

## The role of nano-components in contaminated mine water outflow crossing a redox boundary

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Especially in the last 15 years, Earth scientists have been exploring the role of nano-sized materials in a number of environment-related processes, including the transport and transformation of organic and inorganic contaminants. In this study, with both the geochemistry and microbiology in mind, we chose to study a highly dynamic environmental system (Ronneburg Mining District, Germany) where groundwater outflow from a former uranium mine is negatively impacting the downstream environment. The outflow contains high amounts of Fe(II) and, upon exposure to air at pH 5.8-6.0, iron oxyhydroxide particles form. Our principal goal was to determine the role that nanoparticulate formation has on the (bio)geochemistry of this complex and dynamic system. From June to October of 2011, water and sediment was carefully collected at four sites along portions of the flow path of greatest interest: at the groundwater outflow point, at rust-colored terraces where the outflow water flowed over a creek bank, from the creek adjacent to the terrace, and from the creek about 1 km downstream. A multi-scale approach was used to analyze the samples including XRD, ICP-MS, SEM and analytical TEM (HR-TEM, EDS, and SAED).

The first indication of nanocrystalline particles comes from the broad XRD peaks of the sediment samples, many of which match goethite and akaganeite. XRD of suspended particles shows even broader diffraction maxima that cannot readily be identified, but do indicate the predominance of nano- and/or very poorly crystalline or amorphous particles. TEM corroborates this to a point, but also reveals very important details. For example, suspended particles (40-300 nm) in terrace and creek sites tend to be roughly spherical, and found in aggregates of amorphous iron oxyhydroxides intimately mixed with and sometimes coated by amorphous silica. Various types of nanocrystalline phases were found in the sediment samples as well, including nanoneedles of goethite growing from 100-300 nm spherical particles, and even smaller and smoother spherical particles that are clearly mixtures of amorphous silica and the very earliest stages of iron oxyhydroxide crystallization manifested by uniform lattice fringes that can be traced over only 2 to 5 nanometers. Interestingly, in the groundwater outflow, suspended nanometer-thin ferrous sulfate pseudo-hexagonal platelets (containing small amounts of Zn) were discovered. We have tentatively identified these as the mineral rozenite using electron diffraction analysis.

As these rozenite particles in the outflow become unstable, they are an important source of Zn, which is the metal with the fourth-highest concentration downstream. Zn and Ni were not primarily associated with larger suspended particles (> 0.1 µm), unlike the metals at trace concentrations (U, Cu, Cr, and Pb). Interestingly, Sn oxide oval-shaped nanoparticles (5-20 nm) were found multiple times in terrace site water samples, and their significance is presently being investigated.

In this ongoing study, we have shown again why knowledge of the formation, transformation, reactivity, and dissolution of the nano-components are important in understanding the behavior and evolution of the entire system.

## From mineral interfaces to 200 million tons per year: A geologic perspective of the surface-catalyzed iron redox cycle

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Evidence for redox-driven reactions at the mineral-fluid interface of iron oxides may be found in the largest iron deposits on Earth, banded iron formations (BIFs), which were largely deposited in the Neoproterozoic and Paleoproterozoic. The insights gained by detailed, mechanistic studies of mineral-fluid reactions demonstrate that the major volume of BIF deposits was not formed by "passive" accumulation of iron oxide minerals on the seafloor but instead record an extensive redox history during formation and early diagenesis prior to lithification. Redox-driven reactions are the fundamental process that inhibits iron oxides from behaving as "inert" particles, and, in fact determine not only the isotopic compositions of redox-sensitive elements such as Fe, but also the O isotope compositions through breakage of Fe-O bonds. In addition, the structural changes that occur in iron oxides upon substitution of Si, an important component in marine environments in the Precambrian, produce significant changes in stable isotope compositions. Redox-driven reactions between aqueous Fe(II) and Fe(III) oxides that are catalyzed by biology may produce significantly different end products and elemental mass balance than abiogenic Fe(II)-Fe(III) oxide interactions, and this contrast may be expressed as distinct isotopic compositions. In the case of BIFs, the isotopic fingerprints of microbially-catalyzed redox cycling is expressed in fine-scale isotopic heterogeneity that produces compositions out of equilibrium with ambient seawater. Importantly, the end product of extensive biological reduction of Fe(III) oxides are not mixed Fe(II)-Fe(III) minerals such as magnetite, which are produced at moderate extents of reduction, but Fe(II)-bearing carbonates (siderite, ankerite). Although perhaps not immediately obvious, iron carbonates actually contain the best evidence for the magnitude of microbially-catalyzed redox cycling of iron oxides in BIFs, and C, O, and Fe isotope compositions clearly indicate biological Fe(III) reduction. The C, O, and Fe isotope compositions of the largest BIFs, the 2.5 Ga Brockman (Pilbara craton, Australia) and Kuruman (Kaapvaal craton, South Africa) iron formations, indicate that virtually all of the Fe in these deposits has been cycled by microbes. These BIFs provide the majority of the world's iron, in economic deposits that reflect later hydrothermal mobilization, oxidation, and deposition. These BIFs are mined at a rate of ~200 million tons per year in the Pilbara craton alone, an impressive testament to the importance of surface-catalyzed redox cycling.