

Effect of sorbed arsenic species on bacterial reduction of HFO

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The geochemistry that controls the partitioning of arsenic species between solid and aqueous phases in sediment-porewater systems can be strongly influenced by bacterial processes. Particularly, bacteria can control redox cycling of both arsenic and soil minerals, which can in turn strongly affect the ultimate mobility of arsenic. The release of arsenic into the aqueous phase has created a serious health problem in several countries throughout the world.

One proposed mechanism for the mobilization of arsenic from the surface of an iron (oxy)hydroxide mineral is through the reductive dissolution of the iron mineral, which has been linked to bacterial respiration. However, arsenic mobility also depends on its redox state (mainly inorganic As(III) or As(V)), which can also be microbially controlled. Bacterial respiration is potentially an important route for the reduction of As(V) to As(III) in the environment [1,2].

This study investigates the rates of reductive dissolution of hydrous ferric oxide (HFO) by *Shewanella* sp. ANA-3 in laboratory incubations with either As(V), As(III), or a mixture of As(V) and P(V). Iron and arsenic speciation were measured in both the solid and dissolved phases. In addition, ambient bacteria from Haiwee Reservoir, a field site known to have a population capable of iron reduction and arsenate respiration [3,4], were inoculated into a similar As(V)/HFO slurry experiment.

In both *Shewanella* ANA-3 and Haiwee incubations, As(V) was initially reduced before HFO. A fraction of the total HFO was also reduced over the course of the experiment. The relative rates of reductive dissolution will be presented.

References

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A general rate law for bacterial Fe(III) oxide reduction

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Recent experimental studies of synthetic and natural Fe(III) oxide reduction permit development of a general reaction-based rate law for bacterial Fe(III) oxide reduction at circumneutral pH. The findings collectively support a rate law that differs fundamentally from those applied to abiotic reductive dissolution as a result of two basic phenomena: (1) the relatively minor influence of oxide mineralogical and thermodynamic properties on surface area-normalized rates of enzymatic reduction compared to abiotic reductive dissolution; and (2) the major limitation which sorption and/or surface precipitation of biogenic Fe(II) on residual oxide and Fe(III)-reducing bacterial (FeRB) cell surfaces poses to enzymatic electron transfer in the presence of excess electron donor. Parallel studies with two major FeRB genera (*Shewanella* and *Geobacter*) lead to common conclusions regarding the importance of these phenomena in regulating the rate and long-term extent of Fe(III) oxide reduction. Models in which rates of enzymatic reduction are limited kinetically by the abundance of "available" oxide surface sites (as controlled by oxide surface area and the abundance of surface-bound Fe(II)) and by FeRB cell density provide an adequate macroscopic description of controls on the initial rate and long-term extent of oxide reduction. Although thermodynamic limitations posed by accumulation of aqueous reaction end-products (e.g. Fe(II) and alkalinity) cannot generally account for the slow-down and cessation of Fe(III) oxide reduction over time in batch reaction systems, a thermodynamic term (e.g. a TST function) or some other kind of switch must nevertheless be incorporated into the general rate law in order accurately simulate long-term patterns of reduction.