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

Ferriss, Plank, Newcombe, Walker

# 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.

## Section on Megan’s methods

# 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] for bulk H and all major peaks (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 (Figure 5). The choice of baseline is well known as a major source of error in FTIR analyses, and associated errors in the resulting peak heights and areas may be as high as 30%, consistent across profiles. All profiles were normalized to a relatively homogeneous starting profile. The data in these profiles represent a ratio of two areas, with resulting propagated errors for each data point up to ~40%, again consistent across the profile. This error is omitted for clarity in all profile figures. Path-integrated 3-dimensional diffusion modeling was then performed on each profile to estimate the rate of hydrogen movement after each heating step (Figures 6 through 10 and Supplement). These efforts are described in more detail for each sample in the sections below. Due to the large uncertainty in the individual data points (40%) and frequent failure of least-squares fitting efforts to converge, we estimate the true error on each estimate of the rate of H movement at plus or minus one order of magnitude. While this error is very large, it is consistent, i.e., too large or too small for all estimates. Thus, comparisons, e.g., an observation of H moving more slowly out of one incorporation mechanism than another, is meaningful.

Much of the resulting data show H+ loss rates that are *intermediate* between “pp” and “pv” mechanism diffusivities. Most of these rates could be fit reasonably well using the following constraint: all H+ loss profiles are assumed to represent a linear mixture of pp and pv mechanism 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. This approach yielded satisfying fits for data for bulk H, [Ti], and [Si] mechanisms, but not the [tri] peaks in the Kilauea Iki olivine, which was highly irregular and near isotropic.

|  |  |
| --- | --- |
| 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. All spectra, baselines, profile data and best-fit curves are provided in the supplement. Selected profile data are shown in comparison with expected proton-polaron mechanism profiles in Figure 6, and all estimated diffusivities are shown as a function of heating time in Figure 7.

The [Si-Fe2+] peak 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 in the profile data, compare the close correspondence of the [Ti-3525] data with the expected “pp” curves at 7 hours with the large difference between the data and the “pp” curves at 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 7), moving from 100%pp initially to only 25%pp at 68 hours.

Profiles for the other [Ti] peak and additional [Si] peaks in SC1-2 are not shown but behave similarly to [Ti-3525].

The bulk H curves, which consist of a combination of peaks, are typically less symmetric than the [Si] and [Ti] profiles. During initial dehydration stages, when the [Si-Fe2+] peak at 3600 cm-1 was a relatively minor component, the bulk H could be modeled reasonably well with 100%pp before slowing to only 20%pp at 68 hours, intermediate between the final [Ti-3525] and [Si-Fe2+] mechanism diffusivities. The final bulk H concentration was modeled using 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 infrequently to model with confidence.

### Experimental 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 Kilauea Iki 800°C [tri] loss on reorganization rates started out relatively fast, around 10-11.0 m2/s || c at 1 hour before dropping to 10-12.5 m2/s at 8 hours. This drop in the [tri] movement rate suggests that the large majority of the internal hydrogen reorganization had been completed. The relative flatness of all of the profiles suggests that the movement was occurring everywhere throughout the crystal simultaneously, consistent with reorganization. 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 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. These fits are shown in Figure 8 for the 6 hour data, and the rest are provided in the Supplement. The [Si-Fe2+] loss profiles in Kilauea Iki (Figure 8 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 performed 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.

## Section on Megan’s results

## Estimated bulk H diffusivity during dehydration of natural olivine

We use the H diffusivities determined at the end of each experiment, i.e., the data in San Carlos olivine SC1-2 after 68 hours of heating at 800°C and in the Kilauea Iki olivine after 8 hours of heating at 1000°C, combined with the estimate || a for Kilauea Iki olivine at 1200°C, to estimate rough Arrhenius laws for bulk H in natural Fe-bearing olivine in all three directions during dehydration (Figure 9, Table 3). The errors on these estimates are very large and difficult to estimate with only 2 to 3 points. Additional data, particularly at high temperatures, would be very useful. For convenience, we assume a constant activation energy of 130 kJ/mol and vary the pre-exponential factor D0, which, as plotted in Figure 9, is 10-5.4 m2/s || a, 10-6.9 m2/s || b, and 10-6.6 m2/s || c. The final diffusivity estimates for [Ti] and [Si] are similar to those for bulk H and so are likely to follow similar Arrhenius laws.

