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Tobelite, a new ammonium dioctahedral mica

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Abstract

Mineralogical properties of tobelite, a new ammonium-dominant dioctahedral mica, found in the Ohgidani pottery stone deposit at Tobe, Ehime Prefecture, Japan, are described.

This mineral, accompanied by quartz, occurs as a hydrothermal alteration product of a biotite andesite dyke. Wet chemical analysis gives a structural formula: $((NH_4)_{0.53}K_{0.19}Na_{0.01}\square_{0.27})_{1.00}(Al_{1.97}Ti_{0.00}Fe^{3+}{}_{0.03}Mg_{0.05})_{2.05}(Si_{3.17}Al_{0.83})_{4.00}O_{10}(OH)_2$. The low interlayer charge is explained with its poorly crystallized nature. The X-ray powder diffraction pattern is very close to that of synthetic $NH_4Al_2Si_3AlO_{10}(OH)_2$ by Eugster and Munoz (1966), and is satisfactorily indexed on 1M polytype cell having $a=5.219$Å, $b=8.986$Å, $c=10.447$Å and $\beta=101.31°$. Space group may be $C2/m$. Tobelite is characterized by its larger unit layer thickness (10.25Å) than that of potassium dioctahedral mica. This material yields an endothermic reaction and absorption bands specific to ammonium in DTA curve and infrared spectrum, respectively. Optically it is biaxial, negative, $2V_{calc.}=28°$. Refractive indices are $\alpha=1.555$, $\beta=1.575$, $\gamma=1.581$, all$\pm$ 0.002.

Mineralogical description is made also on tobelite from the Horo pyrophyllite deposit, Hiroshima Prefecture, Japan, which is well crystallized as compared with the Tobe material and is tentatively determined to be of $2M_2$ polytype.

Introduction

Ammonium has been considered to be able to occupy interlayer position of mica structure. Vedder (1964) first confirmed the presence of ammonium in natural muscovite by means of infrared spectrophotometry. Yamamoto (1967) reported common presence of ammonium in dioctahedral micas associated with Roseki (pyrophyllite) deposits of western Japan. Higashi (1978) also described dioctahedral mica minerals with considerably high ammonium content from the Ohgidani Toseki (pottery stone) deposit at Tobe, Ehime Prefecture, Japan, showing distinctive properties due to substitution of ammonium for potassium. The author recently found an ammonium-dominant dioctahedral mica from the same deposit, of which the mineralogical properties are close to those of synthetic ammonium-muscovite (Eugster and Munoz, 1966; Barrer and Dicks, 1966). This mineral has been named tobelite after the locality. The mineral and the name have been approved by the Commission of New Minerals and Mineral Names of

IMA. Type material is preserved at the National Science Museum, Tokyo, Japan.

The second occurrence of tobelite has been recognized in the Horo pyrophyllite deposit, Hiroshima Prefecture, Japan. This paper presents mineralogical description of tobelite from the two localities.

Modes of occurrence

Tobelite was collected from the Ohgidani pottery stone deposit at Tobe, Ehime Prefecture and the Horo pyrophyllite deposit at Toyosaka, Hiroshima Prefecture. The Ohgidani deposit is a hydrothermally altered biotite andesite dyke of Miocene age, which is mainly composed of ammonium-bearing dioctahedral mica minerals (Higashi, 1978), quartz and graphite. Tobelite coexists with only quartz. Tobelite from the Horo deposit, accompanied by ammonium-bearing dioctahedral mica and quartz, occurs as a hydrothermal alteration product of Cretaceous rhyolitic tuff in the foot wall of the deposit. Principal constituents of the deposit are pyrophyllite, diaspore, kaolinite, corundum, andalusite, ammonium-bearing dioctahedral mica and quartz.

Optical properties

Tobelite is clayey material ranging in colour from white (Tobe specimen) to various shades of yellowish green (Horo specimen). Purified powder has a silky luster. In thin section, it is nearly colourless. It commonly occurs as aggregates of minute flakes (a few micron order) in a groundmass or replacing feldspar and biotite phenocrysts, and occasionally forms lamellar crystals up to 0.1 mm (Tobe specimen) and 0.2 mm (Horo specimen) in diameter. Cleavage {001} is perfect. Sign of elongation is positive. Refractive indices of tobelite measured by the immersion method are listed in Table 1 together with calculated 2V. These values are comparable to those of potassium dioctahedral mica.

