

The Occurrence of Kinoshitalite from Hokkejino, Kyoto Prefecture, Japan

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Introduction

Kinoshitalite, $\text{BaMg}_3[(\text{OH}, \text{F})_2|\text{Al}_2\text{Si}_2\text{O}_{10}]$, first described by YOSHII *et al.* (1973) from the Noda-Tamagawa mine, Iwate Prefecture, was found in a contact metamorphosed manganese ore from a small bedded manganese ore deposit at Hokkejino, Kyoto Prefecture, where a granodiorite body has two roof pendants on it, and one of them includes the metamorphosed ore deposit in hornfels of chert and slate origin.

The chemical analysis showed it to be closer to barium-magnesium end member with the relation $\text{F} > \text{OH}$ in mole ratio, which is unique in minerals of brittle mica group.

Geological Setting

The contact metamorphosed bedded manganese ore deposit at Hokkejino has been already exhausted out. Judging from the position of portals, the ore body was located in hornfels of chert origin, which is a dominant member of the roof pendant on a fine-grained biotite-granodiorite body. In the south of the deposit is another roof pendant. The main part of hornfels is exposed about 3 km east of the locality, where the effect of contact metamorphism is also prominent as seen from the development of biotite hornfels occasionally including andalusite. The structure of hornfels is significantly disturbed near the contact as well as in roof pendants. The strike and dip measured on one exposure near the deposit are $\text{N } 30^\circ\text{W}$ and 60°W , respectively.

Hornfels and granodiorite are covered unconformably by Quaternary sedimentary deposits belonging to Osaka Group in the south to southeast of the locality. In Fig. 1 is given the geologic sketch map around the locality, which is at the left side of the Kizu River about 2 km WNW of Kamo railway station.

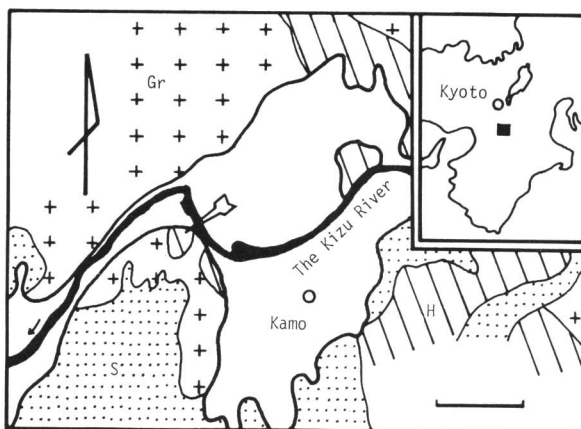


Fig. 1. Geologic sketch map around Hokkejino, Kyoto Prefecture. After NAKAJIMA (1960) with minor corrections. (Arrow indicates the situation of ore deposit.) H: Hornfels of chert and slate origin, Gr: Granodiorite, S: Sedimentary deposits belonging to the Osaka Group. (Scale: 1 km.)

Mode of Occurrence

Kinoshitalite occurs in close association with tephroite as light grayish yellow scales reaching a few millimeters long or hexagonal tablets of several millimeters across with or without alabandite, and the material of the former occurrence was analysed and studied by X-ray.

The scales are concentrated in certain layers in light yellowish gray tephroite, which is banded with rhodonite and light grayish yellow manganoan diopside. A small amount of wine coloured sonolite is present in place of tephroite and includes kinoshitalite scales as well (Fig. 2a). In tephroite bands is sometimes present alabandite band composed of separated subround grains reaching a few millimeter across within or at the margin of tephroite band. Kinoshitalite is also found in association with alabandite, where the grain size is larger than in the previous case. As seen in Fig. 2b, the tephroite band also contains coarse-grained rhodonite band within itself and is surrounded by fine-grained rhodonite bands, occasionally including diopside band encompassed by phlogopite films. Outside the rhodonite band is developed quartz with minor spessartine.

Under the microscope, kinoshitalite scales are interstitially present in tephroite grains forming a mosaic-like texture (Fig. 3a and 3b). The aggregate is also partaken by smaller subround grains of celsian which are liable to gather by themselves within the tephroite band. Besides them, minor rhodochrosite, hübnerite and rhodonite are found in tephroite bands and all of these minerals are in direct contact with kinoshitalite. Among minerals found in the dump derived from the deposit, spessartine, phlogopite, manganoan diopside, pyrophanite, manganoan tremolite and quartz are not in direct contact with kinoshitalite.

