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MANGANILVAITE, $\mathrm{CaFe^{2+}Fe^{3+}(Mn,Fe^{2+})(Si_2O_7)O(OH)}$, A NEW MINERAL OF THE ILVAITE GROUP FROM Pb–Zn SKARN DEPOSITS IN THE RHODOPE MOUNTAINS, BULGARIA

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ABSTRACT

Manganilvaite, $\mathrm{CaFe^{2+}Fe^{3+}(Mn,Fe^{2+})(Si_2O_7)O(OH)}$, is a new mineral species, the Mn end-member of the ilvaite group of minerals. It was found in the Pb–Zn–(Mn) skarn deposits of the central Rhodope Mountains, Bulgaria, and especially in the Ossikovo and Mogilata deposits (Madan ore district) and the Govedarnika deposit (Laki district). In the marble-hosted distal skarn-type orebodies, it is closely associated with Mn-rich clinopyroxene (hedenbergite–johannsenite) ± rhodonite, and with the products of their retrograde alteration (manganoan amphiboles and chlorites, bustamite, manganoan carbonates, quartz). The mineral is black, with a vitreous luster, brittle, with a distinct cleavage. It has Mohs hardness of 5½–6 and a micro-indentation hardness ($\mathrm{VHN_{100}}$) of 868 kg/mm^2. The measured density D_x is 3.92 g/cm^3. In reflected light, it is opaque with moderate pleochroism, from bluish gray to grayish brown, strongly anisotropic in grayish blue to pale reddish brown colors and with red internal reflections. It is homogeneous in BSE images and in thin sections under the IR microscope, where it is transparent. The reflectance is low, in the range 8.3–5.7% for $\mathrm{R_{min}}$ (// *c*) and 10.0–9.3% for $\mathrm{R_{max}}$ (// *a*). In some cases, well-shaped dipyramidal crystals occur, with a prismatic habit along *c* and forms *r*{011}, *m*{110}, *s*{210} and *o*{111}. The average results of 62 and 17 electron-microprobe analyses of manganilvaite from Ossikovo and Govedarnika, respectively, are (in wt.%): MgO 0.48, 0.45; $\mathrm{Al_2O_3}$ 0.20, 0.34; $\mathrm{SiO_2}$ 29.65, 29.48; CaO 12.62, 13.06; $\mathrm{TiO_2}$ 0.02, 0.04; MnO 11.99, 13.54; FeO 40.93, 39.31, ($\mathrm{H_2O}$ 2.21), total 98.10, 98.43. The MnO content varies in the ranges 9.02–14.96 and 12.57–14.86%, respectively, the amount of Mn attaining 0.85 *apfu*. The mineral is of ilvaite-type structure, monoclinic, $P2_1/a$, with cell-edge parameters *a* 13.0250(7), *b* 8.8514(5), *c* 5.8486(3) Å, β 90.167(1)°, *V* 674.28 Å^3, $Z = 4$, as determined by composite X-ray and neutron powder-diffraction studies (see the companion paper). Manganese occupies the *M*2 octahedral position together with some Fe^{2+}. Ilvaite and manganilvaite form a continuous solid-solution series, and gradations between them can be observed even in a single crystal. The strongest eight lines of the X-ray powder-diffraction pattern [*d* in Å(I)(*hkl*)] are: 2.875(85)(130), 2.848(90)(401), 2.718(100)(112), 2.687(70)(230), 2.442(33)(231), 2.180(48)(140,402), 2.111(47)(322,412), and 1.475(48)(060,252). As a product of retrograde alteration of the early-skarn pyroxenes, manganilvaite indicates evolution of the hydrothermal process from reduction to more oxidized and hydrated environment. The mineral name recalls its composition and relation to ilvaite.

Keywords: manganilvaite, new mineral species, ilvaite–manganilvaite solid-solution series, electron-microprobe data, reflectance, X-ray data, Ossikovo mine, Govedarnika mine, central Rhodope Mountains, Bulgaria.

SOMMAIRE

La manganilvaïte, $\mathrm{CaFe^{2+}Fe^{3+}(Mn,Fe^{2+})(Si_2O_7)O(OH)}$, esr un nouvelle espèce minérale, le pôle manganifère du groupe de l'ilvaïte. Nous l'avons découverte dans des gisements à Pb–Zn–(Mn) de type skarn dans les montagnes Rhodope centrales, en Bulgarie, plus particulièrement dans les gisements de Ossikovo et Mogilata (district minéralisé de Madan) et de Govedarnika (district de Laki). Trouvé dans les parties distales de ces gîtes minéraux, développés aux dépens de marbre, ce minéral est étroitement associé au clinopyroxène manganifère (hédenbergite–johannsenite) ± rhodonite, et aux produits de leur altération rétrograde

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(amphiboles et chlorites manganifères, bustamite, carbonates manganifères, quartz). C'est un minéral noir, à l'éclat vitreux, cassant, avec un clivage distinct. Sa dureté de Mohs est entre 5½ et 6, et sa dureté mesurée par micro-indentation (VHN_{100}) correspond à 868 kg/mm^2. La densité mesurée D_x est 3.92 g/cm^3. En lumière réfléchie, la manganilvaïte est opaque, avec pléochroïsme moyen allant de gris bleuâtre à brun grisâtre, avec une forte anisotropie du bleu grisâtre à brun rougeâtre pâle et des réflexions internes rouges. La manganilvaïte est homogène selon les images à électrons rétrodiffusés et en lames minces examinées dans un microscope dans l'infrarouge, où elle est transparente. La réflectance R_{min} (// *c*) est faible, entre 8.3 et 5.7%, et R_{max} (// *a*) est entre 10.0 et 9.3%. Nous avons trouvé des cristaux bipyramidaux idiomorphes, avec une morphologie prismatique *c* et montrant les formes *r*{011}, *m*{110}, *s*{210} et *o*{111}. Une moyenne des résultats de 62 et de 17 analyses de la manganilvaïte de Ossikovo et de Govedarnika, respectivement (données obtenues à la microsonde électronique en termes pondéraux), est: MgO 0.48, 0.45; Al_2O_3 0.20, 0.34; SiO_2 29.65, 29.48; CaO 12.62, 13.06; TiO_2 0.02, 0.04; MnO 11.99, 13.54; FeO 40.93, 39.31, (H_2O 2.21), pour un total de 98.10, 98.43. La teneur en MnO varie dans les intervalles 9.02–14.96 et 12.57–14.86%, respectivement, la quantité de Mn atteignant 0.85 *apfu*. Le minéral possède une structure de type ilvaïte, monoclinique, $P2_1/a$, avec les paramètres réticulaires *a* 13.0250(7), *b* 8.8514(5), *c* 5.8486(3) Å, β 90.167(1)°, *V* 674.28 Å^3, *Z* = 4, déterminés par étude combinée des spectres de diffraction X et neutronique (méthode des poudres; voir l'article connexe). Le Mn occupe la position octaédrique *M*2, de même qu'un peu de Fe^{2+}. L'ilvaïte et la manganilvaïte forment une solution solide continue, avec passages graduels d'un à l'autre même dans un monocristal. Les huit raies les plus intenses du spectre de diffraction X (méthode des poudres) [*d* en Å(I)(*hkl*)] sont: 2.875(85)(130), 2.848(90)(401), 2.718(100)(112), 2.687(70)(230), 2.442(33)(231), 2.180(48)(140,402), 2.111(47)(322,412), et 1.475(48)(060,252). Comme produit de l'altération rétrograde de pyroxènes précoces dans ces skarns, la manganilvaïte indique une évolution du processus hydrothermal, au départ dans un milieu réducteur, vers un milieu davantage oxydant et hydraté. Le nom du minéral rappelle la composition et la relation avec l'ilvaïte.

(Traduit par la Rédaction)

Mots-clés: manganilvaïte, nouvelle espèce minérale, solution solide ilvaïte–manganilvaïte, données de microsonde électronique, réflectance, diffraction X, mine Ossikovo, mine Govedarnika, montagnes Rhodope centrales, Bulgarie.

INTRODUCTION

Manganilvaite, a new mineral species, the Mn-dominant end-member of the ilvaite group of minerals, was found and systematically studied in lead–zinc skarn deposits of the central Rhodope Mountains, Bulgaria. By means of a detailed analysis of its structure, a combined X-ray and neutron diffraction, as well as Mössbauer spectroscopy, we have established that like ilvaite, it is a mixed-valence iron sorosilicate, $CaFe^{2+}Fe^{3+}(Mn,Fe^{2+})(Si_2O_7)O(OH)$, in which Mn^{2+} occupies dominantly the *M*2 octahedral site, which in Mn-free ilvaite is occupied only by Fe^{2+} cations (Zotov *et al.* 2005).

In this paper, we present the mineralogical description and paragenetic relationships of the mineral. These aspects are important for a full understanding of its genesis and the zonation sequence in skarn bodies. The structural analysis, which proved the ordered distribution of Mn, is presented in a companion paper (Zotov *et al.* 2005).

BACKGROUND INFORMATION

Ilvaite ("lievrite" in the older literature) has been well known for a long time as a constituent of various Fe, Zn, and Pb–Zn skarn-type ore deposits. It was described for the first time from the island of Elba (Ilva in Latin) as early as in 1811 (Gaines *et al.* 1997). Though not developed in large quantities, it was also found in many other similar skarn deposits in Italy (Tuscany and Sardinia), Greece, Russian Far East, Japan, and USA (Chukhrov 1979, Einaudi *et al.* 1981, Gaines *et al.* 1997, Larsen & Dahlgren 2002). In addition, it was found in quartz–magnetite veins in the Fossum iron ore deposits (Norway), as a product of late alteration of various magmatic rocks (Naslund *et al.* 1983, Agata & Adachi 1995, Larsen & Dahlgren 2002), and in some metamorphic stratiform Pb–Zn deposits (Plimer & Ashley 1978).

Manganese is the most common substituent for Fe in ilvaite at many of these deposits. The earliest descriptions of manganoan ilvaite are from the Bulgarian Pb–Zn skarn deposits in the Rhodope Mountains: the Lakavitsa deposit in the Laki district, with 12.25 wt.% MnO (Marinova-Petrova & Hristova 1961) and the Sharenka deposit in the Madan district, with 12.77 wt.% MnO (Velchev 1962). These are the Mn-richest members noted in Chukhrov (1979). Later, Stoinova (1986) also mentioned ilvaite from the Laki district with 12.06 wt.% MnO.

