

# Morimotoite, $\text{Ca}_3\text{TiFe}^{2+}\text{Si}_3\text{O}_{12}$ , a new titanian garnet from Fuka, Okayama Prefecture, Japan

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## Abstract

Morimotoite,  $\text{Ca}_3\text{TiFe}^{2+}\text{Si}_3\text{O}_{12}$ , has been found in contaminated rocks which are considered to be a kind of endoskarn at Fuka, Bitchu-Cho, Okayama Prefecture, Japan. Morimotoite is derived from andradite,  $\text{Ca}_3\text{Fe}_2^{3+}\text{Si}_3\text{O}_{12}$ , by the substitution  $\text{Ti} + \text{Fe}^{2+} = 2\text{Fe}^{3+}$ . It is associated with calcite, vesuvianite, grossular, wollastonite, hematite, prehnite, fluorapatite, perovskite, zircon, baddeleyite and calzirtite. It is cubic with space group  $la3d$ . The unit cell dimension  $a$  is 12.162(3) Å. Its refractive index  $n$  is 1.995(2) and the density 3.75(2)  $\text{g cm}^{-3}$  (meas.), 3.80  $\text{g cm}^{-3}$  (calc.). The Mohs' hardness is 7.5. Calculation of the analytical data on the basis of twelve oxygen atoms and eight cations shows that this mineral has a simplified chemical formula  $\text{Ca}_3(\text{Ti,Fe}^{2+},\text{Fe}^{3+})_2(\text{Si,Fe}^{3+})_3\text{O}_{12}$  where  $\text{Ti} > \text{Fe}^{2+} > 0.5$ . Morimotoite was synthesized at low oxygen fugacities, 650 and 700°C and 1 kbar total pressure.

KEYWORDS: morimotoite, titanium, garnet, skarn, Okayama Prefecture, Japan.

## Introduction

In titanian andradite, it is usual that titanium is mainly in the octahedral position replacing ferric iron and the ferric iron in the tetrahedral position replacing the silicon (Koenig, 1886; Huggins *et al.*, 1977a; Flohr and Ross, 1989). The coupled substitution results in the schorlomite component,  $\text{Ca}_3\text{Ti}_2\text{Fe}_2^{3+}\text{Si}_3\text{O}_{12}$ . Morimotoite is the titanian garnet distinct from schorlomite and contains more than 50 mol. % of the morimotoite component,  $\text{Ca}_3\text{TiFe}^{2+}\text{Si}_3\text{O}_{12}$ .

We have named this new mineral morimotoite for Dr Nobuo Morimoto (1925- ), Emeritus Professor of Osaka University, in recognition of his outstanding contributions to the fields of mineralogy and

crystallography. The mineral species and its name have been approved by the Commission on New Mineral and Mineral Names, International Mineralogical Association, in July 1992. The type material of morimotoite is deposited at the National Science Museum, Tokyo, Japan.

Syntheses of schorlomite,  $\text{Ca}_3\text{Ti}_2\text{Fe}_2^{3+}\text{Si}_3\text{O}_{12}$ , and garnets with compositions intermediate between that and andradite,  $\text{Ca}_3\text{Fe}_2^{3+}\text{Si}_3\text{O}_{12}$ , have been carried out by Ito and Frondel (1967), Huckenholz (1969) and others. However, titanian garnet with the morimotoite component has not been synthesized.

The present paper deals with the mineralogical properties and mode of occurrence of the morimotoite found at Fuka. The result of preliminary synthesis of morimotoite at low oxygen fugacity is described.

