LAMELLAR MINERALS OF THE CUPROBISMUTITE SERIES AND RELATED PADĚRAITE: A NEW OCCURRENCE AND IMPLICATIONS

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Abstract

An assemblage consisting of bismuthinite derivatives, mainly in the range gladite – oversubstituted bismuthinite ($Cu_{0.833}Pb_{0.833}Bi_{19.167}S_{30}$), makovickyite, and intergrowths of cuprobismutite and paděraite, with minor hodrushite, occurs in the Paulus mine, Ocna de Fier skarn deposit, southwestern Romania. Even though intimately intergrown with one another as sets of lamellae of varying thickness, with back-scattered electron images strongly suggesting that lamellar intergrowths of the two minerals extend below the size of the microprobe beam, homogeneous parts of lamellae or well-developed acicular crystals allow compositional characterization of the components. These are cuprobismutite, $Cu_{8.07}(Ag_{0.99}Pb_{0.21}Bi_{12.72})_{\Sigma13.92}S_{24.01}$, paděraite, $Cu_{7.11}(Ag_{0.36}Pb_{1.20})_{\Sigma1.56}Bi_{11.28}S_{22.05}$, and hodrushite, $(Cu_{7.80}Fe_{0.23})_{\Sigma8.03}(Ag_{0.35}Pb_{0.12}Cd_{0.02}Bi_{11.49})_{\Sigma11.98}S_{21.99}$. Hodrushite is the least abundant component, containing minor but persistent Fe, up to 0.41 wt.%. An inverse correlation between Ag and Pb is seen between cuprobismutite (Ag_{min} 2.34 wt.%, Ag_{max} 2.75 wt.%) and paděraite (Pb_{min} 5.37 wt.%, Pb_{max} 7.34 wt.%). Compositions for each phase diverge somewhat from previously published data, suggesting that varying degrees of incorporation of Ag and, to a lesser extent, Pb, are features of the cuprobismutite homologous series and of the related paděraite. Ag appears to be an essential component of cuprobismutite, our data showing that 1 *apfu* Ag occupies the Bi position ($\Sigma14$ *apfu*). Hodrushite differs from the type-locality material ($Cu_{8.12}Fe_{0.29}Bi_{11.54}S_{22}$), showing that the composition can depart from the ideal compositions within certain limits, with incorporation of Ag, Pb and Fe in the structure. Significantly, the number of Cu atoms is less than 8 *apfu* in the Ocna de Fier material, with Fe located at the Cu position and minor Ag and Pb at the Bi position. For paděraite, the Ocna de Fier material also differs from type-locality material in that Cu occupancy is 7, instead of 6 *apfu*, and Ag is less than 1 *apfu*, based on 42 *apfu*. Together with a consideration of other published and unpublished data, this information gives an amended ideal formula for paděraite: $Cu_7(Ag_{0.4}Pb_{1.2})_{\Sigma1.6}Bi_{11.4}S_{22}$. Two possible substitutions, $3Ag^+ \rightarrow Bi^{3+}$ and $Ag^+ + Pb^{2+} \rightarrow Bi^{3+}$ can be written for the cuprobismutite homologues. Furthermore, the substitution $Fe^{2+} \rightarrow Cu^+ + \square$ can be considered for hodrushite with Cu deficiency (<8 *apfu*), as in our material. In type-locality hodrushite, however, the Bi position is filled by an excess of Cu over 8 *apfu*, together with Fe, following the substitution $Cu^+ + Fe^{2+} \rightarrow Bi^{3+}$. We believe that this association, involving costability and intergrowths among minerals with closely allied structures, constitutes a paragenesis formed in a field of oscillatory chemical gradients of Cu, Pb, Ag and Bi, in which the pavonite series is represented only by makovickyite, with the fixed composition $Cu_{1.34}Ag_{0.76}Pb_{0.14}Bi_{5.21}S_{9.64}$.

Keywords: Bi-sulfosalts, cuprobismutite, hodrushite, paděraite, bismuthinite derivatives, makovickyite, compositional data, Ocna de Fier, Romania.

Sommaire

Nous documentons un assemblage contenant des dérivés de la bismuthinite, surtout ceux de l'intervalle gladite – bismuthinite sur-substituée ($Cu_{0.833}Pb_{0.833}Bi_{19.167}S_{30}$), makovickyite, et des intercroissances de cuprobismutite et de paděraïte, avec des quantités mineures de hodrushite, provenant de la mine Paulus, exploitant le gisement de type skarn de Ocna de Fier, dans le sud-ouest de la Roumanie. Quoiqu'ils sont en intercroissance intime l'un avec l'autre sous forme de lamelles d'épaisseur variable, les images des minéraux formés à partir des électrons rétrodiffusés laissent supposer que les intercroissances des deux minéraux se poursuivent à une échelle inférieure au rayon du faisceau d'électrons, les parties homogènes des lamelles ou les cristaux aciculaires bien développés permettent la caractérisation des composants. Il s'agit de cuprobismutite, $Cu_{8.07}(Ag_{0.99}Pb_{0.21}Bi_{12.72})_{\Sigma13.92}S_{24.01}$, paděraïte, $Cu_{7.11}(Ag_{0.36}Pb_{1.20})_{\Sigma1.56}Bi_{11.28}S_{22.05}$, et hodrushite, $(Cu_{7.80}Fe_{0.23})_{\Sigma8.03}(Ag_{0.35}Pb_{0.12}Cd_{0.02}Bi_{11.49})_{\Sigma11.98}S_{21.99}$. La hodrushite, la phase la moins abondante, contient des quantités faibles mais constantes de Fe, jusqu'à 0.41% (poids). Une corrélation inverse entre le Ag et le Pb caractérise la cuprobismutite (Ag_{min} 2.34%, Ag_{max} 2.75%) et la paděraïte (Pb_{min} 5.37%, Pb_{max} 7.34%). Les compositions de chaque phase s'écartent quelque peu des compositions déjà dans la littérature, ce qui témoigne d'un taux variable d'incorporation de Ag et, à un degré moindre, Pb, comme caractéristiques de la série d'homologues de la cuprobismutite ainsi que de la paděraïte, qui lui est apparentée. L'argent semble être un élément essentiel de la cuprobismutite, nos données indiquant qu'un atome de Ag par unité formulaire (*apuf*) occupe le site Bi ($\Sigma14$ *apuf*). La hodrushite diffère de l'holotype ($Cu_{8.12}Fe_{0.29}Bi_{11.54}S_{22}$), ce qui montre que sa composition peut s'écarter de la composition idéale à l'intérieur de

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certaines limites, avec incorporation de Ag, Pb et Fe dans la structure. Fait significatif, la proportion d'atomes de Cu est inférieur à 8 *apuf* dans le matériau d'Ocna de Fier, le Fe étant situé à la position du Cu, et des quantités mineures de Ag et Pb, à la position du Bi. Dans le cas de la padĕraïte, le matériau de Ocna de Fier diffère aussi de l'holotype; sa teneur en Cu est 7, plutôt que 6 *apuf*, et la proportion d'Ag est inférieure à 1 *apuf*, sur une base de 42 *apuf*. En considération d'autres données publiées ou non, cette information mène à une formule idéale corrigée pour la padĕraïte: $Cu_7(Ag_{0.4}Pb_{1.2})_{\Sigma1.6}Bi_{11.4}S_{22}$. On peut écrire deux substitutions possibles, $3Ag^+ \rightarrow Bi^{3+}$ et $Ag^+ + Pb^{2+} \rightarrow Bi^{3+}$, pour rendre compte des homologues de la cuprobismutite. De plus, on peut considérer la substitution $Fe^{2+} \rightarrow Cu^+ + \square$ pour la hodrushite ayant un déficit en Cu (<8 *apuf*), comme c'est le cas ici. Toutefois, dans la hodrushite holotype, la position du Bi est remplie au delà de 8 *apuf* par un excédent de Cu, avec le Fe, selon la substitution $Cu^+ + Fe^{2+} \rightarrow Bi^{3+}$. Nous croyons que cette association, impliquant une co-stabilité et des intercroissances parmi des minéraux dont les structures sont voisines, constitue une paragenèse formée dans un milieu de gradients chimiques oscillatoires impliquant Cu, Pb, Ag et Bi, dans lequel la série de la pavonite n'est représentée que par la makovickyite, avec une composition fixe, $Cu_{1.34}Ag_{0.76}Pb_{0.14}Bi_{5.21}S_{9.64}$.

INTRODUCTION

Cuprobismutite ($Cu_{2.58}Bi_{3.14}S_6$; Ozawa & Nowacki 1975) and hodrushite (ideal formula $Cu_8Bi_{12}S_{22}$; Kodĕra *et al.* 1970, Makovicky & MacLean 1972) and the structurally related mineral padĕraïte ($Ag_{1.3}Cu_{5.9}Pb_{1.6}Bi_{11.2}S_{22}$; Mumme & Žák 1985, Mumme 1986), although uncommon, are not so rare in nature (Table 1). Despite this, only very few occurrences have been sufficiently well documented to provide insight into compositional variation among the minerals, their paragenetic position in the ores in question, and their conditions of formation. The operating mechanisms of substitution and natural compositional limits of these three species remain under uncertainty.

The Fe–(Cu) skarn deposit at Ocna de Fier, southwestern Romania, recently dated at 76.6 ± 0.3 Ma (Ciobanu *et al.* 2002a), contains a number of Cu–Pb–Bi and Ag–Pb–Bi sulfosalts and complex intergrowths thereof (Petrulian *et al.* 1979, Ciobanu 1999, Ciobanu & Cook 2000). In rare cares, these cm-scale "nests" of massive Bi-sulfosalts within magnetite skarn ores are of sufficient size to permit adequate documentation of mineral composition, habit, intergrowth relationships and equilibrium associations. Ciobanu & Cook (2000) characterized a number of sulfosalt-bearing assemblages, including intergrowth textures among bismuthinite derivatives. We suggested that some fine intergrowths might reflect self-organization phenomena and represent microscopic analogues of Liesegang banding textures. Other textures among bismuthinite derivatives, and also lillianite homologues, were interpreted as the consequence of a breakdown reaction during prolonged retrograde overprinting and reworking of the ores.

