Speciation of 38 elements in eight GSJ geochemical sedimentary reference materials determined using a sequential extraction technique

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A sequential extraction procedure developed by the European Community Bureau of Reference (BCR) was applied to eight sediment geochemical reference materials provided by the Geological Survey of Japan, AIST (JLk-1, JSd-1–4, JMs-1, JMs-2, and JSO-1). The study aimed to provide reference materials of widely varied geological materials in order to enhance the utility of the sequential extraction procedure in environmental studies. The concentrations of 38 elements extracted by BCR protocols were determined for the eight reference materials. The BCR scheme is designed to extract elements of the intended phase using acetic acid (step 1), hydroxylammonium chloride (step 2), and hydrogen peroxide and ammonium acetate (step 3). The residue of the step 3 extraction was further digested using hydrofluoric acid, perchloric acid, and nitric acid (step 4). The relative standard deviations of elemental concentrations in each extraction stage were generally <30% for steps 1 and 3 and <20% for steps 2 and 4. The sums of the elemental concentrations for the four steps (the total recoveries) ranged from 70% to 100% of the bulk compositions. The speciation of elements in the reference materials obtained by BCR protocols was strongly affected by sediment origin, mineralogical composition, sedimentary environment, and anthropogenic activity. Accordingly, sequential extraction based on the BCR procedure is effective for environmental studies. Eight geochemical reference materials certified/recommended for bulk composition are now further available as reference materials for the sequential extraction procedure.

Keywords: BCR protocol, geochemical reference material, sequential extraction, speciation

INTRODUCTION

The distribution of elemental abundance in the earth's surface is fundamental and essential information for mineral exploration and environmental assessment because the surface layer relates closely to the living beings that exist there. Spatial distribution patterns of elemental concentrations (geochemical maps), even at a sub-continental scale, have been prepared in many countries for various purposes (e.g., Fauth *et al.*, 1985; Lahermo *et al.*, 1990; Lis and Pasieczna, 1995; Reimann *et al.*, 1998; Salminen *et al.*, 2005; Weaver *et al.*, 1983; Webb *et al.*, 1978; Xie *et al.*, 1997). In Japan, the Geological Survey of Japan, National Institute of Advanced Industrial Science and Technology (AIST), conducted nationwide geochemical mapping at 1:2,000,000 scale using stream and marine sediments (Imai *et al.*, 2004, 2010). The purpose of the map is to obtain natural geochemical baselines on the surface of the earth. In order to evaluate the effects of anthropogenic pollution, it is necessary to accurately understand the background values of naturally

occurring elements. For this purpose, in terrestrial areas, stream sediment has been used for making geochemical maps. Stream sediment has been used because its geochemistry is assumed to represent the averaged composite elemental composition of the watershed (e.g., Howarth and Thornton, 1983). On the other hand, rock has not been used as sample media because its geochemistry reflects only the local area, is too inhomogeneous to create nationwide geochemical maps, and provides no information about contamination.

Ohta *et al.* (2005, 2011) successfully identified contamination by P, Cu, Zn, As, Mo, Cd, Sn, Sb, Hg, Pb, and Bi in stream sediments collected from urban areas by applying a statistical test to the geochemical data. However, some parent lithologies elevate the concentrations of these elements in stream sediments. For example, stream sediments originated from ultramafic rock contain several thousand milligrams per kilogram of Cr and Ni (Ohta *et al.*, 2005). In addition, an element in sediments can occur in various physicochemical forms: exchangeable ion, adsorbed ion, carbonate, Fe–Mn oxide, sulfide, organic matter, mineral lattice, and so on (e.g., Tessier *et al.*, 1979). The toxicity of pollutants also changes with their chemical species. For these reasons, the bulk composition provided by geochemical maps is insufficient to elucidate a risk assessment for heavy metals. In areas

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Table 1. List of 8 Geological Survey of Japanese reference materials

Name	Category	Preparation	Note	Reference
JLk-1	Lake sediment	1987	Muddy lake sediments collected from the Lake Biwa	Ando <i>et al.</i> (1990)
JSd-1	Stream sediment	1988	Originating from granitic rocks	Terashima <i>et al.</i> (1990)
JSd-2	Stream sediment	1989	Originating from metamorphic rocks associated with Hitachi Cu mine	Terashima <i>et al.</i> (1990)
JSd-3	Stream sediment	1989	Originating from sedimentary rocks (melange matrix of accretionary complexes)	Terashima <i>et al.</i> (1990)
JSd-4	Stream sediment	2010	Collected from alluvial plain in Kanto District	
JMs-1	Marine sediment	1999	Muddy clay-rich marine sediments collected from the Tokyo Bay	Terashima <i>et al.</i> (2002)
JMs-2	Marine sediment	2000	Pelagic and zeolitic clay collected from Penrhyn Basin in the South Pacific	Terashima <i>et al.</i> (2002)
JSO-1	Soil	1997	Kuroboku soils (Andosol) originated from volcanic ash and rich in organic materials	Terashima <i>et al.</i> (2002)

where speciation geochemical maps have been prepared, it is possible to explore mineral occurrence and elucidate the potential hazard of toxic elements more directly (Ohta *et al.*, 2007).

Imai *et al.* (2004) prepared simple speciation geochemical maps using the 0.1 M hydrochloric acid soluble fraction of elements in stream sediments. Although this method has the advantage of being a simple and rapid procedure, it is unclear which components are extracted. Alternatively, sequential extraction schemes, such as a five-stage Tessier protocol (Tessier *et al.*, 1979), have been widely used as effective speciation techniques. The disadvantage of sequential extraction methods is that the results obtained from different schemes are not always consistent with one another, even in the same laboratories (López-Sánchez *et al.*, 1993; Mester *et al.*, 1998; Usero *et al.*, 1998). Thus, standardization of the sequential extraction procedure and interlaboratory comparison has been evaluated for the three-step extraction procedure of lake sediments developed by the Community Bureau of Reference (BCR) (Crosland *et al.*, 1993; Ure *et al.*, 1993). The precision and accuracy of the analytical data for elemental concentrations extracted using the BCR scheme are confirmed using reference material BCR-701. BCR-701 was prepared using lake sediment (Lake Orta Piemonte, Italy) and was certified for Cd, Cr, Cu, Ni, Pb, and Zn concentrations for the three steps (Sutherland, 2010). Unfortunately, it is the only currently available reference material for the sequential extraction procedure. The availability of a wide variety of reference materials is important for quality control of speciation studies. Indeed, future speciation geochemical mapping of the earth's surface requires a wide range of reference materials, such as stream sediment, marine sediment, and soil, for speciation. Thus, we applied the BCR protocol to sediment geochemical reference materials provided by the Geological Survey of Japan, AIST. The provision of reference values for many elements extracted by sequential extraction would be beneficial for many geochemists who conduct speciation geochemistry of sediments.

SAMPLE MATERIALS

Eight Japanese sediment geochemical reference materials were used for this sequential extraction study. Table 1 summarizes their features, origin, and sedimentary environment. JLk-1 is a lake sediment collected from Lake Biwa, which is the largest lake in Japan (Ando *et al.*, 1990). JSd-1–4 are stream sediment reference materials collected from drainage basins with granitic rocks (JSd-1), the Hitachi Copper Mine (JSd-2), sedimentary rocks (JSd-3), and an alluvial plain in the Kanto District (JSd-4) (Terashima *et al.*, 1990). JMs-1 and JMs-2 are marine sediments collected from Tokyo Bay and the Penrhyn Basin (South Pacific Ocean), respectively (Terashima *et al.*, 2002). JSO-1 is a soil reference material, categorized as an andosol (Kuroboku) soil (Terashima *et al.*, 2002). All materials were well dried in the ambient condition; however, JSO-1 and JMs-1 and JMs-2 were further dried for one week at about 40°C (Terashima *et al.*, 2002) at the time of issue. These reference samples were not intended for speciation chemistry of elements, and the possibility that changes of speciation of elements in soil materials could occur during drying has been suggested. However, the long-term stability of extracted results has been confirmed in dried certified reference materials (Rauret *et al.*, 2000). Therefore, the speciation of elements in our reference materials archived in dried conditions also should not change after their release. We also addressed the binding fraction of the elements in each sample from the stepwise leaching technique. The precision and accuracy of the analytical results for elemental concentrations extracted by the BCR scheme were confirmed using certified reference material BCR-701, which was obtained from the Institute for Reference Materials and Measurements (IRMM).

EXPERIMENTAL METHODS

The sequential extraction was performed in conformity with the BCR scheme proposed by Thomas *et al.*

Fig. 1. Flow diagram of the BCR sequential extraction protocol.

(1994) and Ure *et al.* (1993) and modified by Rauret *et al.* (1999) and Sahuquillo *et al.* (1999). Thirty-eight elements were extracted from the eight sediment geochemical reference materials and BCR701 based on the BCR scheme (defined by Rauret *et al.* (1999)), except that a 0.5 g sample was used instead of a 1 g sample and the shaking was performed at 80 rpm because the sample was not suspended in solution at 30 rpm. Furthermore, the water used for washing the residue was added into the extracted solution without discarding to improve the recovery rate. A brief summary of the method, shown schematically in Fig. 1, is given in the following section. The extracting reagents such as acetic acid, hydroxyammonium chloride, hydrogen peroxide, and ammonium acetate were prepared from analytical grade according to Rauret *et al.* (1999). Deionized ultrapure water (e.g., Milli-Q water) was used throughout.

Sequential extraction procedure (the BCR scheme)

Step 1: This fractionation intends to extract elements in carbonates or those weakly adsorbed on materials (exchangeable elements). 0.5 g of powdered sample, which

was dried at 105°C for 3 h, is added to a 50 mL PFA tube. 20 mL of acetic acid (0.11 mol L⁻¹) is then added to the cool material and a screw-on lid is placed on the PFA tube. The PFA tube is shaken for 16 h at room temperature (25 ± 2°C) in an end-over-end mechanical shaker at a speed of 80 rpm to suspend the sample in the solution. The sample sank to the bottom of the PFA tube at a speed of 30 rpm, which was proposed in the original protocol (Rauret *et al.*, 1999). Supernatant solution is then separated from the solid residue by centrifugation at 3500 rpm for 25 min, removed with a pipette, and then filtrated using a cellulose acetate-type membrane filter (ø = 0.2 µm). The solution is stored in a 100 mL polyethylene volumetric flask. The residue is washed with 10 mL of water by shaking for 15 min (80 rpm) and then centrifuged. The wash solution is filtered into the volumetric flask containing the first extracted solution. Finally, 5 mL of 7 mol L⁻¹ nitric acid is added to the solution and it is made up to 100 mL with water.

Step 2: This fractionation is used to extract the reducible phase and target the elements bound to iron and manganese oxides that would be released when the redox condition changes. Hydroxylammonium chloride solution (0.5 mol L⁻¹, adjusted to pH 1.5 with 1 mol L⁻¹ nitric acid) is prepared immediately before use, and 20 mL of this reagent is added to the residue obtained from step 1. The subsequent extraction procedure is performed as in the case of step 1. 12.5 mL of 7 mol L⁻¹ nitric acid is then added to the supernatant solution and it is made up to 250 mL with water in a polyethylene volumetric flask.

Step 3: This fractionation pertains to the oxidizable phase. Metal sulfides and metals bound to organic matter that would be released into the environment under oxidizing conditions are extracted in this process. 5 mL of hydrogen peroxide (8.8 mol L⁻¹, adjusted to pH 2–3 with 1 mol L⁻¹ nitric acid) is added, in small aliquots, to the residue of step 2 in the centrifuge tube. The screw-on lid on the PFA tube is loosened to release the gases produced during reaction with sulfides and organic matter. In order to avoid violent reactions, the PFA tube is put in a water bath for moderate digestion at ambient temperature (20–30°C) with occasional manual shaking for 1 h. Subsequently, the tube is put in a modular heating block and heated on a hot plate at 85°C for 1 h. The screw-on lid is then removed and the tube contents are evaporated to a small volume (~0.5 mL). After cooling, a second aliquot of 5 mL of hydrogen peroxide is added and the same procedure is repeated. 25 mL of ammonium acetate solution (1.0 mol L⁻¹, adjusted to pH 2.0 with conc. nitric acid) is then added to the cool residue and a screw-on lid is put on the PFA tube. The tube is shaken for 16 h at room temperature (25 ± 2°C) on the shaker, which is operated at a speed of 80 rpm. The extraction procedure and separation of supernatant are repeated as in the case of step 1.

12.5 mL of 7 mol L⁻¹ nitric acid is then added to the supernatant solution and it is made up to 250 mL with water in a polyethylene volumetric flask.

Step 4: This fractionation is associated with the crystalline structure of minerals. This fraction is not part of the target for the BCR extraction scheme, so we call the residue of the step 3 extraction "step 4." 10 mL of hydrofluoric acid, 6 mL of nitric acid, and 4 mL of perchloric acid are added to the residue of step 3 in the PFA tube. The tube, with its screw-on lid loosely attached, is put in a modular heating block on a hot plate at 120°C for 3 h. The solution is then evaporated to dryness, with occasional stirring, at 180°C. The dried residue is dissolved in 5 mL of 7 mol L⁻¹ nitric acid on a hot plate at about 100°C and made up to 100 mL in a polyethylene volumetric flask; 5 mL of the solution and 2.2 mL of 7 mol L⁻¹ nitric acid are then poured into a polyethylene volumetric flask, and diluted to 50 mL with water.

To confirm the recovery of elements extracted by the BCR protocol, bulk compositions of samples are also determined. 0.2 g of powdered sample, which was dried at 105°C for 3 h, is digested using an HF–HNO₃–HClO₄ mixture in a Teflon beaker. The digestion is the same as the procedure of step 4. The dried residue is then dissolved with 5 mL of 7 mol L⁻¹ nitric acid and made up to 100 mL with water in a polyethylene volumetric flask.

Determination of elements

Concentrations of 38 elements extracted at each step were determined using ICP-AES and ICP-MS by the calibration-curve method. Although As, Sn, Sb, and Hg are interesting subjects for environmental assessment, these were not covered in this study. The reason why these elements were not covered is because As, Sn, Sb, and Hg (also Ti, Nb, and Ta) in stream sediments and soil materials are readsorbed on particles during the extraction procedure or scarcely extracted by the three-step BCR protocol (Gómez-Ariza *et al.*, 1999; Marin *et al.*, 1997; Ohta *et al.*, 2007).

Standard and blank solutions for each extraction step were prepared as calibration solutions. Stock solutions containing the 38 elements, prepared by consecutive dilution of 1000 mg L⁻¹ standard solutions, were obtained from Merck Ltd. or Kanto Chemical Co. Inc. The standard solution was prepared by appropriate dilution of the stock solution before analysis. The matrix reagents used in each step were further added to the standard solution at a concentration equal to that of the sample solution for each step. The extractant solution obtained for each step of extraction without geochemical reference materials was used for the blank solution.

For the determination of Na, Mg, Al, P, K, Ca, V, Mn, Fe, Sr, and Ba, a simultaneous echelle type ICP-AES (Nippon Jarrell Ash Model IRIS Advantage AP) was used.

The respective wavelengths (axial plasma viewing) chosen for determination were as follows: Na 589.592 nm, Mg 285.213 nm, Al 237.312 nm, P 213.618 nm, K 766.49 nm, Ca 315.887 nm, V 310.230 nm, Mn 260.569 nm, Fe 259.940 nm, Sr 407.771 nm, and Ba 455.403 nm. The standard solution was inserted as every 10th sample for quality control, correcting drift of the signal intensity. The internal standard method was not applied to ICP-AES measurement.

