***ab initio* Thermodynamics of Magnesium Carbonates and Hydrates in Water-
Saturated Supercritical CO₂ and CO₂-Rich Regions**

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Abstract. *ab initio* thermodynamics is used to determine how free energies of magnesium carbonates and hydrates in a CO₂-rich environment change with water concentration across a range temperature and pressure relevant to geochemistry and carbon sequestration (275 K to 375 K and pCO₂ of 1 to 210 bar). The methodology is based on first principles density-functional theory (DFT) calculations of the total energies and vibrational entropy of periclase, magnesite, brucite, nesquehonite, and hydromagnesite coupled to the experimental chemical potentials of CO₂ and H₂O. The impact of water in supercritical CO₂ (scCO₂), even though less than 1% at saturation, is found to have a significant impact on the stability of hydrated carbonate minerals. Hydromagnesite and nesquehonite are found to be more thermodynamically stable than periclase and brucite in water-saturated scCO₂ and hence may be expected to result kinetically from carbonation of these minerals during CO₂ sequestration. Under dehydrating conditions nesquehonite destabilizes rapidly, whereas hydromagnesite is much more likely to persist in a CO₂-rich environment, consistent with the observations that hydromagnesite is widespread in nature and nesquehonite is relatively rare.

Keywords. Ab initio thermodynamics, density-functional theory, carbon sequestration, carbonates, hydrates, supercritical carbon dioxide

1. Introduction

At the present time, geological trapping appears to be the most promising option for large-capacity sequestration of point source CO₂ emissions to mitigate climate change. (Bachu, 2002; Bachu, 2008; Bachu and Adams, 2003) Subsurface options include saline aquifers, oil and gas recovery sites, unmineable coal seams, and mafic and basalt formations, many of which are globally widespread near population and power generation centers with many successful demonstration projects online. (Goldberg et al., 2010; McGrail et al., 2006; Oelkers et al., 2008) There are also efforts to study the feasibility of using reactive carbonate-forming minerals such as serpentine, olivine, and brucite in ultramafic mine tailings in processing plants at the surface. (Béarat et al., 2002; Harrison et al., 2013; Sturgeon et al., 2010) CO₂ can be trapped underground structurally, stratigraphically, hydrodynamically, or dissolved in aquifers or petroleum recovery sites. Mineralization of CO₂ to form carbonates, however, constitutes the greatest long-term storage security for both surface and subsurface systems. (Bachu, 2008) Understanding the reactivity of periclase (MgO) and brucite (Mg(OH)₂) with CO₂ and the products' long-term stability is also important for the integrity of nuclear waste repositories. In addition, understanding the formation of carbonate minerals in a CO₂-rich environment where the amount of water may have fluctuated greatly is key to linking the current mineral composition of Mars to conditions in the planet's geological past. (Calvin et al., 1994)

The kinetics and thermodynamics of carbonate mineral formation has been observed to vary greatly depending upon conditions. Under ambient conditions, magnesium and carbonate ions will precipitate exclusively as hydrates (barringtonite MgCO₃•2H₂O, nesquehonite MgCO₃•3H₂O, and lansfordite MgCO₃•5H₂O) or basic hydroxides

(hydromagnesite $\text{Mg}_5(\text{CO}_3)_4(\text{OH})_2 \cdot 4\text{H}_2\text{O}$), artinite ($\text{Mg}_2(\text{CO}_3)(\text{OH})_2 \cdot 3\text{H}_2\text{O}$), dypingite ($\text{Mg}_5(\text{CO}_3)_4(\text{OH})_2 \cdot 5\text{H}_2\text{O}$), and several more basic carbonates analogous to dypingite but with additional water molecules. (Cheng and Li, 2009; Hales et al., 2008; Hnchen et al., 2008; Langmuir, 1965; Montes-Hernandez et al., 2012; Sandengen et al., 2008) Up to 325 K in magnesium bicarbonate solutions, nesquehonite will precipitate; at 325 K or above in vacuum or aqueous solution, nesquehonite will transform to hydromagnesite. (Davies and Bubela, 1973) Botha and Strydom (Botha and Strydom, 2001) systematically investigated the impact of temperature, pH, and drying temperature on the products of CO_2 sparging of brucite, and determined that conditions could easily be tailored to synthesize nesquehonite, hydromagnesite, or another unidentified hydrated basic carbonate (likely dypingite). Similarly (Hopkinson, Kristova et al. 2012) found CO_2 sparging of a brucite suspension at 298 K yields a hydromagnesite precipitate followed by nesquehonite upon heating the solution to 331 K; rapid CO_2 degassing of the solution results in the disappearance of nesquehonite and the appearance of dypingite, hydromagnesite, and a more disordered structure with similar stoichiometry. Above 438 K dypingite will transform to hydromagnesite without loss of CO_2 . (Ballirano et al., 2013)

Despite the appearance of hydrated and basic carbonates under aqueous conditions, magnesite is thermodynamically the most stable under these conditions. Magnesite is, however, difficult to synthesize from aqueous solution, as it is kinetically inhibited from forming. (Christ and Hostetler, 1970; Montes-Hernandez et al., 2012; Qafoku et al., 2015) This difficulty was also encountered by Giammar and coworkers who found that forsterite (Mg_2SiO_4) under aqueous conditions exposed to a headspace pCO_2 of 1 or 100 bar would only precipitate magnesite under high temperature and high pCO_2 . (Giammar et al., 2005)

Hence the formation and persistence of these carbonate minerals in aqueous systems is highly dependent upon changes in temperature and $p\text{CO}_2$.

Carbonation processes in CO_2 -rich systems, however, can be very different from aqueous systems with dissolved carbonate. CO_2 -rich conditions need to be considered as they may be of equal if not greater importance than aqueous systems for subsurface carbon sequestration. (McGrail, 2009) Naturally CO_2 pressure can vary from atmospheric concentration to several bar subsurface due to microbial respiration and volcanic or magma activity. When CO_2 is injected into geological formations, it can form a supercritical fluid, with temperatures and pressures above the critical point ($P > 73.9$ bar and $T > 304.25$ K) or as a liquid below the critical point. Some minerals have been shown to react with anhydrous supercritical CO_2 (scCO_2), such as anorthite ($\text{CaAl}_2\text{Si}_2\text{O}_8$) and portlandite ($\text{Ca}(\text{OH})_2$), though portlandite generates water during the reaction process. (Regnault et al., 2005) Brucite, however, has been shown not to carbonate and form magnesite in dry scCO_2 at temperatures below 373 K. (Loring et al., 2012; Schaef et al., 2011) Brucite will carbonate in dry conditions only after exposure to temperatures sufficiently high to effect dehydroxylation, namely 650 K, and a $p\text{CO}_2$ above 54.4 bar. (Bearat, McKelvy et al. 2002)

Supercritical CO_2 injected subsurface, however, is not likely to remain dry. It is a low-density superfluid that once injected can migrate extensively in geological formations, extracting any water that is present. Even though water is only slightly soluble in scCO_2 , (less than 1% by mass), at equilibrium the water in CO_2 has the same chemical potential as pure liquid water and has been demonstrated to have the same reactivity. Development of high-pressure *in situ* X-ray diffraction (Schaef et al., 2011), NMR (Kwak et al., 2010), and vibrational spectroscopy (Loring et al., 2011; Schaef et al., 2011) has enabled monitoring the

reactivity of minerals such as brucite and forsterite (Mg_2SiO_4) in scCO_2 under conditions where the concentration of water is tightly controlled. (Schaef, Windisch et al. 2011) observed that introduction of trace amounts of water into scCO_2 at 82 bar resulted in partial carbonation of brucite, followed by complete carbonation as the water concentration was increased to saturation at 323 K. Raising the temperature to 348 K resulted in complete conversion of nesquehonite to magnesite. (Loring, Thompson et al. 2011) found that at 100 bar pCO_2 brucite will carbonate to form nesquehonite as low as 308 K, and at 343 K form an amorphous hydrated carbonate in addition to magnesite.

