardite, may provide a low-energy supply of carbonate precursors for the subsequent fluid phase nucleation and growth of carbonate crystallites. These concepts will be further explored and validated using advanced simulation techniques.

ARTICLES, ABSTRACTS, PRESENTATIONS, AND STUDENT SUPPORT

Conference Presentations

- "Atomic-level Understanding of CO_2 Mineral Carbonation Mechanisms from Advanced Computational Modeling", Andrew V.G. Chizmeshya, Michael J. McKelvy, Otto F. Sankey, George H. Wolf, Renu Sharma, Hamdallah Bearat, Jason Diefenbacher, and R.W. Carpenter, *Proceedings of the 27th International Technical Conference on Coal Utilization & Fuel Systems*, p.803-814, Clearwater, Florida, March 4-7, 2002.
- "Mineral Sequestration: Atomic Level Mechanistic Insight from Advanced First Principles Computer Simulation ", Andrew V.G. Chizmeshya, Michael J. McKelvy, Otto F. Sankey. Abstract: *University Coal Research Contractors Review Conference*, Pittsburgh, Pennsylvania, June 4-5, 2002.

Students Supported under this Grant

- Deirdre Gormley, graduate student in the Science and Engineering of Materials Graduate Program, Arizona State University.