The Yokokawa Analytical Systems Model HP4500 ICP-MS was used for the determination of other minor elements (⁴⁵Sc, ⁵³Cr, ⁵⁹Co, ⁶⁰Ni, ⁶³Cu, ⁶⁶Zn, ⁸⁵Rb, ⁸⁹Y, ⁹⁷Mo, ¹¹¹Cd, ¹³³Cs, ¹³⁹La, ¹⁴⁰Ce, ¹⁴¹Pr, ¹⁴⁶Nd, ¹⁴⁷Sm, ¹⁵¹Eu, ¹⁵⁷Gd, ¹⁵⁹Tb, ¹⁶³Dy, ¹⁶⁵Ho, ¹⁶⁷Er, ¹⁶⁹Tm, ¹⁷³Yb, ¹⁷⁵Lu, ²⁰⁸Pb, and ²⁰⁹Bi). The blank, standard and sample solutions were mixed with 100 µg/L indium solution and diluted fivefold with water using an automatic dilution system. The solution containing indium was prepared as an internal standard for correction of the matrix effect by coexistence of major elements and drift of the signal intensity. As described above, the standard solution was inserted as every 10th sample for quality control. The ⁵⁹Co, ⁶⁰Ni, and ⁶³Cu results may be interfered respectively by ⁴³Ca¹⁶O, ⁴⁴Ca¹⁶O, and ⁴⁰Ar²³Na. Incidentally, the oxide generation rates of ⁴³Ca and ⁴⁴Ca were 0.1% and 0.05% respectively. Therefore, this interference was negligible in most cases. Exceptionally, the count of ⁶⁰Ni in JMs-2 extracted at step 1 increased to 6% because of the interference of ⁴⁴Ca¹⁶O. The Ni concentration was corrected appropriately. The interference of ¹⁵¹Eu, ¹⁵⁷Gd, and ¹⁵⁹Tb by ¹³⁵Ba¹⁶O, ¹⁴¹Pr¹⁶O, and ¹⁴³Nd¹⁶O were not corrected in this study. The oxide generation rates of ¹³⁵Ba, ¹⁴¹Pr, and ¹⁴³Nd were 0.08%, 0.8%, and 0.06%, respectively. Because the Eu/Ba, Gd/Pr, and Tb/Nd concentration ratios in extractant were constant at roughly 0.002, 1.0, and 0.04, respectively, we prepared standard solution having the identical Eu/Ba, Gd/Pr, and Tb/Nd ratios. Accordingly, it is presumed that there are no significant differences in the results.

Handling of outliers

The sequential extraction procedure provides a large variation in extracted data (e.g., Marin *et al.*, 1997), and the determination of the mean and standard deviation (σ) from the data is largely influenced by far outliers. For this reason, the median and median absolute deviation (MAD) were used to eliminate outliers (Miller and Miller, 2010). These statistical parameters are influenced by the data distribution. The MAD is defined by the following equation:

$$\text{MAD} = \text{median} [|x_i - \text{median}(x_i)|],$$

where median(x_i) means the median values of all data sets.

Table 2. Concentrations (mg kg⁻¹) and 95% confidence intervals for six elements in BCR-701 extracted using mechanical shaker operated at 30 rpm and 80 rpm; significance probabilities (*p*) of *t*-test

Step 1	80 rpm	<i>N</i>	30 rpm	<i>N</i>	<i>p</i> ^a	All	<i>N</i>	Ref ^c	<i>N</i> ^c	<i>p</i> ^b
Cr	3.71 ± 0.70	3	2.81 ± 0.72	4	0.02	3.20 ± 0.55	7	2.26 ± 0.16	14	0.006
Ni	17.1 ± 0.5	4	16.3 ± 1.2	4	0.125	16.7 ± 0.6	8	15.4 ± 0.9	13	0.014
Cu	52.8 ± 14.8	4	49.4 ± 9.5	4	0.557	51.1 ± 6.2	8	49.3 ± 1.7	14	0.528
Zn	213 ± 12	4	202 ± 16	4	0.134	208 ± 9	8	205 ± 6	14	0.576
Cd	7.59 ± 0.34	4	7.44 ± 0.49	4	0.453	7.51 ± 0.21	8	7.34 ± 0.35	14	0.36
Pb	3.85 ± 0.41	4	3.69 ± 0.17	4	0.28	3.77 ± 0.17	8	3.18 ± 0.21	14	<0.001
Step 2										
Cr	46.9 ± 1.8	4	43.0 ± 5.5	4	0.077	45.0 ± 2.7	8	45.7 ± 2.0	12	0.626
Ni	28.8 ± 1.2	4	27.8 ± 2.8	4	0.375	28.3 ± 1.1	8	26.6 ± 1.3	12	0.056
Cu	109 ± 9	4	119 ± 14	4	0.098	114 ± 8	8	124 ± 3	14	0.003
Zn	112 ± 7	4	109 ± 13	4	0.601	111 ± 5	8	114 ± 5	12	0.331
Cd	3.69 ± 0.09	4	3.72 ± 0.32	3	0.77	3.70 ± 0.08	7	3.77 ± 0.28	14	0.627
Pb	127 ± 3	4	126 ± 4	4	0.703	126 ± 2	8	126 ± 3	11	0.79
Step 3										
Cr	156 ± 13	4	155 ± 2	3	0.378	156 ± 5	7	143 ± 7	12	0.011
Ni	16.1 ± 1.5	4	15.8 ± 3.2	4	0.764	16.0 ± 1.2	8	15.3 ± 0.9	13	0.332
Cu	59.9 ± 17.7	4	48.8 ± 37.0	4	0.424	54.4 ± 15	8	55.2 ± 4.0	13	0.901
Zn	47.2 ± 7.8	4	49.4 ± 10.7	3	0.823	48.3 ± 4.6	7	45.7 ± 4.0	11	0.652
Cd	0.34 ± 0.06	4	0.28 ± 0.10	4	0.132	0.31 ± 0.05	8	0.27 ± 0.06	13	0.292
Pb	7.30 ± 1.09	4	8.38 ± 0.55	3	0.115	7.76 ± 0.71	7	9.3 ± 2.0	13	0.131
Step 4										
Cr	109 ± 7	4	112 ± 21	3	0.553	110 ± 6	7	62.5 ± 4.5	13	<0.001
Ni	50.7 ± 1.3	4	49.8 ± 5.5	3	0.473	50.3 ± 1.4	7	41.4 ± 2.7	11	<0.001
Cu	49.6 ± 8.2	4	40.3 ± 11.6	3	0.058	45.6 ± 6.2	7	38.5 ± 6.5	14	0.145
Zn	115 ± 8	4	113 ± 26	3	0.743	114 ± 7	7	95 ± 8	13	0.003
Cd	0.19 ± 0.10	4	0.201 ± 0.002	4	0.282	0.20 ± 0.03	8	0.13 ± 0.06	9	0.045
Pb	22.6 ± 3.1	4	20.7 ± 7.4	3	0.347	21.7 ± 2.2	7	11.0 ± 3.0	14	<0.001

N, number of determinations.

^aSignificance probabilities of *t*-test applied to extracted data obtained from different shaking speed.

^bSignificance probabilities of *t*-test applied to all extracted data and certified data (Sutherland, 2010).

^cCertified data are cited from Sutherland (2010).

A bold-faced type means that the null hypothesis is rejected for *p* = 0.05.

The MAD is calculated from the median of the absolute value of deviations of each value (x_i) from the median values of all data sets (median(x_i)). The MAD is a robust estimator of 0.6745σ , estimated from distribution free data. On an empirical basis, median ± 5 MAD is used as the threshold of the outliers.

RESULTS

Sequential extraction result of CRM-701

Shaking speed The BCR protocol recommends that the shaker is operated at 30 ± 10 rpm (e.g., Rauret *et al.*, 1999). Quevauviller *et al.* (1997) proposed that the sample materials should be continually in suspension during

the extraction. However, the Japanese geochemical reference materials in PFA tube with extractant were not adequately suspended at 30 rpm. By increasing the shaking speed gradually, it was determined that 80 rpm is the minimum necessary speed to suspend samples in experimental solutions. Therefore, the speed of 80 rpm was adopted in this study. In fact, however, the effect of shaking speed on the sequential extraction procedure remained unclear. In order to elucidate the effect of shaking speed, we extracted elements in CRM-701 using an end-over-end mechanical shaker operated at speeds of 30 and 80 rpm. Table 2 summarizes the concentrations of Cr, Ni, Cu, Zn, Cd, and Pb extracted at each step. The *t*-test was applied to compare the means of the two results. When

Table 3. The concentrations in step 1 obtained from BCR extraction procedure

Elements	Unit	D.L.	BCR701		JLk-1		JSd-1		JSd-2	
			Mean $\pm$ 95%*	N	Mean $\pm$ 95%*	N	Mean $\pm$ 95%*	N	Mean $\pm$ 95%*	N
Na	wt%	0.00003	0.0057 $\pm$ 0.0004	7	0.0066 $\pm$ 0.0003	5	0.024 $\pm$ 0.001	7	0.027 $\pm$ 0.002	9
Mg	wt%	0.00003	0.081 $\pm$ 0.001	8	0.029 $\pm$ 0.0006	6	0.035 $\pm$ 0.002	8	0.056 $\pm$ 0.005	9
Al	wt%	0.0004	0.021 $\pm$ 0.002	8	0.022 $\pm$ 0.002	6	0.135 $\pm$ 0.005	8	0.10 $\pm$ 0.01	9
P	mg kg ⁻¹	1	233 $\pm$ 5	7	4.3 $\pm$ 1.2	4	3.5 $\pm$ 1.4	6	21 $\pm$ 3	7
K	wt%	0.0001	0.011 $\pm$ 0.001	7	0.026 $\pm$ 0.001	6	0.027 $\pm$ 0.001	6	0.027 $\pm$ 0.004	9
Ca	wt%	0.0001	0.752 $\pm$ 0.006	7	0.145 $\pm$ 0.003	7	0.110 $\pm$ 0.001	7	0.80 $\pm$ 0.04	9
Sc	mg kg ⁻¹	0.05	0.17 $\pm$ 0.03	8	0.29 $\pm$ 0.07	6	0.47 $\pm$ 0.14	8	1.7 $\pm$ 0.1	7
V	mg kg ⁻¹	1	n.d.	—	n.d.	—	n.d.	—	n.d.	—
Cr	mg kg ⁻¹	0.07	3.2 $\pm$ 0.55	7	0.19 $\pm$ 0.07	6	0.31 $\pm$ 0.05	8	1.84 $\pm$ 0.42	9
Mn	mg kg ⁻¹	0.02	201 $\pm$ 2	8	1260 $\pm$ 10	7	92 $\pm$ 3	7	151 $\pm$ 7	9
Fe	wt%	0.00004	0.021 $\pm$ 0.004	8	0.029 $\pm$ 0.001	5	0.032 $\pm$ 0.003	8	0.46 $\pm$ 0.09	9
Co	mg kg ⁻¹	0.004	2.6 $\pm$ 0.2	8	1.17 $\pm$ 0.08	7	0.85 $\pm$ 0.02	7	12.4 $\pm$ 0.4	8
Ni	mg kg ⁻¹	0.06	16.7 $\pm$ 0.6	8	1.13 $\pm$ 0.08	7	0.26 $\pm$ 0.04	7	10.1 $\pm$ 0.3	9
Cu	mg kg ⁻¹	0.2	51.1 $\pm$ 6.2	8	5.13 $\pm$ 0.22	7	1.32 $\pm$ 0.12	8	176 $\pm$ 17	9
Zn	mg kg ⁻¹	0.1	208 $\pm$ 9	8	5.69 $\pm$ 0.3	5	11.8 $\pm$ 0.7	8	434 $\pm$ 65	9
Rb	mg kg ⁻¹	0.002	0.38 $\pm$ 0.01	8	0.63 $\pm$ 0.04	7	0.38 $\pm$ 0.03	8	0.45 $\pm$ 0.07	9
Sr	mg kg ⁻¹	0.01	48.9 $\pm$ 0.3	7	7.84 $\pm$ 0.09	7	14.2 $\pm$ 0.4	7	15.3 $\pm$ 0.5	9
Y	mg kg ⁻¹	0.002	0.44 $\pm$ 0.07	8	1.9 $\pm$ 0.3	6	0.65 $\pm$ 0.03	7	1.10 $\pm$ 0.07	9
Mo	mg kg ⁻¹	0.004	0.035 $\pm$ 0.009	8	0.009 $\pm$ 0.005	5	0.005 $\pm$ 0.002	5	0.076 $\pm$ 0.021	9
Cd	mg kg ⁻¹	0.002	7.51 $\pm$ 0.21	8	0.34 $\pm$ 0.01	7	0.047 $\pm$ 0.002	7	1.29 $\pm$ 0.07	9
Cs	mg kg ⁻¹	0.0003	0.0053 $\pm$ 0.0006	8	0.0055 $\pm$ 0.0006	7	0.0015 $\pm$ 0.0011	6	0.0023 $\pm$ 0.0008	7
Ba	mg kg ⁻¹	0.08	22.2 $\pm$ 0.6	8	22.9 $\pm$ 0.9	7	45.3 $\pm$ 0.9	7	107 $\pm$ 8	9
La	mg kg ⁻¹	0.003	0.32 $\pm$ 0.04	8	1.1 $\pm$ 0.1	6	1.4 $\pm$ 0.1	8	0.63 $\pm$ 0.05	9
Ce	mg kg ⁻¹	0.005	0.68 $\pm$ 0.1	8	2.6 $\pm$ 0.4	6	1.6 $\pm$ 0.1	7	1.1 $\pm$ 0.1	9
Pr	mg kg ⁻¹	0.0006	0.072 $\pm$ 0.011	8	0.29 $\pm$ 0.04	6	0.29 $\pm$ 0.01	8	0.17 $\pm$ 0.01	9
Nd	mg kg ⁻¹	0.003	0.31 $\pm$ 0.05	8	1.2 $\pm$ 0.2	6	1.1 $\pm$ 0.1	8	0.72 $\pm$ 0.06	9
Sm	mg kg ⁻¹	0.001	0.065 $\pm$ 0.011	8	0.32 $\pm$ 0.05	6	0.19 $\pm$ 0.01	8	0.17 $\pm$ 0.01	9
Eu	mg kg ⁻¹	0.0003	0.013 $\pm$ 0.002	8	0.050 $\pm$ 0.008	6	0.050 $\pm$ 0.001	6	0.052 $\pm$ 0.005	9
Gd	mg kg ⁻¹	0.001	0.074 $\pm$ 0.014	8	0.35 $\pm$ 0.05	6	0.17 $\pm$ 0.01	8	0.19 $\pm$ 0.01	9
Tb	mg kg ⁻¹	0.0002	0.010 $\pm$ 0.001	8	0.053 $\pm$ 0.008	6	0.021 $\pm$ 0.001	8	0.028 $\pm$ 0.002	9
Dy	mg kg ⁻¹	0.0008	0.058 $\pm$ 0.012	8	0.31 $\pm$ 0.04	6	0.11 $\pm$ 0.01	8	0.17 $\pm$ 0.01	9
Ho	mg kg ⁻¹	0.0002	0.012 $\pm$ 0.002	8	0.058 $\pm$ 0.009	6	0.021 $\pm$ 0.001	8	0.036 $\pm$ 0.002	9
Er	mg kg ⁻¹	0.0009	0.033 $\pm$ 0.007	8	0.16 $\pm$ 0.03	6	0.057 $\pm$ 0.002	8	0.10 $\pm$ 0.01	9
Tm	mg kg ⁻¹	0.0001	0.0046 $\pm$ 0.0008	8	0.022 $\pm$ 0.004	6	0.0078 $\pm$ 0.0003	8	0.015 $\pm$ 0.001	9
Yb	mg kg ⁻¹	0.001	0.031 $\pm$ 0.006	8	0.13 $\pm$ 0.02	6	0.047 $\pm$ 0.002	8	0.095 $\pm$ 0.007	9
Lu	mg kg ⁻¹	0.0001	0.0047 $\pm$ 0.0009	8	0.019 $\pm$ 0.003	6	0.0071 $\pm$ 0.0004	8	0.014 $\pm$ 0.001	9
Pb	mg kg ⁻¹	0.05	3.77 $\pm$ 0.17	8	0.98 $\pm$ 0.09	7	0.077 $\pm$ 0.020	6	10.9 $\pm$ 1.4	9
Bi	mg kg ⁻¹	0.006	0.010 $\pm$ 0.002	8	0.014 $\pm$ 0.004	7	0.0069 $\pm$ 0.0027	7	0.014 $\pm$ 0.002	9

the probability obtained by *t*-test was less than 0.05, we could conclude that the two means differed significantly. The results of the statistical test suggest that only concentrations of Cr extracted in step 1 differed significantly (Table 2). Although all elements, except for Cr, Ni, Cu, Zn, Cd, and Pb, are not certified for CRM-701; Mo, Y, and the lanthanides (Ln) also showed the same results as Cr extracted in step 1. However, the ratios of these elemental concentrations extracted in step 1 to bulk concentrations were less than 1.5%. For example, the percentages of Cr concentrations in step 1 to bulk composition at the speeds of 30 and 80 rpm were 1.2% and 0.9%, respectively. Therefore, although the concentrations of

several elements extracted in step 1 varied significantly by shaking speed, we judged that it was of no major consequence for discussion of the extraction percentage.