In this paper, we present new micro-analytical data and relevant back-scattered-electron (BSE) images in order to document a paragenetic association of Bi-sulfosalt minerals from the Paulus mine (distal Zn–Pb skarn), in the northern part of the Ocna de Fier orefield.

The sample material comes from the Fe-zone of the deposit, intermediate between the core Cu–Fe zone and marginal ores subjacent to the Zn–Pb zones (Cook & Ciobanu 2001). Although prominent in these samples, cuprobismutite, hodrushite and related padĕraite have not been previously described from Ocna de Fier. The new data add significantly to existing knowledge on compositional variation of cuprobismutite homologues and coexisting padĕraite. Furthermore, as the minerals display fine, repetitive, banded and meshed textures comparable to those reported for bismuthinite derivatives in the same deposit, observed textural relationships present a rare opportunity to better understand their genesis and paragenesis, not least in terms of a hypothesis that fluctuation of mineralizing parameters during skarn formation is a suitable mechanism to explain compositional variation in Bi-sulfosalts.

BACKGROUND

Cuprobismutite was initially proposed as a mineral with the formula $3(Cu,Ag)_2S•4Bi_2S_3$ (Hillebrand 1884). Nuffield (1952) obtained structural data on type material and contended that cuprobismutite is dimorphous with emplectite, *i.e.,* $CuBiS_2$. The status and composition of cuprobismutite were, however, subjects of debate in ensuing decades. The principal reason was that phases with a Cu:Bi ratio consistently <1 were readily synthesized: $Cu_6Bi_8S_{15}$ (Godovikov & Federova 1969), $Cu_{10}Bi_{12}S_{23}$ (Sugaki & Shima 1972, Goodell 1975), $Cu_4Bi_5S_{10}$ (Mariolacos *et al.* 1975), $Cu_9Bi_{11}S_{21}$ (Sugaki *et al.* 1984) and $Cu_{24}Bi_{26}S_{51}$ (Mariolacos 1980). Chang & Hoda (1977) synthesized stoichiometric $CuBiS_2$ at 400°C, and this phase was considered by them and by Chen & Chang (1974) to be part of a limited solid-solution series along the $Cu_2S–Bi_2S_3$ join. Ozawa & Nowacki (1975), who defined the structure of the phase synthesized by Godovikov & Federova (1969), showed that excess Bi is inherent to the "cuprobismutite" structure, and proposed the formula $Cu_{2.58}Bi_{3.14}S_6$. Wang

TABLE 1. REPORTED OCCURRENCES OF CUPROBISMUTITE-GROUP MINERALS AND PADĚRAITE

Locality	References	Cuprobismutite series				Pad	Occurrence or type of deposit
		Kpk	Hod	Cbs	High. Hom.		
N		1	1.5	2	2.5 (?)		
Hall's Valley, Colorado, U.S.A. (cuprobismutite type-locality)	Hillebrand (1884), Nuffield (1952)			X* (?)			
Banská Hodruša, Slovakia (hodrushite type-locality)	Koděra et al. (1970), Makovicky & MacLean (1972)		**X**				Zn–Pb–Cu veins
	Kovalenker et al. (1993)		X			X	
Băiţa Bihor, Romania (paděraite type-locality)	Mumme & Žák (1985), Mumme (1986)		X		**X**		Cu(–Mo) skarn
	Žák et al. (1994)		X		X		
	Cioflica et al. (1997)		X (?)				
	Ilinca (1998)	X	X			X	
Valea Seacă, Romania	Ilinca (1998)		X			X	
Ohio mining district, Tunnel Extension, Utah, U.S.A.	Taylor et al. (1973)			**X**			Au–Ag veins
Zidarovo, Bulgaria	Tarkian & Breskovska (1995)			X			Cu–Zn–Pb–(Au) veins
Tunaberg, Sweden	Dobbe (1991)			X (?)			Cu skarn
Adrasman, Tajikistan	Borodaev & Mozgova (1971)				X (Phase IV)		Cu–Bi epithermal
Various, central Asia	Kovalenker (1986)		X				
Kayragach, Uzbekistan	Kovalenker et al. (1987)		X				Cu–Zn–Pb epithermal (veins?)
Tomnadashan, Scotland, U.K.	Pattrick (1984)	?**	?**	?**	?**	?**	Granite-related Cu-rich veinlets
Felbertal, Austria (kupčikite type-locality)	Topa (2001), Topa et al. (in prep.)	**X**	**X**	**X**			Metamorphosed W deposit
Ocna de Fier, Romania	This study		X	X		X	Fe–(Cu) skarn
Swartberg, northern Cape Province, South Africa	Ciobanu & Cook (2002a)		X			X	Li–Be-bearing granitic pegmatite
Huangshaping, China	Gu Xiang-Ping et al. (unpubl.), written commun., 2003		X (?)		X		Zn-skarn and Pb–Zn–Ag veins
Vurly Bryag, Bulgaria	Ciobanu et al. (2002b)				X		Cu–(Au) veins

* given as original type-locality with different formula; confirmation on type material required. ** identity of analyzed phases is highly uncertain. ? Indicates difficulty in readily assigning the published micro-analytical data to a given mineral. Crosses in bold attest to confirmation by X-ray diffraction or single-crystal refinement.
The occurrence of hodrushite from Bisbee, Arizona, U.S.A., is supported by unpublished micro-analytical and powder-diffraction data (R. Graeme, pers. commun., 2003). Other unconfirmed occurrences of hodrushite (as reported in the amateur and mineral collector literature) include: Julcani (Peru) and Rodnikovoe (Russian Far East). Note also: Anthony et al. (1960) mentioned the occurrence of cuprobismutite from Krupka (Czech Republic). Unconfirmed occurrences of cuprobismutite include: Ste. Marie-aux-Mines, Chrétien mine and Gabe Gottes mine, Vosges, France, the Clara mine, Oberwolfach, Hagendorf-Sud, and the Grüneau mine, Siegerland, Germany. Symbols: Kpk kupčikite, Hod hodrushite, Cbs cuprobismutite, High. Hom. Higher homologue, Pad paděraite.

(1994) demonstrated that a solid-solution series, $(Cu,Bi)_8S_9$, may be stable over a considerable range in temperature, albeit at relatively high fugacity of sulfur, thus explaining the contradictory results of earlier experimental work.

A second, closely related phase, hodrushite, was discovered at Banská Hodruša, Slovakia, and accepted as a distinct species with the empirical formula $Cu_{8.12}Fe_{0.29}Bi_{11.54}S_{22}$, ideally $Cu_8Bi_{12}S_{22}$ (Kupčik & Makovicky 1968, Koděra *et al.* 1970, Makovicky & MacLean 1972). [Note that although "hodrušite" has been considered a correct spelling in some reference works, "hodrushite" is preferred, in keeping with the first descriptions of the phase. "Hodrušhite" (*e.g.,* Mandarino 1999) is incorrect.] Electron-microprobe analyses show small amounts of Fe to be consistently present in hodrushite, which has a close structural relationship with both cuprobismutite and synthetic $Cu_4Bi_5S_{10}$ of Mariolacos *et al.* (1975). It was recognized that all structures contain a layer with Cu atoms linked by chains of Bi_2S_4, the so-called "C" layer (Koděra *et al.* 1970, Ozawa & Nowacki 1975, Mariolacos *et al.* 1975). These layers alternate with a second type of layer, in which Cu atoms are linked to ribbons of Bi with octahedral and square-pyramidal coordination.

Mumme & Žák (1985) described another related mineral, paděraite, and gave the empirical formula obtained from micro-analytical data as $Cu_{5.5}Ag_{1.1}Pb_{1.2}Bi_{11.0}S_{22}$, calculated for 22 sulfur atoms. Although a Pb-bearing phase, paděraite has unit-cell dimensions closely resembling those of hodrushite (Kupčik & Makovicky 1968). However, the structural refinement for paděraite (Mumme 1986) was based upon a slightly different chemical composition: an ideal formula of $Cu_6AgPb_2Bi_{11}S_{22}$, assuming a ratio of *Me*:S equal to 20:22, rather than 19:22 derived from the empirical formula. The empirical formula was recalculated as $Cu_{5.9}Ag_{1.3}Pb_{1.6}Bi_{11.2}S_{22}$, to match both the charge balance and structural data. Mumme (1986) recognized the same "C" layer as in $Cu_4Bi_5Bi_{19}$, cuprobismutite, and hodrushite, alternating with a thicker layer, in which the two atoms of Pb are included with distorted octahedral coordination. However, Mumme (1986) interpreted the "C" layers differently from the previous authors. He considered that $CuBiS_{10}$ lozenges, formed by pairs of BiS_6 octahedra attached to a square pyramidal Cu, are arranged *en échelon* at the margin of this layer (with pairs of Bi_2S_7 and CuS_4 groups in the middle part). He stressed that two $CuBiS_{10}$ lozenges give a common 17.5 Å repeat in the structures for all minerals discussed, including paděraite. He also recognized layers one octahedron in width (the "D" layers) with $(111)_{PbS}$ configuration as being present in cuprobismutite, hodrushite and paděraite, yet absent in $Cu_4Bi_5Bi_{10}$. Even though paděraite is distinct from the other three minerals by the presence of 2 Pb atoms per formula unit

(*apfu*), the Pb sites are incorporated within the "D" layers. Thus, Mumme (1986) derived the cuprobismutite series, in which each phase has a characteristic stacking sequence of the "C" and "D" layers. This was the first polytypic approach applied to a series of Bi sulfosalts.

