

## Momoiite and nagashimalite from the Tanohata mine, Iwate Prefecture, Japan

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**Abstract** Momoiite and nagashimalite occur in rhodonite-quartz ore in association with V-bearing aegirine, V-bearing allanite, V-bearing titanite, Sr-bearing fluorapatite, pyrophanite, hyalophane and unidentified REE-Sr-Ti-V silicate from the metamorphosed manganese ore deposit of the Tanohata mine, Iwate Prefecture, Japan. Vanadium-bearing garnet including momoiite ( $\text{Mn}_3\text{V}_2\text{Si}_3\text{O}_{12}$ ) occurs as dark green grains up to 2 mm across in rhodonite-quartz ore. The chemical composition of V-bearing garnet varies widely especially in Mn/Ca and V/Al. An electron microprobe analysis for the most Mn- and V-rich area corresponding to momoiite component gave  $\text{SiO}_2$  34.04,  $\text{TiO}_2$  0.93,  $\text{Al}_2\text{O}_3$  6.96,  $\text{V}_2\text{O}_5$  19.85, FeO (as total Fe) 1.11, MnO 23.73, MgO 0.10, CaO 13.64, total 100.36 wt.%. The empirical formula is:  $(\text{Mn}_{1.70}\text{Ca}_{1.24}\text{Fe}^{2+}_{0.05}\text{Mg}_{0.01})_{\Sigma 3.00}(\text{V}_{1.35}\text{Al}_{0.60}\text{Ti}_{0.06})_{\Sigma 2.01}(\text{Si}_{2.88}\text{Al}_{0.09}\text{Fe}^{3+}_{0.03})_{\Sigma 3.00}\text{O}_{11.96}$  on the basis of total metal=8 with separating  $\text{Fe}^{2+}$  (for X<sup>18l</sup>-site) and  $\text{Fe}^{3+}$  (for T<sup>4l</sup>-site). The powder X-ray diffraction peaks appear rather broad in accordance with heterogeneity of the chemical composition. The five strongest diffractions are [ $d(\text{\AA})$ , ( $I$ ),  $hkl$ ]: 2.97(60)400, 2.66(100)420, 2.43(30)422, 1.585(29)642 and 1.481(10)800. Nagashimalite is found as dark greenish prismatic crystal up to 1 mm long in association with V-bearing garnet and quartz. The average of 12 electron microprobe analyses gave  $\text{SiO}_2$  33.56,  $\text{TiO}_2$  5.29,  $\text{Fe}_2\text{O}_3$  (as total Fe) 2.33,  $\text{B}_2\text{O}_3$  4.56,  $\text{V}_2\text{O}_5$  12.15, MnO 0.17, BaO 39.76, SrO 1.01, Cl 1.98,  $-\text{O}=\text{Cl}$  0.44, total 100.55 wt.%. The cell parameters of nagashimalite are,  $a=13.929(8)$ ,  $b=12.150(9)$ ,  $c=7.119(4)\text{\AA}$ ,  $V=1204.8(13)\text{\AA}^3$ .

**Key words:** momoiite, nagashimalite, Tanohata mine

### Introduction

Momoiite,  $(\text{Mn}^{2+}, \text{Ca})_3(\text{V}^{3+}, \text{Al})_2\text{Si}_3\text{O}_{12}$ , was recently described by Tanaka *et al.* (2010) from the Kurase mine of Ehime Prefecture, the Hokkejino mine of Kyoto Prefecture and the Fujii mine of Fukui Prefecture, Japan. In 1964, Momoi reported the occurrence of Mn- and V-rich garnet from the Yamato mine, Kagoshima Prefecture, Japan and proposed a new name of “yamatoite” for the hypothetical end-member,  $\text{Mn}^{2+}_3\text{V}^{3+}_2\text{Si}_3\text{O}_{12}$ . The reported Mn- and V-rich garnet from the Yamato mine, however, did not exceed 50% of  $\text{Mn}^{2+}_3\text{V}^{3+}_2\text{Si}_3\text{O}_{12}$  mole (Momoi, 1964). There-

fore, the Commission on New Minerals, Nomenclature and Classification, International Mineralogical Association approved the proposal by Tanaka *et al.* (New Mineral 2009-026), that is, a mineral name of  $\text{Mn}^{2+}_3\text{V}^{3+}_2\text{Si}_3\text{O}_{12}$  is momoiite instead of “yamatoite”.