Precision and accuracy of extracted data Table 2 also includes the results of repeated analyses of the BCR-701 reference samples for the certified six elements calculated from all data. The relative standard deviations (RSDs) for the six elements extracted in these three steps were less than $\pm 10\%$ in most cases; 95% confidential intervals obtained in this study were comparable to the certified values (Table 2). However, the worse RSDs were determined for Cr extracted in step 1; for Cu in steps 1, 3, and 4; and for Cd in steps 3 and 4 (15–33%).

Table 3. (continued)

Elements	Unit	JSd-3		JSd-4		JMs-1		JMs-2		JSO-1	
		Mean $\pm$ 95%*	N	Mean $\pm$ 95%*	N	Mean $\pm$ 95%*	N	Mean $\pm$ 95%*	N	Mean $\pm$ 95%*	N
Na	wt%	0.003 $\pm$ 0.001	6	0.75 $\pm$ 0.05	7	1.86 $\pm$ 0.05	6	2.69 $\pm$ 0.07	6	0.0079 $\pm$ 0.0005	8
Mg	wt%	0.010 $\pm$ <0.001	4	0.65 $\pm$ 0.02	8	0.36 $\pm$ 0.01	8	0.47 $\pm$ 0.01	7	0.029 $\pm$ 0.001	8
Al	wt%	0.110 $\pm$ 0.005	7	0.069 $\pm$ 0.01	8	0.080 $\pm$ 0.001	5	0.031 $\pm$ 0.002	7	0.22 $\pm$ 0.02	9
P	mg kg ⁻¹	2.9 $\pm$ 0.3	5	8.1 $\pm$ 2.6	8	6.0 $\pm$ 0.8	6	73 $\pm$ 16	8	4.5 $\pm$ 1.7	8
K	wt%	0.026 $\pm$ 0.001	5	0.118 $\pm$ 0.008	8	0.22 $\pm$ 0.02	7	0.22 $\pm$ 0.03	8	0.022 $\pm$ 0.002	8
Ca	wt%	0.062 $\pm$ 0.001	7	2.57 $\pm$ 0.04	8	0.61 $\pm$ 0.02	8	1.14 $\pm$ 0.04	8	0.520 $\pm$ 0.002	7
Sc	mg kg ⁻¹	0.28 $\pm$ 0.04	7	0.73 $\pm$ 0.15	9	0.60 $\pm$ 0.01	5	0.80 $\pm$ 0.07	7	0.70 $\pm$ 0.06	6
V	mg kg ⁻¹	n.d.	—	1.3 $\pm$ 0.4	3	1.9 $\pm$ 0.7	4	1.5 $\pm$ 0.6	3	n.d.	—
Cr	mg kg ⁻¹	0.217 $\pm$ 0.05	6	50 $\pm$ 12	9	3.05 $\pm$ 0.51	8	1.14 $\pm$ 0.09	7	0.35 $\pm$ 0.1	8
Mn	mg kg ⁻¹	190 $\pm$ 10	7	179 $\pm$ 10	9	159 $\pm$ 5	8	370 $\pm$ 100	6	140 $\pm$ 13	9
Fe	wt%	0.0023 $\pm$ 0.0002	6	0.037 $\pm$ 0.008	9	0.034 $\pm$ 0.004	8	0.0004 $\pm$ 0.0001	7	0.008 $\pm$ 0.002	9
Co	mg kg ⁻¹	2.5 $\pm$ 0.3	8	2.9 $\pm$ 0.2	9	2.2 $\pm$ 0.2	8	0.74 $\pm$ 0.31	5	1.4 $\pm$ 0.3	8
Ni	mg kg ⁻¹	0.69 $\pm$ 0.06	6	23.2 $\pm$ 1.9	8	4.47 $\pm$ 0.35	8	51.3 $\pm$ 9.9	8	0.70 $\pm$ 0.03	6
Cu	mg kg ⁻¹	84.6 $\pm$ 3.4	6	55.3 $\pm$ 8.9	9	5.44 $\pm$ 0.87	8	8.73 $\pm$ 0.99	6	1.14 $\pm$ 0.33	8
Zn	mg kg ⁻¹	11.4 $\pm$ 1.5	7	458 $\pm$ 61	9	80.7 $\pm$ 4.0	8	6.3 $\pm$ 1.1	7	4.8 $\pm$ 1.0	8
Rb	mg kg ⁻¹	2.48 $\pm$ 0.09	7	0.89 $\pm$ 0.03	8	1.10 $\pm$ 0.05	8	0.48 $\pm$ 0.05	7	0.79 $\pm$ 0.07	8
Sr	mg kg ⁻¹	3.6 $\pm$ 0.1	7	81.4 $\pm$ 0.8	8	53.1 $\pm$ 1	8	130 $\pm$ 4	8	84 $\pm$ 1	9
Y	mg kg ⁻¹	1.1 $\pm$ 0.1	8	1.4 $\pm$ 0.2	9	1.5 $\pm$ 0.2	8	11 $\pm$ 2	8	0.34 $\pm$ 0.07	8
Mo	mg kg ⁻¹	0.005 $\pm$ 0.002	3	0.016 $\pm$ 0.006	8	0.012 $\pm$ 0.007	6	0.024 $\pm$ 0.006	7	0.008 $\pm$ 0.006	5
Cd	mg kg ⁻¹	0.54 $\pm$ 0.02	7	4.36 $\pm$ 0.38	9	0.78 $\pm$ 0.03	8	0.088 $\pm$ 0.013	7	0.067 $\pm$ 0.009	7
Cs	mg kg ⁻¹	0.070 $\pm$ 0.004	8	0.0081 $\pm$ 0.0006	8	0.0064 $\pm$ 0.0013	6	0.0017 $\pm$ 0.0009	6	0.018 $\pm$ 0.004	7
Ba	mg kg ⁻¹	24.6 $\pm$ 0.6	7	12.9 $\pm$ 1.3	8	4.5 $\pm$ 0.2	8	1.1 $\pm$ 0.1	8	80 $\pm$ 3.5	8
La	mg kg ⁻¹	0.73 $\pm$ 0.07	8	0.88 $\pm$ 0.14	9	1.0 $\pm$ 0.1	8	3.2 $\pm$ 0.5	7	0.17 $\pm$ 0.03	8
Ce	mg kg ⁻¹	1.1 $\pm$ 0.1	8	1.3 $\pm$ 0.2	9	2.1 $\pm$ 0.3	8	0.29 $\pm$ 0.09	7	0.15 $\pm$ 0.04	8
Pr	mg kg ⁻¹	0.16 $\pm$ 0.02	8	0.18 $\pm$ 0.03	9	0.24 $\pm$ 0.03	8	0.70 $\pm$ 0.06	6	0.037 $\pm$ 0.007	8
Nd	mg kg ⁻¹	0.64 $\pm$ 0.08	8	0.80 $\pm$ 0.14	9	1.0 $\pm$ 0.1	8	3.9 $\pm$ 0.1	5	0.18 $\pm$ 0.04	8
Sm	mg kg ⁻¹	0.14 $\pm$ 0.02	8	0.18 $\pm$ 0.03	9	0.23 $\pm$ 0.03	8	0.86 $\pm$ 0.08	6	0.040 $\pm$ 0.009	8
Eu	mg kg ⁻¹	0.037 $\pm$ 0.005	8	0.046 $\pm$ 0.009	9	0.06 $\pm$ 0.01	8	0.22 $\pm$ 0.02	6	0.016 $\pm$ 0.002	8
Gd	mg kg ⁻¹	0.17 $\pm$ 0.02	8	0.21 $\pm$ 0.04	9	0.27 $\pm$ 0.03	8	1.3 $\pm$ 0.1	6	0.044 $\pm$ 0.006	7
Tb	mg kg ⁻¹	0.025 $\pm$ 0.004	8	0.029 $\pm$ 0.005	9	0.039 $\pm$ 0.005	8	0.165 $\pm$ 0.001	5	0.0068 $\pm$ 0.0011	6
Dy	mg kg ⁻¹	0.16 $\pm$ 0.02	8	0.17 $\pm$ 0.03	9	0.22 $\pm$ 0.03	8	1.07 $\pm$ 0.02	5	0.041 $\pm$ 0.009	8
Ho	mg kg ⁻¹	0.031 $\pm$ 0.003	7	0.035 $\pm$ 0.006	9	0.044 $\pm$ 0.005	8	0.27 $\pm$ 0.01	5	0.0088 $\pm$ 0.001	7
Er	mg kg ⁻¹	0.090 $\pm$ 0.010	8	0.10 $\pm$ 0.02	9	0.11 $\pm$ 0.01	8	0.81 $\pm$ 0.01	5	0.024 $\pm$ 0.004	7
Tm	mg kg ⁻¹	0.012 $\pm$ 0.001	7	0.013 $\pm$ 0.002	9	0.015 $\pm$ 0.002	8	0.10 $\pm$ 0.01	6	0.0036 $\pm$ 0.0008	7
Yb	mg kg ⁻¹	0.076 $\pm$ 0.009	8	0.082 $\pm$ 0.014	9	0.091 $\pm$ 0.013	8	0.66 $\pm$ 0.01	5	0.025 $\pm$ 0.005	8
Lu	mg kg ⁻¹	0.011 $\pm$ 0.002	8	0.014 $\pm$ 0.002	9	0.014 $\pm$ 0.002	8	0.125 $\pm$ 0.004	5	0.004 $\pm$ 0.0006	7
Pb	mg kg ⁻¹	2.49 $\pm$ 0.24	8	2.60 $\pm$ 0.26	9	1.09 $\pm$ 0.12	8	<0.09	2	0.082 $\pm$ 0.004	3
Bi	mg kg ⁻¹	0.036 $\pm$ 0.003	7	0.010 $\pm$ 0.002	8	0.0093 $\pm$ 0.0021	7	0.0061 $\pm$ 0.0016	6	0.0060 $\pm$ 0.0019	7

N, number of determinations; *D.L.*, detection limit; *n.d.*, not determined; *95% confidence interval.

Next, the *t*-test was applied to confirm how our data compared to the certified values for respective elements and respective steps. The statistical results suggest that the concentrations of Cr, Ni, and Pb extracted in step 1 and those of Cr in step 3 were significantly higher than the certified values. This occurred because the water used for washing the residue was added into the extracted solution without discarding. Meanwhile, the concentration of Cu obtained at step 2 was significantly lower than the certified value. The concentrations of Cr, Ni, Cu, Zn, and Pb in step 4 were a reasonable amount higher than the certified values because the residue from step 3 was di-

gested not by HF but by aqua regia in the BCR protocol. Accordingly, we can conclude that the obtained data are consistent with the certified values.

Precision and recovery of sequential extraction results of Japanese geochemical reference materials

The sequential extraction results of the eight geochemical reference samples and CRM-701 are presented in Tables 3–6. Figure 2 shows the RSDs obtained from repeated measurements for the 38 elements in each step. The RSDs for most elements were less than 30% for steps 1 and 3 and less than 20% for steps 2 and 4. The