This "cuprobismutite series" (Mumme 1986) gave way to the "cuprobismutite homologous series" (Makovicky 1989), defined as periodic intergrowth of $(331)_{PbS}$-like layers of octahedra with layers of metals in tricapped trigonal–prismatic coordination, giving the general formula $Cu_8Me_{4(N-1)+2}{}^{(quasi)octahedral}Bi_8{}^{square-pyramidal}S_{4N+16}$. Synthetic $Cu_4Bi_5S_{10}$ (Mariolacos *et al.* 1975) and cuprobismutite (Ozawa & Nowacki 1975) are the N_1 and N_2 homologues, respectively. Hodrushite is the $N_{1.5}$ homologue obtained by alternative intergrowths between the layers of octahedra of the two members with integral N, and the "C" layers. Later, Makovicky (1997) described polysomatism within the cuprobismutite series as coherent intergrowths of incremental slabs of octahedra with trigonal prismatic slabs, and denoted the species by the combinatorial triplet: N_1, N_2 = (1,1), (1,2), (2,2). Paděraite is regarded as a related structure with possible merotypic affinities to the cuprobismutite series, sharing the "C" layer.

SAMPLE DESCRIPTION AND COMPOSITION

The sample GS contains large cm-scale masses of Bi-sulfosalt minerals: bismuthinite derivatives (BD) mainly within the range between gladite and bismuthinite (compositional mean $Cu_{0.833}Pb_{0.833}Bi_{19.167}S_{30}$; BD_{10}), the ^4P pavonite homologue makovickyite, and three minerals that correspond, compositionally, to cuprobismutite, paděraite and hodrushite. Cuprobismutite, paděraite and subordinate amounts of hodrushite occur as coarse to acicular blades, up to 1 mm in size, which form aggregates scattered as a more-or-less regular framework within a matrix of bismuthinite derivatives. Minor magnetite, as rounded and fragmented grains, completes the assemblage and documents the extent of retrograde reworking within the ores. The entire assemblage occurs as a nest within magnetite ore hosted by andradite skarn. Our investigation was undertaken using BSE images, owing to the gross similarities of the various minerals in reflected light.

Electron-probe micro-analyses were carried out using the CAMECA SX–50 instrument at the Institute for Mineralogy, University of Würzburg, Germany, the JEOL JXA 8600 instrument at the Department of Earth Sciences, University of Bristol, U.K., and the JEOL JXA 8600 microprobe at the Mineralogical Institute, University of Salzburg, Austria. Operating conditions were 15 nA and 15 kV, 20 nA and 15 kV and 20 nA and 25 kV, respectively. Standards and wavelengths used for micro-analysis in the three laboratories are summarized in Table 2.

Bismuthinite derivatives and makovickyite

The sample matrix is composed of Cu–Pb-poor bismuthinite derivatives, both as mm-scale areas of homogeneous composition and as various morphological intergrowths between discrete derivatives (Figs. 1a–e). The most abundant mineral in the matrix of the sample is $Cu_{0.833}Pb_{0.833}Bi_{19.167}S_{30}$, *i.e.*, $n_{aik} = 10$, occupying an intermediate position between bismuthinite and pekoite along the bismuthinite–aikinite line in the compositional triangle Cu_2S–PbS–Bi_2S_3 (Table 2, Fig. 2). This was earlier described as "Phase 88.6" by Ciobanu & Cook (2000) from the same Paulus occurrence. However, this composition (BD_{10}) can best be assigned to the upper limit of the solid-solution field of bismuthinite (*i.e.,* oversubstituted bismuthinite). Structural refinement of crystals with similar composition from Felbertal, Austria (Topa 2001, Topa *et al.* 2002) indicated neither structural modification from the parent bismuthinite cell nor any indication of a supercell with this composition.

Bulk compositions in the range between gladite and BD_{10} (Fig. 2) are obtained from the fine areas of intergrowths, which are found randomly as patches across the matrix. Nevertheless, stoichiometric gladite is found in minor amounts in three distinct positions: (i) as sets of short lamellae cross-cutting the fields of intergrowths (Figs. 1c, d), (ii) as larger grains with halos of intergrowths (Fig. 1e), and (iii) as a marginal shadow-like rim between inclusions of makovickyite and intergrowth-free BD_{10} (Fig. 1f).

Other masses of BD_{10} contain coarse mm-scale areas of intergrowths, each consisting of μm-scale intergrowths of bismuthinite derivatives. The fields of intergrowths are μm-scale sets of lamellae or blebs of composition in the range between gladite and BD_{10}. Most commonly, the lamellae are pencil-like in morphology (Fig. 1a), extending across large portions of the BD_{10} grains. There is always an intergrowth-free rim between the areas of intergrowths and the acicular aggregates of cuprobismutite and padĕraite. Many of these areas of pencil-like intergrowths are enclosed within, but never touching, the bundles of cuprobismutite and padĕraite, suggesting that they, as a kind of framework, may play the role of a chemical barrier during intergrowth formation. The lamellae may also appear as oriented, elongate blebs, or perpendicular sets of worm-like blebs, some tens of μm in length (Figs. 1b–d).

Within the intergrowths of bismuthinite derivatives, two compositionally distinct lamellae can be distinguished in BSE images. A finer, dominant set of lamellae, never more than 2 μm wide, gives bulk compositions intermediate between gladite and BD_{10}; a second, generally coarser set (3–5 μm wide), cross-cutting the earlier set of lamellae, has the composition of stoichiometric gladite (Fig. 1e). The composition of finer lamellae is difficult to characterize unequivocally, since the size of the microprobe beam is generally greater than the width of the lamellae. Although we wish to avoid speculation without complementary microstructural data, the thin lamellae may well be pekoite, or alternatively, a phase intermediate between gladite and pekoite. A homogeneous phase, with a composition close to $CuPbBi_7S_{12}$, was described by Ciobanu & Cook (2000), and termed "phase70".

Makovickyite, the [4]P pavonite homologue, forms subidiomorphic crystals within the matrix, characteristically rimmed by narrow margins of gladite (Fig. 1f). Makovickyite has an extremely homogeneous composition throughout the sample. Sixty-four spot analyses from 29 grains gave a generally tight compositional cluster, within the compositional range previously reported from Ocna de Fier (Ciobanu & Cook 2000), although somewhat richer in Cu and poorer in Pb than in the earlier study. The mean composition is $Cu_{1.34}Ag_{0.76}Pb_{0.14}Bi_{5.21}S_{9.64}$. Makovickyite appears to be the most homogeneous phase in the material, and may play an effective role in buffering the compositions of associated minerals.

TABLE 2. COMPOSITION OF BISMUTHINITE DERIVATIVE (BD_{10}) FROM OCNA DE FIER, ROMANIA

	representative individual compositions								mean comp.	
	GS 1.6	GS 2.1	GS 5.4	GS 6 *n* = 2	GS 7.1	GS 8 *n* = 3	GS 9 *n* = 2	GS 10 *n* = 2	GSA 1 *n* = 9	GSA 1a *n* = 9
Cu wt.%	1.19	1.01	0.84	0.96	0.92	0.89	1.13	0.98	0.89	1.02
Pb	3.03	3.07	2.49	2.83	2.84	2.52	2.95	2.91	2.88	3.32
Bi	76.09	76.41	77.16	76.30	76.35	77.11	76.45	77.10	77.83	77.09
S	18.43	18.26	18.66	18.57	18.39	18.68	18.60	18.67	19.01	19.03
Total	98.74	98.75	99.15	98.66	98.50	99.20	99.13	99.66	100.61	100.46
Cu at.%	1.87	1.59	1.32	1.51	1.45	1.40	1.78	1.54	1.41	1.61
Pb	1.46	1.48	1.20	1.37	1.37	1.22	1.42	1.40	1.39	1.60
Bi	36.41	36.56	36.92	36.51	36.53	36.90	36.58	36.89	37.24	36.89
Σ*Me*	39.75	39.63	39.45	39.39	39.35	39.52	39.78	39.84	40.04	40.10
S	57.49	56.96	58.20	57.92	57.36	58.27	58.02	58.23	59.30	59.36
% Cu$_2$S	4.54	3.87	3.25	3.71	3.55	3.44	4.31	3.74	3.39	3.85
% PbS	7.10	7.21	5.91	6.70	6.73	5.97	6.91	6.81	6.71	7.69
% Bi$_2$S$_3$	88.36	88.93	90.83	89.59	89.71	90.59	88.77	89.45	89.90	88.47
Cu *apfu*	0.98	0.84	0.68	0.78	0.76	0.72	0.92	0.79	0.71	0.81
Pb	0.76	0.78	0.62	0.71	0.72	0.63	0.74	0.72	0.70	0.81
Bi	19.00	19.26	19.03	18.91	19.11	19.00	18.92	19.01	18.84	18.64
Σ*Me*	20.74	20.88	20.33	20.40	20.58	20.35	20.57	20.52	20.26	20.27
S	30.00	30.00	30.00	30.00	30.00	30.00	30.00	30.00	30.00	30.00

