Journal of Mineralogical and Petrological Sciences, Volume 98, page 142-150, 2003

Watatsumiite, $KNa_2LiMn_2V_2Si_8O_{24}$, a new mineral from the Tanohata mine, Iwate Prefecture, Japan

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Watatsumiite, $KNa_2LiMn_2V_2Si_8O_{24}$, the V- and Mn-analogue of neptunite, is found in metamorphosed manganese ore deposit of the Tanohata mine, Iwate Prefecture, Japan. The mineral is monoclinic, *Cc*, a = 16.450(16) Å, b = 12.492(7) Å, c = 9.995(8) Å, β = 115.32(6)°, V = 1857(2) Å^3 and Z = 4. The seven strongest lines in the X-ray powder diffraction pattern are [d (Å), (I), (hkl)]: 9.58(84)(110), 4.52(85)(002), 3.52(63)(131), 3.19(100)(330, $\bar{1}32$), 2.94(90) ($\bar{2}23$), 2.90(66)(222, 510) and 2.49(93)($\bar{4}41$, $\bar{6}21$). Electron microprobe analysis and laser ablation microprobe-inductively coupled plasma-mass spectrometry gave SiO_2 52.64, TiO_2 3.13, VO_2 15.10, FeO 0.35, MnO 12.28, MgO 1.61, CaO 0.03, BaO 0.88, Na_2O 7.10, K_2O 4.89, Li_2O 1.6, total 99.61 wt.%, corresponding to $(K_{0.94}Ba_{0.05})_{\Sigma 0.99}Na_{2.08}Li_{0.97}(Mn_{1.57}Mg_{0.36}Fe_{0.04})_{\Sigma 1.97}(V_{1.66}Ti_{0.36})_{\Sigma 2.02}Si_{7.97}O_{24}$ on the basis of O = 24. Watatsumiite is transparent and yellowish green with vitreous luster. The streak is white with greenish tint. The cleavage is poor. The fracture is conchoidal and brittle. The hardness is VHN_{100} 707-946 kg/mm^2 (Mohs 5½-6). The calculated density is 3.24 g/cm^3. Watatsumiite has moderate pleochroism from yellowish tint to pale yellowish green, and is optically biaxial positive with $2V$ = 60(5)°, α = 1.686 (2), β (calc) = 1.694, γ = 1.720 (5), v > r perceptible. Watatsumiite occurs as short prismatic or massive aggregates in veinlets composed mainly of quartz, K-feldspar and potassicleakeite.

Introduction

During the survey in 2000 at the Tanohata mine, we found two unfamiliar minerals. One of them was described as a new mineral, potassicleakeite (Matsubara et al., 2002). The other mineral resembling olivine is named as watatsumiite from Watatsumi, the Japanese god of the sea. Watatsumiite is the V- and Mn-analogue of neptunite which was named for Neptune, the Roman god of the sea. The mineral data and its name have been approved by the Commission on New Minerals and Mineral Names of IMA (no. 2001-043). The type specimen is deposited in the National Science Museum, Tokyo, under the registered number NSM-M28187.

Occurrence

The upper Jurassic ore bodies of the Tanohata mine are contact metamorphosed and metasomatized by the intrusion of Cretaceous granodiorite (Nambu et al., 1969).

Watatsumiite was collected at the dump derived from No.3 (Matsumaezawa) orebody where various V-rich minerals such as suzukiite (Watanabe et al., 1973), roscoelite, V-bearing aegirine (Nakai et al., 1976) and V-bearing potassicleakeite (Matsubara et al., 2002) are found. A small amount of watatsumiite is closely associated with potassicleakeite.

Watatsumiite occurs as short prismatic crystals less than 0.8 mm in length or as massive aggregates less than 2 mm in diameter in veinlets composed mainly of quartz, K-feldspar, serandite, and minor potassicleakeite, suzukite, roscoelite, copper, chalcopyrite and yarrowite. The prismatic crystal is elongated along c-axis and is often terminated by pyramidal faces (Fig. 1).

Physical and optical properties

The mineral is transparent and yellowish green in color with vitreous luster. The streak is white with greenish tint. The fracture is conchoidal and brittle. The cleavage is poor. Vickers microhardness is 707-946 kg/mm^2 (100

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g load), corresponding to 5½-6 on the Mohs scale. The calculated density is 3.24 g/cm^3, using the empirical formula. It is optically biaxial positive with $2V = 60(5)°$. The refractive indices are $\alpha = 1.686$ (2), β (calc) = 1.694, $\gamma = 1.720$ (5). Pleochroism is moderate with yellowish tint to pale yellowish green.

Chemistry

Lithium content in the mineral was determined by applying a laser ablation microprobe-inductively coupled plasma-mass spectrometry (LAM-ICP-MS), and the other elements were analyzed with an electron microprobe using energy dispersion methods. The LAM-ICP-MS analyses were performed at the Venture Business Laboratory, the University of Tsukuba, using a perkin-Elmer Sciex ELAN6000 ICP-Ms instrument equipped with a frequency quadrupled Nd:YAG laser microprobe (266 nm). The electron microprobe analyses were made by using Link Systems energy dispersive X-ray spectrometer (QX-2000). The analytical conditions, procedures and standard materials for two equipments have been reported in the description of potassic leakeite (Matsubara et al., 2002). The average of six measurements by LAM-ICP-MS and by the electron microprobe leads to the empirical formula, $(K_{0.94}Ba_{0.05})_{\Sigma 0.99}Na_{2.08}Li_{0.97}(Mn_{1.57}Mg_{0.36}Fe_{0.04})_{\Sigma 1.97}(V_{1.66}Ti_{0.36})_{\Sigma 2.02}Si_{7.97}O24$ on the basis of O = 24. The simplified formula is written as $KNa_2LiMn_2V_2Si_8O_{24}$. Table 1 gives the average composision of watatsumiite together with those of neptunite (Slansky and Glen, 1982) and mangan-neptunite (Bussen et al., 1965) for comparison. The chemistry and crystal structure permit to consider watatsumiite as a V- and Mn-analogue of neptunite.

