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Diffusion of Zr and Hf in Clinopyroxene and Orthopyroxene

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Along with REE, Zr and Hf in pyroxenes have been widely used to study partial melting, magma differentiation and subsolidus reequilibration of mantle and mantle derived rocks. To aid geochemical interpretaions, we have undertaken a systematic study of Zr and Hf diffusion in clinopyroxene and orthopyroxene of near endmember and mantle-like compositions. Thin source diffusion experiments were conducted at 1050-1300°C in air and under NNO buffered conditions and for times ranging from a few hours to two months. Diffusion profiles were measured using Rutherford Backscattering Spectrometry. We found that diffusivities of Zr and Hf in pyroxenes are relatively insensitive to crystallographic orientation, oxygen fugacity, and pyroxene composition. To within experimental uncertainty, diffusivities of Zr and Hf in clinopyroxene are very smilar to those in orthopyroxene. Diffusivities of Hf are also comparable to diffusivities of Zr in both enstatite and diopside. Similarities in our measured Zr and Hf diffusivities maybe attributed to ionic size and charge and M1 site of the two pyroxenes. To a good approximation, diffusivities of Zr in clinopyroxene and orthopyroxene can be described by the same Arrhenius equation with diffusion parameters $D_0 = 8.25 \times 10^{-10}$ m^2/s and Ea = 384 kJ/mol. Similarly diffusvities of Hf in diopside and enstatite can be described by the common diffusion parameters $D_0 = 4.33 \times 10^{-12}$ m^2/s and Ea = 279 kJ/mol. Our measured Hf diffusivities are factors of 3.8 and 7 smaller than Hf diffusivities in diopside reported in [1] at 1300°C and 1050°C, respectively. Depending on temperature, Zr diffusion in diopside is comparable to or slower than Ce diffusion in diopside [2], whereas Zr diffusion in enstatite is 1~2 orders of magnitude slower than REE diffusion in enstatite [3]. Hence Zr and Hf have higher closure temperatures than REE in the same pyroxene grains. During disequilibrium partial melting and subsolidus reequilibration, Zr and Hf can be fractionated from REE by equilibrium partitioning at pyroxene surfaces and diffusion through pyroxene grains. An example will be presented.

[1] Bloch & Ganguly (2014), EPSL 397,173-183. [2] Van Orman et al. (2001), CMP 141, 687-703. [3] Cherniak & Liang (2007), GCA 71, 1324-1340.