TABLE 1. Optical properties of tobelite.

	Tobe	Horo
α	1.555(2)	1.560(2)
β	1.575(2)	1.587(2)
γ	1.581(2)	1.595(2)
$2V_{calc.}$	(−)28°	(−)30°

Chemical composition

Purification of tobelite for chemical and other analyses was attempted by usual sedimentation method. Fractionation to less than one micron size was, however, not sufficiently effective for complete removal of quartz in the Tobe specimen and ammonium-bearing dioctahedral mica and quartz in the Horo specimen. Amounts of these impurities are estimated by X-ray analysis using the method of standard addition.

TABLE 2. Chemical analyses of tobelite and ammonium-bearing dioctahedral mica.

	1	2	3	4	5
SiO_2	49.61	48.40	48.41	48.34	46.65
TiO_2	0.02	0.02	0.25	0.30	0.05
Al_2O_3	35.30	36.27	37.42	37.87	37.75
Fe_2O_3	0.56	0.57	0.91	1.02	0.50
MgO	0.51	0.52	0.09	0.11	0.02
CaO	0.00	0.00	0.00	0.00	0.00
Na_2O	0.04	0.04	0.06	−0.01	0.36
K_2O	2.24	2.30	4.39	3.25	9.20
$(NH_4)_2O$	3.41	3.51	3.15	3.85	0.50
H_2O+ (105°C)	6.23	6.40	4.89	4.96	4.90
H_2O- (105°C)	1.92	1.97	0.32	0.31	0.35
Total	99.84	(100.00)	99.89	(100.00)	100.08

	6		7		8	
Si	3.17	4.00	3.09	4.00	3.06	4.00
Al(IV)	0.83		0.91		0.94	
Al(VI)	1.97	2.05	1.95	2.02	1.99	2.02
Ti	0.00		0.01		0.00	
Fe^{3+}	0.03		0.05		0.03	
Mg	0.05		0.01		0.00	
Ca	0.00	0.73	0.00	0.84	0.00	0.89
Na	0.01		0.00		0.04	
K	0.19		0.27		0.77	
NH_4	0.53		0.57		0.08	

1. Tobelite from Tobe, containing 2.5% quartz.
2. Tobelite from Tobe, corrected for quartz impurity.
3. Tobelite from Horo, containing 20% ammonium-bearing dioctahedral mica and 1% quartz.
4. Tobelite from Horo, corrected for impurities.
5. Ammonium-bearing dioctahedral mica from Horo.
6. Cation numbers of tobelite from Tobe on the basis of $O_{10}(OH)_2$.
7. Cation numbers of tobelite from Horo on the basis of $O_{10}(OH)_2$.
8. Cation numbers of ammonium-bearing dioctahedral mica from Horo on the basis of $O_{10}(OH)_2$.

Chemical analysis of tobelite was carried out by the ordinary wet method with the result shown in Table 2. Ammonium was determined by the Kjehldahl distillation method after Higashi (1978). In the table is also given the analysis of an ammonium-bearing dioctahedral mica from the Horo deposit. This mineral has a basal spacing (10.05 Å) very close to that of dioctahedral mica impurity contained in the Horo specimen, and is used as a standard substance both for estimation of the amount of the impurity in the X-ray analysis and for correction of tobelite composition in the chemical analysis.

Calculation of cation numbers on the basis of $O_{10}(OH)_2$ for tobelite composition, corrected for impurities, leads to the following structural formulae;

Tobe material: $((NH_4)_{0.53}K_{0.19}Na_{0.01}\square_{0.27})_{1.00}(Al_{1.97}Ti_{0.00}Fe^{3+}_{0.03}Mg_{0.05})_{2.05}(Si_{3.17}Al_{0.83})_{4.00}O_{10}(OH)_2$*,

Horo material: $((NH_4)_{0.57}K_{0.27}Na_{0.00}\square_{0.16})_{1.00}(Al_{1.95}Ti_{0.01}Fe^{3+}_{0.05}Mg_{0.01})_{2.02}(Si_{3.09}Al_{0.91})_{4.00}O_{10}(OH)_2$*.

