

## Preliminary study for speciation geochemical mapping using a sequential extraction method

Atsuyuki Ohta<sup>1\*</sup>, Noboru Imai<sup>1</sup>, Shigeru Terashima<sup>1</sup> and Yoshiko Tachibana<sup>1</sup>

Atsuyuki Ohta, Noboru Imai, Shigeru Terashima and Yoshiko Tachibana (2007) Preliminary study for speciation geochemical mapping using a sequential extraction method. *Bull. Geol. Surv. Japan*, vol. 58 (7/8), p.201-237, 7 figs, 3 tables, 5 appendix tables.

**Abstract:** Sequential extraction is useful to assess the potential hazard of toxic metals and metal mobility in sediments. The extraction procedure developed by the Community Bureau of Reference (BCR) has been applied to the extraction of 51 elements from 30 stream sediments that were collected mainly for nationwide geochemical mapping in Japan. The geochemical reference samples, JSd-1, JSd-2 and JSd-3, were used to estimate the reproducibility of the elemental concentrations obtained using the BCR method. The BCR scheme is designed to extract elements in the intended phase using acetic acid (step 1), hydroxylammonium chloride (step 2), hydrogen peroxide and ammonium acetate (step 3), and hydrofluoric acid, perchloric acid, and nitric acid (step 4). The relative standard deviations of elemental concentrations in each extraction stage were generally less than  $\pm 10 - 25 \%$ ; the sums of elemental concentrations in respective steps (the total recoveries) ranged from 80 to 130 % of the bulk compositions in most cases. The extraction results for respective elements showed relative uniformity among the samples originated from various geological and lithological units, suggesting the limited influence of geology on the speciation of elements. In contrast, significant differences in the extraction results were found in samples from rural and urbanized areas even though they were all from sedimentary rock areas. Samples from urban areas were characterized by a higher proportion of Co, Ni, Zn and Cd extracted in step 1 and those of Cr, Cu, and Pb in step 3, probably indicating heavy-metal contamination in their watersheds. Stream sediments near mining sites also showed a distinctive pattern in the extraction results. This study suggested that the BCR scheme is helpful for detecting the possible contamination of Cr, Ni, Cu, Zn, Cd, and Pb and exploring for mineral deposits bearing Zn, Cd and Pb.

**Keywords:** speciation, BCR scheme, geochemical map, stream sediment, pollutant, mineral deposit

### 1. Introduction

A geochemical map provides essential and fundamental information for mineral exploration and environmental assessment on the earth's surface (Webb *et al.*, 1978; Weaver *et al.*, 1983; Fauth *et al.*, 1985; Bølviken, *et al.*, 1986; Thalmann *et al.*, 1988; Reimann *et al.*, 1998; Gustavsson *et al.*, 2001). The Geological Survey of Japan, National Institute of Advanced Industrial Science and Technology (AIST) collected approximately 3000 stream sediments; measured the concentrations of 53 elements; conducted a nationwide geochemical mapping at a 1:2,000,000 scale (Imai *et al.*, 2004a, 2004b). The major controlling factors of respective elemental concentrations have been closely examined by comparing them with geological, mineral resources and land use maps (Ohta *et al.*, 2004a, 2004b; 2005a, 2005b; Ujiie-Mikoshiba *et al.*, 2006).

Ohta *et al.* (2004a, 2004b; 2005a, 2005b) applied a significant statistical test to objectively and quantitatively interpret the geochemical maps. Ohta *et al.* (2005a) identified contamination of P, Cu, Zn, As, Mo, Cd, Sn, Sb, Hg, Pb and Bi in sediments collected from the urban areas by applying a statistical test to the geochemical data. However, an element occurs in sediments in various physicochemical forms: exchangeable ion, adsorbed ion, carbonates, Fe-Mn oxides, sulphide, organic matters, mineral lattice and other forms (*e.g.* Tessier *et al.*, 1979). Therefore, the bulk composition of stream sediments is insufficient to elucidate the metal mobility, which is essential to assess the potential hazard of heavy metals. If speciation geochemical maps are prepared, we will explore a mineral occurrence and more directly elucidate the potential hazard of toxic elements.

Recently, Ohta *et al.* (2003) and Imai *et al.* (2004a) conducted simple speciation geochemical mapping

<sup>1</sup>AIST, Geological Survey of Japan, Institute of Geology and Geoinformation

\*Correspondence should be addressed to Atsuyuki Ohta (Tel. +81-298-61-3848, Fax. +81-298-61-3566, e-mail a.ohta@aist.go.jp)

using the 0.1 M hydrochloric acid (HCl) soluble fraction of stream sediments. This method is a simple and rapid procedure, but is disadvantageous because it is unclear which components are extracted. In order to identify respective chemical forms of heavy metals, we have applied a sequential extraction scheme to stream sediments in Japan. Although many sequential extraction schemes have been proposed, a five-stage Tessier protocol (Tessier *et al.*, 1979) and three-step extraction developed by the Community Bureau of Reference (BCR) (Ure *et al.*, 1993; Thomas *et al.*, 1994) have been widely used. However the results obtained by the different schemes are not always consistent to one another even in the same laboratories (López-Sánchez *et al.*, 1993; Mester *et al.*, 1998; Usero *et al.*, 1998). Besides, the lack of uniformity in the different sequential extraction procedure has led to many criticisms: the results obtained by different laboratories are hardly compared. The standardization (harmonization) of the sequential extraction procedure and interlaboratory comparison have been evaluated for the BCR scheme (*e.g.* Crosland *et al.*, 1993; Ure *et al.*, 1993). In this study, we applied the BCR scheme to the examination of the speciation of elements in stream sediments as a preliminary study for speciation geochemical mapping. The purpose of this study is to (1) examine the effect of lithology on the speciation of elements in sediments, (2) elucidate the efficacy of the BCR scheme to detect the contamination of heavy metals, and (3) apply the sequential extraction method to mineral exploration.

## 2. Materials and methods

### 2.1 Samples

The stream sediment samples which were collected for nationwide and regional geochemical mapping are presented in Fig. 1 and Table 1. Their bulk and 0.1 M HCl soluble compositions are presented in Appendix A (Ohta *et al.*, 2002; Imai *et al.*, 2004a, 2004b). Most elements have different concentrations in stream sediments when specific rock types or mineral resources are exposed in their drainage basins (Imai *et al.*, 2004a, 2004b). We selected samples derived from drainage basins where a specific rock type outcrops in 85 - 100 % of the time. The intended lithology in the present study was accretionary complexes (mainly sedimentary rocks), ultramafic rocks associated with accretionary complexes, granite, felsic and mafic volcanic rocks, two kinds of metamorphic rocks and sedimentary rock (Table 1). Although ultramafic rock associated with accretionary complexes only crops out in a small area, it strongly affects the Mg, Cr, Co and Ni contents in sediments (Ohta *et al.*, 2004a). We selected three samples whose drainage areas have 30 - 50 % of the outcrops of ultramafic rock for the extraction study.

Stream sediments collected from the urban areas, where an alluvial deposit typically covers, have occasionally high concentrations of heavy metals such as Cu, Zn, Cd and Pb (Ohta *et al.*, 2005a). Three sediment samples having high Cr, Ni, Cu, Zn, As, Mo, Cd, Sn, Sb, Hg, Pb and Bi concentrations were prepared as possibly contaminated sediment. The samples associated with a large-scale mineral deposit are highly abundant in Cu, Zn, As, Mo, Cd, Sn, Sb, Hg, Pb and Bi (Ohta *et al.*, 2004a, 2004b; Ujiie-Mikoshihba *et al.*, 2006). We used three samples associated with the Kamioka mine (Skarn type), Ikuno mine (hydrothermal type) and Kosaka mine (Kuroko type) as a “pseudo contaminated” sediment whose origins of heavy metals are known. The reproducibility of elemental concentrations obtained using the BCR scheme was elucidated using JSd-1, -2 and -3, which are geochemical reference samples and composed of stream sediments collected from the north Kanto region (Imai *et al.*, 1996).

### 2.2 Sequential extraction procedure (the BCR scheme)

Sequential extraction was performed in conformity to the BCR scheme proposed by Ure *et al.* (1993) and Thomas *et al.* (1994). The detailed process is as follows.

**Step 1:** This fraction intends to extract elements bound to carbonate or weakly adsorbed on materials (exchangeable elements). A 10 ml volume of acetic acid (0.11 M) was added to 0.25 g dry sediment in a 15 ml PFA tube. The PFA tube was shaken for 16 hr (overnight) at room temperature (25 °C) on a (end-over-end) mechanical shaker at a speed of 30 rpm. The supernatant was separated from the solid residue by centrifugation at 3,500 rpm for 25 min; removed with a pipette and filtrated using a cellulose acetate-type membrane filter ( $\phi = 0.2 \mu\text{m}$ ). The liquid was acidified using nitric acid ( $\text{HNO}_3$ ) and stored in a clean polyethylene bottle before analysis. The residue was washed with 5 ml Milli-Q water by shaking for 15 min, centrifuged and filtered. The washings were not discarded to prevent trace element losses. They were stored with the first extraction.

**Step 2:** This fraction is used to extract elements bounded to iron and manganese oxides that would be released when the oxidative-reductive condition changes. A 10 ml volume of hydroxylammonium chloride (0.1 M, adjusted at pH 2 with  $\text{HNO}_3$ ) was added to the residue from step 1. The extraction procedure was repeated as described above.

**Step 3:** This fraction relates to metals bound to the organic matters and sulfurs which would be released into environment if the condition becomes oxidative. A 2.5 ml volume of hydrogen peroxide (8.8 M) was added to the residue of step 2. The tube was covered with Parafilm with a hole in it. In order to avoid a

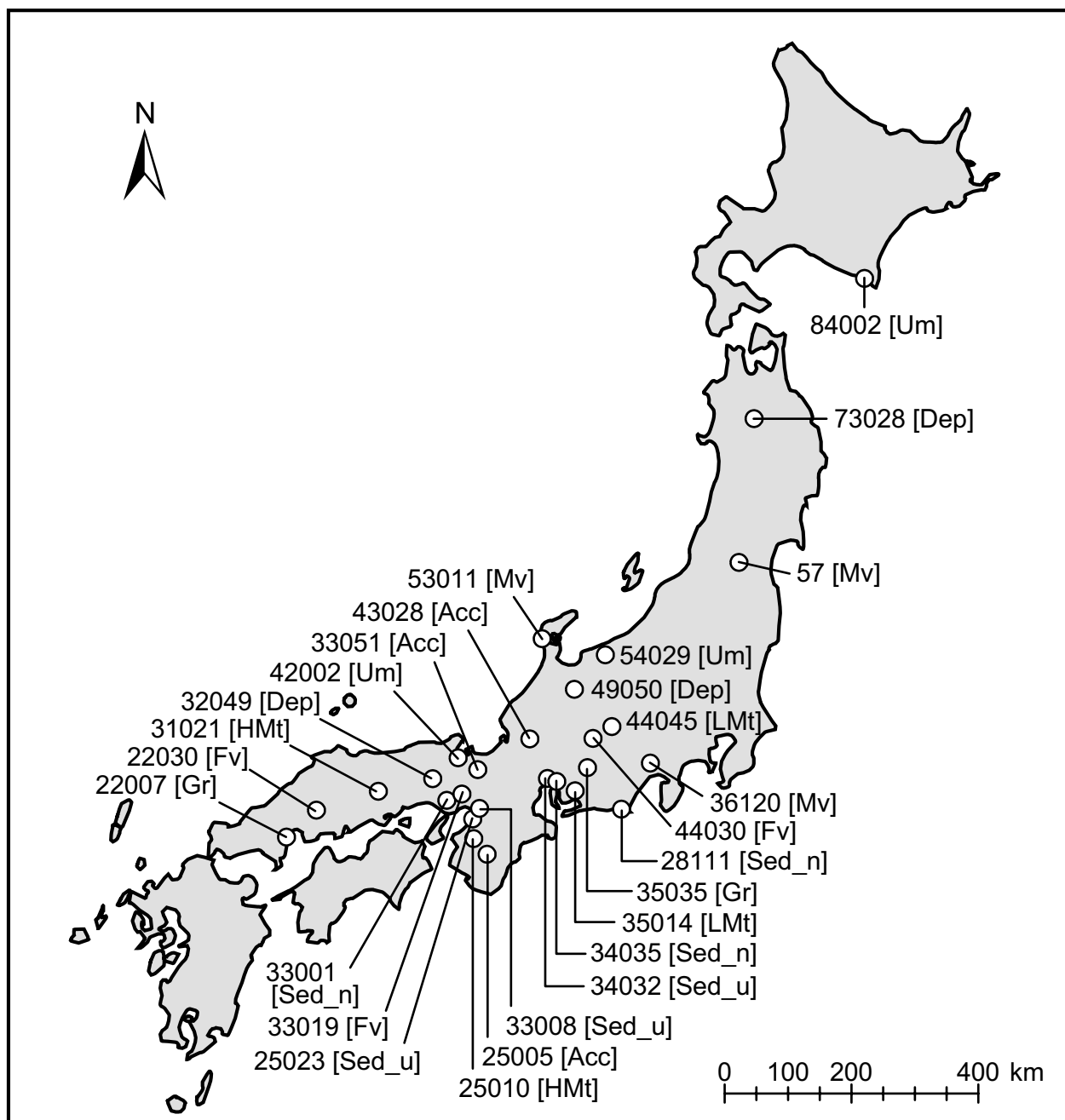


Fig. 1 Sampling location of stream sediments. The abbreviations are the same as Table 1.

violent reaction with sulfides and organic matters, the tube was put in a water bath and digested moderately at ambient temperature (20 - 30 °C) for 1 hr with an occasional manual shaking. The procedure was continued by heating the tube at 85 °C for 1 hr in a modular block. The Parafilm was removed, and the solution is reduced to almost to dryness. A second aliquot of 2.5 ml hydrogen peroxide was added, and the same procedure is repeated. A 12.5 ml volume of ammonium acetate (1 M, adjusted at pH 2 with HNO<sub>3</sub>) was added to the cool residue. The separation of supernatant was conducted as described above.

**Step 4:** This fraction is associated with the crystalline structure of minerals. The residue of step 3 was digested using hydrofluoric acid (HF), perchloric acid (HClO<sub>4</sub>) and HNO<sub>3</sub> solutions at 120 °C for 2 hr (Imai, 1990). The degraded product was evaporated to dryness under 200 °C, and the residue was dissolved with 100 ml of 0.35 M HNO<sub>3</sub> solution. The stored liquids in steps 1, 2 and 3 were filled up to 50 ml with 7 ml of 2 M HNO<sub>3</sub> and Milli-Q water.

Concentrations of 51 elements were determined using ICP-AES (Na, Mg, Al, P, K, Ca, Ti, Mn, Fe, V, Sr and Ba) and ICP-MS (Li, Be, Sc, Cr, Co, Ni, Cu, Zn,

Table 1 Sampling locations of stream sediments with river name and major geology in their watersheds.

Sample no. <sup>a</sup>	Latitude	Longitude	Location	River	Geology [abbreviation]
22007	34° 15' 30.3" N	132° 13' 35.4" E	Yamaguchi Pre.	Megumi Riv.	Granite [Gr]
22030	34° 39' 27.4" N	132° 44' 15.1" E	Hiroshima Pre.	Toshima Riv.	Felsic volcanic rocks [Fv]
25005	34° 2' 30.1" N	135° 42' 31.2" E	Nara Pre.	Kanno Riv.	Sedimentary rocks in accretionary complexes [Acc]
25010	34° 16' 2.8" N	135° 28' 48.6" E	Wakayama Pre.	Yomura Riv.	High-pressure type metamorphic rocks [HMt]
25023	34° 33' 8" N	135° 27' 42.7" E	Osaka Pre.	Ishizu Riv.	Sedimentary rocks in urban area [Sed_u]
28111	34° 39' 16.1" N	138° 3' 45" E	Shizuoka Pre.	Kiku Riv.	Sedimentary rocks [Sed_n]
31021	34° 56' 47.6" N	133° 48' 42.5" E	Okayama Pre.	Asahi Riv.	High-pressure type metamorphic rocks [HMt]
32049	35° 7' 57.2" N	134° 45' 44.1" E	Hyogo Pre.	Ichi Riv.	Accretionary complexes associated with Ikuno mine [Dep]
33001	34° 49' 9.9" N	135° 0' 44" E	Hyogo Pre.	Minou Riv.	Sedimentary rocks [Sed_n]
33008	34° 42' 10.3" N	135° 35' 5.5" E	Osaka Pre.	Furu Riv.	Sedimentary rocks in urban area [Sed_u]
33019	34° 54' 33.9" N	135° 16' 37" E	Hyogo Pre.	Hatsuka Riv.	Felsic volcanic rocks [Fv]
33051	35° 15' 40.8" N	135° 33' 26.9" E	Kyoto Pre.	Yura Riv.	Sedimentary rocks in accretionary complexes [Acc]
34032	35° 7' 24" N	136° 46' 42.4" E	Aichi Pre.	Nikkoh Riv.	Sedimentary rocks in urban area [Sed_u]
34035	35° 4' 38.2" N	136° 56' 22.8" E	Aichi Pre.	Tenpaku Riv.	Sedimentary rocks [Sed_n]
35014	34° 56' 12.1" N	137° 15' 36.9" E	Aichi Pre.	Oto Riv.	Low- to medium-pressure type metamorphic rocks [LMt]
35035	35° 15' 57.4" N	137° 29' 12.1" E	Aichi Pre.	Kamimura Riv	Granite [Gr]
36120	35° 18' 21.4" N	138° 35' 39.1" E	Shizuoka Pre.	Urui Riv.	Mafic volcanic rocks [Mv]
42002	35° 26' 8.3" N	135° 12' 33.3" E	Kyoto Pre.	Hinoki Riv.	Ultramafic rocks in accretionary complexes [Um]
43028	35° 41' 49.9" N	136° 28' 44.6" E	Gifu Pre.	Ibi Riv.	Sedimentary rocks in accretionary complexes [Acc]
44030	35° 41' 13.3" N	137° 35' 46.8" E	Nagano Pre.	Adera Riv.	Felsic volcanic rocks [Fv]
44045	35° 50' 57.8" N	137° 56' 12.9" E	Nagano Pre.	Ozawa Riv.	Low- to medium-pressure type metamorphic rocks [LMt]
49050	36° 23' 53.8" N	137° 17' 13.1" E	Gifu Pre.	Takahara Riv.	Felsic volcanic rocks associated with Kamioka mine [Dep]
53011	37° 8' 13.8" N	136° 43' 42.2" E	Ishikawa Pre.	Togi Riv.	Mafic volcanic rocks [Mv]
54029	36° 53' 10" N	137° 51' 26.5" E	Niigata Pre.	Ohtokoro Riv.	Ultramafic rocks in accretionary complexes [Um]
73028	40° 11' 8.2" N	140° 46' 7" E	Akita Pre.	<i>unnamed small river</i>	Mafic volcanic rocks associated with Kosaka mine [Dep]
84002	42° 4' 56.7" N	143° 2' 24.4" E	Hokkaido Pre.	Horoman Riv.	Ultramafic rocks in accretionary complexes [Um]
57 <sup>b</sup>	38° 8' 7.6" N	140° 20' 20.2" E	Yamagata Pre.	Zao Riv.	Mafic volcanic rocks [Mv]

<sup>a</sup> The samples except for no.57 are collected for a nation-wide geochemical mapping (Imai *et al.*, 2004a, b)<sup>b</sup> Ohta *et al.* (2002)

Ga, Rb, Zr, Nb, Y, Mo, Cd, Sn, Sb, Cs, lanthanide (Ln: La–Lu), Hf, Ta, Tl, Pb, Bi, Th and U).

### 2.3 A single extraction using 0.1 M HCl

The chemical extraction procedure using 0.1 M HCl was conducted to stream sediment samples according to the official protocol by the Ministry of Agriculture, Forestry and Fisheries, Japan (a ministerial ordinance no. 47, the Ministry of Agriculture, Forestry and Fisheries, 2000). A 10 ml volume of 0.1 M HCl was added to 1 g sediment in a 20 ml polyethylene tube. The tube was shaken for 1 hr at 30 °C by an end-over-end mechanical shaker. The supernatant was separated from the solid by filtration using a cellulose acetate-type membrane filter ( $\phi = 0.45 \mu\text{m}$ ) and dried. A 5 ml of 7 M HNO<sub>3</sub> solution was added to the dried samples and diluted to 100 ml with Milli-Q. However, the single extraction using HCl was not conducted for geochemical reference samples (JSd-1, -2 and -3) and sample 57 collected in Yamagata Prefecture.

## 3. Results

### 3.1 Reproducibility of the BCR method using JSd-1, -2 and -3

Three geochemical reference samples, JSd-1, JSd-2 and JSd-3 (Imai *et al.*, 1996), were used to examine the reproducibility of elemental concentrations obtained by using the BCR method. The results are presented in Tables 2 and 3. The extraction results showed that the fourth fraction (step 4) was the most dominant species in all elements except Cd. The precision of the technique was estimated on the basis of the relative standard deviations (RSDs) ( $n=5$ ) for 51 elements. The RSDs estimated for heavy metal concentrations were less than  $\pm 10\%$  in steps 1 and 4 and less than  $\pm 25\%$  in steps 2 and 3. These results are comparable to the previous report (Marin *et al.*, 1997). The precision obtained for Na, K, Ti, Zr, Nb, Mo, Sn, Sb, Hf and Ta in extraction steps 1, 2 and 3 was worse; their RSDs ranged from  $\pm 30\%$  to  $\pm 70\%$ . It could be explained by the lower concentration extracted in each step.

Total recovery rates (the total amounts extracted in four steps) for JSd-1, -2 and -3 ranged from 70 % to 240 % of the bulk compositions for 51 elements, but in most cases they range from 80 to 130 % (Table 3). The results are comparable to the previous reports (Davidson *et al.*, 1994; Marin *et al.*, 1997). Overall, the means and standard deviations ( $n=5$ ) of the sum concentrations of the four steps were in agreement with those of the bulk compositions ( $n=5$ ) for most elements. The total recoveries of 30 stream sediment samples had almost the same result as that of the geochemical reference samples (see Appendixes A1 and B5). Their total

recovery rates ranged from 50 % to 240 % of the bulk compositions (80 - 140 % in most cases). The sum of Pb and Bi concentrations obtained from the four steps ranged from 110 % to 140 %, which were rather higher than those of the other elements. A similar result was reported by Davidson *et al.* (1998).

### 3.2 Sequential extraction results

It has been a fundamental problem whether each reagent used in the sequential extraction procedure can appropriately extract the corresponding phase or not (Kheboian and Bauer, 1987; Martin *et al.*, 1987; Nirel and Morel, 1990; Whalley and Grant, 1994; Coetzee *et al.*, 1995). All papers pointed out that the selectivity of the reagents is not sufficient to extract the metals bound to the intended phases. However, Coetzee *et al.* (1995) concurrently suggested that chemical distribution (relative percentage of elemental concentrations in each step to the total amount) obtained by the BCR protocol is a very important and useful parameter to distinguish effectively between anthropogenically introduced metals and inert metals or metals integrally contaminated in the natural mineral fraction. Therefore, we have a short discussion concerning metal speciation and explore mainly the potential of environmental assessment using the BCR scheme. The concentrations of elements extracted in each step are shown in Appendix B, and their relative percentages in the sum of the total amount released in the four steps (chemical distribution) are presented in Figures 2 - 7.

#### 3.2.1 Distribution of major elements in sediments

Sodium, Mg, K, Al and Ti were primarily extracted in the residual fraction, whose concentrations in step 4 amount to 90 - 100 % of the total concentrations (Fig. 2). In contrast, a significant amount of P, Ca and Mn was extracted in steps 1, 2 and 3 (Figs. 2 and 3). The 10 - 60 % of the total concentrations for Ca was found in step 1 and only 10 % of the total content of Ca was extracted in steps 2 and 3. The 10 - 70 % of the total P concentration was associated with the second fraction and 10 - 20 % of the total P content was obtained in step 3. For Mn, the 10 - 40 % of the total concentrations was detected in step 1 and 10 - 70 % in step 2. The extremely high proportion of Mn in sediments derived from sedimentary rocks in accretionary complexes was extracted in step 2, especially for sample 33051. The details of these anomalous distributions will be discussed later. Iron existed primitively in the residual fraction approximately 90 % of their total content. The only 10 % of the total concentration of Fe was extracted in step 2. Sample 25023 collected from an alluvial plain was characterized by having an extremely high proportion of Na, Mg, K, Ca and Mn in step 1 and relatively high proportion of Fe in step 2. The high proportion of Na and K detected in step 1 is

Table 2 Speciation results of geostandard materials obtained by using the BCR scheme.

