

**ASSESSMENT OF SEPIOLITE AS A CARBON DIOXIDE STORAGE
MATERIAL**

by

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fulfillment of the requirements for the degree of Master of Science in Geology

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Today's dreams are tomorrow's reality.

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ABSTRACT

Due to the dynamics of Earth's natural carbon cycle, levels of carbon dioxide in the atmosphere have varied over geologic time. An analysis of the geologic record indicates that warm periods in Earth's history are correlated with relatively high levels carbon dioxide in the atmosphere. Since the onset of the industrial revolution the natural rate of carbon dioxide accumulation in the atmosphere has been augmented by human activity. Several approaches have been proposed to offset the anthropogenic contribution to the rise in atmospheric carbon dioxide, including underground and ocean sequestration, and storage in synthetic porous materials such as zeolites and metal-organic-frameworks (MOFs). In this work we assess the possibility of utilizing natural porous materials for the storage of carbon dioxide; namely, the clay mineral sepiolite whose structure prominently features water filled pores. Molecular dynamics simulations are used to determine whether a thermodynamic driving force exists for replacing the water in these channels with carbon dioxide. Our results indicate that along the carbon dioxide liquid-vapor curve as much as 10% of the water in sepiolite may be replaced by carbon dioxide. We show that the incorporation of carbon dioxide into the mineral structure is primarily driven by favorable entropic terms at these concentrations. Based on this result we estimate that it may be possible to sequester up to 0.986 mmol of carbon dioxide per gram of sepiolite, which is approximately twice the experimental value reported for montmorillonite clay under similar conditions.

Chapter 1

CONTEMPORARY APPROACHES TO CARBON CAPTURE AND STORAGE

1.1 Relationship Between Atmospheric Carbon Dioxide and Mean Surface Temperature

The concentration of carbon dioxide in Earth's atmosphere has risen steadily since the onset of the industrial revolution (IPCC 2014) (Figure 1.1). During this period, the rate of CO₂ production has been correlated strongly with observed increases in the global mean surface temperature (Hansen et al, 2010). This dynamic correlation is anticipated to continue well into the foreseeable future and to result in sea level rise, severe shifts in weather, and additional ecological pressures for a variety of flora and fauna. Therefore, elevated surface temperatures are likely to have a drastic and lasting influence on human and animal life worldwide (IPCC 2014).

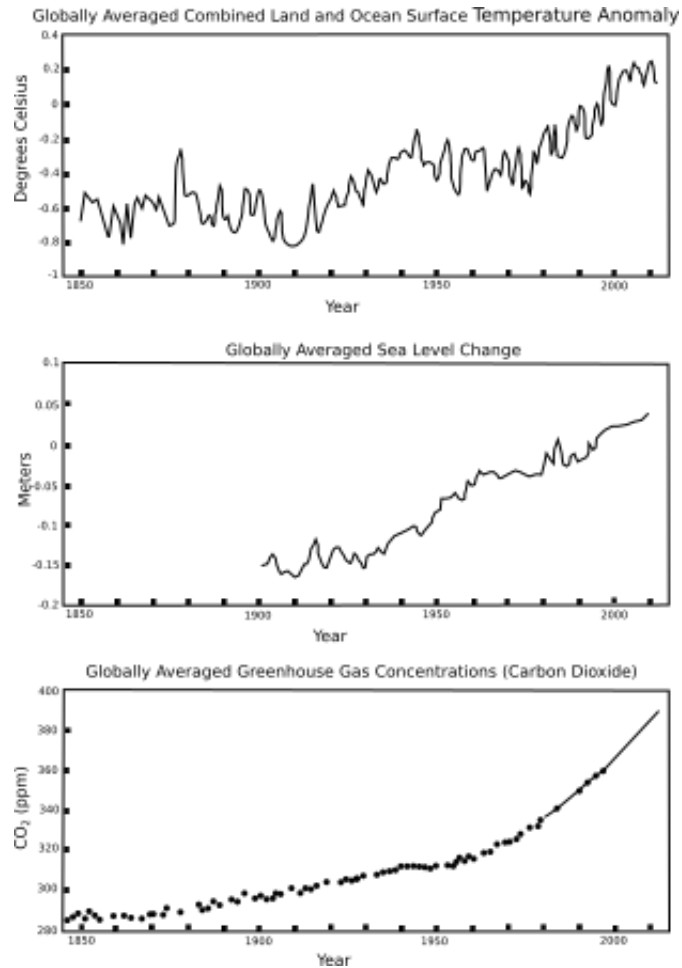


Figure 1.1 From top to bottom: (a) Land and ocean temperature anomalies from 1850 to 2010 (b) Sea level change from 1900 to 2010, and (c) Greenhouse gas concentrations from 1850 to 2010. All three display a high correlation to each other. After IPCC, 2014.

1.2 Methods of Carbon Capture and Storage (CCS)

As levels of atmospheric carbon dioxide continue to rise, numerous strategies have been proposed to remove atmospheric CO₂ via various sequestration methods, thereby mitigating, or possibly even reversing, the current trajectory of climate change (Lal, 2008). On the large-scale, industrially produced CO₂ could be stored within geological reservoirs. Korbøl and Kaddour as well as Marchetti have suggested a mechanism/method for pumping high concentrations of gaseous CO₂ into deep

sedimentary formations or seafloor environments via wells and injection into thermohaline currents respectively (Korbøl & Kaddour, 1995; Marchetti, 1977). The storage capacity of the ocean is at minimum 1000 Gt but may go as high as 5600 Gt, whereas deep sedimentary formations should be able to hold between 1000 and 10000 Gt (Adams & Caldeira, 2008; Benson & Cole, 2008). Seifritz (1990) and Lackner et al. (1995) have suggested chemical incorporation of carbon into insoluble geologic minerals. This is a process that happens naturally and results in sequestration of 0.1 Gt of CO₂/year, but the reaction rates are slow. This is due in part to the requirement that the metal-silicate mineral involved dissolves first so that the CO₂ can react with the metal ions released (Oelkers, Gislason, & Matter, 2008). On a smaller but more immediate scale, other approaches have focused on improving the efficiency of the initial capture of CO₂ from industrial sources. In this manner, one method pioneered by Eddaoudi and others uses engineered mesoporous materials (e.g. zeolitic materials and metal organic frameworks (MOFs)) to absorb and hold carbon dioxide within their pores (Eddaoudi et al., 2002; Li et al., 1998; Yaghi et al., 1999).

1.2.1 Deep Ocean Storage

The ocean, whose total volume is estimated to be on the order of 1.3 billion km³, is capable of absorbing tremendous amounts of carbon dioxide, and is currently doing so in response to elevated concentrations of atmospheric CO₂ (Adams & Caldeira, 2008). This is because carbon dioxide is soluble to some extent and the ocean is very, very large. At standard temperature and pressure conditions (25°C, 0.1 MPa) the solubility of CO₂ in water is quite modest (~0.1 mol %). However, at the pressures and temperatures characteristic of deep ocean environments (~4-10°C, > 10MPa) water is capable of

holding ~ 2.0 mol % CO_2 or more. Conditions in the deep ocean are also potentially favorable for the formation of liquid CO_2 and CO_2 -clathrates. If the conditions are favorable enough to form liquid CO_2 and CO_2 -clathrates, the density of the two are great enough to be more than that of the surrounding ocean water, which will limit the mobilization of the sequestered carbon dioxide.

While promising, long-term storage of CO_2 in the ocean itself poses several potential drawbacks. Currently the surface ocean is experiencing a pH drop due to increased carbon dioxide concentrations (IPCC 2015), resulting in major stress for surface ocean ecosystems. Though injecting carbon dioxide in liquid plumes or even as a lake would slow its rate of dispersal, this downward pH shift would be ultimately continued, and even accelerated, by eventual diffusion of CO_2 throughout the global ocean body (Oelkers & Cole, 2008). Impacts of acidification to biological, hydrological, and geological systems would thus eventually be exacerbated, but to an unknown extent, with no currently understood mechanism to test ecosystem impacts on a large experimental scale. Additionally, such injection does not represent a permanent sequestration method, as some of the injected CO_2 will eventually outgas to the atmosphere (Adams & Caldeira, 2008).

1.2.2 Entrapment in Deep Saline Aquifers

Carbon dioxide sequestration has been done in deep (≥ 800 m) sedimentary rock formations by well injection (DePaolo & Cole, 2013). At this depth, it is hypothesized that the supercritical carbon dioxide will be forced into pores in the sedimentary rock that were initially occupied by brine (DePaolo & Cole, 2013). Supercritical carbon dioxide is less dense than the pore fluids at this depth and is relatively insoluble within them. As a

result it is necessary to deposit it at depths greater than or equal to 800 m to retain some solubility within the pore liquids and stay in the supercritical state. Even so, this density difference necessitates that a candidate formation have an impermeable cap rock to keep the CO₂ from outgassing (e.g., depleted oil and gas reservoirs). Benson and Orr (2008) suggest that the ideal stratigraphic sequence for geological carbon sequestration is a deep layer of sandstone underneath a layer of mudstone, siltstone, or evaporite rock. Sandstone is porous and permeable enough for the carbon dioxide to move through, whereas the impermeable rock layer above it acts as the caprock and prevents the carbon dioxide from moving upward once injected (Benson & Orr, 2008).

As the CO₂ disperses through the system, it initiates new chemical conditions and induces fluid-rock reactions to move towards a new equilibrium (Benson & Cole, 2008; DePaolo & Cole, 2013). This becomes a concern with regards to certain rock types. For example, carbonate cements will dissolve with the addition of CO₂ to the system, and the release of metal ions from silicate mineral dissolution may result in the precipitation of carbonate minerals which decrease porosity and permeability (Benson & Cole, 2008). Thus, geological carbon sequestration sites require constant monitoring, both geophysical and geochemical, to ensure that there are no leaks into the surrounding environment, either of CO₂ itself or of mineralization byproducts. Leaks can have lasting impacts on the groundwater and ecosystems and can be costly to remediate. Furthermore, there are not yet any contingency plans for leak control, a critical component for the future viability of this technology (Benson & Cole, 2008).

Naturally, modeling the effects of geological carbon sequestration on the sequestration materials has become a topic of active research. For example, two-dimensional computer modeling of an idealized CO₂ sequestration formation consisting of a sandstone reservoir with an intact mudstone caprock and an injection well at the base of the sandstone was created to study these effects (Shukla et al., 2011). It was found that

the geologic capture system remained intact over a 30-year injection and 70-year monitoring period (Shukla et al., 2011). Shukla et al. (2011) observed that the injection pressure of the CO₂ had a negligible effect on the cap rock in the system, while surrounding rock was not stressed sufficiently to become fractured. (Shukla et al., 2011). Following this, Ranjith and Perera (2011) built an apparatus to mimic in situ conditions for deep formation sequestration at appropriate temperatures and pressures. The apparatus was ultimately a success at measuring strength and deformation properties under deep ground conditions, opening the door for more effective characterization of formations as well as better predictions of behavior in these areas (Ranjith & Perera, 2011).

1.3 Mineral Carbonation

Mineral carbonation is the most stable solution for long-term carbon dioxide sequestration. It occurs naturally as a consequence of rock weathering, with up to three hundred million tonnes of CO₂ sequestered every year (Power et al., 2013). It is a thermodynamically favored process, but a slow one. Mafic and ultramafic rock, such as peridotite, are favored to react with water and carbon dioxide to form serpentines and carbonates (Figure 1.2).