X-ray crystallography and crystal structure

The powder X-ray diffraction pattern for watatsumiite was obtained by a Gandolfi camera of 114.6 mm diameter employing Ni-filtered Cu$K\alpha$ radiation. The data were recorded on an imaging plate and processed with a Fuji BAS-2500 bio-imaging analyzer and with a computer program written by Nakamuta (1999). The X-ray diffraction data of watatsumiite are given in Table 2 with those of neptunite (Slansky and Glen, 1982) for comparison. The unit cell parameters were refined from the powder X-ray diffraction data with internal Si standard (NBS, #640b) using a computer program written by Toraya (1993).

The intensity data of a single crystal were collected with a Rigaku RASA-7R four-circle diffractometer using graphite monochromatized Mo$K\alpha$ radiation (56 kV, 270 mA). Experimental details pertaining to the collection for single crystal diffraction intensity data with the lattice parameters determined by least-squares refinement of the 2θ values of 25 strong reflections are given Table 3. The data reductions to Fo^2 with corrections for Lorentz, polarization and absorption (ψ-scan procedure) were made with a computer

Table 1. Chemical compositions of watatsumiite, neptunite and mangan-neptunite

wt. %	1	(Range)	2	3
SiO_2	52.64	52.10-53.23	53.10	52.54
TiO_2	3.13	2.50-3.85	17.26	17.22
VO_2	15.10	14.31-15.66		
Al_2O_3	n.d.		0.01	0.43
Fe_2O_3				0.07
FeO	0.35*	0-0.81	13.38*	4.28
MnO	12.28	11.79-12.93	1.06	11.14
MgO	1.61	1.32-1.92	0.76	0.04
CaO	0.03	0-0.18	0.01	0.09
BaO	0.88	0-1.34		
Na_2O	7.10	6.95-7.29	7.70	6.32
K_2O	4.89	4.61-5.02	4.25	4.98
Li_2O	1.6	1.4-1.7	2.00	1.61
Nb_2O_5	n.d.			0.07
F	n.d.			0.05
H_2O+				0.53
H_2O-				0.22
$-O=F$				0.02
total	99.61		99.53	99.57

n.d., Not detected.
* Total Fe.
1 Watatsumiite from the Tanohata mine, Japan (This study).
2 Neptunite from Woodsreef, Australia (Slansky and Glen, 1982).
3 Mangan-neptunite from Kola Peninsula, Russia (Bussen et al., 1965).

Table 2. Powder X-ray diffraction data of watatsumiite

			Watatsumiite*			Neptunite**	
h	k	l	I	$d_{obs.}$	$d_{calc.}$	I	$d_{obs.}$
1	1	0	84	9.58	9.56	78	9.57
$\bar{1}$	1	1	38	7.71	7.71	21	7.73
1	1	1	16	5.81	5.82	9	5.81
$\bar{2}$	2	1	11	4.81	4.81	6	4.81
2	2	0				7	4.79
$\bar{1}$	1	2	24	4.60	4.60	6	4.60
0	0	2	85	4.52	4.52	18	4.51
1	3	0	5	4.01	4.01	16	4.02
$\bar{2}$	2	2	28	3.84	3.86	18	3.845
$\bar{1}$	3	1			3.83	15	3.837
$\bar{4}$	0	2			3.77	16	3.779
4	0	0	5	3.73	3.72	9	3.703
0	2	2	4	3.65	3.66		
1	3	1	63	3.52	3.52	46	3.519
$\bar{4}$	2	1	5	3.44	3.43		
$\bar{3}$	3	1	39	3.31	3.31	25	3.311
3	3	0	100	3.19	3.19	100	3.192
$\bar{1}$	3	2			3.19		
$\bar{5}$	1	1			3.16	24	3.162
$\bar{1}$	1	3			3.13	5	3.129
$\bar{5}$	1	2	52	3.09	3.09	14	3.091
$\bar{3}$	3	2	16	3.03	3.03	8	3.033
$\bar{2}$	2	3	90	2.94	2.94	34	2.942
2	2	2	66	2.90	2.91	24	2.903
5	1	0			2.89	22	2.886
1	3	2	44	2.84	2.84	29	2.839
3	3	1			2.78	8	2.771
$\bar{5}$	1	3	38	2.73	2.73	19	2.734
3	1	2			2.73	15	2.726
$\bar{2}$	4	2	7	2.63	2.63	7	2.640
$\bar{3}$	3	3	29	2.56	2.57		
$\bar{1}$	3	3			2.55	11	2.554
$\bar{6}$	2	2			2.49	18	2.493
$\bar{4}$	4	1	93	2.49	2.49	17	2.485
$\bar{6}$	2	1			2.48	21	2.477
5	1	1			2.47	17	2.470
$\bar{4}$	0	4	11	2.45	2.45		
$\bar{3}$	1	4			2.45	17	2.449
$\bar{1}$	5	1			2.42	3	2.428
$\bar{4}$	4	2	15	2.41	2.40	8	2.405
4	4	0			2.39	4	2.388
$\bar{1}$	1	4	23	2.35	2.35	4	2.345
1	5	1			2.34	4	2.337
$\bar{5}$	3	3			2.32	4	2.326
$\bar{7}$	1	2	34	2.31	2.31	9	2.305
$\bar{5}$	1	4			2.31		
1	3	3	14	2.28	2.28	10	2.284
$\bar{2}$	4	3			2.28	11	2.279
$\bar{3}$	5	1			2.27	7	2.273
2	4	2			2.26	4	2.263
$\bar{7}$	1	1	20	2.26	2.26	6	2.256‡
$\bar{1}$	5	2	6	2.23	2.23	3	2.230
$\bar{7}$	1	3	12	2.21	2.21	3	2.212
4	4	1			2.17	17	2.167
0	4	3	52	2.17	2.17		
3	1	3			2.16	3	2.152
5	3	1			2.16		
1	5	2	9	2.10	2.10	3	2.101
7	1	0			2.09	6	2.087

