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Selenium Content and Its Oxidation State in Igneous Rocks, Rock-Forming Minerals, and a Reservoir Sediment

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The selenium content of 188 samples (115 igneous rocks, 46 sedimentary rocks, and 27 sediments, including 38 rock-forming minerals and 25 rock reference materials) issued from the Geological Survey of Japan were determined. In these samples selenium was distributed over a wide range of concentrations, 0.1—19500 ng g^{-1}. Especially, selenium was rich in alkali-feldspar (7.5—149 ng g^{-1}) as well as in plagioclase (3.6—147 ng g^{-1}), though not in mica (2.4—14.8 ng g^{-1}) and quartz (0.6—6.4 ng g^{-1}). Selenium, rich in feldspar, was easily dissolved as selenite with CO$_2$-bubbling water. In a reservoir sediment-core (from the surface to 15-cm depth), selenite and much organically-complexed selenium were dissolved with 0.1 M[a] hydrochloric acid and the subsequent 1 M sodium hydroxide solutions, respectively.

Though selenium is widely distributed in nature, it does not occur evenly throughout the lithosphere.[1] Both basic and acidic rocks contain 0.1 ppm of selenium; sedimentary rocks also contain slightly high (0.4 ppm) selenium.[2] An estimation of the selenium content of igneous rocks has been reported to be in the range of 0.03 to 0.8 ppm, with an average of 0.09 ppm by Goldschmidt and Strock (1935),[3] and Wedepohl (1967).[4] The value was recently modified to 0.05 ppm by Taylor (1964)[5] and Lakin (1973).[6] These probable data seem to depend on the lack of developing highly-sensitive analyses.[7] For the determination of nanogram levels of selenium in rocks and sediments, neutron activation analysis with a post extraction of selenium[8] and a further sensitive fluorometric analysis with 2,3-diaminonaphthalene[9,10] have been established. Fluoro metry was applied to Japanese rocks (121 samples), showing a mean selenium content of 0.0091 ppm; the enrichment of this element in sedimentary rocks, rather than in igneous types, was reported.[11] As a source of rich selenium in sedimentary rocks, chemical weathering of igneous rocks and leaching by rain water,[1] or the transfer of volcanic gases containing selenium to soils by rain water,[12] have been suggested.

In this work, the distribution of selenium content in all 188 samples (such as feldspar, mica, quartz, granite, granodiorite, quartz diorite, rhyolite, andesite, basalt, peridotite, gabbro, shale, sandstone, tuff, carbonate rocks, and sediments) was investigated by using sensitive fluorometric analysis.[10] The solubility of selenium in feldspar, andesite, and basalt with CO$_2$-bubbing water, while considering chemical weathering, was studied through a leaching experiment.[13] From the same rocks and feldspar sodium, potassium, calcium, and magnesium dissolved with this CO$_2$-water were analyzed, and a relation between land-water quality and its surrounding rock-geology was studied.[14]

As a model of chemical weathering-sedimentation of selenium, a reservoir, which had been investigated for arsenic(III) and arsenic(V) in water and sediment,[15] was selected in this study. In the sediment collected the oxidation states of selenium, selenite, selenate, and organically-complexed selenium, were investigated through a leaching experiment using 0.1 M hydrochloric acid and subsequent 1 M sodium hydroxide solutions.[15,16]

Experimental

Samples of Rocks, Reservoir-Sediment, and -Water. Most of the Japanese rock samples were available from Nihon-Chikagaku-Sha Ltd., Kyoto. These rocks were crushed, powdered to pass through a 100-mesh size sieve made by plastics, and homogenized by a reported method.[8,10] The rock reference materials ("Igneous Rock Series"[17] and "Sedimentary Rock Series"[18]) issued from the Geological Survey of Japan (GSJ) were used without additional sample preparation described above. Details of the sampling locations of these rocks have been described elsewhere.[11,17,18] A sediment core (15-cm length) sample was collected from the bottom of a reservoir (water-depth of 30.5 m), located in Hyogo Prefecture and used as a drinking-water supply. The wet core was cut into sections (1.5-cm depth); each divided core was subjected to a leaching experiment without drying. Water samples collected from the surface to a depth of 30.5-m in the reservoir (200 cm^3) were freeze-dried; the resultant residues were packed with polyethylene films as samples for neutron activation analysis. The sampling methods of both the water and the sediment-core were described elsewhere.[15]

