

## Determination of Major and Minor Elements on the Six GSJ Rock Reference Samples

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**Abstract:** Major and minor elements have been analyzed on the six rock reference samples of Geological Survey of Japan (GSJ), JA-1, JB-2, JB-3, JGb-1, JR-1 and JR-2. Major elements were determined by atomic absorption spectrometry or wet chemical method. Combustion and infrared absorption photometry was used for carbon and sulfur determinations, flame emission spectrometry for cesium and rubidium, and atomic absorption spectrometry for arsenic, beryllium, bismuth, cadmium, copper, lithium, nickel, lead, tin, strontium, vanadium and zinc. The results are compared to the preliminary data reported recently, showing that they are in good agreement.

### 1 Introduction

Recently, six GSJ rock reference samples, JA-1 (andesite), JB-2 (basalt), JB-3 (basalt), JGb-1 (gabbro), JR-1 (rhyolite) and JR-2 (rhyolite) were produced in 1982, and a tentatively compiled report for major and some minor elements was published by ANDO *et al.* (1983). However, the analytical data reported were few, suggesting that the data have not been certificated. A list of six GSJ rock reference samples is shown in Table 1.

In this study, thirteen major and sixteen minor elements on the six GSJ rock reference samples were analyzed using high accurate routine procedures with new methods developed in our laboratory, and analytical results are compared with the reported data.

### 2 Analytical Method

#### 2.1 Major elements

Silicon was determined by a combined method with both gravimetry and atomic

absorption spectrometry, and titanium, aluminium, magnesium, calcium, sodium and potassium were analyzed by atomic absorption spectrometry. Other components were determined using a titrimetry for ferrous iron, absorption spectrophotometry for phosphorus, Penfield method for combined water and gravimetry for moisture. The analytical procedures for the major elements mentioned above have previously been described in detail (TERASHIMA, 1979).

The analytical procedures for the determination of total iron and manganese are as follows. Take out 0.3-1.0 g of sample into a Teflon beaker, and add 10 ml of HF, then evaporate to dryness. Add 10 ml of HF, and repeat evaporation. Add 20 ml of HCl and 2 ml of H<sub>2</sub>O<sub>2</sub>. After covering with a Teflon plate, heat the mixture for about 1 hour. Evaporate to dryness, then dissolve the residue by heating with 20 ml of 5 M HCl and filter. Dilute the filtrate to a fixed volume with 0.5 M HCl, and determine iron and manganese by atomic absorption spectrometry (YAMASHIGE *et al.*, 1983). A portion of the solution containing less than 200 µg of iron is taken into a 50 ml flask, then iron was also determined by conventional o-phenanthroline spectrophotometric method.

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Table 1 A list of six GSJ rock reference samples.

JA-1	Andesite	Hakone Volcano Manazuru-Machi, Ashigarashimo-Gun, Kanagawa-Ken, Japan
JB-2	Basalt	Ōsima Volcano, Tholeiitic basalt Miharayama, Ōshima-Machi, Tokyo-To, Japan
JB-3	Basalt	Fuji Volcano, High alumina basalt Narusawa-Mura, Minamitsuru-Gun, Yamanashi-Ken, Japan
JGb-1	Gabbro	Utsukushigatake Utsukushigatake, Tamura-Gun, Fukushima-Ken, Japan
JR-1	Rhyolite	Wada-Toge Obsidian Northern part of Wada-Toge, Chiisagata-Gun, Nagano-Ken, Japan
JR-2	Rhyolite	Wada-Toge Obsidian Southern part of Wada-Toge, Suwa-Shi, Nagano-Ken, Japan

## 2. 2 Minor elements

The minor amounts of carbon and sulfur were analyzed by combustion and infrared absorption photometry (TERASHIMA, 1978), and tin was determined by atomic absorption spectrometry using an argon-hydrogen flame after extraction of tin (IV) as iodide with benzene (TERASHIMA, 1975 and 1982a). Outline of the procedures for other minor elements is given below.

