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Influence of Natural Organic Matter on the Fate of Cadmium During Microbial Ferrihydrite Reduction

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Ferrihydrite (Fh) is a short-range ordered Fe(III) oxyhydroxide which is often associated with significant amounts of trace metals in soils and sediments. Fh is frequently observed to be unstable under reducing conditions and can be transformed into secondary Fe minerals, during which associated trace metals are either redistributed in the minerals or released into solution. Natural organic matter (NOM), often coexisting with Fe minerals, is known to alter the transformation pathways of Fh, however, its effect on associated trace metals is not well known. Here we investigated how cadmium (Cd) is redistributed when Fh undergoes microbial Fe(III) reduction in the presence of NOM. Incubation with the Fe(III)-reducing bacteria Geobacter sulfurreducens showed that the rate and extent of reduction of Cd-loaded Fh were enhanced by increasing concentrations of NOM (i.e. increasing C/Fe ratio). Under low C/Fe ratios, only 3-5% of Fe(III) was reduced, but around 70% of pre-adsorbed Cd was released into the aqueous phase due to Fh transformation to lepidocrocite. At high C/Fe ratio (1.6), the Fe(III) reduction rate in the first 6 hours became nearly 3 times faster than in the absence of NOM, and more than 35% of Fe(III) was reduced over 5 days, possibly because the adsorbed NOM decreased the size of aggregates and the residual NOM in solution worked as electron shuttle. No Fh transformation was observed (using Mössbauer spectroscopy or X-ray diffraction) suggesting NOM could impede Fh crystal growth, and there was only negligible Cd release into solution. Lower concentrations of aqueous Cd lowered the metal's toxicity toward Geobacter sulfurreducens thus enabling more prolonged microbial reduction. The negligible Cd released during microbial Fh reduction might be due to recapture of Cd (initially bound to Fh) by NOM adsorbed on Fh. In summary, our study suggests the presence of NOM can be beneficial for the stability of Cd adsorbed to Fh under reducing conditions.