Nagashimalite is a V-analogue of taramellite and was described as a new mineral from the metamorphosed manganese ore deposit of the Mogurazawa mine, Gumma Prefecture, Japan by Matsubara and Kato (1980).

During the survey on the manganese minerals from the Tanohata mine, Iwate Prefecture, Japan, we have found momoiite and nagashimalite in

rhodonite-quartz ore.

The present paper deals with the second occurrence of both momoiite and nagashimalite in the world and brief discussion on the chemical composition and crystallography of momoiite.

### Occurrence

The manganese ore deposits of the Tanohata mine are contact metamorphosed and metasomatized by granodiorite (Nambu *et al.*, 1969). We collected the studied specimens from the dump of No. 3 (Matsumaezawa) orebody where new V-rich minerals such as suzukiite (Watanabe *et al.*, 1973), V-bearing potassicleakeite (Matsubara *et al.*, 2002) and watatsumiite (Matsubara *et al.*, 2003) are found. These minerals occur in quartz-rich pegmatite-like veins including rhodonite, serandite, V-bearing aegirine, V-bearing titanite, yoshimuraite, V-bearing allanite, an unidentified REE-Sr-Ti-silicate, K-feldspar, hyalophane, Sr-bearing fluorapatite and pyrophanite.

The aggregates of V-rich garnet including momoiite component is found as dark green grain less than 2 mm across (Fig. 1). Under the microscope the aggregates is pale yellowish green to pale green (Fig. 2) and shows partially distinct anisotropic property in crossed polars (Fig. 3). Nagashimalite occurs as dark green prismatic or anhedral crystals less than 1 mm length. It has remarkable pleochroism with yellowish brown to greenish brown color under the microscope (Fig. 4).

### X-ray Crystallography

The powder X-ray diffraction patterns of two aggregates of V-rich garnet including momoiite were obtained by using a Gandolfi camera, 114.6 mm in diameter, employing Ni-filtered Cu- $K\alpha$  radiation. This diffraction patterns indicate those of general garnet (Table 1), but appear distinctly broad in compare with a normal spessartine (Fig. 5). The representative unit cell parameters calculated in the cubic system are as follows:  $a=11.88 \text{ \AA}$  (Tanohata3). Compared with the unit

cell parameters of synthetic  $\text{Mn}_3\text{V}_2\text{Si}_3\text{O}_{12}$   $a=11.83 \text{ \AA}$  (ICDD 37-220), goldmanite  $a=12.03 \text{ \AA}$  (ICDD 16-714) and V-rich spessartine  $a=11.69 \text{ \AA}$  (ICDD 47-1815) (Table 1), the parameter of the present V-rich garnet including momoiite is located between those of synthetic  $\text{Mn}_3\text{V}_2\text{Si}_3\text{O}_{12}$  and goldmanite.

Also the powder X-ray diffraction pattern of nagashimalite was obtained by using the Gandolfi camera. The pattern resembles that of the original nagashimalite from the Mogurazawa mine, Gumma Prefecture, Japan (Matsubara and Kato, 1980) (Table 2). The unit cell parameters are calculated in the orthorhombic system as follows:  $a=13.929(8)$ ,  $b=12.150(9)$ ,  $c=7.119(4) \text{ \AA}$ ,  $V=1204.8(13) \text{ \AA}^3$ . Compared with the unit cell parameters of the Mogurazawa material,  $a$ -axis is slightly shorter, and  $b$ - and  $c$ -axes are slightly longer.

