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THE MINERALS OF THE NODA-TAMAGAWA MINE, IWATÉ PREFECTURE, JAPAN

III. Yoshimuraite, a New Barium-Titanium-Manganese Silicate Mineral

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ABSTRACT

Yoshimuraite, a new barium-titanium-manganese complex silicate mineral, was found in an alkali-pegmatitic facies bordering the bedded manganese deposit of the Misago ore body of the Noda-Tamagawa mine. Yoshimuraite occurs as dark-brownish platy to tabular crystals, or sometimes in the stellate groups embedded in coarse aggregates of barium-bearing potash-feldspar, quartz, richterite, urbanite, rhodonite etc.

It resembles lamprophyllite and astrophyllite which usually occur in alkali-pegmatites. It is orange brown in colour, brittle and has a perfect cleavage parallel to {010} and distinct cleavages on {10$\bar{1}$} and {101}. Polysynthetic twinning on {010} is common. Hardness, 4½; Sp. gr., 4.13 (obs.) and 4.21 (calc.). Triclinic, with $a_0=7.00$, $b_0=14.71$, $c_0=5.39$Å, $\alpha=93.5°$, $\beta=90.2°$, $\gamma=95.3°$, and $a:b:c=0.476:1:0.366$. Space group, $P\bar{1}$. Biaxial positive with $\alpha=1.763$, $\beta=1.777$, $\gamma=1.785$, $(+)2V=85°\sim90°$ $\rho>\upsilon$, and absorption $X<Y\leqq Z$. Optical orientation, γ' nearly parallel to c-axis, α' nearly parallel to a-axis. Pleochroism, α bright yellow, β orange-brown, γ brown.

Chemical analysis by J. Ito gave SiO_2 18.25, TiO_2 10.00, Fe_2O_3 1.32, FeO 1.47, MnO 17.64, MgO 0.56, ZnO 0.50, BaO 33.51, SrO 4.62, Na_2O 0.16, K_2O 0.03, P_2O_5 3.98, SO_3 5.40, Cl 0.41, $H_2O(\pm)$ 2.34, less for Cl 0.09, total 100.10%. The results indicate a formula of approximately $X_2Y_2(Ti, Fe)O(Si_2O_7)[(P,S)O_4](OH)$ or $X_2Y_2(Ti, Fe)(SiO_4)_2[(P,S)O_4](OH)$, where X=Ba, Sr and Na, Y=Mn, Fe, Mg and Zn.

The mineral is named after Professor Toyofumi Yoshimura who has contributed much to the study of manganese minerals in Japan.

Introduction

In 1953, in the course of his investigation on manganese ores from the Misago ore body of the Noda-Tamagawa mine, the senior author (T. W.) discovered a platy brown mineral in peculiar alkali-pegmatites consisting mainly of barium-bearing potash-feldspar, quartz, richterite, urbanite and rhodonite (Plate V, Fig. 3). The mineral resembles astrophyllite in appearance but has distinctive chemical and physical properties and has been determined as a new species, a complex silicate of barium, titanium and manganese. Long after the discovery of this mineral at Noda-Tamagawa in 1953, a similar mineral was discovered by F. Hirowatari in 1959 in the Taguchi mine, Aichi Prefecture. X-ray studies of the former mineral had been carried out by the late Dr. H. Mori of our Mineralogical Institute, but discontinued because of his death in 1954. Owing partly to this sad event the completion of the present study has greatly been delayed. Later on one of the authors (Y. T.) took over the X-ray studies of that mineral and obtained the results which will be given in the following section. The name, yoshimuraite, is given in honour of Professor Toyofumi Yoshimura at the Kyushu University, who first studied in early 1930's the manganese minerals from the Noda-Tamagawa mine and has greatly contributed to the study of manganese minerals in Japan.

In this paper a brief description of the new mineral is given and, with the description of the yoshimuraite from the Taguchi mine, it will be discussed in detail in a future paper of this journal.