No Sb, Se or Te was detected in any of the samples analyzed. Formula calculated on basis of 30 S atoms per formula unit (*apfu*). The following standards and peaks were used: Bi_2S_3 (Bi*L*α), PbS (Pb*L*α, S*K*α), FeS$_2$ (Fe*K*α), CuFeS$_2$ (Cu*K*α), CdS or CdTe (Cd*L*α), Bi$_2$Te$_3$ (Te*L*α), Bi$_2$Se$_3$ (Se*L*α), Ag (Ag*L*α), and Sb$_2$S$_3$ (Sb*L*α). *n*: number of analyses.
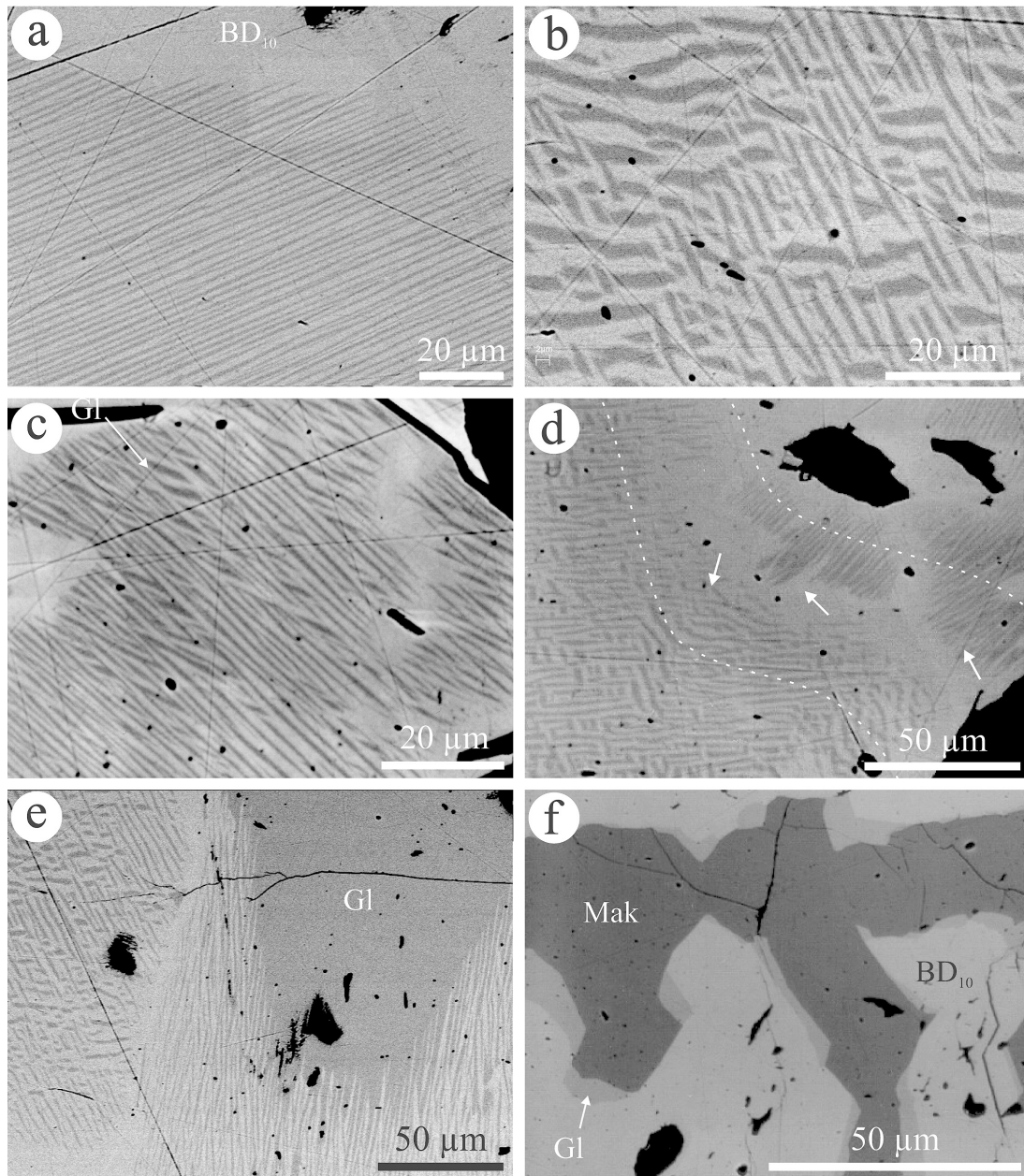
FIG. 1. Back-scattered electron images showing the occurrence of bismuthinite derivatives. (a) Detail of pencil-like lamellae (with composition between gladite and BD_{10}) within a matrix BD_{10}. (b) Worm-like lamellae of variable composition oriented in two dimensions within a matrix of BD_{10}. (c) Pencil-like lamellae within BD_{10} matrix. Two sets of lamellae can clearly be seen; a dominant, thin variety (composition between gladite and BD_{10}) and a slightly thicker set of lamellae (gladite), which cross-cut the thinner variety. (d) Two different morphologies within fields of intergrowths among BDs (see text). Retrograde overprinting is indicated by a slight curvature of some lamellae in both areas of intergrowths toward mutual grain-boundaries (arrow). This is accentuated by coarsening of gladite lamellae (*cf.* Fig. 1a). (e) Patch of homogeneous gladite (Gl) with halos of intergrowths outward of the matrix of BD_{10}. (f) Subidiomorphic crystals of makovickyite (Mak) in a matrix of homogeneous BD_{10}. Note the occurrence of homogeneous gladite (Gl) at grain boundaries between the two minerals.
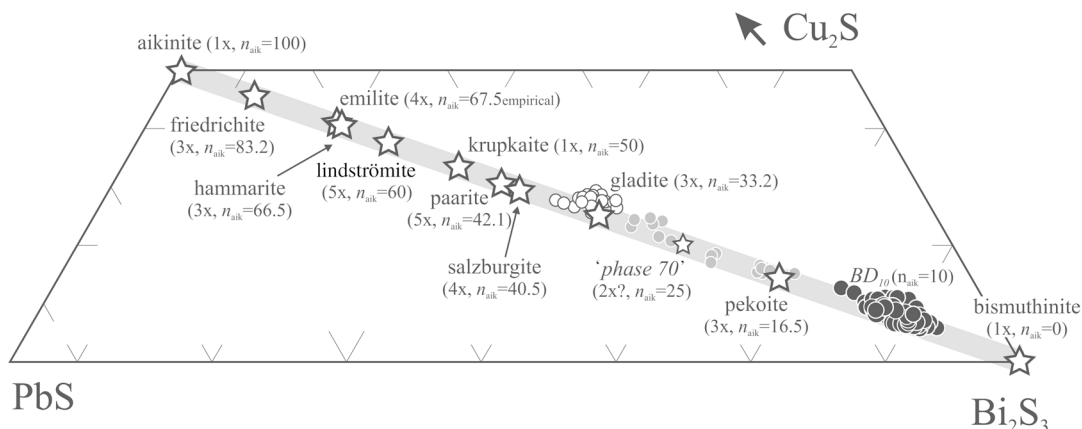
FIG. 2. Compositional plot for bismuthinite derivative $n_{aik} = 10$ (BD_{10}) from homogeneous areas (filled circles; individual compositions) plotted in Cu_2S–PbS–Bi_2S_3 space. Also shown are compositions of homogeneous gladite (white circles) and "bulk" compositions from points within the intergrowths (grey circles). The position of recognized minerals within the aikinite–bismuthinite series (with corresponding n_{aik} values) are indicated by stars. The a repeat of each supercell is given as $1\times$, $3\times$, $4\times$ or $5\times$. "Phase 70" refers to the homogeneous phase in the series reported by Ciobanu & Cook (2000).

Cuprobismutite, padĕraite and hodrushite

Aggregates of acicular blades, several hundred μm in length, are present as bundles or radial "sprays" throughout the sample, hosted within the bismuthinite derivatives (Figs. 3a, b). Although apparently homogeneous in reflected light, BSE photographs show that the blades consist of lamellar intergrowths of two discrete phases in approximately equal proportions ("lighter" and "darker" strips in the BSE images), and a third, much less common, "darkest" phase (Fig. 3). All are intimately intergrown with each other as a series of irregular lamellae. The size of the individual, compositionally homogeneous lamellae attains 1000 μm in length; widths range from more than 100 μm to less than 1 μm. Both the "lighter" and "darker" varieties in the BSE images are observed at the outer margin of the bundles, in contact with BD_{10}.

Micro-analysis of the homogeneous acicular or lamellar minerals allows for identification of cuprobismutite, padĕraite and hodrushite, even though compositions differ somewhat from previously published data for these minerals. The dataset, summarized in Tables 3 and 4, shows evidence of two distinct clusters (Fig. 4). These are centered on a Pb-poor, Ag-rich mineral with a mean composition, based on 46 $apfu$, of $Cu_{8.07}(Ag_{0.99}Pb_{0.21}Bi_{12.72})_{\Sigma13.92}S_{24.01}$ (cuprobismutite), and a Pb-rich, Ag-poor mineral with a mean composition, based on 42 $apfu$, of $Cu_{7.11}(Ag_{0.36}Pb_{1.20})_{\Sigma1.56}Bi_{11.28}S_{22.05}$ (padĕraite).

A small population extends between the two clusters. These data are partly from lamellae that are apparently homogeneous on the microscopic scale. Other lamellae giving compositions intermediate between cuprobismutite and padĕraite contain very fine

intergrowths. Corresponding back-scattered electron images strongly suggest that lamellar intergrowths of the two minerals extend below the sub-μm scale, $i.e.,$ well below the size of the microprobe beam. The variation in composition between lamellae in an individual bladed aggregate is illustrated in Figure 5. The levels of concentration of Pb and Ag display an inverse correlation between the two minerals (Fig. 5b).

Importantly, none of the analyzed grains of cuprobismutite and padĕraite contain Fe at concentrations above the minimum limit of detection. In contrast, hodrushite has the mean composition $(Cu_{7.80}Fe_{0.23})_{\Sigma8.03}$ $(Ag_{0.35}Pb_{0.12}Cd_{0.02}Bi_{11.49})_{\Sigma11.98}S_{21.99}$, based on 42 $apfu$.

