

Fluid/mineral isotope exchange kinetics at *bulk chemical* equilibrium

F. M. STAMM^{1*}, T. ZAMBARDI², J. CHMELEFF¹, J. SCHOTT¹, AND E.H. OELKERS^{1,3}

¹GET, CNRS/UMR 5563, Université Paul Sabatier, 14 avenue Edouard Belin, 31400 Toulouse, France (*correspondence: franziska.stamm@get.omp.eu)

²LEGOS, OMP, 14 avenue Edouard Belin, 31400 Toulouse, France

³Earth Sciences, University College London, Gower Street London WC1E 6BT, UK

Isotope exchange between fluid and co-existing minerals does not stop at *bulk chemical* equilibrium. Fluid/mineral isotope exchange will continue until *isotopic* equilibrium is attained in the system. The determination of the rates at which isotopic equilibrium is attained at *bulk chemical* equilibrium may provide insight into the mechanisms controlling this process and thus the conditions at which mineral isotopic signatures are preserved in natural systems.

Isotope exchange experiments at *bulk chemical* equilibrium were performed 1) between aqueous fluids of various compositions enriched in ²⁵Mg and brucite (Mg(OH)₂) and 2) between fluids enriched in ²⁹Si and amorphous silica (SiO_{2,am}) adopting the ‘three-isotope method’ at both 25 and 75°C^[1]. The rates of isotope exchange were quantified using a first order rate law^[2]. Isotope exchange is initially rapid and consistent with the corresponding bulk solid dissolution rates, indicating that the rate of exchange is driven by the breaking and creating of metal-oxygen bonds at the fluid/solid interface. Over time, the rates slow suggesting they become limited by the transport of material within the solid. The measured exchange rates are closely related to the surface area and reactivity of the solids in the experimental system. The isotopic evolution of these fluid-solid systems attained from 30 to 100% of their experimentally determined equilibrium isotope fractionation value during the experiments, which lasted less than 1.5 years. These results suggest that fluid-mineral isotopic equilibration may be equally fast in natural systems. As such the preservation of the original isotopic signatures in natural water-rock systems may require either the system’s isolation or indicate the existence of an ill defined mineral surface reaction arresting mechanism.

[1] Matsuhisa, Goldsmith & Clayton (1978), *Geochim. Cosmochim. Acta* **42**, 173–182.

[2] Cole & Chakraborty (2001), *Rev. Mineral Geochim.* **43**, 83–223.