**Arsenic (YAMASHIGE *et al.*, 1981):** Take 0.3 g of sample into a Teflon beaker, and add 15 ml of HF, 10 ml of HNO<sub>3</sub> and 2 ml of H<sub>2</sub>SO<sub>4</sub>. After letting stand for about 30 min., add 2 ml of 0.3% potassium permanganate solution, and place for 10–20 min on a hot plate at about 150°C. Add more permanganate solution, if necessary, to maintain the violet color, then evaporate the solution to about 10 ml by heating. Add 5 ml of HNO<sub>3</sub> and 1 ml of permanganate solution, and evaporate nearly to dryness. Dissolve the residue by heating with 20 ml of 0.5 M HCl. After filtrating, dilute to 50 ml with 0.5 M HCl. Take a portion of the sample solution containing less than 0.3 μg of arsenic into a reaction vessel, and add 3 ml of 12 M HCl, 2 ml of 20% potassium iodide solution and 1 ml of 20% ascorbic acid solution. After displacing air by nitrogen, add 7 ml of 1% sodium borohydride solution, then determine arsenic by arsine generation and atomic absorption spectrometry using a heated quartz cell atomizer.

**Beryllium (TERASHIMA, 1982b):** Decompose

0.5 g of sample with 5 ml of HClO<sub>4</sub>, 3 ml of HNO<sub>3</sub> and 8 ml of HF, and evaporate to dryness. Add 2 ml of HClO<sub>4</sub> and 2 ml of saturated H<sub>3</sub>BO<sub>3</sub> solution, and repeat evaporation. Dissolve the residue by heating with 5 ml of 1.5 M HCl. Transfer the solution into a separatory funnel, and add 1 ml of aluminium chloride solution (Al 20 mg/ml), 10 ml of 20% EDTA solution, 2 ml of 10% acetylacetone solution, and 0.5 ml of 0.05% bromocresol green solution. Add 20% NaOH solution dropwise until a permanent blue colour is appeared; add 0.4 ml in excess. Shake with 5 ml of MIBK for 3 min. Determine beryllium in the organic phase by atomic absorption spectrometry using a nitrous oxide-acetylene flame.

**Bismuth (TERASHIMA, 1984):** Decompose 0.1–0.5 g of sample with 3 ml of HClO<sub>4</sub>, 3 ml of HNO<sub>3</sub> and 8 ml of HF in a Teflon beaker, and evaporate to dryness. Dissolve the residue by heating with 5 ml of 3 M HCl. Transfer the solution to a 25 ml volumetric flask, and add 5 ml of aluminium chloride solution (Al 20 mg/ml). After diluting the solution with water to about 20 ml, add 2 ml of 10% ascorbic acid solution and mix to reduce iron (III). Then add 2 ml of 8% thiourea solution, and make up to 25 ml and mix. Determine bismuth by hydride generation and atomic absorption spectrometry using an automated hydride generator with a heated quartz cell atomizer.

**Cadmium (TERASHIMA, 1983a):** Decompose 0.5 g of sample with 5 ml of HNO<sub>3</sub> and 8 ml

of HF, and evaporate to dryness. Add 3 ml of HNO<sub>3</sub> and 2 ml of saturated H<sub>3</sub>BO<sub>3</sub> solution, and repeat evaporation. Dissolve the residue by heating with 5 ml of H<sub>3</sub>PO<sub>4</sub>. Cool, and add about 10 ml of water, then heat to minimize the residual salts. Transfer the solution into a separatory funnel, and add 2 ml of 25% hydroxylamine hydrochloride solution, then dilute to about 18 ml with water. After mixing, add 2 ml of 2 M sodium iodide solution, and mix. Shake with 5 ml of MIBK for 3 min. Determine cadmium in the organic phase by atomic absorption spectrometry using an air-acetylene flame. If the content of cadmium in organic phase is less than 0.02 µg, cadmium can be determined by a carbon tube atomizer.

