Site-specific dehydration of olivines from San Carlos and Kilauea Iki

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# Introduction

The diffusivity of hydrogen in olivine is a fundamental physical quantity critical for understanding a wide range of earth and planetary processes. Hydrogen can affect global-scale phenomenon such as melting relations and strength, and so in turn may control mantle rheology and the occurrence of plate tectonics (Keppler and Smyth 2006; Bell and Rossman 1992). Accurate knowledge of the diffusivity of hydrogen also has great potential to serve as a chronometer to determine magma ascent times from hydrogen diffusion profiles in olivine phenocrysts (Rosen 2016).

Hydrogen, as H+, is incorporated into the olivine lattice in a variety of ways that can be distinguished by differences in the absorbances of O-H bonds as measured by Fourier transform infrared spectroscopy (FTIR) (Berry et al. 2005; Ingrin et al. 2013). Broadly, H+ incorporation mechanisms fall into two categories: relatively high wavenumber peaks produced associated with silicon vacancies and relatively low wavenumber peaks associated with magnesium vacancies. A doublet of peaks at 3525 and 3573 cm-1 has been linked to the presence of 2 H+ ions, a Si4+ vacancy, and Ti4+ on the metal site (Berry et al. 2007). This mechanism, labeled [Ti], has been suggested to control mantle rheology (Faul et al. 2016). Multiple other high wavenumber peaks (3450-3620 cm-1) represent 4 H+ ions charge-balanced by a Si4+ vacancy and are labeled [Si]. Some lower wavenumber peaks (3300-3400 cm-1) appear when a Mg2+ vacancy is charge-balanced by a H+ and a trivalent cation on a Mg2+ site (Blanchard et al. 2017), and these are labeled [tri]. Low wavenumber peaks between 3200 and 3250 cm-1 have been associated with 2 H+ charge-balancing a Mg2+ vacancy, and these are labeled [Mg]. The different mechanisms are important because the rate at which H+ moves through the lattice may depend at least in part on its incorporation mechanism (Padrón-Navarta, Hermann, and O’Neill 2014). All of these mechanisms for hydrogen incorporation are thermodynamically closely related to water, and therefore this incorporated hydrogen is sometimes referred to as “water”.

Previous work on the diffusivity of H+ in olivine has produced a 6-order-of-magnitude range of measurements, from 10-9.7 m2/s during the first hour of hydrating San Carlos olivine at 1000°C (Mackwell and Kohlstedt 1990) to 10-15.7 m2/s for [Si] loss from synthetic forsterite at the same temperature (Padrón-Navarta, Hermann, and O’Neill 2014), and the calculated activation energies suggest even larger discrepancies at lower temperatures. This range has led to considerable disagreement about the correct diffusivity and approach to apply to a given application. The observation of differences in H+ loss profiles for different FTIR peaks (Tollan et al. 2015) is particularly important because if FTIR peaks must be resolved and analyzed individually, then H+ data from secondary ion mass spectrometry (SIMS), a common and powerful technique, becomes significantly more difficult to interpret because SIMS measures only total, or bulk, hydrogen.

Bulk hydrogen diffusion in natural olivine is often thought to occur by one of two mechanisms: a rapid “proton-polaron” or “pp” mechanism that involves electron movement parallel to [100], and a relatively slow “proton-vacancy” or “pv” mechanism that relies on metal vacancy diffusion parallel to [001] (Kohlstedt and Mackwell 1998; Demouchy and Bolfan-Casanova 2016; Thoraval and Demouchy 2014; Demouchy and Mackwell 2006). Yet even within this “pp” versus “pv” framework, significant disagreement exists. For example, in studies of olivine phenocrysts, Le Voyer et al. (2014); Lloyd et al. (2013); and Hauri (2002) conclude that the most rapid H+ diffusion mechanism, the “proton-polaron” or “pp” mechanism (Kohlstedt and Mackwell 1998), is likely operational, whereas Mironov et al. (2015); Portnyagin et al. (2008); Chen et al. (2011); and Gaetani et al. (2012) suggest that relatively slow “proton-vacancy” or “pv” diffusion is dominant. The major goal of this work is to better understand which diffusivity to use for a given application of H diffusion in natural olivine, with particular emphasis on phenocrysts and their potential to serve as clocks for quantifying magma ascent times.

# Experimental methods

We provide, for the first time, time-series data showing water loss from the same single crystal of Fe-bearing olivine. We do this for two olivines: partially hydrated xenolithic olivine from San Carlos and phenocrysts from Kilauea Iki.

