

TABLE 2. Electron microprobe chemical data for 'ferrazite' and gorceixite

	1	2	Range	Probe standard
BaO	30.00	23.52	(22.46–24.99)	BaF <sub>2</sub>
PbO		0.53	(0.00–1.65)	galena
SrO		1.81	(1.29–2.25)	celestine
CaO		0.76	(0.66–0.84)	wollastonite
Na <sub>2</sub> O		0.06	(0.00–0.19)	andesine
K <sub>2</sub> O		0.10	(0.06–0.12)	microcline
Al <sub>2</sub> O <sub>3</sub>	29.91	31.25	(29.54–32.42)	corundum
Fe <sub>2</sub> O <sub>3</sub>		3.76	(1.11–8.40)	hematite
P <sub>2</sub> O <sub>5</sub>	27.76	26.19	(25.13–27.28)	InP
SiO <sub>2</sub>		0.95	(0.65–1.18)	wollastonite
H <sub>2</sub> O	12.33	(11.07)		
Total	100.00	100.00		

1. Gorceixite, ideal composition BaAl<sub>3</sub>(PO<sub>4</sub>)(PO<sub>3</sub>OH)(OH)<sub>6</sub>.
2. 'Ferrazite' from Diamantina, Minas Gerais, Brazil (Average of 10 analyses: H<sub>2</sub>O by difference)..

Ba by gravimetry with precipitation of PbSO<sub>4</sub> and BaSO<sub>4</sub>, thus confusing Ba with Pb.

In conclusion, ferrazite is identical to gorceixite. The name gorceixite (Hussak, 1906) was published before ferrazite and therefore has historical priority.

KEYWORDS: ferrazite, gorceixite, Minas Gerais, Brazil.

This nomenclature proposal (number 95-F) was approved by CNMMN - IMA.

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## Comment on 'Morimotoite, Ca<sub>3</sub>TiFe<sup>2+</sup>Si<sub>3</sub>O<sub>12</sub>, a new titanian garnet from Fuka, Okayama Prefecture, Japan' by Henmi *et al.* (1995)

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HENMI *et al.* (1995) described a new titanian garnet end-member whose composition can be derived from

andradite by the substitution  $Ti + Fe^{2+} = 2 Fe^{3+}$  on octahedral sites, leading to the formula

$\text{Ca}_3\text{Ti}^{4+}\text{Fe}^{2+}\text{Si}_3\text{O}_{12}$ . This component, previously called 'Fe-melanite' as a hypothetical end-member by Huckenholz (1969), was named morimotoite by Henmi *et al.* (1995) and accepted by the Commission on New Minerals and Mineral Names, I.M.A. as a new mineral. In their paper, Henmi *et al.* claimed that "titanian garnet with the morimotoite component has not been synthesized". Single-phase Ti-andradites in the system Ca-Fe-Ti-Si-O-H, however, were synthesized at different oxygen fugacities by Kühberger *et al.* (1988, 1989). These Ti-andradites contain up to 48.3 mole % of a  $3\text{Ca}:1\text{Fe}:1\text{Ti}:3\text{Si}:12\text{O}$  component at 750°C and 3 kbar and oxygen fugacities of the iron-quartz-fayalite buffer (TA13 in Kühberger *et al.*, 1989). The pure end-member with that bulk chemistry was found not to be stable at oxygen fugacities of the IQF buffer in the pressure and temperature range 1 to 7 kbar and 500 to 1000°C respectively. The stable phase assemblages include Ti-andradites of intermediate compositions, plotting in the pseudo-ternary system  $3\text{Ca}:2\text{Fe}:3\text{Si}:12\text{O}$  (andradite) –  $3\text{Ca}:2\text{Fe}:1.5\text{Ti}:1.5\text{Si}:12\text{O}$  (schorlomite) –  $3\text{Ca}:1\text{Fe}:1\text{Ti}:3\text{Si}:12\text{O}$ , besides perovskite, wollastonite, magnetite, and titanite. These results are in accordance with preliminary synthesis experiments of Henmi *et al.* (1995) at 650 to 700°C and 1 kbar, IQF buffer. Unfortunately the associated phases or other run data were not reported by them. Their microprobe analyses of the limiting Ti-andradite solid solution reveal slightly higher Ti and slightly lower Fe than in single-phase Ti-andradite, TA13, of Kühberger *et al.* (1989), as shown in Table 1. The unit cell parameters of the two synthetic Ti-garnets also exhibit similar values of 12.17 Å and 12.166 Å for TA13 respectively and correspond with the value of 12.162 Å for morimotoite (see Table 1). The composition of morimotoite is close to the synthetic Ti-garnets, as shown in Table 1.

