The whole-block approach to measuring hydrogen diffusivity in nominally anhydrous minerals

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Abstract

A method is developed for determining the diffusivity of infrared-active species by transmission Fourier transform infrared spectroscopy (FTIR) in samples prepared as rectangular prisms without cutting the sample. The primary application of this “whole-block” or “3D-WB” method is in measuring the diffusion of hydrogen (colloquially referred to as “water”) in nominally anhydrous minerals, but the approach is applicable to any IR-active species. The whole-block method requires developing a 3-dimensional model that includes the integration of the beam signal through the sample, from rim to core to opposite rim. The analysis is carried out using both forward and tomographic inverse modeling techniques. Measurements collected from central slices cut from the whole block are simpler to interpret than whole-block measurements, but slicing requires destructive sample analysis. Because the whole-block method is nondestructive, this approach allows a time-series of diffusion experiments on the same sample.

The potential pitfalls of evaluating whole-block measurements without correcting for path integration effects are explored using simulations. The simulations demonstrate that diffusivities determined from whole-block measurements without considering path-averaging may be up to half an order of magnitude too fast. The largest errors are in fast and/or short directions, in which
the diffusion profiles are best developed. A key characteristic of whole-block measurements is
that the central values in whole-block traverses always change before the concentration of the
IR-active species changes in the block’s center because of signal integration that includes
concentrations in the sample rims. The resulting plateau in the measurements is difficult to fit
correctly without considering path integration effects, ideally by using 3D whole-block models.

However, for early stages of diffusion with less than 50% progress, diffusivities can be
accurately determined within 0.5 log units using a 1D approximation and the whole-block central
plateau values because diffusivities are more dependent on profile shape than absolute
concentrations.

To test the whole-block method, a dehydration experiment was performed on an oriented
piece of diopside from the Kunlun Mts with minimal zoning, cracks, or inclusions. The
experiment was performed in a gas mixing furnace for 3 days at a temperature of 1000 °C and
oxygen fugacity of $10^{-11.1}$ bar (QFM). First, whole-block analysis was performed by taking FTIR
traverses in three orthogonal directions. Then, a slice was cut from the center of the sample, and
hydrogen profiles were measured by FTIR and secondary ion mass spectrometry (SIMS). The
results of FTIR and SIMS measurements on the slice are in good agreement both with each other
and with diffusion profiles calculated based on the results of forward and inverse models of the
whole-block FTIR measurements. Finally, the new method is applied to previous whole-block
measurements of hydrogen diffusion in San Carlos olivine using both the forward and inverse
approaches.
Keywords

Transmission FTIR, diffusion, hydrogen, water in nominally anhydrous minerals, diopside, olivine

Introduction

Diffusion is an important transport mechanism and has numerous applications to the geological sciences (e.g., Watson and Baxter 2007). The mechanisms and rates of diffusion for many chemical species in geologically relevant systems are known (e.g., Zhang and Cherniak 2010), but diffusivities, also called diffusion coefficients, are still poorly constrained for many systems. Determination of the relatively slow diffusivities in crystalline materials has been tackled with a variety of techniques (Ryerson 1987), some of which are still emerging (Watson and Dohmen 2010). All of these methods require both an experimental approach that results in diffusion and a way to measure the extent of that diffusion.

Experimental methods may be divided into two broad categories: time-series or mass-loss experiments, which measure changes in concentration with time at a particular point, usually the center, of the sample, and diffusion profile experiments, which measure changes in concentration with distance at a given time. Sample geometry is a key factor in all diffusion experiments and is usually chosen in a way that simplifies the final diffusion analysis from Fick’s 2nd Law, $\frac{\partial v}{\partial t} = D \frac{\partial^2 v}{\partial x^2}$, where $D$ is the diffusivity, $v$ is the concentration, $t$ is the time, and $x$ is the distance.

Solutions are available for many geometries and boundary conditions in Carslaw and Jaeger 1959 and Crank 1975.
Experiments that are designed to measure diffusion profiles have the significant advantage that they can be directly compared to profiles calculated from the solution to Fick’s 2nd Law, and transport that is unrelated to diffusion is readily apparent (Ryerson 1987). Time series experiments are, however, still useful to obtain an initial approximation for diffusivity and as a complimentary technique for confirming interpretations based on diffusion profile measurements (e.g., Woods et al. 2000). Other approaches useful for validation of diffusivity estimates include cross-checking with multiple experimental methods, varying the sample geometry, and zero-time experiments, in which the sample is removed from the experiment immediately after run conditions are achieved (Hofmann 1980). Although diffusion profiles are preferable to time-series measurements, profiles are more difficult to obtain because they traditionally require that the sample be cut through the middle after the experiment, which requires careful manipulation to avoid sample fracture or loss and also prevents the sample from being re-used in future diffusion experiments, e.g., to generate time-series measurements or perform a reversal.

Hydrogen (H⁺; colloquially often referred to as “water”) diffusivities in nominally anhydrous minerals (NAMs) are most often determined using measurements from transmission Fourier-transform infrared spectroscopy (FTIR) because this method is non-destructive, commonly available, inexpensive, more sensitive to hydrogen (> ppm level) than most other techniques, and can provide some structure and speciation information (see review by Rossman 2006). Reflectance FTIR may also be used to measure hydrogen and carbon speciation and concentration in glasses, but the detection limits for this method are generally too high (~1000 ppm wt. H₂O) for measuring hydrogen or carbon in nominally anhydrous minerals (Grzechnik et al. 1996; Hervig et al. 2003; King and Larsen 2013; Lowenstern and Pitcher 2013). Experimental methods and measurement techniques for hydrogen diffusion experiments in NAMs are
reviewed by Ingrin and Blanchard 2006 and Farver 2010. In the standard approach, a slice is cut from the center of a sample prior to diffusion profile measurements to minimize the effect of profile overlap (also called signal accumulation or integration) along a transmission path (Movie 1). By cutting, profile overlap effects are eliminated if the hydrogen has not diffused into the center of the slice and is of constant concentration in the thickness direction of the slice. Non-constant slice profiles can still be evaluated, but non-path-integrated three dimensional models must be used instead of relatively simple one dimensional models; see description below.

This paper describes how to acquire and interpret diffusion profile measurements for species measured by transmission FTIR without cutting the sample after a diffusion experiment (Figure 1). This approach, which we refer to as the whole-block method, takes advantage of the fact that the measured transmission FTIR concentration, normalized to thickness, represents a path-averaged value in the sample. We focus on hydrogen in nominally anhydrous minerals cut in the form of a rectangular parallelepiped, but other systems measured using a transmitted signal moderated by absorption such as carbon by FTIR or a heavy element by X-rays, and other sample geometries could also be evaluated using this approach. We explore this method using simulated data, test it experimentally by dehydrating diopside, and then apply it to published measurements on the hydration of olivine.

The whole-block approach

Signal accumulation in FTIR measurements provides an opportunity to obtain diffusion profiles without cutting the sample, which typically is a rectangular parallelepiped oriented with respect to crystallographic or morphologic axes of the material. These profiles (Figure 1) will be called “whole-block” here to distinguish them from “slice” profiles measured on the central slice.
of a sample cut after the diffusion anneal. In this section we describe the advantages of using whole-block measurements as well as the details of the method. The whole-block method involves (1) measurements of hydrogen concentration profiles through the entire, uncut sample block, (2) forward modeling to obtain diffusivity estimates, and (3) inversion of the whole-block measurements to provide an independent determination of the internal concentration structure of the sample.