DISCUSSION

The cuprobismutite series and related padĕraite: chemical composition and occurrences

The number of confirmed occurrences of cuprobismutite remains, to this day, extremely small (Table 1). The occurrence described by Taylor $et~al.$ (1973) from the Tunnel Extension Number Two mine, Ohio Mining District, Utah, U.S.A., was said to have the ideal formula of $Cu_{10}Bi_{12}S_{23}$ but, significantly, the empirical formula $(Cu_{20.8}Ag_{0.97}Pb_{0.35}Mn_{0.22}Bi_{26.7}Sb_{0.06}Te_{0.05}$ $Se_{0.55}S_{50.4})$ also contains both Ag and Pb. Taylor $et~al.$ (1973) carried out an X-ray determination of the phase, which was concordant with the data of Nuffield (1952). Dobbe (1991) reported "sulfosalt Y" $(Cu_{7.9}Ag_{2.2}$ $Fe_{0.6})_{10.7}(Bi_{12.6}Pb_{0.1})_{12.7}(S_{23.7}Se_{0.3})_{24}$, from Tunaberg, Sweden, and tentatively assigned this to cuprobismutite. Tarkian & Breskovska (1995) described "cuprobismutite" from the Zidarovo deposit, Bulgaria, and fur-
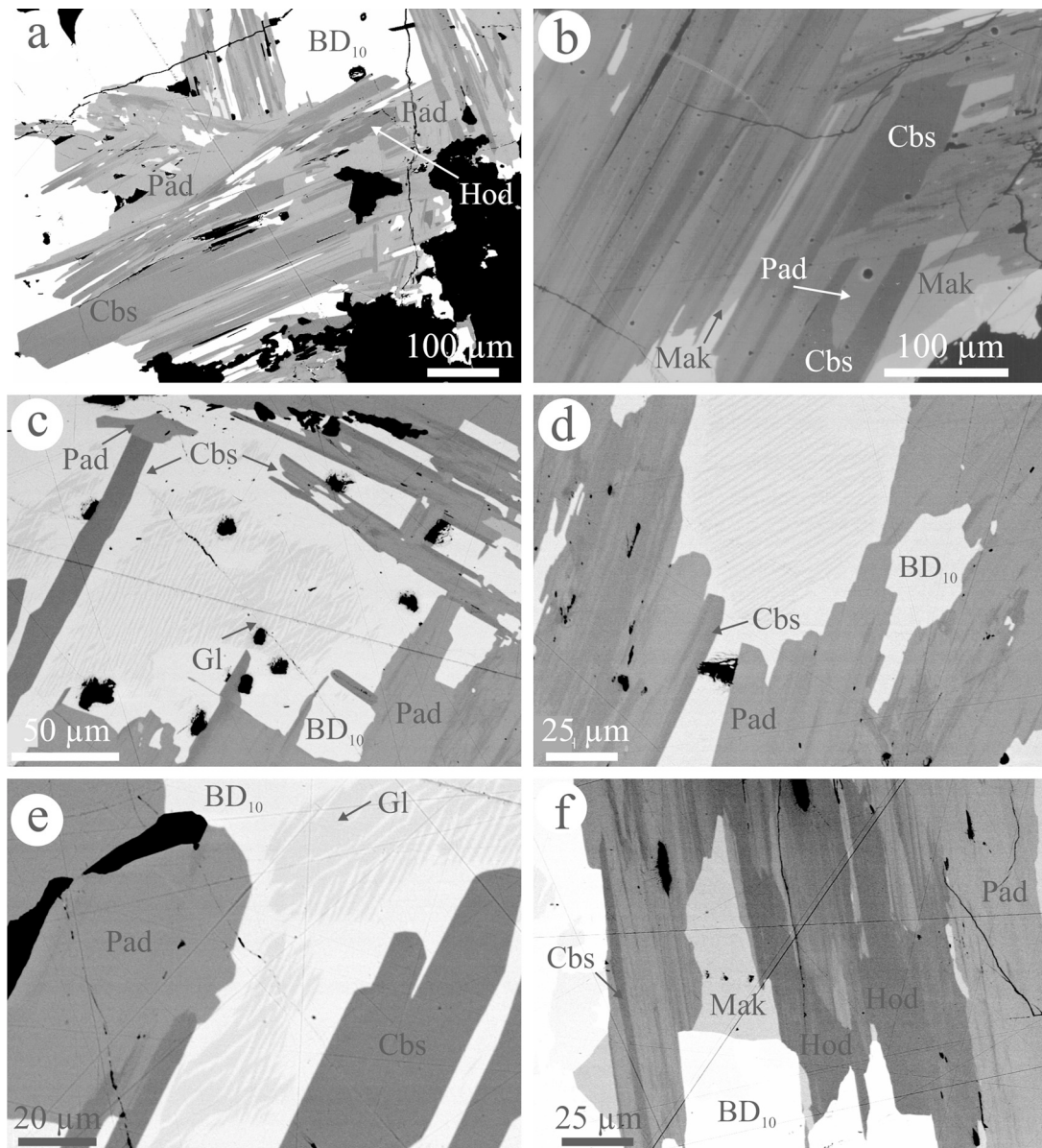
FIG. 3.   Back-scattered electron images showing the occurrence and paragenesis of cuprobismutite, hodrushite and paděraite. (a) Aggregate of cuprobismutite and paděraite (Cbs, Pad), with subordinate hodrushite (Hod), within matrix of BD_{10}. Aggregates of cuprobismutite and paděraite show preferential arrangement of blades at ~45% and ~90% to one another. Width of individual lamellae vary from <100 μm down to a submicrometer scale. (b) Detail showing intergrown character within a single lath from an aggregate similar to that shown in (a). Makovickyite (Mak) occurs between lamellae of cuprobismutite (Cbs) and paděraite (Pad). (c) Field of pencil-like intergrowths of BDs within matrix BD_{10} framed by orthogonal laths of paděraite (Pad). Needles of cuprobismutite (Cbs) mark the margins of the laths. (d) Field of pencil-like intergrowths of BDs within matrix BD_{10} nested by "bundles" of cuprobismutite and paděraite. (e) Detail of area similar to (d) showing thicker, homogeneous paděraite and thinner cuprobismutite, both as crystals with prismatic edges. (f) Detail of an aggregate showing coexistence of the three identified minerals, hodrushite (Hod), cuprobismutite (Cbs) and paděraite (Pad). Retrograde overprinting (by diffusion?) has reshaped mutual boundaries among the three phases. Makovickyite (Mak) occurs between lamellae, as in (b).

TABLE 3. COMPOSITIONS OF CUPROBISMUTITE, PADĚRAITE AND HODRUSHITE
FROM OCNA DE FIER, ROMANIA

cuprobismutite: representative individual compositions

	GS 1.2	GS 1.20a	GS 1.8A	GS 8.3	GSA 6 2	GSA 12 3	GSN 2.4	GSN 2.5	GSN 6.25	GSN 6.26	GSN 19.16
Cu wt.%	12.27	12.36	12.38	12.25	12.20	12.40	11.96	12.68	12.65	12.63	12.62
Ag	2.68	2.50	2.61	2.57	2.60	2.43	2.53	2.54	2.62	2.52	2.71
Cd	n.a.	n.a.	n.a.	n.a.	0.40	0.30	<0.10	<0.10	<0.10	<0.10	<0.10
Pb	0.67	0.62	0.63	0.78	0.90	0.90	1.25	1.25	0.80	1.01	0.98
Bi	65.74	65.91	65.07	64.68	66.30	65.40	64.62	63.74	63.86	64.40	63.45
S	18.54	18.58	18.57	18.76	18.50	18.40	18.25	18.88	18.69	18.47	18.70
Total	99.90	99.97	99.26	99.04	100.90	99.83	98.61	99.10	98.61	99.04	98.44
Cu *apfu*	7.97	8.02	8.05	7.95	7.90	8.07	7.89	8.17	8.20	8.23	8.19
Ag	1.03	0.96	1.00	0.98	0.99	0.93	0.99	0.96	1.00	0.97	1.03
Cd	-	-	-	-	0.15	0.11	-	-	-	-	-
Pb	0.13	0.12	0.13	0.16	0.18	0.18	0.25	0.25	0.16	0.20	0.19
Bi	12.99	13.00	12.87	12.77	13.05	12.95	12.98	12.49	12.60	12.75	12.52
Σ*Me*	22.12	22.10	22.05	21.86	22.27	22.24	22.11	21.87	21.96	22.15	21.95
S	23.88	23.90	23.95	24.14	23.74	23.75	23.89	24.12	24.04	23.85	24.05

padĕraite: representative individual compositions

	GS 1.7	GS 1.10	GS 1.11	GS 3.6	GS 9.1	GS 10.1	GSA 6.1	GSA 6.7	GSA 12.7	GS 6.18	GS 6a.1
Cu wt.%	11.58	11.65	11.66	11.59	11.77	11.69	11.7	11.8	11.7	11.87	11.80
Ag	0.88	1.09	0.91	0.84	0.92	0.92	0.75	1.07	0.83	0.98	1.12
Pb	6.31	6.01	6.13	6.62	6.83	6.08	7.1	6.1	7.1	6.64	6.02
Bi	62.85	62.75	61.74	61.42	60.61	60.95	62.5	62.8	61.6	61.02	61.25
S	18.56	18.19	18.37	18.30	18.54	18.69	18.1	18.2	18.4	18.18	18.31
Total	100.18	99.69	98.81	98.77	98.67	98.33	100.15	99.97	99.63	98.68	98.49
Cu *apfu*	6.95	7.06	7.07	7.05	7.09	7.05	7.10	7.13	7.06	7.22	7.15
Ag	0.31	0.39	0.33	0.30	0.33	0.33	0.27	0.38	0.30	0.35	0.40
Pb	1.16	1.12	1.14	1.23	1.26	1.12	1.32	1.13	1.31	1.24	1.12
Bi	11.48	11.57	11.38	11.36	11.10	11.17	11.53	11.54	11.31	11.28	11.29
Σ*Me*	19.90	20.14	19.92	19.94	19.78	19.67	20.22	20.18	19.98	20.09	19.96
S	22.09	21.86	22.08	22.06	22.13	22.33	21.77	21.81	22.02	21.91	22.04

