Journal of Mineralogical and Petrological Sciences, Volume 105, page 92–96, 2010

LETTER

Momoiite, $(Mn^{2+},Ca)_3(V^{3+},Al)_2Si_3O_{12}$, a new manganese vanadium garnet from Japan

Hidekazu TANAKA[*], Shunsuke ENDO[**], Tetsuo MINAKAWA[***], Masaki ENAMI[**],
Daisuke NISHIO-HAMANE[†], Hiroyuki MIURA[*] and Akihito HAGIWARA[‡]

[*] *Department of Natural History Sciences, Faculty of Science, Hokkaido University, Sapporo 060-0810, Japan*
[**] *Department of Earth and Planetary Sciences, Nagoya University, Nagoya 464-8602, Japan*
[***] *Department of Earth Science, Faculty of Science, Ehime University, Matsuyama 790-5877, Japan*
[†] *The Institute for Solid State Physics, the University of Tokyo, Kashiwa 277-8581, Japan*
[‡] *Irinotani 1-1, Taki-cho, Okazaki, Aichi 444-3173, Japan*

Momoiite, $(Mn^{2+},Ca)_3(V^{3+},Al)_2Si_3O_{12}$, an Mn^{2+}- and V^{3+}-rich analog of silicate garnet, was found in three localities: the Kurase (type locality), Hokkejino, and Fujii mines that are respectively located in Ehime, Kyoto, and Fukui Prefectures, Japan. Momoiite is greenish-yellow to emerald-green in color, and it occurs in the form of an aggregate having a size of up to 1 mm in a vein having a thickness of several millimeters with calcite and tephroite. Momoiite is optically isotropic, with n = 1.86(1). Its calculated density is 4.01 g/cm^3, and its hardness on the Mohs scale is 6.5. The representative empirical formula of momoiite from the Kurase mine is $(Mn_{1.80}Ca_{1.12}Mg_{0.04})_{\Sigma 2.96}(V_{1.51}Al_{0.52})_{\Sigma 2.03}Si_{3.00}O_{12}$ on the basis of O = 12 per formula unit. The mineral is cubic with a space group of $Ia\bar{3}d$, a = 11.9242(7) Å, V = 1695.5(3) Å^3, and Z =8. The strongest seven lines in the X-ray powder diffraction pattern [d *in* Å (I/I_0) (hkl)] are 2.982 (78) (400), 2.668 (100) (420), 2.435 (42) (510), 2.178 (20) (521), 1.935 (21) (611), 1.654 (20) (640), and 1.594 (30) (642). A momoiite solid solution substantially exists at relatively low pressure; however, extremely high momoiite content may not be formed in the pressure conditions of ore deposits in the Kurase, Hokkejino, and Fujii mines even if V and Mn are highly concentrated in the ore.

Keywords: Momoiite, Mn- and V-rich analog of silicate garnet, Kurase mine, Hokkejino mine, Fujii mine

INTRODUCTION

The silicate garnet group minerals are important rock-forming silicate minerals and they exhibit a wide range of solid-solutions. The general formula of silicate garnet is written as $X_3Y_2Si_3O_{12}$, where the X site has 8-fold dodecahedral coordination occupied by divalent cations and the Y site has 6-fold octahedral coordination occupied by trivalent cations in the common natural garnet. Common natural garnet has been discussed in terms of two series: ugrandite ($Ca_3Cr_2Si_3O_{12}$–$Ca_3Al_2Si_3O_{12}$–$Ca_3Fe_2Si_3O_{12}$) and pyralspite ($Mg_3Al_2Si_3O_{12}$–$Fe_3Al_2Si_3O_{12}$–$Mn_3Al_2Si_3O_{12}$), whereas the solid-solutions between these two series are limited in a small compositional range (Meagher, 1980). On the other hand, Momoi (1964) found a substitution between Ca and Mn in V-dominant garnet from the Yamato mine, Kagoshima Prefecture, Japan. Its solid solution can be expressed by two end-members: $Mn_3V_2Si_3O_{12}$ and $Ca_3V_2Si_3O_{12}$, which is called as goldmanite (Moench and Meyrowitz, 1964). However, $Mn_3V_2Si_3O_{12}$ was still a hypothetical end-member, because Mn occupancy in the X site was less than 50% in this garnet.