**Advantages**

Whole-block measurements are useful for the following reasons: (1) whole-block measurements can be obtained nondestructively and thus permit multiple experiments using the same sample, e.g., a time series of progressively longer experiments or reversal of diffusion flux by change of external reservoir concentration to promote diffusion into or out of a specimen. (2) The cut slice may be too thin to provide a high quality FTIR signal for samples with low, ppm-level hydrogen concentrations. (3) The diffusivities in three orthogonal directions can be estimated from the same sample. Measurements for the third direction otherwise requires either a second experiment or a slice taken from one of the butts left from the original slice. (4) In dehydration experiments, the initial profile can be measured directly. (In hydration experiments on pre-annealed samples, the initial concentration is 0 everywhere.)

The whole-block method also allows some independence from the following problems that can sometimes result in high error in measurements taken near the edge of sample slices. The rim hydrogen concentration may be very low after a dehydration experiment, which causes high errors in FTIR calibrations. Rims are also less likely to be perfectly flat than the center of a polished block because of chipping during cutting and/or polishing and/or quenching. If the
sample block shape is wedged and does not have near-perfect 90° angles, then the FTIR beam does not sample the full thickness at some rims, resulting in artificially low values. Further, in some thicker samples, scattering of the infrared beam near edges and cracks may result in artificially low values.

Whole-block measurements taken in the center of the sample always show an apparent decrease for dehydration experiments or increase for hydration in hydrogen content in the center of a whole-block profile (see discussion and illustrations below) and therefore provide diffusion information in the ray path direction without the problems associated with rim measurements. While whole-block measurements also include rim effects, the central values, which include integrated values from the rims, provide additional measurements to improve the overall interpretation. Because the whole-block method is non-destructive, the sample can always be sliced to confirm the final interpretation and resolve any ambiguity.

**Whole-block profile measurements**

Whole-block concentration measurements are constructed by normalizing the peak area of the FTIR absorbance spectra of interest obtained after the experiment to the maximum hydrogen concentration, which is the initial concentration for diffusion out of the sample or the solubility for diffusion into the sample. The relevant OH vibrations occur between wavenumbers 3000 and 4000 cm\(^{-1}\). The resulting area ratios can be used directly in subsequent forward and inverse analyses, or these values can be scaled up to the maximum hydrogen concentration and expressed in concentration units such as ppm wt. H\(_2\)O or H/10\(^6\) Si.

Diffusion studies have somewhat more leeway in how FTIR spectra are evaluated than studies concerned with absolute hydrogen concentrations because the diffusivity estimate
depends on the overall shape, not the absolute values, of the concentration profiles. Thus, approaches likely to introduce errors in absolute concentration values are often permissible as long as they are applied uniformly to all spectra in the profile. For instance, linear baselines are unusual in concentration studies but common in diffusion studies because they provide consistency among measurements both along the profile and before and after the experiment (e.g., Ingrin et al. 1995). The resulting concentration profiles may not be entirely accurate in their absolute concentrations, but they still provide good estimates of the diffusivities, even after diffusion has reached the center of the sample, in which case a 3-dimensional model such as one described below is required.

Also unlike concentration studies, either polarized or unpolarized infrared radiation may be used, even in highly birefringent or anisotropic samples. In the case of unpolarized radiation, which can be slightly polarized due to prisms and mirrors along its optical path, the absorbance spectrum changes with ray path $R$, which is also called the propagation direction or thickness direction. Polarized radiation has the advantages of providing more meaningful additional structural and concentration information and allowing consistent spectra between profiles if the electric vector $E$ is maintained in a constant direction, ideally the direction with the strongest absorbance. However, unpolarized radiation typically has a higher signal-to-noise ratio and may be necessary in samples with very low concentrations. Woods et al. (2000) measured hydrogen diffusion profiles in diopside using both polarized and unpolarized radiation and obtained the same diffusivity within error.

Forward modeling to obtain diffusivities requires whole-block profiles (Figure 1) measured parallel to three orthogonal directions. The simplest geometry for obtaining these profiles is a centered cross of measurements using one infrared ray path and a line of measurements through
the center of the sample using a second ray path. Profiles obtained using three separate ray paths, additional off-center profiles, and/or full concentration maps are not necessary to produce diffusivity estimates but would contribute to and support the final analysis, particularly for the inverse approach described below.

**Forward models**

**Whole-block profiles (3D-WB)**

Whole-block profiles can be calculated from a 3-dimensional (3D) array of hydrogen concentrations determined from standard three-dimensional models (given below) by taking the arithmetic mean of the concentrations in the direction parallel to the infrared beam ray path ($R$) for each measurement. For example, for a whole-block point (x,y) measured with $R // [100]$, the whole-block (3D-WB) concentration $v_{3D-WB}$ equals the average of all concentration points along [100] at (x,y). Unlike slice profiles, whole-block profiles can often be conveniently obtained with $R$ parallel to two different directions, e.g., a traverse // [100] with $R // [010]$ and a traverse // [100] with $R // [001]$. Because they represent averages, these two profiles may differ significantly, particularly when diffusion is strongly anisotropic.

This averaging must take place in the absorbance $A$ domain, which is linearly related to the concentration $v$ according to the Beer-Lambert law ($A = v \times$ molar absorption coefficient $\varepsilon$ $\times$ thickness), rather than in the transmission domain. In FTIR, the transmission $T$ is the variable that is actually measured, and $T = I / I_0$ where $I$ is the intensity of measured light and $I_0$ initial intensity. The absorbance $A = -\log_{10}T$; although other log scales may also be used with an appropriate conversion factor for $\varepsilon$ when calculating $v$ from $A$. The absorbance is conventionally reported by most commercial software for FTIR spectrometers. For each unit step through the
sample, the intensity is changed by a percentage of the initial value entering that unit, resulting in an exponential change in the transmission.

The concentration of the diffusing species being measured, and hence the extent of that exponential change, varies along each unit step-size in the integrated whole-block path after a diffusion experiment. To understand the mathematics involved, consider the simplified example of a zoned sample with three distinct parts, in which each part has a different concentration of the IR-active species and hence different transmittances. The IR radiation first passes through Part 1 to produce transmittance $T_1 = I_1 / I_0$, then passes through Part 2 to produce transmittance $T_2 = I_2 / I_1$, and finally through Part 3 to produce $T_3 = I_3 / I_2$. The generic sample in this example does not have to be symmetric, although a symmetrical diffusion profile is assumed in the whole-block diffusion forward models. The final transmittance, $T_{total} = T_1 \times T_2 \times T_3 = I_3 / I_0$. (Following this equation, whole-block path-integrated values may be calculated in the transmission domain by using the product, not the average, of transmittance values along the ray path.) Because $A$ is related to $T$ on a log scale ($A = -\log T$), the total absorbance $A_{total}$ is determined from the component $A$ values as a sum rather than a product: $A_{total} = -\log(T_{total}) = -\log(T_1 \times T_2 \times T_3) = -\log T_1 + -\log T_2 + -\log T_3 = A_1 + A_2 + A_3$. For a system with $n$ concentration zones, $A_{total} = \sum_{i=1}^{n} A_i$. Therefore, the integrated absorbance or concentration divided by the sample thickness represents the arithmetic mean of absorbance or concentration values in the ray path of the measurement, assuming that the grid size used to calculate the profile is evenly spaced and sufficiently fine-scale that the concentration in each division is approximately uniform.
Production of the 3D-WB profiles described above assumes some knowledge of the internal concentration structure of the sample, which can be determined using standard 3-dimensional models for diffusion in a rectangular parallelepiped such as those found in Carslaw and Jaeger (1959) Section 6.4, Crank (1975) Section 2.5.1, and Demouchy et al. (2006). These models are based on either infinite sums of sines and cosines or error functions. In general, error functions are preferred for the early stages of diffusion, and the infinite sum more accurately represents diffusion at later stages (Crank 1975, Section 2.1). All models discussed here assume that the diffusivity is independent of the concentration of the diffusing species. This assumption may not hold for hydrogen diffusion in all NAMs (e.g., mantle-derived pyrope, Wang et al. 1996) and is certainly incorrect for silicate glasses (e.g., Doremus 1975; Lanford et al. 1979; Zhang et al. 1991, Anovitz et al., 1999).