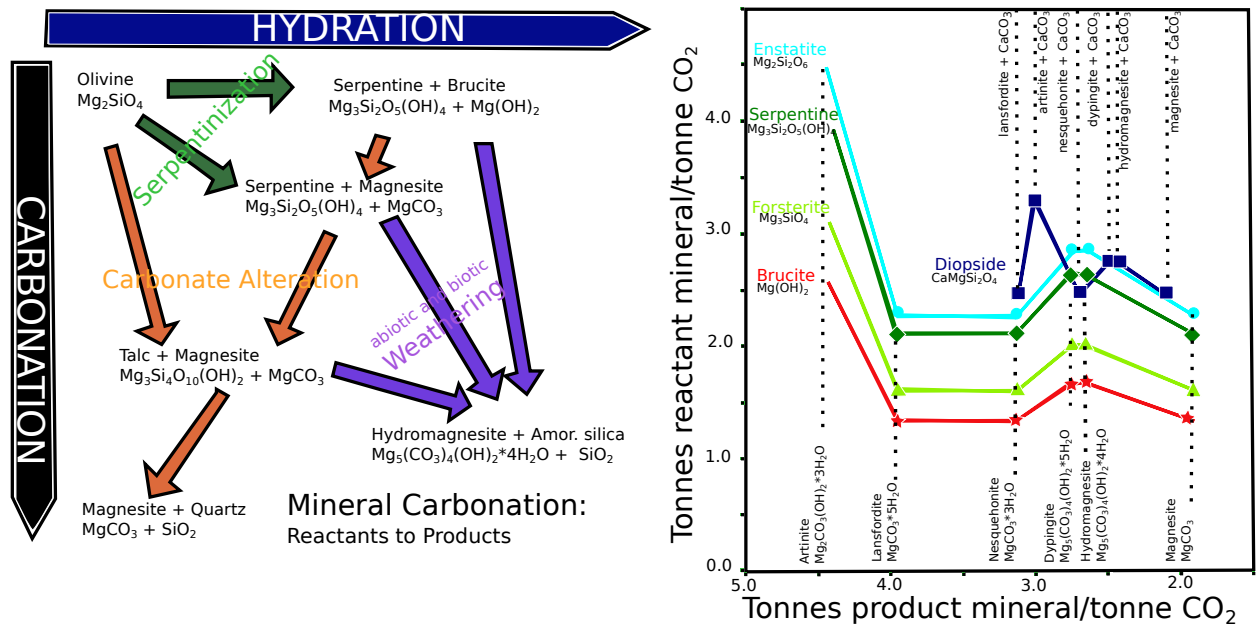


Figure 1.2. Mineral carbonation reactants and products of ultramafic rock. After Power et. al, 2013.

These materials have been used widely for CCS research but are difficult to work with because of slow reaction kinetics. To increase the rate of the carbonation reaction, they must be mechanically altered to increase surface area. Serpentine, a mineral that is a product of mafic rock weathering, should also be heat treated to remove chemically bound water (Gerdemann et al, 2007). Both of these processes are high energy and contribute to the financial cost of carbon dioxide sequestration (Krevor & Lackner, 2011) (Eikeland et al., 2015).

More efficient ways of dissolving and carbonating ultramafic rocks involve the addition of salts to the reaction. One experiment showed that addition of citrate and EDTA increased the serpentine dissolution rate and kept the pH threshold low enough that carbonate ions could remain in solution (though carbonation itself was not in the scope of this experiment) (Krevor & Lackner, 2011). Jia et al (2004) discovered that the addition of NaHCO_3 and NaCl to peridotite or serpentine facilitated the carbonation reaction more efficiently than if the materials were treated with carbonic acid alone,

though the extent of the carbonation was difficult to quantify due to the differences in the mineralogic composition of samples (Jia et al., 2004). Later, in 2015, Eikeland and others found that, at supercritical conditions of 190° C and 100 bar, olivine particles ground to <10µm were fully carbonated in under 4 h, with the addition of NaHCO₃ to provide more carbonate ions. Furthermore, due to the conditions, carbonic acid was perpetually generated in the system and thus eliminated the need to add more reactants (Eikeland et al., 2015). Carbonation of ultramafic and mafic rocks presents a promising solution to the sequestration issue, but one that is ultimately hindered by slow reaction rates.

Another option for producing mineral carbonates involves injecting carbon dioxide into a porous, permeable host rock that contains easily dissolved metal cations for the carbon dioxide to react with. In this vein, basalts and ultramafic rocks show a significant amount of promise. As with deep formation sequestration, this process requires the presence of an impermeable cap rock to limit the mobilization of toxic metals into the surrounding environment (Benson & Cole, 2008).

1.4 Mesoporous Materials in Gas Storage Applications

A significant amount of research has gone into evaluating mesoporous materials, that is, materials with existing pores or channels in which to store carbon dioxide. Those that have undergone the most research in this regard consist of metal-organic frameworks and clay minerals.

1.4.1 Metal-Organic Frameworks in CCS

Metal-organic frameworks (MOFs) are customizable, manufactured substances, engineered to be crystalline, porous materials with high surface area, relatively high thermal and chemical stability, high void volume (or pore space), and low density. Structurally, they consist of metal ion nodes connected by organic molecules. There are four major types of MOFs: rigid, flexible, surface functionalized, and open metal. Rigid MOFs have a stable structure with a permanent porosity, making them the best choice for molecular sieving of CO₂. On the other hand, flexible MOFs “breathe” or change shape contingent on gas adsorption, which restores their porosity when gas is adsorbed. Surface-functionalized MOFs have a functional group specifically grafted onto the surface with a high affinity for CO₂ to enhance capture rates, whereas open-metal MOFs separate polar and nonpolar gases such as a mixture of carbon dioxide and methane, which can be generated concurrently from waste streams. The addition of water to the structure of flexible MOFs enhances CO₂ capture at open metal sites, where the quadrupole moment of CO₂ interacts with the electric field created by the water molecules, which themselves coordinate the open metal site. MOFs can also be engineered to possess inherent carbon dioxide selectivity, either by kinetic separation, utilizing size exclusion principles such that only molecules of a certain size can pass through the framework, or by thermodynamic separation, which utilizes favorable gas-pore surface interactions via quadrupole moments. Another advantage of MOFs is that they allow a high selectivity for carbon dioxide sequestration with minimal experimentation (Sabouni, Kazemian, & Rohani, 2014). However, MOFs, while targeted and efficient in potential for their CO₂ sequestration are not thermally, chemically, or mechanically stable enough for long-term carbon dioxide storage using current techniques and technologies. In comparison, though inefficient and less energetically favorable, mineral carbonation by natural materials provides an extremely long term if

not permanent solution to CO₂ storage (Eddaoudi et al., 2002; Eikeland et al., 2015). Natural materials are also much more abundant than MOFs, which need to be made for each use.

1.4.2 Use of Naturally Occurring Mesoporous Materials

Naturally occurring mesoporous materials such as clays have enormous CCS potential. Though inefficient and less energetically favorable in comparison to MOFs, mineral carbonation by natural materials provides a long-term, possibly permanent solution to CO₂ storage (Eddaoudi et al., 2002; Eikeland et al., 2015). Sequestration using clays may also prove to be the most cost-effective approach, given their natural abundance. Most current CCS research has focused on the use of clay minerals with interlayers that allow swelling, such as montmorillonite. Montmorillonite has been heavily researched as a CCS medium both with physical experiments and theoretical simulations. Physical experiments have yielded promising results. In one study, up to 0.45 mmol CO₂/g of clay could be sequestered by Ca-montmorillonite at 50° C and between 5 and 8 bar, subcritical conditions for CO₂ (Schaef et al., 2015). Similar results could be achieved for Na-montmorillonite, but only at higher, supercritical pressures (90 bar). Molecular dynamics simulations have also examined the CCS potential of montmorillonite under a wide variety of conditions. Schaef et al. (2015) found that, in MD simulations using similar conditions as their experimental parameters, water displaces CO₂ from cation saturation shells as hydration increases, and that increasing concentrations of CO₂ in the interlayer lead to a lack of mixing between water and CO₂, likely due to CO₂'s low solubility. Kadoura et al. (2016) found that montmorillonite absorbed CO₂ in preference to CH₄ after the clay had absorbed water, in both singular

pure component simulations as well as CO₂/CH₄ mixtures (Kadoura, Nair, & Sun, 2016). However, they also suggest that sorption sites and/or available interlayer space may be filled preferentially by water molecules when present.

Though clay minerals with structures of interlayers have been heavily studied, little research exists to investigate the CCS potential of mesoporous materials that do not have interlayers. One such mineral, sepiolite, (structure Mg₄Si₆O₁₅(OH)₂*nH₂O) is the focus of this research.

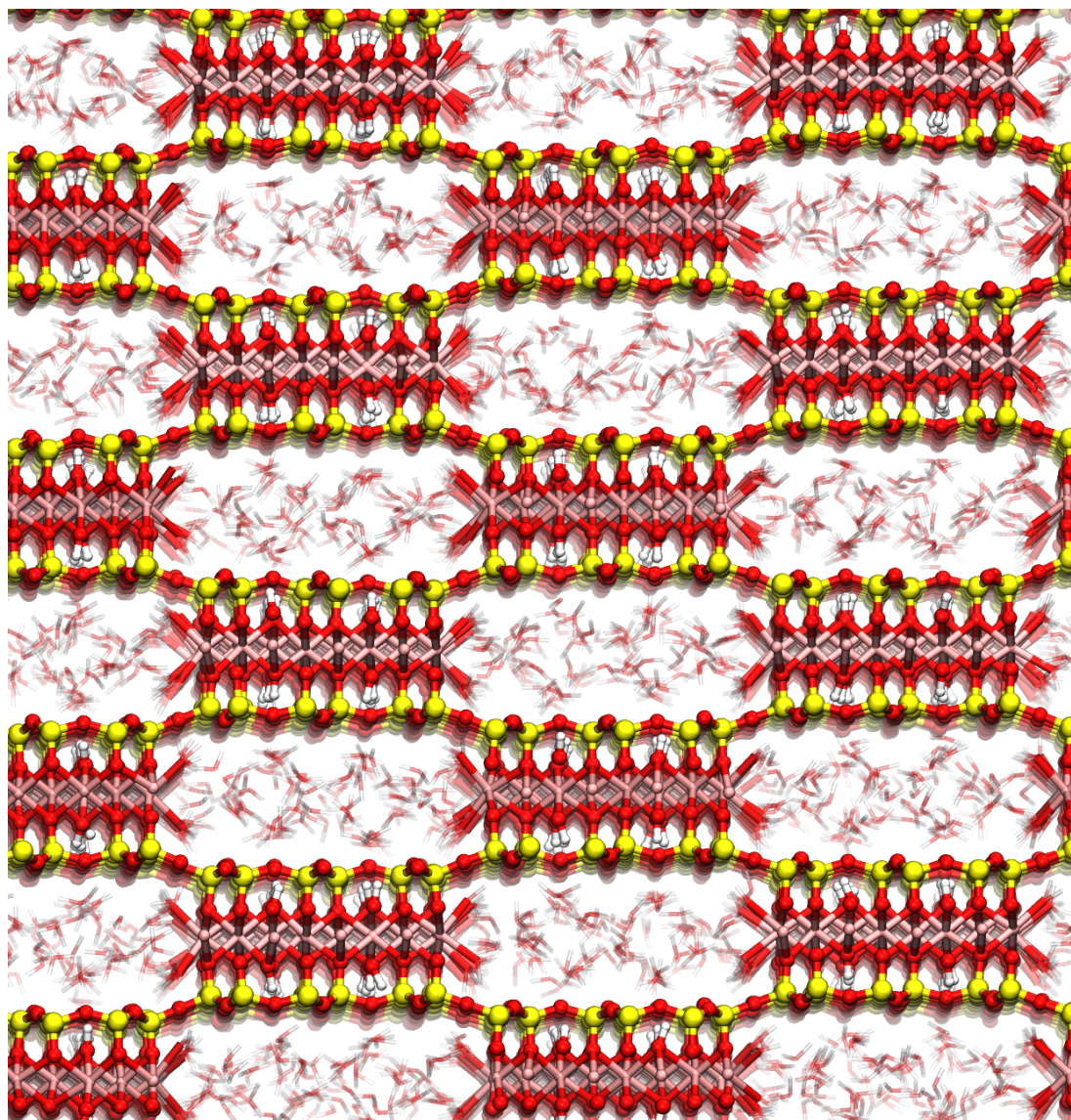


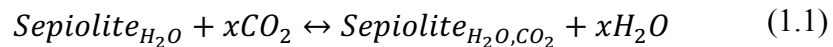
Figure 1.3. A cross section of the sepiolite mineral structure. Water is contained inside the nanopores formed by magnesium-silicate framework.

