*Thortveitite from Kobe, Omiya, Kyoto, Japan**

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In 1960, T. Hisano, an amateur mineral collector in Kyoto, presented several mineral specimens gathered from Shiroishi pegmatite at Kobe, Omiya, Naka-gun, Kyoto, to the first author for identification. Of these, a small greenish gray crystal, after being subjected to X-ray diffraction, X-ray fluorescent and emission spectrochemical studies, turned out to be the first thortveitite fonnd in Japan.

Thortveitite, a soro-silicate of the scandium and yttrium group rare earths, was first described by Schetelig1) in 1911 as gathered from a pegmatite at Iveland, Saetersdalen, Norway. Since then, only one locality, Befanamo, Madagascar, has been added, by Lacroix2). The material from this locality, containing more zirconium and less yttrium than that from Iveland material, was called by the variety name of befanamite.

In 1924, Goldschmidt and Thomassen showed the selective assemblage of rare earth elements in this mineral, the surprisingly high content of ytterbium, and the higher contents of scandium and yttrium3). Also, Goldschmidt alone has demonstrated an average of as much

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1) J. Schetelig, *Vidensk. Skrift*, No. 151 (1922).

2) A. Lacroix, *Compt. rend.*, **171**, 421 (1922).

3) V. M. Goldschmidt and L. Thomassen, *Videndsk. Skrift. I. Mat. -naturv. Klasse*, No. 5 (1924).

as 20 p. p. m. scandium in the gabbro-amphibolite of Iveland and has suggested that the scandium in the thortveitite did not originate from granitic residual material but from the surrounding gabbro-amphibolite penetrated by the pegmatite dikes[4].

The peculiarity of this rare silicate is also found in its unusually high HfO_2/ZrO_2 ratio[5,6], which reaches 0.5 in the Norwegian thortveitite associated with zircons, with $HfO_2/ZrO_2=0.02$ as an average. Furthermore, as is frequently mentioned in textbooks of crystal chemistry, this mineral is one of the most representative species among soro-silicates[7,8].

Occurrence

The Shiroishi pegmatite is enclosed by a late Cretaceous biotite granite overlain by Miocene volcanic sediments about 10 km. north of the pegmatite[10]. The granite body contains many pegmatites, as at Oro, Mie, Morimoto, Ushio Mine, and also this Shiroishi pegmatite.

The pegmatite from which this mineral was derived is called Shiroishi pegmatite and is composed chiefly of perthite, quartz, biotite, muscovite and many such rare accessory minerals as kobeite[10,11], perrierite[12,13], euxenite, monazite, radioactive zircon, allanite, tourmaline, magnetite and ilmenite.

There are only two specimens that have been identified as thortveitite. One is a prismatic crystal 10×4×3.5 mm. in size, while the other is much smaller, 9×2×2 mm. Minute crystals of zircon are attached to the surface of the latter. Because both of them were found in the waste of the quarry, the minerals in the paragenetic relation are uncertain except for the zircon. The fresh surface is greenish gray in color with a glassy luster, but when altered it turns somewhat brownish. The streak color is white.

Emission Spectrochemical Analysis

As the amount of the sample available was so small, the emission spectrochemical technique was applied for the estimation of the scandium, yttrium, ytterbium, zirconium and hafnium. Sodium chloride contaminated by 0.01% palladium as the internal standard was used as the spectrochemical buffer to depress the intensities of the cyanogen bands, which may interefere with many sensitive lines of rare earth elements.

A graduated standard series covering the 0.002∼2.0% range as the oxide of each element was prepared by diluting a mixture of scandium oxide, yttrium oxide, ytterbium oxide, zirconium oxide and hafnium oxide with a buffer. Samples were mixed according to one of the following ratios: (a) one part of sample to 9 parts of buffer, or (b) one part of sample to 99 parts of buffer. The wall of the cavity of the graphite electrode was cut as thin as possible so as to aid the quick burning of the sample, and higher amperage was applied to reduce the volatility differences between the elements.