			Watatsumiite*			Neptunite**	
h	k	l	I	$d_{obs.}$	$d_{calc.}$	I	$d_{obs.}$
3	5	1			2.08	8	2.077
$\bar{6}$	2	4			2.08	8	2.081
1	1	4	43	2.07	2.07		
$\bar{1}$	3	4			2.07		
$\bar{8}$	0	2	52	2.06	2.06	9	2.053
$\bar{6}$	4	2			2.05		
6	2	1			2.05	6	2.049
$\bar{5}$	3	4			2.04		
$\bar{6}$	4	1			2.04	7	2.039
$\bar{2}$	6	1			2.01		
2	6	0	17	2.01	2.00	7	2.007
$\bar{5}$	5	1	14	1.986	1.985	6	1.9860
$\bar{1}$	5	3			1.977	8	1.9783
$\bar{3}$	1	5	8	1.968	1.969	5	1.9713
$\bar{5}$	5	2			1.966	5	1.9685
2	0	4			1.943		
6	4	0			1.941	3	1.9403
$\bar{5}$	1	5	6	1.936	1.937		
$\bar{2}$	6	2	31†	1.911	1.916	10	1.9187
2	6	1			1.911	11	1.9130
7	3	0	3	1.891	1.892	5	1.8887
1	3	4			1.878		
$\bar{1}$	1	5	21	1.871	1.872		
$\bar{2}$	2	5			1.869	5	1.8701
2	2	4			1.855		
1	5	3	2	1.850	1.844	3	1.8420
$\bar{7}$	3	4	3	1.833	1.835	3	1.8386
$\bar{9}$	1	2	7	1.805	1.804		
$\bar{8}$	2	4			1.804	6	1.8029‡
$\bar{6}$	4	4			1.800		
$\bar{3}$	3	5			1.799		
6	2	2			1.785	6	1.7848
3	1	4			1.769	3	1.7687
$\bar{3}$	5	4			1.766		
$\bar{2}$	6	3	10	1.762	1.765	3	1.7671
2	6	2			1.759		
$\bar{1}$	7	1			1.756	5	1.7586
5	1	3			1.754		
$\bar{9}$	1	1			1.747		
0	2	5	5	1.736	1.736	2	1.7399
$\bar{1}$	5	4			1.727	2	1.7304‡
4	6	1	3	1.718	1.713		
$\bar{7}$	5	2	3	1.712	1.711		
1	1	5	16	1.694	1.693		
$\bar{8}$	4	3			1.692		
$\bar{7}$	5	1			1.692	5	1.6914
$\bar{8}$	4	1			1.682		
$\bar{4}$	4	5	9	1.684	1.681		
$\bar{1}$	7	2			1.679	5	1.6811
$\bar{7}$	5	3			1.670	6	1.6723
$\bar{4}$	0	6	16†	1.662	1.665	6	1.6670
4	4	3			1.663	5	1.6626
$\bar{7}$	3	5	16	1.653	1.660		
$\bar{3}$	7	2			1.654	5	1.6551
$\bar{6}$	6	2			1.653		
$\bar{6}$	6	1			1.649	4	1.6505
3	5	3			1.647	4	1.6437
$\bar{3}$	3	4	7†	1.638	1.642	3	1.6413
$\bar{10}$	0	2			1.635		

and those of neptunite for comparison

			Watatsumiite*			Neptunite**	
h	k	l	I	$d_{obs.}$	$d_{calc.}$	I	$d_{obs.}$
$\bar{6}$	0	6	8†	1.634	1.634		
7	5	0	11	1.621	1.618	4	1.6166
3	7	1			1.609	3	1.6120
$\bar{2}$	6	4			1.593	5	1.5946
$\bar{10}$	2	3	30	1.585	1.587	7	1.5859
2	6	3			1.587		
$\bar{10}$	2	2			1.582	5	1.5799
$\bar{7}$	5	4			1.582		
1	3	5			1.581		
$\bar{6}$	2	6			1.581	6	1.5814
$\bar{7}$	1	6			1.578		
$\bar{3}$	7	3	12	1.566	1.566	4	1.5697
0	4	5			1.564		
0	8	0			1.562	4	1.5629
$\bar{3}$	5	5	19	1.558	1.559	3	1.5590
6	2	3			1.556		
$\bar{1}$	1	6			1.555		
$\bar{10}$	2	4	8	1.544	1.544		
$\bar{5}$	5	5			1.542		
$\bar{3}$	3	6	16	1.533	1.534	6	1.5376
$\bar{8}$	0	6			1.534		
$\bar{10}$	2	1			1.531	4	1.5280
7	5	1			1.510		
0	0	6	55	1.507	1.506		
$\bar{5}$	7	3			1.504	7	1.5064
$\bar{8}$	4	5	28	1.487	1.501	11	1.5031
8	4	1			1.482		
0	8	2	8	1.471	1.476		
$\bar{7}$	5	5			1.466		
$\bar{11}$	1	4	12	1.460	1.459		
7	1	3			1.456		
4	4	4			1.454		
$\bar{8}$	6	3	5	1.447	1.447		
$\bar{9}$	5	1	5	1.442	1.441		
$\bar{2}$	6	5			1.427		
$\bar{9}$	5	4	14	1.425	1.424		
2	6	4	7	1.415	1.420		
$\bar{11}$	1	1			1.420		
$\bar{5}$	1	7			1.419		
$\bar{7}$	7	1			1.410		
$\bar{11}$	1	5	8	1.402	1.401		
$\bar{4}$	8	3	9	1.397	1.392		
$\bar{7}$	1	7			1.392		
4	8	1	22	1.387	1.387		
$\bar{6}$	2	7			1.385		
1	9	0	14	1.381	1.382		
$\bar{3}$	5	6			1.377		
$\bar{1}$	9	1			1.374		
7	7	0	9	1.368	1.366		
9	1	2			1.366		
6	2	4	14	1.364	1.364		
1	9	1	14	1.358	1.358		
$\bar{9}$	5	5			1.353		
$\bar{2}$	2	7	5	1.339	1.342		
$\bar{8}$	2	7			1.338		
$\bar{1}$	9	2	5	1.335	1.336		
$\bar{3}$	7	5			1.330		
$\bar{7}$	3	7			1.327		
$\bar{9}$	1	7			1.322		
$\bar{4}$	8	4			1.317		
1	9	2			1.307		
3	9	1	7	1.299	1.301		
$\bar{4}$	6	6			1.300		
9	5	1	6	1.296	1.295		
$\bar{4}$	4	7	6	1.290	1.294		
3	5	5	6	1.287	1.288		
$\bar{6}$	6	6			1.285		
0	8	4			1.284		
$\bar{9}$	7	2	13	1.276	1.275		

