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Chemical Studies of Minerals Containing Rarer Elements from the Far East District. LXI. Yttrofluorite from Suishoyama, Kawamatamachi, Fukushima Prefecture, Japan

Keiji UETANI,* Yoshiko OGIMURA,** Akira KATO* and Kozo NAGASHIMA***

* *Department of Geology, National Science Museum, Ueno Park, Tokyo*

** *Department of Chemistry, Faculty of Science, The University of Tokyo, Hongo, Tokyo*

*** *Department of Chemistry, Faculty of Science, Tokyo Kyoiku University, Otsuka, Tokyo*

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A very rare yttrium mineral, yttrofluorite, from granite pegmatite found at Suishoyama, Fukushima Prefecture, was studied. Chemical analysis: Ca 35.50%, $\sum$ Rare earths 18.84%, Mg 0.42%, Fe 0.34%, Al 0.15%, Mn 0.08%, F (remainder) 44.67%. Cell constant calculated from the X-ray powder data: $a_0=5.500$ Å. Specific gravity: 3.51 (measured), 3.62 (calculated). Refractive index: $n=1.454$. The distribution pattern of lanthanide elements studied by the X-ray fluorescent method disclosed that the mineral is poor in cerium group lanthanide, rich in yttrium group with maxima at dysprosium and erbium. The mineral occurs as aggregates of small crystals in spessartine garnet embeded in large crystals of feldspars.

In spite of the many detailed chemical studies of pegmatite minerals from Japan, yttrofluorite was hitherto not reported, except for one⁽¹⁾ from Yamaguchi-mura, Nagano Prefecture, which was assumed because of the high refractive index (although the sample was too small to be analyzed).

Suishoyama pegmatite, Kawamata-machi, Fukushima Prefecture, is found in a Mesozoic biotite granite body, has a zonal arrangement of felsic minerals, and has been worked for quartz and feldspar for many years. The pegmatite is also well-known for the production of many rare element minerals, such as abukumalite (type locality), yttrialite, fergusonite, tengerite, thorogummite, allanite, uraninite, zircon, gadolinite, keilhauite, thalenite,⁽²⁾ and some secondary uranium minerals such as autunite, torbernite, zeunerite, and a mineral⁽³⁾ very close to uranophane, but which has higher refractive indices and larger d values obtained from X-ray powder diffraction.

The mineral herein described was collected from a waste outside the quarry, so the mode of occurrence or the paragenesis of minerals is not certain. The mineral usually occurs as irregularly shaped, fine grained agglomerate in spessartine garnet of a dark red brown color, and contains a small amount of yttrium group rare earths. The largest aggregate reaches 3 cm in size, but individual grains are too small to see with the naked eye.

The spessartine garnet is usually embeded in potash feldspars. This occurrence of yttrofluorite is very similar to that of tengerite⁽⁴⁾ in Suishoyama pegmatite suggesting a close relationship between these two minerals.

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1) H. Shibata, *J. Geol. Soc. Japan,* **46**, 558 (1939). (in Japanese)

2) K. Nagashima and A. Kato, This Bulletin, **39**, 925 (1966). Literatures describing these minerals from Suishoyama are cited in this paper.

3) K. Nagashima, A. Kato and M. Chiba, *Chigaku-kenkyu,* **17**, Nos. 10, 11, 12, p. 95 (1966). (in Japanese)

4) T. Iimori, *Sci. Pap. Inst. Phys. Chem. Research,* **34**, 832 (1938).

The mineral yttrofluorite is also important as an example of a complete assemblage of rare earth elements in which the yttrium earths are of the same abundance as the cerium earths. This kind of complete assamblage is known as "yttrofluorite type" (Goldschmidt and Thomassen[5]). However, as shown by Semenov,[6] the distribution of rare earth elements in fluorite is quite variable. In Dana's "System of Mineralogy,"[7] both yttrofluorites rich in yttrium group rare earths, $\sum Y_2O_3$ 17.35%, $\sum Ce_2O_3$ 1.68%, and those rich in cerium group rare earths, $\sum Y_2O_3$ 8.10%, $\sum Ce_2O_3$ 16.45% are described.

Optical and X-Ray Powder Studies

As the grains composing the aggregates are so small, clevages characteristic of fluorite is hardly observable with the naked eye. The color of the aggregates, and that of the powder is gray. The refractive index is 1.454. The value is much higher than that of the usual fluorite, and agrees with values, 1.4572, 1.4425, or 1.4483 for yttrofluorites of other localities.[7]

X-Ray powder diffraction measurements were made on a Norelco X-ray Diffractometer. The diffraction data are compared with those of pure artificial calcium fluoride in Table 1. *D* values and intensities of the present mineral are very close to those of calcium fluoride, but the *d* values of the mineral are definitely a little larger than those of artificial fluorite suggesting substitution of calcium by larger rare earth elements. From the *d* values, a_0 was calculated to be 5.500 Å.

