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The Determination of Major and Minor Elements on the Two Geochemical Reference Samples, JA–1 and JB–2, and Six Geochemical Exploration Reference Samples

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Abstract

The major and minor elements have been analysed on the two Japanese reference samples, JA–1 and JB–2, and the six geochemical exploration reference samples. Silicon was determined by a combined method with both gravimetric and atomic absorption method, and titanium, aluminium, total iron, manganese, magnesium, calcium, sodium, potassium, arsenic, cobalt, copper, lithium, nickel, lead, rubidium, strontium and zinc were analysed by atomic absorption method. Other elements were determined using a spectrophotometry for phosphorus, chlorine and fluorine, combustion-infrared absorption photometry for carbon and sulfur, titrimetry for ferrous iron, and gravimetry for water. The results of analyses are tabulated in Tables from 2 to 6. Reported values for these elements are not in good agreement in many cases.

1. Introduction

Recently, OHMORI (1976) and TAKAMATSU (1978) reported some of the data for major elements on the two Japanese Geological Survey standard reference samples JA–1 (andesite) and JB–2 (basalt). However an agreement is very poor for several elements.

ALLCOTT and LAKIN (1974 and 1978) compiled the data by 85 and 109 laboratories for six geochemical exploration reference samples GXR–1 (jasperoid), GXR–2 (soil), GXR–3 (hot spring deposit), GXR–4 (porphyry copper ore), GXR–5 (soil) and GXR–6 (soil). However, most part of the data has been obtained by rapid method for geochemical exploration, and the results are not in good agreement.

In this study, major and minor elements were determined using a high accuracy routine method in our laboratory, and the results are compared with reported values.

2. Analytical method

References for the analytical methods are listed in Table 1. The outline of the procedures in this study is given below.

Silica and **Titanium**: Fuse 0.5 g sample with 2 g Na_2CO_3 and 0.3 g H_3BO_3 and dissolve by 20 m*l* HCl (1 + 1). Heat on the steam bath until completion of formation of gelatinous silica. Separate the gelatinous silica by filtration after addition of polyethylene oxide solution. Determine silica as the gelatinous by gravimetric method, and the fraction in the filtrate by atomic absorption method. Determine titanium in the filtrate by atomic absorption method.

Aluminium: Fuse 0.1 g sample with 2 g Na_2CO_3 and 0.3 g H_3BO_3, and dissolve by heating with 20 m*l* HCl (1 + 1). Dilute to 200 m*l* with water, and determine by atomic absorption method.

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Table 1 Analytical methods of this study.

Elements	Methods	References
Si	A.A. + Grav.	TERASHIMA (1972)
Ti, Al	A.A.	TERASHIMA (1972)
T.Fe, Mn, Mg Ca, Na, K	A.A.	TERASHIMA (1970)
FeO	Titr.	MAEDA *et al.* (1969)
P	Photom.	BAADSGAARD *et al.* (1954)
H_2O+, H_2O-	Grav.	MAEDA *et al.* (1969)
LOI	Grav.	MAEDA *et al.* (1969)
As	A.A.	TERASHIMA (1976)
C, S	Comb.	TERASHIMA (1978)
Cl, F	Photom.	TERASHIMA (1974)
Co, Cu, Li, Ni Pb, Sr, Zn	A.A.	TERASHIMA (1971)
Rb	A.A.	TERASHIMA (1973)

A.A.: Atomic absorption spectrometry
Grav.: Gravimetry
T.: Total
Titr.: Titrimetry
Photom.: Absorption spectrophotometry
LOI: Loss on ignition
Comb.: Combustion-infrared absorption photometry

Iron (total), **Manganese, Magnesium, Calcium, Sodium** and **Potassium**: Decompose 0.1 g sample with 3 m*l* $HClO_4$, 3 m*l* HNO_3 and 5 m*l* HF. Evaporate to dryness, and dissolve by heating with 2.5 m*l* HCl (1 + 1) and 10 m*l* water, then add 5 m*l* strontium chloride solution (Sr 40 mg/m*l*). Dilute to 50 m*l* with water, and determine the six elements by atomic absorption method.

Ferrous Iron: Decompose 0.5 g sample with 5 m*l* H_2SO_4 (1 + 1) and 10 m*l* HF in a covering 30 m*l* platinum crucible on the hot plate. Transfer the crucible to a beaker containing 10 m*l* saturated boric acid solution and 300 m*l* water. Determine ferrous iron by titrating with N/20 potassium permanganate solution.

