

Behaviour of microbial cells as geochemically reactive solids

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The transport, bioavailability, toxicity and ultimate fate of inorganic contaminants such as trace metals and radionuclides, are intimately tied to the nature of reactions occurring between the contaminant and the solid phase (1). In recognition of the importance of reactions at solid surfaces; aquatic surface chemistry (2) has provided both the conceptual framework for the emerging paradigm and more importantly, the ability to quantitatively assess metal impacts in aqueous environments through the development of the surface complexation - precipitation models (SCM - SPM; 3).

These models quantify metal-solid partitioning by describing sorption and subsequent precipitation reactions between functional groups or reactive sites at the solid surface and the charged contaminant species, and use classical thermodynamic equilibria as the controlling principles to predict when such associations are likely to occur. To date, this modelling approach has had demonstrated success for inorganic surfaces, Fe oxides in particular (4). However, a wide variety of potentially geochemically reactive substrates other than Fe oxyhydroxides occur in aquatic environments. If the SCM-SPM approach is to emerge as the guiding paradigm for metal geochemistry its applicability to other likely important solid surfaces, e.g. Mn oxides, and organic matter - both live and dead, must be evaluated.

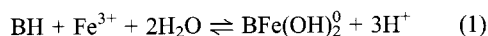
In particular, evidence of a significant microbial involvement in aqueous metal reactions is inferred by the body of largely descriptive evidence showing them to be encrusted with a variety of metal containing minerals (5,6). Investigations into the geochemical reactions occurring at bacterial surfaces have revealed a strong microbial mediation of a wide variety of mineral precipitation reactions, which, according to the geologic record, stretch back 4 million years. It is becoming increasingly evident from such qualitative information, that bacterial precipitation of mineral phases provides a secondary sorbent phase that may play a key role in the transport of a wide variety of compounds.

Bacteria are, at the very least, as widely distributed and probably as reactive as Fe oxyhydroxides in aquatic environments; and thus reactions that occur at

microbial surfaces will be extremely important for chemical contaminant issues. The role of bacteria in subsurface aqueous environments, is likely to be especially important, as in these systems, the spatial distribution of reactive substrates plays a critical role in determining transport and fate of contaminants like trace metals and radionuclides. While microbial surfaces have been implicated as potentially significant metal sorbents in a wide variety of aquatic environments, they have, as yet, to be considered in any geochemically quantitative sense.

If surface complexation of geochemical reactions at bacterial surfaces then a quantitative insight into the continuum between sorption and precipitation of dissolved metals on bacterial surfaces can be elicited. Thus far, in any conceptual understanding of metal behaviour in aquatic systems, is the implicit assumption that reactions should proceed homogeneously. However, reactions such as surface precipitation of secondary mineral phases on bacterial surfaces will proceed heterogeneously. To date no quantitative understanding of the reactions at bacterial surfaces has emerged. Yet this kind of work will provide the missing link between pure chemical precipitation and the formation and synthesis of biominerals. Integration of these biological entities as another reactive substrate in developing geochemical models of aqueous contaminant behaviour will vastly improve our ability to accurately predict contaminant transport, fate and likely impacts in aquatic systems.

We report here that solid phase partitioning of Fe(III) as hydrous ferric oxides (HFO) is enhanced in the presence of a variety of bacteria with differing surface characteristics. Further, the formation of HFO's on bacterial surfaces was found to be amenable to the geochemical SPM modelling approach using a simple mass action expression based on a single generalized bacterial surface site (see equation 1).



where BH represents a bacterial surface site (analogous to SOH for Fe oxides) and $\text{BFe}(\text{OH})_2^0$ is bacterially associated Fe. The corresponding

apparent surface complex formation constant, K_{Fe}^s is given by:

$$K_{\text{Fe}}^s = \frac{[\text{BFe}(\text{OH})_2][\text{H}^+]^3}{[\text{BH}][\text{Fe}^{3+}]} \quad (2)$$

The reactions of Fe with bacterial surfaces follow a clear continuum of sorption, nucleation and precipitation, consistent with the SPM approach (Fig. 1), indicating that metal reactions at bacterial surfaces can be quantitatively described using geochemical principles. Our results provide the first demonstration of the continuum among sorption, nucleation and precipitation of HFOs on microbial cell surfaces, and allowed quantification of the ability of microbes to enhance HFO formation.

We suspect that our results using ordinary heterotrophic bacteria in the laboratory, are analogous to metabolically mediated HFO production in nature, by Fe (III) oxidizing bacteria. The biologically produced Fe (III) probably sorbs to the bacterial surface and ultimately precipitates according to the same principles we have demonstrated with heterotrophic bacteria under non growth conditions. Furthermore, we presume that HFO precipitates on bacteria have similar sorptive capacities for metals and radionuclides as abiotically produced HFOs. Overall, these results have important consequences for aqueous geochemical modelling, especially in subsurface environments where microbially controlled reactions often play a key role in determining the fate and transport of contaminants. An important implication of this work is that physical and environmental factors regulating the spatial distribution and abundance of microorganisms are apt to profoundly influence the deposition of HFO, and thus the chemical reactivity of aquatic systems. The concept of microbial control on the rates and locations of geochemical reactions (e.g. sorption, precipitation) has thus far, been largely ignored in any paradigm development for reactive transport in natural systems.

References

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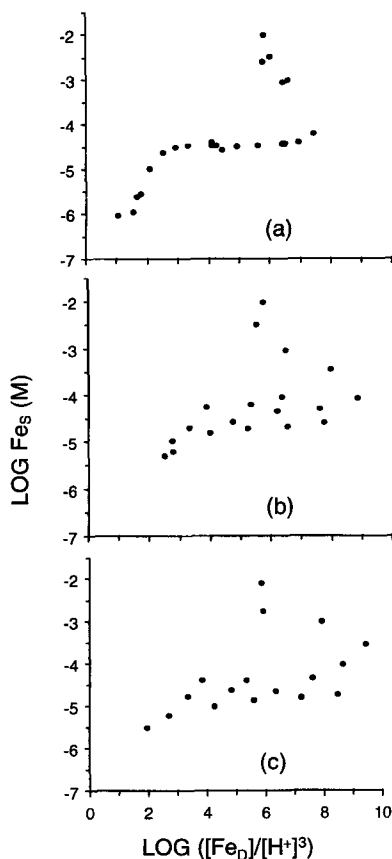


FIG. 1. Log particulate Fe (Fe_s) (M) as a function of log dissolved Fe (Fe_D) normalized for pH ($[\text{Fe}_D]/[\text{H}^+]^3$) for the three bacterial strains examined: *B. subtilis* (a); *B. licheniformis* (b); and *P. aeruginosa* (c). The data points are from the series of experiments in which both total Fe, Fe_T and pH were varied. The modelling of Fe sorption, nucleation and precipitation to these microbial surfaces is achieved with a simple mass action expression that uses a generalized bacterial surface site (equation 1). Data are more variable for the two encapsulated species (*B. licheniformis* and *P. aeruginosa*), probably due to some breakage of the capsules during analyses. Results indicate that Fe reactions with live biological surfaces follow langmuir type isotherm behaviour.

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