Evaluating the Role of the Subterranean Estuary on the Redox Cycling of Uranium

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Introduction

In coastal aquifers, the interface between fresh ground water and more saline surface or ground water is referred to as a subterranean estuary [1]. This mixing zone is generally characterized by steep gradients of pH, Eh, and ionic strength due to the contrast in the geochemistry of the fresh and saline water end-members; these gradients affect the transport and transformation of dissolved constituents (e.g. nutrients and metals). Uranium is a redox sensitive actinide with two pre-dominant valence states, U^{4+} and U^{6+}, and three naturally occurring isotopes, $^{234, 235, 238}U$. Although the $^{235}U/^{238}U$ activity ratio (AR) is fairly ubiquitous in both water and rock, the $^{234}U/^{238}U$ AR is highly variable due to fractionation by alpha recoil across solid/liquid phase boundaries (^{234}U is the second generation decay product of ^{238}U) and increased vulnerability to solution (e.g. recoil displacement and redox chemistry). We are currently examining the effects that a subterranean estuary, which extends 30 m offshore beneath Indian River Lagoon, FL, has on the spatial and temporal cycling of dissolved uranium (bulk concentration and isotopic abundance).

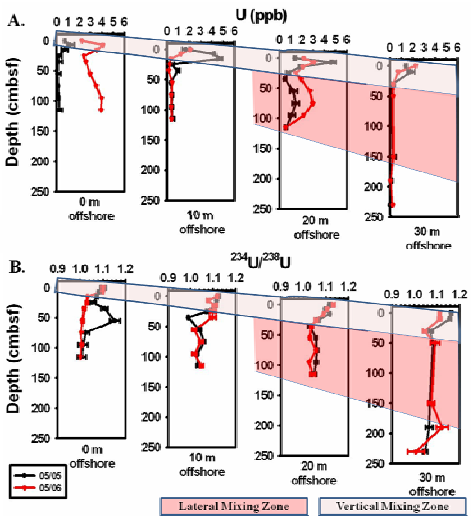

Figure 1: *Cross-section of shore-normal transect showing the vertical pore water distribution of dissolved U (A) and $^{234}U/^{238}U$ activity ratio (B)*

Results and Discussion

A total of 265 pore and surface water samples have been analyzed for natural U isotopes (234, 235, and 238) at the Geochemistry Division, NHMFL using the Finnigan ELEMENT ICP-MS; approximately 50 sediment samples are still awaiting analyses. Salinity distribution in the pore waters show two distinct mixing zones (Fig. 1): 1) an upper, fresh ground water – saline surface water mixing zone (0 to 35 cmbsf) and 2) a lateral, fresh ground water – saline ground water mixing zone (17.5 to 30 m offshore). Dissolved uranium concentration increases in both mixing zones; pore water uranium maxima are observed at 15 cmbsf for all offshore sampling locations and a deeper pore water maximum is observed 75 cmbsf at 20 m offshore (Fig. 1A). Surprisingly, the release of uranium to the pore waters does not greatly affect the $^{234}U/^{238}U$ activity ratio (Fig. 1B). The uranium maxima occur where dissolved oxygen concentrations and higher redox potentials are observed suggesting that the release of uranium is mediated by the oxidation of U^{4+} to U^{6+}. The more oxic conditions in the upper mixing zone are sustained by exchange of oxygen across the sediment-water interface by physical and biological processes [2]. The (sub)oxic conditions observed 75 cmbsf at 20 m offshore are more difficult to explain and we are still looking at other data sets (dissolved Fe, Mn, NO_3^-/NO_2^-, NH_4^+, and others) to better understand redox framework within the lateral mixing zone. Temporally, dissolved uranium concentrations increase significantly at the shoreline site between the May-2005 and May-2006 sampling trips (Fig. 1A), suggesting a significant change in the geochemistry of the ground water that discharges at the shoreline site. This apparent influx of uranium dampens the May-2005 $^{234}U/^{238}U$ AR of 1.17 observed at 55 cmbsf to equilibrium in May-2006 (Fig. 1B). Smith et al. [3] noted the landward migration of the lateral mixing zone at this site during the passage of Tropical Storm Tammy and Hurricane Wilma. We hypothesize these events also changed the redox framework of the subterranean estuary and the increase in uranium at the shoreline site during May-2006 is a reflection of these events. The spatial and temporal variations of uranium reflect two, geochemically-dynamic interfaces between fresh ground water and more saline surface or ground water.

References

[1] W. S. Moore, Marine Chemistry **65**, 111-125 (1999).
[2] C.G. Smith et al., Marine Chemistry, (in prep)
[3] C.G. Smith et al., Limnology and Oceanography, (in press, 2008).