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2 *Temperature Trends for Reaction Rates, Hydrogen Generation, and*
3 *Partitioning of Iron During Experimental Serpentinization of Olivine*

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6 Thomas M. McCollom¹, Frieder Klein², Mark Robbins¹, Bruce Moskowitz^{3,4}, Thelma S.
7 Berquó⁵, Niels Jöns⁶, Wolfgang Bach⁷, and Alexis Templeton⁸

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11 ¹Laboratory for Atmospheric and Space Physics and ⁸Department of Geological Sciences,
12 University of Colorado, Boulder CO 80309, USA; ²Department of Marine Chemistry and
13 Geochemistry, Woods Hole Oceanographic Institution, Woods Hole, MA 02543; ³Department of
14 Earth Sciences and ⁴Institute for Rock Magnetism, University of Minnesota, Minneapolis, MN
15 55455; ⁵Department of Physics, Concordia College, Moorhead, MN 56562; ⁶Department of
16 Geology, Mineralogy and Geophysics, Ruhr-Universität Bochum, 44800 Bochum, Germany;
17 ⁷Department of Geosciences and MARUM, University of Bremen, 28334 Bremen, Germany

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20 **Abstract** – A series of laboratory experiments were conducted to examine how partitioning of Fe
21 among solid reaction products and rates of H₂ generation vary as a function of temperature
22 during serpentinization of olivine. Individual experiments were conducted at temperatures

ranging from 200 to 320 °C, with reaction times spanning a few days to over a year. The extent of reaction ranged from <1% to ~23%. Inferred rates for serpentinization of olivine during the experiments were 50-80 times slower than older studies had reported but are consistent with more recent results, indicating that serpentinization may proceed more slowly than previously thought. Reaction products were dominated by chrysotile, brucite, and magnetite, with minor amounts of magnesite, dolomite, and iowaite. The chrysotile contained only small amounts of Fe ($X_{\text{Fe}}=0.03-0.05$, with ~25% present as ferric Fe in octahedral sites), and displayed little variation in composition with reaction temperature. Conversely, the Fe contents of brucite ($X_{\text{Fe}}=0.01-0.09$) increased steadily with decreasing reaction temperature. Analysis of the reaction products indicated that the stoichiometry of the serpentinization reactions varied with temperature, but remained constant with increasing reaction progress at a given temperature. The observed distribution of Fe among the reaction products does not appear to be entirely consistent with existing equilibrium models of Fe partitioning during serpentinization, suggesting improved models that include kinetic factors or multiple reaction steps need to be developed. Rates of H₂ generation increased steeply from 200 to 300 °C, but dropped off at higher temperatures. This trend in H₂ generation rates is attributable to a combination of the overall rate of serpentinization reactions and increased partitioning of Fe into brucite rather than magnetite at lower temperatures. The results suggest that millimolar concentration of H₂ could be attained in moderately hot hydrothermal systems like Lost City during fluid circulation on timescales of a few years.

1. Introduction

Fluids circulating through actively serpentinizing ultramafic rocks are commonly enriched in reduced volatile compounds, particularly hydrogen (H_2) and methane (CH_4) (e.g., Neal and Stanger, 1983; Abrajano et al., 1990; Charlou et al., 2002, 2010; Kelley et al., 2005; Proskurowski et al., 2008; Lang et al., 2010; Etiope et al., 2011; Morrill et al., 2013). These compounds are capable of supporting communities of chemolithoautotrophic microorganisms in serpentinite-hosted settings such as deep-sea hydrothermal vents, alkaline springs, and the deep subsurface (Kelley et al., 2005; Brazelton et al., 2006, 2013; McCollom, 2007; Tiago and Veríssimo, 2012; Schrenk et al., 2013; Morrill et al., 2013; McCollom and Seewald, 2013; Crespo-Medina et al., 2014; Klein et al., 2015a). The elevated abundance of H_2 in these environments is also thought to facilitate the abiotic reduction of inorganic carbon into methane and other abiotic organic compounds (Berndt et al., 1996; McCollom and Seewald, 2001, 2007, 2013; Foustoukos and Seyfried, 2004; Etiope and Sherwood Lollar, 2013). Additionally, the capacity of serpentinization environments to support chemolithoautotrophy and abiotic synthesis of organic compounds are two of the principal reasons that serpentinites are considered to be strong candidates as the site of the origin of life on Earth (Martin and Russell, 2006; Martin et al., 2008; Russell et al., 2010).

Although H_2 is central to all of these processes, the chemical reactions that control the processes, amounts, and rates of H_2 production during serpentinization remain poorly understood. In particular, although it is widely recognized that the production of H_2 is tightly coupled to the oxidation of ferrous Fe (Fe^{II}) from the reacting rocks into ferric Fe (Fe^{III}) that is precipitated in product minerals, the factors that regulate how much of the Fe^{II} is oxidized during serpentinization under different conditions are not well constrained. At various times, it has been

suggested that factors such as the Fe content of source minerals, activity of silica, and thermodynamic equilibrium among mineral phases may exert a strong influence on the fate of Fe during serpentinization (e.g., Moody, 1976b; Evans and Trommsdorf, 1972; Frost and Beard, 2007; Evans, 2008; McCollom and Bach, 2009; Klein et al., 2013). However, these ideas remain largely untested by laboratory experiments.

Similarly, experimental study of the rates of H₂ production during serpentinization and how these rates might vary under different reaction conditions has been very limited. While there have been numerous laboratory simulations of serpentinization performed over the last several decades, only a handful of these studies have monitored the production of H₂ during the reaction, and so far these studies encompass only a very limited range of reaction conditions (Berndt et al., 1996; McCollom and Seewald, 2001, 2003; Allen and Seyfried, 2003; Seyfried et al., 2007; Okamoto et al., 2011; Klein et al., 2015b). Furthermore, it has been only recently that detailed analyses of the distribution of Fe among the product phases has been included in experimental studies that allow the production of H₂ to be correlated with the fate of Fe as serpentinization proceeds (e.g., Seyfried et al., 2007; Marcaillou et al., 2011; Malvoisin et al., 2012a,b).

To gain a better understanding of the processes that regulate the generation of H₂ during serpentinization, laboratory experiments were undertaken to monitor the production of H₂ and the partitioning of Fe among product phases during serpentinization of olivine. To focus on the impact of temperature on H₂ production and mineral compositions, a series of experiments were performed at temperatures ranging between 200 and 320 °C while keeping other reaction conditions essentially constant. The results are used to examine trends in the distribution of Fe among reaction products and in rates of H₂ generation as a function of temperature. One of the principal objectives of the study was to test whether current models of Fe partitioning during

serpentinization, which are largely based of thermodynamic equilibrium, accurately portray the fate of Fe during the reactions and can predict the Fe contents of brucite and serpentine.

The results presented here describe experiments conducted using only olivine as the mineral reactant. Olivine is the predominant mineral of most ultramafic rocks, and serpentinization of this phase can be summarized by the general reaction:

where the stoichiometric parameters w , x , y , and z depend on how Fe is partitioned among the reaction products. The production of H_2 during serpentinization of olivine chiefly results from the oxidation of ferrous Fe (Fe^{II}) to ferric Fe (Fe^{III}) through reaction with water, liberating H_2 . This process can be expressed as:

where $(\text{Fe}^{\text{II}}\text{O})$ and $(\text{Fe}^{\text{III}}_2\text{O}_3)$ represent components of primary and secondary minerals, respectively. Magnetite is often the major reservoir of Fe^{III} among the products of serpentinization, but under some circumstances a significant fraction of the Fe^{III} generated during alteration of ultramafic rocks can be incorporated as a component of serpentine minerals (Seyfried et al., 2007; Evans, 2008; Klein et al., 2009; Andreani et al., 2013a; Klein et al., 2014).

2. Methods

A suite of ten experiments designed to encompass a range of temperatures and reaction times were conducted for this study, as summarized in Table 1. In these experiments, powdered olivine was heated in the presence of NaCl- and NaHCO₃-bearing aqueous solutions at temperatures between 200 and 320 °C at a nominal pressure of 35 MPa, with durations ranging from 43 to 8183 hours. The fluid composition and H₂ production was monitored during the experiments. Solids were recovered at the end of the experiments and analyzed for their mineral and chemical composition. At temperatures of 230 and 300 °C, both short- and long-term experiments were performed in order to investigate variations in composition of mineral products with increasing extent of reaction. Most experiments were conducted with crushed olivine in the 53-212 µm size range, but two experiments were conducted at 200 and 230 °C with finer grained powders (<53 µm) in order to achieve more extensive reaction progress.

All experiments were conducted in a flexible-cell hydrothermal apparatus using a gold reaction cell with titanium fittings (Supplemental Fig. S1; Seyfried et al., 1987). The reaction cell was contained within a stainless steel pressure housing, with water used as an external pressurizing fluid. The flexibility of the gold reaction cell allows fluids to be sampled from the reaction cell without loss of pressure, and eliminates the presence of a vapor headspace so that reactions are confined to the aqueous phase. Although substantial amounts of H₂ were generated during the experiments, aqueous concentrations remained well below the solubility limits which, at 35 MPa, ranges from ~400 to ~800 mmol kg⁻¹ over the range of experimental temperatures (Seward and Frank, 1981). The cell was equipped with a capillary tube attached to a valve through which fluid samples were taken during the experiments in order to monitor reaction progress over time. The titanium fittings that were exposed to reactants during the experiments were heated in air for at least 48 hours at 350°C prior to use in order to form a relatively inert

TiO₂ surface layer. Although the target pressure for the experiments was 35 MPa, the pressure in a few experiments dropped by up to 2 MPa between samples, presumably owing to volume changes produced by changes in mineral volumes and incorporation of water into solid phases. The pressure was returned to 35 MPa at each sampling point.

To approximate seawater salinity and provide a source of carbon, the initial fluids contained 485 mmol NaCl/kg and 19.4 mmol NaHCO₃/kg. The relative proportions of fluid to rock in the initial experimental charge ranged from 1.6 to 2.9 by weight, although the proportions within the reaction vessel decreased during the experiments as fluid aliquots were removed for chemical analysis and as water was incorporated into secondary phases. However, since the olivine was only partially reacted during the experiments, the effective fluid:rock ratios (in terms of amount of fluid per amount of reacted olivine) during the experiments would have been much higher than these values indicate.

The experiments were conducted using olivine from San Carlos, Arizona, which has an approximate composition of Mg_{1.82}Fe_{0.18}SiO₄ (Fo₉₁). The material used in the experiments were tumbled olivine separates purchased either from Wards Natural Science (Rochester, NY, USA) or Excalibur Minerals (Charlottesville, VA, USA). Only olivine crystals larger than ~4 mm in diameter were used for the experiments, and were hand-picked under a binocular microscope to exclude grains with obvious signs of weathering or inclusions of other minerals. The crystals were crushed by hand using a ceramic mortar and pestle, always avoiding the use of metal tools that might result in contamination of the reactants with particles of metal. For most experiments, the resulting powders were sieved to achieve grain sizes between 53 and 212 μm, and washed repeatedly with deionized water to remove small particulates (Supplemental Fig. S2). One experiment at 230 °C was performed with the <53 μm fraction resulting from the sieving of the

larger particles and was not rinsed, and one experiment conducted at 200 °C was performed with a mineral fraction wet sieved to between 38 and 53 μm . The surface area of olivine for the 53-212 μm fraction used in most experiments was determined by the conventional BET method with N_2 as the adsorptive species. The surface area was found to be $0.59 \pm 0.02 \text{ m}^2 \text{ g}^{-1}$, similar to values reported by other studies (Brantley and Mellott, 2000).

Although the minerals were hand-picked to exclude phases other than olivine, detailed examination of the reactants by scanning electron microscope (SEM) equipped with electron dispersive X-ray spectroscopy (EDS) indicated that trace amounts ($<1 \text{ vol}\%$) of orthopyroxene (Opx), clinopyroxene, and spinel were present among the reactants. In addition to the powders, two experiments (OLIV300_med and OLV300_short) also included polished slabs of olivine for high-resolution examination of alteration phases. These slabs were mounted on 1.6 mm O. D. Ti-tubing that had been baked at 350 °C for $>48 \text{ h}$ and were attached to the tubing using Au wire. The slabs were placed so that they were not in direct contact with the powdered minerals during the experiments. Analyses of the reacted slabs will be reported elsewhere.