Table 4. The concentrations in step 2 obtained from BCR extraction procedure

Elements	Unit	D.L.	BCR701		JLk-1		JSd-1		JSd-2	
			Mean $\pm$ 95%*	N	Mean $\pm$ 95%*	N	Mean $\pm$ 95%*	N	Mean $\pm$ 95%*	N
Na	wt%	0.0001	0.0009 $\pm$ 0.0002	6	0.0013 $\pm$ 0.0003	6	0.0079 $\pm$ 0.0004	5	0.023 $\pm$ 0.004	9
Mg	wt%	0.00003	0.077 $\pm$ 0.005	8	0.067 $\pm$ 0.007	6	0.082 $\pm$ 0.007	7	0.13 $\pm$ 0.01	9
Al	wt%	0.0003	0.38 $\pm$ 0.01	8	0.37 $\pm$ 0.01	5	0.38 $\pm$ 0.01	7	0.41 $\pm$ 0.01	9
P	mg kg ⁻¹	1	1540 $\pm$ 110	7	450 $\pm$ 100	5	293 $\pm$ 12	5	261 $\pm$ 41	5
K	wt%	0.0001	0.016 $\pm$ 0.002	8	0.027 $\pm$ 0.001	5	0.035 $\pm$ 0.001	5	0.049 $\pm$ 0.005	8
Ca	wt%	0.0001	0.189 $\pm$ 0.005	8	0.076 $\pm$ 0.003	6	0.094 $\pm$ 0.002	7	0.52 $\pm$ 0.04	9
Sc	mg kg ⁻¹	0.09	0.27 $\pm$ 0.24	5	0.86 $\pm$ 0.34	6	0.65 $\pm$ 0.41	7	2.9 $\pm$ 0.6	8
V	mg kg ⁻¹	0.8	12 $\pm$ 1	5	19 $\pm$ 2	5	8.4 $\pm$ 2.0	6	8.3 $\pm$ 1.8	7
Cr	mg kg ⁻¹	0.7	45 $\pm$ 2.7	8	4.8 $\pm$ 1.9	6	1.39 $\pm$ 0.55	5	11.7 $\pm$ 0.2	5
Mn	mg kg ⁻¹	0.03	136 $\pm$ 4	7	361 $\pm$ 11	7	99 $\pm$ 2	6	174 $\pm$ 6	8
Fe	wt%	0.00002	0.82 $\pm$ 0.02	7	1.44 $\pm$ 0.12	6	0.41 $\pm$ 0.02	6	1.83 $\pm$ 0.07	8
Co	mg kg ⁻¹	0.007	3.2 $\pm$ 0.1	8	4.2 $\pm$ 0.2	6	1.55 $\pm$ 0.05	7	15.8 $\pm$ 0.5	9
Ni	mg kg ⁻¹	0.08	28.3 $\pm$ 1.1	8	4.08 $\pm$ 0.12	5	0.94 $\pm$ 0.22	7	34.7 $\pm$ 1.4	9
Cu	mg kg ⁻¹	0.2	114 $\pm$ 8	8	15.7 $\pm$ 0.7	6	7.58 $\pm$ 0.74	7	237 $\pm$ 22	9
Zn	mg kg ⁻¹	0.3	111 $\pm$ 5	8	26.4 $\pm$ 1.3	5	16.9 $\pm$ 1.3	6	1325 $\pm$ 91	9
Rb	mg kg ⁻¹	0.01	2.2 $\pm$ 0.1	8	4.0 $\pm$ 0.2	6	3.5 $\pm$ 0.2	6	2.3 $\pm$ 0.1	8
Sr	mg kg ⁻¹	0.02	14.7 $\pm$ 0.5	7	7.9 $\pm$ 0.3	6	4.85 $\pm$ 0.08	7	17.9 $\pm$ 0.8	9
Y	mg kg ⁻¹	0.005	7.6 $\pm$ 0.3	8	17.5 $\pm$ 0.4	7	2.03 $\pm$ 0.05	7	2.38 $\pm$ 0.07	9
Mo	mg kg ⁻¹	0.01	0.13 $\pm$ 0.03	8	0.074 $\pm$ 0.024	7	0.018 $\pm$ 0.007	3	0.66 $\pm$ 0.06	9
Cd	mg kg ⁻¹	0.003	3.66 $\pm$ 0.13	8	0.140 $\pm$ 0.012	6	0.035 $\pm$ 0.007	6	1.03 $\pm$ 0.03	8
Cs	mg kg ⁻¹	0.0008	0.35 $\pm$ 0.01	8	0.35 $\pm$ 0.02	7	0.11 $\pm$ 0.01	6	0.121 $\pm$ 0.004	7
Ba	mg kg ⁻¹	0.07	118 $\pm$ 3	8	121 $\pm$ 2	6	53 $\pm$ 1	8	718 $\pm$ 16	9
La	mg kg ⁻¹	0.008	6.5 $\pm$ 0.2	8	14.6 $\pm$ 0.3	7	2.80 $\pm$ 0.06	7	1.61 $\pm$ 0.06	9
Ce	mg kg ⁻¹	0.02	17.5 $\pm$ 0.7	8	35 $\pm$ 1	7	5.9 $\pm$ 0.3	7	3.1 $\pm$ 0.1	9
Pr	mg kg ⁻¹	0.001	1.69 $\pm$ 0.03	8	3.81 $\pm$ 0.09	7	0.74 $\pm$ 0.01	7	0.44 $\pm$ 0.01	9
Nd	mg kg ⁻¹	0.01	6.8 $\pm$ 0.2	8	15.0 $\pm$ 0.5	7	2.93 $\pm$ 0.05	7	1.84 $\pm$ 0.06	9
Sm	mg kg ⁻¹	0.004	1.55 $\pm$ 0.04	8	3.64 $\pm$ 0.14	7	0.59 $\pm$ 0.02	7	0.45 $\pm$ 0.02	9
Eu	mg kg ⁻¹	0.001	0.24 $\pm$ 0.01	8	0.55 $\pm$ 0.02	7	0.11 $\pm$ 0.01	7	0.15 $\pm$ 0.01	9
Gd	mg kg ⁻¹	0.005	1.59 $\pm$ 0.04	8	3.69 $\pm$ 0.08	7	0.54 $\pm$ 0.02	7	0.47 $\pm$ 0.02	9
Tb	mg kg ⁻¹	0.0005	0.24 $\pm$ 0.01	8	0.56 $\pm$ 0.01	7	0.072 $\pm$ 0.003	7	0.071 $\pm$ 0.002	9
Dy	mg kg ⁻¹	0.002	1.48 $\pm$ 0.03	8	3.25 $\pm$ 0.07	7	0.39 $\pm$ 0.01	7	0.45 $\pm$ 0.01	9
Ho	mg kg ⁻¹	0.0006	0.274 $\pm$ 0.005	8	0.61 $\pm$ 0.01	7	0.075 $\pm$ 0.005	7	0.090 $\pm$ 0.001	9
Er	mg kg ⁻¹	0.001	0.75 $\pm$ 0.01	8	1.64 $\pm$ 0.03	7	0.20 $\pm$ 0.01	7	0.26 $\pm$ 0.01	9
Tm	mg kg ⁻¹	0.0005	0.099 $\pm$ 0.003	8	0.22 $\pm$ 0.01	7	0.026 $\pm$ 0.005	8	0.035 $\pm$ 0.002	9
Yb	mg kg ⁻¹	0.005	0.63 $\pm$ 0.01	8	1.33 $\pm$ 0.03	7	0.17 $\pm$ 0.01	7	0.22 $\pm$ 0.01	9
Lu	mg kg ⁻¹	0.0003	0.081 $\pm$ 0.003	8	0.19 $\pm$ 0.01	7	0.023 $\pm$ 0.001	5	0.030 $\pm$ 0.001	9
Pb	mg kg ⁻¹	0.1	126 $\pm$ 2	8	32.3 $\pm$ 1.4	7	4.56 $\pm$ 0.29	6	104 $\pm$ 5	9
Bi	mg kg ⁻¹	0.006	0.91 $\pm$ 0.08	8	0.69 $\pm$ 0.02	7	0.034 $\pm$ 0.011	7	0.27 $\pm$ 0.02	9

worse coefficients of variance were determined for P, V, and Cr in steps 1, 2, and 3; for Sc in steps 1 and 2; for Fe and Bi in steps 1 and 3; for Na and Mo in steps 2 and 3; and for Cd in steps 1, 3, and 4. The worse RSDs for elements extracted in steps 1 and 2 can be explained by their lower concentrations in each step. The third step in the BCR protocol has cumbersome procedures compared to the other steps, which results in worse RSDs.

Figure 3 shows the recovery rates of the 38 elements. The recovery rate is the ratio of the total amount extracted in the four steps (sum of the four steps) and the bulk con-

centration, which are summarized in Table 7. The elements on the horizontal axis of Fig. 3 are arranged in ascending order of median value of the recovery rate determined for nine samples. The estimated recovery rate for samples ranged from 52% to 137% of the bulk composition (Fig. 3). Extreme overestimation of the recovery rate (137%) occurred only for P in JSd-2. We suspected that the wavelength of P (213.618 nm) was interfered by that of Cu (213.598 nm); the Cu concentration in JSd-2 is very high. However, significant improvement did not occur even after correction of the interference. We thus pre-

Table 4. (continued)

Elements	Unit	JSd-3		JSd-4		JMs-1		JMs-2		JSO-1	
		Mean $\pm$ 95%*	N	Mean $\pm$ 95%*	N	Mean $\pm$ 95%*	N	Mean $\pm$ 95%*	N	Mean $\pm$ 95%*	N
Na	wt%	0.0005 $\pm$ 0.0004	7	0.021 $\pm$ 0.001	7	0.049 $\pm$ 0.003	7	0.47 $\pm$ 0.01	6	0.0008 $\pm$ 0.0005	6
Mg	wt%	0.008 $\pm$ 0.001	7	0.63 $\pm$ 0.01	8	0.20 $\pm$ 0.01	8	0.22 $\pm$ 0.01	8	0.042 $\pm$ 0.004	9
Al	wt%	0.28 $\pm$ 0.01	8	1.03 $\pm$ 0.04	8	0.75 $\pm$ 0.01	7	0.75 $\pm$ 0.02	6	1.69 $\pm$ 0.02	7
P	mg kg ⁻¹	39 $\pm$ 7	6	386 $\pm$ 38	7	272 $\pm$ 37	6	1990 $\pm$ 600	7	52 $\pm$ 14	9
K	wt%	0.014 $\pm$ 0.001	6	0.061 $\pm$ 0.004	8	0.112 $\pm$ 0.001	5	0.63 $\pm$ 0.01	6	0.006 $\pm$ 0.001	8
Ca	wt%	0.020 $\pm$ 0.002	8	0.225 $\pm$ 0.008	7	0.13 $\pm$ 0.01	8	0.95 $\pm$ 0.02	8	0.066 $\pm$ 0.002	8
Sc	mg kg ⁻¹	<1.0	3	1.3 $\pm$ 0.3	7	0.87 $\pm$ 0.24	6	1.1 $\pm$ 0.2	7	1.5 $\pm$ 0.3	8
V	mg kg ⁻¹	4.2 $\pm$ 2.2	5	45 $\pm$ 6	7	25 $\pm$ 4	6	54 $\pm$ 3	5	46 $\pm$ 3	6
Cr	mg kg ⁻¹	1.40 $\pm$ 0.63	4	356 $\pm$ 31	9	20.7 $\pm$ 3.3	7	1.85 $\pm$ 0.80	5	2.60 $\pm$ 0.62	6
Mn	mg kg ⁻¹	268 $\pm$ 12	8	173 $\pm$ 6	9	135 $\pm$ 7	8	14780 $\pm$ 50	6	610 $\pm$ 30	9
Fe	wt%	0.22 $\pm$ 0.03	8	1.40 $\pm$ 0.12	9	0.91 $\pm$ 0.06	8	1.5 $\pm$ 0.1	7	0.61 $\pm$ 0.06	9
Co	mg kg ⁻¹	4.1 $\pm$ 0.2	7	5.4 $\pm$ 0.1	8	3.8 $\pm$ 0.3	8	211 $\pm$ 4	7	11.4 $\pm$ 0.5	9
Ni	mg kg ⁻¹	2.23 $\pm$ 0.24	7	42.7 $\pm$ 1.6	9	7.08 $\pm$ 0.49	8	202 $\pm$ 3	7	1.68 $\pm$ 0.22	8
Cu	mg kg ⁻¹	92.5 $\pm$ 11.8	8	200 $\pm$ 6	7	23 $\pm$ 3.2	8	221 $\pm$ 4	6	2.87 $\pm$ 0.80	8
Zn	mg kg ⁻¹	11.8 $\pm$ 1.9	8	781 $\pm$ 44	9	82.2 $\pm$ 2.6	7	51.7 $\pm$ 2.4	7	9.3 $\pm$ 1.0	8
Rb	mg kg ⁻¹	6.4 $\pm$ 0.5	8	2.9 $\pm$ 0.2	9	4.6 $\pm$ 0.3	8	4.2 $\pm$ 0.3	6	0.90 $\pm$ 0.07	8
Sr	mg kg ⁻¹	1.6 $\pm$ 0.2	7	33.4 $\pm$ 0.7	8	14.5 $\pm$ 0.5	6	122 $\pm$ 4	7	15.4 $\pm$ 0.3	8
Y	mg kg ⁻¹	2.6 $\pm$ 0.1	7	6.2 $\pm$ 0.2	9	7.66 $\pm$ 0.24	8	206 $\pm$ 3	7	2.9 $\pm$ 0.5	9
Mo	mg kg ⁻¹	n.d.	—	0.057 $\pm$ 0.012	8	0.041 $\pm$ 0.010	7	0.43 $\pm$ 0.07	8	n.d.	—
Cd	mg kg ⁻¹	0.211 $\pm$ 0.006	6	1.90 $\pm$ 0.25	9	0.141 $\pm$ 0.018	7	0.307 $\pm$ 0.007	6	0.128 $\pm$ 0.007	8
Cs	mg kg ⁻¹	1.8 $\pm$ 0.1	7	0.17 $\pm$ 0.01	9	0.14 $\pm$ 0.01	8	0.018 $\pm$ 0.003	6	0.23 $\pm$ 0.01	9
Ba	mg kg ⁻¹	26.7 $\pm$ 0.8	8	379 $\pm$ 12	9	25.0 $\pm$ 0.4	8	415 $\pm$ 5	5	84 $\pm$ 6	9
La	mg kg ⁻¹	2.1 $\pm$ 0.1	8	4.6 $\pm$ 0.1	9	6.0 $\pm$ 0.2	8	109 $\pm$ 2	7	1.4 $\pm$ 0.2	9
Ce	mg kg ⁻¹	6.1 $\pm$ 0.3	7	8.4 $\pm$ 0.3	9	15 $\pm$ 0.4	8	107 $\pm$ 5	7	1.2 $\pm$ 0.2	9
Pr	mg kg ⁻¹	0.60 $\pm$ 0.04	8	1.05 $\pm$ 0.04	9	1.75 $\pm$ 0.04	8	29.7 $\pm$ 0.4	7	0.23 $\pm$ 0.04	9
Nd	mg kg ⁻¹	2.4 $\pm$ 0.2	8	4.3 $\pm$ 0.2	9	7.3 $\pm$ 0.2	8	126 $\pm$ 3	7	0.93 $\pm$ 0.19	9
Sm	mg kg ⁻¹	0.57 $\pm$ 0.04	8	0.92 $\pm$ 0.04	9	1.69 $\pm$ 0.05	8	28.6 $\pm$ 0.6	7	0.19 $\pm$ 0.04	9
Eu	mg kg ⁻¹	0.14 $\pm$ 0.01	8	0.24 $\pm$ 0.02	9	0.38 $\pm$ 0.01	8	6.6 $\pm$ 0.2	7	0.060 $\pm$ 0.014	9
Gd	mg kg ⁻¹	0.56 $\pm$ 0.02	7	1.04 $\pm$ 0.05	9	1.76 $\pm$ 0.04	8	32.0 $\pm$ 0.9	7	0.26 $\pm$ 0.06	9
Tb	mg kg ⁻¹	0.092 $\pm$ 0.005	8	0.16 $\pm$ 0.01	9	0.26 $\pm$ 0.01	8	4.9 $\pm$ 0.1	7	0.041 $\pm$ 0.009	9
Dy	mg kg ⁻¹	0.57 $\pm$ 0.04	8	0.98 $\pm$ 0.03	9	1.55 $\pm$ 0.02	8	31.7 $\pm$ 0.7	7	0.29 $\pm$ 0.06	9
Ho	mg kg ⁻¹	0.11 $\pm$ <0.01	7	0.20 $\pm$ 0.01	9	0.29 $\pm$ 0.01	8	6.6 $\pm$ 0.1	7	0.066 $\pm$ 0.014	9
Er	mg kg ⁻¹	0.29 $\pm$ 0.02	8	0.56 $\pm$ 0.02	9	0.76 $\pm$ 0.02	8	18.9 $\pm$ 0.5	7	0.20 $\pm$ 0.04	9
Tm	mg kg ⁻¹	0.04 $\pm$ 0.002	7	0.075 $\pm$ 0.004	9	0.099 $\pm$ 0.004	8	2.58 $\pm$ 0.06	7	0.027 $\pm$ 0.008	9
Yb	mg kg ⁻¹	0.26 $\pm$ 0.01	7	0.47 $\pm$ 0.02	9	0.61 $\pm$ 0.02	8	16.3 $\pm$ 0.6	7	0.17 $\pm$ 0.04	9
Lu	mg kg ⁻¹	0.034 $\pm$ 0.001	7	0.066 $\pm$ 0.003	9	0.082 $\pm$ 0.003	8	2.51 $\pm$ 0.09	7	0.023 $\pm$ 0.005	8
Pb	mg kg ⁻¹	27.5 $\pm$ 1.4	8	149 $\pm$ 6	9	37.1 $\pm$ 0.8	7	37.2 $\pm$ 1.9	8	2.17 $\pm$ 0.33	8
Bi	mg kg ⁻¹	4.0 $\pm$ 0.3	8	0.071 $\pm$ 0.009	8	0.26 $\pm$ 0.04	8	0.010 $\pm$ 0.002	4	n.d.	-

N, number of determinations; *D.L.*, detection limit; *n.d.*, not determinated; *95% confidence interval.

sumed that the cause of the overestimation was analytical errors of concentration in the bulk composition and extractant in each step. Only 14 elements, such as Co and Cu, had high enough recovery rates (median value > 90%). Insignificant recovery rates were obtained for Al, Ca, Sc, Cr, Rb, Sr, Y, Mo, Cs, Ln (La–Lu), and Pb (median values were 70–90%). In this study, we used a 50 mL PFA tube to digest the step 3 residue without transporting it to a Teflon beaker. As a result, the contact area of residue

with mixed acid in the PFA tube was much smaller than that in a Teflon beaker. Thus, these low recovery rates can be attributed in part to incomplete decomposition reaction in the PFA tube. Therefore, when we calculated the relative percentages of each extracted fraction for Al, Ca, Sc, Cr, Rb, Sr, Y, Mo, Cs, Ln, and Pb, their concentrations in step 4 were calculated by the subtraction of the concentrations of steps 1, 2, and 3 from bulk concentrations.