## Sample selection and preparation

Olivines from San Carlos, AZ and Kilauea Iki were chemically characterized and used for H diffusion experiments. The San Carlos olivine similar to that used in previous hydration experiments (Mackwell and Kohlstedt 1990; Kohlstedt and Mackwell 1998) was provided by David Kohlstedt. Here we extend that work by examining site-specific dehydration behavior. The Kilauea Iki olivines were collected from scoria from the 1959 Episode 1 eruption of Kilauea Iki and have been described in detail by David Ferguson (Ferguson et al. 2016), who provided the samples. The Kilauea Iki samples are of great interest because they provide the first direct experimental measurements of H diffusion in all 3 crystallographic directions of inclusion-free olivine phenocrysts.

A large crack and inclusion-free piece of San Carlos olivine, SC1 (IGSN: IEFERSCO1), was oriented by Laue camera at Cornell University and then cut into a series of smaller pieces approximately 2-3 mm long on each side using a diamond saw. One of the resulting sub-pieces, SC1-1 (IGSN: IEFERJAI3), was polished with 0.25 μm diamond paste and used to estimate the initial water concentration by FTIR. Additional pieces of SC1 were used to test the hydration procedure, and pieces SC1-7 (IGSN: IEFERJAI9) and SC1-2 (IGSN: IEFERJAI4) were partially hydrated and then polished with 0.25 μm diamond paste for FTIR. SC1-2 was then sequentially dehydrated with FTIR profiles measured after each dehydration step and afterwards analyzed by EMPA and SIMS.

A large, relatively clear piece of the Kilauea Iki olivine, Kiki (IGSN: IEFERJAIC), was oriented based on morphology and polished into a block shape of dimensions 2 × 1 × 1.3 mm. The orientations were then confirmed by electron backscatter diffraction (EBSD) at the American Museum on Natural History (AMNH). The untreated Kiki sample was characterized by EMPA, SIMS, and polarized FTIR prior to dehydration. The sample was initially zoned in hydrogen, and the low hydrogen rims were polished off to create a homogeneous initial block.

Sample thicknesses in all three directions were measured with a digital micrometer accurate to within ± 5 μm. Additional details for all samples, including images and sample dimensions, are available online at geosamples.org.

## Electron microprobe analysis

Major elements of SC1-2 and Kiki were analyzed by electron microprobe at AMNH along traverses parallel to those on which water measurements were made to confirm homogeneity of the samples. The beam current was 20 nA, and the accelerating voltage was 15 kV.

## Initial water concentrations

The initial water concentration in each olivine was estimated using both polarized FTIR and SIMS. Polarized FTIR measurements were performed at AMNH using the Thermo Nicolet Nexus 670 infrared spectrometer and Thermo Nicolet Continuum 15× infrared microscope with a resolution of 4 cm-1, spot sizes of 100 × 100 μm, an average of 200 scans, and a ZnSe polarizer. Initial water concentrations were estimated from 3 orthogonal polarized measurements (Libowitzky and Rossman 1996; Shuai and Yang 2017) by applying the Bell and Withers calibrations (Bell et al. 2003; Withers et al. 2012). To account for the large error associated with baseline choice, 3 different baselines were drawn, and the resulting areas were averaged. Traverses along all three directions did not show significant zonation in bulk or peak-specific water in the untreated samples.

Erik Hauri measured the C, H, F, P, and Cl concentrations by nanoSIMS along traverses parallel to [001] in SC1-2 and parallel to [010] in Kiki as part of the CIDER workshop on electrical conductivity in hydrous olivine. SIMS measurements were made before Kiki was dehydrated but after the final dehydration heating step for SC1-2. The area under the O-H stretching peaks with the electric vector E || [100] is equal to that of both the untreated SC1-1 (7±5 cm-2) and of the partially hydrated and then dehydrated SC1-2 (7±6 cm-2). Therefore, the SIMS measurements of the hydrated and then dehydrated SC1-2 were taken as a reasonable estimate of the initial water concentration in SC1.

## Hydration of San Carlos olivine

Two pieces of previously oriented San Carlos olivine SC1, SC1-2 and SC1-7, were partially hydrated in a ¾” Boyd-type piston cylinder apparatus with a BaCO3 pressure medium using a procedure broadly similar to that of Jollands et al. (2016). Here the samples were placed in copper capsules and surrounded by liquid distilled H2O and a powdered mixture of Ni and NiO to control oxygen fugacity and San Carlos olivine and enstatite to control silica activity (Figure 1). Temperatures were controlled with aD-type (W3%Re-W25%Re) with control precision of ±2°C and probable accuracy of ±20°C. After rapid quenching followed by relatively slow decompression, the capsules were pierced with a drill to confirm water was still present and then dissolved overnight in a mixture of 1:1 H2O to HNO3. The rectangular parallelepiped samples were then mounted in CrystalBond, polished with 0.25 μm diamond paste on all sides, and cleaned in acetone.