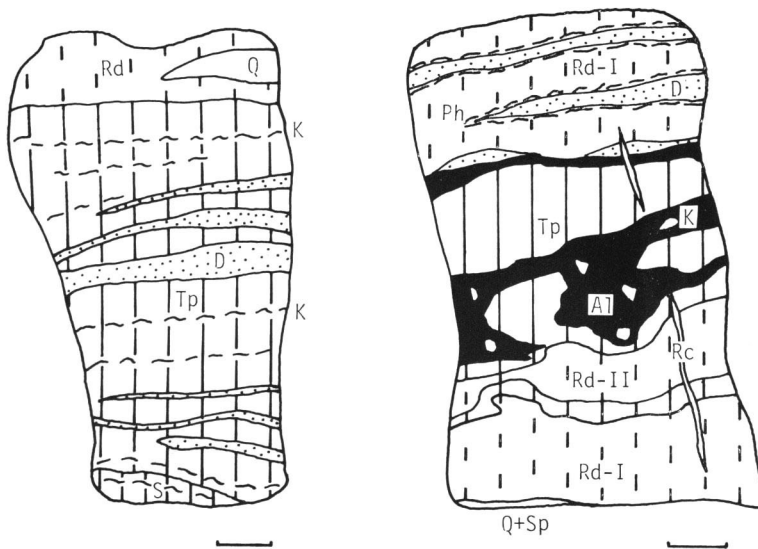


Fig. 2. Sketches of kinoshitalite-bearing specimens. (Scale: 1 cm)

- a (left). Kinoshitalite scales (K) and manganoan diopside (D) in tephroite (Tp) with sonolite (S). Rhodonite (Rd) and quartz (Q) are not in direct contact with kinoshitalite.
- b (right). Larger kinoshitalite tablets (K) in alabandite (Al)-rich part in tephroite (Tp), which includes coarse-grained rhodonite (Rd-II) and is in direct contact with manganoan diopside (D) and fine-grained rhodonite (Rd-I). Phlogopite (Ph) rims diopside (D). Quartz-spessartine (Q+Sp) band is developed outside of rhodonite band. Minor rhodochrosite veinlet (Rc) cuts tephroite, diopside and rhodonite.

Chemical Analysis

About 2 grams of light grayish yellow scales purified by hand-picking and heavy liquid separation was analysed by the third author as shown in Table 1. The result calculated on the basis of $O+OH+F=12$ satisfied well the ideal formula except the lesser amount of aluminum and the larger amount of potassium replacing barium, suggesting the existence of a coupled substitution of KSi for $BaAl$. Besides this, minor valency adjustment may be partaken by the oxygen replacing ($F+OH$).

As compared to the analysis of original material from the Noda-Tamagawa mine in Table 2, the present kinoshitalite contains more BaO and MgO , specifying itself to be closer to barium-magnesium end member.

Another characteristics of this kinoshitalite is the dominance of fluorine over hydroxyl radical in mole ratio, although the difference is so small. All the available chemical analyses of brittle micas have the relation $F < OH$ irrespective of the common existence of $F > OH$ relation in ordinary micas.

