

Tamaite, the Ca-analogue of ganophyllite, from the Shiromaru mine, Okutama, Tokyo, Japan

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Tamaite, $(\text{Ca}, \text{K}, \text{Ba}, \text{Na})_{3-4}\text{Mn}_{24}(\text{Si}, \text{Al})_{40}(\text{O}, \text{OH})_{112} \cdot 21\text{H}_2\text{O}$, the Ca-analogue of ganophyllite, is found from the Shiromaru mine, Okutama, Tokyo, Japan. It is monoclinic, $P2_1/a$, $a = 16.64(1)$, $b = 27.11(2)$, $c = 25.35(2)\text{\AA}$, $\beta = 98.74(7)^\circ$, $Z = 4$. The strongest lines in the X-ray powder diffraction pattern are 12.6 (vvs) (002), 3.46 (m) (027), 3.13 (s) (008), 2.84 (s) (38 -2), 2.69 (vs) (38 -4), 2.60 (s) (602), 2.46 (s) (60 -6), 2.38 (m) (604), 1.623 (m) (98 -2), 1.609 (m) (3 10 11). Electron microprobe and Karl-Fischer analyses gave SiO_2 41.23, Al_2O_3 7.79, FeO 0.16, MnO 35.17, MgO 0.23, CaO 1.94, BaO 2.03, Na_2O 0.34, K_2O 0.82, H_2O 11.07, total 100.78 wt%, and lead to the empirical formula, $(\text{Ca}_{1.65}\text{K}_{0.83}\text{Ba}_{0.63}\text{Na}_{0.53})_{\Sigma 3.64}(\text{Mn}_{23.71}\text{Mg}_{0.27}\text{Fe}_{0.11}\text{Al}_{0.12})_{\Sigma 24.21}(\text{Si}_{32.81}\text{Al}_{7.19})_{\Sigma 40.00}\text{O}_{95.27}(\text{OH})_{16.73} \cdot 21\text{H}_2\text{O}$ on the basis of $\text{O} = 133$. It is transparent and colorless to pale yellowish brown in color with vitreous to pearly luster. The streak is white and cleavage perfect on {001}. The Mohs' hardness is about 4. The measured and calculated densities are 2.85(5) g/cm³ and 2.83 g/cm³, respectively. It is colorless in thin section and optically biaxial negative with $\beta = 1.612(2)$ and $2V < 15^\circ$. It occurs as veinlets up to 1.5 mm thick composed of micaceous platy crystals under 0.5 mm in diameter and as spotted crystals in celsian-barian orthoclase veinlets cutting host rocks of metamorphosed manganese ore deposit. The mineral is considered to be formed during later stage activity of low grade metamorphism.

Introduction

From the metamorphosed manganese ore deposit of the Shiromaru mine such rare Ba- and/or Sr-dominant minerals as cymrite, celsian, banalsite, edingtonite, strontianite, and strontiopiemontite have been found (Matsubara, 1985; Kato et al., 1987; Matsubara and Kato, 1991). The first author already recognized the occurrence of Ca-dominant ganophyllite during the descriptive work on banalsite and other Ba-rich minerals from the Shiromaru mine (Matsubara, 1985), but he could not confirm the mineralogical properties due to lack of suitable amounts. In January of 1998 at the time of water clearance, one of the author (H.I.) had a chance to collect many specimens including Ca-domi-

nant ganophyllite directly from the outcrop of the ore deposit usually under water of the Shiromaru Dam.

Two other occurrences of Ca-dominant ganophyllite are known to date except the present case. Ganophyllite from the Benallt mine, Carnavonshire, England, with CaO 2.67 wt.% obtained by Haga (in Kato, 1980) is apparently Ca-dominant ganophyllite, but no detailed description has been published.

Mottana et al. (1990) reported the occurrence of Ca-dominant ganophyllite from the manganeseiferous metacherts of Molinello mine, Italy. The chemical composition of their material resembles our studied one except containing Cu and lacking Ba, but the crystallography is different, that is, the symmetry is orthorhombic with space group $Pnam$ or $Pna2_1$.