	Watatsumiite*	Neptunite**
a	= 16.450(16) Å	= 16.43 Å
b	= 12.492(7) Å	= 12.51 Å
c	= 9.995(8) Å	= 10.00 Å
β	= 115.32(6)°	= 115.32°
V	= 1857(2) Å^3	= 1857.94 Å^3

* Tanohata, Japan (Present study).

**Woodsreef, Australia (Slansky and Glen, 1982).

† Data with external Si-standard.

‡ Indices given in the original paper, 7 7 1, 8 2 4, and 3 5 1, may have been mistaken.

program written by Prof. Kazumasa Sugiyama of the University of Tokyo (personal communication). The atomic positional parameters of neptunite (Kunz et al., 1991) were used as the initial parameters for the refinement of the structure. The computer program, SHELXL-97 (Sheldrick, 1997), was employed for the refinement of crystal structure. Scattering factors for neutral atoms and anomalous dispersion factors were taken from The International Tables for Crystallography, Volume C (1992). Full-matrix least-squares refinement was performed by refining positional parameters, scale factor, and displacement parameters.

The refinement was started with the centric $C2/c$ model to clarify the symmetry of crystal structure, centric or acentric. The site occupancies of $M1$ and $M2$ sites were fixed as $Mn_{0.80}Mg_{0.18}Fe_{0.02}$ and $V_{0.83}Ti_{0.17}$, respectively, by considering the chemical composition and $M1$–O and $M2$–O distances. The refinement with anisotropic displacement parameters was converged to $R1$ = 0.0424 for the 3371 reflections unique for centric symmetry. An extraordinary anisotropy in the displacement parameters were observed for the O4 site in the centric model, as that in the $C2/c$ model of neptunite (Kunz et al., 1991).

Table 3. Crystallographic data and experimental details

a (Å)	16.454(3)
b (Å)	12.5114(19)
c (Å)	9.9951(19)
β (°)	115.332(12)
V (Å^3)	1859.7(5)
Space group	Cc
Z	4
Formula	$(K_{0.95}Ba_{0.05})Na_2Li(Mn_{1.56}Mg_{0.44})(V_{1.66}Ti_{0.34})Si_8O_{24}$
D_{calc} (g/cm^3)	3.234
μ(cm^{-1})	3.073
Crystal dimension (mm)	0.04 x 0.03 x 0.01
Diffractometer	Rigaku AFC-7R
Radiation	Mo$K\alpha$ (graphite)
Scan mode, rate (°/ min in ω)	2θ-ω, 2
2θ range	5 – 65
Reflection range	$-24 \le h \le 24$
	$-18 \le k \le 18$
	$-15 \le l \le 15$
No. of measured reflections	13191
No. unique reflections	6732
No. of observed reflections [$I > 2\sigma(I)$]	5154
R_{int}	0.0308
Variable parameters	363
$R1$ [$I > 2\sigma(I)$], R1(all reflections)	0.0332, 0.0538
w$R2$ (all reflections)	0.1186
Weghting parameters, a, b	0.1, 0
Goodness of Fit	0.865
Final $\Delta\rho_{min}$ (e/Å^3)	-0.673
Final $\Delta\rho_{max}$ (e/Å^3) 1.278	

$R1 = \Sigma \, | \, |F_o| - |F_c| \, | \, / \, \Sigma \, |F_o|$
$wR2 = \Sigma \, [w(F_o^2 - F_c^2)^2] \, / \, \Sigma \, [w(F_o^2)^2]^{0.5}$
$w = 1 \, / \, [\sigma^2(F_o^2) + (aP)^2 + bP]$
$P = [2F_c^2 + F_o^2] \, / \, 3$

Then, the result of $C2/c$ model was translated into the acentric Cc model, in which all of the sites except for the K1 and Li1 are divided into pairs of sites related by pseudo-centric symmetry. As the scattering powers of the transition metals , V, Mn, Fe and Ti are similar to each other, their distributions in the $M1$, $M1$a, $M2$ and $M2$a sites were examined by referring to the chemical composition (Table 1) and interatomic distances. The $M1$–O and $M2$–O distances indicate that the central cations in the $M1$ and $M2$ octahedra are displaced from the ideal center of the octahedral, as the Ti atoms in the $M1$ and $M2$ octahedra of neptunite, which shows a strong off-center displacement (Kunz et al., 1991). Subsequently, V, the substituent of Ti in watatsumiite, and Ti are regarded to occupy the more distorted and smaller $M1$ and $M2$ sites. Because of the similarity in the scattering powers of Ti and V, the Ti/V ratio was not refined in the calculation, and the ratio was fixed to that derived from chemical composition. Atoms of Mn, Fe and Mg are considered to occupy the other octahedral M sites, $M1$a and $M2$a. The occupancy parameters for the $M1$a and $M2$a were refined with scattering curves of Mn and Mg. The small amounts of Fe atoms, whose scattering power can not be distinguish with that of Mn, are calculated as Mn in the refinements. The refinements with acentric distribution of cations in the M sites, V and Ti atoms in the $M1$ and $M2$ sites and Mn and Mg atoms in the $M1$a and $M2$a sites, converged with $R1$ = 0.0538 for the 6732 reflections unique for acentric symmetry. The final result of refinement is summarized in Table 3. The final positional parameters, equivalent isotropic displacement parameters and anisotropic displacement parameters are given in Table 4. No significant extraordinary anisotropy was observed for the displacement parameters in the Cc model. The selected interatomic distances are summarized in Table 5. The chemical composition yielded from the refinement, $(K_{0.95}Ba_{0.05})Na_2Li(Mn_{1.56}Mg_{0.44})(V_{1.66}Ti_{0.34})Si_8O_{24}$, is consistent with the chemical analyses (Table 1).

