

Geochemical characteristics determined by multiple extraction from ion-adsorption type REE ores in Dingnan County of Jiangxi Province, South China

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Abstract: This article reports results of the multiple six-step extraction and single step extraction experiments conducted on five ion-adsorption ores and three weathered granite samples collected from the Dingnan County in Jiangxi Province, China. The six-step extraction consists of ion-exchangeable (reacted with sodium acetate) fraction, organic-matter (sodium pyrophosphate) fraction, amorphous Fe oxide and Mn oxide (hydroxylamine at 30°C) fraction, Fe and Mn oxides (hydroxylamine at 60 °C) fraction, clays-sulfide (aqua regia) fraction and silicates (mixture acid) fraction. The five ion-adsorption ores from a mining site contained the ion-exchangeable elements by sodium acetate solution ranging from 174 to 388 ppm REY (43 – 68 % relative to whole-rock contents), from 1.1 to 3.5 ppm Th (3.7 – 9.4 %) and from 0.44 to 1.0 ppm U (14 – 25 %). Concentrations of the extracted elements from the ores by ammonium sulfate solution (single step) range from 170 to 346 ppm REY (42 – 64 %), from 0.03 to 0.31 ppm Th (0.1 – 0.8 %) and from 0.25 to 0.71 ppm U (8 – 18 %). The ion-exchangeable fraction is remarkably depleted in Ce relative to the other REY, and is slightly depleted in HREE and Y, compared with the whole-rock compositions. Thorium is dominantly present in the organic-matter fraction, and is moderately contained in the clay-sulfide fraction and in residue. Uranium is extensively present in the residue, silicates fraction, ion-exchangeable fraction, clays-sulfides fraction, and organic-matter fraction. Results of three weathered granite samples outside of a mine are not significantly different although the REY contents or percentages of ion-exchangeable REY are lower than the ores.

Keywords: REE, Th, U, ion-adsorption ore, granite, weathering, adsorption, extraction, South China

1. Introduction

Rare earth elements (REE: La - Eu) can be classified into light REE (LREE: La - Eu) and heavy REE (HREE: Ga - Lu), and HREE-producing deposits are mostly confined to ion-adsorption type in the world (Roskill, 2011). The ion-adsorption type REE deposits have been economically mined in South China, consisting of weathered granite which is called an ion-adsorption ore. The ore grade is generally several hundred ppm and locally reaches up to 3800 ppm (Wu *et al.*, 1990; Bao and Zhao, 2008). Since REE and Y (REY) are adsorbed on weathering products such as kaolin in the ore, they are extracted by ion-exchange with electrolyte solution like ammonium sulfate solution (Chi and

Tian, 2009). The percentage of ion-exchangeable REY relative to the whole-rock grade is generally over 50% (Wu *et al.*, 1990; Bao and Zhao, 2008; Chi and Tian, 2009).

Several publications have reported the results of extraction experiments on the ion-adsorption ores from South China (Wu *et al.*, 1990; Chi and Tian, 2009; Moldoveanu and Papangelakis 2012; 2013a), from Southeast Asia (Sanematsu *et al.*, 2009; 2013; Imai *et al.*, 2013), and from Africa (Le Couteur, 2011; Moldoveanu and Papangelakis, 2013b). Wu *et al.* (1990) conducted extraction experiments and discussed the genesis of ion-adsorption ores. Chi and Tian (2009) summarized the extraction experiments and metallurgical process of the ores. Recently, Moldoveanu and Papangelakis (2012; 2013a) con-

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ducted the extraction experiments to compare the results in different reagents, pH, concentrations and temperatures. Their results suggest that LREE are more adsorbed than HREE and Y. Few previous works except Hoang *et al.* (1989) and Sanematsu *et al.* (2009; 2013) reported the REE-source minerals in the parent rocks. Mineral assemblage of the REE-bearing minerals is important because it strongly influences the fractionation of REE in the ore formation process (Hoang *et al.*, 1989; Sanematsu *et al.*, 2013). Considering the variety of ion-adsorption ores in different localities, specific geochemical data and mineralogical description are still insufficient to understand a proportion of ion-exchangeable REY, fractionation between LREE and HREE, and impurities in the extracted solutions. It is necessary to investigate the fractionation of REE, because HREE are more precious than LREE. Impurities, particularly Th and U, are not desirable in the extracted solutions.

In this article, we report the extraction results of the six-step and single step extraction experiments on five ion-adsorption ores from a REE mine and three weathered granite outside of the mine in South China, in order to discuss the geochemical characteristics of the ion-adsorption ores and extracted solutions. Residual REE-bearing minerals are also described using a SEM-EDS so that we can presume the REE-source minerals in the ores.

2. Geological background of the studied samples

The Phanerozoic igneous rocks are distributed in South China, and were formed by three major tectonic events: the Middle Paleozoic Kwangshian, Triassic Indosinian and Jurassic-Cretaceous Yanshanian events (e.g., Zhou *et al.*, 2006; Wang *et al.*, 2011; Zhang *et al.*, 2012). The productive ion-adsorption type REE deposits were found in the Nanling Range of the Yanshanian granitoid area, however they are not common in the Kwangshian and Indosinian granitoid areas.

The Yanshanian magmatism is spatiotemporally related to metallogeny in South China, resulting from the southwestward subduction of the Pacific Plate and intraplate tectonics (Wang *et al.*, 2011). The Yanshanian period is divided into the Early Yanshanian (180 – 142 Ma) and Late Yanshanian (142 – 67 Ma) periods (Zhou *et al.*, 2006). Major REE deposits were found in the Early Yanshanian granite area rather than the Late Yanshanian one. The HREE-rich deposit area in the Early Yanshanian age is confined to the middle (southern Jiangxi and northern Guangdong) and south of the Nanling Range (Wu *et al.*, 1992). Some of the Early Yanshanian granite plutons were formed by extensional rift-type intraplate magmatism, consisting of calc-alkaline granite, A-type granite, alkali granite, and syenite (Zhou *et al.*, 2006; Guo *et al.*, 2012). Parent granites

of the ion-adsorption ores consist mainly of calc-alkaline granite and alkali granite based on the chemical compositions (Huang *et al.*, 1989; Bao and Zhao, 2008; Ishihara *et al.*, 2008).

3. Experimental and Analytical Methods

3.1 Sample descriptions

A total of eight weathered granite samples including ion-adsorption ores were selected from the previously studied samples of Murakami and Ishihara (2008). They were collected from weathering profiles of granite in Dingnan County, Jiangxi Province, China. Three samples of 1130S0 to 1130S2 (abbreviated to S0 – S2) were collected from a weathering profile outside of an ion-adsorption type deposit. Five samples of 1130S3 to 1130S7 (abbreviated to S3 – S7) are “ion-adsorption ores” taken from two different weathering profiles are collected from the ion-adsorption type deposit. These sampling locations are in the Early Yanshanian granite area (Murakami and Ishihara, 2008).

The weathered granite samples consist mainly of quartz, K-feldspar and kaolinite, and biotite and plagioclase were rarely identified by X-ray diffraction (Murakami and Ishihara, 2008). Whole-rock chemical compositions (REY, Th and U) of the studied samples are listed in Table 1.

3.2 Conditions of SEM-EDS

Polished mounts of ion-adsorption ores were prepared to observe the occurrences of REE-bearing minerals by using the JEOL JSM-6610LV scanning electron microscope. A qualitative and semi-quantitative analysis was performed by using the Oxford Instruments X-max energy dispersive X-ray spectroscopy system at an accelerating voltage of 15 kV.

3.3 Multiple six-step extraction

Multiple six-step extraction and single step extraction experiments were conducted on the pulverized weathered granite and ion-adsorption ore samples. The extraction experiments and ICP-MS analysis of extracted solutions were conducted in Activation Laboratories Ltd. Procedure of the six-step extraction is shown in Table 2. At the step 1, firstly, exchangeable ions were extracted by 1 M sodium acetate (CH_3COONa) solution of pH = 5 for 1 hour. At the step 2, elements were extracted predominantly by decomposing humic and fulvic acids with alkaline (pH = 10) 0.1 M sodium pyrophosphate ($\text{Na}_4\text{P}_2\text{O}_7$) solution for 1 hour. This alkaline solution may decompose silicate minerals because the solubility of silicate minerals is high in alkaline solution. At step 3, elements were extracted by predominantly leaching amorphous Fe oxides and Mn oxides with 1.24 M hydroxylamine (NH_2OH) at 30 °C for 2 hours. Because the hydroxylamine is a reducing agent, it may dissolve the solids

Table. 1 REY, Th and U contents of studied samples collected from Dingnan County of Jiangxi Province, South China (Murakami and Ishihara, 2008).

Sample #	Rock type	Depth (m)	Y (ppm)	La (ppm)	Ce (ppm)	Pr (ppm)	Nd (ppm)	Sm (ppm)	Eu (ppm)	Gd (ppm)	Tb (ppm)	Dy (ppm)	Ho (ppm)
1130S0	Weathered granite	0.3	64.9	42.4	100	7.62	28.7	6.83	0.45	7.54	1.53	10.6	2.15
1130S1	Weathered granite	0.6	71.2	78.6	235	13.7	49.3	10.1	0.65	10.8	1.85	11.6	2.31
1130S2	Weathered granite	1	59.5	79.0	205	13.4	48.4	9.82	0.59	9.51	1.56	9.68	1.89
1130S3	Ion-adsorption ore	0.25	49.8	48.7	204	10.1	42.4	10.1	1.99	9.58	1.73	10.1	1.89
1130S4	Ion-adsorption ore	0.1	56.6	126	149	26.0	102	20.0	3.28	17.1	2.39	12.6	2.19
1130S5	Ion-adsorption ore	0.3	46.0	58.9	207	12.7	51.6	10.5	1.91	9.66	1.48	8.54	1.60
1130S6	Ion-adsorption ore	0.1	62.0	96.8	172	22.2	92.0	18.3	2.98	15.6	2.18	11.8	2.14
1130S7	Ion-adsorption ore	0.2	62.3	113	300	22.8	89.5	17.6	2.82	15.3	2.18	11.7	2.06

Sample #	Er (ppm)	Tm (ppm)	Yb (ppm)	Lu (ppm)	Th (ppm)	U (ppm)	LREE (ppm)	HREE (ppm)	REE (ppm)	REY (ppm)	Ce/Ce*	Eu/Eu*	La _N /Yb _N
1130S0	6.30	0.993	6.13	0.835	49.9	5.4	186	36.1	222.1	287	1.36	0.19	4.96
1130S1	6.81	1.05	6.41	0.877	51.2	5.1	387	41.7	429.1	500	1.76	0.19	8.80
1130S2	5.46	0.834	4.98	0.692	51.3	4.8	356	34.6	390.8	450	1.54	0.19	11.4
1130S3	5.43	0.90	5.93	0.858	36.8	4.7	317	36.4	353.7	404	2.26	0.62	5.89
1130S4	6.11	0.907	5.80	0.828	30.2	3.2	426	47.9	474.2	531	0.64	0.54	15.6
1130S5	4.46	0.69	4.28	0.608	36.8	4.2	343	31.3	373.9	420	1.86	0.58	9.87
1130S6	5.81	0.851	5.15	0.709	34.2	3.8	404	44.2	448.5	511	0.91	0.54	13.5
1130S7	5.45	0.774	4.59	0.614	28.6	2.8	546	42.7	588.4	651	1.45	0.53	17.7

$Ce/Ce^* = Ce_N / (La_N \times Pr_N)^{1/2}$ and $Eu/Eu^* = Eu_N / (Sm_N \times Gd_N)^{1/2}$, where subscript N represents normalization by C1-chondrite (Sun and McDonough, 1989).

Table. 2 Experimental conditions of the multiple six-step extraction. The series of these experiments were conducted in Activation Laboratories Ltd. in Vancouver, Canada.

Extraction step #	Reagent	pH	Reaction time (hrs)	Dominantly reacting materials
1	1M sodium acetate	5	1	Ion-exchangeable materials
2	0.1M sodium pyrophosphate	10	1	Organic matter (humic and fulvic substances)
3	1.24M hydroxylamine (30°C)	1	2	Amorphous Fe oxide and Mn oxide
4	1.24M hydroxylamine (60°C)	1	2	Fe and Mn oxides
5	Aqua regia	-	2	Clays and sulfides
6	Mixture acid (HF, HNO ₃ , HClO ₄ and HCl)	-	19	Acid-soluble silicates and remaining materials

whose solubilities are high in reduced conditions. At step 4, elements were extracted by leaching remaining crystalline Fe and Mn oxides with 1.24 M hydroxylamine at 30 °C for 2 hours. At the step 5, elements incorporated in clays, sulfides and some remaining materials were leached by aqua regia for 2 hours. Because the aqua regia is an oxidizing agent, it may dissolve the solids whose solubilities are high in oxidized conditions. Lastly, at the step 6, elements incorporated in silicates and some remaining materials were leached by mixture acid consisting of HF, HNO₃, HClO₄ and HCl after 19-hours reaction. We are able to estimate the dominantly-reacted materials from the results of

the individual extraction steps, however it is generally difficult to clarify the reacted materials and to know whether the materials are reacted completely.

3.4 Single-step extraction

In order to check the concentrations of ion-exchangeable elements using a different electrolyte solution, a single step extraction and solution ICP-MS analysis were done by authors in Geological Survey of Japan, AIST. Procedure of the single-step extraction is shown in Table 3. Weathered granite samples were pulverized by an agate mortar and were dried at 105 °C

Table. 3 Experimental condition of the single step extraction using ammonium sulfate solution.