Examples for several boundary conditions are written out in Carslaw and Jaeger (1959) section 6.4 for diffusion in an isotropic rectangular parallelepiped. Carslaw and Jaeger (1959) further note that the same approach (i.e., the multiplication of known one-dimensional problems, with a proof given in their Section 1.15) is also applicable to anisotropic media, given the critical assumption that the main axes of diffusion are parallel to the coordinate planes of the parallelepiped. For instance, for the region $La > x > 0$, $Lb > y > 0$, $Lc > z > 0$ with unit initial concentration and zero surface concentration, the concentration at all positions in the crystal $v(x,y,z)$ is as follows:
where \( t \) is time and \( D_a, D_b, D_c \) are the diffusivities parallel to each direction. Throughout this manuscript, we refer to this model as three-dimensional non-path-integrated (3D-NPI).

For individual non-path-integrated concentration profiles (e.g., slice profile measurements along a single dimension) in which the concentration of the diffusing species in the center of the sample remains constant throughout the experiment, then the diffusivity can be determined more simply using a 1-dimensional (1D) model, e.g.,

\[
v(x, y, z) = \text{erf} \left( \frac{x}{2 \sqrt{D_a t}} \right) + \text{erf} \left( \frac{L_a - x}{2 \sqrt{D_a t}} \right) \text{erf} \left( \frac{y}{2 \sqrt{D_b t}} \right) + \text{erf} \left( \frac{L_b - y}{2 \sqrt{D_b t}} \right) \text{erf} \left( \frac{z}{2 \sqrt{D_c t}} \right)
\]

\( Eq. 1 \)

\[
v(x)_{1D} = \left( \text{erf} \left( \frac{x}{2 \sqrt{D_a t}} \right) + \text{erf} \left( \frac{L_a - x}{2 \sqrt{D_a t}} \right) \right)
\]

\( Eq. 2 \)

**Inverse models: Geochemical tomography**

Inversions similar to those used to evaluate geophysical tomography data constitute a complementary analysis technique to the forward models described above. While inverse models cannot by themselves provide diffusivity estimates, they produce independent estimates of the internal concentration structure that provide a useful constraint and check on the concentration profiles and true center concentration values predicted by forward models. Unlike forward models, inverse models require no assumptions about diffusion or any concentration changes over the course of the experiment. The data \( d \) constraining our model are the whole-block estimates of path-averaged concentrations obtained as described above. As in all inverse modeling, errors in the observations arising from the measurement technique and assumptions
will lead to some level of uncertainty in the final model. For example, in our case we assume that our sample is a single crystal with uniform mineral composition to produce integrated concentration estimates from FTIR.

A more complete treatment of discrete inverse theory and examples for geophysical data may be found in Menke (1984). Here we include only a brief overview of the technique. The sample, a rectangular prism, is subdivided into a series of regularly spaced miniature prisms or blocks of equal volume, and each of these sub-blocks is assumed to have uniform concentration. Each whole-block observation represents the average concentration through a subset of these blocks. The problem is then formulated as the equation $G \cdot m = d_{\text{obs}}$, where $d_{\text{obs}}$ is an $n \times 1$ matrix containing $n$ whole-block observations, $m$ is a $k \times 1$ coefficient matrix containing $k$ concentration values (1 for each subdivision of the sample; these are the values we solve for), and $G$ is an $n \times k$ sensitivity matrix that describes the contribution of each of the $k$ sample subdivisions to the whole-block measurements $d_{\text{obs}}$. The grid spacing, which determines $k$, is varied in each direction with the goal of describing the measurements as simply as possible, i.e., with a smallest value of $k$ that adequately describes the measurements.

The internal concentration values are determined by minimizing a goodness of fit measure related to the variance $\sigma^2 = \frac{\sum (d_{\text{obs}} - d_{\text{pred}})^2}{d_{\text{obs}}^2} \left(\frac{1}{k}\right)$, where $d_{\text{pred}}$ represents the whole-block values predicted from the model results, $k$ is number of degrees of freedom (i.e., the number of grid cells used to model the measurements), and $d_{\text{obs}}$ is the mean of the observed measurements, which serves as a scaling factor to compare the goodness of fit between data sets. The error $\sigma_i$ on each concentration value $i$ is evaluated as $\sigma_i = d_{\text{obs}} \sqrt{C(i,i)}$, where $C$ is the covariance matrix $C = [G^T G] \cdot \sigma^2$, and $G^T$ is the transpose of $G$. The formal error $\sigma_i$ on each value is a minimum value.
because it only includes the diagonal elements of the covariance matrix. To better assess the true error, comparable whole-block data can be simulated and then inverted using the same approach as that used to invert the measurements of interest.

Ideally, whole-block profiles would be obtained with at least three lines measured along three different orthogonal planes of the sample block as well as additional, off-center profiles. Newer FTIR spectrometers are equipped with digital stages and software that can rapidly produce hydrogen measurement maps of entire surfaces with consequent improvement in the accuracy of internal concentrations determined from the inversion. However, many laboratories will be limited to the bare minimum required to apply the whole-block forward models: a cross of measurements with one ray path and a single line of measurements with a different ray path.

A successful inversion is possible with a limited set of analyses by applying model constraints to the rim values, symmetry, and/or smoothness of the model, following standard practice in geophysical tomography. A rim value constraint encourages the model to match the concentration in the subdivisions along the outermost rim of the sample to a known value. A symmetry constraint gives preference to model outputs that are symmetrical along any orthogonal line through the sample. A smoothness constraint causes the model to expect that neighboring subdivisions contain similar values. Damping the model output through the application of these constraints does not force the results ($m$) to comply exactly with the constraints, and a weighting factor $\lambda$ can be included and varied to evaluate the importance of these constraints during the calculation. Each of the three constraints can be removed or weighted separately to evaluate their effects on the fit individually. The value of $\lambda$ should be kept as low as possible so that the results are influenced primarily by the observed measurements.
Methods

Simulations were performed to provide more general insight into the potential for error when applying 3D-NPI and 1D diffusion models to path integrated measurements. Then, the whole-block approach was tested experimentally by dehydrating a diopside crystal and comparing the resulting whole-block profiles with slice profiles. In the final section, we review previously published whole-block profiles on hydrogen diffusion in olivine.

Numerical simulations

To investigate the usefulness and potential pitfalls of applying non-path-integrated diffusion models to path-integrated measurements, 40,000 sets of 3D-WB data were simulated and then fit using NPI models. In each simulation, 100 data points were generated along each of three orthogonal whole-block profiles. Then, NPI profiles were fit to these simulated 3D-WB data using the non-linear least squares fitting routine available in MATLAB curve-fitting toolbox. This least squares method is objective but somewhat biased toward fitting points closer to the sample rim where the points and the fit line can show the largest deviations from each other.

Simulations were performed assuming diffusion into the sample for isotropic and anisotropic materials, equant and inequant samples, and early to later stages of diffusion (up to 80% saturation, at which point the profiles are approaching a straight line, and error functions no longer produce good fits). Two different NPI fitting approaches were tested using different initial concentrations during the NPI fit: a 3D-NPI fit that uses the true, known initial value of zero, and a set of three 1D-NPI fits (one for each profile direction) that use the plateau in the 3D-WB data in place of the initial value during the fit.
Experiments

Sample preparation

A dehydrogenation experiment was performed on a diopside from the Kunlun Mountains, China, similar samples to which were used in previous diffusion experiments (Van Orman et al. 1998, 2001). The sample was prepared as a 3.5 mm × 1.6 mm × 1.8 mm orthogonal prism with faces perpendicular to [100]* (which is ~16° from [100]), [010], and [001], and polished using 1 μm diamond paste.

