

STRUCTURE AND CATION ORDER IN MANGANILVAITE: A COMBINED X-RAY-DIFFRACTION, NEUTRON-DIFFRACTION AND MÖSSBAUER STUDY

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ABSTRACT

The crystal structure of manganilvaite, $\text{CaFe}^{2+}\text{Fe}^{3+}(\text{Mn}^{2+},\text{Fe}^{2+})(\text{Si}_2\text{O}_7)\text{O}(\text{OH})$, from the Ossikovo Pb–Zn skarn deposit, Rhodope Mountains, Bulgaria, was refined in space group $P2_1/a$, with a 13.0250(7), b 8.8514(5), c 5.8486(3) Å, β 90.167(1)°, V 674.28(7) Å³, $Z = 4$, using combined neutron and X-ray powder diffraction as well as single-crystal X-ray-diffraction data. The empirical chemical formula proposed on the basis of the Rietveld refinements is: $(\text{Ca}_{0.9}\text{Mn}^{2+}_{0.1})(\text{Fe}^{2+}_{0.83}\text{Fe}^{3+}_{0.17})(\text{Fe}^{2+}_{0.17}\text{Fe}^{3+}_{0.83})(\text{Mn}^{2+}_{0.51}\text{Fe}^{2+}_{0.49})(\text{Si}_2\text{O}_7)\text{O}(\text{OH})$. The occupancy of the M11 site ($0.83\text{Fe}^{2+} + 0.17\text{Fe}^{3+}$) corresponds to an order parameter Q of 0.65(10). The high Mn content leads to strong enhancement (14%) of $\text{Fe}^{2+} \rightarrow \text{Fe}^{3+}$ charge transfer in comparison to Mn-free ilvaite from Seriphos, Greece, as observed by Mössbauer spectroscopy.

Keywords: manganilvaite, combined X-ray and neutron powder diffraction, single-crystal X-ray diffraction, Mössbauer spectroscopy, Rietveld refinement, Ossikovo mine, Bulgaria.

SOMMAIRE

Nous avons affiné la structure cristalline de la manganilvaïte, $\text{CaFe}^{2+}\text{Fe}^{3+}(\text{Mn}^{2+},\text{Fe}^{2+})(\text{Si}_2\text{O}_7)\text{O}(\text{OH})$, provenant du gisement à Pb–Zn de type skarn de Ossikovo, dans les montagnes Rhodope, en Bulgarie, dans le groupe spatial $P2_1/a$, avec a 13.0250(7), b 8.8514(5), c 5.8486(3) Å, β 90.167(1)°, V 674.28(7) Å³, $Z = 4$, en utilisant des données obtenues par diffraction X et neutronique sur poudre ainsi que par diffraction X sur monocristal. La formule chimique empirique proposée selon les résultats obtenus d'affinements de Rietveld est: $(\text{Ca}_{0.9}\text{Mn}^{2+}_{0.1})(\text{Fe}^{2+}_{0.83}\text{Fe}^{3+}_{0.17})(\text{Fe}^{2+}_{0.17}\text{Fe}^{3+}_{0.83})(\text{Mn}^{2+}_{0.51}\text{Fe}^{2+}_{0.49})(\text{Si}_2\text{O}_7)\text{O}(\text{OH})$. Le site M11 contient ($0.83\text{Fe}^{2+} + 0.17\text{Fe}^{3+}$), ce qui correspond à un paramètre d'ordre Q de 0.65(10). La teneur élevée en Mn mène à un transfert accru des charges de Fe^{2+} à Fe^{3+} (14%), en comparaison du cas de l'ilvaïte dépourvue de Mn provenant de Seriphos, en Grèce, selon la spectroscopie de Mössbauer.

(Traduit par la Rédaction)

Mots-clés: manganilvaite, combinaison de diffraction X et neutronique sur poudre, diffraction X sur monocristal, spectroscopie de Mössbauer, affinement de Rietveld, mine Ossikovo, Bulgarie.

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INTRODUCTION

Ilvaite is a mixed-valence iron-dominant sorosilicate, $\text{CaFe}^{2+}_2\text{Fe}^{3+}(\text{Si}_2\text{O}_7)\text{O}(\text{OH})$, common in Fe, Cu, and Pb–Zn skarn-type ore deposits. Manganilvaite, $\text{CaFe}^{2+}\text{Fe}^{3+}(\text{Mn}^{2+}, \text{Fe}^{2+})(\text{Si}_2\text{O}_7)\text{O}(\text{OH})$, from the Rhodope Mountains, Bulgaria was described by Bonev *et al.* (2005) as a new mineral species, the manganese-dominant member of the ilvaite group of minerals. Here, we provide crystal-chemical characterization of this mineral with high Mn content and resolve the problem concerning the distribution of Mn using combined neutron and X-ray refinements, as well as Mössbauer spectroscopy. Neutron diffraction is particularly suited for this problem because Mn has a negative neutron-scattering length ($b_{\text{Mn}} = -3.73$ fm) and can be readily distinguished from Fe, in contrast with X-ray-diffraction techniques.

PREVIOUS WORK

The crystal structure of orthorhombic ilvaite was first determined by Belov & Mokeeva (1954) (space group *Pbnm*) and re-investigated by Beran & Bittner (1974) and Haga & Takéuchi (1976). Bartholomé *et al.* (1968) established the existence of a monoclinic ilvaite-type phase in space group *P2₁/a*, with only small deviation from the orthorhombic *Pnam* symmetry (in the space group *Pnam*, the *a* and *b* axes are interchanged compared to *Pbnm*, and $a > b > c$). The monoclinic structure was later refined by Finger *et al.* (1982), Takéuchi *et al.* (1983, 1993, 1994), Ghose *et al.* (1984, 1985, 1989), Finger & Hazen (1987), Carrozzini (1994), and Bonazzi & Bindi (1999). Crystal-chemical relationships between the cation-order parameter *Q* and the angle β (Finger & Hazen 1987, Carrozzini 1994), as well as effects of heat treatment on *Q*, have been reported (Bonazzi & Bindi 1999). The structure of orthorhombic ilvaite consists of double chains of edge-sharing Fe octahedra (*M1* site) running along the *c* axis and cross-linked by additional Fe octahedra (*M2* site), ¹⁷Ca polyhedra and [Si₂O₇] sorosilicate groups. In the structure of monoclinic ilvaite, the *M1* site splits into two sites, *M11* and *M12* (Fig. 1). Divalent Mn is the most common and quantitatively relevant impurity in natural ilvaite, substituting mainly for Fe²⁺ and, to a lesser extent, Ca²⁺ (Cocco & Garavelli 1954). The Mn content of natural ilvaite is usually below ~2 wt.% MnO, but higher contents, up to 14.96 wt.% MnO, have been reported (Bonev *et al.* 2005). The pattern of order of Mn²⁺ among the *M11*, *M12* and *M2* octahedral sites is still somehow contradictory. In ilvaite, Mn²⁺ substitutes for Fe²⁺ predominantly at the *M2* site (Haga & Takéuchi 1976, Carrozzini 1994, Bonazzi & Bindi 2002), although more disordered distributions of Mn were reported by Takéuchi *et al.* (1993) for crystals from Tochibara (Japan) and by Carrozzini (1994) for

