

EGU22-8313, updated on 23 May 2022

<https://doi.org/10.5194/egusphere-egu22-8313>

EGU General Assembly 2022

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Using Raman spectra of isotopically enriched transformation products to trace mineral reactions

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Isotopic doping is a powerful tool to identify newly formed mineral phases during fluid-mediated mineral transformation reactions. In particular, Raman spectroscopy of isotopically doped minerals can reveal incorporation of the isotopes into the structure of the minerals themselves, rather than enrichment of a fluid within a pore (1). In fluid mediated mineral transformations, dissolution of the reactant mineral enables O isotope exchange between water and dissolved oxyanions (e.g., CO_3). Incorporation of the isotopically enriched oxyanions can result in crystals with different isotopic enrichments if the rate of the exchange in the fluid occurs on a similar timescale to the duration of the experiment and the crystals form at different times. This means that the amount of isotopic enrichment can be used as an internal stop clock and demonstrates the relative timings of precipitation in ex-situ analysis (2). In this presentation we will use previous examples to explore how fluid-mediated mineral transformation reactions can be followed using isotopic enrichment traced with Raman spectroscopy, including new data after deformation experiments. Using new data obtained from in-situ analysis of ^{18}O exchange into dissolved carbonate species we will also show the importance of the solution chemistry on exchange kinetics in the fluid. In addition, we will use density functional theory calculations to explore how the mineral structure may influence the isotopic signature obtained from the Raman spectra.

(1) King H.E. & Geisler T. (2018) *Minerals*, 8. 158.

(2) King H.E., Mattner D.C., Plümper O., Geisler T., Putnis A., (2014) *Crystal Growth & Design*, 14, 3910.