Alginate impacts on hematite crystallisation and bioreduction by *Shewanella oneidensis* MR-1

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Microbial dissimilatory iron reduction (DIR) is widespread in oxygen poor soil and aquatic environments, contributing to Fe and C cycling and the distribution of nutrients and trace metals. While DIR rates and yields have been well assessed for several microbial DIR strains, different iron substrates, as well as changing water chemistries, much less is known about how this dissolution process is affected by tightly associated organic matter (OM). This is however important because OM is ubiquitous in soil and water, where iron minerals form, and thus most iron substrates will likely be partially if not completely covered by OM.

Here, we first determined the effects of alginate on hematite crystallization, and specifically on hematite crystal size and associated alginate content. After, the stability of these co-precipitates was tested by exposure to *Shewanella oneidensis* MR-1. We found that the presence of alginate substantially reduces hematite crystal and particle size due to alginate molecules acting as nucleation sites. Overall, this leads to the formation of closely associated alginate-hematite composites. In experiments with *S. oneidensis*, we see that the initial reduction rate (over 24 h) is dramatically lower in the presence of these composites (~30-50%, depending on composites' alginate content) compared to the alginate-free, pure hematite. Interestingly, however, reduction ceased already after 2 days in the pure hematite system, while reduction in experiments with alginate-hematite composites continued upto 8 days, and possibly longer, indicating a higher overall DIR yield for the composite material. We explain the lower initial DIR rates by alginate physically hindering direct contact between bacterial cells and hematite surfaces. This could also explain the prolonged DIR reaction, i.e., higher DIR yields, in the presence of alginate, because the lower rate likely reduces quick passivation of cell and/or mineral surfaces by Fe(II) adsorption and/or surface precipitates as observed in the pure hematite system. Overall, this study highlights that alginate, a common natural organic molecule, can largely impact hematite crystal formation and the so formed co-precipitates have very different DIR stabilities compared to pure, inorganic hematite.