

# NEW DATA ON "PLUMOSITE" AND OTHER SULPHOSALT MINERALS FROM THE HERJA HYDROTHERMAL VEIN DEPOSIT, BAIA MARE DISTRICT, ROMANIA

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**Abstract:** Compositional data on a range of sulphide and sulphosalt minerals from the hydrothermal vein deposit of Herja in the Baia Mare metallogenic area are presented. The presence of zinkenite, chalcostibite, diaphorite, fülöppite, boulangerite, bournonite, electrum and manganite are confirmed in the Herja ores for the first time. In addition, compositions close to veenite, twinnite and heteromorphite have been identified — possibly representing the first report of these minerals on Rumanian territory. Fibrous Sb-sulphosalts, which are trace phases in massive polymetallic ores and are the main component of the abundant vugs and cavities, are dominantly jamesonite, although boulangerite, berthierite and zinkenite are also present in lesser amounts. Arsenopyrite associated with the Sb-sulphosalts is commonly enriched in Sb (to 6 wt. %). Fahlore phases were determined to be tetrahedrite, with Ag contents ranging from 7 to 20 wt. %. All Sb-sulphosalts are free of As. The loose felty matted masses of acicular needles, „plumosite“, which occur widely throughout the vein systems are confirmed to be jamesonite. This mineral is characterized by a conspicuous Mn content, equivalent to 4-8 % mol. % benavidesite. This has been partially confirmed by X-ray diffraction patterns, which showed a slight shift from those of some reference patterns for (Mn-free) jamesonite. However, a quantitative correlation between cell parameters and extent of Mn substitution is prohibited by discrepancies in the various peak patterns, resulting from differing experimental conditions. Although „plumosite“ has been regarded as synonymous with boulangerite in recent years, it is proposed that the descriptive name „plumosite“ be used for all such felted masses of Pb-Sb sulphosalts, including those with the compositions of jamesonite and berthierite. No supportive evidence for the existence of the problematic mineral parajamesonite was found in the examined samples. Geothermometry based on the S-isotope compositions of coexisting pyrite-galena pairs indicated temperatures of  $417 \pm 75$  °C and  $320 \pm 70$  °C, which are regarded as close to the maximum temperatures at the onset of mineralization. The stibnite and sulphosalt parageneses, however, are believed to have formed at temperatures below 220 °C.

**Key words:** Rumania, Herja, hydrothermal vein mineralization, Pb-Sb sulphosalts, jamesonite, plumosite.

## Introduction

The Herja deposit, formerly known by the Hungarian names Kisbánya and Herzsabánya, has been mined since medieval times. It is one of the largest of the hydrothermal vein systems of Pannonian age hosted within Samartian-Pannonian volcanic rocks and Neogene and Paleogene sediments in the metallogenic district surrounding the city of Baia Mare in Maramureş County, northern Rumania. The polymetallic mineralized veins at Herja contain a wide variety of Pb-Sb sulphosalts and Herja is the type locality for fizelyite ( $\text{Pb}_{14}\text{Ag}_5\text{Sb}_{21}\text{S}_{48}$ ) as well as the poorly constrained parajamesonite ( $\text{FePb}_4\text{Sb}_6\text{S}_{14}$ ).

Despite the mineralogical complexity and the notoreity of beautiful and spectacular museum specimens (c.f. Huber & Mureşan 1996), the mineralogy of the Herja ores has not been studied in detail using modern microanalytical methods and compositional data on component phases are largely lacking. Although this preliminary study on a limited number of samples cannot in any way claim to be representative of the entire vein system, it represents a first contribution to the

study of mineral compositions within the Herja deposit and serves as a basis for future work.

In this short paper, our aim is firstly to report compositional data on a number of sulphide and sulphosalt phases from Herja, in many cases for the first time. Our preliminary study is based on investigation of massive Pb-Zn rich ores and the cavity fillings containing stibnite and other Sb-bearing minerals. Eight further Pb-sulphosalt minerals not previously reported from Herja (zinkenite, fülöppite, boulangerite, bournonite, heteromorphite, veenite, diaphorite, twinnite) have been found in samples from recently opened parts of the mine. These are also described and compositional data presented. Veenite, heteromorphite and twinnite have not been previously reported on Rumanian territory. Chalcostibite is also described from Herja for the first time, although its presence was mentioned by Udubaşa et al. (1992). Secondly, new data on the abundant „plumosite“ at Herja is presented, with a suggested redefinition of this term. The existence of both jamesonite and its dimorph parajamesonite at Herja is discussed in the light of new data. In addition, new estimates for the temperature of crystallization are available, based on the S-isotope composition of sulphide pairs from the Herja ores.