Chemical Composition

Chemical analyses were carried out on the handpicked material. Fluoride was not analyzed directly, but determined by subtracting analyzed

TABLE 1. X-RAY POWDER DATA

(1) Artificial CaF_2		(2) Yttrofluorite from Suishoyama				
d Å	*I*	*d* Å	*I*	Q_{obs}	Q_{calcd}	*hkl*
3.153	94	3.171	100	0.0995	0.0992	111
—	—	2.751	2	0.1321	0.1323	200
1.931	100	1.943	60	0.2648	0.2645	220
1.647	35	1.658	10	0.3637	0.3637	311
—	—	1.586	2	0.3974	0.3968	222
1.366	12	1.375	6	0.5292	0.5290	400
1.253	10	1.262	3	0.6281	0.6282	331
—	—	1.230	1	0.6615	0.6613	420
1.150	16	1.123	6	0.7935	0.7935	422
ASTM, No. 4-0864 Cu/Ni radiation $a_0=5.4626$ Å		Cu/Ni radiation $a_0=5.500$ Å				

TABLE 2. CHEMICAL ANALYSIS

	%	%/Formula weight		×0.9154 (=1/1.092)
Ca	35.50	0.8857	1.0924	0.811
ΣR.E.*	18.84	0.1762		0.161
Fe(III)	0.34	0.0061		0.005
Al	0.15	0.0056		0.005
Mn	0.08	0.0015		0.001
Mg	0.42	0.0173		0.016
F (remainder)	44.67	2.3511		2.152
Total	100.00			

* Mean atomic weight = 99.7

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[5] V. M. Goldschmidt and L. Thomassen, *Vidensk. Skrifter I. Mat.-naturv. Klaase,* **1924,** No. 5.

[6] E. I. Semenov, *Geohkimiya,* **1958,** 452.

[7] C. Palache, H. Berman and C. Frondel, "Dana's System of Mineralogy," 7th ed., Vol. II, John Wiley, New York (1951), p. 32.

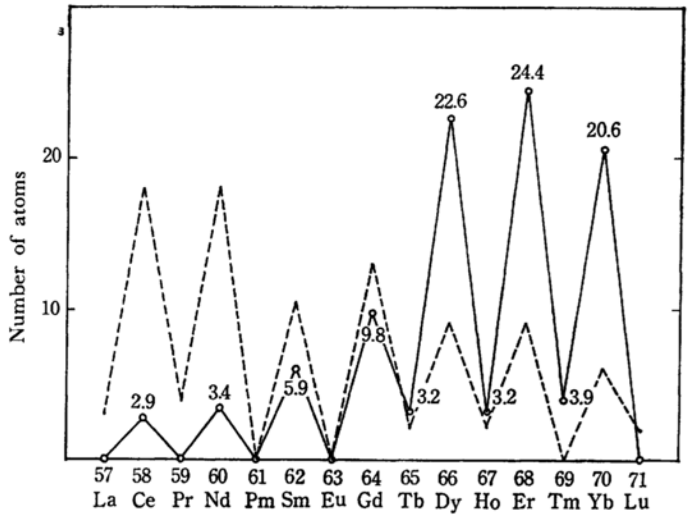

Fig. 1. Distribution of rare earth elements.

—— Yttrofluorite type observed (this work) Total lanthanoids=100 atoms
---- Yttrofluorite type (by V. M. Goldschmidt and Thomassen)

cations from 100%. The average atomic weight of the rare earth elements was determined by titrating the weighed mixed oxides with an EDTA standard solution after dissolving them in hydrochloric acid.

The results of the analyses are given in Table 2, together with the molecular ratios of the components. The experimental formula of the yttrofluorite from Suishoyama calculated on the bases of $\sum$ cation=1.00 is $(Ca_{0.8107}, \sum R.E._{0.1613}, Mg_{0.0158}, Fe, Al, Mn)_{1.00}F_{2.1524}$. The content of rare earth elements as fluoride is 28%, and the atomic ratio of rare earth elements to calcium reaches 1 : 5.04. This ratio is almost the same as that for the yttrofluorite from Hundholmen, Norway, in which (Y, Ce) : Ca is 1 : 6.0, and the yttrofluorite (more correctly cerium fluorite) from Fahlum, Sweden, in which the ratio is 1 : 5.2.

The Distribution Pattern of Rare Earth Elements

The distribution of lanthanum series elements was determined by the X-ray fluorescent technique. Cerium, neodymium, samarium, gadolinium, terbium, dysprosium, holmium, erbium, thulium, and ytterbium (with the maxima at dysprosium and erbium) were found. Lutetium may be present, but could not be confirmed due to the overlapping diffractions of other spectra. A quantitative estimation, with the relative error of less than 10%, is given in Fig. 1, in which the atomic % of the elements is plotted. In the figure, the yttrofluorite type distribution pattern of rare earth elements by Goldschmidt and Thomassen⁵⁾ is also shown. As seen in the figure, the present mineral is richer in yttrium group rare earths than the so called yttrofluorite type. The higher concentration of the yttrium group in the mineral might be a reflection of the high concentration of yttrium group rare earths in the original solution of the Suishoyama pegmatite.

Specific Gravity

When divalent calcium ions in fluorite are substituted by trivalent rare earth ions, excessive fluoride ions are thought to enter the interstitial sites in the fluorite structure. This type of structural model is called the interstitial model. There could be another model —a vacant cation model— in which 1/3 of the lattice points of substituted calcium are left vacant. The phase relationship of the YF_3-CaF_2 system was studied by Short and Roy.8) They also compared the measured specific gravity of a CaF_2-YF_3 solid solution with theoretical values calculated on the basis of the interstitial fluoride model, and the vacant cation model, and showed a beautiful agreement between the measured, and interstitial model values.

The specific gravity of the present yttrofluorite measured by the pycnometric technique is 3.51. The calculated value, adopting the interstitial model, and the concentration, and mean atomic weight of rare earth elements is 3.62. The difference may be explained by the fine, powdery nature of the specimen.

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8) J. Short and R. Roy, *J. Phys. Chem.*, **67**, 1860 (1963).