Extraction step #	Reagent	pH	Reaction time (hrs)	Dominantly reacting materials
1	0.5M ammonium sulphate	5.7	24	Ion-exchangeable materials

for 12 hours to evaporate water. The individual samples of 1 g was soaked in 40 ml volume of 0.5 M (6.6 wt%) ammonium sulfate $[(\text{NH}_4)_2\text{SO}_4]$ solution of pH = ~5.7 in a 50 ml centrifuge tube. The centrifuge tubes were mechanically shaken at room temperature for 24 hours so that the solid sample can react with solution sufficiently. The extract was separated from the solid samples by centrifugation for 15 minutes. The supernatant solution was filtered by using a cellulose acetate-type membrane filter ($\phi=0.22 \mu\text{m}$), and the membrane filter was rinsed repeatedly with 50 ml of ultra pure water. The filtered solution was acidified using HNO_3 and was kept in a polypropylene container. Ultra pure water and In standard solution (Wako) as an internal standard was added to the acidified sample solution, and it was prepared to 1 % HNO_3 equivalent before analysis.

Concentrations of extracted elements at the single step extraction were determined by the Agilent Technologies 7500cx ICP-MS at the Geological Survey of Japan, AIST. Flow rates of carrier gas and the ion-lens setting of the ICP-MS were optimized to maximize the signal intensity of Ce and to minimize the oxide production rate ($^{140}\text{Ce}^{16}\text{O}/^{140}\text{Ce} < 0.01$). We monitored ^7Li , ^{23}Na , ^{24}Mg , ^{27}Al , ^{29}Si , ^{31}P , ^{39}K , ^{43}Ca , ^{45}Sc , ^{47}Ti , ^{51}V , ^{53}Cr , ^{55}Mn , ^{57}Fe , ^{59}Co , ^{60}Ni , ^{63}Cu , ^{66}Zn , ^{69}Ga , ^{72}Ge , ^{75}As , ^{85}Rb , ^{88}Sr , ^{89}Y , ^{90}Zr , ^{93}Nb , ^{95}Mo , ^{107}Ag , ^{111}Cd , ^{115}In (internal standard), ^{133}Cs , ^{137}Ba , ^{139}La , ^{140}Ce , ^{141}Pr , ^{146}Nd , ^{147}Sm , ^{153}Eu , ^{157}Gd , ^{159}Tb , ^{163}Dy , ^{165}Ho , ^{166}Er , ^{169}Tm , ^{172}Yb , ^{175}Lu , ^{181}Ta , ^{182}W , ^{205}Tl , ^{208}Pb , ^{209}Bi , ^{232}Th and ^{238}U . Calibration lines were made by multi-element standard solutions of XSTC-1, -8 and -15 (SPEX). The combination of analogue and pulse-counting mode of the ICP-MS was used for monitoring the minor elements and the detector mode was switched to the analog-counting mode automatically when abundant elements were monitored.

4. Results

4.1 Results of SEM-EDS

Backscattered electron images of residual or secondary REE-bearing minerals are shown in Figure 1. Zircon (ZrSiO_4) is the most common REE-bearing mineral in the studied ion-adsorption ores. It is rarely altered and the grain size ranges from 10 to 100 μm (Fig. 1A, 1B, 1C and 1F). Thorium silicate (ThSiO_4 ; thorite or huttonite) is partly found (Fig. 1B). Monazite-(Ce) $[(\text{Ce,Th})\text{PO}_4]$ is relatively uncommon and this is not significantly altered (Fig.

1D and 1E). Apatite $[\text{Ca}_5(\text{PO}_4)_3(\text{F,Cl})]$ is uncommon as well and is partly weathered and degraded (Fig. 1F). Xenotime (YPO_4) is more scarce than monazite and apatite. REE phosphate-silicate is found (Fig. 1F and 1G) and is likely britholite-(Ce) $[(\text{Ce,Ca,Th})(\text{SiO}_4\text{PO}_4)(\text{OH,F})]$. REE fluorocarbonates are partly observed and they are considered to be synchysite-(Ce) $[\text{CaCe}(\text{CO}_3)_2\text{F}]$, parasite-(Ce) $[\text{CaCe}_2(\text{CO}_3)_3\text{F}_2]$ and/or bastnasite-(Ce) $[\text{Ce}(\text{CO}_3)\text{F}]$. These carbonates exhibit fine-grained ($<20 \mu\text{m}$) anhedral shape and occur in the cavities and fractures in K-feldspar. K-feldspar is partly or wholly kaolinitized (Fig. 1H and 1I). Secondary REE-bearing minerals consist of CeO_2 and Mn oxy-hydroxide. They are enriched in Ce(IV) but other REE(III) are rarely incorporated in these materials. CeO_2 is considered to Th-poor cerianite (if it is crystalline) and occurs as aggregates of fine-grained particles. The aggregates of CeO_2 are commonly found with kaolinite, K-feldspar or Mn oxy-hydroxide (Fig. 1K and 1J). Ce-bearing Mn oxy-hydroxide occurs as aggregates of platy crystals (Fig. 1J) or exhibits dendritic texture (Fig. 1L).

4.2 Results of extraction experiments

Results of the extraction experiments are summarized in Tables 4 and 5, and individual element data are presented in Appendix. Percentages of extracted REY, Th and U relative to whole-rock contents are shown in Figures 2, 3 and 4, respectively. Results of the six-step extraction indicate that REY were extracted predominantly from the ion-exchangeable fraction (step 1) and from the organic-matter fraction (step 2) in most of the samples (Fig. 2). The other fractions were relatively poor in REY although the Fe-Mn-oxides fractions (steps 3 and 4) were rich in Ce. Thorium was extracted predominantly from the organic-matter fraction and from the clays-sulfides fraction (step 5), and was present in a residual fraction (Fig. 3). The residual fraction was estimated by subtracting the extracted concentrations (step 1 to step 6) from the whole-rock contents (Table 4). Negative values of the residual fraction in the weathered granite (S0, S1 and S2) and ion-adsorption ore (S6) were attributed to sampling the heterogeneous portions between the whole-rock analysis and extraction experiment. Uranium was extracted from the ion-exchangeable fraction, organic-matter fraction, Fe-Mn-oxides fractions, clays-sulfides fraction and silicates fraction, and was also present in the residual fraction.

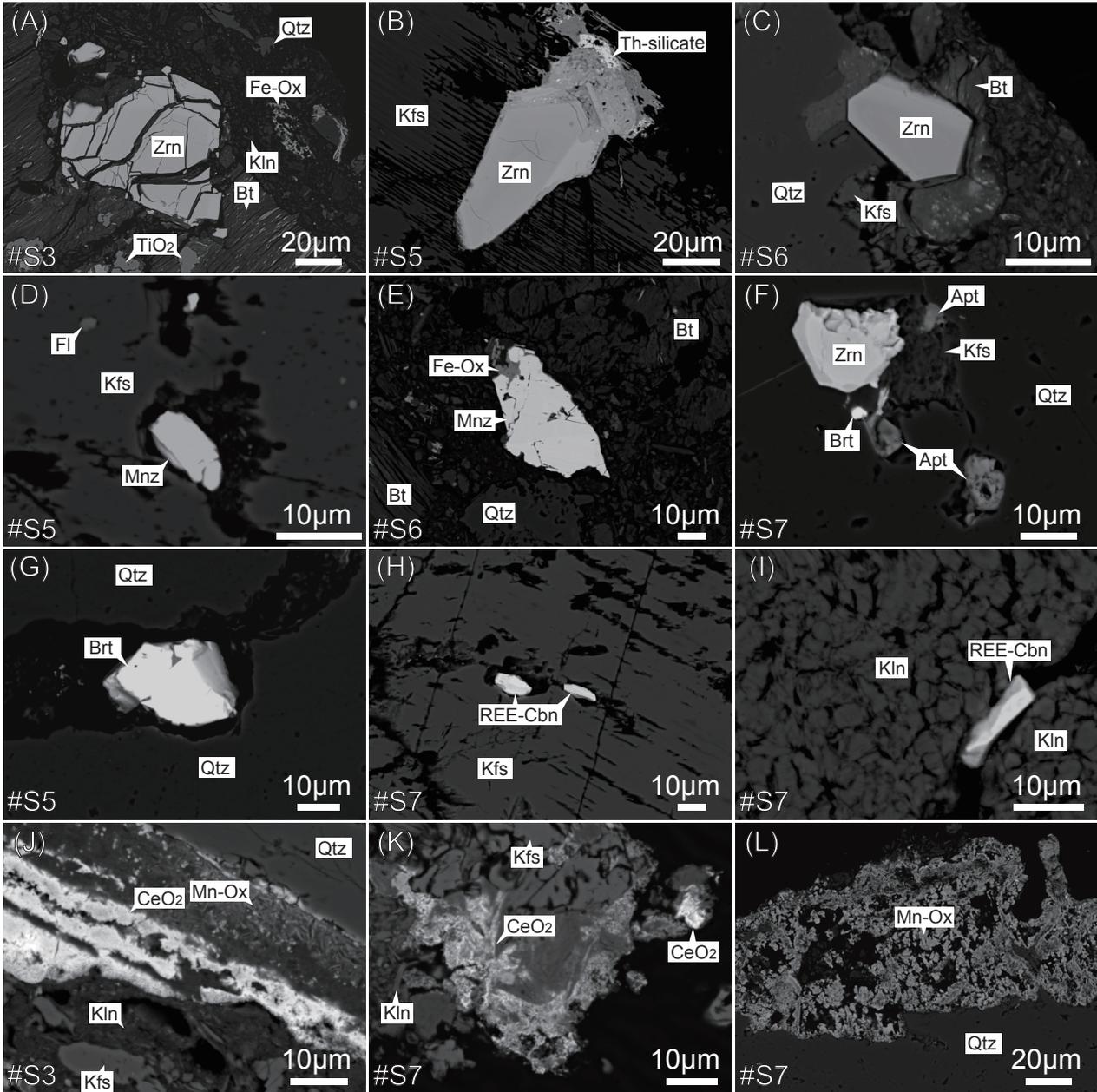


Fig. 1 Backscattered electron images of the ion-adsorption ores. The residual REE-bearing minerals consist mainly of (A, B, C) zircon with lesser amounts of (D, E) monazite-(Ce), (F) apatite, (G) britholite-(Ce) and (H, I) REE fluorocarboxates. The secondary Ce-bearing minerals consist of (J, K) CeO₂ (probably cerianite) and (J, L) Mn oxyhydroxide. Sample numbers (#s) are shown on the individual images. Abbreviations: Zrn, zircon; Kln, kaolinite; Qtz, quartz; Fe-Ox, Fe oxyhydroxide; Bt, biotite; Kfs, K-feldspar; Mnz, monazite-(Ce); Fl, fluorite; Apt, apatite; Brt, britholite-(Ce); REE-Cbn, REE fluorocarboxate-(Ce); Mn-Ox, Mn oxyhydroxide.

4.2.1 Ion-exchangeable fraction

Concentrations of the extracted elements from the five ion-adsorption ores by sodium acetate solution (step 1) range from 174 to 388 ppm REY (43 – 68 % relative to whole-rock contents; the same shall apply hereafter), from 1.1 to 3.5 ppm Th (3.7 – 9.4 %) and from 0.44 to 1.0 ppm U (14 – 25 %). Concentrations

of the extracted elements from the ores by ammonium sulfate solution (single step) range from 170 to 346 ppm REY (42 – 64 %), from 0.03 to 0.31 ppm Th (0.1 – 0.8 %) and from 0.25 to 0.71 ppm U (8 – 18 %).

Concentrations of the extracted elements from the three weathered granite samples by sodium acetate solution (step 1)

Table. 4 Results of the six-step extraction experiment. The other elements are listed in Appendix. Note that negative values of the estimated residual fraction are attributed to sampling the heterogeneous portions between the whole-rock analysis and extraction experiment. See Table 2 for the experimental conditions.

