BULLETIN OF THE CHEMICAL SOCIETY OF JAPAN VOL. 42 1561—1569 (1969)

Scandium Content of Igneous Rocks and Some Oceanic Sediments

Tsuneo SHIMIZU

Department of Chemistry, Faculty of Education, Gunma University, Maebashi, Gunma

(Received October 23, 1968)

Based on the analyses of 105 individual samples and 5 composites, totaling 158 rock samples, the following averages of scandium for various types of Japanese igneous rocks have been obtained (in ppm): granites 5.6, granodiorites 7.4, liparites 6.1, quartz diorites and diorites 11.4, dacites 14.1, andesites 21.8, gabbros 26.9, basalts 27.2 and ultramafic rocks 9.5. Scandium is determined by a combined ion-exchange-spectrophotometric method. Using Poldervaart's suggested ratio of rock types, an abundance figure of 17 ppm Sc for the crust is suggested. The results on the abundance values for scandium in various types of igneous rocks confirm generally the figures given by Norman and Haskin in 1968. Analyses are also performed on Pacific oceanic sediments, giving as averages 18.7 ppm Sc for 4 red clays, 12.1 ppm Sc for 2 volcanic muds and 13.1 ppm Sc for 2 globigerina oozes. Brief discussion on the geochemistry of scandium is given.

A considerable amount of data has been reported for the abundance of scandium in igneous rocks, mostly based on spectrochemical methods. However, data on the abundance of scandium in granitic rocks is rather unreliable because of lack of sensitivity in usual spectrochemical methods. Fryklund and Fleischer[1] have reviewed the previous works involving the geochemistry of scandium prior to 1962, and presented the abundance figures for various igneous rock clans and for the earth's crust as a whole. Currently, averages and concentration ranges for scandium as well as many other elements have been reported

---

[1] V. C. Fryklund, Jr. and M. Fleisher, *Geochim. Cosmochim. Acta*, **27**, 643 (1963).

by Kolbe and Taylor[2] for granites and granodiorites from Australia and South Africa using an improved spectrographic technique. Detailed geochemistry of scandium was not discussed.

Recent development in neutron activation analysis has facilitated the accurate determination of scandium in rocks and minerals, yielding and accumulating reliable data for scandium in materials of geochemical interest. Thus, Stueber and Goles[3] have analyzed 113 ultramafic rocks for sodium, manganese, chromium, scandium, and cobalt by a neutron activation method. Discussing the effect of serpentinization on the abundances of the elements, these authors revealed that scandium abundance is highly dependent on mineral composition and also that the pre-serpentinization mineral composition determines the scandium abundance in the serpentine. Norman and Haskin[4] have reported the results of neutron activation analyses for scandium and iron in 76 samples of igneous and sedimentary rocks, including 9 composites. The highest scandium contents (average, 30 to 40 ppm) were found in basalts and gabbros and the lowest in nepheline syenites and limestones (−1 ppm). Despite increasing amount of data for scandium in igneous rocks, there is still much controversy among the authors as to a possible geochemical relationship between Sc^{3+} and Fe^{2+}, Mg^{2+}, or other major elements or ions in igneous rocks. Taylor[5] gives a general review of the geochemistry of elements including scandium as well as a survey of the analytical data published previously.

In order to develop a routine analytical method for scandium, which is comparable in accuracy to neutron activation analysis, a combined ion-exchange-spectrophotometric method has been worked out for scandium in rocks.[6] Furthermore, 158 igneous rock samples including 5 composites and 8 pelagic sediments from the Pacific Ocean have been analyzed for scandium in order to define the occurrence and abundance of scandium in the igneous rocks and sediments of Japan. It is also intended to summarize the geochemical behavior of scandium. Average abundance figures are suggested for various types of igneous rocks and for the earth's crust as a whole. The results on the abundance values for scandium in various types of igneous rocks confirm generally the figures given by Norman and Haskin.[4]

Analytical Method

The procedure has been described in detail elsewhere.[6] In brief, after 0.5 to 1.5 g of a powdered rock sample is decomposed by means of perchloric-hydrofluoric acid digestion, the resulting residue is dissolved in dilute hydrochloric acid. When any undissolved residue is found, it is put into solution by fusion with sodium carbonate. Traces of scandium in the solution are separated from all interferences by successive cation- and anion-exchange chromatographic techniques in acid ammonium sulfate media. Scandium in the effluent then is coprecipitated together with ferric hydroxide and separated from the ferric ion by an anion-exchange in hydrochloric acid medium. Finally, scandium is determined spectrophoto-

TABLE 1. SCANDIUM IN THE ROCK STANDARDS (in ppm)