TABLE 1. Chemical analyses of morimotoite and representative analyses of the rim garnets. The composition of morimotoite is the mean result of seven analyses

	Morimotoite	Rim garnets					
		1	2	3	4	5	6
SiO <sub>2</sub>	26.93(0.12)	35.95	33.45	28.39	29.18	28.70	28.60
TiO <sub>2</sub>	18.51(0.17)	1.99	5.37	10.78	12.87	19.07	19.59
ZrO <sub>2</sub>	1.48(0.12)	0.47	1.27	3.19	1.00	0.02	0.03
Al <sub>2</sub> O <sub>3</sub>	0.97(0.05)	6.69	6.62	3.81	4.36	1.02	0.10
Fe <sub>2</sub> O <sub>3</sub> *	11.42(0.37)	20.24	17.82	18.46	11.06	8.22	8.77
FeO*	7.78(0.30)	0.27	1.37	2.90	8.25	9.66	9.78
MnO	0.23(0.03)	0.09	0.04	0.11	0.15	0.01	0.01
MgO	0.87(0.04)	0.27	0.41	0.50	0.68	0.31	0.22
CaO	31.35(0.16)	34.52	33.91	32.48	32.72	32.22	32.53
Total	99.54	100.49	100.26	100.62	100.35	99.22	98.62
Atomic proportions (O=12)							
Si	2.321	2.291	2.747	2.404	2.449	2.456	2.450
Ti	1.199	0.122	0.332	0.686	0.812	1.227	1.261
Zr	0.062	0.019	0.051	0.132	0.041	0.001	0.001
Al	0.095	0.640	0.641	0.380	0.431	0.103	0.010
Fe <sup>3+</sup>	0.740	1.237	1.101	1.176	0.967	0.529	0.565
Fe <sup>2+</sup>	0.560	0.018	0.094	0.205	0.265	0.691	0.700
Mn	0.017	0.006	0.003	0.008	0.011	0.001	0.001
Mg	0.112	0.033	0.050	0.063	0.085	0.040	0.028
Ca	2.894	3.004	2.983	2.946	2.940	2.953	2.984

\* Fe<sup>3+</sup> and Fe<sup>2+</sup> calculated based on stoichiometry of 8 cations per 12 oxygens.

### Occurrence

Skarns were formed on both sides of the quartz monzonite dykes that penetrated in limestones at Fuka. The skarns consist mainly of gehlenite and spurrite. Some parts of the skarns are altered to retrograde minerals such as garnet, vesuvianite, bicchulite (Henmi *et al.*, 1973), fukalite (Henmi *et al.*, 1977) and others. Contaminated rocks occur between the quartz monzonite and skarns. The contaminated rock was derived from a magma which intruded the limestone and subsequently changed its composition during the formation of skarns. The contaminated rock may be identical to that reported at Crestmore, California, by Burnham (1959). It usually consists of pyroxene and feldspar and some times contains various amounts of grossular, vesuvianite and wollastonite.

Morimotoite occurs in the contaminated rock and is associated with clinopyroxene, feldspar, vesuvianite, grandite garnet, wollastonite, prehnite and with small amounts of perovskite, titanite, apatite, biotite, epidote, hematite, zircon, baddeleyite and calzirtite.

### Physical and optical properties

Morimotoite occurs as euhedral or subhedral grains up to 15 mm with or without rims of grandite garnet. The mineral is black in colour with adamantine lustre. Cleavage is not observed. It is isotropic with refractive index  $n = 1.955(2)$  measured with Na light (589 nm). Vickers microhardness is 1070–1150 Kg mm<sup>-2</sup> (50 g load) and the Mohs' hardness is 7.5. The density measured with heavy liquids is 3.75(2) g cm<sup>-3</sup>. The calculated density is 3.80 g cm<sup>-3</sup>.

The IR spectra of morimotoite are measured using the conventional KBr method for the region 4000 to 650 cm<sup>-1</sup>. The spectra are very similar to those for schorlomite reported by Tarte *et al.* (1979).

