Characteristics and mechanisms of arsenic behavior during the microbial oxidation-reduction of iron

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ABSTRACT: The (bio)geochemical cycling of arsenic (As) and iron (Fe) is generally coupled in high As groundwater. However, characteristics and mechanisms of As sequestration-release behavior during formation-reduction of biogenic Fe(III) minerals (bio-FeM) are poorly understood. The *Pseudogulbenkiania* sp. strain 2002 induced the formation of binary bio-FeM, facilitating As immobilization compared to single Fe(III) minerals. Net As release was found during reduction of binary bio-FeM by *Shewanella oneidensis* strain MR-1, which was affected by secondary iron mineral formation and competitive adsorption. We suggested that bio-FeM deserve more attention due to their outstanding potential roles in controlling As behavior in aquatic systems.

1 INTRODUCTION

High arsenic (As) groundwater (As concentration > 10 $\mu\text{g L}^{-1}$) is one of the major worldwide concerns. Arsenic (bio)geochemical cycling is often coupled to the cycling of iron (Fe) (Zhu *et al.*, 2017). For instance, natural ferric (hydro)oxides, mainly consisting of various biogenic Fe(III) minerals (bio-FeM), possess high sorption reactivity, which have the potential to coprecipitate or adsorb As (Feris, 2005; Xiu *et al.*, 2015; Xiu *et al.*, 2016; Sowers *et al.*, 2017). Whereas, dissimilarly reductive dissolution of Fe(III) (hydro)oxides is of utmost importance in controlling As enrichment in groundwater under reducing condition (Islam *et al.*, 2004; Postma *et al.*, 2010; Schaefer *et al.*, 2017). However, characteristics and mechanisms of As sequestration-release behavior during the formation-reduction of biogenic Fe(III) minerals are poorly understood. The Objectives of this study are to (i) characterize As sequestration by biogenic Fe(III) minerals as well as related mechanisms of As sequestration; (ii) explore the character and mechanisms of As release during bio-reduction of biogenic Fe(III) minerals.

2 METHODS/EXPERIMENTAL

2.1 Sources of microbes

The anaerobic Fe-oxidizer, *Pseudogulbenkiania* sp. strain 2002, was retrieved from lab stock (20% glycerol at -80°C , Geomicrobiology Lab at the China University of Geosciences, Beijing) and routinely cultivated at 30°C using freshwater basal medium with nitrate and acetate as electron acceptor and donor, respectively.

The facultative dissimilarly iron reducer, *Shewanella oneidensis* MR-1 was routinely cultured aerobically in Luria-Bertani (LB) broth (pH = 7.0) at 30°C . Once cell growth reached the mid to late log phase, centrifuged in anaerobic chamber (filled with N_2/H_2 , 92.5%/7.5% (v/v), Coy Laboratory Products, USA), washed three times with deoxygenated bicarbonate buffer (2 g L^{-1} NaHCO_3 and 0.08 g L^{-1} KCl, pH = 7.0) to remove residual LB, and resuspended in buffer to a final concentration of $\sim 2 \times 10^8$ cells mL^{-1} . In selected treatments, AQDS (Sigma) was added separately.

2.2 Experiential setups

To obtain the As-containing bio-FeM, anaerobic cultures with 1 mg L^{-1} As(V) and approximately initial 3.0 mM Fe(II) (initial molar ratio of Fe(II)/As(V) around 225) were incubated with later log-phase cells of strain 2002 (5%, v/v). The bio-FeM was sampled by repeated centrifugation (1000 rpm for 10 min), following by rinsing with deionized water, dried in an anaerobic glove box until analyzed within one week. Reduction of bio-FeM was conducted in bicarbonate buffer containing bio-FeM (~ 100 mg mL^{-1}) and MR-1 cells ($\sim 2 \times 10^8$ cells mL^{-1}). Tubes were purged with N_2/CO_2 gas mix (80:20) and sealed with thick butyl rubber stoppers. The control consisted of one tube that received 1 mL of sterile bicarbonate buffer in place of MR-1 cells.

2.3 Analytical methods

Suspension were anoxically taken at different time intervals and divided into two equivalents. One was filtered with 0.22 μm membrane filter, and analyzed for dissolved As species, dissolved Fe species. The other

Figure 1. Changes of dissolved As and Fe(II) during strain 2002-induced Fe(II) oxidation: (left) changes of dissolved Fe(II); (right) changes of dissolved As.

was used to monitor the progress of Fe(III) reduction, following the 1,10-phenanthroline assay. The bio-FeM were sampled and analyzed by scanning electron microscopy (SEM), X-ray photoelectron spectroscopy (XPS), frontier transform IR spectra (FTIR), X-ray diffraction (XRD), and As and Fe K-edge XANES and EXAFS.

3 RESULTS AND DISCUSSION

3.1 As immobilization during the formation of biogenic Fe(III) minerals

Results showed that a rapid decrease in Fe(II) concentration was observed in early stage (before 24 h) and thereafter, Fe(II) concentrations dropped relatively placid after 24 h, forming the mixture of two-line ferrihydrite and goethite. Simultaneously, As(V) was efficiently removed from solutions through adsorption onto and/or co-precipitation with biogenic ferrihydrite-goethite bimineral (Fig. 1), forming binuclear bidentate corner sharing As-Fe complexes ($2C$). The $As_{\text{immobilized}}/Fe_{\text{precipitated}}$ at the end of incubation (168 h) achieved 0.005, which was higher than that in poorly crystalline or even amorphous biogenic Fe(III) oxides under similar condition. No detectable redox transformations of As(V) were observed.

3.2 Reduction of biogenic Fe(III) minerals

Result showed that Fe(III) reduction occurred when log phase of MR-1 was reached. A rapid increase in Fe(II) concentration was observed in early stage (< 72 h), and thereafter dropped, possibly due to the formation of secondary iron minerals. Simultaneously, As release occurred before 24 h (mainly As(V) resulting from iron reduction), and then released As was re-immobilized into secondary iron minerals, and finally As was mobilized from secondary iron minerals possibly via competitive adsorption (Fig. 2).

4 CONCLUSIONS

The *Pseudogulbenkiania* sp. strain 2002 induced the formation of binary bio-FeM, facilitating As immobilization compared to single Fe(III) minerals. Net As release was found during reduction of binary bio-FeM by *Shewanella oneidensis* strain MR-1, affected by secondary iron mineral and competitive adsorption.

Figure 2. Changes of dissolved As and Fe(II) during MR-1-induced Fe(III) reduction: (left) changes of dissolved Fe species; (right) changes of dissolved As species.

ACKNOWLEDGEMENTS

The study is financially supported by the National Natural Science Foundation of China (Nos. 41702272, 41672225, 41222020 and 41172224) and the Fundamental Research Funds for the Central Universities (No. 53200759026, 2652013028).

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