

Speciation study of zinc in Japanese geochemical reference materials

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1. Introduction

We have determined the concentrations of 38 elements extracted by a sequential extraction procedure for Japanese geochemical reference materials sediment series [1]. A three-step extraction developed by the Community Bureau of Reference (BCR) [2] has been used for this purpose. This method can elucidate the chemical binding forms in sediments including soils, however it might give misleading results because the reagent used in this procedure is not enough to extract the metals bound to the intended phases [3]. In this work, XANES spectroscopy was measured to identify whether Zn is successfully extracted from intended phases by sequential extraction procedure.

2. Sample materials and experimental methods

The Zn in 8 geochemical reference materials (JLk-1: lake sediment, JSd-1–4: stream sediments, JMs-1–2: marine sediments, JSO-1 and -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 ₃ COOH (0.11 mol/L), 16 h
2	NH ₂ OH·HCl (0.5 mol/L), 16 h
3	H ₂ O ₂ (8.8 mol/L), 1h at 20–30 °C and 1h at 85 °C, followed by CH ₃ COONH ₄ (1 mol/L), 16 h
4	HF-HNO ₃ -HClO ₄ , 3h 120°C

The residue after each step of extraction was filtrated by a 0.45 μm PTFE membrane filter and freeze dried. The samples were stored in a refrigerator until XAFS analysis. As model compounds, several kinds of zinc compounds (e.g., Zn(NO₃)₂·6H₂O and Zn 1000 ppm solution), Zn doped Fe hydroxide (FeOOH), Zn doped Mn dioxide (MnO₂), Zn doped humic materials, and JLs-1 and JZn-1 that are geochemical reference materials of carbonate and zinc sulfide respectively, were also prepared. The Zn K-edge XANES spectra were recorded in a fluorescence mode at the BL-12C of KEK-PF. The fluorescence X-ray was measured by a 19 element pure-Ge SSD.

3. Results and discussion

BCR protocol presumes that metals in sediment and soil materials exist as a mixture of carbonate or exchangeable (weakly absorbed on mineral surface) phase (step 1), Fe-Mn (hydro-) oxide phase (step 2), organic and sulfide phase (step 3) and crystalline minerals (step 4). Table 2 summarizes the analytical data on Zn concentrations extracted using the BCR scheme for the

eight geochemical reference materials [1]. The final residual phase (step 4) was the most dominant specie for many samples. However, JSd-2, JSd-4, and JMs-1 had high percentages of Zn extracted in steps 1 and 2. Although JSd-2 is a stream sediment material collected from drainage basin that contains the Hitachi Copper Mine, the percentage of Zn in step 3 was low. Because JSd-4 and JMs-1 are influenced by anthropogenic activities, the BCR analysis suggests that pollutant Zn exists as exchangeable (or carbonate) and Fe-Mn (hydro-) oxide phases.

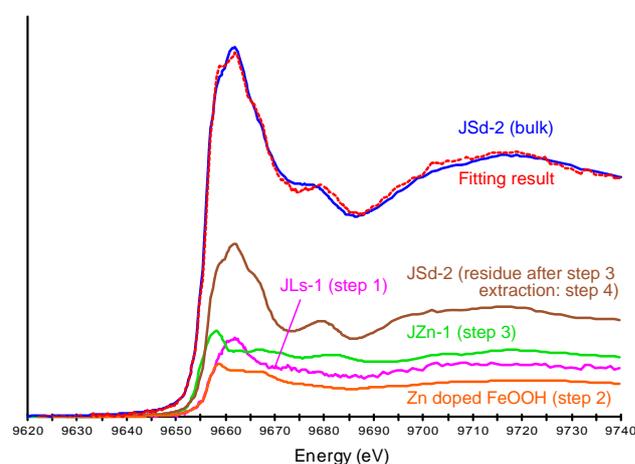


Fig. 1. Linear combination fitting of bulk samples for JSd-2, calculated from a set of model compounds for Zn bounded fractions and residues from step 3 extraction process (step 4).

Next, the accuracy of Zn speciation in geochemical reference materials obtained by the BCR protocol was evaluated using XANES spectroscopy method. The XANES spectra of bulk geochemical reference materials were analyzed using a linear combination fitting of the spectra of model compounds. The Zn 1000 ppm solution, Zn doped FeOOH, and Zn bound humic substance were used as substitutes for Zn binding forms of steps 1, 2, and 3, respectively. Aside from these, JLs-1 was used as a model compound of carbonate phase (step 1) for JSd-2, JMs-1 and 2 because these samples contain calcium carbonate material. In addition, JZn-1 was used as a substitute of sulfide phase (step 3) for JSd-2. Figure 1 shows the XANES fitting result of bulk JSd-2. The XANES spectrum of bulk JSd-2 seems not to be fitted well: especially in the regions of the white line (9657–9663eV) and the shoulder peak at 9670–9685 eV. Although all fitting results are not shown here, the

XANES features of all geochemical reference materials could not be explained satisfactorily by the linear combination fitting of several model substances as with the case of JSd-2.

The linear combination fitting results of XANES spectra of all geochemical reference materials were summarized in Table 2. As a whole, the relative percentages of the final residue (step 4) were overestimated for all samples as compared with the BCR result. XANES fitting results considerably underestimated the proportions of Zn in steps 1 and 2. Those results suggest that BCR protocol could not degrade significantly the intended materials such as carbonate and humic substances. However, Ohta et al. [4] suggested that speciation of Cu in stream sediment determined by BCR method possesses higher reliability. The contradictory finding suggests that Zn binds with calcium carbonate, Fe-Mn (hydro-) oxides, and organic materials weaker (or stronger) than Cu does. In other words, Zn bound to Fe-Mn oxides and humic substances may be extracted in the earlier step, otherwise Zn bound to these materials may be scarcely extracted in steps 1–3. Actually, Coetzee et al. [3] suggested that Zn bound to humic substances is partly extracted in step 1 unlike in the case of Cu: Zn binds to humic substances weakly as compared with Cu. However, even if that is the case, the total extraction percentages of Zn in steps 1, 2, and 3 obtained by BCR protocol should be comparable to those determined by XANES spectroscopy method; actually this is not true (Table 2). It is alternative possibility that the model compounds provided here are too simple to express natural Zn speciation in sediment and soil materials. Further investigation should be needed.

Table 2: Relative percentages of Zn in each step for geochemical reference materials determined using the BCR scheme and XANES spectroscopy methods

Sample	Method	Step 1	Step 2	Step 3	Step 4
JLk-1	BCR	4%	19%	12%	65%
	XANES	0%	0%	0%	100%
JSd-1	BCR	13%	19%	7%	61%
	XANES	5%	10%	0%	85%
JSd-2	BCR	21%	65%	6%	7%
	XANES	20%	14%	25%	41%
JSd-3	BCR	8%	9%	9%	75%
	XANES	0%	3%	0%	97%
JSd-4	BCR	32%	55%	7%	6%
	XANES	7%	0%	0%	93%
JMs-1	BCR	32%	33%	9%	25%
	XANES	0%	21%	14%	65%
JMs-2	BCR	4%	33%	3%	59%
	XANES	0%	37%	0%	63%
JSO-1	BCR	5%	9%	5%	82%
	XANES	0%	0%	0%	100%

References

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