Kwak and coworkers determined that forsterite exhibited reactivity similar to brucite, in that no reaction was observed in dry scCO_2 at 97 bar and 353 K in 7 days. (Kwak et al., 2010) ^{13}C NMR revealed that saturating the system with water resulted in formation of dypingite as an intermediate, followed by formation of magnesite. Felmy and coworkers observed that nesquehonite and magnesite were formed from carbonation of forsterite at 308 K in 3-4 days in water-saturated scCO_2 at 91 bar, followed by complete conversion to magnesite at 14 days; this is the lowest known temperature for magnesite synthesis, having implications for stability of subsurface mineral carbon capture. Loring and coworkers measured the reactivity of forsterite as a function of water film thickness, and determined that a water film of $76 \mu\text{mol}/\text{m}^2$ was necessary at 323 K and 90 bar pCO_2 to effect dissolution of the Mg^{2+} cations from the forsterite and initiate carbonation reactivity beyond surface complexation. (Loring et al., 2015) Qafoku and coworkers (Qafoku et al., 2014) examined carbonation of forsterite at 308 - 353 K for both water saturated with scCO_2 and scCO_2 saturated with water at 91 bar. The dominant phase in the first case was nesquehonite across the temperature range with only a few crystals of magnesite observed at 353 K. In

water-saturated scCO₂, however, nesquehonite dominated only at 308 K with magnesite being the dominant phase at 323 and 353 K. In this amount of water, the magnesite exhibited extremely uniform submicron sized particles that were not consistent with nucleation and growth on the forsterite surface. These experiments underscore the critical nature of the presence of water in scCO₂ to effect subsurface carbon capture.

Given that this highly reactive water can lead to the formation of hydrated minerals and affect the relative stabilities of carbonate minerals, a reliable means to predict the interactions of CO₂ with mineral phases to form carbonates in both dry and water-bearing CO₂-rich environments, and the conditions under which they remain stable, are important for the development of technology to achieve long-term sequestration of CO₂ in geological formations or surface processing plants. (Bachu, 2008) Most of the focus on the thermodynamics of the MgO-H₂O-CO₂ system has historically been on H₂O-rich systems with dissolved concentrations of CO₂, however, and not on CO₂-rich systems. Many thermodynamic measurements have been conducted (Bénézech et al., 2011; Bénézech et al., 2013; Gautier et al., 2014; Hänchen et al., 2008; Königsberger et al., 1999) and thermodynamic models have been developed to predict formation of magnesium carbonate species in water. (Chaka and Felmy, 2014; Hänchen et al., 2008; Königsberger et al., 1999) Even so, the data are somewhat limited and can be highly variable with unknown reliability. For example, recent work by Bénézech highlighted that literature values reported for the solubility product of magnesite at room temperature varied by over five orders of magnitude from 10^{-10.3} to 10^{-5.1}, indicating the need for more reliable measurements. (Bénézech et al., 2011) One predictive technique, *ab initio* thermodynamics (AIT) has been shown to be capable of addressing this gap and the variability in measured data based on knowledge of

the mineral structure.(Chaka and Felmy, 2014) AIT relies on a combination of first principles density-functional theory (DFT) calculations and experimental values for the chemical potential of water and CO₂, and has demonstrated the ability to extend the predictive capability beyond the aqueous conditions measured in experiment to obtain free energies of formation for conditions ranging from ultra-high vacuum to the reference states of 1 bar H₂O and CO₂.(Chaka and Felmy, 2014) DFT is used to calculate the 0 K heats of formation, zero point vibrational energies, and the changes in free energy of the mineral as a function of temperature, as well as the 0 K heat of formation of the water and CO₂ molecules. Experimental data are used for the chemical potentials of water and CO₂ as a function of temperature and pressure. AIT has enabled reliable determination of the free energies of minerals such as nesquehonite and hydromagnesite above the 300 K experimental measurement, and for lansfordite from 0 to 1000 K, including its expected decomposition temperature relative to MgO.

This reactivity of minerals in contact with water-bearing scCO₂ is fundamentally different from the aqueous phase where dissolution/precipitation processes that depend on solution phase ion transport do not occur. Measurements of mineral solubility and ion activity are problematic in dry or water-bearing scCO₂.(McGrail, 2009) AIT, however, derives the thermodynamic values for minerals from the intrinsic properties of the crystalline structure itself calculated quantum mechanically, and does not rely on solubility measurements. All that is needed are the chemical potential values for water and CO₂ under supercritical conditions to predict mineral thermodynamics. Recently Springer and coworkers (2012) addressed this gap and determined the chemical potential of variable concentrations of water in CO₂-rich systems utilizing a combination of experimental

measurements and theoretical modeling.(Springer et al., 2012) This has enabled the development of a thermodynamic equilibrium model that yields chemical potentials for the water/CO₂ system from pure water to pure CO₂, including water-saturated scCO₂, from 273-573 K and 1 to 4000 bar. This model, OLI with Mixed Solvent Electrolyte database has been incorporated into OLISystems software.(OLI Software: Stream Analyzer and ESP (Electrolyte Simulation Program), 2012)

In this work we utilize the values of the water and CO₂ chemical potentials based on the work of Springer et al. (2012) to calculate the first phase diagrams for the Mg carbonates and their hydrates as a function of the chemical potentials of water and CO₂ from 1 bar total pressure at 275 K to 210 bar at 375 K for two conditions: water-saturated CO₂ (WS-CO₂) and for trace amounts of water (TW-CO₂) corresponding to a mole fraction of 10⁻⁹. Three phases of CO₂ occur along this spectrum: vapor, liquid, and supercritical fluid, spanning the conditions that would be encountered in subsurface CO₂ sequestration down to the deepest sites currently under consideration. For WS-CO₂ these phases are always in equilibrium with liquid water. For the TW-CO₂ condition, the small amount of water is present as a vapor at low temperature and pressure when CO₂ is the gas phase, or it is dissolved in the liquid or supercritical CO₂ at higher pressures.

