

S2 Derivation of the effective binary interdiffusion coefficient

Plagioclase consists primarily of an albite ($\text{Ab}=\text{NaAlSi}_3\text{O}_8$) and anorthite ($\text{An}=\text{CaAl}_2\text{Si}_2\text{O}_8$) component, with a minor portion of orthoclase ($\text{Or}=\text{KAlSi}_3\text{O}_8$). Even though K is diffusing slightly faster than Ca in plagioclase (see overview of Cherniak, 2010), it can be neglected in the consideration of the diffusion coefficient due to the combination of its relatively slow diffusion coefficient ($D_{\text{Li}}^* \gg D_{\text{Na}}^* \gg D_{\text{K}}^* > D_{\text{Ca}}^*$; Behrens et al., 1990; Giletti and Shanahan, 1997) and low concentration. Therefore, we are only considering the three components $\text{LiAlSi}_3\text{O}_8$, $\text{NaAlSi}_3\text{O}_8$ and $\text{CaAl}_2\text{Si}_2\text{O}_8$ for our model of effective binary diffusion in a ternary solid solution. The thermodynamic factor is ignored since the albite/anorthite component can be considered fixed.

The molar fraction X_i of a components i can then be calculated by

$$X_{\text{Li}} + X_{\text{Na}} + X_{\text{Ca}} = 1 \quad (\text{S2.1})$$

The flux of Li in this system is given by

$$\begin{aligned} J_{\text{Li}} &= -D_{\text{Li-Li}} \frac{\partial X_{\text{Li}}}{\partial x} - D_{\text{Li-Na}} \frac{\partial X_{\text{Na}}}{\partial x} - D_{\text{Li-Ca}} \frac{\partial X_{\text{Ca}}}{\partial x} \\ &= -D_{\text{Li-Li}} \frac{\partial X_{\text{Li}}}{\partial x} - D_{\text{Li-Na}} \frac{\partial X_{\text{Ab}}}{\partial x} - D_{\text{Li-Ca}} \frac{\partial X_{\text{An}}}{\partial x} \\ &= -D_{\text{Li-Li}} \frac{\partial X_{\text{Li}}}{\partial x} - D_{\text{Li-Na}} \frac{\partial X_{\text{Li}}}{\partial x} \frac{\partial X_{\text{Na}}}{\partial X_{\text{Li}}} - D_{\text{Li-Ca}} \frac{\partial X_{\text{Li}}}{\partial x} \frac{\partial X_{\text{Ca}}}{\partial X_{\text{Li}}} \\ &= -\left(D_{\text{Li-Li}} + D_{\text{Li-Na}} \frac{\partial X_{\text{Na}}}{\partial X_{\text{Li}}} + D_{\text{Li-Ca}} \frac{\partial X_{\text{Ca}}}{\partial X_{\text{Li}}}\right) \frac{\partial X_{\text{Li}}}{\partial x} \end{aligned} \quad (\text{S2.2})$$

Here D_{i-i} and D_{i-j} are the main and cross diffusion coefficients of the components i and j in the diffusion matrix for multi component diffusion.

Now D_{EB} is the effective binary diffusion coefficient with

$$J_{\text{Li}} = -D_{\text{EB}} \frac{\partial X_{\text{Li}}}{\partial x} \quad (\text{S2.3})$$

Then

$$D_{\text{EB}} = D_{\text{Li-Li}} + D_{\text{Li-Na}} \frac{\partial X_{\text{Na}}}{\partial X_{\text{Li}}} + D_{\text{Li-Ca}} \frac{\partial X_{\text{Ca}}}{\partial X_{\text{Li}}} \quad (\text{S2.4})$$

Due to the large difference in diffusivity between Li and Ca (see overview of Cherniak, 2010) we can assume $D_{\text{Li-Ca}} \sim 0$ and therefore

$$D_{\text{EB}} = D_{\text{Li-Li}} + D_{\text{Li-Na}} \frac{\partial X_{\text{Na}}}{\partial X_{\text{Li}}} \quad (\text{S2.5})$$

Due to the low variation in X_{Li} (variation only through diffusing Li), as well as X_{Ca} being constant and the close to ideal Ab-An solution (Holland and Powell, 1992) we can assume no activity coefficient gradients for the Li component (Dohmen and Blundy, 2014), as well as a near ideal solution ($\gamma \approx 1$). This leads to the following equations for $D_{\text{Li-Li}}$ and $D_{\text{Li-Na}}$ (Lasaga, 1979).

