Limited Reduction of Ferrihydrite Encrusted by Goethite in Freshwater Sediment

SAKIKO KIKUCHI[1]*, HIROKO MAKITA[1], UTA KONNO[1], FUMITO SHIRAISHI[2], AKIRA IJIRI[1], KEN TAKAI[1] AND YOSHIO TAKAHASHI[3]

[1]Japan Agency for Marine-Earth Science and Technology (JAMSTEC), Japan (*correspondence: skikuchi@jamstec.go.jp)
[2]Hiroshima University, Japan
[3]The University of Tokyo, Japan

Microbial reduction of Fe(III) oxyhydroxides is an important process in Fe and carbon cycles of aquatic sediments. However, the factors controlling the extent of Fe(III) oxyhydroxide reductions in natural sediment is not well understood. The surface precipitation of secondary Fe minerals on Fe(III) oxyhydroxides have been suggested to limit the extent of microbial Fe(III) reduction, but this phenomenon has not been observed in nature. Here we report secondary Fe mineral (goethite) encrustation on ferrihydrite surface within freshwater sediment.

This study identified vertical changes in Fe-mineral composition at freshwater sediment up to 10 cm deep, using two modes of Fe K-edge extended X-ray absorption fine structure (EXAFS): (i) transmission (TR) mode which provides bulk Fe-mineral information, and (ii) conversion electron yield (CEY) mode for Fe minerals formed at the particle surface. The sediment at depths above 3 cm was characterized by the predominance of ferrihydrite with biogenic stalks and sheaths. At depths below 3 cm, goethite and siderite were detected by TR-EXAFS. The change in the bulk Fe-mineral composition was restricted to sediment depths between 3 and 4 cm, and ferrihydrite remained as a dominant Fe-mineral phase at depths below 4 cm. In contrast to the results obtained from TR-EXAFS analysis, CEY-EXAFS for the 10 cm depth detected goethite as a dominated Fe-mineral phase, suggesting coatings of goethite at the particle surface. An increase in CH_4 concentration was observed at sediment deeper than 6 cm. Stable isotopic analysis of CH_4 in the pore water indicated that acetoclastic CH_4, which is usually inhibited in the presence of dissimilatory Fe(III) reducing bacteria, occurred at sediment depths below 7 cm. Based on these results, the incomplete reduction of ferrihydrite below depth of 4 cm was not due to the lack of organic carbon, but was possibly due to the surface encrustation of goethite on ferrihydrite [1].

[1] Kikuchi et al. (2016) *Geobiology*, in press.