Microbial redox cycling of surface Fe-ions in magnetite nanoparticles

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Iron is an essential element for all microbes, with different oxidation states by some even used as an electron source or as a terminal electron acceptor. The phototrophic iron-oxidizer *Rhodopseudomonas palustris* TIE-1 uses energy from light and electrons from ferrous Fe(II) for growth and respiration, whilst *Geobacter sulfurreducens* combines the oxidation of organic compounds or hydrogen with the reduction of ferric Fe(III). Iron is almost exclusively observed to be bioavailable to the bacteria as aqueous Fe(II) or in poorly crystalline Fe(III) (oxyhydr)oxides such as ferrihydrite. More crystalline iron minerals such as magnetite or siderite are not usually considered to be biologically active. Magnetite is a mixed valent iron oxide $Fe^{II}(Fe^{III})_2O_4$ which is often seen as the end member product of the microbial reduction of ferrihydrite, though very rarely as a result of microbial oxidation of Fe(II).

This study focuses on the oxidation of superparamagnetic magnetite nanoparticles (~20 nm) by strain TIE-1 and the potential mineralogical changes which result. Through *in situ* magnetic measurements and iron extraction methods, we found that the cells are capable of directly oxidizing the surface of magnetite nanoparticles and thereby decrease the overall magnetic susceptibility of the mineral. This effect occurs in the absence of any aqueous Fe(II) in the growth medium and only magnetite provided as the electron donor. Significantly, this process can be reversed through Fe(III) reduction by *G. sulfurreducens*, which in turn leads to an enhancement of the magnetic properties of the nanoparticles. Changes in magnetic properties were also detected in experiments using magnetite with varying stoichiometric ratios (i.e. Fe^{II}/Fe^{III}). Such effects were not observed in abiotic experiments which did not contain any bacteria.

These results demonstrate that iron ions bound at the surface of crystalline minerals such as magnetite are bioavailable for microbial respiration and can potentially be used as a source of iron in reducing or oxidizing conditions, with the potential to cycle the surface redox properties depending on the conditions present. Such modifications may provide a route towards enhancing remediation strategies that are based on the highly reactive surface of magnetite. These effects may also have implications on paleomagnetic measurements in microbially active environments.

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