The associated tephroite and manganoan diopside were analysed by microprobe

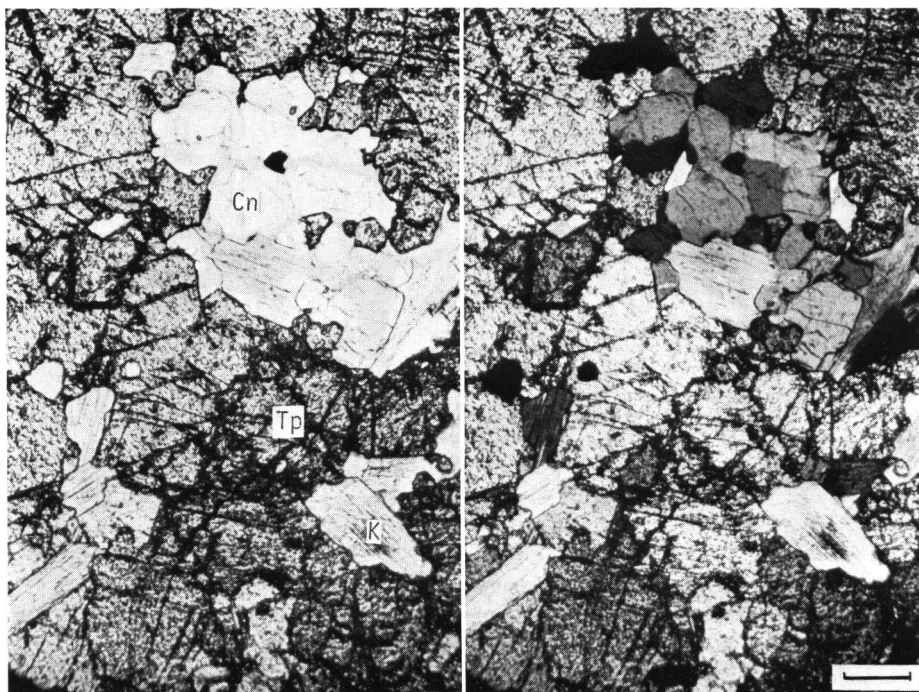


Fig. 3. Photomicrographs of kinoshitalite-bearing specimen. (Scale 0.1 mm)
 a (left). Mosaic aggregate of tephroite grains (Tp) including kinoshitalite scales (K) and aggregate of celsian (Cn). Thin section was prepared perpendicular to the plane of banding in the ore. One polar.
 b (right). Ditto. Crossed polars.

work of Dr. K. FUJINO (Tables 3 and 4). According to FUJINO, SADANAGA and KATO (1976), the tephroite has an ordered structure along with the site occupancy of magnesium, which is remarkably concentrated in the smaller cation site in the tephroite.

The chemical analysis of diopside informs that a part of calcium is replaced by a smaller ion, possibly manganese in view of its ionic radius closer to calcium than magnesium. This suggests that the substitution of manganese for calcium takes place under such a presumed temperature condition as in contact aureole of a granite intrusion.

X-ray Studies

A part of purified material was subjected to X-ray single crystal study, which showed it to be monoclinic, possible space group Cm or C2/m and 1 M type. The unit cell constants refined after the X-ray powder study are $a_0 = 5.344(2) \text{ \AA}$, $b_0 = 9.200(2) \text{ \AA}$, $c_0 = 10.15(1) \text{ \AA}$, $\beta = 100.20(5)^\circ$, $Z = 1$. In Table 5 the X-ray powder data obtained by diffractometer method (Cu/Ni radiation) is compared with those for the Noda-Tamagawa material.

Table 1. Chemical analysis of kinoshitalite from Hokkejino, Kyoto Prefecture, Japan. (Analyst: K. NAGASHIMA)

	wt. %	Molecular quotient	Metal number	Oxygen number	Metal number on the basis of (O+F+OH)=12	
SiO ₂	26.91	0.4479	0.4479	0.8957	2.276	1.724 } 4.000
Al ₂ O ₃	17.74	0.1740	0.3480	0.5220	1.768	
TiO ₂	0.53	0.0066	0.0066	0.0133	0.034	0.044 } 3.083
Fe ₂ O ₃	0.49	0.0031	0.0061	0.0092	0.031	
MnO	4.73	0.0667	0.0667	0.0667	0.339	2.635 } 1.084
MgO	20.90	0.5186	0.5186	0.5186	2.635	
CaO	0.83	0.0148	0.0148	0.0148	0.075	0.746 } 1.084
BaO	22.53	0.1469	0.4169	0.1469	0.746	
SrO	0.02	0.0002	0.0002	0.0002	0.001	0.008 } 1.084
Na ₂ O	0.05	0.0008	0.0016	0.0008	0.008	
K ₂ O	2.35	0.0249	0.0499	0.0249	0.254	0.760 } 1.084
F	2.84	0.1495			0.760	
H ₂ O(+)	1.33	0.0739	0.1478	0.0739	0.751	
	101.25					
—O=F ₂	—1.20					
Total	100.05					

Empirical formula on the basis of (O+F+OH)=12:
(Ba_{0.746}K_{0.234}Ca_{0.075}Na_{0.005}Sr_{0.001}) Σ 1.084
(Mg_{2.635}Mn_{0.339}Ti_{0.034}Fe_{0.031}Al_{0.044}) Σ 3.083
(Si_{2.276}Al_{1.724}) Σ 4.000O_{10.000}(O_{0.459}F_{0.780}(OH)_{0.751}) Σ 2.000

Table 2. Chemical compositions of kinoshitalites from the Noda-Tamagawa mine and Hokkejino, and of theoretical end member