	hodrushite: representative individual compositions					**"bulk" composition of fine intergrowths of cuprobismutite–padĕraite**		
	GS 6.3	GS 12.4	GS 6.17	GS 6.20	GS 6.21	GS 1.5	GS 1.8B	GSA 1.17
Cu wt.%	13.00	13.10	12.82	13.55	13.58	12.18	11.99	12.43
Ag	1.14	0.99	1.54	0.85	0.00	1.74	1.88	1.81
Fe	0.40	0.39	0.16	0.40	0.39	0	0	0
Cd	0.30	0.30	0.00	0.00	0.00	0	0	0
Pb	0.60	0.30	1.59	0.40	0.49	3.54	3.28	3.63
Bi	65.90	65.70	64.14	65.53	64.95	62.31	64.29	61.72
S	18.90	19.50	18.76	18.92	18.97	18.74	18.67	19.96
Total	100.24	100.28	99.01	99.65	98.38	98.51	100.11	99.55
Cu *apfu*	7.58	7.53	7.57	7.90	7.97			
Ag	0.39	0.34	0.54	0.29	0			
Fe	0.27	0.26	0.11	0.27	0.26			
Cd	0.10	0.10	0	0	0			
Pb	0.11	0.05	0.29	0.07	0.09			
Bi	11.69	11.49	11.52	11.61	11.60			
Σ*Me*	20.14	19.77	20.03	20.14	19.92			
S	21.86	22.23	21.97	21.86	22.08			

No Sb, Se or Te was detected in any of the samples analyzed. The formulae of cuprobismutite were calculated on basis of 46 atoms, those of padĕraite and hodrushite, on the basis of 42 atoms. n.a.: not analyzed for.
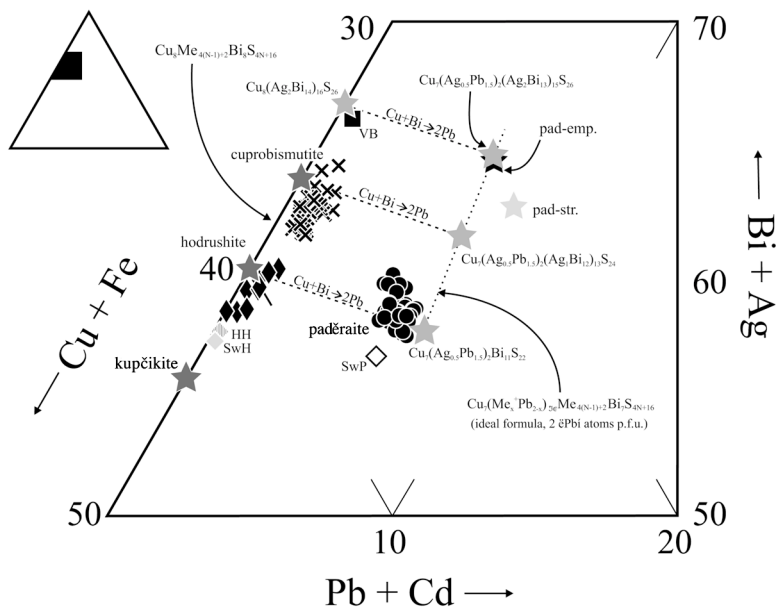
FIG. 4.   Compositions of cuprobismutite, hodrushite and paděraite from Ocna de Fier plotted in (Cu + Fe) – (Bi + Ag) – (Pb + Cd) space. Filled circles show the compositions (individual data-points) of paděraite, crosses are cuprobismutite, and filled rhombs are hodrushite. Stars represent ideal, end- member compositions of the minerals and phases discussed (see text). For paděraite, empirical formulae based on results of electron-probe micro-analysis, $Cu_{5.5}Ag_{1.1}Pb_{1.2}Bi_{11}S_{22}$ (pad–emp.) and structure determination, $Cu_{5.9}Ag_{1.3}Pb_{1.6}Bi_{11.2}S_{22}$ (pad–str.) are given for comparison (Mumme & Žák 1985, Mumme 1986, respectively). VB: phase with mean composition $Cu_{7.94}(Ag_{1.91}Pb_{0.21}Bi_{13.76})_{\Sigma 15.88}S_{26.17}$ from Vurly Bryag, Bulgaria. SwP: Ag-free paděraite from Swartberg, South Africa, with mean composition $Cu_{7.24}Pb_{1.36}Bi_{11.27}S_{22.12}$. SwH: hodrushite from Swartberg $(Cu_{8.13}Fe_{0.33}Ag_{0.04}Pb_{0.09}Bi_{11.44}S_{21.96})$. HH: holotype hodrushite from Banská Hodruša, Slovakia $(Cu_{8.12}Fe_{0.29}Bi_{11.54}S_{22})$.

nished two compositions of a silver-bearing sulfosalt. Cioflica *et al.* (1997) analyzed material that they believed to be cuprobismutite from Băiţa Bihor, Romania. However, because of the difficulty of confirming the presence of a species by micro-analysis, given the complex and varied mechanisms of substitution, the possibility of unnoticed microscopic or submicroscopic intergrowths, and also analytical uncertainties attached to some of the published data, the diagnosis in the latter three occurrences should be approached with caution. The occurrence of cuprobismutite described by Taylor *et al.* (1973) is the sole example to be supported by diffraction data.

A natural, Fe-bearing N_1 homologue in the Felbertal deposit, Austria, has recently been defined as the mineral kupčikite, with the formula $(Cu_{6.8}Fe_{1.2})_{\Sigma 8}Bi_{10.8}S_{20}$ (Topa 2001, in prep.), which can be considered equivalent to Phase "Z", $Cu_{8.4}Fe_{1.2}Bi_{10.8}S_{22}$, of Sugaki *et al.* (1981, 1984). Ilinca (1998) described hodrushite from two Romanian occurrences, Băiţa Bihor and the nearby

deposit of Valea Seacă. Hodrushite from both these occurrences also contains Fe. At Băiţa Bihor, hodrushite occurs both as homogeneous grains and as intergrowths with a similar but more Fe-rich phase, identified by Ilinca (1998) as a probable natural analogue of Phase "Z", *i.e.,* before the same mineral was identified from Felbertal.

Published compositional data for "hodrushite" from the type locality of Banská Hodruša, Slovakia, in both the original descriptions, and in a later publication by Kovalenker *et al.* (1993), indicate that most analyzed samples contain up to 1 wt.% Fe and Ag, but only very minor Pb. Conspicuously, "hodrushite" compositions from Băiţa Bihor given by Žák *et al.* (1994), again without accompanying X-ray data, do not contain Fe. Similarly, "hodrushite" from further occurrences in central Asia (Kovalenker 1986, Kovalenker *et al.* 1987) reveal only minor Fe, placing some uncertainties on their true identities, or upon the role played by Fe to stabilize hodrushite in natural specimens. Pattrick (1984) has

TABLE 4. COMPOSITIONS OF CUPROBISMUTITE, PADĚRAITE AND HODRUSHITE
FROM OCNA DE FIER: MEANS, MAXIMA, MINIMA AND STANDARD DEVIATIONS

	cuprobismutite				padĕraite				hodrushite			
	Mean $n = 30$	Std. Dev	Max.	Min.	Mean $n = 37$	Std. Dev.	Max.	Min.	Mean $n = 10$	Std. Dev.	Max.	Min.
Cu wt.%	12.41	0.19	12.69	11.96	11.74	0.42	12.07	9.23	13.30	0.28	13.72	12.82
Ag	2.59	0.09	2.75	2.34	1.00	0.14	1.31	0.75	1.01	0.43	1.54	<0.10
Fe	0.00	-	-	-	0.00	-	-	-	0.34	0.08	0.41	0.16
Cd	0.06	0.04	0.40	<0.10	0.01	0.05	0.20	0.00	0.06	0.13	0.30	<0.10
Pb	0.91	0.33	1.40	0.55	6.47	0.51	7.34	5.37	0.65	0.41	1.59	0.30
Bi	64.34	0.99	66.30	61.97	61.24	1.03	63.95	59.72	64.41	1.02	65.90	63.35
S	18.62	0.33	19.60	18.25	18.35	0.18	18.69	18.00	18.90	0.23	19.50	18.70
Total	98.93				98.81				98.67			
Basis of formula	46 atoms				42 atoms				42 atoms			
Cu *apfu*	8.07	0.13	8.27	7.84	7.11	0.23	7.30	5.77	7.80	0.19	8.09	7.53
Ag	0.99	0.04	1.07	0.90	0.36	0.05	0.47	0.27	0.35	0.15	0.54	-
Fe	0.00	-	-	-	0.00	-	-	-	0.23	0.05	0.28	0.11
Pb (+Cd)	0.21	0.19	0.39	0.11	1.20	0.09	1.35	1.00	0.14	0.08	0.29	0.06
Bi	12.72	0.06	13.05	12.27	11.28	0.22	12.15	10.99	11.49	0.11	11.69	11.35
ΣMe	21.99	-			19.95	-	-	-	20.01	-	-	-
S(+Te)	24.01	0.22	24.57	23.72	22.05	0.18	22.67	21.69	21.99	0.11	22.23	21.86

n: number of analyses.

given electron-microprobe data for a Fe-rich phase within a Cu-sulfide occurrence at Tomnadashan, Scotland, whose composition does not closely match any recognized minerals within the group. A larger statistical base with which to verify compositional variation and limits, with supporting X-ray data, is clearly required.