crystals from Oridda, Sardinia (Italy), whereas synthetic Mn-doped ilvaite exhibits very different distributions of cations (Ghazi-Bayat *et al.* 1989, Cesena *et al.* 1995). The temperature of the monoclinic–orthorhombic phase transition depends also on the Mn²⁺ content (Ghose *et al.* 1984, 1989, Finger & Hazen 1987, Ghazi-Bayat *et al.* 1989, 1992, Amthauer *et al.* 1998).

MATERIAL

The description of manganilvaite and of its occurrence is given by Bonev *et al.* (2005). The material used for structural studies was selected from the bulk sample Os–8 (Bonev *et al.* 2005); it is rather enriched in the mineral, making it possible to pick out the large quantities necessary for powder neutron and X-ray diffraction. Electron-microprobe analysis of mm-sized single crystals showed variations in the Mn content, from 9.02 up to 12.58 wt.% MnO. However, the variations are gradual and are not visible either in back-scattered images or in thin doubly polished sections under the infrared microscope. The mean composition, as determined from 26 electron-microprobe analyses, is (in wt.%): CaO 12.57, MnO 10.79, MgO 0.44, Al₂O₃ 0.31, FeO_{tot} 41.06, sum 94.74. The amount of H₂O (2.20 wt.%) was measured separately by heating. The ICP analysis of this material gave MnO 10.52 wt.%. However, other specimens from the same locality exhibit higher Mn contents (reaching nearly 15 wt.% MnO; see Bonev *et al.* 2005), although such material present as disseminated small grains.

A nearly stoichiometric Mn-free ilvaite from the Seriphos ilvaite deposit, in the Cyclade Isles, Greece, also was studied by X-ray and neutron powder-diffraction as well as by Mössbauer spectroscopy. We established its chemical homogeneity by electron-microprobe analysis; it contains only a low content of Mg (0.1 wt.% MgO, see Table 5 of Bonev *et al.* 2005).

EXPERIMENTAL

The X-ray powder-diffraction measurements were done in transmission geometry with a PSD detector in the range $12^\circ \leq 2\theta \leq 120^\circ$, step size of 2θ 0.02° and 10 s per step at room temperature on a Stoe X-ray powder diffractometer equipped with Ge monochromator using CoK α_1 radiation ($\lambda = 1.78897$ Å), operating at 40 kV and 30 mA. The neutron-diffraction measurements were done on the time-of-flight ROTAX diffractometer at the ISIS spallation source, Rutherford Appleton Laboratory (UK). The ROTAX instrument is equipped with three banks of detectors at average 2θ positions 28.8° (bank A), 72.8° (bank B) and 122.3° (bank C). The powdered samples were loaded into vanadium cans 8 mm in diameter. Both the manganilvaite and the Seriphos ilvaite were measured at room temperature for about 12 h, and the intensities were normalized against a vanadium stan-

ard. The back-scattering bank C allowed us to collect data with good statistics for a wider momentum-transfer range than is normally the case with X rays.

Combined refinement of the X-ray and three neutron powder-diffraction datasets was done using GSAS (Larson & Von Dreele 1987). The X-ray peak profiles were fitted with the Thompson–Cox pseudo-Voigt function, whereas the neutron peak profiles were fitted with double-exponential pseudo-Voigt convolution function (Larson & Von Dreele 1987). The profile parameters for each histogram were refined in the initial stages of the refinements, and then fixed. During the final cycles of least-squares refinement, the scale factors, the background coefficients (fifth-order polynomials) and the zero shifts for all histograms, lattice parameters, positional parameters, occupancy factors and isotropic-displacement factors were refined. The isotropic-displacement parameters of each of the Fe, Si and O atoms were kept equal during refinements.

A single-crystal X-ray-diffraction study of manganilvaite was done using a Bruker P4 rotating-anode four-circle diffractometer operating at 50 kV and 250 mA, with an 18 kW generator. The high-intensity source was monochromated by a vertical incident-beam graphite monochromator. The wavelength is calibrated against an IUCr ruby standard before and after cell-parameter measurements. The cell parameters of three different crystals of manganilvaite from the Ossikovo mine were determined by least-squares fitting the centered positions of 20 or 30 low-angle reflections ($2\theta < 30^\circ$), and show some variability at the 5σ level due to variability in composition. The crystal showing the sharpest diffraction-peak profiles and measuring about $60 \times 80 \times 120$ mm was selected for intensity data collection using variable-speed θ – 2θ scans (from 4 to 10° per minute) on the twice-redundant hemisphere ($h + 20, k \pm 14, l \pm 9$) out to $2\theta_{\max} = 70^\circ$, resulting in 6333 reflections in total, with 2673 considered unique and having $I > 2\sigma(I)$. The data were corrected for Lorentz, polarization and absorption effects. An analytical absorption correction was applied using the indexed faces and measured distances of the crystal,

after which the data merging of equivalent reflections gave a discrepancy factor $R_{int} = 0.081$. The structure was refined from the starting positions reported by Finger & Hazen (1987) using SHELX-97 (Sheldrick 1997) and $w = 1.0/(\sigma^2(F) + 0.000030F^2)$ weighting scheme and converged to $R_w = 3.4\%$.