The authors re-examined the chemical compositions of manganese garnets from three metamorphosed manganese ore deposits in Japan, namely, Kurase, Hokkejino, and Fujii mines that are respectively located in the Ehime, Kyoto, and Fukui prefectures. We found a Mn- and V-dominant garnet with the compositions plotted in the $Mn_3V_2Si_3O_{12}$–$Ca_3V_2Si_3O_{12}$–$Ca_3Al_2Si_3O_{12}$–$Mn_3Al_2Si_3O_{12}$ system, and confirmed a new garnet with $(Mn,Ca)_3(V,Al)_2Si_3O_{12}$ composition. This garnet is called "momoiite" in honor of Professor Hitoshi Momoi (1930–2002), who first recognized the presence of $Mn_3V_2Si_3O_{12}$ molecules in the garnet. The new mineral data and its name, momoiite, have been approved by the Commission on New Minerals, Nomenclature and Classification, International Mineralogical

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doi:10.2465/jmps.091015a

H.Tanaka, tanakite@mail.sci.hokudai.ac.jp Corresponding author

Association (#2009-026). The type specimen of momoiite has been stored at the Hokkaido University Museum, Sapporo, Japan (#Mineral-07401). The type locality is registered at Kurase mine, Ehime Prefecture, Japan. Here, we describe a new Mn- and V-dominant member of the momoiite garnet.

ORE MINERALIZATION AND OCCURRENCE

The three momoiite localities in Japan are shown in Figure 1. The Kurase mine (lat. 33°48′N, long. 133°02′E), located approximately 1 km north of Natsuyabu, Saijo City, Ehime Prefecture, is a small-scale manganese ore deposit developed in the pelitic schist of the Sambagawa belt (Hara et al., 1992). The main constituent minerals of the ore at the Kurase mine are rhodonite, calcite, tephroite, goldmanite, spessartine, and vuorelainenite. The Hokkejino mine in Kyoto prefecture (lat. 34°45′N, long. 135°51′E) is a thermally metamorphosed manganese ore deposit embedded in the metachert of the Ryoke metamorphic belt (Nakajima, 1960). The manganese ore consists of rhodonite, tephroite, celsian, rhodochrosite, and pyrophanite. The Fujii mine (lat. 35°32′N, long. 135°51′E) located in Fukui prefecture is a bedded manganese deposit developed mainly in the chert of the Tamba accretionary complex. Ore deposits suffer a moderate grade of contact metamorphism due to the intrusion of granite (Matsubara and Kato, 1986). The associated minerals in the Fujii mine are classified into two types based on the presence or absence of quartz: those in type 1 are rhodonite, tephroite, rhodochrosite, spessartine, and nickeline, and those in type 2 are rhodonite, quartz, molybdenite, rhodochrosite, spessartine, and Mn-rich vanadoallanite-(La).

In Kurase mine, momoiite occurred in the form of aggregates having a size of up to 1 mm in a vein having a thickness of several millimeters with calcite and tephroite (Fig. 2), and a single crystal exhibits a subhedral shape having a size of 10-150 μm (Fig. 3). In Hokkejino mine, it occurs in the grain boundaries of tephroite and rhodonite in the form of aggregates having a size of up to 1 mm that are closely associated with spessartine. In the Fujii mine, it occurs in both types of mineral assemblages in the form of euhedral to subhedral grains having a diameter of up to 0.2 mm.

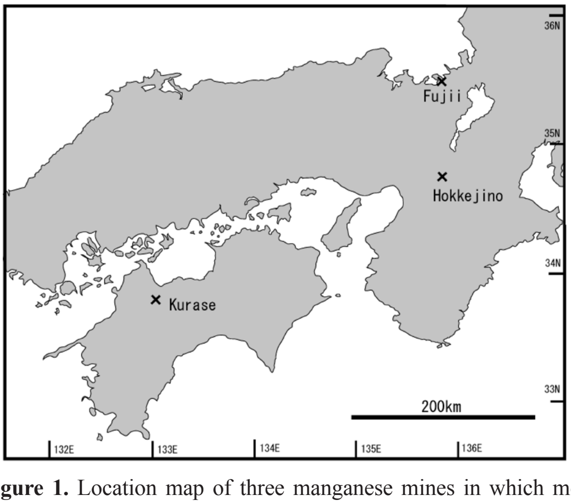

Figure 1. Location map of three manganese mines in which momoiite was found.