SC1-2 was hydrated at a nominal temperature of 800 °C and 10 kbar pressure, which corresponds to a water fugacity of 1.6 GPa (Withers 2013), for 17.5 hours. That time was chosen in order to reach, but not pass, what Kohlstedt and Mackwell (1998) call “metastable equilibrium”, the point at which all of the initial Fe3+ is reduced as H+ diffuses into the sample following the proton-polaron mechanism. If the model used by Kohlstedt and Mackwell (1998) is correct, the hydrogen concentration in SC1-2 after the piston cylinder experiment should be homogeneous, and the concentration should be lower than the true solubility and presumably determined by the initial concentration of ferric iron. If the “metastable equilibrium” hydrogen concentration is both large enough to easily measure and homogeneous, then SC1-2 is a suitable starting material for step-wise dehydration experiments.

SC1-7 was heated for 7 hours at 10 kbar and temperature readings of 1000°C, but the experiment ended when capsule began to melt, suggesting the true temperature in the capsule was closer to 1085°C, the melting point of copper or, more likely, the Cu was contaminated, perhaps with a small amount of oxygen, resulting in freezing point depression. This temperature range and pressure correspond to water fugacities of 1.9-2.0 GPa (Withers 2013). Within this temperature range, given the dimensions of the sample and the diffusivities reported by Kohlstedt and Mackwell (1998), the experiment time of 7 hours should allow the completion of proton-polaron diffusion and enter into the stage of diffusion dominated by the slower proton-vacancy mechanism without fully saturating the sample. This experiment allows a direct comparison with previous work (Kohlstedt and Mackwell 1998; Demouchy and Mackwell 2006).

## Dehydration

Olivine samples SC1-2 (the same sample that was partially hydrated according to the procedure described above) and Kiki (untreated) were dehydrated in increments using the vertical furnace used in previous dehydration experiments (Ferriss 2015), and oxygen fugacity was controlled with a mixture of CO and CO2. The partially hydrated sample SC1-2 was heated at 800 °C for 1, 3, 7, 13, 19, 43, and 68 hours at an oxygen fugacity 10-16.5 bars, equivalent to NNO-2.6, where NNO is the nickel-nickel oxide buffer. Kiki was heated at 800°C for 1 and 8 hours; then 3, 6, 7, and 8 hours at 1000°C. All heating steps for Kiki were conducted at oxygen fugacity of NNO-2.6 except for the final step at 1000°C, which was conducted at relatively oxidizing conditions, NNO+2.

## FTIR and diffusion modeling

Before heat treatment and in between each heating step, samples were analyzed by polarized FTIR along 3 orthogonal traverses parallel to the three crystallographic directions in the uncut crystal. These analyses use the same conditions described above for estimating the initial water and were in all cases conducted with polarized radiation with the electric vector E || [100]. Quadratic baselines were drawn based on the curve of the spectrum of the untreated and/or the dehydrated sample, with typical wavenumber ranges of 3200-3700 cm-1, and the resulting areas were scaled up to approximate hydrogen concentrations by comparison with the corresponding area measured in the same way in the untreated sample, for which hydrogen concentrations are known.

Each profile was normalized to the initial measurements to produce a ratio of the final to initial area A/A0 and scaled up to a true concentration based on the initial concentrations, A0, determined above. These “whole-block” concentrations represent the average concentration through the entire path of the infrared beam, and the forward models used to determine hydrogen diffusivities in each direction are modified accordingly following the models described in E. Ferriss et al. (2015) and Elizabeth Ferriss, Plank, and Walker (2016) and implemented using the free, open-source software package pynams (Ferriss 2015).

