

## Fast Pathways of Exchange

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Diffusion is the dominant mechanism for chemical and isotope exchange if minerals don't experience reaction or recrystallization. Numerous models employing experimental data and Fick's Law are available to evaluate volume diffusion in solids with applications including mineral growth, geochronology, and fluid-rock interaction. In some instances, grains can be modeled as homogeneous with a single rate law, but in others, intragrain variability and multiple domains provide fast pathways of exchange, invalidating a simple model. Fast pathways are often cryptic and vary from micron- to atom-scale; their identification and understanding is a fundamental challenge for geochemistry.

Multi-domain oxygen isotope exchange has been studied by correlated techniques in many minerals. 1) Dislocation arrays in metamorphic magnetite adjacent to rheologically hard minerals locally enhance oxygen exchange (SIMS, TEM)[1]. 2) O and Pb diffuse at ~the same rate, but deformation lamellae disrupt otherwise smooth gradients in  $\delta^{18}\text{O}$  and  $^{206}\text{Pb}/^{238}\text{U}$  in metamorphic titanite (SIMS)[2]. 3) Deformation-twin boundaries act as grain boundaries in polymetamorphic calcite (SEM, SIMS) [3]. 4) Radiation damaged domains in zircon have little effect on micron-scale exchange if  $\alpha$ -dose is below the first percolation point ( $\sim 2\text{E}15$   $\alpha$ -events/mg), but open the crystal to rapid exchange of O, Pb and other elements if accumulated dose is higher, forming continuous pathways (SIMS, APT, SEM)[4]. For each of these examples, in situ analysis reveals interesting hidden domains that affect bulk-exchange rates. These features can be avoided for the sake of modelling or studied in their own right.

[1] Valley & Graham (1993) *Science* 259, 1729-1733; Sitzman et al. (2000) *Am Min* 85, 14-21; [2] Bonamici et al. (2015) *Chem Geol* 298, 70-84; [3] Graham et al. (1998) *CMP* 132, 371-389; [4] Valley et al. (2015) *Am Min* 100, 1355-1377. Blum et al. (2018) this meeting.