Fe redox cycling revealed by ligand-promoted microbial Fe(II) oxidation in clay mineral

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Nitrate-dependent Fe(II) oxidation is important for environmental processes. Past research has focused on microbial oxidation of either aqueous Fe^{2+} or solid-phase Fe(II), however, the effects of organic ligands are not well understood. The aim of this research was to determine the effects of oxalate (OXA) and nitrilotriacetic acid (NTA) on the oxidation of structural Fe(II) in reduced nontronite (rNAu-2) by *Pseudogulbenkiania* sp. strain 2002. Microbial oxidation of structural Fe(II) in rNAu-2 was coupled with reduction of nitrate. The presence of OXA and NTA enhanced Fe(II) oxidation rate through: 1) the ligand-promoted dissolution of rNAu-2 and the formation of Fe(II)-ligand complex; 2) oxidation of Fe(II)-ligand complex to Fe(III)-ligand complex; 3) reduction of Fe(III)-ligand complex to Fe(II)-ligand complex by structural Fe(II) in rNAu-2. The oxidation kinetics of Fe(II)-ligand complex displayed a two-stage pattern – an initially fast and a subsequently slow stage. In the first stage, the fast rate was likely achieved through a combination of rapid oxidation of aqueous Fe(II)-ligand complex and instantaneous re-reduction of resulting Fe(III)-ligand back to Fe(II)-ligand by edge-Fe(II) in rNAu-2. Once edge-Fe(II) was exhausted, electron hopping from structural interior of rNAu-2 to edge-Fe(III) was slow and limited the rate of Fe(II)-ligand oxidation. Nitrate was predominantly reduced to N_2. The ratio of oxidized Fe(II) to reduced nitrate was non-stoichiometric, due to heterotrophic nitrate reduction by cell-stored carbon. The results of this study highlight the importance of organic ligands on microbially-mediated Fe(II) oxidation pathway, kinetics, and mineral transformation, with important implications for iron and nitrogen biogeochemical cycles in natural environments.