The Ca-dominant ganophyllite from the Shiromaru mine is named as tamaite after the Tama district where it is found. The mineral data and the name have been approved by the Commission on New Minerals and Mineral Names of the International Mineralogical Association (no. 99–011). The type specimen is de-

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posited at the National Science Museum, Tokyo, under the registered number NSM-M 27936.

Occurrence

Tamaite is found from the outcrop of weakly metamorphosed manganese ore deposit at the Shiromaru mine (about Lat. 35°48'30"N, Long. 139°7'30"E), Okutama Town, Tama district, Tokyo, located about 60 km NWW from the center of Tokyo Metropolitan. The ore deposit is developed in Triassic chert block enclosed in middle to upper Jurassic sandstone, a member of accretionary complex of Kanto Mountains. The mine operation was closed about 45 years ago. Main ore mineral was banded braunite with brick red gangue composed of very minute celsian, cymrite, barian orthoclase, albite, hematite, aegirine, manganoan andradite, ganophyllite members and analcime. Numerous veinlets of quartz, banalsite, celsian, orthoclase, edingtonite, calcite, strontianite, datolite, members of ganophyllite group, serandite, marsturite (Matsubara and Kato, 1990), rhodonite and strontio Piemontite are observed in ores and gangue. The sequence of rock units including ore deposit has reported by Kato et al. (1987).

Tamaite firstly recognized occurs as micaceous mineral of a minor component of brick red gangue near by banalsite veinlet. Major two occurrences of tamaite were found afterward; one forms veinlets up to 1.5 mm thick composed of micaceous platy crystals under 0.5 mm in diameter in association with celsian, barian orthoclase, aegirine and manganoan grossular (Fig. 1); the other forms spotted subhedral crystal approximately 0.1 mm across in celsian-barian orthoclase veinlets in

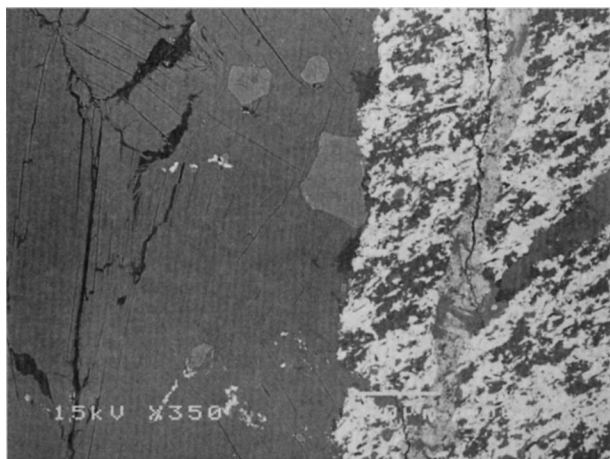


Figure 1 Back-scattered electron image of tamaite (gray of left side), manganoan andradite (light gray of grains near center) and aggregates composed of minute celsian (light), barian orthoclase (gray), orthoclase (dark), etc. Field view: approximately: 0.37×0.28 mm.

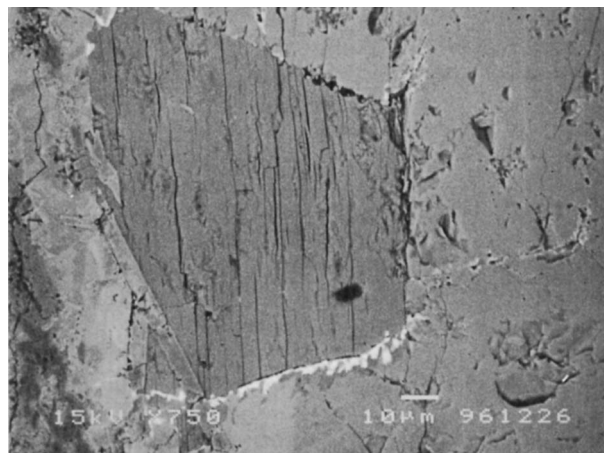


Figure 2 Back-scattered electron image of tamaite (subhedral crystal at center) enclosed in barian orthoclase (gray of mainly right side), pottasian celsian (light gray of left side) and celsian (frame like bright parts along boundary of tamaite and barian orthoclase). Field view: approximately 0.17×0.13 mm.

association with native copper and strontio Piemontite (Fig. 2). Micaceous aggregates of the former occurrence frequently include Na-dominant and K-dominant phases corresponding to chemical compositions of eggletonite and ganophyllite, respectively. Chemical composition and optical observations suggest that they are substantially eggletonite and ganophyllite, though they are not confirmed by X-ray study. Large micaceous crystals up to 2 mm in diameter of eggletonite and ganophyllite are also found in calcite veins.

