

## Mass transport experiments in low permeability shale

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### Introduction

The process of understanding sorption and its role in the transport of radionuclides in Canadian sedimentary rocks under saline conditions requires a combination of batch sorption experiments and mass transport tests to demonstrate that sorption coefficients ( $K_d$ ) can be applied to explain mass transport. Although sorption in low permeability shale is diffusion dominated, transport tests with induced hydraulic flow are performed using the High Pressure Radioisotope Migration (HPRM) apparatus [1] in an attempt to obtain transport information on a shorter time scale than possible with diffusion tests. Tests are performed on core samples by pumping fluid through the core (along the core axis) using pressures as high as 4.5 MPa. The rock matrix permeability is calculated from the measured pressure differential between the inlet and outlet side of the core, and from the flow rate determined by the volume of eluted water [1]. Mass transport tests are performed by injecting a combination of sorbing and non-sorbing tracers and monitoring their eluted concentrations.

### Results and Discussion

Initial tests were performed with a core sample of Queenston Formation. First deionized water was pumped through the sample to remove existing brine from pore spaces so that Cl from the subsequent brine injection could help define porosity. The deionized water was followed by 300 g/L TDS Na-Ca-Cl brine solution, and then same brine solution with uranine dye tracer. The average flow rates of water through the rock sample varied from 0.004 to 0.05 mL/day. The permeability varied from  $1.0 \times 10^{-21}$  to  $7.5 \times 10^{-21}$  m<sup>2</sup> and although the viscosity in permeability calculations was not increased for higher salinity, the resulting permeability values were not significantly affected by fluid composition. The sample pore volume estimated by the initial breakthrough of Cl from the brine injection was  $0.22 \pm 0.03$  cm<sup>3</sup>, which is in agreement with the 7 % porosity of a 2.5 cm diameter core with a length of 0.6 cm. In the mass transport test, uranine breakthrough was slower than that of Cl (assumed to be non-sorbing), producing a retardation factor of  $1.44 \pm 0.31$  for uranine. Using a bulk mass density of 2.66 g/cm<sup>3</sup> for Queenston shale, this retardation factor corresponds to a sorption coefficient ( $K_d$ ) of  $0.167 \pm 0.036$  cm<sup>3</sup>/g. This value is in agreement with batch measurements of uranine sorption on dolomite, calcite and quartz in the presence of Dead Sea brine solution [2]. Results of ongoing migration tests in shale using a brine solution containing a mixture of conservative (Li) and sorbing (Ni, Cu, Pb, Bi, Zr, U) tracers will be reported. These tests are aimed at demonstrating the role of sorption in mass transport processes by comparing the derived  $K_d$  values to that obtained from the batch sorption tests.

[1] Vilks & Miller (2007) *Nuclear Waste Management Organization TR-2007-11*. [2] Magal, Weisbrod, Yakirevich & Yechieli (2008) *Journal of Hydrology* **358**, 124-133.

## Geochronology and hydrochronology of metamorphic and metasomatic rocks

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Metamorphism, metasomatism, retrogression, and aqueous alteration are based on the same underlying mechanism at the atomic scale; their different names depend on the large-scale context. They all require recrystallization, which can be viewed as nano-scale dissolution/reprecipitation, mediated by an aqueous fluid [1].

What drives compositional or isotopic modification? Even if 19<sup>th</sup> century chemistry emphasized “diffusion”, mass balance arguments made it quickly clear that changes in stoichiometry need a chemically open system, i.e. advection, rather than diffusion. Aqueous fluids are the main control on the formation of metamorphic parageneses [2], and on isotope exchange in minerals [3]. The reason is that the rate constants for fluid-mediated isotope transport are orders of magnitude larger, and activation energies much smaller, than those for diffusion. Recrystallisation is energetically less costly at almost any temperature than diffusive reequilibration [3].

In a companion abstract [4], it is argued that stepwise release and spatially resolved analyses are a decisive tool in understanding the petrologic processes controlling isotope exchange. However, unambiguous constraints can also derive from petrology alone, provided one knows what to look for. Diffusion is detectable against a background of faster transport only when water was absent and P-T-A-X calculations give an “asterisk” (an overdetermined set of independent reaction equilibria, all intersecting in one point) as proof of retrogression-free rocks.

The observations demonstrate that only in rare cases diffusion is the sole promoter of isotope resetting. Further, the observations require a major shift in perspective on the significance of mineral ages. Just as the “diffusionist” view that zircon discordance is due to thermal disturbances [5] was superseded by the petrological understanding that it is due to recrystallization [6], interpretations of intra-mineral age variations in terms of a purely thermal history neglecting the microchemical-petrogenetic context is no longer tenable.

Because fluid-mediated dissolution/reprecipitation depends mainly on water activity and only very loosely on temperature, isotope data provide a geohyrometric but not an unambiguous geothermometric datum.

[1] Putnis A (2009) *Rev Mineral Geochem* **70**, 87-124. [2] Lasaga A (1986) *Mineral Mag* **50**, 359-373. [3] Cole DR et al (1983) *Geochim Cosmochim Acta* **47**, 1681-1693. [4] Villa IM (2012) this meeting, Theme 17. [5] Steiger RH, Wasserburg GJ (1969) *Geochim Cosmochim Acta* **33**, 1213-1232. [6] Mezger K, Krogstad EJ (1997) *J Metam Geol* **15**, 127-140.