**Reaction kinetics and diffusive transport in low permeability geological systems**

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Mass transport by aqueous fluids is a dynamic process in shallow crustal systems, redistributing

nutrients as well as contaminants. Rock matrix diffusion into fractures (void space) within crystalline

rock has been postulated to play an important role in the transient storage of solutes. The reacted

volume of host rock involved, however, will be controlled by fluid-rock reactions. Here we present the results of two studies which focus on providing fundamental parameters to describe rock matrix diffusion. The first study1 sought to define the length scale over which rock matrix diffusion operates within crystalline rock over timescales that are relevant to safety assessment of radioactive and other long-lived wastes. Through detailed chemical and structural analysis of natural specimens sampled at depth from an active system (Toki Granite, Japan), we show that, contrary to commonly proposed models, the length scale of rock matrix diffusion may be extremely small, on the order of centimetres, even over timescales of millions of years. This implies that in many cases the importance of rock matrix diffusion will be minimal. Additional analyses of contrasting crystalline rock systems (Carnmenellis Granite, UK; Borrowdale Volcanic Group, UK) corroborate these results. In the second study2 a micro-fluidic method known as the Micro-Reactor Simulated-Channel (MRSC) method, has been employed to rapidly determine the effective diffusion coefficients in three representative low permeability lithologies including: Melechov granite (Czech Republic), Borrowdale tuff, and Land's End Cornish granite (both UK). The concept of MRSC is similar to the micro chemical reactor which enables fast measurements to be done on a small intact sample. Effective diffusion coefficients were measured and comparisons between the MRSC results and conventional column methods showed excellent agreement. Our measured effective diffusion coefficient for Melechov granite is 1.7 x 10-12 m2/s, directly comparable to previous conventional measurements. However the measurement time of the MRSC method is at least one order of magnitude faster than the conventional method and only requires small reaction volumes (as small as 10 ml). In addition, by exploiting the advantages of the MRSC method, the effects of velocity and concentration on diffusive transport for the two different UK rock types have also been investigated. Depending on flow rate and inlet tracer concentration, the effective diffusion coefficient for lithium in the Cornish granite ranges between 0.9 and 1.5 x 10-11 m2/s while that measured for the Borrowdale tuff varies between 1.2 and 1.6 x 10-11 m2/s. The physical and chemical parameters determined in these two completely different sets of experiments will be compared and discussed in terms of creating consistent descriptions of the process of RMD across different scales of time and space.

1. Wogelius RA, Milodowski AE, Field LP, Metcalfe R, Lowe T, van Veelen A, Carpenter G, Norris S, and Yardley B (2020) “Mineral reaction kinetics constrain the length scale of rock matrix diffusion,” *Scientific Reports* **10** (1), 1-19.
2. Zou B, Ohe T and Wogelius RA, “Effects of velocity and concentration on diffusive transport in low permeability geological systems,” *Applied Geochemistry* **63**, 357-365.