Sample	Fraction	LREE		HREE		REE		Y		REY		Th		U		Ce/Ce*	Eu/Eu*	La _N /Yb _N
		(ppm)	(%)															
Weathered granite S0	Ion-exchangeable (Na acetate)	76.7	41.2	12.8	35.4	89	40.3	20.3	31.3	110	38.2	3.3	6.7	0.85	15.7	0.35	0.16	15.7
	Organic matter	107	57.3	2.3	6.4	109	49.0	2.8	4.3	112	38.9	22.3	44.7	0.7	12.9	13.3	0.13	10.4
	Amorphous Fe-Ox & Mn-Ox	8.9	4.8	0.34	0.94	9.2	4.2	0.49	0.7	9.7	3.4	0.14	0.3	0.05	0.9	6.6	0.16	12.7
	Fe and Mn oxides	20.5	11.0	0.19	0.52	20.7	9.3	0.16	0.2	20.9	7.3	0.11	0.2	0.07	1.3	15.2	0.14	13.8
	Clays and sulfides	4.8	2.6	1.2	3.4	6.0	2.7	2.0	3.1	8.0	2.8	11.5	23.0	0.7	12.9	1.8	n.d.	2.9
	Silicates	4.4	2.3	3.4	9.4	7.8	3.5	4.3	6.6	12.1	4.2	2.8	5.6	1.2	22.2	1.2	0.62	0.81
	Estimated residual	-36	-19	16	44	-20	-9.0	35	54	15	5.2	9.7	19	1.8	34	n.d.	n.d.	n.d.
	Whole-rock content	186	100	36	100	222	100	65	100	287	100	50	100	5.4	100	1.4	0.19	5.0
Weathered granite S1	Ion-exchangeable (Na acetate)	173	44.6	21.1	50.7	194	45	30.4	43	224	44.8	3.6	7.0	0.94	18.3	0.32	0.16	26.5
	Organic matter	163	42.2	3.4	8.2	167	39	4.0	5.6	171	34.1	27.6	53.9	0.8	15.7	10.8	0.12	16.1
	Amorphous Fe-Ox & Mn-Ox	13.2	3.4	0.48	1.1	13.7	3.2	0.61	0.9	14.3	2.9	0.20	0.4	0.05	1.0	5.6	0.18	17.7
	Fe and Mn oxides	31.5	8.1	0.25	0.60	31.8	7.4	0.17	0.2	31.9	6.4	0.13	0.3	0.09	1.7	15.5	0.14	16.6
	Clays and sulfides	4.7	1.2	1.1	2.6	5.8	1.4	1.7	2.3	7.4	1.5	10.8	21	0.7	13.7	3.3	n.d.	2.2
	Silicates	5.5	1.4	3.1	7.4	8.6	2.0	5.3	7.4	13.9	2.8	2.9	5.7	1.3	25.5	1.1	0.75	1.2
	Estimated residual	-3.5	-0.9	12	29	8.7	2.0	29	41	38	7.6	6.0	12	1.2	24	n.d.	n.d.	n.d.
	Whole-rock content	387	100	41.7	100	429	100	71.2	100	500	100	51.2	100	5.1	100	1.8	0.19	8.8
Weathered granite S2	Ion-exchangeable (Na acetate)	208	58.4	20.1	58.2	228	58.4	26.7	44.9	255	56.6	5.4	10.6	1.2	24.3	0.57	0.16	28.7
	Organic matter	133	37.4	3.4	9.9	137	35.0	4.4	7.3	141	31.3	23.2	45.2	0.8	16.8	6.5	0.13	20.3
	Amorphous Fe-Ox & Mn-Ox	7.6	2.1	0.35	1.0	7.9	2.0	0.43	0.7	8.4	1.9	0.16	0.3	0.04	0.9	3.6	0.27	19.1
	Fe and Mn oxides	17.6	4.9	0.23	0.67	17.8	4.6	0.22	0.4	18.0	4.0	0.10	0.2	0.06	1.3	8.4	0.18	19.5
	Clays and sulfides	4.2	1.2	1.5	4.3	5.7	1.4	2.4	4.0	8.1	1.8	8.8	17.2	0.8	16.8	1.1	n.d.	2.4
	Silicates	6.0	1.7	3.3	9.5	9.3	2.4	5.1	8.6	14.4	3.2	3.9	7.6	1.2	25.2	1.0	0.53	1.3
	Estimated residual	-20	-5.7	5.7	16	-15	-3.8	20	34	5.6	1.2	9.7	19	0.7	15	n.d.	n.d.	n.d.
	Whole-rock content	356	100	34.6	100	391	100	59.5	100	450	100	51.3	100	4.8	100	1.5	0.19	11.4
Ion-adsorption ore S3	Ion-exchangeable (Na acetate)	119	37.5	24.1	66.3	143	40.5	30.5	61.2	174	43.0	3.2	8.7	0.71	15.3	0.57	0.51	8.4
	Organic matter	112	35.4	4.3	11.8	117	33.0	4.3	8.6	121	30.0	13.3	36.1	0.4	8.6	8.9	0.47	6.2
	Amorphous Fe-Ox & Mn-Ox	18.0	5.7	0.86	2.4	18.9	5.3	0.86	1.7	19.7	4.9	0.18	0.5	0.03	0.7	7.2	0.49	7.0
	Fe and Mn oxides	24.1	7.6	0.39	1.1	24.4	6.9	0.35	0.7	24.8	6.1	0.05	0.1	0.05	1.0	11	0.45	8.0
	Clays and sulfides	11.9	3.8	1.4	3.8	13.3	3.8	1.7	3.5	15.0	3.7	6.2	16.8	0.8	17.2	1.1	n.d.	6.7
	Silicates	13.6	4.3	2.1	5.8	15.7	4.4	2.7	5.4	18.4	4.6	2.7	7.3	1.0	21.5	0.62	0.89	5.6
	Estimated residual	18	5.7	3.3	8.9	21	6.1	9.4	19	31	7.7	11.2	30	1.7	36	n.d.	n.d.	n.d.
	Whole-rock content	317	100	36.4	100	354	100	49.8	100	404	100	36.8	100	4.7	100	2.3	0.6	5.9
Ion-adsorption ore S4	Ion-exchangeable (Na acetate)	243	57.0	34.3	71.7	277	58.5	38.0	67.9	315	59.5	1.1	3.7	0.45	13.8	0.05	0.49	26.0
	Organic matter	94	22.1	4.7	9.9	99.0	20.9	4.8	8.6	104	19.6	11.4	37.7	0.2	6.2	3.91	0.50	11.3
	Amorphous Fe-Ox & Mn-Ox	17.1	4.0	1.4	2.9	18.5	3.9	1.5	2.7	20.0	3.8	0.17	0.6	0.04	1.3	1.83	0.51	13.3
	Fe and Mn oxides	35.8	8.4	0.82	1.7	36.6	7.7	0.70	1.2	37.3	7.0	0.09	0.3	0.06	1.9	5.09	0.47	12.3
	Clays and sulfides	17.5	4.1	2.5	5.1	19.9	4.2	2.3	4.1	22.2	4.2	10.4	34.4	0.7	21.7	0.63	0.41	9.9
	Silicates	2.7	0.6	0.8	1.7	3.5	0.7	0.70	1.3	4.2	0.8	0.40	1.3	0.5	15.5	0.49	n.d.	1.9
	Estimated residual	15.9	3.7	3.4	7.1	19	4.1	8.0	14	27	5.1	6.6	22	1.3	40	n.d.	n.d.	n.d.
	Whole-rock content	426	100	47.9	100	474	100	56.0	100	530	100	30.2	100	3.2	100	0.64	0.54	15.6
Ion-adsorption ore S5	Ion-exchangeable (Na acetate)	173	50.5	20.4	65.1	193	51.7	24.6	53.5	218	51.9	3.5	9.4	1.03	24.7	0.56	0.45	21.1
	Organic matter	124	36.1	3.5	11.2	127	34.0	3.9	8.4	131	31.2	17.7	48.1	0.8	19.2	7.7	0.44	13.3
	Amorphous Fe-Ox & Mn-Ox	15.8	4.6	0.54	1.7	16.3	4.4	0.56	1.2	16.9	4.0	0.15	0.4	0.06	1.4	6.7	0.44	13.6
	Fe and Mn oxides	17.4	5.1	0.23	0.75	17.7	4.7	0.19	0.4	17.9	4.3	0.06	0.2	0.07	1.8	10	0.41	14.8
	Clays and sulfides	11.7	3.4	1.0	3.2	12.7	3.4	1.1	2.3	13.8	3.3	7.4	20.1	0.4	9.6	1.2	n.d.	9.3
	Silicates	5.4	1.6	1.3	4.2	6.7	1.8	1.9	4.1	8.6	2.1	1.1	3.0	0.5	12.0	0.88	1.68	2.7
	Estimated residual	-4.3	-1.3	4.4	14.0	0.1	0.0	14	30	14	3.3	6.9	19	1.3	31	n.d.	n.d.	n.d.
	Whole-rock content	343	100	31.3	100	374	100	46.0	100	420	100	36.8	100	4.2	100	1.9	0.58	9.9
Ion-adsorption ore S6	Ion-exchangeable (Na acetate)	268	66.3	37.0	84	305	68.0	43.4	70.0	349	68.3	3.0	8.7	0.90	23.9	0.24	0.46	22.0
	Organic matter	113	27.9	4.0	9.1	117	26.0	4.9	7.8	122	23.8	16.1	47.1	0.6	15.9	5.1	0.46	15.3
	Amorphous Fe-Ox & Mn-Ox	14.3	3.5	0.66	1.5	14.9	3.3	0.74	1.2	15.7	3.1	0.23	0.7	0.05	1.4	4.1	0.41	15.1
	Fe and Mn oxides	21.4	5.3	0.30	0.68	21.7	4.8	0.25	0.4	21.9	4.3	0.07	0.2	0.08	2.2	8.2	0.37	14.8
	Clays and sulfides	12.3	3.0	1.0	2.3	13.3	3.0	1.4	2.2	14.7	2.9	8.2	24.0	0.5	13.2	1.3	n.d.	9.3
	Silicates	8.4	2.1	2.0	4.5	10.4	2.3	2.8	4.5	13.2	2.6	2.1	6.1	0.8	21.2	1.0	1.8	2.6
	Estimated residual	-33	-8	-0.8	-1.7	-34	-7.5	8.6	14	-25	-4.9	4.5	13	0.8	22	n.d.	n.d.	n.d.
	Whole-rock content	404	100	44	100	449	100	62.0	100	511	100	34.2	100	3.8	100	0.91	0.54	13.5
Ion-adsorption ore S7	Ion-exchangeable (Na acetate)	298	54.5	39.3	92.1	337	57.3	51.0	81.9	388	59.6	1.7	5.9	0.44	15.8	0.11	0.45	30.3
	Organic matter	66.9	12.3	3.2	7.5	70.1	11.9	4.3	6.8	74.3	11.4	9.1	31.8	0.3	10.7	3.0	0.46	19.5
	Amorphous Fe-Ox & Mn-Ox	26.5	4.9	1.1	2.6	27.6	4.7	1.3	2.1	28.9	4.4	0.27	0.9	0.08	2.8	4.3	0.43	19.0
	Fe and Mn oxides	86.0	15.8	0.65	1.5	86.7	14.7	0.32	0.5	87.0	13.4	0.17	0.6	0.12	4.3	17.0	0.34	17.0
	Clays and sulfides	16.9	3.1	1.3	3.0	18.1	3.1	1.6	2.6	19.8	3.0	10.7	37.4	0.5	17.8	5.8	n.d.	2.9
	Silicates	4.3	0.8	1.7	4.0	6.0	1.0	2.0	3.2	8.0	1.2	1.2	4.2	0.7	24.9	1.4	2.3	0.96
	Estimated residual	48	8.7	-4.5	-11	43	7.3	1.8	2.9	45	6.9	5.5	19	0.7	24	n.d.	n.d.	n.d.
	Whole-rock content	546	100	42.7	100	588	100	62.3	100	651	100	28.6	100	2.8	100	1.45	0.53	17.7

Ce/Ce* = Ce_N/(La_N×Pr_N)^{1/2}, Eu/Eu* = Eu_N/(Sm_N×Gd_N)^{1/2}, where subscript N represents normalization by C1-chondrite (Sun and McDonough, 1989). Whole-rock content data are from Murakami and Ishihara (2008). n.d., Not determined.

Table. 5 Results of the single step extraction showing extracted element concentrations (ppm) and percentages (%) to the whole-rock contents. The other elements are listed in Appendix. See Tables 3 for the experimental conditions.

Sample	Fraction	LREE		HREE		REE		Y		REY		Th		U		Ce/Ce*	Eu/Eu*	La _N /Yb _N
		(ppm)	(%)															
Weathered granite	S0 Ion-exchangeable (ammonium sulfate)	73.3	39.4	11.6	32.1	84.8	38.2	18.4	28.3	103	36.0	0.23	0.45	0.55	10.1	0.38	0.16	17.2
	S1 Ion-exchangeable (ammonium sulfate)	160	41.2	19.3	46.2	179	41.7	28.7	40.4	208	41.5	0.17	0.33	0.64	12.5	0.35	0.15	26.9
	S2 Ion-exchangeable (ammonium sulfate)	187	52.5	18.3	52.9	205	52.5	26.0	43.6	231	51.4	0.34	0.67	0.83	17.4	0.58	0.15	28.8
Ion-adsorption ore	S3 Ion-exchangeable (ammonium sulfate)	119	37.6	22.1	60.8	141	40.0	28.5	57.3	170	42.1	0.25	0.68	0.37	7.9	0.70	0.48	9.4
	S4 Ion-exchangeable (ammonium sulfate)	220	51.6	30.9	64.4	251	52.9	35.6	63.5	286	54.0	0.03	0.10	0.25	7.7	0.06	0.48	26.5
	S5 Ion-exchangeable (ammonium sulfate)	163	47.7	18.3	58.6	182	48.6	23.5	51.2	205	48.9	0.31	0.84	0.71	17.1	0.63	0.45	21.5
	S6 Ion-exchangeable (ammonium sulfate)	256	63.3	34.4	77.8	290	64.7	35.1	56.6	325	63.7	0.20	0.57	0.66	17.5	0.26	0.45	22.0
	S7 Ion-exchangeable (ammonium sulfate)	270	49.4	36.6	85.7	306	52.1	39.5	63.4	346	53.1	0.12	0.41	0.35	12.4	0.12	0.44	29.6

Ce/Ce* = Ce_N/(La_N×Pr_N)^{1/2}, Eu/Eu* = Eu_N/(Sm_N×Gd_N)^{1/2}, where subscript N represents normalization by C1-chondrite (Sun and McDonough, 1989).

