

## Textural and kinetic controls on stable isotope fractionation during carbonate replacement

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The alteration of carbonates (e.g., aragonite replaced by dolomite) during diagenesis and metamorphism affects not only the element but also the isotope signature of the original carbonate phase. In a set of experiments Ca-carbonate was replaced by Mg-rich carbonates. We study the kinetics of this reaction and how this affects the element and isotope composition of the reaction products.

Aragonite samples with different textural and microstructural properties (inorganic aragonite single crystal, shell of the bivalve *Arctica Islandica* and skeleton of the coral *Porites* sp.) as well as calcite single crystals were reacted with a solution with 0.8 - 1.0 M MgCl<sub>2</sub> at 200 °C. Cross sections of the solid reaction products were investigated by scanning electron microscopy and electron microprobe. In addition, fluid chemistry was analysed with ICP-OES and the Mg isotopes of the reacted fluids as well as the solid products were analysed using the Thermo Fisher Scientific Neptune MC-ICP-MS (for solids following the procedure of [1]).

The reaction products as well as the reaction rate strongly depends on the porosity and permeability of the test carbonate, which controls the rate of exchange of the carbonate forming elements Ca and Mg between the fluid at the reaction interface and the bulk solution surrounding the test material. From these observations and earlier experiments [2], we infer a concentration gradient within the pore fluid across the solid reactant. The reaction rate is basically diffusion controlled and thus, kinetic isotope fractionation effects could be expected [3]. Magnesium isotope values of the reactant products show systematic evolution with time and are discussed in terms of simple mass balance models (bulk equilibrium and Rayleigh fractionation) as well as by a reaction-diffusion model [3].

[1] Geske *et al.* (2015) *Geochim Cosmochim Acta* **149**, 131-151. [2] Jonas *et al.* (2015) *Geology* **43**, 779-782. [3] Pogge von Strandmann *et al.* (2015) *J Petrol* **56**, 33-58.