Rare Earth Element uptake during olivine/water hydrothermal interaction

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Keywords: olivine, serpentinization, kinetic rate constants, surface adsorption, Rare Earth Element

Abstract

Ultramafic-hosted hydrothermal vent systems link the hydrosphere with the peridotitic mantle via serpentinization. Here, the fractionation and mobility of selected trace (Nd, Sm, Gd, Dy, Yb, Sr and Ba) and major cations (Si, Ca, Mg, Fe, Ni) during seawater-peridotite interaction was investigated through a series of experiments where natural olivine grains were reacted with an artificial seawater solution at a range of temperatures (15-90 °C) and grain size distributions. No evidence for any significant olivine dissolution or precipitation of carbonate and, Fe-oxy-hydroxide phases was observed in these experiments. Experimental data show a strong decoupling of REE (Nd, Sm, Gd, Dy, and Yb) from Sr and Ba under all experimental conditions, with Sr and Ba remaining quantitatively in solution. The REE were removed from the solution and were adsorbed onto olivine surface with kinetic rate constants (i.e. uptake over time) that increase with increasing temperature and increasing surface area (i.e. decreasing particle size). Dysprosium and Yb (heavy REE; HREE) were removed from solution with a faster rate than Nd and Sm (light REE; LREE). Gadolinium is decoupled from this trend, with a slower kinetic rate constant than Sm. The activation energies (E_a) of REE adsorption on olivine were higher for Nd and Sm than Dy and Yb. This suggests that the adsorbance of LREE is generally more dependent on temperature than the HREE. The E_a correlates well with the summed 1^{st}, 2^{nd} and 3^{rd} ionization energies of REE suggesting a link between kinetic rates of element adsorption and electron configuration of the 4*f*-orbitals. Gadolinium has higher E_a than the other analyzed REE, consistent with the electron configuration of Gd^{3+} where all 4*f*-orbitals are filled with one electron each. These experimental data suggest that REE are adsorbed on the surface of olivine via inner sphere complexes under low-temperature hydrothermal conditions, when alteration

34 processes are limited or extremely slow. Scavenging and fractionation of REE may occur within
35 the recharge zone of peridotite-hosted hydrothermal systems at relatively low temperatures
36 (<100 °C), leading to fluids with progressively higher LREE/HREE which could impose
37 seawater-derived LREE enrichments in serpentinized peridotites during high temperature, high
38 pressure water/rock interaction deeper in the oceanic lithosphere.

1.0 Introduction

In oceanic basins, at subduction zones, axial, off-axis and rift systems seawater reacts with the peridotitic portion of the oceanic lithosphere linking the hydrosphere and the Earth's mantle. Hydrothermal circulation of seawater in peridotites results in the formation of reducing hydrothermal fluids enriched in dissolved volatiles (e.g., H_2, CH_4), and with a chemical composition distinctively different from basalt-hosted hydrothermal systems (Allen and Seyfried, 2005; Alt et al., 2013; Bach et al., 2004; Delacour et al., 2008; Evans et al., 2013; Foustoukos et al., 2008). Also, seawater - peridotite reaction at elevated temperatures (>180 °C) results in alteration of primary silicate minerals (e.g., olivine, clinopyroxene, and orthopyroxene) to secondary (or alteration) minerals (e.g., chrysotile, brucite, and magnetite) (Foustoukos et al., 2008; Janecky and Seyfried, 1986; Kadko et al., 1994; Paulick et al., 2006; Seyfried et al., 2007; Snow and Dick, 1995). However, high temperature basalt- and peridotite-hosted hydrothermal systems at oceanic spreading centers are thought to account for only 25-30 % of the total magmatic heat flow from the cooling lithosphere (Alt, 2003; Bach and Früh-Green, 2010; Johnson and Pruis, 2003; Mottl and Wheat, 1994; Rosenberg et al., 1993). The remaining 70-75 % of the total magmatic heat flow is thought to originate from more diffuse, lower-temperature hydrothermal advection at ridge flanks and within oceanic basins. Due to their larger areal coverage, such low temperature hydrothermal systems potentially result in much greater elemental exchange between oceanic crust, lithosphere and seawater than their on-ridge counterparts (Alt, 2003; Elderfield and Schultz, 1996; Johnson and Pruis, 2003; Mottl and Wheat, 1994). Yet, mantle peridotite-seawater interaction at relatively low temperature conditions (<100 °C) has been little studied.

In natural aqueous environments, rare earth elements (REE) have been proven useful tracers of both processes and pathways (Alibo and Nozaki, 1999; Elderfield and Greaves, 1982; Elderfield et al., 1990; German et al., 1990; Johannesson et al., 2011; Schijf and Marshall, 2011; Shiller, 2003; Sonke and Salters, 2006). Their effectiveness as tracers lies in their similar geochemical behavior (3^+ charge, with Ce and occasionally Eu as exceptions), and their gradual decrease in ionic radius from La to Lu (i.e., lanthanide contraction). Several studies (at ambient temperatures and pressures) have demonstrated that REE are highly particle reactive, e.g., adsorption of REE with marine particulates (De Baar et al., 1985a; De Baar et al., 1985b; Elderfield et al., 1990; Erel and Morgan, 1991; Sholkovitz et al., 1994), aquifer sands (Duncan and Shaw, 2003; Tang and Johannesson, 2005), mineral surfaces (silica beads, Schijf and Marshall, 2011; clays, Coppin et al., 2002; basaltic glass, Tertre et al., 2008) and organic macromolecules (Sonke and Salters, 2006; Stern et al., 2014; Stern et al., 2007). The relative depletion of light REE (LREE) over heavy REE (HREE) in seawater compared to an average continental crust shale rock (e.g. Alibo and Nozaki, 1999; Byrne and Kim, 1990; De Baar et al., 1985b; Sholkovitz et al., 1994) is generally attributed to the stronger complexation of HREE over LREE with carbonate complexes (e.g. Cantrell and Byrne, 1987; Luo and Byrne, 2004) leaving LREE more susceptible to scavenging by surface ligands (Sholkovitz et al., 1994). In the absence of strong organic and carbonate complexes, however, some studies have shown preferential removal of HREE over the LREE onto mineral substrates (Byrne and Kim, 1990; Coppin et al., 2002; Tertre et al., 2008). Rare earth elements also show a high affinity for hydrated oxide minerals (e.g., Fe-oxyhydroxide) that increases with increasing pH (Bau, 1999; Koeppenkastrop and De Carlo, 1993; Quinn et al., 2006b; Schijf and Marshall, 2011) and

temperature (Quinn et al., 2007). Although HREE generally have higher affinity than the LREE for Fe-oxyhydroxides, the available data does not always show a simple monotonic increase in partitioning with increasing atomic number and often exhibits maximum at Sm relative to the HREE (Bau, 1999; Quinn et al., 2004).