Table 5. The concentrations in step 3 obtained from BCR extraction procedure

Elements	Unit	D.L.	BCR701		JLk-1		JSd-1		JSd-2	
			Mean $\pm$ 95%*	N	Mean $\pm$ 95%*	N	Mean $\pm$ 95%*	N	Mean $\pm$ 95%*	N
Na	wt%	0.0001	0.004 $\pm$ 0.001	7	0.004 $\pm$ 0.002	6	0.010 $\pm$ 0.003	8	0.009 $\pm$ 0.002	8
Mg	wt%	0.00003	0.066 $\pm$ 0.005	6	0.047 $\pm$ 0.003	5	0.034 $\pm$ 0.004	6	0.037 $\pm$ 0.004	6
Al	wt%	0.001	0.14 $\pm$ 0.03	7	0.15 $\pm$ 0.02	6	0.07 $\pm$ 0.01	6	0.14 $\pm$ 0.01	6
P	mg kg ⁻¹	3	189 $\pm$ 40	7	100 $\pm$ 60	7	44 $\pm$ 22	7	109 $\pm$ 59	9
K	wt%	0.0001	0.014 $\pm$ 0.003	8	0.010 $\pm$ 0.003	6	0.012 $\pm$ 0.005	7	0.004 $\pm$ 0.003	5
Ca	wt%	0.0002	0.021 $\pm$ 0.002	8	0.031 $\pm$ 0.002	6	0.072 $\pm$ 0.004	7	0.036 $\pm$ 0.004	8
Sc	mg kg ⁻¹	0.08	1.2 $\pm$ 0.2	7	2.8 $\pm$ 0.4	6	0.43 $\pm$ 0.15	6	1.8 $\pm$ 0.3	9
Cr	mg kg ⁻¹	0.2	155 $\pm$ 1	5	3.57 $\pm$ 0.49	6	0.84 $\pm$ 0.26	7	2.31 $\pm$ 0.22	7
V	mg kg ⁻¹	1	<3	2	3.1 $\pm$ 2.9	4	4.4 $\pm$ 2.8	4	<4	2
Mn	mg kg ⁻¹	0.02	26.6 $\pm$ 1.0	5	102 $\pm$ 11	5	26.1 $\pm$ 2.2	5	26.9 $\pm$ 7.2	6
Fe	wt%	0.00005	0.17 $\pm$ 0.08	8	0.11 $\pm$ 0.04	6	0.016 $\pm$ 0.009	6	0.52 $\pm$ 0.18	7
Co	mg kg ⁻¹	0.006	1.57 $\pm$ 0.07	7	2.5 $\pm$ 0.14	6	0.45 $\pm$ 0.1	7	5.7 $\pm$ 0.7	8
Ni	mg kg ⁻¹	0.02	16.0 $\pm$ 1.2	8	3.93 $\pm$ 0.35	6	0.38 $\pm$ 0.21	7	15.6 $\pm$ 2.1	8
Cu	mg kg ⁻¹	0.2	54.4 $\pm$ 15	8	13.1 $\pm$ 3.5	7	1.78 $\pm$ 0.73	5	549 $\pm$ 75	9
Zn	mg kg ⁻¹	0.1	48.3 $\pm$ 4.6	8	16.1 $\pm$ 2.3	6	5.84 $\pm$ 2.3	6	132 $\pm$ 12	8
Rb	mg kg ⁻¹	0.002	1.9 $\pm$ 0.2	7	2.0 $\pm$ 0.2	6	1.1 $\pm$ 0.1	6	0.50 $\pm$ 0.18	8
Sr	mg kg ⁻¹	0.03	2.1 $\pm$ 0.2	8	1.4 $\pm$ 0.2	5	2.4 $\pm$ 0.2	7	3.8 $\pm$ 0.5	8
Y	mg kg ⁻¹	0.003	1.4 $\pm$ 0.2	8	2.4 $\pm$ 0.11	7	1.8 $\pm$ 0.4	8	0.56 $\pm$ 0.08	8
Mo	mg kg ⁻¹	0.01	0.88 $\pm$ 0.28	6	0.28 $\pm$ 0.13	5	0.23 $\pm$ 0.02	6	0.43 $\pm$ 0.12	8
Cd	mg kg ⁻¹	0.003	0.312 $\pm$ 0.049	8	0.025 $\pm$ 0.011	6	0.016 $\pm$ 0.006	6	0.52 $\pm$ 0.04	8
Cs	mg kg ⁻¹	0.003	0.29 $\pm$ 0.07	8	0.54 $\pm$ 0.11	6	0.049 $\pm$ 0.026	7	0.035 $\pm$ 0.002	6
Ba	mg kg ⁻¹	0.1	14.3 $\pm$ 0.4	7	7.2 $\pm$ 0.6	6	7.1 $\pm$ 0.8	7	33 $\pm$ 3	8
La	mg kg ⁻¹	0.004	1.2 $\pm$ 0.1	7	1.75 $\pm$ 0.05	6	0.50 $\pm$ 0.19	6	0.27 $\pm$ 0.03	7
Ce	mg kg ⁻¹	0.006	3.6 $\pm$ 0.3	7	4.80 $\pm$ 0.09	6	0.77 $\pm$ 0.36	6	0.52 $\pm$ 0.06	7
Pr	mg kg ⁻¹	0.0008	0.37 $\pm$ 0.04	7	0.54 $\pm$ 0.02	7	0.26 $\pm$ 0.08	7	0.09 $\pm$ 0.02	8
Nd	mg kg ⁻¹	0.004	1.6 $\pm$ 0.2	7	2.25 $\pm$ 0.07	7	1.2 $\pm$ 0.2	7	0.33 $\pm$ 0.03	7
Sm	mg kg ⁻¹	0.002	0.41 $\pm$ 0.06	7	0.60 $\pm$ 0.02	7	0.30 $\pm$ 0.05	7	0.089 $\pm$ 0.009	7
Eu	mg kg ⁻¹	0.0006	0.064 $\pm$ 0.011	7	0.094 $\pm$ 0.003	7	0.083 $\pm$ 0.014	7	0.028 $\pm$ 0.004	8
Gd	mg kg ⁻¹	0.002	0.39 $\pm$ 0.08	8	0.56 $\pm$ 0.01	7	0.33 $\pm$ 0.06	7	0.10 $\pm$ 0.02	8
Tb	mg kg ⁻¹	0.0003	0.055 $\pm$ 0.004	6	0.089 $\pm$ 0.002	7	0.054 $\pm$ 0.007	6	0.017 $\pm$ 0.003	8
Dy	mg kg ⁻¹	0.001	0.33 $\pm$ 0.02	6	0.53 $\pm$ 0.02	7	0.36 $\pm$ 0.06	7	0.12 $\pm$ 0.02	8
Ho	mg kg ⁻¹	0.0003	0.062 $\pm$ 0.008	7	0.102 $\pm$ 0.004	7	0.064 $\pm$ 0.015	8	0.022 $\pm$ 0.002	7
Er	mg kg ⁻¹	0.0009	0.16 $\pm$ 0.01	6	0.27 $\pm$ 0.01	7	0.20 $\pm$ 0.03	7	0.061 $\pm$ 0.004	7
Tm	mg kg ⁻¹	0.0002	0.023 $\pm$ 0.004	8	0.039 $\pm$ 0.004	7	0.029 $\pm$ 0.004	7	0.009 $\pm$ 0.001	7
Yb	mg kg ⁻¹	0.001	0.17 $\pm$ 0.01	7	0.27 $\pm$ 0.02	7	0.20 $\pm$ 0.03	7	0.062 $\pm$ 0.009	8
Lu	mg kg ⁻¹	0.0003	0.022 $\pm$ 0.002	7	0.036 $\pm$ 0.003	7	0.025 $\pm$ 0.005	8	0.008 $\pm$ 0.002	8
Pb	mg kg ⁻¹	0.06	7.76 $\pm$ 0.71	7	2.52 $\pm$ 0.63	6	0.52 $\pm$ 0.43	5	3.57 $\pm$ 0.74	7
Bi	mg kg ⁻¹	0.006	0.29 $\pm$ 0.05	7	0.066 $\pm$ 0.007	6	0.015 $\pm$ 0.008	7	0.11 $\pm$ 0.017	7

Distribution of 38 elements in geochemical reference materials

Distribution of Cr, Ni, Cu, Zn, Cd, and Pb in sediments

Figure 4 shows the distributions of Cr, Ni, Cu, Zn, Cd, and Pb concentrations in samples for the four fractions obtained from the BCR scheme. The BCR-701 sample was certified for the Cr, Ni, Cu, Zn, Cd, and Pb concentrations for the three steps (Sutherland, 2010). The remaining metals amount in the residue could not be certified due to high variability between results obtained by different laboratories (Sahuquillo *et al.*, 1999). Cr was

extracted primarily from the residual fraction, from which mobility is low under environmental conditions (Morillo *et al.*, 2004). However, the intensive feature was found in the distribution of Cr in BCR-701, JSd-4, and JMs-1. The high proportion of Cr in these samples was extracted in step 2 (10–30%) and in step 3 (20–50%). A similar distribution of Cr in urban soils was reported by Davidson *et al.* (1994, 2006). The Ni in JLk-1, JSd-1, and JSO-1 was dominantly associated with the residual fraction (step 4). However, a higher percentage of Ni was extracted in step 1 (10–25%) and in step 2 (35–70%) for JSd-2, JSd-

Table 5. (continued)

Elements	Unit	JSd-3		JSd-4		JMs-1		JMs-2		JSO-1	
		Mean $\pm$ 95%*	N	Mean $\pm$ 95%*	N	Mean $\pm$ 95%*	N	Mean $\pm$ 95%*	N	Mean $\pm$ 95%*	N
Na	wt%	0.002 $\pm$ 0.001	6	0.012 $\pm$ 0.002	8	0.020 $\pm$ 0.003	8	0.024 $\pm$ 0.004	8	0.002 $\pm$ 0.001	8
Mg	wt%	0.006 $\pm$ 0.003	6	0.14 $\pm$ 0.04	8	0.09 $\pm$ 0.02	7	0.104 $\pm$ 0.005	6	0.025 $\pm$ 0.006	8
Al	wt%	0.11 $\pm$ 0.03	7	0.51 $\pm$ 0.11	7	0.37 $\pm$ 0.01	6	0.63 $\pm$ 0.06	6	1.7 $\pm$ 0.2	8
P	mg kg ⁻¹	10 $\pm$ 7	6	210 $\pm$ 87	7	73 $\pm$ 28	6	620 $\pm$ 90	6	165 $\pm$ 33	8
K	wt%	0.006 $\pm$ 0.003	7	0.011 $\pm$ 0.004	9	0.009 $\pm$ 0.003	6	0.18 $\pm$ 0.01	7	0.003 $\pm$ 0.001	8
Ca	wt%	0.008 $\pm$ 0.002	7	0.054 $\pm$ 0.013	8	0.056 $\pm$ 0.001	5	0.057 $\pm$ 0.011	7	0.013 $\pm$ 0.001	8
Sc	mg kg ⁻¹	1.34 $\pm$ 0.06	5	3.1 $\pm$ 0.7	8	4.9 $\pm$ 0.3	8	1.3 $\pm$ 0.1	6	15 $\pm$ 3	9
Cr	mg kg ⁻¹	1.53 $\pm$ 0.54	8	523 $\pm$ 50	9	32.2 $\pm$ 2.8	8	1.33 $\pm$ 0.15	6	14 $\pm$ 2	7
V	mg kg ⁻¹	3.4 $\pm$ 3.3	3	6.9 $\pm$ 1.5	6	<3	2	5.4 $\pm$ 4.0	4	68 $\pm$ 21	4
Mn	mg kg ⁻¹	43 $\pm$ 11	7	45 $\pm$ 14	7	89 $\pm$ 12	7	363 $\pm$ 40	8	99 $\pm$ 13	8
Fe	wt%	0.032 $\pm$ 0.016	6	0.16 $\pm$ 0.05	6	0.44 $\pm$ 0.06	6	0.022 $\pm$ 0.013	5	0.45 $\pm$ 0.05	8
Co	mg kg ⁻¹	0.79 $\pm$ 0.16	7	2.0 $\pm$ 0.4	8	1.6 $\pm$ 0.1	7	4.0 $\pm$ 0.7	8	2.0 $\pm$ 0.2	7
Ni	mg kg ⁻¹	3.31 $\pm$ 0.87	8	12.7 $\pm$ 1.8	8	5.58 $\pm$ 0.69	7	13.0 $\pm$ 2.4	8	1.62 $\pm$ 0.29	8
Cu	mg kg ⁻¹	57.6 $\pm$ 9.5	7	152 $\pm$ 19	9	30.4 $\pm$ 6.2	8	8.6 $\pm$ 2.5	5	65 $\pm$ 14	9
Zn	mg kg ⁻¹	11.8 $\pm$ 4.8	8	93 $\pm$ 17	9	23.6 $\pm$ 2.2	7	5.2 $\pm$ 2.0	5	4.98 $\pm$ 0.81	6
Rb	mg kg ⁻¹	2.3 $\pm$ 0.3	7	1.4 $\pm$ 0.1	8	2.7 $\pm$ 0.4	8	6.4 $\pm$ 0.6	8	0.17 $\pm$ 0.03	9
Sr	mg kg ⁻¹	0.80 $\pm$ 0.18	7	4.6 $\pm$ 1.0	8	3.4 $\pm$ 0.7	8	13 $\pm$ 2	8	2.5 $\pm$ 0.5	9
Y	mg kg ⁻¹	0.45 $\pm$ 0.12	8	2.0 $\pm$ 0.2	9	1.6 $\pm$ 0.1	8	18 $\pm$ 2	8	13 $\pm$ 1	7
Mo	mg kg ⁻¹	0.18 $\pm$ 0.11	8	0.28 $\pm$ 0.12	7	0.060 $\pm$ 0.023	6	0.95 $\pm$ 0.58	5	0.027 $\pm$ 0.006	5
Cd	mg kg ⁻¹	0.12 $\pm$ 0.03	7	0.11 $\pm$ 0.02	8	0.012 $\pm$ 0.008	6	0.012 $\pm$ 0.005	5	0.029 $\pm$ 0.012	5
Cs	mg kg ⁻¹	1.1 $\pm$ 0.2	7	0.28 $\pm$ 0.05	8	0.59 $\pm$ 0.06	8	0.21 $\pm$ 0.02	8	0.13 $\pm$ 0.01	9
Ba	mg kg ⁻¹	5.6 $\pm$ 0.8	7	77 $\pm$ 8	8	0.31 $\pm$ 0.29	6	865 $\pm$ 67	6	11.9 $\pm$ 1.2	8
La	mg kg ⁻¹	0.39 $\pm$ 0.14	8	1.45 $\pm$ 0.06	6	1.1 $\pm$ 0.2	7	10.4 $\pm$ 0.8	7	5.2 $\pm$ 0.5	7
Ce	mg kg ⁻¹	1.8 $\pm$ 0.5	8	3.4 $\pm$ 0.2	6	3.5 $\pm$ 0.3	7	17 $\pm$ 4	8	5.3 $\pm$ 1.5	8
Pr	mg kg ⁻¹	0.10 $\pm$ 0.03	7	0.54 $\pm$ 0.08	9	0.45 $\pm$ 0.04	7	3.1 $\pm$ 0.5	8	1.6 $\pm$ 0.3	9
Nd	mg kg ⁻¹	0.44 $\pm$ 0.14	8	2.4 $\pm$ 0.3	9	2.0 $\pm$ 0.2	7	13 $\pm$ 2	8	8.3 $\pm$ 0.5	6
Sm	mg kg ⁻¹	0.11 $\pm$ 0.036	8	0.64 $\pm$ 0.08	9	0.57 $\pm$ 0.04	7	3.4 $\pm$ 0.5	8	2.3 $\pm$ 0.3	7
Eu	mg kg ⁻¹	0.023 $\pm$ 0.008	7	0.15 $\pm$ 0.02	9	0.13 $\pm$ 0.01	7	0.83 $\pm$ 0.12	8	0.58 $\pm$ 0.11	9
Gd	mg kg ⁻¹	0.11 $\pm$ 0.03	8	0.58 $\pm$ 0.07	9	0.51 $\pm$ 0.04	7	3.4 $\pm$ 0.5	8	2.4 $\pm$ 0.1	6
Tb	mg kg ⁻¹	0.015 $\pm$ 0.004	7	0.09 $\pm$ 0.011	9	0.074 $\pm$ 0.007	8	0.54 $\pm$ 0.08	8	0.39 $\pm$ 0.05	7
Dy	mg kg ⁻¹	0.081 $\pm$ 0.009	6	0.54 $\pm$ 0.07	9	0.44 $\pm$ 0.05	8	3.5 $\pm$ 0.5	8	2.5 $\pm$ 0.3	7
Ho	mg kg ⁻¹	0.017 $\pm$ 0.005	7	0.10 $\pm$ 0.01	9	0.079 $\pm$ 0.008	8	0.68 $\pm$ 0.09	8	0.49 $\pm$ 0.01	5
Er	mg kg ⁻¹	0.050 $\pm$ 0.012	7	0.28 $\pm$ 0.03	9	0.21 $\pm$ 0.02	8	2.0 $\pm$ 0.3	8	1.4 $\pm$ 0.1	6
Tm	mg kg ⁻¹	0.0072 $\pm$ 0.0025	7	0.041 $\pm$ 0.004	9	0.030 $\pm$ 0.003	8	0.28 $\pm$ 0.04	8	0.20 $\pm$ 0.02	7
Yb	mg kg ⁻¹	0.045 $\pm$ 0.005	6	0.27 $\pm$ 0.03	9	0.21 $\pm$ 0.01	7	1.9 $\pm$ 0.3	8	1.3 $\pm$ 0.1	6
Lu	mg kg ⁻¹	0.0065 $\pm$ 0.0022	7	0.04 $\pm$ 0.003	9	0.029 $\pm$ 0.002	8	0.28 $\pm$ 0.04	8	0.18 $\pm$ <0.01	5
Pb	mg kg ⁻¹	2.8 $\pm$ 1.1	7	46 $\pm$ 11	9	<0.5	3	20.3 $\pm$ 1.8	6	4.18 $\pm$ 0.85	8
Bi	mg kg ⁻¹	0.53 $\pm$ 0.08	7	0.44 $\pm$ 0.08	7	0.076 $\pm$ 0.023	7	0.035 $\pm$ 0.008	7	0.021 $\pm$ 0.008	8