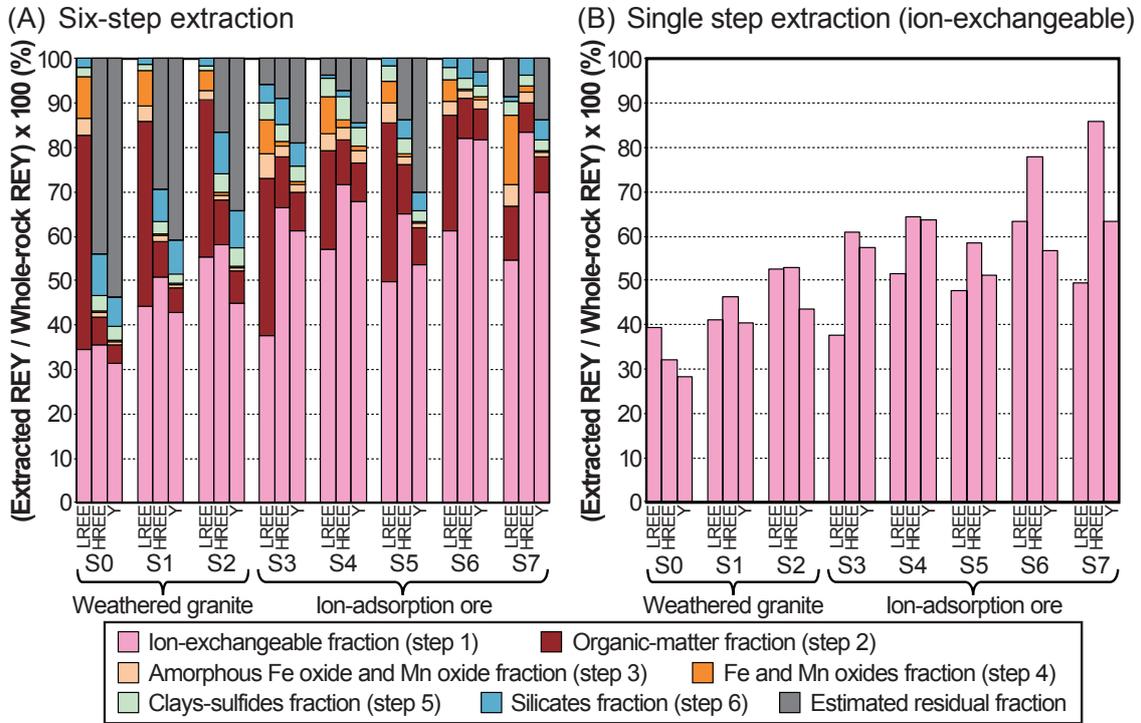


Fig. 2 (A) Percentages of extracted LREE, HREE and Y concentrations relative to their whole-rock contents, determined by the results of (A) the six-step extraction and (B) single step extraction. See Tables 2 and 3 for the experimental conditions. Note that the multiple-extraction columns with total concentrations exceeding 100 % are forcibly corrected to 100 % in total.

range from 110 to 255 ppm REY (38 – 57 %), from 3.3 to 5.4 ppm Th (6.7 – 11 %) and from 0.85 to 1.2 ppm U (16 – 24 %). Concentrations of the extracted elements from the weathered granites by ammonium sulfate solution (single step) range from 103 to 231 ppm REY (36 – 51 %), from 0.17 to 0.34 ppm Th (0.3 – 0.7 %) and from 0.5 to 0.8 ppm U (10 – 17 %).

Depletion of Ce is significant in the ion-exchangeable fraction

and is represented by negative Ce anomalies ($Ce/Ce^* = Ce_N / (La_N \times Pr_N)^{1/2} = 0.05 - 0.57$, where the subscript N represents normalization by C1-chondrite hereafter; Sun and McDonough, 1989). Percentages of extracted Ce concentrations relative to the whole-rock contents are less than 35 %. La_N/Yb_N ratios, which indicate the fractionation between LREE and HREE, in ion-exchangeable fraction range from 8.4 to 30 in all the samples.

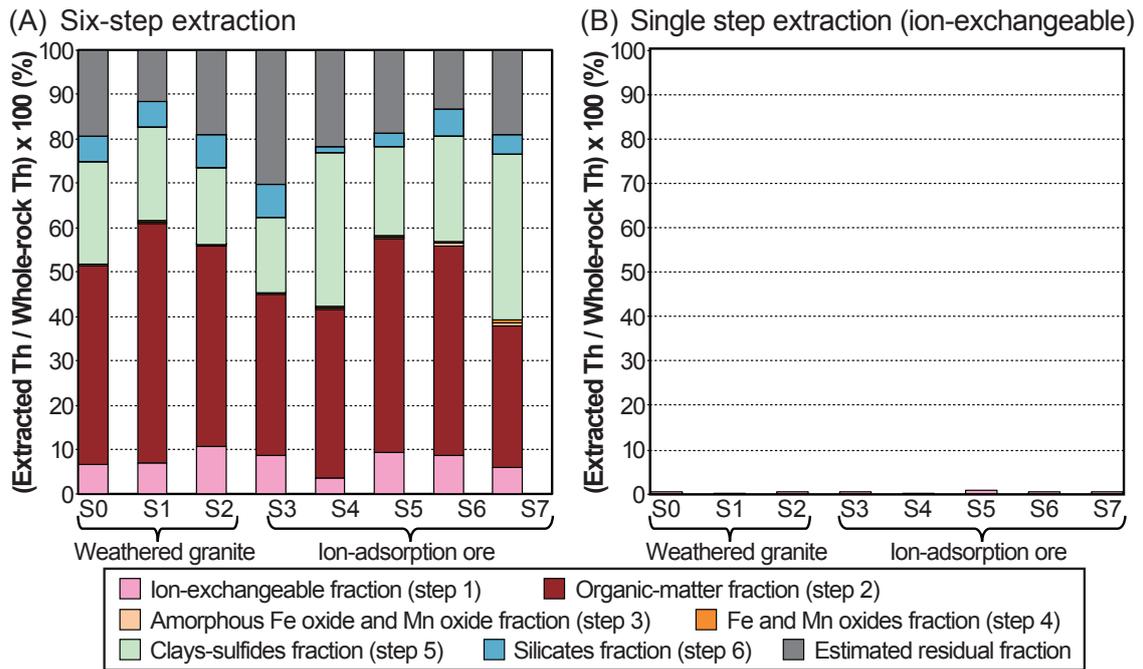


Fig. 3 Percentages of extracted Th concentrations relative to the whole-rock Th contents, determined by the results of (A) the six-step extraction and (B) single step extraction. See Tables 2 and 3 for the experimental conditions.

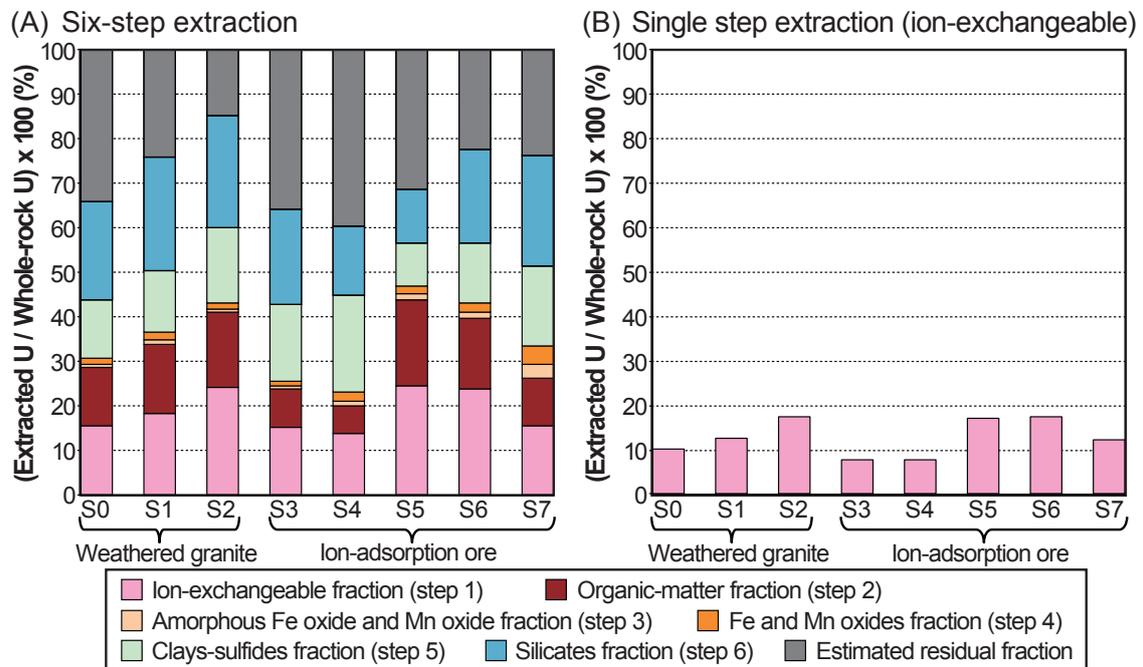


Fig. 4 Results of the sequential extraction showing percentages of extracted U concentrations relative to their whole-rock U contents, determined by the results of (A) the six-step extraction and (B) single step extraction. See Tables 2 and 3 for the experimental conditions.

4.2.2 Organic-matter fraction

In the organic-matter fraction (step 2), concentrations of extracted elements from ion-adsorption ores range from 74 to 131 ppm REY (11 – 31 %), from 9.1 to 18 ppm Th (32 – 48 %) and from 0.2 to 0.8 ppm U (6 – 19 %). Concentrations of extracted elements from weathered granite samples range from 112 to 171 ppm REY (31 – 39 %), from 22 to 28 ppm Th (45 – 54 %) and from 0.7 to 0.8 ppm U (13 – 17 %). All the samples show positive Ce anomalies ($Ce/Ce^* = 3.0 - 13$) and La_N/Yb_N ratios ranging from 6.2 to 20.

4.2.3 Fe-Mn-oxides fraction

Concentrations of REY, Th and U extracted in Fe-Mn-oxides fractions (steps 3 and 4) of all the samples are lower than the first two fractions (steps 1 and 2) except for Ce (Table 4). Cerium is enriched in the steps 3 and 4, showing positive Ce anomalies ($Ce/Ce^* = 1.8 - 17$). La_N/Yb_N ratios range from 7.0 to 20. Results of the step 4 (reaction temperature 60 °C) give higher concentrations of REY and U and lower concentrations of Th than those of the step 3 (reaction temperature 30 °C).

4.2.4 Clays-sulfides fraction

In the clays-sulfides fraction leached by aqua regia (step 5), the ion-adsorption ores show the element concentrations ranging from 14 to 22 ppm REY (3 – 4 %), from 6.2 to 11 ppm Th (17 – 37 %) and from 0.4 to 0.8 ppm U (10 – 22 %). The weathered granites show the element concentrations ranging from 7.4 to 8.1 ppm REY (1 – 3 %), from 8.8 to 12 ppm Th (17 – 23 %) and from 0.7 to 0.8 ppm U (13 – 17 %). La_N/Yb_N ratios range from 2.2 to 9.9, and they are significantly lower than the previous fractions of the extraction steps 1 – 4 in most of the samples.

4.2.5 Silicates fraction

The last step of the six-step extraction is the silicates fraction leached by mixture acid (step 6). Ion-adsorption ores show the concentrations of leached elements ranging from 4 to 18 ppm REY (1 – 5 %), from 0.4 to 2.7 ppm Th (1 – 7 %) and from 0.5 to 1.0 ppm U (12 – 22 %). Weathered granites show the concentrations of leached elements ranging from 12 to 14 ppm REY (3 – 4 %), from 2.8 to 3.9 ppm Th (6 – 8 %) and from 1.2 to 1.3 ppm U (22 – 25 %). Eu anomalies ($Eu/Eu^* = 0.53 - 2.3$ except the sample S3) are significantly higher than those of the other fractions. La_N/Yb_N ratios range from 0.81 to 5.6, and they are lower than the ratios of the other fractions.

5. Discussion

5.1 REE and Y in ion-adsorption ores

Extracted REY concentrations by ammonium sulfate solution

(pH = 5.7) are systematically lower than those by sodium acetate solution (pH = 5.0). This difference in the extracted concentrations is attributed to the differences in ion-exchangeable reagents, solution pH and/or drying temperatures before the experiments. An experimental study indicated that REY are more exchanged by NH_4^+ than by Na^+ from ion-adsorption ores (Moldoveanu and Papangelakis, 2012). This is inconsistent with our extraction results (Fig. 3; Table 4). Extracted REY concentrations are influenced not only by the exchangeable cations (NH_4^+ , Na^+ , etc) but also by the reagents (sulfate, acetate, chloride, etc). It is difficult to compare the ion-exchange efficiency of ammonium sulfate and sodium acetate. Moldoveanu and Papangelakis (2012) also indicated that more REY are extracted from the ores with decreasing pH of solutions. In the present study, the difference in extracted REY concentrations is likely to result from the differences in the reagents and solution pH between sodium acetate solution (pH = 5) and ammonium sulfate solution (pH = 5.7).