At intervals throughout the experiments, several fluid aliquots (0.3-1 g each) were taken directly into gas-tight glass syringes and analyzed for the abundance of: (1) dissolved H_2 , (2) total dissolved CO_2 ($\Sigma\text{CO}_2 = \text{CO}_{2(aq)} + \text{HCO}_3^- + \text{CO}_3^{2-}$), CH_4 , and $\text{C}_2\text{-C}_6$ hydrocarbons, (3) room temperature pH ($\text{pH}_{25^\circ\text{C}}$), and (4) the major elements present in the starting materials, following procedures described in detail in the Supplemental Materials. Briefly, volatile compounds were analyzed by gas chromatography (GC) using either thermoconductivity detection (TCD) or Flame Ionization Detection (FID), with estimated analytical errors $\pm 5\%$. For comparative purposes, the measured H_2 concentrations were normalized to the total number of moles of H_2 generated per gram of olivine to account for variations in the amount of solid reactants used in

different experiments and for the changing mass of fluid present in the reaction vessel as aliquots are removed during sampling (see Supplemental Materials). The $\text{pH}_{25^\circ\text{C}}$ was measured using a Ross micro combination electrode at room temperature with an uncertainty of approximately ± 0.1 units of the reported value. Dissolved SiO_2 was measured using spectrometry immediately after sampling, and total dissolved Na, Ca, Mg, Fe, Si, and K were analyzed by Inductively Coupled Plasma – Optical Emission Spectroscopy (ICP-OES) on acidified sub-samples.

At the termination of each experiment, the solids were removed, filtered, and gently rinsed with DI water. A variety of methods were employed to investigate the mineralogy, chemical composition, and morphology of the solid products, including SEM/EDS, Electron Microprobe Analysis (EMPA), confocal Raman Spectroscopy, thermogravimetric analysis (TGA), Mössbauer spectroscopy, and investigation of magnetic properties. Details of the analytical methods are provided in the Supplemental Materials.

Calculations to estimate in situ pH and silica activity were performed with the computer program EQ3 (Wolery and Jarek, 2003). The calculations were performed in two steps. First, fluid speciation calculations were performed at 25°C using the measured fluid compositions including the room temperature pH, and adjusting for charge balance with Na. The total dissolved Na calculated at 25°C was then used with other measured concentrations to respeciate the fluid at the reaction temperature, with charge balance determining the in situ pH. Because Mg, Ca, and Fe were below detection limits in most cases, the total dissolved abundance of these elements were assumed to be either $1\ \mu\text{mol kg}^{-1}$ (Mg, Ca) or $0.1\ \mu\text{mol kg}^{-1}$ (Fe), representing maximum values based on the detection limits. Mineral stability diagrams were constructed using the computer program Geochemist's Workbench (Rockware Inc.). All calculations were performed using a database of thermodynamic parameters for 35 MPa as described in McCollom

and Bach (2009). Thermodynamic data for assembly of the database are derived primarily from Helgeson et al. (1978), Shock and Helgeson (1988) and Shock et al. (1989, 1997). Thermodynamic properties for solid solutions were calculated from end-member data assuming ideal site mixing.

3. Results

The following sections describe the compositions of fluids obtained as the experiments progressed and of minerals obtained after the termination of the experiments. To provide additional context for interpretation of the data, results of two previously unpublished experiments performed using similar methods but with highly elevated H₂ concentrations are provided in the supplemental materials (OLIV300_H2sat1, OLIV300_H2sat2), along with additional analyses of the mineral products of previous experiments reported by McCollom and Seewald (2001) (OLIV300_MS). These other experiments attained a much greater degree of reaction progress and higher H₂ levels than the experiments performed for this study, and allow assessment of the role of these factors in relation to the distribution of Fe among reaction products.

3.1. Variation of fluid composition with reaction temperature

Fluid compositions during a series of long-term experiments conducted at temperatures ranging from 200 to 320 °C with uniform grain size (53-212 µm) are summarized in Table 2. The amounts of dissolved H₂ generated during experiments performed at 230 °C and higher are shown in Figures 1a and 1b. Results from the 200 °C experiment (OLIV200) are not shown in the figure since only a very small amount of H₂ was produced before the first measurement (0.16 µmol/g olivine) and no detectable increase in H₂ was observed during the remaining 2400 h of

heating (Table 2). The 230 °C experiment (OLIV230) initially followed a similar pattern, producing only a small amount of H₂ (0.23 µmol/g) during the first 479 h of heating with a barely detectable increase of 0.34 µmol/g during the following 2000 h. However, the rate of H₂ generation in this experiment then began to increase substantially, reaching a steady, linear rate of increase after about 4000 h that continued until the experiment was terminated at 8159 h (Fig. 1b). Additional fluid was injected into this experiment at 4013 h to replenish fluid removed during sampling, but this did not appear to have a significant impact on the rate of H₂ generation since the trend towards increasing H₂ was apparent before the injection and continued at a similar rate after the injection.

Experiments conducted at temperatures of 265 °C and above generated considerably larger amounts of H₂, and the lag period prior to the onset of H₂ accumulation observed in the 230 °C experiment was not evident at higher temperatures (Fig. 1a). The rate of H₂ generation was similar in experiments at 265 °C and 320 °C, while substantially greater amounts were generated in the 300 °C experiment. The rate of H₂ generation was approximately constant throughout the 265 and 320 °C experiments, but appeared to decrease slightly with increasing reaction progress at 300 °C.

Concentrations of dissolved SiO₂ were very low during all of the experiments in this series, with most measurements in the 20-80 µmol/kg range (Fig. 1c; Table 2). In experiment OLIV230, there was a sharp increase in SiO₂ concentration following the injection of fluid at 4013 h, but the concentration quickly returned to lower levels consistent with the trend established prior to injection. Concentrations of dissolved Na and Cl were nearly constant within analytical error throughout the experiments at levels consistent with the initial fluid, confirming that the reactors did not leak during heating (otherwise, the concentrations would have decreased

through dilution by the pressurizing fluid). Concentrations of dissolved Mg, Fe, and Ca were close to or below the detection limit throughout most of the experiments ($<1\text{-}10\text{ }\mu\text{mol/kg}$), while concentrations of K showed considerable variability, ranging from values below the detection limit to $>200\text{ }\mu\text{mol kg}^{-1}$. Concentrations of dissolved Al were below the detection limit in most experiments but higher levels were observed in experiment OLIV265, suggesting that trace amounts of an Al-bearing contaminant may have been present. Measured values of $\text{pH}_{25^\circ\text{C}}$ remained mildly alkaline and fairly constant during each of the experiments (Table 2).

With the exception of the 320°C experiment, ΣCO_2 concentrations decreased during the experiments, which appeared to be primarily attributable to precipitation of carbonate minerals (Table 2). At lower temperatures (200 and 230°C), the ΣCO_2 decrease occurred relatively rapidly, while at higher temperatures ΣCO_2 decreased more gradually throughout the experiments. However, the limited number of samples analyzed for ΣCO_2 in some experiments makes it difficult to track its behavior in detail (ΣCO_2 was not analyzed at all sample points in order to conserve fluid in the reaction cell). Only very small amounts of CH_4 were observed during the experiments, with concentrations increasing slightly as the experiments progressed (Table 2). Other dissolved volatile hydrocarbons were either below detection or present in trace amounts just above the detection limit.

3.2. Fluid compositions during short-term and fine-grain-size experiments

In order to more closely examine fluid compositions and mineral products during the early stages of reaction, a few additional short-term experiments were performed at 230°C and 300°C (Table 3). A short-term experiment conducted at 230°C (OLIV230_short) generated H_2 at a substantially greater rate than had been observed in the early stages of the long-term experiment at this temperature (Fig. 1b). However, the rate of H_2 production was very similar to that

observed between ~4000 and 8159 hours in the longer-term experiment. Like the longer-term experiment at 230 °C, there was a lag period prior to the onset of H₂ accumulation in OLIV230_short; however, the delay was substantially shorter than was observed in experiment OLIV230 (Fig. 1b). The SiO₂ concentration in a fluid sample taken 23 hours after initiation of the short-term experiment was much higher (170 μmol kg⁻¹) than had been observed in the first samples for other experiments, but in this instance the first sample was taken after much shorter reaction time than in the other experiments. Concentrations of SiO₂ in subsequent samples of OLIV230_short were similar to those observed in other experiments (29-43 μmol/kg). Other aspects of the fluid chemistry were similar to those observed in experiment OLIV230.

The two short-term experiments conducted at 300 °C accumulated H₂ at amounts that were consistent with the trend observed in the initial stages of the long-term experiment at this temperature (Fig. 2a). As observed at 230 °C, dissolved SiO₂ concentrations measured within a day after the onset of heating were elevated (81-290 μmol kg⁻¹), but concentrations rapidly decreased to lower levels similar to those observed in longer term experiments (35-48 μmol kg⁻¹) (Fig. 2b). In all other aspects, the fluid composition in the short-term experiments at 300 °C were similar to those observed in the initial stages of the long-term experiment (Table 3).

Two additional experiments were performed using olivine with a fine grain size, which were intended to increase the reactive surface area of the olivine and thereby achieve a greater extent of reaction. One of these experiments was performed at 200 °C with a grain size of 38-53 μm (OLIV200_fine) (Table 3). While the experiment conducted at this temperature with a larger grain size (53-212 μm; OLIV200) did not produce any detectable H₂ increase after the initial sample, the fine-grain experiment resulted in substantial and steady production of H₂ (Fig. 3a).

After the initial sample, SiO₂ concentrations in this experiment were measured at low levels comparable to those observed in other experiments (Fig. 3c).

The other small-grain experiment was performed at 230 °C (OLIV230_fine), and utilized olivine powder that had been dry sieved to <53 µm. Generation of H₂ in this experiment began immediately after heating without the lag observed in the larger-grain experiments performed at the same temperature, and it accumulated at a rate that was much faster than observed with the larger grain size (Fig. 3b). The total amount of H₂ generated in this experiment (40.7 µmol/g olivine) was more than 5 times greater than that attained in OLIV230, even though the duration of the experiment was only half as long. After an initial spike, the concentration of dissolved SiO₂ in OLIV230_fine decreased to a level similar to that observed in the other experiments (Fig. 3c). Concentrations of all other fluid components were similar to those observed in the other 230 °C experiments.

3.3. Solid reaction products

Following the experiments, all of the solids were clumped together at the end of the reaction cell opposite the titanium fitting, and in most cases were cemented together by secondary precipitates into one solid lump. Examination of the solids after termination of the experiments confirmed that serpentine, brucite, and magnetite were the principal secondary phases, although the abundances, crystal habit, and chemical composition of these products varied somewhat among the experiments. Also identified among the reaction products were small amounts of carbonates and iowaite. In addition to these products, a large fraction of the original olivine remained at the termination of each experiment (~77-98%; Table 4), indicating that reaction of olivine had not approached completion despite the prolonged reaction times. In many cases, secondary minerals occurred only as a thin veneer on the surfaces of partially reacted olivine

crystals. Compositional information on the solid reaction products are summarized in Table 4, with the relative Mg and Fe contents of the minerals expressed as Mg# [=100 × Mg/(Mg+Fe) on a molar basis; Fe is total Fe]. Representative electron microprobe analyses of olivine, serpentine, brucite and magnetite are given in Table 5.

Serpentine occurred primarily as fibrous mats coating the surfaces of partially reacted olivine grains (Fig. 4a,b). The serpentine precipitated initially as short, stubby fibers (~5-10 μm long by ~0.1 μm wide) that evolved into elongated fibers with more extensive reaction. Based on morphology and Raman bands at 232, 391, 689, and 3698 cm⁻¹, the serpentine phase present was predominantly chrysotile in all experiments (Supplemental Fig. S3) (Auzende et al., 2004; Groppo et al., 2006). In a few instances, a spherical phase that appeared to be polyhedral serpentine (cf. Andreani et al., 2008) was observed (Supplemental Fig. S4). This phase, however, was found exclusively in reaction rims surrounding trace amounts of Opx present as contaminants in the reactant minerals. In these instances, EDS analysis indicated that the serpentine contained trace amounts of Cr not typically observed in the fibrous serpentine, consistent with observations of polyhedral serpentine formed in association with Opx in natural samples (Andreani et al., 2008). With the exception of the 200 °C experiments, the measured compositions of serpentine were nearly identical at all temperatures with Mg# ≈ 97 (Fig. 5). The serpentine in the 200 °C experiments, however, appeared to have slightly higher Fe contents, with Mg# = 95-96.

