Serpentinization as a reactive transport process: The brucite silicification reaction

Benjamin M. Tutolo[1,*], Andrew J. Luhmann[2], Nicholas J. Tosca[1], William E. Seyfried, Jr.[3]

[1]University of Oxford Department of Earth Sciences, South Parks Road, Oxford UK OX1 3AN

[2]Department of Earth and Environmental Science, New Mexico Institute of Mining and Technology, 801 Leroy Place, Socorro, NM 87801, USA

[3]Department of Earth Sciences, University of Minnesota, 310 Pillsbury Drive SE, Minneapolis, MN 55455, USA

[*]Present address: University of Calgary Department of Geoscience, 2500 University Dr. NW, Calgary, AB T2N 1N4, Canada

Abstract

Serpentinization plays a fundamental role in the biogeochemical and tectonic evolution of the Earth and perhaps many other rocky planetary bodies. Yet, geochemical models still fail to produce accurate predictions of the various modes of serpentinization, which limits our ability to predict a variety of related geological phenomena over many spatial and temporal scales. Here, we utilize kinetic and reactive transport experiments to parameterize the brucite silicification reaction and provide fundamental constraints on SiO_2 transport during serpentinization. We show that, at temperatures characteristic of the sub-seafloor at the serpentinite-hosted Lost City Hydrothermal Field (150°C), the assembly of Si tetrahedra onto $MgOH_2$ (i.e., brucite) surfaces is a rate-limiting elementary reaction in the production of serpentine and/or talc from olivine. Moreover, this reaction is exponentially dependent on the activity of aqueous silica ($a_{SiO_{2(aq)}}$), such that it can be calculated according to the rate law:

$$Rate = 2.3 \times 10^{-4}\, a_{SiO_{2(aq)}}^{1.5} \text{ (mol/m}^2\text{/s)} .$$

Calculations performed with this rate law demonstrate that both brucite and Si are surprisingly persistent in serpentinizing environments, leading to elevated Si concentrations in fluids that can be transported over comparatively large distances without equilibrating with brucite. Moreover, applying this rate law to an open-system reactive transport experiment indicates that advection, preferential flow pathways, and reactive surface area armoring can diminish the net rate of Si uptake resulting from this reaction even further. Because brucite silicification is a fundamentally rate-limiting elementary reaction for the production of both serpentine and talc from forsterite, our new constraints are applicable across the many environments where serpentinization occurs. The unexpected but highly consequential behavior of this simple reaction emphasizes the need for considering serpentinization and many other hydrothermal processes in a reactive transport framework whereby fluid, solute, and heat transport are intimately coupled to kinetically-controlled reactions.

1. Introduction

As seawater infiltrates exhumed mantle rocks, a variety of chemical and physical processes ultimately convert mafic minerals (i.e., olivine and pyroxene) to serpentine and accessory phases (Evans et al., 2013; O'Hanley, 1996). For most of Earth's history, this process, known generally as "serpentinization," has played a central role in the long-term evolution of atmospheric, oceanic, and lithospheric properties. Serpentinites and serpentinite-hosted hydrothermal systems host unique, microbial ecosystems (Kelley, 2005; Schrenk et al., 2013), and figure prominently in chemical scenarios for the origins of life on Earth (Martin et al., 2008; Sleep et al., 2011; Sojo et al., 2016) as well as in models for the early chemical evolution of the atmosphere (Kump and Barley, 2007). At a broader level, serpentinizing systems strongly modify the strength and rheological characteristics of the oceanic crust (Escartín et al., 2001),

which, once subducted, influences both the oxidation state and water content of Earth's mantle (e.g., Rüpke et al., 2004). Because the principal reactants and drivers are thought to be common across a range of planetary bodies, some view serpentinization as a fundamental process influencing planetary evolution more generally (e.g., Oze and Sharma, 2005; Sleep et al., 2011; Waite et al., 2017).

Nonetheless, in spite of decades of dedicated research into serpentinization and its wide-ranging implications, the various modes of serpentinization cannot yet be quantitatively predicted from a process-oriented point of view. This, in turn, limits the confidence with which we can extrapolate our knowledge of serpentinization over geologically relevant scales of space and time.

An important example illustrating the disparity between theoretical predictions and field measurements for serpentinizing systems involves the reaction between brucite and dissolved silica ($SiO_2(aq)$). Considering only the magnesian end-members, the isochemical serpentinization reaction may be written:

$$\text{2 olivine} + 3\ H_2O = \text{brucite} + \text{serpentine}\ .$$
$$2\ Mg_2SiO_4 + 3\ H_2O = Mg(OH)_2 + Mg_3Si_2O_5(OH)_4 \quad (1)$$

However, silica sourced from adjacent pyroxene or plagioclase often either precludes brucite formation through a contemporaneous reaction:

$$\text{3 olivine} + SiO_2(aq) + 4\ H_2O = \text{2 serpentine}\ ,$$
$$3\ Mg_2SiO_4 + SiO_2(aq) + 4\ H_2O = 2\ Mg_3Si_2O_5(OH)_4 \quad (2)$$

or silicifies brucite through later-stage infiltration or a fracture reactivation event:

$$\text{3 brucite} + 2\ SiO_2(aq) = \text{serpentine} + H_2O\ .$$
$$3\ Mg(OH)_2 + 2\ SiO_2(aq) = Mg_3Si_2O_5(OH)_4 + H_2O \quad (3)$$

Through either pathway, the extreme reactivity of brucite across a broad range of SiO_2 concentrations dictates that either SiO_2 should be quantitatively removed from solution (if brucite is the excess component) or brucite should be quantitatively converted to serpentine (if SiO_2 is the excess component) (Fig. 1a). However, although petrographic studies have demonstrated the operation of reactions 1-3 and their higher $a_{SiO_2(aq)}$, talc-producing analogues during oceanic serpentinization (e.g., Katayama et al., 2010; Klein et al., 2009), recent measurements of Lost City fluids (Seyfried et al., 2015) suggest that elevated levels of SiO_2(aq) can persist in serpentinizing environments, even after flowing through brucite-bearing fractures and massive brucite chimney structures (Ludwig et al., 2006). This, in turn, suggests that "Lost City-type" hydrothermal fluids are not always in equilibrium with their geologic surroundings, and, indeed, that fluid and solute transport in concert with kinetically-controlled geochemical reactions—i.e., reactive transport—govern fluid compositions observed at the seafloor.

Reactive transport models have long shown promise for the quantitative prediction of hydrothermal processes, but this ultimate functionality has, to date, remained elusive. Amongst the grand challenges in the continually evolving field of reactive transport modelling, perhaps the most difficult to reconcile involves the estimation of the surface area within a particular rock that will participate in a reaction, which is a function not only of the mineral's intrinsic surface area but also other factors such as flow path geometry (e.g., Helgeson et al., 1984; Noiriel et al., 2009; White and Peterson, 1990). Because this fundamental parameter ultimately dictates the overall pace and extent of geochemical reactions within a particular system, the accuracy of reactive transport simulations hinge largely upon the accuracy of the utilized reactive surface area estimate. This is particularly evident in serpentinizing systems, where most of the reactive

surface area within the rock is generated through feedbacks associated with flow paths generated by the serpentinization reaction itself (Tutolo et al., 2016).