Author	Method*	G-1	G-2	GSP-1	AGV-1	W-1	BCR-1	PCC-1	DTS-1
Brunfelt and Steinnes[a]	NA	2.8	3.4	5.6	11.5	33.3	31.0	7.4	3.0
Flanagan[b]	S	—	2—6	6—15	9—25	—	29—53	8—11	2—7
Gordon *et al.*[a]	NA	—	3.5±0.2	6.0±0.3	11.7±0.4	34.8±0.8	32.5±0.5	—	—
Fleischer[d]	R	3	—	—	—	34	—	—	—
This work		2.8	4.1	6.4	13	34	35	6.1	2.9
			3.7	5.9	10	33	32	5.6	2.6
			3.4	5.8	10	33	29	5.5	2.3
			av. 3.7	av. 6.0	av. 11	av. 33	av. 32	av. 5.7	av. 2.6

a) A. O. Brunfelt and E. Steinnes, *Geochim. Cosmochim. Acta*, **30**, 921 (1966).
b) F. J. Flanagan, *ibid.*, **31**, 289 (1967).
c) G. E. Gordon, K. Randle, G. G. Goles, J. B. Corliss, M. H. Beeson and S. S. Oxley, *ibid.*, **32**, 369 (1968).
d) M. Fleischer, *ibid.*, **29**, 1263 (1965).
* NA=neutron activation; S=spectrographic; R=recommended value; —=not determined.

---

2) P. Kolbe and S. R. Taylor, *Contr. Mineral. Petrol.*, **12**, 202 (1966).

3) A. M. Stueber and G. G. Goles, *Geochim. Cosmochim. Acta*, **31**, 75 (1967).

4) J. C. Norman and L. A. Haskin, *ibid.*, **32**, 93 (1968).

5) S. R. Taylor, "The Application of Trace Element Data to Problems in Petrology." Physics and Chemistry of The Earth, Vol. VI, p. 135. Pergamon Press, London (1965).

6) T. Shimizu, *Talanta*, **14**, 473 (1967).

metrically with bromopyrogallol red as a color reagent.

In order to obtain information about the accuracy and precision of the procedure, 8 standard rock samples, G-1 (granite), G-2 (granite), GSP-1 (granodiorite), AGV-1 (andesite), W-1 (diabase), BCR-1 (basalt), PCC-1 (peridotite) and DTS-1 (dunite), were analyzed for scandium. The results are quoted in Table 1. For comparison, earlier literature values for scandium in the rock standards are also listed in Table 1. Generally agreement with previous values is excellent. The following standard deviations (in ppm) indicated by ± sign for three types of igneous rocks also give a general idea of precision of the present method: av. 34.7±1.2 for basalt (8 detens.), av. 20.7±1.3 for andesite (13 detens.), av. 11.9±1.2 for quartz diorite (8 detens.).

Analytical Results

Analytical results are presented in Tables 2 to 6 along with necessary descriptions. Marine sediments of the Pacific Ocean were collected in 1925—1928 through the deep sea expedition carried out by the Hydrographical Department of the former Japanese Navy.

Discussion

Abundance of Scandium. From the values listed in Table 2 the following averages for ultramafic rocks are obtained:

	Sc, ppm	Range
7 Peridotites	10.0	5.5—13.5
Dunite	8.5	
Cortlandite	6.9	
All ultramafic rocks (9 samples)	9.5	5.5—13.5

For an average abundance figure of scandium in ultramafic rocks, Turekian and Wedepohl⁷⁾ give 15 ppm on the basis of the data of Pinson, Ahrens and Frank.⁸⁾ Vinogradov⁹⁾ gives 10 ppm Sc. Vinogradov¹⁰⁾ also gives a value of 5 ppm Sc, deriving this figure from Borisenko,¹¹⁾ who estimated the average scandium contents of ultramafic rocks of the Soviet Union to be 5 ppm for peridotites, 3 ppm for dunites, and 52 ppm for pyroxenites. Compiling the determinations of Pinson, Ahrens and Frank,⁸⁾ Liebenberg,¹²⁾ and Borisenko and Rodionov,¹³⁾ Fryklund and Fleischer¹⁾ give an average scandium abundance of 9 ppm for peridotites, of 30 ppm for perknites and of less than 5 ppm for olivine dunites. Stueber and Goles³⁾ give an average of 5.4 ppm Sc for 14 dunites, of 42 ppm Sc for 9 pyroxenites, and of 15.7 ppm Sc for all ultramafic rocks studied. Norman and Haskin⁴⁾ have reported measurement for scandium in 3 peridotites (all about 12 ppm Sc), 2 pyroxenites (8 and 56 ppm Sc), 2 dunites (9.1 and 3.6 ppm Sc) and 3 perknites (3.4, 3.7 and 17.1 ppm Sc) from various locations. The values found in this work all fall within the range for individual samples analyzed by the above authors. Because of the large number of determinations involved, the overall average given by Stueber and Goles³⁾ may at the present time provide a sound representation of ultramafic rocks of variable mineralogical composition. However, the striking preference of scandium for pyroxene is now well established so that the compiled averages given by Fryklund and Fleischer¹⁾ for dunites, peridotites and perknites may provide a better basis for comparison between averages for the individual rock classes. An average for scandium obtained in this work (9.5 ppm) is in good agreement with their average (9 ppm) for peridotites.