Occurrence and paragenesis

On the foot-wall side of the manganese ore zone of the Noda-Tamagawa mine there occurs occasionally a dark grey massive hornfels containing manganiferous minerals such as manganophyllite, richterite and urbanite. In many places along the boundary between the manganese ore and this hornfels, very coarse-grained pegmatitic rocks with peculiar mineral paragenesis have been found. As shown in Fig. 1, the pegmatitic rocks often cut the layered manganese ore-

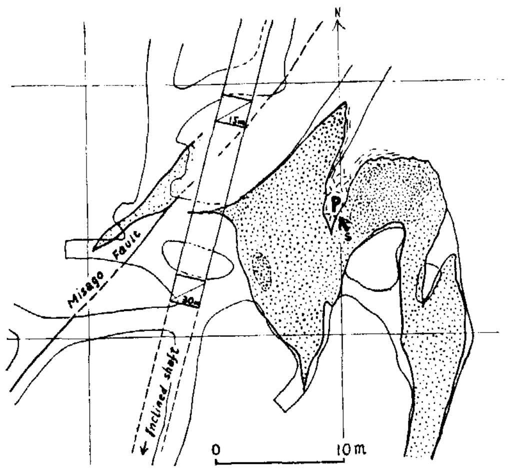


Fig. 1. Underground map showing the Misago ore body (dotted) at 30 m. Level of the Noda-Tamagawa mine, and the location of yoshimuraite-bearing alkali-pegmatite (P). Arrow (S) indicates the position of the sketch shown in Fig. 2.

bodies consisting of tephroite, rhodonite, braunite, hausmannite and other manganese minerals. The development of zoned manganese skarns along the boundaries between the pegmatitic facies and manganese ore-bodies is commonly observed as following;

quartzite or manganiferous hornfels	yoshimuraite-bearing alkali-pegmatite	rhodonite	tephroite	braunite ore or hausmannite-pyrochroite ore
	1～2 m	1～10cm	1～30cm	

The yoshimuraite occurs in blade or in mica-like form with length up to 5 cm. in the alkali-pegmatite facies which is found in the folded zone of the Misago ore body at 150 m. Level and is embedded in potash-feldspar, quartz, rhodonite, urbanite, richterite etc.

Only one well-formed crystal of yoshimuraite has hitherto been separated from a specimen of the Taguchi mine. The study of

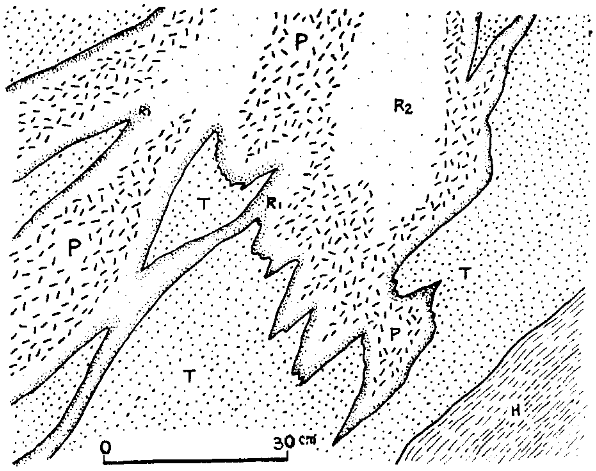


Fig. 2. Diagrammatic sketch representing development of zoned manganese-skarn around yoshimuraite-bearing alkali-pegmatite. P: alkali-pegmatite consisting of barium-potash-feldspar, quartz, urbanite, richterite, yoshimuraite, etc. T: tephroite ore. R_1: rhodonite-rim surrounding the tephroite ore. R_2: rhodonite-rich part in the alkali-pegmatite. H: manganiferous hornfels.

the relation between its crystal form and optical properties is now under way.

Physical properties

The hardness of yoshimuraite is 4½ on Moh's scale. Measurements of specific gravity by pycnometer method gave a value of 4.13. Refractive indices measured by immersion method are α 1.763, β 1.777, γ 1.785; $(+)2V=85°\sim90°$, $\rho>\upsilon$. The pleochroic scheme is as follows: α bright yellow, β orangebrown, γ brown with absorption $X<Y\leqq Z$. Since no well-formed crystal has been found from Noda-Tamagawa, the optical orientation has not been accurately determined.

