MgSi Paper Supplement

1 Equilibrium Reactions

$$K_1 = \frac{a_{Mg}a_O}{a_{MgO}} = \frac{X_{Mg}X_O}{X_{MgO}} = \frac{M_{Mg}M_O M_m}{M_{MgO}M_c^2} \tag{1}$$

$$K_2 = \frac{a_{Si}a_O^2}{a_{SiO_2}} = \frac{X_{Si}X_O^2}{X_{SiO_2}} = \frac{M_{Si}M_O^2 M_m}{M_{SiO_2}M_c^3} \tag{2}$$

$$K_3 = \frac{a_{Fe}a_O}{a_{FeO}} = \frac{X_{Fe}X_O}{X_{FeO}} = \frac{M_{Fe}M_O M_m}{M_{FeO}M_c^2} \tag{3}$$

$$K_4 = \frac{a_{MgO}a_{SiO_2}}{a_{MgSiO_3}} = \frac{X_{MgO}X_{SiO_2}}{X_{MgSiO_3}} = \frac{M_{MgO}M_{SiO_2}}{M_{MgSiO_3}M_m} \tag{4}$$

$$K_5 = \frac{a_{FeO}a_{SiO_2}}{a_{FeSiO_3}} = \frac{X_{FeO}X_{SiO_2}}{X_{FeSiO_3}} = \frac{M_{FeO}M_{SiO_2}}{M_{FeSiO_3}M_m} \tag{5}$$

1.1 Change with Temperature

$$\frac{(\partial_T K_1)}{K_1} = \frac{(\partial_T M_{Mg})}{M_{Mg}} + \frac{(\partial_T M_O)}{M_O} + \frac{(\partial_T M_m)}{M_m} - \frac{2(\partial_T M_c)}{M_c} - \frac{(\partial_T M_{MgO})}{M_{MgO}} \tag{6}$$

$$\frac{1}{K_2}\partial_T K_2 = \frac{1}{M_{Si}}\partial_T M_{Si} + \frac{2}{M_O}\partial_T M_O + \frac{1}{M_m}\partial_T M_m - \frac{3}{M_c}\partial_T M_c - \frac{1}{M_{SiO_2}}\partial_T M_{SiO_2} \tag{7}$$

$$\frac{1}{K_3}\partial_T K_3 = \frac{1}{M_{Fe}}\partial_T M_{Fe} + \frac{1}{M_O}\partial_T M_O + \frac{1}{M_m}\partial_T M_m - \frac{2}{M_c}\partial_T M_c - \frac{1}{M_{FeO}}\partial_T M_{FeO} \tag{8}$$

$$\frac{1}{K_4}\partial_T K_4 = \frac{1}{M_{MgO}}\partial_T M_{MgO} + \frac{1}{M_{SiO_2}}\partial_T M_{SiO_2} - \frac{1}{M_{MgSiO_3}}\partial_T M_{MgSiO_3} - \frac{1}{M_m}\partial_T M_m \tag{9}$$

$$\frac{1}{K_5}\partial_T K_5 = \frac{1}{M_{FeO}}\partial_T M_{FeO} + \frac{1}{M_{SiO_2}}\partial_T M_{SiO_2} - \frac{1}{M_{FeSiO_3}}\partial_T M_{FeSiO_3} - \frac{1}{M_m}\partial_T M_m \tag{10}$$

$$\tag{11}$$

1.2 Molar Continuity

$$0 = \partial_T M_{Mg} + \partial_T M_{MgO} + \partial_T M_{MgSiO_3} + (\partial_T M_{MgO})_{erosion} + (\partial_T M_{MgSiO_3})_{erosion} \tag{12}$$

$$0 = \partial_T M_{Si} + \partial_T M_{SiO_2} + \partial_T M_{MgSiO_3} + \partial_T M_{FeSiO_3} + (\partial_T M_{SiO_2})_{erosion} + (\partial_T M_{MgSiO_3})_{erosion} + (\partial_T M_{FeSiO_3} \tag{13}$$

$$0 = \partial_T M_{Fe} + \partial_T M_{FeO} + \partial_T M_{FeSiO_3} + (\partial_T M_{FeO})_{erosion} + (\partial_T M_{FeSiO_3})_{erosion} \tag{14}$$