Discussion

All pairs of the sites are related mutually by the pseudo centric-symmetry, other than the pair of O4 and O4a (Table 4). Significant displacements from the imaginary position corresponding to the O4 position of the centric $C2/c$ model were observed in the case of the acentric Cc model for the positional parameters of O4 and O4a sites.

Table 4. Final atomic coordinates and displacement parameters (Å^2)

	x	*y*	*z*	U_{eq}	U_{11}	U_{22}	U_{33}	U_{23}	U_{13}	U_{12}
Na1	0.2629(3)	0.1966(3)	0.3055(5)	0.0194(9)	0.014(2)	0.025(2)	0.021(2)	-0.0026(16)	0.0091(17)	-0.0027(15)
Na2	-0.2649(3)	-0.1975(3)	-0.3064(5)	0.0171(8)	0.0139(19)	0.0178(18)	0.019(2)	-0.0084(15)	0.0068(16)	-0.0079(14)
K1*	-0.0004(2)	0.42412(7)	0.2496(3)	0.02870(18)	0.0121(2)	0.0537(5)	0.0190(3)	-0.0047(13)	0.0055(2)	0.0025(12)
Li1	0.4963(16)	0.4348(6)	0.249(2)	0.0198(17)	0.015(3)	0.021(3)	0.022(3)	0.014(7)	0.007(3)	0.000(6)
*M*1*	0.34007(9)	0.31650(14)	0.09554(15)	0.0115(3)	0.0060(6)	0.0158(7)	0.0136(7)	0.0065(6)	0.0052(6)	0.0037(5)
*M*1a*	-0.34011(9)	-0.31677(14)	-0.09590(15)	0.0119(3)	0.0088(7)	0.0161(7)	0.0116(7)	0.0059(5)	0.0050(6)	0.0040(5)
*M*2*	0.08647(9)	0.05687(13)	0.11034(15)	0.0110(3)	0.0085(7)	0.0149(7)	0.0094(7)	-0.0029(6)	0.0037(6)	-0.0007(5)
*M*2a*	-0.08659(9)	-0.05667(13)	-0.11019(15)	0.0087(3)	0.0028(7)	0.0147(8)	0.0083(7)	-0.0046(6)	0.0021(5)	-0.0005(5)
Si1	0.14605(15)	0.40656(18)	0.0631(2)	0.0057(4)	0.0052(10)	0.0045(9)	0.0075(10)	-0.0016(7)	0.0027(9)	-0.0002(7)
Si1a	-0.14623(16)	-0.40574(19)	-0.0636(3)	0.0079(4)	0.0069(11)	0.0079(10)	0.0092(11)	0.0023(8)	0.0037(9)	0.0004(8)
Si2	0.52314(15)	0.22613(19)	0.0840(3)	0.0074(4)	0.0066(11)	0.0065(9)	0.0092(11)	0.0004(8)	0.0034(9)	-0.0002(8)
Si2a	-0.52323(15)	-0.22624(18)	-0.0842(3)	0.0066(4)	0.0039(10)	0.0065(9)	0.0081(10)	-0.0018(8)	0.0013(8)	-0.0012(7)
Si3	0.76904(14)	0.4744(2)	0.1074(2)	0.0080(4)	0.0046(10)	0.0082(10)	0.0099(11)	-0.0004(8)	0.0018(8)	0.0006(8)
Si3a	-0.76895(14)	-0.47445(19)	-0.1068(2)	0.0056(4)	0.0059(10)	0.0055(9)	0.0055(9)	0.0013(8)	0.0026(8)	0.0001(8)
Si4	0.89541(15)	0.15009(18)	0.0838(3)	0.0060(4)	0.0061(10)	0.0045(10)	0.0076(11)	-0.0006(8)	0.0032(9)	-0.0011(7)
Si4a	-0.89530(16)	-0.15001(18)	-0.0841(3)	0.0074(4)	0.0053(10)	0.0081(10)	0.0087(11)	0.0002(9)	0.0028(9)	0.0013(8)
O1	0.9540(4)	0.0476(5)	0.0733(7)	0.0120(12)	0.012(3)	0.009(3)	0.017(3)	0.000(2)	0.009(2)	0.007(2)
O1a	-0.9549(4)	-0.0480(5)	-0.0739(6)	0.0071(11)	0.005(2)	0.007(2)	0.007(2)	0.0001(18)	0.0001(19)	-0.0033(17)
O2	0.4578(4)	0.3266(6)	0.0683(8)	0.0163(14)	0.011(3)	0.022(3)	0.018(3)	0.000(3)	0.008(3)	0.001(2)
O2a	-0.4574(4)	-0.3280(4)	-0.0687(7)	0.0076(11)	0.008(3)	0.000(2)	0.013(3)	-0.0033(18)	0.003(2)	0.0021(17)
O3	0.1090(4)	0.1682(5)	0.2615(7)	0.0102(11)	0.013(3)	0.010(2)	0.010(3)	-0.004(2)	0.006(2)	-0.003(2)
O3a	-0.1095(5)	-0.1697(5)	-0.2618(8)	0.0144(13)	0.014(3)	0.016(3)	0.016(3)	0.005(2)	0.009(3)	0.000(2)
O4	0.3705(3)	0.4325(4)	0.2287(5)	0.0211(10)	0.0123(16)	0.020(2)	0.035(3)	0.0211(18)	0.0139(18)	0.0081(15)
O4a	-0.3784(3)	-0.4547(4)	-0.2674(5)	0.0159(8)	0.0157(16)	0.0154(17)	0.0165(17)	-0.0037(12)	0.0068(13)	-0.0014(12)
O5	0.2067(4)	0.0760(5)	0.0937(7)	0.0108(12)	0.005(2)	0.014(3)	0.012(3)	0.004(2)	0.002(2)	0.004(2)
O5a	-0.2049(4)	-0.0749(5)	-0.0932(7)	0.0107(12)	0.010(3)	0.005(2)	0.016(3)	-0.006(2)	0.005(2)	0.0003(19)
O6	0.7110(4)	0.3660(5)	0.0435(7)	0.0110(12)	0.008(3)	0.010(2)	0.010(3)	0.005(2)	-0.001(2)	-0.001(2)
O6a	-0.7086(4)	-0.3672(5)	-0.0406(7)	0.0112(12)	0.006(2)	0.006(2)	0.021(3)	-0.002(2)	0.005(2)	-0.0008(19)
O7	0.2094(4)	0.3069(5)	0.0752(8)	0.0133(13)	0.008(3)	0.012(3)	0.021(4)	0.003(2)	0.008(3)	0.001(2)
O7a	-0.2094(5)	-0.3055(5)	-0.0757(8)	0.0136(13)	0.018(3)	0.009(3)	0.018(3)	0.006(2)	0.011(3)	0.010(2)
O8	0.8316(4)	0.4912(4)	0.0183(7)	0.0097(12)	0.007(3)	0.003(2)	0.018(3)	0.0028(19)	0.005(2)	-0.0015(17)
O8a	-0.8300(4)	-0.4934(5)	-0.0166(6)	0.0105(12)	0.012(3)	0.012(2)	0.011(3)	0.0044(19)	0.009(2)	0.003(2)
O9	0.1610(4)	0.4495(5)	0.2285(6)	0.0123(12)	0.009(3)	0.016(3)	0.010(2)	0.0037(19)	0.003(2)	0.005(2)
O9a	-0.1589(4)	-0.4491(5)	-0.2223(6)	0.0120(12)	0.009(3)	0.019(3)	0.005(2)	-0.0074(19)	-0.0004(19)	-0.006(2)
O10	0.3972(5)	0.2088(5)	0.2551(8)	0.0139(12)	0.010(3)	0.018(3)	0.012(3)	0.003(2)	0.003(2)	0.001(2)
O10a	-0.3955(4)	-0.2073(5)	-0.2575(7)	0.0117(12)	0.008(3)	0.012(2)	0.010(3)	-0.003(2)	-0.002(2)	-0.002(2)
O11	0.4622(4)	0.1181(5)	0.0250(7)	0.0124(12)	0.004(2)	0.013(3)	0.019(3)	0.000(2)	0.004(2)	-0.0028(18)
O11a	-0.4593(4)	-0.1184(4)	-0.0219(6)	0.0080(11)	0.010(3)	0.003(2)	0.008(2)	-0.0039(17)	0.002(2)	-0.0022(17)
O12	0.9294(4)	0.2561(5)	0.0325(7)	0.0112(12)	0.011(3)	0.010(2)	0.015(3)	-0.001(2)	0.008(2)	-0.003(2)
O12a	-0.9294(4)	-0.2596(5)	-0.0309(7)	0.0099(11)	0.013(3)	0.005(2)	0.017(3)	0.001(2)	0.010(2)	0.000(2)