To explore possible differences among various hydrogen incorporation mechanisms, the same normalization and fitting procedures were applied to individual peaks using the peak heights relative to the quadratic baseline. Particular emphasis was placed on peaks at the following 4 wavenumbers: 3600, 3525, 3356, and 3236 cm-1. The peak at 3600 cm-1, designated [Si-Fe2+], is most likely 4H+ in a Si4+ vacancy with a nearby Fe2+ (Blanchard et al. 2017). The peak at 3525 cm-1, designated [Ti-3525], is one of two prominent peaks produced by 2H+ coupled with a Si4+ vacancy and a Ti4+ on a metal site. We focus on this peak both to minimize interferences with nearby [Si] peaks and to more directly compare with the results of Padrón-Navarta, Hermann, and O’Neill (2014). The 3356 cm-1 peak, designated [tri-Fe3+-3356], is the most prominent peak in a doublet associated with a Mg2+ vacancy charge-balanced by H+ and Fe3+ substituting on a metal site (Blanchard et al. 2017), and the 3236 cm-1, designated [Mg], is likely 2H+ charge-balanced by a Mg2+ vacancy (Berry et al. 2005).

All of the raw FTIR spectra and computer code used to produce all calculations and figures reported in this paper will be made available on GitHub.

# Results

## Characterization of the starting material

Microprobe analysis did not reveal any significant zonation along the measured profiles and were generally consistent with previous work (Ruprecht and Plank 2013; Ferguson et al. 2016) with somewhat lower forsterite numbers: 87.7±0.2 in SC1-2 and 86.2±0.2 in Kiki. The San Carlos olivine used in previous H diffusion experiments had a reported approximate composition with forsterite number 91 (Mackwell and Kohlstedt 1990). This large difference in forsterite content suggests that the San Carlos olivine that we are using came from a different xenolith than the samples used in previous work. The initial water concentration was estimated from the polarized FTIR measurements and baselines shown in Figure 2 using both the Bell calibration and the Withers calibration and also by nanoSIMS (Table 1). These three estimates were averaged to produce initial water concentration estimates of 15±2 ppm H2O in the Kilauea Iki olivine and 4±1 ppm H2O in the San Carlos olivine. These low concentrations are consistent with previous work on San Carlos olivine (Peslier and Luhr 2006; Kurosawa, Yurimoto, and Sueno 1997)**.** The hydrogen concentration in the Kilauea Iki sample, for which the low rims had been polished off to prepare the sample as a rectangular parallelepiped, was homogeneous by both SIMS and FTIR.

Several different O-H peaks were observed in the initial materials. The prominent peaks at wavenumbers 3525 and 3573 cm-1 oriented primarily || [100] in both Kilauea Iki and San Carlos olivine correspond to the [Ti] incorporation mechanism, and the high-wavenumber peaks that primarily appear as shoulders on the [Ti] peaks correspond to [Si] (Berry et al. 2005). A very small peak at 3600 cm-1 present in both samples has been ascribed to [Si] with nearby Fe2+ (Blanchard et al. 2017). Because of the association with Fe2+, we label this peak [Si-Fe2+]. The Kilauea Iki olivine, but not the untreated San Carlos olivine, contains prominent [tri] peaks. These peaks at 3356 and 3329 cm-1 correspond exactly to the peak locations that Blanchard et al. (2017) associate with Fe3+, and which we therefore designate [tri-Fe3+]. No [Mg] peaks were present initially.

Table 1. Water concentration estimates for Kilauea Iki olivine and San Carlos olivine based on polarized FTIR areas (Figure 2) and SIMS measurements.

|  |  |  |  |
| --- | --- | --- | --- |
|  | Kilauea Iki olivine; Kiki | San Carlos olivine; sub-samples of SC1 | |
| FTIR area E || [100] (cm-2) | 52+/-10 | 7+/-5  55+/-17  24+/-8  7+/-6 | untreated SC1-1  partially hydrated SC1-7  partially hydrated SC1-2  dehydrated SC1-2 |
| FTIR area E || [010] (cm-2) | 31+/-13 | 8+/-5 | untreated SC1-1 |
| FTIR area E || [001] (cm-2) | 18+/-9 | 9+/-4 | untreated SC1-1 |
| FTIR area summed over 3 directions (cm-2) | 101+/-19 | 24+/-8 | untreated SC1-1 |
| Water, Bell calibration (ppm H2O) | 19+/-4 | 4.5+/-1.5 | untreated SC1-1 |
| Water, Withers calibration (ppm H2O) | 12+/-2 | 3+/-1 | untreated SC1-1 |
| Water, SIMS (ppm H2O) | 14+/-1 | 5+/1 | dehydrated SC1-2 |
| Average initial water (ppm H2O) | 15+/-2 | 4+/-1 | SC1 |
| Ratio of water in ppm H2O to area in cm-2 with E || [100] | 0.3 | 0.6 | SC1-1 |
| Average water (ppm H2O) after piston cylinder experiment | Not treated with pressure | 32+/-23  14+/-10 | partially hydrated SC1-7  partially hydrated SC1-2 |

