

## Speciation of sulfur in sediments under the hypoxia revealed by XANES spectra

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### Introduction

Hypoxia, which is water mass contained little dissolved oxygen (<2 ml of O<sub>2</sub> / liter) [1], is known as dead zone in coastal sea. In Tokyo bay, grand-scale dredging operations had been done in 1970s, then, severe hypoxia has observed in annual summer seasons. Though strong hypoxia is especially observed in dredged area, influence of dredged area is not revealed against hypoxia. To understand relation between hypoxia and dredged area, methods which can estimate coastal environment in dredged area are needed.

When organic matters accumulate at the seabed, chemical states of elements are altered by various reduction reactions. Sulfur exists as sulfate ion of good solubility. Sulfate ion reduces to sulfide ion of difficult solubility by the sulfate reduction reaction, as redox condition become to reduction. Chemical states of sulfur in sediments have often been used as index to evaluate redox condition in water. Therefore, by separation of chemical states of sulfur in sediments by XANES, we evaluate redox condition in dredged area from obtained spectra with respect to each depositional age.

### Experimental

The sediment samples were collected at dredged area in Makuhari off (35°37'33"N, 140°1'11"E, depth 26 m) and reference site near the Chiba port (35°36'4"N, 140°4'17"E, depth 17 m), which is compared with dredged area, on July 2010 in Tokyo bay. Sediments were collected by a core sampler at each point. Core length of each core was 35 cm and 50 cm at dredged and reference point, respectively. The sediments were divided at intervals of 3 cm and cryopreserved. All sediments were measured at sulfur K-edge XANES spectra without any chemical modification of the samples in order to prevent from being oxidized by air. Samples were put into a prolene film and sealed. Beam line was used at BL9A, and the spectra collected in fluorescence mode using a Lytle type detector at room temperature.

### Results and Discussion

Figure shows depth profile of K-edge XANES spectra of sulfur in the sediments (0-3cm, 15-18 cm, 30-33 cm below sea floor) at dredged(red) and reference(blue) point. Two peaks at 2471 eV and 2780 eV can be assigned to sulfide and sulfate, respectively [2]. It is indicated that poorly-soluble sulfide was mainly contained in sediments and soluble sulfate ion was resolved in pore water. By a

comparison of spectra between dredged and reference point, the ratio of sulfate in dredged point was more than reference point in all layers. Although we thought of dredged area as reductive condition, these facts indicated that dredged area had more oxidative environment than reference site. To compare with the study of Bostick et al., (2005) [3], it is estimated that dredged point was oxidative and reference point was highly reductive. From that, reference site can be regarded as dredged place, because water depth at reference point is deeper than surrounding natural seabed. These results are scientifically interesting because reductive environment of seabed more than dredged area was found at the Chiba port. We expect that this method can be applied to other sea or coastal area with development of hypoxia.

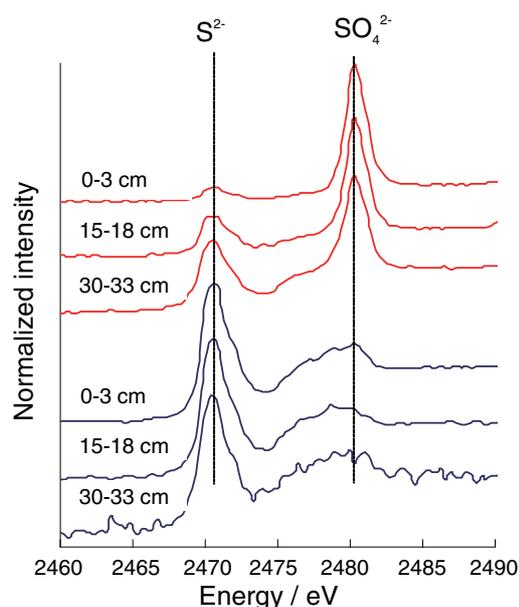


Figure. Depth profile of K-edge XANES spectra of sulfur in the sediments.

Red lines; dredged point, Blue lines; reference point

### References

- [1] R.J. Daiz et al., *Science*, 321, 926-929 (2008)
- [2] S. Matsumoto et al., *Tetsu-to-Hagane*, 93, 62-67 (2007)
- [3] B.C. Bostick et al., *Chem. Geo.*, 219, 163-174 (2005)

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