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Tokyoite, $Ba_2Mn^{3+}(VO_4)_2(OH)$, a new mineral from the Shiromaru mine, Okutama, Tokyo, Japan

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Tokyoite, $Ba_2Mn^{3+}(VO_4)_2(OH)$, the Mn^{3+}-analogue of gamagarite, is found from the Shiromaru mine, Okutama, Tokyo, Japan. It is monoclinic, $P2_1/m$, $a = 9.10(4)$, $b = 6.13(2)$, $c = 7.89(5)$ Å, $\beta = 112.2(5)°$, Z = 2. The strongest lines in the powder X-ray diffraction pattern are 3.73 (15) (111), 3.31 (100) ($\bar{1}12$), 3.08 (20) (020), 3.00 (16) (301, $\bar{2}12$, 102), 2.90 (19) (120), 2.80 (62) (121, 300), 2.16 (18) ($\bar{3}21$), 1.963 (15) ($\bar{2}04$). Electron microprobe analysis gave V_2O_5 31.77, SiO_2 0.15, Al_2O_3 0.07, Fe_2O_3 2.33, Mn_2O_3 11.27, CaO 0.07, BaO 51.91, SrO 0.22, Na_2O 0.13, H_2O (calc.) 1.59, total 99.51 wt. %, and lead to the empirical formula, $(Ba_{1.92}Na_{0.02}Sr_{0.01}Ca_{0.01})_{\Sigma 1.96}(Mn^{3+}_{0.81}Fe^{3+}_{0.17}Al_{0.01})_{\Sigma 0.99}[(V_{1.99}Si_{0.01})O_{7.92}](OH)_{1.00}$ on the basis of V + Si = 2 and (OH) = 1. It is translucent and black red in color with a vitreous luster. The streak is dark brownish red and cleavage is not observed. The Mohs' hardness is about 4 to 4.5. The calculated density is 4.62 g/cm^3. It has distinct pleochroism, from reddish orange to dark brownish red in thin section and the calculated mean refractive index is 2.03. It occurs as irregular grains under 15 μm, and the aggregates are up to 250 μm wide in association with braunite, hyalophane and tamaite. The mineral is formed under the later stage activity of low grade metamorphism.

Introduction

From the Shiromaru mine such rare minerals as cymrite, banalsite, edingtonite, strontiopiemontite, marsturite, tamaite and eggletonite, have been found (e.g. Matsubara et al., 2000). During a survey of braunite-ore, newly obtained directly from the outcrop of the ore deposit in February of 2003 at the time of water clearance of the Shiromaru Dam, we found an unfamiliar Ba- and Mn-bearing vanadate. Chemical and X-ray diffraction studies indicated that it is a Mn^{3+}-analogue of gamagarite, which is a member of the brackebuschite group described from Gamagara Ridge, South Africa (de Villiers, 1943).

The Mn^{3+}-analogue of gamagarite from the Shiromaru mine was named as tokyoite for the locality, Tokyo. The mineral data and the name have been approved by the Commission on New Minerals and Mineral Names of the International Mineralogical Association (no. 2003-036). The type specimen is deposited at the National Science Museum, Tokyo, under the registered number NSM-M 28569.

Occurrence

Tokyoite is found from an outcrop of abandoned manganese ore deposit in the Shiromaru mine (~Lat. 35°48′30″N, Long. 139°7′30″E), at the river bed of the Tama River, Okutama Town, Tokyo. The ore deposit was developed in the Trias chert block enclosed in middle to upper Jurassic sandstone, a member of the accretionary complex of the Kanto Mountains (Ozawa and Kobayashi, 1985; Kato et al., 1987; Matsubara et al., 2000). The main ore mineral was banded or brecciated braunite with brick red gangue composed of very minute celsian, cymrite, hyalophane, albite, hematite, aegirine, manganoan garnets, ganophyllite, tamaite and analcime. Numerous veinlets of quartz, banalsite, celsian, hyalophane, edingtonite, calcite, strontianite, barite, datolite, members of the ganophyllite group, serandite, marsturite, rhodonite and strontiopiemontite are observed in the ores and gangue.