The analytical results of all the samples indicate that the majority of REY except Ce is present in the ion-exchangeable fraction (Fig. 2; Table 4). Ion-exchangeable REY excluding Ce range from 136 to 363 ppm (68 - ~100 % relative to whole-rock contents). The significant depletion of ion-exchangeable Ce is recognized in all the samples and it is common in the ion-adsorption type ores (Wu *et al.*, 1990; Sanematsu *et al.*, 2013). The depletion of Ce can be explained by the precipitation of CeO_2 under oxidized conditions (Fig. 1J and 1K) during weathering because the solubility of CeO_2 is lower in oxidized conditions than in reduced conditions in the pH range of soil water (Brookins, 1988). Ce(IV) is present in Mn oxyhydroxide (Fig. 1L), because Ce(III) is commonly adsorbed on Mn oxide and the oxidized Ce(IV) is incorporated in the Mn oxide (Ohta and Kawabe, 2001). Cerium is most abundant in the organic-matter fraction (step 2), and this result implies that CeO_2 was leached by sodium pyrophosphate solution. This fraction has the second highest REY concentrations following the ion-exchangeable fraction (step 1), however Ce accounts for the majority of REY. Cerium is enriched in Fe-Mn-oxides fractions (steps 3 and 4) as well. This Ce enrichment is probably due to the incorporation of Ce into Mn and Fe oxides.

La_N/Yb_N ratios of the ion-exchangeable fraction are significantly higher than those of the other fractions and whole-rock compositions, suggesting that ion-exchangeable REY except Ce are enriched in LREE and depleted in HREE and Y. The depletion of HREE can be recognized in chondrite-normalized REE patterns (Fig. 5), and this mainly results from a difference of weathering resistances between REE fluorocarbonate and zircon. REE fluorocarbonate enriched in LREE was mostly degraded by chemical weathering (Fig. 1H and 1I), in contrast, zircon

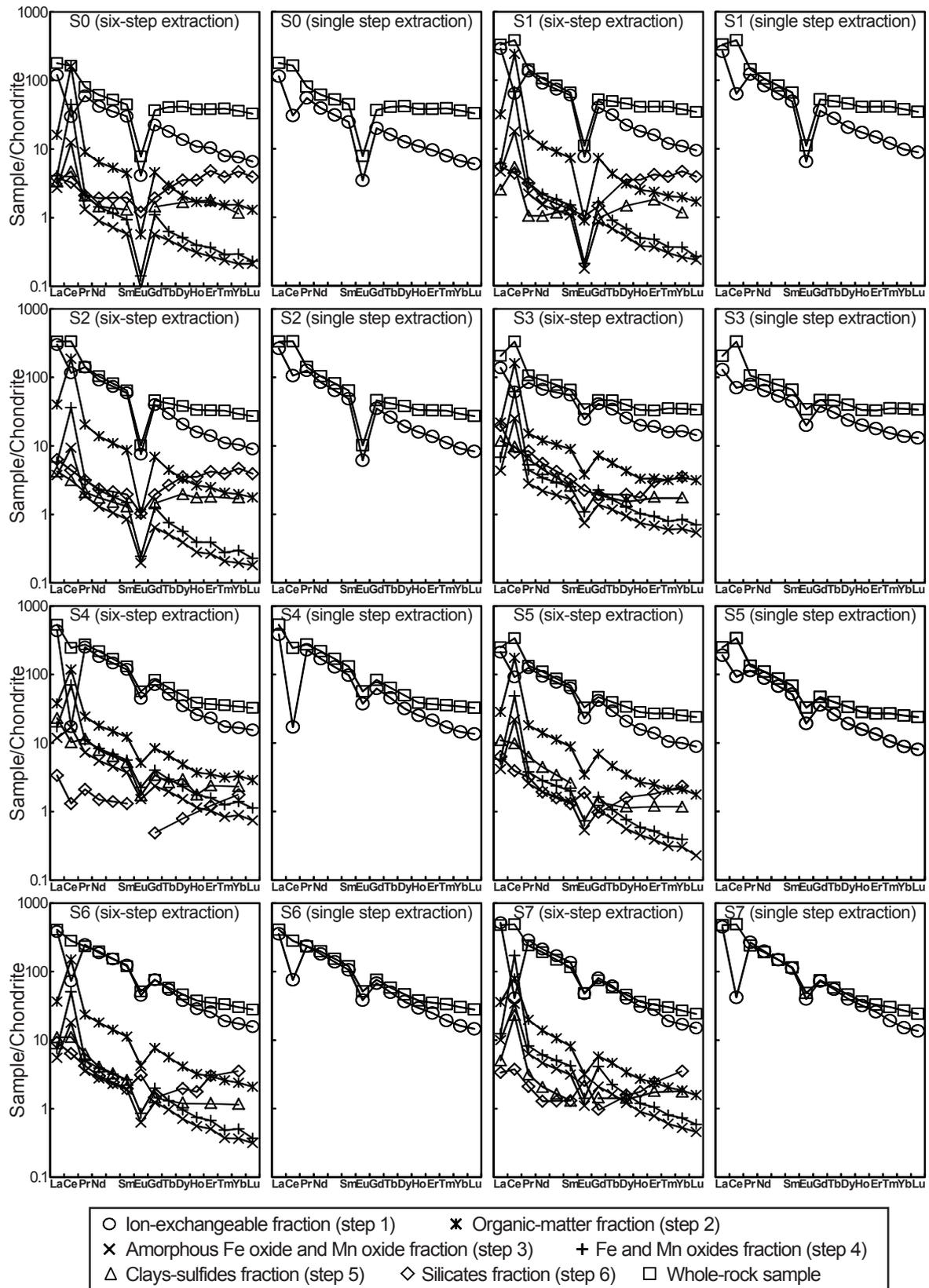


Fig. 5 Chondrite-normalized REE patterns of the each extracted fraction and whole-rock samples in the six-step extraction and single step extraction. The C1-chondrite values are from Sun and McDonough (1989). See Tables 2 and 3 for the experimental conditions.

did not undergo chemical weathering significantly (Fig. 1A, 1B, 1C and 1F). The enrichment of HREE can be seen in the silicates-fraction (step 6), represented by low La_N/Yb_N ratios of 1.0 – 5.6 and chondrite-normalized REE patterns (Fig. 5). This is likely to result from zircon partly leached by the mixture acid. Since zircon was not totally degraded by the acid, large amounts of HREE are present in the estimated residual fraction (Table 4). Huang *et al.* (1989) indicated that typical HREE-rich ion-adsorption ores in Longnan were derived from fractionated granite abundant in synchysite-(Y), which is HREE-rich fluorocarbonate. The ion-exchangeable fraction of these ores would be enriched in HREE because synchysite-(Y) was soluble in soil water and HREE were adsorbed on clays. Sanematsu *et al.* (2013) indicated that LREE-rich ion-adsorption ores in Phuket of Thailand were formed by the parent granite containing abundant fluorocarbonate which is enriched in LREE. These results suggest that the fractionation between LREE and HREE in ion-adsorption ores is constrained by LREE or HREE abundances in primary REE-bearing minerals and their resistances to chemical weathering.

Whole-rock contents of Eu and ion-exchangeable Eu concentrations are low in all the samples. This is consistent with typical ion-adsorption ores depleted in Eu (Wu *et al.*, 1990; Bao and Zhao, 2008). A significant amount of Eu was extracted from the mixture acid fraction (step 6) as well (Table 4), and this suggests that residual plagioclase, the dominant Eu-bearing mineral, was leached by the acid.

Scandium can be included in one of rare earth elements in a broad sense, however the ion-exchangeable Sc concentrations are estimated to be low (up to 0.3 ppm Sc; Appendix). In general, Sc is incorporated in pyroxene and amphibole of ultramafic or mafic rocks, and granite is not enriched in Sc (Sanematsu *et al.*, 2012). These results suggest that ion-adsorption ores rarely have a potential to recover Sc with REY in terms of amount of resource.

These geochemical features of the ion-adsorption ores are not significantly different from the three weathered granite samples collected outside from a mining site. The grades of the studied ion-adsorption ores are lower than the typical ores of South China, reported by Wu *et al.* (1990) and Bao and Zhao (2008).

5.2 Th and U in ion-adsorption ores

Thorium was ion-exchanged by sodium acetate solution (3.7 – 9.4 % of whole-rock content), but was rarely ion-exchanged by ammonium sulfate solution (<1 % of whole-rock content) as shown in Figure 3. This significant difference in the concentrations is presumably due to the different ligands of acetate and sulfate ligands rather than to different pH. Thorium is predominantly present by complexing with organic and inorganic ligands

in solution at a room temperature (Langmuir and Herman, 1980). Thorium(IV) is complexed with acetate at a wide range of pH (Portanova *et al.*, 1975; Rao *et al.*, 2004). In contrast, Th-sulfate complex is insignificant at $pH > \sim 5.5$ (Langmuir and Herman, 1980), and this caused low Th concentrations extracted by ammonium sulfate solution of $pH=5.7$.

Thorium is dominantly present in the organic-matter fraction, and is moderately contained in the clays-sulfides fraction and estimated residual fraction (Fig. 3). The residual fraction may suggest the occurrence of insoluble Th silicates (thorite and/ore huttonite). The host materials of Th are not well understood in the organic-matter fraction and clays-sulfides fraction.

Uranium was ion-exchanged by both sodium acetate and ammonium sulfate solutions and the extracted concentrations are lower in the ammonium sulfate solution. This difference results from the differences in reagents and pH. Uranium(VI) is likely to exist as uranyl (UO_2^{2+}) ion, uranyl-acetate complex or uranyl-sulfate complex in the extracted solutions, because these ion and complexes are common as well as other organic and inorganic complexes at room temperature (Langmuir, 1978; Nguyen-Trung *et al.*, 1992). Since the stability constants of uranyl-acetate and sulfate complexes are not significantly different (Nguyen-Trung *et al.*, 1992), the difference in pH (5.0 and 5.7) may have more influenced the extracted REY concentrations.

Uranium is extensively present in the estimated residual fraction, silicates fraction, ion-exchangeable fraction, clays-sulfides fraction, and organic-matter fraction, however it is rarely present in the Fe-Mn-oxides fractions (Fig. 4). Uranium in the residual and silicates fractions may be derived from zircon and other minerals. Fergusonite ($YNbO_4$), uraninite (UO_2) and coffinite[(U,Th)SiO₄·nH₂O] are relatively common U-bearing minerals in granites, however they were not found on the polished mounts by SEM-EDS. The host materials of U are not well understood in the clays-sulfides fraction and organic-matter fraction.

6. Conclusions

Extraction experiments were conducted on the five ion-adsorption ore samples from South China. The concentrations of ion-exchangeable elements by 1 M sodium acetate solution ($pH = 5$) range from 174 to 388 ppm REY (43 – 68 % relative to whole-rock contents), from 1.1 to 3.5 ppm Th (3.7 – 9.4 %) and from 0.44 to 1.0 ppm U (14 – 25 %). The concentrations of the ion-exchangeable elements by ammonium sulfate solution ($pH = 5.7$) range from 170 to 346 ppm REY (42 – 64 %), from 0.03 to 0.31 ppm Th (0.1 – 0.8 %) and from 0.25 to 0.71 ppm U (8 – 18 %).

The ion-exchangeable fraction is significantly depleted in

Ce because Ce was immobilized as Ce(IV) during weathering before the other REE(III) and Y were adsorbed on weathering products in the ores.

The ion-exchangeable fraction is slightly depleted in HREE and Y relative to whole-rock compositions. The fractionation between LREE and HREE is most likely to be constrained by weathering resistances of primary REE-bearing minerals in the studied samples.

Non-ion-exchangeable REY in the ores are present in residual minerals such as fluorocarbonates-(Ce), monazite-(Ce), REE phosphate-silicate (probably britholite-(Ce)), cerianite and zircon. HREE and Y are dominantly contained in zircon.

The majority of Th and U in the ores are present in organic matter, acid-leachable minerals (e.g., clays, sulfides, silicates) and insoluble minerals. The extracted Th and U concentrations are influenced by the reagents and solution pH.

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Appendix Concentrations of extracted elements in the six-step and single step extraction experiments.