Analytical Method. The selenium content of the rocks and sediments were determined by fluorometry with 2,3-diaminonaphthalene.[10] A leaching experiment of the rocks and sediments were carried out by the reported methods with CO$_2$-bubbling water,[14] as well as with 0.1 M hydrochloric acid and the subsequent 1 M sodium hydroxide solutions,[15] respectively. The selenium dissolved with 25 cm^3 of the leaching solution (prepared by repeating the treatment five times) from one gram of a powdered sample was also determined by fluorometry. The selenium concentrations of the reservoir water were determined by neutron activation analysis[19] for the freeze-dried samples of the water.

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[a] This unit is defined to 1 M=1 mol dm^{-3}.

Table 1. Selenium Content of GSJ Rock Reference Materials[a]

GSJ samples	Se content/ppb	
	This work	Reference value
"Igneous rock series"		
Granite, JG-1	2.6 ±1.6 (n=3)	2.8[b]
Granite, JG-1a	2.7 ±0.6 (n=4)	
Granite, JG-2	10.5 ±0.5 (n=4)	
Basalt, JB-1	21.4 ±3.9 (n=5)	26[b]
Basalt, JB-1a	26.1 ±5.1 (n=5)	
Basalt, JB-2	167 ±5 (n=3)	180[b]
Basalt, JB-3	82.9 ±1.8 (n=3)	80[b]
Andesite, JA-1	8.6 ±1.8 (n=5)	8.6[b]
Andesite, JA-2	6.2 ±0.6 (n=5)	
Andesite, JA-3	29.9 ±2.2 (n=5)	
Rhyolite, JR-1	5.9 ±1.2 (n=4)	5.9[b]
Rhyolite, JR-2	2.6 ±0.6 (n=4)	2.6[b]
Gabbro, JGb-1	168 ±1 (n=3)	170[b]
Peridotite, JP-1	6.3 ±0.9 (n=4)	Less than 78[c]
Feldspar, JF-1	10.8 ±2.3 (n=5)	
Feldspar, JF-2	7.5 ±1.2 (n=5)	
"Sedimentary rock series"		
Dolomite, JDo-1	44.3 ±1.4 (n=3)	50[c]
Limestone, JLs-1	3.9 ±0.6 (n=5)	Less than 18[c]
Lake sediment, JLk-1	618 ±1 (n=6)	880[c]
River sediment, JSd-1	97.7 ±0.3 (n=4)	
River sediment, JSd-2	19.5 ±1.2 (n=8)$\times 10^3$	
River sediment, JSd-3	1.54±0.01 (n=4)$\times 10^3$	
Slate, JSl-1	664 ±1 (n=4)	
Slate, JSl-2	338 ±9 (n=4)	
Chart, JCh-1	6.8 ±0.5 (n=5)	

a) Value: Average±standard deviation. n: Number of determinations. b) Ando et al.[17] c) Suzuki et al.[20]

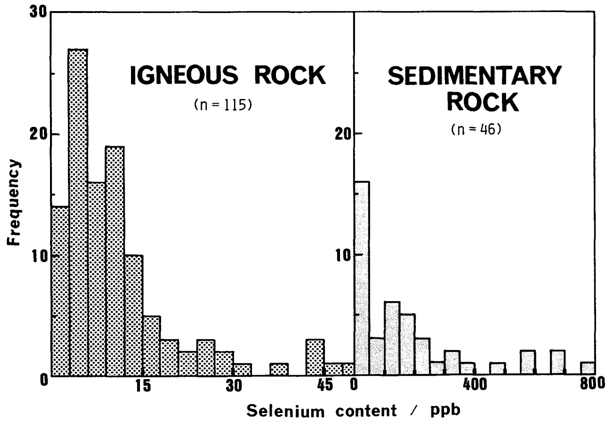

Fig. 1. Histograms of selenium content of igneous rocks (7 samples: >50 ppb) and sedimentary rocks (3 samples: >800 ppb).