Despite these data, the behavior of REE during peridotite-seawater interaction is less understood. Experiments on the reaction of serpentinized peridotite with fluids at temperatures greater than 300 °C show LREE enrichment in the resulting hydrothermal fluid that was attributed to a complex interplay between dissolved REE species in the Na-Mg bearing fluid and precipitation of secondary mineral phases, such as talc and chrysotile (Allen and Seyfried, 2005). Enrichments in LREE in hydrothermal fluids were further attributed to mobilization of REE from the interstitial secondary minerals of serpentinized peridotite (Bach and Irber, 1998). In contrast, field studies of Paulick et al. (2006), Frisby et al. (2016a) and Frisby et al. (2016b) suggested that serpentinization under high integrated water/rock mass ratios results in REE uptake from seawater and enrichments in altered peridotites. This was particularly exemplified by the overprint of the mantle-like Nd isotope composition of peridotites by a seawater component (Frisby et al., 2016a). The apparent REE mobilization during peridotite serpentinization (Allen and Seyfried, 2005) appears at odds with the strong adsorption of REE onto mineral surfaces, and field studies discussed above. It is unclear whether this discrepancy is driven by precipitation or dissolution of mineral species (e.g. serpentine group minerals, carbonates, etc.; Allen and Seyfried, 2005; Zhong and Mucci, 1995) or surface related reactions controlled by temperature and fluid pH conditions (Marmier et al., 1999; Ridley et al., 2005).

In order to gain further insights into the extent of elemental fractionation between seawater and natural peridotite, and especially test whether there is REE uptake or not during olivine – seawater interaction, we present time-series reaction experimental data for Sr, Ba, Nd, Sm, Gd, Dy and Yb between fresh, natural forsteritic olivine and Na-Mg-Ca-Cl-bearing aqueous solutions at vapor-saturated pressure conditions, and as a function of temperature (15, 60 and 90 °C) and reactive surface area. The starting solutions were of seawater composition for the major cations, however, without SO_4^{2-} which may act as strong ligand for REE aqueous complexation (Migdisov et al., 2016) and open to the atmosphere so bicarbonate, carbonate ions are present but at lower concentrations than typical seawater. The experiments were designed to constrain the relative fractionation and mobility of selected REE at conditions reflecting low temperature peridotite-seawater interaction at hydrothermal environments (i.e., off-axis, ridge flank settings, diffuse flow) that are thought to dominate the global oceanic hydrothermal heat flux (Bach and Früh-Green, 2010; Elderfield and Schultz, 1996; Johnson and Pruis, 2003; Kadko et al., 1995; Mottl and Wheat, 1994; Stein and Stein, 1994). Strontium and Ba were determined in addition to the REE to contrast their generally more conservative behavior relative to REE in seawater (in the absence of precipitating carbonates). The experimental data are used to derive the activation energy of the surface area-normalized kinetic constants for the REE adsorption to olivine and the implications of these data towards seawater – peridotite interaction.

2.0 Methods

2.1 Starting Material

125 Olivine mineral separates with typical upper mantle peridotite composition (Mg#=0.91,
126 where Mg# = Mg/(Mg+Fe) cation mole; Table 1) were obtained from a large fresh spinel
127 peridotite xenolith (88SAL 1-1) from Salt Lake Crater, Hawaii (e.g. Bizimis et al., 2004 and
128 references therein). The peridotite was crushed and hand sieved to obtain three size fractions
129 (<200 μm, 200-350 μm and 500-850 μm). The two larger fractions were magnetically separated
130 with a Frantz isodynamic separator to concentrate olivine. Olivine grains were handpicked for
131 clarity under a binocular microscope, and to be devoid of alteration or inclusions. In order to
132 remove any surface alteration or adsorbed metals, the picked olivine grains were leached in a 10
133 wt% HCl solution and sonicated for ten minutes, and subsequently rinsed and sonicated several
134 times in 18 MΩ H_2O. The grains were dried at 90 °C and were sieved again with a clean
135 polypropylene sieve to better constrain the size fraction by separating any smaller grains that
136 may have mechanically broken off during sonication. To obtain the "fine" fraction of olivine
137 used in the experiments, a hand-picked olivine fraction was processed through an agate ball-mill
138 until a <30 μm powder was achieved. Average grain size for the three fractions was determined
139 using a Beckman Coulter LS 100Q laser particle size analyzer using the diffractometry laser
140 method (Beuselinck et al., 1998). Surface area measurements are based on the assumption of
141 sphere shape of the counted particles, and reflect the sum of particles' surface area divided by the
142 sum of particles' volume (Foustoukos and Stern, 2012). Repeated analyses of the material were
143 reproducible to better than 1% relative. The geometric surface area (GSA) was determined by
144 accounting for olivine's specific gravity of 3.33 (Klein and Dutrow, 2008).
145 Aqueous solution with seawater-like composition was prepared by dissolving NaCl
146 (99.99%), $MgCl_2$ (99.99%), and $CaCl_2$ (99.99%) (Alfa Aesar) in 18 MΩ H_2O to obtain the

concentrations of dissolved Na^+ (0.42 mol/L), Mg^{2+} (0.05 mol/L), Ca^{2+} (0.01 mol/L), and Cl^- (0.54 mol/L) found in average seawater (Table 2; Wilson, 1975). We did not added sulfate for simplicity and because it is not thought to be a major REE ligand in seawater (Millero et al., 2009). An aliquot of this solution was spiked with Sr, Ba, Nd, Sm, Gd, Dy, and Yb, to a concentration of 100 ppb each while maintain the pH at ~7.5.

At the water/rock mass ratios of these experiments (~40) the total dissolved REE content (2.5 μg) in the starting solution is about 100 times higher than the total REE content of the olivine used for this investigation (<37 ng, Table 1 and Supplementary Table S1). Therefore olivine contributions to the REE concentrations in solution (even if all olivine was to dissolve) were relatively insignificant.

2.2 Experiment Protocols

2.2.1 Olivine Time-series experiments

All experiments were performed in a trace metal free, HEPA filtered air clean lab at the Center for Elemental Mass Spectrometry, University of South Carolina. In these experiments 125 mg of olivine grains with GSA ranging from 28.2 to 3339 cm^2/g were added in 5ml of reactant aqueous solution, resulting in a water-to-rock mass ratio (W/R) of ~40 (Table 3). The experiments were performed in Savillex 7ml PFA (Teflon) vials. The beakers were set on an aluminum block, capped to ensure even heat transfer. Temperatures were set at 15 °C (ambient lab temperature, controlled within 1 degree), 60 °C and 90 °C. The actual solution temperatures were found constant and reproducible to better than 2 °C for the 90 °C experiments. Before adding the mineral grains to the reaction PFA vial, the solution was heated to the temperature of

169 the experiment. An aliquot of the solution was taken to establish the initial composition of the
170 solution, then the olivine was added to the vial and the vial was capped. Time series samples
171 were collected during the course of the experiment (a total of 131 analyzed aliquots) and in
172 varied intervals: 30-minute intervals for the first hour, every 3 hours for the next 24 hours, then
173 every 6 hours over 3 days followed by every 24 hours out to 14 days total experiment time.
174 Sampling of the fluid consisted of opening the vials, withdrawing 50 µl of the solution with a
175 pre-cleaned polypropylene pipette tip, and recapping the vial. Therefore during sampling the
176 experiments were exposed to atmosphere. The 50 µl sample extraction was chosen to minimize
177 change in the volume of the solution in the experiment (1% of the experiment volume per
178 analysis).