Fraction	Li ppm	Na ppm	Mg ppm	Al ppm	Si ppm	P ppm	K ppm	Ca ppm	Sc ppm	Ti ppm	V ppm	Cr ppm	Mn ppm
S0 Ion-exchangeable (sodium acetate)	<0.1	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.	<0.2	<0.4	<0.02	<0.1	22
S0 Organic matter	1	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.	2.3	n.a.	1.6	<0.5	106
S0 Amorphous Fe oxide and Mn oxide	0.11	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.	<0.2	0.6	<0.5	<5	34
S0 Fe and Mn oxides	0.16	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.	<0.2	<0.5	<0.5	<5	4
S0 Clays and sulfides	1.5	20	20	840	n.a.	n.a.	20	n.a.	0.3	n.a.	3	3	13
S0 Silicates	6.4	310	80	2680	n.a.	n.a.	1330	n.a.	n.a.	n.a.	3	4.1	14
S0 Whole-rock content	n.a.	1039	1210	75700	361000	87	34700	140	n.a.	1500	15	<20	85
S0 Ion-exchangeable (ammonium sulfate)	n.a.	12	22	69	226	<18	318	8	<0.05	<1.5	<0.2	<0.2	26
S1 Ion-exchangeable (sodium acetate)	<0.1	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.	<0.2	<0.4	<0.02	<0.1	17
S1 Organic matter	<1	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.	2.2	n.a.	1.8	<0.5	48
S1 Amorphous Fe oxide and Mn oxide	0.07	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.	<0.2	0.5	<0.5	<5	14
S1 Fe and Mn oxides	0.07	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.	<0.2	<0.5	<0.5	<5	2
S1 Clays and sulfides	1.4	10	10	700	n.a.	n.a.	20	n.a.	0.2	n.a.	3	1	6
S1 Silicates	8.1	400	90	2680	n.a.	n.a.	1370	n.a.	n.a.	n.a.	6	4.2	8
S1 Whole-rock content	n.a.	1039	1330	76400	364000	87	31500	140	n.a.	1380	13	<20	116
S1 Ion-exchangeable (ammonium sulfate)	n.a.	15	22	76	252	<18	325	5	<0.05	<1.5	<0.2	<0.2	20
S2 Ion-exchangeable (sodium acetate)	<0.1	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.	<0.2	<0.4	<0.02	<0.1	29
S2 Organic matter	1	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.	2.5	n.a.	2	0.7	56
S2 Amorphous Fe oxide and Mn oxide	<0.05	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.	<0.2	<0.5	<0.5	<5	20
S2 Fe and Mn oxides	0.12	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.	<0.2	<0.5	<0.5	<5	2
S2 Clays and sulfides	1.6	10	10	660	n.a.	n.a.	20	n.a.	0.2	n.a.	<1	0.7	8
S2 Silicates	8.1	410	100	2660	n.a.	n.a.	1070	n.a.	n.a.	n.a.	3	4.4	11
S2 Whole-rock content	n.a.	890	1390	79400	356000	87	29800	210	n.a.	1380	14	<20	93
S2 Ion-exchangeable (ammonium sulfate)	n.a.	16	19	92	237	<18	260	4	<0.05	<1.5	<0.2	<0.2	36
S3 Ion-exchangeable (sodium acetate)	0.5	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.	0.3	<0.4	<0.02	<0.1	105
S3 Organic matter	3	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.	2.9	n.a.	2.5	0.8	205
S3 Amorphous Fe oxide and Mn oxide	0.22	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.	<0.2	1.2	<0.5	<5	84
S3 Fe and Mn oxides	0.42	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.	<0.2	1.1	<0.5	<5	13
S3 Clays and sulfides	5	10	20	1010	n.a.	n.a.	20	n.a.	1.5	n.a.	5	2.9	27
S3 Silicates	14.3	410	110	2740	n.a.	n.a.	670	n.a.	n.a.	n.a.	4	4.6	34
S3 Whole-rock content	n.a.	742	1450	89000	326000	87	24200	140	n.a.	2640	16	<20	503
S3 Ion-exchangeable (ammonium sulfate)	n.a.	10	23	85	220	<18	203	2	0.11	<1.5	<0.2	<0.2	157
S4 Ion-exchangeable (sodium acetate)	0.3	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.	<0.2	<0.4	<0.02	<0.1	34
S4 Organic matter	4	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.	2.4	n.a.	1.7	1.2	136
S4 Amorphous Fe oxide and Mn oxide	0.37	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.	<0.2	1.6	<0.5	<5	69
S4 Fe and Mn oxides	0.67	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.	<0.2	1	<0.5	<5	10
S4 Clays and sulfides	9.2	10	40	1180	n.a.	n.a.	40	n.a.	1.5	n.a.	2	1.7	42
S4 Silicates	13.2	240	30	1280	n.a.	n.a.	1640	n.a.	n.a.	n.a.	6	5.3	25
S4 Whole-rock content	n.a.	1040	1630	75900	345000	131	34400	140	n.a.	2460	10	<20	395
S4 Ion-exchangeable (ammonium sulfate)	n.a.	13	28	47	254	<18	288	2	<0.05	<1.5	<0.2	<0.2	39
S5 Ion-exchangeable (sodium acetate)	0.8	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.	0.3	<0.4	<0.02	<0.1	35
S5 Organic matter	3	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.	3.5	n.a.	3.2	0.7	70
S5 Amorphous Fe oxide and Mn oxide	0.2	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.	<0.2	0.7	<0.5	<5	26
S5 Fe and Mn oxides	0.39	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.	<0.2	<0.5	<0.5	<5	9
S5 Clays and sulfides	3.7	10	40	810	n.a.	n.a.	30	n.a.	0.9	n.a.	3	2.2	26
S5 Silicates	9.1	420	60	2180	n.a.	n.a.	1390	n.a.	n.a.	n.a.	4	3.4	12
S5 Whole-rock content	n.a.	1630	1870	85400	329000	87	32800	140	n.a.	2340	17	<20	240
S5 Ion-exchangeable (ammonium sulfate)	n.a.	13	47	180	248	<18	366	3	0.13	<1.5	<0.2	<0.2	44
S6 Ion-exchangeable (sodium acetate)	0.1	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.	<0.2	<0.4	<0.02	<0.1	33
S6 Organic matter	2	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.	2.7	n.a.	2.4	0.5	72
S6 Amorphous Fe oxide and Mn oxide	0.15	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.	<0.2	1.1	<0.5	<5	20
S6 Fe and Mn oxides	0.32	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.	<0.2	<0.5	<0.5	<5	6
S6 Clays and sulfides	4.7	20	40	820	n.a.	n.a.	50	n.a.	1.3	n.a.	3	2	32
S6 Silicates	9.6	340	110	3350	n.a.	n.a.	1200	n.a.	n.a.	n.a.	3	5	22
S6 Whole-rock content	n.a.	1930	1390	89700	333000	87	37100	210	n.a.	2340	14	<20	209
S6 Ion-exchangeable (ammonium sulfate)	n.a.	15	35	120	207	<18	350	3	0.09	<1.5	<0.2	<0.2	49
S7 Ion-exchangeable (sodium acetate)	0.2	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.	<0.2	<0.4	<0.02	<0.1	34
S7 Organic matter	2	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.	1.7	n.a.	1	<0.5	117
S7 Amorphous Fe oxide and Mn oxide	0.44	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.	<0.2	1.1	<0.5	<5	108
S7 Fe and Mn oxides	0.72	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.	<0.2	0.6	<0.5	<5	19
S7 Clays and sulfides	7.2	10	60	1070	n.a.	n.a.	70	n.a.	1.5	n.a.	5	3.1	47
S7 Silicates	8.7	320	80	3510	n.a.	n.a.	1410	n.a.	n.a.	n.a.	2	6.8	27
S7 Whole-rock content	n.a.	2230	1690	75200	353000	87	42300	140	n.a.	2160	9	<20	441
S7 Ion-exchangeable (ammonium sulfate)	n.a.	18	41	113	174	<18	392	5	<0.05	<1.5	<0.2	<0.2	47

See Tables 2 and 3 for the experiment conditions.

Whole-rock content data are from Murakami and Ishihara (2008).

n.a., not analyzed.

Appendix (continued)

Fraction	Fe ppm	Co ppm	Ni ppm	Cu ppm	Zn ppm	Ga ppm	Ge ppm	As ppm	Rb ppm	Sr ppm	Y ppm	Zr ppm	Nb ppm
S0													
Ion-exchangeable (sodium acetate)	n.a.	0.53	<0.03	<0.1	<2	0.51	0.05	0.13	2.7	0.3	20.3	<0.08	<0.001
Organic matter	n.a.	3.0	<1	<0.6	18	2.8	<0.3	0.5	27	0.2	2.8	1.2	0.25
Amorphous Fe oxide and Mn oxide	n.a.	0.73	<0.08	<0.04	<0.5	0.23	<0.01	<0.04	1.0	<0.1	0.49	<0.4	0.006
Fe and Mn oxides	n.a.	0.08	<0.08	<0.04	0.8	0.23	<0.01	<0.04	1.2	<0.1	0.16	<0.4	0.012
Clays and sulfides	380	0.5	0.5	0.41	10.9	3.4	<0.1	5.1	14	1.7	2.0	0.9	0.2
Silicates	190	0.5	0.6	<0.2	7.2	9.9	0.1	79	74	32.4	4.3	60	23.7
Whole-rock content	15700	57	< 20	< 10	50	25	1.8	<5	291	12	64.9	179	51.8
Ion-exchangeable (ammonium sulfate)	<6	0.24	<0.2	<0.4	0.43	2.3	n.a.	0.40	5.3	0.23	18.4	<0.5	<0.004
S1													
Ion-exchangeable (sodium acetate)	n.a.	0.33	<0.03	<0.1	<2	0.46	0.12	0.25	2.5	0.2	30.4	<0.08	<0.001
Organic matter	n.a.	1.5	<1	<0.6	13	2.6	<0.3	0.60	24	0.1	4.0	1.3	0.24
Amorphous Fe oxide and Mn oxide	n.a.	0.30	<0.08	<0.04	<0.5	0.22	<0.01	<0.04	0.9	<0.1	0.61	<0.4	0.006
Fe and Mn oxides	n.a.	0.05	<0.08	<0.04	<0.5	0.25	<0.01	<0.04	1.1	<0.1	0.17	<0.4	0.013
Clays and sulfides	260	0.3	0.4	0.29	6.9	2.4	<0.1	2.5	10	1.2	1.65	0.7	0.2
Silicates	140	0.5	0.7	<0.2	6.2	9.3	0.1	75	76	36.3	5.30	63	19.7
Whole-rock content	14100	60	< 20	< 10	30	25	1.5	<5	253	12	71.2	172	49.2
Ion-exchangeable (ammonium sulfate)	<6	0.12	<0.2	<0.4	<0.3	2.2	n.a.	0.88	5.6	0.17	28.7	<0.5	<0.004
S2													
Ion-exchangeable (sodium acetate)	n.a.	0.86	0.04	<0.1	3	1.3	0.12	0.23	2.9	0.2	26.7	<0.08	<0.001
Organic matter	n.a.	3.0	<1	<0.6	19	3.0	<0.3	0.7	22	0.1	4.4	1.7	0.23
Amorphous Fe oxide and Mn oxide	n.a.	0.39	<0.08	<0.04	<0.5	0.13	<0.01	<0.04	0.8	<0.1	0.43	<0.4	0.002
Fe and Mn oxides	n.a.	0.10	<0.08	<0.04	<0.5	0.18	<0.01	<0.04	0.9	<0.1	0.22	<0.4	0.010
Clays and sulfides	380	0.6	0.5	0.22	9.8	2.4	<0.1	1.8	8.5	0.9	2.4	0.7	0.1
Silicates	230	1.1	0.9	<0.2	8.7	8.5	<0.1	79	54	31.1	5.1	51	16.2
Whole-rock content	16000	53	140	70	50	25	2	<5	239	12	59.5	143	37.1
Ion-exchangeable (ammonium sulfate)	<6	0.56	<0.2	0.8	0.71	2.3	n.a.	0.92	5.7	0.19	26.0	<0.5	<0.004
S3													
Ion-exchangeable (sodium acetate)	n.a.	0.47	<0.03	<0.1	<2	0.16	0.09	0.16	3.4	0.2	30.5	<0.08	<0.001
Organic matter	n.a.	2.8	<1	0.7	16	3.2	<0.3	0.9	26	0.2	4.3	2.2	0.43
Amorphous Fe oxide and Mn oxide	n.a.	1.1	<0.08	0.06	<0.5	0.32	<0.01	<0.04	1.0	<0.1	0.86	<0.4	0.009
Fe and Mn oxides	n.a.	0.09	<0.08	0.06	0.8	0.31	<0.01	<0.04	1.7	<0.1	0.35	<0.4	0.016
Clays and sulfides	840	0.5	0.7	0.55	19.1	4.7	<0.1	3.2	18	1.6	1.7	2.2	0.3
Silicates	260	0.3	0.8	<0.2	10.4	8.6	<0.1	67	34	40.1	2.7	41	1.2
Whole-rock content	31300	56	< 20	< 10	70	29	2.4	<5	189	24	49.8	474	43.9
Ion-exchangeable (ammonium sulfate)	<6	0.55	<0.2	<0.4	0.43	0.81	n.a.	0.69	5.1	0.15	28.5	<0.5	<0.004
S4													
Ion-exchangeable (sodium acetate)	n.a.	0.11	<0.03	<0.1	4	1.2	0.24	0.51	2.2	0.2	38.0	<0.08	<0.001
Organic matter	n.a.	1.06	<1	<0.6	22	3.5	<0.3	0.5	12	0.2	4.8	1.1	0.21
Amorphous Fe oxide and Mn oxide	n.a.	0.47	<0.08	0.06	1.3	0.47	0.02	<0.04	1.0	<0.1	1.5	<0.4	0.003
Fe and Mn oxides	n.a.	0.05	<0.08	0.07	1.7	0.42	<0.01	<0.04	1.2	<0.1	0.70	<0.4	0.007
Clays and sulfides	1160	0.6	0.6	0.34	27	5.72	<0.1	2.8	12	1.4	2.3	2	<0.1
Silicates	380	0.3	0.7	<0.2	13.8	12	0.1	78	40	28.2	0.7	39	21.6
Whole-rock content	29200	52	< 20	< 10	50	24	1.9	<5	183	27	56.6	400	39.9
Ion-exchangeable (ammonium sulfate)	<6	<0.05	<0.2	<0.4	0.57	2.0	n.a.	1.9	3.6	0.20	35.6	<0.5	<0.004
S5													
Ion-exchangeable (sodium acetate)	n.a.	2.5	0.1	0.1	3	0.44	0.14	0.26	3.5	0.2	24.6	<0.08	<0.001
Organic matter	n.a.	6.7	<1	1.3	27	3.5	<0.3	1.1	20	0.3	3.9	4.4	0.34
Amorphous Fe oxide and Mn oxide	n.a.	1.4	<0.08	0.08	<0.5	0.27	<0.01	<0.04	1.3	<0.1	0.56	<0.4	0.004
Fe and Mn oxides	n.a.	0.23	<0.08	0.11	1.1	0.22	<0.01	<0.04	1.2	<0.1	0.19	<0.4	0.010
Clays and sulfides	810	1.0	0.6	1.1	24.9	3.5	<0.1	3.2	10	1.3	1.05	2.2	0.1
Silicates	160	0.4	<0.5	<0.2	6.4	8.4	<0.1	63.7	40	36.6	1.9	40	2.9
Whole-rock content	29200	59	< 20	< 10	50	27	1.5	<5	213	32	46	358	35.3
Ion-exchangeable (ammonium sulfate)	<6	1.61	<0.2	<0.4	0.78	2.2	n.a.	0.9	8.0	0.19	23.5	<0.5	<0.004
S6													
Ion-exchangeable (sodium acetate)	n.a.	0.80	0.04	<0.1	2	0.81	0.26	0.55	3.5	0.3	43.4	<0.08	<0.001
Organic matter	n.a.	3.8	<1	1	22	2.9	<0.3	0.9	19	0.3	4.9	3.3	0.34
Amorphous Fe oxide and Mn oxide	n.a.	1.3	<0.08	0.04	<0.5	0.26	<0.01	<0.04	1.2	<0.1	0.74	<0.4	0.004
Fe and Mn oxides	n.a.	0.13	<0.08	0.24	1.2	0.24	<0.01	<0.04	1.3	<0.1	0.25	<0.4	0.012
Clays and sulfides	980	0.8	0.8	1.2	26.6	3.9	<0.1	3.4	14	1.9	1.36	2.2	0.1
Silicates	240	0.3	<0.5	<0.2	9.8	13.8	0.2	74	54	46.4	2.8	51	7.3
Whole-rock content	25700	61	< 20	< 10	60	25	1.8	<5	228	37	62	384	35.2
Ion-exchangeable (ammonium sulfate)	<6	0.77	<0.2	<0.4	0.58	3.6	n.a.	2.0	6.9	0.21	35.1	<0.5	<0.004
S7													
Ion-exchangeable (sodium acetate)	n.a.	0.42	<0.03	<0.1	4	1.5	0.30	0.66	2.8	0.5	51	<0.08	0.006
Organic matter	n.a.	2.4	<1	<0.6	17	2.3	<0.3	0.4	11	0.3	4.3	1.5	0.26
Amorphous Fe oxide and Mn oxide	n.a.	2.2	<0.08	0.09	1.8	0.41	0.01	<0.04	1.4	<0.1	1.3	<0.4	0.003
Fe and Mn oxides	n.a.	0.32	0.08	0.13	3.4	0.51	<0.01	<0.04	1.4	<0.1	0.32	<0.4	0.013
Clays and sulfides	1200	0.9	0.9	1.2	40.5	5.6	<0.1	4.8	19	1.5	1.6	2.9	0.1
Silicates	350	0.3	<0.5	<0.2	11.4	16.8	0.2	73	49	41.7	2	52	10.1
Whole-rock content	22900	79	< 20	< 10	80	24	2.1	<5	239	44	62.3	375	35.4
Ion-exchangeable (ammonium sulfate)	<6	0.22	<0.2	<0.4	0.72	2.8	n.a.	2.2	4.7	0.47	39.5	<0.5	<0.004

