



# Water and carbon dioxide adsorption at olivine surfaces



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## ABSTRACT

Divalent cation-rich silicate minerals such as olivines have a high potential for carbonation reaction and thus their reactivity with water/carbon dioxide mixed fluids is critical to understanding chemical interactions relevant to carbon dioxide capture and sequestration. Therefore, plane-wave density functional theory (DFT) calculations were performed to simulate water and carbon dioxide adsorption at the (010) surface of five olivine minerals, namely, forsterite ( $\text{Mg}_2\text{SiO}_4$ ), calcio-olivine ( $\text{Ca}_2\text{SiO}_4$ ), tephroite ( $\text{Mn}_2\text{SiO}_4$ ), fayalite ( $\text{Fe}_2\text{SiO}_4$ ), and Co-olivine ( $\text{Co}_2\text{SiO}_4$ ). Adsorption energies per water molecule obtained from energy minimizations varied from  $-100 \text{ kJ mol}^{-1}$  for tephroite to  $-148 \text{ kJ mol}^{-1}$  for calcio-olivine at sub-monolayer coverage and became less exothermic as coverage increased. In contrast, carbon dioxide adsorption energies at sub-monolayer coverage ranged from  $-44 \text{ kJ mol}^{-1}$  for fayalite to  $-83 \text{ kJ mol}^{-1}$  for calcio-olivine. Therefore, the DFT calculations show a strong driving force for carbon dioxide displacement by water at the surface of all olivine minerals in a competitive adsorption scenario. Additionally, adsorption energies for both water and carbon dioxide were found to be more exothermic for the alkaline-earth (AE) olivines than for the transition-metal (TM) olivines and to not correlate with the solvation enthalpies of the corresponding divalent cations. However, a correlation was obtained with the charge of the surface divalent cation indicating that the more ionic character of the AE cations in the olivine structure relative to the TM cations leads to greater interactions with adsorbed water and carbon dioxide molecules at the surface and thus more exothermic adsorption energies for the AE olivines. For calcio-olivine, which exhibits the highest divalent cation charge of the five olivines, ab initio molecular dynamics simulations showed that this effect leads both water and carbon dioxide to react with the surface and form hydroxyl groups and a carbonate-like species, respectively.

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## 1. Introduction

Olivines are orthosilicate minerals that are common in the Earth's subsurface and are particularly abundant in the Earth's upper mantle. In the olivine structure, silica tetrahedra are not polymerized and are instead connected by divalent metal cations in octahedral coordination. This structural feature is thought to lead to their weak resistance to weathering, as the olivine structure can be broken down simply by rupture of the weaker metal–oxygen bonds. Therefore, olivines are a significant source of divalent cations and are thus susceptible to undergo carbonation reactions. This makes olivine minerals of particular interest in the context of carbon capture and sequestration, as their high reactivity and divalent cation content could enable long-term carbon sequestration by mineral trapping via carbonation reactions (Oelkers et al., 2008). For example, despite low porosity and permeability, formations consisting predominantly of the ultramafic rock peridotite are potentially attractive sites for permanent carbon dioxide sequestration because of their high olivine content and thus significant potential for carbon dioxide mineralization (Matter and Kelemen, 2009).

Consequently, much effort has been concentrated on studying the carbonation of olivine minerals in contact with carbon dioxide-saturated aqueous solutions (Giammar et al., 2005; Béarat et al., 2006; Dufaud et al., 2009; Prigiobbe et al., 2009; King et al., 2010; Daval et al., 2011; Olsson et al., 2012). However, the caprock's pore space near the injection bore well at a supercritical carbon dioxide ( $\text{scCO}_2$ ) injection site is expected to be permeated by  $\text{scCO}_2$  containing varying amounts of water as the injected dry  $\text{CO}_2$  migrates and creates dehydration fronts (Nordbotten and Celia, 2006). Therefore, the reactivity of caprock minerals with water-bearing supercritical  $\text{CO}_2$  fluids (WBSF) constitutes a critical aspect of the chemistry of carbon sequestration (McGrail et al., 2009). As a result, there has been recently an increasing focus on mineral reactivity in WBSF with water contents up to water saturation concentration (Regnault et al., 2005; McGrail et al., 2009; Regnault et al., 2009; Schaefer et al., 2011; Loring et al., 2012; Miller et al., 2013), including several studies carried out at our laboratory on the reactivity of members of the olivine series (Kwak et al., 2010, 2011; Loring et al., 2011; Felmy et al., 2012; Qafoku et al., 2012, in press; Schaefer et al., 2013).