The brucite silicification reaction (reaction 3) presents a tractable yet realistic opportunity to experimentally examine reactive transport processes during serpentinization and illustrate the effects of reactive surface area estimates on predicted results. Here, we utilize both closed- and open-system reactive transport experiments to examine the rates and evolution of this reaction at 150°C, a temperature characteristic of the subsurface at the Lost City Hydrothermal Field (Seyfried et al., 2015), where upwelling hydrothermal fluids are interacting with serpentinized oceanic crust (Früh-Green et al., 2016). We show that, although this reaction is rapid at 150°C, it is orders of magnitude slower than the rates of olivine dissolution and brucite precipitation. Surprisingly, strong reactive surface area feedbacks can decrease the net rate of this reaction even further, in spite of continued kinetic and thermodynamic drive in its favor. This interesting behavior implies that brucite and elevated SiO_2(aq) concentrations can be surprisingly persistent in serpentinizing systems, which helps to explain the elevated SiO_2(aq) concentrations measured at LCHF, and in turn, implies unexpected alteration phase assemblages and, potentially, limited amounts of H_2 production in some serpentinizing systems

2. Methods

2.1 Characterization procedures

Mineral reactants for experiments were characterized by both Fourier transform infrared (FTIR) spectroscopy and powder X-ray diffraction (XRD) to determine mineralogical composition, and chemical composition of experimental fluids and solids were determined using inductively coupled plasma-optical emission spectroscopy (ICP-OES). FTIR spectra were acquired in transmission mode on optically translucent KBr disks, which were prepared by first

mixing ~2 mg of sample into 200 mg of dried (at 200°C) KBr powder, and then compressing the mixture under vacuum to 7 tons in a hydraulic press. XRD measurements were performed at the University of Oxford using a Panalytical Empyrean Series 2 outfitted with a spinning reflection-transmission stage. Samples were mounted on polished silicon background substrates and analyses were performed using a Co Kα source at 40 kV and 40 mA. 5-point Brunauer-Emmett-Teller (BET) specific surface area was measured with N_2 gas on the brucite powder (dried at 60°C) used in the closed-system experiments at the University of Oxford Begbroke Science Park. The measured specific surface area, 5.41 ± 0.06 m^2/g, was used to calculate the silica uptake rate in the closed-system experiments.

Mg, Ca, Na, and SiO_2 concentrations in selected fluid samples and the solid brucite ore used in the open-system reactive transport experiment were analyzed by ICP-OES at the Scottish Universities Environmental Research Centre in Glasgow, UK (for the closed-system experiments) and in the University of Minnesota Department of Earth Sciences (for the reactive transport experiment). In the closed-system experiments, Ca concentrations were below the detection limit and variations in Na concentration were smaller than analytical errors and hence neither element is reported. In several samples from the flow-through experiment, SiO_2 was measured spectrophotometrically using the molybdate blue method with metol as the reducing agent (Mullin and Riley, 1955) in order to supplement data provided by ICP-OES. Solution pH was measured using a Thermo Scientific™ Orion™ 8103BN ROSS™ Combination semi-micro (Oxford) or micro (Minnesota) pH electrode, calibrated using NIST-traceable 7 and 10 pH buffers. X-ray computed tomography (XRCT) imaging was performed on the core assembly described below in the University of Minnesota XRCT laboratory in order to infer extents of physical and chemical evolution that occurred over the course of the flow-through experiment.

The core assembly was imaged in a dry state prior to the experiment, and subsequently imaged in a water-saturated state directly after the experiment and again after it had been flushed with deionized water and dried at 60°C. The dry core images showed significantly better grayscale contrast than the water-saturated images without any noticeable difference in other volume features and are thus used exclusively in experimental interpretations below. In addition, pre- and post-experiment subsamples of the fracture fill material were analyzed using a Scanning Electron Microscope (SEM) coupled to an Energy Dispersive Spectrometer in the Characterization Facility at the University of Minnesota.

2.2 Experimental Methods

The goal of this study is to provide insight into the reactive transport process of serpentinization using experimental observations of the elementary brucite silicification reaction. Because no data exist within the literature to calculate the rate of this reaction in even ideal conditions, we first present a series of well mixed, closed-system experiments to quantify its rate. The measured evolution of fluid chemistry as a function of time during these closed-system experiments permits the derivation of a rate law for calculating the rate of silica depletion during brucite silicification as a function of brucite surface area and the activity of aqueous silica. Subsequently, we present an open-system reactive transport experiment that inherently incorporates reactive transport processes, such as surface area armoring and preferential flow pathways. The parameterization derived from the closed-system experiments enables the quantitative interpretation of surface area evolution during the open-system reactive transport experiment. Together, these experimental results provide direct insight into serpentinization in natural systems.

2.2.1 Closed-system experiments

163 Reactant fluid in all experiments was prepared to match seawater chloride concentration
164 (0.547 mol Cl/kg solution) by addition of reagent grade NaCl. Consistent with the absence of
165 measurable Mg in LCHF vent fluids (Seyfried et al., 2015), the experimental solutions contained
166 no Mg and were hence undersaturated with respect to the reactant brucite. Other species typical
167 to seawater and the LCHF vent fluids, such as Ca, K and SO_4, were also left out of reactant
168 solutions because they are not expected to impact the progress of the focus brucite silicification
169 reaction.
170 Closed-system reactor experiments were performed at the University of Oxford in a 100 mL
171 pressure vessel manufactured by the Parr Instrument Company (Model 4793). All internal
172 wetted parts are constructed of inert Ti, which were heated in air at 350°C for ~4 hours prior to
173 the experiments in order to produce a thin, oxidized surface coating. A flat PTFE gasket creates
174 a seal between the upper and lower portions of the reaction vessel, which was heated by an
175 external band heater coupled to a K-type thermocouple inserted into a Ti well in direct contact
176 with the reactant fluid. Internal pressure is equilibrium steam saturation pressure, ~4.8 bar.
177 High-purity (95%) brucite (102 mg and 105 mg for Expts. 3 and 4, respectively) and a PTFE-
178 coated stir bar were loaded into the vessel prior to sealing. Once sealed, the vessel was secured
179 in an upright position on a magnetically controlled stirrer, the experimental fluid (75.75 g and
180 75.43 g in Expts. 3 and 4, respectively) was injected through a port in the top of the vessel, and
181 the temperature controller was set to 150°C. Total time between fluid loading and reaching
182 150°C was ~20-25 minutes. Throughout the experiments, fluid samples (~1 mL) were obtained
183 through a Ti dip tube fitted with a 10 μm Ti filter positioned within the reactant fluid in order to
184 observe the real-time evolution of fluid chemistry within the vessel. Each fluid sample was
185 preceded by a ~1 mL rinse sample in order to clear stagnant fluid from within the dip tube prior

186 to sample acquisition, causing the total mass of reactant fluid to decrease by ~2 mL after each
187 sample and the fluid/solid ratio to decrease accordingly. Rate calculations take these masses into
188 account. pH was measured on a ~0.5 mL aliquot immediately upon sampling, and the remainder
189 of the sampled fluid was acidified and diluted to preserve for later analyses.

