

XAFS study of early-stage diagenesis of pelagic sediments

Katsumi SHOZUGAWA*¹, Yuji SANO², Akihito KUNO¹ and Motoyuki MATSUO¹

¹Graduate School of Arts and Sciences, The University of Tokyo, 3-8-1 Komaba, Meguro-ku, Tokyo 153-8902, JAPAN

²Ocean Research Institute, The University of Tokyo, 1-15-1 Minamidai, Nakano-ku, Tokyo 164-8639, JAPAN

Introduction

Organic matters in the sea sediments are oxidized in the sequential order. After sedimentation, there are several steps of redox reaction in the sediments. Timescale of these reactions, which are named early-stage diagenesis, depends on several parameters, *e.g.*, counter anion, environment of sediment such as potential temperature, salinity, water pressure, oxidation-reduction potential (ORP) and dissolved oxygen (DO). In early-stage diagenesis, there is the stage that sulfate ion sulfurates heavy metals, such as iron, manganese, in the sediments.

XAFS technique is one of the powerful methods for chemical speciation of elements in the sediments [1]. In our previous work, we clarified the environment of sedimentation with the object of the chemical states of iron in the sediments [2]. In case of sample with long sedimentation age, XAFS study aimed on heavy metals in the sediments is meaningful. However, in case of samples with relatively short sedimentation age, sulfate reduction stage in the early-stage diagenesis has been proceeding in the sediments.

In this study, in order to elucidate the degree of the sulfate reduction of each sedimentation depth, vertical distribution of chemical states of sulfur in pelagic sediments were analyzed with XANES spectra.

Experimental

JAMSTEC (Japan Agency for Marine-Earth Science and Technology) and Ocean Research Institute, the University of Tokyo collected sediment cores at the pelagic sea located 39°59.57'S., 169°59.85'W. in 2005. Core length was 30cm, and water depth at collection point was 4500m. Cores were collected in much attention; therefore, these cores had no disconcertion. All samples were cut by 1cm (*ca.* 150mg) for each immediately, and were kept 4 °C until the measurement, and were sealed by prolene. Also being kept N₂ atmosphere prevents oxidization with air. XAFS measurement was performed using synchrotron radiation ring at BL-9A, Photon Factory, KEK. A Si (111) double-crystal monochromator was used. XANES of sulfur K-edge spectra of the samples were measured in a fluorescence mode using a Lytle-type detector at room temperature under atmospheric pressure. For the low concentration (*ca.* 500ppm) of sulfur in the sediments, measurements were twice for each, and spectra for analysis are on average. Standard reagents are Fe₂(SO₄)₃ and FeS₂[pyrite] for a class of sulfate and sulfide.

Results and Discussion

We ignored the influence of human activity over the whole sediments, taking account of sampling area. Sulfur K-edge XANES spectra of sediments and Fe₂(SO₄)₃ and FeS₂[pyrite] are shown in figure. Pre-edge (shown with an arrow) indicates the existence of sulfide in the sediments; however, all spectra of sediments are similar to those of sulfate rather than those of sulfide. Sediments tend to be influenced by sulfate ion in the seawater at the surface.

Note the region of higher energy than K-edge. It is obvious that the spectra of sediments had a difference in this region by depth of sediments. XANES spectra of other sediments which had much longer sedimentation age were hardly different in the correspond region at every depth in the sediments. These behaviors of spectra in this region imply that counter cations of sulfur changed in the sediments [3]. Therefore, in this study, XANES spectra of pelagic sediments suggested that chemical states of sulfur changed slightly by the early-stage diagenesis.

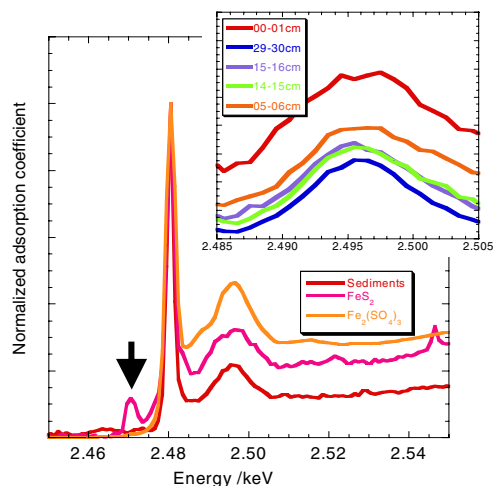


Figure Normalized sulfur K-edge XANES spectra of pelagic sediments and standard reagents

References

- [1] M. Kataoka et al., J. Radioanal. Nucl. Chem., **255**, 283-286(2003)
 - [2] K. Shozugawa et al., PF Activity Report, **23B**, 23(2006)
 - [3] Y. Takahashi et al., Environ. Sci. Technol., **40**, 5052-5057(2006)
- *shozum@dolphin.c.u-tokyo.ac.jp