Tobelite is an ammonium-dominant dioctahedral mica. Namely, more than half of interlayer positions are occupied by ammonium, and the ratio of ammonium ions to total interlayer cations is 0.73 for the Tobe material and 0.68 for the Horo material. Accordingly, the following ideal formula of tobelite is given: $(NH_4, K, \square)Al_2(Si, Al)_4O_{10}(OH)_2$, where $NH_4 > K$, $\square$ and $Si \geqq 3$. The high water content and low interlayer charge of the Tobe material would be attributed to its poorly crystallized nature as compared to the Horo material and to interlayering with a very small amount of smectite layer as shown in the next section.

X-ray powder studies

X-ray properties of tobelite were examined with a Rigaku diffractometer using $CuK\alpha$ radiation.

Fig. 1 shows the basal reflection patterns of the Tobe and Horo tobelite materials, which are obtained from oriented aggregates prepared on glass slides. When compared to usual potassium dioctahedral mica, tobelite is characterized by larger basal spacing (unit layer thickness) and relatively strong intensity of the first order reflection. Average basal spacing calculated from the four reflections excluding the first order reflection is 10.26 Å for the Tobe material and 10.24 Å for the Horo material. These features are similar to those of synthetic ammonium-muscovite (Eugster and Munoz, 1966). The intensity data agree also

* Presence or absence of actual interlayer vacant sites is a matter of some debate in the case of mica clay mineral. At least, a part of them may be occupied by water molecule. Excess $H_2O(+)$ content of the Tobe material may support this interpretation.

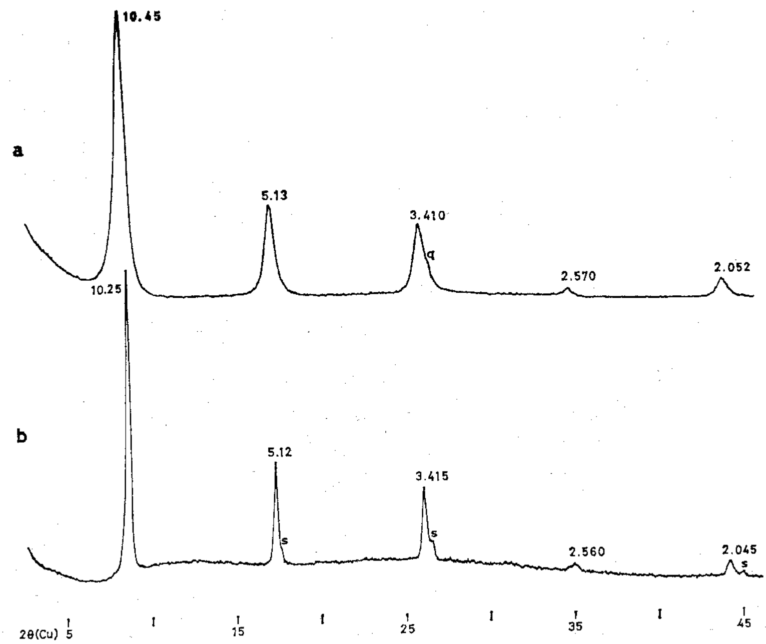

FIG. 1. X-ray diffraction pattern of tobelite (oriented aggregates). q, quartz. s, ammonium-bearing dioctahedral mica. a. Tobe specimen (under 60% relative humidity). b. Horo specimen (in air-dried condition).

with the results of structure factor calculation on potassium-ammonium dioctahedral mica series (Higashi, 1979). The two materials, however, yield noticeable differences as recognized in Fig. 1. The reflections of the Tobe material are broad in profile and are not exactly rational in spacing; particularly, the first order reflection deviates markedly from the average basal spacing of the higher order reflections. These phenomena are, as commonly known, indicative of smaller particle size, i.e., poorly crystalline state of the Tobe material as compared with the Horo material. In addition, on glycerolation the Tobe material shows a shift of the 10.45 Å reflection to 10.20 Å and slight changes of line profiles of the higher order reflections, which is interpreted as an interstratification with a very small amount of smectite layer.

