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Chemical Analysis of Thortveitite from Oro, Mineyama-cho, Naka-gun, Kyoto Prefecture, Japan

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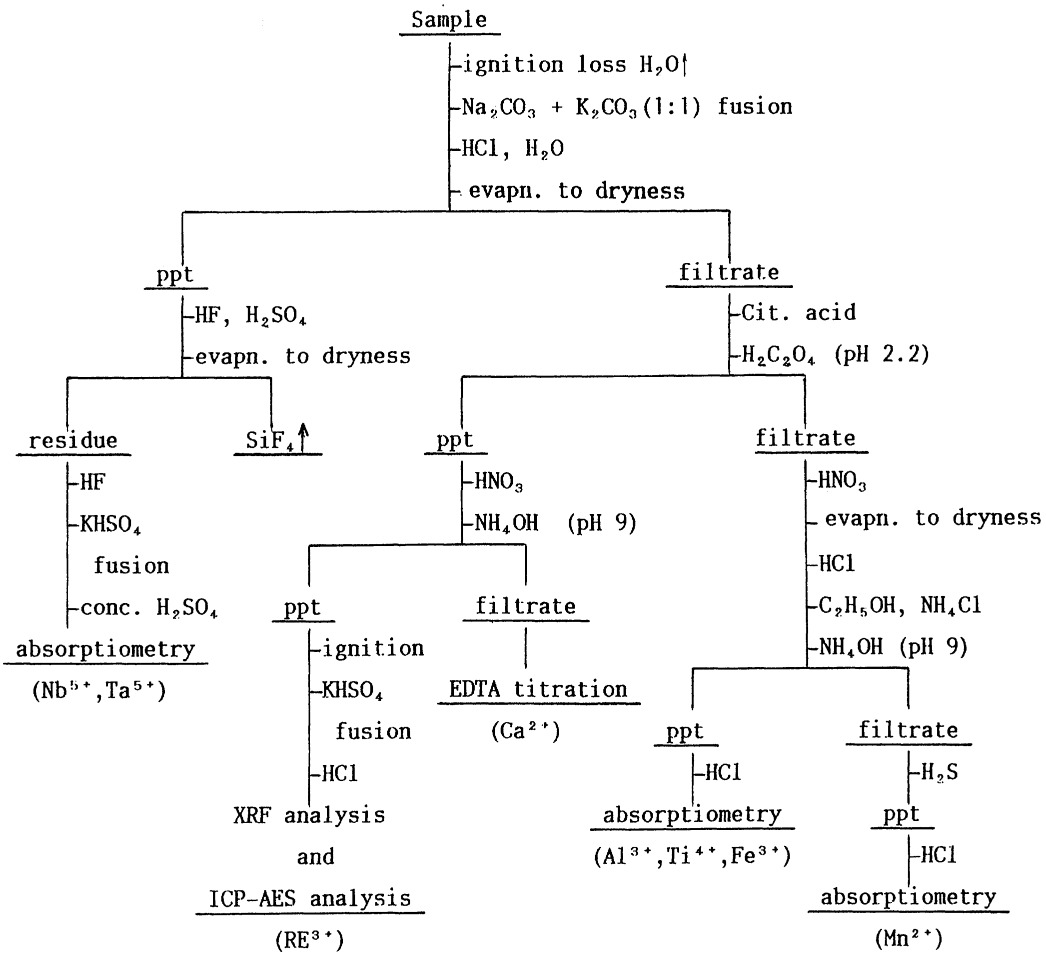
The geochemically interesting rare mineral, thortveitite, from Oro, Kyoto Prefecture was studied. Major constituents, scandium, yttrium, and lanthanoids, niobium, tantalum, aluminum, titanium, iron, calcium, and manganese were determined. The chemical analysis of the mineral assemblage gave Sc_2O_3 18.20, Y_2O_3 0.72, Σ Ln_2O_3 1.70, FeO 0.97, MnO 0.54, Nb_2O_5 trace, Ta_2O_5 9.96, Al_2O_3 3.02, CaO 1.72, TiO_2 0.83, SiO_2 58.31, and H_2O 4.20; total 100.17%. This sample contained tantalite 11.47, anorthite 8.37, rutile 0.83, and quartz 37.91% in addition to thortveitite 37.40%. Scandium–tantalum substitution is suggested to occur similarly to yttrium–niobium substitution in earth acid minerals.