In this study we focus on the magnesium-based minerals for several reasons. Mg and its minerals are geologically abundant, with Mg being the seventh most common element, MgO the fifth to seventh most abundant mineral in most of the earth's crust, and forsterite is the most abundant mineral above 400 km in the earth's mantle. Olivines and serpentines such as forsterite are widely available and can be economically mined on several continents for use in carbon capture. In addition, Mg forms the largest, most diverse group of hydrated

carbonate minerals among the divalent metals. How the stabilities of these minerals change in a liquid or scCO₂ environment with a range of water concentrations is not known.

Although AIT provides a thermodynamic framework, it can also provide insight into which mineral phases are metastable under given conditions and may be formed kinetically. For example, under aqueous conditions AIT indicated whether nesquehonite or hydromagnesite would be produced kinetically during the carbonation of brucite under different conditions, consistent with experimental observations.(Chaka and Felmy, 2014) In experiments with scCO₂, the carbonation of brucite yielded nesquehonite in one experiment(Schaefer et al., 2011) and magnesite in another.(Loring et al., 2012) The difference in product formation was hypothesized to be due to variation in the amount of water present. AIT can quantify the amount of water necessary to make nesquehonite metastable to brucite under different reaction conditions.

In this study we perform AIT calculations in a CO₂-rich environment on brucite, nesquehonite, hydromagnesite, and magnesite with respect to the oxides MgO, CO₂, and H₂O. This study complements our previous work on the thermodynamics of magnesium carbonates and hydrates under aqueous and UHV conditions.

2. Methods

2.1 Thermodynamic Properties of CO₂ and H₂O.

The newly parameterized OLI model was used to calculate the mole fractions, fugacity/activity coefficients, and phases for water and CO₂ from total pressures of 1 to 210 bar and temperatures from 275 K to 375 K for two conditions bracketing the range of water concentration: WS-CO₂ (water-saturated) and TW-CO₂ (trace water, 10⁻⁹ mole fraction

water). The fugacity for dry CO₂ was also obtained from the OLI model and compared to the real gas values in the IUPAC International Thermodynamic Tables of the Fluid State of Carbon Dioxide (Angus et al., 1976). In this work we also compare the impact of using the ideal gas properties on the mineral stabilities. The ideal gas thermodynamics pressure p and temperature T was determined by using the JANAF (Chase et al., 1985a; Chase et al., 1985b) values for water vapor at 1 bar as the reference state $p^0 = 1$ bar and applying the ideal gas law:

$$\Delta\mu_i(T, p) = \Delta\mu_i(T, p^0) + k_B T \ln(p/p^0) \quad (1)$$

An analogous procedure was followed for CO₂ using the IUPAC values for the $p^0 = 1$ bar reference state.

It is important to clarify the state used as the zero enthalpy reference $H^\circ(T_r)$ in the thermodynamic tables listing the chemical potentials for CO₂ and water in this work, as conventions can vary widely. JANAF assigns the vapor phase H₂O and CO₂ molecules at 298.15 K and 1 bar pressure to have zero enthalpy. The IUPAC convention for CO₂ is to assign the enthalpy reference state for enthalpy to be the same as entropy, namely the perfect crystal at 0 K. For this work it is most convenient to assign the enthalpy reference state to be the sublimated gas at 0 K, namely the single molecule, which is most accurately calculated by DFT. Therefore changing the JANAF reference state at 298.15 K to 0 K for water requires subtracting -9.904 kJ/mol for all the $H-H^\circ(T_r)$ values listed. For CO₂, the enthalpy of sublimation, 26.250 kJ/mol was subtracted from the values listed in the IUPAC tables. It should be noted that the Gibbs free energies used to determine the chemical potentials in the subsequent *ab initio* thermodynamics analysis are calculated from $H-H^\circ(T_r)$ and the entropy, rather than the Gibbs free energies of formation from the elements.

For a portion of the water-saturated $\text{H}_2\text{O}-\text{CO}_2$ system below T_c for CO_2 , CO_2 becomes a liquid at 205 K by 45 bar and by 75 bar at 300 K. For the liquid CO_2 phase region, the OLI model reports activities for water and dissolved CO_2 in equilibrium with water in the liquid CO_2 . To maintain a consistent set of values for the enthalpy reference state and the chemical potentials, the vapor pressures of water and CO_2 in equilibrium with the liquid water phase were calculated from the activities. The values calculated by the OLI model for $\mu_{\text{H}_2\text{O}}$ and μ_{CO_2} in the water-saturated and trace-water scCO_2 systems are given in Tables A.1-A.4 in the Appendix.

2.2 *Ab initio* Thermodynamics

Periodic all-electron *ab initio* calculations were performed using the generalized gradient approximation to the density functional of Perdew, Burke, and Ernzerhof (PBE)(Perdew et al., 1996) as implemented in the DMol³ code(Delley, 1990; Delley, 2000). A double-zeta plus polarization quality numerical atom-centered basis set with a real-space cut off of 4.4 Å was used. Lattice optimizations were performed using converged k-point sampling within the Monkhorst-Pack scheme.(Monkhorst and Pack, 1976)

A benchmarking of factors required to improve the reliability of DFT calculations for magnesite, periclase, brucite and the hydrated magnesium carbonates was conducted by Chaka and Felmy.(Chaka and Felmy, 2014) They determined the importance of including the zero-point vibrational energy (ZPE), which increases in proportion to the number of water molecules and hydroxyl groups and thus achieves a considerable magnitude in these hydrated mineral structures. In addition, including dispersion in the DFT Hamiltonian to describe the hydrogen bonding and $\text{Mg}\cdots\text{O}$ interactions improved the overall average of the

calculated structures and energies, with the method of Grimme(Grimme, 2004; Grimme, 2006; Grimme et al., 2010) yielding more accurate results than the Tkatchenko-Scheffler(Tkatchenko and Scheffler, 2009) approach. Including the Grimme dispersion improved 0 K heats of formation for brucite, magnesite, and nesquehonite, although hydromagnesite became worse. At first glance this would seem to be counter-intuitive that including dispersion would result in greater underestimation of the heat of formation given the number of water molecules and hydrogen bonding in hydromagnesite. In hydromagnesite, however, the $\text{Mg}_5(\text{CO}_3)_4(\text{OH})_2 \cdot 4\text{H}_2\text{O}$ stoichiometry indicates that there is less than one water molecule per Mg cation, plus the hydroxyl groups do not engage in hydrogen bonding. The heat of formation for nesquehonite, in contrast, which has three water molecules per Mg cation, does exhibit improvement in the heat of formation from an error of -8.59 to -7.33 kJ/mol.

The actual GGA error per hydrogen bond or $\text{Mg} \cdots \text{O}$ interaction is quite small using PBE with the Grimme dispersion, -5.0 kJ/mol and 4.4 kJ/mol respectively. In large unit cells such as hydromagnesite, however, these errors accumulate. These small errors are undoubtedly due to exchange/correlation (XC), as the exact XC functional is not yet known. Post-GGA functionals such as hybrids incorporating exact exchange or the Hubbard correction DFT+U have shown some improvement for some properties such as ordering of magnetic states and band gaps(Tran and Blaha, 2009), but have not shown systematic improvement for solid state thermodynamics over the efficient PBE used in this study.(Chaka et al., 2012; Lemire et al., 2005; Marsman et al., 2008) This is discussed in greater detail in the Appendix.