190 In two initial experiments (Expts. 1 and 2), the initial $pH_{21°C}$ of the reactant solution was set
191 to ~8 in order to approximate the pH of seawater, and SiO_2 concentration of the initial reactant
192 fluid was set to amorphous silica saturation (~1.8 mmol/kg solution (Gunnarsson and Arnórsson,
193 2000)) using Na metasilicate nonahydrate ($Na_2SiO_3 \cdot 9H_2O$). However, approximately half of
194 this SiO_2 was removed prior to reaching 150°C, preventing acquisition of meaningful rate data.
195 These experiments will not be discussed further. The presented experiments (Expts. 3 and 4)
196 were performed with an initial $pH_{21°C} \approx 9.8$, which, because it is near the pK for silicic acid at
197 room temperature (~9.86), permitted a much higher initial SiO_2(aq) concentration without
198 precipitating amorphous silica. Although quartz was ~2x supersaturated in the initial samples
199 from both closed-system experiments, the rate of quartz precipitation this close to equilibrium is
200 slow (Rimstidt and Barnes, 1980) and we therefore do not expect that precipitation of this
201 mineral could have affected our results. In order to capture the rapid rates of reaction at high
202 SiO_2(aq) concentrations, an aggressive sampling protocol was planned for Expt. 3, such that a
203 total of 9 samples were taken within the first 3 hours. Expt. 4 was sampled less frequently and
204 hence was able to continue for longer prior to termination while maintaining similar volumes of
205 experimental fluid.

206 **2.2.2 Reactive transport experiment**

207 A single-pass, hydrothermal flow-through apparatus (Fig. 2a) located in the University of
208 Minnesota Department of Earth Sciences, which has been described in several previous studies

(Luhmann et al., 2017, 2014; Tutolo et al., 2015), was utilized to examine the effect of reactive transport processes on the brucite silicification reaction (Fig. 1b). In brief, the apparatus makes use of a set of 4 Teledyne Isco syringe pumps to facilitate fluid injection and pressurization. A constant outlet pressure (150 bars in this study) is controlled by a model 500D pump, constant confining pressure (200 bars in this study) is maintained by a model 260D pump, and an additional set of 2 model 260D pumps are used to inject the experimental solution at a constant rate (0.05 mL/min in this study) into the core assembly, which is contained within a stainless steel pressure vessel. In the present study, the pressure vessel was maintained at 150°C throughout the duration of the experiment by a set of 4 thermocouple-linked Watlow band heaters. While flowing through the heated pressure vessel and reacting with the brucite, the experimental solution only contacted corrosion-resistant pieces made from titanium, Teflon, and PEEK. Permeability was continuously measured during the experiment, and fluid samples were collected after passing through the core. Furthermore, a set of two inert Ti separators with internal, o-ring sealed Ti pistons were utilized on the upstream and downstream side of the pressure vessel in order to prevent the corrosive reactant fluid from coming into contact with the stainless steel interior of the syringe pumps. During typical experiments run with this apparatus (e.g., Luhmann et al., 2014), deionized water is flowed through the core at room temperature prior to the experiment in order to establish baseline permeability. However, in this study, due to the high reactivity of brucite in deionized water at even room temperature, this could not be done without potentially dissolving significant brucite. Thus, the core was pressurized immediately prior to experiment initialization.

To facilitate digitization and approximate the fractures characteristic of serpentinization environments, we designed a special Teflon PTFE core assembly with a planar, 1.5 mm x 24.9

mm x 11.34 mm section of the cylindrical "core" filled with ground brucite ore, held in place with Ti frit endcaps (Fig. 2b). This natural brucite, from Brucite Mine, Nevada, was analyzed by ICP-OES to contain 62.2% MgO, 2.8% CaO, 2.0% SiO_2, and 0.6% FeO. It consisted of 90-95% brucite, minor Mg-bearing carbonates, and trace lizardite and was previously used for carbonation experiments by Harrison et al. (2013). The material was first ground and then wet-sieved to select particles in the 75 μm-150 μm size range, which were aggregates of many much smaller brucite particles (Fig. 2c), as evidenced by their complete disaggregation during an initial attempt to sonicate them to remove surface particles. A total of 781 mg (dry mass) of brucite was loaded into the core assembly and loaded into a cylindrical Teflon sheath. Assuming a brucite density of 2.368 g/cm^3 (Robie and Hemingway, 1995), the total porosity of the planar fracture was 0.22, and this value is assumed to be constant in the relevant calculations below. Harrison et al. (2013) report a specific surface area of 6.6 m^2/g for this material, and we utilize this value for the relevant calculations below. The reactant solution in this experiment was a 547 mmol NaCl/kg seawater analogue solution, to which 1.7 mmol SiO_2/kg had been added in the form of silica gel. To facilitate silica dissolution into the solution, we initially raised the pH of the solution above 10 and heated it in a sealed polyethylene bottle to 60°C for several days. The $pH_{21°C}$ solution was then lowered to 8 by HCl addition in order to simulate the pH of seawater. In total, 500 mL (i.e., the approximate total volume of the two injection pumps) of fluid were injected into the core over the course of the experiment, yielding a cumulative water-to-rock mass ratio of ~640. The Darcy velocity in this experiment, ~1550 m/yr, is reasonable, given the (limited) constraints on fluid residence times at T > 150°C in mid-ocean ridge hydrothermal systems (1-3 years (Kadko and Butterfield, 1998)) and an assumed upflow path at LCHF of less than several kilometers (e.g., Seyfried et al., 2015).