## Hydration

Changes in FTIR absorbance indicate that hydrogen was successfully incorporated into San Carlos olivine samples SC1-7 and SC1-2 (Figure 3A). To construct hydrogen profiles, quadratic baselines were drawn to match both the curve of the spectrum of the untreated sample and the middle baselines used to determine the initial water concentration in Figure 2. Typical baselines are illustrated in Figure 3B and C, and all spectra and baselines are shown in the supplement. The area under each curve was determined and scaled to an estimated H concentration by multiplying by 0.6, following the ratio of concentration to area with E || [100] reported for San Carlos olivine in Table 1.

The partially hydrated sample SC1-2 was sufficiently homogeneous for both bulk H and individual peaks to serve as a reasonable starting material for subsequent dehydration experiments (Figure 4). If we ignore the uncertainties associated with baseline choice and use only the quadratic baseline shown in Figure 3C, the water concentration across hydrated SC1-2 is 15±1 ppm H2O. Although there is a small increase in area around the [tri] peaks, the large majority of the hydrogen in the hydrated SC1-2 is incorporated as [Ti] and [Si], and these profiles are also homogeneous.

In contrast, hydrogen zonation in SC1-7 is clearly observed, with water concentrations of 38±7 ppm H2O using the quadratic baseline shown in Figure 3B. The variations in concentration are most apparent || [001] (Figure 4), consistent with previously work showing [001] is the fast direction during proton-vacancy mechanism diffusion (Kohlstedt and Mackwell 1998; Demouchy and Mackwell 2006).

Quantifying the diffusivities in SC1-7 requires major assumptions about both the solubility and metastable equilibrium concentrations. Here we assume a metastable equilibrium concentration of 15±1 ppm H2O, the observed concentration in SC1-2 after hydrating to saturate the pp mechanism. This value is much higher than the 0.4 ppm H2O (7 H/106Si) reported by Kohlstedt and Mackwell (1998), possibly because of differences in the forsterite content and/or the calibrations used to determine H concentrations from FTIR spectra in the two studies. The accepted values for the pv mechanism (Table 2) fit our data reasonably well if we assume a final solubility of 150 ppm H2O, which is possible, particularly given the still large uncertainties in the solubility of H in olivine (Tollan et al. 2017:20; Zhao, Ginsberg, and Kohstedt 2004; Mosenfelder et al. 2006). Figure 4 shows a fit to our whole-block SC1-7 data that assumes a final concentration equal to the maximum observed concentration of 58 ppm H2O. This fit requires higher diffusivities than are generally associated with the pv mechanism, particularly || [010]. Diffusivities higher along [010] than [100] are unexpected but not entirely without precedent (e.g., Demouchy et al. 2016; Demouchy and Mackwell 2003) and not well constrained by three interior points.  All calculated diffusivities for both hydration and dehydration are provided in a supplementary table.

## Dehydration

SC1-2 and Kiki, two homogeneous blocks of olivine with similar initial starting hydrogen concentrations but very different histories, compositions, and distributions of hydrogen, were sequentially dehydrated in a gas-mixing furnace (Figures 5, 6, and 7). All profiles were normalized to a relatively homogeneous starting profile, and path-integrated 3-dimensional diffusion modeling was performed to estimate the rate of hydrogen movement after each heating step (Figures 8 and 9).

Much of the resulting data show H+ loss rates that are *intermediate* between “pp” and “pv” mechanism diffusivities. These diffusivities could be fit reasonably well using the following constraint: all H+ loss profiles are assumed to represent a linear mixture of pp and pv end-members. These end-member diffusivities are calculated using the standard equation D = D0exp(-Ea/RT), where D is the diffusivity, D0 is the pre-exponential factor, Ea is the activation energy, R is the gas constant, and T is the temperature. For the pp mechanism diffusivity, Dpp, the D0 and Ea were calculated from data in Kohlstedt and Mackwell (1998) and Demouchy and Mackwell (2006), and for the pv mechanism diffusivity, Dpv, we use the values reported by Demouchy and Mackwell (2006) (Table 2). The diffusivity in any given direction was then allowed to vary with the percentage of pp, %pp, following Eq 1. In this way, a single number, %pp, was fit for each set of data. The %pv, equal to 100-%pp, could also be used.

|  |  |
| --- | --- |
| D = (Dpp \* %pp/100) + (Dpv \* (1 - %pp/100)) | (Eq. 1 ) |

