Fe-Mg interdiffusion in orthopyroxene

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ABSTRACT

We have measured Fe-Mg interdiffusion coefficients, $D_{\text{Fe-Mg}}$, parallel to the three main crystallographic axes in two natural orthopyroxene single crystals [approximately En 98Fs1 ($X_{\text{Fe}} = X_{\text{Mg}} = 0.01$) and En91Fs9] using diffusion couples consisting of a 20–90 nm thick silicate thin film deposited under vacuum on polished and oriented pyroxene single crystals. The thin films were prepared using pulsed laser ablation of polycrystalline olivine pellets (composition: Fo 30Fa70). Samples were annealed for 4–337 h at 870–1100 °C under atmospheric pressure in a continuous flow of CO + CO2 to control the oxygen fugacity, $f_{\text{O2}}$, between $10^{-11}$ and $10^{-7}$ Pa within the stability field of pyroxene. Film thickness and compositional profiles were measured using Rutherford backscattering spectroscopy (RBS) on reference and annealed samples, and Fe concentration depth profiles were extracted from the RBS spectra and fitted numerically considering a compositional dependence of $D_{\text{Fe-Mg}}$ in orthopyroxene. We obtain an Arrhenius relationship for both types of crystals, but only for the more Fe-rich composition a dependence on $f_{\text{O2}}$ could be clearly identified. For diffusion along [001] in the composition Fs9, least-squares regression of the log $D_{\text{Fe-Mg}}$ vs. reciprocal temperature yields the following Arrhenius equation:

$$D_{\text{Fe-Mg}} [\text{m}^2/\text{s}] = 1.12 \times 10^{-6} (f_{\text{O2}} [\text{Pa}])^{0.053 \pm 0.027} \exp[-308 \pm 23 [\text{kJ/mol}]/(RT)].$$

$D_{\text{Fe-Mg}}$ in Opx with $X_{\text{Fe}} = 0.01$ obeys a relationship that does not depend on $f_{\text{O2}}$:

$$D_{\text{Fe-Mg}} [\text{m}^2/\text{s}] = 1.66 \times 10^{-4} \exp[-377 \pm 30 [\text{kJ/mol}]/(RT)].$$

Diffusion along [001] is faster than diffusion along [100] by a factor of 3.5, while diffusion along [010] is similar to that along [001]. Comparison of $D_{\text{Fe-Mg}}$ and rates of order-disorder kinetics indicates that for $f_{\text{O2}}$ around the IW buffer and lower, diffusion in natural orthopyroxene becomes insensitive to $f_{\text{O2}}$, which could be related to a transition in the diffusion mechanism from a transition metal extrinsic (TaMED) domain to a pure extrinsic (PED) domain. This behavior is analogous to that observed for Fe-Mg diffusion in olivine and this complexity precludes the formulation of a closed form expression for the composition and $f_{\text{O2}}$ dependence of $D_{\text{Fe-Mg}}$ in orthopyroxene at present. We were not able to quantitatively constrain the dependence of $D_{\text{Fe-Mg}}$ on the $X_{\text{Fs}}$ content from the profile shapes, but consideration of the experimentally measured diffusion coefficients along with the data for order-disorder kinetics suggests that the compositional dependence is weaker than previously estimated, at least for orthopyroxene with $X_{\text{Fs}} < 0.5$. For the major element compositional $T$ and $f_{\text{O2}}$ range of available experimental data, Fe-Mg interdiffusion in orthopyroxene is slower than in olivine and aluminous spinel, comparable to garnet, and faster than in clinopyroxene.

Keywords: Orthopyroxene, Fe-Mg diffusion, diffusion chronometry, geothermometry, cooling rates

INTRODUCTION

Fe-Mg interdiffusion in silicate minerals is of interest in petrological studies for determining the closure temperature of geothermometers and for determining cooling rates or durations of processes such as residence times at peak metamorphic conditions or in magma chambers (e.g., Dodson 1973, 1986; Lasaga 1983; Ganguly and Tirone 1999). Fe-Mg diffusion in orthopyroxene has been used to infer these parameters (e.g., Smith and Barron 1991; Pattison and Begin 1994; Rietmeijer and Champness 1982) as well as to determine crystal residence times in magmas from compositional profiles (e.g., Saunders et al. 2012; Allan et al. 2013; Chamberlain et al. 2014) and thermal histories of meteorites (e.g., Ganguly et al. 2013). It is also relevant for studies of the physical properties of silicates, such as rheology or electrical conductivity (Mackwell 1991; Skemer and Karato 2007; Dai and Karato 2009; Farla...