Elements	Unit	JSd-1			
		Step 1	Step 2	Step 3	Step 4
Li	ppm	0.57 ± 0.04	1.1 ± 0.3	0.6 ± 0.2	22.2 ± 0.8
Be	ppm	0.066 ± 0.005	0.06 ± 0.02	0.023 ± 0.008	1.10 ± 0.06
Na	%	0.020 ± 0.001	0.006 ± 0.001	0.006 ± 0.001	1.82 ± 0.06
Mg	%	0.056 ± 0.017	0.064 ± 0.03	0.042 ± 0.016	1.23 ± 0.29
Al	%	0.13 ± 0.01	0.19 ± 0.03	0.043 ± 0.005	6.18 ± 0.76
P (◇100)	%	0.026 ± 0.009	1.97 ± 0.25	0.40 ± 0.09	2.06 ± 0.27
K	%	0.025 ± 0.003	0.018 ± 0.001	0.010 ± 0.002	1.53 ± 0.05
Ca	%	0.105 ± 0.002	0.080 ± 0.003	0.065 ± 0.006	1.77 ± 0.10
Sc	ppm	0.30 ± 0.06	0.14 ± 0.06	0.3 ± 0.1	9.76 ± 0.63
Ti (◇10)	%	<0.001	<0.001	0.051 ± 0.023	3.65 ± 0.14
V	ppm	1.1 ± 0.5	5.2 ± 0.7	7.5 ± 4.3	67.9 ± 7.2
Cr	ppm	0.44 ± 0.11	0.72 ± 0.29	0.65 ± 0.22	21.4 ± 1.7
Mn (◇100)	%	0.73 ± 0.15	0.64 ± 0.13	0.236 ± 0.042	5.24 ± 0.20
Fe	%	0.058 ± 0.023	0.208 ± 0.063	0.026 ± 0.005	3.09 ± 0.20
Co	ppm	0.96 ± 0.04	1.16 ± 0.21	0.34 ± 0.06	8.97 ± 0.18
Ni	ppm	0.31 ± 0.04	0.63 ± 0.15	0.39 ± 0.13	6.66 ± 0.42
Cu	ppm	1.67 ± 0.10	5.1 ± 1.4	0.76 ± 0.15	17.0 ± 0.3
Zn	ppm	12.6 ± 0.8	14.0 ± 3.3	2.67 ± 0.6	71.0 ± 1.9
Ga	ppm	0.08 ± 0.04	0.2 ± 0.1	0.17 ± 0.02	16.0 ± 0.5
Rb	ppm	0.6 ± 0.2	1.6 ± 0.3	1.1 ± 0.3	57.2 ± 10.0
Sr	ppm	12.9 ± 0.8	3.1 ± 0.2	2.3 ± 0.6	282 ± 25
Y	ppm	0.76 ± 0.04	2.0 ± 0.2	2.4 ± 0.3	9.3 ± 0.8
Zr	ppm	0.023 ± 0.009	0.026 ± 0.013	0.046 ± 0.047	18.5 ± 0.8
Nb	ppm	0.015 ± 0.009	0.02 ± 0.01	0.14 ± 0.05	8.7 ± 1.24
Mo	ppm	<0.001	0.05 ± 0.04	0.5 ± 0.3	0.76 ± 0.37
Cd	ppm	0.037 ± 0.010	0.016 ± 0.002	0.014 ± 0.008	0.037 ± 0.012
Sn	ppm	<0.001	<0.001	<0.001	1.96 ± 0.12
Cs	ppm	<0.001	0.013 ± 0.006	0.04 ± 0.01	1.64 ± 0.16
Ba	ppm	44 ± 1	42 ± 3	8.2 ± 0.8	408 ± 15
La	ppm	1.5 ± 0.1	2.0 ± 0.3	1.2 ± 0.3	11.3 ± 1.0
Ce	ppm	1.7 ± 0.1	3.8 ± 0.6	2.3 ± 0.8	23.3 ± 2.3
Pr	ppm	0.29 ± 0.02	0.51 ± 0.08	0.44 ± 0.10	2.74 ± 0.2
Nd	ppm	1.1 ± 0.1	2.2 ± 0.3	2.1 ± 0.4	11.1 ± 0.9
Sm	ppm	0.18 ± 0.01	0.42 ± 0.07	0.49 ± 0.09	2.39 ± 0.14
Eu	ppm	0.052 ± 0.004	0.09 ± 0.01	0.13 ± 0.02	0.69 ± 0.05
Gd	ppm	0.17 ± 0.01	0.42 ± 0.08	0.45 ± 0.07	2.08 ± 0.14
Tb	ppm	0.023 ± 0.001	0.064 ± 0.009	0.08 ± 0.02	0.35 ± 0.02
Dy	ppm	0.11 ± 0.01	0.30 ± 0.04	0.38 ± 0.06	1.73 ± 0.09
Ho	ppm	0.020 ± 0.001	0.057 ± 0.008	0.07 ± 0.01	0.32 ± 0.02
Er	ppm	0.056 ± 0.002	0.16 ± 0.02	0.20 ± 0.03	0.90 ± 0.05
Tm	ppm	0.008 ± 0.001	0.023 ± 0.003	0.032 ± 0.006	0.14 ± 0.01
Yb	ppm	0.048 ± 0.004	0.13 ± 0.02	0.20 ± 0.03	0.82 ± 0.06
Lu	ppm	0.007 ± 0.001	0.021 ± 0.004	0.029 ± 0.004	0.12 ± 0.01
Hf	ppm	<0.001	0.002 ± 0.001	<0.001	0.59 ± 0.04
Ta	ppm	<0.001	<0.001	<0.001	0.67 ± 0.17
Tl	ppm	<0.002	0.008 ± 0.001	0.005 ± 0.004	0.37 ± 0.02
Pb	ppm	0.25 ± 0.10	3.06 ± 1.10	1.77 ± 0.45	15.2 ± 0.6
Bi	ppm	<0.001	<0.001	0.002 ± 0.001	0.13 ± 0.02
Th	ppm	0.024 ± 0.005	0.004 ± 0.002	0.023 ± 0.015	3.90 ± 0.24
U	ppm	0.055 ± 0.002	0.03 ± 0.02	0.27 ± 0.01	0.50 ± 0.02

Results expressed as the mean ± S.D. (n=5)

Table 2 Continued.

Elements	Unit	JSd-2			
		Step 1	Step 2	Step 3	Step 4
Li	ppm	0.74 ± 0.03	0.8 ± 0.2	1.9 ± 0.3	18.3 ± 0.5
Be	ppm	0.088 ± 0.006	0.09 ± 0.03	0.11 ± 0.02	0.64 ± 0.02
Na	%	0.024 ± 0.002	0.010 ± 0.001	0.009 ± 0.002	1.58 ± 0.05
Mg	%	0.086 ± 0.025	0.067 ± 0.035	0.078 ± 0.024	1.80 ± 0.34
Al	%	0.109 ± 0.010	0.074 ± 0.024	0.191 ± 0.011	4.94 ± 0.65
P (◇100)	%	0.065 ± 0.042	0.198 ± 0.127	0.221 ± 0.040	3.64 ± 0.09
K	%	0.025 ± 0.004	0.020 ± 0.002	0.005 ± 0.004	0.78 ± 0.03
Ca	%	0.786 ± 0.023	0.266 ± 0.047	0.137 ± 0.026	1.23 ± 0.05
Sc	ppm	0.6 ± 0.2	0.3 ± 0.1	1.0 ± 0.2	15.5 ± 0.8
Ti (◇10)	%	<0.001	<0.001	0.008 ± 0.002	3.10 ± 0.11
V	ppm	1.7 ± 0.8	6.9 ± 1.3	1.7 ± 0.7	116 ± 13
Cr	ppm	2.21 ± 0.18	1.2 ± 1.1	3.72 ± 0.49	86.2 ± 2.9
Mn (◇100)	%	1.46 ± 0.13	0.925 ± 0.042	0.578 ± 0.041	7.14 ± 1.01
Fe	%	0.477 ± 0.044	0.837 ± 0.118	0.197 ± 0.031	5.83 ± 0.53
Co	ppm	14.0 ± 0.5	7.0 ± 1.9	12.1 ± 1.7	18.4 ± 0.8
Ni	ppm	11.7 ± 0.8	8.2 ± 2.7	36.8 ± 3.6	36.7 ± 1.1
Cu	ppm	220 ± 33	1.8 ± 1.3	817 ± 105	207 ± 22
Zn	ppm	496 ± 32	740 ± 210	470 ± 89	422 ± 58
Ga	ppm	0.07 ± 0.04	0.05 ± 0.04	0.19 ± 0.03	13.2 ± 0.3
Rb	ppm	0.56 ± 0.08	1.2 ± 0.3	0.7 ± 0.2	24 ± 3
Sr	ppm	13.4 ± 1.4	8.5 ± 1.5	5.0 ± 0.8	155 ± 8
Y	ppm	1.45 ± 0.07	1.1 ± 0.2	2.3 ± 0.4	11.7 ± 0.6
Zr	ppm	0.16 ± 0.12	0.029 ± 0.015	0.018 ± 0.010	28.7 ± 3.6
Nb	ppm	0.006 ± 0.003	0.003 ± 0.003	0.01 ± 0.01	3.1 ± 0.1
Mo	ppm	0.09 ± 0.05	0.14 ± 0.07	<0.001	15.8 ± 2.6
Cd	ppm	1.03 ± 0.35	0.36 ± 0.05	0.94 ± 0.46	0.21 ± 0.04
Sn	ppm	0.08 ± 0.02	<0.001	0.067 ± 0.03	31.2 ± 2.2
Cs	ppm	0.002 ± 0.001	0.027 ± 0.006	0.05 ± 0.006	0.82 ± 0.02
Ba	ppm	113 ± 14	396 ± 53	62.9 ± 6.3	603 ± 56
La	ppm	0.74 ± 0.05	0.7 ± 0.2	0.8 ± 0.2	8.3 ± 0.5
Ce	ppm	1.3 ± 0.2	1.2 ± 0.3	1.8 ± 0.3	15.4 ± 2.2
Pr	ppm	0.19 ± 0.01	0.15 ± 0.04	0.28 ± 0.05	2.1 ± 0.13
Nd	ppm	0.85 ± 0.05	0.7 ± 0.2	1.3 ± 0.2	9.1 ± 0.5
Sm	ppm	0.20 ± 0.01	0.15 ± 0.04	0.36 ± 0.08	2.1 ± 0.1
Eu	ppm	0.062 ± 0.007	0.07 ± 0.03	0.096 ± 0.02	0.66 ± 0.04
Gd	ppm	0.21 ± 0.01	0.16 ± 0.04	0.37 ± 0.08	2.07 ± 0.07
Tb	ppm	0.037 ± 0.001	0.029 ± 0.007	0.07 ± 0.01	0.37 ± 0.01
Dy	ppm	0.20 ± 0.01	0.15 ± 0.03	0.39 ± 0.08	2.0 ± 0.1
Ho	ppm	0.039 ± 0.002	0.032 ± 0.009	0.076 ± 0.009	0.40 ± 0.01
Er	ppm	0.12 ± 0.01	0.09 ± 0.02	0.22 ± 0.04	1.15 ± 0.04
Tm	ppm	0.017 ± 0.001	0.014 ± 0.003	0.034 ± 0.007	0.17 ± 0.01
Yb	ppm	0.107 ± 0.005	0.08 ± 0.02	0.20 ± 0.04	1.02 ± 0.03
Lu	ppm	0.016 ± 0.001	0.011 ± 0.002	0.025 ± 0.002	0.13 ± 0.01
Hf	ppm	0.005 ± 0.002	0.003 ± 0.001	<0.001	0.75 ± 0.07
Ta	ppm	0.007 ± 0.003	0.005 ± 0.002	<0.001	0.32 ± 0.02
Tl	ppm	0.012 ± 0.002	0.06 ± 0.01	0.06 ± 0.01	0.38 ± 0.01
Pb	ppm	17.1 ± 1.5	26 ± 11	45.1 ± 1.9	146 ± 7
Bi	ppm	0.009 ± 0.002	<0.001	0.13 ± 0.03	1.21 ± 0.17
Th	ppm	0.021 ± 0.003	<0.001	0.11 ± 0.03	2.06 ± 0.21
U	ppm	0.11 ± 0.003	0.023 ± 0.009	0.22 ± 0.02	0.57 ± 0.02

Results expressed as the mean ± S.D. (n=5)

Table 2 Continued.

Elements	Unit	JSd-3			
		Step 1	Step 2	Step 3	Step 4
Li	ppm	0.60 ± 0.03	1.1 ± 0.2	2.1 ± 0.6	183 ± 27
Be	ppm	0.35 ± 0.02	0.32 ± 0.07	0.23 ± 0.05	7.4 ± 0.6
Na	%	0.002 ± 0.001	<0.001	<0.001	0.28 ± 0.03
Mg	%	0.014 ± 0.004	0.006 ± 0.003	0.005 ± 0.002	0.88 ± 0.24
Al	%	0.078 ± 0.005	0.133 ± 0.010	0.078 ± 0.008	3.86 ± 0.48
P (◇100)	%	0.021 ± 0.003	0.098 ± 0.066	0.227 ± 0.135	2.70 ± 0.13
K	%	0.023 ± 0.003	0.009 ± 0.001	0.004 ± 0.001	1.25 ± 0.04
Ca	%	0.058 ± 0.002	0.015 ± 0.001	0.008 ± 0.001	0.26 ± 0.02
Sc	ppm	0.09 ± 0.03	0.08 ± 0.04	0.8 ± 0.1	9.3 ± 0.9
Ti (◇10)	%	<0.001	<0.001	<0.001	2.10 ± 0.10
V	ppm	1.1 ± 0.4	2.8 ± 0.6	1.0 ± 0.3	58.8 ± 7.1
Cr	ppm	0.20 ± 0.02	0.24 ± 0.14	0.94 ± 0.09	36.9 ± 2.5
Mn (◇100)	%	1.27 ± 0.30	1.97 ± 0.45	0.426 ± 0.094	6.14 ± 0.35
Fe	%	0.010 ± 0.009	0.092 ± 0.020	0.023 ± 0.005	2.79 ± 0.17
Co	ppm	2.22 ± 0.11	4.47 ± 0.62	1.17 ± 0.2	5.53 ± 0.20
Ni	ppm	0.66 ± 0.05	1.41 ± 0.28	2.47 ± 0.35	15.9 ± 2.5
Cu	ppm	82.6 ± 5.0	78.8 ± 17.7	66.2 ± 13.4	224 ± 12
Zn	ppm	10.1 ± 0.7	9.85 ± 2.09	10.9 ± 3.4	113 ± 6
Ga	ppm	0.04 ± 0.03	0.21 ± 0.15	0.22 ± 0.02	13.4 ± 0.3
Rb	ppm	2.8 ± 0.5	4.1 ± 0.9	2.7 ± 0.5	281 ± 45
Sr	ppm	3.7 ± 0.5	1.1 ± 0.2	0.60 ± 0.12	43.5 ± 3.4
Y	ppm	0.90 ± 0.05	2.4 ± 0.4	1.5 ± 0.3	6.4 ± 0.7
Zr	ppm	0.037 ± 0.011	0.084 ± 0.025	0.13 ± 0.09	40.4 ± 3.4
Nb	ppm	0.0023 ± 0.0005	0.005 ± 0.001	<0.001	5.1 ± 0.6
Mo	ppm	<0.001	<0.001	<0.001	2.1 ± 0.5
Cd	ppm	0.38 ± 0.14	0.17 ± 0.05	0.11 ± 0.05	0.13 ± 0.02
Sn	ppm	<0.001	<0.001	<0.001	100 ± 6
Cs	ppm	0.08 ± 0.02	0.64 ± 0.1	1.5 ± 0.2	23.9 ± 1.9
Ba	ppm	22.5 ± 0.6	22.9 ± 1.2	4.2 ± 0.7	382 ± 12
La	ppm	0.53 ± 0.03	1.6 ± 0.2	0.9 ± 0.3	15.8 ± 1.3
Ce	ppm	0.72 ± 0.04	3.4 ± 0.6	3.8 ± 0.7	32.2 ± 3.3
Pr	ppm	0.10 ± 0.01	0.37 ± 0.07	0.31 ± 0.07	3.5 ± 0.3
Nd	ppm	0.44 ± 0.03	1.5 ± 0.3	1.4 ± 0.3	13.0 ± 1.0
Sm	ppm	0.092 ± 0.007	0.31 ± 0.07	0.36 ± 0.10	2.4 ± 0.2
Eu	ppm	0.026 ± 0.003	0.08 ± 0.02	0.08 ± 0.02	0.48 ± 0.04
Gd	ppm	0.107 ± 0.001	0.36 ± 0.08	0.32 ± 0.08	1.94 ± 0.2
Tb	ppm	0.019 ± 0.001	0.07 ± 0.01	0.06 ± 0.02	0.31 ± 0.08
Dy	ppm	0.102 ± 0.002	0.36 ± 0.07	0.31 ± 0.08	1.34 ± 0.09
Ho	ppm	0.021 ± 0.001	0.07 ± 0.02	0.05 ± 0.01	0.24 ± 0.03
Er	ppm	0.059 ± 0.004	0.20 ± 0.04	0.17 ± 0.04	0.67 ± 0.07
Tm	ppm	0.009 ± 0.001	0.029 ± 0.006	0.024 ± 0.005	0.10 ± 0.01
Yb	ppm	0.049 ± 0.007	0.17 ± 0.04	0.15 ± 0.03	0.74 ± 0.08
Lu	ppm	0.007 ± 0.001	0.022 ± 0.004	0.021 ± 0.005	0.10 ± 0.01
Hf	ppm	0.002 ± 0.002	0.003 ± 0.001	<0.001	1.03 ± 0.10
Ta	ppm	<0.001	<0.001	<0.001	0.35 ± 0.08
Tl	ppm	0.05 ± 0.01	0.17 ± 0.03	0.07 ± 0.01	2.1 ± 0.1
Pb	ppm	2.24 ± 0.2	30.5 ± 6.1	6.96 ± 1.10	89.1 ± 4.8
Bi	ppm	0.033 ± 0.006	0.051 ± 0.02	1.3 ± 0.1	14.1 ± 1.4
Th	ppm	0.007 ± 0.002	0.004 ± 0.002	0.26 ± 0.06	6.1 ± 0.8
U	ppm	0.036 ± 0.001	0.044 ± 0.015	0.15 ± 0.01	1.0 ± 0.1

Results expressed as the mean ± S.D. (n=5)



explained by sea salt contamination because the sampling location is nearby the sea.

### **3.2.2 Distribution of V, Cr, Co, Ni, Cu and Zn in sediments**

Davidson *et al.* (1994) reported that a small amount of V was found in both the reducible and oxidizable phases. Figure 3 shows that most dominant species of V was the residual phase, and a small amount of V (10 - 20 %) was extracted in step 2 or step 3. Davidson *et al.* (1994) and Yuan *et al.* (2004) reported that Cr in sediments dominantly occurred in the mineral phase. Our result (see Cr in Fig. 4) is consistent with their reports. However, the intensive feature is found in the distribution of Cr in sediments collected from the urban area: a considerable amount of Cr (30 - 50 %) for these samples was extracted in step 3.

In contrast to V and Cr, Ni and Zn were found in all fractions (*e.g.* Usero *et al.*, 1998; Davidson *et al.*, 1994; Davidson *et al.*, 1998). Approximately 10 % of the total concentrations of Ni and Zn was detected in steps 1 and 2, and 10 - 20 % of their total concentrations was extracted in step 3 (Figs. 4 and 5). A significant proportion of Co and Cu was also found in all fractions. The 10 - 20 % of the total concentration of Co was detected in steps 1, 2 and 3. The high proportion of Co in step 2 (20 - 50 %) appeared in the sediments derived from accretionary complexes (mainly sedimentary rocks), which was similar to the extraction result for Mn (Fig. 3). Usero *et al.* (1998) and Morillo *et al.* (2004) suggested that Cu was extracted in all steps and especially had a high proportion in the step 3. Figure 4 shows that the 10 - 20 %, 10 - 20 % and 10 - 30 % of total concentrations of Cu were detected in steps 1, 2 and 3, respectively. The percentages to the total amount of Cu in the four steps are consistent with the previous reports (*e.g.* Usero *et al.*, 1998; Morillo *et al.*, 2004).

The sediments collected in the urban area are abundant in Cr, Ni, Cu and Zn (Ohta *et al.*, 2005a). For these samples, the high proportion of Cr (30 - 50 %) and Cu (40 - 60 %) was extracted in step 3 and that of Co (20 - 30 %), Ni (20 - 40 %) and Zn (40 - 70 %) was obtained in step 1. The sediment samples influenced by metalliferous deposits are abundant in Cu and Zn but not in Cr, Ni and Co. The distributions of Cu and Zn were fundamentally similar to the samples in the urban area. The sediments associated with metal deposits had 90 - 100 % of Cr to the total content retained in the residual phase, and a small percentage (10 %) of the total concentration of Ni was extracted in step 1.

### **3.2.3 Distribution of Mo, Cd, Sn, Sb, Tl, Pb and Bi in sediments**

Davidson *et al.* (1994) and Yuan *et al.* (2004) suggested that Mo and Sn were scarcely extracted in steps 1, 2 and 3, and dominantly existed in the residual phase.

Our results also suggested that Mo, Sn, Sb and Tl were dominantly found in the residual fraction (Figs. 5 and 6). Almost 100 % of the total contents of Sn and Sb existed in the residual fraction. However, some samples had high proportions of Mo and Tl in step 3 and step 2, respectively.

It is known that Cd is extremely unstable in sediments, that is, it is easy to be dissolved into water and be adsorbed on materials (Davidson *et al.*, 1998; Morillo *et al.*, 2004). Figure 5 shows that the proportion of Cd extracted in step 1 was extremely high (20 - 80 %) for most samples. The samples from the urban area had a small percentage (less than 10 % except 34035) of the total Cd concentration in step 4. The samples influenced by mineral deposits had a high proportion of the total Cd concentration in step 3. In contrast, the samples derived from mafic volcanic rocks and ultramafic rocks had a small percentage of Cd in step 1 (5 - 30 %) and high proportion of Cd in step 4 (40 - 90 %).

Hudson-Edwards *et al.* (1996) and Morillo *et al.* (2004) reported that Fe-Mn hydrous oxides are important scavengers of Pb in sediments. Figure 6 shows that 10 - 40 % of the total concentration of Pb was extracted in step 2; lead detected in step 1 was a minor species in sediments. The results are also consistent with the previous reports (Marin *et al.*, 1997; Davidson *et al.*, 1998; Usero *et al.*, 1998; Morillo *et al.*, 2004; Yuan *et al.*, 2004). The distribution of Bi was different from those of Mo, Cd, Sn, Sb, Tl and Pb. The 10 - 30 % of the total Bi concentrations was extracted in step 3, and the rest appeared in the residual phase.

### **3.2.4 Distribution of the other elements in sediments**

The Li, Rb and Cs were found in association with residual materials similar to Na and K. Martin *et al.* (1997) reported that a slight amount of Cs was detected in the steps 1, 2 and 3 using the BCR scheme. The extraction results of Be and Ba in sediments were similar to that of Mg. In contrast, the distribution of Sr was consistent with that of Ca. Lithium, Be, Rb, Cs and Ba in sample 25023 were not abundant in step 1, which is different from Na and K because sea salt and calcium carbonate are not concentrated in these elements. The distributions of Ga, Zr, Nb, Hf and Ta in stream sediments resembled to that of Ti. Marin *et al.* (1998) applied the BCR scheme to the extractions of REE, U and Th in river sediments whose river basin is covered by granitic rocks with U deposits. They suggested that a significant proportion of REE and U in sediments was associated with the organic matter (step 3). In contrast, the most dominant species of Th was the residual fraction because Th is contained in heavy minerals such as monazite (Martine *et al.*, 1998). Our results (Fig. 7) show that Sc, Y and lanthanide (Ln) in the sediments were extracted in step 2 (10 - 20 %) and

Table 3 Comparison of the total amount extracted in four steps (n=5) and the bulk compositions (n=5).

Elements	Unit	JSd-1			JSd-2			JSd-3		
		BCR <sup>a</sup>	Bulk comp.	Ref. <sup>b</sup>	BCR <sup>a</sup>	Bulk comp.	Ref. <sup>b</sup>	BCR <sup>a</sup>	Bulk comp.	Ref. <sup>b</sup>
Li	ppm	24.5 ± 0.9	25.0 ± 1.9	22.8	21.8 ± 0.3	22.6 ± 1.7	19.2	187 ± 28	197 ± 25	151
Be	ppm	1.25 ± 0.07	1.32 ± 0.07	1.4	0.93 ± 0.04	0.99 ± 0.04	1.04	8.3 ± 0.6	8.9 ± 1.5	9.08
Na	%	1.85 ± 0.06	1.91 ± 0.05	2.023	1.62 ± 0.05	1.70 ± 0.05	1.809	0.28 ± 0.027	0.301 ± 0.028	0.305
Mg	%	1.39 ± 0.35	1.50 ± 0.07	1.093	2.03 ± 0.42	2.15 ± 0.05	1.647	0.91 ± 0.25	0.965 ± 0.044	0.706
Al	%	6.55 ± 0.77	6.83 ± 0.73	7.753	5.32 ± 0.66	5.55 ± 0.57	6.515	4.15 ± 0.48	4.32 ± 0.18	5.244
P (◇100)	%	4.37 ± 0.50	5.15 ± 0.10	5.32	4.04 ± 0.20	4.94 ± 0.09	4.58	3.04 ± 0.09	3.34 ± 0.09	3.57
K	%	1.58 ± 0.05	1.64 ± 0.02	1.812	0.827 ± 0.028	0.891 ± 0.016	0.951	1.28 ± 0.04	1.30 ± 0.03	1.636
Ca	%	2.02 ± 0.11	2.07 ± 0.07	2.168	2.42 ± 0.08	2.54 ± 0.06	2.614	0.342 ± 0.023	0.333 ± 0.029	0.400
Sc	ppm	10.5 ± 0.6	10.4 ± 0.8	10.9	17.3 ± 0.5	17.6 ± 0.9	17.5	10.2 ± 0.9	8.6 ± 1.4	10.5
Ti (◇10)	%	3.70 ± 0.13	3.95 ± 0.05	3.85	3.11 ± 0.11	3.24 ± 0.21	3.68	2.10 ± 0.10	2.16 ± 0.14	2.42
V	ppm	79.7 ± 7.6	82.6 ± 9.0		126 ± 13	132 ± 7		63.2 ± 7.8	78.8 ± 8.4	
Cr	ppm	23.0 ± 1.8	22.4 ± 1.5	21.5	93.3 ± 3.5	95.6 ± 8.1	108	38.0 ± 2.5	39.3 ± 2.9	35.3
Mn (◇100)	%	6.85 ± 0.36	7.15 ± 0.14	7.16	10.1 ± 0.9	9.12 ± 0.31	9.29	9.8 ± 1.2	10.7 ± 0.6	11.5
Fe	%	3.36 ± 0.22	3.45 ± 0.14	3.539	7.34 ± 0.55	8.11 ± 0.25	8.149	2.91 ± 0.16	2.94 ± 0.15	3.055
Co	ppm	11.4 ± 0.3	11.8 ± 0.6	11.2	51.5 ± 1	52.7 ± 2.3	48.4	13.4 ± 0.6	14.0 ± 0.6	12.7
Ni	ppm	7.99 ± 0.54	8.18 ± 0.59	7.04	93.2 ± 1.7	96.4 ± 4.5	92.8	19.9 ± 3.1	21.0 ± 1.6	19.6
Cu	ppm	24.3 ± 1.5	26.3 ± 1.3	22	1246 ± 119	1465 ± 159	1117	451 ± 24	565 ± 91	426
Zn	ppm	100 ± 6	104 ± 5	96.5	2128 ± 106	2399 ± 338	2056	144 ± 8	154 ± 9	136
Ga	ppm	16.4 ± 0.5	16.9 ± 0.6	17.2	13.6 ± 0.2	14.0 ± 0.5	15.3	13.8 ± 0.4	14.0 ± 0.5	13.5
Rb	ppm	60 ± 10	79 ± 7.4		26 ± 3	31 ± 3		291 ± 45	408 ± 72	
Sr	ppm	301 ± 25	293 ± 26		182 ± 8	188 ± 13		48.9 ± 4	42.1 ± 5	
Y	ppm	14.5 ± 1.0	15.6 ± 1.6	14.8	16.6 ± 0.7	17.9 ± 1.3	17.4	11.2 ± 0.8	9.8 ± 1.0	14.9
Zr	ppm	18.6 ± 0.8	20.2 ± 1.1	132	28.9 ± 3.6	27.7 ± 1.8	111	40.7 ± 3.4	42.3 ± 6.0	124
Nb	ppm	8.8 ± 1.2	10.6 ± 0.4	11.1	3.13 ± 0.09	3.56 ± 0.25	4.56	5.1 ± 0.6	6.1 ± 0.5	7.8
Mo	ppm	1.3 ± 0.7	0.58 ± 0.20	0.669	16 ± 3	14 ± 4	11.5	2.1 ± 0.5	1.5 ± 0.4	

Results expressed as the mean ± S.D. (n=5)

<sup>a</sup> BCR indicate the sums of the total amount released in the four steps

<sup>b</sup> Imai *et al.* (1996)

Table 3 Continued.