X-ray studies

The specimens suitable for X-ray experiments were made out of a lamellar single crystal. Examination of X-ray precession photographs ($\lambda = 1.5418$Å.) revealed a triclinic symmetry of the crystal. Since it is most desirable to describe a lattice by a reduced cell, three shortest non coplanar translations of the lattice of yoshimuraite were chosen, and their periods which were measured in the precession films are listed in Table 1. The longest axis being chosen as b and shortest one c, the index of the perfect cleavage plane corresponds to {010} (Plate V, Fig. 4 (a)) and those of distinct cleavage planes are {101} and {$10\bar{1}$}.

Table 1. Crystallographic data for yoshimuraite.
Symmetry : triclinic.

	$a_0 = 7.00 \pm 0.01$Å.	$a^* = 14.372 \times 10^{-2}$
	$b_0 = 14.71 \pm 0.02$Å.	$b^* = 6.849 \times 10^{-2}$
	$c_0 = 5.39 \pm 0.01$Å.	$c^* = 18.595 \times 10^{-2}$
	$\alpha = 93.5 \pm 0.2°$	$\alpha^* = 86.5°$
	$\beta = 90.2 \pm 0.2°$	$\beta^* = 89.5°$
	$\gamma = 95.3 \pm 0.2°$	$\gamma^* = 84.7°$
Unit cell volume	$V = 549.8$Å^3	$V^* = 1819 \times 10^{-6}$
Space group	$P\bar{1}$	
Axial ratio	$a_0 : b_0 : c_0 = 0.476 : 1 : 0.366$	
Density (obs.)	4.13 g. cm^{-3}.	
(calc.)	4.21 (See text)	

In the zero level of the a-axis precession photographs, very weak and diffuse reflections were observed on the lattice rows parallel to the b^*-axis at the positions which make the period of the b^*-axis one-third (Plate V, Fig. 5). This makes one impress that the true period of the b-axis is three times of the period given by the sharp reflections. However, as shown in Fig. 6(a), these reflections occur only if $l \neq 3n$, and, in a certain lattice row parallel to b^*, they appear only either at the points $nb^* + \frac{1}{3}b^*$ or at $nb^* + \frac{2}{3}b^*$, where n is an integer. These reflections appear in higher levels of the a-axis precession photographs and in the c-axis photographs as well. In these cases, positions of the reflections show slight deviations from the above particular positions in the reciprocal space. It is then suspected that, with the analogy to the X-ray reflections from polysynthetic-

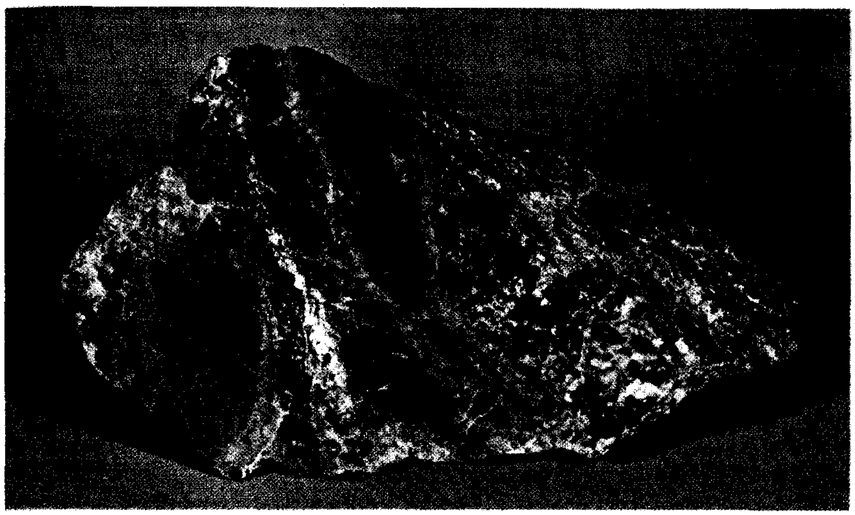


Fig. 3. Polished hand specimen, showing the occurrence of yoshimuraite-bearing pegmatitic rock including massive tephroite ore from the Misago ore-body (×½). Brown fine-grained part: tephroite ore, pinkish rim surrounding tephroite ore: rhodonite, coarse-grained part: alkali-pegmatitic rock.

