*Notes on the Geochemistry of Germanium**

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(Received April 7, 1956)

To Goldschmidt and Peters[1] we owe most of the present knowledge of the geochemistry of germanium. A value of 7 ppm. for the abundance of germanium in the lithosphere was reported by Goldschmidt[2,3]. This value is based on the content of a composite of shales in which germanium was found to be enriched. Goldschmidt and Peters showed that germanium replaces silicon and forms GeO_4 tetrahedra. Wickman[4] pointed out that, on the whole, germanium is preferably substituted for silicon in the least-linked silicate tetrahedra. Harris[5] found that germanium is enriched relative to silicon, in olivines (isolated tetrahedra), and pyroxenes (silicate chains), but is impoverished in feldspars and quartz (silicate networks). This confirms Wickman's supposition. In view of this new fact, it appeared to the present author that Goldschmidt and Peters' earlier observation indicating that silicic rocks are richer than subsilicic rocks in germanium, should be reexamined. This would lead to a further study on the germanium content of common igneous rocks (compare Fleischer[6]). Fortunately a sensitive and accurate photometric method for determination of germanium has now been made available.

The more pertinent abundance data for germanium are summarized in Table I. Goldschmidt and Peters' values were obtained by the spectrographic method having a sensitivity limit of about 1 ppm. Ge. This limit is not considered very sensitive. The spectrographic method of Preuss[7] involves fractional distillation of 1–3 g. samples. Harris used the spectrochemical determination after chemical concentration. His method had a sensitivity limit of 0.1 ppm. and the accuracy of ±10%. The results of the Noddacks[8,9] were obtained by an unspecified method. In the paper of the geochemistry of rhenium[10], they gave the germanium content of various geomaterials including meteorites. However, those values are not shown in Table I.

TABLE I

SUMMARY OF LITERATURE DATA ON ABUNDANCE OF GERMANIUM

Material	Ge, ppm.	Author
Igneous Rocks		
Igneous rocks, average	1	Noddacks (1930)[8]
Granites, average	3.5	Goldschmidt and Peters (1933)[1]
Composite of 14 German granites	3	Preuss (1940)[7]
Pitchstones, 3 samples	1.5, 1.4, 1.4	Harris (1954)[5]
Hypersthene-augite-dacite-pumice, Japan	1.7	Harris (1954)[5]
Andesite, New Zealand	1.4	Harris (1954)[5]
Nephelin syenites, average	2	Goldschmidt and Peters (1933)[1]
Basic plagioclase rocks, average	2	Goldschmidt and Peters (1933)[1]
Composite of 11 German gabbros	2	Preuss (1940)[7]
Greisen, average	35	Goldschmidt and Peters (1933)[1]
Sedimentary Rocks		
36 Shales, average	7	Goldschmidt and Peters (1933)[1]
Composite of 36 German shales	7	Preuss (1940)[7]
Red clay, Challenger Exp., Station 353	3.5	Goldschmidt and Peters (1933)[1]
Composite of 23 German sandstones	2	Preuss (1940)[7]
Meteorites		
Nickel-iron, average	500	Goldschmidt and Peters (1933)[1]
Troilite, average	40	Goldschmidt and Peters (1933)[1]
Meteorites, average	79	Goldschmidt (1937)[2]
Meteorites, average	55	Goldschmidt (1954)[3]
Chondrites, average	31	Noddacks (1934)[9]

* Presented at the 9th Annual Meeting of the Chemical Society of Japan in April, 1956.

1) V.M. Goldschmidt and C. Peters, *Nachr. Ges. Wis. Göttingen, Math.-physik. Kl.* IV, 1933, 141.

2) V.M. Goldschmidt, *Skr. Norske Videnskaps-Akad. Oslo, I. Mat.-naturv. Kl.*, No. 4. Geochemische Verteilungsgesetze der Elemente, IX (1937).

3) V.M. Goldschmidt, ed. by A. Muir, "Geochemistry", Oxford Univ. Press, London (1954), p. 379.

4) F. Wickman, *Geol. Fören. Stockh. Förh.*, 65, 371 (1943).

5) P.G. Harris, *Geochim. et Cosmochim. Acta*, 5, 185 (1954).

6) M. Fleischer, *Geol. Soc. Amer. Sp. Paper*, No. 62, 145 (1955).

7) E. Preuss. *Z. angew. Mineral.*, 3, 8 (1940).

8) I. Noddack and W. Noddack, *Naturw.*, 18, 757 (1930).

9) I. Noddack and W. Noddack, *Svensk. Kem. Tid.*, 46, 173 (1934).

10) I. Noddack and W. Noddack, *Z. physik. Chem.*, A154, 207 (1931).

Goldschmidt and Peters[11] found a strong enrichment of germanium in coals. Due to the growing importance of this element in the electrical industry, a few extensive studies on the occurrence of germanium in American[12] and Japanese coals[13] have recently been made. The germanium contents of coals are variable, ranging from a few parts per million to as much as several per cent in the ashes. It appears that there is a regional variation in the abundance of germanium. Occurrence of germanium in ore-minerals has been studied by Kimura and some other workers[14,15,16,17].

The present paper supplies data on the germanium content of the common igneous and sedimentary rocks, and of chondrites.