Working conditions were as follows:

Instrument: Shimadzu Littrow type spectrograph.
Spectral region: 4400∼2700 Å.
Electrode: National Carbon's special-grade 1/8 inch graphite electrode.
Loaded sample: About 10 mg.
Analytical gap: 3 mm.
Voltage: 230 V. D. C.
Current: 9 amp. anode excitation.
Exposure: 0∼50 sec.
Photographic plate: Fuji Spectroscopic Process.

In the sample with 1:9 dilution, such elements as aluminum, calcium, dysprosium, erbium, iron, hafnium, lutetium, magnesium, manganese, scandium, silicon, yttrium, ytterbium and zirconium were detected. Of these, except for silicon, scandium, yttrium and ytterbium the main components of this mineral, the lines of only iron and manganese were strong enough to be estimated as much as the order of 1%. Beryllium, often reported in this mineral, was not found.

Adopting the line pairs of Sc 3365/Pd 3481, Y 3242/Pd 3481, Yb 3298/Pd 3481, and Zr 3391/Pd 3481, smooth calibration curves were drawn for each element except hafnium at lower concentrations. Taking account of the previous lack of study of error for actual analysis, the range of values for each oxide is shown in Table I.

TABLE I. SPECTROCHEMICAL ANALYSIS

Sc_2O_3	10 %
Y_2O_3	3∼10 %
Yb_2O_3	3∼10 %
ZrO_2	0.1∼0.3 %
HfO_2	0.01∼0.03%

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[4] V. M. Goldschmidt, *Geol. Foren. Forh.*, **56**, 385 (1934).

[5] G. von Hevesy and V. Thal Jantzen, *Z. anorg. Chem.*, **136**, 387 (1924).

[6] M. Fleischer, *U. S. Geol. Survey Bull.*, No. 1021 (1955).

[7] W. H. Zachariasen, *Z. Krist.*, **73**, 1 (1930).

[8] F. Liebau, *Acta Cryst.*, **14**, 1103 (1961).

[9] O. Hirokawa and K. Kuroda, Geological Map of Miyazu (1/50000) and Explanatory Text, Geol. Survey of Japan (1960) (in Japanese).

[10] J. Takubo, Y. Ukai and T. Minato, *J. Geol. Soc. Japan*, **56**, 509 (1950) (in Japanese).

[11] K. Masutomi, K. Nagashima and A. Kato, *Mineral. J.*, **3**, 139 (1961).

[12] J. Takubo and S. Nishimura, *J. Min. Soc. Japan*, **1**, 51 (1953) (in Japanese).

[13] S. Bonatti, *Am. Mineral.*, **44**, 115 (1959).

Such other minerals as kobeite, monazite, zircon, ilmenite, and feldpars were analyzed in the same way; only in kobeite 0.1～0.3 % scandium oxide was determined.

X-Ray Powder Studies

A very small fraction of the thortveitite was examined by X-ray powder study using a Norelco X-ray diffractometer. These powder data were compared with those of the thortveitite from Befanamo, Madagascar,[14] as given in Table II.

As may easily be seen, there are consistent discrepancies in the respective corresponding diffractions; that is, their *d*-values are always smaller in the Befanamo material. The discrepancies are to be ascribed to the increase of lattice constants due to the substitution for the smaller ion ($Zr^{4+}=0.86$ Å) of the larger ion ($Y^{3+}=1.00$ Å), both of which replace scandium.

TABLE II. X-RAY POWDER DATA FOR THORTVEITITES FROM BEFANAMO, MADAGASCAR AND KOBE, KYOTO, JAPAN

1		2	
d, Å	*I*	*d*, Å	*I*
5.13	100	5.18	30
4.57	5	4.57	20
4.48	5		
4.29	5		
3.45	5	3.45	20
3.36	10	3.35	10
3.14	90	3.16	50
3.12	100	3.13	100
2.93	80	2.96	80
2.60	30	2.62	40
2.55	80	2.59	50
		2.44	10
2.17	30	2.19	30
2.13	5	2.15	5
2.09	10b	2.11	20
2.05	30	2.08	20b
1.932	10		
1.975	10	1.883	10
		1.768	10
1.700	40	1.738	10vb
1.694	30	−1.708	
1.646	30	1.660	20b
1.594	20	1.590	10b
1.572	10		
1.552	10	1.537	30
1.509	20	1.510	10
1.422	20	1.434	10
1.358	40	1.346	10b

