Sulfur Contents of Volcanic Rocks in Japan

Yoshiko Arikawa
Department of Chemistry, Faculty of Home Economics, Japan Women's University,
Mejiro-dai, Bunkyo-ku, Tokyo 112

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The total sulfur content was determined for 140 samples of Japanese volcanic rock by the mercury(II) thiocyanate photometric method of hydrogen sulfide formed by a wet reduction of the sample by tin(II)–strong phosphoric acid. Though determined values are widely scattered from 5390 down to 10 ppm (or less), the cumulative frequency distribution of the sulfur contents shows lognormality. The geometric and arithmetic means are 26 ppm (mg kg^{-1}) and 116 ppm, respectively. The alkaline rocks have high sulfur contents, the geometric mean of which is 62 ppm. Little significant difference was observed among the rhyolitic rock, the andesite and the trachyte, and the basaltic rock. Japanese and foreign standard rock samples were analyzed for sulfur. Almost all results were in good agreement with those obtained by other authors. In this case foreign standard samples also have higher sulfur contents than those of Japanese samples. The fact that the sulfur contents of Japanese volcanic rocks are lower than the previously accepted values seems to be characteristic of the islands arc of volcanism.

From the geochemical point of view sulfur is one of the most interesting and important volatile components of magma and is released as a volcanic gas into the atmosphere in the form of either sulfur dioxide or hydrogen sulfide. However, certain amounts are considered to be fixed in igneous rocks in such a form as sulfate or sulfide during the course of crystallization of magma.

Ever since the first work involving a determination of the sulfur in igneous rocks by Clark and Washington,[1] many authors have reported sulfur contents in igneous rocks. Especially, from numerous samples Goldschmidt[2] has determined the average value of the sulfur contents in igneous rocks to be 520 ppm. However, his data, together with those of others, were widely scattered over more than one order of magnitude; thus, these determination methods seemed to lack reliability.

It was until the late 1950's when standard rock samples were prepared by geological surveys in several countries that the accuracies of individual determination methods could be compared with each other by using these standard samples. As a consequence, the reliability and accuracy of the determination method were much improved.[3–14] Ricke[7] has attempted a separate determination of the sulfate and sulfide sulfur in various kinds of igneous rocks; he found the total sulfur contents to be 300 ppm. From a series of such investigations he concluded that sulfur was generally inclined to be contained in alkaline rocks. He further pointed out that sulfide sulfur was more abundant in alkaline rocks whereas sulfate sulfur was rich in silicic rocks. Moore and Fabbi[8] reported the sulfur contents in deep ocean-floor erupted basalts to be 800±100 ppm. Recently Ueda and Sakai[9] pointed out that the sulfur contents of Quaternary volcanic rocks from the Japanese Islands Arc were less than 40 ppm, much lower than those of ocean-floor basalts.

The total sulfur contents of standard rock samples were summarized in review papers by Fleisher,[15] Abbey,[16] and Flanagan.[17] All of these determined values were not always in good agreement among individual standard samples and fell, as a whole, in the range from several tens to several hundreds ppm. However, the total sulfur contents of the standard samples prepared by the Geological Survey of Japan showed with no doubt lower values by one order of magnitude than those of the foreign standard samples.

To find a reliable and feasible method of determining the total sulfur in rocks, we investigated and established several different methods by means of: (1) the photometric method,[18] (2) the sulfide ion selective electrode method,[19] and (3) the fluorometric method.[20] Each of these are based on a wet reduction of the sample by tin(II)–strong phosphoric acid. A fourth method, the UV-photometric method[21] is used after the combustion of a sample with vanadium pentaoxide. The determined values by these methods showed excellent agreement.

In this paper we present the total sulfur contents mainly determined by the photometric method[18] for 140 volcanic rocks in Japan.

Experimental

Detailed descriptions of each method for the determination of the total sulfur in volcanic rocks can be found in previous papers;[18–21] thus, only brief analytical description of the photometric method will be presented in this section.