Cesium, Lithium, Rubidium, Strontium and Vanadium (TERASHIMA, 1979; TERASHIMA and MITA, 1981): Decompose 0.5 g of sample with 5 ml of HClO<sub>4</sub>, 3 ml of HNO<sub>3</sub> and 10 ml of HF, and evaporate to dryness. Dissolve the residue by heating with 5 ml of HCl (1+3), and dilute to 25 ml with water. Determine vanadium in the sample solution by atomic absorption spectrometry. Take a 10 ml of the sample solution into a volumetric flask (25 ml), and add 2.5 ml of potassium chloride solution (K 30 mg/ml), and make up exactly to 25 ml. Determine cesium and rubidium by flame emission spectrometry, and lithium by atomic absorption spectrometry. Transfer a 2 ml of the master sample solution into another volumetric flask (25 ml). After adding 2.5 ml of lanthanum chloride solution (La 50 mg/ml), determine strontium by atomic absorption spectrometry.

Copper, Nickel, Lead and Zinc (YAMASHIGE et al., 1983): Decompose 1–1.5 g of sample by the same procedures described for iron and manganese. Determine zinc directly from the sample solution by atomic absorption spectrometry. For other elements, take a portion of the sample solution into a beaker, and evaporate to about 2 ml. Transfer the solution into a separatory funnel, and add 20 ml of 12 M HCl. Shake with 20 ml of isopentyl acetate for 3 min to extract iron. Transfer the aqueous phase into a beaker, and wash the organic phase twice with 5 ml of 12 M HCl. Discard the

organic phase, and evaporate the combined aqueous phase to about 5 ml, and transfer into a separatory funnel. Dilute to 40 ml with water, and add 10 ml of 10% ammonium citrate solution, 0.5 ml of 0.1% bromothymol blue solution. After mixing, add NH<sub>4</sub>OH (1+9) dropwise until a permanent blue colour is obtained. Add 3 ml of 10% diethyldithiocarbamate solution, then shake the solution with 10 ml of n-butyl acetate for 5 min. Determine copper, nickel and lead in the organic phase by atomic absorption spectrometry using an air-acetylene flame.

### 3 Results and Discussion

Analytical results for total iron by atomic absorption spectrometry and absorption spectrophotometry in this study are tabulated in Table 2 for comparison with the values of titrimetry (ANDO et al., 1983). It can be pointed out that the data of present study and previous titration method are fairly in good agreement.

Analytical results for manganese are shown in Table 3, with the previously reported data for comparison. A systematic discrepancy is

Table 2 Comparison of results for total iron as Fe<sub>2</sub>O<sub>3</sub> (%).

Method	JA-1	JB-2	JB-3	JGb-1	JR-1	JR-2
A.A.	7.06	14.42	11.91	15.57	0.91	0.76
Photom.	7.00	14.29	11.86	15.12	0.87	0.74
Tit.	6.95	14.34	11.88	15.16	0.96	0.86

A.A.: Atomic absorption spectrometry.

Photom.: Absorption spectrophotometry.

Tit.: Titrimetry (Taken from ANDO et al., 1983).

Table 3 Comparison of results for manganese as MnO (%).

Method	JA-1	JB-2	JB-3	JGb-1	JR-1	JR-2
A.A. (1)	0.163	0.226	0.187	0.198	0.104	0.116
A.A. (2)	0.158	0.222	0.181	0.190	0.101	0.111
Photom.	0.15	0.20	0.16	0.17	0.10	0.11

A.A. (1): Atomic absorption spectrometry.

A.A. (2): Atomic absorption spectrometry (Added strontium chloride solution).

Photom.: Absorption spectrophotometry (Taken from ANDO et al., 1983).