## Geological setting of the mineralization

The deposit, situated in the Gutâi Mts., about 6 km NE of Baia Mare consists of two major groups of veins along ENE-WSW oriented fractures related to a subvolcanic body of pyroxene andesite and porphyritic quartz microdiorite (Figs. 1-2). The southern vein group, including the veins Şâlan (also known as vein 10), Zincos (vein 20), Ignaşiu (vein 40), Clementina (vein 60), Boromei (vein 80), and Mächtige (vein 100), which were the source of historic production, are enclosed by the porphyritic quartz microdiorite body. The northern vein group (numbered 30, 50, 70, ... up to 170) lies within altered sedimentary rocks of Pannonian, Sarmatian and Eocene age. Descriptions of host rock geology, structural controls and hydrothermal alteration have been given by Petruşian (1934), Szöke (1968), Borcoş & Lang (1973), Borcoş et al. (1975) and Lang (1979). A comprehensive account of geology, petrology, geochemistry and mineralogy has recently been presented by Damian (1996). Age constraints have recently become available (Edelstein et al. 1992; Lang et al. 1994); andesitic volcanism in the Gutâi Mountains extended between 13.4 and 9.0 Ma. Hydrothermal activity in the area took place between 11.5 and 8.0 Ma; the Herja mineralization having been dated by Edelstein et al. (1992) using K-Ar methods on illite at  $8.8 \pm 0.6$  Ma.

Borcoş et al. (1975) described the main veins in the southern part of the Herja deposit in some detail. Unlike other deposits in the Baia Mare metallogenic area (e.g. Cavnic, Baia Sprie), there is little evidence of vertical zonation within the vein system, with Pb and Zn being rather evenly distributed over the depth of the system, which probably exceeds 1000 m and a width of more than 1200 m. A total of more than 180 veins have been identified to date. The polymetallic ores are characterized by the geochemical signature  $Zn > Pb \pm Cu, Ag, Au$ , with significant enrichment in Sb, As, Cd, Bi, Ga, In, Mn, W and Tl. Borcoş et al. (1975) recognized a single phase of mineralization, beginning with the deposition of pyrite and pyrrhotite and followed by intense crystallization of sphalerite and galena, followed in turn by stibnite and various sulphosalts at lower temperatures. Idiomorphic chalcopyrite, galena, marcasite and quartz were deposited later in the sequence. Temperatures of mineralization were previously estimated to be in the range 250–350 °C on the basis of fluid inclusion data (e.g. Pomârleanu 1971). Vein thickness may attain dimensions as large as 2 m, but are significantly lower in the many minor vein branches, where thicknesses of only 1–2 cm are common.

Alongside massive ore composed of sphalerite, galena and subordinate chalcopyrite, with pyrite, pyrrhotite and marcasite, in which Ag-bearing tetrahedrite and other sulphosalts are minor components, the mineralization also contains abundant vugs and mineralized cavities in which a large variety of Pb-Sb sulphosalts phases are well developed. The Herja mine is particularly famous for centimeter-sized tetrahedrite, needle-like jamesonite, berthierite and stibnite, semseyite and the abundant felted masses of „plumosite“ (Federerz). The vug associations are accompanied by quartz, spheroidal black and white calcite and also siderite. The sulphosalt and stibnite-containing vugs were particularly abundant at upper levels which are now largely mined out. Antimony was the most important product of mining prior to 1928. Other ore minerals re-

ported include arsenopyrite, mackinawite, bournonite, molybdenite, pyrrargyrite, argentite, fülöppite, gold and electrum. Dolomite, rhodochrosite, flourite, gypsum and vivianite are accessory gangue phases.

Our sample suite is drawn from both the northern and southern vein groups. Massive ores varied petrographically from massive galena, galena-chalcopyrite and galena-sphalerite varieties, with or without pyrite, to marcasite- and pyrrhotite-rich types. Other samples contained only quartz with minor sulphides. Samples with coarse stibnite, jamesonite and berthierite crystals were collected from cavities as were felty masses of „plumosite“.

## Analytical methods

All electron probe microanalyses were carried out on the CAMECA SX-50 instrument in Würzburg. Standards and radiations used were as follows: pure Bi (M $\alpha$ ), pure PbS (Pb-M $\alpha$ ), AsGa (As-L $\alpha$ ), FeS<sub>2</sub> (Fe-K $\alpha$ , S-K $\alpha$ ), pure Cu (K $\alpha$ ), ZnS (Zn-K $\alpha$ ), pure Ni (K $\alpha$ ), pure Co (K $\alpha$ ), pure Te (L $\alpha$ ), pure Se (L $\alpha$ ), pure Ag (L $\alpha$ ), pure Au (M $\alpha$ ), HgS (Hg-M $\alpha$ ), Sb<sub>2</sub>S<sub>3</sub> (Sb-L $\alpha$ ), MnTi (Mn-K $\alpha$ ). No other elements were detected in any of the minerals analysed. A beam current of 15 nA and an accelerating voltage of 15 kV were used. All mineral grains and standards were analysed under the same operating conditions. Minimum detection limits are ca. 0.1 wt. % for all elements. At least one analysis was carried out on each grain. Tables 1 to 5 contain analyses representative of the total data suite.

Determination of sulphur isotope concentrations was made on 9 sulphide separates which are considered to be representative. The coarse grain size and high degree of purity permitted the separation by hand-picking of grains. All S-isotope analyses were carried out on a Finnegan MAT-251 gas spectrometer at the Institut für Geochemie, Universität Göttingen. Analytical errors are approximately 0.1–0.2 ‰  $\delta^{34}\text{S}$ .

