



Stable isotope fractionation during porous flow with fluid-solid reaction

Madeleine S. Bohlin and Mike J. Bickle

Department of Earth Sciences, University of Cambridge, Downing Street, Cambridge, CB2 3EQ (msb56@cam.ac.uk)

Chemical weathering of the crust plays an important part in geochemical cycling by redistributing elements between Earth's surface reservoirs. On a geological time scale chemical weathering buffers Earth's climate as atmospheric CO₂ is consumed during the breakdown of silicate minerals and eventually stored as carbonates in the ocean. However there are fundamental problems in estimating chemical weathering fluxes and their climatic impact. These include distinguishing between silicate and carbonate sources of riverine dissolved loads, understanding the nature of element cycling along groundwater and river flow paths, and understanding the couplings between climate and chemical weathering rates.

An emerging field in studying chemical weathering is the use of light stable isotopes whose fractionations add additional constraints on weathering processes. Lithium isotopes have been highlighted in recent years as they almost exclusively reflect silicate weathering and have been shown to correlate with weathering intensity (e.g. Huh et al., 2001, *Geochimica et Cosmochimica Acta*). However, in order to understand the relationship between weathering intensity and lithium isotopic fractionation it is important to have appropriate physical models for the interaction of fluids and minerals in weathering environments.

Weathering reactions likely take place continuously within catchments with water flowing through a range of shallow to deep paths as rock is progressively exhumed through these flow paths. To model this it is necessary to consider how kinetically-limited fluid-mineral reactions will evolve along individual water flow paths and to understand the range of inputs to river systems. We present a simple one-dimensional transport reaction model to calculate Li-isotopic fractionation in a plausible weathering setting. The modelling reveals the key controlling parameters and predicts the isotopic evolution along the water flow paths.

The model shows that for such a one-dimensional constant reaction-rate flow path the Li isotopic composition of water produced is only dependent on the distance of fluid flow and two dimensionless variables, one Damköhler number representing the ratio of reaction rate to flow rate and the second describes the fraction Li taken up by clay minerals compared to the fluid. The modelling shows that the final Li-isotopic composition of the water is a function of both the Damköhler number and the fraction of Li taken up by secondary clay minerals. River compositions comprise mixtures of waters which will have experienced variations in both these parameters and care must be taken in interpretation of such arrays of natural data.