### Chemical composition

Seven chemical analyses were carried out by an electron microprobe analyser using the following standards: CaSiO<sub>3</sub> (Ca, Si), TiO<sub>2</sub> (Ti), Zircon (Zr), Al<sub>2</sub>O<sub>3</sub> (Al), Fe<sub>2</sub>O<sub>3</sub> (Fe), MnO (Mn) and MgO (Mg). The mean result is given in Table 1. No absorption

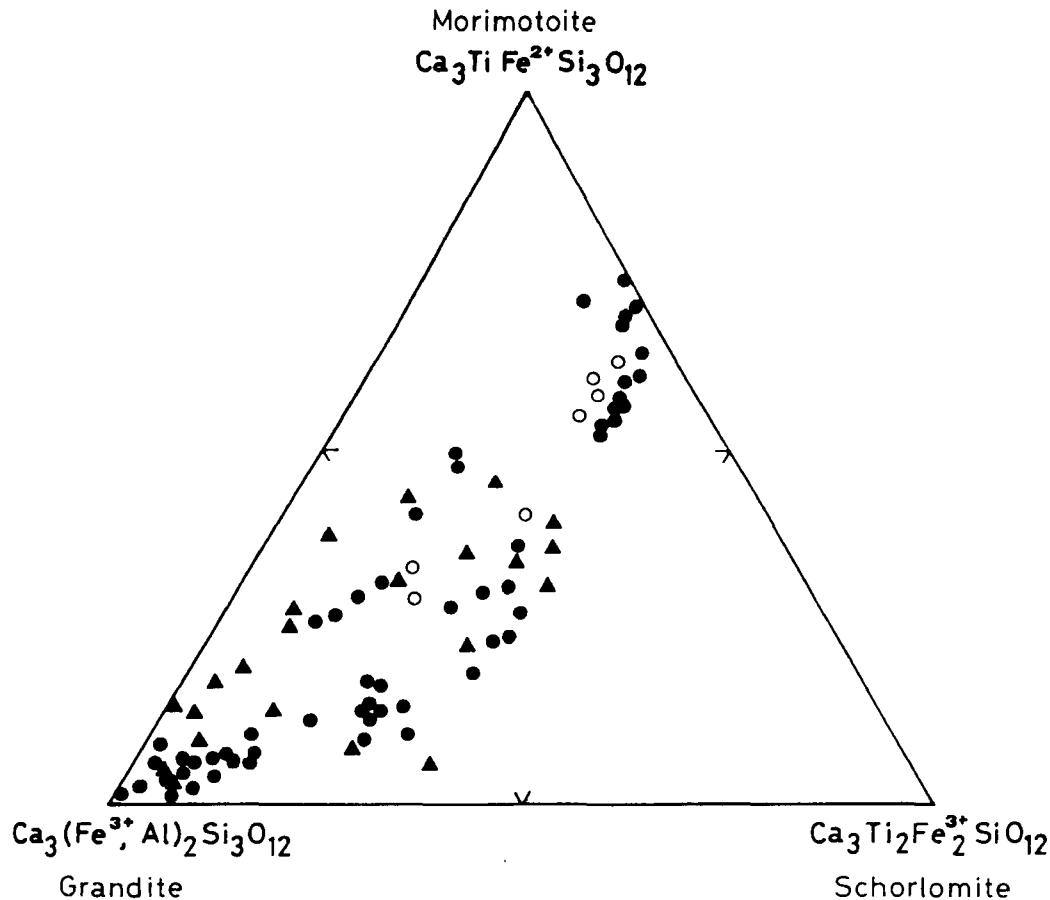


FIG. 1. The relative proportions of the morimotoite, grandite (grossular + andradite) and schorlomite components for garnets. Solid circles indicate the garnets from Fuka. Triangles indicate garnets taken from the previous studies (Huckenholz, 1969; Dowty, 1971; Huggins *et al.*, 1977b; Deer *et al.*, 1982; Dawson *et al.*, 1992). Open circles indicate those synthesized in the present study.