Analytical Method

For determination of germanium in silicate rocks, the photometric procedure described by Schneider and Sandell[18] was adopted with minor modifications. The method consists in decomposition of a 0.5 g. sample with sulfuric-nitric-hydrofluoric acid, extraction of germanium tetrachloride from 9 M hydrochloric acid solution of the residue, transfer of germanium to aqueous solution by shaking the carbon tetrachloride with water, and final photometric determination with phenylfluorone. Instead of gum arabic to disperse germanium-phenylfluorone complex, aqueous polyvinyl alcohol solution[19] was used. Absorbance measurements were made with a Hirama photoelectric colorimeter (517 mμ filter) in a 1 cm. cell. Recoveries of germanium were slightly low, and a correction of 10% was made. For 1 to 2 ppm. Ge the error should be within 20 to 10%.

Shale composites (0.4 g. each) were heated in an oven at 550°C[20] for about one hour to destory organic matter. The residue was then treated with sulfuric-nitric-hydrofluoric acid. To ensure the validity of this method, 3.0 μg. of Ge and 1 mg. of sodium chloride were added to a 0.50 g. shale sample (1.0 ppm. Ge) containing a considerable amount of organic matter, and after carrying out the above procedure, duplicate values of 7.8 and 7.8 ppm. Ge were obtained.

For determination of total germanium in chondrites, the sample (0.25 g.) was first treated with nitric and sulfuric acid and the solution was evaporated to slight fumes. The residue was treated with hydrofluoric acid and germanium extracted with carbon tetrachloride after elimination of hydrofluoric acid, followed by photometric determination.

Discussion

Igneous Rocks.—Table II–VI list the germanium content of igneous rocks arranged according to rock class. Silica contents of some silicic rocks are based on Shibata, Okada, and Hara's analyses[21]. A summary of igneous averages is given in Table VII. The frequency distribution of germanium in silicic, mafic, and ultramafic rocks is shown in Fig. 1.

TABLE II
GERMANIUM IN RHYOLITES AND GRANITIC ROCKS

	SiO_2, %	Ge ppm.
Rhyolites		
Rhyolite, composite of 12 beach pebbles, 5 miles east of Grand Marais, Minn.		1.0
Rhyolite, White Pine, Nevada		1.3
Granitic Rocks		
Japan		
Quartz porphyry, Hatasa, Okumyo-mura, Gifu Prefecture		1.2
Quartz porphyry, Hatasa, Okumyo-mura, Gifu Pref.		0.9
Quartz porphyry, Hatasa, Okumyo-mura, Gifu Pref.		1.0
Two mica-granite, Ouchi, Ishikawa-machi, Fukushima Pref.	73.89	1.3
Granite, pink, Fusamata, Kawamata-machi, Fukushima Pref.	71.29	1.2
Granite, Ono-shinmachi, Fukushima Pref.		1.0
Granite, Soma-gun, Fukushima Pref.		1.4
Granite, Soma-gun, Fukushima Pref.		1.5
Granite, Tanakura-machi, Fukushima Pref.		1.0
Granite, Tanakura-machi, Fukushima Pref.		1.3
Granite, Higashishirakawa-gun, Fukushima Pref.		1.1
Two mica-granite, Yamamoto, Nanae-mura, Ibaraki Pref.	72.82	1.3, 1.3
Two mica-granite, Hongo, Sanso-mura, Ibaraki Pref.	72.30	1.4

11) V.M. Goldschmidt and C. Peters, *Nachr. Ges. Wis. Göttingen, Math.-physik. Kl.* IV, 1933, 371.
12) T. Stadnichenko, K.J. Murata, P. Zubovic and E.L. Hufschmidt, *U.S. Geol. Survey Circ.*, 272 (1953). A considerably extensive bibliography is found there.
13) M. Inagaki, *J. Chem. Soc. Japan (Pure Chem. Sect.)* 74, 19 (1953).
14) K. Kimura, T. Nakamura and T. Kushibe, ibid., 52, 55 (1931).
15) K. Kimura and Y. Koyama, ibid., 57, 1190 (1936).
16) K. Kimura, O. Nagashima, K. Saito, M. Shima and S. Nakai, ibid., 73, 589 (1952).
17) E.H. Strickland, *Analyst*. 80, 548 (1955).
18) W.A. Schneider, Jr. and E.B. Sandell, *Microchim. Acta*, 1954, 263.
19) Y. Oka and T. Kanno, *J. Chem. Soc. Japan (Pure Chem. Sect.)* 76, 874 (1955).
20) Cf. H. Almond, H.E. Crowe and C.E. Thompson, *U.S. Geol. Survey Bull.*, 1036-B (1955).
21) H. Shibata, S. Okada and K. Hara, *Sci. Repts. Tokyo Kyoiku Daigaku*, Sect. C. 3, No. 22, 141-172 (1954).