Manganese-enriched ilvaite with up to 10.6 wt.% Mn also has been described in the Tetyukhe ore district (now, Dalnegorsk) in the Russian Far East (Khetchikov 1956, Mozgova & Borodaev 1965, Chukhrov 1979). Remarkable crystals of ilvaite from this locality are exposed in many mineralogical museums. Evidently, the "Techukhe" specimen with 0.29 *apfu* Mn studied by Takéuchi *et al.* (1983) comes from the same deposit. Manganoan ilvaite also was found in the Broken Hill deposits, with 13.55 wt.% MnO, and at Ban Ban (both in Australia), with 10.97–12.42 wt.% MnO (Plimer & Ashley 1978, Ashley 1980), in the Zn skarns of the Groundhog Zn–Pb–Cu–Ag mine, New Mexico, with 9.19–11.79 wt.% MnO (Meinert 1987, Franchini *et al.* 2002), and from the Campiglia Marittima skarns in Italy, with 13.97 wt.% (Capitani & Mellini 2000). Recently, Larsen & Dahlgren (2002) also reported the occurrence of ilvaite with a high average content of MnO, 12.24 wt.%, from the Konnerrud contact Cu–Pb–Zn deposit in the Oslo Graben in Norway, without presenting results of analyses. No crystallographic or structural data were given for all these finds. Such data were obtained by single-crystal X-ray-diffraction studies of manganoan ilvaite from two Sardinian skarn deposits: Oridda, for material containing up to 10 wt.% MnO (Carrozzini 1994), and Perda Niedda, with 9.43–12.86 wt.% MnO (Bonazzi & Bindi 2002). Synthetic Mn-bearing ilvaite was produced and studied by Ghazi-Bayat *et al.* (1989) and Cesena *et al.* (1995).

During our systematic studies of the skarn mineralogy of the Rhodope Pb–Zn deposits, in the Madan and Laki districts, we established the presence of members of the ilvaite group with high to extremely high Mn content (Vassileva *et al.* 2001), which provided adequate material with which to characterize this new mineral. It was named *manganilvaite* after its composition and the close relation to ilvaite. The mineral and its name have been approved by the IMA Commission on New Minerals and Mineral Names (IMA 2002–016). The type specimens are deposited in the collections of the Geological Institute, Bulgarian Academy of Sciences, Sofia, under catalogue number M1.2003.5–6.

OCCURRENCE

The Rhodope Mountains are an important sector of the Alpine – Carpathian – Balkan metallogenic province. This sector contains large, economically significant lead–zinc deposits of vein and replacement type. In the central Rhodope Mountains, such deposits cross-cut the high-grade metamorphic rocks of the old (presumably Precambrian) Rhodopian complex and partly are overlain by Tertiary clastic sediments (Kolkovski *et al.* 1996, Ivanov 2000). These deposits are related to several separate hydrothermal ore-forming systems of Tertiary (about 30 Ma) age and relatively shallow depth (1000 m and more). The ore districts of Madan (in the southern part) and Laki (in the northern part) are the largest and most important in this sector (Fig. 1).

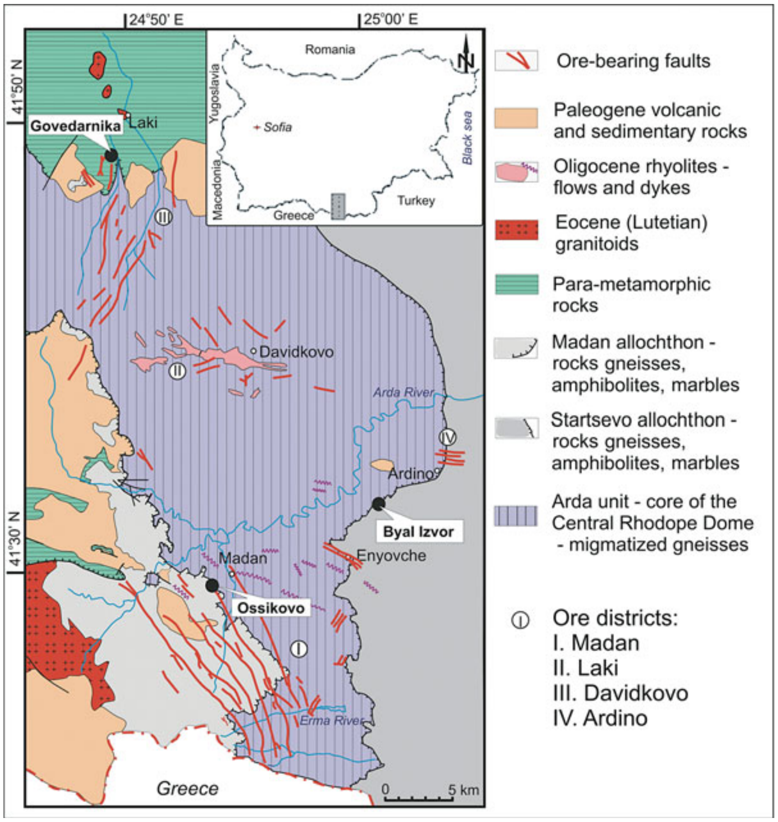

FIG. 1. Geological map of the Central Rhodopes, with location of the skarn Pb–Zn ore deposits in which manganilvaite was found (modified after Ivanov 2000).

The Rhodopian metamorphic complex consist of two parts, a lower one, Arda unit, composed of migmatized gneisses in the core of the Madan–Davidkovo (Central Rhodopian) dome, and an upper, overthrust part, cropping out in the western and eastern parts of the dome (Madan and Startsevo allochthons, respectively), and composed of various gneisses, amphibolites, mica schists and marbles. The main ore-controlling structures are large, steeply dipping faults enclosing ore veins. Layers of marble in the different parts of the massif are the host rocks for rich replacement-type skarn-ore beds and irregular bodies located along the ore veins (Fig. 2). No direct link between these skarns and magmatic rocks has been established so far.

In the Madan district, the larger of the two, six major ore-controlling faults of north-northwest orientation and up to 10–15 km long are known. The replacement skarn-type orebodies are related to three different marble horizons, only the upper two of which are accessible and worked at present (Bonev 2003). Manganilvaite was found and studied in the metasomatic deposits of the adjacent Ossikovo and Mogilata mines, in the northern part of the district, not too far from the former Sharenka mine. In the last year, these mines were abandoned and closed as well.

In the Laki district, the ore-controlling faults are submeridional to north-northeast-oriented, and the replacement bodies are related to one upper marble horizon. Manganilvaite was found in the largest mine, Govedarnika, in addition to the earlier finds from the abandoned Lakavitsa and Goranska Padina deposits. In these deposits, the mineral occurs only as very small black grains associated with bustamite, formed as a replacement product after manganoan hedenbergite in the skarn. Mineralogically, the two districts are very similar (Kolkovski *et al.* 1996, Bonev 2003, Vassileva & Bonev 2003a). The pre-ore marble-hosted skarn bodies consist of highly to extremely Mn-rich clinopyroxenes (manganoan hedenbergite to end-member johannsenite) in fibroradial to spherulitic aggregates or in dense masses. Minor rhodonite also occurs. Locally (*e.g.*, in Ossikovo), some marble horizons contain graphite flakes, which are preserved as unchanged relics also in the pyroxene skarns.

During intensive retrograde alteration of the skarns, various Mn-rich silicate and carbonate minerals were formed, including manganoan amphiboles, pyroxenoids, chlorites, garnet (retrograde manganoan andradite), together with abundant manganoan carbonates and quartz. These alterations are nearly contemporaneous with the main sulfide ores. The mineralization consists mainly of galena, sphalerite, pyrite, and chalcopyrite, deposited with quartz as open-space filling in the ore veins, and metasomatically replacing the early skarns. The temperature of ore-formation is rather high, 350–300–280°C, according to fluid-inclusion studies (Kolkovski *et al.* 1996). A late, low-temperature (200–220°C and lower) quartz–carbonate stage with minor sulfides also is widespread.

Manganilvaite is invariably closely associated with skarn assemblages and products of their alteration (Vassileva & Bonev 2003a). In the Ossikovo and Mogilata deposits, it occurs usually as a minor mineral component in the distal parts of the skarn orebodies (Figs. 2, 3), as: 1) single grains or nests within the pyroxene aggregates, mainly in their interstices, 2) single crystals or groups of crystals at the skarn–marble front, and 3) crystals at the periphery of small carbonate or quartz nests included in the pyroxene or rhodonite aggregates. In Govedarnika, ilvaite is closely associated with bustamite, which also is a product of pyroxene alteration. In some specimens from Ossikovo, the volume of the ilvaite-group minerals reaches up to 5% and even more, whereas in Govedarnika, it is below 1%. However, in many of the skarn orebodies of the two districts, this mineral was not observed.

In another small skarn deposit of the same area, Byal Izvor (Fig. 1), Mn-bearing ilvaite is a major mineral, occurring as large, black crystals of rhombic habit, reaching up to 10 cm along the *c* axis. It is associated with hedenbergite, garnet, hematite, magnetite, and small amounts of sulfides (chalcopyrite, pyrite, galena). However, the Mn content of this mineral is not higher than 5 wt.% MnO (Vassileva *et al.* 2001).

PHYSICAL AND OPTICAL PROPERTIES

Manganilvaite from the Rhodope deposits is black, and has a vitreous luster. The streak is black to brownish black. The mineral is brittle, with a distinct (100) cleavage and an uneven fracture. It has a Mohs hardness of 5½ to 6 and a micro-indentation hardness (VHN_{100}) of 868 kg/mm^2 (mean value of 10 measurements between 824 and 946 kg/mm^2). The measured density is 3.92 g/cm^3, and the calculated density is 3.93 g/cm^2. The mineral is easily recognizable in hand specimens owing to its separate grains and black color. It becomes gelatinized with HCl.

In reflected light, the mineral is opaque, gray to bluish gray, with red internal reflections. It shows pleochroism from bluish gray to lilac-brown and strong anisotropy in grayish blue to pale reddish brown. In transmitted light in very thin sections at the rim of crystals, it is semitransparent with a brown-red color. In thin sections under the infrared microscope, manganilvaite is transparent, and seems homogeneous, as well as in BSE images.