Brucite occurred as platy, euhedral crystals that in many instances displayed hexagonal terminations (Fig. 4c). Individual brucite crystals ranged from ~10 μm up to several hundred μm across, and were a few to ~20 μm thick. The crystals were clear in transmitted light. Brucite was fairly common in most of the experiments, although few crystals were found among the

products of the 320 °C experiment (OLIV320) and no brucite was found during inspection of the solid products of the short-term experiments (OLIV230_short, OLIV300_med) by SEM. The Fe contents of brucite displayed much greater variation than serpentine, with Mg# ranging from 92 to 99 and exhibiting a trend towards increasing Fe content (lower Mg#) with decreasing temperature (Fig. 5). In all cases, however, the Mg# of brucite was greater than that of the original olivine. Within individual experiments, analyses of multiple brucite crystals yielded essentially the same compositions within analytical uncertainties, with Mg# typically varying by no more than a unit or two between individual crystals. In addition, analysis of multiple points on individual brucite crystals using EDS and EMPA indicated no evidence of compositional zoning, and backscattered electron images of individual brucite crystals similarly showed no variation in relative brightness that might be indicative of variation in Fe abundance across individual crystals (Fig. 4c).

Analysis of brucite crystals from the experiments indicated that it was often intergrown with iowaite, a mineral that is structurally similar to brucite but contains Fe^{III} and Cl (ideal molecular formula $\text{Mg}_6\text{Fe}^{\text{III}}_2\text{Cl}_2(\text{OH})_{16} \cdot 4\text{H}_2\text{O}$; Braithwaite et al., 1994). Initially, the occurrence of iowaite was suspected because of elevated Cl contents during EDS analysis of brucite crystals, and its presence was subsequently confirmed by Raman spectroscopy (Supplemental Fig. S5). Iowaite appeared to be fairly widespread in those experiments where it was found, although only some of the brucite crystals from any particular experiment analyzed by Raman or EDS showed evidence for this phase. In all cases, the iowaite was intimately intergrown with brucite, and no separate phase clearly identifiable as iowaite was observed using SEM, light microscopy, or Raman spectroscopy. Because this phase contains Fe^{III}, it is possible that it formed after cooling of the experiments and exposure of brucite to air, but incubation

experiments that exposed iowaite-free brucite crystals to Cl-bearing fluid under oxic conditions for 48 hours failed to produce iowaite, suggesting that it was formed during the experiments. Further details on analysis of this phase and its potential implications are provided in the Supplemental Materials

Magnetite was present in the reaction products from all of the experiments, with abundances measured using saturation magnetization listed in Table 4. Magnetite primarily occurred in the experimental products as euhedral crystals dispersed throughout the fibrous serpentine mats that coated the surface of reacted olivine (Fig. 4a,d). In most experiments, however, isolated areas with dense accumulations of magnetite were also observed (Fig. 4f). In the lower temperature experiments (265 °C and below), magnetite occurred as octahedral crystals (Fig. 4e), although it primarily occurred as truncated octahedra at higher temperatures (Fig. 4f). The size of the magnetite crystals ranged from <1 to ~20 µm in diameter, with the majority in the 2-8 µm range (Fig. 4e,f).

Magnetization analyses at low-temperature (10-300K) indicated that the samples contained both pure and cation-substituted magnetite, with the cation-substituted phase prevalent in most cases. The distinct, low-temperature (~120 K) Verwey transition observed in stoichiometric pure magnetite is either missing or lowered to a temperature <50 K (e.g., Dunlop and Özdemir, 1997). Elemental analysis of magnetite crystals by EMPA and EDS usually indicated the presence of a few wt% of Mg and Si (e.g., Table 5), but it could not be determined whether these elements were present within the magnetite or represented small amounts of fine-grained serpentine intergrown with the magnetite. Many magnetite crystals were also found to contain up to a few wt% Ti by EDS. High-temperature Curie point analyses were consistent with a small amount of Ti-substitution in magnetite, with an approximate composition of $\text{Fe}_{2.95}\text{Ti}_{0.05}\text{O}_4$. The minor

amount of Ti-substitution is also consistent with observed remanence transition near 50 K (Moskowitz et al., 1998). Potential sources of Ti include the mineral reactants as well as parts of the reaction cell, including the closure piece and the tubes used to mount polished slabs in some experiments.

Small amounts of carbonate minerals were found by SEM/EDS scattered among the solids in most experiments (Fig. 4d), although none were identified during inspection of the products of the 320 °C experiment. Analysis of the carbonates by EDS indicated that two separate populations were present, one containing Mg as the predominant cation (presumably magnesite) and the other with approximately equal amounts of Mg and Ca (presumably dolomite), with the Ca possibly derived from trace amounts of pyroxenes or other phases present in the reactants. Trace amounts of Fe and Mn (<1 wt%) were also present in both groups of carbonates, and both phases were present in each of the experiments where carbonates were found.

In an effort to determine the extent of reaction during the experiments, the amounts of secondary minerals among the solid products were estimated using a combination of thermogravimetric analysis (TGA) and gravimetric methods (see Supplemental Materials). For those experiments with sufficient reaction progress, TGA was used to quantify the amounts of serpentine and brucite in the reacted solids. Results of the TGA are shown in Supplemental Fig. S6 and summarized in Table 6, with estimates of the amount of olivine reacted based on these measurements listed in Table 4. For all experiments, gravimetric methods were used to quantify the mass of secondary products and estimate the amount of olivine reacted, with results also listed in Table 4. In those cases where both gravimetric and TGA methods were used to estimate the extent of reaction, the results were in close agreement. Based on these measurements, the amount of olivine reacted during the experiments ranged from 1.8% to 9.3%.

To obtain additional constraints on the distribution of Fe among product phases, the products were analyzed using Mössbauer (MB) spectroscopy. Initial Mössbauer measurements performed on bulk product samples were dominated by unreacted olivine, making it difficult to discern the signature of the secondary reaction products. Therefore, subsequent analyses were performed on the fraction of secondary minerals separated from the bulk solids, except for those experiments where small grain size of the olivine reactant precluded separation of the reaction products. Results of these analyses are summarized in Table 7. Because the separation procedure only partially recovered magnetite produced in the experiments, the relative amounts of magnetite in the MB analyses were not representative of the bulk reaction products.

Two doublets were identified in the MB spectra from each experiment, with similar values of isomer shift (IS) and quadrupole splitting (QS) for the doublets in all experiments (Table 7). One doublet with $QS = 2.72\text{--}2.86$ mm/s and $IS = 1.09\text{--}1.18$ mm/s was assigned to Fe^{II} while the other doublet with $QS = 0.66\text{--}0.70$ mm/s and $IS = 0.26\text{--}0.32$ mm/s was assigned to Fe^{III} . These values are consistent with hyperfine parameters for Fe^{II} ($QS = 2.64 \pm 0.47$ mm/s, $IS = 1.10 \pm 0.19$ mm/s) and octahedral Fe^{III} ($QS = 0.68 \pm 0.31$ mm/s, $IS = 0.3 \pm 0.13$ mm/s) in chrysotile (O'Hanley and Dyar, 1998). No doublets were observed that would be consistent with tetrahedral Fe^{III} in chrysotile ($QS = 0.32 \pm 0.10$ mm/s, $IS = 0.17 \pm 0.05$ mm/s), indicating that ferric Fe was present predominantly in the octahedral site. The separated fractions also included small amounts of relict olivine (~5-15%) ($QS = 3.00$ mm/s, $IS = 1.18$ mm/s) as well as brucite ($QS = 2.94$ mm/s, $IS = 1.15$ mm/s; Blaauw et al., 1979) that contributed to the Fe^{II} doublet.

The Mössbauer results can be used to constrain the relative proportions of Fe^{II} and Fe^{III} in the serpentine phase, but this requires accounting for the contributions of olivine and brucite to the Fe^{II} measurement. Owing to uncertainties in the amount of relict olivine in the MB samples

and incomplete recovery of brucite in the separated fraction, the $\text{Fe}^{\text{II}}:\text{Fe}^{\text{III}}$ ratio of serpentine could not be precisely calculated. However, the observations can be used to make reasonable estimates. The MB results indicate that molar $\text{Fe}^{\text{II}}:\text{Fe}^{\text{III}}$ ratios in the separated fractions (exclusive of magnetite) were approximately 3:1 (Table 7). Because some of the measured Fe^{II} is attributable to relict olivine in the samples, this is an upper bound on the $\text{Fe}^{\text{II}}:\text{Fe}^{\text{III}}$ ratio for the secondary phases. The observed mineral compositions and mass balance constraints (see below) indicate that the amount of Fe in brucite relative to that in serpentine varies with temperature, with approximate molar proportions of 1:2 at 200 °C, 2:3 at 230 °C, 1:3 at 265-300 °C, and ~1:10 at 320 °C. If it is assumed that approximately 15% of the Fe^{II} is attributable to olivine, the ratio of Fe^{II} to Fe^{III} in serpentine can be estimated to be 3.5:1 at 200 °C, 1.7:1 at 230 °C, 4:1 at 265 °C, and 2.6:1 at 300 °C and 320 °C. Owing to the uncertainties, these values should be considered rough approximations. Nevertheless, the estimated $\text{Fe}^{\text{II}}:\text{Fe}^{\text{III}}$ ratios are similar to those observed for MB analyses of natural chrysotile by O'Hanley and Dyar (1998), although in most cases the Fe^{III} in the natural samples is distributed more or less evenly between octahedral and tetrahedral sites.

In all cases, a large fraction (~77-98%) of the original olivine remained unreacted at the end of the experiments. Some surfaces of relict olivine grains remained fairly smooth with few etch pits or other indications of dissolution, while other surfaces were deeply etched and developed dentate features similar to those previously reported for olivine dissolution (Velbel, 2009; Malvoisin et al., 2012b; Klein et al., 2015b) (Supplemental Fig. S7). These features indicate a strong preference for dissolution along specific crystal faces (cf. King et al., 2014). In addition, while the starting materials were sieved to a uniform grain size of 53-212 μm for most experiments, many relict olivine fragments in these experiments had grain diameters much

smaller than 53 μm , indicating that most of the initial grains were fractured during the experiments. As a consequence, the surface area of olivine exposed to the fluid likely increased significantly as the experiments proceeded. Analyses by EMPA provided no indication that the Mg# of relict olivine grains changed during any of the experiments, even along grain boundaries.

Despite considerable effort to purify the starting materials, trace amounts of Opx were present in the reactant minerals, and partially reacted Opx crystals were found among the products of some experiments during inspection by SEM. Notably, isolated grains of Opx in the reaction products typically exhibited much more extensive reaction than olivine within the same experiment. A curious observation was that, in several cases, relict Opx crystals were found to be coated with deposits determined by EDS to be composed predominantly of Mg and O with little or no Si (Supplemental Fig. S8). The EDS results suggest that this phase may be brucite, which is generally thought to be incompatible with relatively Si enriched minerals like Opx

The reactant minerals also included trace amounts ($<<1\%$) of spinel, which is a widespread minor component of mantle xenoliths from San Carlos that were the source of the olivine used in the experiments. Spinel minerals from San Carlos generally have Mg- and Al-rich compositions that fall in the range of $(\text{Mg}_{0.7}\text{Fe}_{0.3})(\text{Al}_{1.8}\text{Cr}_{0.2})\text{O}_4$ to $(\text{Mg}_{0.8}\text{Fe}_{0.2})(\text{Al}_{1.1}\text{Cr}_{0.9})\text{O}_4$ (e.g., Uchida et al., 2005), and semi-quantitative analyses of spinel present in the experiments using EDS were consistent with these compositions. Examination of spinels in the reacted samples did not reveal any evidence of etch pits or other indications that they had reacted during the experiments, but the surfaces of many spinel crystals were partly coated with overgrowths of magnetite (Fig. 4c; Fig. 6). In some instances, spinel crystals that were extensively covered with magnetite overgrowths could be found in direct contact with olivine that was free of magnetite (e.g., Fig. 6b), suggesting preferential nucleation of magnetite on the surfaces of spinel. It should be

emphasized, however, that only a very small fraction of the magnetite formed in the experiments precipitated on the surfaces of spinel crystals, and the vast majority of the magnetite was embedded in serpentine mats formed on the surfaces of olivine not spatially associated with spinel.