Thortveitite, a sorosilicate mineral which has scandium and yttrium-group rare earths as its major constituents, mainly occurs in the pegmatite layer of Norway and Madagascar.[1)] The crystallographic and physical properties of thortveitite are as follows: monoclinic system; space group: *C*2/*m*; hardness on Mohs' scale: 6—7; specific gravity: 3.58.[2)]

The distribution pattern of lanthanoid elements in thortveitite, by Goldschmidt and Thomassen,[3)] has been reported to be extremely specific and selective (Goldschmidts' classification: thortveitite type), with a remarkably high content of ytterbium. Other constituents of this geochemically and mineralochemically very rare mineral type are alvite and yttrotitanite.



Scheme 1. Chemical analysis of thortveitite.

In Japan, thortveitite was first collected from the Shiroishi pegmatite zone at Kobe, Omiya-cho, Naka-gun, Kyoto Prefecture, analyzed and identified by Sakurai et al.[4] In Oro, Mineyama-cho, Naka-gun, Kyoto Prefecture, granites containing pegmatite are widely distributed, and some rare element minerals such as fergusonite, zircon (yamaguchilite) and yttrofluorite have been found.[5—7] There are two ore bodies, both of which consist of graphic, feldspar, and quartz zones.[8] The feldspar zone of the ore body A contained bastnaesite, zircon, and small amounts of ilmenite, monazite, and xenotime. The feldspar zone of the ore body B had biotite and magnetite containing fergusonite, zircon, and allanite.

The thortveitite examined here was collected from the ore body A of Oro and its identity was confirmed by Yamada et al. in 1980.[8] Emission spectrochemical analysis of thortveitite from the Shiroishi pegmatite zone at Kobe has been performed in detail by Nagashima et al.[4] and the detailed distribution of lanthanoid elements in the mineral has been reported. The present paper describes the results of chemical analysis, X-ray fluorescence analysis, and ICP analysis of lanthanoids in thortveitite from the ore body A, Oro, Mineyama-cho, Naka-gun, Kyoto Prefecture.

Experimental

In order to clarify the content of thortveitite as [$(Sc,Y,Ln)_2Si_2O_7$; Ln=lanthanoids] and the contents of other minerals found together with it in the ore body A, a total chemical analysis of the thortveitite sample was performed. The analytical procedure of the mineral sample is shown in Scheme 1. A portion (0.1086 g) of the powdered sample was taken in a platinum crucible, and fused with the fusing mixture $Na_2CO_3+K_2CO_3$. The melt was treated with hydrochloric acid and water. The insoluble matter was obtained by filtration, converted to oxides by ignition and weighed as the sum of silicic anhydride and earth acid metal oxides ($Nb_2O_5+Ta_2O_5$). The oxides were treated with hydrofluoric acid and sulfuric acid to remove SiO_2 as SiF_4. After the earth acid metal oxides had been fused with potassium hydrogensulfate, the melt was treated with concentrated sulfuric acid, and niobium(V), and tantalum(V) were determined by hydrogen peroxide-absorptiometry.[9] Ten milliliters of 1 mol dm^{-3} oxalic acid was added to the filtrate, and rare earth ions and calcium ion were precipitated as oxalates at pH 2.2. The precipitates were treated with 10 cm^3 of concentrated nitric acid and heated until the oxalic acid was completely decomposed. To separate calcium ion from lanthanoid ions, the pH of the solution was adjusted to 9.0 with aqueous ammonia and the lanthanoid ions were precipitated as hydroxides. Calcium ion was determined by the EDTA titration method. Lanthanoid hydroxides were converted to the oxides and fused with potassium hydrogensulfate, and, then, the trivalent ions were collected with hydroxyiminodiacetic acid (HIDA)-chelating resin. Scandium(III), and yttrium(III), and ytterbium(III) ions on the HIDA-chelating resin were determined by X-ray fluorometry (XRF analysis) as described in previous papers.[10,11] The trace amounts of other rare earth ions were determined by the ICP-AES method.[12] Aluminum, iron, and titanium ions were determined by 2-methyl-8-quinolinol[13] and 8-quinolinol[14] absorptiometry, and manganese ion was measured by potassium permanganate absorptiometry.[15]

Analytical Results and Discussion

(1) Total Analysis of Thortveitite: The results are summarized in Table 1. With the generally accepted composition of thortveitite, $(Sc,Y,Ln)_2Si_2O_7$, the four components of thortveitite amount to Sc_2O_3 18.20%, Y_2O_3 0.72%, ΣLn_2O_3 (Ln_2O_3 0.94%+Yb_2O_3 0.76%) and SiO_2 16.78% of the total oxide. The overall content of thortveitite in this mineral sample was, then, 37.40%.