Tokyoite is found as minute aggregates composed of very minute irregular grains under 15 μm. Aggregates up to 250 μm wide occur along the rim of brecciated braunite (Fig. 1) or in veinlets composed of hyalophane and/or tamaite cutting braunite (Fig. 2). Very minute two grains corresponding to gamagarite composition are found

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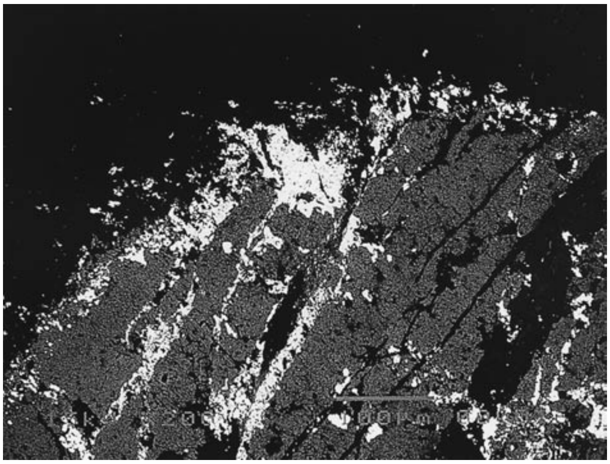

Figure 1. Back-scattered electron image of tokyoite (white), braunite (gray) and aggregates composed of minute hyalophane and tamaite etc (dark). Field view: approximately: 0.63 × 0.49 mm.

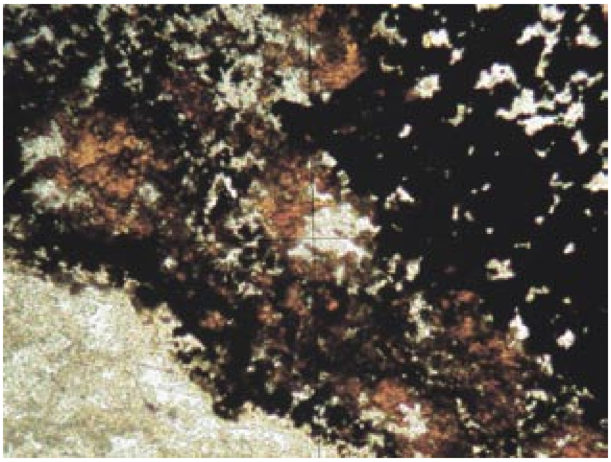

Figure 3. Photomicrograph of tokyoite (brownish red) in association with braunite (black) and minute aggregates of hyalophane and tamaite (colourless). One polar. Field view: approximately 1.0 × 0.8 mm.

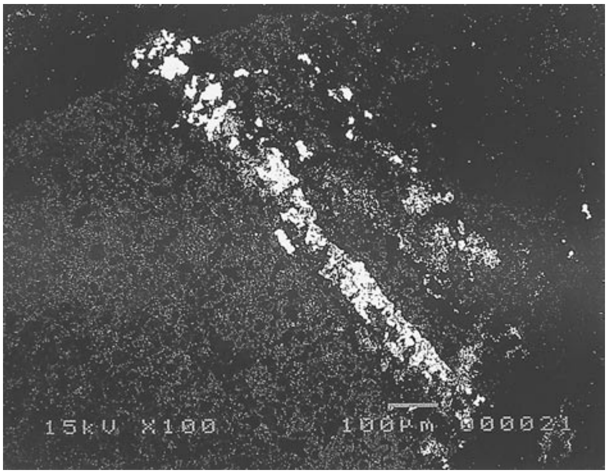

Figure 2. Back-scattered electron image of a veinlet composed of tokyoite (white) and hyalophane (gray) cutting braunite (dark gray). Field view: approximately 1.3 × 0.97 mm.

Table 1. Reflectance values for tokyoite

	Air		Oil	
	Max	Min	Max	Min
400 nm	14.7	14.3	4.6	4.3
420 nm	14.1	13.6	4.0	3.7
440 nm	13.6	13.7	3.7	3.4
460 nm	13.3	12.9	3.6	3.3
470 nm	13.2	12.8	3.5	3.3
480 nm	13.1	12.7	3.5	3.3
500 nm	12.9	12.6	3.5	3.2
520 nm	12.8	12.4	3.4	3.2
540 nm	12.8	12.3	3.4	3.1
546 nm	12.6	12.3	3.4	3.1
560 nm	12.5	12.3	3.4	3.1
580 nm	12.5	12.2	3.5	3.1
589 nm	12.5	12.2	3.6	3.1
600 nm	12.4	12.2	3.6	3.1
620 nm	12.5	12.2	3.9	3.3
640 nm	12.5	12.3	4.1	3.5
650 nm	12.6	12.5	4.3	3.6
660 nm	12.7	12.6	4.3	3.6
680 nm	12.8	12.7	4.6	3.8
700 nm	13.0	12.9	4.8	4.0

in association with tamaite-ganophyllite aggregate.

