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# Compositional controls on hydrogen generation during serpentinization of ultramafic rocks



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#### ABSTRACT

Where ultramafic rocks are exposed to water at temperatures <400 °C, they inevitably undergo serpentinization reactions to form serpentine  $\pm$  brucite  $\pm$  talc  $\pm$  magnetite (in addition to minor or trace phase like chlorite, tremolite, secondary diopside, garnet, Ni-Fe sulfides, alloys). In many circumstances, this process releases substantial amounts of hydrogen. Since the compositional controls of the primary lithology on the secondary mineralogy, fluid composition, Fe-distribution, and H<sub>2</sub> formation are not well established, we used thermodynamic computations to examine the equilibrium mineral assemblages, mineral compositions and the chemistry of fluids during serpentinization of 21 different ultramafic rock compositions and 10 distinct compositions of olivine between 25 °C and 400 °C at 50 MPa. Our models predict some systematic differences between serpentinization of olivine-dominated lithologies (i.e. peridotite) and of orthopyroxene-dominated lithologies (i.e. pyroxenite). Most notably, it is predicted that serpentinization of peridotite causes the formation of serpentine having elevated  $Fe^{+3}/(Fe^{+3} + Fe^{+2})$  values, Fe-bearing brucite (at temperatures  $\leq$  ca. 320 °C), and magnetite (at temperatures > ca. 200 °C), while serpentinization of pyroxenite does not produce magnetite, but instead forms Fe-rich serpentine with relative low  $Fe^{+3}/(Fe^{+3} + Fe^{+2})$  values and Fe-poor talc. The predicted activities of dissolved hydrogen  $(aH_{2(aq)})$ , dissolved silica  $(aSiO_{2(aq)})$ , as well as the pH vary accordingly. At temperatures  $\leq$  ca. 350 °C, fluids interacting with peridotite are more reducing, have lower aSiO<sub>2(aa)</sub> and higher pH than fluids interacting with pyroxenite. A direct correlation between the iron content of olivine, its stability relative to water, temperature and  $aH_{2(aq)}$  is apparent from our calculations. In contrast to forsterite-rich olivine, fayalite-rich olivine can be stable to temperatures as low as 180 °C in the presence of water. As a consequence, the predicted  $aH_{2(aq)}$  for serpentinization of fayalite is maximal at temperatures  $\leq 180$  °C.

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#### 1. Introduction

Among the more distinctive characteristics of serpentinization are the creation of geochemical conditions with vanishingly low oxygen fugacities (Eckstrand, 1975), a pH (measured at 25 °C) ranging from 3 at temperatures  $\geq$  350 °C to 13.1  $\pm$  0.1 at 2.4 °C (Charlou et al., 2002; Mottl, 2009), and the lowest activities of dissolved silica (*a*SiO<sub>2(*aq*)</sub>) in terrestrial silicate systems at temperatures <200 °C (Frost and Beard, 2007). The reducing nature of serpentinization is indicated by the common presence of Ni-Fe alloys in serpentinite (Ramdohr, 1950) and by serpentinization fluids revealing high concentrations of molecular hydrogen [H<sub>2(*aq*)</sub>] (Barnes et al., 1967; Charlou et al., 2002). Hydrogen forms during the oxidation of ferrous iron in olivine and orthopyroxene to ferric iron in secondary minerals through reaction with water. This can be represented by the general reaction:

$$2 \operatorname{FeO} + \operatorname{H}_2 \operatorname{O} \rightarrow \operatorname{Fe}_2 \operatorname{O}_3 + \operatorname{H}_{2(aq)} \tag{R1}$$

The high pH measured in low-temperature serpentinization fluids (Barnes et al., 1967; Cox et al., 1982; Kelley et al., 2001; Mottl et al., 2004), and high concentrations of dissolved Ca characteristic of many serpentinization systems are controlled by the serpentine–brucite–diopside equilibrium illustrated in Fig. 1:

$$\label{eq:caMgSi_2O_6} \begin{array}{c} CaMgSi_2O_6 + 2\,Mg(OH)_2 + 2H^+ = Ca^{2+} + Mg_3Si_2O_5(OH)_4 + H_2O, \\ diopside & brucite & serpentine \end{array} \tag{R2}$$

which includes the serpentine-brucite equilibrium buffering of  $aSiO_{2(aq)}$ :

$$Mg_{3}Si_{2}O_{5}(OH)_{4} + H_{2}O = 3 Mg(OH)_{2} + 2 SiO_{2(aq)}.$$
serpentine
brucite
(R3)