The X-ray diffraction data obtained on „plumosite“ was obtained on a Philips PW 1710 diffractometer with secondary graphite monochromator. Filtered Cu K $\alpha_{1,2}$  radiation was used;  $\lambda = 1.5418$  Å. Instrumental conditions were 40 KV and 30 mA. Measurement was carried out between  $2\theta$  values of 4–80°, in steps of 0.02° and a counting time of 5 secs at each step. The sample material was held in a single crystal quartz plate. 407 reflections were recorded (within the interval  $9.55 < d > 1.87$ ). Peak positions and intensities were indexed by the diffractometer computation program. Our methods are thus comparable to those used to obtain diffraction spectra for jamesonite (Berry 1940; Garavelli 1958) with which the diffraction data for „plumosite“ will be compared in this paper, although complete analytical details are not given for these earlier patterns. In contrast, the reference pattern for benavidesite (Oudin et al. 1982) was obtained by powder film methods.

## Sulphide mineral compositions

### Sphalerite

Two compositional varieties of sphalerite were recognised (Table 1, columns 1–3). The earlier, and more abundant vari-

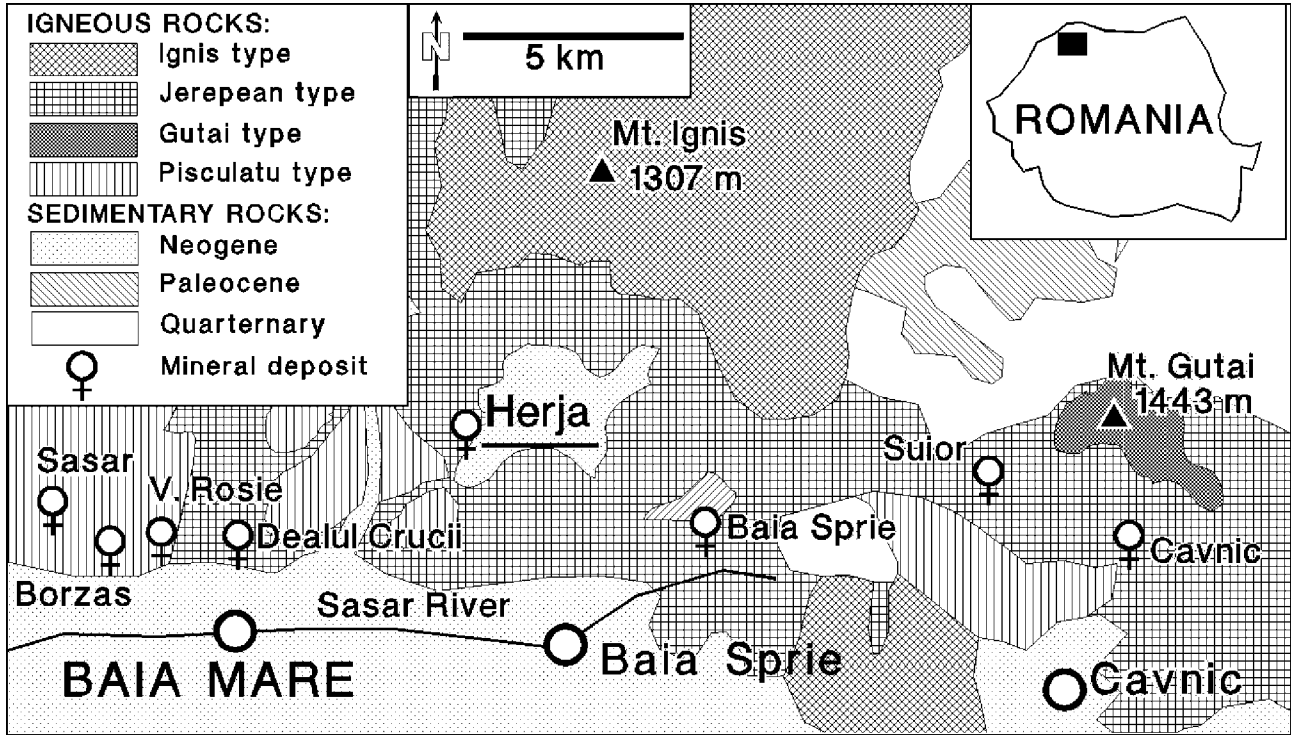


Fig. 1. Geological sketch map showing the location of the Herja mine.