Elements	Unit	JSd-1			JSd-2			JSd-3		
		BCR <sup>a</sup>	Bulk comp.	Ref. <sup>b</sup>	BCR <sup>a</sup>	Bulk comp.	Ref. <sup>b</sup>	BCR <sup>a</sup>	Bulk comp.	Ref. <sup>b</sup>
Cd	ppm	0.094 ± 0.012	0.114 ± 0.013	0.146	2.55 ± 0.73	2.28 ± 0.2	3.06	0.79 ± 0.22	0.72 ± 0.09	1.045
Sn	ppm	1.96 ± 0.12	2.04 ± 0.13	2.77	31.3 ± 2.2	34.5 ± 4.9	32.5	100 ± 6	109 ± 7	195
Sb	ppm	0.25 ± 0.05	0.07 ± 0.09		10.6 ± 2.1	0.6 ± 0.3	12.5	1.7 ± 0.3		2.78
Cs	ppm	1.69 ± 0.16	1.95 ± 0.17	1.89	0.90 ± 0.03	0.99 ± 0.08	1.07	26.1 ± 2.1	30.1 ± 2.8	30.6
Ba	ppm	503 ± 18	520 ± 13		1176 ± 24	1215 ± 32		431 ± 14	428 ± 18	
La	ppm	16.0 ± 1.2	16.3 ± 0.9	18.1	10.5 ± 0.7	10.9 ± 0.9	11.3	18.9 ± 1.4	15.5 ± 1.6	19.8
Ce	ppm	31.1 ± 2.3	30.6 ± 1.9	34.4	19.7 ± 2.3	20.9 ± 1.9	23.4	40.1 ± 3.3	29.3 ± 5.0	42
Pr	ppm	3.98 ± 0.25	4.07 ± 0.2	4.05	2.7 ± 0.2	2.9 ± 0.2	2.4	4.2 ± 0.3	3.4 ± 0.4	3.09
Nd	ppm	16.5 ± 1.1	16.9 ± 1.0	17.6	11.9 ± 0.6	12.3 ± 0.9	13.2	16.3 ± 1.1	12.9 ± 1.3	15.7
Sm	ppm	3.48 ± 0.18	3.57 ± 0.21	3.48	2.8 ± 0.1	2.9 ± 0.2	2.68	3.2 ± 0.2	2.5 ± 0.3	3.26
Eu	ppm	0.95 ± 0.05	1.00 ± 0.06	0.925	0.88 ± 0.07	0.95 ± 0.04	0.81	0.68 ± 0.05	0.57 ± 0.07	0.686
Gd	ppm	3.12 ± 0.18	3.22 ± 0.16	2.71	2.8 ± 0.1	2.8 ± 0.2	2.67	2.72 ± 0.21	2.33 ± 0.2	2.63
Tb	ppm	0.52 ± 0.03	0.54 ± 0.03	0.431	0.51 ± 0.02	0.54 ± 0.03	0.44	0.46 ± 0.08	0.36 ± 0.04	0.368
Dy	ppm	2.51 ± 0.12	2.64 ± 0.16	2.23	2.8 ± 0.1	2.9 ± 0.2	2.86	2.11 ± 0.10	1.72 ± 0.19	2.22
Ho	ppm	0.47 ± 0.02	0.49 ± 0.02	0.318	0.55 ± 0.01	0.58 ± 0.03	0.678	0.38 ± 0.03	0.31 ± 0.03	0.443
Er	ppm	1.31 ± 0.06	1.42 ± 0.12	0.906	1.58 ± 0.04	1.68 ± 0.16	1.48	1.10 ± 0.07	0.84 ± 0.16	1.07
Tm	ppm	0.20 ± 0.01	0.21 ± 0.01	0.13	0.23 ± 0.01	0.25 ± 0.01	0.23	0.17 ± 0.02	0.14 ± 0.01	0.155
Yb	ppm	1.21 ± 0.08	1.29 ± 0.09	1.18	1.4 ± 0.03	1.48 ± 0.09	1.67	1.11 ± 0.08	0.91 ± 0.10	1.4
Lu	ppm	0.17 ± 0.01	0.18 ± 0.01	0.186	0.18 ± 0.01	0.19 ± 0.02	0.252	0.15 ± 0.01	0.13 ± 0.01	0.196
Hf	ppm	0.60 ± 0.03	0.66 ± 0.03	3.55	0.76 ± 0.07	0.73 ± 0.05	2.7	1.0 ± 0.1	1.1 ± 0.2	3.21
Ta	ppm	0.67 ± 0.17	0.90 ± 0.09	0.893	0.33 ± 0.02	0.40 ± 0.03	0.515	0.35 ± 0.08	0.48 ± 0.05	0.687
Tl	ppm	0.39 ± 0.02	0.39 ± 0.01	0.407	0.50 ± 0.02	0.50 ± 0.02		2.4 ± 0.1	2.4 ± 0.1	
Pb	ppm	20.3 ± 1.5	16.5 ± 4.1	12.9	235 ± 6	212 ± 40	146	129 ± 6	113 ± 20	82.1
Bi	ppm	0.13 ± 0.02	0.11 ± 0.02		1.35 ± 0.19	1.04 ± 0.08		15.5 ± 1.5	12.4 ± 1	23.8
Th	ppm	3.95 ± 0.23	4.32 ± 0.32	4.44	2.19 ± 0.21	2.46 ± 0.13	2.33	6.3 ± 0.7	5.3 ± 0.7	7.79
U	ppm	0.86 ± 0.02	0.89 ± 0.03	1.0	0.93 ± 0.02	0.95 ± 0.05	1.1	1.3 ± 0.1	1.2 ± 0.1	1.66

Results expressed as the mean ± S.D. (n=5)

<sup>a</sup> BCR indicate the sums of the total amount released in the four steps

<sup>b</sup> Imai *et al.* (1996)

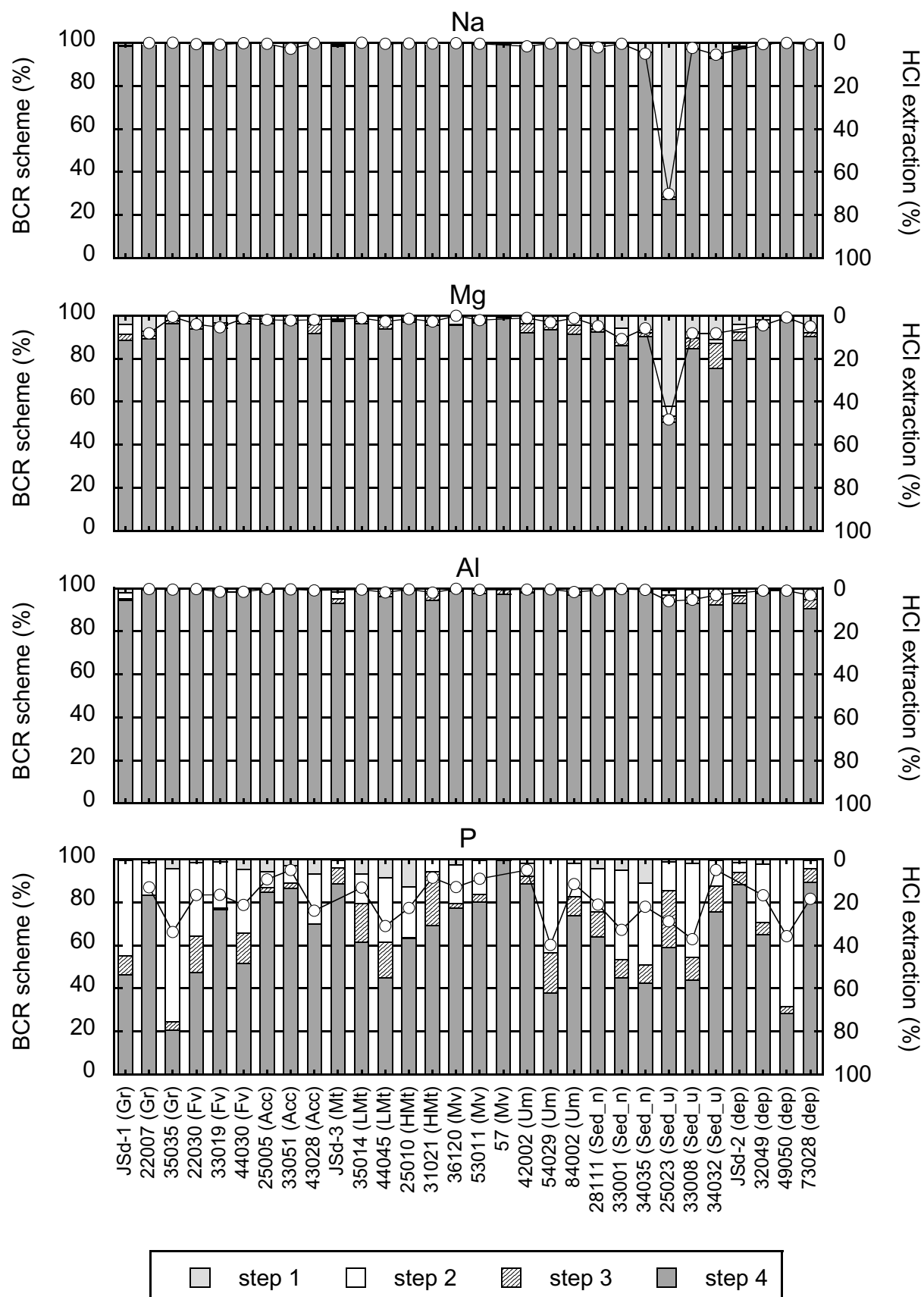


Fig. 2 Distribution of Na, Mg, Al and P concentrations in stream sediments for four fractions obtained by the BCR scheme and for a single extraction using 0.1 M HCl solution. The abbreviations are the same as Table 1.

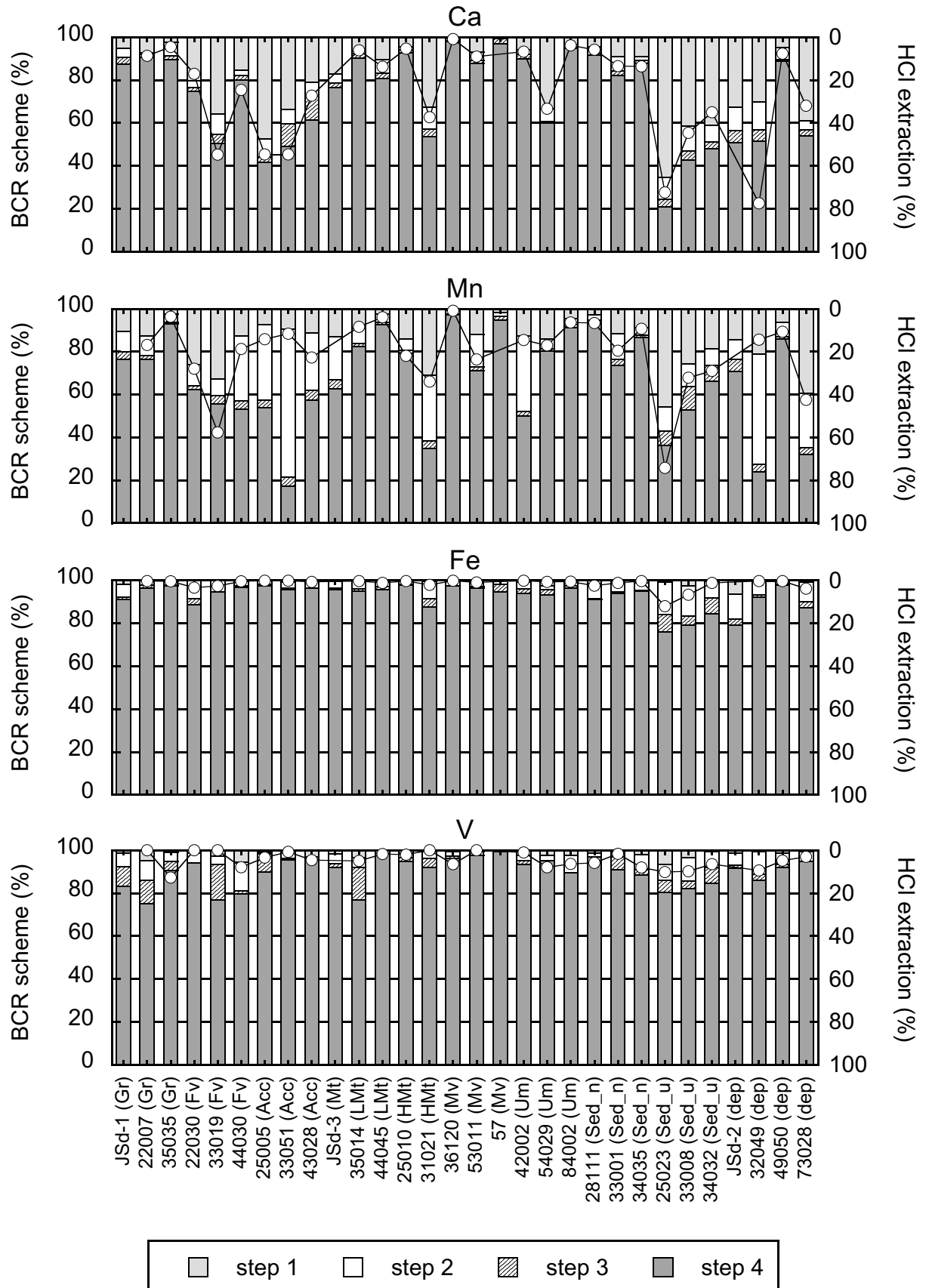


Fig. 3 Distribution of Ca, Mn, Fe and V concentrations in stream sediments for four fractions obtained by the BCR scheme and for a single extraction using 0.1 M HCl solution. The abbreviations are the same as Table 1.

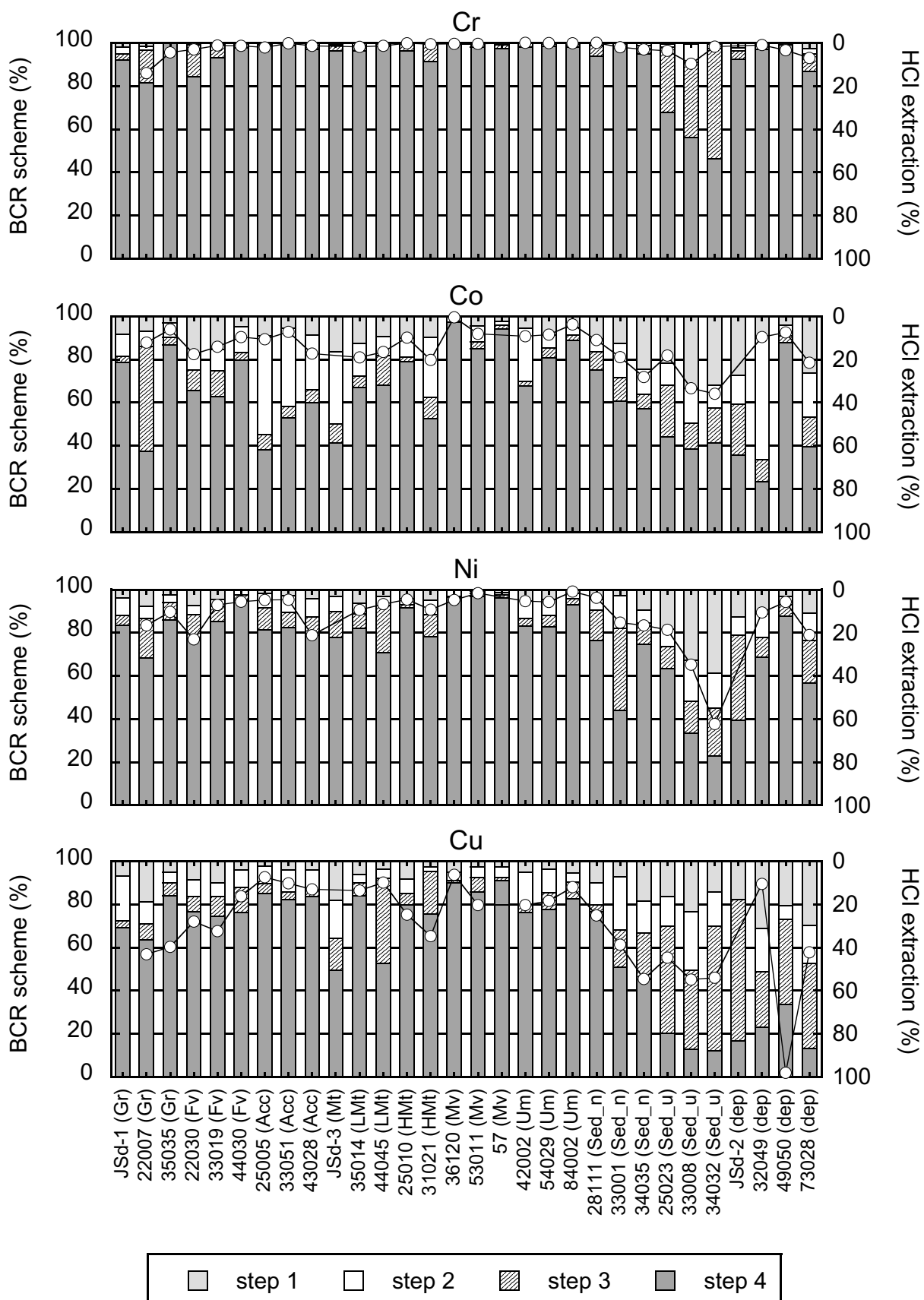


Fig. 4 Distribution of Cr, Co, Ni and Cu concentrations in stream sediments for four fractions obtained by the BCR scheme and for a single extraction using 0.1 M HCl solution. The abbreviations are the same as Table 1.

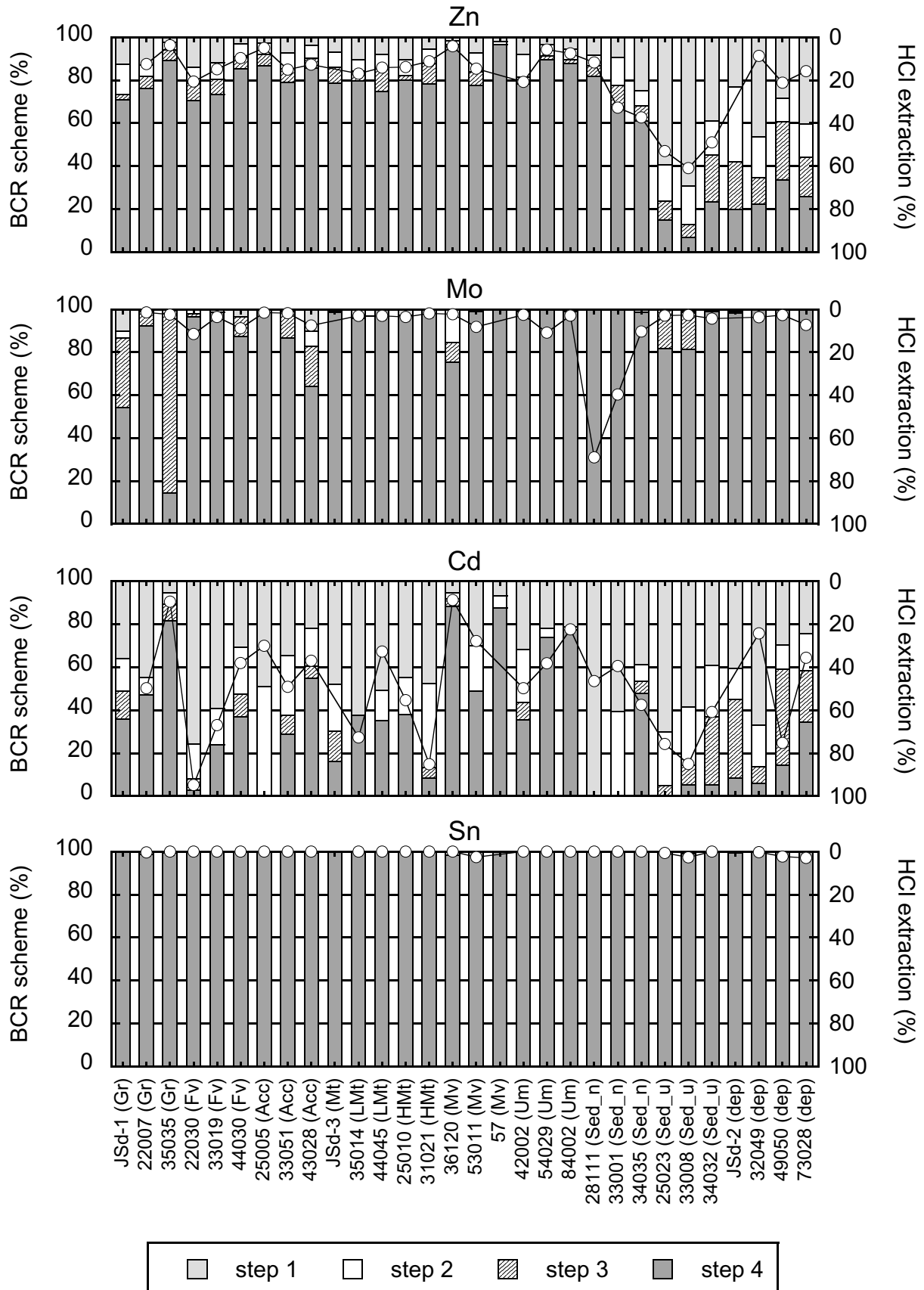


Fig. 5 Distribution of Zn, Mo, Cd and Sn concentrations in stream sediments for four fractions obtained by the BCR scheme and for a single extraction using 0.1 M HCl solution. The abbreviations are the same as Table 1.

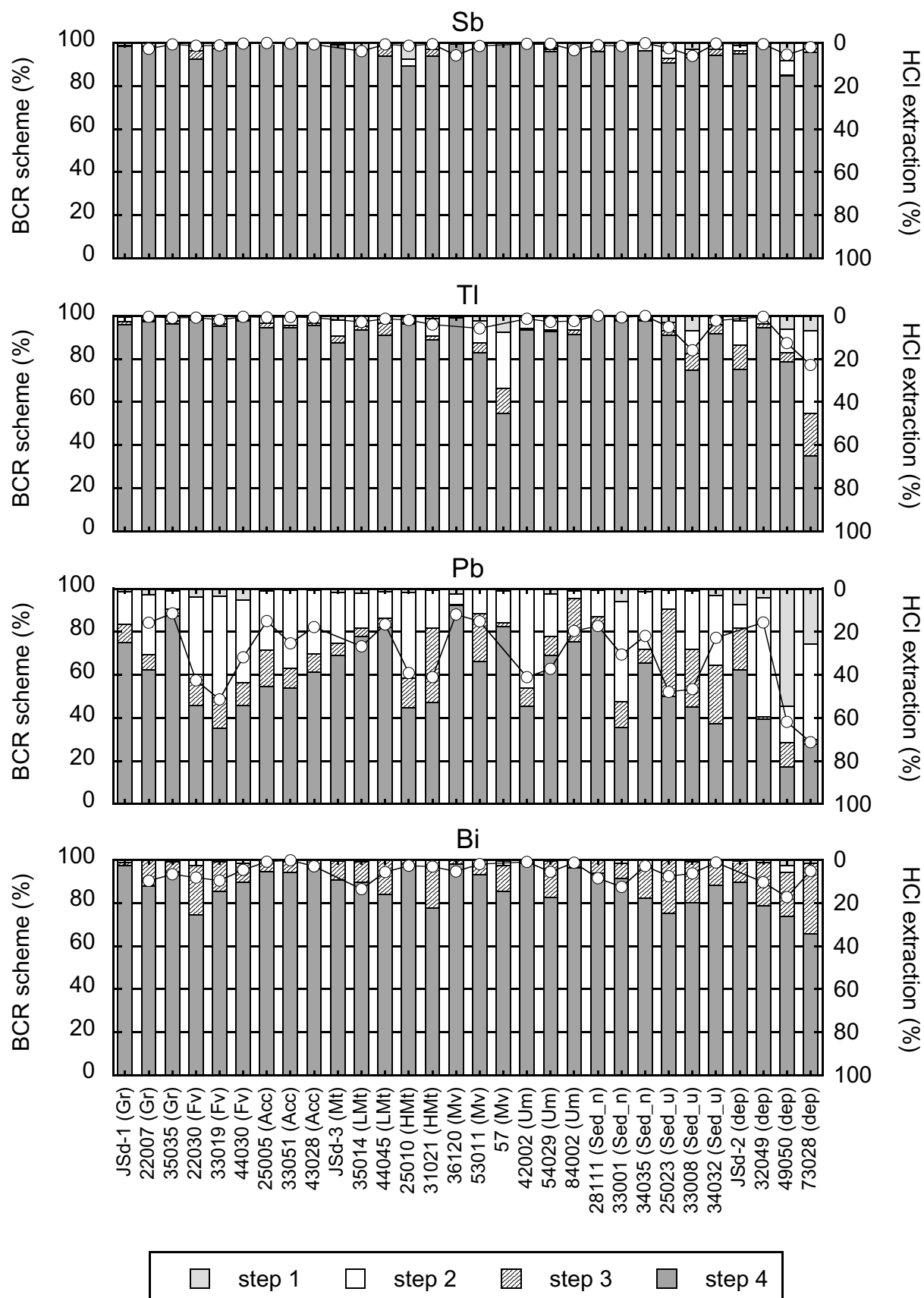


Fig. 6 Distribution of Sb, Tl, Pb and Bi concentrations in stream sediments for four fractions obtained by the BCR scheme and for a single extraction using 0.1 M HCl solution. The abbreviations are the same as Table 1.