# Discussion

Most of the observed hydrogen loss in San Carlos olivine in bulk H, [Ti], and [Si] occurred at rates that were intermediate between the proton-vacancy and proton-polaron mechanisms, pv and pp. The pv mechanisms are always active but are relatively slow (see the dashed and dotted lines on Figure 9) because they rely on the diffusion of metal vacancies through the crystal. The pp rate is well established to shut off after a certain threshold level during incorporation (Kohlstedt & Mackwell 1998; Figure 4), but neither the change in rate that we observe during dehydration (Figure 7) nor diffusivities that appear to correspond to a mixture of pp and pv have been previously documented.

The rates at which the [Ti] and eventually the [Si] move are significantly higher than those expected from vacancy diffusion in forsterite (Figure 9), even allowing for reactions between the two sites (Padrón-Navarta et al. 2014). Here we propose some possible mechanisms by which this rapid movement is occurring, and we assume, following Kohlstedt and Mackwell’s 1998 original model, that, in addition to slower movement associated with vacancy diffusion (the pv mechanism), there are fast paths in which only H+ and electrons are moving. We also discuss the implications of these fast diffusivities for geochronometry and the retention of hydrogen in xenoliths and water in olivine-hosted melt inclusions.

Throughout the discussion, we use Kröger-Vink notation, in which crystal defects are described as follows: V is a vacancy, a superscript \* Indicates a negative charge relative to an ideal crystal, ‘ indicates a positive charge relative to an ideal crystal, and x no charge difference from an ideal crystal. Subscripts indicate different sites: M for octahedral metal sites, T for tetrahedral. Atoms that are not involved any reactions are typically ignored. For simplicity, all equations describing H incorporation here will assume H+ is occupying a related vacancy rather than an interstitial site. For example, the [Ti] site which involves a Ti4+ on a metal site, 2H+, and a Si vacancy, may be represented as (Ti4+M)\*\*(2H+T)’’. Also, all equation describing H loss by the pp mechanism are written assuming that H leaves as H2 gas, following Kohstedt and Mackwell 1998: 2H+ + 2Fe2+ → H2 + 2Fe3+.

## Proton-polaron diffusion and different H+ incorporation mechanisms

Prior to this work, the proton-polaron mechanism first proposed by Kohlstedt and Mackwell 1998, 2H+ + 2Fe2+ = H2 + 2Fe3+ with a fast direction || [100], could reasonably be expected to (1) operate on all H+ incorporated mechanisms and (2) begin immediately upon the start of dehydration by heating at 1 atm and proceed until the maximum amount of Fe3+ the crystal can accommodate has been reached. However, during the sequential dehydration the Kilauea Iki olivine, we observe a clear fast direction || [100] only in the Group I bands, not the [tri] peaks, which produce noisy, isotropic profiles with diffusivities that are, while still faster than would be expected from vacancy-controlled diffusivities in forsterite, are roughly an order of magnitude slower || [100] than the [Ti] and [Si] peaks. This difference in anisotropy suggests that the dominant mechanism by which H leaves [tri] is different from that by which H leaves the Group I bands.

A review of FTIR spectra in hydration and dehydration experiments suggests that the canonical proton-polaron mechanism is in fact closely tied to the movement of [Ti] specifically, and to a lesser extent [Si]. See, for example, Fig 3 and the FTIR spectra in Mackwell and Kohlstedt 1990. The reason for this close association is not entirely clear, but likely the hydrogens associated with Si vacancies have better access to the octahedral Fe2+ required for pp to occur than the [tri] hydrogens that are associated with Mg vacancies and nearby Fe3+, the presence of which may also impede further local Fe oxidation.