Unlike most sheet silicates, whose structures exhibit continuous planar layers, the silicate framework within the sepiolite-palygorskite group is corrugated, seen in Figure 1.3 (Post et al., 2007; Post & Heaney, 2008). This condition results in the presence of nanoscopic channels within the structure that are filled with molecular water. It is here in these water-filled channels that the CO_2 would have room to be sequestered before

possibly reacting with the surrounding magnesium-silicon matrix. Sepiolite is a fairly common mineral, found in numerous deposits worldwide, especially in Spain, Turkey, and Greenland, though it is not particularly abundant (Murray et al., 2011). Sepiolite can also be found in certain soils, continental lakes, shallow seas, and continental slope and deep sea sediments (Velde, 1977). Sepiolite may form stable associations with montmorillonite and serpentine, and is also frequently associated with evaporites and carbonate formations as it is the first silicate to precipitate out of silicate-rich seawater. It forms in systems dominated by inert components in a continuous compositional series with palygorskite, another clay mineral. Sepiolite has many industrial uses, ranging from chemical fertilizers, catalyst support, adsorbents for liquid spills, and in household uses that exploit its absorbent nature (pet litter and floor absorbents) (Alvarez et al., 2011).

Existing studies on sepiolite seek to elucidate the locations of the water contained in the channels (Zhou, Lu, & Boek, 2016) as well as the nature of the interaction between water and the mineral lattice (Ockwig et al., 2009). An initial investigation on the potential of sepiolite as a CO₂ sequestration medium found that, when the mineral lattice is exposed to a CO₂/CH₄ mix using a pressure swing apparatus, CO₂ is preferentially sequestered, leaving a very high purity CH₄ gas behind (Delgado, Uguina, Sotelo, Ruíz, & Rosário, 2007). Despite this promising result, the CCS capacity of sepiolite has not, to our knowledge, been investigated further and thus remains unknown.

Our study seeks to determine the viability of sepiolite as a sequestration material by investigating the magnitude of the thermodynamic driving force for replacing water in sepiolite channels with carbon dioxide. This is described by the following reaction:



To achieve this aim we use atomistic simulations methods to compute the free energy change for this reaction under conditions relevant to CCS. At present, high-level treatments of interatomic interactions by quantum mechanical methods are too impractical to be applied to the large scale systems required for this work. Therefore, this research utilizes classical molecular dynamics simulations in conjunction with empirically derived interatomic potentials.

Chapter 2

THEORETICAL BACKGROUND

2.1 Molecular Dynamics Simulations

In the molecular dynamics simulations described herein, atomic positions were updated in time by integrating Newton's equations of motion using the Large-scale Molecular Massively Parallel Simulator (LAMMPS) code developed at Sandia National Laboratory in New Mexico (Plimpton, 1995). Unless stated otherwise, a time step of 1.0 femtosecond was used. Simulations were performed in both the isothermal and isothermal-isobaric ensembles with the temperature and pressure maintained by application of a CSVR thermostat (Bussi, Donadio, & Parrinello, 2007) and Berendsen barostat (Berendsen, Postma, van Gunsteren, DiNola, & Haak, 1984) using relaxation constants of 0.1 and 1000 picoseconds respectively.

2.1.1 Interatomic Potentials

The energy of the mineral-CO₂-H₂O system was described through the application of several established empirical force fields. The sepiolite clay was described with the CLAYFF forcefield (Cygan, Liang, & Kalinichev, 2004) which was originally designed for use with a flexible version of the rigid simple point charge (SPC) model for liquid water (Berendsen et al., 1987). Therefore we also elected to use a flexible version of SPC water; however we chose to replace the native water model in CLAYFF with SPC/Fw, which has been shown to provide a superior description of liquid water properties near

standard conditions (298K and 1 bar) than other simple models (Wu et al., 2006). Carbon dioxide was described with a fully flexible version of the EPM2 model (Huang et al., 2011) originally developed to reproduce the properties of CO₂ along the liquid-vapor coexistence curve (Harris & Yung, 1995). The interactions between SPC water and EPM2 carbon dioxide were previously optimized by Lucas Vlcek (Vlcek et al., 2011) and were used here without modification. However, the interactions between carbon dioxide and sepiolite molecules have not been explicitly optimized previously. We therefore followed the approach taken by previous studies of CO₂-mineral systems and obtained these interactions through application of the standard Lorentz-Berthelot combining rules (Cygan et al., 2012; Makaremi et al., 2015; Myshakin et al., 2013; Rao & Leng, 2016; Sena et al., 2015; Yang et al., 2015). The complete set of force field parameters utilized in this study are shown in Table 2.1.

The total energy of the system can be defined as the sum of the following components:

$$E_{total} = E_{bond} + E_{angle} + E_{vdW} + E_{coulomb} \quad (2.2)$$

where the subscripts *bond* and *angle* refer to the energy associated with two- and three-body motions within water and carbon dioxide molecules in addition to O-H bonds and Mg-O-H angles in the mineral structure. In all cases the energy was described by a harmonic function:

$$E_{ij(k)} = \sum K(x - x_{eq})^2 \quad (2.3)$$

where x refers to the value of the bond distance between atoms i and j or the angle between atoms i , j , and k , and the subscript eq denotes the equilibrium value of the bond

distance or angle. K is a force constant that determines the frequency of vibration for a given bond stretching or angle bending motion. The total bond and angle energies are obtained by summing over all bonds and angles in the simulation.

The vdW subscript in equation 2.1 denotes the contribution to the total energy from van der Waals interactions, which were described by the Lennard-Jones 12-6 pair potential.

$$E_{ij} = \sum_{i \neq j} 4\epsilon \left[\left(\frac{\sigma}{r_{ij}} \right)^{12} - \left(\frac{\sigma}{r_{ij}} \right)^6 \right] \quad r < r_{cut} \quad (2.4)$$

In the above expression the interaction energy of atoms i and j (which are not members of the same molecule) is described as a function of the separation distance, r_{ij} , up until a threshold value, r_{cut} , beyond which the interaction does not contribute to the total energy. The epsilon and sigma are parameters which determine the depth of the potential energy well (ϵ) and the distance at which the repulsive portion of the potential returns a value of zero (σ).

Electrostatic interactions between non-bonded pairs of atoms were computed using Coulomb's Law (equation 2.5) up until the cutoff distance, beyond which the long-range contribution to the electrostatic energy was computed with the PPPM Ewald summation method (Hockney & Eastwood, 1988) with a precision of 10^{-5} .

$$E_{ij} = \frac{e^2}{4\pi\epsilon_0} \sum_{i \neq j} \frac{q_i q_j}{r_{ij}} \quad r < r_{cut} \quad (2.5)$$

In the above representation of the short-range coulomb energy, e is the charge of the electron, q_i and q_j are the partial charges on atoms i and j respectively, and ϵ_0 is the dielectric permittivity of a vacuum.

2.2 Calculation of Thermodynamic Potentials from Molecular Dynamics Simulations: Overview

Thermodynamic potentials such as the free energy, enthalpy and entropy can be obtained from the phonon density of states (DoS). The DoS is an accounting of all the distinct types of collective atomic motions and their frequencies. Because the frequency of a vibration, ν , is proportional to its energy (i.e. $E = h\nu$) the DoS is equivalent to the statistical mechanical partition function which is an accounting of all the microstates in the system, their energy levels, and statistical weights. In the solid state it is reasonable to describe all the vibrational motions in the system within the harmonic approximation (Dove, 1993). In so doing, the DoS can be computed directly and thermodynamic functions such as the constant volume heat capacity (C_v), enthalpy (H), entropy (S) and free energy (A) may be determined (Berens et al., 1983). However, in the liquid state, collective particle motions exhibit a large degree of anharmonicity and application of the harmonic approximation leads to significant errors in computed thermodynamic properties. Therefore, to calculate the thermodynamic properties of the combined liquid phases present in our simulations, we employ the two-phase thermodynamic model (2PT), which more accurately accounts for the anharmonicity inherent to liquid systems by decomposing the total density of states into solid- and gas-like components (Huang et al., 2011; Lin et al., 2003; Lin et al., 2010).

2.2.1 The Phonon Density of States (DoS)

To calculate the density of states, $S(\nu)$, from a molecular dynamics simulation we must first keep track of all the collective particle motions in the simulation. To this end, we record the positions and velocities of each atom in the system during the course of the simulation. For each atom, l , we compile a function, $v_l^k(t)$, that tracks the velocity of the atom as a function of time. The superscript, k , is a placeholder for the x, y, and z directions, and therefore for each atom three such functions are computed. Taking the Fourier transform of $v_l^k(t)$ (equation 2.6) produces a new function, $s_l^k(\nu)$, which quantifies the frequency with which specific velocities are attained with respect to direction k .

$$s_l^k(\nu) = \lim_{\tau \rightarrow \infty} \frac{1}{2\tau} \left| \int_{-\tau}^{\tau} v_l^k(t) e^{-i2\pi\nu t} dt \right|^2 \quad (2.6)$$

The second step in the computation of $S(\nu)$ requires that we sum $s_l^x(\nu)$, $s_l^y(\nu)$, and $s_l^z(\nu)$ together and weight the result by the atomic mass, m_l , of species l (this step is the inner summation shown in equation 2.7). To obtain $S(\nu)$, this operation is repeated and summed with the results from each of the N atoms in the simulation (outer summation in equation 2.7).

$$S(\nu) = \frac{2}{k_B T} \sum_{j=1}^N \sum_{k=1}^3 m_l s_l^k(\nu) \quad (2.7)$$

The normalization factor, $2/k_B T$, is required to cancel out the normalization factor from the Fourier transform of $v_l^k(t)$ (equation 2.6) and to ensure that the final units of $S(\nu)$ are in Hertz (i.e. sec^{-1}). It is standard practice, however, to scale $S(\nu)$ by the speed of light, c , as shown in Figure 2.1, so that integration of $S(\nu)$ with respect to ν results in a dimensionless value.