$$0 = \partial_T M_O + \partial_T M_{MgO} + \partial_T M_{FeO} + 2\partial_T M_{SiO_2} + 3\partial_T M_{MgSiO_3} + 3\partial_T M_{FeSiO_3} + (\partial_T M_{MgO})_{erosion} + (\partial_T M_{Fe} \tag{15}$$

$$0 = \partial_T M_m + \partial_T M_{MgO} + \partial_T M_{FeO} + \partial_T M_{SiO_2} + \partial_T M_{MgSiO_3} + \partial_T M_{FeSiO_3} + (\partial_T M_{MgO})_{erosion} + (\partial_T M_{FeO})_e \tag{16}$$

$$0 = \partial_T M_c + \partial_T M_{Mg} + \partial_T M_{Fe} + \partial_T M_{Si} + \partial_T M_O \tag{17}$$

$$\tag{18}$$

1.3 Erosion Term

$$(\partial_t M_i)_{erosion} = \frac{sgn(M_{b,i} - M_i)}{\tau}[(|M_i/M_{b,i} - 1| + 1)^2 - 1] \tag{19}$$

$$(\partial_T M_i)_{erosion} = (\partial_t M_i)_{erosion}\Big/\frac{T_c}{dt} \tag{20}$$

1.4 Solution

With total moles in the mantle M_m and core M_c, There are eleven components M_i in the system and eleven equations. This system is solved to obtain a system of first-order nonlinear ODEs of the form $\partial_T M_i = f(M_i, K_j)$ where M_i represent each molar species in the mantle and core and K_j is each equilibrium value. Due to the highly non-linear nature of this set of equations, this results in the solution including several thousand terms each. Further simplification of the equations may be possible, but there is no significant performance penalty so it was not considered a problem. Note that $K_j = K_j(T_c)$ is an analytic function of temperature.

2 Coupled Thermo-Chemical Evolution

The chemical reactions are incorporated into the core-mantle thermal evolution model. With two temperatures T_{CMB} and T_{UM}, and nine molar species, this creates and eleven-component state vector **x**. At each timestep, the mantle uses T_{CMB} and T_{UM} to compute a heat flux at the surface and core-mantle boundary and uses this to compute $\partial_t T_{UM}$. Then, the system of chemical reaction equations uses the current T_{CMB} and molar concentrations M_i to compute $\partial_T M_i$.

The core uses Q_{CMB} from the mantle and $\partial_T M_i$ from exsolution of light elements to compute $\partial_t T_{CMB}$. Finally, this change in temperature is used to compute the change in molar concentrations with time by $\partial_t M_i = \partial_T M_i \partial_t T_{CMB}$. This allows for the computation of $\partial_t \mathbf{x}$ at any state.

We compute the heat release with change in CMB temperature using $\tilde{Q}_{g,i} \partial_t T_c = Q_{g,i}$ where $\tilde{Q}_{g,i}$ depends upon the change in wt% of the light element with temperature (see Nimmo 2015 eq. 73). This is easily computed given $\partial_T M_i$. Then, we include these in addition to the inner-core and secular cooling terms to obtain
$$\tilde{Q}_T = \tilde{Q}_s + \tilde{Q}_g + \tilde{Q}_L + \tilde{Q}_{g,MgO} + \tilde{Q}_{g,FeO} + \tilde{Q}_{g,SiO2} + \tilde{Q}_{L,MgO} + \tilde{Q}_{L,FeO} + \tilde{Q}_{L,SiO2}$$
which is used the the calculation of the core energy budget (see Nimmo 2015 eq. 73).

In a similar manner, we modify the expression for entropy in the core by including terms for exsolution of light elements $\tilde{E}_T = \tilde{E}_s + \tilde{E}_g + \tilde{E}_L + \tilde{E}_H + \tilde{E}_{g,MgO} + \tilde{E}_{g,FeO} + \tilde{E}_{g,SiO2}$

(see Nimmo 2015, eq. 72). As noted in the main text, we do not allow light elements to diffuse into the core because they would form a thin stratified layer and fail to mix into the bulk core. We implement this by requiring that $\partial_t M_i \leq 0$ for i=Mg,Si,O. We do allow Fe to diffuse into the core, but this happens only rarely as a result of changing mantle composition due to mantle overturn in our models and must be matched by exsolution of light elements. Oxygen cannot diffuse into the core and therefore the O concentration cannot increase, which requires that any FeO entering the core be matched by MgO or SiO2 pulling Oxygen out at the same or faster rate.