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Challenging the distribution coefficient: Kinetic fractionation during mineral replacement reactions

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The growth of orthopyroxene (Opx) rims between olivine (Ol) and quartz (Qtz) was the topic of several experimental studies by a number of authors over the last decade [1,2,3,4,5]. Initially the rim growth method was used as a means to measure diffusion in polycrystalline fabrics in time-dependent experiments. Subsequent studies increased the understanding of details in rim formation. We are now in a position to use Opx rim growth as a standard reaction to study various effects, such as trace amounts of water, external stress fields or reaction-induced stress, on the growth rates, growth modes and resulting microstructures. In this respect, this reaction is not only a model for reaction rim formation but for aspects of solid-solid reactions in general.

A few preceding experiments used pure forsterite, but mostly fo-rich olivine solid solutions were used as a reactant. Our present runs were carried out with fo90fa10 olivine. We present observations on the Fe-Mg partitioning in the Opx rims and apply a kinetic model to explain the observed chemical zoning.

Experiments were performed in a piston-cylinder apparatus. Polished sections were investigated using electron back scatter diffraction (EBSD) and field-emission electron microprobe (FE-EMP) that allowed a spatial resolution of 400 nm for spot analyzes and X-ray mapping of compositional contours. Further details were studied by TEM in foils cut vertically from the samples by a focused ion beam (FIB).

Opx crystallizes Fe-rich (En88Fs12) at the Opx-Qtz interface and comparatively Fe-poor (En92Fs08) at the Opx-Ol interface with a prominent step at the initial Ol-Qtz interface. Due to Fe/Mg buffering at the Opx-Ol interface, excess Fe diffuses across the rims towards the Opx-Qtz interface where consequentially the highest Fe concentrations in Opx are attained. Remarkably, Fe diffusion on fast grain boundary pathways proceeds without noticeable Fe-Mg exchange within the Opx rims despite complete En-Fs miscibility. Over longer timescale, the Fe-rich Opx forms a secondary diffusion reservoir for limited back-diffusion of Fe that again uses grain-boundaries and modifies the Fe/Mg step at the initial interface. FE-EMP X-ray maps show concentrical Fe-enrichment in 1 μm large Opx grains near the initial interface.

The general relevance of the described mechanism lies in the fact that it potentially concerns any chemical component that is released in excess at a reactant-product interface in a mineral replacement reaction. Its efficiency depends on the respective grain boundary diffusivities of the chemical species and potentially provides a way of kinetic fractionation of chemical species or even light isotopes by grain boundary diffusion across the rim. If the position of Qtz would be replaced with a silica-rich melt, it could take up chemical or possibly isotopic signatures that are not inherent to the reactant or product phases but rather depend on the grain boundary diffusion kinetics of the respective species.

Ref.s

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