Hence the small errors in pairwise interactions for PBE for the hydrated magnesium carbonates are at the current limit of accuracy for DFT. One of the aims of AIT is to link the performance of DFT functionals with macroscopic thermodynamics to provide another means to validate theoretical developments in addition to electronic spectroscopy and drive the science of electronic structure forward. AIT is also intended to provide a framework that can incorporate experimental data as available to improve the thermodynamic predictions, and provide reasonable predictions on the basis of first principles calculations in the absence of such data, particularly for defects, substitutions, solid solutions, surfaces, nanoparticles, and hypothetical structures such as the Mg analogues of the calcium minerals monohydrocalcite and ikaite.(Chaka and Felmy, 2014) Therefore to improve the thermodynamic predictions and our understanding of the behavior of magnesium hydrates and carbonates in CO₂-rich environments, we apply the heat of formation corrections as reported in Chaka and Felmy. These corrections are best applied to the 0 K total energy of the mineral structures, as the calculated DFT vibrational partition functions for finite temperature effects was found to be very reliable. These corrected calculations are herein referred to as the PBE-G06-HFC level of theory, for the PBE functional, Grimme 2006 dispersion method (G06), and heat of formation corrections (HFC).

The methodology used for the AIT was originally developed to calculate free energies of nonstoichiometric, hydrated, or reconstructed surfaces of metal oxides (Reuter and Scheffler, 2002; Wang et al., 2000). How the AIT methodology was extended to hydrated carbonate minerals is described in detail in (Chaka and Felmy, 2014), and summarized briefly here. For the AIT calculations, the minerals are considered to be formed from reactions of the oxides, MgO, H₂O, and CO₂. Hence a mineral's free energy is

described as a function of the chemical potentials μ_{MgO} , μ_{H_2O} , and μ_{CO_2} . The chemical potentials for the oxides MgO, H₂O, and CO₂ are considered to be independent and the chemical potential of oxygen is treated as a dependent variable, as the geological conditions of interest are not in the temperature and pressure realm where the oxides would break down into Mg metal, H₂, elemental carbon, and O₂, respectively. In addition, the minerals investigated are stoichiometric with respect to MgO, H₂O, and CO₂ and do not undergo redox reactions. Hence the energy of the crystalline phase is defined as:

$$G_{xtl}(T, p, n_i) = E_{xtl}^{Total, 0K} + E_{xtl}^{vib} - n_1 \mu_{MgO}(T, p) - n_2 \mu_{H_2O}(T, p) - n_3 \mu_{CO_2}(T, p) \quad (2)$$

where n_i are the coefficients of MgO, H₂O, and CO₂ in the stoichiometric formula for the mineral, E_{xtl}^{vib} is the ZPE at 0 K plus the vibrational entropy and enthalpy at finite temperature and pressure for the mineral phase, and $\mu_i(T, p)$ is the chemical potential of species i obtained from

$$\mu_i(T, p) = E_i^{Total, 0K} + E_i^{ZPE} + \Delta\mu_i(T, p) \quad (3)$$

where $E_i^{Total, 0K}$, E_i^{ZPE} and $\mu_{MgO}(T, p)$ are calculated from GGA-G06-HFC, and $\Delta\mu_{H_2O}(T, p)$ and $\mu_{CO_2}(T, p)$ are taken from experimental thermodynamic tables or the OLI model. The real gas Gibbs free energies for $\Delta\mu_{H_2O}(T, p)$ are determined from the mole fractions χ_i and fugacity coefficients γ_i from the OLI model to determine the ideal gas pressure with the same free energy as the real gas. The free energy of the ideal gas is then calculated using the ideal gas law in Eq. 1 with $p^0 = 1$ bar reference values taken from the JANAF(Chase et al., 1985a; Chase et al., 1985b) tables. These values are shown in Tables A.1 and A.3 in the Appendix. Similarly for $\mu_{CO_2}(T, p)$, the OLI model was used to obtain the mole fractions and fugacities for CO₂ for saturated water conditions and for trace water,

i.e. 10^{-9} mole fraction of water. These values are presented in Tables A.2 and A.4 in the Appendix. The values found using the ideal gas law approach analogous to that for water above were compared with the real gas values from the IUPAC tables for CO_2 , and are presented in Tables 1 and 2. The IUPAC real gas values were used for the AIT analysis.

3.0 Results and Discussion

The results are organized into three subsections. The first section presents the chemical potential values and phases obtained for CO_2 and water. The second discusses the mineral thermodynamics from 275 K to 375 K and 1 to 210 bar for WS- CO_2 and for TW- CO_2 . The third section discusses using ideal gas approximations for real gas free energies.

3.1 Chemical potentials, phases, and reactivity of saturated- and low-water CO_2

In WS- CO_2 the concentration of water varies widely across the range of 275 K – 375 K and pressures from 1 to 210 bar, being high at low pressure and dropping rapidly as $p\text{CO}_2$ increases since water is not very miscible in a CO_2 -rich environment. The water concentrations calculated from the Springer et al. (2012) data in the OLI model are shown in Fig. 1. At 325 K (above T_c for CO_2) the highest water mole fraction is at a pressure of 1 bar (0.134) and drops more than 10-fold to 0.0100 by 15 bar, and half again to 0.0057 at 30 bar and higher. At 350 K the water concentration is slightly higher as water is more soluble in CO_2 at higher temperature, but follows the same trend; highest concentration of water is a mole fraction of 0.414 at 1 bar, dropping to 0.0302 by 15 bar and 0.0167 and below above 30 bar. 375 K is just above the boiling point of water, so at 1 bar total pressure the system

contains almost all water (0.8645 mole fraction) and little CO₂. But by 15 bar, the water fraction has dropped to 0.0771 and decreases down to 0.0199 at 210 bar.

At first glance it may seem that when water drops to these very low mole fractions in water-saturated liquid and scCO₂, the reactivity is also reduced and can be ignored. As long as the small amount of water in the CO₂-rich phase is in equilibrium with liquid water, however, it will have the same chemical potential and reactivity. This is reflected in the water chemical potential across the range of pressures shown in Fig. 2a and in Table 2 where despite the water phase changes and dramatic differences in mole fraction across the pCO₂ range, the water chemical potential changes very little irrespective of whether water is the dominant phase or less than a 2% mole fraction in scCO₂. For every 25 K increase in temperature, there is roughly a 2 kJ/mol decrease (more negative) in chemical potential of water.

The trace water system where water is *not* in equilibrium with liquid water, however, does exhibit very different reactivity across the range of conditions. The chemical potential of water at a 10⁻⁹ mole fraction is 25.33 kJ/mol lower (more negative) at 275 K and 50.24 kJ/mol lower at 375 K and 90 bar total pressure. Hence we expect CO₂-H₂O systems with trace amounts of water to dehydrate minerals to a much greater extent than water-saturated CO₂-H₂O, and the extent of this dehydration can be quantified. Intermediate concentrations of water will have intermediate reactivities.