TABLE 2. SCANDIUM IN ULTRAMAFIC ROCKS

Rock mark	Sample	Sc (ppm)
HOK	Orthopyroxene peridotite Horoman, Hokkaido	13.5
HK56081904	Peridotite, Besshi, Ehime	13.3
YN64010907	Peridotite, Toba, Mie	12.5
HK56081902	Enstatite bearing peridotite, Besshi, Ehime	11.7
HK51031101	Peridotite, Kamogawa, Chiba	7.3
10127	Peridotite, Ogawa, Saitama	6.2
Tamura 95	Peridotite, Miharu, Fukushima	5.5
49110-189	Dunite, Oshika, Nagano	8.5
TA-4	Cortlandite, Miharu, Fukushima	6.9

Averages for mafic rocks are computed from Table 3 as follows:

	Sc, ppm	Range
15 Basalts	27.2	15.5—42.5
10 Gabbros	26.9	16.6—32.3
9 Diabases	18.1	17.7—18.5
All mafic rocks (34 samples)	25.4	15.5—42.5

For average abundance figures of scandium for "basaltic rocks" Vinogradov⁹,¹⁰⁾ gives 24 ppm,

---

7) K. K. Turekian and K. H. Wedepohl, *Geol. Soc. Am. Bull.*, **72**, 175 (1961).

8) W. H. Pinson, L. H. Ahrens and M. L. Frank, *Geochim. Cosmochim. Acta.*, **4**, 251 (1953).

9) A. P. Vinogradov, *Geokhimiya*, **1**, 6 (1956).

10) A. P. Vinogradov, *ibid.*, **7**, 555 (1962).

11) L. F. Borisenko, *ibid.*, **No. 7**, 623 (1959).

12) C. J. Liebenberg, *Publ. Univ. Pretoria*, **12**, 79 (1960).

13) L. F. Borisenko and D. A. Rodionov, *Geokhimiya*, **No. 9**, 765 (1961).

TABLE 3. SCANDIUM IN MAFIC ROCKS

Rock mark	Sample	Sc (ppm)
200714	Basalt, Tateyama, Toyama	42.5
KB-1	Basalt, Toyooka, Hyogo	35.8
NB-2	Basalt, Mt. Mihara, Izu-oshima Island	32.8
OB-2	Basalt, Hata, Shizuoka	31.9
NB-1	Basalt, Ajiro, Shizuoka	28.0
OB-1	Basalt, Fudo, Shizuoka	21.3
OB-3	Basalt, Karatsu, Saga	16.3
OB-4	Basalt, Karatsu, Saga	15.5
HG-1	Gabbro, Shisaka Island, Ehime	32.3
3302	Olivine gabbro, Kamioka, Gifu	29.7
KG-1	Gabbro, Miharu, Fukushima	26.7
SH135	Picrite gabbro, Hidaka Hokkaido	16.6
65081902	Diabase, Katashina Gunma	18.5
	Basalt, composite of 7, Japan	21.5
	Gabbro, composite of 6, Japan	19.4
	Diabase, composite of 8, Japan	17.7
OB-5	Basalt, Hawaii, U.S.A.	17.0
666-SC-11	Gabbro, South California U.S.A.	17.0

and Turekian and Wedepohl[7] give 30 ppm. Borisenko[11] gives 20 ppm Sc for gabbros, and Hamaguchi and his collaborators[14] give a neutron activation value of 32 ppm Sc for a composite of 7 Japanese basaltic rocks. Fryklund and Fleischer[1] give a figure of 38 ppm Sc for 99 basalts. Norman and Haskin[4] have recently reported that 8 oceanic sub-alkaline basalts have more than 35 ppm Sc, ranging 35 to 50 ppm; five of 8 continental and island alkali basalts contain less than 30 ppm Sc, ranging from 10 to 55 ppm; a composite of 282 continental (alkali and tholeiitic) basalts contains 30 ppm Sc.

With 36 mafic rocks scandium contents obtained here range from 16 to 42 ppm, the difference involved being a factor of approximately three. The average 24 ppm for 36 mafic rocks is somewhat lower than those given by Fryklund and Fleischer,[1] and Norman and Haskin.[4] This average is also considerably lower than the activation value for the composite of 7 basaltic rocks given by Hamaguchi and his collaborators.[14] The scandium contents of two American mafic rocks are somewhat lower than the average reported here.