The reflectance (R) was measured from oriented polished sections with a Leica microscope spectrophotometer in air from 400 to 700 nm using WTiC reference standard (Table 1). The value R_{min} is measured parallel to *c*, and R_{max}, parallel to *a*. The R values are low, with reflectance curves slightly descending to the higher wavelengths, more noticeable for R_{min}. The R data are very close to the data collected for Mn-free ilvaite from Seriphos (Picot & Johan 1982) and low-Mn ilvaite from Rio Marina, Italy (Beran 1980, Bonazzi *et al.* 2001) and Artikutza, Spain (Pesquera & Velasco 1986). However, specific differences can be noticed (Fig. 4). The R_{max} values of manganilvaite are slightly (0.1–0.3) lower in the 580–700 nm range, whereas the R_{min} values are generally higher, increasing from 0.1 at 460, to 0.3 at 540–590, and to 0.9 at the 600–660 range, and then decreasing to 0.3 again at 700 nm. The R data for Mn-bearing ilvaite from Tetyukhe–Dalnegorsk (Mozgova & Borodaev 1965, Chvileva *et al.* 1988) show similar trends but with smaller differences between R_{min} and R_{max}.

The infrared spectrum of powder manganilvaite was measured in the interval 400–3500 cm^{-1} and compared to that of Mn-free ilvaite from Seriphos, Greece (Table 2, Fig. 5). The two spectra are very similar and in agreement with the data of Mozgova & Borodaev (1965), Kräutner & Medeşan (1969), and Güttler *et al.* (1989) for ilvaite of various deposits. We note that some of the bands in the manganilvaite spectrum in the range 800–1100 cm^{-1}, commonly assigned to the asymmetric Si–O stretching vibrations in sorosilicates (Lazarev 1972), are slightly lower in intensity than those in Mn-free ilvaite. A similar trend is observed comparing Mn-free ilvaite from Rio Marina (Elba) with Mn-enriched ilvaite (7 wt.% MnO) from Rushita (Kräutner & Medeşan 1969).

CRYSTAL MORPHOLOGY

Well-shaped crystals of manganilvaite formed by free crystallization occur in small nests of calcite or quartz in the altered skarns of the Ossikovo deposit. Such crystals were extracted by selective dissolution of the enclosing calcite with acetic acid. They are up to 1–2 mm long and could be measured by optical goniometry. Crystals are dipyramidal, with a prismatic habit and rather simple morphology, elongate along the *c* axis. The main forms are *r*{011}, *m*{110} and *s*{210} (in the structural setting). Minor *o*{111} are also developed in some crystals. The prismatic faces have strong longitudinal *m*:*s* oscillation striation, and the *r* faces are striated along [011]. In some crystals, the *b*{010} faces also occur with rough horizontal *r:b* striation. Note that authors of all morphological descriptions of ilvaite crystals available in the mineralogical literature, for example the older ones (summarized by Goldschmidt 1918), and also the later ones, summarized by Chukhrov (1979), and Kostov & Kostov (1999), and supplemented by Larsen & Dahlgren (2002), traditionally used the old morphological orthorhombic axial setting of crystals (space group *Pbnm*, and $c < a < b$), with interchanged *a* and *b* axes, as compared to the now-accepted structural orientation, consistent with the space group $P2_1/a$ (Table 3) and with only slight monoclinic deviation (β 90.17°). Typical shapes of the manganilvaite crystals examined are shown in Figure 6 (with *b* axis toward the reader, for direct comparison with other published drawings of ilvaite crystals). There is an evident similarity in the known morphologies of ilvaite from different deposits: ilvaite from Seriphos, manganoan ilvaite from Tetyukhe (Mozgova & Borodaev 1965, Chukhrov 1979) and from Norway (Larsen & Dahlgren 2002). However, as shown by Goldschmidt (1918), some ilvaite crystals from Elba and Greenland have a more complex morphology, owing to the development of additional forms in the terminal parts and in the prismatic [001] zone.

Since manganilvaite was deposited at a *T* above the orthorhombic – monoclinic transition (60–117°C for ilvaite, according to Ghose *et al.* 1984), this is the original orthorhombic morphology of the crystals. The inference of Takéuchi *et al.* (1994) in favor of submicroscopic polysynthetic twinning seems very reasonable, but we could not find evidence for it.

Usually, the coarse-grained aggregates of manganilvaite replacing masses of pyroxene have irregular subhedral to anhedral outlines. Only some grains, where formed in small open vugs, have well-developed flat faces.

TABLE 1. REFLECTANCE OF MANGANILVAITE FROM OSSIKOVO

λ (nm)	R min // *c*	R max // *a*	λ (nm)	R min // *c*	R max // *a*
400	8.3	10.0	560	7.3	9.7
420	8.4	10.1	580	7.0	9.7
440	8.3	10.0	*589*	6.9	9.7
460	8.3	10.0	600	6.7	9.7
480	8.2	9.9	620	6.4	9.5
500	8.0	9.9	640	6.1	9.5
520	7.9	9.8	*650*	6.0	9.4
540	7.5	9.8	660	5.9	9.4
546	7.5	9.7	680	5.7	9.4
			700	5.7	9.3

TABLE 2. INFRARED SPECTRA OF Mn-FREE ILVAITE FROM SERIPHOS AND MANGANILVAITE FROM OSSIKOVO

Ilvaite	Manganilvaite	Ilvaite	Manganilvaite
433	424	901	900
450	449	968	950
480 sh	480 sh	981	981
496	493	-	1005 sh
-	503 sh	1028	1040
-	513 sh	1121	1121
538	534	1380	1377
573	571	1459	1454
706	700	1651	1635
820	820	1794	1739
880 sh	880 sh	3440	3446

sh: shoulder. The frequency of the absorptions is expressed in cm^{-1}.

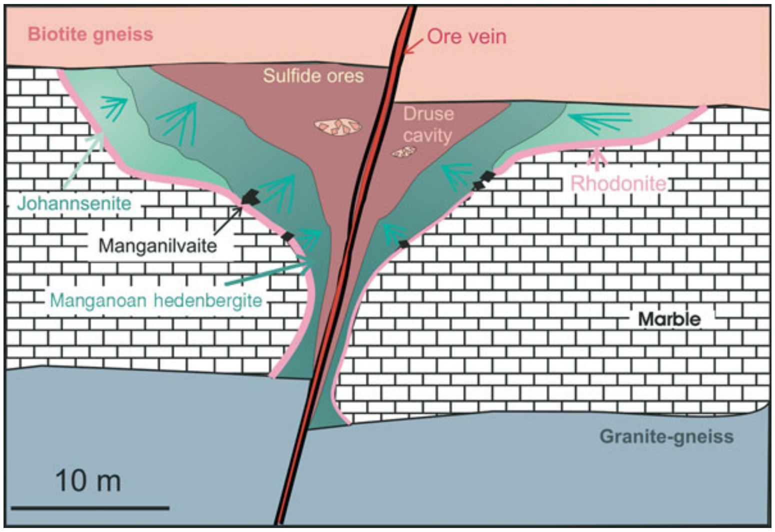

FIG. 2. Generalized cross-section of a skarn-type orebody in the Ossikovo deposit, showing the complexity of zoning.

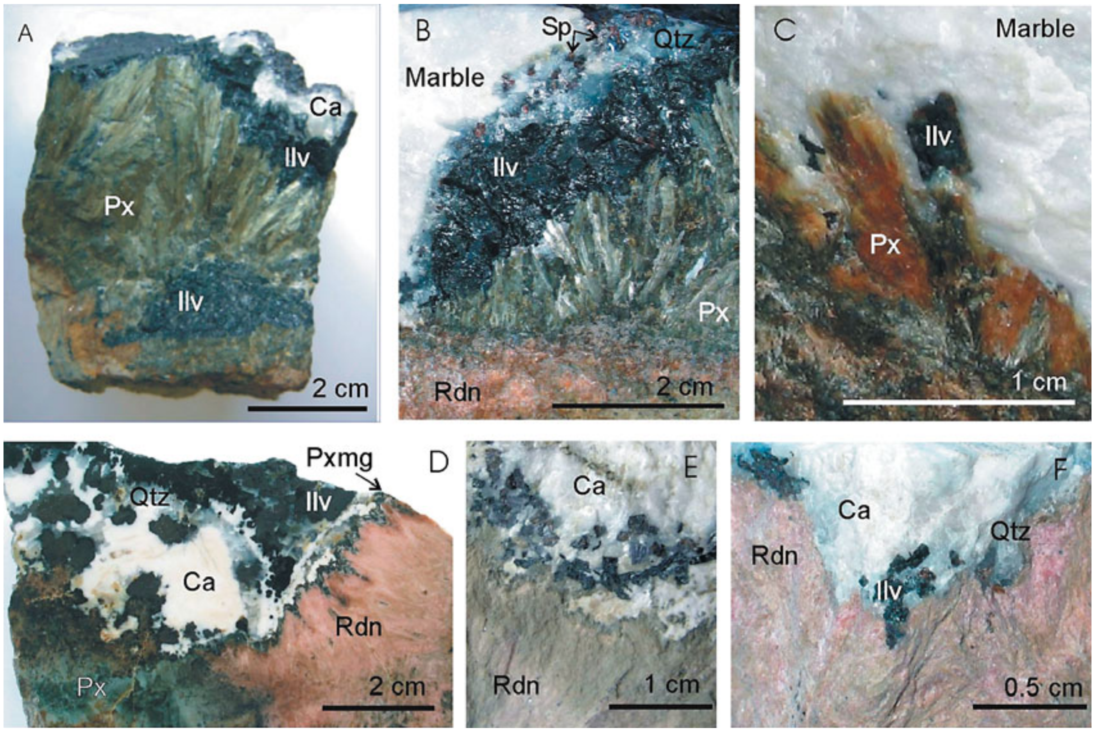

FIG. 3. Position of manganilvaite crystals and aggregates within the radiating pyroxene–rhodonite skarns and around the pyroxene–marble metasomatic front. Hand specimens from Ossikovo. Px: pyroxene, Ilv: manganilvaite, Rdn: rhodonite, Pxmg: pyroxmangite, Qtz: quartz, Ca: calcite, and Sp: sphalerite.

X-RAY POWDER-DIFFRACTION DATA

Unit-cell parameters for manganilvaite, as determined from refinements of combined X-ray and neutron powder-diffraction data, are given in Table 3, along with the parameters of Mn-free ilvaite from Seriphos, Greece. A detailed discussion of the differences observed is given in Zotov *et al.* (2005). The X-ray powder-diffraction data of manganilvaite (Co$K\alpha_1$ radiation) are given in Table 4. The *hkl* values are determined taking into account the calculated intensities from the structure refinements. The interplanar distances of manganilvaite are similar to those of pure ilvaite from Gruba, Oberhalstein (PDF 25–0149).