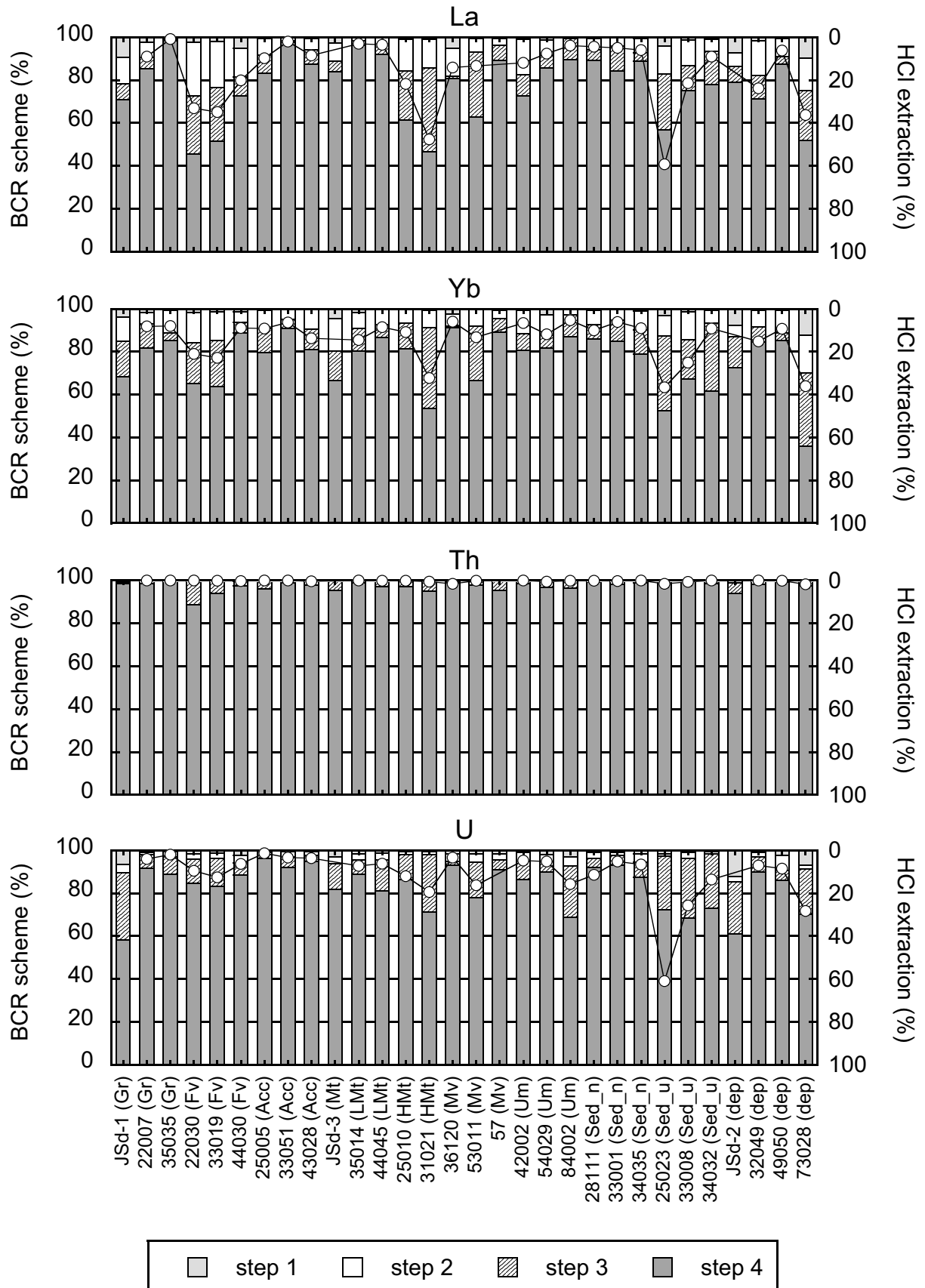


Fig. 7 Distribution of La, Yb, Th and U concentrations in stream sediments for four fractions obtained by the BCR scheme and for a single extraction using 0.1 M HCl solution. The abbreviations are the same as Table 1.

step 3 (10 - 40 %); Th in the sediments existed dominantly in the residual phase, and a small amount of Th (<10 %) was detected in step 3; the 10 - 30 % of the total U concentration in the sediments was obtained in step 3. The chemical distribution of these elements is consistent with the reports by Marin *et al.* (1997) and Martin *et al.* (1998).

### 3.3 Single extraction results

The proportions of most elements in the 0.1 M HCl soluble fractions are plotted between step 1 and step 2 (Figs. 2 - 7). A small amount of Na, K, Ti, Sn and Th was extracted in the 0.1 M HCl soluble fractions (see Appendix A). The percentages of Cr, Cu, REE, Bi and U (partly for Mg, Ni, Zn and Pb) extracted in the 0.1 M HCl soluble fractions to their total contents exceeded the sums of metal amounts in steps 1 and 2. Their excess extraction may be attributed to less effectiveness in the extraction of elements existing in step 2 using 0.1 M hydroxylammonium chloride at pH=2 (Sahuquillo *et al.*, 1999). Sahuquillo *et al.* (1999) proposed that 0.5 M hydroxylammonium chloride at pH=1.5 is more effective to extract heavy metals such as Cr, Cu and Pb. A serious problem using 0.1 M HCl soluble fractions was found in the extraction result of Mo. The 0.1 M HCl fraction of Mo to the total content exceeded the proportion of the sum of Mo concentration in steps 1, 2 and 3. It is unclear which methods have a problem in extraction of Mo in sediments; further investigation will be needed in this problem. Overall, the 0.1 M HCl soluble fractions were equivalent to the sums of elemental concentrations extracted in step 1 and partly in step 2.

Ohta *et al.* (2003) elucidated the features of the 0.1 M HCl extracted fractions of the stream sediments around Sendai city. They reported that the 40 - 70 % of the total concentrations of Mn, P, Cu, Zn, Tl and Pb were extracted; approximately 20 - 40 % of Co, Y, Ln and U were obtained in the 0.1 M HCl fraction; a small amount (10 - 20 %) of Mg, Fe, Ni, Sr, Mo and Ba were found in the eluate; the other elements were mainly found in the residual fraction. These results are comparable to the present study. They also reported that a high proportion of Na and K were extracted using 0.1 M HCl in the samples collected nearby the sea because of sea salt contamination. A similar finding appears in sample 25023 (Fig. 2). Ohta *et al.* (2003) further reported that bulk P concentration and percentage of 0.1 M HCl soluble fraction to the total content were systematically high in sediments collected nearby the rice field on the alluvial plain. It could be explained by the organic fertilizers. Although elemental abundance in sediments adjacent to the rice field is not taken into consideration in the present study, similar findings would probably appear in sediments collected in areas

neighboring a rice field in a nationwide geochemical mapping.

## 4. Discussion

### 4.1 Chemical species of elements in stream sediments

As mentioned above, little systematic differences in the chemical distributions were apparent among the samples originated from different geological materials. The fact indicates that the speciation of elements in stream sediments is not influenced by the lithology. In addition, the dominant species of all elements except Cd were in the residual phase (step 4). The result suggests that elements except Cd in stream sediments have fundamentally low mobility, that is, they are stable in sediments. However, the second dominant phase (occasionally the ternary phase) of the chemical distribution characterizes the past geochemical records of elements in the sediments besides pollution. For example, the percentages of Ca, Mg and Mn extracted in step 1 and percentages of Fe found in step 2 for the samples collected from an urban area were higher than those for the other samples. This result might indicate the contribution of calcareous shells and salt precipitation of Fe hydroxides to sediments because these samples were collected from the river mouth. The mixing of river and seawater attributes to the high proportion of Na, K, Mg, Ca and Mn in step 1 and Fe in step 2 for Sample 25023. However, such extraction results were not found in samples 34035 and 28111 that were under similar conditions. We assume that the pH and Eh conditions of the rivers in the urban area possibly differed from those in the other area.

Figure 3 shows that a considerable amount of Mn in stream sediments was extracted both in step 1 and step 2. The result indicates that Mn has affinity to the sediment surface or calcium carbonate because the oxidation of Mn(II) is much slower than that of Fe(II) (Tessier *et al.*, 1979; Usero *et al.*, 1998; Yuan *et al.*, 2004). The proportion of Mn and Co obtained in step 2 for sediments derived from accretionary complexes was obviously higher than those for the other samples. The 70 % of the total Mn concentrations in sample 33051 was extracted in step 2. Sample 33051 was collected from the Tanba and Mino Belts that consist of sedimentary rocks in accretionary complexes and contain a large number of small-bedded Mn deposits (over 1,000) (Nakazawa *et al.*, 1987; Ohta *et al.*, 2005a). Although no significant enrichment of Mn was recognized in the spatial distribution pattern (Ohta *et al.*, 2005a), the extraction result using the BCR method suggested the presence of bedded Mn deposits. The bedded Mn deposits associated with the Tanba and Mino belt is considered to be formed by hydrothermal activity on the ocean floor. In the process,

Co might have been oxidized and coprecipitated with Mn oxides. However, the percentages of Mn and Co in the 0.1 M HCl soluble fraction were not comparable to those retained in step 2 by the BCR scheme: No characteristic extraction results using 0.1 M HCl were found in these samples. Therefore, the sequential extraction method can be utilized to find a hidden mineral deposit more effectively than the 0.1 M HCl extraction.

#### **4.2 Identification of pollutant in stream sediments using the BCR scheme**

Heavy metals such as Cr, Co, Ni, Cu and Zn are highly elevated in sediments derived from mafic volcanic, ultramafic and high pressure type metamorphic rocks (Ohta *et al.*, 2004a, 2004b, 2005a). Sediments from ultramafic rocks have several thousands ppm of Cr and Ni, which are much higher than sediments collected from the urban area that are possibly polluted. Therefore, the distribution of pollution in sediments from heavy metal enrichments using the bulk composition has difficulty in some cases. However, the extraction results obtained using the BCR scheme revealed that the distribution of these elements in possibly contaminated sediments clearly differed from that in sediments from mafic volcanic and ultramafic rocks. High percentages of the total concentrations of Co, Ni and Zn in step 1 and those of Cr and Cu in step 3 were extracted for possibly polluted samples. The previous studies suggested that extracted Cu in contaminated sediments is mainly associated with the oxidizable phase (step 3), where it is likely to occur as organically complexed metal species (Davidson, *et al.*, 1994; Morillo *et al.*, 2004; Usero *et al.*, 1998). It has been confirmed that a significant proportion of Cu bounded to humic acid can be extracted in step 3 (Whalley *et al.*, 1994; Coetzee *et al.*, 1995). However, the high proportions of Cr retained in step 3 do not immediately indicate that Cr in possible polluted sediments binds to organic material or sulfur because Cr associated with reducible minerals such as goethite can be extracted in step 3 of the BCR scheme (Coetzee *et al.*, 1995). In conclusion, we can easily recognize the pollution of Co, Ni and Zn using their proportion in step 1. Similarly, the pollution of Cr and Cu in sediments can be estimated using their proportion in step 3. These chemical distributions do not always indicate the exact extraction result of metals bound to the respective phases. The single extraction method using the diluted HCl is also useful to identify these elements except for Cr. The 0.1 M HCl soluble fraction suggests that Co, Ni and Zn in sediments collected in the urban area are more effectively extracted than samples related to metal deposits.

The Mo, Cd, Sn, Sb, Pb and Bi are highly abundant in the samples collected from the urban area (Ohta *et*

*al.*, 2005a). The high percentage (30 - 40 %) of the total Pb concentrations in step 3 and the small percentage (less than 10 %) of the total Cd concentration in step 4 were recognized in the chemical distribution of possibly polluted samples. The distribution of Mo, Sn, Sb and Bi in sediments did not differ largely among all samples. Unfortunately, the BCR scheme was not useful to find pollution of these elements in sediments. The extraction result obtained using the BCR scheme suggests that Mo, Sn and Sb are hardly released into water. However, it is possible that a slight amount of Mo, Sn and Sb extracted in steps 1, 2 and 3 was caused by a re-adsorption and re-distribution process during the experimentation. Terashima *et al.* (1996) and Gómez-Ariza *et al.* (1999) reported that the concentrations of Cr, As, Sb, Pb and Hg extracted in each step were fairly low due to their re-adsorption and redistribution processes. There is an ample room for further improvement in the BCR scheme for these elements.

#### **4.3 Differences and similarities of chemical distribution of heavy metals between stream sediments collected from the urban area and those associated with mineral deposits.**

The heavy metals such as Cu, Zn, Mo, Cd, Sn, Sb, Pb and Bi are abundant in sediments collected from the urban area and those influenced by metalliferous deposits. As described above, step 3 is intended to extract elements bound to sulfides, and organic matters were not the major chemical species of heavy metals in sediments related to mineral deposits. Davidson *et al.* (1998) suggested that erosion and mixing with sediments might promote the oxidation of sulfides of Pb; convert them to more labile species. The significant percentages of Cu, Zn, Cd and Pb detected in steps 1 and 2 in sediments associated with mineral deposits possibly suggest that sulfides of these elements are easily oxidized; released in water and finally re-adsorbed on or deposited in the sediments. As a result, the distribution of these metals is similar between the samples in the urban area and samples associated with mineral resources. However, some elements in sediments associated with metalliferous deposits have a different distribution. The proportion of Zn existing in step 1 (20 - 40 %) and 0.1 M HCl soluble fraction of Zn (10 - 20 %) for the samples associated with mineral deposits were systematically smaller than those of the possibly polluted sediments. Although the distribution of Cd largely varied among the samples, a slight amount of Cd in the residual fraction (0 - 10 %) was found in possibly polluted samples. The sediments associated with mineral deposits had the higher proportion of Pb in step 1 (5 - 50 %) and lower percentage of Pb in step 3 (0 - 20 %) than the samples collected in the urban area. These

differences reflect a different contamination process of these elements to sediments due to the variation of pH or Eh condition in rivers.

## 5. Conclusion

We have conducted a sequential extraction analysis (the BCR scheme) for stream sediments collected throughout Japan to identify the chemical forms of heavy metals and elucidate their potential hazard. The most dominant species of elements except Cd in sediments were the residual phase (step 4). This result suggests that most elements are fundamentally stable in stream sediments. However, the second or third dominant proportion of the elemental concentrations to the bulk compositions provides valuable information on the potential mobility in sediments. A significant amount of Ca, Mn, Co, Zn and Cd was extracted by acetic acid (step 1). They are more likely to be released into water. Potassium, Mn, Co, Cd and Pb in sediments had high proportion in the hydroxylammonium chloride soluble phase (step 2). A considerable amount of P, Co, Ni, Cu, Zn, Pb, Bi, REE and U was extracted by hydrogen peroxide and ammonium acetate (step 3). These elements detected in steps 2 and 3 are rather stable than those existing in step 1; they will be released in water when the oxidative-reductive condition changes. Overall, the chemical distribution (the relative percentage of elemental concentrations in each step to the total amount) did not differ largely among the samples. The significantly high percentages of Mn (30 - 70 %) and Co (20 - 40 %) in the sediments derived from accretionary complexes were extracted in step 2. This fact suggests that these sediments are influenced by bedded Mn deposits. Therefore, the chemical distribution obtained by the BCR protocol is a very important and useful parameter to identify complicated controlling factors of elemental concentrations in stream sediments.

Sequential extraction using the BCR scheme is useful not only to elucidate the detailed chemical species in sediments but also to recognize the contamination of Cr, Ni, Cu, Zn, Cd and Pb. The possibly contaminated sediments had a significantly high proportion of the total concentrations of Co (20 - 30 %), Ni (20 - 40 %) and Zn (40 - 70 %) in step 1 and those of Cr (30 - 50 %), Cu (30 - 60 %) and Pb (30 - 40 %) in step 3, compared with the other samples. However, the distributions of Mo, Sn, Sb and Bi obtained using the BCR scheme did not give sufficient information to assess the pollution. The contamination of these elements in sediments should be assessed using a statistical test on the bulk compositions as Ohta *et al.* (2005a) proposed.

**Acknowledgements:** The authors are grateful to Takashi Okai, Masumi Ujiie-Mikoshihara and Ran Kubota (Geological Survey of Japan, AIST) for their useful suggestions which improved the manuscript.

## References

- Bølviken, B., Bergström, J., Björklund, A., Kontio, M., Lehmuspelto, P., Lindholm, T., Magnusson, J., Ottesen, R. T., Steenfelt, A. and Volden, T., 1986. Geochemical Atlas of Northern Fennoscandia. Geological Surveys of Finland, Norway and Sweden, Helsinki, Trondheim and Stockholm, 19p. with 144 maps.
- Coetzee, P. P., Gouws, K., Plüddemann, S., Yacoby, M., Howell, S. and den Drijver, L. (1995) Evaluation of sequential extraction procedures for metal speciation in model sediments. *Wat. SA.*, **21**, 51-60.
- Crosland, A. R., McGrath, S. P. and Lane, P. W. (1993) An interlaboratory comparison of a standardized EDTA extraction procedure for the analysis of available trace elements in two quality-control soils. *Int. J. Environ. Anal. Chem.*, **51**, 153-160.
- Davidson, C. M., Thomas, R. P., McVey, S. E., Perala, R., Littlejohn, D. and Ure, A. M. (1994) Evaluation of a sequential extraction procedure for the speciation of heavy metals in sediments. *Anal. Chim. Acta*, **291**, 277-286.
- Davidson, C. M., Duncan, A. L., Littlejohn, D., Ure, A. M. and Garden, L. M. (1998) A critical evaluation of the three-stage BCR sequential extraction procedure to assess the potential mobility and toxicity of heavy metals in industrially-contaminated land. *Anal. Chim. Acta*, **363**, 45-55.
- Fauth, H., Hindel, R., Siewers, U. and Zinner, J. (1985) *Geochemischer Atlas Bundesrepublik Deutschland*. BGR, Hannover, 79 p.
- Gómez-Ariza, J. L., Giráldez, I., Sánchez-Rodas, D. and Morales, E. (1999) Metal readsorption and redistribution during the analytical fractionation of trace elements in oxic estuarine sediments. *Anal. Chim. Acta*, **399**, 295-307.
- Gustavsson, N., Bølviken, B., Smith, D. B. and Severson, R. C. (2001) *Geochemical landscapes of the conterminous United States – New map presentations for 22 elements*. USGS Prof. Paper 1648, 38 p.
- Hudson-Edwards, K. A., Macklin, M. G., Curtis, C. D. and Vaughan, D. J. (1996) Processes of formation and distribution of Pb-, Zn-, Cd-, and Cu-bearing minerals in the Tyne Basin, northeast England: Implications for metal-contaminated river systems. *Environ. Sci. Technol.*, **30**, 72-80.
- Imai, N. (1990) Multi-element analysis of rocks with the use of geological certified reference material by ICP-MS. *Anal. Sci.*, **6**, 389-395.

- Imai, N., Terashima, S., Itoh, S. and Ando, A. (1996) 1996 compilation of analytical data on nine GSJ geochemical reference samples, sedimentary rock series. *Geostand. Newsl.*, **20**, 165-216.
- Imai, N., Terashima, S., Ohta, A., Mikoshihara, M., Okai, T., Tachibana, Y., Togashi, S., Matsuhisa, Y., Kanai, Y. and Kamioka, H. (2004a) *Geochemical map of Japan*. Geological Survey of Japan, AIST, 209 p (in Japanese, with English abstr.).
- Imai, N., Terashima, S., Ohta, A., Mikoshihara, M., Okai, T., Tachibana, Y., Togashi, S., Matsuhisa, Y., Kanai, Y. and Kamioka, H. (2004b) *Database of elemental distribution (geochemical map) in Japan*. Available at <http://www.aist.go.jp/RIODB/Geochemmap/>.
- Kheboian, C. and Bauer, C. F. (1987) Accuracy of selective extraction procedures for metal speciation in model aquatic sediments. *Anal. Chem.*, **59**, 1417-1423.
- López-Sánchez, J. F., Rubio, R. and Rauret, G. (1993) Comparison of two sequential extraction procedures for trace-metal partitioning in sediments. *Int. J. Environ. Anal. Chem.*, **51**, 113-121.
- Nakazawa, K., Ichikawa, K. and Itihara, M. (1987) *Regional Geology of Japan Part 6 (KINKI)*. Kyoritsu Shuppan Co., Ltd. 310 p (in Japanese).
- Nirel, P. M. V. and Morel, F. M. M. (1990) Pitfalls of sequential extractions. *Wat. Res.* **24**, 1055-1056.
- Marin, B., Valladon, M., Polve, M. and Monaco, A. (1997) Reproducibility testing of a sequential extraction scheme for the determination of trace metal speciation in a marine reference sediment by inductively coupled plasma-mass spectrometry. *Anal. Chim. Acta*, **342**, 91-112.
- Martin, J. M., Nirel, P. and Thomas, A. J. (1987) Sequential extraction techniques: Promises and problems. *Mar. Chem.*, **22**, 313-341.
- Martin, R., Sanchez, D. M. and Gutierrez, A. M. (1998) Sequential extraction of U, Th, Ce, La and some heavy metals in sediments from Ortigas river, Spain. *Talanta*, **46**, 1115-1121.
- Mester, Z., Cremisini, C., Ghiara, E. and Morabito, R. (1998) Comparison of two sequential extraction procedures for metal fractionation in sediment samples. *Anal. Chim. Acta*, **359**, 133-142.
- Morillo, J., Usero, J. and Gracia, I. (2004) Heavy metal distribution in marine sediments from the southwest coast of Spain. *Chemosphere*, **55**, 431-442.
- Ohta, A., Imai, N., Okai, T., Endo, H., Kawanabe, S., Ishii, T., Taguchi, Y. and Kamioka, H. (2002) The characteristics of chemical distribution patterns in and around Yamagata city – Geochemical map in the southern area of Yamagata Basin –. *Chikyukagaku (Geochemistry)*, **36**, 109-125 (in Japanese, with English abstr.).
- Ohta, A., Imai, N., Okai, T., Endo, H., Ishii, T., Taguchi, Y., Kamioka, H., Mikoshihara (Ujiie), M. and Terashima, S. (2003) Investigation of elemental behaviors around the Sendai City based on geochemical maps utilizing stream sediments. *Earth Science*, **57**, 61-72 (in Japanese, with English abstr.).
- Ohta, A., Imai, N., Terashima, S., Tachibana, Y., Ikehara, K. and Nakajima, T. (2004a). Geochemical mapping in Hokuriku, Japan: Influence of surface geology, mineral occurrences and mass movement from terrestrial to marine environments. *Appl. Geochem.* **19**, 1453-1469.
- Ohta, A., Imai, N., Terashima, S. and Tachibana, Y. (2004b) Investigation of elemental behaviors in Chugoku region of Japan based on geochemical map utilizing stream sediments. *Chikyukagaku (Geochemistry)*, **38**, 203-222 (in Japanese, with English abstr.).
- Ohta, A., Imai, N., Terashima, S. and Tachibana, Y. (2005a) Application of multi-element statistical analysis for regional geochemical mapping in Central Japan. *Appl. Geochem.*, **20**, 1017-1037.
- Ohta, A., Imai, N., Terashima, S. and Tachibana, Y. (2005b) Influence of surface geology and mineral deposits on spatial distributions of elemental concentrations in stream sediments of Hokkaido, Japan. *J. Geochem. Explor.*, **86**, 86-103.
- Reimann, C., Åyräs, M., Chekushin, V., Bogatyrev, I., Boyd, R., Caritat, P. De, Dutter, R., Finne, T. E., Halleraker, J. H., Jæger, Ø., Kashulina, G., Lehto, O., Niskavaara, H., Pavlov, V., Räsänen, M. L., Strand, T. and Volden, T. (1998) *Environmental Geochemical Atlas of the Central Barents Region*. Geological Survey of Norway, Trondheim, Norway, 745 p.
- Sahuquillo, A., López-Sánchez, J. F., Rubio, R., Rauret, G., Thomas, R. P., Davidson, C. M. and Ure, A. M. (1999) Use of a certified reference material for extractable trace metals to assess sources of uncertainty in the BCR three-stage sequential extraction procedure. *Anal. Chim. Acta*, **382**, 317-327.
- Terashima, S. and Taniguchi, M. (1996) Evaluation of sequential extraction for speciation of arsenic and antimony in geological reference samples. *Bunseki Kagaku*, **45**, 1051-1058 (in Japanese, with English abstr.).
- Tessier, A., Campbell, P. G. C. and Bisson, M. (1979) Sequential extraction procedure for the speciation of particulate trace metals. *Anal. Chem.*, **51**, 844-851.
- Thomas, R. P., Ure, A. M., Davidson, C. M., Littlejohn, D., Rauret, G., Rubio, R. and López-Sánchez, J. F. (1994) Three-stage sequential extraction procedure for the determination of metals in river sediments. *Anal. Chim. Acta*, **286**, 423-429.
- Thalman, F., Schermann, O., Schroll, E. and Hausberger, G. (1988) *Geochemical Atlas of the Republic of Austria*. Geological Survey of Austria, 141 p. with 35 maps.
- Ujiie-Mikoshihara, M., Imai, N., Terashima, S., Tachibana, Y.

- and Okai, T. (2006) Geochemical mapping in northern Honshu, Japan. *Appl. Geochem.*, **21**, 492-514.
- Ure, A. M., Quevauviller, P. H., Muntau, H. and Griepink, B. (1993) Speciation of heavy metals in soils and sediments. An account of the improvement and harmonization of extraction techniques undertaken under the auspices of the BCR of the Commission of the European Communities. *Int. J. Environ. Anal. Chem.*, **51**, 135-151.
- Usero, J., Gamero, M., Morillo, J. and Gracia, I. (1998) Comparative study of three sequential extraction procedures for metals in marine sediments. *Environ. Int.*, **24**, 487-496.
- Weaver, T. A., Broxton, D. E., Bolivar, S. L. and Freeman, S. H. (1983) *The Geochemical Atlas of Alaska*. Geochemical Group, Earth and Space Sci. Div., Los Alamos Nat. Lab., GJBX-32(83) US DOE, 57 p
- Webb, J. S., Thornton, I., Thompson, M., Howarth, R. J. and Lowenstein, P. L. (1978) *The Wolfson Geochemical Atlas of England and Wales*. Oxford Univ. Press, Oxford, 74 p.
- Whalley, C. and Grant, A. (1994) Assessment of the phase selectivity of the European Community Bureau of Reference (BCR) sequential extraction procedure for metals in sediment. *Anal. Chim. Acta*, **291**, 287-295.
- Yuan, C., Shi, J., He, B., Liu, J., Liang, L. and Jiang, G. (2004) Speciation of heavy metals in marine sediments from the East China Sea by ICP-MS with sequential extraction. *Environ Int.*, **30**, 769-783.

Received March 26, 2007

Accepted October 11, 2007

## 逐次溶解法を用いた元素存在形態別地球化学図作成のための予察的研究

太田充恒・今井 登・寺島 滋・立花好子

### 要 旨

有害元素の潜在的危険性や堆積物中の金属元素の存在形態・移動性などを評価するにあたり、逐次溶解法は有効である。本研究では、The Community Bureau of Reference (BCR) によって開発された抽出手順（手順1～4）を、主として全国地球化学図作成用に採取された日本の河川堆積物へ適用することを試みた。BCR法を30河川堆積物中の51元素の抽出に適用したところ、良好な結果を得たので報告する。BCR法は対象とした相（物質）に含まれる元素を、酢酸（手順1）、塩酸ヒドロキシルアミン（手順2）、過酸化水素・酢酸アンモニウム（手順3）、フッ酸・過塩素酸・硝酸（手順4）を用いて抽出する事を目的としている。BCR法を用いた繰り返し測定の実験については、3種類の地球化学標準物質（JSd-1, -2, -3）を用いて検討を行った。その結果、各抽出段階における元素濃度の分析誤差はおおむね10～25%以下で、回収量（各手順で抽出された元素濃度の合計）は、ほとんどの場合80～130%であった。各元素の逐次溶解法の結果は、河川堆積物の供給源である地質・岩相が様々に異なっても違いはほとんど見られなかった。この結果は、地質の違いが河川堆積物中の元素存在形態に与える影響は少ないことを示している。これに対し、都市域で採取された河川堆積物は、堆積岩が背景地質として分布する地域で採取された試料であるが、他の試料とは明らかに異なる抽出結果を示した。都市域で採取された試料は、コバルト、ニッケル、亜鉛、カドミウムが非常に高い割合で手順1において抽出され、クロム、銅、鉛が手順3で抽出されるなどの特徴を示し、金属元素汚染の結果を反映していると考えられる。鉱山の近くで採取された河川堆積物もまた、特徴的な抽出結果を示した。本研究の結果より、BCR法を用いた逐次溶解法は、クロム、ニッケル、銅、亜鉛、カドミウム、鉛汚染の見極めや、亜鉛、カドミウム、鉛を産出する鉱床探査に大変有効であることが明らかとなった。

Appendix A1 Bulk compositions of stream sediment samples.