X-ray powder diffraction data of tobelite are tabulated in Table 3 along with the data of synthetic ammonium-muscovite (Eugster and Munoz, 1966). For the Tobe material, indexing is possible on 1M polytype cell belonging to space group $C2/m$, and the unit cell parameters determined by least square refinement are a=5.219(4) Å, b=8.986(3) Å, c=10.447(2) Å and β=101.31(1)°. These values are consistent with those of the synthetic ammonium-muscovite (Table 4), but

TABLE 3. X-ray powder diffraction data of tobelite and ammonium-muscovite.

Tobelite (Horo)		Tobelite (Tobe)				Ammonium-muscovite*	
$d_{obs.}$ (Å)	I	hkl	$d_{calc.}$ (Å)	$d_{obs.}$ (Å)	I	d_{obs} (Å)	I
10.28	100	001	10.24	10.44	100	10.4	100
5.13	50	002	5.12	5.12	70	5.163	50
4.491	70	020	4.493	4.486	70	4.498	50
4.374	5	$11\bar{1}$	4.360	4.360	30	4.365	25
4.287	5	021	4.115	4.131	5	4.13	5
3.934	20	$11\bar{2}$	3.683	3.685	30	3.698	30
3.760	10	003	3.415	3.408	60	3.444	50
3.690	20	112	3.106	3.103	35	3.117	20
3.557	20	$11\bar{3}$	2.963	2.969	8	2.98	3
3.414	45	023	2.719	2.720	10	2.736	5
3.352 3.219	30, s 20	$13\bar{1}$ 004	2.568 2.561	2.566	45	2.573	35
3.094	10, b	$20\bar{2}$**	2.493	2.487	8		
2.877	25, b	131	2.450	2.452	15	2.46	15
2.584 2.434	55 25, b	$13\bar{2}$ $11\bar{4}$	2.406 2.404	2.402	15	2.412	15
2.252	10	201	2.375	2.374	10	2.37	3
2.202	5	040**	2.247	2.243	5		
2.089 2.048	15 25	220 132	2.224 2.221	2.224	2		
2.017	10, s	$13\bar{3}$	2.167	2.167	10		
1.8235	5	005	2.049	2.048	20	2.067	15
1.7268	5, b	$20\bar{4}$	2.019	2.020	10		
1.7051	15	133**	1.9694	1.9746	10		
1.6710	5	$13\bar{4}$	1.9168	1.9155	5		
1.6386	10	$22\bar{4}$**	1.8416	1.8436	5		
1.6180	5	$13\bar{5}$	1.6892	1.6894	15	1.70	10
1.5909	5	151**	1.6557	1.6515	10		
1.5440	5	060	1.4977	1.4977	20	1.503	15
1.5029	25						

* Data from Eugster and Munoz (1966). ** Not used for least square refinement. b, broad reflection. s, basal reflection of ammonium-bearing dioctahedral mica.

the parameter c is shortened a little because a small amount of potassium is contained in the interlayer. The powder pattern of the Horo material apparently differs from that of the Tobe material, and resembles, in essence, that of $2M_2$ mica, e. g., a lepidolite reported by Bailey (1980), though it is more or less complicated owing to the impurities. Further structural investigation on this material is in progress.

The unit cell parameters of tobelite (Tobe material) and related dioctahedral

TABLE 4. Unit cell parameters and specific gravity of tobelite and related dioctahedral micas.

	1	2	3
a(Å)	5.219(4)	5.217(3)	5.208
b(Å)	8.986(3)	9.001(3)	8.995
c(Å)	10.447(2)	10.540(2)	10.275
β(°)	101.31(1)	101.37	101.58
V(Å^3)	480.44	485.33	471.52
Z	2	2	2
S. G.$_{calc.}$	2.617	2.581	2.804

1. Tobelite from Tobe, Ehime Prefecture, Japan (the present paper).
2. Synthetic ammonium-muscovite (Eugster and Munoz, 1966).
3. Synthetic muscovite (Yoder and Eugster, 1955).

micas are summarized in Table 4 together with specific gravity calculated from the unit cell data and the normalized empirical formula. Measurement of specific gravity using pycnometer gives 2.58 for the Tobe material and 2.62 for the Horo material when corrected for impurities. Specific gravity of tobelite is smaller than that of potassium dioctahedral mica.