Results and Discussion

Selenium Content of the GSJ Rock Reference Materials. Table 1 lists the analytical results of the selenium content of the GSJ rocks and sediment determined by this fluorometric method, in which the detection limit is 0.05 ng of selenium. In this table, the arithmetic mean of the repeated determinations for a sample is indicated along with the standard deviation. For some of the samples the content determined in this work almost agreed with the reference values by various methods[17] of neutron activation analysis, atomic absorption spectrometry, and fluorometry, as well as by neutron activation analysis.[20]

Distributions of Selenium Content of Igneous Rocks and Sedimentary Rocks. Figure 1 shows two histograms of the selenium content of 115 igneous rocks and 46 sedimentary rocks; the selenium content of each rock is summarized in the Appendix. As can be seen in this figure, the histograms give a log-normal distribution, the highest frequency of which is in the range 3—6 ng g^{-1} selenium for igneous rocks and 0—50 ng g^{-1} for sedimentary rocks. As an estimation of the average selenium content of those rocks, accordingly, a geometric mean is recommended, rather than an arithmetic one. The results of calculating the geometric mean gave 8.6 ng g^{-1} for igneous rocks and 88.1 ng g^{-1} for sedimentary rocks.

Table 2 summarizes the selenium content of rock groups with their concentration range, geometric mean, and arithmetic mean. Regarding igneous rocks, selenium seems to be more enriched in basalt than in granite, granodiorite, rhyolite, and andesite. Especially, high-alumina basalt and tholeiite basalt tend to contain greater amounts of selenium than in olivine basalt. In feldspar groups the mean selenium

Table 2. Selenium Content of Igneous Rocks and Sedimentary Rocks/ppb

Sample	Geometric mean	Arithmetic mean	Range	Number of samples
Igneous rocks				
Granitic rocks	5.9	9.1	0.1— 43.4	27
Biotite granite	5.3	7.3	0.1— 25.5	20
Granodiorite	8.1	14.3	2.7— 43.4	7
Quartz diorite	19.4	26.8	8.3— 45.2	2
Rhyolite	5.5	7.4	0.7— 14.8	9
Andesite	6.4	13.0	0.8— 72.2	16
Basalt	19.1	27.4	4.8— 123	18
Olivine basalt	9.5	10.7	4.8— 20.6	7
Peridotite	5.4	5.5	4.4— 6.3	3
Gabbro	27.6	70.8	5.6— 136	2
Rock-forming minerals				
Feldspar	13.1	26.7	3.6— 149	22
Alkali-feldspar	12.2	27.9	7.5— 149	9
Plagioclase	13.8	25.9	3.6— 147	13
Mica	8.3	9.5	2.4— 14.8	9
Quartz	3.1	4.0	0.6— 6.4	7
Sedimentary rocks				
Shale	194	264	41.7— 811	20
Mudstone	456	598	172 — 1280	6
Slate	188	299	34.7— 160	4
Sandstone	27.3	117	2.8— 593	6
Tuff	17.5	43.1	4.4— 143	4
Carbonate rocks	7.1	12.4	2.2— 44.3	6
Sediments				
River and lake sediment	273	1570	85.9—19500	15
Deep sea sediment	135	158	53 — 430	12

