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Preservation of organic matter in nontronite against iron redox cycling

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Abstract

It is generally believed that clay minerals can protect organic matter from degradation in redox active environments, but both biotic and abiotic factors can influence the redox process and thus potentially change the clay-organic association. However, the specific mechanisms involved in this process remain poorly understood. In this study, model organic compound 12-Aminolauric acid (ALA) was selected to intercalate into the structural interlayer of nontronite (an iron-rich smectite, NAu-2) to form an ALA-intercalated NAu-2 composite (ALA-NAu-2). *Shawanella putrefaciens* CN32 and sodium dithionite were used to reduce structural Fe(III) to Fe(II) in NAu-2 and ALA-NAu-2. The bioreduced ALA-NAu-2 was subsequently re-oxidized by air. The rates and extents of bioreduction and air re-oxidation were determined with wet chemistry methods. ALA release from ALA-NAu-2 via the redox process was monitored. Mineralogical changes after iron redox cycle were investigated with X-ray diffraction, infrared spectroscopy, and scanning and transmission electron microscopy. At the beginning stage of bioreduction, *S. putrefaciens* CN32 reductively dissolved small and poorly crystalline particles and released intercalated ALA, resulting a positive correlation between ALA release and iron reduction extent (<12%). The subsequent bioreduction (reduction extent from 12~30%) and complete air re-oxidation showed no effect on ALA release. These results suggest that released ALA was largely from small and poorly crystalline NAu-2 particles. In contrast to bioreduction, chemical reduction did not exhibit any selectivity in reducing ALA-NAu-2 particles, and a considerable amount of reductive dissolution was responsible for a large amount of ALA release (>80%). Because bacteria are the principal agent for mediating redox process in natural environments, our results demonstrated that the structural interlayer of smectite can serve as a potential shelter to protect organic matter from oxidation.

Keywords: Nontronite, iron redox cycle, organic matter preservation