Thermal analysis

DTA curves of the present tobelite materials, recorded with a Shimazu simultaneous macro TG-DTA apparatus using 250 mg of specimen, are given in Fig. 2. There appear two adjacent endothermic peaks in the range between 500°C and 650°C. Similar curve with two well dissociated peaks was reported for synthetic ammonium-muscovite by Barrer and Dicks (1966). As described

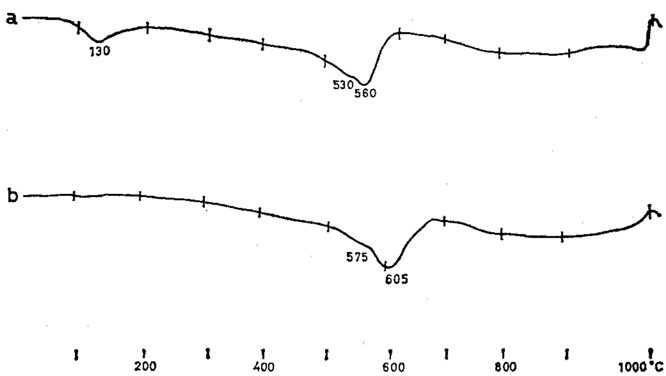

FIG. 2. Macro DTA curve of tobelite. a. Tobe specimen. b. Horo specimen.

previously on the thermal behaviour of ammonium in dioctahedral mica minerals (Higashi, 1978), the earlier endothermic reaction may be correlated to the detachment of ammonium from the structure, which is immediately followed by the prominent reaction due to dehydroxylation in the 2:1 layer. Temperature of the two reactions is higher in the well crystallized Horo material. The Tobe material, having higher water content owing to the poorly crystallized nature and to the interstratified smectite layer, gives an additional endothermic peak at 130°C.

Infrared absorption analysis

Infrared absorption spectra of tobelite are shown in Fig. 3. Measurement was made with a Nihonbunko infrared spectrophotometer using the KBr pellet technique. As demonstrated by previous studies (Erd *et al.*, 1964; Vedder, 1965; Yamamoto, 1967; Higashi, 1978; etc.), ammonium in silicates can be detected by infrared absorption analysis. The present materials yield characteristic absorption bands of ammonium in the spectral region between 3400 cm^{-1} and 2800 cm^{-1} and at around 1400 cm^{-1} (Fig. 3). The bands of ammonium in the two spectra are almost identical. Spectral differences related to polytype are obscure.

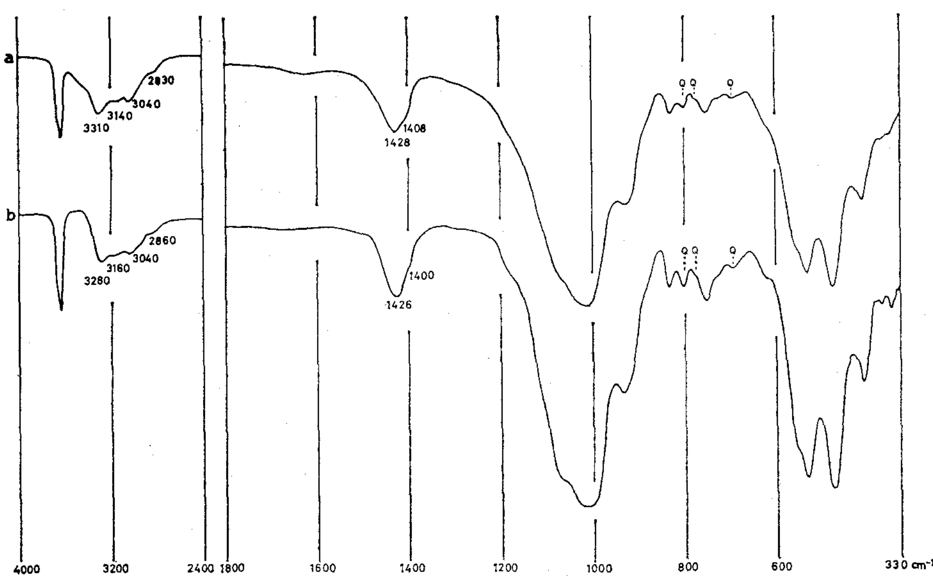

FIG. 3. Infrared absorption spectrum of tobelite. Q, quartz. Symbols are the same as in Fig. 2.

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