Physical and optical properties

Tokyoite is black red with a dark brownish red streak. It is translucent with a vitreous luster. Cleavage is not observed. The density could not be measured because of small grain size. The calculated density is 4.62 g/cm^3. The hardness is VHN$_{25}$ 363-390 kg/mm^2, corresponding to Mohs 4-4½. Under the microscope it has distinct pleochroism, from reddish orange to dark brownish red in thin section (Fig. 3). This property leads to easy distinction between strontiopiemontite existing in the same thin section because of its reddish yellow to purplish red pleochroism. Some optical properties could not be measured, but refractive indices are higher than 1.99. The mean index is 2.03 by calculation from Gladstone-Dale constants (e.g. Mandarino, 1981). Compared with the mean index of gamagarite (2.06), that of tokyoite is lower. Reflectance spectra in air and oil (Nikon nD = 1.515) for tokyoite were measured relative to a SiC standard (Zeiss No.851) (Table 1).

X-ray crystallography

The powder X-ray diffraction pattern for tokyoite was obtained using a Gandolfi camera, 114.6 mm in diameter, employing Ni-filtered Cu $K\alpha$ radiation. It resembles that of gamagarite (Table 2). No single crystal study was carried out because of the small crystal size. It is considered to be monoclinic with space group, $P2_1/m$ in analogy with gamagarite. The unit cell parameters are: a = 9.10 (4), b = 6.13 (2), c = 7.89 (5) Å, β = 112.2 (5)°, V = 408(3) Å^3, Z = 2. Compared with those of gamagarite, a = 9.12, b = 6.14, c = 7.84 Å, β = 112.9° (Basso et al., 1987), the c- and b-axes of tokyoite are slightly shorter but the a-axis is slightly longer.

Chemical composition

Chemical analyses were carried out with a JEOL JXA-8800M WDS electron microprobe analyzer (15 kV, 20 nA, beam diameter 1 μm). The average of 6 analyses and

Table 2. X-ray powder diffraction data for tokyoite and gamagarite

h	k	l	Tokyoite* I	Tokyoite* $d_{obs.}$	Tokyoite* $d_{calc.}$	Gamagarite** I	Gamagarite** $d_{obs.}$
1	0	0				2	8.409
0	0	1	6	7.26	7.26		
$\bar{1}$	0	1				2	6.975
1	1	0	14	4.97	4.94	15	4.961
0	1	1	10	4.67	4.66	10	4.678
1	0	1				10	4.654
$\bar{1}$	1	1	10	4.61	4.61	4	4.606
$\bar{2}$	0	1				2	4.468
2	0	0	11	4.22	4.20	3	4.204
$\bar{1}$	0	2	6	3.93	3.95	4	3.917
1	1	1	15	3.73	3.71	20	3.709
0	0	2	6	3.62	3.63		
$\bar{2}$	1	1				3	3.609
$\bar{2}$	0	2	5	3.54	3.52	7	3.477
2	1	0	26†	3.46	3.46	7	3.477
$\bar{1}$	1	2	100	3.31	3.32	100	3.302
2	0	1	13	3.15	3.14	8	3.140
0	2	0	20	3.08	3.06	32	3.070
$\bar{3}$	0	1			3.05		
$\bar{2}$	1	2	16	3.00	3.05	51	3.041
1	0	2			2.94	6	2.932
1	2	0	19	2.90	2.87	10	2.885
0	2	1				13	2.825
$\bar{1}$	2	1	62	2.80	2.80	53	2.799
3	0	0			2.80		
$\bar{3}$	1	1	40†	2.71	2.73	3	2.726
1	1	2	7	2.66	2.65	14	2.644
$\bar{2}$	0	3	11	2.57	2.58		
1	2	1			2.56	10	2.553
$\bar{2}$	2	1	14	2.54	2.53	9	2.531
2	2	0	4	2.45	2.47	1	2.480
0	2	2	14†	2.35	2.34	26	2.338
2	0	2	10†	2.32	2.33		
$\bar{4}$	0	2				5	2.233
$\bar{3}$	1	3	8	2.20	2.19	4	2.176
$\bar{3}$	2	1	18	2.16	2.16	23	2.160
$\bar{4}$	1	1	15†	2.12	2.13	17	2.128
1	0	3			2.11	8	2.108
$\bar{3}$	2	2	8	2.08	2.07	3	2.069
1	1	3	7	2.00	1.998	5	1.992
4	1	0				3	1.986
1	3	0					
$\bar{2}$	0	4	15	1.963	1.974	8	1.959
$\bar{4}$	1	3				15	1.919
$\bar{3}$	0	4				4	1.889
0	2	3					
1	3	1				2	1.873
$\bar{3}$	2	3	7	1.859	1.861	7	1.855
3	2	1					
$\bar{1}$	1	4				3	1.839
2	3	0					
$\bar{4}$	2	1	7	1.822	1.823	2	1.826
$\bar{1}$	3	2	7	1.799	1.811	11	1.813
$\bar{2}$	3	2	5	1.759	1.763	5	1.761
4	1	1			1.756		
$\bar{4}$	0	4				16	1.739
1	2	3	8	1.747	1.739		
2	3	1	8	1.722	1.709	7	1.715
$\bar{4}$	2	3				3	1.682
5	0	0					
$\bar{2}$	2	4	12†	1.659	1.658	19	1.651
3	0	3				7	1.553
$\bar{5}$	2	1	6	1.546	1.551		
0	4	0				8	1.536
$\bar{6}$	0	2				7	1.521
4	1	2					
$\bar{6}$	1	3				3	1.448
$\bar{4}$	3	3				3	1.439
4	2	2				6	1.399
$\bar{3}$	4	1				4	1.371
$\bar{3}$	1	6	8	1.279	1.286	7	1.275
3	1	4			1.277		
0	3	5				4	1.180

