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Encrustation of goethite on ferrihydrite surface in freshwater sediment

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1. Introduction

Microbial reduction of Fe(III) oxyhydroxides is a key process in the cycle of Fe and carbon in anoxic sediments. One of the important factors controlling the extent of microbial Fe(III) oxyhydroxides reduction is the accessibility of Fe(III) oxyhydroxides to dissimilatory Fe(III)-reducing bacteria. The surface precipitation of secondary Fe minerals on Fe(III) oxyhydroxides has been suggested to limit the accessibility of microbial Fe(III) reduction. However, only a few studies have investigated the relationship between the surface encrustation of secondary Fe minerals and the extent of Fe(III) oxyhydroxide reduction because of the difficulty in quantitative estimations of Fe mineral encrustation on Fe(III) oxyhydroxides. This study aimed to examine the presence of surface encrustation of secondary Fe minerals on Fe(III) oxyhydroxide surface in freshwater sediments, 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 surfaces.

2 Experiment

Sediment samples were collected from Budo Pond at Hiroshima University, Japan. The sampling site is characterized by copious amount of Fe(III) oxyhydroxides deposits near the groundwater discharged point [1]. Sediment core (10 cm depth) was sectioned at 1 cm intervals using a spatula in an anoxic chamber. The Tr and CEY Fe K-edge EXAFS spectra were obtained using beamline BL-12C at the Photon Factory and BL01B1 at the SPring-8.

3 Results and Discussion

In the bulk Fe K-edge EXAFS analysis (Tr-mode), ferrihydrite was the only Fe-mineral species at depths above 2 cm (Fig. 1). At depths below 3 cm, however, goethite and siderite were detected. This result suggests that goethite and siderite precipitated as secondary Fe minerals, possibly during the microbial Fe(III) reduction. The change in the bulk Fe-mineral composition was observed only between depths of 3 and 4 cm, and most of the ferrihydrite remained at depths below 4 cm. Quantitative Fe mineral speciation at particle surface (CEY-mode) for the 10 cm depth detected goethite as a dominated Fe-mineral phase. This result is different of the dominance of ferrihydrite in the bulk Fe-mineral composition, suggesting that goethite selectively precipitated on the surface of mineral particles, whereas ferrihydrite was mainly present inside the particles. Therefore, ferrihydrite surface was suggested to be encrusted by goethite at deeper sediment, which may have limited the extent of microbial ferrihydrite reduction below depths of 4 cm [2].

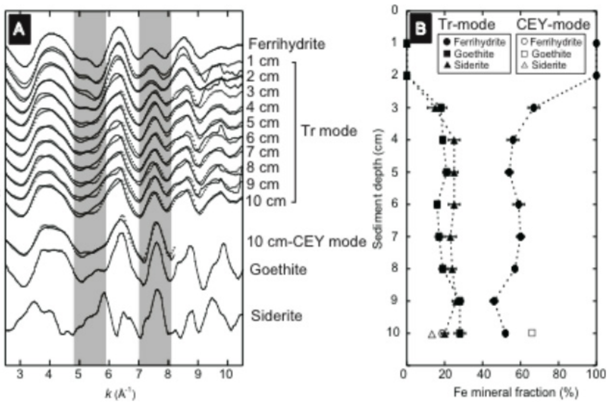

Fig.1. Fe K-edge EXAFS spectra of the sediments and reference minerals obtained by measurements in Tr and CEY modes. The solid lines denote the raw EXAFS spectra, and dotted lines denote the linear combination fittings. The gray shades highlight the spectral features showing variations in each layer. (B) Percentages of Fe minerals in each layer.

References

[1] Y Takahashi et al., *Chemical Geology* (2007)
[2] S Kikuchi et al., *Geobiology* (2016)

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