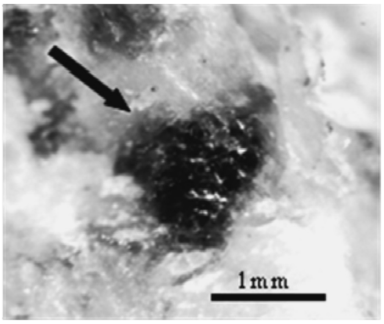

Figure 2. Photomicrograph of momoiite from Kurase mine. Momoiite (dark) occurs as an aggregate having a size of up to 1 mm in a calcite vein together with rhodochrosite (light) and tephroite (gray). Arrows indicate momoiite aggregates, and the bar indicates 1 mm.

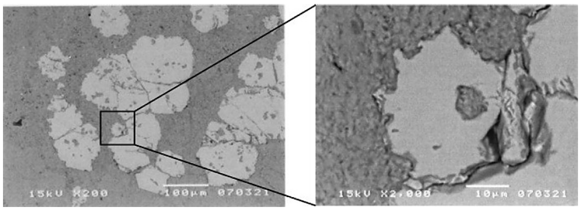

Figure 3. Backscattered electron image of momoiite from the Kurase mine. Momoiite (light) associated with rhodochrosite (dark).

OPTICAL AND PHYSICAL PROPERTIES

The optical and physical properties of momoiite were obtained from the sample collected from Kurase mine. Momoiite exhibits a translucent greenish-yellow to emerald-green color (Fig. 2), reflecting the chemical variations; however, most typically, it exhibits a green color. It exhibits a greenish tinge that increases with the V content, whereas it exhibits a yellowish color similar to that of spessartine with low V content. The streak of momoiite is also dull green in color, and the luster is vitreous and transparent. Momoiite is optically isotropic with $n = 1.86(1)$, 589 nm. Its hardness on the Mohs scale is 6.5 and the calculated density is 4.01 g/cm^3.

Table 1. Representative chemical compositions of Momoiite from the Kurase, Hokkejino, and Fujii mines

	Kurase		Hokkejino		Fujii	
	wt%	Range*	wt%	Range*	wt%	Range*
SiO_2	35.02	33.10-36.89	34.93	34.18-36.34	36.24	34.47-36.86
TiO_2	-	-	0.52	0.30-0.76	0.15	0.06-0.31
Al_2O_3	5.12	2.65-9.12	7.74	6.41-9.33	6.03	5.41-6.39
Cr_2O_3	-	-	1.33	0.79-1.77	0.29	0.17-0.40
V_2O_3	21.96	16.98-25.76	15.95	14.33-16.98	19.83	18.89-20.62
FeO	0.05	0-0.66	0.18	0.13-0.21	0.35	0.26-0.48
MnO	24.74	21.74-29.54	27.23	25.21-29.36	23.85	20.21-25.80
CaO	12.24	12.24-17.42	11.40	9.93-12.55	14.12	12.60-17.34
MgO	0.28	0-0.28	0.27	0.21-0.34	0.08	0.04-0.13
Total	99.41		99.55		100.94	
	O = 12		O = 12		O = 12	
Si	3.001		2.975		3.035	
Ti	-		0.033		0.009	
Al	0.517		0.777		0.595	
Cr	-		0.090		0.019	
V	1.509		1.089		1.331	
Fe	0.003		0.013		0.025	
Mn	1.796		1.964		1.692	
Ca	1.124		1.040		1.267	
Mg	0.036		0.034		0.010	
Total	7.986		8.014		7.983	

* Range of 10, 12, and 13 analyses for momoiite from Kurase, Hokkejino, and Fujii mines, respectively.

CHEMICAL PROPERTIES

The chemical analyses of the type specimen from Kurase mine were performed using a JEOL JXA5400 electron microprobe at Ehime University, and the ZAF method was used for correction. The analytical conditions were an accelerating voltage of 15 kV and a beam current of 0.4 nA. The live time was set to 120 s. The standard materials were $CaSiO_3$, corundum, vanadium metal, iron metal, manganese metal, $CaSiO_3$, and MgO for Si, Al, V, Fe, Mn, Ca, and Mg, respectively. The chemical variations of garnets from Kurase mine along with those from Hokkejino and Fujii mines are shown in Figure 4. The garnet compositions are plotted in the $Mn_3V_2Si_3O_{12}$-$Ca_3V_2Si_3O_{12}$-$Ca_3Al_2Si_3O_{12}$-$Mn_3Al_2Si_3O_{12}$ system as the formula was calculated on the basis of O = 12 per formula unit, and many garnets correspond to momoiite. The microprobe analyses of momoiite are shown in Table 1. Momoiite is characterized by high V_2O_3 and MnO contents as compared to spessartine and goldmanite, respectively (Fig. 4). The representative empirical formula of momoiite from the Kurase mine is $(Mn_{1.80}Ca_{1.12}Mg_{0.04})_{\Sigma 2.96}(V_{1.51}Al_{0.52})_{\Sigma 2.03}Si_{3.00}O_{12}$; this is simplified as $(Mn,Ca)_3(V,Al)_2Si_3O_{12}$. The ideal formula of momoiite ($Mn_3V_2Si_3O_{12}$) corresponds to the Mn-analog of goldmanite and the V-analog of spessartine.