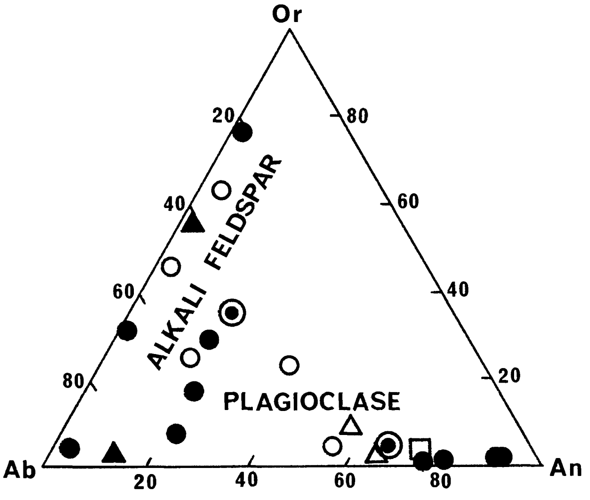

Fig. 2. Or-Ab-An diagram for selenium content of feldspar. Range of selenium content/ppb, ●: 0—9, ○: 10—19, △: 20—29, ▲: 30—39, □: 40—49, ⊙: 100—150.

concentration of the plagioclase is nearly equal to that of alkali-feldspar, and that of these feldspar groups is higher than that of mica and quartz groups. The distribution of the selenium content of all the feldspars is represented with a diagram of Or(Orthoclase, $KAlSi_3O_8$)-Ab (Albite, $NaAlSi_3O_8$)-An (Anorthite, $CaAl_2Si_2O_8$) in Fig. 2. A high concentration of selenium [such as 147 ng g^{-1} (MX-408) and 149 ng g^{-1} (MX-402)] was found in plagioclase as well as in alkali feldspar.

Regarding sedimentary rocks, considerably high amounts of selenium were detected in mudstone, shale, and slate, compared with that in sandstone, tuff, and carbonate rocks. The origin of such rich selenium seems to have a biological origin; e.g., black mudstone (S-22, 963 ng g^{-1}), flintic mudstone (RX-503, 1280 ng g^{-1}), tetragraptus shale (S-1, 811 ng g^{-1}), carboniferous shale (S-4, 786 ng g^{-1}), flintic shale (S-21, 581 ng g^{-1}), and black slate (JSl-1, 664 ng g^{-1}), as listed in Appendix of this paper. In leaching experiments of these sedimentary rocks with 0.1 M hydrochloric acid solution and, subsequently, a 1 M sodium hydroxide solution, considerable amounts (30—50% of the total selenium amounts) were dissolved in a sodium hydroxide solution; e.g., 14% of the total selenium was leached with the acid solution from the RX-503 sample, whereas 38% of that was leached with the alkaline solution. In addition to these experimental results, there was a positive correlation (γ=0.99) between the selenium content and the total sulfur content[18] of nine GSJ sedimentary rock series samples. Therefore, appreciable amounts of biological-origin selenium seem to exist in sedimentary rocks. On the other hand, rich selenium is also recognized in cryustal tuff (RX-404, 143 ng g^{-1}) and glauconite sandstone (RX-509, 593 ng g^{-1}) rather than lapilli tuff (RX-401 and 402, 10.1 and 14.8 ng g^{-1}) and arkose sandstone (RX-506, 13.1 ng g^{-1}), probably derived from granite.

Dissolution of Selenium by Chemical Weathering of Rocks. Table 3 shows the experimental results for selenium(IV) and selenium(VI) dissolved with CO_2-bubbling water from feldspars and igneous rocks. Though no selenium(VI) was detected in any of the rocks, considerable amounts of selenium(IV) were easily dissolved, especially from alkali feldspar (sanidine, MX-401) and plagioclase (albite, MX-408). An extremely low amount of selenium(IV) was leached only from andesite (JA-3) and basalt (JB-2, JB-3), except for the JGb-1 and JB-1a samples. In addition to the leaching experiment with carbonic acid, a residual sample was dissolved with 6 M hydrochloric acid by the same leaching method; after using hydrochloric acid, 56 ng of selenium(IV) was dissolved from the sanidine and 42 ng from the albite. Accordingly, selenium seems to partially occur as selenium dioxide in feldspars, and may exist in andesite, gabbro, and basalt, probably as some occluded state that is insoluble in carbonic acid. In conclusion, the results of these leaching experiments suggest that though selenium in igneous rocks is difficult to dissolve by chemical weathering, vanishingly small amounts of selenite are leachable from feldspars.