bands for OH were observed in the IR spectra. The  $\text{Fe}_2\text{O}_3$  and FeO contents were calculated based on the stoichiometry (O = 12 and total cations = 8). The relative preference for the tetrahedral site are considered to be in the order  $\text{Al} > \text{Fe}^{3+} > \text{Ti}$ , according to Huggins *et al.* (1977a) and Gongbao and Baolei (1986). The empirical formula is  $(\text{Ca}_{2.89}\text{Mg}_{0.11})_{3.00}(\text{Ti}_{1.20}\text{Fe}_{0.56}^{2+}\text{Fe}_{0.16}^{3+}\text{Zr}_{0.06}\text{Mn}_{0.02})_{2.00}(\text{Si}_{2.32}\text{Fe}_{0.58}^{3+}\text{Al}_{0.10})_{3.00}\text{O}_{12.00}$ . The simplified formula is  $\text{Ca}_3(\text{Ti}, \text{Fe}^{2+}, \text{Fe}^{3+})_2(\text{Si}, \text{Fe}^{3+})_3\text{O}_{12}$ . The analytical data represent material which contains more than 50 mole percent of the ideal end-member,  $\text{Ca}_3\text{TiFe}^{2+}\text{Si}_3\text{O}_{12}$ .

Morimotoite crystals are generally homogeneous in composition at the core, but compositional

variations are observed in the rims. Representative chemical analyses for the rims are listed in Table 1. The rims are usually rich in the grandite component (1 to 4) and rarely rich in the morimotoite component (5 and 6). Garnet compositions from Fuka are shown in the triangular diagrams (Figs 1 and 2). The compositions are compared with those of previous workers (Huckenholz, 1969; Dowty, 1971; Huggins *et al.*, 1977b; Deer *et al.*, 1982; Dawson *et al.*, 1992).

#### X-ray studies

Precession and Weissenberg photographs show that morimotoite is cubic with the space group  $la3d$ . The X-ray powder diffraction data for morimotoite are

