

**APPENDIX B:  
MODEL DESCRIPTION AND EXAMPLE MATLAB OUTPUT**

Here we describe our model for diffusive re-equilibration of H<sub>2</sub>O and  $f_{O_2}$  within an olivine-hosted melt inclusion found in the MATLAB file ‘DiffusiveEquilibration.m’. For simplicity, a spherical olivine crystal with a spherical melt inclusion located at the center of the olivine is considered and spherically symmetric transport assumed. The computational domain consists only of the olivine. Isotropic diffusion of protons and metal vacancies is allowed to occur through the olivine crystal. Experimentally determined diffusivities  $D_{H[001]}$  and  $D_{V[001]}$  are used in the model (Demouchy and Mackwell, 2006; Wanamaker, 1994). The interior boundary between the melt inclusion and the host olivine is a flux boundary, following Qin et al. (1992). The olivine-external melt boundary conditions are constant over the entire surface of the olivine crystal and set to be in equilibrium with the external environment. H<sub>2</sub>O contents in the olivine are calculated using an experimentally determined partition coefficient (Hauri et al., 2006). Metal vacancy concentrations in olivine involved in  $f_{O_2}$  re-equilibration are calculated using Equation 18 from Dohmen & Chakraborty (2007). Notably, their calibration for equilibrium metal vacancy concentration is for anhydrous olivines, but there are no studies for equilibrium vacancy concentrations in hydrous olivine as a function of  $f_{O_2}$ , therefore the anhydrous olivine concentrations are used as a best estimate. As the  $f_{O_2}$  of the melt inclusion changes with time, the equilibrium metal vacancy concentration at the olivine-melt inclusion boundary is recalculated at every time step using the  $f_{O_2}$  of the melt inclusion calculated at the previous time step. Dimensions of the olivine and melt inclusion were constrained using the average smallest radii from the experiments. Details and values of the parameters used are given in Table B1.

The oxidation state of the melt inclusion is calculated using oxygen mass balance. For every O incorporated at the olivine-melt inclusion boundary, one metal vacancy is created. This results in the reduction of two Fe<sup>3+</sup>, therefore the moles of Fe<sup>3+</sup> and Fe<sup>2+</sup> in the melt inclusion at time  $t$  are related to their initial concentrations in the following manner:

$$m_{Fe^{3+}}^t = m_{Fe^{3+}}^i - 2 * m_{V_{Me}}^t \quad (B.1)$$

$$m_{Fe^{2+}}^t = m_{Fe^{2+}}^i + 2 * m_{V_{Me}}^t \quad (B.2)$$

where  $m_{V_{Me}}^t$  is the number of metal vacancies created at the olivine-melt inclusion interface since the beginning of re-equilibration ( $t = 0$ ), an  $i$  and  $t$  superscripts indicates initial conditions and conditions at time  $t$ , respectively. A “potential” amount of vacancies required to diffuse in order for complete equilibration to occur is calculated based on the difference in  $Fe^{3+}/Fe^{2+}$  ratios between the external melt (or the equilibrium value) and the initial melt inclusion:

$$\frac{m_{Fe^{3+}}^{eq}}{m_{Fe^{2+}}^{eq}} = \frac{m_{Fe^{3+}}^i - 2 * m_{V_{Me}}^{potential}}{m_{Fe^{2+}}^i + 2 * m_{V_{Me}}^{potential}} \quad (B.3)$$

where  $m_{V_{Me}}^{potential}$  is the “potential” moles of metal vacancies to be created at the melt inclusion-olivine interface and the  $eq$  superscript indicates equilibrium values of the external melt. Eq. B.3 can be rearranged to give an expression of “potential” moles of metal vacancies:

$$m_{V_{Me}}^{potential} = \frac{1}{2} \frac{\left( m_{Fe^{3+}}^i - \frac{m_{Fe^{3+}}^{eq}}{m_{Fe^{2+}}^{eq}} * \left( \frac{1}{m_{Fe^{2+}}^i} \right) \right)}{\left( 1 + \frac{m_{Fe^{3+}}^{eq}}{m_{Fe^{2+}}^{eq}} \right)} \quad (B.4)$$

Absolute values for oxygen fugacity within the melt inclusions are determined using Eq. 7 from Kress & Carmichael, (1991).