See Tables 2 and 3 for the experiment conditions.

Whole-rock content data are from Murakami and Ishihara (2008).

n.a., not analyzed.

Appendix (continued)

Fraction	Mo ppm	Sn ppm	Sb ppm	Cs ppm	Ba ppm	La ppm	Ce ppm	Pr ppm	Nd ppm	Sm ppm	Eu ppm	Gd ppm	Tb ppm	
S0	Ion-exchangeable (sodium acetate)	<0.02	<0.01	<0.005	0.035	15	28.5	18.2	5.66	19.5	4.59	0.24	4.60	0.67
	Organic matter	0.38	n.a.	<0.02	0.84	5.5	3.82	98.1	0.86	3.01	0.68	0.033	0.94	0.11
	Amorphous Fe oxide and Mn oxide	<0.02	<0.1	<0.005	0.06	1.4	0.64	7.6	0.13	0.42	0.089	0.006	0.12	0.018
	Fe and Mn oxides	<0.02	<0.1	<0.005	0.08	<0.05	0.33	19.8	0.08	0.25	0.054	0.003	0.11	0.006
	Clays and sulfides	0.33	0.34	0.05	0.33	2.8	0.8	2.9	0.2	0.68	0.2	<0.1	0.3	<0.1
	Silicates	0.2	4	3.6	1.3	78	0.9	2	0.2	0.9	0.3	0.07	0.4	0.1
	Whole-rock content	< 2	4	3	4.8	93	42.4	100	7.62	28.7	6.83	0.453	7.54	1.53
	Ion-exchangeable (ammonium sulfate)	<0.4	n.a.	n.a.	0.31	11	27.1	18.7	5.24	18.3	3.76	0.20	4.09	0.60
S1	Ion-exchangeable (sodium acetate)	<0.02	<0.01	<0.005	0.041	13	68.8	39.1	12.9	42.1	9.25	0.446	8.29	1.17
	Organic matter	0.46	n.a.	<0.02	1.6	4.5	7.5	148	1.5	5.2	1.1	0.052	1.5	0.16
	Amorphous Fe oxide and Mn oxide	<0.02	<0.1	<0.005	0.07	1.13	1.1	11	0.21	0.71	0.16	0.010	0.18	0.026
	Fe and Mn oxides	<0.02	<0.1	<0.005	0.11	<0.05	0.34	31	0.091	0.31	0.066	0.002	0.16	0.008
	Clays and sulfides	0.37	0.17	0.03	0.7	2.2	0.60	3.3	0.1	0.49	0.2	<0.1	0.2	<0.1
	Silicates	0.2	4	2.7	1.3	73	1.3	2.7	0.3	0.9	0.2	0.06	0.3	<0.1
	Whole-rock content	< 2	4	1	6.3	88	78.6	235	13.7	49.3	10.1	0.645	10.8	1.85
	Ion-exchangeable (ammonium sulfate)	<0.4	n.a.	n.a.	0.43	11	62.4	38.7	11.7	38.9	7.5	0.4	7.4	1.0
S2	Ion-exchangeable (sodium acetate)	<0.02	<0.01	<0.005	0.031	39	71.3	71.3	13.4	42.6	9.06	0.44	8.2	1.11
	Organic matter	0.62	n.a.	<0.02	0.83	10.9	9.5	114	1.9	6.5	1.3	0.059	1.42	0.17
	Amorphous Fe oxide and Mn oxide	<0.02	<0.1	<0.005	0.05	3.1	0.89	5.8	0.18	0.61	0.13	0.011	0.13	0.019
	Fe and Mn oxides	<0.02	<0.1	<0.005	0.08	<0.05	0.49	16.4	0.13	0.45	0.096	0.003	0.13	0.009
	Clays and sulfides	0.49	0.17	0.03	0.26	2.5	1	1.9	0.2	0.82	0.2	<0.1	0.3	<0.1
	Silicates	0.4	3	2.3	1.1	57	1.5	2.7	0.3	1.1	0.3	0.06	0.4	0.1
	Whole-rock content	3	3	3.4	5.0	115	79.0	205	13.4	48.4	9.82	0.591	9.51	1.56
	Ion-exchangeable (ammonium sulfate)	<0.4	n.a.	n.a.	0.35	11	62.7	64.9	12.0	39.6	7.44	0.36	7.24	0.98
S3	Ion-exchangeable (sodium acetate)	<0.02	<0.01	<0.005	0.18	4	32.6	37.5	7.99	31.1	8.41	1.42	8.47	1.28
	Organic matter	0.21	n.a.	<0.02	3.3	6.2	5.2	99	1.4	5.6	1.4	0.22	1.49	0.21
	Amorphous Fe oxide and Mn oxide	<0.02	<0.1	<0.005	0.18	1.01	1.03	15	0.27	1.03	0.26	0.044	0.29	0.044
	Fe and Mn oxides	<0.02	<0.1	<0.005	0.31	<0.05	0.58	23	0.16	0.57	0.13	0.020	0.18	0.018
	Clays and sulfides	0.23	1.25	0.06	1.9	5.3	2.8	6.0	0.6	2.13	0.4	<0.1	0.4	<0.1
	Silicates	<0.1	<0.1	0.2	1.4	160	4.7	4.9	0.8	2.6	0.5	0.13	0.4	<0.1
	Whole-rock content	< 2	4	4.7	11.6	362	48.7	204	10.1	42.4	10.1	1.99	9.58	1.73
	Ion-exchangeable (ammonium sulfate)	<0.4	n.a.	n.a.	0.87	4	30.6	43.2	7.5	29.9	6.82	1.16	7.79	1.15
S4	Ion-exchangeable (sodium acetate)	<0.02	<0.01	<0.005	0.12	36	103.0	10.6	23.8	85.0	18.1	2.59	14.6	1.91
	Organic matter	0.08	n.a.	<0.02	1.9	12.4	8.9	73	2.3	8.3	1.9	0.30	1.7	0.2
	Amorphous Fe oxide and Mn oxide	<0.02	<0.1	<0.005	0.20	4.03	2.8	10	0.69	2.6	0.57	0.088	0.48	0.073
	Fe and Mn oxides	<0.02	<0.1	<0.005	0.24	<0.05	1.3	33	0.36	1.3	0.29	0.043	0.34	0.038
	Clays and sulfides	0.14	1.55	0.05	2.0	14.6	5.5	6.3	1.1	3.68	0.8	0.1	0.7	<0.1
	Silicates	0.2	3	3.7	1.3	321	0.8	0.8	0.2	0.7	0.2	<0.05	0.1	<0.1
	Whole-rock content	< 2	4	2.3	8.3	522	126	149	26.0	102	20.0	3.28	17.1	2.39
	Ion-exchangeable (ammonium sulfate)	<0.4	n.a.	n.a.	0.52	10	91.3	10.4	21.8	79.3	14.9	2.17	12.8	1.70
S5	Ion-exchangeable (sodium acetate)	<0.02	<0.01	<0.005	0.12	12	50.1	56.2	11.9	43.8	9.68	1.34	8.59	1.10
	Organic matter	0.2	n.a.	0.02	2.8	9.6	6.7	107	1.7	6.6	1.4	0.20	1.4	0.17
	Amorphous Fe oxide and Mn oxide	<0.02	<0.1	<0.005	0.20	4.4	0.98	13.4	0.24	0.90	0.21	0.031	0.21	0.029
	Fe and Mn oxides	<0.02	<0.1	<0.005	0.27	<0.05	0.39	16.4	0.11	0.42	0.09	0.012	0.12	0.010
	Clays and sulfides	0.17	0.84	0.78	1.3	4.4	2.6	6.04	0.6	2.09	0.4	<0.1	0.3	<0.1
	Silicates	<0.1	<0.1	0.5	1.4	294	1.5	2.4	0.3	0.9	0.2	0.11	0.2	<0.1
	Whole-rock content	< 2	3	2.2	12.8	550	58.9	207	12.7	51.6	10.5	1.91	9.66	1.48
	Ion-exchangeable (ammonium sulfate)	<0.4	n.a.	n.a.	1.35	11	45.2	57.0	10.8	41.4	7.88	1.12	7.39	0.98
S6	Ion-exchangeable (sodium acetate)	<0.02	<0.01	<0.005	0.12	24	90.7	44.6	23.5	87.7	19.0	2.61	15.6	2.05
	Organic matter	0.17	n.a.	<0.02	2.5	10.7	8.7	92	2.2	8.4	1.7	0.25	1.6	0.21
	Amorphous Fe oxide and Mn oxide	<0.02	<0.1	<0.005	0.17	1.75	1.31	11	0.34	1.3	0.29	0.036	0.25	0.036
	Fe and Mn oxides	<0.02	<0.1	<0.005	0.29	<0.05	0.47	20	0.14	0.53	0.11	0.013	0.16	0.013
	Clays and sulfides	0.21	1.04	0.06	1.4	5.3	2.6	6.8	0.6	1.9	0.40	<0.1	0.30	<0.1
	Silicates	<0.1	<0.1	1.2	1.6	379	2.2	3.9	0.4	1.4	0.3	0.18	0.3	<0.1
	Whole-rock content	< 2	2	2.3	10.2	628	96.8	172	22.2	92	18.3	2.98	15.6	2.18
	Ion-exchangeable (ammonium sulfate)	<0.4	n.a.	n.a.	0.94	18	84.3	46.4	22.4	84.2	16.2	2.2	13.9	1.86
S7	Ion-exchangeable (sodium acetate)	<0.02	<0.01	<0.005	0.07	42	122	25.2	27.4	99.3	20.9	2.76	16.6	2.31
	Organic matter	0.07	n.a.	<0.02	1.1	21.6	8.5	49	1.9	6.5	1.3	0.18	1.2	0.17
	Amorphous Fe oxide and Mn oxide	<0.02	<0.1	<0.005	0.17	17.7	2.4	21	0.60	2.2	0.48	0.064	0.43	0.061
	Fe and Mn oxides	<0.02	<0.1	<0.005	0.23	0.84	0.58	84	0.18	0.67	0.16	0.018	0.41	0.023
	Clays and sulfides	0.28	1.39	0.06	1.6	5.2	1.2	14	0.3	0.97	0.2	<0.1	0.3	<0.1
	Silicates	<0.1	<0.1	1.7	1.5	436	0.8	2.3	0.2	0.6	0.2	0.15	0.2	<0.1
	Whole-rock content	< 2	2	3.8	6.6	774	113	300	22.8	89.5	17.6	2.82	15.3	2.18
	Ion-exchangeable (ammonium sulfate)	<0.4	n.a.	n.a.	0.40	14	106	25.7	25.4	92.6	17.2	2.31	14.9	2.07

See Tables 2 and 3 for the experiment conditions.

