

## **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 three-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 <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