* Occupancy:
K1, 0.95K + 0.05Ba; *M*1, 0.83V + 0.17Ti; *M*1a, 0.846(7)Mn + 0.154Mg; *M*2, 0.83V + 0.17Ti; *M*2a, 0.723(7)Mn + 0.277Mg

The displacements of O4 and O4a sites are the main factor for the reduction of symmetry. The drifts of O4 and O4a sites from the imaginary centric-symmetry positions, ca. 0.2 Å, shorten the *M*1–O4 and *M*2–O4a distances, resulting in enhancements of the distortions of the corresponding octahedra. In addition, the distribution of cations in the octahedral M sites disturbs the centric symmetry of the crystal structure of watatsumite. The *M*1a and *M*2a sites are occupied with Mn and Mg instead of V and Ti, which occupy their respective imaginary centric-symmetric sites, *M*1 and *M*2. The space group of watatsumiite is, therefore, concluded as acentric *Cc*. These structural features in lowering the symmetry from *C*2/*c* to *Cc* observed for watatsumiite are the same as those for neptunite (Kunz et al., 1991).

The crystal structure of watatsumiite is isomorphous with that of neptunite. It consists of chains of the edge-shared octahedra of Li, V, Ti, Mn, Mg and Fe, and chains of the corner-shared SiO_4 tetrahedra. Both of the octahedral- and tetrahedral-chains run along [110] and [$\bar{1}$10]. The octahedral-chains are linked by corner-sharing along [001] to form a three-dimensional framework. The octahedral framework is interwoven by a similar tetrahedral framework consisting of the tetrahedral-chains (Fig. 2). The Na and K atoms are located in the spaces of the framework.

