

S3 Derivation of mass balance boundary condition between glass and crystal

Parameters

$[Li_i^{\blacksquare}]$	Interstitial Li per formula unit plagioclase in the crystal
$[Li_{A1}^x]$	Li on A1 sites per formula unit plagioclase in the crystal
$[Li^{pl}]$	Total Li per formula unit plagioclase in the crystal
$[Li^{gl}]$	Li per formula unit plagioclase in the glass
$[V'_{A1}]$	Vacancies on A1 sites per formula unit plagioclase in the crystal
K	Equilibrium constant for the partitioning of Li between A1 and interstitial sites
$K_i^{pl/gl}$	Partition coefficient of the interstitial Li species between crystal and glass
$K_{A1}^{pl/gl}$	Partition coefficient of the A1 Li species between crystal and glass
D_{gl}	Diffusion coefficient of Li in the glass
D_{Li}^i	Diffusion coefficient of the interstitial mechanism in the crystal
D_{Li}^A	Diffusion coefficient of the vacancy mechanism in the crystal
Δx	Distance between grid points
x_{if}	Position of the interface

Local equilibrium at the interface at $x = x_{if}$

Internal partitioning equilibrium of Li between the two sites:

$$[Li_{A1}^x] = K [Li_i^{\blacksquare}] [V'_{A1}] \quad (S3.1)$$

Partitioning of the two Li species between plagioclase and glass:

$$[Li_i^{\blacksquare}] = K_i^{pl/gl} [Li^{gl}] \quad (S3.2)$$

$$[Li_{A1}^x] = K_{A1}^{pl/gl} [Li^{gl}] \quad (S3.3)$$

For the total Li in the plagioclase, $[Li^{pl}] = [Li_i^{\blacksquare}] + [Li_{A1}^x]$, at the interface we obtain from the last two equations:

$$[Li^{pl}] = [Li_i^{\blacksquare}] + [Li_{A1}^x] = (K_i^{pl/gl} + K_{A1}^{pl/gl}) [Li^{gl}] = K^{pl/gl} [Li^{gl}] \quad (S3.4)$$

Mass balance equation at the interface $x = x_{if}$:

We assume diffusion in a fixed-volume reference frame, which is reasonable as diffusive exchange of Li as a trace element is hardly affecting the molar volume of the glass and the plagioclase. In that case, we can assume mass balance of the diffusive fluxes on both sides of the interface when concentrations are considered as moles or atoms per volume of glass and plagioclase, respectively. Since the molar volume of glass and plagioclase are slightly different to be exact, we would need to convert the concentrations in atoms per formula unit to concentrations in atoms or moles per volume (mol/cm^3). This introduces a correction factor, for example for $[Li^{gl}]$, which is equal to the ratio of the molar volume of plagioclase divided by the molar volume of glass. Ignoring this for the moment, the mass balance at the interface is, as follows:

$$D_{gl} \frac{\partial [Li^{gl}]}{\partial x} = D_{Li}^i \frac{\partial [Li_i^{\blacksquare}]}{\partial x} + D_{Li}^A \frac{\partial [Li_{A1}^x]}{\partial x} = F(x_s, t), x = x_{if} \quad (S3.5)$$

Equations (S3.2), (S3.3), and (S3.5) are the boundary conditions at the interface for the set of diffusion equations for Li in the glass and Li_i^\square and Li_{A1}^x in the plagioclase. For the vacancies on the A1 site we assume a zero flux at the interface as diffusion of a vacancy in plagioclase into a glass is meaningless.

To solve the set of diffusion equations we applied the method of finite differences by an explicit scheme. The grid scheme and notations for the grid points is illustrated in the Fig. S3.1 below.