### Chemical Composition

Excluding B, chemical analyses of the present V-rich garnet and nagashimalite were carried out using a Link Systems energy dispersive X-ray spectrometer (QX-2000) for Mn, Fe, V, Al, Ti, Ba, Sr, Cl, Ca and Si. The standard materials used were Mn for Mn,  $\text{Fe}_2\text{SiO}_4$  for Fe, V for V, sillimanite for Al,  $\text{TiO}_2$  for Ti,  $\text{BaF}_2$  for Ba,  $\text{SrF}_2$  for Sr, vanadinite for Cl and wollastonite for Ca and Si, respectively. Boron was analyzed with a WDS (JXA 8800) using danburite standard. Table 3 and Table 4 show the representative result for goldmanite-momoiite and the average of 12 analyses of nagashimalite compared with data of the original momoiite from the Kurase mine and nagashimalite from the Mogurazawa mine, respectively. The empirical formula of the highest momoiite component (Tanohata3-21) is  $(\text{Mn}_{1.70}\text{Ca}_{1.24}\text{Fe}^{2+}_{0.05}\text{Mg}_{0.01})_{\Sigma 3.00}(\text{V}_{1.35}\text{Al}_{0.60}\text{Ti}_{0.06})_{\Sigma 2.01}(\text{Si}_{2.88}\text{Al}_{0.09}\text{Fe}^{3+}_{0.03})_{\Sigma 3.00}\text{O}_{11.96}$  on the basis of total metal=8 with separating  $\text{Fe}^{2+}$  (for X<sup>[8]</sup>-site) and  $\text{Fe}^{3+}$  (for T<sup>[4]</sup>-site). The empirical formula of nagashimalite is  $(\text{Ba}_{3.71}\text{Sr}_{0.14})_{\Sigma 3.85}(\text{V}_{2.32}\text{Ti}_{0.95}\text{Fe}_{0.42}\text{Mn}_{0.03})_{\Sigma 3.72}\text{Si}_8\text{B}_{1.88}\text{O}_{28.28}\text{Cl}_{0.80}$  on the basis of Si=8. In comparison with the formula of the



Fig. 1. Microphotograph of the aggregate of V-rich garnet including momoiite. Field view: approximately  $2.9 \times 4.8$  mm.

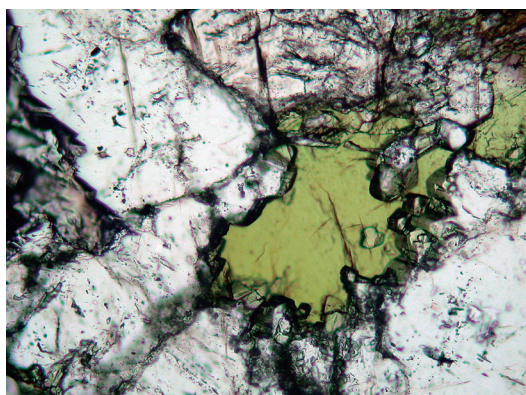


Fig. 2. Microphotograph of the thin section of V-rich garnet including momoiite. One polar. Field view: approximately  $1.2 \times 0.9$  mm.

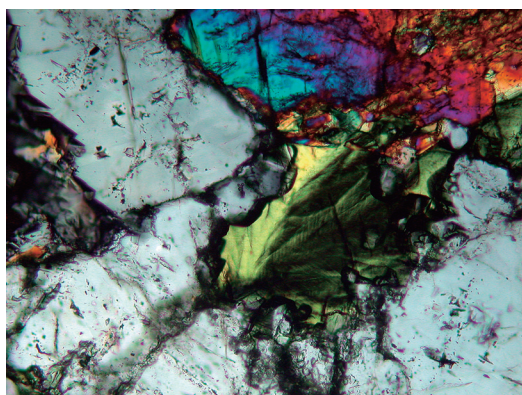


Fig. 3. Microphotograph of the same thin section to Fig. 2. Anisotropic property is visible under crossed polars. Field view: approximately  $1.2 \times 0.9$  mm.