The Mössbauer spectroscopy was done on an electromechanical Wissel (Wissenschaftliche Elektronik GmbH) spectrometer at room temperature. A $^{57}\text{Co}/\text{Cr}$ source with an activity 10 mCi was used with α -Fe as a standard. The experimental spectra were fitted as a sum of Lorentzians using the least-squares method.

RESULTS

Diffraction studies

The lattice parameters of the Seriphos ilvaite (Table 1) are in close agreement with the powder neutron-diffraction results of Ghose *et al.* (1984) and with the single-crystal X-ray data of Carrozzini (1994). In agreement with previous studies (Carrozzini 1994, Bonazzi & Bindi 2002), increasing Mn content correlates with an increase in the b parameter (Fig. 2), whereas a and c remain practically unchanged.

Several models for the Mn occupancy in manganilvaite were examined using combined neutron and X-ray powder refinements (Finney 1995). Simultaneous refinement of the Mn occupancies at the $M11$, $M12$ and $M2$ sites failed, indicating that Mn occurs only at the $M2$ site. The structure was refined with Mn only at the $M2$ site, and the refinement converged to $R_{wp} = 2.3\%$. Mn was then allowed to substitute for Ca at the seven-coordinated site. The residual R_{wp} converged to 2.1%, with $R_{wp} = 4.8\%$ for X-ray and R_{wp} of 2.3, 2.4 and 1.7% for neutron banks A, B and C, respectively. In the Mn-free ilvaite from Seriphos, the refinement converged to an overall R_{wp} of 2.4%. The X-ray-diffraction pattern for manganilvaite is shown together with the fitted intensities in Figure 3a. The low- 2θ neutron-diffraction pattern (bank A), which is the most sensitive to the occupancy factors, together with the fitted intensities, is shown in Figure 3b.

Atom parameters are listed in Table 2. The coordinates for the structural model derived from the combined neutron + X-ray powder-diffraction data are in good agreement with the single-crystal data. The refined occupancies for manganilvaite and for the Seriphos ilvaite are given in Table 3.

The $\langle M11\text{--O} \rangle$ distance in manganilvaite is very similar to that in the Seriphos ilvaite (Table 4) and other samples of Mn-poor ilvaite (Takéuchi *et al.* 1983, Finger & Hazen 1987, Carrozzini 1994, Bonazzi & Bindi 1999), which supports the premise that Mn^{2+} does not occur at the $M11$ site, despite the very large total Mn content. The substitution of Mn^{2+} for Fe^{2+} at $M2$ increases $\langle M2\text{--O} \rangle$, reflecting the greater ionic radius of Mn^{2+} (0.830 versus 0.780 Å, respectively; Shannon

TABLE 1. REFINED LATTICE PARAMETERS FOR ILVAITE AND MANGANILVAITE

	Ilvaite, Seriphos		Manganilvaite, Ossikovo	
	Powder neutrons ⁵	Powder X-ray + neutrons	Powder X-ray + neutrons	Single-crystal X-ray
a , Å	13.0207(7)	13.0146(3)	13.0250(7)	13.015(2)
b	8.8121(4)	8.8046(2)	8.8514(5)	8.8430(8)
c	5.8609(3)	5.8588(2)	5.8486(3)	5.8396(5)
β°	90.25(1)	90.28(1)	90.167(1)	90.11(1)
V , Å ³	672.48(8)	671.34(3)	674.28(7)	672.12(10)
R_{wp} , %	14.7	2.4	2.1	3.4 (R_w 3.5)

⁵ Ghose *et al.* (1984). The space group, in each case: $P2_1/a$.

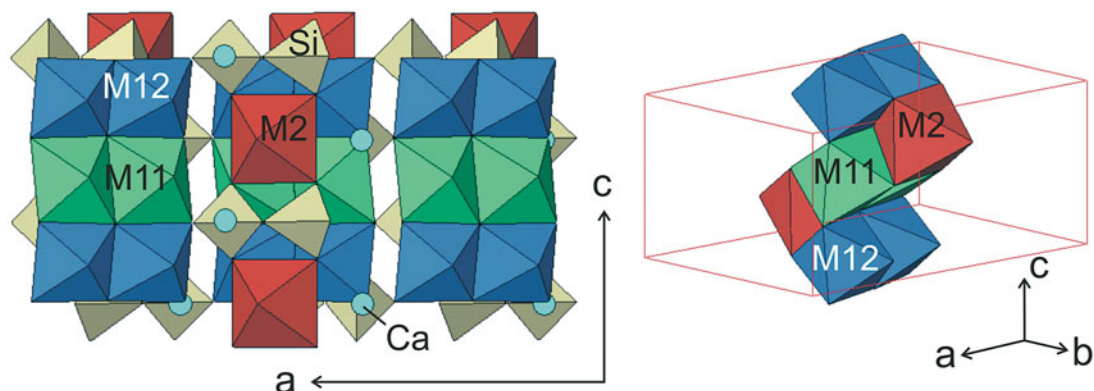


FIG. 1. The crystal structure of manganilvaite and view of one of the double chains of edge-sharing octahedra $M11$ – $M12$ and $M2$.

