Chemical speciation of heavy metals (Zn and Cu) in sediments in Majuro Atoll

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1. Introduction

Atoll is vulnerable for natural disasters since its altitude is generally as low as 1-2 m, which is harsh environment for human habitation. Majuro Atoll is located at latitude 7°05' N, longitude 171°23' E in the Central Pacific and has one of the oldest human history among atolls, which has lasted for about 2000 years [1]. We focus on the impact of urbanization on the atoll and examined the chemical speciation of heavy metals that has contaminated the sediments to identify their origins.

2. Sample

The samples were taken from surface layers of center part of 3 islands in Majuro Atoll, which were named as Laura, Calalen, and Delap. These 3 islands have different characteristics. Laura has one of the longest human settlement history in atolls around the world [1], while Calalen is an isolated island in Majuro Atoll which has less population. Delap is highly populated area which has 15,000 people living at present [2]. The all surface layers are black-colored sediments and well-vegetated especially in Laura and Calalen. The grain size is medium to fine sand.

3. Experiment

Zinc (Zn) and copper (Cu) K edges XANES spectra were obtained at BL-4A at Photon Factory. The samples were mounted in resin and sliced into thin sections. The samples were excited by monochromatized X-rays with a Si(111) double crystal monochromator. The beam size was 5×5 μm. The incident beam energy was 13.5 keV for the mapping to identify the highly concentrated points of Zn and Cu. The absorbance of Zn and Cu was measured every 0.3 and 0.8 eV, respectively. XANES spectra of standard materials and sediment samples were measured in transmission mode using ionization chamber and in fluorescence mode using a Si(Li) detector, respectively. Pattern fitting analysis of XANES spectra was carried out using REX2000 software (Rigaku Co., Ltd.).

4. Results and Discussion

Figure 1 shows the Zn K edge XANES spectra of six sediment samples and standard materials. The XANES spectra for all the samples of Laura 1-3 contained more than 50% of ZnS. Laura 1 and 3 also contain Zn coprecipitated with calcite. On the other hand, Laura 2 contains $ZnSO_4$. The samples of Delap 1-2 also contained ZnS. In addition, Delap 1 and 2 contained 50% of $Zn_3(PO_4)_2 \cdot H_2O$ and Zn(0), respectively. The sample of Calalen is speciated as metallic zinc.

Figure 2 shows the Cu K edge XANES spectra of six sediment samples and standard materials. The sample of Laura, Calalen, and Delap 1-2 is speciated as the mixture of Cu(0) and CuS. The ratio of the former is about 80%. On the other hand, Delap 3 is speciated as the mixture of Cu(0) (9%), Cu_2O(28%), CuO(30%), and CuS(33%). Considering that atolls are closed system where sediments are mainly composed of $CaCO_3$, both chemical species of Zn and Cu are considered to be anthropogenic. Especially, ZnS is considered to be delivered from tire ware, because ZnS is added to the tire during vulcanization and 10–20% of total rubber of tire is estimated to enter the environment due to abrasion within 3 years [3]. The number of cars in this atoll is about 300 per 1 km^2 at present [4]. Zinc is also used along with Cu to make the brass [5]. The distribution of Cu is often correlated with Zn. Therefore, brass (from building materials) is considered to be mixed with sediments.

It is difficult to identify the anthropogenic materials in the urbanized area (e.g. Tokyo). However, in Majuro, which has been isolated island, the anthropogenic effect can be readily evaluated.

References

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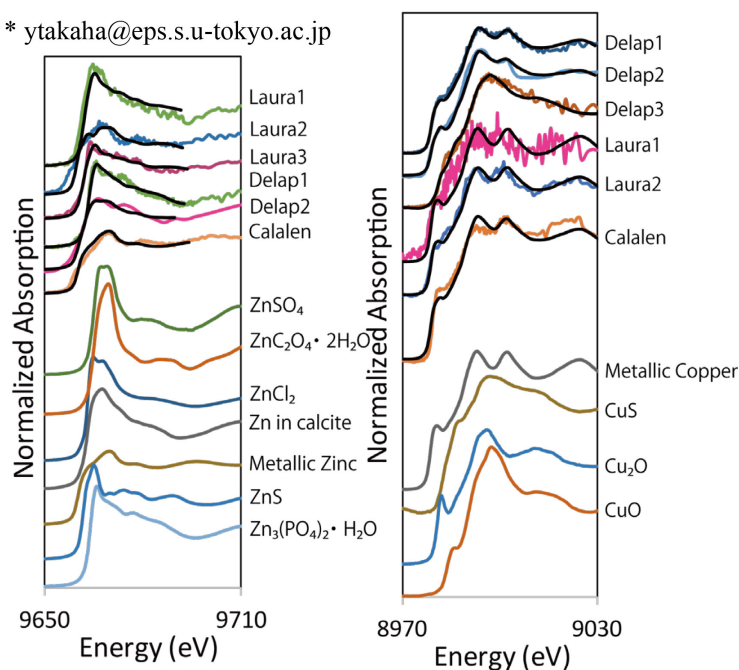
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Fig. 1 Zn-K edge XANES spectra

Fig. 2 Cu-K edge XANES spectra