Finely powdered rock samples are accurately weighed (100—300 mg) and heated with tin(II)–strong phosphoric acid at 280 °C for 15 min in a flow of carbon dioxide or nitrogen gas. Both the sulfate and sulfide sulfur contained in rock samples are separated from other components in a form of hydrogen sulfide. The hydrogen sulfide, thus formed, is absorbed in a zinc sulfate solution to be fixed as a zinc sulfide. In order to completely separate micro amounts of zinc sulfide by means of a centrifugal separator, a zinc hydroxide is coprecipitated by adding a sodium hydroxide solution to the absorbing solution. After separating the supernatant solution, an acetic acid, a mercury(II) thiocyanate–methyl alcohol solution and iron(III) nitrate–

perchloric acid solution are added to the precipitation. The mixture is shaken and diluted with redistilled water. Then, carbon tetrachloride is added and shaken vigorously to adsorb the suspending mercury(II) sulfide on the surface of small drops of carbon tetrachloride. After centrifugation, the absorbance of the supernatant solution is measured at the wavelength of 460 nm against the redistilled water as a reference. A standard sample to make a calibration curve is prepared as follows. Barium sulfate is mixed in an agate motor with a finely powdered obsidian in which no sulfur is assured to be detected by this method. The mixture is diluted with the obsidian several times until the sulfur content becomes 300 ppm. The lowest detectable limit of this method is 10 ppm for total sulfur. The coefficient of variation for five repeat analysis is 5% for a sulfur content of 200 ppm. The determination of the sulfur was performed in association with the main components and other elements such as halogen[22] and boron[23] for samples which were widely gathered from many locations in Japan by people listed in the acknowledgements.

Results and Discussion

Sulfur Contents of Volcanic Rocks in Japan. The total sulfur contents of volcanic rocks in Japan are summarized in Table 1. As should be apparent from Table 1, the determined values are widely scattered from the maximum value of 5390 ppm to the lowest detectable limit of 10 ppm. The sulfur contents of the volcanic rocks can be fairly well expressed as a log-normal type distribution when they are plotted on a logarithmic scale (log S ppm) on a cumulative frequency diagram (Fig. 1). Strictly, this curve seems to be composed of two straight lines with different slopes having a bend around log S=2.0. This feature can also be observed in other volatile components of volcanic rocks. For example, the cumulative frequency distribution of boron deviates from lognormality and the curve is composed of three straight lines; this is well understood by classifying rocks into three groups: alkaline rocks, glassy rocks and the other rocks.[23] However, in the case of sulfur the bend in the curve could not be explained by such a classification into two groups, i.e., alkaline rocks and the rest other rocks, because both curves also showed a bend around log S=2.0 (Fig. 1). The mean value of log S was estimated to be 1.41. The geometric mean of the total sulfur content is 26 ppm with a standard deviation of 0.64 ppm, while the arithmetic mean is 116 ppm. This does not seem to reflect a good representative value of a statistical measure. It should be noted here that there are considerable numbers of samples that contain a total sulfur content less than this lowest limit. Threrefore, a more sensitive method is required in order to determine the exact distribution and geometric mean of the sulfur contents. Alkaline rocks have high sulfur contents, as pointed out by Ricke,[7] and Ueda and Sakai.[9] Their geometric mean is 62 ppm and can be clearly distinguished from those of other rocks by an inspection at the significant level 0.01. Moreover, the rocks from the Circum-Japan Sea Province have a geometric mean of the sulfur contents of 41 ppm, also showing a significant difference from the geometric mean of other rocks (at the significant level 0.05). In Fig. 2 are given the frequency distributions of each of the sulfur contents of three types of rocks classified by the silica content, i.e., rhyolitic rock, andesite and trachyte, and basaltic rock.

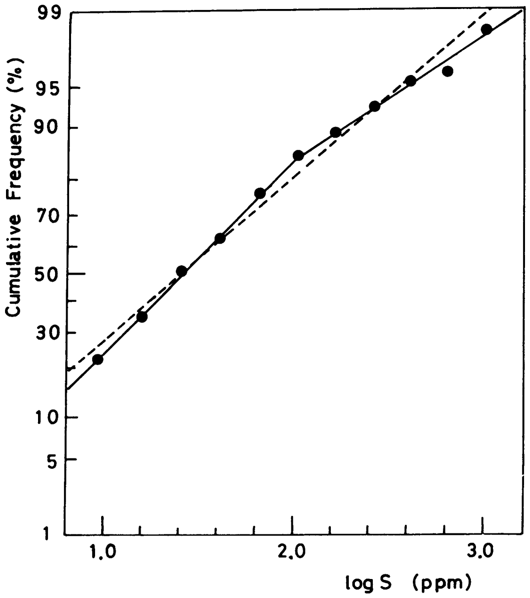

Fig. 1. Cumulative frequency distribution of sulfur contents of volcanic rocks.