One of the major findings of these recent studies is that the reactivity of olivine minerals with WBSF is dependent on the water content, whereby the rate and extent of reaction increase with increasing water content (Loring et al., 2011). This observation is attributed to the presence

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of thin water films at the olivine surfaces with thicknesses that correlate with water content. Molecular dynamics (MD) simulations (Kerisit et al., 2012) and infrared spectroscopy data (Loring et al., 2011) indicate that the thin water films can begin to form even before the supercritical CO<sub>2</sub> fluid becomes saturated with water. These thin water films appear to offer a unique reactive environment that can lead to carbonation reaction mechanisms and products that differ from those observed in CO<sub>2</sub>-saturated aqueous solutions. For example, Felmy et al. (2012) observed the formation of magnesite following the reaction of H<sub>2</sub>O-saturated scCO<sub>2</sub> with nanoparticles of synthetic forsterite at temperatures for which only hydrated magnesium carbonate phases are observed in aqueous solutions.

However, forsterite and fayalite have been shown to exhibit different reaction products as a function of temperature when in contact with WBSF. When forsterite and fayalite were reacted with H<sub>2</sub>O-saturated scCO<sub>2</sub>, the respective anhydrous carbonate phases (i.e. magnesite and siderite) were the only reaction products at high temperature (80 °C). At low temperatures (35 and 50 °C) however, magnesite was formed from forsterite but no carbonate formation was observed for fayalite (Felmy et al., 2012; Qafoku et al., 2012). Because of the critical role of water thin film formation in the reactivity of olivine minerals, one important question to address is whether forsterite and fayalite, and more generally different olivine minerals, exhibit different propensities for water film formation. Key parameters that will influence the propensity for water film formation are the energetics of water adsorption as a function of surface coverage as well as the energetics of the competitive adsorption between water and carbon dioxide, in other words, the magnitude of the driving force for carbon dioxide displacement by water at the surface. Therefore, the aim of this work is to quantify the adsorption energy of water and carbon dioxide at the surface of olivine minerals in order to compare and contrast the formation of thin water films at the surface of different olivine minerals in the context of carbonation reactions. Our previous work (Kerisit et al., 2012) focused on classical MD simulations of forsterite surfaces in contact with mixed H<sub>2</sub>O/scCO<sub>2</sub> fluids and thus considered water films of varying thicknesses for only one end-member of the olivine series. In this study, we extend our work to a range of olivine minerals (X<sub>2</sub>SiO<sub>4</sub>, X=Ca, Mn, Fe, Co, and Mg) and concentrate on the onset of formation of the water films, before dissolution begins to take place, by carrying out density functional theory calculations at surface coverages of up to two monolayers of water, for which water molecules interact directly with the mineral surface.

## 2. Computational methods

All the calculations presented in this work were carried out using the pseudo-potential plane-wave density functional theory module (NWPW) of the NWChem computational chemistry package (Valiev et al., 2010; Bylaska et al., 2011). The calculations made use of the generalized gradient approximation (GGA) exchange–correlation potential of Perdew, Burke, and Ernzerhof (PBE) (Perdew et al., 1996, 1997) and also included the DFT-D2 method of Grimme (2006) to account for dispersive forces (for reference, all the results obtained without dispersion corrections are shown in the Supporting Information in Tables S7 to S19). Valence–core interactions were described by generalized norm-conserving pseudo-potentials modified into a separable form as suggested by Kleinman and Bylander (1982). Softened Hamann pseudo-potentials (Hamann, 1989) were used for silicon (10), carbon (2) (Bylaska et al., 1996), oxygen (2) (Lubin et al., 2000), and hydrogen (0) (Lubin et al., 2000), with the number of core electrons shown in brackets. These pseudo-potentials were constructed using the following core radii:  $r_{cs} = 1.07$  a.u. and  $r_{cp} = r_{cd} = 1.286$  a.u. for Si;  $r_{cs} = 0.8$  a.u., and  $r_{cp} = r_{cd} = 0.85$  a.u. for C;  $r_{cs} = r_{cp} = r_{cd} = 0.7$  a.u. for O; and  $r_{cs} = r_{cp} = 0.8$  a.u. for H. Troullier–Martins pseudo-potentials (Troullier and Martins, 1991) were used for magnesium (10), calcium (18), manganese (18), iron (18), and cobalt (18). The following core radii were used to generate these pseudo-potentials:

$r_{cs} = r_{cp} = r_{cd} = 2.592$  a.u. for Mg;  $r_{cs} = 2.870$  a.u.,  $r_{cp} = 3.462$  a.u., and  $r_{cd} = 3.017$  a.u. for Ca;  $r_{cs} = 2.475$  a.u.,  $r_{cp} = 2.948$  a.u., and  $r_{cd} = 2.077$  a.u. for Mn;  $r_{cs} = 2.292$  a.u.,  $r_{cp} = 2.835$  a.u., and  $r_{cd} = 2.292$  a.u. for Fe; and  $r_{cs} = 2.379$  a.u.,  $r_{cp} = 2.942$  a.u., and  $r_{cd} = 2.047$  a.u. for Co. Semi-core corrections were also included in these pseudo-potentials with semi-core radii of 2.56, 1.73, 1.30, 0.80, and 0.80 a.u. and semi-core charges of 1.085, 0.707, 4.345, 8.949, and 8.327 for Mg, Ca, Mn, Fe, and Co, respectively.