Tokyoite*	Gamagarite**
a = 9.10(4) Å	a = 9.121(2) Å
b = 6.13(2) Å	b = 6.142(1) Å
c = 7.89(5) Å	c = 7.838(2) Å
β = 112.2(5)°	β = 112.88(2)°
V = 408(3) Å^3	V = 405(1) Å^3

* Tokyo, Japan (Present study).

** Eastern Liguira, Italy (Basso et al., 1987).

† Intensities are enhanced by admixed braunite.

Table 3. Chemical composition for tokyoite

Constituent	Wt.%	Range	S.D.*	Std.**
V_2O_5	31.77	29.99-33.03	1.085	V metal
SiO_2	0.15	0.06 - 0.24	0.073	wollastonite
Al_2O_3	0.07	0.03 - 0.15	0.042	sillimanite
Fe_2O_3	2.33	1.55 - 3.35	0.723	Fe_2SiO_4
Mn_2O_3	11.27	10.48 - 12.15	0.698	Mn metal
CaO	0.07	0.06 - 0.08	0.008	wollastonite
BaO	51.91	51.28 - 52.72	0.468	BaF_2
SrO	0.22	0.09 - 0.39	0.115	slawsonite
Na_2O	0.13	0.08 - 0.19	0.039	albite
H_2O (calc.)	1.59			
Total	99.51			

* Standard deviation.
** Standard material.

Table 4. Brackebuschite group minerals and their cell parameters

	VO_4	PO_4	SO_4	AsO_4	*a*	*b*	*c*	β
Bearthite[a]		$Ca_2Al(PO_4)_2(OH)$			8.26	5.73	7.23	112.6
Goedkenite[b]		$Sr_2Al(PO_4)_2(OH)$			8.45	5.74	7.26	113.7
Tsumebite[c]		$Pb_2Cu(SO_4)(PO_4)(OH)$			8.70	5.80	7.85	111.5
Arsentsumebite[d]			$Pb_2Cu(SO_4)(AsO_4)(OH)$		8.85	5.92	7.84	112.6
Feinglosite[e]			$Pb_2Zn(SO_4)(AsO_4)(OH,H_2O)$		8.97	5.95	7.77	112.2
Arsenbrackebuschite[f]				$Pb_2(Fe,Zn)(AsO_4)_2(OH,H_2O)$	9.02	6.05	7.76	112.5
Brackebuschite[g]	$Pb_2Mn(VO_4)_2(OH)$				8.86	6.14	7.65	111.8
Calderonite[h]	$Pb_2Fe(VO_4)_2(OH)$				8.93	6.12	7.66	112.0
Bushmakinite[i]	$Pb_2Al(VO_4)(PO_4)(OH)$				8.69	5.81	7.73	112.1
Gamagarite[j]	$Ba_2Fe(VO_4)_2(OH)$				9.12	6.14	7.84	112.9
Tokyoite[k]	$Ba_2Mn(VO_4)_2(OH)$				9.10	6.13	7.89	112.2