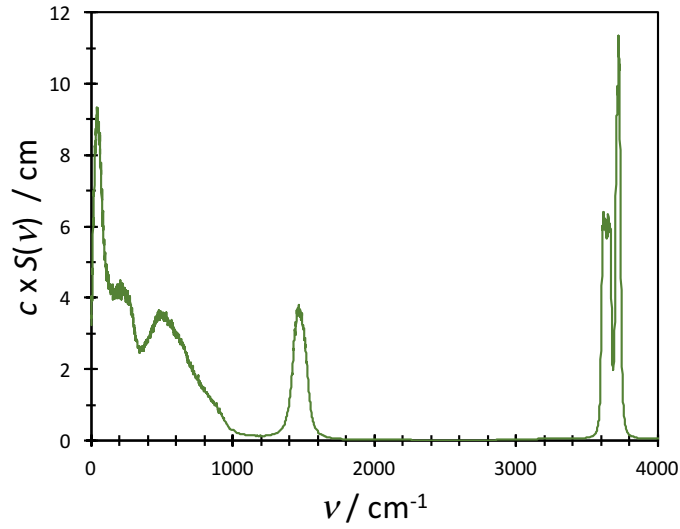


Figure 2.1: The density of states distribution calculated for 512 molecules of SPC/Fw water.

2.2.2 Accounting for Translational, Rotational, and Intramolecular Vibrations

In systems containing molecules rather than isolated atomic species, the total DoS is in fact the superposition of the DoS for the three types of motion: translation, rotation, and intramolecular vibration. These components are shown for SPC/Fw water in figure 2.2.

$$S(\nu) = S(\nu)_{trans} + S(\nu)_{rot} + S(\nu)_{imv} \quad (2.8)$$

The translational density of states, $S(\nu)_{trans}$, is obtained exactly as in the case of the monoatomic system with two exceptions: (1) the mass of atom l is replaced by the mass of molecule j ; and (2) the center of mass velocity of molecule j is utilized rather than the velocity of the atomic species. Therefore, equation 2.9 defines the translational density of

states for a molecular system; note however that this equation results from the composition of equations 2.6 and 2.7 and that the asterisk denotes that the velocity corresponds to that of the center of mass. Additionally, the outer sum now runs to M (the number of molecules in the system) rather than N (the number of atoms in the system).

$$S_{trans}(\nu) = \frac{1}{k_B T} \sum_{j=1}^M \sum_{k=1}^3 \lim_{\tau \rightarrow \infty} \frac{m_j}{\tau} \left| \int_{-\tau}^{\tau} v_j^{*k}(t) e^{-i2\pi\nu t} dt \right|^2 \quad (2.9)$$

The rotational density of states is computed via an analogous expression as shown in equation 2.10. However, we now take the Fourier transform of the rotational velocity $\omega_j^k(t)$ and weight the result by the value principal moment of inertia I_j^k along direction k . In the case of water there are three non-zero principal moments of inertia; however, the linear geometry of the carbon dioxide molecule results in there being only two non-zero moments of inertia. This difference is reflected in the inner summation of equation 2.9.

$$S_{rot}(\nu) = \frac{1}{k_B T} \sum_{j=1}^M \sum_{k=1}^{3(2)} \lim_{\tau \rightarrow \infty} \frac{I_j^k}{\tau} \left| \int_{-\tau}^{\tau} \omega_j^k(t) e^{-i2\pi\nu t} dt \right|^2 \quad (2.10)$$

The density of states for intramolecular vibrational motion, $S(\nu)_{imv}$, is computed in an analogous fashion as the translational density of states provided that the center-of-mass velocities are replaced with the intramolecular vibrational velocities. To obtain these velocities, we subtract the molecular center of mass and rotational velocities from the velocity of each atom l in the molecule.

$$\vec{v}_l^{imv} = \vec{v}_l - \vec{v}_j^* - (\vec{\omega}_j \times \vec{r}_{lj}) \quad (2.11)$$

Then, $S(\nu)_{imv}$ is computed as follows, where the double summation runs over all N atoms in the system and the Fourier transforms are weighted by the atomic mass of atom l rather than mass of molecule j as in the computation of $S_{trans}(\nu)$ and $S_{rot}(\nu)$.

$$S_{imv}(\nu) = \frac{1}{k_B T} \sum_{l=1}^N \sum_{k=1}^3 \lim_{\tau \rightarrow \infty} \frac{m_l}{\tau} \left| \int_{-\tau}^{\tau} v_l^k(t) e^{-i2\pi\nu t} dt \right|^2 \quad (2.12)$$

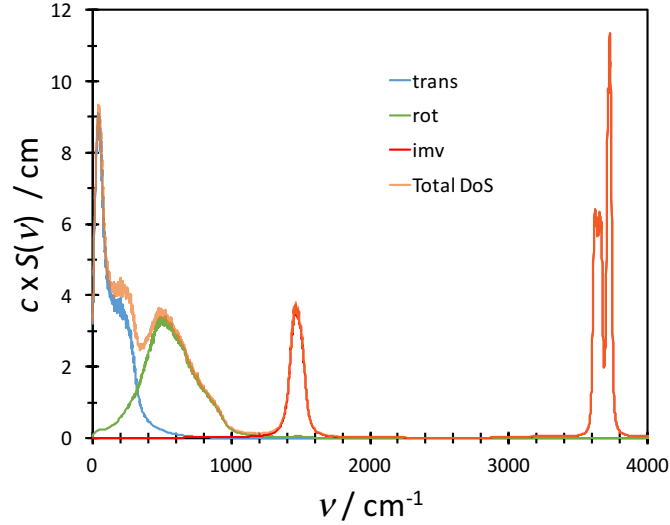


Figure 2.2. Translational, rotational and intramolecular vibrational components of the phonon density of states computed for 512 molecules of SPC/Fw water.

2.2.3 Extracting Thermodynamic Properties from the DoS

The thermodynamic properties of a given system are related to the canonical (isothermal) partition function, Q , as follows:

$$E = k_B T^2 \frac{\partial \ln Q}{\partial T} \quad (2.13)$$

$$C_v = \frac{\partial E}{\partial T} \quad (2.14)$$

$$A = -k_B T \ln Q \quad (2.15)$$

$$S = k_B T \frac{\partial \ln Q}{\partial T} + k_B \ln Q \quad (2.16)$$

where E is the internal energy (equivalent to enthalpy at constant volume), C_v is the constant volume heat capacity, A is the Helmholtz free energy, and S is the entropy. Once the DoS distribution has been obtained, these properties may be determined by taking advantage of the relationship between $S(\nu)$ and the canonical partition function, Q , in the harmonic limit, where each normal vibrational mode in the system is treated as a quantum harmonic oscillator, $q_{HO}(\nu)$.

$$\ln Q = \int_0^\infty d\nu S(\nu) \ln q_{HO}(\nu) \quad (2.17)$$

Substituting equation 2.17 into equations 2.13 – 2.16, one obtains the following expressions for these thermodynamic properties in terms of the density of states distribution, $S(\nu)$, and quantum harmonic oscillator derived weighting functions, $W_i(\nu)$ (Berens et al., 1983).

$$E_m = k_B T \int_0^\infty d\nu S_m(\nu) W_{E,m}(\nu) \quad (2.18)$$

$$C_{v,m} = k_B \int_0^\infty d\nu S_m(\nu) W_{C_v,m}(\nu) \quad (2.19)$$

$$A_m = k_B T \int_0^\infty dv S_m(v) W_{A,m}(v) \quad (2.20)$$

$$S_m = k_B \int_0^\infty dv S_m(v) W_{S,m}(v) \quad (2.21)$$

In these expressions, m stands for the translational, rotational, or intramolecular vibrational density of states distributions as described in section 2.2.2 and their evaluation yields the quantity of each thermodynamic property that is attributable to each type of motion. Therefore, the total value of each thermodynamic property is the sum of contributions from translation, rotation, and intramolecular vibration. E_0 is the reference energy of the system as obtained from a molecular dynamics simulation (S. Lin et al., 2010).

$$E = E_0 + E_{trans} + E_{rot} + E_{imv} \quad (2.22)$$

$$C_v = C_{v,trans} + C_{v,rot} + C_{v,imv} \quad (2.23)$$

$$A = E_0 + A_{trans} + A_{rot} + A_{imv} \quad (2.24)$$

$$S = S_{trans} + S_{rot} + S_{imv} \quad (2.25)$$

2.2.4 Accounting for Anharmonicity in the Liquid State

The methods outlined above are most accurately applied to the solid state where the harmonic approximation is most valid. However, both liquids and gases possess diffusive modes (i.e. low frequency vibrations) that contribute significantly to the

thermodynamic properties of these systems. Therefore, significant errors can result when extracting thermodynamic quantities from the phonon density of states in the harmonic limit. To correct for these effects, Lin and co-workers (Lin et al., 2003) developed the two-phase thermodynamic model (2PT) which decomposes the density of states distribution for each type of molecular motion into solid-like, $S_{s,m}(\nu)$, and gas-like, $S_{g,m}(\nu)$, components (Figure 2.3). Note that intramolecular vibrations are always attributed to solid-like component.

$$S_m(\nu) = S_{s,m}(\nu) + S_{g,m}(\nu) \quad (2.26)$$

The vibrational modes attributed to the solid-like component are then treated as described above, while the diffusive modes in the gas-like component are treated as a hard-sphere fluid. This treatment enables accurate thermodynamic properties to be extracted from the DoS with little additional computational effort.

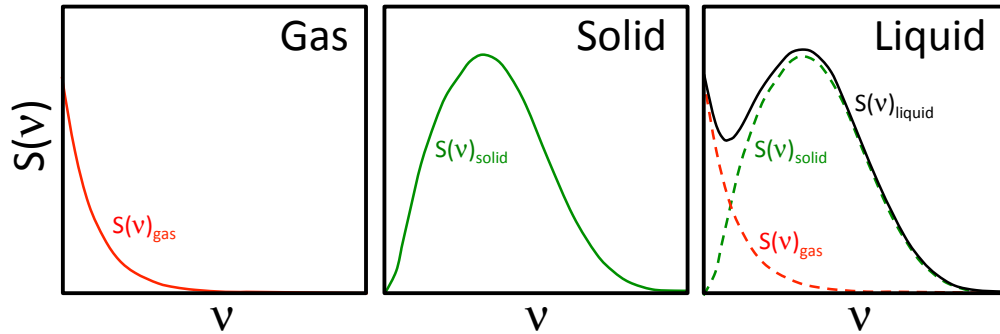


Figure 2.3: Representation of the the DoS of a liquid as the superposition of solid- and gas-like components. After Lin et al., 2003.

