

Radiation damage of iron(III)-organic complexes by hard and soft X-ray microscopy

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1 Introduction

In the field of geochemistry, organic carbons (OC) play an important role in biogeochemical cycles of transition metals through the organic complexations [1]. Recently, speciation experiments of organic complexes with trace metals in the surface environmental samples were conducted by both hard and soft X-ray microscopy. However, many studies reported X-ray radiation damage of target elements, but knowledge of X-ray radiation damage of organic complexes with trace metals are not sufficient [2]. In this study, investigations of radiation damages of Fe(III)-citrate (Fe-cit), Fe(III)-stearate (Fe-ste) and Fe(III)-deferoxamine (Fe-DFO) were conducted by micro X-ray absorption fine structure (μ -XAFS) and scanning transmission X-ray microscope (STXM) because these species were representatives of Fe organic complexes in the environment.

2 Experiments

Iron K-edge experiments were conducted by μ -XAFS at BL-15A1. Iron K-edge spectra were obtained from 7040 eV to 7840 eV by QXAFS. Iron K-edge XANES and EXAFS spectra were recorded in 30 times and measurement time for each scan is 1 min. Shutter was automatically opened and closed, when measurements are started and finished, respectively. Carbon and oxygen K-edges and Fe L-edge experiments were conducted by STXM in BL-13A. Carbon and O K-edge NEXAFS spectra were obtained by image stack in order to understand chemical alteration processes.

3 Results and Discussion

Radiation damages of Fe-ste and Fe-DFO were not found during repetitive scans around Fe K-edge regions. In contrast, serious photoreduction of Fe K-edge spectra were found during repetitive scans by μ -X-ray (Fig. 1a). Basically, photoreduction of Fe-cit can be explained by first-order reaction, but the slope (reactivity constant) were changed after X-ray irradiation for 20 min. It is expected that the process of photodecomposition of Fe-cit is changed when the irradiation dose exceeds the threshold value. One of the potential reason is that formation of an intermediate and its photoreductions, but the actual reason of changing the slope was not be able to clarify in this study.

Carbon and O K-edge NEXAFS spectrum of Fe-cit were also changed by repetitive scans. As a result of X-ray irradiation, intensity of the peak at 285 eV from C 1s $\rightarrow \pi^*$ was slightly increased, whereas the peak position of O 1s

$\rightarrow \pi^*$ was shifted to high energy region (Figs. 2a and b). Iron L-edge NEXAFS spectrum was almost no changed by repetitive scans around C K-edge region, but the spectrum changed by radiation around Fe L-edge. In addition, C K-edge NEXAFS spectrum is drastically changed after O K-edge and Fe L-edge scans. From these results, impacts of X-ray radiation damage can be reduced by conducting experiments from a region with low energy when chemical species of unknown organic complexes in environmental samples were determined. At this stage, we cannot understand detailed process of X-ray radiation processes of Fe-cit, but it is an important advance that the optimization of speciation methods organic complexes of trace metals in environmental samples has progressed.

References

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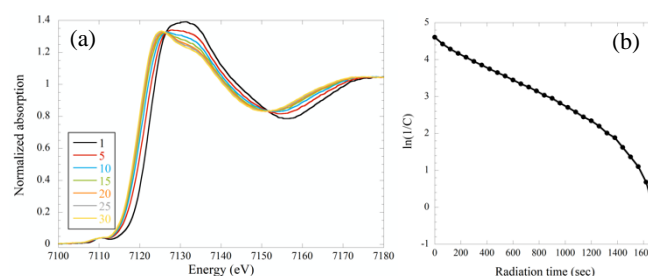


Fig. 1 (a) Fe K-edge XANES spectra and (b) relationship between $\ln(1/\text{Fe-cit conc.})$ and radiation time.

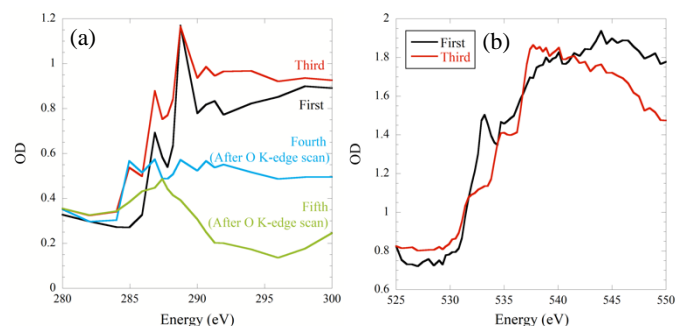


Fig. 2 (a) Carbon K-edge and (b) O K-edge spectrum changes by X-ray irradiation by STXM.

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