N, number of determinations; D.L., detection limit; n.d., not determined; *95% confidence interval.

4, and JMs-2. Figure 4 shows that Cu was extracted in every step, but especially large percentages of Cu for JSd-2 and JSO-1 were extracted in step 3. The presence of Cu in step 3 is consistent with the results of previous studies (Coetzee *et al.*, 1995; Davidson *et al.*, 1994; Morillo *et al.*, 2004). These researchers suggested that Cu can readily form complexes with humic substances, which results in the high abundance in step 3. The distributions of the four fractions for Zn were largely different between the samples. Relatively high proportions of Zn were extracted

in step 1 (5–45%) and in step 2 (10–65%). Cd is extremely unstable in sediments: it is easily dissolved into water and adsorbed on materials. Figure 4 shows that Cd was extracted principally in steps 1 and 2 for all samples. 15–80% of the total concentration of Pb was extracted in step 2; Pb detected in step 1 was a minor species in sediments. These results are consistent with previous studies (Hudson-Edwards *et al.*, 1996; Morillo *et al.*, 2004), which suggested that Fe–Mn hydrous oxides are important scavengers of Pb in sediments. The extraction per-

Table 6. The concentrations in step 4 obtained from BCR extraction procedure

Elements	Unit	D.L.	BCR701		JLk-1		JSd-1		JSd-2	
			Mean $\pm$ 95%*	N	Mean $\pm$ 95%*	N	Mean $\pm$ 95%*	N	Mean $\pm$ 95%*	N
Na	wt%	0.0001	1.48 $\pm$ 0.12	7	0.80 $\pm$ 0.16	7	2.11 $\pm$ 0.27	8	1.75 $\pm$ 0.27	9
Mg	wt%	0.00003	1.08 $\pm$ 0.21	8	0.77 $\pm$ 0.15	6	0.9 $\pm$ 0.12	8	1.39 $\pm$ 0.22	9
Al	wt%	0.0004	3.71 $\pm$ 0.43	6	4.9 $\pm$ 1.0	5	4.23 $\pm$ 0.3	5	3.40 $\pm$ 0.46	6
P	mg kg ⁻¹	1	630 $\pm$ 70	6	440 $\pm$ 116	5	239 $\pm$ 16	5	281 $\pm$ 46	5
K	wt%	0.0003	1.97 $\pm$ 0.06	7	1.96 $\pm$ 0.18	6	1.62 $\pm$ 0.05	6	0.80 $\pm$ 0.04	6
Ca	wt%	0.0002	0.45 $\pm$ 0.07	6	0.13 $\pm$ 0.04	6	1.69 $\pm$ 0.2	6	0.98 $\pm$ 0.15	9
Sc	mg kg ⁻¹	0.02	6.0 $\pm$ 0.7	6	10 $\pm$ 3	5	8.9 $\pm$ 1.9	6	12 $\pm$ 1	6
Cr	mg kg ⁻¹	1	110 $\pm$ 6	7	46.6 $\pm$ 6.5	5	15.2 $\pm$ 7.6	6	74.4 $\pm$ 3.3	5
V	mg kg ⁻¹	0.01	68 $\pm$ 11	7	92 $\pm$ 4	5	68 $\pm$ 3	6	114 $\pm$ 6	7
Mn	mg kg ⁻¹	0.02	342 $\pm$ 42	6	365 $\pm$ 59	5	542 $\pm$ 53	6	545 $\pm$ 46	6
Fe	wt%	0.0001	2.70 $\pm$ 0.08	7	2.96 $\pm$ 0.27	6	2.75 $\pm$ 0.10	5	4.65 $\pm$ 0.2	7
Co	mg kg ⁻¹	0.003	8.9 $\pm$ 0.3	7	9.5 $\pm$ 0.6	7	7.2 $\pm$ 0.5	8	13.2 $\pm$ 0.4	7
Ni	mg kg ⁻¹	0.02	50.3 $\pm$ 1.4	7	26.9 $\pm$ 1.0	6	4.86 $\pm$ 0.57	7	30.3 $\pm$ 2.4	7
Cu	mg kg ⁻¹	0.09	47.3 $\pm$ 5.5	6	31.8 $\pm$ 1.9	5	12.2 $\pm$ 1.8	7	112 $\pm$ 8	7
Zn	mg kg ⁻¹	0.1	114 $\pm$ 7	7	90.7 $\pm$ 8.3	7	55.1 $\pm$ 5.1	7	148 $\pm$ 28	9
Rb	mg kg ⁻¹	0.001	90 $\pm$ 5	6	69 $\pm$ 18	7	44 $\pm$ 6	6	16 $\pm$ 1	7
Sr	mg kg ⁻¹	0.02	74 $\pm$ 4	7	35.3 $\pm$ 7.5	5	231 $\pm$ 23	5	123 $\pm$ 14	6
Y	mg kg ⁻¹	0.003	6.6 $\pm$ 1.2	8	5.1 $\pm$ 1.3	6	5.3 $\pm$ 0.5	7	6.9 $\pm$ 0.6	8
Mo	mg kg ⁻¹	0.01	3.21 $\pm$ 0.40	6	1.39 $\pm$ 0.11	5	0.14 $\pm$ 0.06	5	12.9 $\pm$ 0.9	7
Cd	mg kg ⁻¹	0.002	0.210 $\pm$ 0.019	7	0.091 $\pm$ 0.016	6	0.031 $\pm$ 0.007	6	0.374 $\pm$ 0.067	7
Cs	mg kg ⁻¹	0.0005	4.3 $\pm$ 0.3	7	9.2 $\pm$ 0.7	6	1.4 $\pm$ 0.1	8	0.65 $\pm$ 0.06	9
Ba	mg kg ⁻¹	0.2	378 $\pm$ 16	7	344 $\pm$ 56	5	391 $\pm$ 13	7	350 $\pm$ 30	9
La	mg kg ⁻¹	0.003	18.7 $\pm$ 2.5	7	5.3 $\pm$ 2.2	6	7.1 $\pm$ 0.7	6	5.2 $\pm$ 0.7	7
Ce	mg kg ⁻¹	0.005	37.4 $\pm$ 5.2	7	12 $\pm$ 4	6	16 $\pm$ 1	6	9.7 $\pm$ 1.6	7
Pr	mg kg ⁻¹	0.0004	4.7 $\pm$ 0.6	7	1.5 $\pm$ 0.5	6	1.8 $\pm$ 0.1	6	1.4 $\pm$ 0.2	7
Nd	mg kg ⁻¹	0.002	18 $\pm$ 2	7	5.8 $\pm$ 1.4	6	7.1 $\pm$ 0.5	6	5.8 $\pm$ 0.7	7
Sm	mg kg ⁻¹	0.0009	3.3 $\pm$ 0.4	7	1.2 $\pm$ 0.3	6	1.5 $\pm$ 0.1	7	1.4 $\pm$ 0.1	7
Eu	mg kg ⁻¹	0.0004	0.49 $\pm$ 0.05	6	0.22 $\pm$ 0.03	6	0.45 $\pm$ 0.05	7	0.41 $\pm$ 0.07	7
Gd	mg kg ⁻¹	0.001	2.6 $\pm$ 0.3	7	1.0 $\pm$ 0.2	6	1.3 $\pm$ 0.1	7	1.3 $\pm$ 0.1	7
Tb	mg kg ⁻¹	0.0001	0.32 $\pm$ 0.03	7	0.16 $\pm$ 0.02	6	0.19 $\pm$ 0.02	7	0.21 $\pm$ 0.03	7
Dy	mg kg ⁻¹	0.0007	1.7 $\pm$ 0.2	7	1.2 $\pm$ 0.2	6	1.2 $\pm$ 0.1	7	1.4 $\pm$ 0.2	7
Ho	mg kg ⁻¹	0.0002	0.29 $\pm$ 0.03	7	0.26 $\pm$ 0.03	6	0.22 $\pm$ 0.02	7	0.28 $\pm$ 0.03	7
Er	mg kg ⁻¹	0.0007	0.84 $\pm$ 0.11	6	0.87 $\pm$ 0.1	6	0.61 $\pm$ 0.04	7	0.84 $\pm$ 0.1	7
Tm	mg kg ⁻¹	0.0002	0.10 $\pm$ 0.01	6	0.13 $\pm$ 0.01	6	0.081 $\pm$ 0.013	7	0.11 $\pm$ 0.02	7
Yb	mg kg ⁻¹	0.0009	0.82 $\pm$ 0.08	6	1.0 $\pm$ 0.1	6	0.57 $\pm$ 0.05	7	0.78 $\pm$ 0.10	7
Lu	mg kg ⁻¹	0.0001	0.10 $\pm$ 0.01	6	0.15 $\pm$ 0.02	6	0.072 $\pm$ 0.012	7	0.10 $\pm$ 0.02	7
Pb	mg kg ⁻¹	0.07	21.7 $\pm$ 2.2	7	8.53 $\pm$ 0.99	7	6.9 $\pm$ 1.0	8	32.2 $\pm$ 4	8
Bi	mg kg ⁻¹	0.004	0.91 $\pm$ 0.24	8	0.48 $\pm$ 0.03	6	0.068 $\pm$ 0.034	7	0.58 $\pm$ 0.07	8

centage of Pb in step 3 was 5% or less, except for JSd-4, JMs-2, and JSO-1, which showed relatively high percentages (18–24%).

Distribution of Sc, V, Mn, Fe, Co, Mo, and Bi in sediments
Scandium and V were extracted primarily in the residual fraction (Fig. 5). Of steps 1–3, the relative percentages of Sc in step 3 and those of V in step 2 were the most dominant phases. As for Mn, the geochemical reference materials had the most distinct proportion mutually. In JLk-1, Mn was found mainly in step 1 (around 60%),

which indicates that the mobility of Mn is high. For JSd-1–4 and JMs-1, Mn was distributed equally between step 2 (12–22%) and step 3 (13–22%). In JMs-2, an extremely high proportion of Mn (90%) was extracted in step 2. The soil reference materials had similar proportions of Mn extracted in step 2 (40–50%) and in step 4 (35–45%). In contrast to Mn, only 10–30% of the total concentration of Fe was extracted in step 2. Iron was not extracted effectively in step 1 or step 3. Co had similar extraction results to Mn, although a smaller percentage of Co for

Table 6. (continued)