In the case of translational and rotational motion, the separation of the DoS distributions into solid-like and gas-like components is dependent upon the value of the dimensionless diffusivity constant, Δ , which is a function of several variables, each of which are readily computed from a molecular dynamics simulation.

$$\Delta(T, V, N, M, m_j, S_m(0)) = \frac{2S_m(0)}{9M} \left(\frac{\pi k_B T}{m_j} \right)^{1/2} \left(\frac{N}{V} \right)^{1/3} \left(\frac{6}{\pi} \right)^{2/3} \quad (2.27)$$

In this expression, T and V are the temperature and volume of the system, N is the number of atoms in M molecules of type j , m_j is the mass of molecule type j , and $S_m(0)$ is the value of either the translational or rotational density of states at zero frequency. These diffusivity constants are then used to solve the following relationship for the fluidicity factors, f_{trans} and f_{rot} , which are required to specify the gas-like component of the density of states distributions for translational and rotational motion.

$$2\Delta_m^{-9/2} f_m^{15/2} - 6\Delta_m^{-3} f_m^5 - \Delta_m^{-3/2} f_m^{7/2} + 6\Delta_m^{-3/2} f_m^{5/2} + 2f_m - 2 = 0 \quad (2.28)$$

Once the fluidicity factors are obtained, the gas-like component of the density of states distributions are defined as shown below. The solid-like components are obtained by subtracting the gas-like components from the total translational and rotational DoS distributions. This is shown for SPC\Fw water in figure 2.4.

$$S_m^g(\nu) = \frac{S_m(0)}{1 + \left(\frac{\pi \nu S_m(0)}{6 f_m M} \right)^2} \quad (2.29)$$

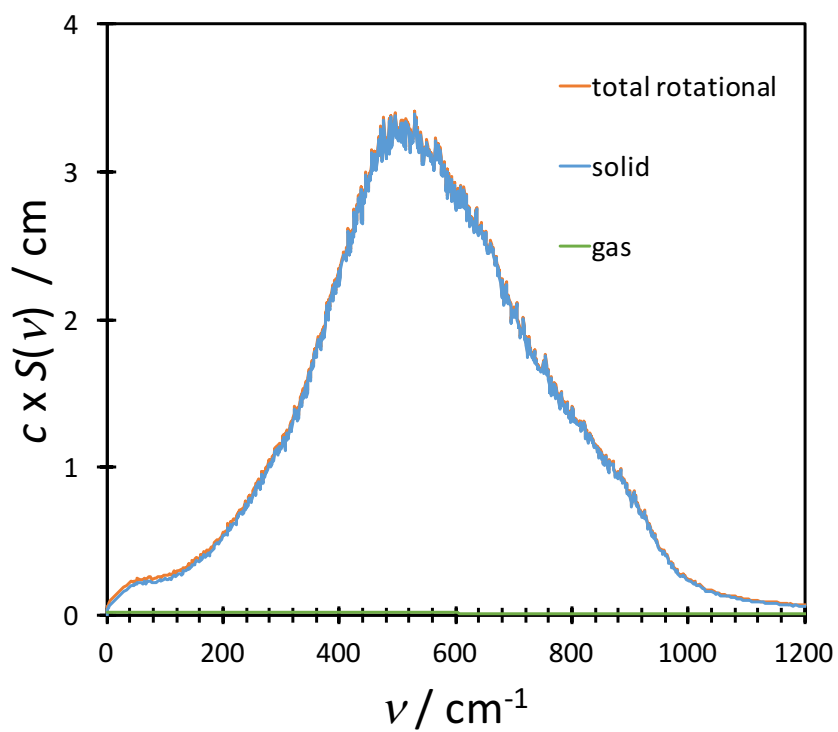
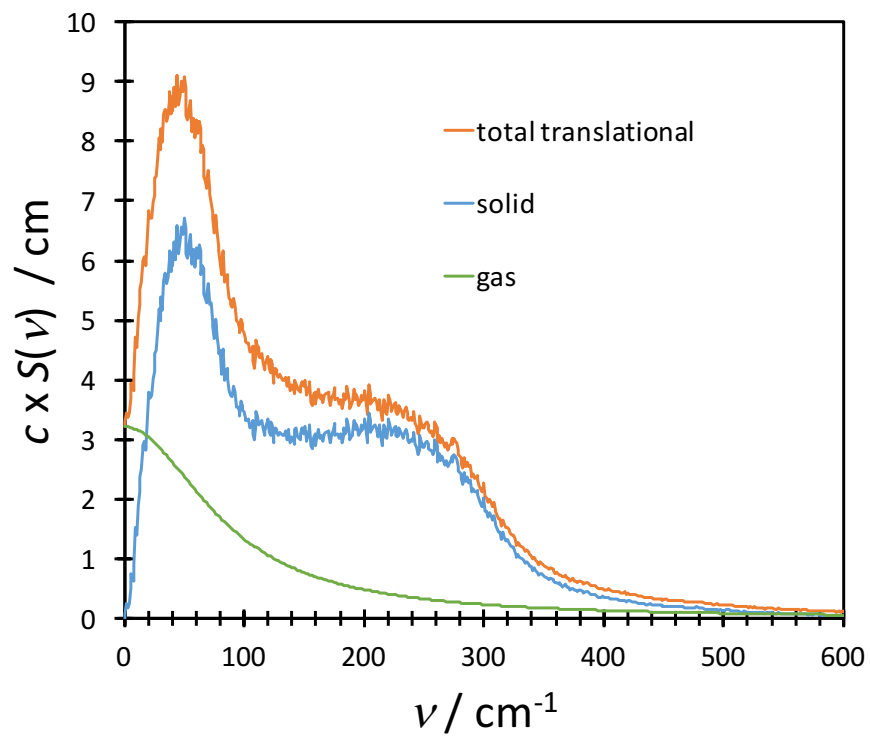


Figure 2.4: Decomposition of the translational and rotational density of states distributions into solid- and gas-like components by the two-phase thermodynamic method.

With the gas- and solid-like components in hand, the thermodynamic properties of the system can be obtained by evaluating the following expressions, which are analogous to equations 2.18 – 2.21, except that we now integrate over the solid- and gas-like DoS distributions separately to utilize weighing functions for the gas-like component that are consistent with a hard sphere fluid.

$$E_m = k_B T \left[\int_0^\infty dv S_m^s(v) W_{E,m}^s(v) + \int_0^\infty dv S_m^g(v) W_{E,m}^g(v) \right] \quad (2.30)$$

$$C_{v,m} = k_B \left[\int_0^\infty dv S_m^s(v) W_{C_v,m}^s(v) + \int_0^\infty dv S_m^g(v) W_{C_v,m}^g(v) \right] \quad (2.31)$$

$$A_m = k_B T \left[\int_0^\infty dv S_m^s(v) W_{A,m}^s(v) + \int_0^\infty dv S_m^g(v) W_{A,m}^g(v) \right] \quad (2.32)$$

$$S_m = k_B \left[\int_0^\infty dv S_m^s(v) W_{S,m}^s(v) + \int_0^\infty dv S_m^g(v) W_{S,m}^g(v) \right] \quad (2.33)$$

Just as before, the total value of each thermodynamic property is the sum of contributions from translation, rotation, and intramolecular vibration as specified in equations 2.21 – 2.24. The weighting functions for the gas-like and solid-like components are defined below (Berens et al., 1983; Huang et al., 2011; Lin et al., 2003; Lin et al., 2010). In the following let $\beta = (k_B T)^{-1}$.

$$W_{E,m}^s(v) = \frac{\beta h v}{2} + \frac{\beta h v}{e^{\beta h v} - 1} \quad (2.34)$$

$$W_{C_v,m}^s(v) = \frac{(\beta h v)^2 e^{\beta h v}}{(1 - e^{\beta h v})^2} \quad (2.35)$$

$$W_{A,m}^s(\nu) = \ln\left(\frac{1 - e^{-\beta h\nu}}{e^{\beta h\nu/2}}\right) \quad (2.36)$$

$$W_{S,m}^s(\nu) = \frac{\beta h\nu}{e^{\beta h\nu} - 1} - \ln(1 - e^{-\beta h\nu}) \quad (2.37)$$

$$W_{E,m}^g(\nu) = W_{C_v,m}^g(\nu) = 0.5 \quad (2.38)$$

$$W_{A,m}^g(\nu) = W_{E,m}^g(\nu) - W_{S,m}^g(\nu) \quad (2.39)$$

$$W_{S,trans}^g(\nu) = \frac{1}{3} \frac{S^{HS}}{k_B} \quad (2.40)$$

$$W_{S,rot}^g(\nu) = \frac{1}{3} \frac{S^R}{k_B} \quad (2.41)$$

Where the gas-like state translational entropy [entropy twice?] weighting function is proportional to the hard-sphere entropy, S^{HS} (equation 2.41a). S^{HS} is further dependent upon the compressibility factor, $z(y)$, from the Carnahan – Starling equation of state (Carnahan & Starling, 1969) for hard-sphere gases (equation 2.1b), which is in turn related to the fluidicity and diffusivity factors for translational motion (equation 2.41c).

$$\frac{S^{HS}}{k_B} = \frac{5}{2} + \ln\left[\left(\frac{2\pi m k_B T}{h^2}\right)^{\frac{3}{2}} \frac{V}{f_{trans} M} z(y)\right] + \frac{y(3y - 4)}{(1 - y)^2} \quad (2.42a)$$

$$z(y) = \frac{1 + y + y^2 - y^3}{(1 - y)^3} \quad (2.42b)$$

$$y = \frac{f_{trans}^{5/2}}{\Delta_{trans}^{3/2}} \quad (2.42c)$$

The gas-like rotational entropy weighting function is proportional to the rotational energy of a rigid body, and takes different forms depending on whether the molecule is non-linear (equation 2.42a) or linear (equation 2.42b) as in the respective cases of H₂O and CO₂.

$$\frac{S^R}{k_B} = \ln \left(\frac{\pi^{1/2} e^{3/2}}{\sigma} \right) \left(\frac{T^3}{\Theta_A \Theta_B \Theta_C} \right)^{1/2} \quad (2.43a)$$

$$\frac{S^R}{k_B} = 1 + \ln \left(\frac{T}{\sigma \Theta} \right) \quad (2.43b)$$

Both expressions for the rotational entropy depend upon the symmetry number, σ , which is the total number of symmetry operations in the rotational subgroup of the molecular point group, and the rotational temperature, $\Theta_i = h^2/(8\pi^2 I_i k_B)$, of which three are defined for non-linear molecules (H₂O) and one for linear molecules (CO₂).

2.2.5 Extension of the 2PT Method to Mixtures

The 2PT method as outlined in the previous sections applies only to homogeneous phases. However, we are interested in mixtures of carbon dioxide and water. Fortunately, the extension of the 2PT method to such mixtures is straightforward and has been demonstrated for mixtures of Lennard-Jones particles (Lai, Hsieh, & Lin, 2012) as well as methanol and water (Pascal & Goddard, 2012). The primary modification required is the use of the partial molar volume for each component rather than the total system volume when post-processing simulation results to obtain thermodynamic properties with the 2PT method. To determine the partial molar volumes of CO₂ and H₂O, we first

determined the change in the molar volume of the mixture, $\Delta \underline{V}_{mix}$, as a function of the mol fraction of carbon dioxide, X_{CO_2} . Thereafter the partial molar volumes of each component were extracted by fitting these data with a Redlich – Kister type polynomial (Sandler, 1999).

$$\Delta \underline{V}_{mix} = x_1 x_2 \sum_{i=0}^n a_i (x_1 - x_2)^i \quad (2.44)$$

Using the partial molar volume instead of the total system volume with the 2PT method results in the generation of partial molar quantities. Assuming ideal mixing, the contributions of each component to the overall thermodynamic properties of the system are defined by the following expressions (Lai et al., 2012), where the overbars denote partial molar quantities and the underbars denote molar quantities.

$$\bar{E}_{mixture} = \sum_i x_i \bar{E}_i \quad (2.45)$$

$$\bar{A}_{mixture} = \sum_i x_i \bar{A}_i - k_B T \sum_i x_i \ln x_i \quad (2.46)$$

$$\bar{S}_{mixture} = \sum_i x_i \bar{S}_i - k_B \sum_i x_i \ln x_i \quad (2.47)$$

Table 2.1: Summary of model parameters used in molecular dynamics simulations of the Sepiolite-H₂O-CO₂ system.