Sample		22007	22030	25005	25010	25023	28111	31021	32049	33001	33008	33019	33051	34032	34035
Geology <sup>a</sup>		Gr	Fv	Acc	HMt	Sed_u	Sed_n	HMt	Dep	Sed_n	Sed_u	Fv	Acc	Sed_u	Sed_n
Li	ppm	33.6	25.6	60.3	25.8	38.9	44.7	48.9	60.4	32.5	51.7	58.0	63.6	20.7	18.6
Be	ppm	3.95	1.78	2.50	1.16	1.48	1.50	2.26	2.23	1.88	2.17	2.42	2.22	2.26	1.02
Na	%	2.85	1.11	1.28	1.57	2.82	1.67	1.33	0.694	1.97	1.22	1.16	0.525	0.803	0.732
Mg	%	0.137	0.265	0.769	2.66	1.04	0.800	1.50	0.754	0.365	0.980	0.446	0.820	0.749	0.533
Al	%	5.04	6.00	8.86	9.23	4.07	3.76	5.86	5.54	6.91	6.21	3.26	3.65	2.35	1.98
P (×100)	%	1.19	3.33	2.91	5.57	24.0	4.15	8.77	5.70	2.13	53.1	2.96	4.14	15.1	3.81
K	%	2.68	3.07	2.39	1.05	1.45	1.73	1.70	2.18	2.13	1.59	2.10	1.79	1.09	1.58
Ca	%	0.582	0.502	0.193	2.94	0.944	0.620	0.790	0.395	1.06	1.70	0.363	0.103	0.888	0.341
Sc	ppm	3.23	5.48	10.4	22.1	6.95	7.00	9.85	8.42	8.69	11.7	5.38	6.76	6.21	4.57
Ti (×10)	%	1.37	3.88	2.34	5.49	2.88	2.43	3.92	1.97	6.87	3.93	2.44	2.26	3.95	8.56
V	ppm	22.0	39.9	66.5	171	57.9	59.8	112	66.5	49.6	79.2	42.5	90.9	84.7	64.1
Cr	ppm	7.79	9.92	75.7	425	121	77.5	106	44.7	39.6	254	36.3	72.9	212	32.5
Mn (×100)	%	4.72	7.21	5.58	14.1	8.43	3.47	17.9	23.6	6.86	6.37	5.16	10.3	7.27	5.78
Fe	%	1.59	1.89	2.89	5.28	3.25	1.99	4.24	4.05	2.25	4.28	1.99	3.11	6.16	2.06
Co	ppm	2.15	4.15	9.53	29.8	12.1	8.66	23.2	28.3	6.51	26.3	8.11	13.3	13.7	7.90
Ni	ppm	3.65	7.54	30.8	133	47.3	25.8	66.7	18.0	12.1	113	15.8	36.1	138	14.6
Cu	ppm	12.4	33.1	42.6	80.3	123	19.4	52.8	481	12.4	652	29.5	50.1	219	19.7
Zn	ppm	87.2	117	107	118	596	92.8	190	2637	81.5	1722	135	111	697	73.4
Ga	ppm	22.5	15.7	23.7	16.3	16.0	15.5	20.8	18.7	17.6	23.9	22.2	18.0	11.8	9.54
Rb	ppm	174	195	130	31.7	74.7	94.3	72.9	175	122	127	166	132	68.0	78.0
Sr	ppm	31.2	68.7	57.7	137	74.3	110	92.1	65.5	151	123	55.2	25.1	70.6	52.0
Y	ppm	38.2	17.9	8.40	24.0	16.4	13.7	22.0	16.8	18.0	34.4	21.5	5.69	25.3	9.73
Zr	ppm	254	78.2	44.6	16.4	60.1	33.0	58.0	69.2	89.3	55.5	86.0	53.8	53.8	52.2
Nb	ppm	15.4	15.5	10.2	8.11	8.97	6.79	8.86	6.22	16.0	14.0	12.0	7.28	9.54	13.4
Mo	ppm	2.66	0.747	2.88	1.45	5.06	0.705	2.26	1.69	0.754	6.01	0.930	1.61	1.63	0.464
Cd	ppm	0.207	0.378	0.090	0.166	0.518	0.058	0.591	7.834	0.095	1.686	0.196	0.128	1.199	0.066
Sn	ppm	6.40	5.35	3.33	7.07	7.72	2.00	4.10	72.6	2.46	60.0	3.33	2.55	38.2	11.2
Sb	ppm	0.311	0.425	1.21	0.411	2.77	0.435	1.10	6.88	0.702	5.76	1.32	1.18	9.60	0.646
Cs	ppm	4.21	5.18	8.54	2.95	5.29	2.89	6.60	16.0	5.14	6.86	8.41	7.20	2.94	2.10
Ba	ppm	172	598	417	236	342	435	433	438	589	855	597	498	420	477
La	ppm	32.9	16.1	11.0	14.7	17.7	42.6	22.8	17.6	26.3	46.1	23.7	18.5	28.4	20.1
Ce	ppm	79.8	28.2	21.6	28.9	21.8	78.9	41.2	36.3	46.8	72.3	30.9	37.6	49.2	38.0
Pr	ppm	9.16	3.49	2.72	3.52	3.67	8.62	5.46	3.84	5.40	10.63	4.92	4.20	6.24	4.61
Nd	ppm	35.6	13.3	10.9	15.0	14.5	31.2	21.9	15.4	19.4	41.1	18.8	15.9	23.5	17.8
Sm	ppm	7.94	2.77	2.46	3.47	2.84	4.98	4.62	3.13	3.42	8.05	3.71	2.75	4.71	3.42
Eu	ppm	0.354	0.524	0.483	0.979	0.576	0.704	0.945	0.687	0.989	1.285	0.655	0.490	0.552	0.446
Gd	ppm	6.63	2.64	2.24	3.77	2.80	3.90	4.28	2.93	3.04	6.91	3.29	1.85	4.45	2.74
Tb	ppm	1.20	0.491	0.365	0.728	0.471	0.561	0.759	0.498	0.525	1.15	0.579	0.267	0.811	0.403
Dy	ppm	6.42	2.66	1.68	3.85	2.45	2.62	3.83	2.53	2.77	5.77	3.03	1.09	4.24	1.84
Ho	ppm	1.30	0.535	0.288	0.787	0.475	0.462	0.727	0.492	0.563	1.08	0.581	0.190	0.838	0.330
Er	ppm	4.32	1.64	0.80	2.34	1.38	1.29	2.08	1.46	1.64	3.12	1.81	0.579	2.49	0.913
Tm	ppm	0.811	0.270	0.117	0.365	0.225	0.197	0.321	0.238	0.278	0.483	0.296	0.100	0.390	0.155
Yb	ppm	5.47	1.78	0.69	2.20	1.45	1.19	1.90	1.51	1.89	2.97	1.93	0.638	2.43	1.00
Lu	ppm	0.962	0.271	0.103	0.306	0.224	0.167	0.273	0.233	0.282	0.424	0.286	0.101	0.343	0.150
Hf	ppm	11.9	2.35	1.39	0.47	1.63	0.985	1.64	1.94	2.37	1.72	2.27	1.40	1.55	1.62
Ta	ppm	1.88	1.26	1.08	0.688	0.870	0.500	0.830	1.24	0.789	1.55	0.649	0.516	0.708	0.933
Tl	ppm	0.912	1.294	0.986	0.374	0.585	0.508	0.789	1.55	0.748	1.01	0.929	0.813	0.455	0.490
Pb	ppm	35.1	45.9	25.9	21.0	63.3	17.3	59.6	469	20.4	186	31.5	20.9	658	29.1
Bi	ppm	0.273	0.527	0.397	0.248	1.249	0.104	0.805	2.733	0.207	2.94	0.218	0.347	0.668	0.166
Th	ppm	48.1	9.38	8.95	3.92	5.27	9.85	6.79	7.87	7.60	15.4	7.77	6.00	11.0	9.19
U	ppm	9.34	3.61	1.90	0.781	0.83	1.48	2.36	1.97	1.83	4.22	2.17	1.75	2.10	1.83

<sup>a</sup> The abbreviations are the same as Table 1.



Appendix A1 Continued.

Sample		35014	35035	36120	42002	43028	44030	44045	49050	53011	54029	73028	84002	57
Geology <sup>a</sup>		LMT	Gr	Mv	Um	Acc	Fv	LMT	Dep	Mv	Um	Dep	Um	Mv
Li	ppm	18.7	24.6	7.23	19.4	37.8	28.1	37.3	23.7	23.0	28.4	28.7	9.53	9.01
Be	ppm	0.861	2.36	0.506	1.08	1.70	2.38	1.52	1.39	0.982	0.966	0.953	0.340	0.463
Na	%	0.729	2.35	1.86	0.954	1.63	1.68	0.854	2.16	1.11	1.18	1.32	0.661	1.13
Mg	%	0.536	1.32	4.75	6.55	1.20	0.343	1.76	1.88	3.09	6.64	1.00	8.51	2.55
Al	%	2.79	6.11	8.63	6.20	4.19	3.31	3.98	4.07	6.97	6.74	7.28	2.96	7.03
P (×100)	%	2.23	9.75	9.88	3.74	4.19	1.06	5.94	6.80	6.36	4.65	7.28	2.16	4.23
K	%	0.933	1.82	0.565	1.05	2.18	2.82	1.24	1.94	0.793	0.980	1.28	0.255	0.610
Ca	%	0.424	2.57	6.57	1.72	0.477	0.177	0.938	2.21	2.40	1.99	1.76	1.48	2.22
Sc	ppm	3.44	29.4	31.7	18.6	7.59	4.34	11.2	10.2	19.5	16.2	11.2	15.1	26.4
Ti (×10)	%	1.40	5.24	7.47	3.81	3.78	1.77	8.36	5.03	10.3	3.12	2.91	1.59	4.79
V	ppm	33.5	64.8	349	115	105	31.1	156	129	257	101	101	72.2	188
Cr	ppm	23.3	16.2	158	1941	60.3	18.0	102	56.0	159	1099	47.4	986	51.6
Mn (×100)	%	8.53	12.1	15.3	15.9	6.39	3.66	25.7	9.59	14.3	9.68	22.6	10.6	8.09
Fe	%	1.28	3.72	9.08	6.60	3.17	1.62	5.50	4.17	7.18	5.11	5.22	5.69	8.75
Co	ppm	4.73	7.45	47.7	55.5	11.4	3.35	16.7	12.1	29.9	56.4	16.5	111	17.2
Ni	ppm	11.1	6.06	75.4	699	24.1	6.21	35.7	21.7	58.7	785	23.6	2401	16.9
Cu	ppm	20.9	11.3	170	47.2	30.5	9.87	47.6	47.8	33.8	32.4	523	19.7	23.5
Zn	ppm	37.6	80.0	98.4	111	70.9	90.9	148	397	153	80.9	5382	68.2	61.6
Ga	ppm	7.56	33.9	17.2	12.5	15.8	16.9	14.8	15.6	19.6	13.1	14.7	6.32	18.4
Rb	ppm	45.3	82.6	11.7	47.1	90.4	186	81.0	83.7	23.9	51.5	50.9	14.4	20.9
Sr	ppm	79.8	163	355	91.4	91.5	32.1	119	195	201	169	99.2	69.0	131
Y	ppm	5.76	106	22.8	17.9	9.04	15.1	21.1	18.5	11.0	13.7	38.5	8.43	16.0
Zr	ppm	6.08	139	75.4	57.0	58.8	59.5	19.7	34.1	108	46.7	67.6	11.1	81.3
Nb	ppm	3.32	17.8	1.43	5.15	7.14	13.2	10.8	8.36	7.73	4.90	5.02	2.47	3.49
Mo	ppm	0.443	0.692	1.10	0.906	1.10	0.565	1.20	2.94	1.05	0.679	8.39	0.697	2.64
Cd	ppm	0.03	0.13	0.07	0.21	0.08	0.15	0.10	0.95	0.13	0.11	19.72	0.07	0.06
Sn	ppm	1.10	3.62	0.671	2.09	1.76	5.35	1.64	2.99	1.65	1.24	168	0.509	2.17
Sb	ppm	0.126	0.356	0.084	0.830	0.91	1.02	0.652	1.24	0.570	1.31	123	0.087	0.221
Cs	ppm	2.06	2.28	0.71	3.64	4.45	5.34	3.90	4.30	1.56	2.94	3.83	0.990	1.31
Ba	ppm	302	485	188	238	446	425	452	492	297	246	525	91.8	327
La	ppm	15.8	390	6.62	13.4	16.0	18.2	37.7	38.1	11.1	14.9	12.6	6.61	7.60
Ce	ppm	33.9	758	16.6	29.7	29.5	40.6	76.3	72.0	20.0	31.2	19.4	14.6	17.0
Pr	ppm	3.60	69.7	2.49	3.30	3.64	4.29	8.64	8.02	2.59	3.61	4.17	1.74	1.98
Nd	ppm	13.7	251	12.6	13.6	13.8	16.5	33.1	29.3	10.2	15.0	19.3	7.06	8.62
Sm	ppm	2.47	40.4	3.39	3.03	2.60	3.54	6.06	5.21	2.07	3.10	5.20	1.52	2.19
Eu	ppm	0.433	1.58	1.08	0.715	0.538	0.287	1.24	0.948	0.680	0.808	1.53	0.377	0.690
Gd	ppm	1.97	33.8	3.81	2.97	2.21	3.21	5.01	4.29	2.04	2.82	5.30	1.45	2.31
Tb	ppm	0.274	4.54	0.698	0.525	0.348	0.546	0.789	0.664	0.355	0.478	1.09	0.267	0.446
Dy	ppm	1.16	20.3	3.81	2.83	1.65	2.77	3.90	3.24	1.86	2.41	6.12	1.37	2.50
Ho	ppm	0.196	3.43	0.758	0.574	0.306	0.533	0.713	0.625	0.367	0.448	1.235	0.279	0.521
Er	ppm	0.500	8.86	2.24	1.72	0.911	1.61	2.04	1.84	1.09	1.27	3.74	0.84	1.35
Tm	ppm	0.076	1.34	0.347	0.278	0.146	0.261	0.311	0.288	0.174	0.189	0.602	0.129	0.260
Yb	ppm	0.478	8.39	2.16	1.78	0.929	1.65	1.84	1.85	1.11	1.11	3.69	0.82	1.74
Lu	ppm	0.061	1.22	0.324	0.262	0.132	0.244	0.259	0.272	0.173	0.168	0.566	0.124	0.258
Hf	ppm	0.176	4.92	1.97	1.57	1.61	2.31	0.547	1.18	2.38	1.20	1.86	0.31	2.08
Ta	ppm	0.185	1.34	0.127	0.549	0.480	0.828	0.992	0.579	0.563	0.564	0.432	0.417	0.280
Tl	ppm	0.300	0.464		0.334	0.623	1.47	0.539	0.664	0.186	0.317	6.54	0.082	0.532
Pb	ppm	13.1	20.0	4.75	22.9	17.8	46.2	18.3	1037	16.8	10.1	7594	7.00	9.08
Bi	ppm	0.139	0.190	0.036	0.389	0.222	0.270	0.257	1.53	0.094	0.266	87.0	0.067	10.3
Th	ppm	5.58	104	0.977	4.37	5.38	10.6	10.2	13.9	2.50	3.26	2.39	2.12	2.61
U	ppm	0.934	9.10	0.366	1.13	1.50	2.83	1.32	1.98	0.846	0.803	0.778	0.379	0.563

<sup>a</sup> The abbreviations are the same as Table 1.

Appendix A2 Extraction concentration by the single extraction using 0.1M HCl.

Sample		22007	22030	25005	25010	25023	28111	31021	32049	33001	33008	33019	33051	34032	34035
Geology <sup>a</sup>		Gr	Fv	Acc	HMt	Sed_u	Sed_n	HMt	Dep	Sed_n	Sed_u	Fv	Acc	Sed_u	Sed_n
Li	ppm	0.326	0.097	0.184	0.147	0.603	0.362	0.261	0.262	0.289	0.703	0.245	0.095	0.224	0.097
Be	ppm	0.176	0.356	0.146	0.104	0.264	0.138	0.580	0.363	0.217	0.449	0.422	0.091	0.162	0.093
Na	%	0.007	0.008	0.007	0.007	1.982	0.037	0.005	0.005	0.012	0.031	0.011	0.015	0.046	0.038
Mg	%	0.011	0.011	0.016	0.042	0.504	0.041	0.043	0.035	0.040	0.082	0.025	0.019	0.063	0.033
Al	%	0.023	0.026	0.040	0.048	0.247	0.035	0.125	0.068	0.033	0.337	0.057	0.021	0.075	0.017
P (×100)	%	0.157	0.559	0.275	1.27	6.96	0.882	0.768	0.964	0.703	19.8	0.493	0.214	0.777	0.847
K	%	0.003	0.009	0.007	0.006	0.138	0.012	0.009	0.006	0.015	0.026	0.010	0.005	0.015	0.009
Ca	%	0.051	0.086	0.106	0.158	0.684	0.037	0.296	0.306	0.143	0.759	0.200	0.056	0.311	0.047
Sc	ppm														
Ti (×10)	%	0.002	<0.001	<0.001	0.004	0.013	<0.001	0.005	0.005	<0.001	0.015	0.002	0.001	0.002	0.002
V	ppm	<0.001	<0.001	2.37	3.56	5.97	3.56	<0.001	6.32	0.83	7.81	<0.001	0.762	5.55	5.15
Cr	ppm	1.10	0.310	1.72	1.42	4.54	<0.001	0.783	0.494	0.851	24.9	0.488	0.270	3.87	1.01
Mn (×100)	%	0.798	2.02	0.790	3.11	6.27	0.232	6.09	3.42	1.34	2.05	2.97	1.20	2.11	0.542
Fe	%	0.005	0.064	0.004	0.018	0.391	0.049	0.091	0.015	0.028	0.285	0.052	0.005	0.075	0.008
Co	ppm	0.266	0.733	1.02	3.00	2.22	0.961	4.71	2.78	1.25	8.80	1.16	0.980	4.94	2.23
Ni	ppm	0.608	1.75	1.52	6.10	8.84	1.02	6.28	1.93	1.86	39.3	1.14	1.72	86.0	2.43
Cu	ppm	5.37	9.33	3.24	20.0	55.0	4.93	18.4	51.2	4.81	359	9.63	5.21	119	10.8
Zn	ppm	11.0	24.3	5.43	16.6	317	10.9	21.4	232	26.8	1050	20.3	16.8	342	27.5
Ga	ppm														
Rb	ppm	0.371	0.626	0.725	0.384	0.976	0.363	0.991	0.693	0.894	1.18	0.950	0.378	0.510	0.310
Sr	ppm	2.24	4.99	10.4	10.1	70.4	5.07	20.3	11.9	9.10	45.3	11.6	5.51	16.3	4.32
Y	ppm														
Zr	ppm														
Nb	ppm														
Mo	ppm	0.038	0.086	0.046	0.052	0.149	0.487	0.044	0.064	0.299	0.167	0.034	0.029	0.071	0.048
Cd	ppm	0.103	0.359	0.027	0.092	0.393	0.027	0.504	1.908	0.038	1.44	0.131	0.063	0.730	0.038
Sn	ppm	0.025	<0.001	<0.001	<0.001	0.056	<0.001	<0.001	0.219	<0.001	1.61	<0.001	<0.001	<0.001	<0.001
Sb	ppm	0.009	0.006	0.002	0.006	0.074	0.005	0.008	0.047	0.011	0.355	0.018	0.005	0.038	0.002
Cs	ppm	0.033	0.044	0.100	0.025	0.010	0.010	0.085	0.123	0.038	0.051	0.073	0.044	0.026	0.010
Ba	ppm	15.0	34.3	60.9	25.3	77.9	5.13	63.1	57.0	20.4	166	58.5	22.4	19.3	4.79
La	ppm	2.99	5.36	1.08	3.21	10.5	1.94	10.9	4.20	1.33	9.92	8.29	0.387	2.57	1.22
Ce	ppm	3.54	9.32	1.13	5.68	18.1	3.15	17.5	6.46	2.70	20.2	14.0	0.825	5.58	2.53
Pr	ppm	0.687	1.07	0.310	0.621	1.81	0.455	2.23	0.887	0.330	2.17	1.69	0.110	0.592	0.270
Nd	ppm	2.74	4.03	1.49	2.42	6.92	1.85	8.83	3.72	1.32	8.67	6.46	0.495	2.38	1.10
Sm	ppm	0.701	0.780	0.463	0.479	1.36	0.416	1.82	0.824	0.283	1.86	1.28	0.153	0.507	0.218
Eu	ppm	0.035	0.104	0.108	0.121	0.257	0.095	0.374	0.162	0.053	0.284	0.214	0.038	0.074	0.046
Gd	ppm	0.796	0.811	0.516	0.574	1.33	0.473	1.96	0.932	0.308	1.77	1.29	0.176	0.517	0.232
Tb	ppm	0.155	0.147	0.089	0.100	0.230	0.081	0.356	0.154	0.051	0.293	0.225	0.031	0.096	0.041
Dy	ppm	0.815	0.774	0.362	0.526	1.18	0.372	1.74	0.723	0.264	1.58	1.11	0.135	0.470	0.207
Ho	ppm	0.164	0.153	0.057	0.103	0.221	0.067	0.334	0.130	0.049	0.297	0.207	0.020	0.094	0.040
Er	ppm	0.490	0.426	0.124	0.285	0.619	0.169	0.867	0.342	0.134	0.857	0.546	0.048	0.266	0.112
Tm	ppm	0.076	0.065	0.014	0.044	0.087	0.022	0.117	0.046	0.021	0.129	0.078	0.008	0.037	0.017
Yb	ppm	0.453	0.375	0.064	0.239	0.533	0.120	0.615	0.229	0.118	0.750	0.442	0.041	0.223	0.092
Lu	ppm	0.063	0.049	0.008	0.032	0.079	0.017	0.079	0.033	0.016	0.106	0.056	0.006	0.030	0.013
Hf	ppm														
Ta	ppm														
Tl	ppm	0.005	0.012	0.008	0.008	0.031	<0.001	0.033	0.008	0.006	0.164	0.019	0.006	0.011	0.001
Pb	ppm	5.56	19.6	3.92	8.25	30.4	3.02	24.5	74.2	6.28	86.8	16.2	5.33	151	6.40
Bi	ppm	0.027	0.044	0.004	0.007	0.097	0.009	0.026	0.289	0.026	0.192	0.021	0.001	0.009	0.005
Th	ppm	0.004	0.010	0.004	0.010	0.083	0.014	0.035	0.007	0.024	0.101	0.016	0.001	0.011	0.003
U	ppm	0.388	0.350	0.028	0.095	0.506	0.172	0.461	0.141	0.098	1.090	0.275	0.062	0.288	0.123

<sup>a</sup> The abbreviations are the same as Table 1.

Appendix A2 Continued.

Sample		35014	35035	36120	42002	43028	44030	44045	49050	53011	54029	73028	84002	57
Geology <sup>a</sup>		LMt	Gr	Mv	Um	Acc	Fv	LMt	Dep	Mv	Um	Dep	Um	Mv
Li	ppm	0.244	0.485	0.050	0.139	0.218	0.188	0.809	0.516	0.149	0.168	2.947	0.122	
Be	ppm	0.063	0.053	0.005	0.130	0.164	0.250	0.087	0.116	0.225	0.087	0.183	0.026	
Na	%	<0.001	0.001	0.005	0.016	0.006	0.005	0.005	0.004	0.006	0.006	0.013	0.004	
Mg	%	0.007	0.009	0.007	0.083	0.025	0.005	0.051	0.017	0.070	0.216	0.052	0.117	
Al	%	0.019	0.044	0.028	0.045	0.046	0.058	0.080	0.048	0.055	0.038	0.243	0.055	
P (×100)	%	0.297	3.31	1.29	0.192	1.01	0.227	1.85	2.44	0.585	1.86	1.35	0.253	
K	%	0.003	0.005	0.002	0.006	0.005	0.005	0.008	0.006	0.010	0.005	0.010	0.004	
Ca	%	0.026	0.121	0.060	0.118	0.130	0.044	0.129	0.171	0.218	0.667	0.564	0.057	
Sc	ppm													
Ti (×10)	%	0.001	0.009	0.010	0.001	<0.001	0.001	0.020	0.006	0.002	0.003	0.016	0.003	
V	ppm	1.68	8.31	23.0	1.26	4.84	2.48	2.82	6.27	<0.001	7.98	3.20	4.64	
Cr	ppm	0.462	0.744	0.809	2.10	0.898	0.255	1.49	1.96	0.867	2.67	3.37	3.03	
Mn (×100)	%	0.728	0.457	0.155	2.33	1.46	0.689	1.02	1.03	3.38	1.66	9.59	0.689	
Fe	%	0.004	0.017	0.014	0.015	0.021	0.008	0.067	0.012	0.067	0.034	0.202	0.033	
Co	ppm	0.909	0.460	0.246	5.23	1.99	0.327	2.79	0.923	2.47	4.82	3.56	4.36	
Ni	ppm	1.06	0.632	3.67	38.1	5.11	0.353	2.44	1.25	1.01	45.6	4.99	22.8	
Cu	ppm	2.86	4.51	10.9	9.66	4.03	1.62	4.79	47.0	6.91	6.02	222	2.40	
Zn	ppm	6.41	3.00	4.19	23.2	9.11	8.90	21.0	84.3	22.6	4.65	854	5.15	
Ga	ppm													
Rb	ppm	0.408	1.08	0.108	0.340	0.534	0.862	0.947	0.818	0.714	0.705	1.28	0.200	
Sr	ppm	1.36	2.74	2.16	7.06	7.24	2.91	7.10	5.69	23.2	32.1	12.2	2.89	
Y	ppm													
Zr	ppm													
Nb	ppm													
Mo	ppm	0.014	0.017	0.026	0.024	0.083	0.050	0.037	0.079	0.086	0.074	0.618	0.021	
Cd	ppm	0.024	0.012	0.006	0.103	0.030	0.056	0.034	0.712	0.036	0.042	7.028	0.015	
Sn	ppm	<0.001	<0.001	<0.001	<0.001	<0.001	<0.001	<0.001	0.070	0.044	<0.001	5.068	<0.001	
Sb	ppm	0.005	0.003	0.005	0.005	0.007	0.005	0.005	0.070	0.009	0.007	2.533	0.003	
Cs	ppm	0.036	0.046	0.011	0.022	0.089	0.078	0.060	0.409	0.024	0.184	0.229	0.020	
Ba	ppm	7.51	10.5	2.70	29.5	34.7	15.3	24.9	21.5	72.2	17.0	47.2	11.3	
La	ppm	0.485	3.70	0.943	1.61	1.39	3.70	1.37	2.42	1.50	1.15	4.60	0.264	
Ce	ppm	0.818	5.36	2.41	2.15	2.63	4.62	2.34	4.69	2.92	2.55	7.48	0.506	
Pr	ppm	0.116	0.964	0.354	0.355	0.420	0.858	0.362	0.606	0.361	0.342	1.61	0.073	
Nd	ppm	0.480	4.37	1.76	1.50	1.96	3.42	1.60	2.50	1.49	1.59	7.68	0.327	
Sm	ppm	0.115	1.23	0.423	0.306	0.505	0.732	0.394	0.519	0.321	0.403	2.016	0.094	
Eu	ppm	0.036	0.071	0.076	0.075	0.114	0.053	0.096	0.075	0.093	0.092	0.572	0.015	
Gd	ppm	0.141	1.37	0.427	0.358	0.499	0.745	0.416	0.506	0.327	0.414	2.506	0.100	
Tb	ppm	0.028	0.277	0.072	0.071	0.093	0.115	0.083	0.091	0.060	0.073	0.459	0.019	
Dy	ppm	0.158	1.48	0.348	0.333	0.422	0.489	0.444	0.422	0.309	0.358	2.458	0.100	
Ho	ppm	0.031	0.295	0.066	0.062	0.072	0.084	0.078	0.082	0.055	0.064	0.497	0.020	
Er	ppm	0.073	0.845	0.177	0.160	0.185	0.196	0.217	0.203	0.171	0.176	1.497	0.053	
Tm	ppm	0.013	0.119	0.024	0.022	0.023	0.025	0.028	0.029	0.025	0.024	0.219	0.008	
Yb	ppm	0.070	0.675	0.130	0.119	0.128	0.147	0.157	0.173	0.148	0.132	1.333	0.045	
Lu	ppm	0.010	0.095	0.018	0.017	0.016	0.021	0.022	0.023	0.021	0.018	0.199	0.007	
Hf	ppm													
Ta	ppm													
Tl	ppm	0.009	0.005	<0.001	0.005	0.006	0.009	0.008	0.085	0.011	0.009	1.495	0.002	
Pb	ppm	3.52	2.31	0.57	9.43	3.20	14.8	3.04	642	2.56	3.74	5418	1.38	
Bi	ppm	0.019	0.013	0.002	0.004	0.007	0.013	0.015	0.268	0.002	0.015	4.62	0.001	
Th	ppm	0.005	0.130	0.016	0.003	0.025	0.033	0.014	0.032	0.004	0.020	0.043	0.003	
U	ppm	0.068	0.194	0.013	0.055	0.057	0.184	0.083	0.170	0.139	0.042	0.221	0.060	

<sup>a</sup> The abbreviations are the same as Table 1.