Table 3. Nanogram Amounts of Selenium Dissolved from One Gram of a Powder Sample with CO_2-Bubbling Water

Sample	Se content	Dissolved	
	ppb	Se(IV)	Se(VI)
Sanidine (MX-401)	149	83	0
Albite-hornblende (MX-408)	147	38	0
Olivine andesite (JA-3)	29.9	7	0
Hornblende gabbro (JGb-1)	168	0	0
Olivine basalt (JB-1a)	26.1	0	0
Tholeiite basalt (JB-2)	167	13	0
High-alumina basalt (JB-3)	82.9	6	0

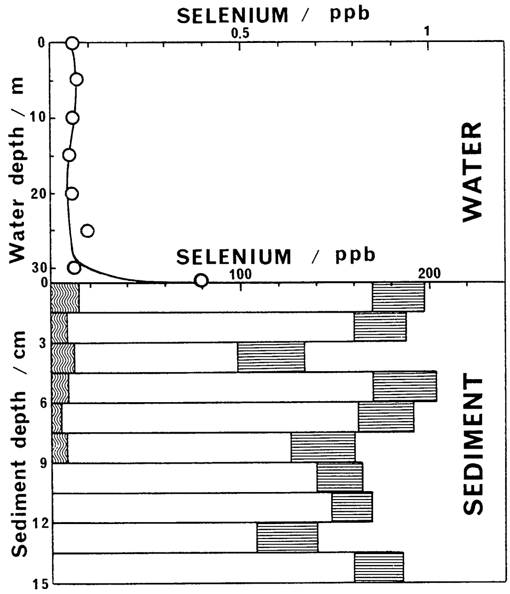

Fig. 3. Vertical distributions of concentrations of selenium in a reservoir water and its sediment. ▨: Acid-soluble fraction detecting only selenite, □: Alkali-soluble fraction, ▤: Silicate fraction.

Selenium in a Reservoir Water and Its Sediment. Figure 3 shows the vertical distribution of the concentration of the total selenium in reservoir water. In the near-bottom water, the increasing change of the selenium is abrupt. This tendency in the same reservoir has been observed for other elements (arsenic, iron, manganese, ammonium, and so on), as has been reported elsewhere.[15] In the reservoir sediment the vertical distributions of selenium in each soluble fraction of the sediment are also shown in Fig. 3 and Table 4: 0.1 M hydrochloric acid (acid-soluble fraction), 1 M sodium hydroxide solution (alkali-soluble fraction) and hydrofluoric acid (silicate fraction). In the acid-soluble fraction which seems to be associated with the sedimentation of selenite and selenate with iron hydroxide, though selenate was not detected small amounts of selenite were found. The same tendency was obtained for arsenite rich in the same sediment core.[15] In the alkali-soluble fraction to leach out organically-complexes selenium, however, about 79% (as an average) of all the selenium was dissolved for the

Table 4. Vertical Distribution of Selenium Amounts in a Reservoir Sediment (ng in 1 g of the dry sediment)

Sediment depth/cm	0.1 M HCl soluble		1 M NaOH soluble Se	Residue Se	Total Se
	Se(IV)	Se(VI)			
0 — 1.5	7	0	156	28	198
1.5— 3.0	8	0	151	27	186
3.0— 4.5	12	0	86	36	134
4.5— 6.0	9	0	160	35	204
6.0— 7.5	5	0	159	29	193
7.5— 9.0	8	0	117	34	159
9.0—10.5	0	0	140	23	163
10.5—12.0	0	0	148	23	171
12.0—13.5	0	0	108	33	141
13.5—15.0	0	0	160	25	185