[a] Chopin et al., 1993; [b] Moore et al., 1975; [c] Nichols, 1966; [d] Bideaux et al., 1966; [e] Clark et al., 1997; [f] Abraham et al., 1978; [g] Foley et al., 1997; [h] Gonzalez Del Tanago et al., 2003; [i] Pekov et al., 2002; [j] Basso et al., 1987; [k] This study.

standard materials are shown in Table 3. Mn and Fe are assigned as trivalent charge, and H_2O is calculated as (OH) =1 per formula in analogy with gamagarite. The empirical formula is $(Ba_{1.92}Na_{0.02}Sr_{0.01}Ca_{0.01})_{\Sigma 1.96}(Mn^{3+}_{0.81}Fe^{3+}_{0.17}Al_{0.01})_{\Sigma 0.99}[(V_{1.99}Si_{0.01})O_{7.92}](OH)_{1.00}$ on the basis of V + Si = 2, and (OH) = 1. The simplified formula is $Ba_2Mn^{3+}(VO_4)_2(OH)$. It is the Mn^{3+}-dominant analogue of gamagarite, and the Ba-dominant analogue of brackebuschite; a member of the brackebuschite group.

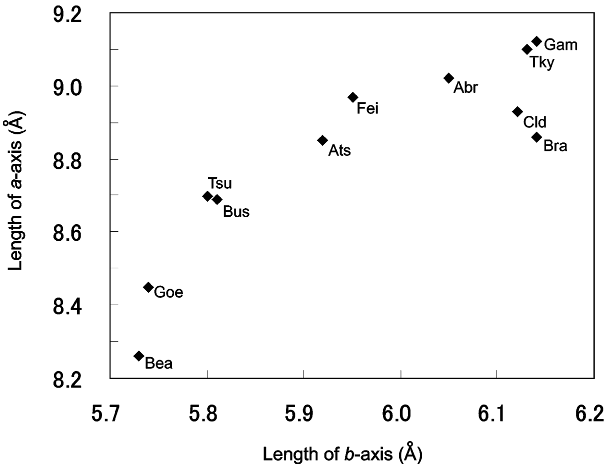

Figure 4. Diagram of *a*-length vs *b*-length in brackebuschite group minerals. Bea, Bearthite; Goe, Goedkenite; Tsu, Tsumebite; Ats, Arsentsumebite; Fei, Feinglosite; Abr, Arsenbrackebuschite; Bra, Brackebuschite; Cld, Calderonite; Bus, Bushmakinite; Gam, Gamagarite; Tky, Tokyoite.

Discussion

Some radiolarian fossils were observed in tokyoite-bearing specimens. Radiolarians are originally made of silica, but the present materials are almost entirely replaced by albite. Moreover, numerous veinlets composed of hyalophane, celsian, albite, marsturite, serandite, tamaite, strontianite and barite cut braunite and gangue, which was originally radiolarian chart. The gangue was changed to dense aggregates of minute albite, celsian, cymrite, hyalophane, hematite, ganophyllite group minerals, aegirine and manganoan garnet grains. The occurrences indicate that these minerals were formed under the later stage hydrothermal activities after diagenesis or low grade metamorphism. Some of the brackebuschite group minerals are considered as a secondary formation at the oxidized zone of ore deposits. In the present case, tokyoite is not a secondary mineral but may be a primary mineral derived from reactions between braunite and Ba- and V-bearing liquid.

According to Basso et al. (1987), the crystal structure of gamagarite is composed of linear double chains of edge-sharing (Fe,Mn)O_6 octahedra and face-sharing Ba-polyhedra elongated to the *b*-axis and flanked VO_4 tetrahedra. The *b*- and *a*-lengths in the brackebuschite group minerals are controlled by the dimension of the [MO_4] ions and polyhedral cations, respectively (Table 4 and Fig. 4).

In Japanese manganese ore deposits, all vanadium ions in rhodonite and/or rhodochrosite ores have trivalent or tetravalent charge and form octahedral coordination in the structures of minerals such as nagashimalite (Matsubara, 1980), haradaite (Takéuchi and Joswig, 1967) and watatsumiite (Matsubara et al., 2003) except for fianelite, which is a typical secondary mineral at the oxidized zone of the Komatsu mine, Saitama Prefecture, Japan (Yamada et al., 2000). Whereas pentavalent vanadium ion forming tetragonal coordination is seen in ardennite and tokyoite in braunite and/or piemontite (or strontiopiemontite) ore. These occurrences are completely due to the oxidation state of the original manganese ore, in which manganese is divalent or trivalent.

Acknowledgments

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