We therefore assume going forward in our discussion that when H moves in or out of the crystal by the pp mechanism, it does so primarily and most readily to or from the location in the olivine associated with the [Ti] peaks at 3525 and 3573 cm-1. This mechanism requires Ti4+ substituting onto an octahedral site (Berry et al. 2007 XANES paper). The fact that H+ is able to to readily enter San Carlos olivine so quickly in the first hours of hydration by pp suggests that at least some octahedral Ti is initially present in San Carlos olivine. If all of the Ti were on the tetrahedral site initially, then some of that Ti would need to change its position in the crystal to create the [Ti] defect, a process that is unlikely to occur under the hour timescales at which pp is observed. Thus, any rapid influx of H+ by pp may be limited not only by the initial quantity of Fe3+ (Kohlstedt and Mackwell 1998) but the initial amount of octahedral Ti.

Although the anisotropy of our [Ti] loss profiles is consistent with pp, the exact values of the diffusivities are inconsistent and often much slower than pp. In the following two sections, we explain how this apparent slowing of the pp mechanism may be explained by the redistribution of H+ from less stable incorporation mechanisms that are unable to access pp efficiently into [Ti].

## San Carlos olivine: Loss followed by redistribution

Immediately prior to dehydration, the H in San Carlos olivine SC1-2 was observed entirely as Group I bands, particularly [Ti], which proved highly mobile. Most of the [Si] peaks were similarly mobile, with the exception of one small peak at 3600 cm-1 (Figure 5). The initial hydrogen loss from [Ti] proceeded by the classic pp mechanism (Figure 6 D-F), increasing the number of open tetrahedral site vacancies near octahedral Ti:

2(Fe2+M)x  + (TiM )’’ + (2H+T)\*\* → 2H2 + 2(Fe3+M)’ + (TiM )’’ + (VT)\*\*\*\*.

The high-wavenumber [Si] peak was initially present in our sample (Figure 2A), and its profile did not change significantly during the initial stages of either hydration or dehydration, perhaps because pp would require the oxidation of four irons, rather than only 2:

4Fe2+M + (4H+T)x→ 2H2 + 4(Fe3+M)\* + (VT)’’’’.

The [Ti] mechanism, in addition to being strongly associated with pp, is known from incorporation studies as a particularly favorable position for H+ (e.g., Berry et al. 2005). Because of the relative stability of [Ti], any H+ that are unable to leave readily by pp from [Si] prefer to move into recently-vacated Si vacancies that bring them closer to the octahedral Ti. As H loss proceeds by pp from [Ti], the number of Si vacancies near octahedral Ti increases, and so the redistribution of H+ from [Si] to [Ti] becomes easier and thus faster.

Such a redistribution would explain the changes in rates that we observe between [Ti] and [Si] in Figure 7. The H leaves quickly from [Ti] by pp throughout the duration of the experiment, but the peak appears to slow down as more and more H+ moves into [Ti] from [Si]. Thus, the observed loss of the [Si] peak may not represent H+ moving out of the sample at all, but rather may indicate rate at which the H+ is redistributing between sites. This redistribution is slow enough to observe over a period of days because this experiment was conducted at the relatively low temperature of 800°C, but at magmatic temperatures and/or in samples with higher concentrations of H+ in relatively unstable incorporation mechanisms, the redistribution rates are likely to be higher.

## Kilauea Iki olivine: Redistribution followed by loss

While H+ loss by pp began promptly in the San Carlos olivine, in the Kilauea Iki olivine, rapid H+ loss was proceeded by a great deal of redistribution among incorporation sites, with a clear drop in [tri] and corresponding increase in [Si]. The [Ti] peaks were essentially immobile after 8 hours of heating at 800°C, in striking contrast to the same peak’s rapid pp movement in San Carlos olivine under the same experimental conditions (profiles in Supplement). After increasing the temperature to 1000°C, the [Ti] exhibited fast, anisotropic loss profiles very similar to what might be expected from the final measurements for the same peak in San Carlos olivine at 800°C: ~10% pp.

