Biotic and abiotic contributions to the reduction of environmental bacteriogenic Fe-oxides at circumneutral pH

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Motivation: Environmental Impacts of Fe Cycling

- The Fe biogeochemical cycle affects carbon cycling, energy flow, and the mobility of nutrients and contaminants[1, 2, 3]
- The chemistry of environmental bacteriogenic Fe-oxides (EBIOS) biomineralized at circumneutral conditions in streams and soils is an important link in this larger cycle

Background: Biotic and Abiotic Fe-oxide Reduction

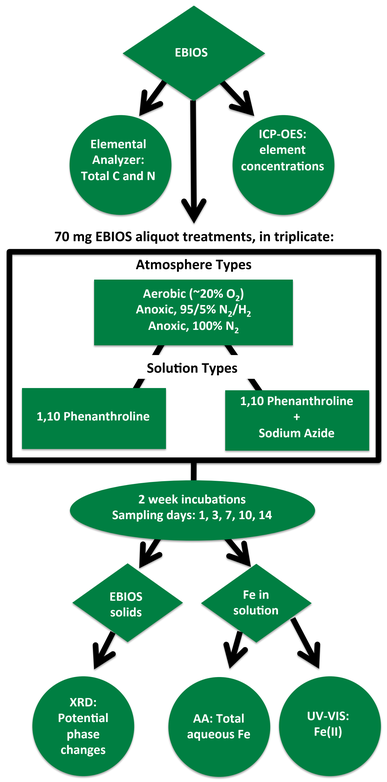
- Fe can be oxidized and reduced abiotically, but also biotically by Fe-oxidizing and reducing bacteria[4]
- The dominant mechanism for the circumneutral reduction of EBIOS is only partially understood

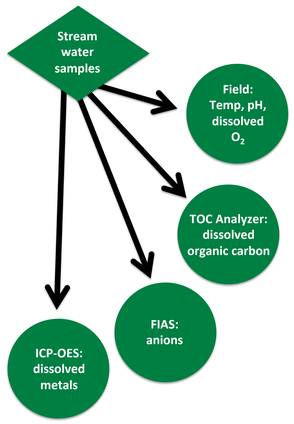
Objectives

- Determine the plausibility of biotic and abiotic mechanisms for EBIOS reduction
- Track kinetics of Fe(II) formation from EBIOS and synthetic two-line ferrihydrite (2LFh)
- Identify potential phase changes during EBIOS reduction

Experiment: EBIOS Reduction Incubations

- EBIOS biofilms and stream water samples collected from Walnut Creek and New Hope Creek in Raleigh



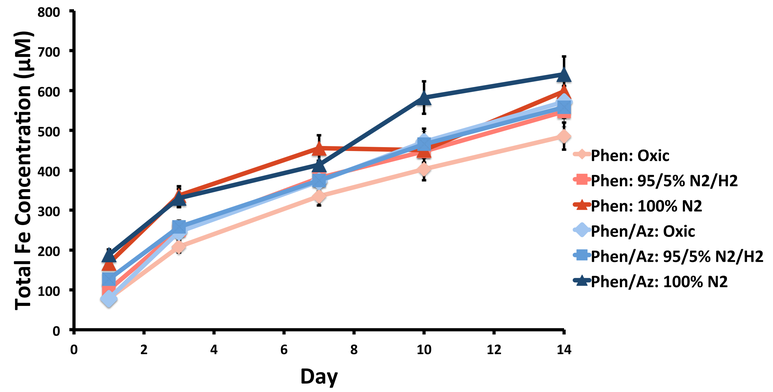


EBIOS forming in Walnut Creek, Raleigh NC

- 1,10 phenanthroline: Fe(II) trapping agent
- Sodium azide: microbial metabolism inhibitor

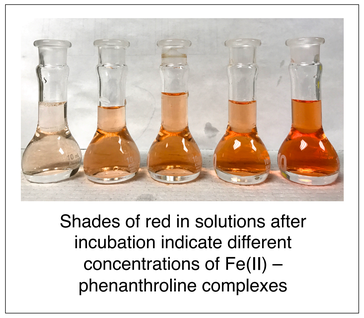
Results

EBIOS Total Aqueous Fe

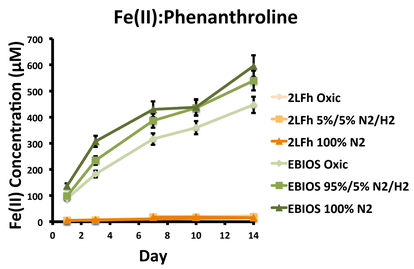


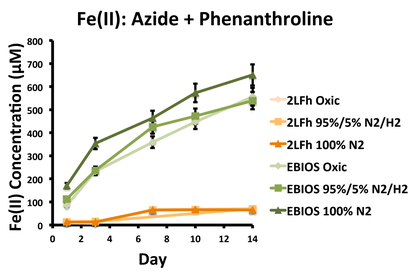
Error bars represent analytical error, estimated as 7%

Fe(II)



Shades of red in solutions after incubation indicate different concentrations of Fe(II) – phenanthroline complexes

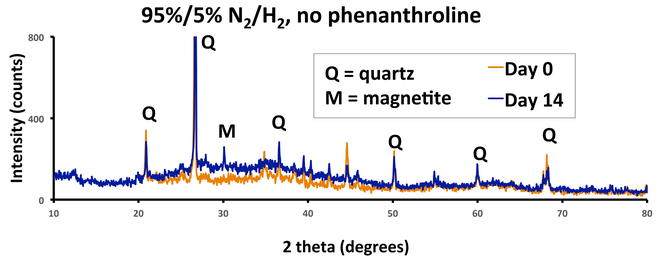


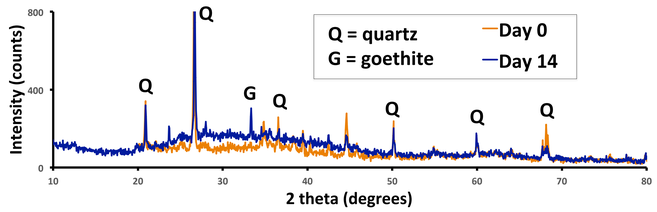


- Fe(II) concentrations equivalent to total Fe concentrations for EBIOS
- Possible correlation between azide and higher Fe(II)
- Minimal 2LFh reduction

Sample Type	Initial Reduction Rate (mol m^{-2} min^{-1})	14-Day Reduction Rate (mol m^{-2} min^{-1})	Reduction Mechanism	Reference
EBIOS (average)	1.65E-10	7.41E-11	–	This study
2-Line Ferrihydrite	4.24E-10	–	Microbial	Roden and Zachara (1996)[5]
2-Line Ferrihydrite	1.19E-10	–	Microbial	Roden (2003)[6]

XRD: Potential Phase Changes?





Conclusions

- While extent of EBIOS reduction is slightly greater under anoxic conditions, atmosphere type did not have a large influence on reduction rates
- The reduction of EBIOS at circumneutral pH is mainly abiotic, since azide did not result in significant changes in reduction
- Small increases in reduction in the presence of azide may indicate reduced activity of Fe-oxidizing bacteria

Hypothesis: EBIOS reduction is abiotic and driven by reactions with organic matter present in the biofilms rather than by microbial processes

Ongoing Work

- EBIOS and 2LFh incubations without the trapping agent 1,10 phenanthroline, to characterize the build-up of Fe(II) in solution under oxic and anoxic conditions
- 2LFh incubations with ascorbate to verify plausibility of reduction via reactions with organic matter

References

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Acknowledgments

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