

Experimental and modeling investigation of conservative and reactive transverse mixing in porous media

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Transverse mixing is of primary importance in many relevant groundwater quality scenarios. For instance, the transport and natural attenuation of organic contaminants is often controlled by the extent of mixing of soluble reactants at the plume's fringe. Conservative and (bio)reactive flow-through experiments have been performed for a detailed investigation of transverse mixing and its coupling with reactive processes. The experiments were carried out at the laboratory bench-scale in quasi two-dimensional flow-through systems, including both homogeneous and heterogeneous saturated porous media. Since the extent of mixing in groundwater systems is typically small, the characteristics of the flow field that result in enhanced mixing are of particular significance. The experiments showed that flow focusing in high-permeability inclusions significantly enhances dilution of conservative tracers as well as transverse mixing of reactants.

Numerical simulations have been performed to extend the experimental results to field-scale scenarios where conservative and reactive transport were evaluated in complex heterogeneous hydraulic conductivity fields. In such systems, measures such as the flux-related dilution index and the flux-related spatial moments have been proposed to quantify mixing [1]. These measures are useful since they allow one to define a mixing-relevant upscaled transverse dispersion coefficient. This parameter accounts not only for the variability of flow in the heterogeneous formation (e.g., flow-focusing in high-permeability inclusions and defocusing in low-conductivity zones) but also for small scale, compound-specific effects. The latter include incomplete dilution in the pore channels, which was investigated in pore-scale simulations and multi-tracer laboratory experiments, and was shown to lead to a non-linear compound-specific parameterization of local transverse dispersion [2]. For reactive transport, the effects of a correct quantification of transverse mixing on the length of reactive solute plumes are illustrated.

[1] Chiogna et al. (2011) *Water Resour. Res.*, 47, W02505, doi:10.1029/2010WR009608.

[2] Rolle et al. (2012) *Transp. Porous Media* (in press).

Incorporation and early diagenesis of Mo and U isotope records in Bahamian carbonate sediments

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Transition metal concentrations and isotopes are widely used to understand past changes in ocean redox. Most of these proxies were developed for use in black shales. However, black shales are not ubiquitous in the geologic record and so our conception of ocean redox evolution may be biased by the conditions of restricted marginal basins in which such shales are often deposited. Along with other groups, we are exploring the use of complementary lithologies, such as carbonates, which are abundant in the geologic record and often deposited along open ocean margins [1-3].

Here, we examine the incorporation and early diagenetic evolution of Mo and U isotopes in shallow Bahamian carbonate sediments. The Bahamas is one of the largest and best studied Holocene carbonate platforms, and its location far from continental land masses results in sediments which contain very little siliclastic detritus. Our sample set consists of a wide variety of modern coral, algae, ooids, and mollusk samples ("primary precipitates") as well as 4 short push cores taken from tidal flats, sea grass meadows, and an organic-rich, tidal pond.

We find that Mo and U concentrations are much higher in shallow carbonate sediments than in primary precipitates, increasing from <0.1 ppm Mo to an average of 5.6 ppm Mo, and from an average of 1.5 ppm U to 4.1 ppm U, respectively. In almost all cases, the lowest sediment Mo and U concentrations were as high or higher than the highest concentrations found in primary precipitates, consistent with authigenic accumulation of Mo and U from reducing porewaters. $\delta^{234/238}\text{U}$ and $\delta^{238/235}\text{U}$ were very close to seawater values in all of the primary precipitates, but $\delta^{238/235}\text{U}$ in sediments was 0.2-0.4‰ heavier than in seawater. $\delta^{98/95}\text{Mo}$ ranged from ~1.0‰ lighter than seawater in a tidal flat core with low organic matter and low porewater sulfide, to values similar to or even slightly exceeding that of seawater in the most organic- and sulfide-rich cores, a pattern also consistent with control by porewater H_2S concentrations.

These results indicate that authigenic accumulation of Mo and U under sulfidic porewater conditions strongly affects Mo and U concentrations and isotopes in carbonate sediments. The extent of this process appears sensitive to porewater H_2S , and thus indirectly to sediment organic content. In the Bahamas, these parameters can vary over 100s of meters, with potential implications for Mo and U isotopic records in the geologic record. For example, in one case $\delta^{98/95}\text{Mo}$ of sediments varied by ~1‰ between a tidal flat region and core in a sea grass meadow ~100m away. To cope with such effects, proxies for porewater redox conditions may be required (e.g. organic content, iron speciation, or trace metal distributions).

[1] Voegelin et al. (2009) *Chemical Geology* 265(3-4), 488-498 [2] Voegelin et al. (2010) *Precambrian Research* 182(1-2), 70-82 [3] Brennecke et al. (2011) *PNAS* 108(43): 17631-17634.