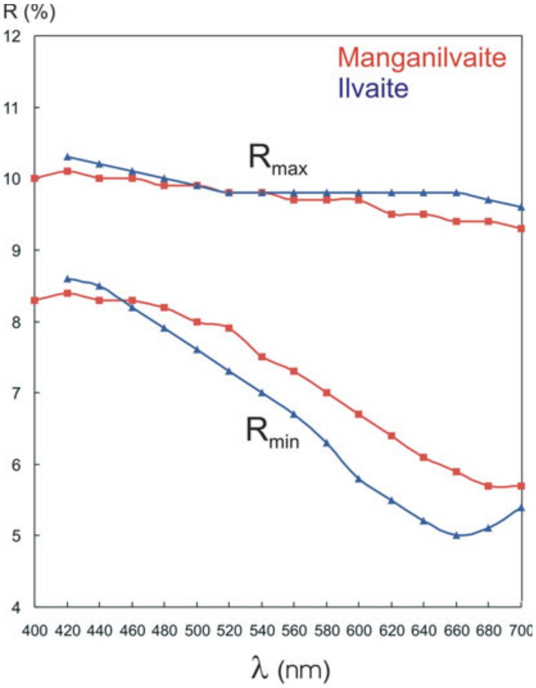

FIG. 4. Reflectance (R in %) of manganilvaite from Ossikovo and Mn-free ilvaite from Seriphos (Picot & Johan 1982).

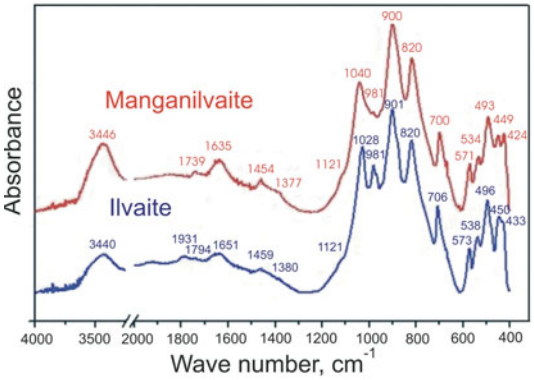

FIG. 5. IR absorption spectra of manganilvaite from Ossikovo and Mn-free ilvaite from Seriphos.

TABLE 3. UNIT-CELL PARAMETERS OF ILVAITE AND MANGANILVAITE

	Ilvaite Seriphos	Manganilvaite Ossikovo
a, Å	13.0146(3)	13.0250(7)
b, Å	8.8046(2)	8.8514(5)
c, Å	5.8588(2)	5.8486(3)
β °	90.28(1)	90.167(1)
V, Å^3	671.34(3)	674.28(7)
Space group	$P2_1/a$	$P2_1/a$
Z	4	4

TABLE 4. X-RAY POWDER-DIFFRACTION DATA OF MANGANILVAITE

I	*d* obs	*d* calc	*hkl*	*I*	*d* obs	*d* calc	*hkl*	*I*	*d* obs
18	7.34	7.320	110	47	2.111	2.125	322	18	1.424
8	6.53	6.512	200			2.116	$\bar{4}12$	50	1.395
5	4.90	4.879	011			2.110	412	11	1.372
8	4.58	4.573	$\bar{1}11$	4	2.055	2.050	132	4	1.358
4	4.20	4.190	120	2	2.021	2.033	601	7	1.334
24	3.901	3.900	211	25	1.973	1.973	$\bar{2}41$	8	1.303
8	3.428	3.408	$\bar{1}21$			1.972	241	19	1.284
20	3.257	3.256	400			1.971	340	5	1.260
		3.247	$\bar{3}11$	12	1.952	1.955	$\bar{4}22$	13	1.249
9	3.102	3.100	221			1.953	530	38	1.211
		3.099	320	20	1.897	1.897	512	5	1.198
16	2.920	2.924	002	6	1.852	1.854	$\bar{5}31$	7	1.185
85	2.875	2.877	130			1.851	531	5	1.176
90	2.848	2.848	$\bar{4}01$			1.848	621	4	1.167
		2.841	401	5	1.818	1.821	710	4	1.140
27	2.737	2.741	$\bar{3}21$	4	1.792	1.784	023	3	1.134
		2.736	321	5	1.768	1.768	$\bar{1}23$	4	1.121
100	2.718	2.717	$\bar{1}12$			1.765	042	12	1.110
		2.714	112	13	1.748	1.749	$\bar{1}42$	10	1.010
70	2.687	2.687	230	39	1.716	1.715	720	3	1.088
15	2.624	2.622	420	5	1.695	1.694	051	4	1.082
5	2.579	2.581	131	29	1.673	1.676	$\bar{6}31$	8	1.073
17	2.553	2.557	$\bar{2}12$			1.675	$\bar{4}03$	5	1.066
		2.552	212			1.670	403	11	1.054
11	2.499	2.498	510	19	1.635	1.639	251	6	1.044
33	2.442	2.443	$\bar{2}31$			1.634	342	9	1.031
		2.441	231			1.628	800	9	1.020
		2.440	022	22	1.623	1.626	$\bar{5}32$	5	1.006
23	2.395	2.400	$\bar{1}22$			1.622	532		
		2.397	122	3	1.600	1.601	810		
		2.395	$\bar{4}21$	14	1.577	1.578	$\bar{2}33$		
		2.391	421			1.577	233		
24	2.337	2.342	$\bar{3}12$	7	1.561	1.562	423		
		2.336	312	7	1.546	1.548	640		
4	2.295	2.300	$\bar{5}11$			1.546	$\bar{8}11$		
		2.296	511	20	1.527	1.528	820		
		2.283	222	35	1.499	1.500	$\bar{6}32$		
4	2.253	2.254	$\bar{3}31$			1.499	$\bar{6}41$		
		2.251	331	48	1.475	1.475	060		
3	2.209	2.213	040			1.475	252		
48	2.180	2.182	140			1.475	$\bar{5}23$		
		2.179	$\bar{4}02$	28	1.462	1.462	004		
		2.173	402						

Stoe powder diffractometer, transmission geometry, Ge monochromator, Co$K\alpha_1$ radiation (λ 1.78897 Å), Δ2θ = 0.02°, 10 s/step. The *d* values are expressed in Å.

CHEMICAL COMPOSITION

The chemical composition of manganilvaite from different localities was studied by electron-probe micro-analysis instruments (Camebax SX and JEOL Superprobe-733, equipped with EDS ORTEC–5000 System), at 15 and 20 kV. Natural standards were employed: diopside, manganoan ilmenite with 11 wt.% MnO or tephroite, K-feldspar, and quartz. Iron concentration was measured as FeO_{total}, and then recalculated as FeO and Fe_2O_3 according to the method of Droop (1987). In BSE images, the samples seem homogeneous. We found that the rim of crystals is slightly Mn-enriched. Representative results of electron-microprobe analyses, including of areas richest in Mn, are presented in Table 5. The amount of H_2O was determined through dehydration by heating in vacuum. The result for a sample from Ossikovo, 2.20 wt.% (mean of 10 determinations), coincides well with the theoretical value (2.21 wt.%).

The following chemical peculiarities were established: 1) the level of Mn in the samples from the Madan and Laki deposits varies in the range 9–15 wt.% MnO, with only minor variations in the various deposits; 2) Ca is in the range 0.92–0.97 *apfu*, invariably slightly below 1; in the Ossikovo samples, Ca is about 0.92 *apfu*, and slightly lower than in the Govedarnika samples (~0.94 *apfu*), whereas in the Mn-free Seriphos ilvaite, Ca is 1 *apfu*; 3) Mg invariably is low (<0.50 wt.% MgO), and 4) Si is nearly stoichiometric (~2 *apfu*).

As established by the combined X-ray-diffraction and neutron-diffraction structural study (Zotov *et al.* 2005), part of the Mn complements the slightly deficient Ca in the largest seven-coordinated Ca polyhedra, whereas the rest of the Mn occupies as Mn^{2+} the larger and distorted *M*2 octahedral site, together with some Fe^{2+}. The distribution of the octahedrally coordinated Fe^{2+}, Fe^{3+} and Mn cations of the investigated samples of manganilvaite is compared with the previous results on ilvaite in Figure 7. The dependence of the Fe^{2+} content *versus* Mn^{2+} content of the Ossikovo and Govedarnika samples is shown in Figure 8.

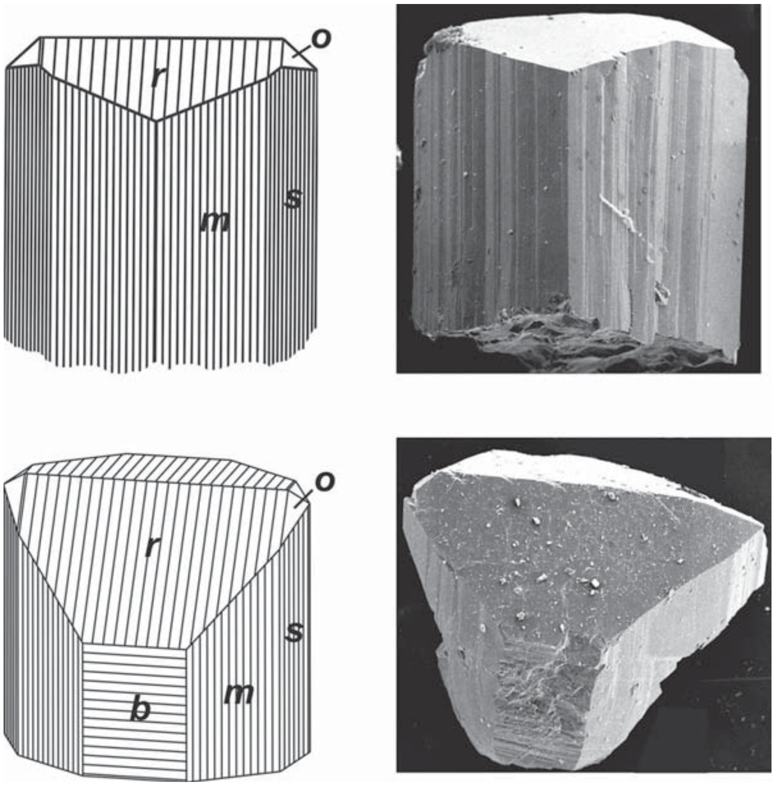

FIG. 6. Morphology of manganilvaite crystals with forms (in the structural setting) *r*{011}, *m*{110}, *s*{210}, *b*{010} and *o*{111}. The crystals are presented with their *b* axis toward the reader (for direct comparison with the crystal drawings of ilvaite published already, given in orthorhombic setting with *a* and *b* axes interchanged and $c < a < b$).