It is of interest to see how the scandium distribute among rock-forming minerals in a basaltic rock. Based on radioactivation analysis, Onuma[15] revealed that an alkali olivine basalt from Takashima, Kyushu, shows a scandium content of 18.1 ppm, while values for scandium in its constituent minerals are:

51.2 ppm	for augite (clinopyroxene)
21.4 ppm	for bronzite (orthopyroxene)
not detected	for plagioclase

The striking preference of scandium for pyroxene, particularly clinopyroxene, is well illustrated. With Skaergaard rocks Wager and Mitchell[16] found scandium in the clinopyroxenes of all basic rocks and in apatites of the later basic differentiates, but not in plagioclase or in olivine or opaque iron minerals.

The following averages are obtained from the data listed in Table 4 for intermediate rocks.

	Sc, ppm	Range
32 Andesites	21.8	12.4—28.6
5 Dacites	14.1	10.0—19.1
7 Quartz diorites and diorites	11.4	5.7—21.6
5 Obsidians	29.9	26.5—34.9
2 Pitchstones	7.6	6.0— 9.2
All intermediate rocks (51 samples)	19.1	5.7—34.9

For average abundance figures of scandium in intermediate rocks, Vinogradov gives values of 15 ppm in 1956[9] and of 2.5 ppm in 1962[10] for "neutral rocks" (diorites+andesites). Borisenko[11] gives 3 ppm Sc for diorites. There is no basis for comparison with Turekian and Wedepohl,[7] as they listed no figure for andesites. Fryklund and Fleischer[1] report averages of 34 ppm Sc for 72 andesites, 21 ppm Sc for 68 dacites, and 14 ppm Sc for 32 rhyodacites. Norman and Haskin[4] give 15 ppm Sc for a composite of 85 intermediate rocks of many localities, consistent with the average obtained in this work for intermediate rocks.

Scandium does not distribute uniformly even in the same province as can be seen from its abundance in the rocks of Mt. Asama, Nagano (Table 4). In andesites of Mt. Asama, scandium content ranges 10 to 35 ppm, the difference involved being a factor of more than three.

There is comparatively little reliable information about the abundance figure of scandium in silicic rocks. As can be seen in Table 5 scandium content in 61 silicic rocks ranges from 2.9 to 13 ppm, and average scandium values are:

---

14) H. Hamaguchi, R. Kuroda, K. Tomura, M. Osawa, K. Watanabe, N. Onuma, T. Yasunaga, K. Hosohara and T. Endo, *Geochim. Cosmochim. Acta*, **23**, 296 (1961).

15) N. Onuma, private communication.

16) L. R. Wager and R. L. Mitchell, *Geochim. Cosmochim. Acta*, **1**, 129 (1951).

TABLE 4. SCANDIUM IN INTERMEDIATE ROCKS

Rock mark	Sample	Sc (ppm)
972705	Andesite, Mt. Asama, Nagano	28.6
KA-3	Andesite, Suwa, Nagano	27.8
AS-214	Andesite, Mt. Asama, Nagano	26.3
EM9822	Andesite, Mt. Asama, Nagano	25.0
7X2204B	Andesite, Mt. Asama, Nagano	24.5
KA-2	Andesite, Tanashita, Gunma	24.5
AS-358	Andesite, Mt. Asama, Nagano	24.0
HA-4	Andesite, Sakurajima, Kagoshima	23.9
EM7701	Andesite, Mt. Asama, Nagano	23.7
770210	Andesite, Mt. Asama, Nagano	23.1
HA-3	Andesite, Mt. Ishizuchi Ehime	22.3
HA-1	Andesite, Shimabara, Nagasaki	21.6
AS-336	Andesite, Mt. Asama, Nagano	20.3
AS-375-3	Andesite, Mt. Asama, Nagano	17.1
KA-1	Andesite, Mt. Haruna, Gunma	17.1
NI44	Garnet-biotite-andesite, Mt. Nijo, Nara	15.8
OA-15	Quartz andesite, Amagi, Izu, Shizuoka	15.2
EM9121	Andesite, Mt. Asama, Nagano	12.4
7X2101	Dacite, Mt. Asama, Nagano	19.1
770204	Dacite, Mt. Asama, Nagano	17.3
47121401a	Garnet-biotite-dacite, Mt. Nijo, Nara	12.9
G1061	Dacite, Mizunami, Gifu	11.2
213	Dacite, Mt. Asama, Nagano	10.0
HI-1	Diorite, Tsushima, Ehime	21.6
7820	Biotite-hornblende-gabbro-diorite Kamioka, Gifu	10.7
TK57	Diorite, Tanakura, Fukushima	9.3
OQ-1	Quartz diorite, Kinkazan, Miyagi	12.4
KQ-1	Quartz diorite, Yubiso, Gunma	11.6
NQ-1	Quartz diorite, Sanriku, Iwate	8.6
55080112	Quartz diorite, Yamakita Kanagawa	5.7
7X2204A	Obsidian, Mt. Asama, Nagano	34.9
7X2205	Obsidian, Mt. Asama, Nagano	32.6
882102A	Obsidian, Mt. Asama, Nagano	28.7
241	Obsidian, Mt. Asama, Nagano	27.0
882102B	Obsidian, Mt. Asama, Nagano	26.5
MT132	Pitchstone, Uchimura, Nagano	9.2
15249	Pitchstone, Izu-shikine Island	6.0
	Andesite, composite of 14, Japan	14.3