(a)
(b)

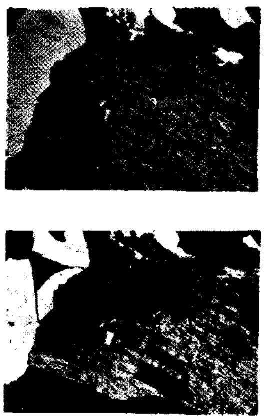


Fig. 4. Photomicrograph of yoshimuraite from the Noda-Tamagawa Mine (×12).
(a) Polarizer only, showing cleavage parallel to {010}.
(b) Crossed nicols, showing polysynthetic twinning on {010}.

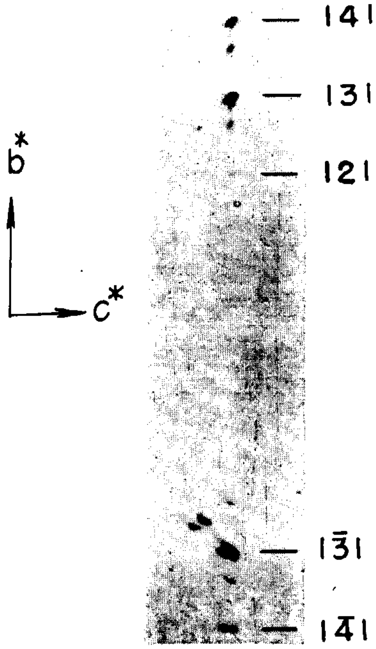
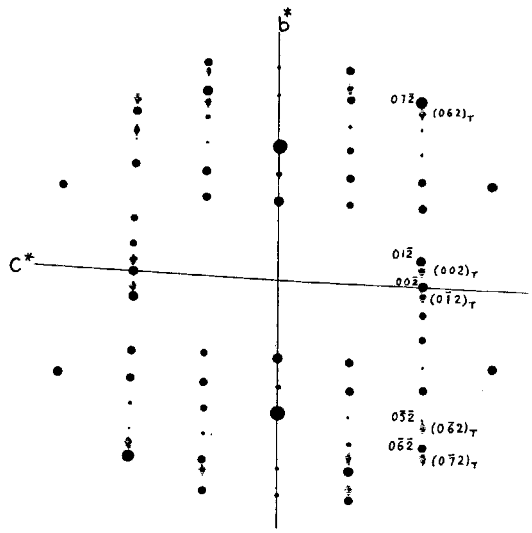


Fig. 5. Part of the a-axis, zero-level precession photograph of yoshimuraite, showing diffuse extra reflections.



(a)

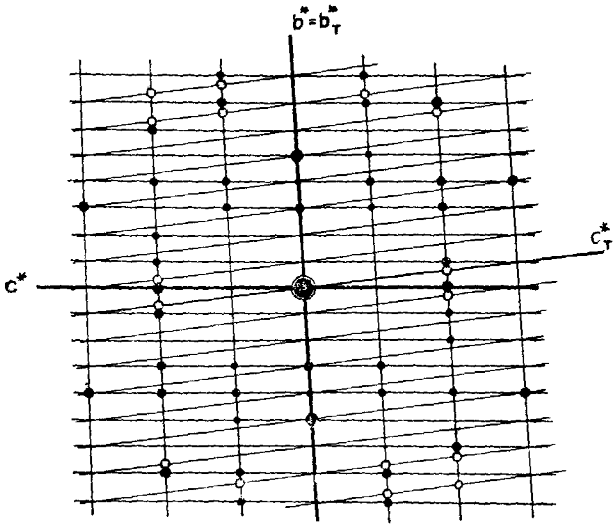
Fig. 6(a). Diffraction spots observed in the Buerger precession of yoshimuraite; a-axis, zero-level. Diffuse spots are indicated by shading.