The reason for this jump in the [Ti] movement rate, from essentially immobile (all pv) to noticeable H+ loss by pp, is not entirely clear but may be the related to the equilibration in the redox state of the crystal, the redistribution of H+ from other sites as discussed above for SC1-2, or both. Unlike San Carlos olivine, the Kilauea Iki olivine began significantly oxidized (Terry knows the reference and fO2) and thus contained a significant amount of initial Fe3+. Hydrogen loss by pp requires Fe2+, and thus the high level of Fe3+ may have impeded loss by this mechanism. Although the experiments were run at relatively reducing conditions, at 800°C the kinetics of Fe oxidation state equilibration may be too sluggish to produce enough Fe2+ for pp to proceed to efficiently. Alternatively, pp may have been occuring from [Ti] at 800°C, but that loss could have been masked by rapid redistribution of H+ from [Si] and/or [tri]. Both possibilities are difficult to test with the current data set. What is clear is that after an initial period of re-equilibration and redistribution and at the higher temperature more relevant to most geologic applications, [Ti] dehydration profiles show a clear fast direction || [100] and diffusivities intermediate between classic pp and pv. This intermediate rate may be explained by a similar redistribution process as occurred in SC1-2: pp loss primarily from [Ti] masked by H+ movement from [tri] into the newly vacated silicon vacancies near the octahedral Ti.

.

## Comparison with previous work

The diffusivities that we suggest using for the interpretation of bulk H diffusion profiles (Figure 9) are consistent with most previous work on the dehydration of natural Fe-bearing olivines. Thoraval and Demouchy 2014 extensively discuss 1- and 3-dimensional modeling of FTIR profiles of natural dehydrated olivine, with specific application to H profiles in Pali-aike olivine measured by Demouchy et al. 2006 and including discussion of H profiles measured by Peslier and Luhr 2006 and Denis et al. 2013. They conclude “The concentration profiles measured for Pali-aiki samples are characteristic of dehydration. However, they are neither consistent with PP process, which is too fast, nor with PV process, since a fast [001] axis is not observed.” These many observations of dehydration rates intermediate between pp and pv in natural samples are fully consistent with the results of our experimental work.

Chen et al. 2011 and Gaetani et al. 2012 determine bulk H diffusivities in unoriented melt-inclusion-bearing olivines based on changes in the water content of the melt inclusion during heating. Their results, which consist of a single diffusivity for each temperature with no anisotropy information, are intermediate between our model’s expected diffusivities for the fast direction [100] and the two slower directions. These authors interpret their dehydration as entirely due to the pv mechanism because their measured diffusivity is similar to that expected for the fast direction [001] in pv. However, no actual FTIR measurements or profiles were taken on the olivine itself to confirm the anisotropy, and thus the fast direction for H loss from their olivine may well have been [100]. Their models also require the assumption that their sample is a perfect sphere of olivine containing a perfectly spherical melt inclusion in its center, and so their measured overall bulk H diffusivity measurement determined from changes in the water concentration of the melt inclusion might not necessarily be the true fast direction diffusivity but rather some diffusivity intermediate between fast and slow direction diffusivities. Given all of the assumptions that went into their diffusivity estimates, the data from these two studies are in rough agreement with our suggested diffusivities.

Le Voyer et al. 2014 used SIMS data to map the bulk H around an olivine-hosted melt inclusion and found strongly anisotropic diffusion with a fast direction of [100]. They interpreted this observed anisotropy as dehydration occuring by pp, but the results presented here demonstrate that dehydration can occur with a fast direction || [100] and diffusivities slower than pp.

Hauri’s 2002 observation of extremely fast diffusion in an unoriented olivine is more difficult to understand, particularly without oriented data and/or FTIR spectra for comparison. One possible explanation is that all of the H in Hauri’s olivine was present as [Ti] and thus was able to leave by pp without any redistribution among sites to slow the bulk movement rate.

While more work remains to better understand and predict the variations in the rate of H loss from olivine, the frequent observation of rapid H loss and anisotropy from natural samples suggests that roughly 10%, and occasionally even more, of the H+ in a typical olivine dehydrating upon ascent is exiting via the proton-polaron mechanism. In the next sections we discuss the implications of these rapid rates of bulk H+ movement on various geologic applications.

Need to revist Portnyagin, maybe Mironov, make sure I caught all of Peslier and Demouchy’s measurements.