The empirical chemical formulae for the average composition of manganilvaite from the Ossikovo and Govedarnika mines, according to these electron-probe results, are:

$(Ca_{0.92}Mn^{2+}_{0.08})(Fe^{2+}_{0.97}Mg_{0.05})(Fe^{3+}_{0.96}Al_{0.02})$
$(Mn^{2+}_{0.61}Fe^{2+}_{0.39})(Si_{2.00}O_7)O(OH)$,

$(Ca_{0.94}Mn^{2+}_{0.06})(Fe^{2+}_{0.94}Mg_{0.05})(Fe^{3+}_{0.99}Al_{0.03})$
$(Mn^{2+}_{0.71}Fe^{2+}_{0.29})(Si_{1.99}O_7)O(OH)$.

The degree of $(Fe^{2+},Fe^{3+},Mn^{2+})$ cation order obtained from the combined structural analysis is discussed in the related paper (Zotov *et al.* 2005). The simplified formula for manganilvaite is: $CaFe^{2+}Fe^{3+}(Mn^{2+},Fe^{2+})(Si_2O_7)O(OH)$.

The trace and rare-earth elements determined by inductively coupled plasma – mass spectrometry (ICP–MS) analysis are in low concentrations, as can be seen from Table 6 and Figure 9. In a comparative study, Bonev *et al.* (2003) established that the *REE* concentrations and *REE* patterns of the enclosing marbles, preceding skarn silicates and ilvaite are very similar, which is evidence for their inheritance in the hydrothermal process, with only slightly enrichment in the later ilvaite. Tin was not detected, though it is known to occur in ilvaite from Tetyukhe and other deposits (Mozgova & Borodaev 1965). Only Pb and Zn were found in increased concentrations (up to 1.06 and 0.77 wt.%, respectively), which is due to mechanical admixtures from galena and sphalerite inclusions, common in the core of ilvaite grains from Ossikovo. The slight enrichment in Ga and Ge contents, not found in the marbles, also are attributable to sphalerite inclusions.

THE ILVAITE–MANGANILVAITE SERIES OF SOLID SOLUTIONS

In the literature, especially in several recent publications, chemical data were published for ilvaite with variable Mn-content from various deposits (Fig. 7). All these results indicate the existence of a continuous solid-solution series between ilvaite and manganilvaite. The distribution of the manganese-rich members is rather dispersed, even in a single deposit.

Taking in consideration the published data on composition and the crystal chemistry of ilvaite, together with the results of the structure refinements of

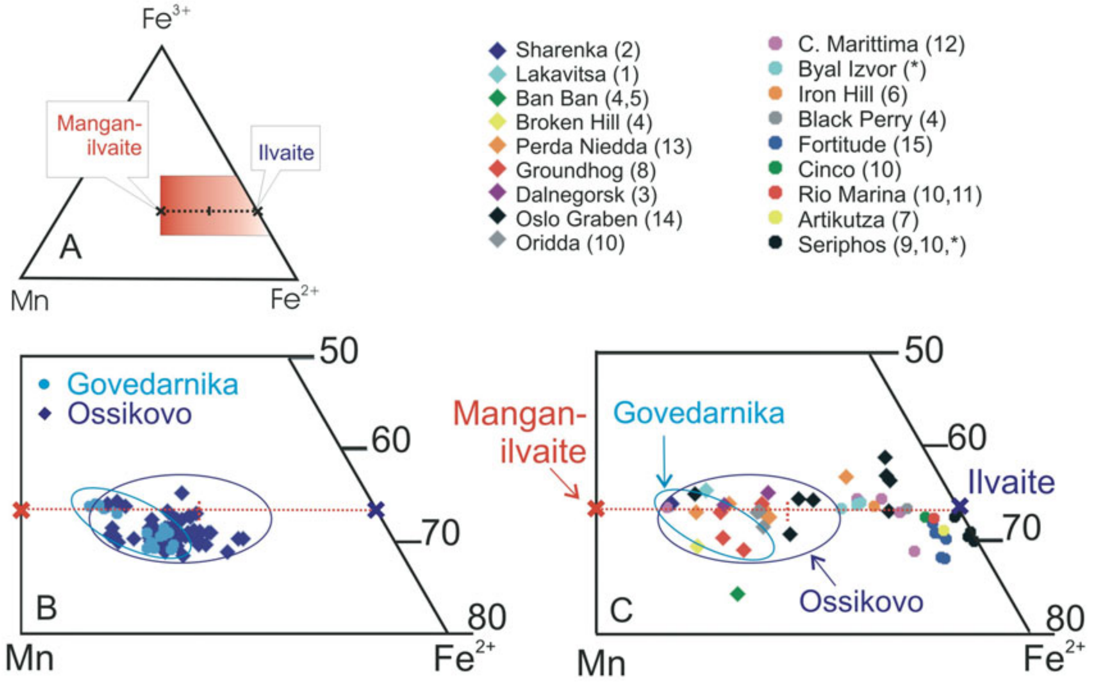

FIG. 7. Compositional diagram (A) for the [6]-coordinated $Mn–Fe^{2+}–Fe^{3+}$ cations in minerals of the manganilvite–ilvaite series. B) Data for Ossikovo and Govedarnika. C) Data for representative deposits according to (1) Marinova-Petrova & Hristova (1961), (2) Velchev (1962), (3) Mozgova & Borodaev (1965), (4) Plimer & Ashley (1978), (5) Ashley (1980), (6) Meinert (1984), (7) Pesquera & Velasco (1986), (8) Meinert (1987), (9) Finger & Hazen (1987), (10) Carrozzini (1994), (11) Bonazzi & Bindi (1999), (12) Capitani & Mellini (2000), (13) Bonazzi & Bindi (2002), (14) Larsen & Dalgren (2002), (15) Franchini *et al.* (2002), and our data (*).

TABLE 5. CHEMICAL COMPOSITION OF Mn-FREE ILVAITE FROM SERIPHOS AND MANGANILVAITE FROM OSSIKOVO AND GOVEDARNIKA

	Theoretical			Seriphos	Ossikovo							Govedarnika						
	Ilv $Mn_{0.0}$	Ilv $Mn_{0.5}$	Mlv $Mn_{1.0}$	S1	Range	Ave. n = 62	Os1	Os2	Os3	Os4	Os5	Range	Ave. n = 17	G1	G2	G3	G4	G5
MgO	0.00	0.00	0.00	0.10	0.15-0.72	0.48	0.57	0.68	0.70	0.26	0.26	0.07-0.84	0.45	0.55	0.33	0.15	0.56	0.26
Al_2O_3	0.00	0.00	0.00	0.59	0.00-0.53	0.20	0.20	0.06	0.00	0.05	0.20	0.00-0.81	0.34	0.70	0.08	0.00	0.13	0.00
SiO_2	29.40	29.43	29.46	29.60	29.20-30.27	29.65	29.32	29.66	29.43	30.11	29.88	29.21-29.89	29.48	29.34	29.36	29.23	29.21	29.29
CaO	13.72	13.73	13.75	13.83	12.01-13.31	12.62	12.96	12.85	12.89	12.79	12.79	12.72-13.86	13.06	12.75	13.63	13.42	13.10	13.38
TiO_2	0.00	0.00	0.00	0.16	0.00-0.17	0.02	0.02	0.08	0.00	0.04	0.00	0.00-0.12	0.04	0.08	0.00	0.06	0.04	0.00
MnO	**0.00**	**8.69**	**17.39**	0.00	9.02-14.96	11.99	9.91	11.33	13.68	14.72	14.96	12.57-14.86	13.54	12.71	13.88	14.07	14.82	14.86
FeO	35.15	26.39	17.61	52.78	38.57-43.45	40.93	41.39	41.94	39.32	38.63	38.60	38.09-40.21	39.31	40.21	39.07	39.48	38.09	38.47
Fe_2O_3	19.53	19.55	19.58															
H_2O	2.20	2.21	2.21	2.20		2.21	2.21	2.21	2.21	2.21	2.21		2.21	2.21	2.21	2.21	2.21	2.21
Total	100.00	100.00	100.00	99.26		98.10	96.58	98.81	98.23	98.81	98.90		98.43	98.55	98.56	98.62	98.16	98.65
Mg	0.00	0.00	0.00	0.01	0.02-0.08	0.05	0.06	0.07	0.07	0.03	0.03	0.01-0.07	0.05	0.06	0.03	0.01	0.05	0.03
Al	0.00	0.00	0.00	0.05	0.00-0.05	0.02	0.02	0.00	0.00	0.00	0.02	0.00-0.06	0.03	0.06	0.01	0.00	0.01	0.00
Si	2.00	2.00	2.00	1.98	1.98-2.03	2.00	2.01	1.99	1.99	2.03	2.01	1.97-2.02	1.99	1.98	1.98	1.98	1.98	1.98
Ca	1.00	1.00	1.00	0.99	0.88-0.96	0.92	0.95	0.93	0.93	0.92	0.92	0.92-0.99	0.94	0.93	0.99	0.97	0.95	0.97
Mn	0.00	0.50	1.00	0.00	0.58-0.85	0.69	0.58	0.65	0.78	0.84	0.85	0.71-0.85	0.77	0.73	0.79	0.81	0.85	0.85
Fe^{2+}	2.00	1.50	1.00	2.04	1.23-1.50	1.36	1.43	1.37	1.21	1.24	1.21	1.17-1.35	1.23	1.28	1.17	1.19	1.12	1.13
Fe^{3+}	1.00	1.00	1.00	0.92	0.86-0.98	0.96	0.95	0.99	1.02	0.94	0.96	0.87-1.04	0.99	0.98	1.03	1.04	1.03	1.04
Σ	6.00	6.00	6.00	6.00		6.00	6.00	6.00	6.00	6.00	6.00		6.00	6.00	6.00	6.00	6.00	6.00

The results of electron-microprobe analyses are first expressed in wt.%, then in atoms per unit formula (*apfu*) calculated on the basis of 8.5 atoms of oxygen. The total amount of Fe is expressed as FeO_{total} and *apfu* Fe^{2+} recalculated according to Droop (1987); H_2O: theoretical value, confirmed by direct measurement in one sample. Symbols: Ilv: ilvaite, Mlv: manganilvaite.