ATOMIC SPECIES			PAIR POTENTIALS (cutoff = 9.0 Å)		
<i>Sepiolite (CLAYFF)</i>			<i>Sepiolite</i>		
	charge		ϵ (eV)	σ (Å)	
Mg	1.05		Mg-Mg	3.9156E-08	5.26432
Si	2.1		Si - Si	7.9810E-08	3.30203
O	-0.95		Mg-Si	5.5902E-08	4.28317
H	0.425		Mg-O	1.6244E-05	4.21493
Obr	-1.05		Mg-Obr	1.6244E-05	4.21493
<i>Water (SPC/Fw)</i>			Si-O	2.3191E-05	3.23378
Ow	-0.82		Si-Obr	2.3191E-05	3.23378
Hw	0.41		O-O	6.7387E-03	3.16554
<i>Carbon Dioxide (Flexible EPM2)</i>			O-Obr	6.7387E-03	3.16554
C	0.6512		Obr-Obr	6.7387E-03	3.16554
Oc	-0.3256		<i>Water</i>		
HARMONIC BOND & ANGLE TERMS			Ow-Ow	6.7400E-03	3.16549
BONDS			<i>Carbon Dioxide</i>		
<i>Sepiolite</i>	K (eV/Å ²)	r_{eq} (Å)	C-C	2.4250E-03	2.75700
O-H	24.02917	1.0	Oc-Oc	6.9380E-03	3.03300
<i>Water</i>			C-Oc	4.1018E-03	2.89500
Ow-Hw	22.965	1.012	<i>Sepiolite-Water</i>		
<i>Carbon Dioxide</i>			Mg-Ow	1.6244E-05	4.21493
C-Oc	55.6518	1.149	Si-Ow	2.3191E-05	3.23378
ANGLES			O-Ow	6.7387E-03	3.16554
<i>Sepiolite</i>	K (eV/rad ²)	θ (deg)	Obr-Ow	6.7387E-03	3.16554
Mg-Obr-H	1.3009	109.47	<i>Sepiolite-Carbon Dioxide</i>		
<i>Water</i>			Mg-C	9.7444E-06	4.01066
Hw-Ow-Hw	1.6455	113.24	Si-C	1.3912E-05	3.02951
<i>Carbon Dioxide</i>			O-C	4.0424E-03	2.96127
Oc-C-Oc	2.452	180	Obr-C	4.0424E-03	2.96127
			Mg-Oc	1.6482E-05	4.14866
			Si-Oc	2.3531E-05	3.16751
			O-Oc	6.8376E-03	3.09927
			Obr-Oc	6.8376E-03	3.09927
			<i>Water-Carbon Dioxide</i>		
			Ow-C	5.7120E-03	2.84120
			Ow-Oc	7.7610E-03	3.15240

Chapter 3

ATOMISTIC MODELING OF CARBON DIOXIDE IN SEPIOLITE

3.1 Introduction

The carbonation of magnesium silicate minerals within ultramafic rocks is one of the most promising routes to CO₂ sequestration involving chemical reaction with natural materials. However, in practice the rate of mineral carbonation is very slow at ambient conditions. Using smaller grains with greater reactive surface areas and increasing the reaction temperature can enhance rates, however, crushing and heating rock is an energy-consuming task. Other proposed strategies endeavor to physically capture CO₂ and store it in porous media, such as deep sedimentary rock formations, and synthetic materials such as zeolites and metal organic frameworks (MOFs). However, the use of naturally occurring porous materials is the most promising. Though their physical properties cannot be tailored for specific applications, sepiolite-palygorskite group clays are of particular interest because of their natural abundance (commonly occurring as minerals in marine and lacustrine sediments), and the fact that infrastructure already exists to exploit the materials in industrial-scale applications. In this work, we have performed molecular dynamics simulations to assess the thermodynamics of the incorporation of CO₂ into a hydrated sepiolite mineral lattice, with the goal of determining whether sepiolite can be utilized for carbon capture and storage applications. To meet this objective we have employed the 2PT method detailed in chapter 2 to determine whether there is a thermodynamic driving force in favor of replacing water in the sepiolite structure with CO₂ using the conditions outlined in Table 3.1.

Simulation	Cooling Time	Temperature (K)	Time Run at Temperature(ns)	2PT Run Time (ps)	Mole Fraction CO ₂
Pure Water	4 ns, cooled from 500 K	280-304	2	20	N/A
Pure Liquid CO ₂	4 ns, cooled from 500 K	220-304	2	20	N/A
Pure Gaseous CO ₂	4 ns, cooled from 500 K	220-304	2.5	20	N/A
Bulk Mixture	5 ns, cooled from 500 K	280-304	6	20	0.0-0.3, 0.05
Water in Sepiolite	N/A	280-304	2	20	N/A
Mixture in Sepiolite	5 ns, cooled from 500 K	280-304	3.5	20	0.025-0.1, 0.15-0.3

Table 3.1. Conditions used for the 2PT simulations. Liquid CO₂ had a cutoff radius of 9Å and gaseous CO₂ had a cutoff radius of 17Å. Liquid and gaseous CO₂ simulations were run at experimental densities along the liquid-vapor curve.

3.2 Validation of 2PT Code

The 2PT method is a relatively new computational tool. While it is becoming increasingly utilized in the literature, there is at present no open source community code implementing this method. For this reason, our research group has developed its own in-house code that we validate below by benchmarking its performance with respect to previously 2PT results for SPC/Fw and EPM2 carbon dioxide.

3.2.1 Liquid Water at 298 K and 1 Bar

Table 3.2 compares results obtained using our in-house 2PT model for SPC/Fw water with those of Pascal et al. (2012). The slight numerical difference between the two sets of results is likely due to small differences in simulation temperatures (e.g. 298 versus 300K) and pressures (1.01325 bar versus 1 bar). We conclude that our model produces thermodynamic values in reasonable agreement with the results of Pascal et al. (2012).

Thermodynamic Values	Pascal and Goddard	This Work
ΔH (kJ/mol)	-30.5 ± 0.3	-31.494 ± 0.029
ΔS (J/mol)	61.7 ± 0.6	63.280 ± 0.0001
ΔG (kJ/mol)	-48.5 ± 0.5	-50.541 ± 0.039

Table 3.2. Comparison of our data to existing data for the SPC/Fw water model.

3.2.2 Liquid Carbon Dioxide Along the Liquid-Vapor Curve

Next, we used our in-house 2PT code to study the behavior of pure CO₂. Figure 3.1 compares our results to those obtained by Huang and Goddard (2011). Our results differ at most by only 3.4% from that of Huang and Goddard's and indicate that our in-house code produces results consistent with previous studies.

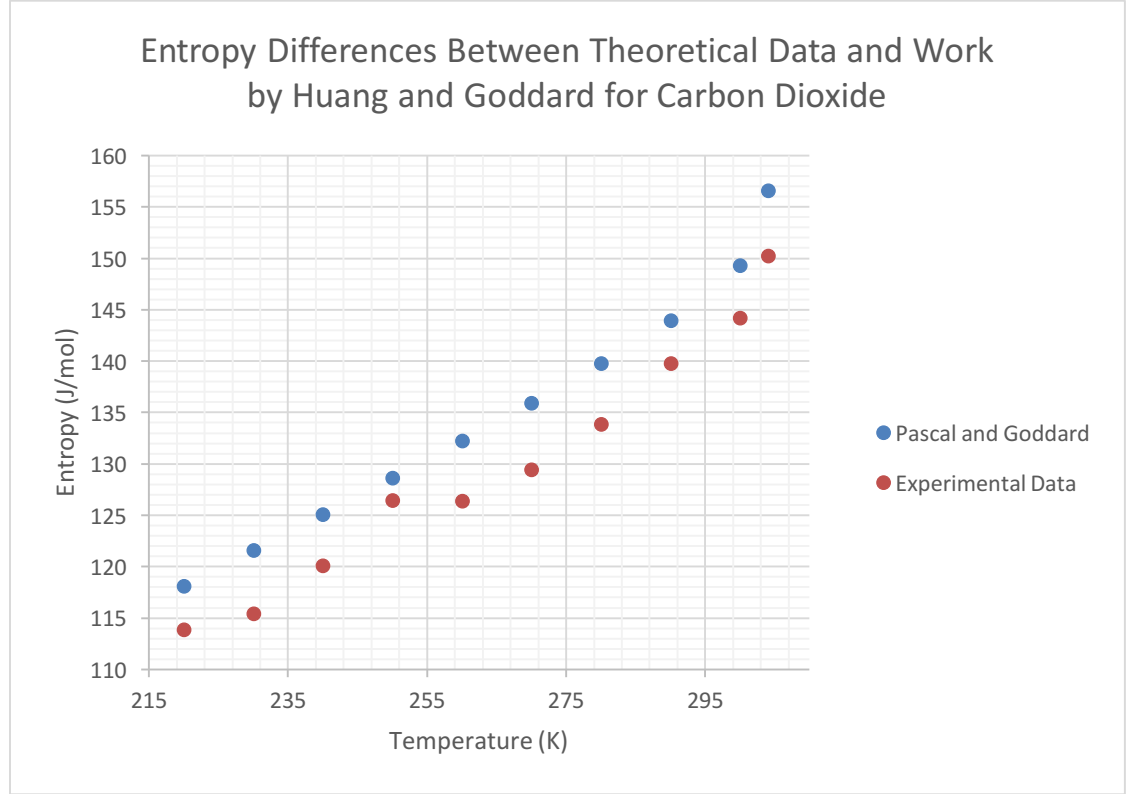


Figure 3.1. Entropy comparison between published work on liquid carbon dioxide by Huang and Goddard (2011) and our data. The data differ by a maximum of 3.4%. Error bars have not been included as they are smaller than the actual point indicators.

3.2.3 Carbon Dioxide-Water Mixtures

While there is no previously published 2PT result for $\text{CO}_2\text{-H}_2\text{O}$ mixtures, to some degree we can benchmark the performance of our model with respect to experimental data. Here, we compare the total volume of our model mixtures to experimentally measured volumes. Table 3.3 compares the total volume of our simulated mixtures to the experimental volume at four temperatures (280, 290, 300, 304K) along the CO_2 liquid-vapor coexistence curve (Duan 2008).