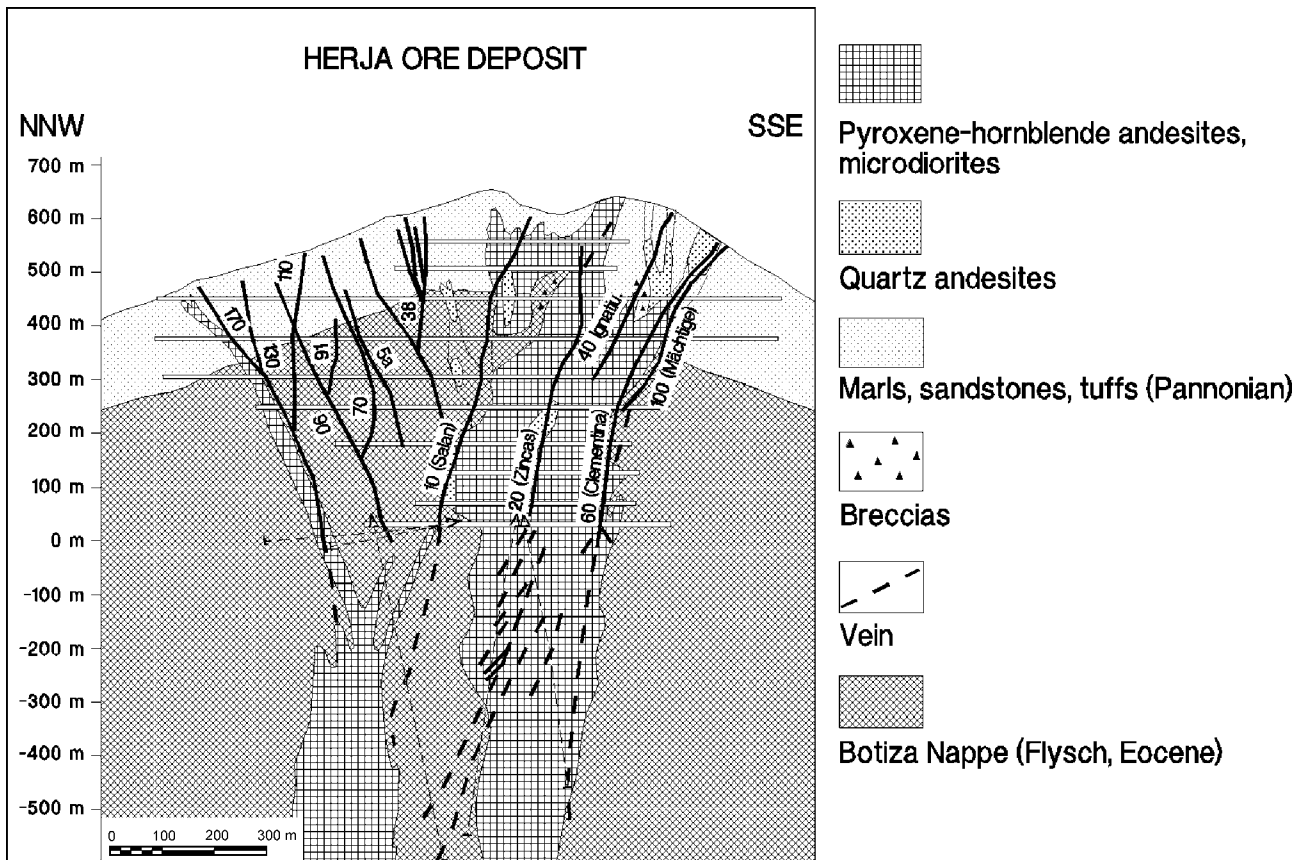
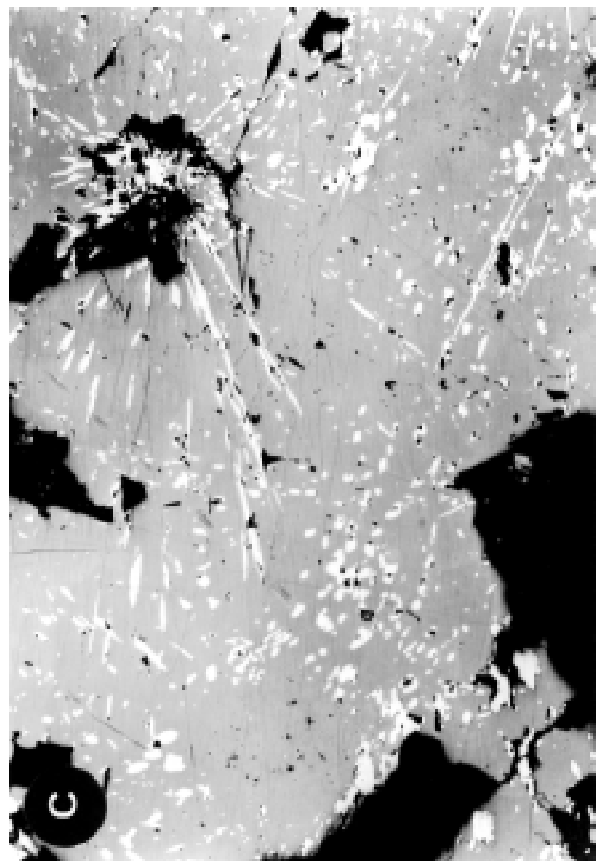
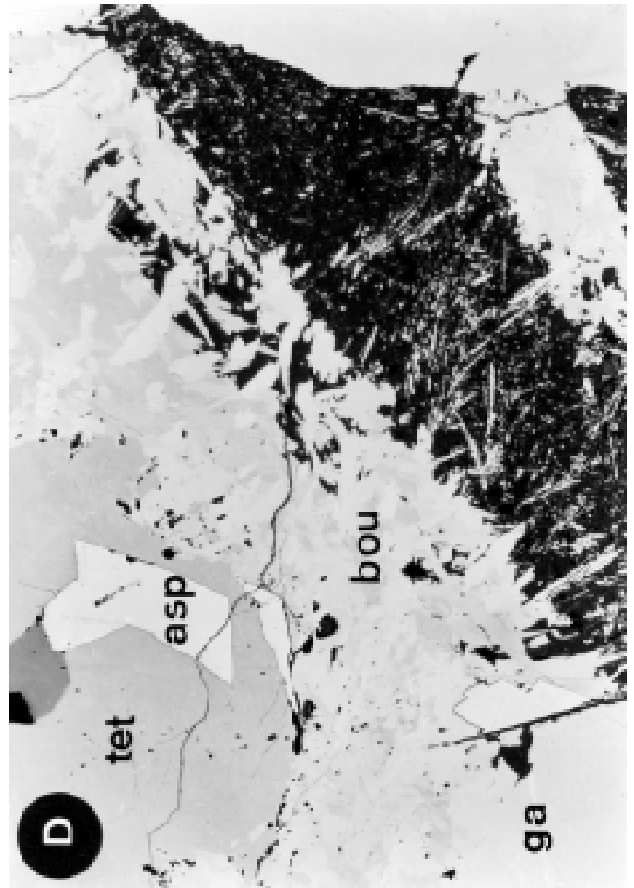