ally twinned micas[2], polysynthetic twinning occurs in yoshimuraite crystals as schematically shown in Fig. 7. Actually, under the microscope polysynthetic twinning on {010} is observed as illustrated in Plate V, Fig. 4(b).

As the matter of fact, in the reciprocal space, the following dimensional specialization exists in the lattice constants of yoshimuraite:

$$6c^* \cos \alpha^* = b^*$$

Similar relation is also approximately held among a^*, γ^* and b^*. Therefore, the twinning about the b^*-axis, with a rotation 180°, will result in giving the composite reciprocal net as shown in Fig. 6(b). If the volumes of the twin-individuals in the twin-orientation are small, the intensities of X-ray reflections from these twin-individuals should be weak and in this way the weak extra reflections of yoshimuraite may be explained as the results of polysynthetic twinning.



(b)

Fig. 6(b). Composite $0kl$ reciprocal net of twinned yoshimuraite. Open circles belong to the reciprocal net in twin-orientation and correspond to the diffuse spots in (a).

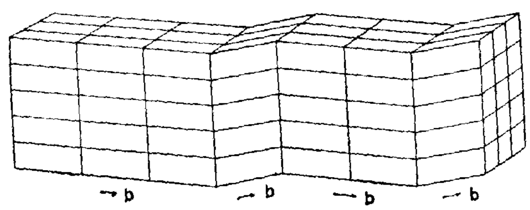


Fig. 7. Schematic representation of polysynthetic twinning of yoshimuraite.

Piezoelectric tests along approximately the three crystallographic axes of the crystal were made on an apparatus built by Iitaka[1] with negative results. If the crystals are noncentrosymmetric, the direction of the b^*-axis must be polar even with the polysynthetic twinning. Accordingly, the negative results strongly suggest the centrosymmetric space group $P\bar{1}$.

Table 2. X-ray powder data for yoshimuraite.

Measured†		Calculated††	
I	*d*	*d*	*hkl*
1	14.8	14.6	010
6	4.90	4.95	011
2	4.28	4.28	$\bar{1}01$
2	4.22	4.23	101
		4.21	021
4	4.11	4.11	$\bar{1}11$
		4.09	$\bar{1}11$
3	3.99	3.96	111
3	3.71	3.73	0 1
2	3.45	3.46	$2\bar{1}0$
10	3.40	3.38	$1\bar{3}1$
2	3.34	3.36	$1\bar{1}0$
		3.32	210
6	3.24	3.22	$\bar{1}30$
4	3.13	3.12	140
4	3.05	3.04	131
10	2.94	2.94	041
		2.94	$\bar{2}01$
2	2.88	2.88	211
6	2.78	2.77	$\bar{3}21$
		2.77	$\bar{1}41$
4	2.71	2.71	002
2	2.65	2.65	$2\bar{4}0$
2	2.62	2.61	012
2	2.42	2.42	231
3	2.24	2.24	$\bar{2}\bar{4}1$
2	2.17	2.17	061
2	2.15	2.15	132
2	2.13	2.13	$2\bar{1}2$
		2.12	301
		2.12	$\bar{1}61$
3	2.11	2.11	$\bar{2}\bar{1}2$
		2.11	$\bar{1}\bar{6}1$
2	2.10	2.10	$\bar{1}\bar{4}2$
		2.10	$2\bar{2}2$
2	2.07	2.07	212
2	2.06	2.06	$\bar{2}22$
1	2.03	2.03	$3\bar{3}1$
1	1.992	1.991	$1\bar{5}2$
1	1.649	1.649	033
		1.649	$0\bar{1}3$
		1.650	$3\bar{1}2$
2	1.595	1.596	$\bar{4}\bar{2}1$
		1.595	$2\bar{1}3$

† $CuK_\alpha = 1.5418$ Å.