	SiO_2, %	Ge, ppm.
Two mica-granite, Mito, Higashinaka-mura, Ibaraki Pref.	73.05	1.4
Two mica-granite, Kitanaka-yama, Nishiyamauchi-mura, Ibaraki Pref.	72.32	1.4
Biotite granite, Higashiiida, Amabiki-mura, Ibaraki Pref.	71.66	1.3
Biotite granite, Ogoto, Kita-yamauchi-mura, Ibaraki Pref.	73.03	1.6
Hornblende biotite granite, Ashio-machi, Tochigi Pref.	67.68	1.1
Granite, Hotokezakikannon, Omachi-shi, Nagano Pref.	75.79	1.2
Hornblende biotite granite, Akazawa, Agematsu-machi, Nagano Pref.	71.27	1.2
Hornblende biotite granite, Haizawa, Agematsu-machi, Nagano Pref.	69.81	1.4
Granite, Kariyasutoge, Oyama-mura, Toyama Pref.	74.52	1.3
Granite, Shomyogawa, Tate-yama, Toyama Pref.	65.08	1.2
Gneissic granite, Mizutani, Tateyama-mura, Toyama Pref.	69.84	0.7
Granodiorite, Tamanoyu, Ono-mura, Fukushima Pref.	62.86	1.2
Granodiorite, Ono-shinmachi, Fukushima Pref.		1.4
Granodiorite, Ono-shinmachi, Fukushima Pref.		1.4
Granodiorite, Ono-shinmachi, Fukushima Pref.		1.4
Granodiorite, Tanakura-machi, Fukushima Pref.		1.8
Granodiorite, Soma-gun, Fukushima Pref.		1.2
Granodiorite, Higashishira-kawa-gun, Fukushima Pref.		1.2
Granodiorite, Higashishira-kawa-gun, Fukushima Pref.		1.2
Granodiorite, Ishikawa-machi, Fukushima Pref.		1.4
Granodiorite, Senzai, Yoshi-hama-mura, Iwate Pref.	66.72	1.6
Granodiorite, Yokoishi, Yoshi-hama-mura, Iwate Pref.	65.18	1.0
Average		1.3
U.S.		
Granite, red, Lower Falls, Snake River, Kanabec Co., Minn.		1.4
Granite, grey, coarse-grained, Benton Co., Minn.		0.9
Granite, red, Stearns Co., Minn.		1.5
Hornblende granite, Freed-hem, Minn.		1.1
Quartz monzonite, Warman, Minn.		1.0
Granite, near Pierz, Minn		1.0
Hornblende granite, Rockport, Mass.		1.8
Granite (standard G-1), Westerly, R.I.		0.9, 1.0
Average		1.2
Average of all		1.3

TABLE III

GERMANIUM IN INTERMEDIATE ROCKS

	SiO_2, %	Ge, ppm.
Japan		
Quartz diorite, Rajotoge, Yoshihama-mura, Iwate Pref.	61.94	1.6
Quartz diorite, Namiita, Okirai-mura, Iwate Pref.	55.96	1.4
Quartz diorite, composite of 7 samples, Miho, Yamakita-machi, Kanagawa Pref.		1.3
Diorite, Soma-gun, Fukushima Pref.		1.6
Diorite, Soma-gun, Fukushima Pref.		1.7
Diorite, Soma-gun, Fukushima Pref.		1.6
Diorite, Tanakura-machi, Fukushima Pref.		1.6
Diorite, Ono-shinmachi, Fukushima Pref.		1.2, 1.4
Diorite, Higashishirakawa-gun, Fukushima Pref.		1.6
Biotite-hornblende gabbro diorite, Kamioka-machi, Gifu Pref.		1.3
Average		1.5
U.S.		
Porphyritic syenite, Wausau, Wis.		2.0
Hornblende tonalite, medium texture, Freedhem, Minn.		0.9
Average of all		1.5

TABLE IV

GERMANIUM IN BASALTS AND DIABASES

	Ge, ppm.
Japan	
Basalt, Ajiro-machi, Shizuoka Prefecture	1.6
Basalt, Ajiro-machi, Shizuoka Pref.	1.7
Basalt (1951 lava) Miharayama, Oshima Volcano, Izu	1.7
Basalt, Tateyama, Toyama Pref.	1.0
Basalt, Tateyama, Toyama Pref.	1.3
Average	1.5

	Ge, ppm.
Localities outside Japan	
Diabase, Grand Marais, Minn.	1.4*
Basalt and diabase, composite of 4 samples, Minn.	1.2
Diabase (standard W-1), Fairfax Co., Va.	1.6, 1.6
Basalt, Columbia River (Nat. Bur. Standards sample no. 4978)	1.2
Triassic diabase (Nat. Bur. Standards sample no. 4984)	1.3
Trap, Deccan (Nat. Bur. Standards sample no. 4985)	1.4
Diabase porphyry, Mt. Etna, Sicily	1.1
Average	1.3
Average of all	1.3

* Triplicate values of 1.4, 1.4, and 1.4_5 have independently been obtained by El Wardani[33].