Table 2. Activation energies (Ea) and pre-exponential factors (D0) for two mechanisms of bulk H diffusion derived from a combination of data from Kohlstedt & Mackwell 1998 and Demouchy & Mackwell 2006 (the “pp” mechanism) and data from Kohlstedt & Mackwell 1998, Demouchy & Mackwell 2003, and Demouchy & Mackwell 2006 (the “pv” mechanism”).

|  |  |  |  |  |  |  |
| --- | --- | --- | --- | --- | --- | --- |
| mechanism | Ea || [100] | Ea || [010] | Ea || [001] | D0 || [100] | D0 || [010] | D0 || [001] |
| “pp” | 143 | 180 | 109 | 1.2E-4 | 1.6E-4 | 1.2E-7 |
| “pv” | 204 | 204 | 258 | 3.2E-5 | 3.2E-5 | 4.0E-2 |

### Dehydration of San Carlos olivine

We determined hydrogen loss curves and diffusivities for bulk H, [Si-Fe2+] at 3600 cm-1, and [Ti-3525] in San Carlos SC1-2 (Figure 6, Figure 9). Most spectra and quadratic baselines are similar to those shown in Figure 5 and described during the initial characterization of the materials. The other [Ti] peak and [Si] peaks profiles in SC1-2 are not shown but are similar to [Ti-3525]. All spectra, baselines, profiles, best-fit models, and diffusivities are provided in the Supplements.

The [Si-Fe2+] peak (Figure 6 G-I) is clearly slower than the rest of the peaks and was essentially immobile for the first 5 heating steps. After 43 hours, when the large majority of the initial H had left the crystal and the bulk of the remaining H was present in the [Si-Fe2+ peak], clear H-loss profiles could be observed, with apparent diffusivities that were relatively fast compared to the initial stages and with a fast direction || [100]. These [Si-Fe2+] loss profiles also differ from the majority of profiles observed in this study in that they did not appear to be going to zero near the edges, but rather to about 40% of the initial, which was the final concentration used when modeling the diffusivities. At 19 hours these [Si] profiles could be modeled as only 2%pp, before increasing to 8%pp at 43 hours and finally 12%pp at 68 hours.

While the [Si-Fe2+] peak sped up, the [Ti-3525] peak slowed down. To observe this decrease in hydrogen loss rate, compare the close correspondence of the [Ti-3525] data with the expected “pp” curves after 7 hours with the large difference between the data and the “pp” curves after 19 hours (Figure 6D-F). The [Si-Fe2+] and [Ti-3525] mechanisms eventually come close to converging, but the [Ti-3525] peak is always faster (Figure 9), moving from 100%pp initially to only 25%pp at 68 hours.

The bulk H curves, which consist of a combination of peaks, are typically less symmetric. During initial dehydration stages, when the [Si-Fe2+] peak at 3600 cm-1 is a relatively minor component, bulk H could be modeled reasonably well with 100%pp before slowing at 68 hours to 20%pp, intermediate between the final [Ti-3525] and [Si-Fe2+] mechanism diffusivites. The final bulk H concentration was modeled as 15% of the initial homogeneous partially hydrated concentration because the [Si-Fe2+] peak does not go to zero, and therefore the bulk H also cannot go to zero. An additional complication in interpreting the bulk H curves is the occasional appearance of spectra with relatively large [tri-Fe3+] peaks and distorted baselines (see Supplementary PDF, e.g., 100 μm from the edge of [100] after 43 hours of heat treatment). This [tri-Fe3+] appeared intermittently near all edges of SC1-2 frequently enough that it is unlikely to be contamination but too infreqently to model with confidence.

### Dehydration of Kilauea Iki olivine

Experimentation on the Kilauea Iki sample took place in two stages. First, the sample was treated exactly the same way as SC1-2 during dehydration: heated at 800°C in a gas-mixing furnace at NNO-2.6. Second, the sample was sequentially heated at 1000°C, initially at NNO-2.6 and then at NNO+1.9. Heating the Kilauea Iki sample at 800°C for 8 hours did not produce any clear loss in bulk H or [Ti-3525] (profiles included in Supplemental PDF), in contrast to the partially hydrated SC1-2 treated the same way (Figure 6). This minimal movement was modeled as having maximum diffusivities of only 2%pp.