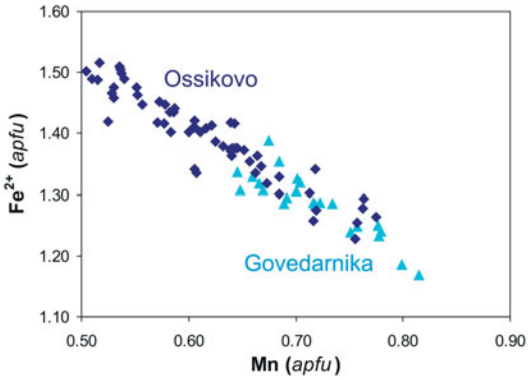

FIG. 8. Extent of substitution of octahedrally coordinated Mn^{2+} and Fe^{2+} in manganilvaite from Ossikovo and Govedarnika.

manganilvaite (Zotov *et al.* 2005), we consider that the manganilvaite member of the series occurs in several of the known deposits. This is the case where the Mn remaining after complementing the $^{[7]}$Ca sites exceeds 0.5 *apfu*.

Thus, we contend that in the Tetyukhe (Dalnegorsk) (Mozgova & Borodaev 1965), Campiglia Marittima (Capitani & Mellini 2000) and Perda Niedda, Sardinia (Bonazzi & Bindi 2002) occurrences, there are members of the series ilvaite–manganilvaite, whereas in the Groundhog (Meinert 1987), Konnerud (Larsen & Dahlgren 2002), Broken Hill and Ban Ban (Plimer & Ashley 1978) deposits, manganilvaite is prevalent. It can be expected that in very high-manganese environments, nearly pure manganilvaite could exist, with Mn reaching 1 *apfu* (*i.e.*, MnO 17.39 wt.%).

Relationships with Associated Minerals

Manganilvaite is invariably closely related to Pb–Zn–(Mn) skarns and the products of their retrograde alteration (Vassileva *et al.* 2001, Vassileva & Bonev 2001, 2003a). Its association with the primary manganese-enriched *clinopyroxenes* is especially characteristic. Located mostly at the periphery or in the interstices of pyroxene aggregates, manganilvaite shows in many cases clear evidence for metasomatic growth. Thus, some manganilvaite grains contain many tiny oriented relics of pyroxene, as shown in Figure 10. In several cases, especially in the Ossikovo deposit, manganilvaite is associated with *rhodonite* and *manganoan hedenbergite* (Fig. 11).

Characteristic products of pyroxene alteration in the deposits are the *manganoan amphiboles*, especially manganoan ferro-actinolite and members of the mangano-cummingtonite–manganogrunerite series (Vassileva &

Bonev 2001). Manganilvaite at Ossikovo is associated with manganoan ferro-actinolite and is formed after it. Fine relict fibers of these amphiboles are present as inclusions in the manganilvaite crystals (Fig. 11). The association of manganilvaite with the abundant *rhodochrosite* and *manganoan calcite* replacing skarn pyroxenes is a close one. Direct relationships with other products of retrograde alteration, like andraditic garnet and manganoan chlorite (Vassileva & Bonev 2003a), were not observed.

In Ossikovo, manganilvaite also is associated with the main sulfides, usually with *sphalerite*. Small grains of sphalerite and galena are common in the central parts of many crystals of ilvaite (Fig. 11). Similarly, where the two minerals form peripheral part of ore nests in skarns, the central part is filled by coarse-grained *calcite*, or in some cases with *quartz*. These relationships are evidence of the contemporaneous formation of manganilvaite and the main sulfides.

An association of manganilvaite with *magnetite* is common in Ossikovo (Fig. 11d). Sets of fine-grained magnetite may replace the central parts of manganilvaite crystals, in some cases also their peripheries, but remaining always within outlines of the ilvaite grains. Calcite and quartz in these areas are abundant. The metasomatic origin of magnetite after manganilvaite is evident and indicates for an increase in $f(O_2)$ during the later stages of mineralization. A still higher increase in $f(O_2)$ occurs at Byal Izvor, where ilvaite is cross-cut and replaced by a network of tiny grains of hematite. *Hematite* as fine flakes is common in altered clinopyroxene in this and the other deposits.

An interesting association of manganilvaite with ferroan *bustamite*, $(Ca_{0.83}Mn_{1.78}Fe^{2+}_{0.39})_{\Sigma 3.00}Si_3O_9$, is observed in the Govedarnika deposit. Bustamite crystallizes late instead of the lower-*T* polymorph, johannsenite, in this deposit (Vassileva & Bonev 2003b), as also in some of the Madan deposits, with clear textural evidence for replacement of the primary pyroxene. In this case, manganilvaite seems to be contemporaneous with, or later than, the bustamite.

DISCUSSION: ZONATION SEQUENCES OF ILVAITE-GROUP MINERALS IN SKARNS

The mineralogical and textural relationships (Figs. 3, 10, 11) clearly determine the position of manganilvaite in the evolution of the ore-forming processes in the Rhodope skarn Pb–Zn deposits. Though closely associated with skarn clinopyroxenes (manganoan hedenbergite to johannsenite), manganilvaite is invariably deposited after them and after rhodonite, mostly replacing the pyroxenes. Thus it is a product of retrograde alteration of the skarns, synchronous with the main episode of deposition of sulfides at rather high *T* (~330–300°C). In some cases, at a later stage, ilvaite is partly replaced by magnetite and even by hematite. As manganilvaite is a minor component occurring in small nests, it does not form well-delimited zones in the skarn bodies, as in other deposits.

There are different and controversial opinions about the genesis of ilvaite-group minerals and their paragenetic sequence in the zoned skarn-type deposits. Machairas & Blais (1966) established that in skarns of Noranda (Quebec, Canada), manganoan ilvaite with 8.3 wt.% MnO is a product of transformation of manganoan (5.3 wt.% MnO) hedenbergite. Einaudi *et al.* (1981), Meinert (1987) and Franchini *et al.* (2002) also considered ilvaite as a typical retrograde, post-skarn mineral.

Of special interest is the classical skarn-type Temperino deposit in Campiglia Marittima, Tuscany, Italy, in which ilvaite is a characteristic component and where, already in 1868, the first description of skarn zoning has been given by vom Rath (Burt 1982). This pattern of zoning has been reported many times since. The mineral zones developed as exoskarn zones in marbles, outward from a quartz porphyry dike: magnetite – ilvaite – clinopyroxene – marble.

Two contrasting explanations for the origin of this zoning have been proposed. (a) Simultaneous development of all major zones as the result of chemical potential gradients set up between the Fe- and Si-rich solutions and limestone host-rocks (Burt 1977, Rose

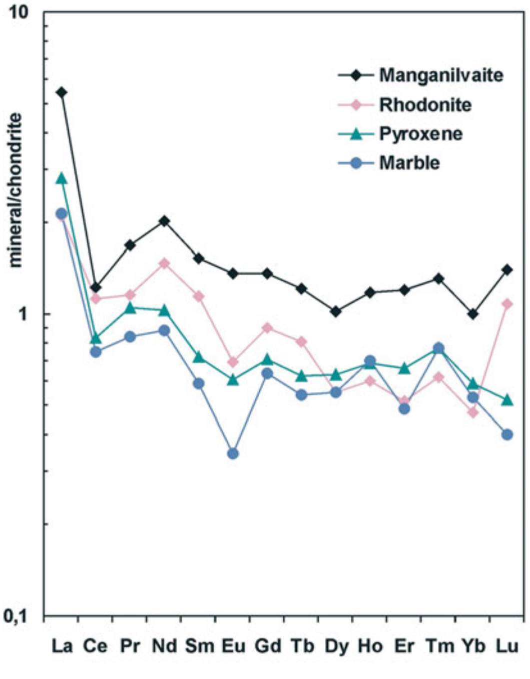

FIG. 9. Chondrite-normalized *REE* contents in manganilvaite, as well as in the precursor marble, skarn pyroxene and rhodonite from Ossikovo.

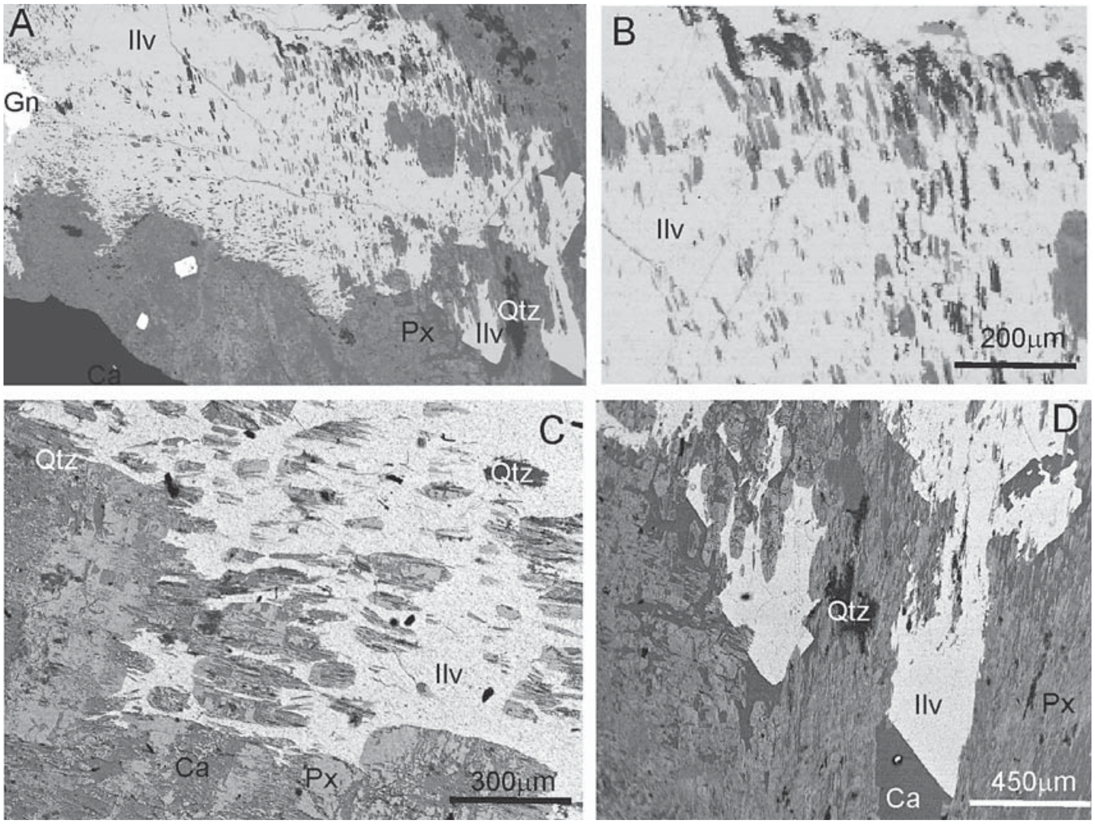

FIG. 10. BSE images of manganilvaite replacing radiating aggregate of pyroxene crystals. We present a general view (A) and details from its upper (B) and lower (C and D) parts. The numerous, partly carbonatized relics of pyroxene preserve their original radiating, slightly fan-like orientation.