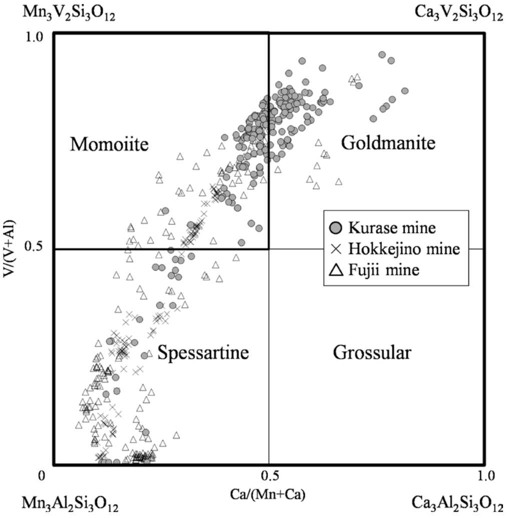

Figure 4. Plot of garnet solid-solution in the $Mn_3V_2Si_3O_{12}$-$Ca_3V_2Si_3O_{12}$-$Ca_3Al_2Si_3O_{12}$-$Mn_3Al_2Si_3O_{12}$ system from Kurase, Hokkejino, and Fujii mines.

X-RAY PROPERTIES

X-ray powder diffraction data of a momoiite sample from Kurase mine, which was mounted on a silicon non-reflection specimen holder, was collected using a Mac Science MX-Labo diffractometer with Cu*K*α radiation (40 kV, 40 mA, 0.5°-0.5°-0.3 mm slit), in a step-scanning mode over a 2θ range of 10–90° in increments of 0.02° (10 s/step). The X-ray intensity was estimated after monochromatization by pyrolytic graphite. The observed *d*-values and intensities are listed in Table 2 together with those of goldmanite (Moench and Meyrowitz, 1964). The X-ray diffraction patterns can be well indexed as a cubic cell and they are in good agreement with those of goldmanite. The observed reflection conditions, *hkl* with $h + k + l = 2n$, $0kl$ with $k = 2n$ and $l = 2n$, and *hhl* with $2h + l = 4n$, uniquely indicate the space group as $Ia\bar{3}d$. The least-square refinement using 17 reflections yielded the unit cell parameters a = 11.9242 (7) Å and V =grossular 1695.5(3) Å^3. Crystallographic data of garnet group minerals are listed in Table 3. Momoiite is slightly smaller than goldmanite and larger than spessartine and in the unit cell.

DISCUSSION

As the chemical analysis revealed that the Mg and Fe contents of momoiite are extremely low, the representative momoiite composition is considered as $(Mn,Ca)_3(V,Al)_2Si_3O_{12}$. Figure 4 shows the distribution of the observed chemical composition in the $Mn_3V_2Si_3O_{12}$–$Ca_3V_2Si_3O_{12}$–$Ca_3Al_2Si_3O_{12}$–$Mn_3Al_2Si_3O_{12}$ system, and the compositional variation indicates a substantial solid solution from spessartine to goldmanite through the momoiite field. It is evident that a part of the observed garnet compositions are plotted in the momoiite region (Fig. 4). Because the ore mineral assemblage suggests that momoiite is formed by the metamorphism of the V-bearing protolith bedded in the manganese ore deposits, high V and Mn concentrations in the ore may suggest high momoiite content in the garnet. However, near end-member momoiite was not found in our samples from three manganese ore deposits despite the presence of vuorelainenite (MnV_2O_4) in some momoiite-bearing samples. This suggests that other conditions are necessary for high momoiite content in addition to high V and Mn concentrations.