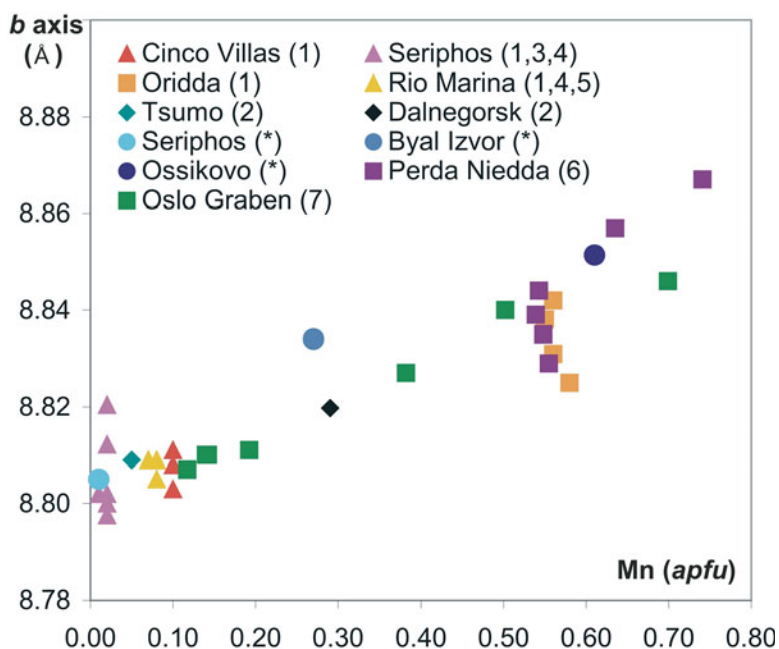


FIG. 2. Variation of b versus Mn content (in $apfu$) in ilvaite–manganilvaite. Data from: (1) Carrozzini (1994), (2) Takéuchi *et al.* (1983), (3) Finger & Hazen (1987), (4) Ghose *et al.* (1984), (5) Bonazzi & Bindi (1999), (6) Bonazzi & Bindi (2002), (7) Larsen & Dahlgren (2002), and the present study (*).

1976). The $\langle M2-O \rangle$ bond length is a linear function of Mn content (Fig. 4), in accord with correlation proposed by Carrozzini (1994) and Bonazzi & Bindi (2002). Also, $\langle M2-O \rangle_{obs}$ equals $2.201(1)$ Å (Table 4), whereas $\langle M2-O \rangle_{calc}$ equals $2.200(1)$ Å using the empirical equation $\langle M2-O \rangle = 2.1869(3) + 0.0266(9)$

$n(\text{Mn}^{2+})$, reported by Bonazzi & Bindi (2002), where $n(\text{Mn}^{2+})$ is the Mn occupancy at the $M2$ site. The $M11$, $M12$ and $M2$ octahedra in the ilvaite structure are not regular. In the Seriphos Mn-free ilvaite, the $M2$ site has the largest bond-length $\langle \Delta l \rangle$ and bond-angle $\langle \Delta \tau \rangle$ distortions among the octahedra (Table 5).

TABLE 2. ATOM COORDINATES AND ISOTROPIC DISPLACEMENT PARAMETERS FOR MANGANILVAITE

	Powder X-ray + neutrons				Single-crystal X-ray			
	x	y	z	Ue*100	x	y	z	Ue*100
Ca	0.8150(3)	0.3729(3)	0.7630(1)	0.54(9)	0.81298(3)	0.36996(5)	0.75154(8)	0.75(1)
M11	0.8912(3)	0.0504(5)	0.0072(4)	0.49(2)	0.89021(2)	0.04995(4)	0.00689(6)	0.734(8)
M12	0.8886(2)	0.0501(5)	0.4953(5)	0.49(2)	0.89018(2)	0.05095(4)	0.49337(6)	0.704(8)
M2	0.9421(3)	0.7395(5)	0.2561(2)	0.49(2)	0.93987(3)	0.73906(4)	0.24925(6)	0.738(8)
Si1	0.9587(2)	0.3693(3)	0.2599(1)	0.37(4)	0.95890(5)	0.36741(7)	0.2495(1)	0.50(1)
Si2	0.6820(3)	0.2262(3)	0.2439(2)	0.37(4)	0.67971(5)	0.22663(7)	0.2511(1)	0.52(1)
O1	0.0100(2)	0.0270(3)	0.7378(7)	0.027(7)	0.0092(1)	0.0264(2)	0.7443(3)	1.02(4)
O21	0.9376(3)	0.2731(6)	0.0140(7)	0.027(7)	0.9366(1)	0.2717(2)	0.0158(3)	0.78(4)
O22	0.9340(3)	0.2722(6)	0.4799(7)	0.027(7)	0.9361(1)	0.2716(2)	0.4844(3)	0.79(4)
O3	0.7764(2)	0.1071(2)	0.2598(7)	0.027(7)	0.7767(1)	0.1081(2)	0.2526(3)	0.77(4)
O41	0.6762(3)	0.3330(5)	0.0208(6)	0.027(7)	0.6715(1)	0.3282(2)	0.0185(3)	0.79(4)
O42	0.6678(3)	0.3258(5)	0.4842(6)	0.027(7)	0.6713(1)	0.3303(2)	0.4821(3)	0.74(4)
O5	0.5836(2)	0.1018(2)	0.2616(7)	0.027(7)	0.5845(1)	0.1018(2)	0.2515(3)	0.68(4)
O6	0.6028(2)	0.0215(2)	0.7605(7)	0.027(7)	0.6033(1)	0.0224(2)	0.7513(3)	1.07(4)
O7	0.7973(2)	0.1120(2)	0.7422(8)	0.027(7)	0.7978(1)	0.1103(2)	0.7474(3)	0.76(4)
H	0.7285(3)	0.0644(4)	0.7549(2)	2.05(10)	0.733(4)	0.094(7)	0.743(11)	0.6(2)

TABLE 3. REFINED CATION-OCCUPANCIES AND CORRESPONDING CRYSTAL-CHEMICAL FORMULAE PROPOSED FOR MANGANILVAITE AND ILVAITE

Method	Ca site	M2 site
Manganilvaite, Ossikovo		
powder X-ray + neutrons	0.903(3) Ca + 0.097(3) Mn	0.503(2) Mn + 0.497(2) Fe
single-crystal X-ray	1Ca	0.56(4) Mn + 0.44(4) Fe
	(Ca _{0.9} Mn _{0.1})(Fe ²⁺ _{0.83} Fe ³⁺ _{0.17})(Fe ²⁺ _{0.17} Fe ³⁺ _{0.83})(Mn ²⁺ _{0.51} Fe ²⁺ _{0.49})(Si ₂ O ₇)O(OH)	
Ilvaite, Seriphos		
powder X-ray + neutrons	1 Ca	0.01(1) Mn + 0.99(1) Fe
	Ca _{1.00} (Fe ²⁺ _{0.86} Fe ³⁺ _{0.14})(Fe ²⁺ _{0.14} Fe ³⁺ _{0.86})(Mn ²⁺ _{0.01} Fe ²⁺ _{0.99})(Si ₂ O ₇)O(OH)	