The comparison of crystal structures of watatsumiite and neptunite reveals that the substitutions of V and Mn for Ti and Fe cause no significant changes

Table 5. Interatomic distances (Å)

K1	— O9a	2.757(7)	Li1	— O4	1.99(2)	Na1 — O3	2.403(7)	Na2 — O10a	2.403(8)
	— O9	2.772(7)		— O2a	2.124(16)	— O5	2.437(8)	— O3a	2.425(8)
	— O8	2.868(7)		— O1a	2.141(19)	— O10	2.473(8)	— O5a	2.463(7)
	— O12a	2.867(6)		— O4a	2.15(2)	— O7	2.498(8)	— O7a	2.485(8)
	— O12	2.885(6)		— O1	2.121(16)	— O6a	2.555(8)	— O6	2.518(7)
	— O8a	2.911(7)		— O2	2.12(2)	— O12	2.772(8)	— O12a	2.729(8)
	— O11	3.112(7)	<Li1—	O	2.108>	— O6	2.956(8)	— O6a	2.975(8)
	— O11a	3.111(6)				— O8	3.044(7)	— O8a	3.056(7)
	— O11a	3.204(6)				<Na1— O	2.642>	<Na2— O	2.632>
	— O11	3.182(7)							
<K1—	O	2.967>				Si1 — O7	1.596(7)	Si1a — O7a	1.600(7)
						— O11a	1.601(6)	— O9a	1.603(6)
*M*1	— O4	1.887(5)	*M*1a	— O10a	2.014(7)	— O8a	1.620(6)	— O11	1.644(6)
	— O10	1.991(7)		— O2a	2.066(6)	— O9	1.654(7)	— O8	1.649(6)
	— O2	2.073(7)		— O7a	2.077(7)	<Si1— O	1.618>	<Si1a— O	1.624>
	— O7	2.075(7)		— O5	2.176(6)				
	— O5a	2.181(6)		— O7	2.188(7)	Si2 — O10a	1.594(7)	Si2a — O10	1.594(7)
	— O7a	2.175(7)		— O4a	2.321(4)	— O11	1.636(7)	— O2a	1.636(6)
<*M*1—	O	2.064>	<*M*1a—	O	2.140>	— O2	1.617(7)	— O12	1.672(7)
						— O12a	1.652(7)	— O11a	1.659(6)
*M*2	— O4a	1.690(4)	*M*2a	— O3a	1.988(7)	<Si2— O	1.625>	<Si2a— O	1.640>
	— O3	1.970(6)		— O1a	2.041(6)				
	— O1	2.053(7)		— O5a	2.037(7)	Si3 — O5	1.602(7)	Si3a — O5a	1.609(6)
	— O5	2.069(6)		— O1	2.112(6)	— O6	1.624(6)	— O9	1.585(6)
	— O1a	2.122(6)		— O4	2.129(5)	— O9a	1.636(6)	— O8a	1.628(6)
	— O2a	2.166(6)		— O2	2.175(8)	— O8	1.637(6)	— O6a	1.631(6)
<*M*2—	O	2.012>	<*M*2a—	O	2.080>	<Si3— O	1.625>	<Si3a— O	1.613>
						Si4 — O3a	1.599(7)	Si4a — O3	1.591(7)
						— O6a	1.643(7)	— O1a	1.639(6)
						— O12	1.606(7)	— O12a	1.653(6)
						— O1	1.634(6)	— O6	1.679(7)
						<Si4— O	1.621>	<Si4a— O	1.641>

Table 6. Comparison of crystallographic data, physical properties and optical properties among watatsumiite, neptunite and mangan-neptunite

	Watatsumiite	Neptunite	Mangan-neptunite
Ideal formula	$KNa_2LiMn_2V_2Si_8O_{24}$	$KNa_2LiFe_2Ti_2Si_8O_{24}$	$KNa_2LiMn_2Ti_2Si_8O_{24}$
Occurrence	Metamorphosed Mn deposit	Syenite, its pegmatite, serpentinite and natrolite vein	Syenite and its pegmatite
Crystal system	Monoclinic	Monoclinic	Monoclinic
Space group	*Cc*	*Cc*	*C*2/*m* or *C*2/*c*
Cell parameters			
a (Å)	16.450(16)	16.427(2) 16.43*	16.38
b (Å)	12.492(7)	12.478(2) 12.51*	12.48
c (Å)	9.995(8)	9.975(1) 10.00*	10.01
β (°)	115.32(6)	115.56(1) 115.32*	115.4
V (Å^3)	1857(2)	1845 1858*	1848
Z	4	4 4	
Color	Yellowish green	Black	Reddish black
Hardness (Mohs)	5.5 ~ 6	5 ~ 6	5 ~ 6
D (g/cm^3)	3.24 (calc)	3.19 ~ 3.23	3.23
Color in thin section	Yellow ~ pale yellowish green	Yellowish orange ~ dark red	Yellowish orange ~ dark red
Refractive indices			
α	1.686(2)	1.697 ~ 1.711	1.691 ~ 1.697
β	1.694(calc)	1.710 ~ 1.721	1.700 ~ 1.710
γ	1.720(5)	1.735 ~ 1.744	1.725 ~ 1.735
2*V* (°)	(+) 60(5)	(+) 45 ~ 65	(+) 35 ~ 45
References	This study	Kunz et al., 1991 * Slansky and Glen, 1982 Gaines et al., 1997	Bussen et al., 1965 Gaines et al., 1997