Table 4 Analytical results of major components

Components (%)	JA-1		JB-2		JB-3	
	This study*	ANDO <i>et al.</i> (1983)	This study*	ANDO <i>et al.</i> (1983)	This study*	ANDO <i>et al.</i> (1983)
SiO <sub>2</sub>	64.15	64.06	53.26	53.20	51.15	51.04
TiO <sub>2</sub>	0.86	0.87	1.20	1.19	1.46	1.45
Al <sub>2</sub> O <sub>3</sub>	15.10	14.98	14.65	14.67	17.03	16.89
Fe <sub>2</sub> O <sub>3</sub>	2.61	2.42	3.32	3.13	3.26	3.10
FeO	3.98	4.08	9.93	10.09	7.86	7.90
MnO	0.16	0.15	0.22	0.20	0.18	0.16
MgO	1.55	1.61	4.63	4.66	5.21	5.20
CaO	5.65	5.68	9.75	9.89	9.73	9.86
Na <sub>2</sub> O	3.87	3.86	2.03	2.03	2.75	2.82
K <sub>2</sub> O	0.80	0.82	0.42	0.43	0.80	0.80
P <sub>2</sub> O <sub>5</sub>	0.16	0.16	0.10	0.10	0.28	0.29
H <sub>2</sub> O+	0.80	0.80	0.26	0.31	0.14	0.20
H <sub>2</sub> O-	0.24	0.26	0.11	0.07	0.06	0.03
Sum	99.93	99.75	99.88	99.97	99.91	99.74
Total Fe as Fe <sub>2</sub> O <sub>3</sub>	7.03	6.95	14.36	14.34	11.99	11.88

\* Average value of 2 to 5 determinations.

Table 5 Analytical results of sixteen minor elements

Element (ppm)	JA-1		JB-2		JB-3	
	This Study*	ANDO <i>et al.</i> (1983)	This Study*	ANDO <i>et al.</i> (1983)	This Study*	ANDO <i>et al.</i> (1983)
As	2.76±0.09	3	2.60±0.08	3	1.50±0.03	
Be	0.50±0.12	0.49	0.30±0.07	0.23	0.78±0.08	0.69
Bi	0.009±0.001		0.033±0.002		0.020±0.002	
C	263±11		194±10		112±8	
Cd	0.094±0.006		0.141±0.008		0.082±0.005	
Cs	0.67±0.06		0.90±0.10		1.26±0.11	
Cu	42.2±0.3	41.7	227±1	230	198±1	197
Li	10.5±0.4	11	8.0±0.5	8	7.2±0.3	
Ni	1.81±0.01	1.9	14.2±0.3	14.6	38.8±0.3	38.5
Pb	5.77±0.04	5.8	5.41±0.06	5.5	5.51±0.08	5.8
Rb	12±2	11.8	7±1	6.2	13±2	13
S	25±5		23±5		10±3	
Sn	0.8±0.1		0.5±0.1		0.8±0.1	
Sr	268±6	266	177±3	173	404±7	395
V	105±3	103	571±9	540	383±7	
Zn	90.6±0.5	88.3	110±1	106	106±1	103

\*Average value of 3 to 5 determinations with standard deviation.

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for Six GSJ rock reference samples.

JGb-1		JR-1		JR-2	
This study*	ANDO <i>et al.</i> (1983)	This study*	ANDO <i>et al.</i> (1983)	This study*	ANDO <i>et al.</i> (1983)
43.50	43.44	75.36	75.41	75.54	75.65
1.62	1.62	0.09	0.10	0.06	0.09
17.61	17.66	12.92	12.89	12.79	12.82
5.07	4.89	0.40	0.40	0.31	0.38
9.25	9.24	0.44	0.50	0.40	0.43
0.19	0.17	0.10	0.10	0.11	0.11
7.82	7.83	0.11	0.09	0.04	0.05
11.86	11.98	0.69	0.63	0.51	0.45
1.20	1.23	4.02	4.10	4.02	4.03
0.24	0.26	4.52	4.44	4.54	4.48
0.05	0.05	0.02	0.02	0.01	0.01
1.30	1.23	1.03	1.05	1.21	1.28
0.09	0.04	0.14	0.13	0.20	0.14
99.80	99.64	99.84	99.86	99.74	99.92
15.35	15.16	0.89	0.96	0.75	0.86

for six GSJ rock reference samples.

