

Microbial reduction of goethite by *Shewanella* Alga BrY: Effects of pH and sorbed Arsenic(III)

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Goethite reduction by *Shewanella* algae BrY under anaerobic conditions coupled to lactate oxidation was investigated in solution pH ranging from 5.5 to 8.0 and As(III) concentration varying from 0 to 500 μM . In the absence of As(III), the rate and extent of goethite reduction decreased with increase in pH from 6.5 to 8.0. The maximum extent of goethite reduction decreased from about 7500 μM at pH 6.5 to 650 μM at pH 8.0. A large fraction of the goethite remained unreduced and a large fraction of Fe(II) was associated with the solid phase at pH 8.0, whereas at pH 6.5, most of the Fe(II) was in the aqueous phase. In contrast, under similar conditions, the rate of anaerobic Fe(III)-NTA reduction and aerobic growth of the cells were independent of pH. A decrease in pH below 6.5 leads to a decrease in the rate and extent of goethite reduction, Fe-NTA reduction rate, and aerobic growth rate of cells; suggesting inability of the cells to synthesize biomass and sustain life functions at these low pH conditions. The relative importance of thermodynamic constraints posed by accumulation of byproducts and the effect of Fe(II) sorption on the rate and extent of goethite reduction are evaluated through modeling simulation for pH conditions between 6.5 to 8.0. Despite large differences in the total maximum Fe(II) concentrations observed at different pH conditions, goethite reduction seems to cease at around $\Delta\text{Gr} \sim -40 \pm 5 \text{ kJ mol}^{-1}$ much below the proposed maximum of -20 kJ mol^{-1} required for ATP synthesis. The effect of sorbed Fe(II) on the rate of goethite reduction was modeled using site density and Fe(II) sorption constants obtained previously in simple electrolyte solutions using the same goethite. The model predicts that goethite reduction seems to cease even when reactive free sites are available. The sorption model is further developed assuming that a reduction of total available surface sites occur under these experimental conditions, rather than the simple chemical conditions under which it was constrained, from a combination of factors including the presence of phosphate, cells, chemicals from bacterial media, and the assumption that all the complexed Fe(II) does not sorb onto goethite surface. With the above assumptions, the model is able to predict both the rate and extent of goethite reduction at pH values ranging from 6.5 to 8.0.

The rate and extent of goethite reduction are not significantly affected by the presence of 250 μM total As(III). At 500 μM total As(III), a small increase in the maximum extent of goethite reduction was observed at pH 7.5 and 8.0. However, both the rate and extent of goethite reduction decreased at pH 6.5 and 7.0. Goethite reduction did not result in the release of excess As(III) into the solution.

Carbonatite and silicate melt metasomatism of depleted mantle surrounding the Hawaiian plume: origin of rejuvenated-stage lavas

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Wyllie [1] first presented a melting model for the Hawaiian plume, predicting formation of trace amounts of volatile-charged incipient melt at depths of 350-150 km as the plume crosses the solidus for peridotite-C-H-O. Wyllie predicted these incipient melts would be swamped by major melting at the center of the plume, but might be detectable on the margins of the plume, where precursory, marginal and rejuvenated-stage volcanics (RSV) erupt. This and subsequent work [2] provides an important framework for interpreting spatial and temporal variation in Hawaiian magmatism as a function of temperature. Building on Wyllie's conceptual framework, we model [3] the generation of RSV by small degrees of melting of depleted peridotite recently metasomatized by a few percent of enriched silicate melt and/or carbonatite derived by incipient melting of carbonated peridotite and eclogite within the Hawaiian plume. The carbonatite component is clearly identified in RSV from Niihau, characterized by enrichments in Ba, Sr, LREE, H₂O and Cl at relatively low concentrations of Th, Nb, Hf, and Ta. High and variable H₂O and Cl may be caused by heterogeneous fluids in the mantle source produced as carbonatite percolates through and interacts with depleted peridotite. Production of carbonatite at depths of incipient generation favors metasomatism of depleted mantle thermally entrained by the plume, rather than shallow lithosphere, consistent with recent isotopic studies.

[1] Wyllie (1988) *J. Geophys. Res.* **93**, 4171-4181. [2] Wyllie & Ryabchikov (2000) *J. Pet.* **41**, 1195-1206. [3] Dixon *et al.* (2008) *G³*, doi:10.1029/2008GC002076.