Although bulk H and [Ti] did not move, heating the Kilauea Iki olivine at 800°C did result in significant re-organization of the H from [tri-Fe3+] to [Si]. The rate of the decrease in [tri-Fe3+] could be modeled to obtain effective reorganization rates. These rates were similar to the estimates for [tri] movement into SC1-7 in that there was typically not a consistent fast direction, and the data could not be fit using the %pp model described above that works well for the [Si] and [Ti] peaks. The Kilauea Iki 800°C [tri] loss on reorganization rates started out relatively fast at 1 hour (10-11.5 m2/s || a; 10-10.6 m2/s || b; 10-11 m2/s || c) before dropping roughly an order of magnitude in all directions after 8 hours to diffusivities that were broadly consistent with the 1000°C results for [tri] in both SC1-7 hydration and in subseqent dehydration steps of the Kilauea Iki olivine. This drop in the [tri] movement rate and the relative flatness of all of the profiles suggests that the large majority of the internal hydrogen reorganization had been completed. These 8 hours profiles from heating at 800°C were used as the ‘initial’ profiles for data collected during a second stage of heating at a higher temperature.

The heating temperature was raised to 1000°C because the maximum 2%pp bulk H diffusivities observed at 800°C were unlikely to produce clear H loss profiles within the relatively short laboratory time scales. The oxygen fugacity was maintained along the same buffer curve, NNO-2.6, for 3 heating steps totaling 3, 6, and 7 hours, and in each of these steps, the bulk H loss could be effectively modeled at 8%pp, the [Si-Fe2+] at 12%pp, and the [Ti] at 7-9%pp. The increase in diffusivity from less than 2%pp at 800°C to 92%pp at 1000°C suggests a higher activation energy for H movement in the Kilauea Iki olivine than in San Carlos. The [Si-Fe2+] loss profiles in Kilauea Iki (Figure 7 J-L), unlike in San Carlos (Figure 6 G-I), appears to go to zero and is moving somewhat faster than [Ti-3525]. The [tri] loss at 1000°C was similar to that observed at 800°C in that it could not be modeled within the %pp framework and did not have an obvious fast direction.

A final heating step of 1 additional hour was perfored for a total of 8 hours heating at 1000°C. This final step was performed under more oxidizing conditions, NNO+1.9. The resulting loss of hydrogen for all mechanisms was consistent with the diffusivities determined under more reducing conditions, which suggests that the role of oxygen fugacity has little effect on the diffusivities, at least for this very late stage of dehydration.

# Figures

Figure 1. Schematic cross-sections illustrating the experimental design for hydrating San Carlos olivine samples SC1-2 and SC1-7 in a piston cylinder apparatus showing the BaCO3 pressure medium, graphite furnace and pyrophyllite sleeve surrounding an unwelded copper capsule containing the sample, liquid water, and a powdered mixture of nickel, nickel oxide, San Carlos olivine, and San Carlos enstatite. The sleeve and capsule are supported by MgO, and D-type W-Re thermocouples (colored lines) extend through cylindrical holes in the MgO.

Figure 2. Polarized FTIR spectra (thick blue) and baselines (black) used to estimate the water concentrations of Kilauea Iki olivine (Kiki) and San Carlos olivine (SC1-1 and SC1-2) reported in Table 1.

Figure 3. (A) Polarized FTIR spectra with electric vector E || [100] averaged across all traverses in three directions of San Carlos olivine SC1 pieces that were untreated (SC1-1, blue); hydrated in a piston cylinder for exactly the amount of time needed to reach “metastable equilibrium” by the proton-polaron mechanism (SC1-2, green) at 800°C; and hydrated long enough to enter into proton-vacancy-dominated diffusion without saturating the sample (SC1-7, orange) with major peaks labeled. The shapes of the quadratic baselines used to calculate the areas under each curve for spectra measured are shown for SC1-7 (B) and SC1-2 (C). Note the differences in the y-axis scale.

Figure 4. Concentration profiles across San Carlos olivine samples SC1-2 and SC1-7 after partial hydration in a piston cylinder as measured through the uncut block. R is the ray path of the infrared beam, and the electric vector E of the polarized beam is in all cases || [100]. Hydrogen concentrations are estimated from polarized FTIR spectra using the areas under the baselines shown in Figure Figure and initial hydrogen contents from Table Table. Black numbers and curves show the expected diffusion curves based on the diffusivities (D) for the proton-vacancy (“pv”) mechanism diffusion at 1000°C, an initial “metastable equilibrium” concentration equal to the mean concentration or peak height in the hydrated SC1-2 (dotted green lines, where all diffusion possible by the proton-polaron, or p.p., mechanism has been completed) and final concentration of 58 ppm H2O. Thin orange lines show curves for the reported diffusivities, assuming the same initial and final concentration as the pv lines. The large difference between the black and orange curves in panel A despite their having the same diffusivity is a result of path integration effects along the ray path, [010], which has significantly different diffusivities for the two models. See Ferriss et al. 2015 for a more complete discussion of this “whole-block” effect.

