

On Tscheffkinite from Kobe-mura, Kyoto Prefecture, Japan

By

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Abstract

A new occurrence of tscheffkinite was discovered in Kobe-mura, Kyoto Prefecture, Japan. The mineral occurs in a pegmatite body intimately associated with other rare element minerals such as fergusonite, kobeite, monazite, xenotime and zircon. According to the chemical analysis, the chemical composition of this mineral is expressed by a formula $(Ca, Fe, Mg, Mn)(Al, Ce, [Ce], [Y])_2(Ti, Si, Sn)_3O_{10}$ indicating a titano-silicate containing rare earth elements. The x-ray spectre analysis gives the cerium-type distribution of the rare earth elements. A powder diffraction pattern was obtained using an automatic recording Philips Geiger Counter Spectrometer.

Introduction

The pegmatites distributed elsewhere in biotite granite region, north-west part of Kyoto prefecture are accompanied with various kinds of rare element minerals as accessory constituent minerals. The tscheffkinite now under consideration, a titano-silicate of the rare earths, was first found by one of the authors (Takubo) in a pegmatite cropped out at 2.2 km east of Kobe, Kobe-mura, Naka-gun, Kyoto prefecture during a geologic survey of this region in 1949. The occurrence at this locality is the first discovery in Japan. Besides of this, some other rare element minerals such as fergusonite, kobeite¹⁾, monazite, xenotime, zircon and moderate amount of illmenite have been also identified in the same pegmatite body.

In far east Asia, for the present, the occurrence of tscheffkinite has been only known in a pegmatite dike in Kogen-do region, Korea. The specimen from this locality was first collected by H. Awazu and it was made clear to be tscheffkinite by Dr. S. Hata²⁾ after his detailed examination and accurate chemical study. The localities reported in the world besides far east Asia include the ilmen Mountains, Russia³⁾; the Salem district of South India⁴⁾; the Tordendrika-Ifasina region of Madagascar⁵⁾; Sabaragemura Province in Ceylon⁶⁾; in the Aquarius Mountains, Mohave County, Arizona and Nelson and Bedford Counties, Virginia in U. S. A⁷⁾.

The present brief report mainly deals with the field occurrence, physical and chemical properties and x-ray study of the mineral specimen collected from the above mentioned locality first discovered in Japan.

Field occurrence and physical properties

The pegmatite associated with this mineral is mainly consisted of rosy microcline perthite, white albite, smoky and white quartz and biotite. Of these minerals, albite and biotite are less abundant comparing with the others. According to the field evidence that the pegmatite is characterized with the titanium-bearing minerals such as kobeite and illmenite, it is natural to postulate that the tscheffkinitite was crystalized out in place of allanite during the period of crystalization from pegmatic fluid. The crystal specimens of this mineral are usually prismatic in habit with dimension having 1 cm in thickness and 5 cm in length. According to rough external faces, most of them are not available for the morphological measurement. They are occasionally grouped in fan-shaped cluster that weights even 1kg. The mineral occurs closely aggregated with kobeite and it sometimes contains individual fine crystals of the latter. Such aggregates of the two occur sporadically in the rosy microcline perthite, surrounding part of which has been always decomposed to the clayey material brownish red colored as commonly seen in the case of the strong radioactive minerals.

The color of tscheffkinitite is black and streak brown. Hardness 5 to 5.5. The cleavage is none and fresh fracture shows somewhat glassy. It breaks with an irregular fracture. If we treat the mineral with hydrochloric acid, it is easily decomposed and geratinized owing to the precipitation of the hydrous silica. In these respects, the mineral is much alike to allanite which is usually found in some other pegmatites distributed in this region. The case being so, the allanite is, in quite general, is coated with a limonite-like substance which is probably produced by weathering decomposition, whereas the tscheffkinitite is thin coated with some titanium oxide yellowish white colored. Under microscope, thin section of the mineral shows moderate preochloism changing their color from redish brown to dark brown. Biaxial and index of refraction is higher than 1.85. With specimen which was perfectly free from the decomposed product coating its surface and closely associated foreign mineral, kobeite, the determination of specific gravity was made. The result is shown as $G_{(20)}^{(20)} = 4.381$. This nearly accords with those previously reported for the minerals from all localities in the world.