4. Discussion

4.1. Serpentinization reaction stoichiometry

The measured compositions of the product phases as well as the lack of any significant accumulation of aqueous species other than H_2 allows the generalized serpentinization reaction (Rxn. 1) to be more explicitly defined for the experimental conditions. Based on the measured mineral compositions, balanced chemical reactions for the experiments as a function of reaction temperature could be closely approximated, as listed in Table 8. Although carbonates and iowaite were observed as reaction products, these mineral phases were present in relatively small amounts (estimated to be <2% of reaction products) that made only a minor contribution to mass balance, and have been disregarded in the reactions. On the basis of the Mössbauer results, a value of 3:1 is adopted for the $Fe^{II}:Fe^{III}$ ratio in serpentine at all temperatures. The value of 3:1 is similar to predicted ratios from thermodynamic models of olivine serpentinization for this temperature range (Klein et al., 2013) as well as ratios reported for many chrysotile occurrences in natural systems (O'Hanley and Dyar, 1998). The excess charge created by Fe^{III} was assumed to be accommodated by vacancies in the octahedral site (Evans, 2008).

The stoichiometry of the reactions in Table 8 yield a chrysotile:brucite weight ratio of about 6 at all temperatures, which is similar to, but slightly smaller than, the ratios determined by TGA (7.4-9.3). This minor discrepancy may reflect partial incorporation of Mg into carbonate minerals rather than brucite, errors in the TGA analyses, or a greater amount of water in the

serpentine structure than is reflected in its nominal formula. The reaction stoichiometries in Table 8 also suggest that about 10-15% of the H₂ production in the experiments at temperatures of 230 °C and above is derived from Fe^{III} incorporated into serpentine rather than magnetite. At 200 °C, the proportion appears to be somewhat higher, and may reach values above 20%. However, owing to uncertainties in the amount of Fe^{III} contained in chrysotile and the relative proportions of the product minerals, these values should be considered to be approximate. For lizardite, which can contain substantially higher Fe^{III} contents than the chrysotile produced in our experiments (O’Hanley and Dyar, 1993; Evans, 2008), the proportion of H₂ derived from serpentine may be significantly higher.

While the reaction stoichiometries shown in Table 8 are derived from the measured mineral compositions that were determined at the end of the experiments, several observations indicate that the stoichiometry did not vary appreciably as the reactions progressed. First, except for the initial phase of the OLIV230 experiment, H₂ generation occurred at nearly constant rates during the experiments, suggesting relatively constant stoichiometry (Figs. 1, 2 & 3). Second, extensive examination of reaction products with EDS did not reveal any evidence of compositional variability or zonation in the mineral products that would indicate change in reaction stoichiometry over time. Third, in those instances where experiments were performed for different durations at the same temperature, the mineral compositions and H₂ generation rates appeared to be similar for different reaction times. Consequently, it appears likely that the serpentinization reactions proceeded with essentially the same stoichiometry throughout the experiments. This apparent constant stoichiometry is consistent with observations of Malvoisin et al. (2012a), who reported that production of magnetite during serpentinization of olivine

increased was nearly linear with reaction progress in many of their laboratory experiments conducted at 250-300 °C.

There does appear, however, to be one minor exception to the general prevalence of constant stoichiometry in this study. The long-term experiment at 230 °C (OLIV230) exhibited a long lag time (~2500 h) prior to the onset of significant H₂ generation that was not observed in experiments at other temperatures (Fig. 1b). Besides the increase in H₂ production, there was no obvious change in the fluid composition, such as a shift in pH or variation in concentrations of other dissolved compounds, that might indicate the cause of the increased H₂ production. Since the fluids at the start of the experiments were exposed to air, the fluid would have contained some O₂ that could have reacted with H₂ produced by fluid-rock interactions in the early stages of the experiments. However, this is unlikely to explain the delayed onset of H₂ accumulation in OLIV230, since the maximum amount of dissolved O₂ present in the fluid (~0.1 mmol kg⁻¹ based on equilibrium with the local atmosphere) is small compared to the amount of H₂ expected to be generated during the first 2500 hours based on rates observed later in the experiments (>3 mmol kg⁻¹). The delayed onset could also be explained by an increase in the reaction rate of olivine as the experiments progressed, but this seems unlikely since there is no obvious reason why the rate would suddenly undergo a steep increase after 2500 h of heating.

Perhaps the most plausible explanation for the delayed onset of H₂ accumulation in OLIV230 is that small amounts of Opx present in the reactant minerals led to the occurrence of different reaction pathways in the early stages of the experiment that did not generate H₂ (for instance, through precipitation of Fe^{II}-enriched serpentine rather than production of magnetite). This was the first experiment performed for this study, and other mineral phases were not as scrupulously removed from the reactant olivine as they were in subsequent experiments. In the

latter stages of OLIV230 (~3800 h to 8159 h), H₂ was generated at a steady rate that would be consistent with a constant reaction stoichiometry. Accordingly, the change in H₂ production rates in this experiment may reflect a transition to the stoichiometry shown in Table 8 following depletion of Opx as the experiment progressed.

4.2. Fluid constraints on reaction pathways

Additional constraints on reaction pathways during the experiments can be derived from evaluation of fluid compositions. Calculated values of in situ pH (pH_{in situ}) for the experiments are listed in Tables 2 and 3. In general, calculated values of pH_{in situ} are slightly lower than the measured pH_{25°C} for experiments performed at temperatures of 200 and 230 °C, but somewhat higher for experiments at temperatures of 265 °C and above. In all cases, however, the calculated pH_{in situ} values are around 8, indicating that the fluids were moderately alkaline at the reaction conditions (neutral pH is ~5.5 in the 200-320 °C range at 35 MPa).

Calculated in situ activities of dissolved silica [*a*_{SiO₂(aq)}] during the longer-term experiments are displayed in Figure 7 along with the relative stability fields of olivine, talc, chrysotile, and brucite as a function of temperature. At all temperatures, silica activities of the initial fluid samples fall within the chrysotile stability field. With continued reaction, the silica concentrations in the experiments dropped rapidly and then leveled off at concentrations around 20-40 μmol kg⁻¹ at all temperatures (Figs. 1c, 2b, and 3c). While the observed *a*_{SiO₂(aq)} values converge towards the boundary for chrysotile-brucite equilibrium, the activities nevertheless remain well above equilibrium values despite prolonged reaction times and the presence of brucite in all of the experiments (Fig. 7).

These results indicate that brucite did not attain equilibrium with chrysotile during the experiments. If brucite in these experiments had attained equilibrium with chrysotile, SiO₂

levels would have been significantly lower than the measured values (Fig. 7). On the other hand, silica activities remained close to levels expected for metastable equilibrium between olivine and brucite, suggesting that reactions between those minerals may have controlled silica activities.

Another perspective on the relationships between fluid compositions and mineral phases is provided in Figure 8, which shows the calculated values of in situ pH and silica activity for the 230-300 °C experiments plotted on mineral stability diagrams for the Mg-Fe-Si-C-O-H system (see Supplemental Fig. S9 for 200 °C and 320 °C results). While it might be expected that the presence of the mineral assemblage of chrysotile+brucite+magnesite in the experiments would be reflected by convergence of the fluids towards the invariant point for equilibrium among these phases, the measured fluid compositions nevertheless remained within the chrysotile stability field (Fig. 8a-c). However, when chrysotile is excluded from the diagrams, the experimental fluid compositions appear to converge on the metastable invariant point for equilibration of the assemblage olivine+brucite+magnesite (Fig. 8d-f). This is most clearly evident in the lower temperature experiments, where the difference between the $a_{\text{SiO}_2(\text{aq})}$ values of the invariant points for chrysotile+brucite+magnesite and olivine+brucite+magnesite is greatest (see also Fig. 7).

In all of the experiments, thermodynamic considerations indicate that brucite should have reacted with dissolved SiO_2 to form chrysotile and lower the silica activity in the fluid, as represented by the general reaction:

brucite

serpentine

where the occurrence of the reactants and products shown in brackets depends on the relative compositions of brucite and serpentine. The persistence of silica activities at values well above brucite-chrysotile equilibrium suggests that this reaction was kinetically inhibited on the

612 olivine brucite serpentine

613 (in accordance with Frost and Beard, the reaction is written for the Mg endmembers only, but
614 inclusion of Fe would not significantly affect the equilibrium level of $a_{\text{SiO}_2(\text{aq})}$). Equilibration of
615 this mineral assemblage would buffer silica activities to very low levels below that of serpentine-
616 brucite equilibrium. According to this scenario, silica activities during active serpentinization
617 would remain very low until olivine is completely eliminated, at which point $a_{\text{SiO}_2(\text{aq})}$ would rise
618 to levels consistent with serpentine-brucite equilibrium. However, in the experiments performed
619 for this study and in other studies as well (Fig. 7), silica activities remained at or above the
620 serpentine-brucite buffer, even though olivine persisted throughout the experiments. Thus, at
621 least under the experimental conditions, the very low silica activities that would be attained by
622 equilibration of Rxn. 5 were not observed, and there was no evidence that olivine, serpentine,
623 and brucite came into simultaneous equilibrium in any of the experiments.

624 *4.3. Partitioning of Fe among reaction products*

625 One of the primary objectives of this study was to determine the partitioning of Fe among
626 mineral products and to evaluate the factors responsible for this distribution. As shown in Figure
627 5, the serpentine produced during the experiments contained relatively small amounts of Fe
628 (Mg# = 95-98) with only limited variation in Fe content with reaction temperature, at least for
629 temperatures ≥ 230 °C. Conversely, brucite exhibited a broader range of compositions (Mg# =
630 91-99), with Fe contents progressively decreasing at higher reaction temperatures. These
631 observations allow proposed models for the partitioning of Fe among product phases during
632 serpentinization to be tested.

633 On initial inspection, the compositions of chrysotile and brucite produced in the experiments
634 appear to be generally consistent with thermodynamic equilibrium models for serpentinization of

ultramafic rocks (McCollom and Bach, 2009; Klein et al., 2009, 2013). These models predict that serpentinization should produce chrysotile with a nearly constant composition of $Mg\# \approx 96$ between 200 and 320 °C while the Fe content of brucite should steadily decrease with increasing temperature from $Mg\# \approx 85$ at 200 °C up to $Mg\# \approx 95$ at 320 °C. However, other aspects of the results are not consistent with computed thermodynamic equilibrium. For instance, the thermodynamic models assume that the Fe component of brucite will maintain equilibrium with magnetite at the ambient abundance of H_2 . This relationship can be represented by the reaction:

where $[Fe(OH)_2]_{\text{brucite}}$ represents the Fe component of brucite. Figure 9 shows the calculated compositions of brucite in equilibrium with magnetite as function of H_2 and reaction temperature, with results from the laboratory experiments shown for comparison. Although a few of the experimental results come close to matching the calculated equilibrium composition of brucite at the measured H_2 concentration, the majority of the experimental data do not show good agreement with equilibrium. Furthermore, experiments that attained higher concentrations of H_2 at a given temperature would be expected to produce brucite with higher Fe contents according to Rxn. 6, but experiments performed at the same temperature generally produced brucite with similar $Mg\#$ despite widely different H_2 concentrations. For instance, experiments OLIV300 and OLIV300_sat2 produced brucite with similar Fe contents ($Mg\# = 96$) even though the latter had much higher H_2 concentrations throughout the experiment. Similarly, experiments OLIV230 and OLIV230_fine both produced brucite with $Mg\# = 92$ despite a greater than four-fold difference in H_2 concentration.

In addition, for serpentinization under nearly closed system conditions (as in the laboratory experiments), thermodynamic equilibrium according to Rxn. 6 requires that brucite should become progressively more enriched in Fe as the reaction proceeds, and the proportion of magnetite produced from each incremental amount of olivine reacted should decrease. That is, as H₂ accumulates with increasing extent of reaction, conditions should increasingly favor the partitioning of Fe into brucite relative to precipitation of magnetite, resulting in changing stoichiometry as the reaction progresses (Rxn. 6; Fig. 9). Yet, experimental results from this study as well as those of Malvoisin et al. (2012a,b) do not show any indication for either an increase in Fe content of brucite or a decrease in the proportion of magnetite produced with increasing extent of reaction (Fig. 10). Instead, the results suggest that the Fe content of brucite and proportion of magnetite produced remained essentially constant as the reaction progresses, regardless of the accumulation of H₂.