Henmi *et al.* (1995) have not found any structurally bound  $(\text{OH})^-$  by means of IR spectra (KBr pellet technique). Contents of  $\text{H}_2\text{O}$  between 0.1 to 0.22 wt.%, however, were measured by Kühberger *et al.* (1989) by means of a solids moisture analyser in synthetic and natural Ti-andradites. The existence of structurally bound  $(\text{OH})^-$  was verified by single crystal FTIR spectroscopy in natural melanite from Kaiserstuhl by Amthauer and Rossman (1994, 1995). Such low  $\text{H}_2\text{O}$  values cannot be detected with the KBr pellet technique due to the hygroscopic nature of KBr, obscuring low  $\text{H}_2\text{O}$  contents of enclosed samples. The valence state of Fe was calculated by Henmi *et al.* (1995) on the basis of 12 oxygens per formula unit and fixed valence of 4 for Ti. They argued that, due to the high crystallization temperatures of morimotoite, electron hopping processes occur and "that no distinction of different valence states of Fe and Ti can be made with respect to cation exchange". This is

not valid, as pointed out by Kühberger *et al.* (1989), because electron hopping processes are unlikely to occur between sites which are sharing common corners only, as octahedral and tetrahedral sites in the garnet structure. Empirical formulae were deduced by Henmi *et al.* (1995) under the assumption that the relative preference for the tetrahedral site in Ti-garnets is  $\text{Al} > \text{Fe}^{3+} > \text{Ti}^{4+}$ . Kühberger *et al.* (1989) determined the valence states and site distributions of Fe by low temperature Mössbauer spectroscopy. The result for their TA13 is depicted in Table 1 and demonstrates that  $\text{Fe}^{2+}$  and  $\text{Fe}^{3+}$  are distributed over octahedral and tetrahedral sites, as dodecahedral sites are completely occupied by Ca.

Charge balance calculations by Kühberger *et al.* (1989) result in appreciable amounts of octahedrally coordinated trivalent Ti, when considering structurally bounded  $(\text{OH})^-$  and experimentally determined ferric/ferrous iron ratios. Additional qualitative XPS study of TA13 clearly confirms two different valence states of Ti (Fehr *et al.*, 1990). Similar results were recently obtained by Malitesta *et al.* (1995), who quantitatively determined the  $\text{Ti}^{3+}/\text{Ti}^{4+}$  and  $\text{Fe}^{3+}/\text{Fe}^{2+}$  ratios by XPS in two natural Ti-garnets. In accordance with Kühberger *et al.* (1989) they also found high amounts of  $\text{Ti}^{3+}$  besides  $\text{Fe}^{3+}$ ,  $\text{Fe}^{2+}$ , and  $\text{Ti}^{4+}$  on octahedral sites. Therefore, the compound  $3\text{Ca}:1\text{Ti}:1\text{Fe}:3\text{Si}:12\text{O}$  consists of two distinct end-members, displaying the formulae  $\text{Ca}_3\text{Ti}^{4+}\text{Fe}^{2+}\text{Si}_3\text{O}_{12}$  and  $\text{Ca}_3\text{Ti}^{3+}\text{Fe}^{3+}\text{Si}_3\text{O}_{12}$ . Both components occur in different portions in synthetic and natural Ti-garnets as well. For instance, the total amount of 48.3 mole%  $3\text{Ca}:1\text{Ti}:1\text{Fe}:3\text{Si}:12\text{O}$  compound in TA13 is distributed into 21.9 mole% of a  $\text{Ca}_3\text{Ti}^{4+}\text{Fe}^{2+}\text{Si}_3\text{O}_{12}$  component and 26.4 mole%  $\text{Ca}_3\text{Ti}^{3+}\text{Fe}^{3+}\text{Si}_3\text{O}_{12}$  component respectively. Müntener and Hermann (1994) determined, on the basis of data from microprobe, Mössbauer spectroscopy, X-ray single crystal and colorimetric measurements, the composition of natural Ti-andradites, revealing 35 to 43 mole%  $\text{Ca}_3\text{Ti}^{3+}\text{Fe}^{3+}\text{Si}_3\text{O}_{12}$  and 42 to 34 mole%  $\text{Ca}_3\text{Ti}^{4+}\text{Fe}^{2+}\text{Si}_3\text{O}_{12}$  component respectively.