entire core depth. This high amount of selenium seems to depend on a biological origin, as was pointed out in a study on arsenic.[15] The concentration of selenium in the silicate fraction was almost constant, regardless of the core depth, in the range 23—36 ng g^{-1}. Since the reservoir is surrounded mainly by rhyolitic tuff and rhyolite rocks, the selenium content of the rhyolite (much weathered R-11 and solid core of R-12 samples) collected from the surrounding area of the reservoir was determined to be 11.2 and 14.8 ng g^{-1} of selenium, as is listed in Appendix. Thus, the dissolution of selenium by natural weathering seems to be poor; this result seems to support the possibility of a biological origin of selenium in the reservoir sediment.

Appendix. Selenium Content of Rocks and Rock-Forming Minerals

Run no.	Sample no.	Sample	Se/ppb
	Feldspar		
1	JF-1	Orthoclase-albite (Nagano)	10.8
2	JF-2	Orthoclase (Ibaraki)	7.5
3	MX-401	Sanidine (Mie)	149
4	MX-402	Orthoclase (Okayama)	7.8
5	MX-403	Microline (India)	1.3
6	MX-404	Microline (Toyama)	5.2
7	MX-405	Anorthoclase (Norway)	13.4
8	MX-406	Orthoclase, moonstone (Toyama)	37.9
9	MX-411	Oligoclase-anorthoclase (Akita)	18.1
10	MX-407	Albite (Niigata)	3.6
11	MX-408	Albite-hornblende (Ehime)	147
12	MX-409	Albite-magnesia-riebeckite (Niigata)	30.4
13	MX-410	Oligoclase (Hokkaido)	4.1
14	MX-412	Andesine (Fukui)	13.6
15	MX-413	Andesine (Fukui)	26.3
16	MX-414	Plagioclase, Labradorite (Canada)	11.7
17	MX-415	Labradorite-augite (Kochi)	43.8
18	MX-416	Bytownite (U.S.A.)	8.3
19	MX-417	Bytownite (Kanagawa)	29.1
20	MX-418	Anorthite (Miyagi)	8.9
21	MX-419	Anorthite (Hokkaido)	5.9
22	MX-420	Anorthite-grossular (Shiga)	4.2
	Mica		
23	MX-301	Muscovite (India)	9.1
24	MX-305	Phlogopite (Canada)	6.1
25	MX-310	Lepidolite (Rhodesia)	5.0
26	M-2	Biotite (Fukui)	14.8
27	M-3	Biotite (Nara)	10.7
28	M-4	Biotite (U.S.A.)	13.3
29	M-5	Biotite (India)	13.9
30	M-6	Muscovite (Fukushima)	2.4
31	M-7	Sericite (Shimane)	10.4
	Quartz		
32	MX-421	Rock crystal (Brazil)	3.2
33	MX-422	Quartz (Kyoto)	6.4
34	MX-426	Quartz (Kyoto)	5.4
35	Q-1	Quartz, crystal (Fukushima)	5.1
36	Q-2	Quartz, crystal (Shiga)	5.6
37	Q-3	Quartz (Kyoto)	0.6
38	Q-4	Quartz (Shiga)	1.5
	Granite		
39	G-2	Biotite granite (Shiga)	2.0
40	G-3	Biotite granite (Gifu)	5.4
41	G-4	Corse-grained biotite granite (Kyoto)	3.1
42	G-5	Porphyritic biotite granite (Yamaguchi)	4.3
43	G-6	Biotite granite (Ibaraki)	4.6
44	G-7	Biotite granite (Kyoto)	9.3
45	G-9	Biotite granite (Hiroshima)	7.9
46	G-10	Biotite granite (Okayama)	7.8
47	G-11	Biotite granite (Shiga)	4.6
48	G-12	Biotite granite (Kyoto)	9.7
49	G-13	Biotite granite (Kyoto)	9.0

Appendix. (Continued)