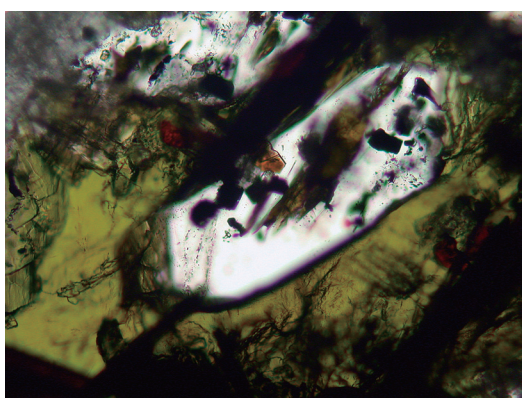


Fig. 4. Microphotograph of the thin section of nagashimalite in quartz crystal enclosed in V-rich garnet including momoiite. One polar. Field view: approximately  $1.2 \times 0.9$  mm.

## Discussion

The chemical variation of momoiite from three localities reported by Tanaka *et al.* (2010) and the Tanohata mine indicate similar trend indicating solid solution from goldmanite to spessartine through the part of momoiite field (Fig. 6). This property may be derived from the similar geological condition, that is, no high pressure and temperature regional or contact metamorphism. We agree the consideration that the formation of near end member of momoiite is undesirable under such low-to medium-metamorphic conditions

Moguraza material,  $\text{Ba}_{4.00}(\text{V}_{3.30}\text{Ti}_{0.51}\text{Mn}_{0.10})_{\Sigma 3.91}\text{Si}_8\text{B}_{1.71}\text{O}_{27.64}\text{Cl}_{0.72}(\text{OH})_{1.28}$ , the present material is characterized of rich in Ti and Fe.

Table 1. Powder X-ray diffraction data for V-rich garnet including momoiite (Tanohata1 and 3), momoiite from the Kurase mine (Tanaka *et al.*, 2010), synthetic  $\text{Mn}_3\text{V}_2\text{Si}_3\text{O}_{12}$  (ICDD 37-220), goldmanite (ICDD 16-714) and V-rich spessartine (ICDD 47-1815).

<i>hkl</i>	V-rich garnet				Momoite		Synthetic		Goldmanite		Spessartine	
	Tanohata1		Tanohata3		Kurase		$\text{Mn}_3\text{V}_2\text{Si}_3\text{O}_{12}$				(V-rich)	
	$d_{\text{obs.}}$	<i>I</i>	$d_{\text{obs.}}$	<i>I</i>	$d_{\text{obs.}}$	<i>I</i>	$d_{\text{obs.}}$	<i>I</i>	$d_{\text{obs.}}$	<i>I</i>	$d_{\text{obs.}}$	<i>I</i>
211	4.86	3									4.787	5
220	4.21	3	4.21	4	4.23	7	4.183	5	4.26	12		
321							3.162	5			3.123	5
400	2.97	60	2.97	70	2.98	78	2.958	70	3.01	65	2.927	45
420	2.66	100	2.66	100	2.67	100	2.646	100	2.688	100	2.617	100
332	2.53	3	2.54	7	2.54	19	2.522	6	2.565	10	2.497	5
422	2.43	30	2.43	34	2.44	42	2.415	45	2.453	40	2.386	20
431	2.33	11	2.33	13	2.34	20	2.321	12	2.357	16	2.292	10
521	2.17	15	2.17	17	2.18	20	2.160	25	2.194	16	2.134	15
440											2.063	2
611	1.93	19	1.929	18	1.94	21	1.919	25	1.951	20	1.896	20
620	1.88	4	1.884	8	1.89	11	1.871	6	1.901	8		
444	1.71	6	1.720	10	1.72	12	1.708	8	1.735	8	1.687	10
640	1.65	17	1.648	25	1.65	20	1.64	30	1.667	18	1.621	20
721							1.61	2				
642	1.59	29	1.588	37	1.59	30	1.581	60	1.607	50	1.561	25
<i>a</i> (Å)	11.9		11.88		11.9242(7)		11.83		12.03		11.69	
ICDD							37-220		16-714		47-1815	

