Nano and Bulk-Scale Characterization of Biogeochemical Processes: A Case Study

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Recent advances in nanotechnology and analytic instrumentation allow biogeochemical processes between microbes, metals and minerals to be probed at remarkable levels of complexity, sensitivity, space and time. One of the dominant trends in geomicrobiology is the detailed characterization and application of biogenic minerals whose characteristic features are at the nanometer scale in at least one dimension. It is therefore important to understand – and ultimately exploit – the unique properties and behavior of a wide range of nanoscale biogenic materials. Central to this trend are the development and application of effective analytic techniques for characterizing the structural and chemical properties of biogenic minerals with (sub)nanometer spatial resolution.

Microbes in the subsurface are involved, directly or indirectly, in a plethora of activities such as metal reduction and oxidation, mineral precipitation and dissolution. These innate capacities of subsurface microbes are often exploited for *in situ* remediation of contaminated sites. During subsurface bioremediation of uranium-contaminated sites, indigenous metal and sulfate-reducing bacteria may produce biogenic minerals such as mackinawite (FeS) which could potentially drive abiotic uranium reduction.

In this work, the propensity of well-characterized biogenic mackinawite to abiotically reduce U(VI) was tested using a suite of electron microscopy and synchrotron based spectroscopy techniques. High-resolution electron microscopy confirmed the formation of nanoparticulate uraninite [UO_2] on the surface of biogenic mackinawite, which was further confirmed with bulk X-ray absorption spectroscopy that revealed the molecular coordination environment of uraninite. X-ray photoelectron spectroscopy confirms that U(IV) reduction was coupled to the oxidation of S^{2-} and not structural Fe(II) within the biogenic mackinawite. The combination of rigorous nano- and bulk-scale characterization provides insights into such biogeochemical processes, that occur during subsurface biostimulation, that are not always possible with bulk-scale analyses alone.

Unravelling complex groundwater recharge and transport of contaminants using combined stable and radioactive isotope tracers

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As part of a project assessing the quality and potential of groundwater, a vital resource in the extremely arid but touristic Namib-Naukluft area, a geochemical study of the surface and groundwaters, plants, soil, and rocks was undertaken. The study indicated excessive nitrate concentrations in about 15% of the 70 groundwaters sampled (several 100's of mg/l). While many of these groundwaters with high NO_3^{-} also have high $\delta^{15}N$ and $\delta^{18}O$ values and are from boreholes close to settlements, others are not. Furthermore, the vegetation also has elevated $\delta^{15}N$ values, making it difficult to identify anthropogenic or animal watses as contaminants. Mean residence times of groundwaters estimated by ^{14}C measurements of DIC have a wide range (recent as >100% modern carbon to about 14'000 yrs b.p.), and also a wide range of $\delta^{13}C$ values (–4.6 to –12.8‰) related to infiltration across soils of typical C3 (mountains) and C4 (savannah-desert) type of vegetation and limestone-derived soils and aquifers ($\delta^{13}C$ of –3 to +2‰). This variation, in addition to drainage across calcrete soils during brief periods of recharge necessitates substantial corrections to the measured ^{14}C ages, but which can be modelled via the concentrations and stable isotope compositions of DIC. Recharge during decadal "extreme events" is suggested by the H- and O-isotope compositions of the groundwaters with low δ-values compared to normal average annual rainfall. Seasonal variations in H- and O- isotope compositions in combination with modern mean residence times and high high nitrate $\delta^{15}N$ and $\delta^{18}O$ values thus do confirm an anthropogenic/animal-waste origin. The complex recharge of the aquifers across different soils, soil organic matter, can hence be unravelled using a combined isotopic tracing approach. In general, a slow, horizontal flow away from the principal mountain-recharge area, but also with locally important vertical recharge, particularly close to settlements and man-made boreholes, is indicated.

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