3D-WB measurements

Unpolarized FTIR measurements were obtained before and after the experiment using a spot size of 100 μm, resolution of 4 cm⁻¹, and averaged over 200 scans on the Nicolet 20 XSB with IR microscope at the American Museum of Natural History. To aid in FTIR spot location in the absence of a digital sample holder, pits were placed along each of the three orthogonal profiles in 100 μm intervals using a laser ablation microprobe. Initial integrated peak areas for unpolarized FTIR spectra with linear baselines range between 20 and 80 cm⁻², depending on the ray path direction. The precision error for the FTIR areas is 2%, based on repeated measurements at the same location according to the following equation: 100×σ/(m×\sqrt{n}), where σ is a single standard deviation and m is the mean area for n=3 measurements.

Dehydration

The prepared sample block was heated in a gold-calibrated (error ± 3°) 1-atm vertical alumina tube furnace for 75 hours at 1000 °C and 10⁻¹¹.¹ bar oxygen fugacity (at the quartz-fayalite-magnetite buffer) using CO/CO₂ mixes of 97.0% CO₂ (Deines et al. 1974). The resulting absorbance values were normalized to the initial profile measurements to generate whole-block
diffusion profiles in three orthogonal directions with concentration units of final absorbance \((A) / (A_0)\). The precision error for \(A/A_0\) concentration values of 3% was determined by propagation of the 2% precision error on each measurement.

**Slice measurements by FTIR and SIMS**

After whole-block profiles were obtained, the sample was sliced perpendicular to [100]*, and slice measurements were obtained parallel to [010] and [001] by unpolarized FTIR and secondary ion mass spectrometry (SIMS). Concentrations profiles for the slice FTIR measurements were generated by normalizing to the initial FTIR absorbance values adjusted for thickness. One potential concern with this approach is that absorbance measurements obtained using unpolarized radiation may not be directly proportional to thickness, at least for grains with unpolarized absorbance greater than 0.15 and linear polarized absorbance greater than 0.3 (Libowitzky and Rossman 1996; Kovacs et al. 2008; Sambridge et al. 2008; Withers 2013; Xia et al. 2013). All initial absorbance values used here are less than 0.13, and therefore should scale directly with thickness.

SIMS measurements were carried out at the Carnegie Institution of Washington (DTM) using the Cameca 6f ion microprobe. The primary beam of Cs⁺ was 5-10 nA. The accelerating voltage was 10 kV, and the final spot size was 20-40 μm. Hydrogen was measured as \(^{16}\text{O}^{1}\text{H}\). The ratio \(^{16}\text{O}^{30}\text{Si}\) was monitored, and concentrations were obtained following the procedures in Wade et al. (2008). The SIMS measurements were calibrated using clinopyroxene standards PMR-53, ROM271-10, -16 and -21. Standard concentrations are given in Aubaud et al. (2007). The calibration factor for SIMS was \(4540 \pm 560 \text{ ppm wt. H}_2\text{O}/(\text{counts/s})\), which corresponds to an accuracy or calibration error of 12%. The SIMS precision errors were determined similarly to
those for FTIR using n=4 to 5 measurements of each data point, and these errors ranged from 1.6
to 7.9 %.

**Initial concentration**

Initial concentration estimates through the untreated whole block of the Kunlun diopside
were complicated by the lack of an infrared polarizer on the FTIR at the time this work was
begun. An initial concentration of 33 ppm wt. H$_2$O was calculated from the average unpolarized
spectra measured along three orthogonal ray paths and using polynomial baselines with the
clinopyroxene calibration of Bell et al 1995. The error associated with estimating the total
absorbance in this way may be considerable but cannot be estimated accurately (Withers 2013).
Nonetheless, this value is nearly identical to the average of the eight SIMS measurements that
create a plateau of 34.3 +/- 0.6 ppm H$_2$O in the central slice of the heated whole block (shown in
Figure 5). When FTIR measurements are scaled to this SIMS value, they overlap in
concentrations, supporting both the initial FTIR estimate, and the initial value still preserved in
the core of the block. Thus to facilitate comparison with the SIMS measurements, the FTIR
concentrations were scaled up from $A/A_0$ to units of ppm wt. H$_2$O using a concentration of 34
ppm wt. H$_2$O.

**Forward models**

Diffusivities were determined from the whole-block diffusion profiles and each of the two
sets of slice profiles (FTIR and SIMS measurements) by least-square fits assuming a starting
concentration of 34 ppm wt. H$_2$O and an equilibrium concentration of 0 ppm and using both 3D-
WB and 3D-NPI approaches. Fits using 1D models are identical to 3D-NPI because diffusion has
not reached the center of the sample.
Inverse models

Inverse analysis of the 3D-WB measurements were performed for both the Kunlun diopside and previously published San Carlos olivine hydration measurements (Demouchy and Mackwell 2006) using comparable parameters, with the main focus on San Carlos olivine. The ray paths for the San Carlos olivine measurements are as follows: for the traverse // [100], R is // [010]; for the traverse // [010], R is // [100]; and for the traverse // [001], R is // [010] (Sylvie Demouchy, personal communication). To determine the best set of parameters, the number of grid cells in each direction was systematically increased, and $\lambda$ was varied to minimize the variance while fitting the olivine profiles as simply as possible (Table 1). Preference was given to odd-numbered grid cell spacing to reduce ambiguity about which values in the central slices were sampled by observations. The maximum number of grid cells was restricted to 5 // [100], 11 // [010], and 9 // [001] to avoid including parameterized sections unconstrained by observations. Final grids were 9 × 9 × 9 in diopside and 5 × 9 × 9 for San Carlos olivine. A constraint weighting factor $\lambda$ of 0.05 was applied for both smoothness and symmetry to both sets of measurements, and the rim value was not constrained for the diopside.

In addition to calculating the formal error $\sigma_i$, which is a minimum value, we assessed the true error on the inversion by simulating a comparable number and distribution of noise-free whole-block hydration profiles followed by inversions. The resulting calculated central value estimate was then compared to the known central value as a function of time and diffusivity // [100] to assess the error. For simplicity, the simulated profiles were produced using only a single-mechanism model of diffusion starting at 0 and increasing to a final solubility of 10 ppm wt. H$_2$O. The diffusivities // [010] and [001] were held constant at $10^{-13.4}$ and $10^{-12.2}$ m$^2$/s, and the diffusivity // [100] was varied from $10^{-11}$ to $10^{-12.5}$ m$^2$/s. Removing the rim value constraint while
Results and Discussion

In the following sections, we first use numerical simulations to determine the errors that might occur in calculated diffusivities if 3D-whole block (3D-WB) data are interpreted using a 3D-non-path-integrated (3D-NPI) model. We then verify both the forward and inverse 3D-WB methods by obtaining both 3D-WB and slice data on a natural diopside sample that has been dehydrated in the laboratory. Finally, we consider some pitfalls that may occur using published 3D-WB data for olivine diffusion.

There are three general issues at stake in interpreting 3D-WB data. One is the effect on calculated diffusivities; another is the effect on calculated concentrations. These are separate issues, and we demonstrate that it is possible to calculate accurate diffusivities from profile shapes, without knowing absolute or even central value concentrations. The final issue is how one interprets 3D-WB data in terms of equilibrium partitioning or solubility. Here accurate determination of absolute concentrations from core to rim is essential.