Based on these considerations, it appears doubtful that brucite and magnetite remain in equilibrium with one another during the experiments, and equilibrium with magnetite does not appear to be controlling the Fe content of brucite under the experimental conditions. Furthermore, as discussed above, brucite appeared to be out of equilibrium with chrysotile in the experiments, providing additional evidence that thermodynamic equilibrium did not prevail during the reactions. Consequently, it appears that the equilibrium thermodynamic relationships proposed by McCollom and Bach (2009) may not be directly applicable to explain the distribution of Fe among secondary minerals under the experimental conditions.

Alternatively, Frost and Beard (2007) have proposed that the relative Fe contents of serpentine and brucite during serpentinization are controlled by equilibrium between these mineral phases as a function of silica activity (see their Fig. 5). While their model is non-

quantitative, it predicts that Fe content of both serpentine and brucite will increase with increasing silica activity, with brucite consistently maintaining a higher Fe:Mg ratio than serpentine. Based on their model, those authors suggest that higher silica activities will favor production of Fe-rich serpentine and brucite without magnetite, while lower silica activities will favor formation of magnetite along with relatively Fe-poor serpentine and brucite.

Because the experiments performed for this study all converge to similar values of silica activity, the results cannot be used to rigorously test the dependence of serpentine and brucite compositions on silica activity proposed by Frost and Beard (2007). However, the experimental data do not exhibit any systematic trend with silica activity as might be expected if this was the primary variable controlling the composition of the minerals (Fig. 11). Although the equilibrium distribution of Fe between serpentine and brucite as a function of silica activity would be expected to vary with temperature and oxidation state, there is no indication that a consistent trend would emerge from the data if these other variables were taken into account. In any case, the experimental results indicate that it is reactions among the minerals that regulate silica activities during serpentinization rather than silica activities controlling the composition of the minerals, as suggested by the proposed scenario of Frost and Beard (2007). As a consequence, the data do not appear to be consistent with silica activity being the major factor controlling the partitioning of Fe among product minerals during the experiments.

As another alternative, Evans and Tromsdorff (1972) have proposed that the relative Fe contents of serpentine and brucite precipitated during serpentinization are regulated by equilibrium partitioning of the Fe between these phases, with a distribution constant (K_D) equal to 0.50. The K_D in this case is defined as:

$$K_D = (X_{Fe}/X_{Mg})_{serpentine}/(X_{Fe}/X_{Mg})_{brucite} \quad (7)$$

where X_{Fe} and X_{Mg} are the mole fraction of Fe and Mg in the minerals. However, since Evans and Tromsdorff (1972) derived this relationship for Fe partitioning in reference to antigorite, it might not be strictly applicable to chrysotile. Nevertheless, comparison of this model with experimental data can still be informative.

Figure 12 shows the relative Fe contents of serpentine and brucite pairs in experiments from this study as well as data from other studies where mineral compositions were reported for experimental serpentinization of olivine. Also shown for comparison are expected values for equilibrium partitioning as proposed by Evans and Tromsdorff (1972). The measured compositions of minerals from the present study exhibit considerable scatter on this plot, and there is no apparent correlation between the compositions of serpentine and brucite in this dataset. When all of the available data are considered collectively, they follow a vague trend parallel to the equilibrium partitioning line but offset to lower values for Mg# of brucite. However, given the considerable scatter in the data, it is difficult to determine whether this might represent a genuine relationship. Overall, there does not appear to be any linear correlation between the Fe contents of serpentine and brucite in the experimental results, which would appear to be consistent with the disequilibrium between brucite and chrysotile inferred from the observed silica activities.

Thus, none of the models that have been proposed to date to explain the distribution of Fe among the mineral products of serpentinization appear to be consistent with laboratory results from this or other experimental studies. All of the proposed models are based on attainment of some degree of thermodynamic equilibrium among the product phases, and it could be argued that longer reaction times in natural systems might allow these phases to equilibrate to a greater extent than is allowed by relatively short laboratory experiments. However, the available

evidence indicates that longer reaction times lead only to a greater extent of reaction with the same stoichiometry (e.g., Fig. 10), so it appears doubtful that more prolonged reactions would lead to equilibrium conditions, unless such equilibration occurred after serpentinization was complete. Of course, the experiments do not replicate all of the conditions present in natural environments, and it is possible that other factors that are not replicated in the experiments might cause serpentinization in natural settings to more closely parallel the predictions of the models. Nevertheless, the results suggest that more complex models may need to be considered to explain the processes controlling mineral composition during serpentinization.

The results of this study and those of Malvoisin et al. (2012a,b) indicate that the stoichiometric partitioning of Fe among the reaction products as well as the proportion of Fe^{II} converted to Fe^{III} remained essentially constant during individual experiments, although this stoichiometry varied for experiments performed at different temperatures. The partitioning of Fe among reaction products is likely regulated by mechanistic factors related to individual reactions and the relative rates of those reactions, rather than equilibrium factors alone. However, because multiple reaction steps appear to be involved, it will require a better understanding of these individual steps to formulate a rigorous model of the overall process.

4.4. Reaction rates for serpentinization of olivine

Few experimental studies have examined reaction rates for serpentinization of olivine, and the rates that have been reported to date are widely divergent (Fig. 13) (Martin and Fyfe, 1970; Wegner and Ernst, 1983; Malvoisin et al., 2012b; Lafay et al., 2012; Andreani et al., 2013b). As a consequence, the rates of serpentinization reactions and how these rates vary with environmental factors such as rock and fluid composition, temperature, etc., remain poorly understood. Because the solids in the present study were only sampled at the endpoint of the

experiments, the results are not ideally suited to quantitative evaluation of reaction rates. Nevertheless, since even provisional rates can provide useful insights, reaction rates for serpentinization and for H₂ generation during the experiments were estimated for comparison with other studies.

Until recently, the only in-depth experimental studies of reaction rates for serpentinization were those of Martin and Fyfe (1970) and Wegner and Ernst (1983). Both of these studies reported reaction rates for serpentinization of olivine at elevated temperatures that were relatively rapid on geologic timescales (Fig. 13). For instance, Martin and Fyfe (1970) reported ~40% conversion of synthetic forsterite to serpentine plus brucite after 8 days at 200 °C, and ~70% conversion after 8 days at 250 °C, using a somewhat smaller average grain size (58-79 µm) than most of the experiments in the present study. Both studies reported that reaction rates increased substantially with increasing temperature up to about 270-300 °C, but decreased steeply at higher temperatures (Fig. 13). The decrease in reaction rates with temperatures above ~300 °C has conventionally been attributed to slowing of the reaction as the temperature approaches the point where olivine can exist in stable equilibrium with water (~360 °C at 35 MPa).

More recently, Malvoisin et al. (2012b) found reaction rates for serpentinization of olivine that were one to two orders of magnitude slower than those reported by Martin and Fyfe (1970) and Wegner and Ernst (1983) (Fig. 13). For instance, Malvoisin et al. (2012b) found that 216 days of reaction were required to achieve 26% reaction of olivine with a grain size of 50-63 µm at 250 °C, which is more than an order of magnitude slower than the rates reported by Wegner and Ernst (1983) and Martin and Fyfe (1970) for similar reaction conditions. While their absolute rates were much slower, Malvoisin et al. (2012b) did find a similar temperature trend to

those reported in the earlier studies, with rates increasing with temperature up to 300 °C and then decreasing at 350 °C. In other recent studies, Lafay et al. (2012) reported reaction rates very similar to those of the earlier studies by Wegner and Ernst (1983) and Martin and Fyfe (1972) during experimental serpentinization of olivine under extremely alkaline conditions ($\text{pH}_{25^\circ\text{C}} = 13.5$) for experiments with comparable grain sizes, while Andreani et al. (2013b) found even higher serpentinization rates when olivine was reacted in the presence of a soluble Al-bearing phase (Fig. 13).

To approximate overall reaction rates during the present study, the amount of alteration products present at the endpoint of the experiments (Table 4) were used to estimate the rates of serpentinization. Since H_2 production was linear in most experiments (Figs. 1, 2 & 3) and there was no indication of a change in reaction mechanism or stoichiometry over time in most cases, it was assumed that reaction rates were linear during the course of the experiments. Malvoisin et al. (2012b) monitored reaction progress in their experiments by measuring the production of magnetite over time. In most of their experiments, magnetite production was roughly linear with only a slight increase over time, indicating that reaction rates were approximately constant during the experiments. In a few cases, however, they found that magnetite accumulation followed a sigmoidal pattern where an initially slow production of magnetite was followed by an increase in production rate that eventually slowed when a large extent of reaction was attained (see, for example, experiments #2 and #22 in Figure 2 from Malvoisin et al., 2012b). This change in reaction rates was attributed to changes in the reactive surface area of the olivine grains during the experiments. Based on H_2 production, the only experiment in this study to display similar behavior was the long-term experiment at 230 °C, which produced little H_2 during the first ~2500 h followed by a steep increase in production rate (Fig. 1b). However, it is not

clear whether this increase in H₂ production reflected a change in the reaction rate of olivine or other factors such as the presence of small amounts of Opx. Consequently, an assumption of relatively constant reaction rates appears to be a valid first-order approximation for the experiments.

Using an assumption of linear reaction rates and estimates of the amount of olivine reacted at termination of the experiments (Table 4), overall reaction rates for conversion of olivine were calculated, with results shown in Figure 13. The reaction rates do not show a consistent trend with temperature, with an anomalously low reaction rate at 265 °C and reaction rates at 200 and 230 °C comparable to those at 300 and 320 °C. While the variation in reaction rates with temperature may reflect a shift in the rate-controlling step for the overall conversion of olivine, the limited data available make it difficult to determine the underlying cause of the temperature trend. Nevertheless, the estimated reaction rates appear to be consistent with the results of Malvoisin et al. (2012b) when grain size effects are taken into account. The smaller grain size employed in the Malvoisin et al. (2012b) experiments shown in Figure 13 (38-50 µm) relative to most of the experiments in this study (53-212 µm) should result in olivine with 3-5 times greater surface area (Brantley and Mellott, 2000), which probably accounts for the ~3-fold higher reaction rates reported in their study. The rate estimates of two experiments in this study that were conducted with smaller grain size agree very well with the rates of Malvoisin et al. (2012b). On the other hand, reaction rates observed in the present study are all significantly slower than those reported previously by Martin and Fyfe (1970) and Wegner and Ernst (1983), by a factor of 50-80 for experiments with comparable grain size. Thus, our results support the conclusions of Malvoisin et al. (2012b) that rates of serpentinization of olivine in natural systems may be

significantly slower than the earlier studies of Martin and Fyfe (1970) and Wegner and Ernst (1983) would suggest.

The reason for the broad discrepancy in reaction rates between recent results and the older studies is not immediately apparent, and direct comparisons among experiments are hampered by differences in experimental design and the lack of information on fluid compositions for many studies. Both Martin and Fyfe (1970) and Wegner and Ernst (1983) estimated the extent of serpentinization in their experiments by the difference in weight of the minerals before and after reaction, and it is possible that the procedures used to dry the products after reaction did not remove all of the reactant fluid, producing anomalously high estimates for the extent of reaction. Alternatively, the minerals formed during their experiments may have contained more structural water than is typical of serpentinites, or may have included trapped water. It is not clear, however, whether these factors could account for the very large differences in reaction rates. Martin and Fyfe (1970) did report slower reaction rates when natural Fe-bearing olivine ($Mg\# = 85$) was used as reactant rather than synthetic forsterite in a few of their experiments, but this decreased rates by less than a factor of three and thus cannot explain the full extent of discrepancy with more recent results. Because neither Martin and Fyfe (1970) nor Wegner and Ernst (1983) provide detailed descriptions of the reaction products, it is difficult to assess the accuracy of the high extent of olivine conversion that they report. Since Lafay et al. (2012) found reaction rates similar to those of the older studies under strongly alkaline conditions (Fig. 13), another possibility is that the experiments of Martin and Fyfe (1970) and Wegner and Ernst (1983) attained strongly alkaline conditions that promoted more rapid reaction. However, no fluid chemistry was reported for the older studies, so this possibility cannot be evaluated further with the available data.