Physical and optical properties

Tamaite is colorless to pale yellowish brown with white streak, and colorless in thin section. The cleavage is perfect on {001}. The luster is vitreous to pearly and fluorescence is not observed under short and long wavelength ultraviolet light. The measured density by Berman balance is 2.85(5) g/cm³ and the calculated one is 2.83 g/cm³. The Mohs' hardness is approximately 4, parallel to cleavage. It is optically biaxial negative with refractive index, $\beta=1.612(2)$, and $2V$ is small ($<15^\circ$). The interference color resembles that of muscovite.

X-ray study

The X-ray powder diffraction pattern for tamaite was obtained using a Gandolfi camera, 114.6 mm in diameter, employing Ni-filtered Cu-K α radiation. It resembles that of ganophyllite (Table 1). X-ray single crystal study was made by Weissenberg, Precession and four-circle methods. It is monoclinic with space group, $P2_1/a$, and unit cell parameters, a 16.64(1), b 27.11(2),

Table 1 X-ray powder diffraction data for tamaite from the Shiromaru mine

h k l	dobs	dcalc	I
0 0 2	12.6	12.5	vvs
0 2 1	12.2	11.9	w
0 4 0	6.81	6.78	vvw
0 0 4	6.22	6.26	vw
3 2 -1	5.13	5.12	w
3 2 -3	4.65	4.64	vvw
0 6 1	4.44	4.45	vw
3 4 0	4.26	4.26	vw
0 0 6	4.19	4.18	w
3 2 3	4.09	4.09	vw
0 6 3	3.96	3.97	w
3 4 2	3.86	3.90	vvwb
3 2 -5		3.85	
3 4 -4	3.72	3.73	vw
0 2 7	3.46	3.46	m
3 4 4	3.34	3.35	vvw
0 0 8	3.13	3.13	s
3 6 -5	2.99	3.00	vw
3 8 -2	2.84	2.86	s
0 6 7	2.81	2.81	w
6 0 0	2.74	2.74	m
3 8 -4	2.69	2.70	vs
6 0 2	2.60	2.60	s
3 8 4	2.55	2.54	vvw
0 0 10	2.51	2.51	vvw
6 0 -6	2.46	2.47	s
3 8 -6		2.47	
3 10 -1	2.44	2.43	vvw
6 0 4	2.38	2.38	m
3 8 6	2.29	2.29	w
6 0 -8	2.23	2.24	w
3 8 -8	2.21	2.21	w
6 0 6	2.15	2.15	vvw
3 10 5	2.13	2.13	vvw
6 2 -9	2.09	2.09	vvw
6 6 -7		2.09	
3 8 8	2.04	2.04	vw
6 0 -10	2.00	2.01	vvw
3 8 -10	1.967	1.970	vvw
6 0 8	1.931	1.923	vvw
3 6 -13	1.757	1.760	vw
3 8 -12		1.759	
6 0 10	1.725	1.724	vvw
0 16 0	1.689	1.694	vw
0 16 2	1.681	1.679	vw
9 8 -2	1.623	1.623	m
9 8 -4		1.611	
3 10 11	1.609	1.609	m
9 8 0		1.609	
0 16 6		1.570	
9 8 2	1.567	1.569	wb
0 0 16		1.566	
6 2 -15	1.529	1.524	vvwb
0 2 17	1.462	1.465	vvwb
6 16 0	1.441	1.441	vvw
6 16 2	1.422	1.419	vvw
9 10 -9	1.405	1.407	vvw
6 16 4	1.379	1.381	w
12 0 -5		1.376	
12 0 -6	1.367	1.365	vw

$$a = 16.64(1), b = 27.11(2), c = 25.35(2) \text{ \AA}, \beta = 98.74(7).$$

$c = 25.35(2) \text{ \AA}, \beta = 98.74(7)^\circ$, derived from the single crystal data. Indexing of the powder pattern is based on intensities of reflections obtained from single crystal study. Compared with ganophyllite and eggletonite, c -axis of tamaite is approximately half of them. The X-ray, physical and optical properties of tamaite, ganophyllite (Eggleton and Guggenheim, 1986) and eggletonite