Elements	Unit	JSd-3		JSd-4		JMs-1		JMs-2		JSO-1	
		Mean $\pm$ 95%*	N	Mean $\pm$ 95%*	N	Mean $\pm$ 95%*	N	Mean $\pm$ 95%*	N	Mean $\pm$ 95%*	N
Na	wt%	0.32 $\pm$ 0.03	8	0.96 $\pm$ 0.13	9	1.03 $\pm$ 0.12	8	0.73 $\pm$ 0.09	8	0.48 $\pm$ 0.04	8
Mg	wt%	0.67 $\pm$ 0.09	8	0.91 $\pm$ 0.15	9	1.00 $\pm$ 0.14	8	1.14 $\pm$ 0.14	8	1.13 $\pm$ 0.13	9
Al	wt%	3.56 $\pm$ 0.24	5	3.11 $\pm$ 0.32	6	4.10 $\pm$ 0.43	6	4.14 $\pm$ 0.71	6	3.34 $\pm$ 0.27	6
P	mg kg ⁻¹	367 $\pm$ 49	5	1200 $\pm$ 390	8	427 $\pm$ 97	6	2880 $\pm$ 180	6	1790 $\pm$ 320	9
K	wt%	1.35 $\pm$ 0.07	8	0.82 $\pm$ 0.06	8	1.29 $\pm$ 0.10	8	1.02 $\pm$ 0.04	7	0.20 $\pm$ 0.01	8
Ca	wt%	0.22 $\pm$ 0.03	8	0.75 $\pm$ 0.13	7	0.41 $\pm$ 0.01	5	1.03 $\pm$ 0.15	8	1.08 $\pm$ 0.11	9
Sc	mg kg ⁻¹	7.4 $\pm$ 0.8	8	9.2 $\pm$ 1.2	6	7.7 $\pm$ 1.3	6	19 $\pm$ 2	5	13 $\pm$ 2	7
Cr	mg kg ⁻¹	24.2 $\pm$ 2.2	6	165 $\pm$ 23	6	57.8 $\pm$ 4.0	8	56.8 $\pm$ 1.2	6	46.7 $\pm$ 2.6	8
V	mg kg ⁻¹	60 $\pm$ 4	7	85 $\pm$ 6	7	92 $\pm$ 3	6	111 $\pm$ 4	7	199 $\pm$ 30	8
Mn	mg kg ⁻¹	697 $\pm$ 69	6	409 $\pm$ 59	6	351 $\pm$ 21	6	507 $\pm$ 38	6	640 $\pm$ 70	7
Fe	wt%	2.71 $\pm$ 0.10	7	3.63 $\pm$ 0.16	6	3.16 $\pm$ 0.11	6	5.57 $\pm$ 0.34	7	6.15 $\pm$ 0.31	7
Co	mg kg ⁻¹	4.6 $\pm$ 0.1	7	8.3 $\pm$ 0.6	9	7.5 $\pm$ 0.3	7	11.1 $\pm$ 0.7	8	18.5 $\pm$ 0.9	8
Ni	mg kg ⁻¹	12.4 $\pm$ 0.6	8	25.5 $\pm$ 2.6	8	35.4 $\pm$ 0.8	6	35.9 $\pm$ 2.2	7	36.1 $\pm$ 1.1	8
Cu	mg kg ⁻¹	183 $\pm$ 10	7	51.0 $\pm$ 7.3	7	25.3 $\pm$ 2.5	7	209 $\pm$ 6	6	78.2 $\pm$ 3.5	8
Zn	mg kg ⁻¹	103 $\pm$ 4	8	83 $\pm$ 12	9	62.7 $\pm$ 8.5	8	92.2 $\pm$ 5.5	7	86.2 $\pm$ 6.3	8
Rb	mg kg ⁻¹	210 $\pm$ 20	6	33 $\pm$ 3	8	52 $\pm$ 9	5	36 $\pm$ 5	6	5.4 $\pm$ 1.8	7
Sr	mg kg ⁻¹	39 $\pm$ 5	8	59 $\pm$ 8	7	53 $\pm$ 2	7	132 $\pm$ 26	8	62 $\pm$ 6	9
Y	mg kg ⁻¹	5.3 $\pm$ 1.1	6	5.0 $\pm$ 0.6	7	5.1 $\pm$ 1.2	6	5.2 $\pm$ 0.5	7	3.8 $\pm$ 0.4	8
Mo	mg kg ⁻¹	1.39 $\pm$ 0.10	8	4.00 $\pm$ 0.33	8	2.53 $\pm$ 0.13	8	18.8 $\pm$ 2.4	8	0.67 $\pm$ 0.13	7
Cd	mg kg ⁻¹	0.183 $\pm$ 0.032	6	0.37 $\pm$ 0.16	8	0.065 $\pm$ 0.009	7	0.198 $\pm$ 0.046	7	0.067 $\pm$ 0.010	8
Cs	mg kg ⁻¹	24 $\pm$ 1	6	2.5 $\pm$ 0.2	9	4.3 $\pm$ 0.3	8	2.3 $\pm$ 0.2	8	0.85 $\pm$ 0.14	9
Ba	mg kg ⁻¹	365 $\pm$ 29	8	338 $\pm$ 30	9	233 $\pm$ 22	7	530 $\pm$ 120	6	72.6 $\pm$ 8.7	9
La	mg kg ⁻¹	11 $\pm$ 2	7	5.5 $\pm$ 0.7	8	5.3 $\pm$ 1.4	7	7.9 $\pm$ 1.4	7	1.9 $\pm$ 0.4	9
Ce	mg kg ⁻¹	22 $\pm$ 4	6	9.7 $\pm$ 1.9	8	11 $\pm$ 3	7	24 $\pm$ 3	6	7.0 $\pm$ 1.2	8
Pr	mg kg ⁻¹	2.5 $\pm$ 0.4	8	1.3 $\pm$ 0.2	8	1.3 $\pm$ 0.3	7	1.9 $\pm$ 0.2	8	0.69 $\pm$ 0.11	9
Nd	mg kg ⁻¹	9.4 $\pm$ 1.4	7	4.9 $\pm$ 0.4	7	5.0 $\pm$ 0.9	6	7.2 $\pm$ 0.7	7	3.1 $\pm$ 0.5	9
Sm	mg kg ⁻¹	1.7 $\pm$ 0.2	8	0.99 $\pm$ 0.08	7	0.98 $\pm$ 0.16	6	1.5 $\pm$ 0.1	7	0.81 $\pm$ 0.14	9
Eu	mg kg ⁻¹	0.35 $\pm$ 0.04	7	0.25 $\pm$ 0.02	9	0.23 $\pm$ 0.03	6	0.53 $\pm$ 0.04	8	0.25 $\pm$ 0.02	8
Gd	mg kg ⁻¹	1.5 $\pm$ 0.2	7	0.91 $\pm$ 0.08	7	0.98 $\pm$ 0.32	6	1.4 $\pm$ 0.1	6	0.84 $\pm$ 0.11	8
Tb	mg kg ⁻¹	0.19 $\pm$ 0.02	7	0.13 $\pm$ 0.02	8	0.13 $\pm$ 0.03	7	0.20 $\pm$ 0.02	7	0.14 $\pm$ 0.01	7
Dy	mg kg ⁻¹	1.1 $\pm$ 0.1	8	0.89 $\pm$ 0.1	9	0.93 $\pm$ 0.13	7	1.3 $\pm$ 0.1	7	0.91 $\pm$ 0.10	8
Ho	mg kg ⁻¹	0.21 $\pm$ 0.03	8	0.18 $\pm$ 0.02	9	0.20 $\pm$ 0.04	7	0.24 $\pm$ 0.03	8	0.16 $\pm$ 0.02	9
Er	mg kg ⁻¹	0.64 $\pm$ 0.09	8	0.58 $\pm$ 0.06	9	0.66 $\pm$ 0.07	7	0.73 $\pm$ 0.08	8	0.53 $\pm$ 0.05	8
Tm	mg kg ⁻¹	0.091 $\pm$ 0.014	7	0.080 $\pm$ 0.014	7	0.10 $\pm$ 0.02	7	0.083 $\pm$ 0.012	7	0.070 $\pm$ 0.005	6
Yb	mg kg ⁻¹	0.71 $\pm$ 0.08	8	0.63 $\pm$ 0.06	9	0.77 $\pm$ 0.10	7	0.69 $\pm$ 0.06	7	0.57 $\pm$ 0.07	8
Lu	mg kg ⁻¹	0.10 $\pm$ 0.02	8	0.083 $\pm$ 0.012	9	0.11 $\pm$ 0.02	7	0.085 $\pm$ 0.014	7	0.077 $\pm$ 0.009	7
Pb	mg kg ⁻¹	46.7 $\pm$ 2.5	8	40.0 $\pm$ 7.3	8	11.6 $\pm$ 1.4	8	23.8 $\pm$ 3	7	9.31 $\pm$ 0.42	6
Bi	mg kg ⁻¹	7.43 $\pm$ 0.51	8	4.40 $\pm$ 0.57	7	0.62 $\pm$ 0.06	7	1.13 $\pm$ 0.06	8	0.17 $\pm$ 0.03	9

N, number of determinations; *D.L.*, detection limit; *n.d.*, not determined; *95% confidence interval.

JLk-1 was extracted in step 1 and a larger percentage of Co for JSd-2–4 was extracted in step 2. Mo was barely extracted in steps 1, 2, and 3; it dominantly existed in the residual phase (Fig. 5). Slightly high proportions of Mo in step 3, especially for JSd-1, compared to those in steps 1 and 2 were found. Bi was extracted primarily in the residual fraction. JLk-1, JSd-1–3, and JMs-1 had a significant amount of Bi extracted in step 2 (25–55%).

Distribution of the alkali elements and the alkali earth elements Sodium, K, Rb, and Cs were extracted primarily in the residual fraction (Fig. 6). The extremely high proportion of Na detected in step 1 for JSd-4, JMs-1, and JMs-2 is explained by sea salt contamination because the sampling location of JSd-4 is near the sea and marine sediments were not desalinated. The alkali earth elements had different distributions from the alkali elements. 5–

Fig. 2. The percentage relative standard deviation (RSD) used to exhibit reproducibility of repeated measurements of elemental concentrations in each step.

70% of the total concentrations for Ca and Sr were found in step 1, which is explained by calcareous materials. A large amount of Mg was found in the residual phase (step 4), except for JSd-4, JMs-1, and JMs-2, which showed a high percentage in steps 1 and 2. The distribution of Ba

among the four fractions varied between the samples. A significant proportion of Ba was extracted in both steps 1 and 2 for JSO-1; in step 2 for Jk-1, JSd-2, and JSd-4; and in both steps 2 and 3 for JMs-2.

Fig. 3. Recovery rates of 38 elements for nine samples. The elements on the horizontal axis are arranged in ascending order of median value of recovery rate determined for nine samples.

Distribution of the other elements Most of the Al was present in the residual fraction (step 4), which accounts for nearly 90% of the total, except for JSO-1 (Fig. 7). JSO-1 had systematically higher proportions of Al in steps 2 and 3 than the other samples. In contrast, phosphorus in JSd-3 and JSO-1 was hardly extracted in steps 1–3. Except for these samples, extractable P was obtained principally in step 2 (20–60%) and in step 3 (around 10%). Figure 7 also shows that Y, La, Ce, Nd, Eu, and Yb in the sediments were extracted largely in step 2 (15–60%) among steps 1–3. However, JSO-1 had high proportions of Y and Ln extracted in step 3 (10–65%). The result of the soil reference material is not likely to be artifact from sequential extraction because similar results of La and Ce in stream sediments have been reported previously (Martin *et al.*, 1998).

DISCUSSION

In earlier sections, we discussed the determination of the value and enumerated the distribution characteristic of each element for geochemical reference materials. In this section, we elucidate how the speciation of elements extracted by the BCR protocol reflects their origin or sedimentary environment.

Speciation of elements in lake sediments: JLk-1

JLk-1 and CRM-701 are Japanese lake (Lake Biwa) and Italian lake (Lake Orta Piemonte) sediments, respectively. Although their sampling positions are distant, the distributions of elements, except for Cr, Mn, Ni, Cu, and Zn, shown in Figs. 5–7 are quite similar mutually. JLk-1 was characterized by having a higher percentage of Mn

and Cd extracted in step 1 and of P, Fe, Y, Ln, Ba, Pb, and Bi in step 2 than the other samples. These results correspond with the results of Nakashima (1982). He suggested that Mn and Cd were extracted mainly in the exchangeable fraction; that Cu, Zn, As, and Pb were extracted largely in Fe–Mn hydroxide fractions; and that Ni existed dominantly in the aluminosilicate fraction. Enrichments of P, Mn, Ni, Cu, Zn, As, Cd, and Pb in surface sediments of Lake Biwa have been known for more than 30 years (e.g., Kobayashi *et al.*, 1975). These were presumed to be caused by early diagenetic processes (Lynn and Bonatti, 1965; Robbins and Callender, 1975). Comprehensively, metals such as Mn, Fe, Co, Ni, Cu, and Zn are dissolved at greater sediment depths under reducing conditions. They then diffuse upward and precipitate on the sediment surface under oxic conditions. In pelagic environments, Mn dioxide precipitates on surface sediments explain the high enrichment of Mn caused by diagenetic process (e.g., Chester, 1999). However, Ohta *et al.* (2006) reported that 95% of the Mn in JLk-1 exists as Mn(II). This result suggests that most of the Mn in JLk-1 was not present as Mn oxides but was weakly absorbed on mineral surfaces. Therefore, P, Fe, Y, Ln, Ba, Pb and Bi seem to be strongly influenced by Fe hydroxides but not by Mn dioxide.

Speciation of elements in stream sediments: JSd-1–4

JSd-1 and JSd-3 are stream sediments collected from drainage basins covered by granitic rocks and sedimentary rocks, respectively. The lowest percentages of elements extracted at steps 1, 2, and 3 for these were obtained among geochemical reference materials, except for P, Co, Cu, Mo, and Cd. These are typical cases of non-polluted sediments. It is notable that a significant amount of Mo was extracted in step 3 for JSd-1 (about 50%). Nevertheless, previous studies found that Mo in stream and marine sediments was barely extracted in steps 1, 2, and 3 and existed dominantly in the residual phase (Davidson *et al.*, 1994; Yuan *et al.*, 2004). A higher percentage of Mo in step 3 was also found in stream sediment samples that originated from granite rocks (Ohta *et al.*, 2007). According to Ishihara (2002), the most common mineral that is composed mainly of Mo is molybdenite (MoS_2), and molybdenite occurs dominantly in granitic rocks. This report is consistent with the result of JSd-1 (granite origin) in this study.

JSd-2 is the stream sediment influenced by Hitachi Cu mines. Omori *et al.* (1986) reported that pyrite and chalcopyrite are major ores in the Hitachi mines. This is why a significant amount of Cu was extracted in step 3 for JSd-2 (about 50%): Cu in the sample exists dominantly as copper sulfide. Indeed, the presence of copper sulfide in JSd-2 was confirmed using X-ray absorption fine structure spectroscopy, and 38% of the total Cu was found to

Table 7. The sum concentration determined in the four steps compared to the bulk concentrations

