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Speciation study of copper in stream sediments

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Introduction

A sequential extraction method has been used widely to elucidate its chemical binding forms in sediments including soil. However, the method might give misleading results due to alteration of the samples during the individual steps of the extraction [1]. In this work, a modified three-step extraction developed by the Community Bureau of Reference (BCR) [2] was investigated using XAFS spectroscopy to identify the Cu species in the residues after each step of the extraction.

Methods

The Cu in 12 geo-standard materials (JLk-1: lake sediment, JSd-1~5: stream sediments, JMs-1~3: marine sediments, JSo-1~3) was extracted using sequential extraction procedure (BCR scheme). Table 1 summarizes the procedure used in this investigation.

Table 1 Outline of the sequential extraction procedure

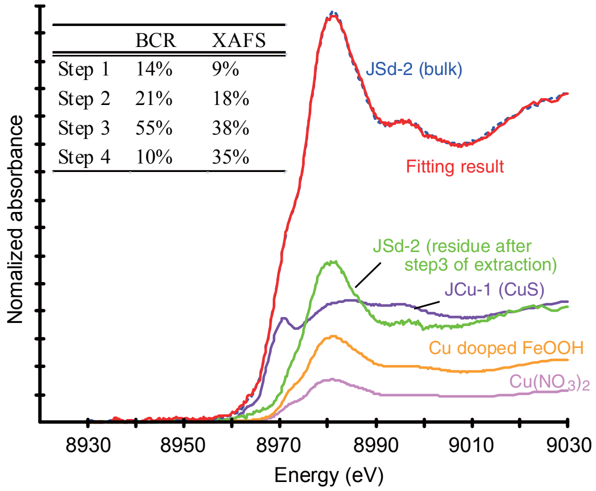
Step	Extractant
1	CH_3COOH (0.11 mol/L), 16 h
2	$NH_2OH{\cdot}HCl$ (0.5 mol/L), pH=2, 16 h
3	H_2O_2 (8.8 mol/L), pH=2, 2h at 85 °C, followed by CH_3COONH_4 (1 mol/L), pH=2, 16 h

The residues after each step of extraction were filtrated by a 0.45 μm PTFE membrane filter and dried under 30-40 °C. They were store in a refrigerator at about 4 °C prior to analysis. As a reference compounds, several kinds of cupper compounds ($Cu(NO_3)_2$ and $CuSO_4$), Cu doped FeOOH, Cu doped MnO_2, Cu doped humic materials, and JCu-1 that is a geochemical reference material of CuS were prepared. A 2.0 mg of Cu was reacted with 3.2 mg of Fe in Fe hydroxides (FeOOH) and Mn in Mn dioxides (MnO_2) at pH 7.0 for 5 days. A 0.2 mg of Cu was reacted with 1 mg of Dando and Inogashira humic acid provided from Japanese Humic Substances Society at pH 6.0 for 5 days. The reactants were filtrated by a 0.1 μm PTFE membrane filter and dried in under vacuum. These reference materials were also store in a refrigerator prior to analysis.

The Cu K-edge XANES spectra were recorded in a fluoresce mode at the BL-12C of KEK-PF under an atmosphere and at room temperature. The fluorescence X-ray was measured by a 19 element pure-Ge SSD.

Results and Discussion

Figure 1 shows the Cu K-edge XANES spectra of bulk JSd-2 and reference materials and its fitting results. JSd-2 is a stream sediment reference material collected from drainage basins having the Hitachi Mine (Cu mine). Ohta et al. [3] suggest that heavy metals released from sulfide ores in sediments to water are weakly sorbed on materials or on Fe iron hydroxides. Therefore, it is expected that Cu in JSd-2 is a mixture of Cu weakly adsorbed on materials (step 1), Cu bound to Fe oxyhydroxide (step 2), chalcopyrite (step 3) and silicate materials (residue). The reference compounds of $Cu(NO_3)_2$, Cu doped FeOOH, JCu-1 are used as substitutes for Cu binding forms of steps 1, 2, and 3, respectively. The linear fitting result was roughly comparable to the results from BCR scheme, although the relative amount of Cu extracted at step 3 is underestimated (see the Table in Fig. 1). It is possible that a part of chalcopyrite (CuS) is oxidized to $CuSO_4$ or that Cu doped Humic acid is probable substitute for Cu binding form in step 3. However, the liner fitting results using XANES spectra of $CuSO_4$ and Cu doped Humic acid instead of that of JCu-1 (chalcopyrite) is not satisfactory. Thus, XAFS spectroscopy is useful to indentify Cu species in sediment residues after each step of BCR extraction.



	BCR	XAFS
Step 1	14%	9%
Step 2	21%	18%
Step 3	55%	38%
Step 4	10%	35%

Figure 1. The Cu K-edge XANES spectra of bulk JSd-2 and the residue of JSd-2 after third step in the BCR scheme, and reference materials. The red line shows the linear combination calculated from the entire set of reference compound spectra.

References

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