TABLE 5. SCANDIUM IN SILICIC ROCKS

Rock mark	Sample	Sc (ppm)
NR-11	Granite, Agematsu, Nagano	10.5
OR-2	Granite, Kofu, Yamanashi	9.9
KR-3	Granite, Sudagai, Gunma	9.8
NR-6	Granite, Ishikawa Fukushima	7.7
HR-2	Granite, Kashiwa Island, Kochi	7.1
NR-15	Granite, Makabe, Ibaragi	6.5
NR-7	Granite, Chiyoda, Ibaragi	6.4
HR-7	Granite, Mt. Okue, Miyazaki	5.9
NR-16	Granite, Kasama, Ibaragi	5.9
HR-10	Granite, Tsushima, Ehime	5.8
HR-8	Granite, Odaira, Oita	5.6
KR-2	Granite, Mt. Tsukuba, Ibaragi	5.5
NR-2	Granite, Oyama Toyama	5.5
NR-9	Granite, Tateyama, Toyama	5.3
NR-13	Granite, Iwase, Ibaragi	5.3
NR-1	Granite, Omachi, Nagano	5.3
HR-9	Granite, porphyry, Mt. Osuzu, Miyazaki	5.3
NR-8	Granite, Niihari Ibaragi	5.2
NR-10	Granite geniss, Tateyama, Toyama	5.1
HR-5	Granite, Omogokei, Ehime	4.8
TK41	Granite, Tanakura, Fukushima	4.7
NR-14	Granite, Kasama, Ibaragi	3.9
KR-1	Granite, Abukuma district	3.9
NR-4	Granite, Kawamata, Fukushima	3.6
NR-12	Granite, Agematsu, Nagano	3.1
NR-3	Granite, Ashio, Tochigi	3.0
KR-4	Granite, Kawaba, Gunma	2.8
NR-5	Granodiorite, Ono, Fukushima	12.8
OR-1	Granodiorite, Tono, Iwate	11.5
OR-3	Granodiorite, Enzan, Yamanashi	11.3
OR-5	Granodiorite, Kamaishi, Iwate	11.3
KR-5	Granodiorite, Sori, Gunma	7.8
ON-2	Granodiorite, Ono, Fukushima	7.4
HR-6	Granodiorite, Omogokei, Ehime	7.1
HR-11	Granodiorite, Namikata, Ehime	6.9
OR-4	Granodiorite, Iwaizumi, Iwate	5.4
OR-7	Granodiorite, Kinkazan, Miyagi	5.0
OR-6	Granodiorite, Mt. Minakami, Iwate	4.0
OR-9	Granodiorite, Sumita, Iwate	3.0
OR-8	Granodiorite, Ofunato, Iwate	2.9
HR-12	Liparite, Tsuzuragawaguchi, Ehime	7.2
G1034	Liparite, Tobi Island, Yamagata	6.7
G1256	Liparite, Naruko, Miyagi	4.3
	Granite and granodiorite, composite of 18, Japan	6.4
666-SC-12	Granodiorite, South California, U.S.A.	4.6

27 granites	5.6 ppm
13 granodiorites	7.4 ppm
composite of 7 granites and 11 granodiorites	6.4 ppm
3 liparites	6.1 ppm

An average for all silicic rocks is 6.3 ppm. Acidic igneous rocks have much less scandium than intermediate and mafic rocks. Hamaguchi and his collaborators[14)] give a neutron activation value of 2.3 ppm for scandium in a composite of 20 Japanese granitic rocks, so there is a difference of a factor of almost three in an average scandium between the composite and 61 silicic rocks reported here.

Borisenko[11)] gives 1 ppm Sc for granites. Turekian and Wedepohl[7)] give 14 ppm Sc for high-calcium granites and 7 ppm Sc for low-calcium granites. Vinogradov gives 7 ppm Sc[9)] and 3 ppm Sc[10)] as the average for scandium in silicic rocks. Fryklund and Fleischer[1)] obtain average scandium values of 11 ppm for 14 quartz latites and 5 ppm for 24 rhyolites. Kolbe and Taylor[2)] have recently given averages and ranges for 32 elements including scandium for granitic rocks of the Snowy Mountains, Australia and South-Western Cape Province, South Africa. Their scandium averages are 13 ppm for 4 gneissic rocks, 13 ppm for 20 granodiorites, and 5 ppm for 8 leucogranites, all from the Snowy Mountains. For Cape granites, they give 6.6 ppm Sc for 17 coarsely porphyritic granites, 4.1 ppm Sc for 6 medium-grained granites, and 2.3 ppm Sc for 8 fine-grained granites. Norman and Haskin[4)] suggest an average value of 5 ppm Sc for granites, based principally on the analyses of the composites. Scandium averages obtained in the present work are well in line with such recent estimates as given by Kolbe and Taylor,[2)] and Norman and Haskin.[4)]