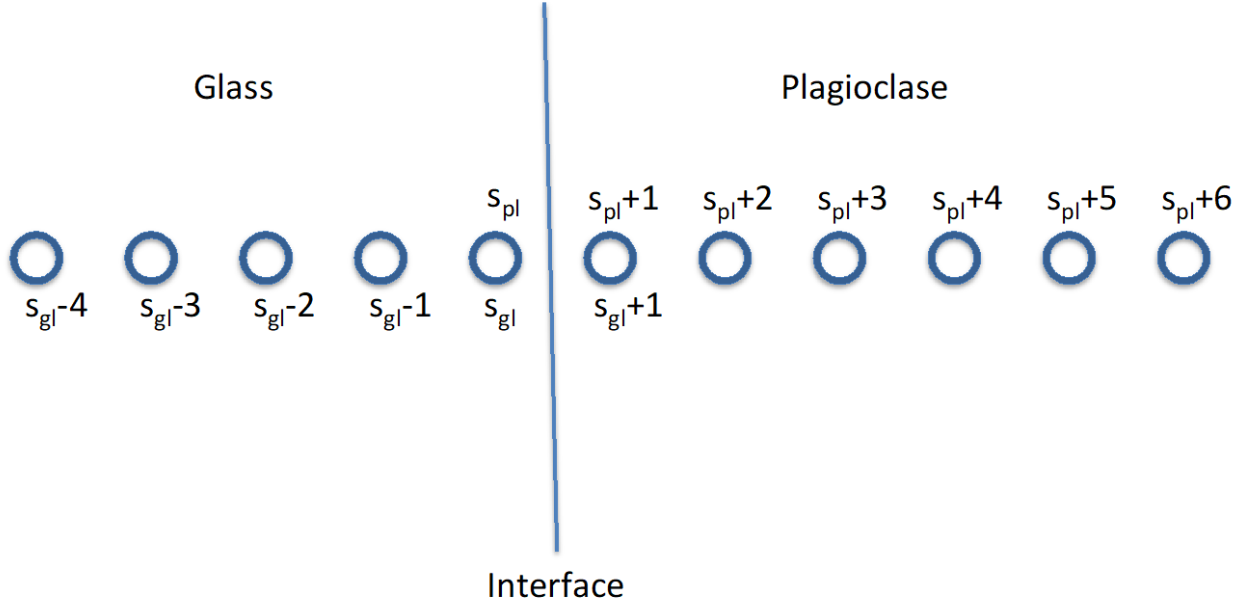


Fig. S3.1: Grid scheme between glass and crystal.

For the replacement of Eq. (S3.5) in a finite difference form we extended both media by one grid point (Δx) into the other medium (one grid point to the right for the glass, point $s_{gl}+1$, and one grid point to the left for the plagioclase, point s_{pl}), as follows (Crank, 1975):

$$D_{gl} \frac{[Li^{gl}]_{s_{gl}+1} - [Li^{gl}]_{s_{gl}-1}}{2\Delta x} = D_{Li}^i \frac{[Li_i^\square]_{s_{pl}+2} - [Li_i^\square]_{s_{pl}}}{2\Delta x} + D_{Li}^A \frac{[Li_{A1}^x]_{s_{pl}+2} - [Li_{A1}^x]_{s_{pl}}}{2\Delta x} = F \quad (S3.6)$$

The finite difference forms of the diffusion equations for the concentrations at the interface are:

$$\frac{\partial [Li^{gl}]_{s_{gl}}}{\partial t} = D_{gl} \frac{[Li^{gl}]_{s_{gl}-1} - 2[Li^{gl}]_{s_{gl}} + [Li^{gl}]_{s_{gl}+1}}{\Delta x^2} \quad (S3.7)$$

$$\frac{\partial [Li^{pl}]_{s_{pl}+1}}{\partial t} = \frac{\partial [Li_i^\square]_{s_{pl}+1}}{\partial t} + \frac{\partial [Li_{A1}^x]_{s_{pl}+1}}{\partial t} = D_{Li}^i \frac{[Li_i^\square]_{s_{pl}} - 2[Li_i^\square]_{s_{pl}+1} + [Li_i^\square]_{s_{pl}+2}}{\Delta x^2} + D_{Li}^A \frac{[Li_{A1}^x]_{s_{pl}} - 2[Li_{A1}^x]_{s_{pl}+1} + [Li_{A1}^x]_{s_{pl}+2}}{\Delta x^2} \quad (S3.8)$$