TABLE V

GERMANIUM IN GABBROS

	Ge, ppm.
Japan	
Gabbro, Higashishirakawa-gun, Fukushima Prefecture	1.3
Gabbro, Higashishirakawa-gun, Fukushima Pref.	0.9
Gabbro, Higashishirakawa-gun, Fukushima Pref.	1.3
Gabbro, Tanakura-machi, Fukushima Pref.	1.3
Gabbro, Miharu-machi, Fukushima Pref.	1.0
Gabbro, Miharu-machi, Fukushima Pref.	1.7
Gabbro, Soma-gun, Fukushima Pref.	1.4
Gabbro, Soma-gun, Fukushima Pref.	1.4
Olivine gabbro, Kamioka-machi, Gifu Pref.	0.9
Gabbro, olivine-bearing? Kamioka-machi, Gifu Pref.	0.9
Gabbro, olivine-free, Kamioka-machi, Gifu Pref.	0.8
Microgabbro, Kamioka-machi, Gifu Pref.	1.3
Average	1.2
Localities outside Japan	
Gabbro, Duluth, Minn., above cement plant	0.8
Gabbro, Duluth, Minn.	1.3
Gabbro, composite of 5 samples, Minn.	1.2
Olivine gabbro, Cripple Creek, Colo.	1.3
Hornblende gabbro, near Shelby, N. Car.	1.8
Hypersthene gabbro (Norite), near Sudbury, Ontario	1.1
Weighted average excluding the first two samples	1.3
Average of all	1.2

TABLE VI

GERMANIUM IN ULTRAMAFIC ROCKS

	Ge, ppm.
Japan	
Peridotite, Horoman, Hidaka, Hokkaido	0.9
Peridotite, Horoman, Hidaka, Hokkaido	1.0
Peridotite, Horoman, Hidaka, Hokkaido	0.8
Peridotite, Miharu-machi, Fukushima Prefecture	0.8
Peridotite, Ogawa-machi, Saitama Pref.	1.1
Cortlandite, Miharu-machi, Fukushima Pref.	1.6
Average	1.0
Localities outside Japan	
Dunite, Balsam, N. Car.	0.7
Dunite (Nat. Bur. Standards sample no. 4975)	1.0
Average	0.9
Average of all	1.0

TABLE VII

IGNEOUS AVERAGES

Rock (number of samples)	Range	Avg. Ge, ppm.
Granitic rocks (43)	0.7–1.8	1.3
Japanese (35)	0.7–1.8	1.3
U.S.A. (8)	0.9–1.8	1.2
Intermediate rocks (12)	0.9–2.0	1.5
Japanese (10)	1.3–1.7	1.5
Basalts and diabases (15)	1.0–1.7	1.3
Japanese (5)	1.0–1.7	1.5
Other localities (10)	1.1–1.6	1.3
Gabbros (20)	0.8–1.8	1.2
Japanese (12)	0.8–1.7	1.2
Other localities (8)	0.8–1.8	1.3
Ultramafic rocks (8)	0.7–1.6	1.0

The amounts and the distribution patterns are much the same for granitic rocks, basalts and diabases, and gabbros. The granitic average (1.3 ppm. Ge) does not differ from the basaltic and gabbroic averages (1.3 and 1.2 ppm.). This is in contrast with the finding of Goldschmidt and Peters showing a larger concentration of germanium in granitic rocks (3.5 ppm.) than plagioclase rocks (2 ppm.).

The average germanium content of the lithosphere probably lies in the range 1–2 ppm., and we may give the most reasonable figure as 1.5 ± 0.5 ppm. Ge. Although the samples studied were mostly from Japan, the same distribution patterns and a small dispersion in the germanium contents are observed for both Japanese and some other samples. Thus, for example, among the granitic and gabbroic rocks analyzed, there are a good number of samples from Fukushima Prefecture or Abu-

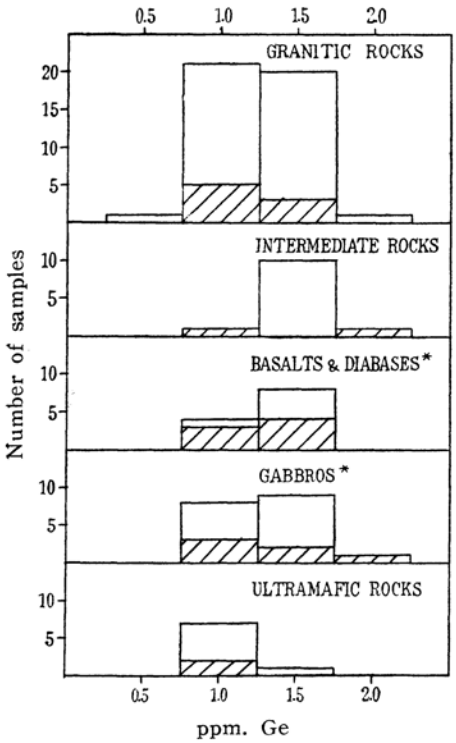

Fig. 1. Frequency distribution of germanium in igneous rocks.

▨ Outside Japan

* Minnesota composite taken as one sample

kuma Plateau. The average of 6 granites from this area is 1.2 ppm. compared to 1.2 ppm. as the average of 8 American granitic rocks. Nine granodiorites from Fukushima Prefecture gave an average of 1.2 ppm. Among 12 Japanese gabbro samples analyzed, 8 were from the same prefecture and an average of 1.3 ppm. is obtained for the latter samples. This value very favorably compares to the weighted average of 1.3 ppm. for 8 American and Canadian gabbros. Such an uniform distribution of germanium in igneous rocks (also compare Fig. 1) is the very basis of the new estimate of the terrestrial abundance of this element. Analysis of a larger number of samples from well-scattered areas of the globe is naturally desirable to get more exact averages. This will also serve as an inter-laboratory test of analyses.