Tanaka *et al.*, 2010

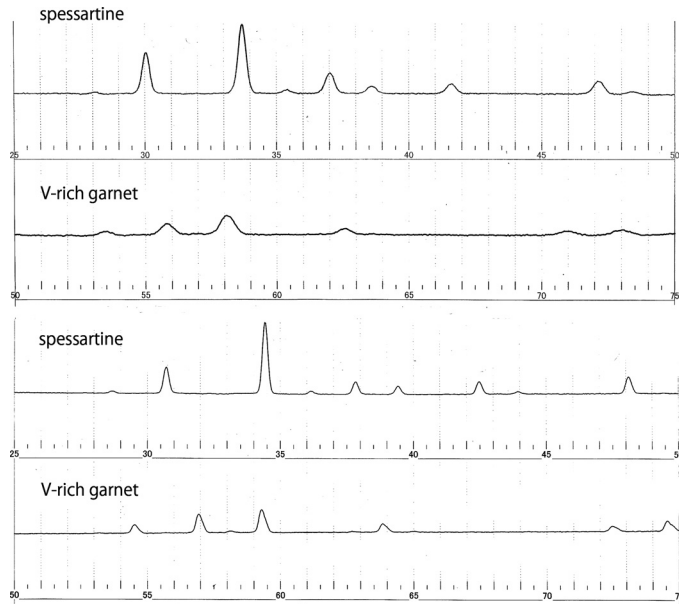


Fig. 5. Comparison of powder X-ray diffraction patterns between spessartine from Kunisaki, Hyogo Prefecture, Japan and V-rich garnet including momoiite.

Table 2. X-Ray powder diffraction data for nagashimalite from the Tanohata and Mogurazawa mine.

$hkl$	Tanohata		Mogurazawa		$hkl$	Tanohata		Mogurazawa	
	$d_{\text{obs.}}$	$I$	$d_{\text{obs.}}$	$I$		$d_{\text{obs.}}$	$I$	$d_{\text{obs.}}$	$I$
1 1 0			9.28	3	4 0 2	2.49	17	2.490	10
2 0 0	6.96	17	6.98	10	3 4 1	2.39	22	2.393	12
1 0 1	6.34	12	6.32	2	3 3 2	2.32	11	2.318	5
0 2 0	6.09	22	6.09	12	5 3 0	2.30	11	2.294	6
1 1 1	5.63	8	5.63	2	4 4 0			2.288	8
0 2 1	4.61	6	4.61	3	6 0 1	2.21	13	2.209	6
1 2 1	4.39	12	4.384	4	4 4 1	2.18	14	2.178	12
3 1 0			4.345	5	5 1 2	2.16	14	2.159	8
2 2 1	3.85	67	3.854	25	2 2 3	2.11	10	2.107	2
3 1 1	3.70	20	3.708	8	3 1 3			2.080	2
0 0 2	3.53	7	3.559	2	6 2 1	2.06	15	2.074	6
0 3 1					3 5 1			2.059	8
4 0 0	3.48	10	3.487	10	0 6 0			2.022	3
1 1 2	3.32	65	3.319	15	1 5 2	1.987	12	1.984	5
3 2 1	3.28	14	3.273	6	7 1 0			1.963	2
2 0 2	3.17	49	3.173	15	0 6 1			1.943	5
2 3 1	3.14	13	3.136	6	1 6 1			1.925	10
0 2 2	3.07	62	3.066	8	7 1 1	1.891	8	1.893	5
0 4 0, 4 1 1	3.02	100	3.030	60	3 3 3	1.875	12	1.873	8
4 2 0			3.020	100	6 4 0	1.844	9	1.845	5
0 4 1	2.79	30	2.791	20	5 5 0			1.830	2
5 1 0	2.71	6	2.717	8	5 0 3, 2 4 3	1.807	24	1.805	8
1 3 2	2.63	18	2.621	6	6 4 1	1.783	21	1.785	15
5 0 1, 2 4 1	2.59	56	2.592	28	4 6 0	1.752	12	1.748	12
5 1 1			2.538	3	8 0 0			1.743	10

Tanohata: this study.