## Implications for phenocryst and xenolith ascent rate calculations

## Implications for H retention in xenoliths and melt inclusions

# 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. Errors of ~30-40% in all y-axis data are omitted for clarity. 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 3 and initial hydrogen contents from Table 1. 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. Errors of ~40% in all y-axis data are omitted for clarity. 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. Estimated rates of hydrogen movement represented as diffusivities in San Carlos olivine SC1-2 with heating time at 800°C and oxygen fugacity of 10-16.5 bars (NNO-2.6) in three crystallographic directions for bulk hydrogen and two peak-specific mechanisms described in the text, [Si] and [Ti], compared with expected diffusivities for the proton-polaron mechanism (“pp”, Table 2). Errors on all diffusivities of ~1 order of magnitude, which should be consistently too high or too low for all data, are ommitted for clarity. 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 for fitting. These [Si] diffusivities increased at 43 and 68 hours, approaching the values for [Ti] and bulk H. The profile data used to obtain these diffusivities are shown in Figure 6 and the Supplement.

Figure 8. 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, and (J-L) the [Si] peak at 3600 cm-1 in an uncut block of Kilauea Iki olivine after 6 hours of heating at 1 atm and 1000°C. Errors of ~40% in all y-axis data are omitted for clarity. 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). Numbers are the diffusivities that correspond to the purple lines fit to the data. The proton-vacancy mechanism (pv, dotted lines) is too slow to account for all of the observed H movement. If the proton-polaron mechanism, pp, were fully active, then all hydrogen would have been lost from the crystal. Baselines and best-fit diffusivities and curves are provided in the Supplements.

Figure 9. Arrhenius diagram for bulk H movement in olivine. Black lines show ranges for previous measurements of the proton-polaron mechanism (“pp”) and the proton-vacancy mechanism (“pv”) during hydration of San Carlos olivine (Table 2) as well as peak-specific measurements from the dehydration of synthetic forsterite (dotted lines, Padrón-Navarta et al. 2014). Pink line shows a fit through the final observed bulk H diffusivity measurements from this study: the experimental dehydration of San Carlos olivine at 800°C (SC1-2, green), the experimental dehydration of Kilauea Iki olivine at 1000°C (Kiki, purple), and the estimated diffusivity in Kilauea Iki || [100] during its ascent at 1200°C (blue star). The activation energies (Ea) and pre-exponential factors (D0) for our fits are provided as a table. An interactive Arrhenius diagram that includes additional measurements and all time-series and peak-specific data is available online at [https://arrheniusdiagram.herokuapp.com](https://arrheniusdiagram.herokuapp.com/).

# Bibliography

Bell, D. R., and G. R. Rossman  
 1992 Water in Earth’s Mantle: The Role of Nominally Anhydrous Minerals. Science 255(5050). WOS:A1992HH74400043: 1391–1397.

Bell, D. R., G. R. Rossman, J. Maldener, D. Endisch, and F. Rauch  
 2003 Hydroxide in Olivine: A Quantitative Determination of the Absolute Amount and Calibration of the IR Spectrum. Journal of Geophysical Research-Solid Earth 108(B2). WOS:000181985400002. ://WOS:000181985400002.

Berry, A. J., J. Hermann, H. S. C. O’Neill, and G. J. Foran  
 2005 Fingerprinting the Water Site in Mantle Olivine. Geology 33(11). WOS:000233059000008: 869–872.

Berry, A. J., A. M. Walker, J. Hermann, et al.  
 2007 Titanium Substitution Mechanisms in Forsterite. Chemical Geology 242(1–2). WOS:000248433400010: 176–186.

Blanchard, Marc, Jannick Ingrin, Etienne Balan, István Kovács, and Anthony C. Withers  
 2017 Effect of Iron and Trivalent Cations on OH Defects in Olivine. American Mineralogist 102(2): 302–311.

Chen, Y., A. Provost, P. Schiano, and N. Cluzel  
 2011 The Rate of Water Loss from Olivine-Hosted Melt Inclusions. Contributions to Mineralogy and Petrology 162(3). WOS:000294216500011: 625–636.

Demouchy, S., and S. Mackwell  
 2003 Water Diffusion in Synthetic Iron-Free Forsterite. Physics and Chemistry of Minerals 30(8). WOS:000185964900006: 486–494.

2006 Mechanisms of Hydrogen Incorporation and Diffusion in Iron-Bearing Olivine. Physics and Chemistry of Minerals 33(5). WOS:000240439000005: 347–355.