Mole Fraction CO ₂	Temperature (K)	Pressure (bar)	Duan 2008 (cm ³ /mol)	This Work (cm ³ /mol)	Percent Difference
0.05	280	41.6	18.678	18.353	1.756
0.1	280	41.6	19.375	18.862	2.682
0.2	280	41.6	20.769	20.466	1.472
0.3	280	41.6	22.163	22.339	0.791

Mole Fraction CO ₂	Temperature (K)	Pressure (bar)	Duan 2008 (cm ³ /mol)	This Work (cm ³ /mol)	Percent Difference
0.05	290	53.1	18.707	18.420	1.546
0.1	290	53.1	19.421	18.959	2.408
0.2	290	53.1	20.848	20.554	1.420
0.3	290	53.1	22.275	21.862	1.870

Mole Fraction CO ₂	Temperature (K)	Pressure (bar)	Duan 2008 (cm ³ /mol)	This Work (cm ³ /mol)	Percent Difference
0.05	300	67.1	18.773	18.527	1.317
0.1	300	67.1	19.521	19.173	1.801
0.2	300	67.1	21.018	20.702	1.513
0.3	300	67.1	22.515	22.108	1.823

Mole Fraction CO ₂	Temperature (K)	Pressure (bar)	Duan 2008 (cm ³ /mol)	This Work (cm ³ /mol)	Percent Difference
0.05	304	73.6	18.806	18.573	1.249
0.1	304	73.6	19.571	19.198	1.923
0.2	304	73.6	21.101	20.821	1.335
0.3	304	73.6	22.632	22.550	0.363

Table 3.3. Comparisons of total volumes from this work and that of Duan 2008.

Using this comparison we determined that our data differed from that of Duan and others by no more than 2.7%.

3.3 H₂O and CO₂-H₂O Mixtures in Sepiolite

Given that we have demonstrated that the simulations accurately reproduce the thermodynamics of bulk pure water and, separately, bulk pure carbon dioxide, as well as the volume of carbon dioxide-water mixtures, we introduced the sepiolite mineral to our modeling system. As described in Chapter 2, we are using high quality models for carbon dioxide, water, and sepiolite and therefore have some confidence that our simulations are

accurate in a qualitative sense; however, our results are ultimately only as reliable as the model is.

Figure 3.2 depicts the density-of-states vibrational spectra for pure water and water in sepiolite. There are two differences that stand out in the spectra. The first is the diffusion coefficient, found using the y-intercept of the DoS in the following equation:

$$S(0) = \frac{12mND}{k_bT} \quad (3.1)$$

Where $S(0)$ is the value of the DoS at zero, k_bT is rate and temperature, m is mass, and N is the number of molecules. $S(0)$ is thus proportional to the diffusivity. As observed in our theoretical spectra, water outside of the sepiolite nanopores exhibits a higher diffusivity than water inside the nanopores. We also observe that the intensity of the translational and rotational components of the DOS are much higher for pure water outside of the mineral than for water in the nanopores. This is not surprising, as confinement in the channels as well as specific interactions with the magnesium in the octahedral layers of the silicate framework would be expected to restrict molecular motion.

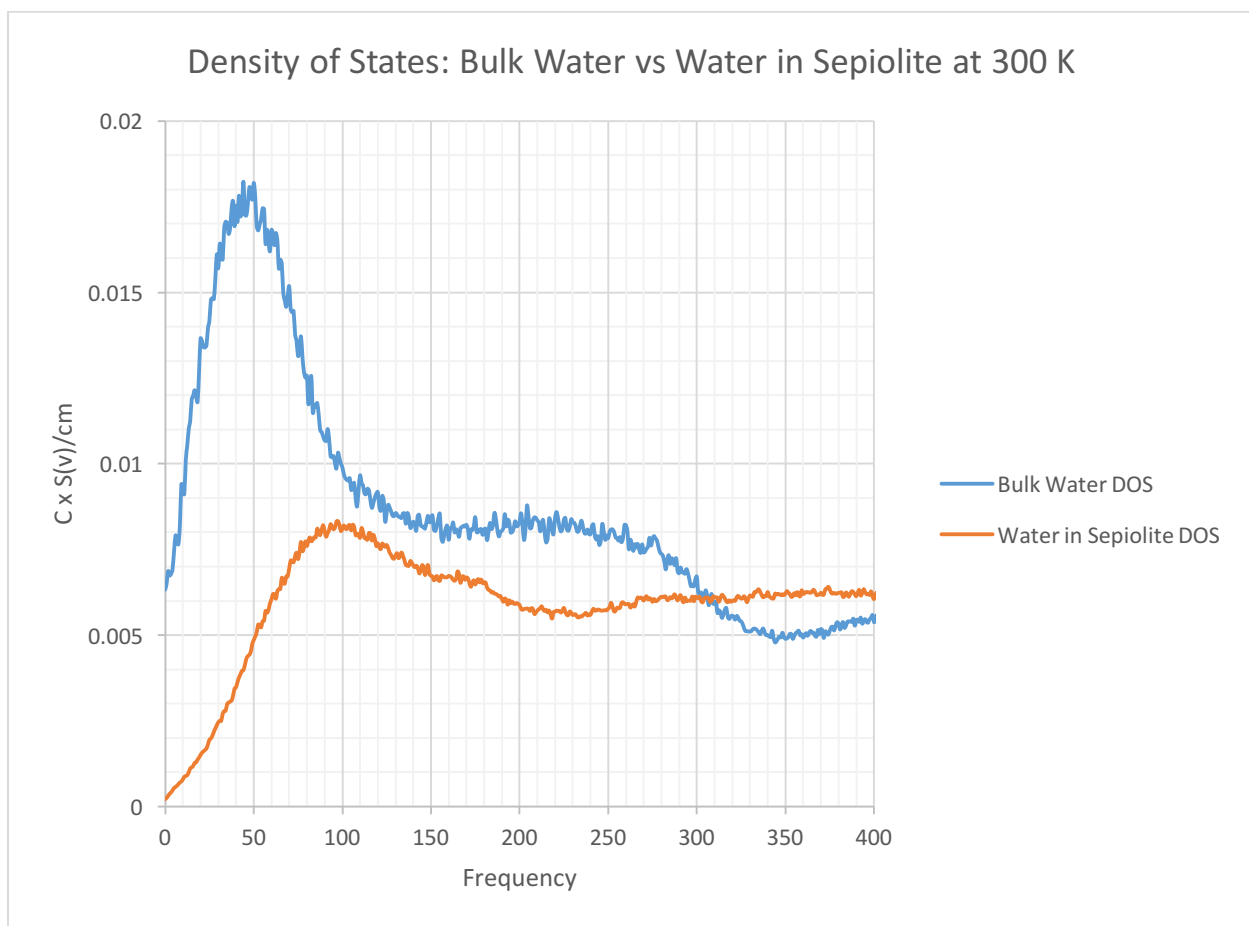


Figure 3.2. A comparison of the DoS for bulk water and water in sepiolite. While the curves are similar in shape, the intensity of the DOS for water in sepiolite is significantly lower than that of bulk water. This is due to translational and rotational motions of water molecules being inhibited by interactions with the mineral as well as confinement within individual channels.

The same trend appears when comparing pure carbon dioxide with the carbon dioxide-water mixture inside the sepiolite nanopores (Figure 3.3). We observe that $S(0)$ for pure liquid carbon dioxide is significantly higher than that of carbon dioxide inside the sepiolite channels, indicating that carbon dioxide molecules in the pure liquid experience greater freedom of motion than that of carbon dioxide inside the channels. When comparing the two DoS spectra, it becomes apparent that the translational

component of motion is inhibited for carbon dioxide within the mineral structure. Thus, our data suggests that carbon dioxide, like water, diffuses more readily outside of the mineral structure than inside of it.

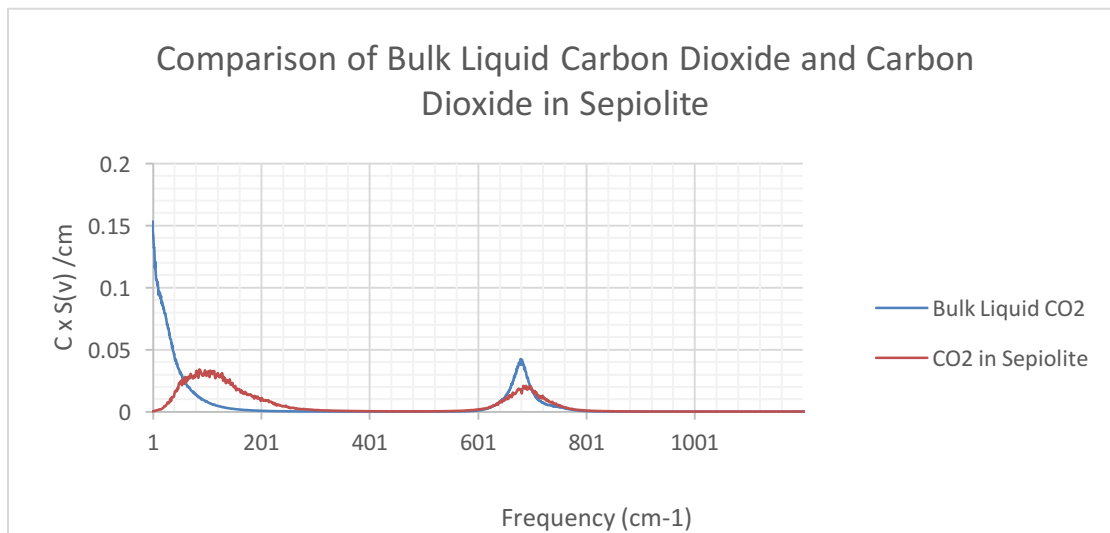


Figure 3.3. A comparison of bulk liquid carbon dioxide against the carbon dioxide in sepiolite. The same diffusivity trend is observed here as when examining the behavior of water inside and outside the sepiolite nanopores. Along with the translational motion inhibition, there is some inhibition at the 700 peak that corresponds to O=C=O bend.

3.3.1 Simulation Results

3.3.1.1 Free Energy of the CO₂-H₂O Mixture Both In and Out of Sepiolite

For bulk mixtures, the free energy of mixing was calculated as the free energy difference between the mixture and its isolated components:

$$\Delta G = G_{Bulk} - (G_{H2O}X_{H2O} + G_{CO2}X_{CO2}) \quad (3.2)$$

The results displayed in Figure 3.4 show that the free energy of mixing is positive, and indicate that a two-phase mixture of water and carbon dioxide is stable under all the conditions modeled in this work.

For mixtures confined within sepiolite, we did not compute the free energy of mixing, but rather the free energy change associated with replacing water within the sepiolite nanopores with carbon dioxide (equation 1.1). The free energy of reaction for this process is defined as follows:

$$\Delta G = (G_{Mix\ in\ Sep} + X_{CO2}G_{H2O}) - (G_{H2O\ in\ Sep} + X_{CO2}G_{CO2}) \quad (3.3)$$

Analogous equations were also used to calculate the entropy and enthalpy change of reaction. From here we compared the free energy change of the pure bulk water to that of the bulk carbon dioxide-water mixture at different concentrations (Figure 3.5).