Numerical simulations

Simulation results are illustrated for 3D-NPI models used to fit simulated 3D-WB data in Figure 2 and for the 1D-NPI models that use the plateau in place of the initial value in Figure 3. The extent of diffusion progress with time is represented by percent saturation of the sample. The absolute values of the errors in the best-fit diffusivity on a log scale were added together across all three orthogonal directions to produce a single summed error for each simulation. The effect
of changing ray paths was also investigated for samples with varying levels of diffusive
anisotropy. The results differ for individual directions, but the final summed errors are the same
as in Figure 2 and Figure 3.

The diffusivities estimated using 3D-NPI applied to 3D-WB simulated data are generally too
large, which corresponds to faster diffusion. This error is concentrated on well-developed
profiles in fast or short directions and results in errors in both the absolute value of the diffusivity
and the apparent anisotropy. This error arises primarily because the 3D-NPI fit requires at least
one diffusion direction fast enough for diffusion to reach the center of the sample to account for
relatively rapid changes in the central value of 3D-WB data.

Changes in the apparent central value

An important potential source of confusion when interpreting 3D-WB measurements comes
from differences between the central values of 3D-WB data and those of slice data. The central
value in a given whole-block profile always changes from the initial value before the
concentration in the actual center of the sample changes because the central measurement
includes the concentration at the rims (Movies 2 and 3; still image in Figure 4). If, for example,
the diffusing species begins to diffuse into a sample block with initial concentration $C_i=0$ from
all sides, then the average value of the concentration measured through the sample thickness in
any given direction necessarily increases from 0. The whole-block profile will then show an
apparent increase in concentration due to contributions from the sample rim in the FTIR
integrated value, but the concentration in the center of the sample may still be 0.

During 3D-NPI analysis of slice measurements, the concentration measured at the center of
each profile must be the same in all three directions because only one central point exists. In
contrast, the central values measured in whole-block profiles, because they represent averages,
may differ for each of the six possible orientations: the profile // [100] with ray path $R$ // [010]; // [100] with $R$ // [010]; // [010] with $R$ // [100]; // [010] with $R$ // [001]; // [001] with $R$ // [100]; and // [001] with $R$ // [010]. This effect is more pronounced when $R$ is parallel to a faster direction.

Effect of diffusion progress

The summed error for the 3D-NPI fit tends to first increase as the difference increases between the central values in the whole-block profiles, which change immediately, and the slice profiles, which remains constant at $C_i=0$ until the total concentration change in the sample reaches ~17% saturation. The error then decreases after diffusion reaches the center of the sample. After hydrogen reaches the center, the shape of the best-fit 3D-NPI profiles are able to match the 3D-WB simulated data much better than in previous stages of diffusion, resulting in improved fits (lower $r^2$ values) and lower summed error (e.g., Figure 2-A1 versus -A2). This improved fit likely results because once hydrogen has reached the center of the sample, the shape of all three orthogonal profiles for both slice and 3D-WB simulated data are controlled by diffusion only in the fast and/or short direction(s) from which hydrogen is infiltrating rather than in all three directions. After the center is reached, diffusivities in the long and/or slow-direction are usually modeled correctly (e.g., // [001] in Figure 2-A1 and -B1), and the error is entirely in the fast or short direction(s). That error in the fast or short direction also tends to decrease with diffusion progress as the system approaches saturation.

Effect of sample geometry and anisotropy

The effect of crystal shape was investigated by holding two sides of a rectangular parallelepiped sample constant at 2.2 mm and varying the length of the third side in a sample
with isotropic diffusion ($\log_{10}D=-14$ in m$^2$/s). The effect of changing anisotropy was investigated in the same way for an equant crystal (each side 2.2 mm) with diffusivities held constant at $\log_{10}D=-14$ m$^2$/s in two orthogonal directions and varied in the third direction (Figure 2B).

The 3D-NPI models typically provide the poorest fit and highest errors in short and/or fast direction(s), which have the most well developed profiles, whereas profiles parallel to slow and/or long directions, which are largely controlled by diffusion from other directions, are relatively easy to fit and do not significantly contribute to the overall error. Equant, isotropic samples have higher error than those with any deviation, perhaps because they lack any direction that is largely controlled by another and so have relatively high errors in all directions. In contrast, 3D-WB data with a single fast direction are modeled remarkably well with 3D-NPI models (right side of Figure 2B) likely because of this low error associated with long/slow directions and because the signal integration, which causes 3D-WB profiles to deviate from slice profiles, is minimized when the ray path is parallel to a slow direction.

In these simulations, the maximum summed error in the diffusivities is around 10% on a log scale. For diffusivities on the order of $10^{-14}$ m$^2$/s, 10% summed log error corresponds to estimated diffusivities in each direction that are about a factor of 5 too fast. This error is concentrated on the fast and short direction(s) of a rectangular parallelepiped, resulting in errors in the calculated extent of anisotropy, and is most pronounced when the concentration in the center of the sample first changes significantly from the initial concentration. These factor of 5 errors are associated with simulated, and therefore perfect, data. As shown in the next section, the error associated with fitting a 3D-NPI model to real 3D-WB measurements may be closer to a full order of magnitude.
A 1D approximation using central plateau values

If the goal is only to extract diffusivities, as opposed to true concentrations, it is possible to obtain better fits using NPI models than those shown Figure 2 by assuming that the central plateau in the 3D-WB data is also the initial value during fitting. This assumption is clearly not the case because the central concentration measured through the whole block is neither the initial nor the true center value, but a path integrated value. Nonetheless, by taking the measured 3D-WB central value as both the initial and final concentration, the fitting procedure becomes entirely dependent on the curvature of the profile, which has enough information to predict a diffusivity that is remarkably accurate, especially for early stages of diffusion. For diffusion progress less than 50%, the total summed error on the three diffusivities is less than 0.5 log units (Figure 3). As diffusion progresses and the shape of the profiles change to become less steep, the assumption of no change in the true central concentration (essentially the approximation here) becomes worse, and the corresponding fits also worsen. A set of three 1D profiles works better than 3D-NPI (which we explored but do not show here) for use in this approximation because it allows greater flexibility to accommodate differences in the 3D-WB profile plateau values (Figure 4). Moreover, with a 1D approximation, profiles are not needed in all three directions to provide a diffusivity estimate. Thus, while the full 3D-WB approach is certainly preferable for obtaining accurate diffusivities and concentrations, the 1D approximation using the central plateau values can provide a reasonable estimate of the diffusivities based on 3D-WB measurements. Interpretations that rely on an understanding of true concentrations, however, still require forward or inverse methods that take path integrations effects into account. Examples of such applications include partitioning, equilibrium solubility, and “metastable equilibrium”, a concept we discuss in the final section on hydrogen diffusion in olivine.
Experiments

After the 3D-WB measurements were obtained for heat-treated Kunlun diopside by FTIR, the central slice of the treated block was cut perpendicular to [100]* and analyzed by both FTIR and SIMS. The resulting hydrogen concentration profiles are reported in Supplementary Table 1 and plotted in Figure 5. When the unpolarized $A/A_o$ FTIR measurements are scaled to a 34 ppm H$_2$O initial value, the central slice zonation and central plateau are very similar to those measured by SIMS, with concentrations overlapping within the analytical precision for many points. Both the SIMS and FTIR measurements show a sudden drop of ~10 ppm wt. H$_2$O near the center of the slice in the profile parallel to [001]. This drop suggests non-diffusive behavior unrelated to measurement precision, although no nearby cracks were visible. The concentrations measured through the treated whole block are lower than the initial value because of path integration through the lower-concentration rims.