Figure 5. Averaged polarized FTIR spectra with electric vector E || [100] of Kilauea Iki olivine (offset for clarity) and partially hydrated San Carlos olivine SC1-2 before and after heating in a gas-mixing furnace.

Figure 6. Path-integrated profiles of (A-C) bulk H, (D-F) the [Ti] peak at 3525 cm-1, and (G-I) the [Si] peak at 3600 cm-1 during step-wise dehydration of an uncut block of partially hydrated San Carlos olivine SC1-2 at 1 atm, 800°C, and NNO-2.6. R is the ray path of the infrared beam. All data are normalized to a best-fit line through the hydrated profile data to account for small amounts of initial zonation. Black lines show expected hydrogen loss curves for the proton-polaron mechanism (diffusivities labeled in A-C). This “pp” mechanism is somewhat too fast to describe the bulk H data and much too fast to describe the [Si] peak data. The [Ti] data is very well described by the pp mechanism after 7 hours of heating, but [Ti] movement slows down by 19 hours. Baselines and best-fit diffusivities and curves are provided in the Supplements.

Figure 7. Path-integrated profiles of (A-C) bulk H, (D-F) the [tri-Fe3+] peak at 3356 cm-1, (G-I) the [Ti] peak at 3525 cm-1, (J-L) the [Si] peak at 3600 cm-1 during step-wise dehydration of an uncut block of Kilauea Iki olivine at 1 atm and 1000°C. R is the ray path of the infrared beam. All profiles are normalized to profile data measured after heating for 8 hours at 1 atm, 800°C, and NNO-2.6, which produced significant re-organization of the hydrogen across different sites (see Supplement). Heat treatment was conducted at QFM – 2 for all steps except the final step at 8 hours, which was more oxidizing at NNO+1.9. Black lines show expected hydrogen loss curves for the proton-polaron mechanism “pp” and proton-vacancy mechanism “pv” at two different times. All of the data show hydrogen loss rates slower than the “pp” mechanism and faster than the “pv” rate. Baselines and best-fit diffusivities and curves are provided in the Supplements.

Figure 8. Arrhenius diagram for selected H diffusivity measurements in olivine parallel to [100] and [001], designated a and c, for bulk H and four different H incorporation mechanisms, labeled in brackets, described in the text. Data for the proton-polaron (“pp” solid lines) and proton-vacancy (“pv” dashed lines) mechanisms are provided in Table 2. The dotted lines show unoriented measurements for three different peak-specific mechanisms in unoriented synthetic forsterite (Padrón-Navarta et al. 2014). The temperature ranges for all lines are restricted to the range of actual measurements. The hydration measurements at 1000°C for San Carlos olivine SC1-7 (orange) are reasonably consistent with expected pv mechanism || [100] but faster than expected || [001]. Dehydration of an olivine from Kilauea Iki (purple) was extremely slow at 800°C for all mechanisms except [tri], which slowed down significantly from 1 hour to 8 hours of heating. At 1000°C, the Kilauea Iki olivine diffusivities for all mechanisms was constant with time, except for [tri] which again slowed down with heating time, and intermediate between pp and pv diffusivities. The dehydration of the partially hydrated San Carlos olivine sample SC1-2 (green), shown in more detail in Figure 9, also changes with time but is generally intermediate between the expected pp and pv mechanism diffusivities. A more detailed and interactive Arrhenius diagram is available online at [https://arrheniusdiagram.herokuapp.com](https://arrheniusdiagram.herokuapp.com/).

Figure 9. Changes in hydrogen diffusivities with heating time at 800°C and oxygen fugacity of 10-16.5 bars (NNO-2.6) in three crystallographic directions for partially hydrated San Carlos olivine sample SC1-2 compared with expected diffusivities for the proton-polaron mechanism (“pp”, Table 2). The anisotropy of the observed diffusivities and pp is similar, with movement || [100] > [001] > [010], but the exact values are not consistent over time. At early heating stages, the bulk H, which is dominated by the mechanism [Ti], is consistent with expected pp values, but over time those diffusivities decrease. In contrast, the [Si] mechanism is initially too slow to be measured confidently, but after 19 hours enough movement could be observed to fit diffusivities. Those diffusivities increased with time, but were consistently lower than the diffusivities observed for [Ti] and bulk H.

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