	1.	2.	3.
SiO ₂	24.58	26.91	23.36
Al ₂ O ₃	22.06	17.74	19.82
TiO ₂	0.16	0.53	
Fe ₂ O ₃	0.71	0.49	
Mn ₂ O ₃	3.24		
FeO	0.04		
MnO	7.38	4.73	
MgO	16.60	20.90	23.51
CaO	0.05	0.83	
BaO	17.85	22.53	29.81
SrO		0.02	
Na ₂ O	0.68	0.05	
K ₂ O	3.30	2.35	
F	0.21	2.84	
H ₂ O(+)	2.90	1.33	3.50
H ₂ O(—)	0.20		
	99.96	101.25	100.00
—O=F ₂	—0.09	—1.20	
Total	99.87	100.05	

1. Kinoshitalite. Noda-Tamagawa mine, Iwate Prefecture, Japan. After YOSHII *et al.* (1973).
Empirical formula (basis (O+OH+F)=12):

$$(\text{Ba}_{0.584}\text{K}_{0.352}\text{Na}_{0.110}\text{Ca}_{0.005})\Sigma 1.051$$

$$(\text{Mg}_{2.065}\text{Mn}_{0.522}\text{Al}_{0.223}\text{Mn}_{0.206}\text{Fe}_{0.045}\text{Ti}_{0.010}\text{Fe}_{0.003})\Sigma 3.074$$

$$(\text{Si}_{2.052}\text{Al}_{1.948})\Sigma 4.000\text{O}_{10.000}(\text{OH})_{1.615}\text{O}_{0.330}\text{F}_{0.055})\Sigma 2.000$$
2. Kinoshitalite. Hokkejino, Kyoto Prefecture, Japan. The present study.
Empirical formula (basis (O+OH+F)=12):

$$(\text{Ba}_{0.746}\text{K}_{0.254}\text{Ca}_{0.075}\text{Na}_{0.005}\text{Sr}_{0.001})\Sigma 1.084$$

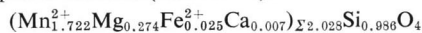
$$(\text{Mg}_{2.635}\text{Mn}_{0.339}\text{Ti}_{0.034}\text{Fe}_{0.031}\text{Al}_{0.944})\Sigma 3.083$$

$$(\text{Si}_{2.276}\text{Al}_{1.724})\Sigma 4.000\text{O}_{10.000}(\text{F}_{0.760}\text{OH})_{0.751}\text{O}_{0.489})\Sigma 2.000$$
3. Theoretical $\text{BaMg}_3[(\text{OH})_2\text{Al}_2\text{Si}_2\text{O}_{10}]$.

Table 3. Electron microprobe analysis of tephroite from Hokkejino, Kyoto Prefecture. Analyst: K. FUJINO.

	Wt. %	Molecular quotient	Oxygen number	Metal number (O=4)
SiO ₂	30.50	0.5076	1.0152	0.986
MgO	5.69	0.1412	0.1412	0.274
FeO	0.92	0.0128	0.0128	0.025
MnO	68.88	0.8864	0.8864	1.722
CaO	0.19	0.0034	0.0034	0.007
Total	100.18			

Empirical formula (basis O=4):

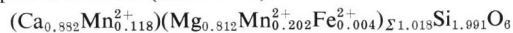


Elements looked for but not found: Al, Cr, K, Na, Ni, and Ti.

Table 4. Electron microprobe analysis of a manganoan diopside from Hokkejino, Kyoto Prefecture. Analyst: K. FUJINO.

	Wt. %	Molecular quotient	Oxygen number	Metal number (O=6)
SiO ₂	53.49	0.8902	1.7805	1.991
MgO	14.63	0.3630	0.3630	0.812
FeO	0.12	0.0017	0.0017	0.004
MnO	10.14	0.1429	0.1429	0.320
CaO	22.11	0.3943	0.3943	0.882
Total	100.49			

Empirical formula (basis O=6):



Elements looked for but not found: Al, Cr, K, Na, Ni, and Ti.

The present kinoshitalite is liable to have preferred orientation, which is of lesser degree of development than in micas. This is also felt when it is pulverized in mortar and recognized by the appearance of fairly clear and reproducible peaks other than basal reflections.