& Burt 1979). The inner zones continuously replace the outer ones, and on the model diagram of Ca–Fe–Si potentials of Burt (1977, our Fig. 12), an arrow (magnetite – ilvaite – hedenbergite – marble) expresses the zoning sequence: (1) outer (frontal) hedenbergite zone, formed first, (2) an ilvaite zone followed after (1), and (3) the inner magnetite zone, deposited latest, replacing (2). (b) Successive emplacement of the three zones in a multistage process (Bartholomé & Evrard 1970, Corsini *et al.* 1980, Capitani & Mellini 2000, Capitani *et al.* 2003). In the sequence of events, given by these authors, there is: (1) first, at the *earliest* stage, deposition of magnetite in the inner zone (preceded by hematite), (2) in the second stage, there is deposition of ilvaite in the middle zone, and (3) at a later stage, there is deposition of hedenbergite in the outer zone (after ilvaite). Thus, there occurs "the general trend of deposition, from more oxidized to more reduced minerals" (Bartholomé & Evrard 1970). In their Figure 2, this trend is represented by the same arrow (magnetite – ilvaite – hedenbergite), but the interpretation of the crystallization sequence is just the opposite. Furthermore, Capitani & Mellini (2000) hypothesized even the temperature conditions for the three successive stages: 460–400–260°C, respectively. However, detailed mineral relationships were not clearly shown.

Our observation in the Rhodope skarn-type ore deposits is conistent with the first sequence of crystallization of minerals presented, but with evidence for some later formation of ilvaite – manganilvaite and magnetite. The sequence Mn-rich clinopyroxenes (in some cases with graphite) – Mn-rich amphiboles – manganilvaite – magnetite – hematite is indicative of evolution of the conditions of the hydrothermal process, from reducing (Fe^{2+}, Mn^{2+}) during the formation of the primary skarns, to hydrated and more oxidizing (with (Fe^{2+}, Mn^{2+} + Fe^{3+}, and then Fe^{3+}) during the overlapping retrograde alterations and deposition of the ore minerals.

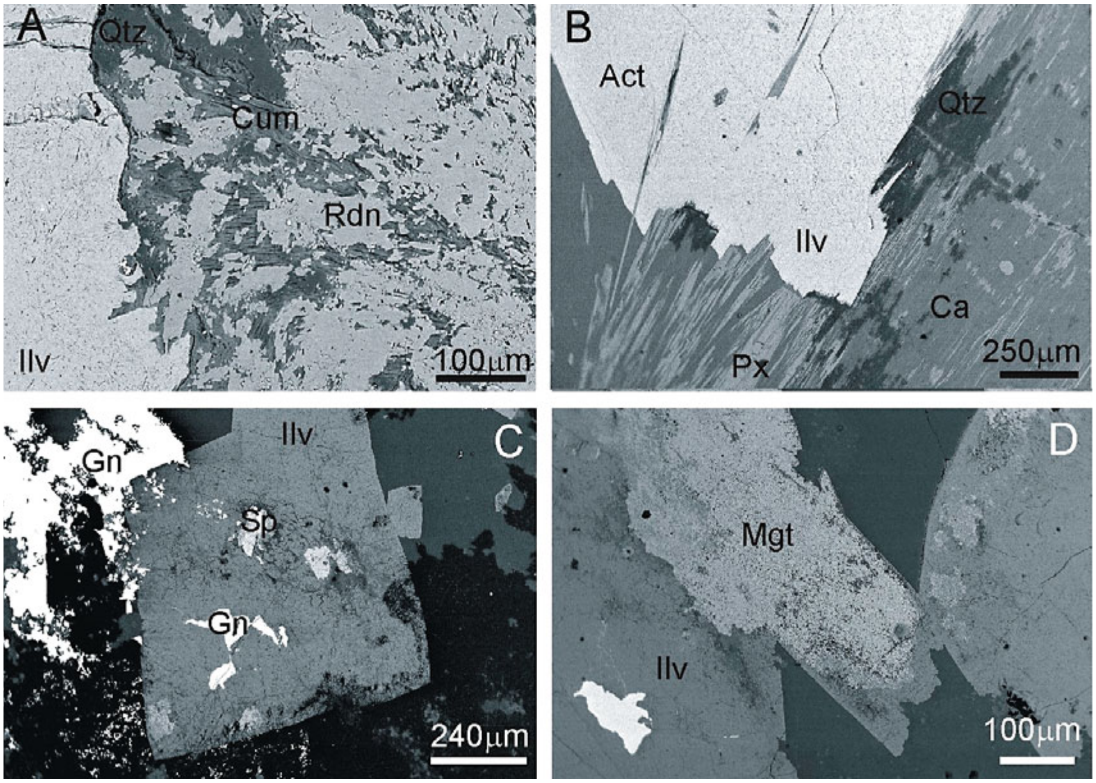

FIG. 11. BSE micrographs showing the relationships of manganilvaite with the main minerals in the skarn-type orebodies. (A) Manganilvaite (Ilv) with rhodonite (Rdn) and manganocummingtonite (Cum) relics. (B) Manganilvaite developed after radiating pyroxene (Px) and later fibrous manganoan ferro-actinolite (Act). (C) Manganilvaite crystal with sphalerite (Sp) and galena (Gn) inclusions. (D) Manganilvaite crystals, the central one intensively replaced by fine-grained magnetite (Mgt).

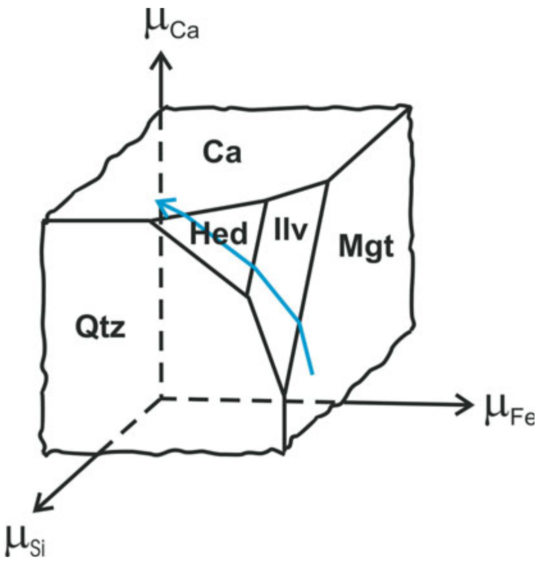

FIG. 12. Diagram of the chemical potentials to account for the zoning sequence magnetite – ilvaite – hedenbergite – marble in the skarns, after Burt (1977) and Rose & Burt (1979).

CONCLUSIONS

1) Manganilvaite is the manganese-dominant member of a continuous solid-solution series in ilvaite-group minerals, with Mn occupying the larger octahedral site *M*2.

2) The chemical composition of the intermediate members of ilvaite group, even in one deposit, may be quite variable. Manganilvaite is typical of the high-Mn to extremely Mn-rich deposits, like the skarn Pb–Zn deposits Ossikovo and Mogilata, Madan district, and Govedarnika, Laki district, central Rhodope, Bulgaria, or Grounghog, New Mexico, USA (Meinert 1987). However, it can form also in other types of Mn-rich environments, such as hydrothermal quartz–magnetite veins (Oslo Graben, Norway: Larsen & Dahlgren 2002) and metamorphosed stratiform Pb–Zn deposits (Broken Hill, Australia: Plimer & Ashley 1978).

3) Manganilvaite in the Rhodope deposits is a product of retrograde alteration of the primary reduced high-manganese clinopyroxene skarns, indicating their later oxidation and hydration, nearly simultaneous with deposition of the main galena – sphalerite – pyrite mineralization.

4) The physical and crystallographic characteristics of manganilvaite differ only slightly from those of the Mn-free and low-Mn members of the ilvaite group.

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REFERENCES

AGATA, T. & ADACHI, M. (1995): Ilvaite from a serpentinized peridotite in the Asama igneous complex, Mikabu greenstone belt, Sambagawa metamorphic terrain, central Japan. *Mineral. Mag.* **59**, 489-496.

ASHLEY, P.M. (1980): Geology of the Ban Ban zinc deposit, a sulfide-bearing skarn, southeast Queensland, Australia. *Econ. Geol.* **75**, 15-29.

BARTHOLOMÉ, P. & EVRARD, P. (1970): On the genesis of the zoned skarn complex at Temperino, Tuscany. *In* Problems of Hydrothermal Ore Deposition. Int. Union Geol. Sci. A, N 2. Schweizerbart, Stuttgart, Germany (53-57).

BERAN, A. (1980): A reflected light investigation of ilvaite. *Tschermaks Mineral. Petrogr. Mitt.* **27**, 225-230.

BONAZZI, P. & BINDI, L. (1999): Structural adjustments induced by heat treatment in ilvaite. *Am. Mineral.* **84**, 1604-1612.

________ & ________ (2002): Structural properties and heat-induced oxidation–dehydrogenation of manganoan ilvaite from Perda Niedda mine, Sardinia, Italy. *Am. Mineral.* **87**, 845-852.

________, ________ & OLMI, F. (2001): Reflectance variations in heat-treated ilvaite. *Mineral. Petrol.* **72**, 249-257.

BONEV, I.K. (2003): Marble hosted skarn Pb–Zn ore deposits in the central Rhodopes, Bulgaria. *In* Mineral Exploration and Sustainable Development (D.G. Eliopoulos, ed.), Proc.7th Biennial SGA Meeting (Athens) **1**. Millpress, Rotterdam, The Netherlands (243-246).

________, VLADYKIN, N.V., VASSILEVA, R.D. & DAIEVA, L.-A. (2003): Rare earth and some trace elements in the metasomatic skarn-ore bodies of the Madan Pb–Zn deposits, Bulgaria. *Geochem. Mineral. Petrol.* (*Sofia*) **40**, 73-85.

