Microbially-mediated iron biogeochemistry

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Iron is a nutritional requirement for life. However for many microorganisms iron is not only a nutritional necessity, but also serves as a source of energy or as a terminal electron acceptor in respiratory microbial metabolisms. Microbially-catalyzed iron redox reactions between the Fe (III) and Fe (II) valence states play a fundamental role influencing modern environmental biogeochemistry in oxic, suboxic, and anoxic zones of aquatic, terrestrial, and subsurface environmental systems. The significance of iron redox cycling to the biogeochemistry of these environmental systems is well established. In the last decade, light-independent microbial Fe (II) oxidation has been recognized to contribute to iron redox cycling not only in the oxic environment but also in environments devoid of molecular oxygen with nitrate serving as the electron acceptor. To date, a diversity of microorganisms in the domain Bacteria and Archaea have been identified from various surface and subsurface environments that are capable of Fe (II) oxidation. These studies hint at the ubiquity of these Fe (II)-oxidizing microorganisms suggesting that metabolic, light independent Fe (II) oxidation reactions have the potential to contribute to suboxic and anoxic Fe (II) oxidative processes on a global scale provided that adequate concentrations of an electron acceptor are readily available. Some of these microorganisms are capable of oxidizing solid-phase Fe (II) bearing minerals including the products of microbial Fe (III) reduction. While oxidation of Fe (II) in suboxic and anoxic environments closes a gap in the iron redox cycle, the oxidative dissolution of these solid-phase Fe (II) minerals is additionally significant to understanding mineral weathering and dissolution reactions in these environments. These processes are not only important to modern biogeochemical cycling, but likely played a significant role throughout geologic time in surface as well as subsurface environments.

Biosignatures within iron-rich concretions originating in a sandstone paleoaquifer: Evidence of microbial oxidative dissolution of Fe(II)-carbonates

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Spheroidal concretions composed of an iron oxide-rich cemented outer rind and a weakly-cemented iron-poor sandstone core are abundant in the Jurassic Navajo Sandstone of the Colorado Plateau. Our recent work in south-central Utah has shown that abundant Fe (II)-carbonates were precipitated within the Navajo Sandstone at sites that lie downflow from massive CO_2 reservoirs. The Fe (II)-carbonate concretions were subsequently altered to Fe (III)-oxide as oxidizing water was transported through the paleoaquifer. Microbial metabolisms have been demonstrated to promote the oxidative dissolution of Fe (II)-carbonate minerals. Elemental analysis of the specimens collected from Spencer Flat, east of Escalante, in south-central Utah revealed elevated carbon (C) as well as nitrogen (N) content with respect to the interior of the concretion (Rind, C, 0.06%, N, 0.006%; Interior, C, 0.009%, N, 0.003%). Elevated C and N values in the rind suggest C-N rich compounds consistent with biomolecules. Average $\delta^{13}C$ values measured from the organic carbon (OC) fraction in triplicate samples (-22.088‰) indicated the iron oxide crust contains OC consistent with a biogenic origin and CO_2 fixation (-20 to -35 ‰). Structures morphologically consistent with bacterial cells have been observed via FE-SEM in association with a matrix that coated sand grains in the iron oxide-rich rind. Similar structures identified using NanoSIMS consists of high CN/C and FeO demonstrating a relationship of Fe minerals and C signature consistent with OC. Together these results support the presence of microorganisms and iron biomineralization in the spheroidal iron oxide concretions. Here we have presented evidence of biosignatures suggesting a role of microbial metabolism transforming the Fe (II)-carbonates which would have subsequently lead to carbonate dissolution in the paleoaquifer. Given the ubiquity of Fe (II)-oxidizing bacteria, this microbial catalyzed process is likely active in modern aquifers and other subsurface environments.