179 The recovered solutions were filtered by centrifugation in a pre-cleaned micro-centrifugal
180 filter (<0.2 µm; Fisher Scientific part #UFC30GV0S with a low hold volume of < 5µl), to filter
181 any submicron suspended material. Thirty (30) µl of the filtered aliquots were then diluted ~80x
182 with sub-boiling, Teflon-distilled 2% (wt/wt) HNO_3 with 2 ppb Indium added as internal
183 standard for elemental analysis. Strontium, Ba, Nd, Sm, Gd, Dy, Yb, Ni, Si, Fe, Mg, and Ca
184 concentrations for all starting materials and reaction fluid products were determined using a
185 combination of external standard calibration with the USGS BIR-1 basalt, and internal drift
186 correction using Indium on a Thermo-ELEMENT 2 HR-ICPMS following established protocols
187 for this lab (Table 4) (Das et al., 2013; Frisby et al., 2016b; Sen et al., 2011). The isotopes ^{88}Sr,
188 ^{137}Ba, ^{146}Nd, ^{147}Sm, ^{157}Gd, ^{163}Dy, and ^{172}Yb were analyzed in low-resolution mode and the
189 isotopes ^{60}Ni, ^{29}Si, ^{57}Fe, ^{25}Mg, and ^{43}Ca in medium-resolution to maximize the signal to
190 background ratio by avoiding isobaric interferences (e.g., $^{40}Ar^{16}OH$ on ^{57}Fe). Detection limits for

191 the experimental solutions were approximately 25 ppt for Nd and Sm, 30 ppt for Gd, and 2 to 5
192 ppt for Dy and Yb. As the starting solution was 100 ppb for each REE we resolved the REE
193 depletion in solution down to a 0.03% to 0.002% of the starting solution. Precision of
194 concentrations as judged by internal statistics of the measurements is from 1 to 6% for the lowest
195 concentrations. However, elemental ratios in each aliquot are precise to better than 3% because
196 some uncertainties in the calculation of the absolute concentrations (e.g. drift correction, plasma
197 noise), effectively cancel out during measurement.

198 The pH of the solutions was measured in-situ at each sampling interval using a micro-pH
199 electrode (Thermo Scientific 8220BNWP) with the exception of the CF-23 experiment (15 °C)
200 (Supplementary Table S1), where the pH of the solution was measured at termination. The
201 analytical uncertainty of the pH measurements was within 0.05 log units (1σ standard deviation).

202 Least-squares fitting of the experimental data was performed utilizing the technical
203 graphic and data analysis software IGOR Pro (Wavemetrics) and Microsoft Excel.

204

205 **2.2.2 Analysis of Solid Samples**

206 To examine the presence of secondary alteration phases, the reactant solids of the high
207 surface area (< 30 μm, i.e. powder) experiment HP (Table 3, Supplementary Table S1) were
208 retrieved at the termination of the experiment, and then dried down at 90 °C overnight in an
209 enclosed HEPA filtered dry down box. Once dry, the solids were rinsed with ~5 ml of 18 MΩ
210 H_2O; to remove remnant chlorides. The solids were analyzed by X-ray diffraction on Shimadzu
211 LabX XRD-6000 (at the University of South Carolina) and for Fe^{+3}/Fe^{+2} by Mößbauer
212 spectrometry (Carnegie Institution of Washington: Geophysical Lab). Mößbauer spectroscopy

213 analysis were conducted with a ~40 mCi ^{57}Co flat source with the drives (Austin Science)
214 operating in constant acceleration mode between −4 and 4 mm/s, and calibrated with metallic Fe
215 at the operational temperature conditions of 25 °C. Data were collected over 1024 channels,
216 which on folding resulted in 512 channels. All Mößbauer spectra were accumulated to a low
217 statistical uncertainty (typically 5 - 7 x 10^6 counts per channel). Samples were prepared by
218 homogeneously mixing the starting olivine and the final reaction-products (15 mg) with
219 transoptic powder (120 mg), and then converted to a 12.7-mm diameter and 1 mm thick pellet at
220 350 bar and 120 °C (Foustoukos and Stern, 2012).

221 The solids from the high temperature (90 °C) coarser olivine experiment CF-19 (Table 3,
222 Supplementary Table S1) where inspected by SEM on a Tescan Vega 3 SBU variable pressure
223 SEM at the Electron Microscopy Center, University of South Carolina (Supplementary Fig.
224 SF1). The grains where compared to the unreacted fractions to test for the presence of newly
225 formed secondary mineral phases.

226

227 **2.2.3 Thermodynamic modeling**

228 Assessment of phase equilibria during the experiments including calculation of mineral
229 solubility and distribution of aqueous species at experimental conditions was performed using
230 Geochemist's WorkBench (GWB) software package (Bethke, 1996). Mathematical derivations
231 and numerical techniques used by the GWB code involve a Newton-Raphson approach to
232 simultaneously solve the grid of non-linear equations that describe chemical equilibria and
233 mineral saturation states, while assessing aqueous speciation through equations of mass and
234 charge balance. This formulation of geochemical modeling is in accordance with previous

numerical algorithms developed to estimate aqueous speciation and approximate mineral-fluid equilibria at elevated temperatures and pressures (e.g. SOLVEQ, EQ3/6) (Reed, 1982; Wolery and Daveler, 1992). The activity coefficients of ionic species were calculated with an extended form of the Debye-Hückel equation ("*B-dot"*) (Helgeson et al., 1981) (additional details in (Foustoukos, 2016). To ensure internal consistency, thermodynamic data on mineral hydrolysis, dissociation reactions of aqueous species and H_2O properties were derived from SUPCRT92 (Johnson et al., 1992) and the 1998 database update (Shock et al., 1997; Sverjensky et al., 1997). The standard state for end-member minerals and liquid H_2O is unit activity of the pure phase at the temperature/pressure conditions of this study (Ding and Seyfried, 1992).

For the thermodynamic properties of chloro- and hydroxyl- bearing REE aqueous complexes we utilized the thermodynamic data of Migdisov et al. (2016) (REE-Cl^{2+}, REE-Cl_2^{+}, $Nd(OH)_{3(aq)}$) along with the dataset of Haas et al. (1995) (REE-OH^{2+}, other chloro-complexes, REE^{3+}). Unfortunately, the recent advances in the thermodynamic properties of REE-carbonate aqueous species (Luo and Byrne, 2004) are limited to ambient temperature/-pressure conditions. Thus, to model the aqueous REE-carbonate species in our hydrothermal experiments, use of the theoretical predictions of Haas et al. (1995) was adopted (see more in (Migdisov et al., 2016)).

3.0 Results

To better illustrate and model the change in dissolved REE concentrations during olivine/fluid interaction, we present the natural logarithm of the solution concentration, *C*, at any given time, normalized to the starting solution concentration, C_0 (i.e., $\ln(C/C_0)$) (Supplementary

256 Table S1). Results are grouped with temperature. In all figures circle symbols depict
257 experimental data at 15 °C, squares data at 60 °C, and triangles data at 90 °C.

258 **15 °C Experiments:** Considering the very sluggish kinetics of olivine hydrolysis at such
259 low temperatures, these experiments served as control experiments to constrain the REE
260 olivine/fluid partitioning and possibly decouple the effects of REE mineral uptake during
261 alteration from surface adsorption at the higher temperatures of 60 and 90 °C. Time series
262 samples collected at 15 °C (ALG, CF-11, CF-20, CF-22, CF-23, AP) (Fig. 1, Supplementary
263 Table S1) showed that Sr and Ba concentrations remained essentially unchanged in the solution
264 for all size fractions. In contrast, the REE are increasingly removed from solution with increasing
265 GSA (i.e. decreasing particle size), with the HREE being preferentially removed over the LREE.
266 For example, as the GSA approximately doubles (from 257 to 577 cm^2/g), the amount of Nd
267 remaining in solution after 1920 minutes decreased from ~30 % to ~ 4 %, respectively, while the
268 $Yb/Nd_{(n)}$ in solution decreased from 0.39 to 0.35 (where n = concentration normalized to C_0)
269 (Fig. 1, Supplementary Table S1). In two extreme cases, experiment ALG (Fig. 1A) with the
270 largest size olivine grains (500 to 850 micron size fraction, GSA = 28.16 2 cm^2/gr) showed no
271 appreciable change in REE and Sr, Ba concentrations in solution, even after 22 days of reaction
272 time; while in experiment AP with the highest GSA = (3339 cm^2/gr) (Fig. 1F) the REE
273 concentrations in solution decreased to 1-2 % of the starting solution concentration within only 6
274 hours (Fig. 1F, Supplementary Table S1). We note that there was no significant difference in the
275 composition of solutions collected from static experiment CF-11, and a continuously agitated
276 experiment CF-20 using the same sized olivine starting solid material (Supplementary Table S1,
277 Fig. 1 A; B), particularly for early on in the experiments where kinetic constants are calculated

(discussed later). We take this to suggest that these static experiments adequately represent the reactivity of REE on olivine.