Table 2. X-ray powder diffraction data for momoiite and goldmanite

			Momoiite			Goldmanite*	
h	*k*	*l*	*I*/*I*o	d_{obs}	d_{calc}	*I*/*I*o	d_{obs}
2	2	0	7	4.225	4.216	12	4.255
4	0	0	78	2.982	2.981	65	3.005
4	2	0	100	2.667	2.666	100	2.688
3	3	2	19	2.541	2.542	9	2.565
4	2	2	42	2.435	2.434	38	2.453
4	3	1	20	2.339	2.339	16	2.357
5	2	1	20	2.178	2.177	16	2.194
6	1	1	21	1.935	1.934	22	1.951
6	2	0	11	1.886	1.885	8	1.901
4	4	4	12	1.722	1.721	8	1.735
6	4	0	20	1.654	1.654	18	1.667
6	4	2	30	1.594	1.593	49	1.607
8	0	0	13	1.49	1.491	10	1.502
8	4	0	11	1.333	1.333	9	1.345
8	4	2	12	1.301	1.301	10	1.312
6	6	4	9	1.271	1.271	4	1.282
10	4	0	8	1.107	1.107	9	1.117
			a = 11.9242(7) Å			a = 12.011 Å	
			V = 1695.5(3) Å^3			V = 1732.8 Å^3	

* Moench and Meyrowitz (1964).

We preliminarily considered the physical conditions required to from near end-member momoiite. Figure 5 shows the existence limit of silicate garnet for ionic radii of the X and Y cations (Novak and Gibbs, 1971) and the stability of the garnet end-member (Schreyer and Baller, 1981) together with our garnet compositions. Novak and Gibbs (1971) proposed an existence limit for garnet based

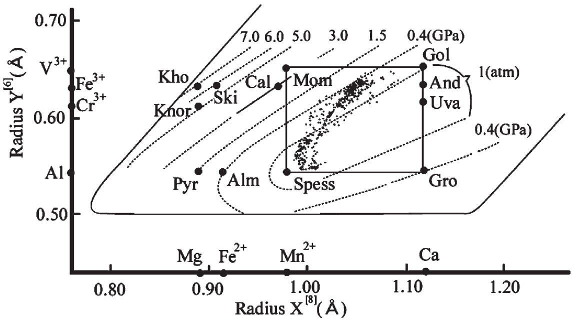

Figure 5. Radii of the 6-fold versus 8-fold coordinated cations for garnet end-members. Solid curve indicate the existence limit for garnet proposed by Novak and Gibbs (1971), and the isobars delineate their low-pressure limits of stability at 1000 °C (after Schreyer and Baller, 1981). The superimposed plots are recalculated from the observed chemical composition shown in Figure 4. Alm, almandine; And, andradite; Cal, calderite; Gol, goldmanite; Gro, grossular; Kho, khoharite; Knor, Knorringite; Mom, momoiite; Pyr, pyrope; Ski, skiagite; Spess, spessartine; Uva, uvarovite.

Table 3. Comparative data of momoiite with some other garnet group minerals

Name	Momoiite	Goldmanite	Spessartine	Grossular
Ideal end-member	$Mn_3V_2Si_3O_{12}$	$Ca_3V_2Si_3O_{12}$	$Mn_3Al_2Si_3O_{12}$	$Ca_3Al_2Si_3O_{12}$
a (Å)	11.9242(7)	12.011	11.612	11.69
V (Å^3)	1695.5(3)	1732.756	1565.745	1597.509
Reference	This study	*	*	*

* Novak and Gibbs (1971).

on the crystal structural constraints, and Schreyer and Baller (1981) added isobars delineating the approximate low-pressure limits of stability of the various garnet end-members for a fixed temperature of 1000 °C. Our momoiite solid solution distributes in a range of 1 atm to 0.4 GPa (Fig. 5), and this is consistent with the deposit formation of Kurase, Hokkejino, and Fujii mines as these deposits did not suffer ultrahigh-pressure metamorphism. On the other hand, the momoiite end-member is plotted around the isobar of 3 GPa in Figure 5. Therefore, extremely high momoiite content may not be found in the garnet solid solution from the Kurase, Hokkejino, and Fujii mines because of the relatively low-pressure formation of the manganese deposits, even if V and Mn are highly concentrated in the ore.

ACKNOWLEDGMENTS

We wish to thank to Dr. S. Matsubara, Department of Geology and Palaeontology, National Museum of Nature and Science for his helpful advice and encouragement. Thanks are also due to Miss. H. Akamatsu for the sample preparation and to Mr. M. Sasaki for assistance with the microscopic examination of the sample.

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Manuscript received October 15, 2009
Manuscript accepted January 21, 2010

Manuscript handled by Hiroharu Matsueda