2.3 Theoretical treatment of rate data

In treating the closed-system experiments, we assumed that the brucite silicification reaction behaves according to the following form of the rate law:

$$Rate = k\ A\ a_{SiO_2(aq)}^{n} \quad (4)$$

where k is the rate constant for the reaction, A is the surface area of the reactant brucite, and n is the reaction order with respect to the activity of aqueous silica ($a_{SiO_2(aq)}$). Equation 4 has the same general form as that derived for the geochemically analogous kaolinite illitization reaction by Chermak and Rimstidt (1990). Following the methodology described by Chermak and Rimstidt (1990), we evaluated the reaction order with respect to $a_{SiO_2(aq)}$ by calculating the Si removal rate in the closed system experiments according to:

$$rate = \frac{\Delta C_{Si} m_{soln}}{\Delta t A} \quad (mol/m^2/s) \quad (5)$$

where ΔC_{Si} is the measured change in Si concentration, m_{soln} is the mass of solution in the reactor, taking into account mass changes due to sampling, Δt is the time between samples, and A is again the surface area of brucite in the reactor, calculated as the product of the measured BET specific surface area and the mass of brucite in the reactor. Attempts to approximate reductions in brucite surface area in the reactor according to stoichiometric Mg-silicate-forming reactions had no effect on the calculated reaction order or rate constant within the uncertainty of the calculation and hence were ignored. This is consistent with the limited amount of reaction permitted stoichiometrically (Reaction 3 and its talc-producing analogue, which requires 1.33 moles of SiO_2(aq) per mole of brucite) between the 1.8 total millimoles of brucite in the reactor and the ~350 total micromoles of Si removed from solution.

Uncertainties on calculated rates were calculated using standard procedures (Rimstidt, 2014), taking into account the standard deviation of measured Si concentrations and uncertainty on BET surface area. Regression of rates as a function of $a_{SiO_2(aq)}$ was performed according to York et al. (2004), taking into account uncertainties on both calculated $a_{SiO_2(aq)}$ (assumed equivalent to the standard deviation of the measured Si concentrations) as well as the uncertainties on the rates calculated using Eqn. 5. We optimized the value of *k* using an iterative, nonlinear least squares data fitting procedure which minimized the difference between the measured number of moles of SiO_2 removed from solution (Table 1) and those calculated using Eqn. 4. In order to remove bias introduced by the variable period between individual samples, a spline function was fit to the measured values as a function of time, and the data were resampled at 10, 100, and 1000 evenly spaced intervals. A significant change in the value of the rate constant was observed between 10 and 100 samples, but not between 100 and 1000 samples, thus, the reported rate constant is the value obtained after fitting to 1000 evenly spaced subsamples.

2.4 Numerical methods

The Geochemist's Workbench version 10.0.10 (Bethke and Yeakel, 2015) and PFLOTRAN (Lichtner et al., 2017) were utilized for aqueous speciation and reactive transport calculations, respectively. Because this study focuses on the role of silica in serpentinization reactions, it is important to ensure that the data that we are using to produce thermodynamic calculations of fluid-mineral equilibria agree with available data for the aqueous speciation of silica over the range of temperatures and pressures applicable to serpentinization reactions. As discussed in detail in Tutolo and Tosca (in review), a geochemical thermodynamic database taking explicit account of recent revisions to the speciation of aqueous silica was created using the DBCreate software package (Kong et al., 2013). Briefly, this database was created using

299 updated SiO_2(aq) thermodynamic properties presented by Sverjensky et al. (2014), which are
300 consistent with the updated low-temperature quartz solubility measurements of Rimstidt (1997).
301 The $NaHSiO_3$(aq) complex was removed from the database due to revised experimental
302 measurements that have drawn its stability in seawater into question (Busey and Mesmer, 1977;
303 Felmy et al., 2001; Zarubin and Nemkina, 1990). This complex has a major effect on the
304 aqueous speciation of silica and the overall solubility of silicate minerals at pH > pK for silicic
305 acid (see Tutolo and Tosca, in review) and it is thus particularly important to avoid including it
306 in aqueous speciation calculations of water-rock interaction in ultramafic-hosted systems.

307 **3. Results and discussion**

308 The conversion of brucite to serpentine (reaction 3) can be conceptualized through a
309 simple, epitaxial reaction (Carrado et al., 2000): Si tetrahedra from solution bind to the surface of
310 octahedrally coordinated Mg (in the form of brucite), forming serpentine (at higher $a_{SiO_2(aq)}$, the
311 resultant mineral is talc (Fig. 1), but the mechanism is identical). This process is exemplified by
312 the results of our closed-system experiments. Specifically, the observed concentrations
313 Nonetheless, in the open-system reactive transport experiment, which was designed to more
314 closely approximate processes characteristic of natural serpentinizing environments, the fluids
315 and reactants are clearly not well-mixed, and only a relatively small proportion of the total
316 brucite surface area is accessible to the flowing fluid. As discussed below, the closed-system
317 experiments provide constraints on the surface-controlled process of brucite silicification under
318 well-mixed conditions, and the laboratory and numerical reactive transport experiments allow us
319 to observe how reactive transport processes can affect the rate and extent of this reaction.

320 **3.1 Closed System Experiments**

In spite of the experimental challenges associated with the brucite silicification reaction, our closed-system experiments provide mutually consistent rate measurements, which, in turn, permit kinetic parameterization. Solution analyses indicate Mg concentrations near detection limits in all samples, which is expected, given that equilibrium brucite solubility in our experimental solutions at $pH_{150°C}$ = 8.2 is ~10 µmol/kg. Thus, within the uncertainty on our calculated $pH_{150°C}$ (on the order of $\pm$0.1 pH unit), the solutions were very close to thermodynamic equilibrium with respect to brucite. Although the $pH_{150°C}$ of all samples from both experiments (Table 1) is above the neutral $pH_{150°C}$ (≈ 5.8), they are all below the $pK_{150°C}$ for silicic acid (8.75) such that SiO_2(aq) accounts for the majority (~70%) of the total aqueous silica in the analyzed solutions, with the remainder existing as $HSiO_3^-$. The initial samples in both experiments are characterized by a notably more rapid rate of reaction than the subsequent samples, consistent with an exponential dependence of the reaction rate upon $a_{SiO_2(aq)}$ according to Eqn. 5. Fitting a line to a plot of the rates calculated according to Equation 4 as a function of the $a_{SiO_2(aq)}$ in solution (Fig. 3a) yields the equation:

$$\log(r) = 1.55(0.08) \log a_{SiO2(aq)} - 3.39(0.28)\,, \qquad (6)$$

where the values in parentheses are the calculated standard error. This result suggests a reaction order (n) of 1.5 with respect to with respect to $a_{SiO_2(aq)}$, and subsequent fitting of Eqn. 4 to the measured SiO_2 concentrations yields the rate law:

$$Rate = 2.3 \times 10^{-4}\, a^{1.5}_{SiO_2(aq)}\ (\text{mol/m}^2\text{/s})\,, \qquad (7)$$

which is applicable at 150°C for values of $a_{SiO_2(aq)}$ at least down to ~10 µmolal at seawater ionic strength. Assuming 1 m^2 of brucite interacting with 1 kg of solution, these data indicate that it would take 5.25 days to reduce the SiO_2(aq) concentration from 1.7 mmol/kg to 170 µmol/kg, another 16.6 days to reach 17 µmol/kg and another 52.4 days to remove the 15.3 micromoles of