60 °C Experiments: The 60 °C time-series experiments at a GSA of 28.2, 57.8, 176 and 3339 cm^2/g (CF-18, CF-12, CF-13, and CF-21; Fig. 2, Supplementary Table S1) also showed that Sr and Ba remain in solution while REE are increasingly removed over time. Again, with increasing GSA the REE are progressively depleted in solution, with preferential depletion of HREE over LREE (Fig. 2). Experiment CF-18 solution concentration with the smallest GSA of 28.2 cm^2/g, remained constant within 5% of the starting solution for the last 3 days of the experiment (from 2800 to 7200 minutes; Fig. 2A).

90 °C Experiments: As in the 15 °C and 60 °C experiments, the 90 °C time-series experiments at a GSA of 28.2, 57.8, 924 and 3339 cm^2/g (CF-17, CF-19, CF-24, and HP; Fig. 3, Supplementary Table S1) showed that Sr and Ba remain quantitatively in solution while REE are progressively removed with increasing GSA, and the HREE are removed preferentially over the LREE (Fig. 3). Experiment CF-17 (Fig. 3A) showed a step-wise decrease in REE concentration at 1200 and 3600 minutes. We speculate that this may be due to breakage of some grains that resulted to an increase in surface area.

Temperature effect: Experiments conducted at a given olivine surface area and at the 3 temperatures (GSA = 57.8 cm^2/g) allow to constrain the effect of temperature on the reactivity of REE (Fig. 4). With increasing temperature the amount of REE removed from the solution increases, while Sr and Ba (as well as Ca^{2+} and Mg^{2+}) remain quantitatively in solution (Fig. 4). Also, REE fractionation increases with increasing temperature, with greater removal of the HREE over the LREE. For example, as the temperature increases from 60 to 90 °C and after

1400 minutes, the Nd concentration in solution decreases from 75 % to 46 % of the starting solution and the $Yb/Nd_{(n)}$ ratio decreased from 0.65 to 0.42, respectively. Note that we cannot perform the same quantitative analysis with the highest GSA (3339 cm^2/g) experiments due to the near quantitative removal of REE from solution at all temperatures, approaching analytical detection limits.

A common observation in all the above experimental data is that the REE solution concentrations change quickly in the beginning of the experiment and the change becomes progressively slower over time, with some experiments (e.g. Figures 1A, 2C, 3C) approaching an apparent steady-state condition. Importantly, the HREE Yb and Dy are removed to a greater extent than the LREE Nd and Sm, implying greater reactivity for the HREE than the LREE.

Olivine Leaching: To confirm the REE adsorption on olivine surface we performed blank experiments where the starting aqueous solution was placed in the PFA vials without olivine. The data showed no change in REE concentrations over time, confirming that REE were not adsorbed on the vial walls, as is also generally known for polyethylene bottles (e.g., Stern et al. 2007). We also performed leaching tests on mineral fractions recovered from experiments CF-12 and CF-13 at 60 °C. The recovered olivine grains were rinsed twice with 18 MΩ H_2O to remove salts, and then dried on HEPA-filtered hot plates at 60 °C. Once dry, a 10 wt% HCl solution was added to each beaker and after an hour the solution was subsampled and analyzed. The total content of the REE, as the sum of those remained in solution at experiment termination and those recovered from the olivine match the REE composition of the starting solution to within 5 % of the starting amount (Table 5). This confirms that the depletion of REE in solution is due to scavenging and adsorption on reactant olivine.

322 **Olivine dissolution and alteration:** Under the temperature conditions of our
323 experiments, olivine dissolution can occur with the potential formation of secondary Fe(III)-
324 (hydr)oxides (Hänchen et al., 2006; Mayhew et al., 2013; Oelkers, 2001; Pokrovsky and Schott,
325 2000; Stopar et al., 2006). In addition, experimental data from Chen and Brantley (2000) show
326 stoichiometric olivine dissolution at pH=2.95 to 5 at 65 °C in HCl media, at conditions generally
327 similar (albeit far more acidic) to ours.
328 Our experimental results, however, do not show stoichiometric dissolution of olivine, or
329 any dissolution for that matter. In all experiments the Mg/Ca in the solution (to account for any
330 instrumental drift) remained effectively unchanged and within measurement uncertainty
331 (Supplementary Figure SF4), of the concentrations in the starting solution (e.g., ~1 % relative),
332 therefore no significant Mg addition for possible olivine dissolution was observed,
333 stoichiometric, or otherwise.
334 Morever, we monitored the concentration of dissolved Ni and Fe in the experimental
335 solution as a proxy for olivine dissolution. Under the circumnatural pH (~7 to 7.8) of the
336 experimental solutions, Fe is highly insoluble and will precipitate from solution as Fe
337 oxyhydroxide while Ni remains soluble (Ji and Cooper, 1996; Takeno, 2005). Ni and Fe are
338 found in high concentrations in olivine but absent in the starting solution (Table 1, 2). The use of
339 medium resolution mode ($\Delta m/m = 4000$) on the ELEMENT2 eliminates isobaric interferences on
340 the analyzed ^{60}Ni and ^{57}Fe isotopes, resulting in low detection limits (typically 2 to 5 ppt). This
341 allows the use of Ni in solution as a sensitive tracer for the amount of olivine dissolution in the
342 experiments. Results show that while Ni in some experiments slowly increased over time (e.g.,
343 CF-18), the Ni concentrations in most experimental solutions (for the time range where kinetic

344 rate constants were calculated, see below) ranged from <1 ppb to 10 ppb with most being less
345 than 3 ppb (Supplementary Table S1). Occasional "spikes" in Ni, Fe and Mn concentrations
346 (e.g., experiment CF-23 at 120 minutes) are likely <0.2μm particles that where not filtered.
347 Considering the high end of Ni concentrations for the filtered experiments (~10 ppb, experiment
348 CF-23, Supplementary Table S1) and assuming stoichiometric dissolution of olivine, our
349 estimations suggest that up to 1.2 μg of olivine could have dissolved which is 0.013 % of starting
350 olivine mass.

351 Solid reaction products were analyzed at the termination of the experiment for selected
352 experiments (CF-19, HP) using SEM, x-ray diffraction (XRD) and Mößbauer spectrometry
353 (Supplementary Figs. SF1, SF2, SF3). There were no distinct textural or compositional variations
354 detected with the SEM images to suggest alteration or precipitation of secondary mineral (e.g.,
355 chrysotile, brucite, magnetite, Fe-oxides) (Supplementary Figs. SF1). Similarly, no secondary
356 minerals or Fe^{3+} contributions in both the XRD and Mößbauer spectra were identified in solid
357 reaction products (Supplementary Figs. SF2, SF3). These results are consistent with the very
358 sluggish kinetic rates of olivine alteration and serpentinization reported in previous low-
359 temperature (<100 °C) experimental studies, in which trace amounts of alteration phases such as
360 Fe^{3+}-(hydro)oxides, talc and serpentine were developed after at least 800 hours of reaction
361 (Mayhew et al., 2013; Neubeck et al., 2014; Miller et al. 2017).