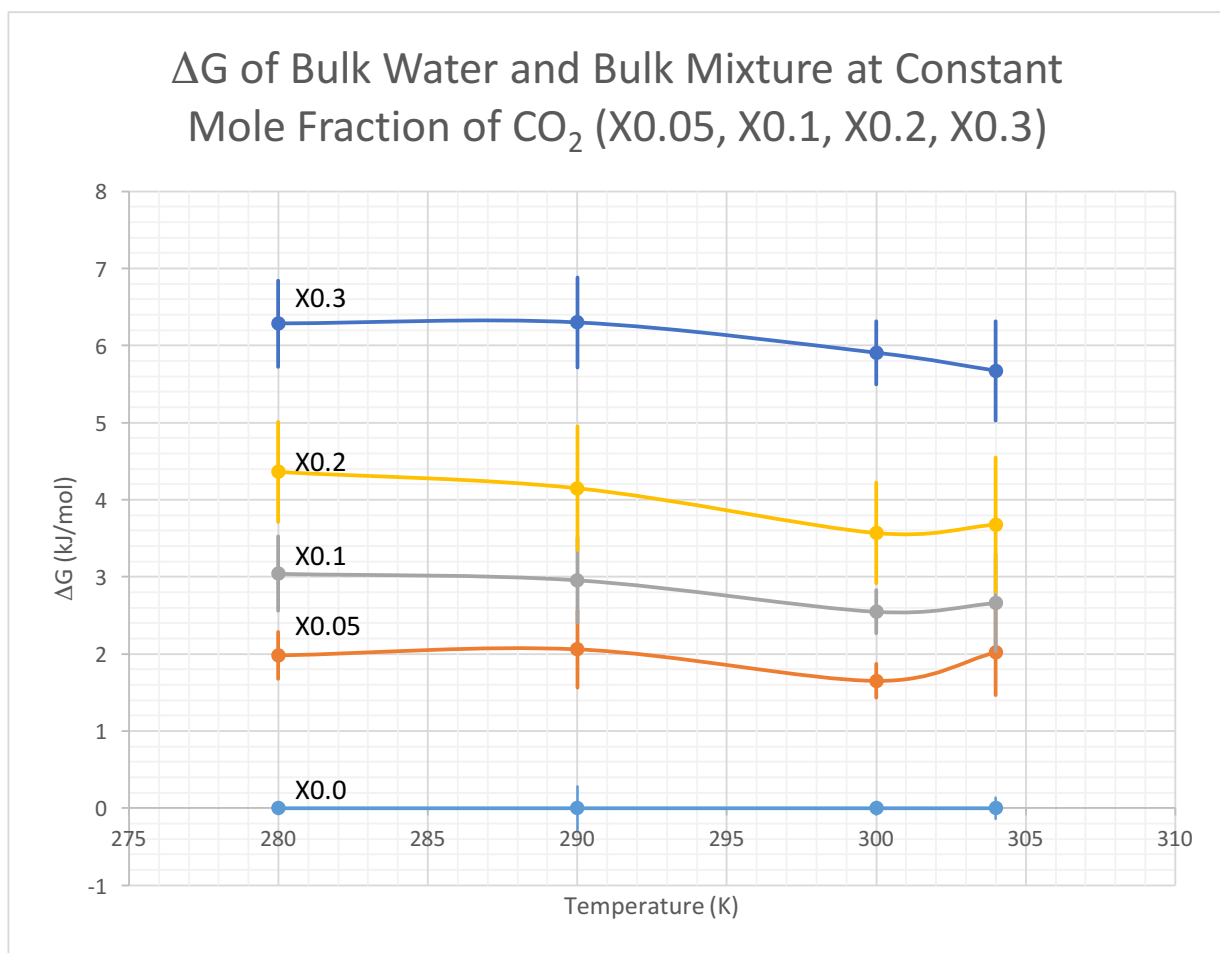


Figure 3.4. Free energy of mixing for pure water and the carbon dioxide-water mixture at various concentrations. The change in pure water is zero and serves as a reference value for the other concentrations.

We found that two of our chosen mole fractions of carbon dioxide (0.05 and 0.1) experience a negative free energy change when exposed to sepiolite in solution, presenting a driving force for carbon dioxide to replace water inside the sepiolite nanopores.

ΔG of Water in Sepiolite and H_2O-CO_2 Mix in Sepiolite at Constant Mole Fraction of CO_2 (0.05, 0.1, 0.2, 0.3)

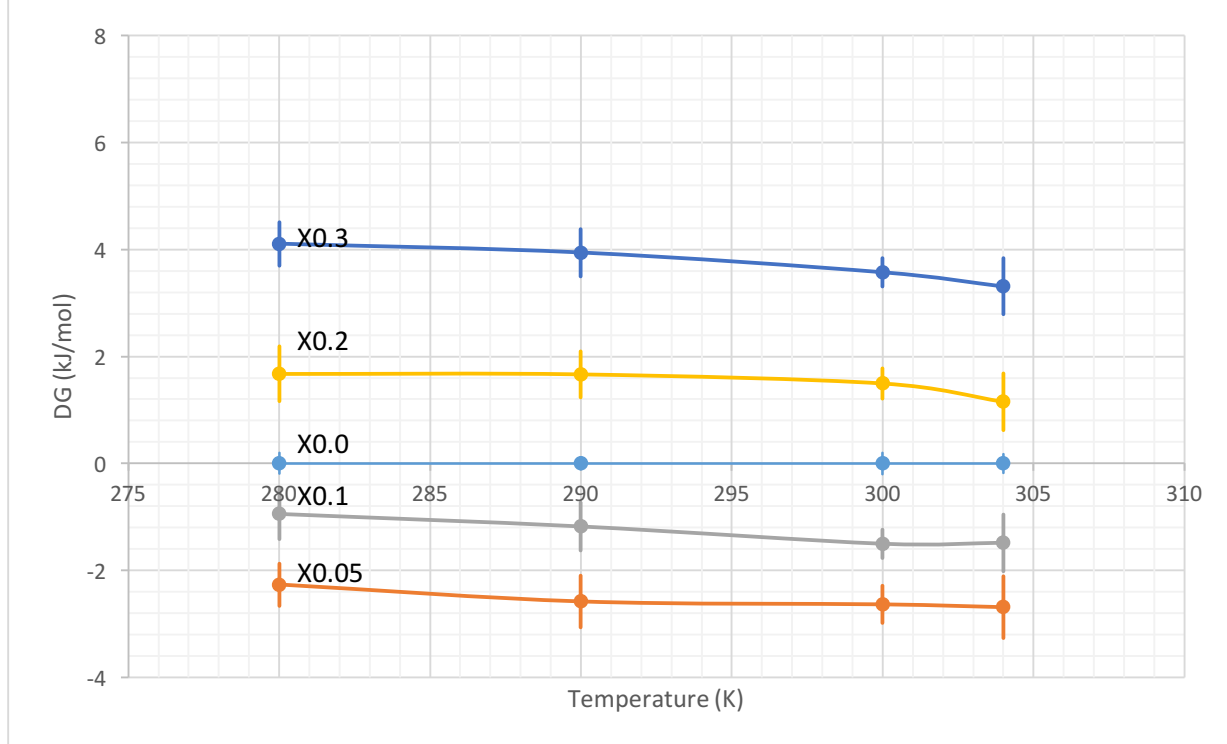


Figure 3.5. The free energy of reaction for exchanging CO_2 for water in sepiolite. Pure water in sepiolite was used as a reference point to compare with various concentrations of carbon dioxide mixtures.

3.3.1.2 Origin of the Thermodynamic Driving Force for CO_2 Incorporation into Mineral Nanopores

To examine why mole fractions up to 0.1 CO_2 experience a thermodynamic driving force to infiltrate the sepiolite nanopores, we present an analysis of the individual thermodynamic values involved in computing the free energy change using the Gibbs free energy equation:

$$\Delta G = \Delta H - T\Delta S \quad (3.4)$$

Temperature (K)	Mole Fraction CO ₂	ΔG (kJ/mol)	ΔH (kJ/mol)	$-T\Delta S$ (kJ/mol)
280	0.05	-2.2645 ± 0.394	0.188 ± 0.370	-2.453 ± 1.236
290	0.05	-2.578 ± 0.471	0.017 ± 0.438	-2.595 ± 1.198
300	0.05	-2.632 ± 0.513	0.015 ± 0.411	-2.647 ± 1.396
304	0.05	-2.684 ± 0.410	-0.095 ± 0.496	-2.589 ± 1.748

Temperature (K)	Mole Fraction CO ₂	ΔG (kJ/mol)	ΔH (kJ/mol)	$-T\Delta S$ (kJ/mol)
280	0.1	-0.943 ± 0.484	-0.56 ± 0.268	-0.382 ± 1.560
290	0.1	-1.178 ± 0.451	-0.942 ± 0.289	-0.235 ± 1.443
300	0.1	-1.501 ± 0.021	-1.252 ± 0.017	-0.249 ± 0.070
304	0.1	-1.482 ± 0.444	-1.495 ± 0.268	0.0127 ± 1.415

Temperature (K)	Mole Fraction CO ₂	ΔG (kJ/mol)	ΔH (kJ/mol)	$-T\Delta S$ (kJ/mol)
280	0.2	1.673 ± 0.347	-1.141 ± 0.183	2.814 ± 0.852
290	0.2	1.665 ± 0.269	-1.855 ± 0.214	3.52 ± 0.844
300	0.2	1.495 ± 0.279	-2.441 ± 0.157	3.936 ± 0.707
304	0.2	1.153 ± 0.263	-2.995 ± 0.191	4.148 ± 0.779

Temperature (K)	Mole Fraction CO ₂	ΔG (kJ/mol)	ΔH (kJ/mol)	$-T\Delta S$ (kJ/mol)
280	0.3	4.104 ± 0.576	-1.993 ± 0.366	6.097 ± 1.965
290	0.3	3.94 ± 0.529	-2.939 ± 0.371	6.879 ± 1.958
300	0.3	3.574 ± 0.531	-3.829 ± 0.371	7.403 ± 1.980
304	0.3	3.311 ± 0.523	-4.748 ± 0.350	8.059 ± 1.904

Table 3.4. Thermodynamic values for various mole fractions of carbon dioxide in sepiolite. Mole fraction increases from the top down as follows: X_{CO_2} 0.05, X_{CO_2} 0.1, X_{CO_2} 0.2, and X_{CO_2} 0.3. The entropy term ($-T\Delta S$) in the equation shifts to a positive value, which results in a positive change in free energy.

As concentration increases, the $-T\Delta S$ (entropy) term shifts to a more positive value, driving the change in free energy to increase (Table 3.4). Though enthalpy

decreases with increasing mole fraction, the entropy term is a much larger factor in determining the change in free energy. The drastic shift toward unfavorable entropy at higher concentrations likely occurs because, as higher concentrations of carbon dioxide are added to the nanopores, the molecules become more crowded in the channels and are physically able to occupy fewer microstates in the system.

3.4 Implications of Model Results

Our model results indicate, at mole fractions of CO₂ less than 0.1, an entropy-driven thermodynamic driving force exists for carbon dioxide to enter the nanopores in the sepiolite structure. We additionally observe that, compared to the bulk liquids and mixtures, the diffusivity of water and carbon dioxide in sepiolite is significantly inhibited, a likely result of restricted translational and rotational motions. This lower diffusivity brings two implications to light. First, once carbon dioxide is inside the mineral structure it is unlikely to come back out. However, the second implication serves as a potential issue for the first: the initial entry of carbon dioxide into the nanopores may be slow.

Our study represents an important initial step in assessing the usefulness of sepiolite as a potential carbon-sequestration material. We have demonstrated herein that sepiolite nanopores possess an inherent affinity for low mole fractions of CO₂, with a capacity of up to 0.926 mmol CO₂/g of material under conditions of 0.1 mole fraction CO₂. Indeed, our results suggest that sepiolite has almost double the CO₂ sequestration capacity as does Ca-montmorillonite (0.45 mmol CO₂/g Ca-montmorillonite, Schaef et al. 2015). Further work on this topic should include experimental physical proof of concept as well as modeling regarding, specifically, the diffusivity of the carbon dioxide in the mineral structure.

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