†† Based on: $a^* = 14.372 \times 10^{-2}$, $b^* = 6.849 \times 10^{-2}$, $c^* = 18.595 \times 10^{-2}$, $\alpha^* = 86.5°$, $\beta^* = 89.5°$, $\gamma^* = 84.7°$.

Table 2 shows the X-ray powder data of yoshimuraite which were obtained by the use of a Norelco diffractometer only for indexing powder peaks by the above lattice constants.

Chemical composition

Spectroscopic analyses of yoshimuraite yield to show the presence of Mg and Zn in addition to the major components Si, P, Mn, Ba, Fe, Ti and Sr. The result of a total chemical analysis is given in the first column of Table 4.

Method of chemical analysis for main elements in yoshimuraite is given schematically in Table 3. Alkalies were determined by flame photometric method after the separation of most of interfering elements with NH_4OH and $(NH_4)_2CO_3$. Chlorine was determined gravimetrically as AgCl after the decomposition with Na_2CO_3 fusion.

From the cell volume and observed density, the molecular weight of the cell contents was calculated to be 1367.5. Based on this value and the results of chemical analysis the chemical formula of yoshimuraite can readily be derived. Account then was made of the total number of each kind of atom in the cell. In determining chemical formula, we must take into account the requirement of space groups, and resultant chemical formula must give the calculated density in reasonable accord with the observed one. Since atoms in the tetrahedral coordination can not lie on the centre of symmetry, number of Si and that of P(S) in the cell with space group $P\bar{1}$ must be even. As seen in Table 4, number of Si in the cell is close enough to four, while that of P+S is 1.68 and much less than two. However, it may be reasonable to assume that there are two of these atoms in the cell. OH groups are, for their polarity, usually not located on the centres of symmetry and it is found that the most reasonable number of the OH groups which is conformable with the results of the chemi-

Table 3. Procedure for chemical analysis of yoshimuraite.

