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SPECIAL COLLECTION: MECHANISMS, RATES, AND TIMESCALES OF GEOCHEMICAL TRANSPORT PROCESSES IN THE CRUST AND MANTLE

Fe-Mg interdiffusion in orthopyroxene

RALF DOHMEN[1,*], JAN H. TER HEEGE[1,2], HANS-WERNER BECKER[3], AND SUMIT CHAKRABORTY[1,3]

[1]Institute for Geology, Mineralogy and Geophysics, Ruhr-University Bochum, 44801 Bochum, Germany
[2]TNO Geo Energy, Princetonlaan 6, 3584 CB, Utrecht, The Netherlands
[3]Zentrale Einheit für Ionenstrahlen und Nuklide, RUBION, Ruhr-University Bochum, 44801 Bochum, Germany

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 $En_{98}Fs_1$ ($X_{\text{Fs}} = X_{\text{Fe}} = 0.01$) and $En_{91}Fs_9$] 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: $Fo_{30}Fa_{70}$). Samples were annealed for 4–337 h at 870–1100 °C under atmospheric pressure in a continuous flow of CO + CO_2 to control the oxygen fugacity, f_{O_2}, 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_{O_2} could be clearly identified. For diffusion along [001] in the composition Fs_9, least-squares regression of the log $D_{\text{Fe-Mg}}$ vs. reciprocal temperature yields the following Arrhenius equation:

$$D_{\text{Fe-Mg}}\,[\text{m}^2/\text{s}] = 1.12 \times 10^{-6}\,(f_{O_2}\,[\text{Pa}])^{0.053 \pm 0.027} \exp[-308 \pm 23\,[\text{kJ/mol}]/(\text{R}T)].$$

$D_{\text{Fe-Mg}}$ in Opx with $X_{\text{Fe}} = 0.01$ obeys a relationship that does not depend on f_{O_2}:

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

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_{O_2} around the IW buffer and lower, diffusion in natural orthopyroxene becomes insensitive to f_{O_2}, 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_{O_2} 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_{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 $X_{\text{Fe}} < 0.5$. For the major element compositional T and f_{O_2} 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