Table 5. X-ray powder data for kinoshitalites from the Noda-Tamagawa mine, Iwate Prefecture and Hokkejino, Kyoto Prefecture, Japan

1.				2.		
d (Å)	I	d(Å)	I	Qobs	Qcal	hkl
10.0	45	10.06	30	0.0099	0.0100	001
5.05	50	5.012	100	0.0398	0.0394	10 $\bar{1}$
					0.0400	002
		4.203	5	0.0566	0.0573	021
3.96	2	3.941	5	0.0644	0.0647	111
3.68	3	3.666	10	0.0744	0.0745	11 $\bar{2}$
		3.400	15	0.0865	0.0867	12 $\bar{1}$
					0.0873	022
3.37	100	3.336	100	0.0899	0.0897	102
					0.0901	003
3.16	5	3.144	16	0.1012	0.1015	112
2.93	5	2.915	15	0.1177	0.1177	11 $\bar{3}$
2.72	4	2.706	12	0.1366	0.1370	122
2.63	3	2.630	8	0.1446	0.1446	200
2.52	55	2.500	80	0.1600	0.1601	004
2.37	1	2.349	5	0.1812	0.1810	11 $\bar{4}$
		2.213	5	0.2042	0.2059	21 $\bar{3}$
		2.199	3	0.2067	0.2074	024
2.183	3	2.174	6	0.2116	0.2117	202
					0.2123	13 $\bar{3}$
2.020	55	1.999	100	0.2502	0.2502	005
					0.2506	20 $\bar{4}$
1.684	15	1.666	35	0.3600	0.3589	13 $\bar{5}$
					0.3603	006
		1.650	6	0.3674	0.3674	125
					0.3674	311
					0.3676	11 $\bar{6}$
		1.566	5	0.4080	0.4075	026
1.546	4	1.533	8	0.4253	0.4253	060
		1.492	5	0.4492	0.4488	116
1.442	2	1.427	6	0.4909	0.4903	007
		1.364	5	0.5376	0.5376	027
1.371	2	1.359	3	0.5418	0.5433	136
		1.308	6	0.5846	0.5855	064
		1.250	25	0.6405	0.6405	008
a _o	5.345Å	a _o	5.344 (2)Å			
b _o	9.250Å	b _o	9.200 (2)Å			
c _o	10.256Å	c _o	10.15 (1)Å			
β	99.99°	β	100.20 (5)°			

1. Kinoshitalite. Noda-Tamagawa mine, Iwate Prefecture. After YOSHII *et al.* (1973).
2. Kinoshitalite. Hokkejino, Kyoto Prefecture. The present study. Cu/Ni radiation. Diffractometer method.

Physical Properties

The present kinoshitalite is markedly different from the original one in colour. Except this, however, physical properties including optical ones are very similar. In Table 6, some physical and crystallographic properties of two kinoshitalites are compared.

Table 6. Crystallographic and physical properties of kinoshitalites from Hokkejino, Kyoto Prefecture and the Noda-Tamagawa mine, Iwate Prefecture.

	Hokkejino	Noda-Tamagawa
Cryst. sys.	Monoclinic	Monoclinic
Space group	Cm or C2/m	C2/m
Unit cell constants	$a_0 = 5.344\text{\AA}$, $b_0 = 9.200\text{\AA}$ $c_0 = 10.15\text{\AA}$, $\beta = 100.20^\circ$	$a_0 = 5.345\text{\AA}$, $b_0 = 9.250\text{\AA}$ $c_0 = 10.256\text{\AA}$, $\beta = 99.99^\circ$
Z	1	1
Polytypes	1 M	1 M, 2 M ₁
Colour	Light gray yellow, translucent	Yellow brown, translucent
Luster	Vitreous	Vitreous
Hardness	2.5–3	2.5–3
Cleavage	{001}, perfect	{001}, perfect
Specific gravity	3.23 (meas.) 3.29 (calc.)	3.30 (meas.) 3.33 (calc.)
Colour in thin section	Colourless	Pleochroic, X = very light yellow Y = Z = light yellow
(–) 2V	Very small	23°
Refractive indices	$\alpha = 1.615$, $\beta = 1.630$, $\gamma = 1.630$	$\alpha = 1.619$, $\beta = 1.633$, $\gamma = 1.635$
Extinction	Parallel	Parallel
Sign of elongation	Positive	Positive

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References

- FUJINO, K., R. SADANAGA, and A. KATO, 1976. Cation ordering in Mn-Mg olivines. *Abstr. Annual Meeting of Mineralogical Society of Japan*, B27 (1976) (In Japanese.)
- NAKAJIMA, W., 1960. Geology of the Northern margin of the Ryoke zone in the Yamato Plateau. *Earth Science (Chikyu Kagaku)*, **49**: 1–14 (In Japanese.)
- YOSHII, M., K. MAEDA, T. KATO, T. WATANABE, S. YUI, A. KATO, and K. NAGASHIMA, 1973. Kinoshitalite, a new mineral from the Noda-Tamagawa mine, Iwate Prefecture. *Chigaku Kenkyu*, **24**: 181–190 (In Japanese.)