Both Fe²⁺ and Fe³⁺ occupy the M11 and the M12 sites. An order parameter Q has been proposed (Takéuchi *et al.* 1983, Ghose *et al.* 1984, Finger & Hazen 1987), depending on the Fe³⁺ occupancy [$n(\text{Fe}^{3+})$] of the M11 site: $Q = 10.5 - n(\text{Fe}^{3+}) / 0.5$; Q equals 1 for complete order, with Fe²⁺ and Fe³⁺ at the M11 and M12 sites, respectively (monoclinic symmetry), whereas Q is 0 for complete disorder (orthorhombic symmetry). The Fe³⁺ occupancy of M11 can be expressed as a function of $\langle M11-O \rangle$ assuming $\langle \text{Fe}^{2+}-O \rangle = 2.135 \text{ \AA}$ and $\langle \text{Fe}^{3+}-O \rangle = 2.025 \text{ \AA}$ (Ghose *et al.* 1984): $n(\text{Fe}^{3+}) = [\langle \text{Fe}^{2+}-O \rangle - \langle M11-O \rangle] / [\langle \text{Fe}^{2+}-O \rangle - \langle \text{Fe}^{3+}-O \rangle]$.

In the Seriphos ilvaite, Q equals 0.73(10). Hence, Fe²⁺ preferably occupies the M11 octahedra (0.86 Fe²⁺ + 0.14 Fe³⁺), whereas the Fe³⁺ ions occupy mostly the M12 position (0.14 Fe²⁺ + 0.86 Fe³⁺) (Table 3). The order parameter for the Seriphos ilvaite is the same

(within 1 σ) as the values of Q reported by Carrozzini (1994) and Ghose *et al.* (1984), 0.58 and 0.69, respectively, but it is larger than the value given by Finger & Hazen (1987), 0.16.

The order parameter for manganilvaite Q = 0.65(10), determined from the combined X-ray and neutron powder-diffraction refinements, shows that substitution of Mn²⁺ at the M2 site slightly increases the Fe²⁺-Fe³⁺ disorder at the M11 and M12 sites (Table 3). The order parameter determined from the X-ray single-crystal refinement is even smaller, Q = 0.26(12), which correlates with the difference in the β angle (Table 1) and suggests that there may be variation of the order parameter in different crystals from the same deposit.

Mössbauer study

Ilvaite has been the subject of numerous ⁵⁷Fe Mössbauer studies (Herzenberg & Riley 1969, Gérard & Grandjean 1971, Grandjean & Gérard 1975, Heilmann *et al.* 1977, Nolet & Burns 1979, Amthauer & Evans 1978, Yamanaka & Takéuchi 1979, Evans & Amthauer 1980, Litterst & Amthauer 1984, Demelo *et al.* 1994, Cesena *et al.* 1995, Amthauer *et al.* 1998, Dotson & Evans 1999). It has been shown that the monoclinic-orthorhombic transition in ilvaite is accompanied by temperature-activated delocalization of electrons (Ghazi-Bayat *et al.* 1989, Güttler *et al.* 1989). The degree of electron delocalization at room temperature can be related to the paragenesis of the mineral (Nolet & Burns 1979).

Following Nolet & Burns (1979) and Amthauer & Rossman (1984), the Mössbauer spectra of the Seriphos ilvaite and of manganilvaite (Fig. 5) were fitted to five quadruple doublets: two corresponding to Fe²⁺ and mixed-valence Fe^{2.5+} ions at the M11 position, two for Fe³⁺ and Fe^{2.5+} ions at the M12 position, and one doublet