Run no.	Sample no.	Sample	Se/ppb
50	G-14	Biotite granite (Gifu)	11.3
51	G-15	Gneissose biotite granite (Kyoto)	25.5
52	G-16	Micrographic biotite granite (Tottori)	7.7
53	G-17	Fine grained biotite granite (Kagawa)	7.4
54	G-18	Two mica granite (Ehime)	7.4
55	G-19	Hornblende granite (Kyoto)	0.1
56	G-25	Biotite granite (Hyogo)	4.5
57	G-101	Biotite granite (Hyogo)	4.0
58	JG-2	Biotite granite (Gifu)	10.5
	Granodiorite		
59	G-20	Granodiorite (Iwate)	5.3
60	G-21	Granodiorite (Toyama)	20.9
61	G-22	Graodiorite (Yamanashi)	2.8
62	G-23	Gneissose granodiorite (Ehime)	43.4
63	G-24	Biotite granodiorite (Kyoto)	21.9
64	JG-1	Granodirite (Gunma)	2.8
65	JG-1a	Granodiorite (Gunma)	2.7
	Quartz diorite		
66	D-2	Quartz diorite (Kanagawa)	8.3
67	RX-116	Hornblende quartz diorite	45.2
	Rhyolite		
68	R-11	Rhyolite (Hyogo)	11.2
69	R-12	Rhyolite (Hyogo)	14.8
70	RX-301	Potash rhyolite (Shizuoka)	0.7
71	RX-302	Moonstone rhyolite (Toyama)	3.4
72	RX-303	Plagiorhyolite (Hyogo)	7.4
73	RX-304	Vesicular biotite rhyolite (Tokyo)	9.0
74	RX-305	Anorthoclase rhyolite (Akita)	12.0
75	JR-1	Rhyolite, obsidian (Nagano)	5.9
76	JR-2	Rhyolite, obsidian (Nagano)	2.6
	Andesite		
77	RX-310	Hornblende two-pyroxene dacite (Shizuoka)	5.7
78	RX-311	Garnet biotite andesite (Nara)	72.1
79	RX-313	Hornblende andesite (Kagawa)	11.5
80	RX-314	Hypersthene hornblende andesite (Kagawa)	0.8
81	RX-316	Two-pyroxene andesite (Akita)	12.3
82	RX-317	Two-pyroxene andesite (Nagano)	3.8
83	RX-318	Two-pyroxene andesite (Kagoshima)	15.5
84	RX-319	Two-pyroxene andesite (Kanagawa)	0.1
85	RX-320	Two-pyroxene andesite (Kanagawa)	9.7
86	RX-321	Basaltic andesite (Osaka)	6.4
87	RX-322	Trachytic andesite (Akita)	13.3
88	RX-323	Hornblende trachytic andesite (Akita)	2.4
89	RX-324	Altered porphyritic pyroxene (Akita)	9.5
90	JA-1	Augite-hypersthene andesite (Kanagawa)	8.6
91	JA-2	Olivine andesite (Kagawa)	6.2
92	JA-3	Olivine-bearing augite andesite (Gunma)	29.9
	Basalt		
93	B-1	Alkali olivine basalt (Ishikawa)	26.5
94	B-2	Olivine trachy basalt (Hyogo)	5.2
95	B-3	Olivine trachy basalt (Nagasaki)	4.8
96	B-4	Olivine trachy basalt (Kyoto)	11.0
97	B-6	Olivine augite diopside basalt (Yamanashi)	9.0
98	B-7	Olivine augite basalt (Shizuoka)	20.6
99	B-8	Olivine augite basalt (Yamanashi)	15.1
100	B-9	Quartz basalt (Ymaguchi)	17.9
101	B-10	Olivine trachy basalt (Shimane)	9.3
102	B-11	Alkali dolerite (Yamagata)	16.5
103	B-12	Picrite basalt (Niigata)	25.9
104	B-13	High-alumina quartz basalt (Niigata)	55.3
105	B-14	Nepheline basalt (Shimane)	50.8
106	B-15	Bronzite basalt (Miyagi)	11.6
107	JB-1	Titanaugite-olivine basalt (Nagasaki)	21.4