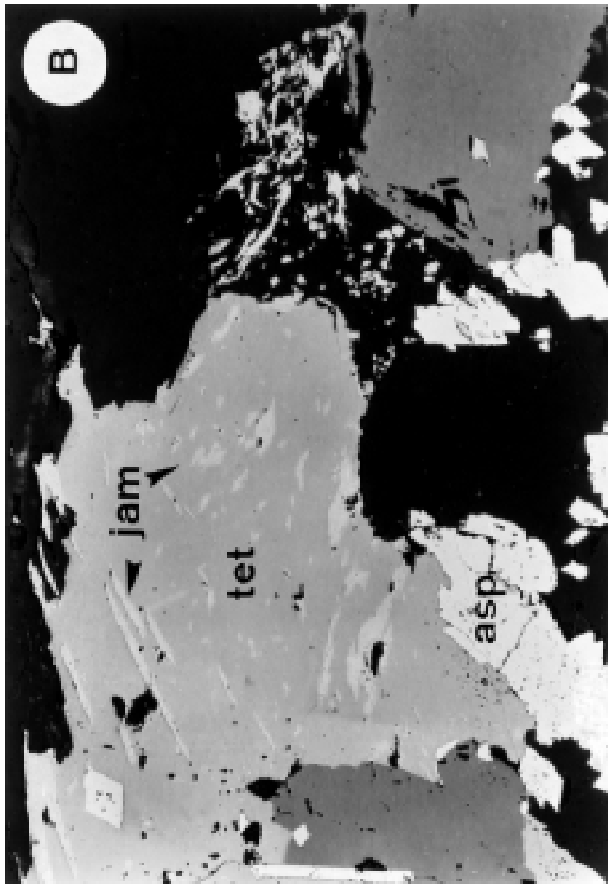
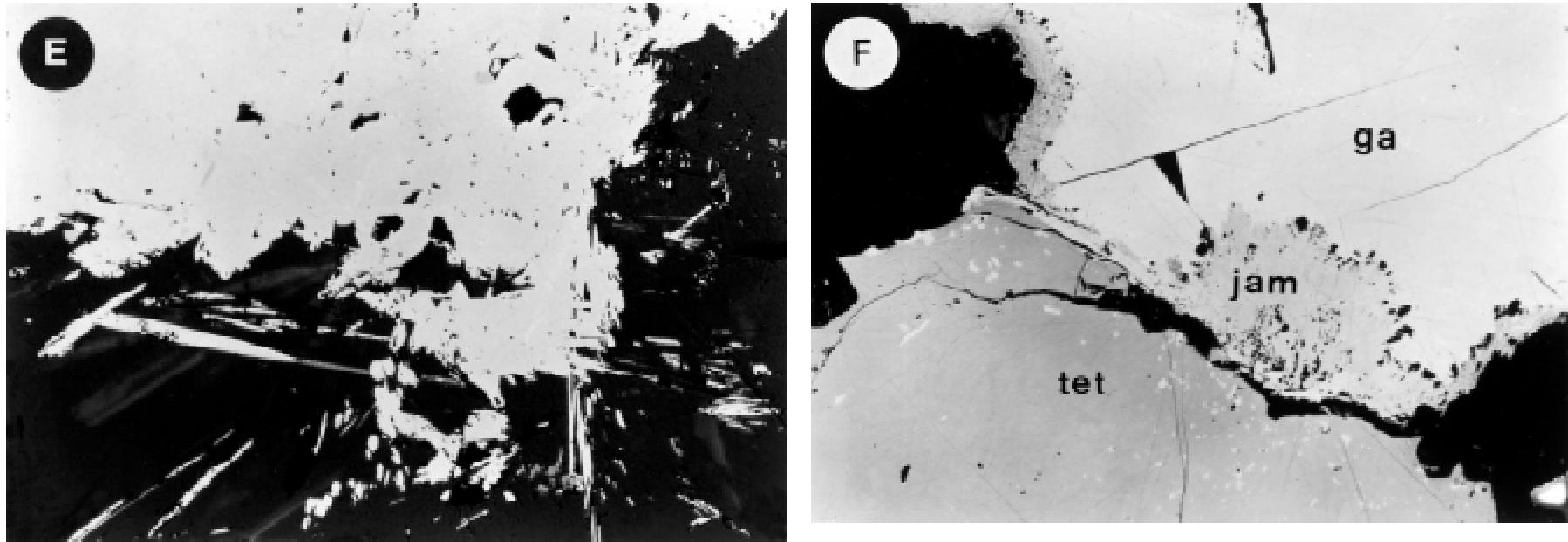