362

363 **4.0 Discussion**

364 Our data show that REE are readily adsorbed on to the surface of olivine, while Sr and Ba
365 remain quantitatively in solution. These findings are consistent with earlier studies (Byrne and

366 Kim, 1990; Tang and Johannesson, 2005; Tertre et al., 2008) that showed in the absence of
367 strong organic and carbonate ligands, REE are particle reactive with HREE being preferentially
368 removed from both seawater and fresh water over LREE by adsorption on to mineral surfaces.
369 The low reactivity of the alkaline earths seen here is consistent with experimental data that show
370 little adsorption of Sr, Ba, Ca, and Mg at circumneutral pH for a variety of mineral reactive
371 surfaces (rutile, goethite, amorphous silica, quartz; Sverjensky, 2006 and references therein for a
372 compilation of experimental data on alkali metal reactivity). These findings are also qualitatively
373 consistent with the well-known long residence time (~4 million years) of Sr and the short
374 residence time (hundreds to thousand years) of REE in seawater (Bruland, 1983; Goldberg,
375 1965). However, our data allows us to quantify REE reaction rates at conditions relevant to low
376 temperature hydrothermal conditions and seawater / rock interaction. In the following, we
377 explore the kinetic rates of REE reaction and the role of carbonates, Fe-hydroxides, and REE
378 aqueous speciation on REE uptake and fractionation during low-temperature olivine/fluid
379 interaction.
380
381 **4.1 Adsorption kinetic rate constants**
382 Experimental data indicate that the concentration of REE in solution (as $\ln(C/C_0)$)
383 changes rapidly at the beginning of the experiments (Figs. 1 to 3), but slows with time, i.e., the
384 kinetics of REE adsorption changes with time from fast to slow. In some cases, especially in the
385 coarser grain (small GSA) experiments (e.g., Fig. 4C), the concentrations approach steady-state
386 conditions where little additional REE removal is observed. This change in adsorption kinetics is
387 clearly not that of a first order reaction, where the natural logarithm of the normalized REE

388 concentrations is expected to show strong linear correlation with reaction time. Thus, we
389 evaluated the possibility of a second order reaction by plotting the $(C/C_0)^{-1}$ for Nd and Yb vs.
390 reaction time for selected experiments (Fig. 5). Some experiments show a strong linearity
391 particularly early in the experiment (Fig. 5E, and F), whereas others show characteristic changes
392 in kinetic rates, as a function of the reaction time (Figs. 5A, B, D, and C; concave down curves).
393 From this, it becomes apparent that the kinetics of REE adsorption on to olivine surface
394 do not follow a first or second order reaction pattern. More complex kinetics with multiple rates
395 were not investigated. However, the essential observation is that during the early stages of
396 reaction conditions of enhanced kinetics are established (Figures 1 through 4). For simplicity,
397 therefore, the adsorption kinetic rate constants were approximated as two pseudo first-order
398 reaction regimes using linear regression between $\ln(C/C_0)$ and reaction time (an example is
399 shown Fig. 6). The transition point between these two reaction regimes was approximated by
400 manually optimizing the fit of a linear regression to the data in the early stage of the experiments
401 to increase the r-squared values of the fitted model. Our only limit to the fit was to include a
402 minimum of 4 points in the first reaction regime, so that the calculated rate constants represent at
403 least 2 hours of reaction time. The initial kinetic rate constants of REE scavenging, k^{REE},
404 calculated for the experiments are given in Table 6.
405 This approach explicitly assumes that k^{REE} are constant for the selected time intervals.
406 While this is obviously not entirely valid as discussed above, nevertheless, the k^{REE} effectively
407 represents an "average" REE adsorption kinetic rate constant over that time interval. As a result
408 of this approximation, some uncertainty in the selection of the transition point between the two
409 reaction regimes (Fig.6) does not significantly affect the estimated values k^{REE} (Table 6). The

uncertainties of the estimated k^{REE} values are calculated assuming a 5-minute sampling time error, whereas the error on the ln(C/C_0) value is calculated by a full error propagation of the analytical uncertainties (1 standard deviation, typically 2-3 % relative). Note that for experiments with the highest GSA (3339 cm^2/g), we were unable to quantify kinetic constants due to the relatively long sampling intervals compared to the rapid rate of REE removal from solution (Figures 1F, 2D, 3D).

4.2. REE adsorption kinetic rate constants and activation energy

The adsorption kinetic rate constants (k^{REE}) increase with both increasing temperature and GSA. This is shown in Figure 7**,** where the experimentally-derived k^{Nd} and k^{Yb} (only Nd and Yb are shown for clarity as the rest of the analyzed REE fall between the two) are plotted against total olivine surface area (SA: mass, multiplied by the GSA of the particular olivine fraction) and as a function of temperature. At a given temperature, the k^{REE} increase approximately linearly with the surface area (Fig. **7**). Based on this linearity, we quantify the effect of temperature on k^{REE} by normalizing k^{REE} to the mineral surface area using a least-squares regression, and for each temperature. The slope of this line defined as k^{REE}/SA, is effectively the "surface area normalized adsorption kinetic rate constant" for a given REE at a given temperature (Fig. 7, Table 7).

Figure 8 shows that the natural *log* of surface-normalized REE adsorption kinetic rate constants, ln(k^{REE}/SA), decrease with the reciprocal of temperature, i.e., the highest k^{REE}/SA are found at the highest temperature experiments. The approximately linear relationship of

431 ln(k^{REE}/SA) with 1000/T suggests that the kinetics of REE olivine surface adsorption may be
432 described through an Arrhenius relationship:

433 $$\ln\left(\frac{k^{REE}}{SA}\right) = \ln(A) - E_a^{REE}/RT \qquad (1)$$

434 where R =8.314 (J/(K*mol), E_a is the activation energy and A is the frequency factor. In Figure
435 8, the E_a is defined as he slope of ln(k^{REE}/SA) vs. 1000/T, and the frequency factor, A, is the
436 intercept. The calculated E_a for each REE are reported in Table 7 and range from 16.3 ± 0.6 to
437 13.1 ± 0.6 kJ/mol. The HREE have lower activation energies and frequency factors than the
438 LREE (Table 7). This suggests that adsorption of HREE is less temperature dependent than the
439 LREE. In other words, the HREE are more readily adsorbed on the surface of olivine than the
440 LREE at the temperature conditions of our experimental study.
441
442 **4.3 Gd decoupling and REE electron configuration**
443 The calculated kinetic rate activation energies decrease with decreasing atom radius (or
444 increasing atomic number) from LREE to HREE (Fig. 9a; i.e., from Nd to Yb). However, Gd
445 falls off this trend having characteristically higher E_a than the neighboring Sm and Dy and higher
446 than all analyzed REE, implying another property of REE, in addition to ionic radius, controls
447 their reactivity as a function of temperature. Instead, the activation energy, E_a^{REE}, yields a strong
448 linear relationship with the sum of the 1st, 2nd, and 3rd ionization potentials (referred herein as
449 total ionization potential) of the REE (Fig. 9b). Gadolinium and Nd with the highest E_a both have
450 the lowest total ionization potential, whereas Yb with the lowest E_a has the highest total
451 ionization potential. The total ionization potential represents the amount of energy required to
452 remove the three outer electrons from the atom and is a function of the electron configuration of

