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Morimotoite, a new titanian garnet? — discussion

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THE valence state and site distribution of titanium in andradite remains a matter of much discussion. In a recent paper, Henmi *et al.* (1995) described a new mineral morimotoite, $\text{Ca}_3\text{TiFe}^{2+}\text{Si}_3\text{O}_{12}$, found in contaminated rocks at Fuka, Bitchu-Cho, Okayama Prefecture, Japan. The morimotoite chemical composition (mean of seven microprobe analyses) and its cell dimensions are presented in Table 1, together with an earlier known titanian andradite (schorlomite

from nepheline syenite, Iivaara, Finland, Deer *et al.*, 1982. N24 after Zedlitz, 1935) shown for comparison.

Apparently, both analyses are closely similar. Note that the wet-chemical analysis from Zedlitz (1935) contains no Fe^{2+} , whereas the analysis of morimotoite includes Fe^{3+} and Fe^{2+} , calculated on the basis of 8 cations per 12 oxygens. Hence, the latter mineral may be either the first find at Fuka or in these rocks,

TABLE 1. Chemical analyses

	Morimotoite	Schorlomite
SiO ₂	26.93	26.88
TiO ₂	18.51	17.3
ZrO ₂	1.48	n.a.
Al ₂ O ₃	0.97	2.83
Fe ₂ O ₃	11.42*	19.42
FeO	7.78*	—
MnO	0.23	0.01
MgO	0.87	0.05
CaO	31.35	32.35
Total	99.54	100.09
a (Å)	12.162	12.167

n.a. not analysed

* calculated on the basis of 8 cations per 12 oxygens

or it may be regarded as just a new way of calculating the cation proportion. Henmi *et al.* (1995) propose this procedure for formula calculation, using a hypothetical end-member $\text{Ca}_3\text{Ti}^{4+}\text{Fe}^{2+}\text{Si}_3\text{O}_{12}$, and presuming that Ti^{4+} and Fe^{2+} may occupy the octahedral site in the garnet structure. Although this possibility does exist (Amthauer *et al.*, 1977; Gongbao and Baolei, 1986), it is only one variant of many other possibilities: the presence of two different valence states of Ti (Howie and Woolley, 1968; Schwartz *et al.*, 1980; Gongbao and Baolei, 1986; Rass, 1986; Waychunas, 1987; Fehr *et al.*, 1990; Malitesta *et al.*, 1995); the occurrence of Ti in the tetrahedral site (Huchenholz, 1969; Dowty, 1971; Amthauer *et al.*, 1977; Tarte *et al.*, 1979; Povarennykh and Shabalin, 1983); the occurrence of octahedral titanium (Amthauer *et al.*, 1977; Huggins *et al.*, 1977; Povarennykh and Shabalin, 1983; Waychunas, 1987; Flohr and Rose, 1989); the occurrence of octahedrally coordinated trivalent titanium (Kühberger *et al.*, 1989); the presence of both octahedral and tetrahedral Fe^{3+} (Amthauer *et al.*, 1977; Gongbao and Baolei, 1986); other speculation concerning the positions of Fe^{2+} , Zr^{4+} and Al^{3+} in the garnet structure.

It is worth noting that most of the methods used (Infrared spectra, Mössbauer study, XANES spectroscopy) provide only possibilities rather than the actual mechanisms. And an XPS study qualitatively confirms two different states of Ti (and Fe), although their quantitative proportions may remain uncertain because of the possible impurity of the samples for XPS analysis (e.g. some perovskite in schorlomite grains, as may often be seen under the microscope). According to Henmi *et al.* (1995), the IR spectra of morimotoite are very similar to those reported by

Tarte *et al.* (1979). But Tarte *et al.* (1979) emphasize that according to their data, Ti should be distributed over tetrahedral and octahedral sites.

To decide between the possibilities encountered in nature, or for the sake of formula calculation, additional evidence is required. Rass (1984) suggested a hypothetical garnet end-member $\text{Ca}_3\text{Ti}_2^{3+}\text{Ti}_3^{4+}\text{O}_{12}$ on the strength of the following arguments: (1) mineralogical – the substitution of (Si+Fe) by Ti, a fact inferred from electron microprobe analysis of zoned garnets (Rass, 1986; Howie and Woolley, 1968); (2) crystallochemical – the above possibilities; (3) an advantage of this hypothetical end-member over the earlier-offered $\text{Ca}_3\text{Fe}_2\text{Ti}_3\text{O}_{12}$, (Huchenholz, 1969) and $\text{Ca}_3\text{Ti}_2\text{Fe}_2\text{SiO}_{12}$ (Ito and Frondel, 1967): when the required Ca atom content is subtracted, the remainder is close to the theoretical andradite formula; (4) the existence of a linear dependence of cell dimension, and refractive index on $\text{Ca}_3\text{Ti}_2\text{Ti}_3\text{O}_{12}$ mole fraction.

This hypothetical garnet end-member does not exist in nature, because its stability field occurs under higher temperatures and lower oxygen fugacities than that of perovskite, which is stable in mantle environments. The conditions of $\text{Ca}_3\text{Ti}_2\text{Ti}_3\text{O}_{12}$ stability are: f_{O_2} –15 to –35 at 1300–900°C, at $\log a_{\text{CaO}}$ –3 in melt, and $\log a_{\text{SiO}_2} < -0.622$ (Rass and Dubrovinskii, 1997).

If even the synthesized compound $3\text{Ca}:1\text{Ti}:1\text{Fe}:3\text{Si}:12\text{O}$ (Kühberger *et al.*, 1989) consists of two distinct end-members and is described by the formulae $\text{Ca}_3\text{Ti}^{4+}\text{Fe}^{2+}\text{Si}_3\text{O}_{12}$ and $\text{Ca}_3\text{Ti}^{3+}\text{Fe}^{3+}\text{Si}_3\text{O}_{12}$ (Fehr and Amthauer, 1996), it is reasonable to expect that natural titanian andradite (melanite and schorlomite) can also consist of the two end-members (with a 'melanitic' silicon deficiency) together with $\text{Ca}_3\text{Fe}_2^{3+}\text{Ti}_3\text{O}_{12}$, $\text{Ca}_3\text{Fe}_2^{3+}\text{Ti}_{1.5}\text{Si}_{1.5}\text{O}_{12}$, and $\text{Ca}_3\text{Ti}_2^{3+}\text{Ti}_3^{4+}\text{O}_{12}$ (in the case of schorlomite).

In any case, a matter of discussion should now be the method of calculation or the predominance of one end-member. A new mineral with its assigned name might be discussed if the type specimen is re-examined, and true valence states of Ti and Fe are established (not calculated), and the presence of more than 50% $\text{Ca}_3\text{Ti}^{4+}\text{Fe}^{2+}\text{Si}_3\text{O}_{12}$ in its composition is proved.

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