The equilibrium constant (log K) of Reaction (R2) decreases more than 13 orders of magnitude between 400 °C and 25 °C at 50 MPa implying that  $aCa^{2+}/a^{2}H^{+}$  ratios increase significantly with a decreasing temperature (cf. Foustoukos et al., 2008). Similarly, the log K of Reaction (R3) decreases more than 8 log units between 400 °C and





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**Fig. 1.** Activity–activity diagram depicting the phase relations in the system CaO–MgO–SiO<sub>2</sub>–H<sub>2</sub>O. This figure illustrates that at any given activity of dissolved Ca<sup>2+</sup>, serpentinization of peridotite buffers pH to markedly higher and silica activity ( $aSiO_{2(aq)}$ ) to markedly lower values than serpentinization of pyroxenite.

25 °C, which reflects a marked decrease in aSiO<sub>2(aq)</sub> with decreasing temperature. Reactions (R2) and (R3) apply only to serpentinization of olivine dominated-rocks or, if geochemical exchange is spatially limited during serpentinization, to olivine-dominated domains within a rock. Serpentinization of orthopyroxene-dominated rocks cannot proceed via Reactions (R2) and (R3), since brucite is not stable in the relatively high-silica environment of orthopyroxene and water (Fig. 1). Instead, talc would form together with serpentine and tremolite, which would buffer pH to lower values and  $aSiO_{2(aq)}$  to higher values (Fig. 1). However, petrographic observations of serpentinized peridotite reveals that talc is usually lacking in hydrothermally-altered orthopyroxene (bastite) indicating that silica is mobile to some extent under most circumstances (Frost and Beard, 2007; Frost et al., 2013-this issue; Klein et al., 2009; Kodolanyi et al., 2012). Silica is mobile because a substantial gradient in *a*SiO<sub>2(aq)</sub> develops during serpentinization between serpentine-talc and serpentine-brucite equilibria (Fig. 1). While serpentinization of olivine commonly produces magnetite, serpentinization of orthopyroxene and orthopyroxene-rich rocks commonly proceeds without the formation of magnetite (Evans et al., 2009; Klein et al., 2009; Kodolanyi et al., 2012). However, serpentinization of olivine does not always result in the formation of magnetite either. A hydrothermal serpentinization experiment using lherzolite as the starting material at 200 °C did not produce any (or only trace amounts) of magnetite, but generated abundant  $H_{2(aa)}$  (Seyfried et al., 2007). Instead of forming magnetite, Fe was distributed into brucite and serpentine (Seyfried et al., 2007). In two of our previous communications (Klein et al., 2009; McCollom and Bach, 2009) we could show that Fe is preferentially partitioned into brucite with decreasing temperature, indicating that the thermodynamic drive for magnetite formation decreases with decreasing temperature. Furthermore, magnetite is not predicted to be part of the serpentinization assemblage at very high water to rock mass ratios (w/r). These relations indicate that serpentinization reactions vary with protolith composition, temperature and fluid flux. This notion is corroborated by magnetic susceptibility-density relations of partly to completely serpentinized olivine-bearing rocks, which suggest that reaction pathways of serpentinization are exceptionally variable (Bach et al., 2006; Beard et al., 2009; Toft et al., 1990).