The new igneous values are consistently lower than those of Goldschmidt and Peters and of Preuss. The reason for this discrepancy is not entirely evident: difference in the standardization could explain it to some extent, and some difference could be attributed to a lower limit of sensitivity of the spectrographic method. For the reason that will be discussed on **Sedimentory Rocks,** a possibility of regional variation may not be so great as one would suspect. As for intermediate rocks, two values obtained by Harris, i.e., 1.7 and 1.4 ppm., are just in the right range of the germanium content of this class of rocks obtained by the present author. Values for three pitchstones reported by Harris, i.e., 1.5, 1.4, and 1.4 ppm. and for rhyolites by the present author (Table II), seem to indicate that silicic volcanic rocks are not particularly high in germanium. This is opposite to the behavior of arsenic which shows a higher arsenic content in silicic volcanic rocks[22].

Goldschmidt's estimate in 1937[2] was based on the results of 12 igneous rocks and 13 sedimentary rocks, but several of the samples were composites. He found an average of 4 ppm. for igneous and 7 ppm. for sedimentary rocks but he preferred the latter for some reason as the abundance of germanium in the lithosphere. Recently Fleischer[5] stated that the Noddacks value for igneous rocks (1 ppm.) would probably be closer to the truth. He did not, however, mention the reason why he preferred Noddacks to Goldschmidt in the germanium abundance. The present data happen to confirm Fleischer's supposition.

Logarithms of the atomic abundances, expressed as parts per million atomic weight, of elements of atomic numbers 29 to 35 and 47 to 53 in igneous rocks are plotted in Fig. 2. The value for tellurium is quite uncertain. The data for selenium, silver, and iodine are not definitely established.

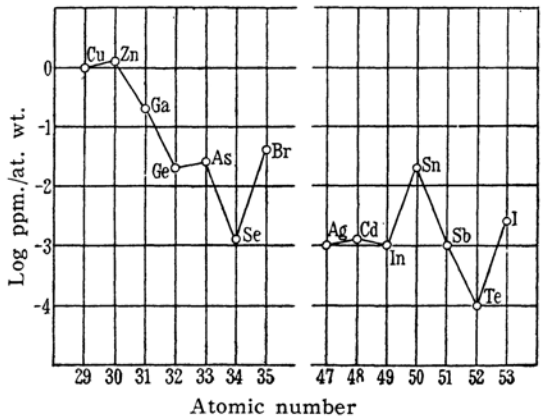

Fig. 2. Log of the atomic abundance, expressed as parts per million/atomic weight, of elements 29–35 and 47–53 in igneous rocks.

The average of 1.5 ppm. of germanium for igneous rocks arrived at above makes the

22) H. Onishi and E.B. Sandell, *Geochim. et Cosmochim. Acta*, 7, 1 (1955).

element definitely less abundant than gallium (15 ppm.), but comparable to arsenic (2 ppm.) in the upper lithosphere. The terrestrial abundances of germanium and tin (2–3 ppm.[23]) are much the same.

As already mentioned in the introductory part of this paper, germanium (using Ahrens' 1952 values for ionic radii[24], Ge^{4+} 0.53 Å) replaces silicon (0.42 Å). The valency of germanium in igneous rocks and magmas is usually quadrivalent, although, according to Ahrens[25], divalent germanium may apparently be found in some sulfide minerals that were formed at low oxidation potentials. Goldsmith[26] has synthesized and determined some of the crystal-chemical properties of Ge^{4+} substituted feldspars. Harris[5] studied the distribution of germanium among coexisting phases of partly glassy rocks such as pitchstone and andesite. Although his findings may not be applied to minerals formed at different stages of the crystallization of the different parent magmas, they deserve careful attention. His results showed that feldspar usually contained ~1 ppm. Ge, whereas olivines and pyroxenes 2–4 ppm. Thus a greater enrichment of germanium relative to silicon, takes place in the latter two minerals. Quartz may contain a fraction of a part per million of germanium, as one would infer from the presence of germanium in cherts and novaculites (0 to 3.0; average 0.4 ppm.)[27]. Also a few parts per million of germanium may be found in sandstones (Table VIII). The feldspar of igneous rocks probably accounts for one-half or more of the total germanium. However, the contribution of olivines and pyroxenes is also considerable, and this is probably the reason that germanium does not show any marked enrichment in a particular class of igneous rocks as shown by the present work.

For granitic rocks whose content of silica had been determined, no relation between germanium and silica was apparent.

In Fig. 3 the germanium contents of some igneous rocks are plotted against arsenic. The substitution of arsenic for silicon has already been indicated. As germanium behaves in the same way, a correlation between the two elements is not unexpected. A general tendency for germanium to rise with arsenic seems to exist, and it may be concluded that the process increasing the arsenic content of magmas also tends to increase the germanium content. Both germanium and arsenic are known to concentrate in the end stages of magmatic differentiation.

