

Green rust formation under anaerobic nitrate-dependent Fe(II) oxidizing conditions

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Recent studies have suggested that both oxidative and reductive microbial Fe metabolisms result in the formation of a mixed valence, layered Fe(II)/Fe(III) hydroxide with anion interlayers known as green rust (GR), however, the extent of either process is unknown. Green rust is predominantly identified in hydromorphic soils and sediments. The contribution of anaerobic nitrate-dependent Fe(II) to iron redox cycling provides an ideal mechanism of GR formation given that microorganisms capable of this metabolism are ubiquitous. Given that nitrate-dependent Fe(II) oxidizing bacteria are ubiquitous as identified by most probable number enumeration, as high as 1.47×10^4 cells (g sediment)⁻¹ in freshwater lake sediment, 2.04×10^3 cells mL⁻¹ in groundwater, and 1.17×10^3 cells (g sediment)⁻¹ in subsurface sediment, and contributes to anaerobic iron redox cycling. Furthermore, a novel autotrophic, nitrate-dependent Fe(II)-oxidizing bacterium, *Cosmobacter millennium* strain 2002, yields a mixed phase Fe(II)/Fe(III) mineral phase, identified as green rust by Mössbauer spectroscopy and X-Ray diffraction. In contrast to the GR biogenically formed by Fe(III) reduction, the biogenic GR product formed via nitrate-dependent Fe(II) oxidation by *C. millennium* strain 2002 did not yield transformation products, i.e., magnetite. X-Ray fluorescence spectroscopy identified chloride and phosphate in association with the GR product. Furthermore, anion analysis of the GR by ion chromatography indicated that 6 mg SO₄²⁻, 32 mg Cl⁻, and 66 mg PO₄³⁻ was associated with the oxidation of 111 mg Fe(II). These results suggest that GR(Cl⁻) was formed. It is currently unknown whether phosphate is adsorbed to the GR surface or intercalated into the interlayer. These results represent the first demonstration of the biogenic formation of green rust in significant quantities providing evidence for the biological mechanism for the production of GR(Cl⁻) in soils and sediments.

Coupling sulfide production and arsenic release in dynamic systems

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Iron (hydr)oxides are a common constituent of clay-rich soils to which toxic metals and metalloids readily adsorb. The influence of microbial populations on the speciation of such adsorbed metals and metalloids under reducing conditions is not well understood. Information of such processes will aid in the understanding of the mobility and retention of toxic metals and metalloids

We have examined arsenic remobilization in a series of column experiments using synthetic mineral suspensions and/or natural sediments from an uncontaminated, though arsenic-impacted, region of Cambodia. Here, we focus on arsenic release induced by the presence of dissolved sulfide production. As(III) and As(V) were adsorbed to ferrihydrite-coated sand within the columns and then reacted with a variety of solutions. These Fe-As systems were subjected to various flow rates, sulfide concentrations and microbial populations in replicate columns. Results indicate that arsenic and iron underwent considerable changes in speciation, and that arsenic mobility was significantly influenced by the presence of sulfide. At relatively high sulfide activities, iron reduction was observed without measurable arsenic release, while arsenic was released to a limited extent under conditions of slow flow and/or low sulfide activities. Changes in mineralogy were identified using X-ray absorption spectroscopy, and the mechanism of As retention also changed rapidly during sulfidization.

For Cambodian sediments, sulfate reduction also was stimulated in situ, and the results contrasted with sterilized controls. Community analysis, using 16S rDNA, was used to identify potential dominant microbial populations capable of reducing arsenic, iron and sulfur. Solid phase analysis using X-ray absorption methods also identified changes in mineralogy and to characterized As retention.