b=broad, vb=very broad

1 Thortveitite (Befanamite), Befanamo. Madagascar. Cu/Ni radiation[14].

2 Thortveitite, Kobe, Kyoto, Japan. Cu/Ni radiation.

Distribution of Lanthanum Series Elements

The distribution of lanthanum series elements was determined by the X-ray fluorescent method. The results are graphically configured in Fig. 1 and compared with those of Goldschmidt and Thomassen. The figure indicates the prevailing dominance of ytterbium among the lanthanide elements and how the elements belonging to the cerium-, gadolinium- and terbium-groups are quite deficient (detection limit: 0.01 % as R_2O_3). Although there are slight discrepancies between the present results and those of Goldschmidt and Thomassen in point of the distribution of the lighter lanthanides, a good coincidence was attained for those of the heavier lanthanides according to Oddo-Harkin's law.

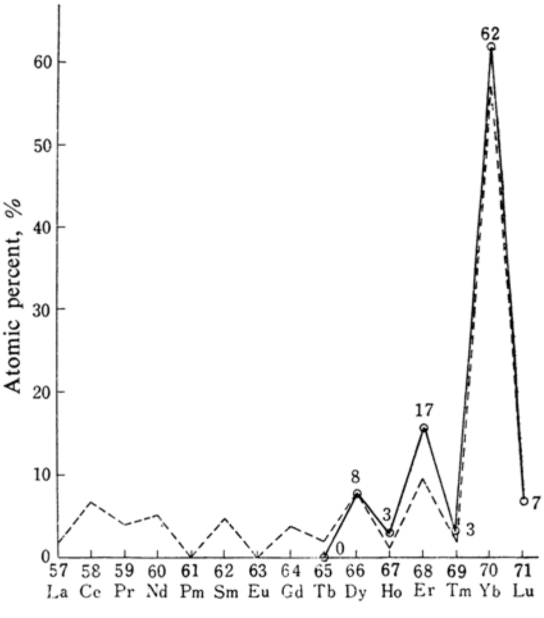

Fig. 1. Distribution of the Lanthanum series elements.
—— Present mineral
- - - Goldschmidt's thortveitite type (recalculated)

Discussion

From the results of X-ray powder study, X-ray fluorescent and emission spectrochemical analyses, it is quite certain that the mineral in question is thortveitite.

As for the contents of the yttrium group of rare earths, that is, a summation of yttrium oxide and the oxides of the yttrium group

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[14] Geological Survey of Japan, X-ray Powder Data for Radioactive Minerals, (1958), p. 112, (unpublished data).

lanthanide elements, values by older analyses fall in the range between 8.89∼17.7 % which range includes the present value.

The zirconium contents in thortveitites vary considerably. For example, Schetelig found 5 % zirconium oxide from the Iveland material[15], but a newer analysis[16] shows the absence of zirconium in other thortveitite from the same locality, suggesting a fluctuation in zirconium content even in samples from the same locality. Therefore, the rather low zirconium content of the present material is not particularly unusual; moreover, as may easily be seen from Table I, the extraordinary concentration of hafnium with respect to zirconium is in good harmony with the results of Hevesy and Jantzen[5].

Our discovery of thortveitite and detection of scandium in kobeite from the Shiroishi pegmatite indicates a notable accumulation of scandium in the magmatic residue of the granitic rock in this area in which no vestige of basic rock is found. In this respect, Goldschmidt's opinion is not applicable to the genesis of the thortveitite from the Shiroishi pegmatite.

Very recently, Neumann[17] has suggested the origin of scandium in several kinds of minerals in pegmatites of the Iveland district, where some thortveitite-bearing pegmatite dikes are developed.

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[15] C. Doelter, "Handbuch der Mineralchemie," III-2, 554 (1917).

[16] J. P. Marble and J. J. Class, *Am. Mineral.*, **27**, 696 (1924).

[17] H. Neumann. *Norsk. Geol. Tidssk.*, **41**, 197 (1961).