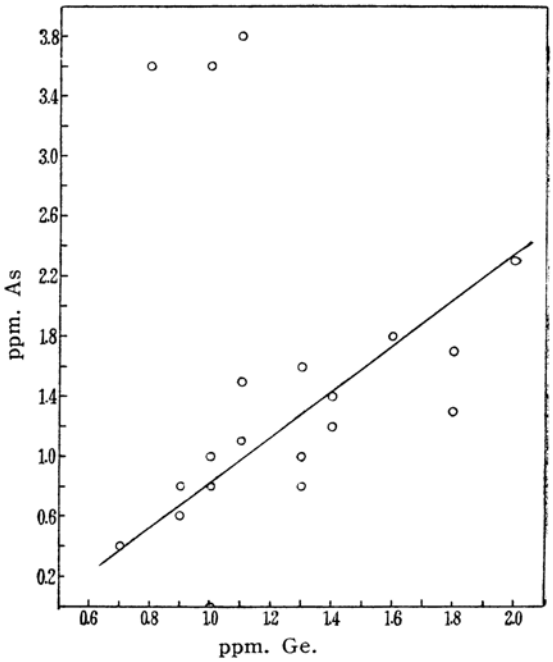

Fig. 3. Germanium as a function of arsenic in igneous rocks.

Replacement of iron (Fe^{3+} 0.64 Å) by germanium appears very probable since 1–3 ppm. Ge was found in magnetites[5]. The ionic radius of Al^{3+} (0.51 Å) suggests the possible substitution of germanium for aluminum. If substitutional disorder (Si–Al) in aluminosilicate is proved, this substitution of germanium for aluminum becomes a good possibility. This is, however, a mere speculation

TABLE VIII

GERMANIUM IN SEDIMENTARY ROCKS

	Ge, ppm.
Graywacke, Hatasa, Okumyo-mura, Gifu Prefecture	0.9, 0.9
Graywacke, Hatta, Hokuse-machi, Mie Prefecture	3.1, 3.5
Sandstone, Mitani-mura, Shiga Pref.	0.8, 0.8
Sandstone, Mitani-mura, Shiga Pref.	1.6, 1.5
Shale, Mitani-mura, Shiga Pref.	1.6, 1.6
Shale, Hatta, Hokuse-machi, Mie Pref.	1.7, 1.6
Shale, Hatta, Hokuse-machi, Mie Pref.	1.5, 1.4
Shale, Hatta, Hokuse-machi, Mie Pref.	1.6, 1.8
Composite of 14 Japanese Paleozoic shales (Minami)	1.6
Composite of 10 Japanese Mesozoic shales (Minami)	1.8
Composite of 36 European Paleozoic shales (Noll)	2.2

23) H. Onishi and E.B. Sandell, *Geochim. et Cosmochim. Acta*, To be published.
24) L.H. Ahrens, ibid., 2, 155 (1952).
25) L.H. Ahrens, ibid., 3, 1 (1953).
26) J.R. Goldsmith, *J. Geol.*, 58, 518 (1950).
27) J.A. Maxwell, Ph. D. Thesis, Univ. of Minnesota (1953).

unless a larger number of analyses of rock-forming minerals have been carried out and more pertinent information on the substitution has been obtained.

Sedimentary Rocks.—Tables VIII and IX list germanium values for sedimentary materials.

TABLE IX
GERMANIUM IN DEEP-SEA DEPOSITS

	Location		Depth, m	
Composite of red clays, Pacific Ocean	30°28.0′N	135°47.0′E	4363	Ge, ppm.
	15°10.0′	154°34.5′	5219	
	31°33.5′	136°20.5′	4096	1.6,
	13°39.5′	158°49.0′	5794	1.6*
Composite of red clays, Pacific Ocean	5°13.0′N	140°40.0′E	4884	
	9°25.5′	126°40.5′	5844	1.4,
	6°47.0′	139°27.0′	4293	1.6*
	6°43.0′	141°27.5′	4743	

* Most of the sodium chloride removed with water before hydrofluoric acid treatment.

The average of 4 shales, of which 3 are from Mie Prefecture and 1 from Shiga Prefecture, is 1.6 ppm. This figure is in good agreement with the weighted average of the two composites prepared by Minami[28] to represent 24 Japanese shales (1.7 ppm.). The composite of 36 European shales prepared by Noll[29] contained 2.2 ppm. The weighted average of the three composites above, based on 60 European and Japanese shales is 2.0 ppm. Here attention should be called to a difference in the results obtained by the previous workers and the present author. Goldschmidt and Peters[1], and Preuss[7] did not describe in detail the shale composites analyzed, but it appears that all three of the samples are the same. As shown in Table I, Goldschmidt and Peters reported 7 ppm. Ge or 0.001% GeO_2. Judging from the description of the analytical procedure they used, it is the impression of the present author that their value is rather approximate; the accuracy may well be 50% or more. However, Preuss' value of 7 ppm. Ge for 36 German shales is claimed to be obtained by a quantitative intensity measurement of the spectrogram. He mentions that the average error of ±50% was obtained for 10 determinations of germanium (as well as of other rare elements) in a shale sample. Considering this, the Preuss' value could be regarded as 7±4 ppm. or 3–11 ppm. Ge. In the present work, the procedure for shales was studied carefully, and, as mentioned in the *Analytical Method*, the recoveries were satisfactory. So the present figure of 2.2 ppm. could well be ±0.4 or 1.8–2.6 ppm. The agreement with Preuss' value is not very satisfactory, and the cause for this discrepancy may be sought elsewhere.