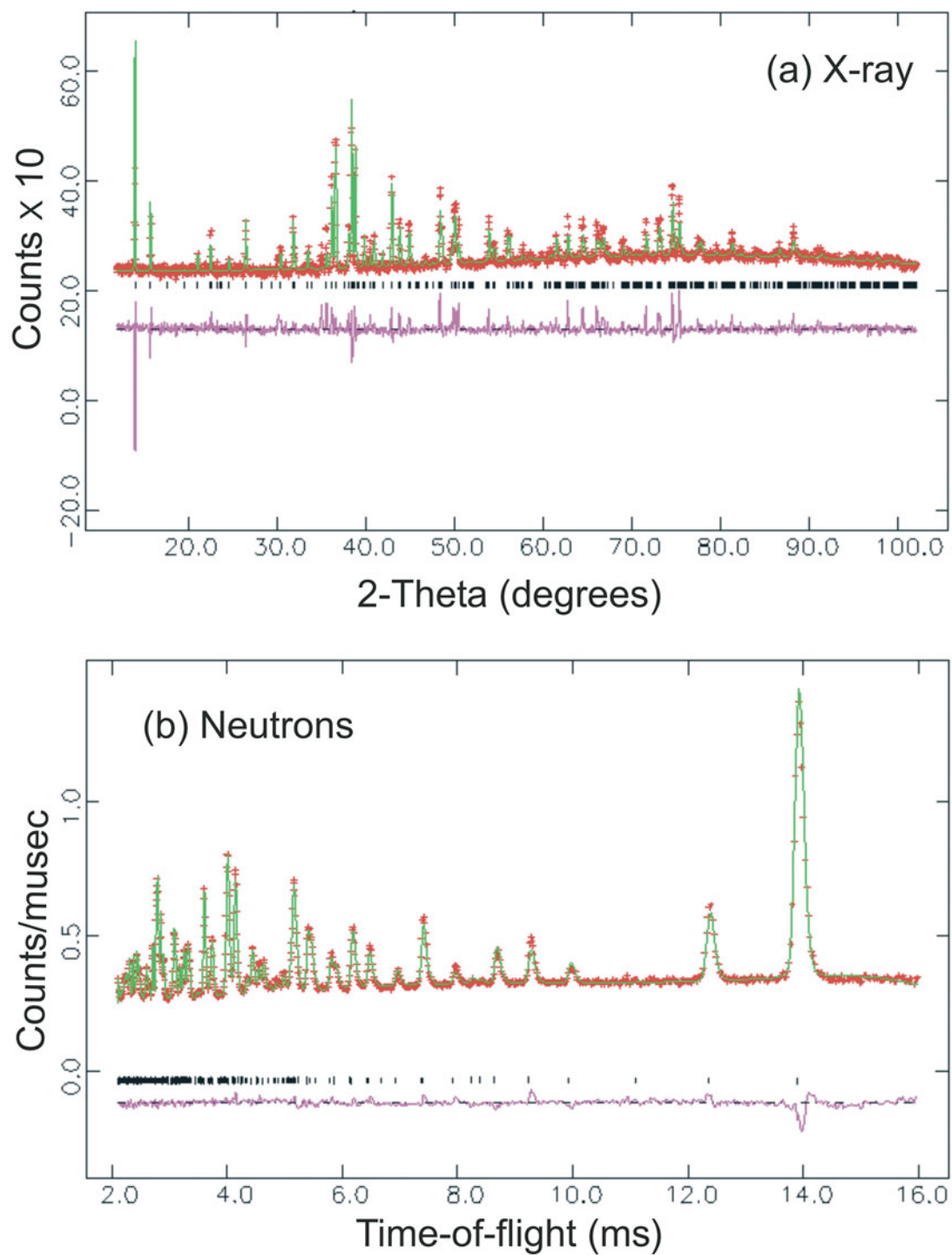


FIG. 3. (a) X-ray and (b) neutron powder-diffraction patterns for manganilvaite (crosses). Also shown are results of the Rietveld-fitted calculated profiles (solid lines, top) and the residual (bottom).

for the Fe^{2+} ions at the $M2$ position. The low degree of occupancy of $M11$ and $M12$ by Fe^{3+} and Fe^{2+} , respectively, makes a seven-doublet model less probable.

The interpretation of the Mössbauer spectrum of manganilvaite shows better agreement between the experimental and fitted spectra if electron-exchange interactions ($\text{Fe}^{2.5+}$ species) are considered. This model is also supported by the results obtained from the X-ray- and neutron-diffraction refinements. The interatomic distances between Fe ions in adjacent $M11$ and $M12$ octahedra along the chains in the manganilvaite structure [2.841(1) and 2.999(1) Å] are close to the optimal values and within the 3 Å limit (Swinnea & Steinfink 1983) necessary for $3d^6\text{Fe}^{2+} \leftrightarrow 3d^5\text{Fe}^{3+}$ electron exchange. The potential for experimental determination of the mixed valence state by Mössbauer spectroscopy depends on the T_L/T_E ratio, where T_L is the Larmor precession time of the 14.4 keV excited state and T_E is

the electron-relaxation time. If the frequency of electron delocalization is higher than 10^{-7} s^{-1} , then the mixed-valence state could be registered in the Mössbauer spectrum with parameters between those characteristic for Fe^{3+} and Fe^{2+} .

The Mössbauer spectra are shown in Figure 5 and the corresponding parameters [isomer shifts (IS), quadrupole splittings (QS) and full widths at half maximum (FWHM)] are listed in Table 6. Doublet 1 exhibits a small isomer shift typical for Fe^{3+} in octahedral coordination (Nolet & Burns 1979, Hawthorne 1988) and can be assigned to Fe^{3+} at the $M12$ site, taking into account the occupancies of the $M12$ site in manganilvaite and the Seriphos ilvaite (Table 3). Doublets 4 and 5 have IS and QS parameters characteristic of high-spin Fe^{2+} (Nolet & Burns 1979, Hawthorne 1988). Doublets 2 and 3 have IS parameters intermediate with respect to Fe^{3+} and Fe^{2+} , *i.e.*, they can be assigned to the mixed-valence $\text{Fe}^{2.5+}$ species. The bond-length and bond-angle distortions of the $M2$ octahedra are almost 50% larger than for the $M11$ octahedra in both the structures of manganilvaite and the Seriphos ilvaite (Table 5). Using empirical relations between the degree of polyhedron distortions and the quadrupole splitting in silicate minerals (Hawthorne 1988), we can easily assign doublet 5 to the $M2$ site and doublet 4 to the $M11$ site. In the Seriphos sample, the bond-length distortion of the $M11$ octahedron is larger than that of the $M12$ octahedron, whereas their bond-angle distortions are practically the same. Thus we tentatively assign doublets 2 and 3 in both samples to the $\text{Fe}^{2.5+}$ species at the $M12$ and $M11$ sites, respectively. The differences in QS parameters for the Seriphos ilvaite and manganilvaite correlate with the corresponding changes in their bond-length distortions (especially for the $M11$ site).

The contribution of mixed-valence ions in the Seriphos spectrum, measured at room temperature, is insignificant (almost within the error limits). Thus the $M1$:

TABLE 4. BOND LENGTHS (Å) FOR ILVAITE AND MANGANILVAITE

	Ilvaite Powder X-ray + neutrons	Manganilvaite Powder X-ray + neutrons	Single- crystal X-ray		Ilvaite Powder X-ray + neutrons	Manganilvaite Powder X-ray + neutrons	Single- crystal X-ray
Ca-O21	2.402(1)	2.339(1)	2.391(1)	M2-O1	2.105(2)	2.159(1)	2.178(1)
Ca-O22	2.397(1)	2.440(1)	2.401(1)	M2-O21	2.219(1)	2.231(1)	2.236(1)
Ca-O3	2.414(1)	2.394(1)	2.408(1)	M2-O22	2.262(1)	2.233(1)	2.242(1)
Ca-O41	2.449(1)	2.384(1)	2.443(1)	M2-O41	2.274(1)	2.381(1)	2.271(1)
Ca-O42	2.478(1)	2.548(1)	2.447(1)	M2-O42	2.298(1)	2.225(1)	2.283(1)
Ca-O5	2.414(1)	2.423(1)	2.446(1)	M2-O6	1.970(1)	2.018(1)	1.997(1)
Ca-O7	2.307(2)	2.324(2)	2.305(1)	<M2-O>	2.188(1)	2.208(1)	2.201(1)
<Ca-O>	2.409(1)	2.407(1)	2.406(1)				
M11-O1	2.250(1)	2.221(1)	2.191(1)	Si1-O21	1.688(1)	1.693(1)	1.631(1)
M11-O11	2.114(1)	2.083(1)	2.067(1)	Si1-O22	1.552(1)	1.581(1)	1.640(1)
M11-O21	2.021(1)	2.062(1)	2.053(1)	Si1-O5	1.662(1)	1.647(1)	1.658(1)
M11-O3	2.149(1)	2.164(1)	2.124(1)	Si1-O6	1.594(1)	1.572(1)	1.592(1)
M11-O41	2.147(2)	2.121(1)	2.124(1)	<Si1-O>	1.624(1)	1.623(1)	1.630(1)
M11-O7	2.040(1)	2.046(1)	2.005(1)				
<M11-O>	2.120(1)	2.116(1)	2.094(1)				
M12-O1	2.122(1)	2.131(1)	2.142(1)	Si2-O3	1.640(1)	1.622(1)	1.641(1)
M12-O11	2.000(1)	2.020(1)	2.029(1)	Si2-O41	1.673(1)	1.613(1)	1.632(1)
M12-O22	2.098(1)	2.055(1)	2.041(1)	Si2-O42	1.649(1)	1.670(1)	1.635(1)
M12-O3	2.059(1)	2.068(1)	2.099(1)	Si2-O5	1.698(1)	1.693(1)	1.659(1)
M12-O42	2.087(1)	2.120(1)	2.114(1)	<Si2-O>	1.632(1)	1.650(1)	1.642(1)
M12-O7	1.948(1)	1.952(1)	1.982(1)				
<M12-O>	2.052(1)	2.058(1)	2.068(1)	O7-H	0.970(1)	0.993(1)	0.854(1)

TABLE 5. AVERAGE BOND-LENGTH $\langle\Delta l\rangle$ (Å) AND O-M-O BOND ANGLE $\langle\Delta\tau\rangle$ ($^\circ$) OCTAHEDRON DISTORTIONS

Site	Distortion index	Ilvaite, Seriphos X-ray + neutrons	Manganilvaite, Ossikovo X-ray + neutrons	single- crystal X-ray
M11	$\langle\Delta l\rangle^*$	0.08	0.06	0.06
	$\langle\Delta\tau\rangle^{\#}$	4.8	4.6	4.0
	$\langle\Delta l\rangle$	0.07	0.06	0.06
M12	$\langle\Delta l\rangle$	4.9	4.1	4.1
	$\langle\Delta\tau\rangle$	0.12	0.12	0.10
M2	$\langle\Delta l\rangle$	7.2	7.7	7.9
	$\langle\Delta\tau\rangle$			

* Average bond-length distortion $\langle\Delta l\rangle = [1/6 \sum (d_{M-O} - \langle d_{M-O} \rangle)^2]^{1/2}$; estimated standard errors in $\langle\Delta l\rangle^* = \pm 0.01$ Å.

Average bond-angle distortion $\langle\Delta\tau\rangle = [1/12 \sum (\tau_{OMO} - \langle\tau_{OMO}\rangle)^2]^{1/2}$; estimated standard errors in $\langle\Delta\tau\rangle = \pm 0.02$ $^\circ$.

TABLE 6. MÖSSBAUER PARAMETERS FOR ILVAITE AND MANGANILVAITE

Doublet	Assignment	IS	QS	FWHM	G (%)
Ilvaite, Seriphos					
1	Fe^{3+} ($M12$)	0.57	1.11	0.30	31.7
2	$\text{Fe}^{2.5+}$ ($M12$)	0.62	1.40	0.30	1.7
3	$\text{Fe}^{2.5+}$ ($M11$)	0.62	1.90	0.30	1.7
4	Fe^{2+} ($M11$)	0.95	2.18	0.39	31.7
5	Fe^{2+} ($M2$)	1.01	2.43	0.30	33.2
Manganilvaite, Ossikovo					
1	Fe^{3+} ($M12$)	0.55	1.25	0.32	28.6
2	$\text{Fe}^{2.5+}$ ($M12$)	0.65	1.43	0.32	14.3
3	$\text{Fe}^{2.5+}$ ($M11$)	0.65	1.99	0.40	14.3
4	Fe^{2+} ($M11$)	0.92	2.10	0.42	28.6
5	Fe^{2+} ($M2$)	1.08	2.33	0.32	14.2

Mössbauer parameters for model with five doublets: IS: isomer shift, QS: quadrupole splitting, FWHM: full width at half maximum, and G: relative weight of the partial Fe components of the spectra. The standard deviations in IS, QS and FWHM are 0.02 mm/s, the standard deviations in G are 0.8.

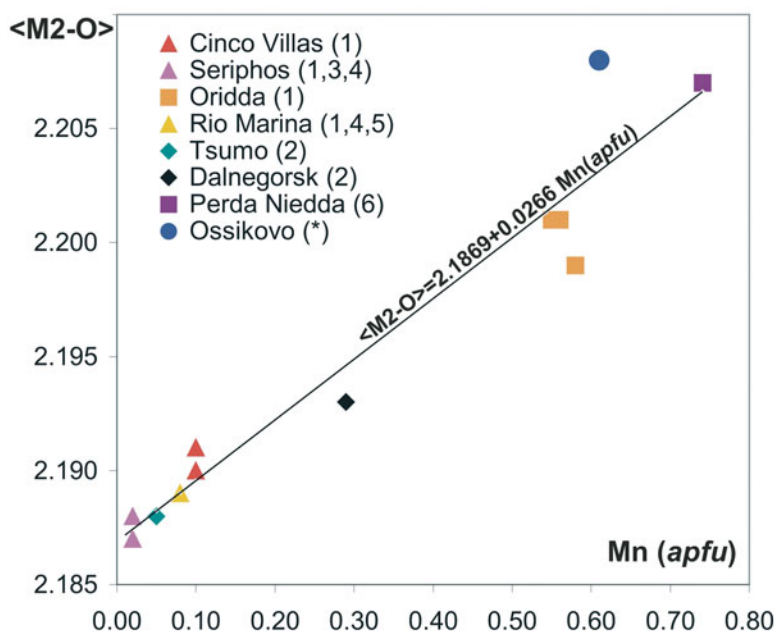


FIG. 4. Variation of $\langle M2-O \rangle$ with Mn content (in *apfu*) in ilvaite–manganilvaite. Data from: (1) Carrozzini (1994), (2) Takéuchi *et al.* (1983), (3) Finger & Hazen (1987), (4) Ghose *et al.* (1984), (5) Bonazzi & Bindi (1999), (6) Bonazzi & Bindi (2002), and the present study (*). The line representing the empirical linear equation $\langle M2-O \rangle = 2.1869 + 0.0266(9) \text{ Mn}^{2+}(\text{apfu})$ is the one proposed by Carrozzini (1994) and Bonazzi & Bindi (2002).