JGb-1		JR-1		JR-2	
This Study*	ANDO <i>et al.</i> (1983)	This Study*	ANDO <i>et al.</i> (1983)	This Study*	ANDO <i>et al.</i> (1983)
1.00±0.03		17.9±0.5	16	20.2±0.7	
0.36±0.08	0.33	3.14±0.09	3.1	3.48±0.08	3.4
0.014±0.002		0.510±0.007		0.652±0.010	
285±13		63±7		50±4	
0.085±0.005		0.017±0.003		0.019±0.003	
0.27±0.05		21.6±0.8		27.2±1.2	
86.8±0.5	85.3	2.07±0.03	1.9	1.37±0.08	1.5
4.3±0.4		66±2	65	83±2	
25.4±0.1	25.7	0.66±0.08	0.6	0.84±0.04	0.8
1.86±0.04	1.9	19.1±0.1	18.7	21.9±0.1	21.1
4±1		254±7		297±9	
1980±20		15±4		8±2	
0.4±0.1		2.6±0.2		2.9±0.2	
321±5		29±1	30	8±1	
640±12		<8		<8	
111±1	103	30.1±0.3	28.8	27.2±0.5	27.3

noticed between the results of atomic absorption spectrometry and absorption spectrophotometry, suggesting the effect of coexisted elements on the absorbance of manganese. Accordingly, manganese is analyzed again after addition of 4 mg/ml of strontium chloride solution to both samples and calibration standards to minimize the effects of concomitant elements, and the results are given in the Table 3. Small discrepancies still remain for three samples of JB-2, JB-3 and JGb-1.

The results of this study and reported data (ANDO *et al.*, 1983) for thirteen major components for the six GSJ rock reference samples are given in Table 4. The previous data by T. OHMORI of the Geological Survey of Japan have been obtained by using conventional wet chemical methods and atomic absorption spectrometry for sodium and potassium. The agreement for all the components between present study and reported data are generally good. The sixteen minor elements of present results are listed in Table 5 for comparison with compiled values (ANDO *et al.*, 1983). The previous data for copper, nickel, lead and zinc were obtained by an another solvent extraction procedure with atomic absorption spectrometry (TERASHIMA, 1983b). The analytical results for arsenic, beryllium, copper, lithium, nickel, lead, rubidium, strontium and zinc are satisfactorily in good agreement with previous data. However, available analytical values for carbon, cadmium, cesium, sulfur, and tin of the reference rocks have not been reported. It is obvious that much more data are needed before the establishment of certified values for all elements.

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\* in Japanese with English abstract.

岩石標準試料 JA-1, JB-2, JB-3, JGb-1, JR-1, JR-2 中の  
主成分と微量成分の定量

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要 旨

最近日本地質調査所で調製された6種の岩石標準試料 JA-1(安山岩), JB-2(玄武岩), JB-3(玄武岩), JGb-1(斑れい岩), JR-1(流紋岩), JR-2(流紋岩)について主成分と微量成分を定量した。SiO<sub>2</sub>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<sub>2</sub>, Al<sub>2</sub>O<sub>3</sub>, Total Fe<sub>2</sub>O<sub>3</sub>, MnO, MgO, CaO, Na<sub>2</sub>O, K<sub>2</sub>O, As, Be, Bi, Cd, Cu, Li, Ni, Pb, Rb, Sn, Sr, V, Zn は原子吸光法で定量した。C及びSは燃焼-赤外吸収分析法, Cs, Rb は炎光光度法, FeO は滴定法, H<sub>2</sub>O+はペンフィールド法, H<sub>2</sub>O-は重量法により定量した。主成分について得られた値は文献値と良好な一致を示した。微量成分のうちいくつかの元素は他の方法による値が公表されておらず比較できなかったが, As, Be, Cu, Li, Ni, Pb, Rb, Sr, Zn についての結果は文献値とほぼ良好な一致を示した。

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