Demouchy, Sylvie, and Nathalie Bolfan-Casanova  
 2016 Distribution and Transport of Hydrogen in the Lithospheric Mantle: A Review. Lithos 240: 402–425.

Demouchy, Sylvie, Catherine Thoraval, Nathalie Bolfan-Casanova, and Geeth Manthilake  
 2016 Diffusivity of Hydrogen in Iron-Bearing Olivine at 3 GPa. Physics of the Earth and Planetary Interiors 260: 1–13.

Faul, Ulrich H., Christopher J. Cline II, Emmanuel C. David, Andrew J. Berry, and Ian Jackson  
 2016 Titanium-Hydroxyl Defect-Controlled Rheology of the Earth’s Upper Mantle. Earth and Planetary Science Letters 452: 227–237.

Ferguson, David J., Helge M. Gonnermann, Philipp Ruprecht, et al.  
 2016 Magma Decompression Rates during Explosive Eruptions of Kīlauea Volcano, Hawaii, Recorded by Melt Embayments. Bulletin of Volcanology 78(10): 71.

Ferriss, E.  
 2015 Pynams: A Python Package for Interpreting FTIR Spectra of Nominally Anhydrous Minerals (NAMs). New York. https://github.com/EFerriss/pynams.

Ferriss, E., T. Plank, D. Walker, and M. Nettles  
 2015 The Whole-Block Approach to Measuring Hydrogen Diffusivity in Nominally Anhydrous Minerals. American Mineralogist 100(4). WOS:000352175700017: 837–851.

Ferriss, Elizabeth, Terry Plank, and David Walker  
 2016 Site-Specific Hydrogen Diffusion Rates during Clinopyroxene Dehydration. Contributions to Mineralogy and Petrology 171(6): 1–24.

Gaetani, G. A., J. A. O’Leary, N. Shimizu, Claire E. Bucholz, and Matthew Newville  
 2012 Rapid Reequilibration of H2O and Oxygen Fugacity in Olivine-Hosted Melt Inclusions. Geology 40(10): 915–918.

Hauri, E.  
 2002 SIMS Analysis of Volatiles in Silicate Glasses, 2: Isotopes and Abundances in Hawaiian Melt Inclusions. Chemical Geology 183(1–4). WOS:000174332300008: 115–141.

Ingrin, J., J. Liu, C. Depecker, et al.  
 2013 Low-Temperature Evolution of OH Bands in Synthetic Forsterite, Implication for the Nature of H Defects at High Pressure. Physics and Chemistry of Minerals 40(6). WOS:000319771000005: 499–510.

Jollands, Michael C., José Alberto Padrón-Navarta, Jörg Hermann, and Hugh St.C. O’Neill  
 2016 Hydrogen Diffusion in Ti-Doped Forsterite and the Preservation of Metastable Point Defects. American Mineralogist 101(7): 1560–1570.

Keppler, Hans, and Joseph R. Smyth  
 2006 Water in Nominally Anhydrous Minerals, vol.62. Reviews in Mineralogy and Geochemistry. Mineralogical Society of America.

Kohlstedt, D. L., and S. J. Mackwell  
 1998 Diffusion of Hydrogen and Intrinsic Point Defects in Olivine. Zeitschrift Fur Physikalische Chemie-International Journal of Research in Physical Chemistry & Chemical Physics 207. WOS:000076569300010: 147–162.

Kurosawa, M., H. Yurimoto, and S. Sueno  
 1997 Patterns in the Hydrogen and Trace Element Compositions of Mantle Olivines. Physics and Chemistry of Glasses 24: 385–395.

Le Voyer, Marion, Paul D. Asimow, Jed L. Mosenfelder, et al.  
 2014 Zonation of H2O and F Concentrations around Melt Inclusions in Olivines. Journal of Petrology 55(4): 685–707.

Libowitzky, E., and G. R. Rossman  
 1996 Principles of Quantitative Absorbance Measurements in Anisotropic Crystals. Physics and Chemistry of Minerals 23(6). WOS:A1996VD85000001: 319–327.