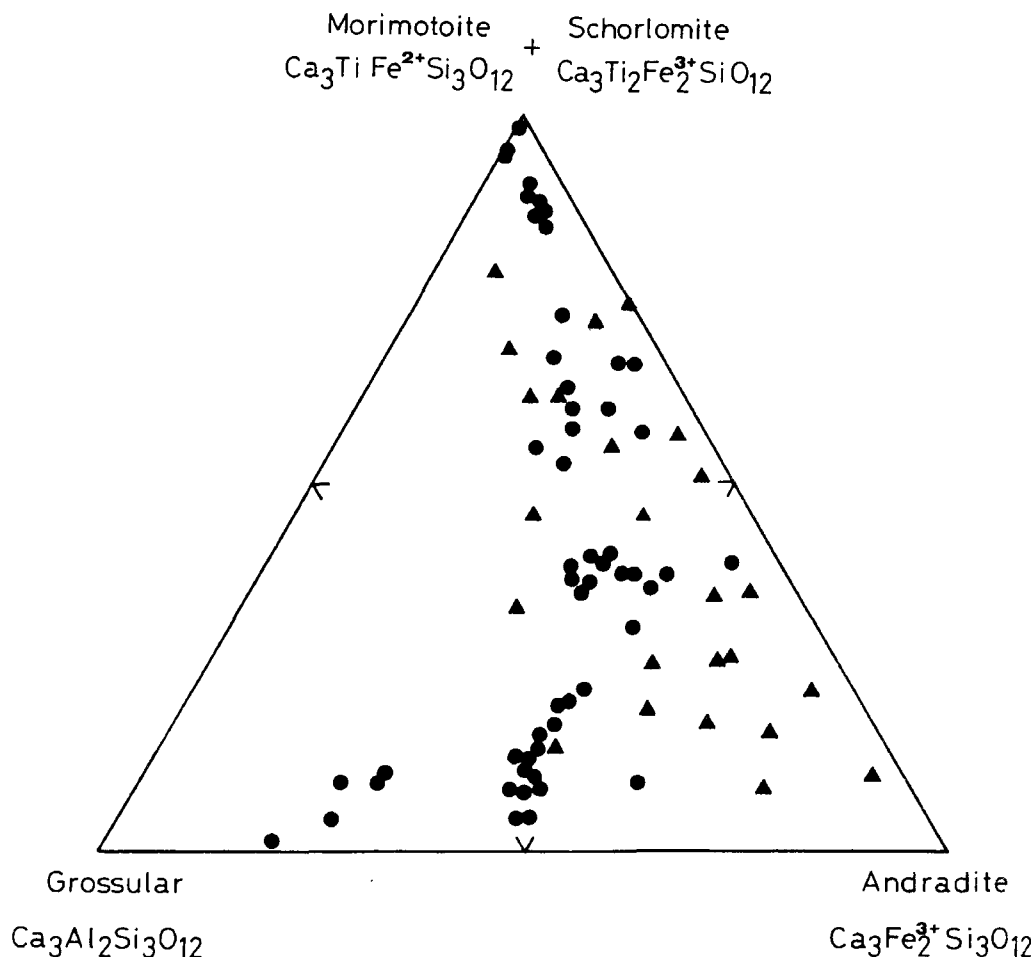


FIG. 2. The relative proportions of titanian garnets (morimotoite + schorlomite), grossular and andradite components for garnets. Solid circles indicate the garnets from Fuka. Triangles indicate garnets taken from the previous studies (Huckenholz, 1969; Dowty, 1971; Huggins *et al.*, 1977*b*; Deer *et al.*, 1982; Dawson *et al.*, 1992).

listed in Table 2. The cell dimension refined from the powder data is:  $a = 12.162(3)$  Å. X-ray data show that morimotoite is one of the garnet group minerals.

#### Synthesis of morimotoite

Hydrothermal synthesis of morimotoite was initially carried out using the iron-wüstite and the iron-quartz-fayalite buffers. The starting materials were prepared using reagent grade silica gel, active alumina, titanium oxide, iron oxide and calcium carbonate. The starting mixtures with the ratio Ca:Fe:Ti:Si = 3:1:1:3 with small amount of water were sealed in

$\text{Ag}_{70}\text{Pd}_{30}$  tubes. The tubes and the buffer were sealed in gold tubes. Runs were restricted at 1 kbar total pressure and at 650°C and 700°C.

Some experiments were carried out at very low oxygen fugacity using metal silicon and metal iron with no buffer. The starting materials with small amounts of water were sealed in gold tubes.

Euhedral crystals of titanian garnet with rhombic dodecahedra were synthesized. The crystals are black in colour and 30–150 µm in diameter. The chemical compositions of the morimotoite crystals synthesized were analysed by means of electron probe micro-analyser. Representative results are listed in Table 3

TABLE 2. X-ray powder diffraction data for morimotoite from Fuka. The calculated values are based on  $a = 12.162 \text{ \AA}$ 

<i>l</i>	<i>d</i> (meas.)	<i>d</i> (calc.)	<i>hkl</i>
13	4.298	4.300	220
72	3.039	3.040	400
100	2.720	2.720	420
19	2.593	2.593	332
51	2.483	2.482	422
21	2.385	2.385	431
18	2.220	2.220	521
24	1.973	1.973	611,532
19	1.923	1.923	620
16	1.756	1.755	444
26	1.687	1.687	640
56	1.626	1.625	642
16	1.520	1.520	800

TABLE 3. Representative analyses of morimotoite synthesized in the present study

	1	2	3	4
SiO <sub>2</sub>	28.50	28.53	28.39	28.97
TiO <sub>2</sub>	18.82	18.45	18.02	16.14
Fe <sub>2</sub> O <sub>3</sub> *	10.50	11.18	12.67	13.99
FeO*	9.95	9.40	8.57	8.22
CaO	32.05	32.24	32.46	31.95
Total	99.82	99.80	100.11	99.27
Atomic proportions (O=12)				
Si	2.446	2.448	2.431	2.499
Ti	1.215	1.191	1.160	1.047
Fe <sup>3+</sup>	0.678	0.722	0.817	0.908
Fe <sup>2+</sup>	0.714	0.675	0.614	0.593
Ca	2.948	2.964	2.978	2.953

\* Fe<sup>3+</sup> and Fe<sup>2+</sup> calculated based on the stoichiometry of 8 cations per 12 oxygens

and Fig. 1. The cell dimension is  $12.17 \text{ \AA}$ . Morimotoite with the end-member composition, Ca<sub>3</sub>TiFe<sup>2+</sup>Si<sub>3</sub>O<sub>12</sub>, has not been synthesized.