In Cu–(Au) veins at Vurly Bryag, Burgas District, Bulgaria, along the same Upper Cretaceous Banatitic Magmatic and Metallogenic Belt that includes the Băiţa Bihor, Valea Seacă, Ocna de Fier, and Zidarovo deposits, the present authors and coworkers (Ciobanu *et al.* 2002b) isolated a phase with the composition $Cu_{7.94}(Ag_{1.91}Pb_{0.21}Bi_{13.76})_{\Sigma 15.88}S_{26.17}$. The phase occurs as <70 μm inclusions within chalcopyrite, and is associated with BD and emplectite. This may correspond to a possible $N = 2.5$ homologue in the cuprobismutite series, theoretically $Cu_8(Ag_2Bi_{14})_{\Sigma 16}S_{26}$, characterized by Cu/(Ag + Bi) value of 8:16, atoms, based on 50 *apfu*. As expected by charge-balance requirements, Ag content increases in the quasi-octahedral position with higher N in the series.

Published compositions of "padĕraite" (Kovalenker *et al.* 1993, Žák *et al.* 1994, both without structural data) from two known occurrences, the type locality, Băiţa Bihor, Romania and Banská Hodruša, Slovakia, show some variation, particularly with respect to Ag and Pb contents. Additional data illustrating compositional variation in padĕraite come from a new occurrence of

Ag-free padĕraite, $Cu_{7.24}Pb_{1.36}Bi_{11.27}S_{22.12}$, coexisting with hodrushite, $Cu_{8.13}Fe_{0.33}Ag_{0.04}Pb_{0.09}Bi_{11.44}S_{21.96}$, in a rare-element pegmatite from Swartberg, South Africa (Ciobanu & Cook 2002a, Ciobanu *et al.* 2002b). The identity of both phases is confirmed by single-crystal diffraction (D. Topa, pers. commun. 2003). The confirmation of padĕraite in the Swartberg specimens indicates that Ag is not essential, provided that other elements, *e.g.,* excess Cu, fulfill the same structural role. In contrast, the Pb-content seems fixed to a certain value, not exceeding 2 *apfu*, as used in the structure refinement for padĕraite. Lead content shows little correlation with Ag.

Ciobanu *et al.* (2002b) accordingly proposed that "padĕraite" occupies a wider compositional range, with the general formula $Cu_7(Me^+_xPb_{1.6-x})_{\Sigma 1.6}Me_{4(N-1)+2.4}Bi_7S_{4N+16}$, derived from the cuprobismutite series *via* the simple substitution $Cu^+ + Bi^{3+} \rightarrow 2Pb^{2+}$. If, as is apparent from a consideration of all published compositional data, there are various values of the ratio between the fixed number of Cu atoms (7) per formula unit, and the corresponding number of Bi atoms, then "padĕraite" may form a discrete homologous series, paralleling the cuprobismutite series, also with variable N (Fig. 4). In the type-locality padĕraite, it would be easy to consider that the 1 Ag atom, together with 6 Cu, fulfills the requirement of 7 "Cu" atoms in the formula above, especially since Mumme (1986) considered that the Ag is in
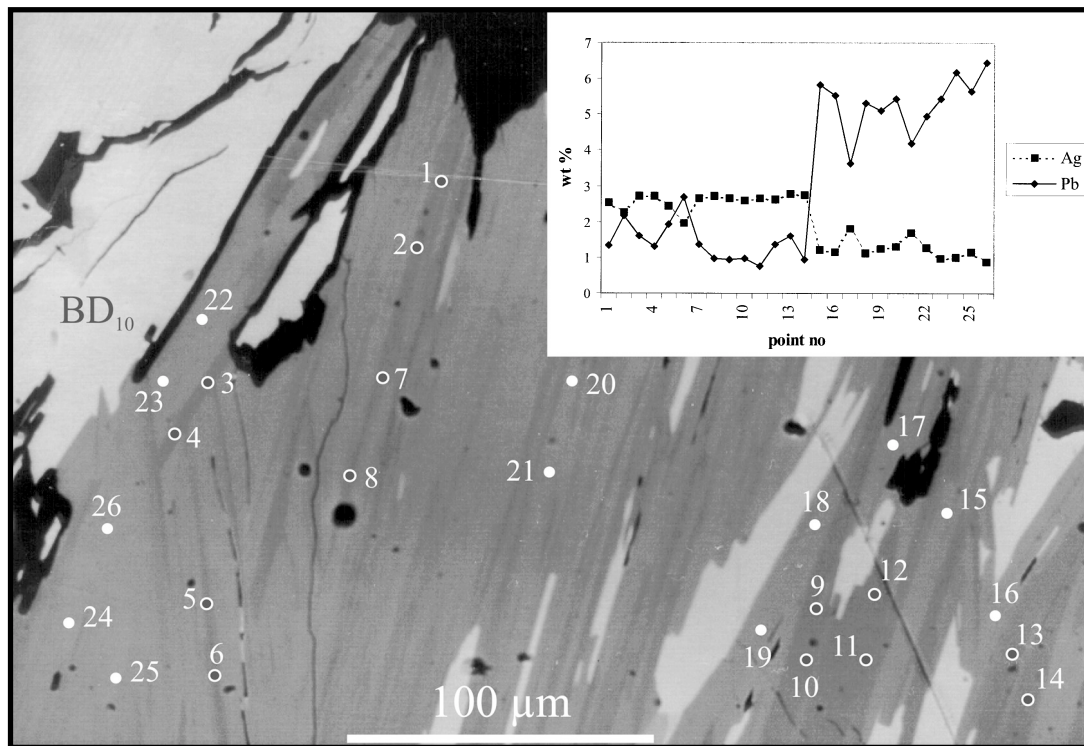
FIG. 5. Compositional variation among intimately intergrown lamellae in a selected lath, indicated by points of micro-analysis on coarser lamellae. Black circles are "dark" lamellae (cuprobismutite); white circles are "light lamellae" (padĕraite). Inset shows variation in proportion of Ag and Pb (wt.%) in the 26 analyzed points (1–14 from cuprobismutite, 15–26 from padĕraite). The size of the individual points analyzed is exaggerated for clarity.

tetrahedral coordination, as is the Cu in the "C" layers. In such an assumption, the holotype padĕraite would plot in the same position in Cu–Bi–Pb space as padĕraite in the Ocna de Fier material or the Ag-free padĕraite from Swartberg (Fig. 4). However, this is a debatable point, given uncertainties about the composition of the holotype material (as expressed by Mumme himself; 1986), and the fact that in other Bi sulfosalt structures, Ag can be more easily incorporated with octahedral coordination (*e.g.,* in the pavonite or lillianite series; Makovicky 1989). Even though the layered structure of padĕraite, and the "C" layer common to all minerals discussed, offers the kind of modularity to reflect incremental changes in Cu:Bi ratio, as in the cuprobismutite series, the limited data for padĕraite available at present are too speculative for further statements.

Ocna de Fier material

BSE images (Fig. 3) and results of electron-microprobe analyses (Tables 3, 4) confirm the presence of two main minerals, cuprobismutite and padĕraite. Inter-

growths of the two, at both the microscopic and submicroscopic scales, are a feature of the described occurrence. A smaller number of hodrushite lamellae, coexisting with the above intergrowths, are recognizable by a minor, but persistent Fe contents. In this section, we will discuss the identities of these minerals and the implications that they have, both for the occurrence of minerals of the cuprobismutite group in nature, and for the genesis of the deposit.

As with other groups of Bi-sulfosalts, plotting of mineral compositions in ternary space is complicated by the need to incorporate operating mechanisms of substitution. For the purposes of simplicity, however, our compositional data have been plotted in terms of (Cu + Fe) – (Pb + Cd) – (Bi + Ag), based upon the empirical formulae presented above. Even though this may not fully reflect all possible substitutions in specimens from other localities, *e.g.,* holotype hodrushite, it efficiently illustrates the deviation, in our material, from the ideal formulae: $(Cu_{8-x}Fe_x)_{\Sigma 8}(Ag_yPb_zBi_{12-y-z})_{\Sigma 12}S_{22}$, with $0 \leq x \leq 0.4$, $0 \leq (y + z) \leq 0.5$ ($N_{1.5}$; hodrushite), and $Cu_8(AgBi_{13})_{\Sigma 14}S_{24}$ (N_2; cuprobismutite). Two possible

substitutions can be written for cuprobismutite homologues: $3Ag^+ \rightarrow Bi^{3+}$ and $Ag^+ + Pb^{2+} \rightarrow Bi^{3+}$. Furthermore, the substitution $Fe^{2+} \rightarrow Cu^+ + \square$ can be considered for hodrushite with Cu deficiency (less than 8 *apfu*), as in our material. The ideal composition considered for the Ocna de Fier hodrushite differs from that of holotype hodrushite, from Banská Hodruša, Slovakia, $Cu_{8.12}Fe_{0.29}Bi_{11.54}S_{22}$, in that Cu is deficient (*i.e.*, less than 8 *apfu*), rather than in excess. In holotype hodrushite, the Bi position is filled by an excess of Cu over 8 *apfu*, together with Fe, following the substitution $Cu^+ + Fe^{2+} \rightarrow Bi^{3+}$, giving $Cu_8(Cu_xFe_yBi_{12-x-y})_{\Sigma12.02}S_{22}$, with $0 \leq (x + y) \leq 0.5$. Crystal-structure refinements for cuprobismutite and hodrushite from Felbertal, Austria, with similar compositions as in our material (D. Topa, pers. commun., 2003) confirms that the Bi octahedral sites can adjust to excess Ag in cuprobismutite, whereas Fe can enter the Cu sites (quasi-octahedral; 0.64/0.36) in hodrushite.