We applied the inverse tomographic method to these whole block measurements to solve for the 3-D concentration structure using a 9 x 9 x 9 grid and symmetry and smoothness constraints with weighting parameter $\lambda=0.05$. The fit to the whole block data is shown Figure 6A, and the predicted profiles in the central slices based on the inversion is shown in Figure 6B. The formal error on the inversion $\sigma^2$ is extremely small, only $5\times10^{-4}$, although this value is a minimum and does not include the 2% error from the FTIR area determination. The formal error $\sigma^2$ is not always so small; see Table 1 for $\sigma^2$ as a function of grid spacing and $\lambda$ for the San Carlos olivine measurements discussed below and the Methods section for a description of simulations to assess the true error in these simulations.

Results for the inverse model of the whole-block measurements produced a good fit to both the whole-block and slice measurements with central values around the initial concentration, 34
ppm wt. H₂O, which is identical to the plateau in the SIMS measurements (Figure 5B). Thus, there is strong coherence among the SIMS and FTIR measurements and the inverse approach for solving for 3D concentration zonation within the whole block. These results agree with the simulations showing that the central value of the 3D-WB measurements decreases from the initial value of as a result of signal integration, while the true central value of the slice measurements remains at the initial value.

The hydrogen diffusivities were then calculated by forward models from the whole-block measurements (Table 2) using both 3D-WB and 3D-NPI approaches and from both the FTIR and SIMS slice data using 1D models, which are adequate given that diffusion did not reach the block center. The FTIR and SIMS slice data yield diffusivities that are within 0.1-0.2 log units of each other. The 3D-WB analysis produced diffusivities that are within error but 0.1 to 0.5 orders of magnitude slower than those determined from the slice measurements. In contrast to the excellent agreement and fits of the whole-block and slice measurements analyses, 3D-NPI fits to the whole-block measurements fail to accurately match the measurements, with a correlation coefficient r² only 0.21 versus 0.64 for 3D-WB, and produce diffusivities almost an order of magnitude too fast // [001] and about a factor of five too fast // [010]. Thus, given real uncertainties in analytical measurements, the whole block effects can lead to order of magnitude summed error in diffusivities when path integration effects are not taken into account.

Attempts to improve the fits by adjusting the diffusivities manually did not yield any clear improvement because in 3D-WB analysis, the profiles are highly interdependent and often a fundamentally different shape than in 3D-NPI. For instance, increasing D₁₀₀₁₀ to closely fit the shape of the 3D-WB profile // [001] results in calculated profiles that are lower than most of the central measurements // [010]. Also, the 3D-NPI fits cannot easily match the squat 3D-WB
profiles, and the resulting error is concentrated in the direction with the most well-developed profile, in agreement with the results of the numerical simulations.

An important source of uncertainty in these FTIR measurements arises from a change in the relative heights of the individual O-H stretching peaks, which are grouped together in this analysis to produce a single bulk hydrogen diffusivity. In some dehydration experiments, the final bulk absorbance area is as large or larger than the initial area measured at the same position and orientation. We attribute this change to a re-distribution of the hydrogen among different crystallographic environments similar to the changes first described in clinopyroxene by Skogby and Rossman (1989). A full peak analysis is beyond the scope of this paper, but this result emphasizes both the need for future work that considers O-H peaks individually and the potential importance of a pre-annealing (heating to dryness) and/or a hydrogen saturation step to allow the point defects to reach equilibrium prior to the main experiment.

**Hydrogen diffusion in olivine**

One potential application of the whole-block method is the diffusion of hydrogen in olivine, which is critical to how the mantle melts and deforms. Experimental measurements of hydrogen diffusion have been performed on San Carlos olivine (Mackwell and Kohlstedt 1990; Kohlstedt and Mackwell 1998; Demouchy and Mackwell 2006; Du Frane and Tyburczy 2012) and synthetic forsterite (Demouchy and Mackwell 2003; Padrón-Navarta et al. 2014). However, significant uncertainty remains about how best to interpret and apply these studies to obtain ascent rates based on olivine dehydration profiles (Le Voyer et al. 2014; Thoraval and Demouchy 2014). Here we apply the whole-block method to the hydration profiles of Demouchy...
and Mackwell (2006) both to gain insight into the system and to provide an example of the whole-block approach.

Although Demouchy and Mackwell (2006) interpreted their measurements using non-path-integrated models, their concentration profiles were obtained through the whole block and must, therefore, be revisited using models that take path integration effects into account. This task is significantly complicated by the proposed existence of two separate hydrogen diffusion mechanisms (Kohlstedt and Mackwell 1998): one ("proton-polaron") that is fast but short-lived and dependent on ferric iron content and one ("proton-vacancy") that is relatively slow and modeled as beginning once the fast mechanism saturates at a concentration value that Kohlstedt and Mackwell (1998) call "metastable equilibrium". Isolating and quantifying diffusivities in this sequential two mechanism model requires using the concentration of the final value in profiles measured over short time scales as the initial profile for diffusion profiles measured over longer times scales. Curiously, the slice profiles of Kohlstedt and Mackwell (1998) are not entirely consistent with this approach (Figure 7), possibly as a result of changes in experimental oxygen fugacity or differences in ferric iron content between their 1 hour and 8 hour samples. Demouchy and Mackwell (2006) demonstrate the principle using a consistent set of experimental parameters and 4 ppm wt. H$_2$O for "metastable equilibrium" (Figure 8A – DM06). However, 4 ppm is not a reasonable initial value for fitting their 20 hour hydration profiles if the minimum concentration in the sample is actually lower.

We applied the inverse tomographic method to these whole block measurements to solve for the true central concentration using a $5 \times 9 \times 9$ grid, symmetry and smoothness model constraints with a weighting parameter $\lambda=0.05$. Tomographic inverse modeling provides a good fit to these measurements (Figure 6B) and indicates that the minimum value in this sample is $3.0 \pm 0.1$ ppm.
wt. H₂O. This value is not in the exact center of the sample, consistent with higher measured
whole-block values in the center of the profile // [010] and perhaps indicating some
heterogeneity within the sample similar to that observed in the slice measurements of Kunlun
diopside. Note that the errors reported here include only the formal error on the inversion, \( \sigma_i \), not
the calibration error on the original concentration estimates based on FTIR, which is on the order
of a few ppm wt. H₂O.

Approximately 25% of the observed 4 ppm wt. H₂O plateau value in the 20 hour San Carlos
olivine hydration profile of Demouchy and Mackwell (2006) is the result of signal integration
through the whole block. This difference, though trivial in absolute terms (3 ppm vs. 4 ppm wt.
H₂O, within calibration error for FTIR measurements), is important for two reasons. First, when
applying whole-block forward models and the sequential two mechanism model, 3 ppm wt. H₂O
is more appropriate than 4 ppm wt. H₂O as a transitional “metastable equilibrium” value. The
error in the central value translates directly into an error in the “metastable equilibrium” state,
and this error is preventable by applying the 3D-WB method. Second, there is actually an
inconsistency in the olivine measurements and their interpretation for a central value of 3 ppm
wt. H₂O. The metastable equilibrium model dictates that the olivine reaches a metastable
saturation value after 1 hour. This value is 3 and not 4 ppm H₂O, based on the inverse modeling
of the 3D-WB measurements. This interpretation is inconsistent with the maximum
concentrations in the 1 hour profiles (4 to 5 ppm wt. H₂O at the rims), which are certainly greater
than the central minimum concentration in the 20 hour sample (3 ppm wt. H₂O). This difference
cannot be dismissed as simply within error for FTIR because calibration error generally affects
all values the same way, i.e., all reported values are wrong by approximately the same amount in
only one direction. Thus, the model in which two diffusion mechanisms operate sequentially and
have some “metastable equilibrium” concentration is likely in error. At stake is not just an
estimate of a particular diffusivity, but a fundamental understanding of how hydrogen diffuses in
Fe-bearing olivine. Does diffusion proceed primarily by one dominant mechanism or multiple?
Assuming multiple mechanisms are important, under what time scales do they operate, and to
what extent can they be separated and individually quantified?