The remainder of the constituents was assigned to several minerals expected to be present in the ore body A: FeO 0.97, MnO 0.54, Nb_2O_5 trace, Ta_2O_5 9.96% →tantalite [$(Fe,Mn)(Nb,Ta)_2O_6$: 11.47%]; Al_2O_3 3.02, CaO≒1.72, SiO_2 3.63%→anorthite [$CaAl_2Si_2O_8$: 8.37%]; TiO_2 0.83%→rutile [TiO_2: 0.83%]; quartz [SiO_2: 37.91%].

The present thortveitite sample was found to be a mixture of tantalite, anorthite, rutile, and quartz. It has been reported that the zirconium content in thortveitite often varies considerably (0.1—5% ZrO_2), and the HfO_2/ZrO_2 ratio is usually high (0.5—0.02).[4,16,17] However, no detectable amounts of zirconium and hafnium were present in the present sample.

(2) Distribution of Scandium, Yttrium, and Lanthanoid Elements: The content of each rare earth element was analyzed by XRF and ICP methods. The results are listed in Table 2 with the contents of other elements in thortveitite under the assumption that the present thortveitite has the composition of $(Sc,Y,Ln)_2Si_2O_7$.

Table 1. Analytical Results of Thortveitite from Oro, Mineyama-cho, Naka-gun, Kyoto Prefecture (Sample taken 0.10859 g)

	Content/%	Mineral assemblage
Sc_2O_3	18.20	
Y_2O_3	0.72	Thortveitite (sorosilicate)
Yb_2O_3	0.76	$(Sc, Y, Ln)_2Si_2O_7$
Ln_2O_3 (Excluding Yb)	0.94	37.40%
FeO	0.97	
MnO	0.54	Tantalite
Nb_2O_5	Trace	$(Fe, Mn) (Nb, Ta)_2O_6$
Ta_2O_5	9.96	11.47%
Al_2O_3	3.02	Anorthite (tectosilicate)
CaO	≒1.72	$CaAl_2Si_2O_8$ 8.37%
TiO_2	0.83	Rutile TiO_2 0.83%
SiO_2	58.31	Quartz SiO_2 37.91%
H_2O	4.20	
Total	100.17	

Scandium in thortveitite from the ore body A, Oro,

Table 2. Analytical Results of Thortveitite $(Sc, Y, Ln)_2Si_2O_7$ (Ln: Lanthanoids)

	Weight/mg	Content/%
Sc_2O_3	19.76	48.66
Y_2O_3	0.78	1.92
La_2O_3	0.01	0.02
Ce_2O_3	0.03	0.07
Pr_2O_3	0.06	0.15
Nd_2O_3	0.06	0.15
Sm_2O_3	0.05	0.12
Eu_2O_3	Trace	Trace
Gd_2O_3	0.06	0.15
Tb_2O_3	0.04	0.10
Dy_2O_3	0.16	0.39
Ho_2O_3	0.05	0.12
Er_2O_3	0.17	0.42
Tm_2O_3	0.08	0.20
Yb_2O_3	0.82	2.02
Lu_2O_3	0.27	0.66
SiO_2	18.21	44.84
Total	40.61	100.00

$(La—Tb)_2O_3$ 0.76%; $[(La—Tb)_2O_3/Ln_2O_3=16.6\%]$
$(Dy—Lu)_2O_3$ 3.82%; $[(Dy—Ln)_2O_3/Ln_2O_3=83.4\%]$

Mineyama-cho, was present in a notable amount; 48.66% as Sc_2O_3. Yttrium-group rare earths (Dy—Lu) were over 80% of the total lanthanoids.

The distribution pattern of lanthanoid elements in the thortveitite is illustrated in Fig. 1. Their amounts were compared with those of Goldschmidt.[3] and Sakurai et al.[4] for thortveitite. Although the aboundance of cerium (Z=58) and praseodymium (Z=59) are reversed, the present results on the distribution of lanthanoid elements generally conform to Oddo-Harkins' law. The ytterbium content is slightly less than that found in other studies. The abundance of an odd-numbered lutetium (Z=71) is found to be higher than those of the neighboring even-numbered dysprosium (Z=66) and erbium (Z=68). According to the Clarke number of these elements, there should be less lutetium than dysprosium and erbium.[18] But the present result may indicate that the mutual camouflage-substitution of the same valent metals in minerals is a more important factor. The camouflage-substitutions of these elements in minerals have been reported and attributed to the similarity in the ionic radius.[19] As the ionic radius of lutetium (0.99 Å) is close to that of ytterbium (1.00 Å) and scandium (0.83 Å), lutetium seems to be more selectively concentrated than other elements in thortveitite in which Yb and Sc are principal constituents.