Si required to achieve a concentration of 1.7 μmol/kg. Regardless of the applicability of these specific water-to-rock ratios, the calculations indicate that significant disequilibrium can be maintained during SiO_2 transport through serpentinizing rocks. For example, at $a_{SiO_2(aq)} \approx 73 \times 10^{-6}$ (i.e., the end-member concentration measured in 116°C vent fluids at the Lost City Hydrothermal Field (Seyfried et al., 2015)), Eqn. 7 yields a reaction rate of $\sim 1 \times 10^{-10}$ mol/m^2/s, which is several orders of magnitude slower than the 150°C dissolution rates of brucite, 8.6×10^{-7} mol/m^2/s (Palandri and Kharaka, 2004) and forsterite, $\sim 1 \times 10^{-6}$ mol/m^2/s (Rimstidt et al., 2012). Assuming that brucite growth rates are within 1-2 orders of magnitude of its dissolution rates (as shown experimentally by Pokrovsky and Schott (2004) at 25°C), this comparison confirms that the assembly of silica tetrahedral sheets onto Mg octahedral sheets (i.e., brucite) is the rate-limiting step during forsterite serpentinization. This assertion is in agreement with the experimental observations of Lin and Clemency (1981) and Saldi et al. (2007), who suggested that the rate-limiting step of the reverse reaction (i.e., antigorite and talc *dissolution*) is the destruction of tetrahedral Si rather than octahedral Mg sheets.

All fluid samples from both closed-system experiments were within the chrysotile stability field in $a_{Mg^{++}}/a_{H^+}^2$ - $a_{SiO_2(aq)}$ space, but the majority of the samples were above the $a_{SiO_2(aq)}$ for talc-chrysotile equilibrium, i.e., 200×10^{-6} (Fig. 1a). Solids recovered from Expt. 3 showed no crystallographic evidence of silicification, consistent with its relatively short duration and extent of reaction. XRD data from Expt. 4, on the other hand, exhibit a low-angle peak at ~10.2 Å, consistent with the formation of kerolite, a hydrated, structurally-related form of talc.

3.2 Reactive transport experiment

In total, 0.87 millimoles of dissolved SiO_2 were injected into the synthetic, brucite-filled fracture during the reactive transport experiment. Models assuming equilibrium between well-

mixed reactants and products predict that the 13.4 millimoles of brucite within the synthetic fracture would deplete Si well below detection levels during flow through the core (see below). Nonetheless, solution chemical analyses consistently indicate SiO_2 concentrations well above those required for brucite stability exiting the experimental reactor during the first ~110 hours of the experiment, and a subsequent, rapid transition to even lower net reactivity (Table 2, Fig. 4a). At the conclusion of the experiment, ~0.62 of the total injected 0.87 millimoles of SiO_2 had been deposited within the core. Assuming serpentine growth (see mineralogical constraints below), this amount of silica uptake accounts for the reaction of ~0.41 millimoles, or ~3%, of the brucite contained within the synthetic fracture.

Mg concentrations in outlet fluids varied from an early-time maximum of 2.3 mmol/kg, down to a minimum of ~44 μmol/kg. These solutions tend to be ~1-2 orders of magnitude undersaturated with respect to brucite and near equilibrium or supersaturated with respect to chrysotile (Table 2). These results, particularly the generally low Mg concentrations and the relatively low supersaturations of chrysotile in the bulk fluid, are consistent with the reaction mechanism discussed above, wherein serpentine is crystallizing by silica condensation upon to brucite surfaces, rather than through heterogeneous crystallization from the bulk fluid phase.

In spite of the surface area effects discussed below, the main reason that SiO_2 concentrations above brucite-serpentine equilibrium are exiting the brucite-filled fracture during the first 110 hours of the experiment is the exponential dependence of the silicification reaction on $a_{SiO_2(aq)}$, as discussed in the previous section. Fig. 4b illustrates the expected surface area-normalized silica uptake rates for the solution samples plotted in Fig. 4a. As a result of this exponential rate dependency, the outlet solutions sampled during the first ~110 hours of the experiment have an expected reaction rate ~2 orders of magnitude lower than that calculated for

390 the injected solution, showing that elevated concentrations of Si can persist even as the solution
391 flows through a packed bed of high-surface-area brucite. After 110 hours of experiment time,
392 however, the outlet SiO_2 concentrations indicate that there is simply much less brucite surface
393 area reacting with the fluid. Even though the bulk of fluid flow during this experiment was
394 apparently confined to a relatively limited portion of the fracture, this result is quite surprising
395 because: 1) XRD and FTIR both indicate that even this more reactive portion of the synthetic
396 fracture was still composed almost entirely of brucite after the experiment, and 2) no apparent,
397 abrupt change in the permeability of the synthetic fracture occurred at this time, which would
398 have represented either significant porosity decreases due to serpentine growth or a change in the
399 dominant fluid flow path within the core (Fig. 5). The decline in permeability measured at the
400 beginning of the experiment, significantly prior to the change in reaction regimes, is consistent
401 with pressurization and compaction of the brucite fracture fill, since the pressurization of the
402 core assembly occurred simultaneously with experiment initialization. Because the fluid
403 injection rate was constant throughout the experiment, this permeability did not directly impact
404 fluid residence time within the reactor.
405 We have labeled the transition from the first reaction regime to the second as
406 "precipitation breakthrough", due to the analogy to "dissolution breakthrough" processes which
407 occur whenever high permeability, low reactivity preferential flow paths are generated in, for
408 example, carbonate aquifers (e.g., Dreybrodt, 1990). Regardless of the mechanism, the fact that
409 such high concentrations of SiO_2 are exiting the reaction vessel indicates that very little brucite
410 surface area was available for reaction during this stage of the experiment, in spite of the fact that
411 abundant brucite remained both in the "reacted" and "unreacted" regions of the core. Although
412 the small amount of serpentine formed during the experiment precludes identification by XRD,

413 the location and topology of the set of peaks at 988 and 1087 cm^{-1} in the post-experiment FTIR
414 spectrum demonstrate serpentine precipitation (Fig. 6c). These principal Si-O absorptions are
415 distinct from all other 2:1 phyllosilicates or modulated versions thereof (i.e., talc, kerolite,
416 sepiolite, etc.; (Farmer, 1974; Russell and Fraser, 1994)) and are instead indicative of poorly
417 crystalline serpentine, akin to the poorly crystalline antigorite identified by Gunnarsson et al.,
418 (2005, 2002) and the proto-serpentine discussed by Andreani et al. (2007) and Plümper et al.
419 (2012).