453 the REE. Gadolinium +3 has an [Xe]4f^7 electron configuration where each of the seven *f*-orbitals
454 are filled with one unpaired electron (i.e., half-filled *f* orbitals). In contrast, the +3 cations of Nd,
455 Sm, Dy and Yb either have some unfilled *f*-orbitals (Nd, Sm) or some of the *f*-orbitals with two
456 electrons (Dy, Yb). This electron configuration likely results in a more symmetric and less
457 polarized electric field for Gd^{+3} (De Baar et al., 1985b), than the other analyzed REE and may
458 account for its relatively lower reactivity (and higher activation energy) compared to Sm and Dy
459 with the nearest atomic number and radius (Bau, 1999)). The relative enrichment of Gd relative
460 to other REE in some Atlantic and Pacific seawaters (Alibo and Nozaki, 1999; De Baar et al.,
461 1985b) has also been attributed to a lower reactivity due to its electron configuration.
462
463 **4.3 Mechanisms of adsorption on olivine.**
464 **4.3.1 REE-complexation by carbonates?**
465 As our experiments were open to the atmosphere, the presence of dissolved CO_2 may
466 stabilize carbonate-bearing REE aqueous species and promote the precipitation of carbonate
467 minerals. However, thermodynamic calculations conducted by accounting for the chemical
468 composition of the sampled aliquots, suggest that calcite is not stable, whereas dolomite and
469 magnesite are. Formation of secondary dolomite could alter the Ca^{2+}/Mg^{2+} of the solution due to
470 preferential uptake of Ca^{2+} over Mg^{2+} in the dolomite crystalline structure. With Ca^{2+}/Mg^{2+} ratio
471 of 0.21 in reactant fluids and the ideal dolomite mineral with Ca^{2+}/Mg^{2+} ratio of 1.65, dolomite
472 precipitation would decrease the Ca^{2+}/Mg^{2+} ratio of the experimental solutions. The Ca^{2+}/Mg^{2+} in
473 our solutions remain unchanged within error (Supplementary Figure SF4) providing no evidence
474 for significant carbonate formation. These data are also consistent with the lack of evidence for

475 carbonates in the experimental solids in the SEM and XRD analyses. Ca-bearing phases, such as
476 dolomite and calcite, should also remove Sr (Foustoukos et al., 2008; Haggerty et al., 1992;
477 Menzies et al., 1993; Scambelluri et al., 2001), and the lack of evidence for Sr removal in our
478 experiments further argues against calcite precipitation.

479 The overall HREE enriched patters of seawater (Alibo and Nozaki, 1999; Nozaki and
480 Alibo, 2003) are attributed to the greater reactivity of LREE than HREE in marine particles,
481 which is opposite to what we observe in our experiments. This has been attributed to the stronger
482 complexation of HREE to carbonate ligands, REE-CO_3^+ and REE-$(CO_3)_2$ which leaves
483 proportionally more LREE than HREE as free 3^+ cations to hydrolyze and react with particle
484 surfaces (Johannesson et al., 2017; Luo and Byrne, 2004; Schijf et al., 2015). This further
485 implies that REE-carbonate ligands do not control the REE reactivity observed in our
486 experiments. We speculate that with higher carbonate activity in solution, more typical of
487 seawater, the stronger complexation of HREE over LREE with carbonate ligands may result in
488 increased LREE uptake, as observed in amorphous ferric hydroxide experiments with increasing
489 carbonate concentration (Quinn et al., 2006b).

490

491 **4.3.1 REE^{+3} scavenging by Fe-oxyhydroxides?**

492 REE have very high affinity for freshly precipitated hydrous ferric oxides (HFO)
493 (Koeppenkastrop and De Carlo, 1993; Quinn et al., 2004; Quinn et al., 2006a; Quinn et al., 2007;
494 Schijf and Marshall, 2011). In our experiments, olivine dissolution would result in the release of
495 Fe into the solution, which would likely form HFO under these experimental conditions (pH~7,
496 open to atmosphere) and precipitate. For example, Fe-(hydr)oxide precipitation has previously

497 reported in low-temperature olivine dissolution (Chen and Brantley, 2000) and peridotite
498 alteration experiments under slightly acidic to neutral pH conditions (pH = 5-7) (Mayhew et al.,
499 2013). However, based on the low amount of dissolved Ni, and the constant Mg concentrations
500 in the experimental solutions (see Results section), olivine dissolution would have released much
501 less than 500 ng of Fe during the course of the experiments. This is far less than the starting
502 amount of REE in solution (2.5 μg total) and we deem unlikely that this amount of Fe could
503 control REE precipitation. Furthermore, the chemical and spectroscopic analysis did not reveal
504 any Fe-bearing secondary minerals or Fe^{3+} contributions in both the XRD and Mößbauer spectra
505 in the solid reaction products (Supplementary Figures SF2, SF3).

506 We can further evaluate the role of possible HFO precipitation by comparing our results
507 with HFO-induced REE scavenging experiments (Koeppenkastrop and De Carlo, 1992;
508 Koeppenkastrop and De Carlo, 1993; Quinn et al., 2004; Quinn et al., 2006b; Quinn et al., 2007).
509 Some of our experiments approached a steady state in REE dissolved concentrations (e.g., Figs.
510 1B, E; Figs. 2A,C,D; Figs. 3B,C), and thus, we use these experimental data to calculate apparent
511 distribution coefficients as: $appD^{REE} = C^{i}_{oli} / C^{i}_{sol}$, where C^{i}_{oli}, is the amount of element *i* removed
512 from solution normalized to the mass of olivine in the experiment, and C^{i}_{sol} is the concentration
513 of REE remaining in solution (Bau, 1999) (Table 8). For experiments where more than 99% of
514 the REE were removed (AP, CF-21, HP, CF-24), $appD^{REE}$ values are less reliable, because
515 $appD^{REE}$ becomes very sensitive to the diminishing C^{REE}_{sol} (Table 8).

516 Figure 11 compares the relative fractionation of the $appD^{REE}$ as D^{Yb}/D^{Nd}, with the
517 magnitude of the $appD^{Gd}$ anomaly, here defined as $log(appD^{Gd})$/Gd*, where Gd* is the expected
518 value for $appD^{Gd}$ if it were to fall between those of $appD^{Sm}$ and $appD^{Dy}$, i.e.: $log[(appD^{Dy} +$

519 appD^{Sm})/2]. Our olivine adsorption data show greater adsorption of HREE over LREE and larger
520 negative Gd anomalies than the D^{REE} from HFO precipitation experiments. Based on the greater
521 HREE over LREE partitioning on olivine surface than HFO, the low amount of Fe released from
522 olivine dissolution and the lack of spectroscopic evidence for secondary minerals evidence, we
523 conclude that precipitation of HFO is unlikely the dominant mechanism of REE removal from
524 solution in our experiments.
525
526 **4.3.2 Insights from REE speciation in solution**
527 Additional insights can be gained by modeling the speciation of REE in solution as a
528 function of temperature and under atmospheric $CO_{2(g)}$ fugacity (Fig. 12). We compare the results
529 with the olivine experiments CF-12 and CF-19 at low GSA (57.8 cm^2/g) where the Gd anomaly
530 is more prominent (e.g. Fig. 10, Fig. 11). At 60 °C and slightly acidic pH conditions REE in
531 solution exist dominantly as 3^+ free species, however at near neutral pH conditions the REE-
532 OH^{2+} species become increasingly abundant and approximately equal to the REE^{3+}. Across the
533 same pH range but at 90 °C the dominant species are the $REEOH^{2+}$. The REE-CO_3^+ species
534 appear to be of less importance in these experimental conditions. This is also consistent with our
535 observations described above where REE-CO_3^+ complexes do not seem to control the REE
536 reactivity.
537 The decrease in the proportion of REE^{3+} to $REEOH^{2+}$ species with increasing
538 temperature coincides with the decrease in the magnitude of the D^{Gd} anomaly with temperature
539 (Fig. 11). In other words, when REE^{3+} are the dominant species in solution, their reactivity to
540 particle surfaces must be dictated by their electron structure. The apparent effect of REE electron