Mogurazawa: Matsubara and Kato (1980).

Table 3. Chemical compositions of momoite (Tanohata3 and 4) and goldmanite (Tanohata1), and momoite from the Kurase mine (Tanaka *et al.*, 2010).

	MOMOIITE				GOLDMANITE	
	Tanohata3		Tanohata4		Kurase*	Tanohata 1
	21	31	48	65		4
SiO <sub>2</sub>	34.04	34.39	34.86	34.45	35.02	35.60
Al <sub>2</sub> O <sub>3</sub>	6.96	9.22	9.89	9.58	5.12	8.30
V <sub>2</sub> O <sub>3</sub>	19.85	16.78	16.58	16.51	21.96	15.55
TiO <sub>2</sub>	0.93	0.67	0.53	0.64	nd	0.71
FeO	1.11	1.37	1.51	1.55	0.05	1.43
MnO	23.73	21.49	23.42	23.93	24.74	21.06
MgO	0.10	0.10	0.10	0.09	0.28	0.09
CaO	13.64	15.62	14.01	14.09	12.24	16.93
Total	100.36	99.64	100.90	100.84	99.41	99.67

\*: Tanaka *et al.* (2010)proposed by Tanaka *et al.* (2010).

In Ca rich-garnet, especially solid solution from grossular to andradite, anisotropic property is commonly observed. Such garnet is generally

not cubic and this suggests the Tanohata V-rich garnet solid solution having broad powder X-ray pattern and partial anisotropic property also to be not cubic. The original momoite was calculated

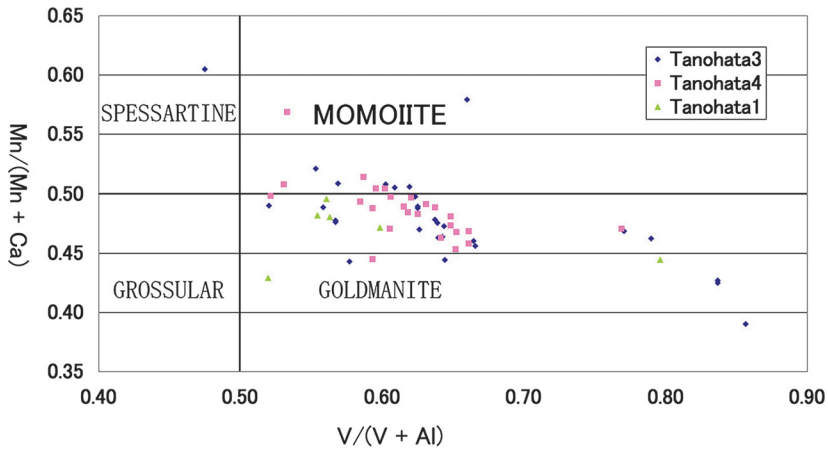


Fig. 6. Mn/(Mn+Ca) vs. V/(V+Al) diagram in V-rich garnets including momoiite.

Table 4. Chemical compositions of nagashimalite from the Tanohata mine and nagashimalite from the Mogurazawa mine (Matsubara and Kato, 1980).

wt.%	Tanohata	Mogurazawa
SiO <sub>2</sub>	33.56	32.37
V <sub>2</sub> O <sub>3</sub>	12.15	16.65
TiO <sub>2</sub>	5.29	2.75
Fe <sub>2</sub> O <sub>3</sub>	2.33	0
MnO	0.17	0.48
BaO	39.76	41.36
SrO	1.01	0
B <sub>2</sub> O <sub>3</sub>	4.56	4.0
Cl	1.98	1.73
H <sub>2</sub> O		0.77*
-O=Cl <sub>2</sub>	-0.44	-0.39
Total	100.55	99.72

as cubic using powder X-ray diffraction data and by observation of isotropic property. Although we tentatively assign V-rich garnet including momoiite to be cubic, it is uncertain whether our material is real cubic or not. In order to solve this problem we have to analyze the structure using a single crystal.

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