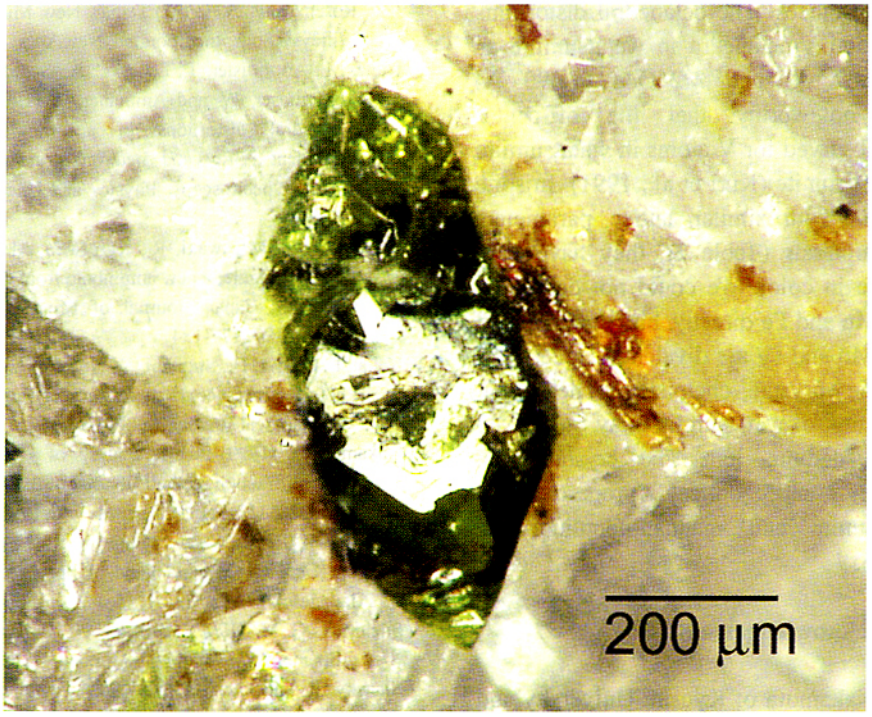

Figure 1. Photomicrograph of watatsumiite. The yellow green prismatic crystal terminated by pyramidal faces is associated with quartz and reddish brown potassicleakeite.

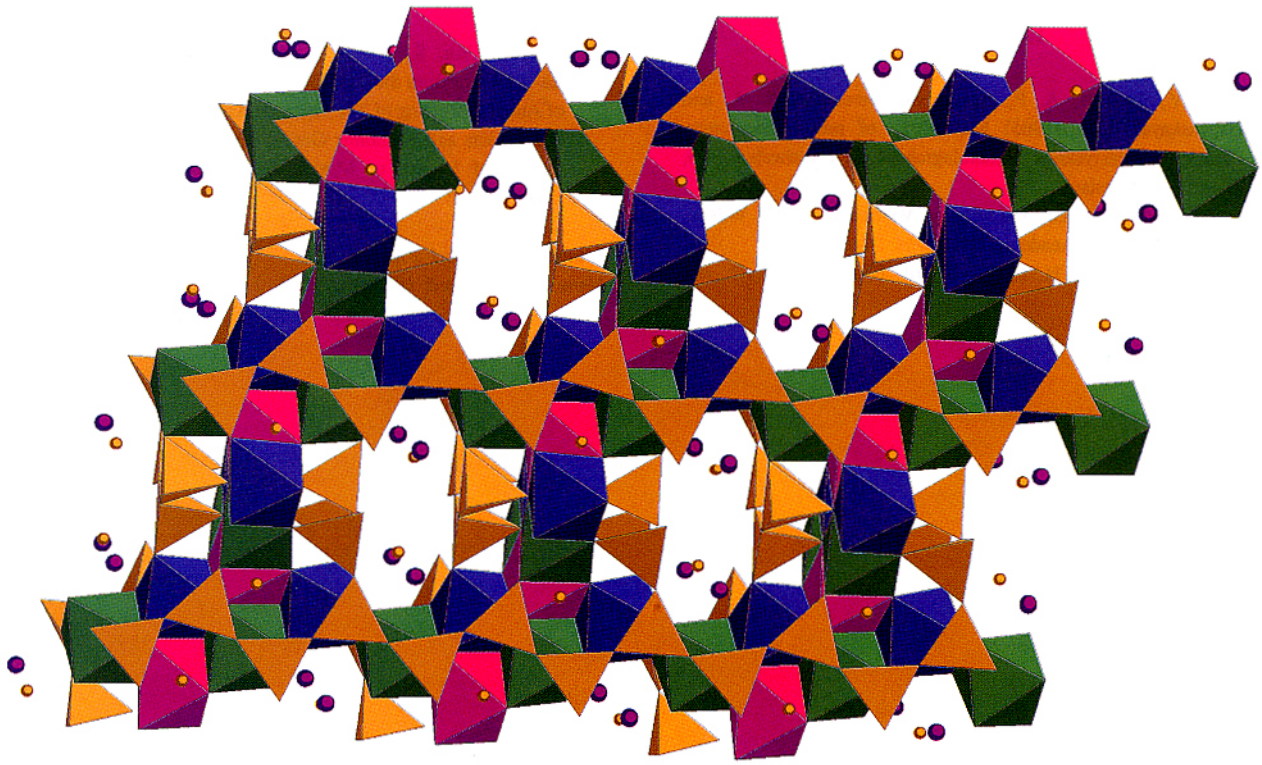

Figure 2. A view of the crystal structure of watatsumiite along [110]. Blue octahedra are $(V,Ti)O_6$ at the *M*1 and *M*2 sites. Green ones are $(Mn,Mg)O_6$ at the *M*1a and *M*2a sites. The LiO_6 are illustrated as pink octahedra. The chains of these octahedra connected at the corner to form three-dimensional framework. The chains of SiO_4 tetrahedra are indicated in ocher color. The (K,Ba) and Na in the cavity of framework are shown as purple and orange balls, respectively.

in the interatomic distances. The octahedral distortions were observed for the V-octahedra in watatsumiite as short *M*1–O4 (1.887 Å) and *M*2–O4a (1.690 Å) distances. It is noteworthy that the off-center displacements are observed for V atoms in watatsumiite as the Ti atoms in neptunite (Kurt et al., 1991). In spite of the isomorphism with similar lattice parameters between the two minerals (Table 2), they have very different appearance in color. We could not determine the valences of V, Mn and Fe directly, but V is assigned as tetravalent, and Mn and Fe are divalent, respectively, estimated from the crystal chemistry. The color, especially greenish tint, of watatsumiite may be derived from tetravalent vanadium ion. The crystal data, physical properties and optical properties of watatsumiite, neptunite and mangan-neptunite are compared in Table 6.

Acknowledgements

We thank Prof. Y. Nakamuta of Kyushu University and Prof. K. Sugiyama of the University of Tokyo for their suggestions on the XRD investigations. We also thank Mrs. M. Shigeoka for her preparing the polished thin section and Mr. Y. Ohara for his providing photograph of watatsumiite.

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Manuscript received; 2 May, 2003
Manuscript accepted; 19 August, 2003