

Multicomponent modeling of *in situ* uranium bioremediation: Findings and challenges

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Microbially mediated immobilization of uranium is being studied as a potential *in situ* remediation option for contaminated groundwater. Several biostimulation field experiments at a former uranium mill tailings site in Rifle, Colorado, USA have provided a basis to develop and test multicomponent biogeochemical reactive transport models of terminal electron accepting processes using acetate as the electron donor. A number of hydrologic, geochemical, and biological factors control the effectiveness of the uranium immobilization, making it a challenge to reliably predict important behaviors during and after bioremediation. The modeling approach accounts for two distinct functional microbial populations and parallel bioreduction of sediment iron associated with layer silicate and iron oxides, of which silicate iron bioreduction is faster and accounts for ~90% bioreduced iron. The model simulates the coupled biotic-abiotic processes in the context of site-specific hydrologic and geochemical conditions. Issues and data needs, such as spatial heterogeneity, stratified water chemistry, and detailed sediment characterization, will be discussed. The development of the modeling capability is part of a research project on long-term uranium immobilization at a U.S. DOE, Office of Science Integrated Field Challenge (IFC) Site. This capability is important to the design of optimal biostimulation strategies for uranium removal from groundwater, and will be continually updated with new knowledge and information.

Rapid recrystallization of carbonates and implications for geochemical proxies

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The alteration of primary chemical and isotopic signatures during the diagenesis of carbonate sediments can substantially affect the fidelity of geochemical proxies, such as Mg/Ca, Sr/Ca, $^{87}\text{Sr}/^{86}\text{Sr}$, and $\delta^{44}\text{Ca}$. The extent of diagenetic alteration, by exchange processes such as dissolution-reprecipitation or solid-state diffusion, depends on (1) mineral reaction rates, (2) the degree to which the solid is out of equilibrium with pore fluid, and (3) time. The current study discusses constraints on the former two factors, using measurements of sediment and pore fluid geochemistry and numerical models that simulate the interaction between pore fluids and carbonate sediments over million-year time scales.

The Ca isotopic composition of pore fluids is a sensitive indicator of recrystallization rates over meter length scales in carbonate-rich sedimentary sections. The measurement and modeling of Ca isotopes can therefore be used to determine bulk carbonate recrystallization rates in young sediments. At ODP Site 807A, recrystallization rates of Pleistocene nannofossil ooze have been constrained to be ~10 times faster (initially 30–40%/Ma, decreasing as a function of age) than older sediments [1]. This implies that the integrated amount of recrystallization in bulk sediments can be 15–30% in the first 2 Ma following deposition.

Since the implications of enhanced rates are considerable, additional work is required to substantiate the initial observations. High-resolution Ca isotope measurements at ODP Site 1171A (South Tasman Rise) indicate that, as at 807A, the Ca isotopic composition of pore fluids rapidly decreases with depth in the sedimentary column from seawater $\delta^{44}\text{Ca}$ values to bulk sediment $\delta^{44}\text{Ca}$ values. Just as at 807A, this decrease occurs over a period of <600 ka, suggesting that initial recrystallization rates are ~40%/Ma at 1171A. That “enhanced” reaction occurs in the upper part of the sedimentary section is significant, since this is the region in which solids and coexisting pore fluids are most likely to be out of equilibrium. Rapid recrystallization may work to alter the fidelity of elemental and isotopic proxies. The degree of alteration, constrained using numerical models, will be discussed.

[1] Fantle & DePaolo (2007) *Geochim. Cosmochim. Acta* 71(10), 2524–2546.