Scandium values for sedimentary rocks and oceanic sediments are listed in Table 6. Scandium content of oceanic clays ranges from 11 to 20 ppm, averaging 19 ppm. Red clays tend to have a little higher value of scandium than volcanic muds. Judging from scandium contents of both igneous rocks and oceanic sediments there seems to be no prominent tendency for scandium to become enriched, relative to average igneous rocks, at the oceanic bottom by some mechanism. Plotting the scandium contents *vs.* iron or manganese for the oceanic clays listed in Table 6 has revealed no positive correlations. As far as the scandium is concerned, coprecipitation along with hydrated oxide of iron or manganese or adsorption (ion-exchange) mechanisms caused by submarine ferromanganese minerals are unlikely to play an important role in accumulating scandium into oceanic sediments.

Turekian and Wedepohl[7)] summarize scandium figures of 13 ppm for shales, 1 ppm for sandstones, and 1 ppm for carbonates, estimating also 2 and 19 ppm for deep sea carbonates and clays, respectively. Horn and Adams[17)] have currently made a new approach to geochemical balancing and to estimation of element abundances using a high speed digital computer. Their computer-derived abundance figures for scandium are 10.1 ppm for shale, 0.733 ppm for sandstone, 0.683 ppm for carbonate, 22.8 ppm for oceanic clay, and 2.09 ppm for oceanic carbonate. Norman and Haskin[4)] took a value of 12 ppm Sc found in the composite of 40 North American shales as a representative value for that rock type. They also found 20 ppm Sc for a composite of 55 North American metamorphosed shales. Their values for scandium in 4 carbonate sediments and 2 carbonate metasediments were quite low, ranging 0.40 to 1.57 ppm. Scandium estimates (14.4 and 11.5 ppm) in the present work for 2 globigerina oozes are markedly higher than the averages just mentioned for oceanic carbonates. High contents of scandium in globigerina ooze can partly be accounted for as due to the con-

TABLE 6. SCANDIUM IN MARINE SEDIMENTS AND SEDIMENTARY ROCKS

Sample record number	Sample	Location	Depth (m)	Sc (ppm)
1666	Red clay	11°19'N, 151°57'E	5893	20.3
1539	Red clay	27°42'N, 147°46'E	5948	19.9
1623	Red clay	10°11'N, 128°12'E	5395	19.0
1620	Red clay	12°26'N, 132°54'E	5640	15.7
712	Volcanic mud	29°45'N, 140°36'E	3181	13.0
709	Volcanic mud	25°49'N, 141°24'E	3191	11.2
1618	Globigerina ooze	8°15'N, 134°27'E	3656	14.4
1654	Globigerina ooze	5°29'N, 146°47'E	4032	11.5
KS-1	Slate	Iwamuro, Gunma		9.1
KS-2	Mudstone	Numata, Gunma		1.8
KS-3	Limestone	Kawaba, Gunma		trace
KS-4	Limestone	Nagatoro, Saitama		trace

---

17) M. K. Horn and J. A. S. Adams, *ibid.*, **30**, 279 (1966).

tribution of red clays included in globigerina ooze.

Computations are carried out to obtain an approximate figure for the crustal bundance of scandium. Assuming the average crust to be composed of equal portions of the continental crust consisting of one part of basaltic and five parts of granitic rocks and the oceanic crust consisting of basaltic rocks only (Hamaguchi and Kuroda[18]), a value has been estimated to be 17.3 ppm for the crustal abundance of scandium. Using Poldervaart's suggested ratio of rock types in the crust (basalt+tholeiite 48.9%; diorite-andesite 10.3%; granodiorite 40.8%),[19] a value of 17.1 ppm for the crustal abundance of scandium has been estimated. The two estimates are in excellent agreement.

The classic abundance values usually given for the crust are 5 to 6 ppm Sc (*e. g.*, Fleischer[20]). Vinogradov[10] gives 10 ppm Sc. These figures refer to the abundance of scandium in the continental crust, based on a 2 : 1 weight ratio of felsic to basic rock abundances. Fryklund and Fleischer[1] suggest a figure of 30 ppm Sc for the crust, using Poldervaart's estimate.[19] Abundances in the continental crust, based on a mixture of equal portions of basaltic and granitic rocks, have been given by Taylor,[21] who gives a value of 22 ppm for scandium. Horn and Adams[17] give 15.1 ppm as the abundance for scandium in igneous rocks. Matsuo and Onuma[22] suggest 22 ppm Sc using Poldervaart's ratio.[19]