It has to be expected that in morimotoite octahedrally coordinated Fe and Ti also occur in different valence states, expressed as  $\text{Ca}_3\text{Ti}^{4+}\text{Fe}^{2+}\text{Si}_3\text{O}_{12}$  and  $\text{Ca}_3\text{Ti}^{3+}\text{Fe}^{3+}\text{Si}_3\text{O}_{12}$  components. Neither the predominance nor the exclusive occurrence of the component  $\text{Ca}_3\text{Ti}^{4+}\text{Fe}^{2+}\text{Si}_3\text{O}_{12}$  in type material morimotoite is verified by Henmi *et al.* (1995). Therefore, additional spectroscopic analyses are required for morimotoite in order to determine exactly its crystal chemistry.

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TABLE 1. Microprobe data and crystal chemistry of Ti-garnets

P(kb)/T (°C)/buffer	Morimotoite <sup>(a)</sup>	Ti-gar <sup>(b)</sup>	TA13 <sup>(c)</sup>
	natural	1/650 - 700/IQF	3/750 /IQF
SiO <sub>2</sub>	26.93	28.39	27.61
TiO <sub>2</sub>	18.51	18.02	16.71
ZrO <sub>2</sub>	1.48		
Al <sub>2</sub> O <sub>3</sub>	0.97		
Fe <sub>2</sub> O <sub>3</sub>	11.42 <sup>(d)</sup>	12.67 <sup>(d)</sup>	23.33 <sup>(e)</sup>
FeO	7.78 <sup>(d)</sup>	8.57 <sup>(d)</sup>	
MnO	0.23		
MgO	0.87		
CaO	31.35	32.46	32.34
H <sub>2</sub> O			0.22
Si <sup>4+</sup>	2.321	2.431	2.391
Ti <sup>4+</sup>			0.168
Fe <sup>3+</sup>	0.580 <sup>(f)</sup>	0.569 <sup>(f)</sup>	0.319
Al <sup>3+</sup>	0.095 <sup>(f)</sup>		
Fe <sup>2+</sup>			0.122
Sum tetrahedral cations	2.996	3.000	3.000
Zr <sup>4+</sup>	0.062		
Ti <sup>4+</sup>	1.199 <sup>(g)</sup>	1.160 <sup>(g)</sup>	0.544
Ti <sup>3+</sup>			0.377
Fe <sup>3+</sup>	0.160 <sup>(d,g)</sup>	0.248 <sup>(d,g)</sup>	0.973
Fe <sup>2+</sup>	0.560 <sup>(d,g)</sup>	0.592 <sup>(d,g)</sup>	0.106
Mn <sup>2+</sup>	0.017		
Sum octahedral cations	1.998	2.000	2.000
Ca <sup>2+</sup>	2.894	2.978	3.000
Mg <sup>2+</sup>	0.112		
Fe <sup>2+</sup>		0.022	
Sum dodecahedral cations	3.006	3.000	3.000
O	12.000	12.000	11.874
(OH)			0.126
Sum anions	12.000	12.000	12.000
Unit cell parameter <i>a</i> <sub>0</sub> (Å)	12.162(3)	12.17	12.166(1)

(a) natural morimotoite (Henmi *et al.*, 1995; Table 1); (b) synthetic limiting Ti-garnet solid solution, associated with other phases not reported (Henmi *et al.*, 1995; Table 3, nr. 3); (c) single phase Ti-garnet TA13, H<sub>2</sub>O determined by means of a solid's moisture analyser; all site distributions of Fe species are determined by means of Mössbauer spectroscopy and Ti valance based on charge balance calculations (Kühberger *et al.*, 1989); (d) Fe<sub>2</sub>O<sub>3</sub> and FeO recalculated on the base of 12 oxygen (Henmi *et al.*, 1995); (e) all iron expressed as Fe<sub>2</sub>O<sub>3</sub>; (f) Fe<sup>3+</sup> and Al<sup>3+</sup> on tetrahedral sites not determined, assignment based on formal occupancy of tetrahedral sites by Al<sup>3+</sup>>Fe<sup>3+</sup>>Ti<sup>4+</sup> (Henmi *et al.*, 1995); (g) Fe<sup>3+</sup>, Fe<sup>2+</sup> and Ti<sup>4+</sup> on octahedral sites not determined, calculated on the base of 12 oxygen (Henmi *et al.*, 1995)

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