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Reduction of structural Fe(III) in nontronite by humic substances in the absence and presence of *Shewanella putrefaciens* and accompanying secondary mineralization

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Abstract

Studies have shown the electron shuttling role of humic substances (HS) in enhancing microbial reduction of solid-phase Fe(III), but it is unknown if native HS can reduce structural Fe(III) in clays and how their chemical properties affect this process and secondary mineralization. The objective of this study was to evaluate the role of natural HS, Leonardite humic acid (LHA), and Pahokee Peat humic acid (PPHA) in reducing structural Fe(III) in nontronite with or without *Shewanella putrefaciens*. The extent of Fe(III) reduction was determined with a wet chemical method. Electrochemical methods, spectroscopy, and mass spectrometry were used to determine the changes of HS electrochemical and molecular composition after bioreduction. X-ray diffraction and electron microscopy were used to observe mineralogical transformations. The results showed that natural HS not only served as an electron donor to abiotically reduce Fe(III) in nontronite but also served as an electron shuttle to enhance Fe(III) bioreduction by *S. putrefaciens*. In the presence of CN32 cells, both the rate and extent of Fe(III) reduction significantly increased. Between the two HS, PPHA was more effective. The final bioreduction extents were 12.2 and 17.8% with LHA and PPHA, respectively, in bicarbonate buffer. Interestingly, when CN32 cells were present, LHA and PPHA donated more electrons to NAu-2, suggesting that CN32 cells were able to make additional electrons of LHA and PPHA available to reduce structural Fe(III). Although LHA reduced less Fe(III), it induced more extensive mineral transformation. In contrast, PPHA reduced more Fe(III) but did not induce any mineralogical change. These contrasting behaviors between the two humic acids are ascribed to their differences in electron-donating capacity, reactive functional group distribution, and metal complexation capacity. A unique set of secondary minerals, including talc, illite, silica, albite, ilmenite, and ferrihydrite formed as a result of reduction. The results highlight the importance of coupled C and Fe biogeochemical transformations and have implications for nutrient cycling and contaminant migration in the environment.

Keywords: LHA, mineralization, nontronite, PPHA, *Shewanella putrefaciens*