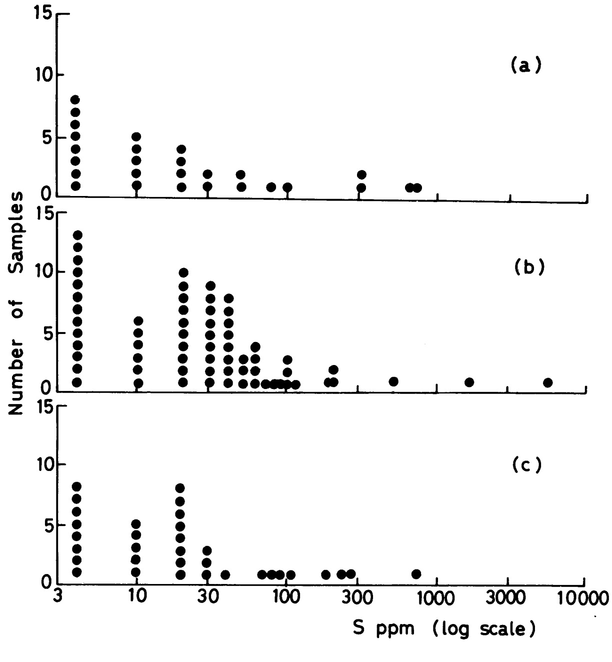

Fig. 2. Frequency distributions of sulfur contents of volcanic rocks.

(a): Rhyolitic rock, (b): andesite and trachyte, (c): basaltic rock.

