**Determining diffusivities, prefactors and ages using FTIR data and a diffusion model**

The time evolution of the concentration of molecular water $C\_{m}$ in a uniform slab of thickness $L$ may be described using a diffusion equation

$$\frac{∂C\_{m}(x,t)}{∂t}=\frac{∂}{∂x}\left[D\_{m}(C\_{m}\left(x\right))\frac{∂}{∂x}C\_{m}(x,t)\right]$$

 Equation S1

where $t$ is time, $x$ is the position across the thickness of the slab and $D\_{m}(C\_{m}(x))$ is the local diffusivity for molecular water which depends on the concentration. In this work, the shards of rhyolite glass are assumed to be surrounded on both sides by water; the concentration at the walls is fixed to the solubility of water $C\_{sat}$ in the glass. The initial concentration of molecular water is set to be $C\_{m}(x,0)=0$ throughout the shard. To find the concentration at some time $t$, we solve the above numerically using a finite difference method to find derivative terms and an explicit Euler scheme to propagate over time.

Two different treatments of diffusivity $D\_{m}(C\_{m})$ are presented for comparison. Firstly, we consider a constant diffusivity which does not vary with local concentration, $D\_{m}\left(C\_{m}\right)=D\_{0}$. Secondly, we use the concentration dependent expression of Zhang and Behrens (2000),

$$D\_{m}\left(C\_{m}\right)=Z×exp\left[\left(14.08-\frac{13,128}{T}-\frac{2.796P}{T}\right)+\left(-27.21+\frac{36,892}{T}+\frac{57.23P}{T}\right)X\right]$$

 Equation S2

where $Z$ is a constant prefactor, $D\_{m}\left(C\_{m}\right)$ is the diffusivity in micrometres squared per second, $P$ is the pressure in megapascals, $T$ is the temperature in kelvin, and $X$ is the mole fraction of total water on a single oxygen basis. To find $X$, we use an effective molecular weight of 32.2094982 for this rhyolite composition and assume a fixed concentration of hydroxyl groups due to minimal interconversion below the glass transition temperature, as explained in the text.

Given a measured thickness $L$ and a known diffusivity for molecular water $D\_{m}(C\_{m})$, it is possible to find $C\_{m}(x,t)$ and an average hydration $\overbar{C\_{m}}$ at any time $t$. Conversely, given an age $t$ and a measured average hydration $C\_{m, FTIR}$, it becomes possible to determine the diffusivity $D\_{0}$ or prefactor $Z$ for the concentration dependent diffusivity in Equation S2. For simplicity, we initially consider the case of a constant diffusivity $D\_{0}$. This may be re-cast as a root-finding problem, where we may define a function

$$f\left(D\_{0},t\right)=\overbar{C\_{m}}\left(D\_{0},t\right)-C\_{m, FTIR}$$

and find the value of $D\_{0}$ where $f\left(D\_{0},t\right)=0$. Since a larger $D\_{0}$ will always lead to greater hydration at a given age, the function $f\left(D\_{0},t\right)$ varies monotonically and will change sign either side of the solution. Thus, we are able to apply an iterative bisection scheme to find the root: initial limits for $D\_{0}$, termed $D\_{u}$ and $D\_{l}$, are chosen such that $f(D\_{u})>0$ and $f(D\_{l})<0$; the value of $f(D\_{1})$ is determined, where $D\_{1}=\frac{1}{2}(D\_{u}+D\_{l})$; if $f(D\_{1})>0$, then the solution lies between $D\_{l}$ and $D\_{1}$, while if $f(D\_{1})<0$, the solution lies between $D\_{1}$ and $D\_{u}$; the process is repeated using the new limits until the desired convergence is reached.

Note that the same process may be applied to find a prefactor $Z$ (Equation S2), or the age of a shard given a pre-determined diffusivity or prefactor. The latter is proposed as a way to date shards using measured thicknesses and hydrations.

When upper and lower estimates for the diffusivity span many orders of magnitude, bisection may require more than a dozen iterations to reach a desired accuracy. Since each iteration requires solution of the diffusion equation, it is desirable to have a fast implementation of the solver. In this work, MATLAB code kindly provided by Michael Hudak (Hudak and Bindemann 2020; Hudak et al 2021) was modified and translated into Fortran, pre-compiled using the Intel oneAPI compiler (ifort) and used to find $\overbar{C\_{m}}(t)$ given a thickness, temperature, pressure, boundary concentration, and a definition of diffusivity. The root-finding itself was implemented using GNU Octave. Code for the solver and bisection scheme may be provided on request.