Fig. 2. Simplified NNW-SSE cross-section across the Herja vein deposit.

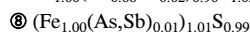
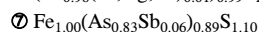
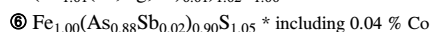
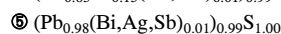
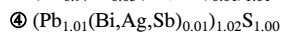
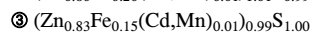
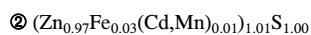
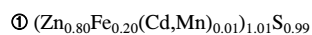




**Fig. 3.** Photomicrographs in reflected light: **a**—Antimonian arsenopyrite (asp) containing enclosed and epitaxial jamesonite (jam). Sample: Hj-12; Field of view: 1.44 mm. **b**— Tetrahedrite (tet) containing needles of jamesonite (jam) with antimonian arsenopyrite (asp). Sample: Hj-13; Field of view: 1.10 mm. **c**—Needle-like aggregates of zinkenite, often radially oriented, within coarse sphalerite. Sample: GV-100; Field of view: 0.69 mm. **d**—Massive twinned, and acicular boulangerite (bou), in association with galena (ga), tetrahedrite (tet) and antimonian arsenopyrite (asp). Sample: Hj-14; Field of view: 1.31 mm, half-crossed nicols. **e**—Massive and needle-like chalcostibite. Sample: Hj-13; Field of view: 0.96 mm. **f**—Rim of fine-grained jamesonite (jam) between galena (ga) and tetrahedrite (tet). Sample: Hj-13; Field of view: 625  $\mu\text{m}$ , oil immersion.

**Table 1:** Electron probe microanalyses of sulphides.

	Sphalerite (8255; GV-100, HJ-13)			Galena (8255, HJ-12)		Arsenopyrite (4, HJ-12)		Marcasite (HJ-11)
	① mean n=2	② mean n=3	③ mean n=2	④ mean n=5	⑤ mean n=12	⑥ mean n=8	⑦ mean n=11	⑧ mean n=5
<b>Cu</b>	0	0.13±0.01	0	0	0	0	0	0
<b>Fe</b>	11.54 ±0.11	1.78 ±0.35	8.66 ±0.29	0	0	35.10±0.65*	34.69 ±0.83	45.66 ±0.52
<b>Zn</b>	53.95 ±0.19	62.78 ±0.46	55.82 ±0.32	0	0	0	0	0
<b>Mn</b>	0.46 ±0.02	0	0.24 ±0.02	0	0	0	0	0
<b>Cd</b>	0.11 ±0.01	0.33 ±0.02	0.28 ±0.01	0	0	0	0	0
<b>Ag</b>	0	0	0	0.12 ±0.07	0.19 ±0.06	0	0	0
<b>Pb</b>	0	0	0	86.84 ±1.00	86.80 ±0.63	0	0	0
<b>Sb</b>	0	0	0	0.16 ±0.07	0.28 ±0.08	1.68 ±1.08	4.90 ±2.22	1.11 ±0.79
<b>As</b>	0	0	0	0	0	41.38 ±1.68	38.36 ±2.49	0.03 ±0.07
<b>Bi</b>	0	0	0	0.33 ±0.10	0.27 ±0.11	0	0	0
<b>S</b>	32.59 ±0.34	32.98 ±0.20	33.58 ±0.44	13.27 ±0.12	13.71 ±0.17	21.22 ±0.79	21.80 ±0.54	52.04 ±0.70
<b>Se</b>	0	0	0	0.10 ±0.06	0	0	0.14 ±0.10	0
<b>Te</b>	0	0	0	0	0.03 ±0.05	0	0	0
<b>Total</b>	98.65	98.00	98.58	100.82	101.28	99.38	99.89	98.84

**Formulae:**

ety is characterized by a deep red colour and high Fe content (mean FeS contents > 18 mol. %), accompanied by enrichment in Mn (0.2–0.5 wt. %). Concentrations of Cd are variable but relatively low. The second, darker, type accompanies the late sulphosalt parageneses and has a mean Fe content of only 3.2 mol. % FeS and no detectable Mn. This type is further characterized by an enrichment in Cd (mean 0.33 wt. %). Enrichment in Cd in a late sphalerite can be related to the strong incompatibility of that element in the latest generation of hydrothermal fluids.

*Galena*

Analyses of galena (Table 1, columns 4, 5) from the total sample suite showed little variation between textural types. In all samples, trace amounts of Ag, Bi, Sb and, occasionally, Se were detected. Typical contents (all in wt. %) are 0.15–0.45 for Bi, 0.10–0.24 for Ag, 0.12–0.28 Sb and < 0.10–0.13 Se.

*Arsenopyrite*

Arsenopyrite was observed in all of the sulphosalt-rich samples, but was absent in massive ores. It is an extremely abundant phase in the sulphosalt-rich suite, occurring as small euhedra in association with jamesonite, boulangerite, berthierite, tetrahedrite or semseyite in a sphalerite-galena matrix, or as larger grains, commonly overgrown by fibrous sulphosalts (Fig. 3a). Compositions are uniformly close to  $\text{Fe}_{1.00}(\text{As},\text{Sb})_{0.90}\text{S}_{1.05}$  (Table 1, columns 6, 7). Considerable localised enrichment in Sb was however noted in a number of samples, up to as much as 6.65 wt. % in some analysed grains, which corresponds to 10.1 % end member gudmundite. Some grains showed evidence of zonation in which the cores were richer in Sb (to 6 wt. %) than the rims (< 1 wt. % Sb). This pattern could not, however, be verified in all grains

on which microanalytical profiles were made. In some cases, there appeared to be no zonation, and in others a rather erratic pattern was evident, possibly related to repeated crystallization and resorption during deposition.