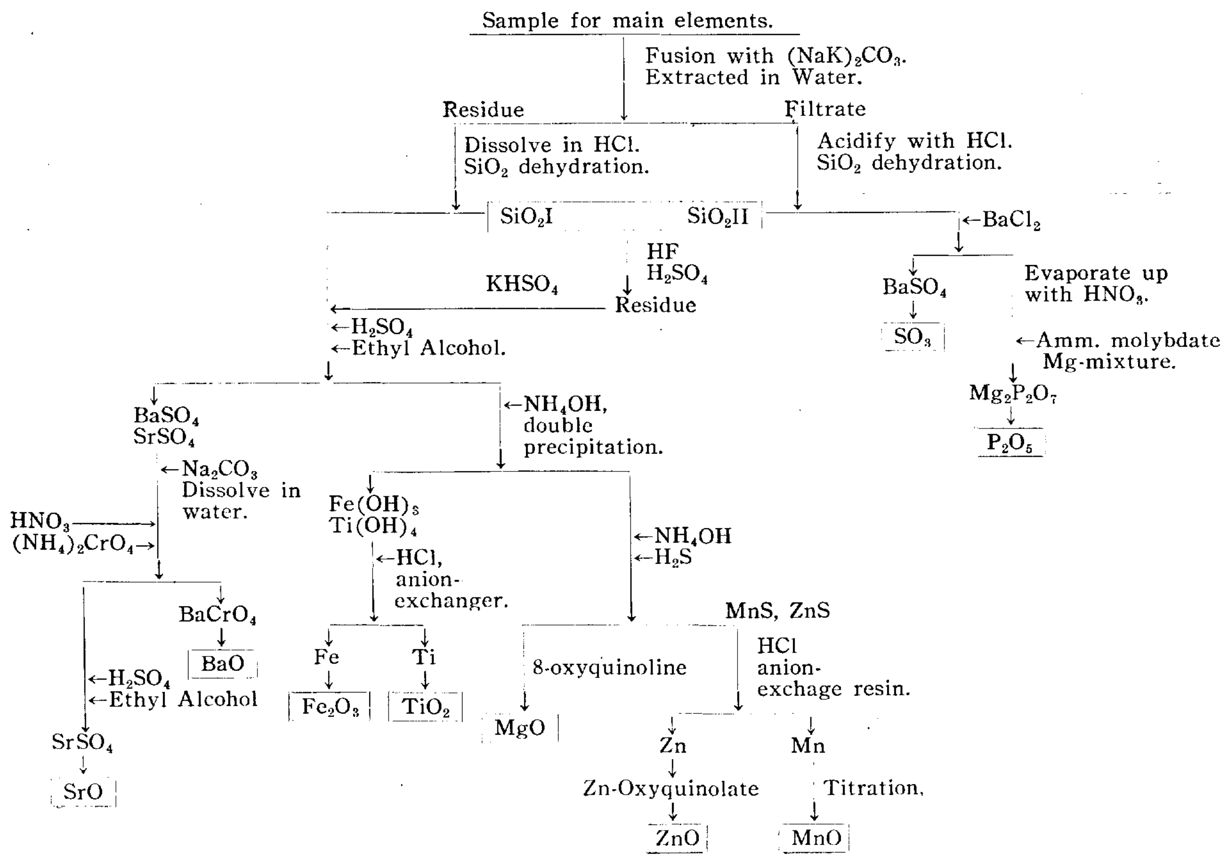


Table 4. Chemical composition of yoshimuraite.

	Wt. %	No. of oxides and Cl per unit cell	Metal atoms per unit cell		Oxygens and Cl per unit cell
SiO_2	18.25%	4.17	4.17		8.34
TiO_2	10.00	1.70	1.70	1.92	3.40
Fe_2O_3	1.32	0.11	0.22		0.33
FeO	1.47	0.28	0.28	3.95	0.28
MnO	17.64	3.40	3.40		3.40
MgO	0.56	0.19	0.19		0.19
ZnO	0.50	0.08	0.08		0.08
BaO	33.51	2.99	2.99	3.68	2.99
SrO	4.62	0.61	0.61		0.61
Na_2O	0.16	0.04	0.08		0.04
K_2O	0.03	0.00	0.00		0.00
P_2O_5	3.98	0.38	0.76		1.90
SO_3	5.40	0.92	0.92		2.76
Cl	0.41	0.16			0.16
$H_2O(\pm)$	2.34	1.37	2.74		1.37
−Cl	−0.09				
Total	100.10%				25.85
Sp. gr.	4.13				

Analyst, J. Ito (1958).

cal analysis is two*. Thus, the ideal chemical formula of yoshimuraite may well be expressed by

$$X_2Y_2(Ti, Fe)O(Si_2O_7)[(P, S)O_4](OH)$$

where X=Ba, Sr and Na,

Y=Mn, Fe, Mg and Zn.

There are two formula units in the cell. If we accept that the total number of Ti in the cell is 1.7 as given by the chemical analysis and

* Previously, a chemical formula,

$$(Ba, Sr)_4Mn_4Ti_2(SiO_4)_4[(P, S)O_4]_2(OH, Cl_3),$$

was tentatively assigned to yoshimuraite and described[3]. However, it is not likely that there are three (OH) groups in the cell from the view point of the space group requirement and the above formula should be withdrawn.

the ratio of P/S is unity, the ideal formula gives the calculated density 4.21 g. cm.$^{-3}$ which is in good agreement with the observed value 4.13 g. cm.$^{-3}$. The ideal formula is fully supported by the chemical composition of yoshimuraite which was later found from the Taguchi mine.

The chemical formula of yoshimuraite can also be given in the form of an orthosilicate,

$$X_2Y_2(Ti,\ Fe)(SiO_4)_2[(P,\ S)O_4](OH),$$

but accurate expression of the formula should await the completion of the structure analysis.

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