(Guggenheim and Eggleton, 1986) are compared in Table 2.

Chemical composition

Chemical analyses were made using Link Systems energy dispersive X-ray spectrometer (QX-2000) for Si, Al, Fe, Mn, Mg, Ca, Ba, Na and K. Standard materials are wollastonite for Si and Ca, sillimanite for Al, Fe_2SiO_4 for Fe, Mn metal for Mn, Mg_2SiO_4 for Mg, BaF_2 for Ba, albite for Na and adularia (orthoclase) for K. The detailed analytical procedure has been reported by Yokoyama et al. (1993). H_2O was measured by Karl-Fischer method for hand-picked material. In Table 3 four analyses and their average of tamaite are demonstrated together with the representative analyses of the associated ganophyllite and eggletonite. The empirical formula of the average is $(\text{Ca}_{1.65}\text{K}_{0.83}\text{Ba}_{0.63}\text{Na}_{0.53})_{\Sigma 3.64}(\text{Mn}_{23.71}\text{Mg}_{0.27}\text{Fe}_{0.11}\text{Al}_{0.12})_{\Sigma 24.21}(\text{Si}_{32.81}\text{Al}_{7.19})_{\Sigma 40.00}\text{O}_{95.27}(\text{OH})_{16.73} \cdot 21\text{H}_2\text{O}$ on the basis of $\text{O} = 133$. Allotment of OH and H_2O was estimated in analogy with ganophyllite, and consequently 21 H_2O was derived based on $\text{O} + \text{OH} = 112$. All of ganophyllite members from the Shiromaru mine are characterized by higher BaO content than those previously reported (e.g., Dunn et al., 1983; Peacor et al., 1984; Mottana et al., 1990).

Discussion

The crystal structure of ganophyllite has been reported by Kato (1980) based on a subcell and by Eggleton and Guggenheim (1986) based on a superstructure. Noe and Veblen (1999) proposed a new subcell and discussed commensurate and incommensurate modulation in the crystal structure of ganophyllite. From the result of Eggleton and Guggenheim (1986) large cations such as K, Na and Ca are located in the interlayer and also in zeolite-like sites. They have considered that complete substitution for potassium is possible, but that for calcium is rather negative due to the differences of cation charge, size or hydration state. Ganophyllite members from the Shiromaru mine, however, include predominantly Ca and Ba in spite of the differences of cation charge and size. This suggests that the structure is kept by occupying alkali earth elements of half value for alkali elements in the interlayer, and furthermore the possibility of Ba-dominant ganophyllite. Bannisterite has a ganophyllite-like structure and composition (Heany and Post, 1992), and actually Ba-dominant bannisterite has been found from the weakly metamorphosed manganese ore deposit of the Kamo mine, Toba City, Japan (Matsubara and Kato, 1989).

Table 2 Comparison of crystal data, physical properties and optical properties of tamaite, ganophyllite and eggletonite