Table 1. Sulfur Contents of Volcanic Rocks

No.	Sample	S/ppm
1	Basalt; Lava of 1950, Mihara-yama, Ō-shima, Tōkyō Metr.	20
2	Basalt; Anei lava, Mihara-yama, Ō-shima	20
3	Basalt; Okata, Ō-shima	40
4	Basalt; Lava of 1962, Miyake-jima, Tōkyō Metr.	10
5	Basalt; Southern coast of Iga-tani, Miyake-jima 660501-9	10
6	Basalt; Southern coast of Iga-tani, Miyake-jima 660501-10	10
7	Basalt; Meiji-lava, Tosa Yuno-hama, Miyake-jima	20
8	Basalt; Kayakuko-ura, Miyake-jima	10
9	Basalt; Oji-ike, Miyake jima	10
10	Basalt; Wall of No. 3 entrance of the crater, Miyake-jima	10
11	Basalt; Northern coast of Ako, Miyake-jima 660501-8-1	20
12	Basalt; Northern coast of Ako, Miyake-jima 660501-8-2	20
13	Basalt; Western foot of Higashi-yama, Hachijō-jima Tōkyō Metr.	30
14	Basalt; Southeastern foot of Nishi-yama, Hachijō-jima	20
15	Basalt; Sakasagawa, Itō. Shizuoka Pref.	10
16	Basalt; Lava of 864, Aokiga-hara, Fuji-san, Yamanashi Pref.; No. 1	<10
17	Basalt; Lava of 864, Aokiga-hara, Fuji-san; No. 2	<10
18	Basalt; Kenmarubi lava, Fuji-yoshida, Fuji-san; No. 3	<10
19	Basalt; Maku-iwa, Fuji-san; No. 4	10
20	Basalt; Shirogane lava, Tokachi-dake, Hokkaidō	20
21	Basalt; Orimoto-tōge lava, Shidara, Aichi Pref.	60
22	Basalt; Orimoto-tōge lava, Shidara	80
23	Basalt; Orimoto-tōge lava, Shidara	210
24	Basalt; Kakuda-yama, Niigata Pref.	10
25	Basalt; Nishimura, Nakamura, Dōgo, Oki, Shimane Pref.	90
26	Basalt; Kuniga, Nishino-shima, Dōdo, Oki	70
27	Basalt; Imazu, Saigō, Oki	30
28	Basalt; Kami-sue, Saigo, Dōgo, Oki	270
29	Basalt; Chika-ishi, Harada, Dōgo, Oki	110
30	Basaltic rock; No. 8 Shimo-motoya, Nakamura, Dōgo, Oki	10
31	Basalt; No. 15 Nishino-shima, Ura-gōri B, Dōgo, Oki	80
32	Basalt; Iwano, Karatsu, Saga Pref.; No. 1	20
33	Basalt; Iwano, Karatsu; No. 2	20
34	Basalt; Taka-shima, Karatsu	20
35	Basalt; Hinode-matsu, Karatsu	<10
36	Basalt; Hanase-zaki Kaimon-dake, Kagoshima Pref.	10
37	Basalt; Trachyandesitic basalt; Intrusive sheet, South of Ōkuwa, Shidara, Aichi Pref.	240
38	Nepheline basalt; Nagahama, Hamada, Shimane Pref.	730
39	Dolerite; Kawai, Shidara, Aichi Pref.	190
40	Basaltic andesite; Dyke, Sukumo-gawa, Hakone, Kanagawa Pref.	<10
41	Chilled margin of dyke No. 31	<10
42	Andesite; Kami-futago-yama, Hakone	60
43	Andesite; Shimo-futago-yama, Hakone	<10
44	Andesite; Nagao-tōge, Hakone	<10
45	Andesite; Southeast of Okimura, Haha-jima, Bonin Islands, Tōkyō Metr.	10
46	Andesite; Kitamuki-kakō lava, Tokachi-dake, Hokkaido	100
47	Andesite; Kami-horokametokku-kabu lava, Tokachi-dake	40
48	Andesite; Kumano-sawa-shita, Tokachi-dake	60
49	Andesite; Lava of parasitic crater (Minami-kakō), Yōtei-zan, Hokkaidō	<10
50	Andesite; Somma lava, Usu, Hokkaidō	<10
51	Andesite; Dome lava, Tarumai-yama, Hokkaidō	30
52	Andesite; Bomb, Tarumai-yama	30
53	Andesite; Eniwa-dake, Hokkaidō	10
54	Andesite; Kenga-mine, Komaga-take, Hokkaidō	20
55	Andesite; Around the crater, Komagatake	20
56	Andesite; Block in a mud flow, Komaga-take	20
57	Andesite; Lava of Yake-yama, Tamagawa Spa, Akita Pref.	40
58	Andesite; Iwaya, Kakuda-yama, Niigata Pref.	20
59	Andesite; Ejecta of Meiji eruption, Azuma-issaikyō-yama, Fukushima Pref.	30
60	Andesite; Lava of 1783, Asama-yama, Gunma Pref.	60
61	Andesite; Dyke, Kuniga, Nishino-shima, Oki, Shimane Pref.	80
62	Andesite; Iimi, Fuse, Dōgo, Oki (epidote, pyrite bearing)	5390
63	Andesite; Chōshi, Harada, Dōgo, Oki	30
64	Andesite; Yunoo, Karatsu, Saga Pref.	<10
65	Andesite; Yakataga-udo, Neko-dake, Aso, Kumamoto Pref.	<10
66	Andesite; South valley of Hinoo-tōge, Neko-dake, Aso	20
67	Andesite; Dyke, Ōshōji-iwa, Yamaguchi-dani, Nekodake, Aso	30
68	Andesite; Chilled margin of dyke, Tengu-iwa, Neko-dake Aso	130
69	Andesite; East valley of Jigoku-dani, Neko-dake, Aso	10
70	Andeside; The 5th valley of western slope of Neko-dake, Aso	10
71	Andesite; Scoria lava of 1958, Neko-dake, Aso	50
72	Andesite; Northern slope of Ōgi-yama, Aso	20
73	Andesite; Sensui-yane, Taka-dake, Aso	30

Table 1. Continued.