3.2 Mineral Stabilities

In this section we quantify how the water and carbon dioxide chemical potentials impact the stability of the hydrated and carbonated magnesium minerals in the CO₂-rich

systems. The results are shown in Fig. 3 and Tables 3 and 4 for magnesite, brucite, nesquehonite, and hydromagnesite for 275-375 K and pressures from 1 bar to 210 bar. The chemical potentials of the minerals are shown relative to MgO and are equivalent to the formation energies from MgO, H₂O, and CO₂. Mineral stability increases the lower (or more negative) the chemical potential. The grey horizontal line at 0 kJ/mol represents the free energy of MgO. Where free energy lines for the other mineral phases cross the MgO reference line, it indicates the temperature at which the mineral becomes unstable with respect to generation of the oxide and release of CO₂ and/or H₂O. Where free energy lines for two minerals cross, that indicates the temperature for the phase boundary between them under the given conditions.

Fig. 3a shows the AIT for these minerals under ambient conditions, where pCO₂ is 400 ppm and μ_{H_2O} is equal to the vapor pressure of water in equilibrium with liquid water at 298.15K and 1 bar, namely 32 mbar. At 1 bar total pressure in the WS-CO₂ system where pCO₂ increases from 400 ppm to 0.965 bar, shown by the solid lines in Fig. 3b, all minerals with the exception of brucite become significantly more stable (lower in energy). Nesquehonite shifts from becoming unstable with respect to brucite at 291 K to 359 K, and to MgO from 325 K to well above 375 K when the pCO₂ increases. These results indicate that shifting the CO₂ concentration from 400 ppm to 0.965 bar increases the temperature range that MgO and brucite can be carbonated to form nesquehonite (kinetically) by 50-60 K. Similarly, hydromagnesite shifts from becoming unstable with respect to brucite at 321 K, to being more stable than brucite across the entire 275-375 K range. Above 360 K where nesquehonite becomes less stable than brucite, carbonation of brucite at higher pCO₂ may result in formation of metastable hydromagnesite. Magnesite, as expected, shifts to lower

chemical potential (more stable) by -23.18 kJ/mol at 275 K and -51.02 kJ/mol at 375 K.

Over time, the kinetic products of brucite carbonation (nesquehonite and hydromagnesite) will transform to magnesite under the right conditions. (Hopkinson et al., 2008; Kazakov et al., 1959; Qafoku et al., 2015; Sandengen et al., 2008; Sayles and Fyfe, 1973; Stevula et al., 1978; Zhang, 2000)

At first it may seem counterintuitive that increasing CO₂ pressure will stabilize the hydrated carbonate minerals relative to liquid water under ambient conditions so much more than brucite, but the lower chemical potential of CO₂ has a significant stabilization effect on the carbonate group in nesquehonite thus lowering its free energy, even above the boiling point of water at 373 K.

The relative stabilities of the hydrated magnesium minerals are dramatically changed in the CO₂-rich environment when the water concentration is lowered from saturation to 10⁻⁹ mole fraction, which at 1 bar total pressure corresponds to 10⁻⁶ mbar. These conditions are represented by the dashed lines in Fig. 3b. Nesquehonite and brucite are completely destabilized with respect to MgO, let alone magnesite. Hydromagnesite is more stable with respect to MgO, H₂O, and CO₂ up to ~320 K, but above that will decompose. Magnesite, on the other hand, becomes slightly more stable, gaining 7 kJ/mol at 375 K. Under these low water conditions, nesquehonite is destabilized relative to brucite across the entire range, so that upon carbonation brucite may kinetically yield hydromagnesite first, followed by slow transformation to magnesite.

Fig. 3b-g shows that as pressure is increased, the stability of mineral phases increases. Under saturated water conditions, nesquehonite and hydromagnesite are comparable in energy at 300 K and below; above 300 K hydromagnesite is more stable than

nesquehonite. These results are consistent with the recent work of Qafoku et al. (2015), who observed that both nesquehonite and hydromagnesite form initially in water in equilibrium with scCO_2 at high pCO_2 (90 and 111 bar) and 308 K and 323 K, before slowly transforming to magnesite over a period of several months.(Qafoku et al., 2015) That nesquehonite forms along with hydromagnesite above 300 K rather than just hydromagnesite supports the hypothesis that metastable products will form more quickly if their structure is simple compared to more complex materials.(Hopkinson et al., 2012)

Brucite stability remains largely unchanged as pCO_2 is increased in the water-saturated conditions. Under trace water conditions, the stability sequence of nesquehonite < brucite < hydromagnesite remains unchanged, with nesquehonite the most destabilized of all minerals. Even at 165 bar total pressure when the water partial pressure increases to 1.79 bar in the trace water case at 10^{-9} mole fraction, nesquehonite is still higher in energy than MgO across the entire temperature range. Hydromagnesite is much less destabilized by the dehydration of the system going from WS- CO_2 to TW- CO_2 , remaining metastable relative to MgO throughout the temperature range. This may be one reason why hydromagnesite is so much more abundant in nature than nesquehonite.(Gautier et al., 2014) If a geological formation loses water to the point where it is no longer in equilibrium with a water reservoir, nesquehonite will become destabilized and likely transform to hydromagnesite, as it did at 325 K in a sealed flask in an experiment by Davies and Bubela.(Davies and Bubela, 1973) This is true for both the ambient aqueous conditions as well as the CO_2 -rich region. Magnesite, of course, remains the most stable throughout, but may be kinetically inhibited from forming from hydromagnesite in very low water environments.

The stability of the minerals brucite, nesquehonite, hydromagnesite, and magnesite respond very differently to changes in temperature, pressure, and water concentration, summarized in Fig 5. At all pressures the change in H₂O concentration has a dramatic effect on nesquehonite stability much more so than differences in temperature or pressure. Changes in hydromagnesite stability are comparable to brucite, and magnesite stability shows little sensitivity to changes in either water mole fraction, temperature, or pressure. So if minerals experience dehydrating conditions subsurface, they will ultimately transform to magnesite or be trapped kinetically as hydromagnesite, thus retaining CO₂ trapped underground.

3.3 Evaluation of the Ideal Gas Approximation

The forces between molecules in a real gas can be considerable, resulting in significant pressure differences between the real and ideal gas, as shown in Fig. 5. For example, the fugacity to ideal gas ratio for CO₂ at 200 bar and 275 K is 0.193. Real gas data, however, are not always readily available. Hence free energies based on the ideal gas can be very convenient to use if the errors introduced do not significantly affect the results. The recent determination of free energies of water in CO₂-rich environments enables the assessment of the error in using the ideal gas approximation for the chemical potentials of water and CO₂ and the impact on mineral thermodynamics, serving as a guide as to when the ideal gas approximation can be used. For CO₂ we also compare the differences between the calculated values for CO₂ from the OLI model and the IUPAC real gas data. The water-saturated scCO₂ data are determined from 325 to 375 (above T_c) for CO₂.