$M2$ G ratio is $\sim 2:1$, as expected from the stoichiometry. The distribution of the Fe ions over the $M1$ ($= M11 + M12$) and $M2$ sites in manganilvaite is practically the same (the G values of the components are normalized to 100% not considering the Mn^{2+} ions occupying $M2$). However, the presence of Mn^{2+} in the ilvaite structure leads to a significant increase in the mixed-valence contribution. The replacement of Fe^{2+} by Mn^{2+} at the $M2$ site results in complex deformations of the $M11$ and $M12$ octahedra (Table 5) as well as some changes in the $M11$ – $M12$ distances. There are two different $M11$ – $M12$ distances along the double chains of octahedra: $M11$ – $M12$ and $M12$ – $M11'$. In the Seriphos ilvaite, $M11$ – $M12 = 3.004(1) \text{ \AA}$ and $M12$ – $M11' = 2.854(1) \text{ \AA}$. The distance $M12$ – $M11'$ remains practically the same [$2.855(1) \text{ \AA}$] in manganilvaite, whereas the $M11$ – $M12$ distance decreases slightly [$2.994(1) \text{ \AA}$], providing more favorable conditions for electron transfer between these ions. Mössbauer studies on synthetic ilvaite of low Mn content ($<0.19 \text{ apfu}$) also suggest that incorporation of Mn^{2+} enhances the valence fluctuations in ilvaite (Ghazi-Bayat *et al.* 1992, Amthauer *et al.* 1998).

CONCLUSIONS

1) The present structural studies confirm that manganilvaite, the new Mn-dominant end-member of the ilvaite group, has the monoclinic ilvaite-type structure.

2) Compositional variations in the ilvaite–manganilvaite series are common among samples from the same deposit and even within a single crystal.

3) In manganilvaite, Mn^{2+} occurs at the $M2$ and Ca sites. The small charge deficit at the Ca^{2+} site, usually existing in Mn-bearing samples, is the result of partial replacement by Mn, whereas the majority of Mn^{2+} substitutes for Fe^{2+} at the $M2$ site.

4) Replacement of Fe^{2+} by Mn^{2+} at the $M2$ sites leads to an increase in bond-angle distortion of the $M2$ octahedron, increase of the Fe^{2+} – Fe^{3+} disorder, and to an increase in $\text{Fe}^{2+} \leftrightarrow \text{Fe}^{3+}$ charge transfer between the $M11$ and $M12$ sites.

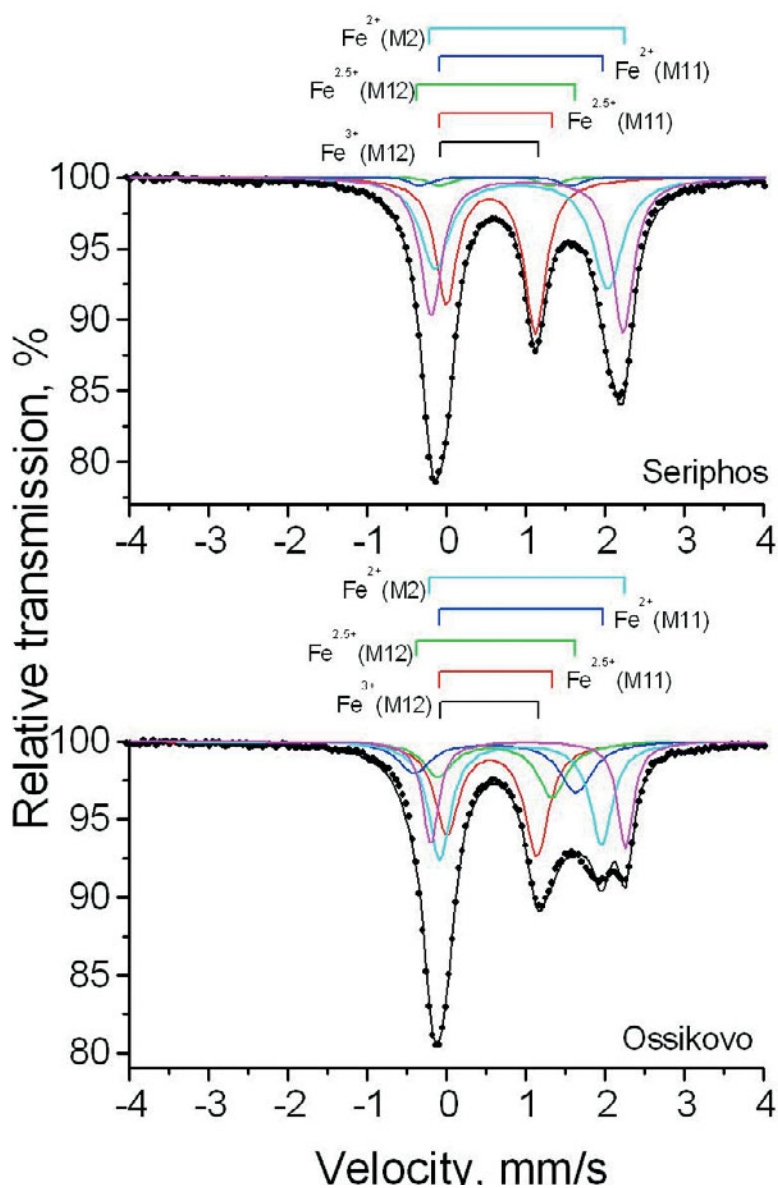


FIG. 5. Mössbauer spectra for Mn-free ilvaite from Seriphos and manganilvaite from Ossikovo.

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