If we adopt the value of 7 ppm. Ge for European shale composite, the result is that it indicates that an extraordinary enrichment of germanium occurred in this sample (compare the data for Japanese shales and oceanic red clays). Of course it may be pointed out that too few shales have been examined in the present work to enable a satisfactory average to be established. Local concentration of germanium may be possible; two Chattanooga shales in which germanium-rich coals (average 470 ppm. in 4 samples) occurred, contained 8 and 18 ppm. Ge[30]. Further investigations of the germanium content of sedimentary rocks, particularly of shales, are very desirable.

The average germanium content of 2 pelagic red clay composites representing 8 individual samples from the Pacific Ocean, is 1.6 ppm. Antimony determination was already made on these composites[31]. A sample of deep-sea red clay contained 2 ppm. according to the analysis of J. A. Maxwell, Geological Survey of Canada[32]. El Wardani[33] has independently obtained the same value for the same sample. A value of 2 ppm. is thus indicated for red clays and this average is comparable to that of shales examined.

As a result of the above observations, it can be pointed out that shales and red clays tend to be rich in germanium compared to igneous rocks. This may be understandable from the fact that some germanium compounds are volatile at relatively low temperatures. Germanium is found in some waters of hot springs. In a mineral water of Senami Spring, Niigata Prefecture, Kuroda[34] found 0.03 mg. Ge per liter or 0.03 ppm. Data of germanium for sea water are scanty. El Wardani found 0.05 μg. Ge in a liter of sea water, corresponding to $\sim 10^{-5}$ ppm.[33] Arsenic is much more abundant in sea water (1–3 μg. As/l.[35,36]) than germanium. The escaping tendency of germanium is less than that of arsenic.

Chondrites.—Table X contains the chandrite data. The frequency distribution is shown

28) E. Minami, *Nachr. Ges. Wis. Göttingen, Math.-physik. Kl.* **IV**, N.F. **1**, 143 (1935).
29) W. Noll, *Chem. Erde*, **8**, 537 (1934).
30) I.A. Breger and J.M. Schopf, *Geochim. et Cosmochim. Acta*, **7**, 287 (1955).
31) H. Onishi and E.B. Sandell, ibid., **8**, 213 (1955).
32) J. A. Maxwell, Private communication to E. B. Sandell.
33) S. A. El Wardani (Scripps Inst. Oceanography, Univ. of Calif.), Private communication to E.B. Sandell.
34) K. Kuroda, This Bulletin, **14**, 303 (1939).
35) A. A. Smales and B. D. Pate, *Analyst*, **77**, 188 (1952).
36) K. Sugawara, Distribution of some minor bio-elements in western Pacific Waters, Regional Symposium on physical oceanography, Tokyo, October, 1955.

in Fig. 4. For the description of some samples, the readers are referred to Prior and Hey[37] or Onishi and Sandell[38].

TABLE X
GERMANIUM IN CHONDRITES

	Ge, ppm. Present work	El Wardani, analyst
Alamogordo, N. Mex.	10.3	
Arriba, Colo.	10.3	9.2*
Cope, Colo.	9.6	9.1*
Gladstone, N. Mex.	11.6	
Gruver, Texas	10.6	
Haven. Kans.	12.4	
Hesston, Kans.	9.6	
Hugoton, Kans.	9.6	
Kanzaki-gun, Saga Prefecture, Japan	10.6	
Kingfisher, Okla.	11.3	
Ladder Creek, Kans.	9.2, 9.2	6.1
Melrose, N. Mex.	10.0	9.4*
Miller, Kans.	12.4	
Morland, Kans.	10.6	
Oshima-gun, Kagoshima Pref., Japan	9.0	
Plainview, Texas	11.2	12.0
Potter, Neb.	11.9	
Roy, N. Mex.	11.2, 11.2	8.8
Average	10.6	
Composite I (Arriba, Beenham, Cope, Cotesfield, Morland, Plainview, Roy)	9.5, 10.0	10.6*
Composite II (Alamogordo, Estacado, Gladstone, Gruver, Kingfisher, Ladder Creek, Melrose)	11.7, 10.9	9.4*

* Average of duplicate analyses.

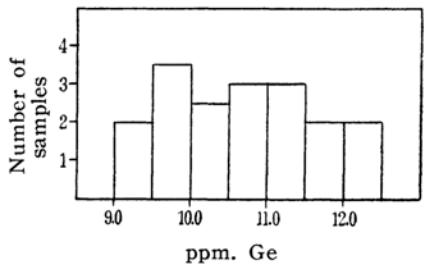

Fig. 4. Frequency distribution of germanium in chondrites.

El Wardani's[33] values were obtained by a photometric method with phenylfluorone after decomposing the sample with hydrofluoric acid only, followed by fusion of the residue with potassium pyrosulfate, and distillation of germanium tetrachloride. The agreement is generally good and this fact was already discussed from the standpoint of the present day trace analysis[39]. The worst agreement is found in the Ladder Creek chondrite which contains 6.1 ppm. (single analysis) according to El Wardani and 9.2, 9.2 ppm. (duplicate analyses) according to the author. For Composite I, a difference between the two analysts' values, taking an average respectively, is 8% with respect to the author's value. For Composite II, it is −17%. The average given by El Wardani for the two composites is 10.0 ppm. and by the author 10.5 ppm. The difference is only −5% which should, in the opinion of the author, be considered very satisfactory.