Even though the empirical formula obtained for padĕraite in Ocna de Fier is closer to ideal Cu_7 $(Ag_{0.4}Pb_{1.2})_{\Sigma1.6}Bi_{11.4}S_{22}$ rather than $Cu_6AgPb_2Bi_{11}S_{22}$ (holotype padĕraite), it involves a *Me*:S ratio of 20:22, which is the same as in the structural formula used for structure refinement (Mumme 1986) and confirmed by single-crystal structure investigation in the Ag-free padĕraite from Swartberg ($Cu_{7.24}Pb_{1.36}Bi_{11.27}S_{22.12}$).

A survey of the limited published data for N_1, $N_{1.5}$ (hodrushite), N_2 (cuprobismutite) and for padĕraite is instructive for the purposes of comparing chemical compositions. Hodrushite, ideally $Cu_8Bi_{12}S_{22}$, may depart from the ideal compositions within certain limits, with substitution of Ag, Pb, Fe and excess Cu in the structure. Significantly, in the Ocna de Fier hodrushite, the number of Cu atoms is less than 8, with Fe located within the Cu position, and the minor Ag and Pb, in the Bi position. It therefore differs from that from holotype hodrushite, and from the Ag-free hodrushite from Swartberg, in which 8 Cu *apfu* is exceeded. If the limited database is truly representative, Ag appears, however, to be an essential component of cuprobismutite. Our data show that the 1 *apfu* Ag position is nearly filled, and the cuprobismutite compositions are similar to those reported from Felbertal (Topa 2001). In the case of padĕraite, the Ocna de Fier material is also different from the holotype material (Fig. 4), in that Cu occupancy is 7 *apfu*. Again, comparison with the Swartberg material is instructive, since this has the highest Cu occupancy yet reported, differing still further from the composition of holotype specimens.

The limits of incorporation of Pb, Ag, Fe (and also Cd?) into the structures of cuprobismutite homologues and padĕraite will likely remain questionable until adequate structural data are obtained on chemically distinct variants of all members of the series. Microanalytical data on additional natural occurrences are also desirable before mechanisms of substitution can be accurately and unambiguously defined.

The intimate association of cuprobismutite, padĕraite and hodrushite in the Ocna de Fier material is evidence for the costability of closely allied structures. Intermediate compositions in the cuprobismutite–padĕraite range, obtained from apparently homogeneous lamellae, strongly suggest that the μm-scale intergrowths observed on the SEM images could be paralleled by lattice-scale intergrowths. As in some silicate groups, order–disorder modularity (stacking and polysomatic disorder) within Bi-sulfosalt series (bismuthinite derivatives, lillianite homologues; *e.g.,* Pring *et al.* 1999, and references therein) can explain extensive compositional fields. Potentially, it can define intermediate compounds between related structures that are not part of the same series (*e.g.,* coherent intergrowths between cosalite and lillianite; Pring & Etschmann 2002).

Genetic considerations

Ocna de Fier is a classic zoned skarn deposit, and temperature estimates for the Fe-zone are in the order of 600–400°C. The sulfosalt assemblage discussed in this paper represents one of the characteristic trace-mineral parageneses within the Fe-zone of the Ocna de Fier deposit. The "GS" association is restricted to preserved cores of prograde andradite skarn in one of the Paulus orebodies. These bodies, consisting of both Fe-ores (in andradite) and Zn–Pb-ores (in hedenbergite), represent the distal, northern end of the deposit, with a more oxidizing character than in the similarly distal, southern end at Dognecea. In Paulus, preserved textures due to reworking superimposed on prograde patterns of oscillatory zonation in both garnet and silica-bearing magnetite, as well as magnetite – hematite – magnetite pseudomorphism, indicate that skarn and ore associations experienced intense carbofracturing assisted by back-flow fluxes throughout the retrograde stage (Ciobanu & Cook 2001). Temperature estimates for the retrograde stage are as high as 371°C, on the basis of single-phase blebs of maldonite (Shunk 1969) positioned along trails that cross-cut magnetite–Bi-sulfosalt assemblages in the Paulus occurrence (Ciobanu & Cook 2002b).

The abundance of cuprobismutite relative to very minor hodrushite, the only sulfosalt identified in this association that can incorporate Fe in the structure, may be constrained by the buffering capacity of magnetite as the host in this case. The presence of padĕraite as the second most abundant mineral, instead of another cuprobismutite homologue, strongly suggests that the comparative stability of these phases is, in our case, controlled by certain critical chemical gradients of Pb and Ag. The intimate and repetitive intergrowths of these minerals within laths, and in similar intergrowths within the aggregates, suggests that during their formation, the chemical gradients responsible for their cocrystallization underwent sustained oscillatory paths. It thus appears that coupled variance between Ag and

Pb gradients favored formation of the two phases that could adjust to an inverse variance of these elements. Pavonite homologues are represented by makovickyite alone, which is homogeneous with only negligible compositional variance with respect to Ag, Cu and Pb. Compared to the bismuthinite derivatives and cuprobismutite series, with their modular potential, the pavonite series appears "inert" in this chemical environment, *i.e.,* unable to produce packages of closely allied structures, even though similarly defined as an accretional series (*e.g.,* Makovicky 1989).

The assemblage discussed in this paper consists of bismuthinite derivatives and their intergrowths (in the range gladite – oversubstituted bismuthinite), cuprobismuthite homologues (cuprobismutite, hodrushite), paděraite and makovickyite. We believe that intergrowths among these minerals constitute a paragenetic association formed in a field of oscillatory chemical gradients of Cu, Pb, Ag and Bi, in which the pavonite series is represented only by makovickyite with the fixed composition $Cu_{1.34}Ag_{0.76}Pb_{0.14}Bi_{5.21}S_{9.64}$. In the same Paulus occurrence, within separate pockets of Bi-sulfosalts, but where krupkaite and intergrowths in the gladite–krupkaite range are additional stable phases in the bismuthinite series, makovickyite starts to shows compositional variance (Cu-rich and Cu-poor varieties; Ciobanu & Cook 2000). Neither cuprobismutite homologues nor paděraite is formed in this assemblage, evidence for the highly localized character of mineral associations formed in a skarn environment.

The relationship between cuprobismutite–paděraite and enclosing bismuthinite derivatives, and among the bismuthinite derivatives themselves, allows some constraints to be placed on the crystallization histories. The textural patterns of gladite indicate that its formation relates to reaction during the micro-shearing that accompanied the retrograde stage of skarn formation. This is based on the observations that gladite occurs conspicuously at the margins of makovickyite and that the sets of gladite lamellae are oriented along and parallel to cracks within the matrix.

The complex, intimate intergrowth textures preserved among these minerals and the accompanying bismuthinite derivatives are specific to the Fe-zone of the deposit. Textural interpretations suggest that the Bi sulfosalt association discussed in this paper is formed during the prograde stage, yet the development of the complete assemblage, as seen today, reflects readjustment and coarsening assisted by local subsolidus diffusion during retrograde overprinting.

CONCLUSIONS

Our micro-analytical data, coupled with back-scattered images, and comparison with available published data, serve to illustrate the complexities involved in identification of minerals of the cuprobismutite series and paděraite using electron-microprobe data, in cases where precise determinations of the structure cannot be undertaken. We have, nevertheless, identified compositional fields for three minerals that, despite their intimately intergrown character, can be characterized as distinct from each another. The compositional limits established assist in defining mechanisms of substitution between homologues in the cuprobismutite series and relative to paděraite. Further refinements of the structural aspects will eventually clarify specific positions and reasoning for limits of substituting elements in natural phases complementary to those found in the synthetic compounds. On the basis of the Ocna de Fier material, and other recent data discussed above, a new formula for paděraite is suggested: $Cu_7(M^+_{0.4}Pb_{1.2})_{\Sigma 1.6} Bi_{11.4}S_{22}$ (M^+ = Ag,Cu), for which existing structural data refined on holotype paděraite (Mumme 1986) remain valuable.

The observed associations and compositions determined for cuprobismutite, hodrushite and paděraite from Ocna de Fier, compared to those described from other localities, strongly suggest that controls on mineral stability, textural habit and relationships with associated minerals are influenced by the buffering effect of the host environment as well as paths of the chemical gradients. Even though we cannot quantify the parameter controlling the deficiency or excess of Cu in natural hodrushite, we attribute this to the buffering effect of the host.

Of relevance to future work on these minerals are questions concerning (1) the compositional limits of natural cuprobismutite, relative to those of kupčikite and hodrushite, (2) the extent to which Fe is required to stabilize natural hodrushite, the position it occupies in the structure, and the limits to which Ag and Pb may enter the structure, (3) whether structural modularity allows for the recognition of substitution line(s) between paděraite (or paděraites?) relative to the cuprobismutite homologous series.

Lastly, skarns are commonly typified by fluctuation of diffusion and infiltration rates, substantial retrograde overprinting and prolonged cooling, if compared with other magmatic–hydrothermal systems. Therefore, mechanisms involved in the mineralizing process at Ocna de Fier will be broadly comparable to those in Băița Bihor – Valea Seacă skarns, yet differing significantly from those involved in vein deposits at Zidarovo, Vurly Bryag, Banská Hodruša, in the Swartberg pegmatite or the metamorphosed or metamorphogenic deposit at Felbertal. An explanation for the speciation among cuprobismutite-series minerals and paděraite in this diverse range of environments of formation provides fertile ground for future research.

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