4.5. Rates of H_2 generation

The fluid measurements also allow rates of H_2 production during the experiments to be estimated and compared with other studies. In most cases, H_2 was generated at a relatively constant, linear rate. The principal exceptions were the larger-grain experiments at 230 °C (OLIV230 and OLIV230_short) where there was a delay in the onset of H_2 production, although H_2 production appeared to occur at a linear rate following the delayed onset. Similarly constant rates of H_2 accumulation have been reported for other olivine serpentinization experiments, at least during the early stages of reaction (Berndt et al., 1996; McCollom and Seewald, 2001; Allen and Seyfried, 2003; Jones et al., 2010; Klein and McCollom, 2013).

Assuming that H_2 generation was linear during the experiments, production rates were calculated as shown in Figure 14. For comparison, the figure also shows calculated production rates for several other experimental studies of olivine serpentinization where H_2 concentrations were reported. To facilitate comparison among studies, the data have all been normalized to show the rate of H_2 production per unit surface area of olivine. Since most other studies did not report surface areas for their olivine reactants, these were estimated based on Brantley and Mellott (2000) (see Supplemental Materials for details of the calculations). While these estimates of surface area introduce some uncertainty into the calculated H_2 production rates, the errors probably affect the absolute values more than the relative values between different experiments. The experiments shown were performed using methods similar to those of the present study, except that the experiments of Jones et al. (2010) were performed in a rocking reaction vessel that was rotated during heating (the frequency of rotation was not reported). Exposure of fresh olivine surfaces during rotation may account for the much higher rates of H_2

production reported by Jones et al. (2010) relative to other experiments at comparable temperatures (Fig. 14).

Although the available data are limited, they indicate that the rate of H₂ production during serpentinization of olivine generally increases up to about 300 °C, and then decreases at higher temperatures. Experiments conducted with a smaller grain size consistently generated H₂ at rates that were substantially faster than the 53-212 µm experiments at the same temperature, by factors ranging from ~10 to ~100. It is unlikely that errors in the surface area approximations can account for the differences in H₂ production rates for different grain sizes, since even a 50% error in surface area changes the estimated rate by only a factor of 2. Malvoisin et al. (2012b) noted that the reactive surface area of olivine sharply increases during hydrothermal experiments owing to two effects: (1) preferential etching of the surface on particular grain boundaries to form dentate structures, and (2) fracturing of larger crystals. In the present study, even those experiments with little extent of reaction contained numerous particles of relict olivine that were much smaller than the initial grain size (see, for example, Supplemental Fig. 10a and 10b). Perhaps these effects had a greater impact on the experiments with initial smaller grain size are responsible for the higher production rates. Nevertheless, the overall trend in the experiments performed with smaller grains parallel those for the 53-212 µm experiments.

Two factors evidently contribute to the observed trend in H₂ production rates seen in Figure 14. First, the temperature trend in H₂ production rates closely parallels the rate of olivine conversion (Fig. 13), reflecting the contribution of overall serpentinization reaction rates to the production of H₂. Second, increased partitioning of Fe into brucite rather than magnetite with decreasing temperature contributes to the decrease in H₂ production with decreasing temperatures.

The results for the large-grained experiment at 230 °C represent somewhat of an anomaly in the general trend of increasing H₂ production rates with increasing temperature. While experiment OLIV230 produced H₂ at a rate lower than the higher temperature experiments during the first ~4100 h, after that time H₂ was produced at a rate faster than observed in the 265 °C and 320 °C experiments (Figs. 1 and 16). Furthermore, after a short lag period, experiment OLIV230_short also produced H₂ at a higher rate than the 265 °C and 320 °C experiments. At this point, it is not clear how to explain these variations in the temperature trend. It is possible that the 265 °C experiment produced anomalously low amounts of H₂ for some reason that is not immediately evident. Alternatively, the reaction mechanism responsible for H₂ generation may undergo a change between 230 °C and 265 °C.

4.6. Implications for natural systems

The reaction rates observed in this study as well as the results of Malvoisin et al. (2012b) suggest that serpentinization of olivine in ultramafic rocks in natural systems may proceed much more slowly than older studies had suggested. For instance, based on their experimental results, Wegner and Ernst (1983) estimated that complete serpentinization of olivine-rich dunites with an average grain diameter of 1 mm in near surface environments would occur in ~4.8 years at 230 °C or 800 years at 25 °C. At these rates, shallowly emplaced dunites would be expected to completely serpentinize on very brief timescales from a geologic perspective. However, the reaction rates observed in this study suggest that much longer timescales would be required for serpentinization to go to completion in near surface environments. For instance, if the approximately 80-fold slower reaction rates observed in recent studies is applied to the above estimates of Wegner and Ernst (1983), nearly 400 years would be required for complete serpentinization of 1 mm grain-size olivine at 230 °C or >60,000 years at 25 °C. Given that

reaction rates in natural systems are often orders of magnitude slower than those measured in laboratory experiments (e.g., White and Brantley, 2003), reaction rates of serpentinization in natural systems may be even slower. Furthermore, the experimental reaction rates were determined using powdered materials with abundant pore space, and rates are expected to be slower in more compact aggregates and coherent rocks where the fluids must penetrate along grain boundaries (e.g., Malvoisin and Brunet, 2014; Klein et al., 2015b).

The slower reaction rates found in recent studies would appear to be more compatible with the widespread occurrence of partially serpentinized rocks in shallow subsurface environments than the more rapid rates reported by Wegner and Ernst (1983). Of course, factors other than temperature, such as fluid and rock compositions, fluid fluxes, and water availability, would be expected to affect reaction rates of serpentinization in natural environments, and the impact of these factors would need to be evaluated before any definitive statements can be made about the timescale of serpentinization in specific settings.

Rates of H₂ generation parallel the trend for overall reaction rates, indicating that the highest rates of H₂ generation during serpentinization of olivine should occur at around 300 °C with rates dropping off at higher and lower temperatures (Fig. 14). Although a number of deep-sea hydrothermal systems have been identified whose fluid compositions appear to be influenced by serpentinization of ultramafic rocks, these occur at temperatures that are either higher (>365 °C) or lower (<~250 °C) than the peak temperature (e.g., Charlou et al., 2002, 2010; Kelley et al., 2005; Foustoukos et al., 2008; McDermott et al., 2015). In high temperature systems such as Rainbow and Logatchev, where hydrothermal fluids vent at temperatures of 365 °C or above (Charlou et al., 2002, 2010), olivine may be stable in the source regions of the fluids, and most of the H₂ may be derived from reactions involving pyroxenes (Allen and Seyfried, 2004). At the

Lost City system, H₂ concentrations up to 15 mmol/kg have been measured in hydrothermal fluids (Kelley et al., 2005). Although the measured temperatures of hydrothermal fluids venting at the seafloor in the Lost City system are around 91 °C, peak temperatures of reaction zones during circulation through the subsurface are thought to be somewhat higher, in the 150-250 °C range (Proskurowski et al., 2006; Foustoukos et al., 2008). If the production rates measured in this study are representative, it appears feasible that the H₂ concentrations observed at Lost City could be attained during circulation of fluids through the crust on timescales of a couple of years. However, detailed models that take into account fluid circulation pathways and environmental factors such as fluid:rock ratios and grain size will be required to rigorously test this possibility.

It is worth noting that the measured concentrations of SiO₂ at Lost City (24-73 µM; Seyfried et al., 2015) are very similar to those observed in the experiments performed for this study. Seyfried et al. (2015) have argued that the measured concentrations, which are elevated relative to values expected for serpentine-brucite equilibrium at the inferred reservoir temperatures (~200 °C), are controlled by equilibration with the mineral assemblage serpentine+diopside+tremolite, driven by reaction of plagioclase with serpentinized peridotite in the subsurface. However, the experimental results indicate that plagioclase is not required to explain the elevated SiO₂ concentrations, which might instead be attributable to olivine-brucite equilibrium (Rxn. 4).

The results also suggest that serpentine replacing olivine should have a lower Fe:Mg ratio than the original olivine, and this proportion should be largely insensitive to temperature of formation. On the other hand, the Fe:Mg ratio for brucite should increase with decreasing temperature of serpentinization. These results appear to be consistent with observations from natural systems. For instance, serpentine in serpentinized mantle rocks predominantly have Mg#

in the range of 94-96, while olivine in the same rocks exhibits a narrow range of Mg# between 88 and 91 (Früh-Green et al., 1996, 2004; Mével and Stamoudi, 1996; Bach et al., 2006; Frost, 2008; Beard et al., 2009; Klein et al., 2009). Conversely, brucite in serpentinites exhibit a broad range of compositions, with Mg# as low as 60 reported in some cases (Hostetler et al., 1966; Page, 1967; Evans and Trommsdorf, 1972; Moody, 1976a,b; D'Antonio & Kristensen, 2005; Bach et al. 2006; Klein et al., 2014). It appears likely that reaction temperature has been a major factor responsible for the variation in Fe content among natural samples, with reaction temperatures <200 °C possibly accounting for brucites with higher Fe contents. However, other factors are likely contribute to variation in the Fe content of brucite, and more work will need to be done to determine how other factors such as rock composition and pH effect Fe content before brucite compositions can be used to make specific inferences about reaction temperatures.

5. Concluding remarks

Perhaps more than anything, the results of this and other recent experimental studies emphasize that serpentization reactions are complex, and reaction pathways can be highly variable when performed under different conditions, for reasons that are not yet well understood. The experiments reported here demonstrate that reaction temperature exerts a strong influence on the composition of product minerals and H₂ production during serpentization, but additional work on the influence of other factors such as pH and the presence of additional reactant minerals (e.g., orthopyroxene, clinopyroxene) on reaction pathways are required in order to form a comprehensive view of the role of environmental factors on product composition. In addition, the experimental results indicate that reaction pathways during serpentization of olivine are controlled by a combination of thermodynamic and kinetic factors. Further progress in understanding the overall process would benefit from a better understanding of the relative

reaction kinetics of the individual reactions involved, such as the reaction of brucite with SiO₂ (Rxn. 4) and reactions between brucite and magnetite (Rxn. 6). Development of numerical models of serpentinization to date have largely relied on an assumption of thermodynamic equilibrium (e.g., Palandri and Reed, 2004; McCollom and Bach, 2009; Klein et al., 2013), but results from this study as well as other recent experimental work indicate that accurate portrayal of serpentinization reactions may require incorporation of kinetic factors and multiple reaction steps into the models.

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1227 **Table 1.** Summary of experimental parameters.

Experiment	Target Temp. (°C)	Duration (h)	Mass olivine (g)	Grain size (µm)	Initial fluid (g)	Initial F:R [#]
OLIV200	200	3331	25.0	53-212	44.7	1.8
OLIV200_fine	200	1823	17.0	38-53	35.8	2.1
OLIV230	230	8183	25.0	53-212	42.4	1.6
OLIV230_short	230	1823	18.0	53-212	39.7	2.2
OLIV230_fine	230	4293	16.0	<53	39.5	2.4
OLIV265	265	4857	17.4	53-212	45.1	2.6
OLIV300	300	2683	20.0	53-212	42.2	2.1
OLIV300_med ^s	300	333	18.0	53-212	40.7	2.2
OLIV300_short ^s	300	41	14.0	53-212	37.8	2.6
OLIV320	320	2087	15.0	53-212	38.3	2.5

[#]Fluid:rock ratio at start of experiment. ^sThese experiments included polished olivine slabs.

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Table 2. Fluid compositions during long-term hydrothermal experiments with 53-212 μm olivine at 200 to 320 $^{\circ}\text{C}$.