The average for 18 chondrites is 10.6 ppm. Ge, with a range from 9.0 to 12.4 ppm. The germanium content is uniform and it is probable that this average is not far from the truth. If we take the average for Haven, Hesston, Hugoton, Kanzaki, Miller, Oshima, and Potter chondrites, all of which are not included in either Composite I or II, a value of 10.8 ppm. is obtained and is comparable with 9.8 and 11.3 ppm. of those composites.

In the present work, no attempt was made to separate silicate, troilite, and metal phases of chondrites, or to determine germanium in these phases.

Some of the chondrite samples used in the present work are considerably weathered and the effect of this alteration on the gallium content was previously discussed[38]. We believed that no important change in the gallium content has occurred. In the case of germanium, no definite relation between the degreen of alteration and the germanium content is apparent. Thus, for example, the Kingfisher chondrite, which is the freshest in our collection, contains 11.3 ppm. Ge, as compared to 11.2 ppm. in the weathered Roy chondrite.

There seems to be no relation between the germanium and arsenic contents of chondrites, and this is in contrast with igneous rocks (see Fig. 3).

The new average germanium content of chondrites or approximate cosmic abundance (10.6 ppm. Ge) is much smaller than the values of 31 ppm. reported by the Noddacks[9] and of 55 ppm. by Goldschmidt[3]. The last value is based on the ratio 10 silicate phase : 2 metal : 1 troilite.

In Fig. 5 the meteoritic abundances of germanium, tin, and their neighbors of both even and odd atomic numbers are plotted. The

37) G. T. Prior and M. Hey, "Catalogue of Meteorites", 2nd ed., British Museum (Natural History), London (1953).

38) H. Onishi and E. B. Sandell, *Geochim. et Cosmochim. Acta* 9, 78 (1956).

39) H. Onishi, *Kagaku*, 26 306 (1956).

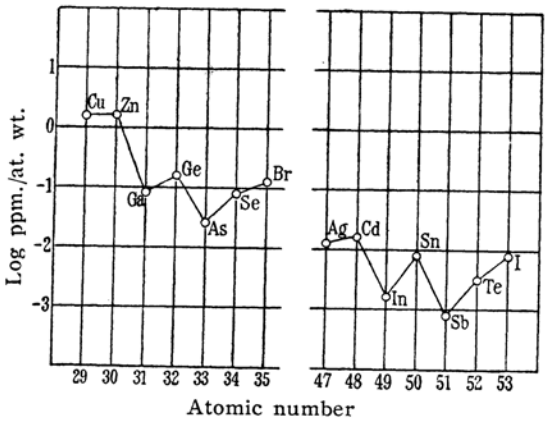

Fig. 5. Log of the atomic abundance, expressed as parts per million/atomic weight, of elements 29–35 and 47–53 in meteorites.

abundances of copper[40], gallium[38], arsenic[22], tin[23], and antimony[31] referred to chondrites. Other values are based on the Goldschmidt's ratio as representing the average of meteorites. Some of the values, e. g., bromine and iodine, are very uncertain. The value for tellurium is an estimate (0.5 ppm.) by the author.

If we adopt the Urey-Craig[41] average for silicon in chondrites, i. e., 18% Si, we obtain the weight ratio $Ge/Si=10.6/18\times10^4=5.9\times10^{-5}$ or the atomic ratio 2.3×10^{-5}.

Germanium (atomic number 32) is more abundant than gallium (A. N. 31) and arsenic (A. N. 33) if the respective contents are taken as 5.3 and 2 ppm. in chondrites.

40) J.M. Shreeve, Unpublished work, Univ. of Minnesota (1955).

41) H.C. Urey and H. Craig., *Geochim. et Cosmochim. Acta*, **4**, 36 (1953).

Summary

Chondrites have uniform germanium contents: the average of 18 samples is 10.6 ppm. Ge, with the range 9.0–12.4 ppm.

The common igneous rocks do not differ greatly in germanium content as shown by the averages: granitic rocks 1.3 ppm., intermediate rocks 1.5 ppm., basalts and diabases 1.3 ppm., gabbros 1.2 ppm., and ultramafic rocks 1.0 ppm. The average for the lithosphere or the crustal rocks may be taken as 1.5 ± 0.5 ppm. Ge.

Shales contain 2 ppm. Ge. Oceanic red clay also contains the similar amount. The germanium content of sedimentary materials seems to be somewhat higher than that of igneous rocks because of the possible escape of germanium in hydrothermal and volcanic emanations.

Special thanks are due Professor E. B. Sandell for generous cooperation in providing rock and meteorite samples and helpful suggestions. Dr. E. Minami kindly provided three composites of European and Japanese shales. Drs. S. S. Goldich, M. Gorai, H. Hamaguchi, and H. Shibata, and Messrs. R. Kuroda and S. Sato supplied various rock samples. Two Japanese meteorites were vigne through the courtesy of the Director, Geological Survey of Japan.

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