Geochemical Behavior of Scandium. Judging from the distribution of scandium in magmatic rocks, it may be reasonably stated that scandium concentrates preferentially into early crystallization products. This behavior of scandium is consistent with the previous knowledge about the geochemical behavior of scandium during magmatic differentiation. However, there is still considerable controversy about the geochemical coherence between scandium and other major elements or ions in igneous rock. Rankama and Sahama[23] state that during magmatic crystallization scandium preferentially enters the early ferro-magnesian minerals, occupyring the Mg-Fe positions, thereby becoming impoverished in residual magma. Because the radius of Sc^{3+} (0.81 Å) is considerably larger than that of Mg^{2+} (0.66 Å) and its electronegativity is also greater ($E_{Sc}=1.3$, $E_{Mg}=1.2$), scandium would be retarded from entering crystals compared to Mg^{2+}. On the other hand, the radius of Fe^{2+} (0.74 Å) is much closer to that of Sc^{3+}, and the electronegativity of Sc^{3+} is much smaller than that of Fe^{2+} ($E_{Fe}=1.65$). Based on these observations Ringwood[24] postulated that scandium should exhibit a far greater tendency to enter a suitable lattice site than iron, and this tendency dominates its behavior.

Reviewing the previous knowledge about the diadochy of scandium with other metal ions, Fryklund and Fleischer[1] indicated that plots of scandium content against total iron actually show a better correlation than those against FeO alone, although they believe the geochemical correlation can be best expressed by saying that Sc^{3+} is in diadochy with Fe^{2+}.

Norman and Haskin[4] stated that the presently available evidence does not support predictions for a close geochemical relationship between Sc^{3+} and Fe^{2+}, Mg^{2+}, or any other major element or ion in igneous rocks. According to these authors there should be obvious correlation between scandium and iron within a single class of rocks, say all basic rocks, or all basalts, as well as over the broader range of rock acidities, if a coherence of scandium with iron is really being observed. In view of the possibility of scandium provinces and the absolute lack of observed correlation between iron and scandium for individual rock types, they concluded that the correlation diagrams such as Fe^{2+} *vs.* Sc, $Fe^{2+}+Fe^{3+}$ vs. Sc are not adequate to establish or to refute the existence of any close geochemical relationship between scandium and iron.

It is true that an ordinary coefficient of correlation, which is computed to obtain a quantitative measure of the strength of a relationship such as Fe^{2+} *vs.* Sc, can lead to extremely misleading conclusions unless it is interpreted carefully. Essentially, we have to deal primarily with many geochemical relations as problems of partial correlation. Therefore, observed geochemical correlations (measured by the coefficient of correlation) should be corrected by converting the ordinary coefficient to the coefficient of partial correlation, which does a fair job of eliminating the disturbing effects of other variables. However, this is not always an easy task in geochemical works. It may be thought that the close geochemical correlation of scandium against Fe^{2+} or total iron revealed by many workers does not exclude the possibility that Fe^{2+} or Fe^{2+} plus Fe^{3+} ions are the cause of enrichment of scandium in mafic rocks by diadochy, although it can imply that high contents of both iron and scandium in mafic rocks are

---

[18] H. Hamaguchi and R. Kuroda, *ibid.*, **17**, 44 (1959).

[19] A. Poldervaart, *Geol. Soc. Am. Special Paper*, **62**, 119 (1955).

[20] M. Fleischer, *U. S. Geol. Surv. Circular*, **285**, (1953).

[21] S. R. Taylor, *Geochim. Cosmochim. Acta*, **28**, 1273 (1964).

[22] T. Matsuo and N. Onuma, *Kagaku (Science)*, **37**, 554 (1967).

[23] K. Rankama and T. G. Sahama, "Geochemistry," Chicago Univ. Press, Chicago (1950).

[24] A. E. Ringwood, *Geochim. Cosmochim. Acta*, **7**, 189 (1955).

merely the effects of some other common cause. This cause is not established at the present time. and if present it is not thought so decisive as to change the sign of the coefficient of correlation usually found in diagrams of Fe^{2+} *vs.* Sc^{3+}.

The anthor does not expect that the whole behavior of scandium is governed strictly by the geochemical behavior of iron. There may be some contribution of other major or minor elements like Mn^{2+} (Taylor,⁵⁾ Liebenberg¹²⁾), which may in part affect the behavior of scandium during magmatic crystallization. Also, even though not appreciable, a certain amount of scandium becomes concentrated in residual magmas, because it acts as network former in magmas rich in volatiles, thus forming big tetrahedral complexes (ScO_4^{5-}), which is not accepted into silicate minerals and is therefore concentrated in residual magmas (Ringwood²⁵⁾).