These questions are difficult to answer unambiguously with the available published profiles.
Figure 8 shows a series of possible fits that all take path integration into account. In Figure 8A
we show 3D-WB profiles that use the revised “metastable equilibrium” value of 3 ppm H$_2$O and
the diffusivities from both the original interpretation of Demouchy and Mackwell (2006; labeled
DM06 3D-WB) and Kohlstedt and Mackwell (1998; labeled KM98 3D-WB). The diffusivities
from Demouchy and Mackwell (2006) provide a much better fit to this set of measurements
($r^2$=0.87) than the diffusivities of Kohlstedt and Mackwell (1998) ($r^2$=0.61). Two examples of
possible alternative fits to the profiles from Demouchy and Mackwell (2006) are also shown in
Figure 8: a single diffusion mechanism and two mechanisms that operate simultaneously and
assume a fast mechanism that has diffusivities taken from Kohlstedt and Mackwell (1998) and
saturates at 3 ppm wt. H$_2$O. These models provide slightly worse $r^2$ values than the 3D-WB
revised sequential model (0.79 for single mechanism and 0.83 for simultaneous vs. 0.87), but
they have the virtue of allowing the concentration at the rims in the 1 hour experiment (4-5 ppm
wt. H$_2$O) to be greater than a “metastable equilibrium” value of 3 ppm H$_2$O. The single
mechanism model is also much simpler to apply. Other fits are certainly possible, e.g., using
different values at which the fast mechanism saturates or by varying the diffusivities, particularly
for the rough 20 hour profiles // [100]. The original fits of Demouchy and Mackwell (2006) are
very similar to many other models, including the one that applies the true central concentration
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of 3 ppm H$_2$O as the “metastable equilibrium” starting concentration in the 20 hour experiments and the model using simultaneously operating mechanisms. This agreement arises because of the success of the 1D approximation using the central 3D-WB plateau value (Figure 3), which is in essence what Demouchy and Mackwell (2006) did. Experiments that show greater diffusion progress would better enable distinction among the different models.

Two conclusions can be drawn from this exercise with regard to hydrogen diffusion in olivine. First, taken in isolation, the hydration profiles reported by Demouchy and Mackwell (2006) can be adequately modeled by a relatively simple (and therefore preferable) single mechanism model. Second, none of the modeling approaches discussed here can satisfactorily explain or reconcile the large (0.9 to 1.8 orders of magnitude) discrepancy between the slow mechanism hydrogen diffusivity in San Carlos olivine observed by Demouchy and Mackwell (2006) and that observed by Kohlstedt and Mackwell (1998) and in forsterite (Figure 10 and Table 3). In particular, Kohlstedt and Mackwell (1998) show a clear change in anisotropy in San Carlos olivine from a fast direction // [100] at 1 hour to a fast direction // [001] at 8 hours that is not as readily apparent in the Demouchy and Mackwell (2006) profiles. Additional experiments, especially those that consider site-specific diffusivity as in Padrón-Navarta et al. (2014), are required to fully understand this system.

**Implications**

A new treatment of whole-block measurements successfully yields hydrogen diffusivities in three orthogonal directions of a rectangular prism without cutting the sample. This approach will simplify future diffusion experiments that rely on FTIR and be bolstered by the results of measurements from cut samples. Multiple hydrogen diffusion experiments are now possible.
using the same sample (e.g., a time series using profiles), which will minimize both the amount
of sample material needed and the error associated with heterogeneity among samples from the
same locale. The efficacy of the method has been demonstrated experimentally for hydrogen
diffusion in diopside. Because the differences between whole-block and slice measurements are
often significant, path integration effects must be considered when evaluating whole-block
measurements. Failure to include these path integration effects may result in errors of half an
order of magnitude or more in fast and/or short directions. In cases where diffusion has not
progressed significantly, it is possible to use a 1D approximation with the whole-block central
plateau to accurately obtain diffusivities with errors less than 0.5 log units because diffusivities
are more sensitive to profile shape than the absolute concentration of the central plateau.
However, in cases where absolute concentrations are required, forward or inverse 3D-WB
models are necessary to recover core concentrations. An important application of these effects is
in the interpretation of olivine diffusion experiments. We use the new whole block forward and
inverse methods to re-evaluate whole block measurements of olivine dehydration (Demouchy
and Mackwell 2006). The resulting diffusivities are within the range of those originally
published for the slower “proton-vacancy” mechanism, but could also be consistent with a
simpler single diffusive mechanism. The newly determined central value concentrations create
inconsistencies with existing interpretations of dual mechanisms and “metastable equilibrium”
concentrations. The whole-block approach is likely to prove very useful for future work on
olivine, pyroxene, and other nominally anhydrous minerals to illuminate the parameters that
define different hydrogen diffusion mechanisms (particularly the role of differing
crystallographic environments as in Padrón-Navarta et al. 2014) for use in broader Earth science
applications such as determining crystal residence times (Danyushevsky et al. 2002), magma
degassing rates (Hauri 2002), and ascent times (Demouchy et al. 2006, Peslier and Luhr 2006, Denis et al. 2013, Chen et al. 2013); interpreting hydrogen concentrations in melt inclusions (Portnyagin et al. 2008, Chen et al. 2011, Gaetani et al. 2012, Bucholz et al. 2013, Lloyd et al. 2013) and mantle xenoliths (review by Peslier 2010); and electrical conductivity (e.g., Karato 1990).

Acknowledgements

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Figure 1. Sketch showing representative depth slices of an initially dry rectangular prism that has been partially hydrated during a diffusion experiment. The whole-block approach developed here evaluates measurements derived from signals that are transmitted and absorbed by all the layers of the entire sample along the transmission direction rather than cutting a slice from the center of the sample.

Figure 2. Sensitivity maps showing summed error in the diffusivities on a log scale for fits to simulated 3D-WB data using a diffusion model that does not take path integration into account (the 3D-NPI model) (A) for isotropic diffusion as a function of sample shape and diffusion progress and (B) in an equant crystal as a function of anisotropy and diffusion progress. Example profiles are labeled and shown below each map. In all simulations, the diffusing species is entering the sample, the initial concentration is 0, and the equilibrium concentration is $S$. $D$ values are the initial diffusivities in $m^2/s$ used to simulate the 3D-WB data (only 20 simulated data points out of 100 are shown for clarity) in each orthogonal direction ($[100]$, $[010]$, and $[001]$; length of crystal along $[100]$ is 2.2 mm in all examples), and $D_{fit}$ is the diffusivity in each direction in $m^2/s$ determined using a least-squares best-fit to the 3D-NPI model. Ray paths $R$ are // $[010]$ for profiles // $[100]$, $R$ // $[100]$ for profiles // $[010]$, and $R$ // $[100]$ for profiles // $[001]$. For comparison, simulated slice profiles (from 3D-NPI equations) are shown for each example.

Figure 3. Sensitivity maps calculated using the same numerical simulation approach as in Figure 2 showing summed error in the diffusivities for a set of three 1D-NPI models fit to 3D-
WB data using the the 3D-WB plateau concentration in place of the true initial value (zero), thus ignoring the apparent drop in the 3D-WB central concentration and emphasizing the profile curvature, which is what primarily determines the calculated diffusivities.

