Modeling reactive transport of biogenic uraninite and its re-oxidation by Fe(III)-(hydr)oxides

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Uranium contamination in the subsurface is a global problem in surface and groundwater, soils, sediments and related ecosystems due to its chemical and radioactive toxicity to human and ecosystem health. A promising strategy for in-situ remediation of U-contaminated subsurface is through stimulating iron and/or sulfate reducing indigenous bacterial species to catalyze the reduction of soluble U(VI) to insoluble U(IV) – uraninite (UO_2), typically accomplished by amending the groundwater with an organic electron donor. Thus, uraninite is generally regarded as the most desirable end product of this bioreductive process due to its low solubility, and hence stability under reducing conditions. However, it has recently been shown that once the electron donor is entirely consumed, the biogenic uraninite can be can be reoxidized (and remobilized) by Fe(III)-(hydr)oxides, which may potentially impede the cleanup efforts. Therefore, it is vital to understand the governing factors that control the redox behavior of the bioreduced uraninite with respect to uranium fate, transport, and long-term stability. Based on the experiments [1], a suitable biogeochemical reaction network was developed to integrate the experimental data and simulate these interactions in subsurface environments focusing on the role of sulfide, Fe(II), Fe(III) (hydr)oxides, and the effect of nanoscale particle size on the stability of biogenic uraninite and its reoxidation [2]. Model results showed that the oxidation of sulfide by Fe(III) directly competed with UO_2 reoxidation as thermodynamically, Fe(III) oxidizes sulfide preferentially to UO_2. The re-oxidation of UO_2 is thus shown to depend on the relative rates of UO_2 and sulfide oxidation by Fe(III), as well as to the activity of Fe(II) in solution [2]. The developed reaction network and the interplay that emerges between flow, physical transport and reactions has been further studied in 2-D numerical experiments that were based on the setting found at the South Oyster site, Eeastern Virgina [3]. These simulations included surface complexation of U(VI) and Fe(II) onto Fe(III) oxides, microbial sulfate reduction using acetate with reductive dissolution of ferrihydrite and considered a highly heterogeneous property distributions.

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Biological productivity in the Subarctic North Pacific and Bering Sea: A proxy evaluation

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The Subarctic North Pacific (SNP) is one of the three principal HNLC (high nutrient low chlorophyll) regions in the modern ocean where biological production is limited. More than 20 years ago, John Martin and co-workers suggested that phytoplankton growth in the SNP is limited by iron which is mainly brought in by atmospheric eolian dust input from East Asian dust sources [1].

Productivity proxies (e.g., opal, carbonate, biogenic barium) show discrepancies in their interpretation from sediment cores in the SNP and Bering Sea for the last ~150 kyr. We will present results from a spatial survey of core-top sediments from 37 stations of the INOPEX cruise, with an extensive coverage of the whole SNP and Bering Sea. We will map and compare results from different productivity proxies (^{230}Th-normalized fluxes of opal, carbonate and biogenic barium) to evaluate the efficiency of the different proxies to reconstruct the spatial pattern in primary and export production with strong gradients across the SNP, as shown in studies of annual primary productivity estimated from the climatology of satellite ocean color observations [2] and of biological drawdown of pCO_2 [3]. Further, comparison with results from sediment trap studies will help to identify possible preservation problems for the different productivity proxies. First results indicate a good correlation between opal fluxes and published data of biological drawdown of pCO_2 in the northwestern and northeastern SNP. Results from this core-top study will be crucial for our ultimate goal to test the dust fertilization hypothesis over the last deglaciation using different dust flux and biological productivity proxies in sediment cores from the SNP.

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