Appendix B1 Results of analysis of the extracts in step 1 obtained by the BCR scheme.

Sample		22007	22030	25005	25010	25023	28111	31021	32049	33001	33008	33019	33051	34032	34035
Geology <sup>a</sup>		Gr	Fv	Acc	HMt	Sed_u	Sed_n	HMt	Dep	Sed_n	Sed_u	Fv	Acc	Sed_u	Sed_n
Li	ppm	0.14	0.077	0.12	0.052	0.95	0.25	0.10	0.56	0.16	0.65	0.18	0.061	0.23	0.087
Be	ppm	0.19	0.24	0.10	0.065	0.15	0.077	0.24	0.29	0.11	0.12	0.23	0.072	0.093	0.081
Na	%	0.004	0.001	0.002	<0.001	1.8	0.040	0.002	0.003	0.006	0.032	<0.001		0.046	0.030
Mg	%	0.009	0.006	0.010	0.032	0.36	0.026	0.028	0.021	0.016	0.10	0.016	0.017	0.050	0.040
Al	%	0.010	0.007	0.006	0.006	0.043	0.008	0.014	0.017	0.004	0.057	0.006	0.004	0.015	0.005
P (×100)	%	0.014	0.047	0.14	0.61	0.29	0.23	0.034	0.12	0.077	1.18	0.038	0.12	0.079	0.44
K	%	0.002	0.009	0.005	0.003	0.18	0.010	0.009	0.004	0.008	0.023	0.006	0.002	0.013	0.006
Ca	%	0.042	0.087	0.090	0.12	0.62	0.026	0.27	0.13	0.082	0.62	0.16	0.039	0.32	0.033
Sc	ppm	0.022	n.d.	0.010	0.020	0.149	n.d.	n.d.	0.022	0.018	0.060	0.043	0.012	0.007	0.008
Ti (×10)	%	<0.001	<0.001	<0.001	<0.001	<0.001	<0.001	<0.001	<0.001	<0.001	<0.001	0.001	<0.001	<0.001	<0.001
V	ppm	1.2	0.65	0.92	2.1	4.6	1.0	0.48	0.36	0.81	2.39	1.4	0.43	0.52	1.2
Cr	ppm	0.1	0.038	0.042	0.3	0.9	0.066	0.1	<0.001	0.048	1.4	0.056	n.d.	1.1	0.009
Mn (×100)	%	0.55	1.4	0.38	1.8	3.7	0.12	5.4	5.0	0.55	1.7	1.8	1.1	1.5	0.59
Fe	%	n.d.	<0.001	0.001	0.027	0.021	0.027	0.006	0.018	0.001	0.103	n.d.	0.016	0.008	0.023
Co	ppm	0.31	0.69	0.68	3.0	2.5	0.70	2.3	2.4	0.62	7.0	0.93	0.72	4.3	2.3
Ni	ppm	0.29	0.23	0.42	5.2	7.5	0.62	3.4	2.0	0.45	31	0.52	1.1	58	1.8
Cu	ppm	2.5	2.9	0.74	7.3	17	1.6	1.4	174	0.93	129	2.1	1.9	34	5.3
Zn	ppm	12	16	2.1	13	306	7.2	10	1079	5.4	1248	12	7.9	272	23
Ga	ppm	0.027	0.014	0.008	0.016	0.034	0.007	0.014	0.101	0.004	0.070	0.027	0.026	0.010	0.033
Rb	ppm	0.31	0.33	0.24	0.22	0.60	0.11	0.35	0.29	0.15	0.47	0.55	0.15	0.25	0.01
Sr	ppm	2.1	4.6	8.4	7.4	59	3.8	16	6.7	4.4	30	9.3	2.4	15	3.8
Y	ppm	2.4	0.48	0.22	0.19	1.1	0.24	0.37	0.41	0.04	0.68	0.58	0.09	0.30	0.29
Zr	ppm	0.002	0.013	0.008	n.d.	0.056	0.012	0.040	0.068	0.026	0.050	0.009	n.d.	0.014	n.d.
Nb	ppm	n.d.	n.d.	0.001	n.d.	<0.001	0.003	0.002	<0.001	n.d.	0.002	n.d.	n.d.	0.004	n.d.
Mo	ppm	0.015	n.d.	n.d.	0.026	0.004	n.d.	n.d.	<0.001	n.d.	0.043	0.011	0.015	0.001	0.015
Cd	ppm	0.088	0.63	0.017	0.069	0.37	0.015	0.272	4.3	0.019	0.82	0.087	0.036	0.61	0.026
Sn	ppm	n.d.	0.004	n.d.	n.d.	n.d.	n.d.	n.d.	0.046	n.d.	0.056	n.d.	n.d.	n.d.	n.d.
Sb	ppm	0.005	0.006	0.002	0.030	0.13	0.005	0.009	0.013	0.006	0.16	0.010	<0.001	0.17	0.006
Cs	ppm	0.011	0.004	0.007	0.003	0.003	<0.001	0.007	0.082	0.002	0.008	0.010	0.005	0.004	n.d.
Ba	ppm	12	27	33	16	30	1.6	24	27	4.7	24	36	16	10	4.6
La	ppm	0.91	0.38	0.11	0.13	1.2	0.17	0.31	0.44	0.027	0.54	0.58	0.045	0.21	0.21
Ce	ppm	0.96	0.60	0.11	0.22	1.7	0.26	0.42	0.51	0.058	0.87	0.90	0.075	0.35	0.39
Pr	ppm	0.19	0.070	0.031	0.022	0.17	0.038	0.054	0.076	0.008	0.10	0.11	0.009	0.031	0.047
Nd	ppm	0.75	0.27	0.16	0.093	0.70	0.16	0.21	0.30	0.034	0.43	0.45	0.049	0.13	0.20
Sm	ppm	0.19	0.049	0.048	0.020	0.13	0.036	0.041	0.055	0.007	0.095	0.084	0.015	0.026	0.038
Eu	ppm	0.008	0.007	0.012	0.005	0.026	0.008	0.009	0.015	0.002	0.015	0.013	0.004	0.004	0.009
Gd	ppm	0.22	0.064	0.060	0.020	0.15	0.049	0.050	0.065	0.009	0.088	0.087	0.014	0.032	0.045
Tb	ppm	0.042	0.010	0.009	0.002	0.021	0.007	0.007	0.010	0.001	0.013	0.014	0.002	0.005	0.007
Dy	ppm	0.24	0.060	0.034	0.015	0.11	0.036	0.037	0.046	0.007	0.071	0.070	0.014	0.025	0.037
Ho	ppm	0.050	0.011	0.005	0.003	0.021	0.006	0.008	0.009	<0.001	0.015	0.014	0.002	0.005	0.007
Er	ppm	0.14	0.033	0.012	0.011	0.067	0.013	0.019	0.021	0.002	0.042	0.036	0.004	0.016	0.022
Tm	ppm	0.023	0.004	<0.001	0.001	0.009	0.002	0.002	0.003	<0.001	0.006	0.006	<0.001	0.002	0.003
Yb	ppm	0.14	0.030	0.005	0.007	0.053	0.009	0.015	0.016	<0.001	0.038	0.030	0.004	0.011	0.018
Lu	ppm	0.017	0.004	<0.001	n.d.	0.009	0.001	0.002	0.002	<0.001	0.006	0.002	<0.001	0.001	0.003
Hf	ppm	0.006	<0.001	n.d.	0.003	<0.001	n.d.	0.001	0.003	n.d.	0.002	0.003	<0.001	n.d.	n.d.
Ta	ppm	n.d.	n.d.	<0.001	n.d.	<0.001	n.d.	n.d.	0.003	n.d.	<0.001	n.d.	0.001	<0.001	<0.001
Tl	ppm	0.006	0.006	0.001	0.004	0.019	n.d.	0.011	0.011	<0.001	0.064	0.010	0.003	0.004	0.002
Pb	ppm	1.6	2.7	0.27	0.64	0.53	0.15	0.50	29	3.1	2.3	1.9	0.20	17	0.56
Bi	ppm	<0.001	0.001	<0.001	n.d.	<0.001	n.d.	n.d.	0.021	n.d.	0.005	0.001	0.001	<0.001	<0.001
Th	ppm	0.005	0.003	<0.001	n.d.	0.004	0.001	0.005	<0.001	0.002	<0.001	<0.001	0.002	<0.001	<0.001
U	ppm	0.18	0.058	0.004	0.007	0.042	0.031	0.017	0.026	0.027	0.040	0.032	0.012	0.021	0.035

<sup>a</sup> The abbreviations are the same as Table 1.

n.d.: not detected

Appendix B1 Continued.

Sample		35014	35035	36120	42002	43028	44030	44045	49050	53011	54029	73028	84002	57
Geology <sup>a</sup>		LMt	Gr	Mv	Um	Acc	Fv	LMt	Dep	Mv	Um	Dep	Um	Mv
Li	ppm	0.044	0.13	0.016	0.074	0.11	0.114	0.14	0.27	0.096	0.082	2.8	0.035	0.078
Be	ppm	0.039	0.041	0.003	0.090	0.10	0.173	0.039	0.069	0.083	0.049	0.144	0.016	0.022
Na	%	n.d.	0.003	<0.001	0.002	<0.001	<0.001	<0.001	0.002	0.005	0.002	0.011	<0.001	0.002
Mg	%	0.004	0.005	0.003	0.10	0.018	0.005	0.012	0.007	0.055	0.20	0.042	0.149	0.002
Al	%	0.006	0.011	0.017	0.004	0.008	0.016	0.007	0.005	0.004	0.011	0.153	0.013	0.008
P (×100)	%	0.14	0.48	0.23	0.052	0.25	0.054	0.52	0.018	0.026	0.012	0.041	0.022	0.003
K	%	0.002	0.003	<0.001	0.003	0.002	0.003	0.005	0.002	0.007	0.005	0.012	0.002	<0.001
Ca	%	0.027	0.055	0.032	0.088	0.11	0.034	0.089	0.093	0.16	0.75	0.63	0.045	0.008
Sc	ppm	n.d.	0.007	0.004	0.023	0.042	0.034	n.d.	0.035	0.062	0.24	0.27	0.098	0.059
Ti (×10)	%	n.d.	<0.001	<0.001	<0.001	0.001	<0.001	<0.001	<0.001	n.d.	<0.001	<0.001	0.001	n.d.
V	ppm	1.2	0.63	2.1	3.5	2.5	2.3	n.d.	1.4	1.0	2.5	0.65	1.6	0.10
Cr	ppm	0.007	<0.001	<0.001	0.529	0.12	n.d.	0.022	n.d.	0.048	1.3	1.4	0.83	0.069
Mn (×100)	%	0.57	0.33	0.11	1.9	0.70	0.51	0.49	0.64	1.7	1.4	7.7	0.45	0.13
Fe	%	n.d.	0.007	0.002	0.055	0.013	0.007	0.007	0.011	n.d.	0.145	0.032	0.007	0.008
Co	ppm	0.61	0.23	0.13	3.1	1.0	0.17	1.6	0.58	1.4	4.6	4.3	4.6	0.36
Ni	ppm	0.71	0.13	0.07	37	0.92	0.06	1.2	0.79	0.41	33	2.7	26	0.21
Cu	ppm	1.3	0.5	9.6	2.7	0.97	0.4	2.0	17	0.91	1.0	147	0.78	0.61
Zn	ppm	4.3	2.0	1.7	11	2.7	2.8	10	89	12	2.3	1855	2.8	1.1
Ga	ppm	0.006	0.059	0.061	0.048	0.012	0.094	0.004	0.038	0.012	0.010	0.084	0.006	0.015
Rb	ppm	0.24	<0.001	<0.001	n.d.	0.41	0.50	0.21	0.16	0.39	0.31	0.71	0.094	0.26
Sr	ppm	1.6	2.4	1.5	2.7	6.0	1.5	6.2	1.8	16	34	12	2.4	0.47
Y	ppm	0.14	1.1	0.82	0.20	0.25	0.83	0.14	0.25	0.082	0.47	6.1	0.051	0.13
Zr	ppm	n.d.	0.022	<0.001	n.d.	0.010	0.007	0.007	0.003	n.d.	0.007	0.093	n.d.	0.017
Nb	ppm	n.d.	<0.001	<0.001	<0.001	0.016	0.002	n.d.	n.d.	n.d.	<0.001	0.007	n.d.	n.d.
Mo	ppm	0.012	<0.001	<0.001	0.011	0.167	0.021	n.d.	<0.001	0.009	n.d.	0.003	0.003	n.d.
Cd	ppm	0.017	0.008	0.004	0.056	0.015	0.037	0.011	0.22	0.035	0.016	6.5	0.009	0.004
Sn	ppm	n.d.	0.018	0.014	n.d.	n.d.	n.d.	n.d.	<0.001	n.d.	n.d.	0.044	n.d.	n.d.
Sb	ppm	0.002	0.002	<0.001	0.002	0.001	0.004	0.006	0.213	<0.001	0.021	0.867	n.d.	n.d.
Cs	ppm	0.011	<0.001	<0.001	n.d.	0.020	0.012	0.003	0.087	0.005	0.015	0.036	0.006	0.013
Ba	ppm	6.8	9.1	2.0	16	22	12	19	15	35	12	33	8.4	0.60
La	ppm	0.065	0.79	0.35	0.13	0.14	1.1	0.065	0.26	0.056	0.19	1.6	0.026	0.037
Ce	ppm	0.080	0.73	0.85	0.17	0.23	1.2	0.095	0.39	0.10	0.38	2.7	0.030	0.12
Pr	ppm	0.011	0.16	0.12	0.028	0.040	0.23	0.015	0.054	0.014	0.054	0.57	0.004	0.015
Nd	ppm	0.041	0.70	0.60	0.13	0.18	0.92	0.063	0.23	0.061	0.26	2.8	0.020	0.075
Sm	ppm	0.005	0.15	0.15	0.028	0.051	0.19	0.013	0.047	0.011	0.071	0.78	0.004	0.020
Eu	ppm	0.004	0.014	0.031	0.009	0.014	0.012	0.005	0.008	0.005	0.024	0.22	<0.001	0.006
Gd	ppm	0.015	0.17	0.15	0.031	0.049	0.18	0.022	0.045	0.010	0.089	0.90	0.011	0.022
Tb	ppm	0.002	0.029	0.025	0.005	0.008	0.028	0.004	0.007	0.001	0.013	0.17	<0.001	0.004
Dy	ppm	0.016	0.15	0.13	0.024	0.041	0.12	0.020	0.036	0.010	0.077	0.85	0.006	0.023
Ho	ppm	0.003	0.030	0.024	0.004	0.008	0.021	0.004	0.007	0.002	0.012	0.17	<0.001	0.004
Er	ppm	0.010	0.084	0.067	0.014	0.013	0.052	0.010	0.018	0.003	0.036	0.52	<0.001	0.012
Tm	ppm	<0.001	0.013	0.010	0.002	0.001	0.005	0.001	0.003	<0.001	0.005	0.07	<0.001	0.002
Yb	ppm	0.008	0.071	0.052	0.011	0.004	0.032	0.006	0.013	0.004	0.034	0.44	n.d.	0.013
Lu	ppm	n.d.	0.010	0.007	0.002	<0.001	0.005	<0.001	0.002	n.d.	0.005	0.068	n.d.	0.002
Hf	ppm	0.002	<0.001	<0.001	n.d.	0.002	0.001	<0.001	<0.001	0.003	<0.001	0.005	0.002	<0.001
Ta	ppm	n.d.	<0.001	<0.001	<0.001	n.d.	0.002	n.d.	<0.001	n.d.	<0.001	0.008	n.d.	n.d.
Tl	ppm	0.005	0.003	<0.001	0.002	0.004	0.006	<0.001	0.047	0.004	0.002	0.575	<0.001	0.041
Pb	ppm	0.37	0.30	0.21	0.15	0.16	3.60	0.29	1153	n.d.	0.30	2430	0.06	0.19
Bi	ppm	<0.001	<0.001	<0.001	n.d.	n.d.	<0.001	n.d.	0.020	n.d.	<0.001	0.546	n.d.	0.036
Th	ppm	n.d.	0.002	<0.001	<0.001	n.d.	0.015	<0.001	0.002	n.d.	0.002	0.004	n.d.	0.002
U	ppm	0.011	0.060	0.006	0.009	0.010	0.073	0.017	0.055	0.014	0.015	0.089	0.009	0.010

<sup>a</sup> The abbreviations are the same as Table 1.

n.d.: not detected

Appendix B2 Results of analysis of the extracts in step 2 obtained by the BCR scheme.

Sample		22007	22030	25005	25010	25023	28111	31021	32049	33001	33008	33019	33051	34032	34035
Geology <sup>a</sup>		Gr	Fv	Acc	HMt	Sed_u	Sed_n	HMt	Dep	Sed_n	Sed_u	Fv	Acc	Sed_u	Sed_n
Li	ppm	0.215	0.099	0.361	0.227	0.371	0.212	0.210	0.564	0.216	0.534	0.228	0.303	0.148	0.061
Be	ppm	0.079	0.194	0.095	0.060	0.219	0.054	0.324	0.215	0.084	0.322	0.179	0.070	0.099	0.052
Na	%	<0.001	<0.001	<0.001	<0.001	0.028	0.001	<0.001	<0.001	0.002	0.002	<0.001	n.d.	0.002	n.d.
Mg	%	0.003	0.002	0.005	0.017	0.038	0.006	0.010	0.018	0.014	0.036	0.005	0.008	0.008	0.007
Al	%	0.020	0.029	0.052	0.040	0.135	0.032	0.113	0.104	0.030	0.268	0.054	0.030	0.076	0.021
P (×100)	%	0.122	0.918	0.181	1.10	3.41	1.03	0.516	1.46	0.598	24.1	0.586	0.342	1.80	1.52
K	%	<0.001	0.002	0.003	0.002	0.022	0.005	0.005	0.003	0.009	0.007	0.003	0.001	0.005	0.001
Ca	%	0.005	0.014	0.017	0.043	0.097	0.008	0.085	0.056	0.064	0.176	0.042	0.008	0.060	0.007
Sc	ppm	0.010	0.012	0.019	0.030	0.073	n.d.	0.062	0.009	0.019	0.058	0.073	0.021	0.036	0.016
Ti (×10)	%	<0.001	<0.001	<0.001	<0.001	<0.001	<0.001	<0.001	<0.001	<0.001	<0.001	<0.001	<0.001	<0.001	<0.001
V	ppm	2.24	2.23	0.627	2.97	5.15	1.23	3.65	6.49	1.45	7.38	2.29	2.29	6.02	4.82
Cr	ppm	0.107	0.020	n.d.	1.33	1.27	0.151	0.324	0.421	n.d.	16.1	0.169	n.d.	5.23	0.498
Mn (×100)	%	0.386	0.519	1.80	0.642	0.930	0.126	5.39	12.3	0.586	0.733	0.441	8.26	0.629	0.252
Fe	%	0.041	0.156	0.046	0.069	0.486	0.155	0.361	0.233	0.085	0.579	0.118	0.086	0.460	0.073
Co	ppm	0.316	0.313	3.42	2.62	1.20	0.396	6.49	15.7	0.791	3.38	0.593	4.62	1.44	1.11
Ni	ppm	0.222	0.135	1.49	3.94	3.26	0.628	4.62	1.96	2.30	18.1	0.379	2.84	24.5	1.10
Cu	ppm	1.31	2.57	2.52	6.17	13.8	1.63	1.19	111	3.09	147	1.36	4.68	38.6	4.26
Zn	ppm	4.88	8.33	4.04	9.24	88.0	4.44	11.7	438	7.47	317	8.07	8.27	112	6.62
Ga	ppm	0.114	0.124	0.066	0.072	0.100	0.043	0.129	0.461	0.046	0.451	0.163	0.249	0.049	0.264
Rb	ppm	0.299	0.760	1.10	0.532	1.06	0.521	1.04	1.91	0.906	1.34	1.13	n.d.	0.649	n.d.
Sr	ppm	0.213	0.791	1.80	4.74	11.2	1.24	7.19	1.57	8.21	17.8	2.90	3.81	9.43	0.674
Y	ppm	6.052	4.269	2.141	3.471	3.650	1.756	4.728	3.985	1.141	5.972	5.417	1.002	1.989	2.482
Zr	ppm	0.006	0.057	0.010	0.004	0.049	0.014	0.057	0.032	0.034	0.044	0.035	0.380	0.016	0.024
Nb	ppm	0.003	0.003	n.d.	n.d.	n.d.	n.d.	n.d.	<0.001	n.d.	<0.001	n.d.	0.002	n.d.	n.d.
Mo	ppm	n.d.	0.032	n.d.	n.d.	0.009	n.d.	n.d.	<0.001	n.d.	0.069	n.d.	n.d.	0.001	n.d.
Cd	ppm	0.016	0.138	0.017	0.026	0.132	n.d.	0.225	1.248	0.013	0.381	0.025	0.029	0.378	0.005
Sn	ppm	0.003	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	0.044	n.d.	0.543	n.d.	0.004	n.d.	0.004
Sb	ppm	0.004	0.010	<0.001	0.012	0.113	0.002	0.019	0.019	0.006	0.136	0.012	0.013	0.216	0.020
Cs	ppm	0.083	0.094	0.166	0.037	0.015	0.016	0.101	1.045	0.055	0.193	0.129	0.131	0.048	0.032
Ba	ppm	3.96	14.1	40.0	13.4	74.0	5.25	67.6	25.1	20.9	203	24.9	27.0	87.6	8.79
La	ppm	2.56	4.27	1.19	2.62	3.98	1.46	4.43	4.46	0.90	5.16	6.47	0.50	1.47	1.96
Ce	ppm	7.18	7.14	1.77	5.25	5.78	2.40	6.04	8.62	2.00	9.25	10.6	1.46	2.61	4.56
Pr	ppm	0.610	0.737	0.336	0.466	0.512	0.335	0.637	0.893	0.220	0.913	1.148	0.148	0.237	0.447
Nd	ppm	2.36	2.71	1.61	1.72	1.91	1.39	2.40	3.47	0.890	3.55	4.13	0.697	0.895	1.83
Sm	ppm	0.571	0.513	0.481	0.345	0.330	0.320	0.405	0.671	0.198	0.709	0.739	0.202	0.156	0.351
Eu	ppm	0.028	0.063	0.109	0.074	0.064	0.069	0.090	0.153	0.034	0.130	0.122	0.053	0.027	0.071
Gd	ppm	0.701	0.562	0.601	0.391	0.398	0.348	0.545	0.751	0.204	0.745	0.845	0.239	0.208	0.360
Tb	ppm	0.132	0.104	0.093	0.073	0.067	0.062	0.098	0.127	0.036	0.133	0.143	0.039	0.036	0.072
Dy	ppm	0.705	0.546	0.392	0.376	0.367	0.294	0.513	0.587	0.184	0.722	0.710	0.173	0.197	0.379
Ho	ppm	0.152	0.106	0.058	0.077	0.073	0.050	0.101	0.108	0.035	0.145	0.138	0.028	0.041	0.071
Er	ppm	0.440	0.325	0.124	0.213	0.203	0.133	0.275	0.274	0.090	0.415	0.370	0.072	0.112	0.198
Tm	ppm	0.068	0.046	0.015	0.031	0.028	0.016	0.035	0.037	0.013	0.062	0.050	0.011	0.016	0.031
Yb	ppm	0.411	0.270	0.075	0.151	0.146	0.093	0.187	0.192	0.082	0.323	0.271	0.048	0.082	0.183
Lu	ppm	0.054	0.038	0.008	0.020	0.022	0.012	0.024	0.025	0.011	0.046	0.037	0.006	0.011	0.025
Hf	ppm	<0.001	0.002	<0.001	n.d.	0.002	n.d.	0.003	0.001	<0.001	0.003	0.001	0.006	n.d.	0.003
Ta	ppm	n.d.	n.d.	<0.001	n.d.	<0.001	n.d.	n.d.	0.002	n.d.	0.002	n.d.	0.001	n.d.	<0.001
Tl	ppm	0.012	0.018	0.025	0.008	0.025	n.d.	0.065	0.051	0.010	0.097	0.021	0.037	0.016	0.008
Pb	ppm	15.8	24.9	8.26	13.7	9.25	3.39	12.6	384	24.9	68.9	24.4	10.2	173	10.6
Bi	ppm	0.011	0.012	<0.001	<0.001	0.001	n.d.	n.d.	0.112	0.002	0.018	0.002	0.002	0.001	0.004
Th	ppm	0.004	0.006	<0.001	<0.001	0.001	<0.001	0.007	0.002	0.002	0.007	0.003	0.007	<0.001	0.001
U	ppm	0.168	0.104	0.011	0.016	0.027	0.068	0.036	0.060	0.039	0.106	0.056	0.051	0.027	0.096

<sup>a</sup> The abbreviations are the same as Table 1.

n.d.: not detected

Appendix B2 Continued.