Appendix. (Continued)

Run no.	Sample no.	Sample	Se/ppb
108	JB-1a	Titanaugite-olivine basalt (Nagasaki)	16.5
109	JB-2	Tholeiite basalt (Tokyo)	123
110	JB-3	High-alumina basalt (Yamanashi)	53.5
	Peridotite		
111	RX-125	Cortlandite (Ibaraki)	5.8
112	RX-216	Albite (Niigata)	4.4
113	JP-1	Peridotite (Hokkaido)	6.3
	Gabbro		
114	RX-121	Labradorite, anorthite (Canada)	5.6
115	JGb-1	Hornblende gabbro (Fukushima)	136
	Shale		
116	RX-502	Shale, Triassic (Kyoto)	59.0
117	S-1	Tetragraptus, Ordovician (U.S.A.)	811
118	S-2	Monograptus, Silurian (New York)	143
119	S-3	Leclercqia, Devonian (New York)	134
120	S-4	Floral fossil, Carboniferous (U.S.A)	786
121	S-6	Coaly shale, Permian (Nagano)	228
122	S-7	Shell fossil, Triassic (Miyagi)	461
123	S-8	Floral fossil, Triassic (Okayama)	164
124	S-9	Triassic (Kyoto)	197
125	S-10	Floral fossil, Triassic (Yamaguchi)	149
126	S-11	Floral fossil, Jurassic (Niigata)	208
127	S-12	Oil shale, Jurassic (Ishikawa)	105
128	S-13	Ammonite, Jurassic (Yamaguchi)	349
129	S-14	Floral fossil, Cretaceous (Ishikawa)	41.7
130	S-15	Floral fossil, Cretaceous (Wakayama)	140
131	S-18	Floral fossil, Palaeogene (Hokkaido)	110
132	S-19	Floral fossil, Palaeogene (Fukushima)	88.0
133	S-20	Oil shale, Palaeogene (Colorado)	165
134	S-21	Flintic shale, Miocene (Akita)	581
135	S-23	Coaly shale, Miocene (Mie)	369
	Mudstone		
136	S-16	Marlstone, Cretaceous (Hokkaido)	273
137	S-17	Black mudstone, Cretaceous (Ehime)	233
138	S-22	Black mudstone, Miocene (Nagano)	963
139	S-24	Gray mudstone, Pliocene (Akita)	668
140	S-25	Foraminiferal, Pliocene (Shizuoka)	172
141	RX-503	Flintic siliceous, Neogene (Akita)	1280
	Slate		
142	S-5	Toyama slate, Permian (Miyagi)	160
143	RX-501	Clay slate, Permian (Miyagi)	34.7
144	JSl-1	Black slate (Miyagi)	664
145	JSl-2	Slate (Miyagi)	338
	Sandstone		
146	RX-504	Fine-grained, Neogene (Wakayama)	14.3
147	RX-505	Medium-grained, Cretaceous (Osaka)	54.9
148	RX-506	Arkose sandstone, Jurassic (Fukui)	13.1
149	RX-507	Red sandstone, Archaeozoic (India)	2.8
150	RX-508	Tuffaceous, Neogene (Shimane)	24.1
151	RX-509	Glauconite, Neogene (Ishikawa)	593
	Tuff		
152	RX-401	Lapilli tuff (Fukui)	10.1
153	RX-402	Lapilli tuff (Hyogo)	14.8
154	RX-403	Vitric massive tuff, (Hyogo)	4.4
155	RX-404	Crystal tuff (Wakayama)	143
	Carbonate rocks		
156	C-1	Iceland spar (Mexico)	2.2
157	C-2	Aragonite (Spain)	13.3
158	C-3	Crystalline, marble (Yamaguchi)	3.6
159	JLs-1	Limestone, calcite (Hokkaido)	3.9
160	JDo-1	Dolomite (Tochigi)	44.3
161	JCh-1	Chert (Tochigi)	6.8

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