$$D_{\text{Li-Li}} = D_{\text{Li}}^* \frac{X_{\text{Li}} D_{\text{Ca}}^* + X_{\text{Na}} D_{\text{Na}}^* + 4X_{\text{Ca}} D_{\text{Ca}}^*}{X_{\text{Li}} D_{\text{Li}}^* + X_{\text{Na}} D_{\text{Na}}^* + 4X_{\text{Ca}} D_{\text{Ca}}^*} \quad (\text{S2.6})$$

$$D_{\text{Li-Na}} = X_{\text{Li}} D_{\text{Li}}^* \frac{D_{\text{Ca}}^* - D_{\text{Na}}^*}{X_{\text{Li}} D_{\text{Li}}^* + X_{\text{Na}} D_{\text{Na}}^* + 4X_{\text{Ca}} D_{\text{Ca}}^*} \quad (\text{S2.7})$$

Now using the derivation $\frac{\partial}{\partial X_{\text{Li}}}$ of Eq. (S2.1), with X_{An} being a constant, we get the numerical approximation

$$\frac{\partial X_{\text{Na}}}{\partial X_{\text{Li}}} = -1 \quad (\text{S2.8})$$

And inserting it into Eq. (S2.5) yields

$$D_{\text{EB}} = D_{\text{Li-Li}} + D_{\text{Li-Na}} \frac{\partial X_{\text{Na}}}{\partial X_{\text{Li}}} = D_{\text{Li-Li}} - D_{\text{Li-Na}} \quad (\text{S2.9})$$

As already previously mentioned the large difference in diffusivity between Li and Ca allows for the assumption $D_{Ca} \sim 0$. Now combining this assumption with Eq. (S2.5), as well as Eq. (S2.6) and Eq. (S2.7), yields

$$D_{EB} = \frac{X_{Na}D_{Li}^*D_{Na}^*}{X_{Li}D_{Li}^* + X_{Na}D_{Na}^*} \quad (S2.10)$$

Further rearranging the equation leads to

$$D_{EB} = \frac{D_{Li}^*}{\frac{X_{Li}}{X_{Na}} \frac{D_{Li}^*}{D_{Na}^*} + 1} \quad (S2.11)$$

This version of the equation clearly shows the influence of the ratios D_{Li}^*/D_{Na}^* and X_{Li}/X_{Na} on D_{EB} . D_{EB} approaches the tracer diffusion coefficient of Li when either or both ratios are small. In other words, D_{EB} slows down in comparison to D_{Li}^* with increasing Li concentration. This difference will be more pronounced the further apart the tracer diffusion coefficients of Li and Na are. Since the D_{Li}^*/D_{Na}^* ratio is temperature dependent, the difference between D_{EB} and D_{Li}^* is also temperature dependent. One important point is that D_{EB} is already affected at low Li concentrations between 1-5 ppm if D_{Na}^* is slow enough in comparison to D_{Li}^* .

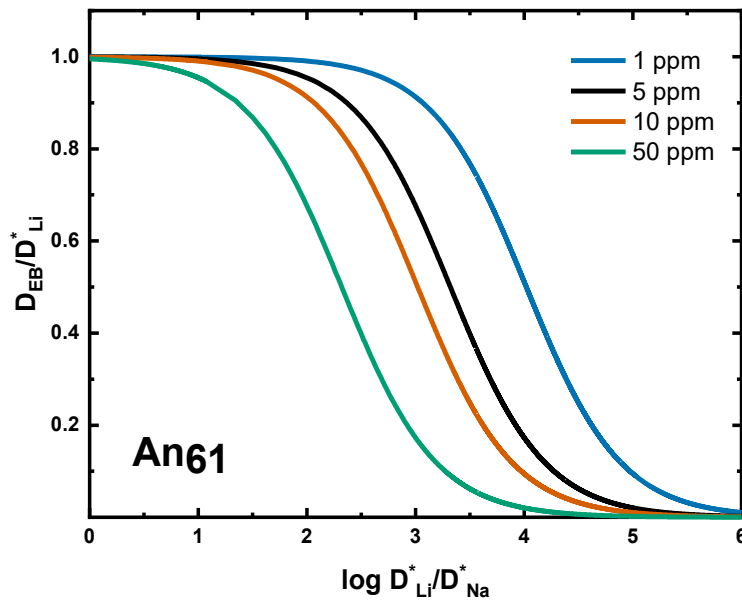


Figure S2.1: Dependence of D_{EB} on D_{Li}^*/D_{Na}^* for an An_{61} labradorite crystal for different Li concentrations. At higher Li concentration, D_{EB} already starts to decrease at D_{Li}^*/D_{Na}^* ratios closer to 1.

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