### Discussion

Morimotoite is defined as a member of garnet group of minerals and contains more than 50% of the morimotoite component Ca<sub>3</sub>TiFe<sup>2+</sup>Si<sub>3</sub>O<sub>12</sub>. This is derived from end-member andradite by the substitution  $\text{Ti} + \text{Fe}^{2+} = 2\text{Fe}^{3+}$ . This substitution is well known in pyroxenes, e.g. the substitution of  $\text{Ti}_{0.5}\text{Fe}_{0.5}^{2+}$  in aegirine results in titanian aegirine (Morimoto, 1988). The substitution is also known in some mineral groups, e.g. the aenigmatite group (Gaeta and Mottana, 1991) and the magnetoplumbite group. Morimotoite is the distinct titanian garnet from schorlomite, Ca<sub>3</sub>Ti<sub>2</sub>Fe<sub>2</sub><sup>3+</sup>SiO<sub>12</sub>, reported from Magnet Cove by Koenig (1886) and Flohr and Ross (1989).

The morimotoite component is identical with one of the garnet end-members which were postulated for titanian andradite solid solutions by Huckenholz (1969), Dowty (1971), Huggins *et al.* (1977b), Platt and Mitchell (1979) and Gongbao and Baolei (1986). Mössbauer spectroscopy suggests that this component occurs as a possible constituent in titanian garnets (Huggins *et al.*, 1977b; Schwartz *et al.*, 1980).

Mössbauer spectroscopic study shows the presence of Fe<sup>2+</sup> in the octahedral site and that of Fe<sup>3+</sup> in the octahedral and tetrahedral sites. Presence of Ti<sup>3+</sup> is possible as described by Howie and Woolley (1968), Huggins *et al.* (1977b), Schwartz *et al.* (1980) and by Gongbao and Baolei (1986). Huggins *et al.* (1977b),

Schwartz *et al.* (1980) and Gongbao and Baolei (1986) described electron-hopping, electron delocalization and charge transfer between Fe cations and presumably Ti cations in titanian andradites. At high temperatures, as morimotoite crystallizes, extensive electron-hopping (or electron delocalization or charge transfer) between Fe and Ti cations occurs rapidly so that no distinction of different valence states of the Fe and Ti cations can be made with respect to cation exchange. Therefore, we consider that the Fe<sup>2+</sup> in the octahedral site represents the total number of reducing cations.

The effect of TiO<sub>2</sub> on the cell-size, refractive index and specific gravity in titanian andradite and schorlomite has been described by Howie and Woolley (1968). The linear relationship between the TiO<sub>2</sub> content and cell-size is also reported by Kusachi *et al.* (1975). Morimotoite is different from schorlomite in that the former has a smaller cell-size, lower refractive index and lower specific gravity than schorlomite with the same TiO<sub>2</sub> content.

Morimotoite crystals are generally homogeneous in composition at the core, but compositional variations are observed in their rims. The rims are usually titanium-poor. Figure 1 and Table 1 show the trend of chemical composition from morimotoite through titanian grandite to grandite. Figure 2 shows that outer rims are grandite (Gr<sub>50</sub>An<sub>50</sub>) or grossular (Gr<sub>70</sub>An<sub>30</sub>). Titanium-rich rims (Table 1, Nos. 5 and 6) have the morimotoite component up to 70 mol. %. Because the titanium-rich rims are thin (about 20 μm), we were unable to determine the physical properties.

The high contents of ferrous iron in morimotoite indicate low oxygen fugacity compared to that for schorlomite. Virgo *et al.* (1976) showed that natural titanian garnets are stable at low oxygen fugacities. The compositions of morimotoite synthesized with the iron-wüstite buffer are similar to that of morimotoite from Fuka. It is concluded that morimotoite was crystallized from a magma at low oxygen fugacity.

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