BURT, D.M. (1977): Mineralogy and petrology of skarn deposits. *Rend. Soc. Ital. Mineral. Petrol.* **33**, 859-873.

________ (1982): Skarn deposits – historical bibliography through 1970. *Econ. Geol.* **77**, 755-763.

CAPITANI, G.C., GROBÉTY, H.B. & MELLINI, M. (2003): Reaction sequences, polysomatic faults and chemical compositions of manganese pyroxenoids from Campiglia Marittima skarn. *Eur. J. Mineral.* **15**, 381-391.

________ & MELLINI, M. (2000): The crystallisation sequence of the Campiglia Marittima skarn. *Neues Jahrb. Mineral., Monatsh.*, 97-115.

CARROZZINI, B. (1994): Crystal structure refinements of ilvaite: new relationships between chemical composition and crystallographic parameters. *Eur. J. Mineral.* **6**, 465-479.

CESENA, M., SCHEPKE, M., DEMELO, M.A.C., LITTERST, F.J. & AMTHAUER, G. (1995): Mössbauer studies of Mn- and Al-doped synthetic ilvaites. *J. Magnetism and Magnetic Materials* **140**, 1889-1890.

CHUKHROV, F.V., ed. (1979): Ilvaite. *In* Minerals Handbook **III–1**. Nauka, Moscow, Russia (692-709; in Russ.).

CHVILEVA, T.N., BEZSMERTNAYA, M.S., SPIRIDONOV, E.M., *et al.* (1988): *A Handbook for Determination of Ore Minerals*. Nedra, Moscow, Russia (in Russ.).

CORSINI, F., CORTECCI, G., LEONE, G. & TANELLI, G. (1980): Sulfur isotope study of the skarn – (Cu–Pb–Zn) sulfide deposit of Valle del Temperino, Campiglia Marittima, Tuscany, Italy. *Econ. Geol.* **75**, 83-96.

DROOP, G.T.R. (1987): A general equation for estimating Fe^{3+} concentrations in ferromagnesian silicates and oxides from microprobe analyses, using stoichiometric criteria. *Mineral. Mag.* **51**, 431-435.

EINAUDI, M.T., MEINERT, L.D. & NEWBERRY, R.J. (1981): Skarn deposits. *Econ. Geol., 75th Anniversary Vol.*, 317-391.

FINGER, L.V. & HAZEN, R.M. (1987): Crystal structure of monoclinic ilvaite and the nature of the monoclinic–orthorhombic transition at high pressure. *Z. Kristallogr.* **179**, 415-430.

FRANCHINI, M.B., MEINERT, L.D. & VALLÉS, J.M. (2002): First occurrence of ilvaite in a gold skarn deposit. *Econ. Geol.* **97**, 1119-1126.

GAINES, R.V., SKINNER, H.C.V., FOORD, E.E., MASON, B. & ROSENZWEIG, A. (1997): *Dana's New Mineralogy* (8th ed.). Wiley, New York, N.Y.

GHAZI-BAYAT, B., AMTHAUER, G. & HELLNER, E. (1989): Synthesis and characterisation of Mn-bearing ilvaite $CaFe^{2+}{}_{2-x}Mn_xFe^{3+}[Si_2O_7/O/(OH)]$. *Mineral. Petrol.* **40**, 101-109.

GHOSE, S., HEWAT, A.W. & MAREZIO, M. (1984): A neutron powder diffraction study of the crystal and magnetic structures of ilvaite from 305 K to 5 K – a mixed valence iron silicate with an electronic transition. *Phys. Chem. Minerals* **11**, 67-74.

GOLDSCHMIDT, V. (1918): Lievrit. *In* Atlas der Kristalformen **5**. Carl Winters Universitätsbuchhandlung, Heidelberg, Germany (p. 151-156, Tables 96-102).

GÜTTLER, B., SALJE, E. & GHOSE, S. (1989): Polarized single crystal absorption spectroscopy of the $Pnam$–$P2_1/a$ transition of ilvaite $Ca(Fe^{2+},Fe^{3+})Fe^{2+}Si_2O_8(OH)$ as measured between 300 K and 450 K. *Phys. Chem. Minerals* **16**, 606-613.

IVANOV, Z. (2000): Structure, Alpine evolution and mineralizations of the Central Rhodopes area (South Bulgaria). *ABCD–GEODE 2000 Workshop* (*Borovets, Bulgaria*), *Guide to excursion* **B**.

KHETCHIKOV, L.N. (1956): On ilvaite from skarn – polymetallic deposits. *Mineral. Sbornik Lvov Mineral. Obshchest.* **10**, 298-304 (in Russ.).

KOLKOVSKI, B., DOBREV, S., PETROV, P. & MANEV, D. (1996): Geology, mineralogy and genesis of Madan ore field. *In* Plate Tectonic Aspects of the Alpine Metallogeny in the Carpatho-Balkan Region. *Proc. Ann. Meeting* (Sofia), *UNESCO IGCP Project 356* **2**, 157-173.

KOSTOV, I. & KOSTOV, R.I. (1999): *Crystal Habits of Minerals*. Pensoft Publ. / Prof. Marin Drinov Academic Publ. House, Sofia, Bulgaria (Bulgarian Acad. Monogr. **1**).

KRÄUTNER, H.G. & MEDEŞAN, A. (1969): Ilvait in den polymetamorphen Eisenerzen der Poiana Ruscă (Rumänien). *Tschermaks Mineral. Petrogr. Mitt.* **13**, 157-164.

LARSEN, A.O. & DAHLGREN, S. (2002): Ilvaite from the Oslo Graben, Norway. *Neues Jahrb. Mineral., Monatsh.*, 169-181.

LAZAREV, A.N (1972): *Vibrational Spectra and structure of silicates*. Consultants Bureau, New York, N.Y.

MACHAIRAS, G. & BLAIS, R. (1966): La transformation de l'hédenbergite manganésifère en ilvaite dans les sulfures de cuivre et de zinc de la région de Noranda (Québec). *Bull. Soc. fr. Minéral. Cristallogr.* **89**, 377-381.

MARINOVA-PETROVA, R. & HRISTOVA, R. (1961): Ilvaite in skarns of the vicinity of the village Laki, near Assenovgrad. *Jahrb. Comm. Geol. Prospecting* **11**, 133-137 (in Bulg.).

MEINERT, L.D. (1984): Mineralogy and petrology of iron skarns in western British Columbia. *Econ. Geol.* **79**, 869-882.

________ (1987): Skarn zonation and fluid evolution in the Groundhog mine, Central mining district, New Mexico. *Econ. Geol.* **82**, 523-545.

MOZGOVA, N.N. & BORODAEV, YU.S. (1965): On some physical properties of ilvaite. *Trudi Mineral. Muz., Akad. Nauk SSSR* **16**, 114-140 (in Russ.).

NASLUND, H.R., HUGHES, J.M. & BIRNIE, R.W. (1983): Ilvaite, an alteration product replacing olivine in the Skaergaard intrusion. *Am. Mineral.* **68**, 1004-1008.

PESQUERA, A. & VELASCO, F. (1986): An occurrence of ilvaite layers in the Cinko Villas metasomatic rocks, western Pyrenees (Spain). *Mineral. Mag.* **42**, 85-88.

PICOT, P. & JOHAN, Z. (1982): *Atlas des Minéraux Métalliques*. BRGM, Orléans, France (Mém. **90**).

PLIMER, I.R. & ASHLEY, P.M. (1978): Manganoan ilvaite from Broken Hill, N.S.W. and Ban Ban, Queensland, Australia. *Mineral. Mag.* **42**, 85-88.

ROSE, A.U. & BURT, D.M. (1979): Hydrothermal alteration of rocks. *In* Geochemistry of Hydrothermal Ore Deposits (H.L. Barnes, ed.; 2nd edition). Wiley, New York, N.Y. (173-235).

STOINOVA, M. (1986): Skarn minerals in the polymetallic deposits of the Laki ore field, northern Rhodopes. *In* Crystal Chemistry of Minerals (J. Minčeva-Stefanova, I. Bonev & B.K. Kamenov, eds.). *Proc. 13th Gen. Int. Mineral. Assoc. Meeting* (*Varna, 1982*). Bulgarian Acad. Sci., Sofia, Bulgaria (411-419).

TAKÉUCHI, Y., HAGA, N. & BUNNO, M. (1983): X-ray study on polymorphism of ilvaite, $HCaFe^{2+}{}_2Fe^{3+}O_2[Si_2O_7]$. *Z. Kristallogr.* **163**, 267-283.

________, SAWADA, H., TANIGUSHI, H., UNO, R. & TABIRA, Y. (1994): Submicroscopic twinning and chemical inhomogeneity of ilvaite, a mixed-valence iron sorosilicate $HFe^{2+}{}_2Fe^{3+}Si_2O_9$. *Z. Kristallogr.* **209**, 861-869.

VASSILEVA, R.D. & BONEV, I.K. (2001): Manganoan amphiboles from the skarn-ore Pb–Zn deposits in the Madan district, central Rhodopes, Bulgaria. *Geochem. Mineral. Petrol.* (*Sofia*) **38**, 45-53.

________ & ________ (2003a): Retrograde alterations of manganoan skarns in the Madan Pb–Zn deposits, South Bulgaria. *In* Proc. 7th Biennial SGA Meeting (Athens) **1**. Millpress, Rotterdam, The Netherlands (403-406).

________ & ________ (2003b): Bustamite, an important mineral in the skarn-ore bodies of the Govedarnika deposit, central Rhodopes. *In* Annual Sci. Conf. Geology – 2003. Bulgarian Geol. Soc., Sofia, Bulgaria (75-77).

________, ________ & ZOTOV, N. (2001): High-Mn ilvaites from the skarn Pb–Zn deposits in the Central Rhodopes. *In* Mineral Deposits at the Beginning of the 21st Century (A. Piestrzynski *et al.* eds.). Swets & Zeitlinger, Lisse, The Netherlands (925-928).

VELCHEV, V. (1962): Ilvaite from the Sharenka deposit, Rhodope Mts. *Rew. Bulgarian Geol. Soc.* **23**, 348-353 (in Bulg.).

ZOTOV, N., KOCKELMAN, W., JACOBSEN, S.D., MITOV, I., PANEVA, D., VASSILEVA, R.D. & BONEV, I.K. (2005): Structure and cation ordering in manganilvaite: a combined X-ray diffraction, neutron diffraction, and Mössbauer study. *Can. Mineral.* **43**, 1043-1053.

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