**Table B1: Model Parameters**

Parameter	Definition	Value	Reference
$K_d^H$	H partition coefficient	0.0015	Hauri et al., 2006
$V_{Me}^n(fO_2)$	Molar concentration of metal vacancies in olivine as function of $fO_2$	e.g. $8.37 \times 10^{-5}$ (at 1100°C and NNO) $1.89 \times 10^{-4}$ (at 1250°C and NNO) $1.23 \times 10^{-4}$ (at 1100°C and NNO+1)	Dohmen & Chakraborty, 2007 (Eq. 18)
$R_{MI}$	Radius of melt inclusion	$6.5 \times 10^{-5}$ m	(Representative dimension from experiments)
$R_{olivine}$	Radius of olivine	$5 \times 10^{-4}$ m	(Representative dimension from experiments)
$D_{H[001]}$	H diffusivity	$6.10 \times 10^{-12}$ m <sup>2</sup> /s (at 1100°C) $5.65 \times 10^{-11}$ m <sup>2</sup> /s (at 1250°C)	Demouchy & Mackwell, (2006)
$D_{V[001]}$	Metal vacancy diffusivity	$6.30 \times 10^{-12}$ m <sup>2</sup> /s (at 1100°C) $5.64 \times 10^{-11}$ m <sup>2</sup> /s (at 1250°C)	Wanamaker, (1994)

## Example Figures Output from MATLAB Script:

Fig. 1: Concentrations in Melt Inclusion

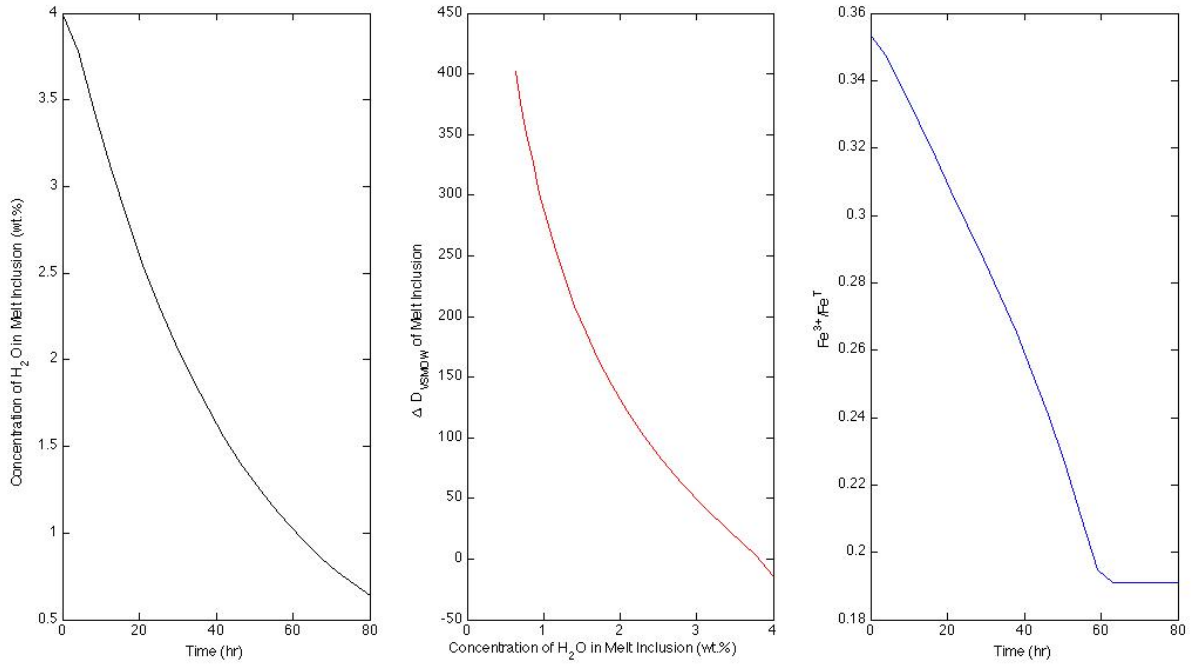


Fig. 2: Concentrations in Olivine