In order to identify the optimal plane-wave cutoff energy and  $k$ -point mesh that maximize computational efficiency for a given accuracy, a series of unit cell minimizations were carried out for forsterite. The root mean square deviation (RMSD) of the percentage difference between the calculated and experimental lattice parameters, shown in Table S1 of the Supporting Information for a range of plane-wave cutoff energies and  $k$ -point mesh sizes, indicates that a plane-wave cutoff energy of 70 Ry together with a  $2 \times 1 \times 2$   $k$ -point mesh are sufficient and thus were employed throughout this work. The density energy cutoff was set to twice the plane-wave energy cutoff. Energy minimizations were performed with a quasi-Newton optimization algorithm to determine the adsorption energies and adsorption geometries of water and carbon dioxide at the olivine surfaces.

Five end-member orthosilicate minerals that adopt the olivine crystal structure were considered in this work, namely, forsterite ( $\alpha$ -Mg<sub>2</sub>SiO<sub>4</sub>), calcio-olivine ( $\gamma$ -Ca<sub>2</sub>SiO<sub>4</sub>), tephroite ( $\alpha$ -Mn<sub>2</sub>SiO<sub>4</sub>), fayalite ( $\alpha$ -Fe<sub>2</sub>SiO<sub>4</sub>), and Co-olivine (Co<sub>2</sub>SiO<sub>4</sub>). The olivine structure is composed of independent SiO<sub>4</sub><sup>4-</sup> tetrahedra connected by divalent cations in octahedral coordination, which are found in two distinct crystallographic sites referred to as M1 and M2 sites (Fig. 1). Tephroite, fayalite, and Co-olivine adopt an antiferromagnetic magnetic structure (Nomura et al., 1964; Santoro et al., 1966) with all transition-metal cations in high-spin configurations. The spin configuration determined by Cococcioni et al. (2003) for fayalite, whereby corner-sharing octahedra are in an antiferromagnetic configuration, was applied to all three transition-metal olivines (Fig. 1). This spin configuration is consistent with neutron diffraction data (Lottermoser et al., 1986; Lottermoser and Fues, 1988).

For the water and carbon dioxide adsorption calculations, the (010) surface (Pbnm space group) was used as a model surface as it is one of the main cleavage planes of olivine minerals, was shown to be the most stable surface of forsterite in previous computational studies (Watson et al., 1997; de Leeuw et al., 2000), and was the surface used in our previous work on forsterite–scCO<sub>2</sub>/H<sub>2</sub>O interfaces (Kerisit et al., 2012). The (010) surface slabs were one-unit-cell thick (~10–11 Å) and had a  $1 \times 1$  surface area (~28–35 Å<sup>2</sup>). A vacuum gap of approximately 15 Å was introduced between the surfaces. Water coverages of up to 2 monolayers (ML) were considered in 0.5 ML increments as well as a carbon dioxide coverage of 0.5 ML. The adsorption energies per H<sub>2</sub>O or CO<sub>2</sub> molecule were calculated as follows:

$$E_{\text{ads.}} = \frac{E_{\text{cov.}}^n - E_{\text{dry}} - nE_{\text{mol.}}}{n} \quad (1)$$

where  $E_{\text{cov.}}^n$  is the total energy of the surface covered with  $n$  H<sub>2</sub>O or CO<sub>2</sub> molecules,  $E_{\text{dry}}$  is the total energy of the bare surface and  $E_{\text{mol.}}$  is the total energy of an isolated H<sub>2</sub>O or CO<sub>2</sub> molecule.

For forsterite, calcio-olivine, and fayalite, the energy-minimized structures obtained for 0.5 ML water coverage and 0.5 ML carbon dioxide coverage were used as starting points for constant-temperature ab initio molecular dynamics (AIMD) simulations with the Car–Parrinello approach (Car and Parrinello, 1985; Blöchl and Parrinello, 1992). These simulations were carried out to investigate whether, given some kinetic energy, the adsorbed water and carbon dioxide molecules could explore the different adsorption energy minima as well as potentially react with the surface. In the AIMD calculations, the plane-wave cutoff energy remained the same but sampling was limited to the  $\Gamma$  point ( $1 \times 1 \times 1$   $k$ -point mesh). An integration time step of 0.12 fs was used for the equations of motion with a fictitious mass of 750 a.u. for the

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