Much progress has been made over the last decade in furthering our understanding of serpentinization reactions (e.g., Bach et al., 2006; Evans, 2008; Frost et al., 2008) and their relevance for accompanying processes such as mineral carbonation (Andreani et al., 2009; Hansen et al., 2005; Klein and Garrido, 2011) and rodingitization (Austrheim and Prestvik, 2008; Bach and Klein, 2009). Furthermore, the concept that aqueous  $CO_2$  can be reduced to hydrocarbons abiotically during serpentinization of olivine has become widely accepted (Foustoukos and Seyfried, 2004; Horita and Berndt, 1999; McCollom and Seewald, 2001; Proskurowski et al., 2008), and it has been hypothesized that low-temperature (<150 °C) off-axis serpentinization systems in the Hadean Ocean represent a likely venue for the emergence of life (Martin and Russell, 2006). Present day seafloor serpentinization reactions support archeal and bacterial communities with H<sub>2</sub>, CH<sub>4</sub> and other sources of energy (Brazelton et al., 2010; Kelley et al., 2005; Perner et al., 2007; Petersen et al., 2011; Takai et al., 2005). Pioneering experiments conducted by Allen and Seyfried (2003), which investigated the hydrothermal alteration of distinct ultramafic protolith compositions at 400 °C and 50 MPa, suggest that serpentinization of pyroxene-rich lithologies leads to low-pH, Si-rich fluids buffered by talc-fluid or talc-tremolite-fluid equilibria. At these temperature and pressure conditions olivine is part of the equilibrium mineral assemblage and will not undergo significant alteration (Allen and Seyfried, 2003), which is reflected in the fluid chemistry. However, the impact of changing protolith compositions on the fluid chemistry, redox conditions and secondary mineralogy during serpentinization has not been explored as a function of temperature, which as pointed out by Allen and Seyfried (2003) plays a key role in mineral solubility and influencing the fluid chemistry. The present communication provides a theoretical perspective on serpentinization processes during fluid-rock interactions for a variety of different lithologies from dunite to pyroxenite and from olivine Fo<sub>90</sub> to fayalite in a temperature range between 25 °C and 400 °C. In order to focus on the role of protolith composition on the chemical composition of fluids, hydrogen generation, and secondary minerals during serpentinization, we present here equilibrium thermodynamic models of serpentinization reactions that exclude other factors such as reaction kinetics, changes in permeability and fluid flow, etc.

#### 2. Modeling background

#### 2.1. Software codes and databases

Reaction path modeling was conducted using the computer code EQ3/6, version 8.0 (Wolery, 1992a, 1992b; Wolery and Daveler, 1992) with a customized thermodynamic database assembled using the software code SUPCRT92 (Johnson et al., 1992). The SUPCRT92 database includes thermodynamic data from Shock and Helgeson (1988), Shock et al. (1989, 1997) and Wolery and Jove-Colon (2004) for aqueous species, and from Helgeson et al. (1978) and Wolery and Jove-Colon (2004) for minerals. Additional modifications include thermodynamic data for NaSO<sub>4</sub><sup>-</sup> and MgSO4 from McCollom (2000), aqueous Al complexes from Tagirov and Schott (2001), thermodynamic data for greenalite [Fe<sub>3</sub>Si<sub>2</sub>O<sub>5</sub>(OH)<sub>4</sub>] and minnesotaite [Fe<sub>3</sub>Si<sub>4</sub>O<sub>10</sub>(OH)<sub>2</sub>] from McCollom and Bach (2009), as well as thermodynamic data for ferroan brucite [Fe(OH)<sub>2</sub>] from Klein et al. (2009). The EQ3/6 database contains log K values for temperatures from 0 to 400 °C in 25 °C increments at a constant pressure of 50 MPa. Activity coefficients of dissolved inorganic species were calculated using the B-dot equation with hard-core diameter, and B-dot and Debye-Hückel parameters from Wolery and Jove-Colon (2004). Activity coefficients are assigned to be unity for neutral species, with the exception for non-polar gaseous species, for which the activity coefficients of CO2 (Drummond, 1981) were assigned. Solid solutions used in the thermodynamic reaction path models include serpentine (containing the end-members chrysotile, greenalite, kaolinite, cronstedtite (to allow substitution of ferric iron at the tetrahedral and octahedral sites)), brucite (Mg-brucite, ferroan brucite), talc (talc, minnesotaite), orthopyroxene (enstatite, ferrosilite), clinopyroxene (diopside, hedenbergite), chlorite (clinochlore, daphnite) and tremolite (tremolite, Fe-actinolite). Trace amounts of Fe in talc might be ferric

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