Elements	Unit	BCR701		JLk-1		JSD-1		JSD-2		JSD-3		JSD-4		JMS-1		JMS-2		JSD-1	
		sum	bulk	sum	bulk	sum	bulk	sum	bulk	sum	bulk	sum	bulk	sum	bulk	sum	bulk	sum	bulk
Na	wt%	1.49	1.36	0.81	0.85	2.15	1.96	1.8	1.74	0.32	0.32	1.74	1.68	2.96	2.79	3.91	3.87	0.49	0.49
Mg	wt%	1.3	1.32	0.92	1.02	1.06	1.06	1.61	1.63	0.7	0.66	2.33	2.38	1.65	1.7	1.93	1.9	1.22	1.21
Al	wt%	4.25	7.22	5.44	8.45	4.81	7.65	4.05	6.43	4.06	5.04	4.72	6.89	5.3	7.42	5.55	7.29	7	9.04
P	mg kg ⁻¹	2590	2660	992	959	580	528	672	492	419	368	1800	1979	778	745	5560	5714	2010	2114
K	wt%	2.01	1.95	2.03	2.04	1.69	1.66	0.88	0.91	1.4	1.38	1.01	1.1	1.64	1.71	2.05	2.13	0.232	0.28
Ca	wt%	1.41	1.72	0.38	0.43	1.97	2.12	2.33	2.58	0.31	0.35	3.6	3.86	1.21	1.4	3.17	3.34	1.68	1.79
Sc	mg kg ⁻¹	7.7	12.1	14	15.2	10.5	10.9	17.9	18.1	9.7	10.6	14.3	16.2	14.1	16.1	21.9	25.4	30.3	33.9
V	mg kg ⁻¹	86.4	84.7	116	112	81	82	127	124	70	73	139	145	121	127	171	188	315	309
Cr	mg kg ⁻¹	314	345	55.2	72.1	17.7	20	90.2	97.4	27.4	35.3	1095	1192	114	133	61.1	64.7	63.7	78.7
Mn	mg kg ⁻¹	705	741	2090	2165	759	699	897	901	1200	1116	806	828	734	721	16000	17290	1490	1456
Fe	wt%	3.71	3.78	4.54	4.87	3.21	3.43	7.45	8.03	2.96	3	5.22	5.64	4.55	4.68	7.14	7.62	7.22	7.84
Co	mg kg ⁻¹	16.2	16	17.3	19.3	10.1	11	47.1	50.9	12	12.8	18.6	20	15.2	15.8	227	240	33.3	36.3
Ni	mg kg ⁻¹	111	105	36	36	6.44	5.54	90.7	90.6	18.6	17.7	104	106	52.6	49.9	303	311	40.1	38.9
Cu	mg kg ⁻¹	267	284	65.8	70.9	22.9	24.2	1074	1179	418	458	458	493	84.1	88.4	448	465	147	170
Zn	mg kg ⁻¹	480	474	139	156	90	100	2039	2095	138	143	1415	1430	249	252	155	165	105	113
Rb	mg kg ⁻¹	94	113	75	145	49.1	67.4	19.3	26.7	222	284	38	52.8	60.7	79.3	46.7	65.5	7.2	13.4
Sr	mg kg ⁻¹	140	178	52.4	64.1	253	333	160	207	45.2	53.1	179	218	124	132	397	442	164	186
Y	mg kg ⁻¹	16	24.3	26.9	37.3	9.8	14.9	10.9	17.6	9.4	12.8	14.7	20	15.8	21.1	241	280	20.2	23.9
Mo	mg kg ⁻¹	4.26	4.01	1.76	1.85	0.39	0.47	14	16.4	1.65	1.77	4.35	5.18	2.65	3	20.2	25.5	0.71	0.82
Cd	mg kg ⁻¹	11.7	11.5	0.6	0.58	0.13	0.16	3.22	3.2	1.05	1.08	6.74	6.59	1	1.01	0.6	0.61	0.29	0.33
Cs	mg kg ⁻¹	4.99	5.52	10.1	11.9	1.56	1.94	0.8	1	27.1	30.2	2.96	3.64	5.06	5.85	2.54	3.35	1.23	1.37
Ba	mg kg ⁻¹	532	559	496	585	497	531	1210	1261	422	458	806	861	263	287	1810	1903	249	250
La	mg kg ⁻¹	26.7	36.1	22.7	30.6	11.7	15.6	7.7	10.6	13.8	17.6	12.4	16.6	13.5	16.8	131	139	8.69	8.81
Ce	mg kg ⁻¹	59.3	77.5	54.1	71.7	24	31.6	14.3	21.7	31.3	39.5	22.8	34	31.4	30.1	148	169	13.7	20.1
Pr	mg kg ⁻¹	6.82	8.89	6.16	7.89	3.1	4.06	2.1	2.87	3.33	4.14	3.05	3.85	3.71	3.76	35.4	37.4	2.59	2.98
Nd	mg kg ⁻¹	26.3	36.2	24.3	32.5	12.3	17.3	8.7	12.8	12.9	16.4	12.3	16.4	15.4	16.3	150	167	12.5	14.8
Sm	mg kg ⁻¹	5.32	7.16	5.71	6.78	2.58	3.53	2.07	2.88	2.54	3.14	2.74	3.42	3.48	3.61	34.3	36.7	3.37	3.74
Eu	mg kg ⁻¹	0.81	1.17	0.91	1.09	0.69	0.95	0.64	0.9	0.55	0.68	0.68	0.91	0.79	0.84	8.18	8.62	0.91	1.11
Gd	mg kg ⁻¹	4.68	6.03	5.6	6.32	2.36	3.18	2.08	2.9	2.31	2.73	2.74	3.33	3.52	3.31	38.1	38.3	3.55	3.89
Tb	mg kg ⁻¹	0.63	0.93	0.87	1.02	0.34	0.45	0.33	0.46	0.32	0.35	0.4	0.52	0.51	0.49	5.82	6.05	0.57	0.68
Dy	mg kg ⁻¹	3.58	5.02	5.28	5.99	2.04	2.63	2.16	2.88	1.92	2.23	2.58	3.27	3.14	3.47	37.5	41.1	3.74	4.27
Ho	mg kg ⁻¹	0.63	0.89	1.02	1.17	0.38	0.51	0.43	0.61	0.36	0.42	0.51	0.66	0.61	0.68	7.74	8.26	0.73	0.86
Er	mg kg ⁻¹	1.78	2.45	2.93	3.44	1.07	1.4	1.26	1.7	1.07	1.21	1.51	1.9	1.75	1.98	22.4	24.3	2.13	2.49
Tm	mg kg ⁻¹	0.23	0.34	0.41	0.5	0.14	0.2	0.17	0.25	0.15	0.18	0.21	0.27	0.24	0.28	3.05	3.34	0.3	0.36
Yb	mg kg ⁻¹	1.64	2.19	2.78	3.24	0.99	1.24	1.15	1.43	1.09	1.17	1.46	1.76	1.68	1.82	19.6	21.2	2.03	2.34
Lu	mg kg ⁻¹	0.21	0.31	0.39	0.47	0.13	0.18	0.15	0.19	0.15	0.17	0.2	0.25	0.23	0.26	3	3.21	0.29	0.34
Pb	mg kg ⁻¹	160	161	44.3	50.8	12	14.7	151	167	79.5	89.7	237	257	50	51.5	81.4	87	15.7	17.7
Bi	mg kg ⁻¹	2.12	2.28	1.25	1.4	0.12	0.12	0.98	1.1	12	12.9	4.92	5.69	0.97	0.95	1.18	1.26	0.2	0.22

sum, the sum concentration of the four steps; bulk, the bulk concentration is determined by HF-HNO₃-HClO₄ digestion.

Fig. 4. Distribution of Cr, Ni, Cu, Zn, Cd, and Pb concentrations in geochemical reference materials for four fractions obtained by the BCR scheme.

exist as a sulfide (Ohta *et al.*, 2010). In contrast, Fe was scarcely extracted in step 3 (about 7%). We assumed that the relative abundance ratio of pyrite and chalcopyrite to crystalline minerals containing Fe (e.g., hornblende, chlorite, epidote, and magnetite) in JSd-2 would be small. Actually, the GSJ Geochemical Reference Samples Database (<https://gbank.gsj.jp/geostandards/>) indicates that distinctive peaks of pyrite and chalcopyrite are not observed. As an example, considering the Cu in step 3 to be totally originated from chalcopyrite, the concentration of Fe from chalcopyrite is calculated to be only about 0.048 wt%. This is considerably lower than the Fe concentra-

tion of step 3 extractant (0.52 wt%, Table 5). Another possible factor is that most of the pyrite was oxidized to Fe oxyhydroxides during the weathering process. In fact, a high percentage of Fe was extracted in step 2 (about 25%). Aside from Cu and Fe, JSd-2 had higher percentages of Co, Ca, and Zn in step 1 and of Co, Ni, Zn, Ba, and Pb in step 2 (Figs. 4, 5, and 6) compared to the other stream sediment reference materials not associated with mine activity (JSd-1 and JSd-3). These results suggest that Ni, Fe, Cu, Zn, Co and Pb released during the refining process adsorb onto mineral surfaces and bind to Fe oxides. The high Ca and Ba extraction in step 2 for JSd-2

Fig. 5. Distribution of Sc, V, Mn, Fe, Co, Mo and Bi concentrations in geochemical reference materials for four fractions obtained by the BCR scheme.

Fig. 6. Distribution of Na, Mg, K, Ca, Rb, Sr, Cs and Ba concentrations in geochemical reference materials for four fractions obtained by the BCR scheme.

is also explained by this same reason because the Hitachi mine also yields a large amount of skarn minerals and barite (Omori *et al.*, 1986).

JSd-4 was collected from an urban area in the Kanto

Plain. Ohta *et al.* (2011) suggested that the stream sediments collected from urban areas in the Kanto Plain are significantly enriched in P, Cr, Ni, Cu, Zn, Sn, Sb, Hg, and Pb because of anthropogenic activities. Actually,

Fig. 7. Distribution of Al, P, Y, La, Ce, Nd, Eu and Yb concentrations in geochemical reference materials for four fractions obtained by the BCR scheme.

JSd-4 has high concentrations of P (1,980 mg kg⁻¹), Cr (1,190 mg kg⁻¹), Ni (106 mg kg⁻¹), Cu (490 mg kg⁻¹), Zn (1,430 mg kg⁻¹), Cd (6.6 mg kg⁻¹), and Pb (260 mg kg⁻¹). Interestingly, the extraction results for these elements in JSd-4 were quite similar to those in JSd-2, except for Cr. JSd-4 had higher fractions of Ni and Zn in step 1; of V, Cr, Ni, Cu, Ba, Zn, and Pb in step 2; and of Cr, Cu, and Pb in step 3. These results suggest that the Ni and Zn released by anthropogenic activities are weakly sorbed on mineral surfaces or bound to Fe–Mn oxide phases; Cr, Cu, and Pb released by anthropogenic activities are bound both to Fe–Mn oxides and to organic materials. It is noteworthy that JSd-4 is also enriched in Mg, Ca, V, and Ba compared with the other stream sediment materials in bulk composition (see Table 7). Significant amounts of Mg, Ca, and Sr in step 1 and of Mg, V, and Ba in step 2 are notable features. The enrichments and distribution features of these elements may be attributable to waste slag because the slag consists of oxides of Mg (3~5%), Al (10~20%), Si (30~55%), and Ca (19~33%) (Nagano *et al.*, 2007; Nishi and Kawabata, 1990) and is associated with heavy metals such as Cr, Ni, Cu, Zn, and Pb. The slag is reutilized for construction materials such as cement and asphalt pavement (Nagano *et al.*, 2007).

Speciation of elements in marine sediments: JMs-1 and JMs-2

JMs-1 was collected from Tokyo Bay, which is surrounded by a highly populated urban area and large-scale industrial zone, and is thus affected by anthropogenic activities. It had speciation features similar to those of JSd-4 (stream sediment), whose sampling location is adjacent to Tokyo Bay. The distributions of Cr in JSd-4 and JMs-1 share a common thread of high extraction percentage in steps 2 and 3. A similar distribution of Cr in soil of areas affected by anthropogenic activities as in JSd-4 and JMs-1 was reported by Davidson *et al.* (1998). We assumed that the Cr was adsorbed on Fe–Mn oxides and humic substances, as discussed by Tokalioğlu and Kartal (2000). The oxidation state and chemical forms of Cr in sediments will be discussed in a following paper.

JMs-2 is pelagic sediment that was collected from the floor of the South Pacific Ocean. It is free from anthropogenic influences. JMs-2 had significant amounts of P, Fe, Mn, Ni, Co, Cu, Zn, Y, Cd, Ln, and Pb extracted at step 2, which is caused by diagenetic process, as described in Subsection “Speciation of elements in lake sediments: JLk-1”. The high percentages of Fe and Mn extracted in step 2 were different from the case of JLk-1. The fact suggests that Fe hydroxides and Mn dioxides precipitate on surface sediments with coprecipitated or adsorbed P, Ni, Co, Cu, Zn, Y, Cd, Ln, and Pb. Different from JMs-1, non-negligible amounts of Na, K, Ca, Sr, Cs, and Ba were also extracted in step 2 for JMs-2. These elements were

also incorporated into Mn dioxide. For instance, Moorby *et al.* (1984) reported that Na, Mg, K, and Ca play an essential role in the crystallographic structure of birnessite, which is a Mn–dioxide mineral that is formed in many environments (of non-marine and marine hydrogenous, diagenetic, and hydrothermal origin). Similarly, Ba is also incorporated into Mn dioxides (Manceau *et al.*, 2007). The high percentage of Ba extracted in step 3 may indicate that a portion of Ba strongly binds to organic materials in deep-sea sediments (Tsunogai *et al.*, 1979).

Speciation of elements in soil: JSO-1

JSO-1 (forest soil) is highly enriched in organic matter (total carbon concentration is 8.91 wt%) (Terashima *et al.*, 2002). The higher proportion of V, Cr, Cu, Y, Ln, and Pb in step 3 for JSO-1 suggests that these elements are present dominantly in organic phases. In fact, it has been confirmed that a significant proportion of the V and Cu bounded to humic acid can be extracted in step 3 (Coetzee *et al.*, 1995; Davidson *et al.*, 1994). Significant amounts of Ca, Sr, and Ba relative to the bulk concentrations were extracted in steps 1 and 2. In contrast to marine sediments, calcareous materials are scarcely included in JSO-1 (Terashima *et al.*, 2002). Accordingly, the extraction result suggests that a significant amount of Ca, Sr, and Ba are incorporated in clay minerals. Phosphate ions react with Al and Fe ions in volcanic ash soils to form insoluble compounds such as aluminum phosphate and iron phosphate. This is the reason that P in JSO-1 is scarcely extracted in steps 1, 2, and 3. The soil reference material has higher Mn extraction in step 2 (40%) than JSd-1–4. Ohta *et al.* (2006) suggested that 66% of the Mn in JSO-1 is in the trivalent state (Mn(III)) and that the rest is hexavalent (Mn(VI)). Almost all of the Mn(VI) and a part of the Mn(III) would be extracted in step 2 (relative extraction rate is 40%).

SUMMARY

We determined the concentrations of 38 elements extracted by the BCR sequential extraction procedure for eight Japanese geochemical reference materials. We essentially followed the procedure proposed by BCR. Exceptionally, the mechanical shaker was operated at a higher speed (80 rpm) than the proposed speed (30 rpm) to keep samples suspended in experimental solutions during the extraction. The effect of the shaking speed and the precision and accuracy of the analytical data were confirmed using a certified reference material (BCR-701). As a result, the shaking speed does not affect the extraction percentage seriously but does slightly enhance the extraction of Cr, Mo, Y, and lanthanide (Ln) in step 1. The estimated concentrations and repeatability errors of Cr, Ni, Cu, Zn, Cd and Pb extracted in respective steps

were comparable to the certified values.

The RSDs obtained from repeated measurements for the 38 elements of eight geochemical reference materials were <30% for steps 1 and 3 and <20% for steps 2 and 4. The RSDs obtained for low concentrations of elements extracted by the BCR scheme showed worse results. The third step in the BCR protocol is a cumbersome procedure that is different from the other steps, resulting in worse RSDs. The estimated recovery rates for samples ranged mostly from 70% to 100% of the bulk compositions. Insignificant recovery rates were obtained for Al, Sc, Cr, Rb, Y, Cs, and Ln. Unfortunately, the step 3 residue remaining in the PFA tubes was not decomposed completely using mixed acids.

The most dominant species of elements in the sediments were the residual phase (step 4). This result suggests that most elements are fundamentally stable in stream sediments. Ca and Sr in the geochemical reference materials were highly extracted in step 1. Significantly high percentages of V, P, Ni, Y, Ba, Ln, and Pb were extracted in step 2. Mn, Co, Zn, and Cd had high proportions in steps 1 and 2; Cu was extracted significantly in all steps. Except for marine geochemical reference materials, the most dominant species of Na, K, Rb, and Cs were the residual phase.

JLk-1 was characterized by having higher percentages of Mn and Cd extracted in step 1 because of diagenetic process. JSd-1 and JSd-3 had the lowest extraction of metals in steps 1–3 among all samples. JSd-2, which is stream sediment influenced by Cu mines, had a significant proportion of Cu in step 3. It is suggested that JSd-4 was affected by anthropogenic activities, as evidenced by the larger percentages of Cr, Ni, Cu, Zn, and Pb extracted in steps 1–3 compared to the other samples. JMs-1 and JMs-2 had high proportions of Na, Mg, K, Ca, and Sr in step 1, which indicates the presence of sea salt and calcareous materials. In addition, significant amounts of Mn, Co, Ni, Cu, Y, Cd, and Ln were extracted in step 2 for JMs-2. This fact suggests that Fe–Mn oxides are important carriers for these elements in pelagic sediments. P in JSO-1 was scarcely extracted in steps 1, 2, and 3 because phosphate ions react with Al and Fe ions in volcanic ash soils to create insoluble compounds. The speciation of elements in reference materials correspond to their origin, mineral composition, and sedimentary environment. Therefore, the recommended values of 38 elements extracted by sequential extraction are beneficial for many geochemists who are conducting speciation geochemistry of sediments.

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