Chemical analysis

To avoid the noticeable impurities, the special caution was paid to prepare the sample for the chemical analysis. The tscheffkinitite specimens which were previously used for the determination of the specific gravity were crashed into the grains of moderate size. Under the binocular microscope, the only those grains, which appear not to be associated with foreign material, were carefully selected. The sample thus obtained was ground to fine powder and the chemical

treatment was conducted with it. The determination of each component of SiO_2 , TiO_2 , Nb_2O_5 , SnO_2 , ThO_2 , rare earths, Al_2O_3 , Fe_2O_3 , MnO , CaO , MgO was made respectively in the course of successive chemical procedure with the sample weighed about 1 g and that of component FeO , with another sample weighed about 0.2 g using the ordinary method. The analytical results are shown in the following table, wherein the published results of tscheffkinite found in Kogen-do region, Korea⁸⁾ and Mohave County, U. S. A⁹⁾. are also quoted for the sake of comparison in the following table.

Table 1.

Component	Kobe-mura, Kyoto Pref. Japan		Kogen-do, Korea	Mohave Co. U. S. A.
	(1)	(2)		
CaO	5.04	4.71	2.12	3.35
MgO	0.81	0.20	0.31	0.74
MnO	1.01	0.70	tr	0.50
FeO	6.07	6.19	9.95	7.76
Fe_2O_3		1.33	8.81	9.56
Al_2O_3	6.01	6.13	0.23	0.93
Ce_2O_3	17.57	19.02	14.21	25.29
$[\text{Ce}]_2\text{O}_3$	16.30	18.51	24.09	18.35
$[\text{Y}]_2\text{O}_3$	6.96	3.49	2.45	1.50
$[\text{Nb},\text{Ta}]_2\text{O}_5$	0.07	0.23	0.63	—
ThO_2	0.20	0.59	0.67	0.82
SnO_2	0.06	0.09	0.25	—
TiO_2	19.84	19.06	17.93	17.08
SiO_2	19.10	19.35	17.66	12.04
$\text{H}_2\text{O}^{(+)}$	0.55	0.25	—	1.50
$\text{H}_2\text{O}^{(-)}$	0.34	0.21	—	$\text{P}_2\text{O}_5=0.38$
Total	99.93	100.06	99.31	99.80

As shown in the above table, the content of component of the mineral is nearly accordant with those of minerals from Kogen-do, Korea as well as from Mohave county, U. S. A. with the exception of the components Al_2O_3 and Fe_2O_3 , the former somewhat larger and the latter somewhat smaller than those of other

two. According to the analytical results, the composition of the mineral can be considered as the titanio-silicate of the rare earth elements and the rare earths are shown by the cerium-type distribution as we see in the allanite. Such a fact was clearly established by the experiment of x-ray spectre analysis undertaken with the rare earths which was prepared by the analytical procedure.

Intensities of the spectres are distinguished by the letters such as ss (very strong), s (strong), m (medium), w (weak), ww (very weak).

Table 2.

Element	Series	Content ratio	α_1	β_1	β_2	α_2	γ_1	β_3	β_4
57 La	L	9.8	s	m	w	w	w	w	ww
58 Ce	L	56.5	ss	ss	ss	s	?	m	ww
59 Pr	L	8.4	m	w	w	ww	ww	ww	—
60 Nd	L	11.1	s	s	s	w	w	w	?
61 Pm	L	—	—	—	—	—	—	—	—
62 Sm	L	3.7	s	m	tr	—	?	—	—
63 Eu	L	1.0	m	?	?	—	tr	—	—
64 Gd	L	4.1	s	w	ww	tr	—	—	—
65 Tb	L	0.45	ww	—	—	—	—	—	—
66 Dy	L	0.90	w	m	ww	tr	—	—	—
67 Ho	L	tr	?	tr	—	—	—	—	—
68 Er	L	0.45	w	w	—	tr	—	—	—
69 Tu	L	rt	?	—	—	—	—	—	—
70 Yb	L	0.52	w	—	—	ww	—	—	—
71 Lu	L	0.13	ww	—	—	—	—	—	—

The content ratio of each element, which is listed in 3rd column in the above table, is obtained by comparing the intensity of the spectre line of the respective element and the relationship between the content ratio and the atomic number is fully held by the well known Harkin's Law.