The pressures for the ideal gases used in the comparison were calculated simply from $p_i = \chi_i p_{tot}$ where p_i is the ideal gas partial pressure of either H₂O or CO₂, χ_i is the mole fraction calculated from the OLI model, and p_{tot} is the total pressure. The free energies of the CO₂ ideal gas were obtained from the ideal gas molar entropies and enthalpies in the IUPAC reference.(Angus et al., 1976) The ideal gas values for water were calculated from the JANAF table values using the ideal gas law in Eq. 1.

The results for the real and ideal gas chemical potential comparisons are shown in Table 1 for the dry CO₂ and trace water (10⁻⁹) case and in Table 2 for the water-saturated scCO₂. The error for the OLI model for CO₂ is very small for both the trace and saturated water cases, being less than 0.2 kJ/mol over most of the range. For the trace water case the error in the OLI model for CO₂ is slightly higher but still under 2 kJ/mol at 300 K and 75-100 bar, and at the highest pressure considered (210 bar) at 375 K. CO₂ values for the OLI model in the water-saturation case are extremely good, less than 0.5 kJ/mol except for the 1 bar values at 350 and 375 K, where the error is -1.47 kJ/mol and -6.14 kJ/mol, respectively. The errors in chemical potential for the ideal gas approximation in the trace water case are also small: less than 0.1 kJ/mol for 300 K and the other temperatures at 1 bar, between 1.4 and 1.9 kJ/mol at 75 bar, and ~3.6-3.6 kJ/mol at higher pressures. In the water-saturated scCO₂ case, the ideal gas approximation still works reasonably well, with errors on the order of 4 kJ/mol at the highest pressures calculated at each temperature, namely 115 to 210 bar. We also tested the variation in the trace water case if the fugacity coefficient from the water-saturated case was used; errors were extremely small in this case as well, being under 0.3 kJ/mol.

The impact on mineral stabilities from the variations in chemical potential due to the ideal gas approximation has been quantified. The results shown in Fig. 6 indicate that these variations from using the ideal gas approximation do not significantly change the mineral thermodynamics. The only difference of note is that nesquehonite in the water-saturated CO₂ case becomes lower in chemical potential by 6.42 kJ/mol, becoming slightly lower in energy (more stable) than hydromagnesite below 345 K. This difference would affect kinetic results seen in laboratory synthesis and increase the likelihood of natural nesquehonite deposits, but not for the long term geological timeframe where the overwhelming stability of magnesite relative to the rest of the hydrated minerals remains unchanged.

4. Conclusions

The presence of water in CO₂-rich systems has a significant impact on the formation and stability of the hydrated magnesium carbonate minerals and magnesite and cannot be ignored. When CO₂ is in equilibrium with water, the CO₂-H₂O system undergoes a series of phase changes as the pressure is increased from 1 to 210 bar in the temperature range of 275 K to 375 K: with CO₂ changing from gas to liquid to supercritical fluid, and water going from high concentration at low pCO₂ to less than 1% by weight in condensed phase CO₂. Throughout these dramatic phase and concentration changes, water maintains the high degree of reactivity consistent with the chemical potential of liquid water. The AIT framework and results presented here quantifies the impact of water chemical potential in CO₂-rich environments on mineral stabilities addressing a gap in available thermodynamic data. Under water-saturated scCO₂ conditions the hydrated minerals exhibit the same

sequence of stability relative to magnesite and MgO: $\text{MgO} < \text{brucite} < \text{nesquehonite} < \text{hydromagnesite} < \text{magnesite}$, except above 359 K at 1 bar where brucite becomes more stable than hydromagnesite. Under low water conditions (10^{-9} mole fraction) where water is not in equilibrium with CO_2 , this sequence of stability changes to $\text{nesquehonite} < \text{brucite} < \text{hydromagnesite} < \text{magnesite}$, with both brucite and nesquehonite unstable with respect to MgO across most of the conditions examined in this study. These stability sequences indicate which carbonate minerals are metastable and may form kinetically when MgO and brucite are carbonated in CO_2 -rich environments. If dehydrating conditions occur in long-term storage, any remaining nesquehonite that has not transformed to hydromagnesite or magnesite will lose both its water and CO_2 and form MgO. Hydromagnesite or magnesite, however, will safely trap CO_2 indefinitely whether under water-saturated or dehydrating conditions at the temperatures and pressures investigated.

Using the free energies for water from the ideal gas approximation does not affect the relative mineral stabilities under CO_2 -rich conditions. It must be emphasized, however, that accurate fugacities are essential for determining the solubility of water in CO_2 and vice versa. But because of water's low solubility in CO_2 , the ideal gas values constitute the upper limit on the solubility and represent a reasonable approximation for predicting mineral stabilities under CO_2 -rich conditions.

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Appendix

A.1. Performance of GGA and post-GGA functionals

The post-GGA functionals (hybrids incorporating exact exchange, the Hubbard correction DFT+U, and the more computationally intensive self-interaction corrections (SIC) and Green's function-based approaches (GW)) designed to correct the self-interaction of localized electrons have improved the known GGA problem of calculating band gaps that are too small or yielding wrong ordering of bulk magnetic states. The improvement is not systematically consistent, however. For MgO band gaps, for example, the post-GGA functionals MBJLDA (Heyd et al., 2005; Tran and Blaha, 2009), HSE (Heyd et al., 2005), G_0W_0 (Marsman et al., 2008), and GW(Shishkin et al., 2007) yield band gaps of 7.17, 6.67, 7.25 and 9.16 eV respectively, compared to the LDA value of 4.70 eV, our PBE value of 5.70 eV, and the experimental value of 7.83 eV.

Unfortunately parameterization procedures to improve band gaps and magnetic ordering on small sets of materials can yield inconsistent or unphysical results on other properties such as thermodynamics. Early work by Heyd and coworkers (Heyd et al., 2003) tested hybrid functionals B3LYP, PBE0, and ω PBEh as well as PBE on the G2 data sets of small molecules and found the hybrid functionals had indeed a better mean average error for heats of formation than PBE. More recent work on the solid state by Marsman and

coworkers, however, compared PBE with three hybrid functionals with varying amounts of exact exchange (PBE0, HSE03, and B3LYP) on a set of metallic and non-metallic solids and found that exact exchange improved some properties for some materials, but not others. The improvement was not systematic, and for heats of atomization PBE had the lowest mean absolute relative error. (Marsman et al., 2008) Others have found that the amount of exact exchange or Hubbard U parameter incorporated in post-GGA functionals needed to correct heats of formation varies with the chemical composition and stoichiometry of the material, even within a given class such as manganese oxides.(Franchini et al., 2007; Haas et al., 2009)