420 **3.3 Reactive transport simulations of brucite silicification**

421 By incorporating the rate law determined above into reactive transport simulations of our
422 flow-through experiment, we can hone in on specific reactive transport phenomena occurring
423 during the experiment. This allows us to fully understand the implications of the quantified
424 brucite silicification reaction for reactive transport in natural serpentinites. To do this, we ran a
425 series of 200 PFLOTRAN simulations that examine the effects of preferential flow paths and
426 reactive surface area armoring on silica uptake. These simulations illustrate that no more than
427 about 15% of the brucite surface area in the synthetic fracture participated in the reaction at any
428 given time (Fig. 7a). Indeed, during the post-precipitation breakthrough reaction regime, very
429 little (i.e., less than ≈1%) of the brucite contained within the core assembly was participating in
430 the reaction, most likely because the easily accessible surface area within this portion of the core
431 had been virtually completely silicified by this time. If, on the other hand, all of the brucite in
432 the synthetic fracture had been participating in the reaction, outlet concentrations would have
433 been on the order of 1 μmolal, or about double the concentration representative of brucite-
434 serpentine equilibrium, and about 50 times lower than the lowest measured concentration. In
435 spite of the fact that only about 1/3 of the fracture showed evidence of silicification in post-

436 experiment imagery (Fig. 6), these simulations show that even within this portion of the core,
437 only a fraction of the brucite was actually participating in the reaction. This latter observation is
438 consistent with the limited (~3%) extent of brucite conversion to serpentine calculated above.

439 The results of these simulations also clearly illustrate the progress of brucite silicification
440 during fluid transport through the core (Fig. 7b). It is particularly interesting to observe the ways
441 in which the coupling between advective Si fluxes, $a_{SiO_2(aq)}$, and brucite reactive surface area
442 availability interact to produce unique equilibration length scales in serpentinizing rocks. For
443 example, these simulations show that in high-flux environments, such as faults, where reactive
444 surface area has been depleted by long-duration fluid fluxes, Si can be transported over great
445 distances and, thus, seafloor samples of these fluids would be quite representative of the
446 subseafloor reaction zone. At the other end of the spectrum, at the scales of individual olivine
447 crystals (i.e., several hundred micrometers), these simulations show that high Si concentrations
448 generated by orthopyroxene-fluid interaction, such as those producing the pattern of
449 serpentinization shown in Fig. 1, can be laterally persistent if rates of advection/diffusion are
450 sufficiently high, or if the existing brucite surface area has been largely armored during prior
451 stages of serpentinization. These two scales of observation can both be tackled with
452 appropriately scaled reactive transport models, and demonstrate the usefulness of treating
453 serpentinization in a reactive transport sense.

454 **5. Geological Implications**

455 The efficiency and pathway of serpentinization can be dictated by a wide array of
456 processes, yet our study offers unique perspectives on the geological mechanisms that underlie
457 the reactions themselves. From an entirely kinetic point of view, our rate data show that the slow
458 rate of brucite silicification relative to both forsterite dissolution and $MgOH_2$

459 dissolution/precipitation allows elevated (i.e., above brucite-serpentine equilibrium)
460 concentrations of Si to persist in moderate-temperature serpentinization environments. That the
461 rate of brucite silicification slows as an exponential function of $a_{SiO_2(aq)}$ indicates that Si can be
462 transported over comparatively large length scales, particularly when considering the reactive
463 transport processes we have discussed.
464 Both our laboratory and numerical reactive transport experiments illustrate that
465 traditional geochemical models of serpentinization cannot produce accurate, process-oriented
466 predictions of serpentinizing systems. For example, the presence of brucite in serpentinized
467 rocks has been used to infer excessively low concentrations of SiO_2 concentrations in reacting
468 fluids (e.g., Beard and Hopkinson, 2000). In addition, at face value, simplified rate formulations
469 (e.g., Martin and Fyfe (1970)) and the activity diagram plotted in Fig. 1 would appear to suggest
470 that serpentinization should proceed rapidly and irreversibly in all seafloor hydrothermal
471 systems, with brucite fully reacting out in the presence of even negligible aqueous silica.
472 However, we have shown that the exponential dependence of the rate of this reaction on
473 $a_{SiO_2(aq)}$, as well as reactive surface area armoring, permit SiO_2 concentrations to remain
474 metastably elevated. As a consequence, these dynamic factors allow brucite to persist in such
475 systems, particularly when the brucite surfaces are separated from primary flow paths by
476 serpentine. From the fluid perspective, our results also help to explain recent reports of elevated
477 Si fluids emitting from orifices in the massive brucite chimneys at the Lost City Hydrothermal
478 Field (Seyfried et al., 2015). Because elevated Si fluxes in serpentinizing environments are
479 thought to govern the partitioning of Fe into alteration phases and, consequently, the amount of
480 H_2 generated from Fe oxidation (Bach et al., 2006; Frost and Beard, 2007; Syverson et al., 2017),
481 our new kinetic and reactive transport constraints suggest that elevated Si and its consequent

effects on H_2 production and biological habitability can be surprisingly prevalent in serpentinizing environments.

Brucite silicification is a fundamentally rate-limiting elementary reaction for the production of both serpentine and talc from forsterite. Thus, our new constraints are applicable across the many environments where serpentinization occurs. The surprising kinetic behavior of this simple reaction, in turn, emphasizes the need for considering serpentinization and many other hydrothermal processes as reactive transport processes in which fluid, solute, and heat transport are intimately coupled to kinetically-controlled serpentinization reactions. Persistent challenges in the application of reactive transport models to geologic systems, particularly the estimation of reactive surface area within geologic media, will thus need to be the subject of continued, focused experimental and computational investigations.

Acknowledgements

This research used samples and/or data provided by the International Ocean Discovery Program (IODP). Portions of this research were supported by the United States National Science Foundation under grant number 1426695. We thank Glenn Hammond for help with the PFLOTRAN simulations, Nicholas Seaton for assistance with SEM analysis, Brian Bagley for assistance with XRCT imaging and processing, and Anna Harrison for providing the brucite used in the reactive transport experiment. The Characterization Facility at the University of Minnesota, where the SEM imaging was performed, receives partial support from NSF through the MRSEC program. The authors wish to thank two anonymous reviewers and Associate Editor Mike Bickle, whose critical evaluation of this manuscript helped to improve its clarity.

References

505 Bach, W., Paulick, H., Garrido, C.J., Ildefonse, B., Meurer, W.P., Humphris, S.E., 2006.
506 Unraveling the sequence of serpentinization reactions: Petrography, mineral chemistry, and
507 petrophysics of serpentinites from MAR 15°N (ODP Leg 209, Site 1274). Geophys. Res.
508 Lett. 33, 4–7. doi:10.1029/2006GL025681

509 Beard, J.S., Hopkinson, L., 2000. A fossil, serpentinzation-related hydrothermal vent, Ocean
510 Drilling Program Leg 173, Site 1068 (Iberia Abyssal Plain): Some aspects of mineral and
511 fluid chemistry. J. Geophys. Res. 105, 16,527-16,539. doi:10.1029/2000JB900073

512 Bethke, C.M., Yeakel, S., 2015. The Geochemist'sWorkbench® Release 10.0 - Reference
513 Manual.

514 Busey, R.H., Mesmer, R.E., 1977. Ionization equilibriums of silicic acid and polysilicate
515 formation in aqueous sodium chloride solutions to 300.degree.{C}. Inorg. Chem. 16, 2444–
516 2450. doi:10.1021/ic50176a004