541 configuration is also most prominent in the coarser olivine grain experiments (lowest GSA). This
542 may suggest that under low GSA conditions the available reactive surfaces are naturally limited,
543 and REE outcompete each other for the few available adsorptive sites. At the higher GSA
544 experiments, as in HFO precipitation experiments (Koeppenkastrop and De Carlo, 1993; Quinn
545 et al., 2004; Quinn et al., 2006a; Quinn et al., 2007; Schijf and Marshall, 2011), the excess of
546 adsorptive sites that result in near complete removal of REE from solution can explain the
547 smaller Gd anomaly.

548 Tertre et al., (2008) suggested that REE adsorption on basalt is controlled by two parallel
549 processes, cation exchange at the surface along Na-saturated sites (>XNa). and surface
550 complexation (>SOH) on hydroxylated sites (Si, Al, Fe), respectively. In their experiments
551 adsorption is enhanced under neutral pH and high ionic strength conditions leading to the
552 preferential adsorption of HREE on mineral surfaces relative to LREE, qualitatively similar to
553 our observations.. Their calculated surface "sorption constants" for REE on to basalt surface
554 hydroxylated sites show greater Nd/Yb fractionation than the HFO precipitation experiments
555 equilibrium constants discussed above and better match with the observed REE systematics (e.g.
556 D^{Yb}/D^{Nd} vs. $log(appD^{Gd})$/Gd*, see Figure 11) of our experiments. Following Tertre et al., (2008),
557 we surmise that the apparent link between REE electron configuration and their adsorption
558 systematics on olivine in our experiments points to surface complexation through inner-sphere
559 type complexes of the REE^{3+} ions on hydroxylated surfaces (Stumm, 1995; Sverjensky and
560 Fukushi, 2006), and in the case of olivine likely those of silicon or iron, as Mg is more soluble
561 and would be removed in solution and Al is typically in very low abundance.
562

5.0 Summary and Implications

During reaction of olivine and seawater in the absence of strong complexing organic ligands (carbonate, sulfate) and precipitation of secondary minerals, Sr and Ba remain in solution while REE are removed from solution on to olivine with increasing kinetic rate constants as both temperature and reactive surface area increase. Based on the behavior of Nd, Sm, Dy and Yb as a function of their ionic radii, the kinetics and the apparent partitioning of Gd on to the olivine surface are lower than expected, but correlate best with the total ionization potential of the REE, which is a function of their electron configuration. As temperature increases the extent of the Gd anomaly coincides with changes in the REE speciation in solution from dominantly REE^{3+} to REE^{3+} and $REEOH^{2+}$ at 60 °C and $REEOH^{2+}$ at 90 °C. The dominance of electron configuration on the reactivity and adsorption of REE^{3+} on olivine implies that inner sphere type surface complexes dominate the adsorptive characteristics under these experimental conditions. In our experimental set up REE-carbonate speciation or Fe-oxyhydroxide precipitation have a minor, if any, effect.

During progressive reaction of seawater with peridotite, the enhanced reactivity of HREE will progressively generate LREE-enriched fluids that may ultimately impart a LREE enriched signature in serpentinized peridotites (Frisby et al., 2016b). We speculate that the variable REE systematics seen in secondary phases in serpentinites (e.g. Gillis et al., 1992; Rouméjon et al., 2015) and the highly variable REE patterns (from LREE depleted to LREE enriched) in hydrothermal vent fluids (Douville et al., 1999) may also be controlled in part by adsorption of REE on to mineral surfaces (at least at near neutral pH conditions) and subsequent incorporation of the adsorbed elements within the structures of the crystallizing secondary minerals. Seawater

585 has REE patterns that are enriched in HREE over the LREE, but they are nonetheless more
586 LREE enriched than typical depleted peridotites (Frisby et al., 2016b). We envision that
587 preferential scavenging of HREE from seawater may take place within the recharge zone at
588 relatively low temperature conditions (<100 °C). As the fluids become progressively LREE
589 enriched, they reach high temperature water/rock interaction zones deep in oceanic crust,
590 imparting seawater-like Nd isotope systematics in peridotites exhibiting high water / rock mass
591 ratio alteration (Delacour et al., 2008; Frisby et al., 2016a). Additional detailed trace element and
592 isotopic studies in serpentinized peridotites, especially a comparison between serpentine and
593 relic fresh minerals, are needed to decipher the origin of their flat LREE patterns, either as melt
594 infiltration (Deschamps et al., 2013), seawater addition (Frisby et al., 2016a; Frisby et al.,
595 2016b), or some combination therefore (Rouméjon et al., 2018) that is depended on tectonic
596 setting. Increasingly complex experiments are also needed, where the role of serpentine
597 formation on REE and other trace element uptake (partitioning) can be distinguished from that of
598 surface adsorption during growth.
599
600 **Acknowledgements:** This work was supported from NSF awards OCE-0928280, OCE-1129280,
601 EAR-1347890, OCE-1624315 to MB. DF acknowledges the NSF awards OCE-0928443, EAR-
602 1347970, OCE-1538671, EAR 1716388 and the Carnegie Institution of Washington – Canada
603 Fund. The peridotite 88SAL-1 was kindly provided by Dr. David Clague. Many thanks to Dr.
604 Raymond Torres and his research group at the University of South Carolina for performing the
605 particle size analyses which were critical in this study. Our sincere thanks to the journal

606 reviewers, Dr. Frieder Klein and Dr. Ivan Savov, for their effort and comments on this work, and
607 to the editor, Dr. Marco Scambelluri for handling this manuscript.

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910 **Figure Captions**

911 **Figure 1:**

912 Sr, Ba, REE normalized concentrations in solution, $\ln(C/C_0)$, vs. time for experiments at
913 15 °C. **A:** ALG, with GSA = 28.2 cm^2/g); **B:** CF-11, with GSA = 57.8 cm^2/g; **C:** CF-20, with
914 GSA 57.8 cm^2/g agitated; **D:** CF-22, with GSA 257cm^2/g; **E:** CF-23, with GSA 577 cm^2/g and
915 **F:** AP with GSA = 3339 cm^2/g. Y-axis scale is fixed for every pair of panels for clarity, but
916 changes in the Y-axes between the panel pairs. X-axes change between panels corresponding
917 with total experiment time. Detection limit (DL) range is indicated in panel F for these analyses.
918 In all cases Sr and Ba concentrations remain constant while REE concentrations decrease over
919 time. Towards the end of the experiments, REE concentrations level off, approaching conditions
920 of steady state. At a given time, REE concentrations are lower in experiments with greater
921 surface area (e.g. compare panels C and D, E and F). Moreover, inter-element REE fractionation
922 increases with increasing surface area.