Although the behavior of scandium is complex, we have no positive reason at the present time to reject the close geochemical coherence between Fe^{2+} (or Fe^{2+} plus Fe^{3+}) and Sc^{3+} ions. Substitution of scandium for iron may dominate its behavior during magmatic crystallization. Norman and Haskin⁴⁾ noted that Goldschmidt's rules, even with corrections, should not be applied to group III transition elements, and a successful theory can not be based solely or mostly on comparison of the general properties of the Sc^{3+} cation with those for major elements in melts. Curtis²⁶⁾ has already drawn attention to the fact that the behavior of certain cations of the transition elements, involving d electrons, is dependent largely on their stabilization energy in six-fold and in four-fold co-ordination. However, with no deposition of its d orbitals in four- or six-fold co-ordination, scandium ion (Sc^{3+}) should not acquire any additional stabilization energy, so that the effects of such stabilization may be negligible.

Recently, Nockolds²⁷⁾ has attempted to estimate bonding energies for metal-oxygen bonds, in which charge, radius, and electronegativity would be involved in a single function, and to use the results to account for behavior of elements during magmatic crystallization. As far as scandium is concerned, a coupled substitution like $X^{3+}Al \rightleftharpoons X^{2+}Si$ or $2X^{3+} \rightleftharpoons 3X^{2+} +$vacant octahedral site must be considered. According to Nockolds,²⁷⁾ when two cations of different valency involving the coupled substitution are capable of substitution in a crystal lattice, that substitution will take place preferentially whose sum of relative total bonding energies is the greater. Accepting Goldschmidt's fifteen per cent tolerance in ionic radius for easy substitution, we may expect that major elements Mg^{2+} and Fe^{2+} in six-fold co-ordination should be replaced by Sc^{3+}. For coupled substitutions of the type $X^{3+}Al \rightleftharpoons X^{2+}Si$, the sums of the relative bonding energies are:

$$ScAl = 600$$
$$MgSi = 580$$
$$Fe^{2+}Si = 560$$
$$Fe^{3+}Al = 545$$

Therefore, scandium should exhibit a markedly preferential entry and would be incorporated preferentially with respect to Mg^{2+} as well as with respect to Fe^{2+}. This kind of substitution must depend on the presence of available aluminum, thus perhaps playing a major role in controlling the behavior of scandium during magmatic differentiation.

It is well established that scandium becomes concentrated in early pyroxenes. Although scandium is substituting for Fe^{2+} in this mineral, it is of interest to see that scandium does not favor the coexisting olivines at levels above the analytical detection limit. This is usually accounted for as due to the difficulty of balancing charges (Taylor⁵⁾). However, if we assume the substitution of the type $2X^{3+} \rightleftharpoons 3X^{2+} +$vacant octahedral site, we might have substitutions involving $3Mg^{2+}$, 606; $2Sc^{3+}$, 600; $3Fe^{2+}$, 534, where numerical values stand for the relative bonding energies. If this substitution could occur in olivine-rich ultramafic rocks, scandium should not show any preferential incorporation with respect to Mg^{2+}. This may account for low abundance of scandium in olivine-rich ultramafic rocks.

Favorable evidence supporting the idea that scandium is replacing Ca^{2+} rather than Mg^{2+} or Fe^{2+} have also been offered by Snyder.²⁸⁾ Based on many available determinations of scandium and calcium in rocks and related minerals, Norman and Haskin⁴⁾ pointed out that scandium contents closely paralleled calcium contents. If scandium substitutes for calcium, the coupled substitution of the type Sc Al=Ca Si must be assumed, the sums of the relative total bonding energies being:

Sc Al, 600 and Ca Si, 580

Therefore, scandium may enter into early fractions in excess of calcium, thus becoming impoverished in the magma. However, this substitution suffers from the embarrassment that scandium is not observed in feldspars, not even in the most calcic plagioclases. This is presumably due to the fact that the effective ionic radius range for substitution of calcium is 0.96 to 1.30 Å, far removed from the radius of scandium (0.81 Å). The substitution Sc Al=Ca Si is not thought to proceed as readily as does the coupled substitution Sc Al=Fe^{2+} Si

---

25) A. E. Ringwood, *Geochim. Cosmochim. Acta.*, **7**, 242 (1955).

26) C. D. Curtis, *ibid.*, **28**, 389 (1964).

27) S. R. Nockolds, *ibid.*, **30**, 267 (1966).

28) J. L. Snyder, *ibid.*, **16**, 243 (1959).

under normal conditions. The apparent correlation between scandium and calcium is thought to be due to some other common cause.

The author is indebted to Professor H. Hamaguchi, The University of Tokyo, and Professor R. Kuroda, University of Chiba, for their helpful discussion, and to Professor Y. Kizaki, Gunma University, Professor K. Horikoshi, Ehime University, Dr. D. Gottfried, U. S. Geological Survey, Dr. H. Ishikawa, Kagoshima University, and Dr. H. Onishi, Japan Atomic Energy Research Institute, for placing numerous rock samples. Thanks are also due to Dr. F. J. Flanagan, U. S. Geological Survey, Washington, D. C., for providing the rock standards, and to Dr. N. Onuma, The University of Tokyo, for permission to use his unpublished data.