Figure 4. Simulated diffusion profiles for the hydration of an initially dry cube in which diffusion is strongly anisotropic. $D$ is diffusivity in each direction, and $R$ is the direction of the ray path of the infrared beam. See Movies 2 and 3 for changes in diffusion profiles with time.

Figure 5. Concentration profiles in diopside after partial dehydration for 75 hours at 1000 °C measured using unpolarized FTIR and SIMS for (A) the uncut block (3D-WB) and (B) a slice cut from the center of the sample. Diffusivities (D) were determined by least square fits in each direction for the 3D-WB FTIR measurements using both the 3D-WB model and the non-path-integrated 3-dimensional model (3D-NPI) and for the slice FTIR and SIMS measurements using 3D-NPI models. The initial concentration is assumed to be 34 ppm wt. H$_2$O and uniform, and the equilibrium concentration is assumed to be 0. The measurements are provided in Supplementary Table 1, and error estimates and correlation coefficients are listed in Table 2.

Figure 6. (A) Results of inverse analyses showing FTIR 3D-WB measurements, predicted values based on inverse model results, and associated residuals for the dehydrated Kunlun diopside from this study. (B) FTIR measurements of a slice cut from the center of the sample and predicted values based on inverse analysis. Light grey dashed lines show the sub-divisions in the $9 \times 9 \times 9$ grid used to model the system, where each block is assumed to contain a uniform concentration. Propagated errors plot within the symbols.
Figure 7. Hydrogen profiles // [100] from central slice FTIR measurements reproduced from Kohlstedt and Mackwell (1998). The original paper used a value of 7 H/10^6 Si (red line) as the initial value when fitting the 8 hour data, but this “metastable equilibrium” value cannot also be used as the final value to fit their 1 hour data. Note the different temperatures, pressures, and oxygen fugacities of the two experiments.

Figure 8. Whole-block FTIR measurements (squares) for hydrogen diffusion experiments at 1 and 20 hours on San Carlos olivine at 200 MPa, the Ni/NiO buffer, 900 °C, and observed initial concentration C_i=0 reproduced from Demouchy and Mackwell (2006), and five different approaches to modeling diffusivities based on these profiles. Error bars are shown in the original text and are omitted here for clarity. (A) “DM06” is the original fit by Demouchy and Mackwell (2006) that does not consider path integration effects and uses 4 ppm wt. H_2O (dotted grid line) as a transitional state between two mechanisms. “DM06 3D-WB” uses the diffusivities estimated from the original fit with the whole-block forward model and a transitional state of 3 ppm wt. H_2O (the central value in the sample determined by tomography; see text). “KM98 3D-WB” uses an identical approach as “DM06 3D-WB” except the diffusivities are those expected from Kohlstedt and Mackwell (1998). “Single mech.” illustrates a possible fit to both the 1 hour and 20 hour profiles using the same diffusivity, initial concentration, and solubility for both sets of concentration profiles. (B) Shows the two mechanisms described by Demouchy and Mackwell (2006) modeled as operating simultaneously rather than sequentially. For simplicity and consistency with previous work, the fast mechanism diffusivities (mech. 1) were held constant at the values expected based on Kohlstedt and Mackwell (1998), and best fit slow diffusivities were
obtained by fitting to both sets of profiles simultaneously. The diffusivity estimates for all models are given in Table 3 and plotted on an Arrhenius diagram in Figure 10.

Figure 9. Observed whole-block measurements for hydrogen diffusion in San Carlos olivine (Demouchy and Mackwell 2006) after 20 hours at 900 °C, predicted whole-block measurements based on inverse model results, and associated residuals. Light grey dashed lines show the sub-divisions in the $5 \times 9 \times 9$ grid used to model the profiles, where each block is assumed to contain a uniform concentration. Propagated errors on the predicted values plot within the symbols.

Figure 10. Arrhenius diagram of hydrogen diffusivity measurements in olivine. Self-diffusivity is from Du Frane and Tyburczy (2012). New diffusivity estimates from this study (Figure 8) based on the measurements of Demouchy and Mackwell (2006; labeled DM06) are shown for both the assumption of a single diffusion mechanism and for a slow mechanism assumed to operate simultaneously with the fast mechanism of Kohlstedt and Mackwell (1998; labeled KM98). PN is Padrón-Navarta et al. (2014), and bracketed elements in PN refer to different H defects inferred from FTIR absorption bands. The five studies in which orientation was not determined (Padrón-Navarta et al. 2014, Gaetani et al. 2012, Hauri 2002, Chen et al. 2011, and Portnyagin et al. 2008, who report a minimum diffusivity) are plotted only on the first panel for comparison.

List of table headings

Table 1. The number of grid cells parallel to each direction and constraint weighting factor $\lambda$ used to model the 20 hour San Carlos olivine hydrogen profiles from Demoucy and Mackwell
(2006), resulting goodness of fit parameter $\sigma^2$, and estimated minimum concentration in the center in ppm wt. H$_2$O.

Table 2. Diffusivities ($D$ in m$^2$/s), associated errors, and correlation coefficients ($r^2$) determined for Kunlun diopside at 1000°C using four different approaches. “3D-WB” is the whole-block path-integrated forward model. “1D” and “3D-NPI” are 1- and 3-dimensional non-path-integrated models. The reported errors are based on 95% confidence intervals in the fitting procedure. Diffusivity estimates // [100]* from slice measurements are not available and are labeled “N/A”.

Table 3. Diffusivity estimates in m$^2$/s for various forward models (Figure 8) to the whole-block measurements of Demouchy and Mackwell (2006). Diffusivities reported by Kohlstedt and Mackwell (1998) are provided for comparison.

Supplementary Table 1. Hydrogen concentration as a function of position in heat-treated Kunlun diopside. Total lengths are 3450±10 μm // [100]*, 1609±5 μm // [010], and 1757±6 μm // [001]. FTIR measurements are reported assuming a uniform initial concentration of 34 ppm wt. H$_2$O. Slice data were not available // [100]* and are labeled “N/A”.
Whole-block profile // [100]
with ray path R // [001]
Fig 3 (1D plateau approximation)

A. Isotropic diffusion, changing shape

B. Equant sample, changing anisotropy

Length of inequant side (% other two sides)

$\Delta \log_{10} D$ from orthogonal directions

Diffusion progress (% saturation)

Summed error in $\log_{10} D_{eff}$
Fig 5

A. 3D-WB profiles (Peak area/Initial)

- // [100]* (mm)
  - logD (m²/s)
    - 3D-WB: -13.0
    - 3D-NPI: -12.8

- // [010] (mm)
  - logD (m²/s)
    - 3D-WB: -13.4
    - 3D-NPI: -13.7

- // [001] (mm)
  - logD (m²/s)
    - 3D-WB: -13.6
    - 3D-NPI: -12.4

B. Slice profiles (Peak area/Initial)

- logD (m²/s)
  - FTIR: -13.1
  - SIMS: -13.3

- // [010] (mm)

- // [001] (mm)
  - ppm wt. H₂O

- FTIR measurement
- SIMS measurement
- 3D-WB fit to 3D-WB
- 3D-WB fit to 3D-NPI
- 1D fit to slice FTIR
- 1D fit to slice SIMS
Fig 9

3D-WB measurements, tomography grid, predicted value (1/grid column), residuals

Hydrogen (ppm wt. H₂O)

// [100] (mm) // [010] (mm) // [001] (mm)
<table>
<thead>
<tr>
<th>grid // [100]</th>
<th>grid // [010]</th>
<th>grid // [001]</th>
<th>$\lambda$</th>
<th>$\sigma^2$</th>
<th>concentration at the center (ppm wt. H2O)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>1</td>
<td>1</td>
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