923 **Figure 2:**

924 Sr, Ba, REE normalized concentrations in solution, $\ln(C/C_0)$ vs. time for experiments at
925 60 °C. **A:** CF-18, with GSA = 28.2 cm^2/g; **B:** CF-12, with GSA = 57.8 cm^2/g; **C:** CF-13, with
926 GSA = 176 cm^2/g; **D:** CF-21, with GSA = 3339 cm^2/g. Y-axis scale is fixed for every pair of
927 panels for clarity, but changes in the Y-axes between the panel pairs. X-axes change between
928 panels corresponding with total experiment time. Detection limit (DL) range is indicated in
929 panel D for these analyses. In all cases Sr and Ba concentrations remain constant while REE
930 concentrations decrease over time. Towards the end of the experiments, REE concentrations
931 level off, approaching conditions of apparent equilibrium. At a given time, REE concentrations

932 are lower in experiments with greater surface area (e.g. compare panels C and D). Moreover,
933 inter-element REE fractionation increases with increasing surface area.

934 **Figure 3:**

935 Sr, Ba, REE normalized concentrations in solution, $\ln(C/C_0)$ vs. time for experiments at
936 90 °C. **A:** CF-17, with GSA = 28.2 cm^2/g; **B:** CF-19, with GSA = 57.8 cm^2/g; **C:** CF-24, with
937 GSA = 924 cm^2/g; **D:** HP, with GSA = 3339 cm^2/g. Y-axis scale is fixed for every pair of panels
938 for clarity, but changes in the Y-axes between the panel pairs. X-axes change between panels
939 corresponding with total experiment time. Detection limit (DL) range is indicated in panel D for
940 these analyses. In all cases Sr and Ba concentrations remain constant while REE concentrations
941 decrease over time. Towards the end of the experiments, REE concentrations level off,
942 approaching conditions of apparent equilibrium. At a given time, REE concentrations are lower
943 in experiments with greater surface area (e.g. compare panels C and D, E and F). Moreover,
944 inter-element REE fractionation increases with increasing surface area.

945 **Figure 4:**

946 Sr, Ba, REE normalized concentrations in solution, $\ln(C/C_0)$ vs. time for experiments at
947 57.8 cm^2/g. **A:** CF-11, at 15 °C; **B:** CF-12, at 60 °C; **C:** CF-19, at 90 °C. Y-axis scale is fixed for
948 all panels, x-axis scale changes between panels reflecting total time of the experiment. Sr and Ba
949 concentrations remain constant while REE concentrations decrease in solution over time. At a
950 given time, REE concentrations are lower in experiments as temperature increases. Moreover,
951 inter-element REE fractionation increases with increasing temperature.

952 **Figure 5:**

953 $(C/C_0)^{-1}$ against time of representative experiments (**A**: CF-11, **B**: CF-12, **C**: CF-19, **D**:
954 CF-23, **E**: CF-13, **F**: CF-24) for Nd and Yb to test for second order reaction processes.
955 Experiments B, C, and F display a near linear trend while A, D, and E have a distinct concave
956 down appearance. The lack of a distinctive linear trend is indicative of these associated reactions to not
957 be purely second order in characteristic.

958 **Figure 6:**

959 $Ln(C/C_0)$ of Nd and Yb against time for representative experiments A: CF-11 (15 °C) and
960 **B**: CF-19 (90 °C) with GSA of 57.8 cm^2/g. Experimental data for each element are treated as the
961 combination of two first order reactions, an initial fast reaction (bold black line) followed by a
962 slower reaction (grey dashed line). Each segment represents an average *k*. Transition point
963 selection (Δk) is further explained in the text, represented here as a dashed arrow.

964 **Figure 7:**

965 Reaction rates for representative elements A: Nd and **B**: Yb at 15, 60 and 90 °C against
966 surface area (m^2 x 1000). Surface area is determined from GSA times the mass of olivine is each
967 experiment. The slope of the line connecting these data points effectively represents the surface
968 area normalized kinetic constants (*k*/SA). The *k*/SA is used to remove the influence of surface
969 area related reactions imposed on the experimental kinetic constant. Represented errors are
970 smaller than data points on figure.

971 **Figure 8:**

972 ln(*k*/SA) for each element plotted against 1000/T (K), to describe the Arrhenius function
973 ($\ln(k/SA)=Ln(A)-(E_a/RT)$ where E_a is the activation energy of the reaction, R is the gas constant
974 8.134 $JK^{-1}mol^{-1}$ and A is the frequency factor. Represented errors are smaller than data points on

figure. Furthermore the figure shows that reaction rate constants are faster for the HREE than LREE.

Figure 9:

The estimated activation energy (kJ/mol) plotted against **A**: Ionic radius (Å) (Sonke and Salters, 2006) and **B**: sum of the first, second and third ionization potentials (eV) for Nd, Sm, Gd, Dy and Yb. Plot A has HREE on the left and LREE on the right. Near linear correlation is displayed between E_a and ionic radius with the exception of Gd showing a positive anomaly. Plot B displays a near linear correlation for E_a and total ionization potentials for all REE where Gd has the higher E_a and second lowest total ionization potential, and Yb has the lowest E_a and highest total ionization potential.

Figure 10:

Reaction rate constants (*k)* plotted against apparent distribution coefficient (D_{REE}) for CF-11, CF-12, CF-19 with GSA 57.8 cm^2/g at 15, 60 90 °C respectively. Experiments with GSA 57.8 are shown that cover all three temperatures and allow reliable D^{REE} calculations The *k* and D_{REE} show a linear correlation for the three temperatures. Gd displays anomalous behavior falling between Nd and Sm for both the determined *k* and D_{Gd} rather than between Sm and Dy.

Figure 11:

REE fractionationas appD_{Yb}/appD_{Nd} for select experiments at 15 °C (blue circles), 60 °C (red squares), and 90 °C (green diamonds) as a function of the Gd anomaly $logD_{Gd}$/Gd*. Symbol size increases with increasing GSA. Data is compared with equilibrium distribution coefficients for REE sorbed on $Fe(OH)_3$ from Quinn et al., 2004 (Q'04) in the absence of dissolved carbonate; Quinn et al., 2006b (Q'06b) in the presence of dissolved carbonate; Quinn et al., 2007

997 in the absence of carbonate at 39.3°C and 10°C (Q'07 a, Q'07 b, respectively); Koeppenkastrop
998 and De Carlo, 1992 (K&DeC'92) for REE sorbed on vernadite and hydroxyapatite; Tertre et al.,
999 2008 (T'08) for REE sorption constants on to basalt surface as inner sphere complexes. All data
1000 is reported in Table 8.

1001 **Figure 12:**

1002 REE speciation of the experimental aqueous solutions in equilibrium with atmospheric
1003 fCO_2 at 60 and 90 °C. At the experimental pH range of 7-7.5 the REE exist predominantly as
1004 $REE(OH)^{2+}$. At higher pH conditions and with increase in temperature, the speciation of
1005 dissolved REE transitions from a) carbonate dominated (60 °C) to b) hydroxyl dominated (90
1006 °C). The distribution of Nd hydroxyl species includes the single complex $Nd(OH)_{3(aq)}$ by
1007 adopting the thermodynamic properties developed by Migdisov et al. (2016). The depicted REE
1008 chloride complexes (e.g. Nd^{3+}, Yb^{3+} Cl^-) correspond to the total concentrations of the dominant
1009 $REECl^{2+}$ and $REECl_2^+$. Species reported are those with concentrations greater than 1 μmolal.