Phosphorus: Decompose 0.5 g sample with 5 m*l* HNO_3 and 10 m*l* HF by evaporating to dryness. Repeat the evaporation with 5 m*l* HNO_3, then dissolve by 10 m*l* HNO_3 (1 + 2) and 5 m*l* saturated boric acid solution. After filtration into a 100 m*l* flask, add 5 m*l* each of ammonium vanadate (0.5%) and ammonium molybdate (10%) solution. Mix, allow to stand for 30 minutes, and measure the absorbance at 460 nm.

Water: Determine water (±) by Penfield method, and water (−) by heating at 105–110°C for 2 hours.

LOI (loss on ignition): Ignite 0.5 g sample at 1000–1050°C for 1 hour.

Carbon and **Sulfur**: Take out 0.1 to 0.5 g sample into a ceramic crucible, add iron powder and tungsten chips accelerators. Determine carbon and sulfur by an infrared absorption method, after combustion in a high-frequency induction furnace.

Chlorine and **Fluorine**: Fuse 0.5 g sample with 3.5 g Na_2CO_3 and 0.6 g ZnO, and dissolve the melt in hot water. After filtration, neutralize by 4.2 m*l* HNO_3, and obtain 50 m*l* of sample solution. Determine chlorine and fluorine by absorption measurement utilizing the stable colored iron (III)

thiocyanate and zirconium-eriochrome cyanine R complex.

Arsenic: Decompose 0.1 to 0.5 g sample with a mixture of 4 m*l* $HClO_4$, 3 m*l* HNO_3, 10 m*l* HF and 2.5 m*l* potassium permanganate solution (2%) in a Teflon beaker, and evaporate nearly to dryness. Dissolve the residue with 6 m*l* water and 3 m*l* HCl, then transfer a portion of the solution to a polyethylene reaction bottle. Determine arsenic by arsine generation-atomic absorption method.

Cobalt, Copper, Lithium, Nickel, Lead, Zinc, Strontium and **Rubidium**: Decompose 0.5 g sample with 8 m*l* $HClO_4$, 5 m*l* HNO_3 and 10 m*l* HF by heating to dryness. Add 5 m*l* HCl (1 + 1) and 10 m*l* water, and heat to dissolve the content. Dilute to 50 m*l* with water and obtain a sample solution. Determine cobalt, copper, lithium, nickel, lead and zinc by atomic absorption method. Pipette a 10 m*l* of the sample solution into a 25 m*l* flask, and add 2.5 m*l* lanthanum chloride solution (La 50 mg/m*l*), then determine strontium by atomic absorption method. Take a 5 m*l* of the sample solution into a 10 m*l* flask. Add 1 m*l* of potassium chloride solution (K 50 mg/m*l*), and determine rubidium by atomic absorption method.

A Nippon Jarrell–Ash AA–781 atomic absorption spectrophotometer with a background corrector was used for all the atomic absorption analyses. Three types of flame were adopted as follows: an argon-hydrogen flame for arsenic, a nitrous oxide-acetylene for silicon, titanium and aluminium, and an air-acetylene for other elements. A Kokusai Electric I.R.-Matic "C–S" VK–111 AS simultaneous analyzer was used for carbon and sulfur.

3. Results and Discussion

Analytical results of this study and other works for major elements on the JA–1 and JB–2 are given in Table 2. The values of OHMORI (1976) are obtained by conventional wet chemical methods. The

Table 2 Results of major elements for JA–1 and JB–2 (%).

	JA–1			JB–2		
	This study	OHMORI (1976)	TAKAMATSU (1978)	This study	OHMORI (1976)	TAKAMATSU (1978)
SiO_2	63.78	63.87		53.54	53.45	
TiO_2	0.86	0.84	1.04	1.22	1.26	1.54
Al_2O_3	15.42	15.50		14.59	14.64	
Fe_2O_3	2.68			3.18		
FeO	4.15			9.96		
MnO	0.17	0.16	0.18	0.22	0.23	0.29
MgO	1.64	1.67		4.63	4.76	
CaO	5.87	5.89	6.09	9.80	9.93	12.39
Na_2O	3.97	3.94		2.05	2.09	
K_2O	0.80	0.82	0.72	0.42	0.42	0.42
P_2O_5	0.17	0.15		0.11	0.11	
H_2O+	0.19			0.06		
H_2O-	0.20			0.04		
Sum	99.90			99.82		
T.Fe as Fe_2O_3	7.29	7.26	8.47	14.25	14.29	16.96

T.: Total

TAKAMATSU's (1978) data are determined by non-dispersive X-ray fluorescence. The agreement for all the elements between present study and OHMORI (1976) are fairly good.