*Pyrite and marcasite*

In the single sample in which it was analysed, pyrite was found to contain minor quantities of As to 0.12 wt. %. Marcasite (Table 1, column 8), which was formed relatively late in the paragenetic sequence was found, in contrast, to contain detectable Sb in almost all cases, at concentrations typically of 0.10 to 0.30 wt. %, but as much as 2.1 wt. % in isolated cases.

*Bournonite*

Analysed bournonite compositions (Table 2, column 1) were stoichiometric  $\text{CuPbSbS}_3$ . Very limited solid solution towards the As end-member, seligmannite and only minor trace Bi and Te were noted.

*Tetrahedrite-tennantite*

Tetrahedrite is abundant in the Herja ores and is probably the most important Ag-carrier in the vein ores. Tetrahedrite is present as euhedral crystals, ranging from 20  $\mu\text{m}$  to several mm in size and commonly contains inclusions of other sulphosalts (Fig. 3b). Microprobe analyses (Table 2, columns 2–5) indicate that Ag-rich tetrahedrites (16–20 wt. % Ag) prevail in the samples studied, although there is a marked inverse correlation between Ag content and grain size, the largest grains (> 2 mm) containing less than 10 wt. % Ag. Contents of As are negligible (< 0.20 wt. %) and atomic Fe/Zn ratios generally exceed 5. The formulae of tetrahedrite from all the representative analyses given in the table give a slight excess of both Sb and S over expected stoichiometry, when calculated to 12 metal at-

**Table 2:** Electron probe microanalyses of sulphosalt minerals.

	Bournonite (8255)		Tetrahedrite (110, 50D, HJ-13, HJ-14)			Semseyite (4, GV-10, SI-480)			Fülöppite (GV-100)
	① mean n=5	② mean n=5	③ n=1	④ mean n=17	⑤ mean n=5	⑥ mean n=5	⑦ mean n=9	⑧ mean n=6	⑨ mean n=9
<b>Cu</b>	13.08±0.31	25.57±0.09	22.09	31.71±1.20	22.97±0.41	0	0	0	0
<b>Fe</b>	0	5.15±0.09	5.12	4.74±0.87	5.47±0.12	0	0	0	0
<b>Zn</b>	0	0.85±0.15	0.65	2.06±1.01	0.86±0.04	0	0	0	0.03±0.05
<b>Ag</b>	0	15.77±0.41	21.21	7.17±1.56	19.57±0.23	0	1.24±1.54	0.10±0.05	0.09±0.12
<b>Pb</b>	42.01±0.38	0	0	0	0	52.31±0.90	52.55±2.36	51.62±0.74	29.29±0.34
<b>Sb</b>	25.07±0.13	27.03±0.22	27.06	29.07±0.28	27.37±0.21	28.32±0.36	27.26±0.64	27.41±0.37	47.50±0.61
<b>As</b>	0.17±0.04	0.12±0.02	0	0.02±0.01	0	0	0.01±0.01	0	0
<b>Bi</b>	0.09±0.09	0.10±0.04	0.26	0.10±0.07	0.12±0.07	0.23±0.05	0.18±0.07	0.20±0.07	0.07±0.09
<b>S</b>	9.42±0.13	23.43±0.27	22.84	24.25±0.23	22.61±0.19	19.08±0.16	18.67±0.35	19.18±0.24	23.09±0.21
<b>Te</b>	0.03±0.04	0.11±0.05	0.16	0	0	0	0	0.10±0.04	0
<b>Total</b>	99.87	98.03	99.23	99.01	98.97	99.94	99.92	98.61	100.08

**Formulae:**

①  $\text{Cu}_{1.02}\text{Pb}_{1.00}(\text{Sb}_{1.02}\text{As}_{0.01})_{1.03}\text{S}_3$

②  $(\text{Cu}_{7.39}\text{Fe}_{1.69}\text{Zn}_{0.24}\text{Ag}_{2.68})_{12.00}(\text{Sb}_{4.07}\text{As}_{0.03}\text{Bi}_{0.01})_{4.11}\text{S}_{13.42}$

③  $(\text{Cu}_{6.46}\text{Fe}_{1.70}\text{Zn}_{0.18}\text{Ag}_{3.65})_{12.00}(\text{Sb}_{4.13}\text{Bi}_{0.02})_{4.15}(\text{S}_{13.24}\text{Te}_{0.02})_{13.26}$

④  $(\text{Cu}_{8.78}\text{Fe}_{1.49}\text{Zn}_{0.55}\text{Ag}_{1.17})_{12.00}(\text{Sb}_{4.20}\text{Bi}_{0.01})_{4.21}\text{S}_{13.26}$

⑤  $(\text{Cu}_{6.63}\text{Fe}_{1.80}\text{Zn}_{0.24}\text{Ag}_{3.33})_{12.00}(\text{Sb}_{4.13}\text{Bi}_{0.01})_{4.14}\text{S}_{12.95}$