No.	Sample	S/ppm
74	Andesite; Northern slope of Narao-dake, Aso	20
75	Andesite; Southern slope of Naka-dake, Aso	30
76	Andesite; The top of Ōgi-yama, Aso	10
77	Andesite; Southeastern slope of Naka-dake, Aso	10
78	Andesite; Southwestern valley of Naka-dake, Aso	20
79	Andesite; The top of Taka-dake, Aso	90
80	Andesite; Eastern slope of Okamado-yama, Aso	10
81	Andesite; Southern slope of Naka-dake, Aso	30
82	Andesite; Road cutting near the Akamizu station, Aso	20
83	Andesite; Kometsuka, Aso	<10
84	Andesite; Bomb, Eastern slope of Ōjō-dake, Aso	30
85	Andesite; Crater wall of Ōjō-dake, Aso	100
86	Andesite; Northeastern Eboshi-dake, Shigetama Spa, Aso	50
87	Andesite; Northern slope of Naka-dake, Aso	10
88	Andesite; Under the bridge on the Kuro-kawa, Aso	20
89	Andesite; Lava of 1946, Sakura-jima, Kagoshima Pref.	190
90	Andesite; Lava of 1914, Sakura-jima	200
91	Andesite; Anei lava, Sakura-jima	110
92	Andesite; Bunmei lava, Sakura-jima	40
93	Andesite; Satsuma-iwō-jima, Kagoshima Pref.	70
94	Andesite; Lava of Iwō-dake, inner cliff of Higashi Spa, Satsuma-iwō-jima	100
95	Andesite; Iwō-dake, Satsuma-iwō-jima	20
96	Andesite; Inamura-dake, Satsuma-iwō-jima	40
97	Andesite; Yahazu-dake lava, Sakamoto, Satsuma-iwō-jima	50
98	Andesite; The uppermost lava of Shin-dake, Kuchino-erabu-shima, Kagoshima Pref.	60
99	Glassy andesite; Southern slope of E-san, Hokkaidō	130
100	Glassy andesite; Shōwa-iwō-jima, Satsuma-iwō-jima, Kagoshima Pref.	70
101	Glassy andesite; Shōwa-iwō-jima, Satsuma-iwō-jima (pumiceous part)	50
102	Dacitic andesite; Sembe-yama, Shimane Pref.	<10
103	Trachyandesite; Suribachi-yama, Iwō-jima, Sulfur Islands, Tōkyō Metr.	500
104	Trachyte; Funakoshi, Nishino-shima, Oki, Shimane Pref.	40
105	Phonolitic trachyte; Tokage-iwa, Tsuzurao-yama, Dōgo, Oki	30
106	Dacite; Dome lava, Shōwa-shinzan, Usu, Hokkaidō	320
107	Dacite; Usu-dake, Usu	20
108	Dacite; Dome lava, Ōusu-dake, Usu	20
109	Dacite; Komaga-take, Hokkaidō	20
110	Dacite; Lava of somma, Akagi-yama, Gunma Pref.	10
111	Dacite; Eboshi-dake, Aso, Kumamoto Pref.	320
112	Dacite; Koeboshi, Aso	20
113	Rhyodacite; Eastern slope of Otogase (Senriga-hama volcano)	30
114	Liparite; Tenjō-san, Kōzu-shima, Tōkyō Metr.	10
115	Liparite; Southeastern foot of Tenjō-san, Kōzu-shima	<10
116	Liparite; South of Naga-hama, Kōzu-shima	20
117	Liparite; Takōdo-yama, Kōzu-shima	<10
118	Liparite; Mae-hama, Nii-jima, Tōkyō Metr.	10
119	Liparite; Nii-jima	10
120	Liparite; Southern coast of Shikine-jima, Tōkyō Metr.	10
121	Liparite; Southeastern coast of Shikine-jima	10
122	Liparite; Nakaya, Fuse, Dōgo, Oki, Shimane Pref.	660
123	Rhyolitic rock; Nishida, Saigō, Dōgo, Oki	50
124	Rhyolitic rock; Igo, Nakamura, Dōgo, Oki; No. 6	10
125	Potash liparite; Manzō-yama, Shimoda, Shizuoka Pref.	30
126	Alkali rhyolite; Madara-jima, Saga Pref.	100
127	Obsidian; Shirataki, Hokkaidō	<10
128	Obsidian; Wada-tōge (pale part)	<10
129	Obsidian; Koshi-dake, Imari, Saga Pref.	<10
130	Obsidian; Hime-shima, Ōita Pref.; No. 1	10
131	Obsidian; In a deposit of ejecta of Kikai Caldera, Satsuma-iwō-jima, Kagoshima Pref.	140
132	Obsidian; Mifune	10
133	Trachyte; Harada, Saigō, Dōgo, Oki, Shimane Pref.	40
134	Trachyte; Funakoshi, Nishino-shima, Dōgo, Oki	40
135	Trachyte; Minato, Nakamura, Dōgo, Oki; No. 5	10
136	Trachyte; Uragōri, Nishino-shima, Dōgo, Oki; No. 14—1	1600
137	Trachyte; Uragōri, Nishino-shima, Dōgo, Oki; No. 14—2	200
138	Trachyte; Kojōga-hana, Saigō, Dōgo, Oki; No. 23	40
139	Peridotide; Horoman, Hokkaidō	10
140	Syenite; Oyama, northeastern foot of Takuhi-yama, Nishino-shima, Oki, Shimane Pref.	1550