The amount of yttrium in the present thortveitite is small, but as no detailed analytical data are available for yttrium and individual lanthanoids on thortveitite,[20—22] simple comparison of these elements with other thortveitite is difficult. The sum of yttrium oxide and heavy rare earth oxides in this thortveitite is less than that for other reported thortveitite samples as shown in Table 3.

Table 3. Comparison of Analytical Results of Various Thortveitite Samples

	(1)	(2)	(3)	(4)
Sc_2O_3	43.63%	48.65%	37.36%	48.66%
Y_2O_3	9.22	0.75		1.92
$(HRE)_2O_3$			10.44	3.82
$(LRE)_2O_3$			1.65	0.76
SiO_2	47.15	50.60	50.55	44.84
Total	100.00	100.00	100.00	100.00

HRE: Heavy rarte earth
LRE: Light rare earth

(1) J. Schetelig: *Videnskapsselsk.-Skr.*, **1922**, No. 151.
(2) C. Boulanger, G. Urbain: *Compt. Rend.*, **174**, 1442 (1922).
(3) K. Kinoshita: "Kobutsu Shigen Jiten," Nippon Kobutsu Shumi no Kai, Kyoto (1965), p. 122.
(4) This work.

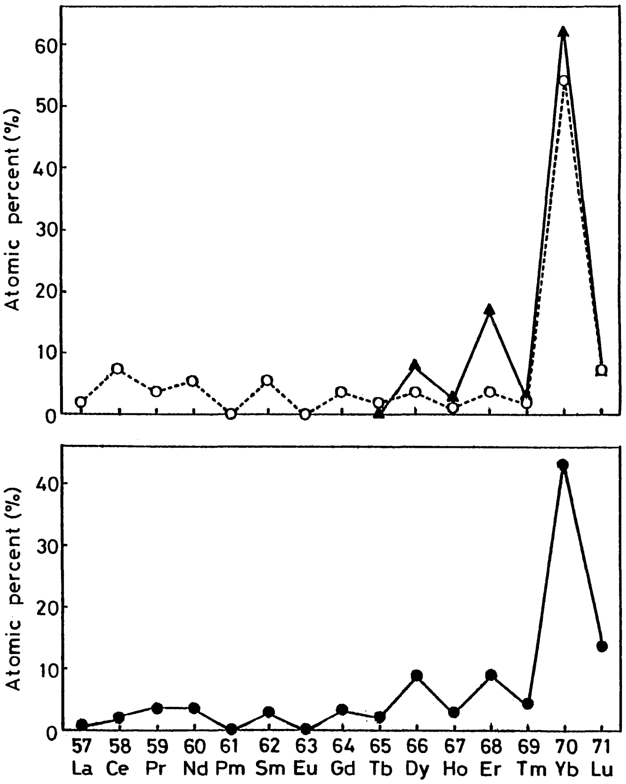


Fig. 1. Distribution of lanthanoid series elements.
—○—: Goldschmidt and Thomassen's thortveitite type (recalculated);
—▲—: Thortveitite from Kobe, Omiya-cho;
—●—: Thortveitite from Oro, Mineyama-cho (This work).

As described in section (1), the authors have assumed that the thortveitite sample from the ore body A contains about 11% tantalite in which tantalum is more aboundant than niobium. In general, earth acid minerals such as fergusonite and columbite are constituted of large quantities of niobium and always contain yttrium as a sub-component.[5,23,24] However, the thortveitite sample analyzed in this work contains a large amount of scandium and a little yttrium. Generally, tantalum (ionic radius: 0.64 Å) seems to be present in minerals with scandium, and niobium (0.64 Å) with yttrium. Scandium has a smaller ionic radius (0.83 Å) than yttrium (0.95 Å) and has a strong affinity for tantalum. It has been reported that Ta_2O_5 easily forms solid solutions with 2—4 mol% of Sc_2O_3 at high temperature,[25] and the crystal structure is stabilized by replacement of some Ta^{5+} by Sc^{3+}.

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