Sample		35014	35035	36120	42002	43028	44030	44045	49050	53011	54029	73028	84002	57
Geology <sup>a</sup>		LMt	Gr	Mv	Um	Acc	Fv	LMt	Dep	Mv	Um	Dep	Um	Mv
Li	ppm	0.192	0.374	0.018	0.503	0.313	0.151	0.748	0.389	0.158	0.268	0.755	0.135	0.031
Be	ppm	0.026	0.035	0.003	0.087	0.079	0.092	0.032	0.054	0.154	0.055	0.081	0.005	0.009
Na	%	n.d.	<0.001	0.002	<0.001	<0.001	<0.001	<0.001	n.d.	<0.001	0.002	0.002	<0.001	n.d.
Mg	%	0.008	0.020	0.200	0.118	0.024	0.007	0.037	0.022	0.024	0.135	0.016	0.404	0.002
Al	%	0.017	0.051	0.064	0.074	0.043	0.044	0.083	0.044	0.055	0.040	0.160	0.041	0.032
P (×100)	%	0.277	7.78	1.75	0.164	0.841	0.331	1.74	4.67	0.833	2.16	0.282	0.185	0.010
K	%	<0.001	0.002	<0.001	0.002	0.002	0.002	0.004	0.002	0.003	0.003	0.005	0.001	<0.001
Ca	%	0.005	0.156	0.077	0.032	0.033	0.006	0.057	0.113	0.089	0.131	0.071	0.017	0.005
Sc	ppm	0.009	0.014	0.059	0.094	0.063	0.039	0.047	0.060	0.087	0.084	0.063	0.278	0.029
Ti (×10)	%	0.001	0.003	0.004	<0.001	<0.001	0.001	0.002	<0.001	<0.001	<0.001	<0.001	n.d.	n.d.
V	ppm	1.76	2.72	7.09	3.45	0.899	5.54	1.75	5.77	4.62	2.37	4.62	5.23	0.284
Cr	ppm	0.271	<0.001	<0.001	4.10	0.526	n.d.	0.722	0.175	0.401	3.25	1.42	2.94	0.324
Mn (×100)	%	0.422	0.513	0.273	5.37	1.67	1.20	0.716	0.699	2.22	0.482	5.02	0.299	0.113
Fe	%	0.044	0.067	0.197	0.200	0.109	0.034	0.123	0.060	0.219	0.101	0.463	0.111	0.126
Co	ppm	0.718	0.464	1.23	13.4	2.97	0.425	1.48	0.685	2.29	3.00	3.36	3.21	0.320
Ni	ppm	0.507	0.177	2.77	55.5	1.89	0.229	1.66	0.946	0.518	51.0	3.08	41.9	0.143
Cu	ppm	0.790	0.514	7.01	7.99	2.51	0.926	2.32	5.68	1.64	3.01	86.6	0.585	1.10
Zn	ppm	2.12	2.73	2.05	14.4	3.98	5.54	8.39	35.1	14.2	3.99	719	2.67	0.873
Ga	ppm	0.030	0.464	0.228	0.341	0.067	0.481	0.050	0.454	0.062	0.045	0.137	0.003	0.157
Rb	ppm	0.322	0.636	0.914	n.d.	0.791	0.196	0.704	n.d.	0.842	0.708	1.45	0.168	0.493
Sr	ppm	0.255	3.25	3.72	2.24	1.65	0.470	1.93	4.22	9.12	6.09	2.80	0.999	0.369
Y	ppm	0.679	13.8	1.80	2.97	2.29	2.26	2.08	3.39	1.80	1.87	8.81	0.451	0.824
Zr	ppm	0.002	<0.001	0.019	0.013	0.019	0.078	0.012	0.024	0.043	0.008	0.147	0.008	0.025
Nb	ppm	0.002	<0.001	0.042	n.d.	0.016	0.002	0.004	n.d.	n.d.	n.d.	0.004	n.d.	n.d.
Mo	ppm	n.d.	<0.001	0.231	n.d.	0.115	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.
Cd	ppm	n.d.	0.008	0.002	0.043	0.012	0.026	0.003	0.086	0.025	0.003	4.707	<0.001	0.004
Sn	ppm	n.d.	<0.001	<0.001	n.d.	n.d.	n.d.	n.d.	0.001	n.d.	n.d.	0.247	n.d.	n.d.
Sb	ppm	<0.001	<0.001	<0.001	0.004	0.003	0.009	n.d.	0.175	<0.001	0.005	3.100	n.d.	0.006
Cs	ppm	0.070	0.109	0.041	0.037	0.215	0.162	0.089	0.532	0.056	0.304	0.361	0.046	0.112
Ba	ppm	2.46	5.46	1.19	25.5	21.2	6.21	11.4	4.53	47.1	11.2	80.4	4.63	3.96
La	ppm	0.222	3.789	0.847	2.35	1.12	2.87	1.09	3.48	0.890	1.05	2.50	n.d.	0.269
Ce	ppm	0.748	8.26	2.25	4.51	2.99	9.80	2.10	7.89	2.75	2.39	4.17	0.313	0.874
Pr	ppm	0.082	1.151	0.321	0.511	0.397	0.700	0.267	0.871	0.310	0.312	0.731	0.038	0.107
Nd	ppm	0.314	5.49	1.61	2.11	1.82	2.71	1.17	3.62	1.22	1.43	3.31	0.152	0.531
Sm	ppm	0.058	1.657	0.388	0.440	0.420	0.629	0.291	0.709	0.251	0.355	0.778	0.042	0.143
Eu	ppm	0.018	0.070	0.067	0.100	0.101	0.039	0.069	0.087	0.067	0.076	0.231	0.003	0.032
Gd	ppm	0.092	1.959	0.365	0.496	0.514	0.611	0.385	0.694	0.276	0.399	1.08	0.046	0.152
Tb	ppm	0.018	0.403	0.064	0.088	0.085	0.097	0.072	0.115	0.049	0.068	0.212	0.010	0.027
Dy	ppm	0.100	2.167	0.304	0.444	0.374	0.431	0.356	0.535	0.259	0.318	1.20	0.052	0.141
Ho	ppm	0.019	0.424	0.059	0.082	0.067	0.072	0.064	0.099	0.049	0.057	0.249	0.010	0.027
Er	ppm	0.048	1.208	0.154	0.202	0.166	0.164	0.168	0.264	0.134	0.150	0.744	0.026	0.073
Tm	ppm	0.008	0.178	0.023	0.030	0.020	0.024	0.022	0.039	0.022	0.021	0.111	0.003	0.012
Yb	ppm	0.041	0.989	0.119	0.158	0.102	0.132	0.129	0.212	0.096	0.118	0.648	0.018	0.074
Lu	ppm	0.006	0.132	0.017	0.019	0.014	0.017	0.017	0.027	0.015	0.016	0.095	0.002	0.011
Hf	ppm	n.d.	0.003	<0.001	<0.001	n.d.	0.003	<0.001	0.002	0.003	n.d.	0.007	n.d.	<0.001
Ta	ppm	n.d.	<0.001	0.002	<0.001	n.d.	<0.001	<0.001	<0.001	n.d.	n.d.	0.005	n.d.	<0.001
Tl	ppm	0.009	0.008	<0.001	0.020	0.016	0.020	0.017	0.084	0.017	0.016	3.22	0.003	0.138
Pb	ppm	3.02	2.24	0.431	18.8	8.07	25.4	2.89	364	2.58	2.52	4197	0.191	3.69
Bi	ppm	<0.001	0.002	<0.001	0.001	<0.001	0.005	n.d.	0.023	n.d.	n.d.	0.114	n.d.	0.197
Th	ppm	n.d.	0.013	0.002	<0.001	0.003	0.032	0.002	0.006	0.002	0.002	n.d.	n.d.	<0.001
U	ppm	0.022	0.195	0.012	0.040	0.028	0.120	0.041	0.174	0.038	0.024	0.017	0.013	0.015

<sup>a</sup> The abbreviations are the same as Table 1.

n.d.: not detected

Appendix B3 Results of analysis of the extracts in step 3 obtained by the BCR schem.

Sample		22007	22030	25005	25010	25023	28111	31021	32049	33001	33008	33019	33051	34032	34035
Geology <sup>a</sup>		Gr	Fv	Acc	HMt	Sed_u	Sed_n	HMt	Dep	Sed_n	Sed_u	Fv	Acc	Sed_u	Sed_n
Li	ppm	0.946	0.207	1.81	0.016	2.98	1.62	0.372	1.52	1.71	3.66	0.659	1.03	4.84	0.638
Be	ppm	0.071	0.093	0.147	0.021	0.166	0.046	0.244	0.110	0.084	0.126	0.093	0.072	0.148	0.038
Na	%	<0.001	n.d.	0.002	n.d.	0.005	0.003	<0.001	<0.001	0.005	<0.001	<0.001	n.d.	0.003	n.d.
Mg	%	0.002	0.004	0.009	0.029	0.025	0.008	0.019	0.018	0.009	0.064	0.006	0.017	0.052	0.012
Al	%	0.018	0.023	0.051	0.020	0.183	0.020	0.180	0.061	0.054	0.219	0.036	0.019	0.195	0.017
P (×100)	%	n.d.	0.452	0.051	0.021	6.74	0.588	2.308	0.300	0.121	5.77	0.021	0.097	1.77	0.335
K	%	0.001	0.004	0.004	0.003	0.005	0.004	0.005	0.002	0.012	0.006	0.003	0.001	0.004	0.001
Ca	%	0.008	0.007	0.004	0.035	0.036	0.016	0.028	0.025	0.018	0.064	0.019	0.012	0.026	0.005
Sc	ppm	0.207	0.559	0.508	0.587	0.472	0.290	1.57	0.491	0.414	0.303	0.588	0.170	0.714	0.226
Ti (×10)	%	n.d.	0.003	<0.001	n.d.	0.001	0.010	0.002	<0.001	0.001	0.001	n.d.	0.012	0.002	0.003
V	ppm	2.64	n.d.	7.40	2.65	3.93	n.d.	4.14	1.87	4.06	2.32	9.43	0.649	6.02	1.96
Cr	ppm	0.953	1.14	0.456	15.7	35.0	0.927	9.05	0.818	0.475	67.5	1.35	0.894	123	1.85
Mn (×100)	%	0.079	0.106	0.186	0.185	0.555	0.075	0.653	0.763	0.123	0.727	0.205	0.496	0.584	0.071
Fe	%	0.023	0.055	0.020	0.013	0.260	<0.001	0.173	0.048	0.015	0.173	n.d.	0.022	0.443	0.015
Co	ppm	2.17	0.381	0.517	0.611	2.75	0.540	2.27	2.77	0.532	2.57	0.720	0.703	2.18	0.617
Ni	ppm	0.708	0.350	2.33	1.55	4.17	1.87	7.24	1.68	5.87	13.9	0.763	2.59	33.1	1.81
Cu	ppm	0.961	2.28	1.44	4.54	50.3	0.492	10.9	143	2.18	201	2.00	1.60	139	6.27
Zn	ppm	4.82	9.49	4.02	2.97	46.1	4.19	17.0	290	5.84	112	6.83	6.85	154	6.35
Ga	ppm	0.088	0.232	0.095	0.108	0.580	0.068	0.793	0.349	0.107	0.689	0.267	0.075	0.877	0.175
Rb	ppm	0.567	0.690	1.36	0.408	1.06	0.412	0.865	0.536	1.28	1.010	0.814	0.277	1.16	0.122
Sr	ppm	0.139	0.463	0.789	1.50	2.64	0.804	2.60	2.12	4.05	4.80	2.47	0.578	3.28	1.43
Y	ppm	8.36	3.83	2.20	3.26	7.10	1.37	13.2	2.38	2.22	5.00	5.33	0.658	5.41	2.82
Zr	ppm	0.162	0.080	n.d.	n.d.	0.346	n.d.	1.23	<0.001	n.d.	0.145	n.d.	n.d.	2.51	n.d.
Nb	ppm	1.54	0.061	n.d.	n.d.	n.d.	0.039	0.013	<0.001	n.d.	<0.001	n.d.	n.d.	n.d.	n.d.
Mo	ppm	0.136	0.024	n.d.	n.d.	0.715	n.d.	n.d.	<0.001	n.d.	1.398	n.d.	0.241	0.032	n.d.
Cd	ppm	n.d.	0.044	n.d.	n.d.	0.026	n.d.	0.029	0.510	n.d.	0.128	n.d.	0.009	0.495	0.004
Sn	ppm	0.068	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	0.017	n.d.	0.048	n.d.	n.d.	n.d.	n.d.
Sb	ppm	0.001	0.015	n.d.	n.d.	0.084	0.012	0.032	0.061	n.d.	0.093	n.d.	n.d.	0.327	n.d.
Cs	ppm	0.094	0.084	1.04	0.004	0.023	0.063	0.097	1.46	0.276	0.255	0.146	0.286	0.157	0.072
Ba	ppm	0.765	4.20	7.08	8.41	31.2	2.98	13.7	3.16	13.4	76.3	6.87	4.36	24.3	5.01
La	ppm	2.02	4.64	1.36	3.97	7.84	1.34	12.8	3.06	2.72	5.14	7.55	0.279	3.93	1.30
Ce	ppm	5.09	9.93	2.46	7.42	14.9	1.96	28.0	7.61	6.05	10.6	15.8	0.881	9.78	3.20
Pr	ppm	0.522	1.13	0.468	0.894	1.61	0.347	3.417	0.853	0.680	1.18	1.79	0.112	1.13	0.355
Nd	ppm	2.24	4.41	2.38	3.67	6.39	1.47	14.1	3.66	2.78	4.94	6.98	0.580	4.82	1.44
Sm	ppm	0.739	0.920	0.791	0.751	1.41	0.328	3.00	0.807	0.552	1.077	1.41	0.184	1.09	0.346
Eu	ppm	0.020	0.117	0.172	0.167	0.252	0.076	0.606	0.181	0.095	0.179	0.223	0.046	0.144	0.070
Gd	ppm	0.795	0.827	0.818	0.648	1.31	0.275	2.95	0.684	0.507	0.906	1.25	0.181	1.08	0.363
Tb	ppm	0.207	0.131	0.123	0.108	0.218	0.056	0.512	0.111	0.089	0.163	0.212	0.031	0.168	0.066
Dy	ppm	1.18	0.688	0.493	0.565	1.09	0.253	2.46	0.491	0.364	0.840	0.964	0.137	0.858	0.364
Ho	ppm	0.257	0.130	0.078	0.113	0.206	0.047	0.457	0.083	0.068	0.165	0.186	0.024	0.168	0.081
Er	ppm	0.842	0.348	0.158	0.352	0.638	0.139	1.18	0.218	0.209	0.483	0.494	0.058	0.483	0.242
Tm	ppm	0.138	0.062	0.022	0.049	0.102	0.020	0.181	0.031	0.028	0.076	0.076	0.009	0.081	0.037
Yb	ppm	0.889	0.366	0.100	0.285	0.563	0.094	0.893	0.169	0.166	0.466	0.438	0.048	0.450	0.236
Lu	ppm	0.132	0.050	0.014	0.035	0.093	0.013	0.118	0.024	0.025	0.072	0.054	0.008	0.073	0.037
Hf	ppm	n.d.	n.d.	n.d.	n.d.	0.005	n.d.	0.012	<0.001	n.d.	0.003	n.d.	n.d.	0.045	n.d.
Ta	ppm	n.d.	0.003	n.d.	n.d.	n.d.	<0.001	0.004	<0.001	n.d.	0.005	n.d.	0.001	n.d.	0.002
Tl	ppm	0.008	0.004	0.019	0.004	0.013	<0.001	0.016	0.028	0.006	0.070	0.009	0.009	0.021	0.004
Pb	ppm	3.94	10.0	5.04	4.87	41.2	0.95	24.9	6.65	6.34	68.4	7.23	2.56	146	2.56
Bi	ppm	0.800	0.113	0.025	0.004	0.223	0.007	0.061	2.07	0.011	0.575	0.060	0.017	0.070	0.027
Th	ppm	0.855	1.06	0.250	0.124	0.082	0.139	0.376	0.169	0.315	0.062	0.599	0.098	0.251	0.143
U	ppm	0.988	0.458	0.035	0.123	0.651	0.117	0.722	0.189	0.124	1.02	0.296	0.107	0.750	0.160

<sup>a</sup> The abbreviations are the same as Table 1.

n.d.: not detected



Appendix B3 Continued.

Sample		35014	35035	36120	42002	43028	44030	44045	49050	53011	54029	73028	84002	57
Geology <sup>a</sup>		LMt	Gr	Mv	Um	Acc	Fv	LMt	Dep	Mv	Um	Dep	Um	Mv
Li	ppm	0.447	1.15	0.014	1.40	0.336	0.786	1.98	1.53	1.13	0.074	4.21	0.076	0.324
Be	ppm	0.016	0.034	0.001	0.196	0.065	0.087	0.088	0.043	0.110	0.007	0.109	<0.001	0.015
Na	%	n.d.	<0.001	<0.001	<0.001	<0.001	0.002	<0.001	n.d.	0.003	n.d.	0.004	n.d.	0.006
Mg	%	0.004	0.013	0.019	0.009	0.038	0.004	0.023	0.018	0.015	0.199	0.014	0.511	0.013
Al	%	0.014	0.017	0.018	0.077	0.010	0.032	0.058	0.022	0.106	0.010	0.248	0.024	0.137
P (×100)	%	0.362	0.440	0.213	1.52	n.d.	0.155	0.962	0.208	0.184	0.933	0.448	0.106	0.021
K	%	0.003	0.004	0.001	0.004	0.003	0.003	0.009	0.003	0.002	0.003	<0.001	0.002	n.d.
Ca	%	0.009	0.039	0.019	0.010	0.056	0.005	0.020	0.019	0.030	0.015	0.042	0.006	0.048
Sc	ppm	0.144	0.247	0.150	0.821	0.702	0.177	0.604	0.189	0.995	0.777	2.12	0.664	0.675
Ti (×10)	%	n.d.	0.036	0.034	0.003	n.d.	0.012	0.010	0.002	n.d.	0.002	0.002	n.d.	0.003
V	ppm	5.47	2.63	3.39	n.d.	n.d.	0.454	n.d.	1.17	n.d.	n.d.	n.d.	n.d.	0.266
Cr	ppm	0.447	<0.001	0.273	29.1	0.971	0.460	0.910	0.416	2.84	12.3	4.55	11.0	0.825
Mn (×100)	%	0.080	0.116	0.026	0.210	0.294	0.149	0.242	0.089	0.275	0.104	0.609	0.145	0.106
Fe	%	0.013	0.013	0.017	0.055	n.d.	0.011	0.062	0.021	0.039	0.140	0.126	0.068	0.238
Co	ppm	0.254	0.241	0.091	0.641	0.704	0.138	2.280	0.435	0.930	2.39	2.27	2.32	0.281
Ni	ppm	0.760	0.391	0.176	0.946	1.82	0.329	8.37	1.35	1.02	40.2	4.93	47.2	0.246
Cu	ppm	1.29	0.639	2.55	2.93	0.660	1.28	21.5	33.4	2.39	2.12	195	1.066	0.364
Zn	ppm	1.76	4.11	0.988	15.4	3.28	5.31	14.7	84.6	10.3	1.27	853	0.835	n.d.
Ga	ppm	0.003	0.355	0.039	0.438	0.080	0.429	0.115	0.182	0.186	0.060	0.376	n.d.	0.316
Rb	ppm	1.06	0.724	<0.001	1.06	0.664	0.464	1.20	0.094	0.659	0.341	0.908	0.154	0.264
Sr	ppm	0.530	1.42	3.70	1.51	1.11	0.282	1.55	1.19	3.10	1.04	2.61	0.306	2.25
Y	ppm	0.471	4.00	0.219	7.51	1.81	1.70	1.33	0.979	3.60	0.854	11.8	0.646	1.13
Zr	ppm	n.d.	<0.001	0.014	0.546	0.008	0.095	n.d.	n.d.	n.d.	n.d.	0.438	n.d.	n.d.
Nb	ppm	n.d.	0.110	0.008	0.001	n.d.	0.065	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.
Mo	ppm	n.d.	7.08	0.137	n.d.	0.315	0.058	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.
Cd	ppm	n.d.	0.012	0.002	0.002	0.004	0.013	n.d.	0.333	n.d.	n.d.	6.46	n.d.	n.d.
Sn	ppm	n.d.	<0.001	<0.001	n.d.	0.010	n.d.	n.d.	n.d.	n.d.	n.d.	0.333	n.d.	n.d.
Sb	ppm	n.d.	<0.001	<0.001	0.017	n.d.	0.002	0.021	0.013	n.d.	0.010	3.419	n.d.	n.d.
Cs	ppm	0.123	0.152	0.044	0.071	0.570	0.232	0.179	0.419	0.246	0.230	1.045	0.004	0.168
Ba	ppm	2.64	3.27	0.492	7.11	5.11	2.02	1.67	2.60	9.54	0.39	29.3	2.46	8.35
La	ppm	0.367	3.77	0.075	7.64	1.49	1.92	1.86	1.44	4.15	0.862	3.82	0.574	0.540
Ce	ppm	0.633	4.28	0.118	15.7	1.75	7.83	3.45	3.04	8.44	1.83	7.84	0.986	2.16
Pr	ppm	0.075	0.825	0.026	2.04	0.354	0.521	0.503	0.372	1.04	0.271	1.56	0.105	0.225
Nd	ppm	0.322	3.34	0.145	8.14	1.70	2.09	2.10	1.49	4.19	1.25	7.57	0.458	1.13
Sm	ppm	0.076	0.684	0.035	1.73	0.458	0.477	0.465	0.267	0.887	0.294	2.15	0.143	0.297
Eu	ppm	0.030	0.036	0.011	0.276	0.104	0.037	0.103	0.040	0.229	0.061	0.573	0.025	0.068
Gd	ppm	0.079	0.768	0.040	1.47	0.458	0.471	0.398	0.263	0.767	0.253	2.20	0.113	0.263
Tb	ppm	0.021	0.121	0.007	0.259	0.073	0.073	0.063	0.038	0.130	0.036	0.420	0.036	0.047
Dy	ppm	0.081	0.610	0.038	1.25	0.312	0.333	0.327	0.169	0.697	0.192	2.23	0.123	0.230
Ho	ppm	0.015	0.119	0.007	0.244	0.055	0.060	0.052	0.033	0.129	0.035	0.433	0.028	0.042
Er	ppm	0.061	0.348	0.019	0.680	0.146	0.152	0.141	0.085	0.366	0.088	1.24	0.080	0.116
Tm	ppm	0.007	0.055	0.003	0.120	0.011	0.024	0.020	0.012	0.057	0.011	0.212	0.006	0.017
Yb	ppm	0.055	0.322	0.017	0.743	0.106	0.134	0.117	0.066	0.311	0.075	1.25	0.065	0.119
Lu	ppm	0.006	0.043	0.003	0.109	0.017	0.018	0.013	0.011	0.042	0.009	0.178	0.006	0.017
Hf	ppm	n.d.	0.002	<0.001	n.d.	n.d.	<0.001	n.d.	n.d.	n.d.	n.d.	0.013	n.d.	n.d.
Ta	ppm	n.d.	<0.001	<0.001	n.d.	n.d.	<0.001	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.
Tl	ppm	0.005	0.005	<0.001	0.007	0.009	0.012	0.028	0.032	0.008	0.002	1.656	0.001	0.061
Pb	ppm	0.697	0.851	0.033	5.24	2.32	6.70	0.960	235	4.96	1.13	228	1.18	0.455
Bi	ppm	0.014	0.012	<0.001	0.099	0.010	0.029	0.014	0.155	0.007	0.009	12.6	0.002	1.15
Th	ppm	0.062	0.086	0.008	1.09	0.164	0.371	0.308	0.137	0.102	0.100	0.096	0.062	0.124
U	ppm	0.049	0.715	0.006	1.76	0.045	0.196	0.186	0.115	0.153	0.037	0.265	0.068	0.028

<sup>a</sup> The abbreviations are the same as Table 1.

n.d.: not detected

Appendix B4 Results of analysis of the extracts in step 4 obtained by the BCR scheme.