To determine the chemical composition of the mineral the molecular ratio of each component was calculated, wherein the molecular ratio of $[Y]_2O_3$ was calculated by the mean atomic weight of the yttrium group elements, which was obtained from the ratio of the weight of unhydrous sulphate to the oxide as

shown as follows, $\sum \frac{R_2O_3}{R_2(SO_4)_3} = 0.546$ $R = 120.4$ (mean atomic weight) and that of $[Ce]_2O_3$ was obtained assuming the mean atomic weight as the mean of the atomic weights of the member belonging to the cerium group. Since the content of Fe_2O_3 may be considered to ascribe to the secondary oxidation, it was assumed as FeO . The result thus obtained is as follows:

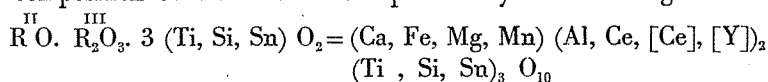
Table 3.

Component	(1)		(2)	
	(%)	Mol. ratio	(%)	Mol. ratio
CaO	5.04	0.0899	4.71	0.0840
MgO	0.81	0.0201	0.20	0.0050
MnO	1.01	0.0142	0.70	0.0090
FeO	6.07	0.0760	6.19	0.0862
Al ₂ O ₃	6.01	0.0590	6.13	0.0602
Ce ₂ O ₃	17.57	0.0535	19.02	0.0579
[Ce] ₂ O ₃	16.30	0.0485	18.51	0.0551
[Y] ₂ O ₃	6.96	0.0241	3.49	0.0138
SnO ₂	0.06	0.0004	0.09	0.0006
TiO ₂	19.84	0.2483	19.06	0.2385
SiO ₂	19.10	0.3180	19.35	0.3222

From the above result, the molecular ratios of $R^{II}O$ (CaO, MgO, MnO) $R_2^{III}O_3$ (Al₂O₃, Ce₂O₃, [Ce]₂O₃, [Y]₂O₃) and (Ti, Si, Sn) O₂ are shown as the following relation:

$$\begin{aligned}
 R^{II}O : R_2^{III}O_3 : (Ti, Si, Sn) O_2 &= 0.2002 : 0.1851 : 0.5667 \quad (1) \\
 & \quad \quad \quad 0.1851 : 0.1958 : 0.5613 \quad (2) \\
 & = 1.08 : 1 : 3.06 \quad (1) \\
 & \quad \quad \quad 0.95 : 1 : 2.87 \quad (2) \\
 & \therefore 1 : 1 : 3
 \end{aligned}$$

So that the composition of the mineral is expressed by the following formula



denoting the salt of the titano-silicic acid $H_8 (Ti, Si, Sn)_3 O_{10}$. The same statement is applicable to the chemical composition of the tscheffkinites found in all other localities in the world.

X-ray study

A powder diffraction pattern of this mineral was obtained using an automatic recording Philips Geiger Counter Spectrometer under copper radiation, nickel filter, 35 Kv, 17 Ma, scan speed 1° per min., angular aperture 1°, receiving slit 0.006 inch, and goniometer radius 170 mm. The relative intensity of diffracted x-ray, the facing angle and the planar spacing in Angstroms are shown in the following tabs.

Table 4.

I	θ°	d(Å)	I	θ°	d(Å)
2	8.212	5.399	2	17.40	2.579
3	8.537	5.195	3	17.87	2.513
1	9.177	4.834	4	18.28	2.458
2	10.83	4.104	2	20.06	2.247
4	12.48	3.566	2	20.21	2.231
4	12.86	3.462	5	20.75	2.176
4	13.08	3.405	4	20.91	2.158
2	13.86	3.217	2	21.44	2.108
5	14.66	3.045	3	23.27	1.952
10	14.98	2.983	2	26.58	1.723
10	15.11	2.956	3	27.68	1.659
7	15.74	2.841	3	28.58	1.612
6	16.06	2.699	2	28.87	1.597

According to the x-ray studies, the tscheffkinite may be found in either amorphous or crystalline state. The mineral from this locality gives marked diffraction pattern as in the case of the same mineral from Arizona, U. S. A. but the results are much differ from those¹⁰⁾ obtained with the latter.

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