The results for major elements in six geochemical exploration reference samples are shown in Table 3. The values of carbon dioxide were calculated from total carbon data. For the case of GXR–2 and GXR–5 samples, the obtained values of the carbon dioxide plus the total water are clearly higher than the loss on ignition. This conflicting result is probably resulted from noncarbonate carbon contained in the samples. The most part of fluorine in the GXR–3 sample was lost by igniting at 1000°C for 2

Table 3 Results of major elements for GXR samples (%).

	GXR–1	GXR–2	GXR–3	GXR–4	GXR–5	GXR–6
SiO_2	48.46	44.44	13.29	65.44	39.43	45.50
TiO_2	0.05	0.47	0.14	0.48	0.38	0.88
Al_2O_3	6.60	37.43	10.80	13.21	40.80	33.82
$T.Fe_2O_3$	36.70	2.63	28.20	4.45	4.77	7.95
MnO	0.12	0.13	3.02	0.02	0.04	0.14
MgO	0.33	1.26	1.29	2.86	1.77	0.90
CaO	1.24	1.24	20.45	1.39	1.09	0.22
Na_2O	0.06	0.75	1.06	0.73	1.00	0.15
K_2O	0.05	1.58	0.90	4.98	0.98	2.18
P_2O_5	0.17	0.18	0.28	0.30	0.09	0.13
LOI	5.27	9.32	17.36	4.72	8.65	8.09
Sum	99.05	99.43	96.79	98.58	99.00	99.96
$T.H_2O$	4.41	4.68	7.91	2.91	5.39	7.64
T.C as CO_2	0.62	9.67	4.87	0.22	6.05	0.66
F	—	—	7.80	—	—	—

T.: Total
LOI: Loss on ignition

Table 4 Results of minor elements for JA–1 and JB–2 (ppm).

	JA–1		JB–2	
	This study	TAKAMATSU (1978)	This study	TAKAMATSU (1978)
As	3.1		3.0	
C	40		31	
Cl	38		273	
Co	15		40	
Cu	43	46	258	234
F	199		118	
Li	11		8	
Ni	5		19	
Pb	6	12	7	40
Rb	11	21	7	9
S	16		19	
Sr	272	353	183	173
Zn	87	97	103	92

Table 5 Comparison of results for five elements in two samples by different digestion methods on the atomic absorption analyses.

Elements	Methods	GXR-1		GXR-5	
		Range	Mean	Range	Mean
Co	A	2–59	22	21–88	37
	B	4–52	21	23–120	47
Cu	A	380–1440	1087	188–638	360
	B	1032–1300	1168	298–675	375
Ni	A	5–140	46	31–155	77
	B	28–140	53	65–160	90
Pb	A	149–1200	728	5–370	36
	B	700–1200	842	12–130	38
Zn	A	120–1050	739	17–124	49
	B	700–1050	841	40–200	65

A: All the digestion method (taken from ALLCOTT and LAKIN, 1974).
B: Digestion with HF plus various other acids (taken from ALLCOTT and LAKIN, 1978).

Table 6 Results of minor elements for GXR samples (ppm).

	GXR-1		GXR-2		GXR-3	
	This study	Others	This study	Others	This study	Others
As	436	303	23	20	3980	3216
Co	6	21	8	23	44	61
Cu	1150	1168	74	89	14	29
Li	9	8	71	54	148	104
Ni	35	53	14	34	59	77
Pb	801	842	648	730	21	51
Rb	4	3	80	46	102	91
S	2436	2600	315	300	2420	2500
Sr	290	261	158	100	1030	776
Zn	833	841	498	566	210	229

	GXR-4		GXR-5		GXR-6	
	This study	Others	This study	Others	This study	Others
As	103	74	12	12	297	233
Co	13	27	28	47	20	34
Cu	6430	6495	342	375	67	75
Li	12	12	55	41	41	32
Ni	38	54	67	90	26	45
Pb	43	64	7	38	99	116
Rb	177	107	41	21	85	42
S	17600	17150	278	300	131	200
Sr	235	239	110	138	44	38
Zn	68	83	46	65	114	141

Others: As (Spectrophotometry) and S(Titrimetry) data from ALLCOTT and LAKIN (1974). Others data (Atomic absorption spectrometry after digestion with HF plus various other acids) from ALLCOTT and LAKIN (1978).

hours.