Sample		22007	22030	25005	25010	25023	28111	31021	32049	33001	33008	33019	33051	34032	34035
Geology <sup>a</sup>		Gr	Fv	Acc	HMt	Sed_u	Sed_n	HMt	Dep	Sed_n	Sed_u	Fv	Acc	Sed_u	Sed_n
Li	ppm	30.3	25.2	45.3	25.6	37.0	29.2	50.1	50.5	22.2	38.6	40.9	58.5	17.0	20.4
Be	ppm	4.06	1.20	1.68	1.01	1.14	2.71	1.71	1.76	1.18	1.45	1.40	1.91	0.939	0.961
Na	%	2.64	0.926	1.11	1.50	0.685	2.48	1.24	0.685	1.80	1.14	1.09	0.508	0.652	0.648
Mg	%	0.106	0.171	0.589	2.52	0.433	0.487	1.17	0.960	0.242	1.10	0.441	1.09	0.340	0.537
Al	%	7.30	5.45	6.65	6.33	5.23	5.49	5.29	7.02	6.04	7.24	5.97	5.37	3.39	3.65
P (×100)	%	0.672	1.27	2.05	2.96	14.9	3.27	6.38	3.48	0.648	24.3	2.10	3.55	11.3	1.70
K	%	2.66	3.04	2.45	1.05	1.18	2.06	1.75	2.12	2.09	1.44	1.98	1.61	1.05	1.40
Ca	%	0.543	0.321	0.079	2.621	0.197	0.547	0.439	0.224	0.762	0.638	0.224	0.057	0.372	0.333
Sc	ppm	3.70	4.78	9.03	23.2	7.47	6.01	10.5	11.2	6.29	12.3	6.7	11.0	5.26	6.74
Ti (×10)	%	1.28	3.36	2.46	5.18	2.99	3.01	4.23	3.11	4.77	3.97	2.41	2.15	3.35	9.88
V	ppm	18.2	46.2	80.3	147	56.5	72.9	96.2	53.2	64.7	55.4	43.2	70.9	68.2	60.3
Cr	ppm	5.20	6.39	49.2	447	77.6	17.6	98.8	40.5	19.0	108	22.1	72.0	111	44.9
Mn (×100)	%	3.31	3.35	2.77	9.84	2.95	4.21	6.15	5.74	3.54	3.58	3.10	2.07	5.30	5.93
Fe	%	1.78	1.67	2.61	5.35	2.42	1.97	3.86	3.54	1.58	3.25	2.15	2.88	4.93	2.10
Co	ppm	1.67	2.62	2.86	23.7	5.07	4.97	12.2	6.37	3.01	8.05	3.76	6.79	5.50	5.33
Ni	ppm	2.65	2.45	18.2	120	25.8	10.1	55.0	12.4	6.78	31.9	9.66	30.9	34.5	13.8
Cu	ppm	8.20	25.2	26.8	71.3	20.4	12.3	41.6	128	6.42	69.7	15.8	38.1	29.2	13.0
Zn	ppm	69.4	80.8	67.1	100	76.4	72.1	138	516	39.0	121	72.9	86.7	162	55.9
Ga	ppm	22.2	14.8	18.0	16.3	14.2	21.0	20.6	17.3	13.4	20.1	17.1	18.0	10.6	11.3
Rb	ppm	193	172	113	61.2	89.5	91.7	94.1	166	87.4	121	129	107	71.8	73.2
Sr	ppm	32.3	62.5	58.3	127	49.1	77.4	78.1	65.5	159	97.6	73.5	28.2	59.9	69.1
Y	ppm	41.2	9.89	5.99	20.9	7.83	9.80	11.2	17.8	11.7	18.4	10.9	8.13	8.28	15.1
Zr	ppm	296	87.1	36.8	14.3	69.3	45.6	57.9	101	63.5	54.9	69.0	56.2	43.4	71.1
Nb	ppm	19.0	13.5	8.18	6.46	11.6	10.1	9.68	10.2	8.52	13.3	9.63	7.41	10.2	12.9
Mo	ppm	1.81	1.53	1.36	0.959	3.26	1.92	1.50	2.40	0.384	6.56	0.898	1.64	3.34	0.98
Cd	ppm	0.093	0.022	n.d.	0.059	n.d.	n.d.	0.048	0.384	n.d.	0.075	0.035	0.030	0.084	0.032
Sn	ppm	5.89	5.63	2.78	2.28	8.58	2.84	4.81	88.7	2.85	69.1	3.79	2.82	30.0	6.34
Sb	ppm	0.314	0.368	0.810	0.356	3.15	0.439	0.953	6.16	0.541	5.40	0.823	1.30	11.5	0.686
Cs	ppm	4.23	4.67	6.06	3.34	4.44	4.41	7.75	10.5	3.24	6.68	6.25	5.31	2.85	2.28
Ba	ppm	159	547	353	223	277	248	366	414	523	481	544	460	277	446
La	ppm	31.7	7.75	13.3	10.8	17.3	25.0	15.4	19.7	19.6	32.6	15.6	36.1	19.9	27.5
Ce	ppm	75.5	16.9	29.7	23.8	37.3	50.8	34.0	43.2	36.7	68.6	31.6	75.5	38.4	54.6
Pr	ppm	8.63	1.79	3.17	2.83	3.63	5.36	3.67	4.34	3.76	7.44	3.42	7.77	4.03	5.97
Nd	ppm	33.9	6.84	12.3	12.5	13.3	19.7	14.3	16.3	13.5	28.8	12.8	28.7	14.7	22.4
Sm	ppm	7.80	1.56	2.20	3.09	2.24	3.38	2.91	3.08	2.19	5.19	2.40	4.59	2.44	3.90
Eu	ppm	0.320	0.343	0.399	0.940	0.430	0.343	0.571	0.675	0.709	0.864	0.424	0.772	0.338	0.526
Gd	ppm	6.92	1.35	1.73	3.39	1.80	2.63	2.43	2.88	1.97	4.48	1.89	3.42	1.89	3.28
Tb	ppm	1.32	0.276	0.266	0.644	0.307	0.396	0.416	0.483	0.338	0.711	0.331	0.397	0.300	0.502
Dy	ppm	7.29	1.53	1.21	3.46	1.53	1.81	2.05	2.81	1.77	3.38	1.76	1.57	1.51	2.36
Ho	ppm	1.48	0.316	0.217	0.698	0.278	0.340	0.405	0.577	0.360	0.600	0.360	0.269	0.265	0.462
Er	ppm	4.93	1.05	0.66	2.04	0.82	1.09	1.23	1.86	1.14	1.80	1.20	0.88	0.82	1.50
Tm	ppm	0.919	0.196	0.103	0.317	0.129	0.180	0.204	0.323	0.200	0.278	0.194	0.152	0.132	0.237
Yb	ppm	6.47	1.26	0.702	1.93	0.840	1.20	1.27	2.07	1.40	1.71	1.30	1.00	0.878	1.65
Lu	ppm	1.08	0.196	0.097	0.255	0.137	0.182	0.188	0.305	0.209	0.244	0.191	0.166	0.130	0.262
Hf	ppm	13.7	2.68	1.22	0.46	1.79	1.55	1.63	2.80	1.88	1.62	2.01	1.45	1.21	2.23
Ta	ppm	2.97	1.13	0.751	0.482	1.16	0.964	0.686	1.34	0.522	1.61	0.862	0.665	0.831	0.845
Tl	ppm	0.992	1.30	0.756	0.370	0.567	0.675	0.734	1.56	0.625	0.682	0.758	0.817	0.458	0.562
Pb	ppm	35.6	31.9	16.3	15.4	51.2	22.6	33.6	273	19.0	114	18.3	15.1	198	26.1
Bi	ppm	5.80	0.371	0.442	0.238	0.678	0.104	0.213	8.05	0.140	2.41	0.365	0.323	0.527	0.147
Th	ppm	72.1	8.39	6.33	4.47	11.5	17.4	7.48	10.9	19.1	14.8	9.33	11.8	19.4	12.6
U	ppm	14.8	3.37	1.30	0.930	1.89	2.53	1.90	2.43	2.58	2.53	1.92	1.94	2.16	1.99

<sup>a</sup> The abbreviations are the same as Table 1.

n.d.: not detected

Appendix B4 Continued.

Sample		35014	35035	36120	42002	43028	44030	44045	49050	53011	54029	73028	84002	57
Geology <sup>a</sup>		LMt	Gr	Mv	Um	Acc	Fv	LMt	Dep	Mv	Um	Dep	Um	Mv
Li	ppm	19.7	21.2	7.45	19.6	35.4	29.8	31.8	21.6	20.5	25.6	24.6	8.37	9.80
Be	ppm	0.82	2.15	0.50	0.91	1.47	2.21	1.28	1.29	0.63	0.73	0.86	0.29	0.44
Na	%	0.706	2.16	1.77	0.891	1.44	1.53	0.787	1.88	1.03	1.25	1.23	0.674	1.02
Mg	%	0.410	1.01	4.67	5.62	0.897	0.424	1.13	1.90	2.74	7.69	0.673	11.0	1.72
Al	%	2.91	6.90	7.96	4.86	5.61	5.83	3.83	6.32	6.98	5.61	5.31	2.52	6.38
P(×100)	%	1.24	2.25	7.42	2.45	2.53	0.574	2.64	1.92	4.18	1.89	6.43	0.876	4.91
K	%	0.862	1.65	0.537	0.963	1.95	2.60	1.25	1.68	0.703	0.976	1.25	0.235	0.524
Ca	%	0.380	2.16	6.07	1.33	0.312	0.181	0.710	1.79	1.99	1.35	0.882	1.29	1.97
Sc	ppm	3.90	30.1	31.4	18.2	8.74	8.08	11.2	11.8	20.7	15.2	10.7	11.6	24.1
Ti(×10)	%	1.32	5.48	7.32	3.60	3.16	1.55	7.04	4.62	10.3	3.22	2.90	1.53	4.04
V	ppm	27.8	58.5	321.2	134	80.8	33.0	128	98.5	236	93.8	96.0	59.9	135
Cr	ppm	19.4	15.3	192	1854	54.9	20.7	96.5	60.7	161	947	48.1	792	47.9
Mn(×100)	%	5.05	12.6	14.6	7.66	3.58	2.13	18.5	8.84	10.4	7.91	6.30	9.43	6.62
Fe	%	1.09	3.57	8.04	5.97	3.33	1.55	4.49	4.16	7.32	5.34	4.34	4.87	6.84
Co	ppm	3.22	6.15	48.4	37.2	7.10	2.88	11.4	12.1	26.3	42.0	6.47	81.3	15.4
Ni	ppm	8.95	4.31	82.8	579	17.5	12.2	27.2	22.1	57.7	594	13.9	1553	15.1
Cu	ppm	17.7	8.76	169	40.9	21.1	8.46	28.8	28.5	29.1	21.3	64.6	11.7	20.7
Zn	ppm	32.2	74.2	106	105	59.2	78.8	98.7	106	127	65.8	1183	45.1	55.7
Ga	ppm	7.75	43.8	15.6	12.0	15.9	17.7	13.9	16.9	18.7	11.9	14.1	4.93	15.9
Rb	ppm	50.1	89.0	17.9	56.7	113	158	80.0	66.1	28.2	40.6	66.0	11.9	20.7
Sr	ppm	85.8	163	328	73.6	114	45.2	86.9	228	189	130	86.9	61.2	125
Y	ppm	5.20	98.7	19.6	10.9	8.39	20.8	17.7	16.7	7.07	9.53	12.2	5.66	13.9
Zr	ppm	6.28	167	74.8	48.0	52.5	62.9	16.9	40.8	105	41.4	83.5	7.87	83.3
Nb	ppm	3.07	20.8	1.94	4.83	6.93	13.4	7.74	6.72	4.92	4.32	7.69	1.59	3.37
Mo	ppm	0.281	1.21	1.12	1.00	1.06	0.55	0.750	2.20	0.947	0.405	8.95	0.326	2.99
Cd	ppm	0.010	0.122	0.065	0.062	0.038	0.045	0.008	0.108	0.057	0.053	9.347	0.034	0.057
Sn	ppm	1.08	3.81	0.863	2.47	1.89	6.94	1.55	3.86	1.76	1.03	164	0.396	2.03
Sb	ppm	0.074	0.390	0.092	1.01	0.667	1.27	0.420	2.20	0.186	0.838	154	0.042	3.12
Cs	ppm	2.11	2.58	0.833	3.17	4.18	4.95	3.56	2.39	1.41	2.41	2.71	0.752	1.08
Ba	ppm	278	460	174	170	401	444	421	434	186	217	378	72	264
La	ppm	17.1	526	5.35	10.4	19.4	15.6	34.9	36.3	8.67	12.4	8.54	5.24	7.02
Ce	ppm	36.0	1009	13.3	24.7	41.0	38.6	70.0	72.2	17.0	24.6	19.1	11.4	14.7
Pr	ppm	3.70	80.3	1.98	2.54	4.21	3.89	7.81	7.46	1.93	2.81	2.04	1.32	1.73
Nd	ppm	13.9	289	9.95	10.6	15.5	15.5	29.6	27.0	7.54	11.2	8.53	5.29	7.60
Sm	ppm	2.32	43.9	2.76	2.20	2.74	3.63	5.39	4.57	1.54	2.23	1.74	1.12	1.89
Eu	ppm	0.432	1.57	0.950	0.509	0.540	0.324	1.01	0.852	0.482	0.617	0.590	0.261	0.609
Gd	ppm	1.79	35.5	3.08	1.94	2.16	3.23	4.18	3.81	1.47	2.03	1.82	1.05	1.89
Tb	ppm	0.238	4.69	0.562	0.349	0.327	0.630	0.672	0.589	0.245	0.323	0.355	0.185	0.383
Dy	ppm	1.00	20.1	3.20	1.90	1.57	3.34	3.07	2.85	1.25	1.70	2.02	0.93	2.19
Ho	ppm	0.164	3.35	0.641	0.370	0.289	0.681	0.600	0.554	0.245	0.334	0.411	0.190	0.468
Er	ppm	0.469	9.11	1.96	1.16	0.865	2.23	1.73	1.59	0.742	1.01	1.25	0.557	1.47
Tm	ppm	0.067	1.33	0.307	0.181	0.147	0.379	0.253	0.277	0.123	0.157	0.206	0.093	0.235
Yb	ppm	0.426	8.10	1.94	1.19	0.915	2.37	1.64	1.69	0.819	1.01	1.30	0.562	1.69
Lu	ppm	0.063	1.16	0.286	0.176	0.142	0.367	0.239	0.262	0.115	0.143	0.203	0.077	0.232
Hf	ppm	0.162	5.89	1.92	1.25	1.436	2.48	0.48	1.35	2.39	1.18	2.24	0.219	2.22
Ta	ppm	0.223	1.50	0.223	0.339	0.571	1.17	0.646	0.486	0.282	0.34	0.643	0.140	0.292
Tl	ppm	0.270	0.423	0.027	0.360	0.591	1.521	0.446	0.595	0.139	0.256	2.923	0.056	0.289
Pb	ppm	14.2	22.9	8.16	18.8	16.7	30.4	19.2	366	14.8	8.76	2624	4.42	20.6
Bi	ppm	0.133	0.231	0.033	0.261	0.271	0.295	0.071	0.560	0.102	0.041	25.4	0.051	7.97
Th	ppm	5.55	128	1.09	3.47	7.36	15.3	10.3	18.0	4.45	3.33	3.72	1.69	2.70
U	ppm	0.660	7.78	0.325	0.784	1.50	2.94	1.05	2.13	0.724	0.679	0.879	0.196	0.535

<sup>a</sup> The abbreviations are the same as Table 1.

n.d.: not detected

Appendix B5 Results of analysis of total contents obtained by the BCR scheme.

Sample Geology <sup>a</sup>		22007	22030	25005	25010	25023	28111	31021	32049	33001	33008	33019	33051	34032	34035
		Gr	Fv	Acc	HMt	Sed_u	Sed_n	HMt	Dep	Sed_n	Sed_u	Fv	Acc	Sed_u	Sed_n
Li	ppm	31.6	25.6	47.6	25.9	41.3	31.3	50.8	53.1	24.3	43.5	42.0	59.9	22.2	21.2
Be	ppm	4.40	1.73	2.03	1.16	1.67	2.88	2.51	2.37	1.45	2.01	1.91	2.12	1.28	1.13
Na	%	2.65	0.928	1.12	1.50	2.53	2.53	1.24	0.689	1.81	1.18	1.09	0.508	0.702	0.678
Mg	%	0.119	0.183	0.613	2.60	0.859	0.527	1.23	1.02	0.281	1.30	0.469	1.14	0.450	0.595
Al	%	7.35	5.51	6.76	6.39	5.59	5.55	5.60	7.21	6.12	7.78	6.06	5.42	3.68	3.69
P (×100)	%	0.808	2.69	2.42	4.69	25.3	5.11	9.23	5.36	1.44	55.4	2.74	4.11	14.9	3.99
K	%	2.67	3.05	2.46	1.06	1.39	2.07	1.76	2.13	2.12	1.48	1.99	1.61	1.07	1.40
Ca	%	0.598	0.429	0.190	2.82	0.949	0.596	0.818	0.437	0.926	1.49	0.443	0.116	0.777	0.378
Sc	ppm	3.94	5.36	9.57	23.9	8.16	6.30	12.1	11.7	6.74	12.7	7.37	11.2	6.01	6.99
Ti (×10)	%	1.28	3.37	2.46	5.18	2.99	3.02	4.24	3.11	4.77	3.97	2.41	2.16	3.35	9.89
V	ppm	24.3	49.1	89.3	155	70.2	75.1	104	61.9	71.0	67.4	56.4	74.2	80.7	68.3
Cr	ppm	6.36	7.59	49.7	465	115	18.7	108	41.8	19.5	193	23.7	72.9	240	47.3
Mn (×100)	%	4.32	5.38	5.14	12.4	8.17	4.52	17.6	23.8	4.80	6.77	5.56	11.9	7.99	6.84
Fe	%	1.85	1.88	2.67	5.46	3.19	2.15	4.40	3.84	1.68	4.11	2.26	3.00	5.84	2.21
Co	ppm	4.46	4.00	7.48	30.0	11.5	6.60	23.3	27.3	4.95	21.0	6.00	12.8	13.4	9.32
Ni	ppm	3.88	3.16	22.5	131	40.8	13.2	70.2	18.0	15.4	95.0	11.3	37.4	150	18.5
Cu	ppm	12.9	33.0	31.5	89.3	101	16.1	55.1	556	12.6	547	21.3	46.3	241	28.9
Zn	ppm	90.9	115	77.3	125	516	88.0	176	2322	57.8	1799	99.4	110	700	91.4
Ga	ppm	22.4	15.1	18.2	16.5	14.9	21.1	21.6	18.2	13.6	21.3	17.5	18.4	11.5	11.8
Rb	ppm	195	174	116	62.3	92.2	92.7	96.4	169	89.7	124	131	107	73.9	73.3
Sr	ppm	34.7	68.4	69.2	140	122	83.3	104	75.8	176	151	88.2	35.0	87.4	74.9
Y	ppm	58.1	18.5	10.6	27.9	19.7	13.2	29.6	24.6	15.1	30.1	22.2	9.9	16.0	20.7
Zr	ppm	296	87.2	36.8	14.3	69.8	45.6	59.2	101	63.6	55.1	69.1	56.6	45.9	71.1
Nb	ppm	20.5	13.5	8.18	6.46	11.6	10.2	9.70	10.2	8.52	13.3	9.63	7.42	10.2	12.9
Mo	ppm	1.96	1.58	1.36	0.99	3.99	1.92	1.50	2.40	0.38	8.07	0.91	1.90	3.38	1.00
Cd	ppm	0.196	0.832	0.034	0.153	0.529	0.015	0.574	6.45	0.032	1.40	0.146	0.103	1.57	0.066
Sn	ppm	5.96	5.63	2.78	2.28	8.58	2.84	4.81	88.8	2.85	69.8	3.79	2.83	30.0	6.35
Sb	ppm	0.323	0.398	0.812	0.398	3.48	0.46	1.01	6.25	0.553	5.80	0.846	1.32	12.3	0.712
Cs	ppm	4.42	4.85	7.27	3.39	4.48	4.49	7.95	13.1	3.57	7.13	6.54	5.74	3.06	2.39
Ba	ppm	176	592	434	261	412	258	471	469	562	785	612	507	399	465
La	ppm	37.2	17.0	15.9	17.5	30.3	28.0	33.0	27.7	23.2	43.4	30.2	36.9	25.5	31.0
Ce	ppm	88.8	34.6	34.0	36.7	59.7	55.4	68.4	59.9	44.8	89.3	58.9	77.9	51.1	62.8
Pr	ppm	9.95	3.73	4.01	4.21	5.92	6.08	7.78	6.16	4.67	9.63	6.47	8.04	5.43	6.82
Nd	ppm	39.3	14.2	16.5	17.9	22.3	22.8	31.1	23.8	17.2	37.7	24.4	30.0	20.5	25.9
Sm	ppm	9.30	3.04	3.52	4.21	4.11	4.06	6.36	4.61	2.95	7.07	4.62	5.00	3.71	4.64
Eu	ppm	0.376	0.530	0.691	1.19	0.772	0.496	1.28	1.02	0.840	1.19	0.783	0.876	0.514	0.675
Gd	ppm	8.64	2.80	3.21	4.45	3.66	3.30	5.97	4.38	2.69	6.22	4.07	3.86	3.21	4.05
Tb	ppm	1.70	0.521	0.490	0.828	0.613	0.521	1.03	0.731	0.464	1.02	0.699	0.469	0.509	0.647
Dy	ppm	9.41	2.82	2.13	4.42	3.09	2.39	5.07	3.93	2.32	5.01	3.51	1.90	2.59	3.14
Ho	ppm	1.94	0.564	0.359	0.891	0.578	0.442	0.970	0.776	0.464	0.925	0.698	0.323	0.478	0.621
Er	ppm	6.35	1.75	0.95	2.62	1.73	1.37	2.70	2.37	1.44	2.74	2.10	1.01	1.43	1.97
Tm	ppm	1.15	0.309	0.140	0.398	0.268	0.218	0.423	0.394	0.241	0.422	0.326	0.173	0.230	0.309
Yb	ppm	7.90	1.92	0.882	2.37	1.60	1.40	2.37	2.45	1.65	2.54	2.04	1.10	1.42	2.09
Lu	ppm	1.29	0.288	0.119	0.311	0.261	0.207	0.332	0.357	0.245	0.369	0.284	0.181	0.215	0.327
Hf	ppm	13.7	2.68	1.22	0.461	1.79	1.55	1.65	2.81	1.89	1.63	2.02	1.45	1.26	2.24
Ta	ppm	2.97	1.13	0.75	0.482	1.16	0.964	0.690	1.34	0.522	1.622	0.862	0.669	0.832	0.848
Tl	ppm	1.02	1.33	0.802	0.385	0.624	0.675	0.826	1.65	0.641	0.913	0.797	0.866	0.500	0.576
Pb	ppm	56.9	69.5	29.9	34.6	102	27.1	71.6	692	53.4	254	51.8	28.0	534	39.8
Bi	ppm	6.61	0.498	0.467	0.243	0.903	0.111	0.274	10.2	0.153	3.01	0.428	0.343	0.598	0.178
Th	ppm	72.9	9.46	6.59	4.59	11.5	17.5	7.87	11.0	19.4	14.9	9.93	11.9	19.7	12.7
U	ppm	16.2	3.98	1.35	1.08	2.61	2.75	2.68	2.71	2.77	3.70	2.31	2.11	2.96	2.28

<sup>a</sup> The abbreviations are the same as Table 1.

n.d.: not detected

Appendix B5 Continued.

Sample		35014	35035	36120	42002	43028	44030	44045	49050	53011	54029	73028	84002	57
Geology <sup>a</sup>		LMt	Gr	Mv	Um	Acc	Fv	LMt	Dep	Mv	Um	Dep	Um	Mv
Li	ppm	20.4	22.8	7.50	20.3	36.1	30.9	34.7	23.8	21.9	26.0	32.4	8.62	10.2
Be	ppm	0.898	2.26	0.504	1.13	1.72	2.56	1.44	1.45	0.982	0.838	1.20	0.314	0.484
Na	%	0.706	2.17	1.78	0.892	1.44	1.53	0.788	1.88	1.04	1.26	1.25	0.675	1.03
Mg	%	0.427	1.05	4.89	6.10	0.977	0.440	1.20	1.95	2.84	8.23	0.746	12.0	1.74
Al	%	2.94	6.98	8.06	4.96	5.67	5.92	3.98	6.39	7.14	5.67	5.87	2.60	6.56
P(×100)	%	2.02	10.9	9.61	2.77	3.62	1.11	5.86	6.82	5.22	5.00	7.20	1.19	4.94
K	%	0.868	1.66	0.54	0.968	1.95	2.61	1.27	1.68	0.716	0.987	1.27	0.239	0.526
Ca	%	0.421	2.41	6.20	1.48	0.507	0.225	0.876	2.01	2.26	2.24	1.63	1.36	2.03
Sc	ppm	4.05	30.3	31.6	18.9	9.54	8.32	11.8	12.1	21.8	16.3	13.2	12.7	24.8
Ti(×10)	%	1.33	5.52	7.36	3.61	3.16	1.56	7.06	4.62	10.3	3.22	2.90	1.53	4.04
V	ppm	36.2	64.5	334	144	84.2	41.3	130	107	241	98.7	101	66.8	136
Cr	ppm	20.1	15.3	192	1888	56.5	21.2	98.2	61.3	165	964	55.5	807	49.2
Mn(×100)	%	6.12	13.5	15.0	15.3	6.23	4.00	19.9	10.3	14.7	9.86	19.6	10.3	6.97
Fe	%	1.14	3.66	8.25	6.34	3.45	1.60	4.68	4.25	7.58	5.72	4.96	5.06	7.21
Co	ppm	4.80	7.08	49.9	54.97	11.8	3.62	16.7	13.8	30.9	51.9	16.4	91.5	16.3
Ni	ppm	10.9	5.00	85.9	698	22.1	12.8	38.5	25.2	59.6	718	24.6	1669	15.7
Cu	ppm	21.1	10.4	188	53.8	25.2	11.1	54.7	85.0	34.0	27.4	493	14.1	22.7
Zn	ppm	40.4	83.0	111	135	69.2	92.5	132	314	163	73.4	4610	51.4	57.7
Ga	ppm	7.79	44.7	15.9	12.6	16.1	18.7	14.1	17.5	19.0	12.0	14.7	4.93	16.4
Rb	ppm	51.7	90.4	18.8	56.7	115	159	82.1	66.3	30.1	42.0	69.1	12.3	21.7
Sr	ppm	88.2	170	337	79.3	123	47.4	96.5	235	217	171	104	64.9	129
Y	ppm	6.48	118	22.5	15.6	12.7	25.5	21.2	21.3	12.5	12.7	38.9	6.81	16.0
Zr	ppm	6.28	167	74.8	48.0	52.5	63.0	16.9	40.8	105	41.4	84.2	7.88	83.4
Nb	ppm	3.07	20.93	1.99	4.83	6.96	13.4	7.74	6.72	4.92	4.32	7.71	1.59	3.37
Mo	ppm	0.292	8.29	1.49	1.01	1.66	0.63	0.75	2.20	0.955	0.405	8.96	0.329	2.99
Cd	ppm	0.027	0.149	0.073	0.176	0.069	0.121	0.021	0.746	0.116	0.072	27.1	0.044	0.065
Sn	ppm	1.08	3.83	0.877	2.47	1.90	6.94	1.55	3.86	1.76	1.03	164	0.396	2.03
Sb	ppm	0.076	0.393	0.092	1.01	0.67	1.28	0.447	2.60	0.187	0.875	162	0.042	3.13
Cs	ppm	2.32	2.84	0.917	3.24	4.99	5.36	3.83	3.43	1.72	2.96	4.15	0.808	1.38
Ba	ppm	290	477	178	216	450	464	453	456	278	241	521	87.4	276
La	ppm	17.8	534	6.63	14.3	22.1	21.5	37.9	41.5	13.8	14.5	16.5	5.84	7.86
Ce	ppm	37.5	1022	16.6	32.1	46.0	57.5	75.7	83.5	28.3	29.2	33.8	12.7	17.9
Pr	ppm	3.86	82.5	2.45	3.47	5.00	5.34	8.60	8.76	3.30	3.45	4.90	1.47	2.08
Nd	ppm	14.6	298	12.3	14.5	19.2	21.3	32.9	32.4	13.0	14.2	22.2	5.92	9.34
Sm	ppm	2.46	46.4	3.33	3.08	3.67	4.94	6.16	5.60	2.69	2.95	5.45	1.31	2.35
Eu	ppm	0.485	1.69	1.06	0.705	0.758	0.411	1.190	0.988	0.782	0.779	1.61	0.290	0.715
Gd	ppm	1.97	38.3	3.64	2.86	3.18	4.50	4.99	4.81	2.53	2.78	6.00	1.22	2.33
Tb	ppm	0.280	5.239	0.658	0.503	0.492	0.827	0.810	0.750	0.426	0.440	1.155	0.231	0.461
Dy	ppm	1.20	23.0	3.68	2.66	2.30	4.22	3.77	3.59	2.21	2.28	6.31	1.11	2.58
Ho	ppm	0.201	3.92	0.732	0.511	0.418	0.834	0.719	0.692	0.425	0.438	1.27	0.229	0.541
Er	ppm	0.589	10.7	2.20	1.52	1.19	2.60	2.05	1.95	1.24	1.28	3.75	0.664	1.67
Tm	ppm	0.082	1.58	0.343	0.234	0.179	0.432	0.297	0.331	0.202	0.195	0.603	0.104	0.266
Yb	ppm	0.530	9.49	2.12	1.47	1.13	2.67	1.90	1.99	1.23	1.24	3.64	0.645	1.90
Lu	ppm	0.074	1.35	0.313	0.212	0.173	0.407	0.270	0.302	0.172	0.173	0.544	0.086	0.262
Hf	ppm	0.164	5.89	1.92	1.25	1.44	2.48	0.477	1.35	2.40	1.18	2.27	0.221	2.22
Ta	ppm	0.223	1.50	0.225	0.340	0.571	1.17	0.647	0.488	0.282	0.340	0.656	0.140	0.292
Tl	ppm	0.289	0.44	0.027	0.386	0.620	1.56	0.491	0.758	0.168	0.276	8.38	0.061	0.529
Pb	ppm	18.3	26.3	8.84	41.3	27.3	66.1	23.3	2119	22.3	12.7	9479	5.86	24.9
Bi	ppm	0.148	0.245	0.034	0.265	0.283	0.329	0.085	0.758	0.109	0.050	38.7	0.053	9.35
Th	ppm	5.61	128	1.10	3.52	7.53	15.7	10.6	18.2	4.56	3.43	3.82	1.75	2.83
U	ppm	0.742	8.75	0.350	0.908	1.58	3.33	1.29	2.47	0.929	0.755	1.25	0.285	0.588

<sup>a</sup> The abbreviations are the same as Table 1.

n.d.: not detected