	tamaite	ganophyllite	eggletonite
Ideal formula	(Ca,K,Ba,Na) ₃₋₄ Mn ₂₄ (Si,Al) ₄₀ (O,OH) ₁₁₂ · 21H ₂ O	(K,Na) ₆ Mn ₂₄ (Si,Al) ₄₀ (O,OH) ₁₁₂ · 21H ₂ O	(Na,K,Ca) ₆ (Mn,Fe) ₂₄ (Si,Al) ₄₀ (O,OH) ₁₁₂ · 21H ₂ O
Occurrence	metamorphosed Mn deposits	metamorphosed Mn deposits	nepheline syenite pegmatite
Crystal system	monoclinic	monoclinic	monoclinic
Space group	<i>P</i> 2 ₁ / <i>a</i>	<i>A</i> 2/ <i>a</i>	<i>A</i> 2/ <i>a</i> or <i>Aa</i>
Cell parameters			
<i>a</i> Å	16.64(1)	16.60	16.647(3)
<i>b</i> Å	27.11(2)	27.13	27.012(4)
<i>c</i> Å	25.35(2)	50.18	50.06(2)
β	98.74(7) ^o	93.96 ^o	94.02(2) ^o
<i>V</i> Å ³	11302.9	22545.0	22455
<i>Z</i>	4	8	8
Color	colorless to pale yellowish brown	light brown, pale pink	dark to golden brown, red-brown
Hardness(Mohs)	~4	4~4.5	3~4
D(calc) g/cm ³	2.83	2.88	2.76
Color in thin section	colorless	dark to pale yellow-brown	colorless to pale brown
Refractive indices			
α		1.571	1.566(2)
β	1.612(2)	1.610	1.606(2)
γ		1.611	1.606(2)
2 <i>V</i>	(-) small (under 15 ^o)	small	9(3) ^o
References		Dunn et al.(1983) Eggleton & Guggenheim (1986)	Peacor et al.(1984) Guggenheim & Eggleton (1986)

Table 3 Chemical compositions of ganophyllite members from the Shiromaru mine

Wt. %	1	2	3	4	average	5	6
SiO ₂	41.64	41.52	41.23	40.54	41.23	41.41	40.34
Al ₂ O ₃	7.82	8.01	7.95	7.36	7.79	6.49	7.61
FeO	0.00	0.64	0.00	0.00	0.16	0.00	0.00
MnO	35.87	34.87	35.12	34.80	35.17	34.46	34.23
MgO	0.00	0.29	0.26	0.37	0.23	0.32	0.40
CaO	1.83	1.93	1.92	2.06	1.94	2.12	2.28
BaO	1.71	1.84	2.59	1.97	2.03	1.24	1.95
Na ₂ O	0.35	0.00	0.54	0.46	0.34	0.88	2.01
K ₂ O	0.94	0.58	0.90	0.86	0.82	2.18	0.54
H ₂ O					11.07		
total	90.16	89.68	90.51	88.42	100.78	89.10	89.36
	Si + Al + Fe + Mn + Mg = 64				O=133	Si+Al+Fe+Mn+Mg=64	
Si	32.80	32.61	32.68	32.74	32.81	33.67	32.72
Al(IV)	7.20	7.39	7.32	7.01	7.19	6.22	7.28
Σ	40.00	40.00	40.00	39.75	40.00	39.89	40.00
Al(VI)	0.06	0.03	0.11		0.12		
Fe		0.42			0.11		
Mn	23.93	23.20	23.58	23.80	23.71	23.73	23.52
Mg		0.34	0.31	0.44	0.27	0.38	0.48
Σ	23.99	23.99	24.00	24.24	24.21	24.11	24.00
Ca	1.55	1.63	1.63	1.78	1.65	1.85	1.98
Ba	0.53	0.57	0.80	0.62	0.63	0.40	0.62
Na	0.54		0.83	0.71	0.53	1.39	3.16
K	0.95	0.59	0.91	0.89	0.83	2.26	0.56
Σ	3.57	2.79	4.17	4.00	3.64	5.90	6.32
H					58.75		
Ca/(Na+K+Ca+Ba)	0.44	0.58	0.39	0.44	0.45	0.31	0.31

1-4, tamaite; 5, ganophyllite; 6, eggletonite.

At the Shiromaru mine, tamaite is generally accompanied by Ba-dominant feldspars such as celsian, banalsite and barian orthoclase, and cymrite. They completely exclude calcium in their constituents, and therefore calcium might be concentrated into tamaite. Whereas ganophyllite members in calcite vein are relatively K- or Na-rich and result ganophyllite or eggletonite. Consequently, the formation of tamaite is due to the chemical composition of coexisting minerals, in which calcium is favored or excluded.

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