For surfaces and solids with defects, substitutions, interstitial impurities, or other sources of nonstoichiometry for which the AIT method has been effectively utilized, the inconsistency of post-GGA functionals can be even more problematic. The increased electron-electron repulsion incorporated into the DFT+U approach to open the band-gap, for example, can cause an excessive destabilization of surfaces and materials with excess oxygen. The oxygen chemical potential required to oxidize the hematite $\alpha\text{-Fe}_2\text{O}_3$ (0001) surface calculated by GGA+U, for example, corresponded to an unphysical $p(\text{O}_2)$ of 200+ bar (Rohrbach et al., 2004), whereas PBE predicted a $p(\text{O}_2)$ of 1 mbar at 1040 K and 10^{-2} mbar at 870 K, in quantitative agreement with experiment.(Lemire et al., 2005) Similarly AIT calculations utilizing PBE were also in quantitative agreement with the experimental conditions for the redox threshold for the SnO_2 (101) surface.(Batzill et al., 2004) The same increased electron-electron repulsion in anions with post-GGA functionals also yielded unphysical results for the incorporation of interstitial oxygens in UO_2 . As described in (Chaka et al., 2012), many of the post-GGA functionals result in endothermic formation

energies for oxygen interstitials in UO_2 , which is inconsistent with the propensity of UO_2 to readily absorb oxygen (10% by weight) and form $\text{UO}_{2.25}$.

Thus it is clear that there is extensive room for improvement in DFT functionals to provide consistent results for *all* properties of materials, and that PBE is still one of the most reliable overall workhorses for thermodynamics at a level of efficiency enabling calculation of large mineral systems despite the underestimation of bandgaps. (GW is prohibitively expensive for most of the minerals modeled in this study.)

Section A.2.

This section contains the numerical data tables for the chemical potentials for CO_2 and H_2O in the water-saturated CO_2 -rich system and with (10^{-9} mole fraction) water.

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Table 1

Comparison of ideal gas chemical potentials for CO₂ and H₂O in the trace water CO₂-rich system with real gas values for dry CO₂ from IUPAC and for H₂O from the OLI model in kJ/mol. In addition, an assessment of the error from using the water fugacity coefficients for the water-saturated CO₂-rich system (WS ϕ_X) for the trace water system (TW ϕ_X).

K	Bar	μ CO ₂ (kJ/mol)					μ H ₂ O (kJ/mol)				
		IUPAC	OLI Model	Error OLI Model	Ideal Gas	Error Ideal Gas	TW ϕ_X	Ideal Gas	Error Ideal Gas	SW ϕ_X	Error SW ϕ_X
300	1	-54.799	-54.736	0.063	-54.753	0.046	-97.930	-97.940	-0.010	-97.933	-0.003
	75	-45.225	-43.950	1.275	-44.881	0.344	-87.134	-87.167	-0.033	-87.134	0.000
	100	-45.084	-43.232	1.852	-44.223	0.861	-86.416	-86.449	-0.033	-86.416	0.000
325	1	-60.175	-60.105	0.070	-60.129	0.045	-106.973	-106.989	-0.016	-106.980	-0.008
	75	-49.341	-49.259	0.082	-50.255	-0.914	-97.163	-95.318	1.846	-97.192	-0.029
	90	-49.045	-49.023	0.022	-49.838	-0.793	-97.475	-94.825	2.650	-97.527	-0.053
	115	-48.821	-48.645	0.176	-49.277	-0.456	-97.962	-94.162	3.799	-98.086	-0.124
350	1	-65.620	-65.542	0.077	-65.572	0.048	-116.064	-116.086	-0.022	-116.081	-0.017
	75	-53.723	-53.622	0.101	-55.697	-1.974	-104.936	-103.517	1.420	-104.985	-0.049
	165	-52.323	-52.133	0.190	-53.893	-1.570	-105.047	-101.221	3.825	-105.238	-0.191
375	1	-71.138	-71.057	0.080	-71.090	0.048	-125.214	-125.240	-0.027	-125.235	-0.021
	90	-57.768	-57.645	0.123	-60.799	-3.031	-112.621	-111.205	1.416	-112.722	-0.100
	210	-57.166	-55.747	1.418	-58.861	-1.695	-112.186	-108.562	3.624	-112.478	-0.292

Table 2

Comparison of ideal gas chemical potentials for CO₂ and H₂O in the saturated-water CO₂-rich system with real gas values for dry CO₂ from IUPAC and for H₂O from the OLI model in kJ/mol.

K	bar	μ CO ₂ (kJ/mol)					μ H ₂ O (kJ/mol)		
		IUPAC	OLI Model	Error OLI Model	Ideal Gas	Error Ideal Gas	OLI Model	Ideal Gas	Error Ideal Gas
325	1	-60.175	-60.495	-0.321	-60.521	-0.026	-56.986	-56.994	-0.008
	75	-49.341	-49.269	0.072	-48.469	0.799	-56.912	-55.038	1.875
	90	-49.045	-48.946	0.099	-47.979	0.967	-56.882	-54.052	2.831
	115	-48.821	-48.623	0.198	-47.318	1.305	-56.833	-52.909	3.924
350	1	-65.620	-67.092	-1.472	-67.126	-0.035	-58.972	-58.977	-0.005
	75	-53.723	-53.649	0.074	-53.031	0.618	-58.872	-57.403	1.469
	90	-53.338	-53.402	-0.064	-52.502	0.900	-58.848	-56.742	2.105
	165	-52.323	-52.164	0.159	-50.740	1.424	-58.725	-54.709	4.017
375	1	-71.138	-77.275	-6.137	-77.326	-0.051	-61.747	-61.752	-0.005
	90	-57.768	-57.707	0.061	-57.120	0.587	-60.961	-59.445	1.517
	210	-56.322	-55.807	0.516	-54.476	1.331	-60.760	-56.844	3.916

Table 3

Mineral chemical potentials at 1 bar in kJ/mol for ambient, WS-CO₂ and TW-CO₂ conditions.

K	Brucite			Magnesite			Nesquehonite			Hydromagnesite		
	Ambient	WS-CO ₂	TW-CO ₂	Ambient	WS-CO ₂	TW-CO ₂	Ambient	WS-CO ₂	TW-CO ₂	Ambient	WS-CO ₂	TW-CO ₂
275	-31.82	-30.33	5.20	-50.93	-69.32	-69.27	-47.65	-51.05	55.60	-44.29	-53.86	-18.29
300	-27.35	-28.97	13.85	-44.98	-64.46	-64.48	-28.50	-48.45	79.96	-35.14	-50.87	-8.07
325	-22.81	-27.96	22.04	-38.97	-59.78	-60.10	-8.36	-40.60	109.09	-25.66	-46.24	3.51
350	-18.28	-26.90	30.22	-32.96	-54.26	-55.74	11.77	-31.70	138.17	-16.18	-40.70	15.23
375	-13.75	-25.12	38.38	-26.95	-45.24	-51.37	31.92	-17.10	167.24	-6.72	-31.63	26.95

Table 4Mineral chemical potentials at 15, 90, and 165 bar in kJ/mol for WS-CO₂ and TW-CO₂.

