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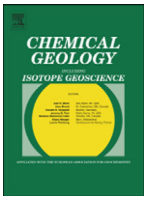

Ab initio thermodynamics of magnesium carbonates and hydrates in water-saturated supercritical CO_2 and CO_2-rich regions

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ABSTRACT

ab initio Thermodynamics is used to determine how free energies of magnesium carbonates and hydrates in a CO_2-rich environment change with water concentration across a range temperature and pressure relevant to geochemistry and carbon sequestration (275 K to 375 K and pCO_2 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 CO_2 and H_2O. The impact of water in supercritical CO_2 ($scCO_2$), 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 $scCO_2$ and hence may be expected to result kinetically from carbonation of these minerals during CO_2 sequestration. Under dehydrating conditions nesquehonite destabilizes rapidly, whereas hydromagnesite is much more likely to persist in a CO_2-rich environment, consistent with the observations that hydromagnesite is widespread in nature and nesquehonite is relatively rare.

1. Introduction

At the present time, geological trapping appears to be the most promising option for large-capacity sequestration of point source CO_2 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). CO_2 can be trapped underground structurally, stratigraphically, hydrodynamically, or dissolved in aquifers or petroleum recovery sites. Mineralization of CO_2 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 CO_2 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 CO_2-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 $MgCO_3 \cdot 2H_2O$, nesquehonite $MgCO_3 \cdot 3H_2O$, and lansfordite $MgCO_3 \cdot 5H_2O$) or basic hydroxides (hydromagnesite $Mg_5(CO_3)_4(OH)_2 \cdot 4H_2O$), artinite ($Mg_2(CO_3)(OH)_2 \cdot 3H_2O$), dypingite ($Mg_5(CO_3)_4(OH)_2 \cdot 5H_2O$), and several more basic carbonates analogous to dypingite but with additional water molecules (Cheng and Li, 2009; Hales et al., 2008; Hänchen 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 (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 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).

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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 pCO_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 be may of equal if not greater importance than aqueous systems for subsurface carbon sequestration (McGrail et al., 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 ($CaAl_2Si_2O_8$) and portlandite ($Ca(OH)_2$), 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 pCO_2 above 54.4 bar (Béarat 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 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 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 $\mu mol/m^2$ 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 $scCO_2$, 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 $scCO_2$ 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 CO_2 with mineral phases to form carbonates in both dry and water-bearing CO_2-rich environments, and the conditions under which they remain stable, are important for the development of technology to achieve long-term sequestration of CO_2 in geological formations or surface processing plants (Bachu, 2008). Most of the focus on the thermodynamics of the $MgO—H_2O—CO_2$ system has historically been on H_2O-rich systems with dissolved concentrations of CO_2, however, and not on CO_2-rich systems. Many thermodynamic measurements have been conducted (Bénézeth et al., 2011; Bénézeth 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 Bénézeth 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 (Bénézeth 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 CO_2, 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 H_2O and CO_2 (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 CO_2 molecules. Experimental data are used for the chemical potentials of water and CO_2 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 $scCO_2$ is fundamentally different from the aqueous phase where dissolution/reprecipitation 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 $scCO_2$ (McGrail et al., 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 CO_2 under supercritical conditions to predict mineral thermodynamics. Recently Springer et al. (2012) addressed this gap and determined the chemical potential of variable concentrations of water in CO_2-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/CO_2 system from pure water to pure CO_2, including