We can now eliminate the fictitious concentrations in the above diffusion equations by rewriting the diffusive flux equation for the glass and the plagioclase separately (Eq. (S3.6)):

$$D_{gl} [Li^{gl}]_{s_{gl}+1} = 2F\Delta x + D_{gl} [Li^{gl}]_{s_{gl}-1} \quad (S3.9)$$

$$D_{Li}^i [Li_i^\square]_{s_{pl}} + D_{Li}^A [Li_{A1}^x]_{s_{pl}} = D_{Li}^i [Li_i^\square]_{s_{pl}+2} + D_{Li}^A [Li_{A1}^x]_{s_{pl}+2} - 2F\Delta x \quad (S3.10)$$

After inserting the left-hand side into the diffusion equations, we obtain:

$$\frac{\partial [Li^{gl}]_{s_{gl}}}{\partial t} = 2D_{gl} \frac{[Li^{gl}]_{s_{gl}-1} - [Li^{gl}]_{s_{gl}}}{\Delta x^2} + \frac{2F}{\Delta x} \quad (S3.11)$$

$$\frac{\partial [Li^{pl}]_{s_{pl}+1}}{\partial t} = 2D_{Li}^i \frac{[Li_i^\square]_{s_{pl}+2} - 2[Li_i^\square]_{s_{pl}+1}}{\Delta x^2} + 2D_{Li}^A \frac{[Li_{A1}^x]_{s_{pl}+2} - 2[Li_{A1}^x]_{s_{pl}+1}}{\Delta x^2} - \frac{2F}{\Delta x} \quad (S3.12)$$

By adding these two equations we obtain:

$$\frac{\partial [Li^{gl}]_{s_{gl}}}{\partial t} + \frac{\partial [Li^{pl}]_{s_{pl+1}}}{\partial t} = 2D_{gl} \frac{[Li^{gl}]_{s_{gl-1}} - [Li^{gl}]_{s_{gl}}}{\Delta x^2} + 2D_{Li}^i \frac{[Li_i^{\blacksquare}]_{s_{pl+2}} - 2[Li_i^{\blacksquare}]_{s_{pl+1}}}{\Delta x^2} + 2D_{Li}^A \frac{[Li_{A1}^x]_{s_{pl+2}} - 2[Li_{A1}^x]_{s_{pl+1}}}{\Delta x^2} \quad (S3.13)$$

And with the assumption for local equilibrium at the interface (Eq. (S3.4)), we finally get an equation for the concentration change of Li in the glass at the interface:

$$\left(1 + K^{pl/gl}\right) \frac{\partial [Li^{gl}]_{s_{gl}}}{\partial t} = 2D_{gl} \frac{[Li^{gl}]_{s_{gl-1}} - [Li^{gl}]_{s_{gl}}}{\Delta x^2} + 2D_{Li}^i \frac{[Li_i^{\blacksquare}]_{s_{pl+2}} - 2[Li_i^{\blacksquare}]_{s_{pl+1}}}{\Delta x^2} + 2D_{Li}^A \frac{[Li_{A1}^x]_{s_{pl+2}} - 2[Li_{A1}^x]_{s_{pl+1}}}{\Delta x^2} \quad (S3.14)$$

We solved this equation in the explicit form of the time derivative. The concentrations of Li and the two respective species at the interface in the plagioclase then follow from the equations for equilibrium partitioning between plagioclase and glass (Eq. (S3.4)), the different sites (Eq. (S3.1)), and assuming a zero flux for the vacancies:

$$[V'_{A1}]_{s_{pl+1}} = [V'_{A1}]_{s_{pl+2}}.$$

Crank, J.: The mathematics of diffusion, Oxford university press 1975.