517 Carrado, K.A., Xu, L., Gregory, D.M., Song, K., Seifert, S., Botto, R.E., 2000. Crystallization of
518 a layered silicate clay as monitored by small-angle X-ray scattering and NMR. Chem.
519 Mater. 12, 3052–3059. doi:10.1021/cm000366a

520 Chermak, J.A., Rimstidt, J.D., 1990. The hydrothermal transformation rate of kaolinite to
521 muscovite/illite. Geochim. Cosmochim. Acta 54, 2979–2990. doi:10.1016/0016-
522 7037(90)90115-2

523 Dreybrodt, W., 1990. The Role of Dissolution Kinetics in the Development of Karst Aquifers in
524 Limestone: A Model Simulation of Karst Evolution. J. Geol. 98, 639–655.
525 doi:10.1086/629431

526 Escartín, J., Hirth, G., Evans, B., 2001. Strength of slightly serpentinized peridotites:

527 Implications for the tectonics of oceanic lithosphere. Geology 29, 1023–1026.
528 doi:10.1130/0091-7613(2001)029<1023:SOSSPI>2.0.CO

529 Evans, B.W., Hattori, K., Baronnet, A., 2013. Serpentinite: What, why, where? Elements 9, 99–
530 106. doi:10.2113/gselements.9.2.99

531 Farmer, V.C., 1974. Infrared Spectra of Minerals. Mineral. Soc. London 149–151.
532 doi:10.1180/mono-4

533 Felmy, A.R., Cho, H., Rustad, J.R., Mason, M.J., 2001. An aqueous thermodynamic model for
534 polymerized silica species to high ionic strength. J. Solution Chem. 30, 509–525.
535 doi:10.1023/A:1010382701742

536 Frost, R.B., Beard, J.S., 2007. On silica activity and serpentinization. J. Petrol. 48, 1351–1368.
537 doi:10.1093/petrology/egm021

538 Früh-Green, G.L., Orcutt, B.N., Green, S., Cotterill, C., 2016. Expedition 357 Preliminary
539 Report Atlantis Massif Serpentinization and Life.

540 Gunnarsson, I., Arnórsson, S., 2000. Amorphous silica solubility and the thermodynamic
541 properties of H_4SiO_4° in the range of 0°to 350°C at P(sat). Geochim. Cosmochim. Acta 64,
542 2295–2307. doi:10.1016/S0016-7037(99)00426-3

543 Harrison, A.L., Power, I.M., Dipple, G.M., 2013. Accelerated carbonation of brucite in mine
544 tailings for carbon sequestration. Environ. Sci. Technol. 47, 126–134.
545 doi:10.1021/es3012854

546 Helgeson, H.C., Murphy, W.M., Aagaard, P., 1984. Thermodynamic and kinetic constraints on
547 reaction rates among minerals and aqueous solutions. II. Rate constants, effective surface

area, and the hydrolysis of feldspar. Geochim. Cosmochim. Acta 48, 2405–2432. doi:10.1016/0016-7037(84)90294-1

Kadko, D., Butterfield, D.A., 1998. The relationship of hydrothermal fluid composition and crustal residence time to maturity of vent fields on the Juan de Fuca Ridge. Geochim. Cosmochim. Acta 62, 1521–1533. doi:10.1016/S0016-7037(98)00088-X

Katayama, I., Kurosaki, I., Hirauchi, K. ichi, 2010. Low silica activity for hydrogen generation during serpentinization: An example of natural serpentinites in the Mineoka ophiolite complex, central Japan. Earth Planet. Sci. Lett. 298, 199–204. doi:10.1016/j.epsl.2010.07.045

Kelley, D.S., 2005. A Serpentinite-Hosted Ecosystem: The Lost City Hydrothermal Field. Science (80-.). 307, 1428–1434. doi:10.1126/science.1102556

Klein, F., Bach, W., Jöns, N., McCollom, T., Moskowitz, B., Berquó, T., 2009. Iron partitioning and hydrogen generation during serpentinization of abyssal peridotites from 15°N on the Mid-Atlantic Ridge. Geochim. Cosmochim. Acta 73, 6868–6893. doi:10.1016/j.gca.2009.08.021

Kong, X.Z., Tutolo, B.M., Saar, M.O., 2013. DBCreate: A SUPCRT92-based program for producing EQ3/6, TOUGHREACT, and GWB thermodynamic databases at user-defined T and P. Comput. Geosci. 51, 415–417. doi:10.1016/j.cageo.2012.08.004

Kump, L.R., Barley, M.E., 2007. Increased subaerial volcanism and the rise of atmospheric oxygen 2.5 billion years ago. Nature 448, 1033–6. doi:10.1038/nature06058

Lichtner, P.C., Hammond, G.E., Lu, C., Karra, S., Bisht, G., Andre, B., Mills, R.T., Kumar, J., Frederick, J.M., 2017. PFLOTRAN Web page.

570 Lin, F.C., Clemency, C. V., 1981. The dissolution kinetics of brucite, antigorite, talc, and
571 phlogopite at room temperature and pressure. Am. Mineral. 66, 801–806.

572 Ludwig, K.A., Kelley, D.S., Butterfield, D.A., Nelson, B.K., Früh-Green, G., 2006. Formation
573 and evolution of carbonate chimneys at the Lost City Hydrothermal Field. Geochim.
574 Cosmochim. Acta 70, 3625–3645. doi:10.1016/j.gca.2006.04.016

575 Luhmann, A.J., Kong, X.Z., Tutolo, B.M., Garapati, N., Bagley, B.C., Saar, M.O., Seyfried,
576 W.E., 2014. Experimental dissolution of dolomite by CO2-charged brine at 100°C and 150
577 bar: Evolution of porosity, permeability, and reactive surface area. Chem. Geol. 380, 145–
578 160. doi:10.1016/j.chemgeo.2014.05.001

579 Luhmann, A.J., Tutolo, B.M., Bagley, B.C., Mildner, D.F.R., Scheuermann, P., Feinberg, J.,
580 Seyfried, W.E., 2017. Chemical and physical changes during seawater flow through intact
581 dunite cores: An experimental study at 150-200°C. Geochim. Cosmochim. Acta.
582 doi:10.1016/j.gca.2017.07.020

583 Maher, K., Steefel, C.I., DePaolo, D.J., Viani, B.E., 2006. The mineral dissolution rate
584 conundrum: Insights from reactive transport modeling of U isotopes and pore fluid
585 chemistry in marine sediments. Geochim. Cosmochim. Acta 70, 337–363.
586 doi:10.1016/j.gca.2005.09.001

587 Martin, B., Fyfe, W.S., 1970. Some experimental and theoretical observations on the kinetics of
588 hydration reactions with particular reference to serpentinization. Chem. Geol. 6, 185–202.
589 doi:10.1016/0009-2541(70)90018-5

590 Martin, W., Baross, J., Kelley, D., Russell, M., 2008. Hydrothermal vents and the origin of life.
591 Nat. Rev. Microbiol. 6, 805–814. doi:10.1038/nrmicro1991

592 Mullin, J.B., Riley, J.P., 1955. The colorimetric determination of silicate with special references
593 to sea and natural water. Anal. chim. Acta 12, 162–176.