Time (h)	Temp ($^{\circ}\text{C}$)	H ₂ (m)	CO ₂ (m)	CH ₄ (μ)	Na (m)	Cl (m)	Si (μ)	Fe (μ)	Mg (μ)	Ca (μ)	Al (μ)	K (μ)	pH (25 $^{\circ}\text{C}$)	pH in situ	H ₂ gen. [#] ($\mu\text{mol/g}$)	Fluid (g)
<i>Experiment OLIV200 (200 $^{\circ}\text{C}$)</i>																
67	200	0.003	20.4	1.8	-	-	-	-	-	-	-	-	8.2	-	0	44.7
933	200	0.10	-	-	530	-	44	<1	<10	<4	<6	68	8.7	8.1	0.16	42.7
1434	200	0.09	-	-	548	-	93	<1	<10	<4	<6	30	8.7	8.0	0.14	40.2
1698	200	0.07	-	-	525	-	65	<1	<10	<4	<6	51	-	-	0.11	38.3
2373	200	0.07	-	-	503	-	54	<1	<10	<4	<6	66	-	-	0.12	36.2
3331	200	0.09	8.1	-	503	-	22	<1	<10	<4	<6	54	9.0	8.7	0.14	33.0
<i>Experiment OLIV230 (230 $^{\circ}\text{C}$)</i>																
2	232	0	17.9	1.4	-	499	-	-	-	-	-	-	-	-	0	42.4
479	232	0.14	-	-	520	-	71	9	9	8	<6	60	8.3	8.1	0.23	40.4
1031	232	0.19	-	-	450	-	55	5	<10	9	<6	55	8.7	7.5	0.30	36.8
1967	231	0.14	1.0	0.3	492	486	24	<1	<10	<4	<6	<20	8.7	7.4	0.23	33.4
2496	232	0.23	-	-	-	-	28	-	-	-	-	-	-	-	0.34	29.5
3386	232	0.79	-	-	502	-	55	<1	<10	<4	<6	<20	8.4	7.3	0.94	27.2
4010	232	1.05	-	-	496	483	52	<1	<10	<4	<6	<20	6.8	7.1	1.20	24.8
4013	<i>Additional fluid injected</i>															
4034	232	0.45	13.4	3.7	508	476	130	<1	<10	<4	<6	<20	7.0	7.7	1.2	42.8
4559	232	1.08	-	-	483	-	43	<1	<10	<4	<6	<20	8.9	8.0	2.2	38.8
5063	232	1.49	-	-	502	-	37	<1	<10	<4	<6	<20	8.8	8.0	2.8	35.9
5735	232	2.43	-	-	518	-	32	<1	<10	<4	<6	<20	8.7	7.9	4.0	33.0
7055	232	4.09	6.6	6.4	494	-	23	<1	<10	<4	<6	<20	8.3	7.7	6.0	30.4
8159	232	5.78	6.0	5.5	-	476	17	-	-	-	-	-	8.0	7.6	7.9	27.8
<i>Experiment OLIV265 (265 $^{\circ}\text{C}$)</i>																
258	265	0.22	18.8	36	523	-	31	<1	<10	<4	140	<20	7.8	8.0	0.51	45.1
955	265	0.70	16.3	18	513	-	37	<1	<10	<4	110	330	7.6	8.0	1.6	41.7
2344	265	1.61	14.4	-	492	-	29	<1	<10	40	60	230	7.7	8.1	3.4	37.8
4857	265	2.45	12.2	16	489	-	27	<1	<10	40	50	150	7.7	7.9	4.9	34.0
<i>Experiment OLIV300 (300 $^{\circ}\text{C}$)</i>																
11	300	0.45	20.2	16	507	-	48	<1	<10	<4	<6	<20	8.4	8.3	0.95	42.2
1172	301	7.2	18.0	22	504	-	34	<1	<10	<4	<6	37	7.6	8.2	14.3	39.3
1891	300	9.0	13.3	25	-	-	28	-	-	-	-	-	7.3	8.1	17.5	35.6
2683	300	11.0	12.5	25	503	486	28	<1	<10	<4	<6	<20	7.1	8.1	20.7	31.9

Experiment OLIV320 (320 °C)

70	320	0.27	17.8	17	500	-	90	<1	<10	<4	<6	<20	7.8	8.4	0.69	38.3
481	320	0.75	20.1	71	500	-	32	<1	<10	<4	<6	<20	7.5	8.4	1.8	34.9
1343	320	1.8	21.0	210	480	-	41	<1	<10	80	<6	<20	7.1	8.4	3.8	31.7
2087	320	2.6	18.1	270	480	490	39	<1	<10	<4	<6	<20	7.0	8.4	5.1	29.0

Concentrations in mmol kg^{-1} (m) or $\mu\text{mol kg}^{-1}$ (μ). Concentrations given as “<1” were below the detection limit of approximately 1 $\mu\text{mol/kg}$. “-“ = not measured. [#]Hydrogen generated per gram of reactant olivine. [†]Amount of fluid in reaction cell at time of sampling.

Table 3. Fluid composition during short-term and fine-grained hydrothermal experiments with olivine at 230 and 300 °C.

Time (h)	Temp. (°C)	H ₂ (m)	ΣCO ₂ (m)	CH ₄ (μ)	Na (m)	Cl (m)	Si (μ)	Fe (μ)	Mg (μ)	Ca (μ)	Al (μ)	K (μ)	pH (25°C)	pH in situ	H ₂ gen. [#] (μmol/g)	Fluid [†] (g)
<i>Experiment OLIV230_short (230 °C, short-term)</i>																
23	230	0	17.0	1.0	479	500	170	<1	<10	<4	<6	-	8.1	7.9	0	39.7
289	230	0.02	-	-	493	-	43	<1	<10	10	<6	210	8.0	7.9	0.04	35.9
935	230	0.31	12.8	8.0	474	-	43	<1	10	10	<6	260	8.6	8.0	0.59	33.6
1366	230	0.69	11.4	10	451	-	41	<1	<10	10	<6	250	8.7	8.0	1.2	30.4
1823	231	1.24	11.0	11	449	470	29	<1	<10	<4	<6	-	7.9	7.8	2.0	26.9
<i>Experiment OLIV300_short (300 °C, short-term)</i>																
0	298	0.001	19.8	4.7	514	-	290	<1	<10	<4	17	150	8.1	8.3	0.003	37.8
19	300	0.21	-	-	511	-	136	<1	<10	8	18	190	8.1	8.3	0.5	33.4
41	300	0.56	19.1	10	-	-	47	<1	<10	<4	15	180	8.1	8.3	1.2	30.0
<i>Experiment OLIV300_med (300 °C, medium-term)</i>																
23	300	0.02	20.0	4.4	505	-	81	<1	7	28	8	270	8.0	8.3	0.05	40.7
93	300	1.02	-	23	507	-	48	<1	<10	<4	8	250	8.1	8.3	2.1	37.5
166	300	1.59	-	32	486	-	35	<1	<10	<4	<6	200	8.0	8.3	3.2	34.5
262	300	2.29	-	36	497	-	39	<1	<10	5	<6	270	7.8	8.2	4.4	29.9
333	300	2.86	17.5	43	504	-	40	<1	<10	<4	5	230	7.9	8.2	5.2	26.5
<i>Experiment OLIV200_fine (200 °C, 38-53 μm grain size)</i>																
50	200	0.0003	19.0	5.5	540	-	140	<1	150	160	<6	<20	6.4	7.1	0.001	46.2
2018	200	0.58	15.8	9.5	512	-	26	<1	<10	60	<6	180	8.8	8.1	1.4	42.2
5621	200	1.25	11.6	12.4	516	-	25	<1	<10	100	<6	-	9.4	8.4	2.9	38.1
7753	200	2.28	10.7	14.5	510	489	15	<1	<10	<4	<6	250	9.3	8.3	4.9	34.1
9219	201	2.94	9.6	14.8	511	-	14	<1	<10	30	50	240	9.2	8.2	5.9	25.6
<i>Experiment OLIV230_fine (230 °C, <53 μm grain size)</i>																
23	229	0.56	18.4	6.0	505	-	67	<1	11	10	<6	160	8.1	7.9	1.4	39.5
263	229	3.5	-	-	510	-	35	<1	<10	10	<6	190	9.0	8.2	7.9	35.9
695	230	6.3	-	-	480	-	43	<1	<10	10	<6	180	9.0	8.2	13.8	32.9
1629	230	10.5	-	6.9	480	-	35	<1	<10	7	<6	170	9.0	8.1	21.8	30.9
3501	230	22.	-	8.9	480	-	23	<1	<10	<4	<6	180	9.0	7.9	42.0	28.6
4293	230	25.	6.8	10	-	460	24	-	-	-	-	-	9.1	7.8	47.3	26.5

Concentrations in mmol kg^{-1} (m) or $\mu\text{mol kg}^{-1}$ (μ). Concentrations given as “<X” were below the detection limit. “-“ = not determined. # Amount of hydrogen generated per gram of reactant olivine. † Amount of fluid in reaction cell at time of sampling.

Table 4. Summary of solid reaction product compositions and inferred reaction parameters.

Experiment	Target Temp. (°C)	Duration (h)	Final H ₂ conc. (mmol/kg)	Total H ₂ generated (μmol/g olivine)	Mg#		wt.% magnetite [†]	Estimated % olivine reacted [‡]	
					Serpentine*	Brucite*		TGA	Grav.
OLIV200	200	3331	0.09	0.14	95 ^{††}	92 ^{††}	0.10	-	2.1
OLIV200_fine	200	9219	2.94	5.9	95 (0.8)	91 (1.1)	0.25	-	9.3
OLIV230	230	8183	5.78	7.9	98 (0.1)	92 (1.6)	0.37	5.4	4.8
OLIV230_short	230	1823	1.24	2.0	-	-	-	-	1.8
OLIV230_fine	230	4293	25	47.3	97 (0.4)	92 (1.2)	1.75	23	-
OLIV265	265	4857	2.45	4.9	97 (1.0)	96 (1.7)	0.12	-	1.8
OLIV300	300	2683	11.0	20.7	98 (0.4)	96 (0.7)	0.41	3.0	2.8
OLIV300_med	300	333	2.86	5.2	97 ^{††}	-	-	-	-
OLIV320	320	2087	2.60	5.1	97 (0.5)	99 (0.5)	0.17	-	2.7
<i>Additional experimental results[‡]:</i>									
OLIV300_MS	300	3192	44	205	98 (0.2)	93 (2.0)	4.44	-	60 [#]
OLIV300_sat1	300	2421	180	>87	97 (0.7)	93 (0.5)	3.33	-	50 [#]
OLIV300_sat2	300	3885	194	>64	97 (0.6)	96 (0.3)	1.63	-	21 [#]

*Based on EMPA measurements, except as noted. Standard deviations given in parentheses. [†]Measured magnetite abundance from saturation magnetization measurements. The weight percent magnetite was determined from the room-temperature bulk saturation magnetization values and the known value for pure magnetite ($M_s=92 \text{ Am}^2/\text{kg}$) as: wt% magnetite = $100\% \times M_s/(92 \text{ Am}^2/\text{kg})$. Minor amounts of cation substitution in the magnetite would increase the calculated wt% by less than 5%. [‡]Estimated of percentage of olivine reacted, based on either TGA results of gravimetric analysis (see txt). [§]See Supplemental Materials for details of these experiments. [#]Estimated from water weight loss after heating to 900 °C. ^{††}The Mg# for these phases was estimated using EDS because reaction products were too sparse and fine-grained to measure by EMPA. “-” = no data. The olivine starting material has a very weak magnetization that was 50 times lower than the magnetization of the weakest reaction run (OLV200).

Table 5. Representative chemical compositions of minerals determined by electron microprobe analysis.

Oxide (wt%)	SC Olivine	Chrysotile ^a	Chrysotile ^b	Brucite ^a	Brucite ^b	Magnetite ^a
SiO ₂	40.6	26.2	28.4	0.03	0.95	2.70
TiO ₂	0.00	0.00	0.00	0.01	0.01	0.05
Al ₂ O ₃	0.03	0.09	0.60	0.16	0.13	0.03
Cr ₂ O ₃	0.00	0.00	0.02	0.01	0.01	0.01
FeO	8.86	1.05	0.76	11.1	5.84	31.1
Fe ₂ O ₃	-	-	-	-	-	62.8
MgO	50.1	29.0	26.2	68.4	73.6	1.95
MnO	0.14	0.03	0.02	0.23	0.42	0.26
CaO	0.07	0.01	0.01	0.02	0.01	-
Na ₂ O	-	0.02	0.06	0.05	0.01	-
K ₂ O	-	0.02	<0.01	<0.01	<0.01	-
NiO	0.38	-	0.15	-	0.29	-
Cl	-	0.08	0.31	0.12	0.02	-
Total	100.1	56.6	56.5	80.1	81.3	98.9
Mg#	91	98	98	92	96	

^aFrom experiment OLIV230. ^bFrom experiment OLIV300. “-“ = not measured.