	Brucite		Magnesite		Nesquehonite		Hydromagnesite	
	WS-CO ₂	TW-CO ₂	WS-CO ₂	TW-CO ₂	WS-CO ₂	TW-CO ₂	WS-CO ₂	TW-CO ₂
<u>15 bar</u>								
275	-30.32	-0.99	-75.31	-75.25	-57.01	31.04	-58.65	-29.26
300	-28.97	7.09	-71.12	-71.06	-55.14	53.11	-56.20	-20.09
325	-27.97	14.72	-67.32	-67.28	-48.18	79.95	-52.28	-9.55
350	-26.92	22.33	-63.49	-63.49	-40.98	106.76	-48.10	1.14
375	-25.79	29.93	-59.56	-59.72	-33.45	133.56	-43.76	11.83
<u>90 bar</u>								
275	-30.42	-5.09	-76.82	-77.15	-58.82	16.84	-59.95	-34.88
300	-29.07	2.62	-74.14	-74.14	-58.44	36.62	-58.71	-27.03
325	-28.06	9.88	-71.33	-71.23	-52.46	61.47	-55.58	-17.56
350	-27.02	17.12	-67.95	-68.02	-45.76	86.59	-51.78	-7.69
375	-25.90	24.34	-64.80	-64.74	-39.03	111.76	-48.07	2.22
<u>165 bar</u>								
275	-30.55	-6.48	-76.67	-77.42	-59.07	12.41	-59.96	-36.49
300	-29.20	1.11	-74.24	-74.46	-58.95	31.76	-58.93	-28.80
325	-28.17	8.24	-71.71	-71.78	-53.16	56.01	-55.91	-19.63
350	-27.14	15.35	-69.19	-68.91	-47.37	80.40	-52.89	-10.17
375	-26.03	22.45	-65.99	-65.89	-40.59	104.95	-49.15	-0.58

Appendix

Table A.1

μCO_2 in the water-saturated CO_2 -rich system (kJ/mol).

Bar	275 K	300 K	325 K	350 K	375 K
1	-49.4310	-54.8250	-60.4952	-67.0915	-77.2748
15	-43.4375	-48.1606	-52.9557	-57.8660	-62.9560
30	-42.1055	-46.6273	-51.2296	-55.9370	-60.7825
45	-41.8429	-45.8292	-50.2955	-54.8752	-59.5860
60	-41.8733	-45.3510	-49.6896	-54.1655	-58.7766
75	-41.9024	-45.1653	-49.2688	-53.6490	-58.2418
90	-41.9327	-45.1454	-48.9459	-53.4015	-57.7070
115	-41.9624	-45.1116	-48.6230	-52.9891	-57.3111
165	-42.0815	-45.0439	-47.8312	-52.1642	-56.5193
210	-42.1706	-44.9833	-47.1186	-51.4516	-55.8067

Table A.2 $\mu\text{H}_2\text{O}$ in the water-saturated CO_2 -rich system (kJ/mol).

Bar	275 K	300 K	325 K	350 K	375 K
1	-53.4359	-55.1278	-56.9856	-58.9720	-61.7469
15	-53.4465	-55.1206	-56.9717	-58.9549	-61.0720
30	-53.4462	-55.1102	-56.9550	-58.9356	-61.0512
45	-53.4276	-55.0952	-56.9368	-58.9153	-61.0298
60	-53.4006	-55.0776	-56.9171	-58.8942	-61.0076
75	-53.3736	-55.0527	-56.9123	-58.8720	-60.9845
90	-53.3466	-55.0255	-56.8824	-58.8475	-60.9615
115	-53.2819	-54.9798	-56.8327	-58.8068	-60.9195
165	-53.2120	-54.8893	-56.8073	-58.7253	-60.8355
210	-53.1311	-54.8142	-56.7576	-58.6846	-60.7599

Table A.3

μCO_2 in the CO_2 -rich system with trace (10^{-9} mole fraction) water (kJ/mol).

Bar	275 K	300 K	325 K	350 K	375 K
1	-49.4798	-54.7990	-60.1746	-65.6195	-71.1375
15	-43.5051	-48.2210	-53.0019	-57.8625	-62.7953
30	-42.1761	-46.6930	-51.2909	-55.9745	-60.7449
45	-41.8116	-45.8950	-50.3621	-54.9320	-59.5905
60	-41.7409	-45.4190	-49.7585	-54.2300	-58.8050
75	-41.6711	-45.2250	-49.3410	-53.7230	-58.2234
90	-41.6018	-45.1410	-49.0450	-53.3380	-57.7679
115	-41.5108	-45.0312	-48.8212	-52.9922	-57.3362
165	-41.2658	-44.7459	-48.4125	-52.3231	-56.4574
210	-41.1921	-44.6646	-48.3269	-52.2292	-56.3224

Table A.4

$\mu_{\text{H}_2\text{O}}$ in the CO_2 -rich system with trace (10^{-9} mole fraction) water (kJ/mol).

Bar	275 K	300 K	325 K	350 K	375 K
1	-88.9688	-97.9402	-106.9888	-116.0856	-125.2403
15	-82.7746	-91.1829	-99.6683	-108.2020	-116.7936
30	-81.1891	-89.4532	-97.7946	-106.1841	-114.6316
45	-80.2617	-88.4415	-96.6985	-105.0037	-113.3669
60	-79.6037	-87.7236	-95.3176	-104.1662	-112.4696
75	-79.0933	-87.1668	-95.3176	-103.5166	-111.7736
90	-78.6762	-86.7119	-94.8248	-102.9859	-111.2049
115	-78.1155	-86.1002	-94.1621	-102.2723	-110.4403
165	-77.2898	-85.1994	-93.1862	-101.2213	-109.3143
210	-76.7382	-84.5976	-92.5343	-100.5192	-108.5621

Figure

Fig. 1. Mole fraction of water in saturated CO₂ from 275 to 375 K calculated from the Springer et al. (2012) data incorporated into the OLI Model.

Fig. 2. Chemical potential of water showing slow variation as pressure increases even though mole fraction can change dramatically.

(a)

(b)

(c)

(d)

(e)

Fig. 3. Results of *ab initio* thermodynamics for mineral stabilities at (a) 1 bar and ambient conditions (Chaka and Felmy, 2014), and (b) 1 bar (c) 15 bar, (d) 90 bar, and (e) 165 bar total pressures under CO_2 -rich conditions.

Fig. 4. Summary of how mineral stabilities change with water concentration, pressure, and temperature. The color of the bars indicates different pressures: green (1bar), purple (30 bar), blue (75 bar), and red (165 bar). The magnitude of the bar indicates the difference in mineral free energy for the water-saturated and the trace water chemical potentials at 275 K and at 375 K, illustrated by the double arrows between the solid and dashed red lines in the insert. The greater the change in mineral free energy (the longer the bar), the more the mineral is destabilized by dehydration.

Fig. 5. Ratio of fugacity to pressure for CO₂.

Fig. 6. Comparison of mineral stabilities calculated using chemical potentials from real gases (solid lines) and the ideal gas approximation (dashed lines).