Lloyd, Alexander S., T. Plank, Philipp Ruprecht, E. H. Hauri, and William Rose  
 2013 Volatile Loss from Melt Inclusions in Pyroclasts of Differing Sizes. Contributions to Mineralogy and Petrology 165: 129–153.

Mackwell, S. J., and D. L. Kohlstedt  
 1990 Diffusion of Hydrogen in Olivine - Implications for Water in the Mantle. Journal of Geophysical Research-Solid Earth and Planets 95(B4). WOS:A1990CZ37500052: 5079–5088.

Mironov, Nikita, Maxim Portnyagin, Roman Botcharnikov, et al.  
 2015 Quantification of the CO2 Budget and H2O–CO2 Systematics in Subduction-Zone Magmas through the Experimental Hydration of Melt Inclusions in Olivine at High H2O Pressure. Earth and Planetary Science Letters 425: 1–11.

Mosenfelder, J. L., N. I. Deligne, P. D. Asimow, and G. R. Rossman  
 2006 Hydrogen Incorporation in Olivine from 2-12 GPa. American Mineralogist 91(2–3). WOS:000235472000007: 285–294.

Padrón-Navarta, Jose Alberto, Joerg Hermann, and Hugh St. C. O’Neill  
 2014 Site-Specific Hydrogen Diffusion Rates in Forsterite. Earth and Planetary Science Letters 392: 100–112.

Peslier, A. H., and J. F. Luhr  
 2006 Hydrogen Loss from Olivines in Mantle Xenoliths from Simcoe (USA) and Mexico: Mafic Alkalic Magma Ascent Rates and Water Budget of the Sub-Continental Lithosphere. Earth and Planetary Science Letters 242(3–4). WOS:000235855100006: 302–319.

Portnyagin, M., Renat Almeev, S. Matveev, and Francois Holtz  
 2008 Experimental Evidence for Rapid Water Exchange between Melt Inclusions in Olivine and Host Magma. Earth and Planetary Science Letters 272: 541–552.

Rosen, Julia  
 2016 Crystal Clocks. Science 354(6314): 822–825.

Ruprecht, Philipp, and Terry Plank  
 2013 Feeding Andesitic Eruptions with a High-Speed Connection from the Mantle. Nature 500(7460): 68–72.

Shuai, Kang, and Xiaozhi Yang  
 2017 Quantitative Analysis of H-Species in Anisotropic Minerals by Polarized Infrared Spectroscopy along Three Orthogonal Directions. Contributions to Mineralogy and Petrology 172(2–3): 14.

Thoraval, Catherine, and Sylvie Demouchy  
 2014 Numerical Models of Ionic Diffusion in One and Three Dimensions: Application to Dehydration of Mantle Olivine. Physics and Chemistry of Minerals 41(9). WOS:000341924800005: 709–723.

Tollan, P. M. E., H. St C. O’Neill, J. Hermann, A. Benedictus, and R. J. Arculus  
 2015 Frozen Melt-Rock Reaction in a Peridotite Xenolith from Sub-Arc Mantle Recorded by Diffusion of Trace Elements and Water in Olivine. Earth and Planetary Science Letters 422. WOS:000355350700018: 169–181.

Tollan, Peter M. E., Rachel Smith, Hugh St C. O’Neill, and Jörg Hermann  
 2017 The Responses of the Four Main Substitution Mechanisms of H in Olivine to H 2 O Activity at 1050 °C and 3 GPa. Progress in Earth and Planetary Science 4(1): 14.

Withers, A. C.  
 2013 The Pitzer and Sterner Equation of State for Water. http://www.geo.umn.edu/people/researchers/withe012/fugacity.htm, accessed August 6, 2013.

Withers, Anthony C, Hélène Bureau, Caroline Raepsaet, and Marc M Hirschmann  
 2012 Calibration of Infrared Spectroscopy by Elastic Recoil Detection Analysis of H in Synthetic Olivine. Chemical Geology 334: 92–98.

Zhao, Y. H., S. B. Ginsberg, and D. L. Kohstedt  
 2004 Solubility of Hydrogen in Olivine: Dependence on Temperature and Iron Content. Contributions to Mineralogy and Petrology 147(2). WOS:000221169500003: 155–161.