Cyclic microbial oxidation and reduction of magnetite nanoparticles

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Iron is essential for microbial life with different oxidation states used by some microorganisms as an electron source or by others as a terminal electron acceptor. The phototrophic Fe(II)-oxidizer *Rhodopseudomonas palustris* strain 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). Magnetite (Fe_3O_4) is a mixed valent iron oxide that is ubiquitous in the environment. As such, its interaction with microbes could be expected to be commonplace however, often the iron within this highly crystalline mineral is not considered to be bioavailable. Instead, iron is almost exclusively observed to be accessible to the bacteria as aqueous Fe(II) or in poorly crystalline Fe(III) (oxyhydr)oxides such as ferrihydrite.

This study demonstrates how iron metabolizing bacteria are able to induce changes in the magnetization, mineralogy and Fe redox stoichiometry of magnetite nanoparticles, and thereby demonstrate that microbial interactions with magnetite are important processes in the natural iron cycle. Through the use of different analytical methods, we show that the Fe(II)-oxidizers are capable of directly oxidizing the surface of magnetite nanoparticles. This effect occurs with magnetite as the sole electron donor and significantly decreases the in-situ magnetic susceptibility and stoichiometry. The addition of Fe(III)-reducing bacteria reverses this process, leading to an increase in the stoichiometry and an enhancement of the magnetic susceptibility of the nanoparticles. Significantly, this process can be repeated over several cycles using the same magnetite.

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 possibility of cycling 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.