The results of present study and TAKAMATSU's (1978) data for minor elements on the JA–1 and JB–2 are listed in Table 4 for comparison. The agreement for copper, strontium and zinc are generally good.

ALLCOTT and LAKIN (1974, 1978) compiled the very varied results on the GXR samples for minor elements determined by atomic absorption spectrometry, emission spectrography, colorimetry and others. The ranges and means of the results obtained by atomic absorption methods are listed in Table 5 as an example. Taking only results of the atomic absorption method into consideration, there is great diversity on the results. The different results on atomic absorption methods are due to digestion of sample, elimination of interference and selection of calibration standard. The data obtained by all the digestion methods including those with diluted nitric acid only, are lower than those obtained with hydrofluoric acid plus various other acids (Table 5). Thus the sample digestion without mixing hydrofluoric acid may provide incomplete decomposition of the siliceous sediments, giving rise to the lower values.

In this study, the digestion of sample and the elimination of interference were carefully done as described in the previous papers. The calibration standards were prepared by reagent materials, and the accuracy is checked by standard reference samples JG–1 (granodiorite) and JB–1 (basalt). The results of this study and selected other data for minor elements on the GXR samples are tabulated in Table 6. The agreement for arsenic, copper, sulfur, strontium and zinc are generally good.

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地球化学的標準試料 JA–1, JB–2 及び 6 種の地化学探査用標準試料中の主成分と微量成分の定量

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最近我国地質調査所で調製された 2 種の地球化学的標準試料 JA–1（安山岩），JB–2（玄武岩）及び米国地質調査所で調製された 6 種の地化学探査用標準試料 GXR–1（ジャスペロイド），GXR–2（土じょう），GXR–3（温泉沈殿物），GXR–4（ポーフィリ・カッパー原鉱），GXR–5（土じょう），GXR–6（土じょう）中の主成分及び微量成分を定量した．

JA–1, JB–2 中の主成分としては，SiO_2, TiO_2, Al_2O_3, Fe_2O_3, FeO, MnO, MgO, CaO, Na_2O, K_2O, P_2O_5, $H_2O(+)$, $H_2O(-)$ を定量し，微量成分としては，As, C, Cl, Co, Cu, F, Li, Ni, Pb, Rb, S, Sr, Zn の13成分を定量した．これら試料について他の方法による分析値の公表は少なく，詳細な比較はできなかったが，主要主成分 9 成分について湿式の化学分析法により得られた値とは良好な一致を示した．

6 種の地化学探査用標準試料中の主成分としては，SiO_2, TiO_2, Al_2O_3, Fe_2O_3, MnO, MgO, CaO, Na_2O, K_2O, P_2O_5, H_2O, CO_2 及び強熱減量を定量し，微量成分としては As, Co, Cu, Li, Ni, Pb, Rb, S, Sr, Zn を定量した．微量成分については，他の方法による多数の分析値が公表されているが，これらのうち As については吸光光度法，イオウについては滴定法，他の成分については試料をフッ化水素酸と他の無機酸で分解した後原子吸光法で定量した結果とほぼ良好な一致を示した．

なお研究では，SiO_2 の定量には重量法と原子吸光法を組合せた方法を用い，TiO_2, Al_2O_3 は亜酸化窒素—アセチレンフレーム，Fe_2O_3, MnO, MgO, CaO, Na_2O, K_2O, Co, Cu, Li, Ni, Pb, Zn, Rb, Sr は空気—アセチレンフレーム，As はアルゴン—水素フレームを用いる原子吸光法で定量した．P_2O_5, Cl, F は吸光光度法，C，S は燃焼—赤外吸収分析法，FeO は滴定法，$H_2O(\pm)$ 及び強熱減量は重量法により定量した．

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