594 Noiriel, C., Luquot, L., Madé, B., Raimbault, L., Gouze, P., Van Der Lee, J., 2009. Changes in
595 reactive surface area during limestone dissolution: An experimental and modelling study.
596 Chem. Geol. 265, 160–170.

597 O'Hanley, D.S., 1996. Serpentinites. Oxford University Press.

598 Oze, C., Sharma, M., 2005. Have olivine, will gas: Serpentinization and the abiogenic production
599 of methane on Mars. Geophys. Res. Lett. 32, 1–4. doi:10.1029/2005GL022691

600 Palandri, J.L., Kharaka, Y.K., 2004. A compilation of rate parameters of water-mineral
601 interaction kinetics for application to geochemical modeling. USGS Open File Rep. 2004–
602 1068, 71. doi:10.1098/rspb.2004.2754

603 Pokrovsky, O.S., Schott, J., 2004. Experimental study of brucite dissolution and precipitation in
604 aqueous solutions: Surface speciation and chemical affinity control. Geochim. Cosmochim.
605 Acta 68, 31–45. doi:10.1016/S0016-7037(03)00238-2

606 Rimstidt, J.D., 2014. Geochemical Rate Models. Cambridge University Press, Cambridge, UK.

607 Rimstidt, J.D., 1997. Quartz solubility at low temperatures. Geochim. Cosmochim. Acta 61,
608 2553–2558. doi:10.1016/S0016-7037(97)00103-8

609 Rimstidt, J.D., Barnes, H.L., 1980. The kinetics of silica-water reactions. Geochim. Cosmochim.
610 Acta. doi:10.1016/0016-7037(80)90220-3

611 Rimstidt, J.D., Brantley, S.L., Olsen, A.A., 2012. Systematic review of forsterite dissolution rate
612 data. Geochim. Cosmochim. Acta 99, 159–178. doi:10.1016/j.gca.2012.09.019

613 Robie, R.A., Hemingway, B.S., 1995. Thermodynamic properties of minerals and related
614 substances at 298.15 K and 1 bar (105 Pascals) pressure and at higher temperatures.

615 Rüpke, L.H., Morgan, J.P., Hort, M., Connolly, J.A.D., 2004. Serpentine and the subduction
616 zone water cycle. Earth Planet. Sci. Lett. 223, 17–34. doi:10.1016/j.epsl.2004.04.018

617 Russell, J.D., Fraser, A.R., 1994. Infrared methods. Clay Mineral. Spectrosc. Chem. Determ.
618 Methods 11–67. doi:10.1007/978-94-011-0727-3_2

619 Saldi, G.D., Köhler, S.J., Marty, N., Oelkers, E.H., 2007. Dissolution rates of talc as a function
620 of solution composition, pH and temperature. Geochim. Cosmochim. Acta 71, 3446–3457.
621 doi:10.1016/j.gca.2007.04.015

622 Schrenk, M.O., Brazelton, W.J., Carolina, N., Lang, S.Q., 2013. Serpentinization, Carbon, and
623 Deep Life. Rev. Mineral. 75, 575–606. doi:10.2138/rmg.2013.75.18

624 Seyfried, W.E., Pester, N.J., Tutolo, B.M., Ding, K., 2015. The Lost City hydrothermal system:
625 Constraints imposed by vent fluid chemistry and reaction path models on subseafloor heat
626 and mass transfer processes. Geochim. Cosmochim. Acta 163, 59–79.
627 doi:10.1016/j.gca.2015.04.040

628 Sleep, N.H., Bird, D.K., Pope, E.C., 2011. Serpentinite and the dawn of life. Philos. Trans. R.
629 Soc. B 366, 2857–2869. doi:10.1098/rstb.2011.0129

630 Sojo, V., Herschy, B., Whicher, A., Camprubi, E., Lane, N., 2016. The origin of life in alkaline
631 hydrothermal vents. Astrobiology 16, 181–197. doi:10.1089/ast.2015.1406

632 Sverjensky, D.A., Harrison, B., Azzolini, D., 2014. Water in the deep Earth: The dielectric
633 constant and the solubilities of quartz and corundum to 60kb and 1200°C. Geochim.

Cosmochim. Acta 129, 125–145. doi:10.1016/j.gca.2013.12.019

Syverson, D.D., Tutolo, B.M., Borrok, D.M., Seyfried, W.E., 2017. Serpentinization of olivine at 300 °C and 500 bars: An experimental study examining the role of silica on the reaction path and oxidation state of iron. Chem. Geol. 475, 122–134. doi:10.1016/j.chemgeo.2017.11.006

Tutolo, B.M., Luhmann, A.J., Kong, X.Z., Saar, M.O., Seyfried, W.E., 2015. CO_2 sequestration in feldspar-rich sandstone: Coupled evolution of fluid chemistry, mineral reaction rates, and hydrogeochemical properties. Geochim. Cosmochim. Acta 160, 132–154. doi:10.1016/j.gca.2015.04.002

Tutolo, B.M., Mildner, D.F.R., Gagnon, C.V.L., Saar, M.O., Seyfried, W.E., 2016. Nanoscale constraints on porosity generation and fluid flow during serpentinization. Geology 44, 103–106. doi:10.1130/G37349.1

Tutolo, B.M., Tosca, N.J., in review Experimental examination of Mg-silicate - carbonate interactions during lacustrine carbonate reservoir formation.

Waite, J.H., Glein, C.R., Perryman, R.S., Teolis, B.D., Magee, B.A., Miller, G., Grimes, J., Perry, M.E., Miller, K.E., Bouquet, A., Lunine, J.I., Brockwell, T., Bolton, S.J., 2017. Cassini finds molecular hydrogen in the Enceladus plume: Evidence for hydrothermal processes. Science (80-.). 356, 155–159. doi:10.1126/science.aai8703

White, A.F., Peterson, M.L., 1990. Role of reactive-surface-area characterization in geochemical kinetic models. Chem. Model. Aqueous Syst. II (eds DC Melchoir RL Bassett) Chap 35, 461–475.

York, D., Evensen, N.M., Martínez, M.L., De Basabe Delgado, J., 2004. Unified equations for

the slope, intercept, and standard errors of the best straight line. Am. J. Phys. 72, 367. doi:10.1119/1.1632486

Zarubin, D.P., Nemkina, N.V., 1990. The solubility of amorphous silica in an alkaline aqueous medium at a constant ionic strength. Russ. J. Inorg. Chem.