Table 6. Results of thermogravimetric analyses.

Experiment	% weight loss		Mass mineral (wt%)		Magnetite (wt%)	Estimated % olivine reacted
	Serpentine	Brucite	Serpentine	Brucite		
OLIV230	0.66	0.18	5.1	0.66	0.37	5.4
OLIV230_fine	2.85	0.90	22.2	3.0	1.75	23.
OLIV300	0.44	0.09	2.8	0.3	0.41	3.1

Table 7. Room-temperature hyperfine magnetic Mössbauer parameters for experimental samples.

Sample	Sample type	B_{HF} (T)	QS (mm/s)	IS (mm/s)	% [†]	Assignment
OLIV200_fine	separate		2.90	1.17	86	Fe ^{II}
			0.58	0.29	14	Fe ^{III}
OLIV230	separate	48.5 42.9	0.08	0.40		Mgt (site A)
			-0.01	0.68		Mgt (site B)
			2.86	1.18	76	Fe ^{II}
			0.66	0.28	24	Fe ^{III}
OLIV230_fine	bulk	49.0 45.9	-0.03	0.25		Mgt (site A)
			-0.02	0.68		Mgt (site B)
			2.97	1.16	100 [#]	Fe ^{II}
OLIV265	separate		2.90	1.16	86	Fe ^{II}
			0.58	0.29	14	Fe ^{III}
OLIV300	separate	49.0 45.7	-0.05	0.30		Mgt (site A)
			-0.06	0.73		Mgt (site B)
			2.86	1.16	80	Fe ^{II}
			0.70	0.26	20	Fe ^{III}
OLIV320	separate	45.4 42.5	-0.03	0.32		Mgt (site A)
			0.01	0.67		Mgt (site B)
			2.72	1.09	77	Fe ^{II}
			0.66	0.32	23	Fe ^{III}
OLIVCO2	bulk	49.1 45.5	-0.02	0.34		Mgt (site A)
			-0.01	0.67		Mgt (site B)
			2.94	1.17	100 [#]	Fe ^{II}
SC olivine			3.00	1.18	100	Fe ^{II}

[†]Relative abundances of Fe⁺² and Fe⁺³ in phases other than magnetite, in percentage. Magnetite was not included in this calculation since it was not quantitatively recovered during the separation procedure used to prepare products for MB analysis. [#]Owing to the fine-grained olivine used as starting materials for these experiments, the fraction analyzed by MB contains a much larger proportion of olivine than the other samples, dominating the spectrum for these samples.

Table 8. Approximate chemical reactions for serpentinization of olivine at different temperatures.

Temp. (°C)	Reaction
200	$\text{Mg}_{1.82}\text{Fe}_{0.18}\text{SiO}_4 + 1.458\text{H}_2\text{O} \rightarrow$ $0.5(\text{Mg}_{0.955}\text{Fe}^{\text{II}}_{0.03}\square_{0.005}\text{Fe}^{\text{III}}_{0.01})_3\text{Si}_2\text{O}_5(\text{OH})_4 + 0.421(\text{Mg}_{0.92}\text{Fe}_{0.08})(\text{OH})_2 + 0.029\text{Fe}_3\text{O}_4 + 0.037\text{H}_2$
230	$\text{Mg}_{1.82}\text{Fe}_{0.18}\text{SiO}_4 + 1.445\text{H}_2\text{O} \rightarrow$ $0.5(\text{Mg}_{0.966}\text{Fe}^{\text{II}}_{0.0225}\square_{0.004}\text{Fe}^{\text{III}}_{0.0075})_3\text{Si}_2\text{O}_5(\text{OH})_4 + 0.405(\text{Mg}_{0.92}\text{Fe}_{0.08})(\text{OH})_2 + 0.034\text{Fe}_3\text{O}_4 + 0.040\text{H}_2$
265-300	$\text{Mg}_{1.82}\text{Fe}_{0.18}\text{SiO}_4 + 1.434\text{H}_2\text{O} \rightarrow$ $0.5(\text{Mg}_{0.966}\text{Fe}^{\text{II}}_{0.0225}\square_{0.004}\text{Fe}^{\text{III}}_{0.0075})_3\text{Si}_2\text{O}_5(\text{OH})_4 + 0.388(\text{Mg}_{0.96}\text{Fe}_{0.04})(\text{OH})_2 + 0.040\text{Fe}_3\text{O}_4 + 0.046\text{H}_2$
320	$\text{Mg}_{1.82}\text{Fe}_{0.18}\text{SiO}_4 + 1.426\text{H}_2\text{O} \rightarrow$ $0.5(\text{Mg}_{0.966}\text{Fe}^{\text{II}}_{0.0225}\square_{0.004}\text{Fe}^{\text{III}}_{0.0075})_3\text{Si}_2\text{O}_5(\text{OH})_4 + 0.376(\text{Mg}_{0.99}\text{Fe}_{0.01})(\text{OH})_2 + 0.044\text{Fe}_3\text{O}_4 + 0.050\text{H}_2$

Figure 1. Generation of H₂ and dissolved SiO₂ concentrations during reaction in long-term experiments with 53-212 μm olivine grains at 200-320 °C. (a) Amounts of H₂ generated per gram of olivine. Only the first 5000 h of the 230 °C (OLIV230) experiment are shown in (a), and results for the 200 °C experiment are not shown since there was no detectable H₂ generation. (b) Production of H₂ during short- and long-term experiments at 230 °C, shown on an expanded horizontal scale from (a) to encompass the entire duration of experiment OLIV230. Additional fluid was injected into the OLIV230 experiment at 4013 h. (c) Concentrations of dissolved SiO₂ in the experiments.

Figure 2. Amounts of dissolved H_2 (a) and SiO_2 concentrations (b) during reaction of olivine in short-, medium- and long-term experiments performed at 300 °C. Only the first 800 hours of the long-term experiment (OLIV300) are shown.

Figure 3. Generation of H_2 (a,b) and SiO_2 concentrations (c) during reaction of olivine at 200 and 230 °C.

Figure 4. Representative back-scattered electron SEM images of solid reaction products from the hydrothermal experiments. (a,b) Mats of fibrous serpentine minerals coating surface of partially reacted olivine, growing into elongated chrysotile fibers. Areas marked “Ol” show etched surfaces of olivine where the serpentine mat has been peeled away, and the inset in (a) shows expanded view of mat (fibers ~5 μm long). (c) Platy, euhedral brucite crystals showing hexagonal terminations. At upper right is a grain of spinel (Spl) coated with magnetite (Mgt). Inset shows layers in a cross-section of a brucite crystal. (d) Magnesite crystal (Mgs) with fibrous serpentine and magnetite (bright spots). (e) Octahedral magnetite crystals magnetically separated from OLIV265 experiment showing typical size range. (f) Truncated octahedral crystals of magnetite on surface of etched olivine (Ol) embedded in mat of fibrous serpentine from OLIV320 experiment, with inset showing expanded view from another location. Scale bars in insets are 5 μm .

Figure 5. Average compositions of (a) serpentine and (b) brucite produced during laboratory experiments, expressed as Mg# [=100 x Mg/(Mg+Fe), molar basis]. Also shown for comparison are compositions of these minerals reported from several other experimental studies of serpentinization of olivine, including data from Okamoto et al. (2011), Malvoisin et al. (2012a) Lafay et al. (2012), and Ogasawara et al. (2013). Some symbols have been offset slightly in temperature to avoid overlap. The dashed line indicates the composition of the initial SC olivine; olivine with a similar composition was also used in the other published experiments shown.

Figure 6. (a) Representative SEM image of spinel (Spl) with coating of euhedral magnetites in experimental reaction products (from OLIV265). Inset shows magnified view of magnetite crystal with truncated octahedral morphology. (b) Magnetite-coated spinel adjacent to olivine that is free from magnetite (from OLIV230_short). The olivine has a thin veneer of chrysotile fibers not clearly visible in image.

Figure 7. Experimental fluid compositions plotted on a diagram of mineral stabilities in the Mg-Fe-Si-O-H systems as a function of temperature and activity of dissolved silica. Shown for comparison are data from prior studies of olivine alteration where this information is available. For clarity, only the first and last measurements from the experimental studies are shown. The stability fields are calculated using representative mineral compositions from the experiments, and are in equilibrium with magnetite and an activity of dissolved H_2 equal to 10^{-3} . For the experiments from this study, the points on the diagram represent activities of $\text{SiO}_{2(\text{aq})}$ calculated from fluid speciation calculations, taking explicit account for formation of complexes. Conversely, data for other studies represent measured dissolved total silica concentrations assuming an activity coefficient of one. The dashed line represents the metastable extension of the olivine-brucite equilibrium.

Figure 8. Calculated in situ fluid compositions for the serpentinization experiments projected onto mineral stability diagrams for the Mg-Fe-Si-O-C-H system at the experimental temperatures plotted as a function of pH and silica activity. The upper set of panels (a-c) show the stable mineral assemblage for the system, while the lower set of panels (d-f) shows metastable assemblages with chrysotile excluded. Compositions of chrysotile and brucite are constrained to those observed in the experiments. For construction of the mineral stability diagrams, concentration of dissolved Mg was set to $1 \mu\text{mol kg}^{-1}$, Fe was assumed to be in equilibrium with magnetite, H_2 was set to 1 mmol kg^{-1} , and total dissolved CO_2 was set to the amount present in the final sample of the experiments and allowed to speciate across the diagram (methane excluded). Changing the assumed concentration of dissolved Mg alters the position of the boundaries in equilibrium with the solution, but does not affect the boundaries between minerals. Dashed blue lines separate predominance fields for $\text{CO}_{2(aq)}$ and HCO_3^- among dissolved carbon species.

Figure 9. Measured concentrations of dissolved H_2 and Mg# values for brucite from the laboratory experiments (symbols), compared with the calculated composition of brucite in equilibrium with magnetite as a function of H_2 (lines). Symbols are color-coded to match the equilibrium line of the same temperature. Equilibrium lines assume an activity coefficient of unity for dissolved H_2 and are calculated for 35 MPa.

Figure 10. Relationships among total amount of magnetite produced, extent of reaction, and Mg# of brucite for this study (triangles) and that of Malvoisin et al. (2012a) (circles). Symbols with the same color represent experiments performed at the same temperature. For the Malvoisin et al. study, the amount of magnetite was determined using magnetic methods while the extent of reaction was estimated by water weight loss.

Figure 11. Relative compositions of serpentine-brucite mineral pairs from olivine experiments as a function of the calculated in situ activity of silica. Serpentine compositions plotted as circles, and brucite as triangles.

Figure 12. Relative compositions of serpentine and brucite for experiments from this study and other published studies of olivine serpentinization where this data is available. In many cases, there are overlapping data points not evident on figure. Also shown for comparison are calculated compositions for equilibrium distribution of Fe between serpentine and brucite with a $K_D = 0.50$ as proposed by Evans and Trommsdorf (1972) (dashed line). Data sources are Okamoto et al. (2011), Lafay et al. (2012), Malvoisin et al. (2012a), and Ogasawara et al. (2013).

Figure 13. Experimentally determined reaction rates for conversion of olivine to serpentine + brucite + magnetite as a function of temperature. Rates estimated for the present study are shown in red, with results from several other experimental studies with comparable grain size shown for comparison. Data from Martin and Fyfe (1970), Wegner and Ernst (1983), Lafay et al. (2012), Malvoisin et al. (2012b), Ogasawara et al. (2013), and Andreani et al. (2013).

Figure 14. Rates of H₂ production during serpentinization of olivine in the present study, with results from several other experimental studies of olivine serpentinization where H₂ production was monitored shown for comparison. Two data points are shown for experiment OLIV230, one reflecting the production rate prior to 4010 h and the other reflecting the higher production rate that occurred after 4010 h (see Fig. 1b). The data point for OLIV200 is a maximum value since no increase in H₂ was detected during this experiment. Additional data from Berndt et al. (1996), McCollom and Seewald (2001), Jones et al. (2010), and Klein and McCollom (2013).