Whole-rock content data are from Murakami and Ishihara (2008).

n.a., not analyzed.

Appendix (continued)

Fraction	Dy ppm	Ho ppm	Er ppm	Tm ppm	Yb ppm	Lu ppm	Hf ppm	Ta ppm	Tl ppm	Pb ppm	Bi ppm	Th ppm	U ppm
S0 Ion-exchangeable (sodium acetate)	3.48	0.62	1.73	0.20	1.30	0.17	0.016	0.003	0.02	14	<0.01	3.3	0.85
S0 Organic matter	0.53	0.096	0.28	0.039	0.26	0.033	0.052	<0.003	0.20	9	0.08	22.3	0.7
S0 Amorphous Fe oxide and Mn oxide	0.095	0.018	0.045	0.006	0.036	0.005	<0.005	<0.0005	0.01	2.6	<0.1	0.14	0.05
S0 Fe and Mn oxides	0.035	0.005	0.016	0.001	0.014	0.001	<0.005	<0.0005	0.01	0.39	<0.1	0.11	0.07
S0 Clays and sulfides	0.43	<0.1	0.3	<0.1	0.2	<0.1	<0.1	<0.05	0.07	1.5	<0.02	11.5	0.70
S0 Silicates	0.9	0.2	0.8	0.1	0.8	0.1	2.5	1.8	0.51	7.8	0.08	2.8	1.2
S0 Whole-rock content	10.6	2.15	6.30	0.993	6.13	0.835	6.4	4.1	1.33	36	0.2	49.9	5.4
S0 Ion-exchangeable (ammonium sulfate)	3.21	0.62	1.59	0.20	1.13	0.15	n.a.	<0.002	<0.02	6.0	<0.06	0.23	0.55
S1 Ion-exchangeable (sodium acetate)	5.62	1.02	2.64	0.31	1.86	0.24	0.024	0.004	0.02	11	<0.01	3.6	0.94
S1 Organic matter	0.79	0.14	0.39	0.052	0.33	0.043	0.062	<0.003	0.20	6	<0.04	27.6	0.8
S1 Amorphous Fe oxide and Mn oxide	0.13	0.022	0.061	0.008	0.045	0.006	<0.005	<0.0005	0.02	1.7	<0.1	0.20	0.05
S1 Fe and Mn oxides	0.040	0.006	0.018	0.002	0.018	0.001	<0.005	<0.0005	0.02	0.4	<0.1	0.13	0.09
S1 Clays and sulfides	0.38	<0.1	0.3	<0.1	0.2	<0.1	<0.1	<0.05	0.07	0.99	<0.02	10.8	0.70
S1 Silicates	0.9	0.2	0.7	0.1	0.8	0.1	2.2	1.2	0.41	5.4	0.06	2.9	1.3
S1 Whole-rock content	11.6	2.31	6.81	1.05	6.41	0.877	6.3	4.3	0.86	15	<0.1	51.2	5.1
S1 Ion-exchangeable (ammonium sulfate)	5.2	0.98	2.5	0.3	1.7	0.23	n.a.	<0.002	<0.02	4.8	<0.06	0.17	0.64
S2 Ion-exchangeable (sodium acetate)	5.29	0.904	2.33	0.28	1.78	0.23	0.024	0.004	0.02	32	<0.01	5.4	1.16
S2 Organic matter	0.84	0.15	0.41	0.053	0.34	0.045	0.067	<0.003	0.20	11	<0.04	23.2	0.8
S2 Amorphous Fe oxide and Mn oxide	0.099	0.016	0.044	0.005	0.033	0.005	<0.005	<0.0005	0.01	2.5	<0.1	0.16	0.04
S2 Fe and Mn oxides	0.045	0.006	0.021	0.002	0.017	0.001	<0.005	<0.0005	0.01	0.46	<0.1	0.10	0.06
S2 Clays and sulfides	0.50	0.1	0.3	<0.1	0.3	<0.1	<0.1	<0.05	0.05	1.5	<0.02	8.8	0.80
S2 Silicates	0.9	0.2	0.7	0.1	0.8	0.1	2.2	1.1	0.34	5.7	0.08	3.9	1.2
S2 Whole-rock content	9.68	1.89	5.46	0.834	4.98	0.692	5.2	3.1	0.95	47	0.2	51.3	4.8
S2 Ion-exchangeable (ammonium sulfate)	4.88	0.90	2.27	0.28	1.56	0.21	n.a.	<0.002	<0.02	13.6	<0.06	0.34	0.83
S3 Ion-exchangeable (sodium acetate)	6.5	1.13	3.18	0.40	2.8	0.37	0.03	0.005	0.07	9.7	<0.01	3.2	0.71
S3 Organic matter	1.1	0.19	0.56	0.081	0.60	0.08	0.086	0.008	0.40	7	0.09	13.3	0.4
S3 Amorphous Fe oxide and Mn oxide	0.24	0.042	0.11	0.015	0.11	0.014	<0.005	<0.0005	0.04	4.3	<0.1	0.18	0.03
S3 Fe and Mn oxides	0.086	0.016	0.042	0.005	0.039	0.004	<0.005	<0.0005	0.03	0.93	<0.1	0.05	0.05
S3 Clays and sulfides	0.39	<0.1	0.3	<0.1	0.3	<0.1	<0.1	<0.05	0.15	2.9	0.08	6.2	0.80
S3 Silicates	0.5	0.1	0.5	<0.1	0.6	<0.1	1.4	<0.1	0.22	6	0.09	2.7	1.0
S3 Whole-rock content	10.1	1.89	5.43	0.902	5.93	0.858	11.9	3.3	1.33	42	0.8	36.8	4.7
S3 Ion-exchangeable (ammonium sulfate)	6.03	1.14	2.96	0.39	2.34	0.33	n.a.	<0.002	0.07	2.3	<0.06	0.25	0.37
S4 Ion-exchangeable (sodium acetate)	8.88	1.46	3.82	0.44	2.84	0.39	0.034	0.007	0.03	2.32	<0.01	1.1	0.45
S4 Organic matter	1.2	0.21	0.58	0.08	0.57	0.073	0.051	0.004	0.20	4	<0.04	11.4	0.2
S4 Amorphous Fe oxide and Mn oxide	0.39	0.065	0.17	0.021	0.15	0.019	<0.005	<0.0005	0.03	2.1	<0.1	0.17	0.04
S4 Fe and Mn oxides	0.20	0.034	0.093	0.011	0.086	0.010	<0.005	<0.0005	0.03	0.53	<0.1	0.09	0.06
S4 Clays and sulfides	0.76	0.1	0.4	<0.1	0.4	<0.1	<0.1	<0.05	0.08	4.8	0.06	10.4	0.7
S4 Silicates	0.2	<0.1	0.2	<0.1	0.3	<0.1	1.4	1.4	0.36	9.2	0.07	0.40	0.5
S4 Whole-rock content	12.6	2.19	6.11	0.907	5.8	0.828	10.4	3.4	0.71	23	0.2	30.2	3.2
S4 Ion-exchangeable (ammonium sulfate)	8.09	1.43	3.56	0.43	2.47	0.34	n.a.	<0.002	<0.02	0.29	<0.06	0.03	0.25
S5 Ion-exchangeable (sodium acetate)	5.29	0.89	2.31	0.27	1.70	0.23	0.024	0.004	0.01	19.8	<0.01	3.5	1.03
S5 Organic matter	0.88	0.15	0.41	0.053	0.36	0.045	0.161	0.007	0.10	9	0.07	17.7	0.8
S5 Amorphous Fe oxide and Mn oxide	0.14	0.026	0.064	0.008	0.052	0.006	<0.005	<0.0005	0.01	4.1	<0.1	0.15	0.06
S5 Fe and Mn oxides	0.05	0.008	0.022	0.003	0.015	<0.0005	<0.005	<0.0005	0.02	1.2	<0.1	0.06	0.07
S5 Clays and sulfides	0.30	<0.1	0.2	<0.1	0.2	<0.1	<0.1	<0.05	0.07	6.1	0.07	7.4	0.4
S5 Silicates	0.4	<0.1	0.3	<0.1	0.4	<0.1	1.3	0.1	0.27	6.9	0.07	1.1	0.5
S5 Whole-rock content	8.54	1.60	4.46	0.690	4.28	0.608	9.3	2.8	0.62	27	0.3	36.8	4.2
S5 Ion-exchangeable (ammonium sulfate)	4.88	0.90	2.23	0.27	1.51	0.21	n.a.	<0.002	<0.02	9.0	<0.06	0.31	0.71
S6 Ion-exchangeable (sodium acetate)	9.61	1.62	4.27	0.49	2.96	0.40	0.042	0.009	0.02	14.1	<0.01	3.0	0.90
S6 Organic matter	1.1	0.18	0.50	0.066	0.41	0.053	0.131	0.007	0.10	7	<0.04	16.1	0.6
S6 Amorphous Fe oxide and Mn oxide	0.18	0.032	0.084	0.010	0.062	0.008	<0.005	<0.0005	0.01	2.3	<0.1	0.23	0.05
S6 Fe and Mn oxides	0.064	0.011	0.027	0.003	0.024	0.001	<0.005	<0.0005	0.01	0.82	<0.1	0.07	0.08
S6 Clays and sulfides	0.31	<0.1	0.2	<0.1	0.2	<0.1	<0.1	<0.05	0.07	5.0	0.06	8.2	0.5
S6 Silicates	0.5	0.1	0.5	<0.1	0.6	<0.1	1.7	0.3	0.38	9.5	0.08	2.1	0.8
S6 Whole-rock content	11.8	2.14	5.81	0.851	5.15	0.709	9.5	2.7	0.83	38	0.3	34.2	3.8
S6 Ion-exchangeable (ammonium sulfate)	9.24	1.67	4.11	0.49	2.75	0.37	n.a.	<0.002	<0.02	5.5	<0.06	0.20	0.66
S7 Ion-exchangeable (sodium acetate)	10.3	1.75	4.59	0.49	2.89	0.38	0.05	0.009	0.02	2.4	<0.01	1.7	0.44
S7 Organic matter	0.86	0.15	0.40	0.052	0.31	0.04	0.069	0.005	0.10	8	<0.04	9.1	0.3
S7 Amorphous Fe oxide and Mn oxide	0.31	0.051	0.13	0.015	0.089	0.012	<0.005	<0.0005	0.05	6.7	<0.1	0.27	0.08
S7 Fe and Mn oxides	0.10	0.017	0.045	0.005	0.035	0.003	<0.005	<0.0005	0.06	1.0	<0.1	0.17	0.12
S7 Clays and sulfides	0.37	<0.1	0.3	<0.1	0.3	<0.1	<0.1	<0.05	0.12	6.2	0.05	10.7	0.5
S7 Silicates	0.4	0.1	0.4	<0.1	0.6	<0.1	2	0.5	0.49	11.6	0.08	1.2	0.7
S7 Whole-rock content	11.7	2.06	5.45	0.774	4.59	0.614	9.3	2.7	1.33	46	0.2	28.6	2.8
S7 Ion-exchangeable (ammonium sulfate)	10.1	1.80	4.29	0.49	2.58	0.34	n.a.	<0.002	0.03	0.59	<0.06	0.12	0.35

See Tables 2 and 3 for the experiment conditions.

Whole-rock content data are from Murakami and Ishihara (2008).

n.a., not analyzed.

南中国江西省定南県の イオン吸着型希土類鉱の多段階抽出実験から得られた地球化学的特徴

実松健造・昆 慶明

要 旨

中国江西省定南県から採取したイオン吸着鉱 5 試料と風化花崗岩 3 試料について、6 段階抽出実験及び 1 段階抽出実験を行った結果を本稿にて報告する。6 段階抽出実験はイオン交換、有機物、非晶質 Fe 酸化物・Mn 酸化物、Fe-Mn 酸化物、粘土・硫化物、珪酸塩のフラクションから構成される。イオン吸着型 REE 鉱床から採取したイオン吸着鉱 5 試料を酢酸ナトリウム水溶液でイオン交換した結果、抽出された元素濃度は REY(REE+Y)で 174–388 ppm (全岩含有量の 43–68 %に相当)、Th で 1.1–3.5 ppm (3.7–9.4 %)、U で 0.44–1.0 ppm (14–25 %)であった。同様にイオン吸着鉱を硫酸アンモニウム水溶液でイオン交換した結果、元素濃度は REY で 170–346 ppm REY (全岩含有量の 42–64 %に相当)、Th で 0.03–0.31 ppm (0.1–0.8 %)、U で 0.25–0.71 ppm (8–18 %)であった。イオン交換フラクションは Ce が他の REY に比べ著しく枯渇しており、また HREE と Y は全岩組成に比べて若干枯渇していた。Th は有機物フラクションに主に存在し、粘土・硫化物フラクション及び残渣にも含まれる。U は残渣、珪酸塩、イオン交換、粘土・硫化物、有機物フラクションに幅広く存在する。鉱床外から採取した風化花崗岩 3 試料の結果も鉱石の結果と大きく変わらなかったが、REY 含有量またはイオン交換性 REY の割合が鉱石よりも若干低かった。