Each geometric mean is 23 ppm (standard deviation $\sigma=0.72$ ppm) for rhyolitic rock, 29 ppm ($\sigma=0.63$ ppm) for andesite and trachyte, and 22 ppm ($\sigma=0.61$ ppm) for basaltic rock, respectively. No significant difference could be observed among these three types of rocks. Though glassy rocks are enriched in such

Table 2. Comparison of Sulfur Contents of Rock Samples

Sample	Sulfur contents This work				ppm References
	a)	b)	c)	d)	
W-1 Basalt	120				135[7], 124[10], 133[11], 113±2[12] 3[26]
G-1 Granite	40				175[7], 74[10], 65[11], 3[26]
JA-1 Andesite		21.4	22		16[16], 25±5[17]
JB-1 Basalt	20				13.1±2.4[12], 14[16], 50[27]
JB-2 Basalt		17.3	16		19[16], 23±5[17]
JB-3 Basalt		11.1			10±3[17]
JG-1 Granite	20				9.3±0.2[12]
JR-1 Rhyolite		11.7			15±4[17]
JR-2 Rhyolite		11.4			8±2[17]
Andesite-1	200	198	200	200	
Andesite-2	110	103		110	

a) Photometric method.[18] b) Sulfide ion selective electrode method.[19] c) Fluorometric method.[20]
d) UV-photometric method.[21]

volatile components as chlorine[22] and boron,[23] the sulfur content of every obsidian, a typical glassy rock, is lower than 10 ppm. This feature is consistent with the experimental result for the sulfur solubility in silicate melts by Katsura and Nagashima,[24] i.e., sulfur has low solubility in silicate melts, especially in silica rich melts. Moreover, sulfur seems to form the heterogeneous phase in silicate rocks even at a fairly low concentration. The sulfur contents of volcanic rocks determined in this study are much lower than those of the igneous rocks reported before. Old data seem to lack reliability concerning the employed determination methods. However, in a recent review by Schneider,[25] the values of the sulfur content of igneous rocks are not so different as the usual values, i.e., about 600 ppm. Samples in his paper are almost entirely from continental, ocean-floor or hot spots; very few are from islands arc. The low sulfur contents of Japanese volcanic rocks may be a characteristic of the islands arc volcanism, as pointed out by Ueda and Sakai.[9] This feature is probably attributed (1) to the extent of an outgassing of sulfur during the course of magmatic emanation and solidification, (2) to the difference of the source magma of the islands arc from those of others, (3) to the isolation of the sulfur containing phase during the fractional crystallization of magma and (4) to the heterogeneous distribution of sulfur in the upper mantle. However, the fact that the sulfur contents of volcanic rocks of the islands arc are low should be discussed more carefully in correlation with the contents of other volatile components.

Comparison of Sulfur Contents of Standard Rock Samples. To confirm the reliability of our determination method, standard rock samples were analyzed by means of three different methods established by the present author;[18–20] the results were compared with those reported by other authors. The sulfur contents of two kinds of andesite were also compared. The results are shown in Table 2. The present three methods (photometric method,[18] sulfide ion selective electrode method,[19] and fluorometric method[20]) are all based on a wet reduction by tin(II)–strong phosphoric acid. These methods together with the UV-photometric method gave good agreeable results for common andesite samples. The results for some standard samples and andesites by the three methods were also in good agreement with each other.

The sulfur content of standard rock sample G-1 (determined by the present author) showed fairly good agreement with those obtained by Frost and Thomas,[10] and Murphy and Sergeant[11] (ranging from 40 to 74 ppm). For the sulfur in W-1, a satisfactory agreement was also obtained between our result and those of Ricke,[7] Frost and Thomas,[10] Murphy and Sergeant,[11] and Ueda and Sakai[12] (showing contents between 120 and 135 ppm). The results of the present author for the standard rock samples of Japan were in good agreement with those by Ueda and Sakai,[12] Terashima,[13] and Terashima et al.[14] (about 20 ppm); this is very close to the geometric mean (26 ppm) of the volcanic rocks in Japan. The sulfur contents of Japanese standard rock samples also show lower values than those of foreign standard rock samples.

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