⑥  $\text{Pb}_{8.91}(\text{Sb}_{8.21}\text{Bi}_{0.04})_{8.25}\text{S}_{21}$

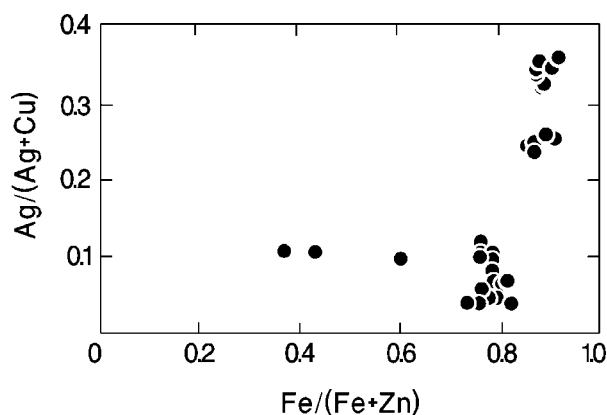
⑦  $(\text{Ag}_{0.42}\text{Pb}_{9.14})_{9.56}(\text{Sb}_{8.07}\text{Bi}_{0.03})_{8.10}(\text{S}_{20.99}\text{Te}_{0.01})_{21}$

⑧  $(\text{Ag}_{0.03}\text{Pb}_{8.78})_{8.81}(\text{Sb}_{7.91}\text{Bi}_{0.03})_{7.94}(\text{S}_{20.97}\text{Te}_{0.03})_{21}$

⑨  $(\text{Zn}_{0.01}\text{Ag}_{0.02}\text{Pb}_{2.94})_{2.98}(\text{Sb}_{8.13}\text{Bi}_{0.01})_{8.14}\text{S}_{15}$

oms; ranging between  $(\text{Ag}_{1.17}\text{Cu}_{8.78}\text{Fe}_{1.49}\text{Zn}_{0.55})_{12}(\text{Sb}_{4.20}\text{As}_{0.01}\text{Bi}_{0.01})_{4.21}\text{S}_{13.26}$  and  $(\text{Ag}_{3.62}\text{Cu}_{6.58}\text{Fe}_{1.60}\text{Zn}_{0.20})_{12}(\text{Sb}_{4.22}\text{S}_{13.60})$ . Higher  $\text{Ag}/(\text{Ag}+\text{Cu})$  ratios tend to correlate positively with higher  $\text{Fe}/(\text{Fe}+\text{Zn})$  ratios in the sample suite, with a dramatic rise in  $\text{Ag}$  content over the  $\text{Fe}/(\text{Fe}+\text{Zn})$  range 0.7 to 1.0 (Fig. 4).

Although the problem was not experienced among the Ag-poorer varieties, some of the tetrahedrites richest in  $\text{Ag}$  gave poor totals. This, and the fact that  $(\text{Fe}+\text{Zn})$  are consistently less than 2.00 atoms p.f.u. in many of these analyses, urges considerable caution in their interpretation; an excess in  $(\text{Cu}+\text{Ag})$  beyond 10 atoms p.f.u. has been reported to be routinely not detected by electron microanalysis (Lind & Makovicky 1982). The choice of microprobe standards used, which did not include synthetic sulphosalt standards, may also infer that some caution be exercised in the interpretation of analytical data.

**Fig. 4.** Plot of  $\text{Fe}/(\text{Fe}+\text{Zn})$  against  $\text{Ag}/(\text{Ag}+\text{Cu})$  for analysed tetrahedrites, indicating silver enrichment in Zn-poor varieties.

#### Semseyite

Semseyite is relatively abundant in the investigated samples, as coarse grains, commonly associated with tetrahedrite, galena or sphalerite and infilling cavities. Compositional variation would appear to be extremely limited in semseyite,  $\text{Pb}_9\text{Sb}_8\text{S}_{21}$  (Table 2, columns 6–8). We note, however, minor contents of  $\text{Ag}$ ,  $\text{Cu}$  and  $\text{Bi}$  in some analyses, one sample containing a particularly Ag-enriched variety. Furthermore, there is minor variation in the  $\text{Pb}/\text{Sb}$  ratio, with some samples showing a consistent slight deficiency in  $\text{Pb}$  below 9 atoms p.f.u. and a corresponding enrichment in  $\text{Sb}$  (Table 2, column 6) and the opposite situation in other samples. Although a systematic analytical error cannot be ruled out, this is considered unlikely as the analyses were accumulated at different times, using different calibrations and operating conditions. Furthermore, other  $\text{Pb}$ - $\text{Sb}$  sulphosalts analysed at the same time gave stoichiometric formulae. The data rather suggest that there may be intergrowths of more than a single  $\text{Pb}$ - $\text{Sb}$ - $\text{S}$  phase present, at the microscopic or sub-microscopic scale, thus resulting in nonstoichiometric compositions.

#### Fülöppite

Fülöppite, which occurs as short prismatic crystals, within a gangue matrix or intergrown with sphalerite, galena, zinkenite and stibnite is essentially stoichiometric in composition ( $\text{Pb}_3\text{Sb}_8\text{S}_{15}$ ), except for very minor  $\text{Ag}$ ,  $\text{Bi}$  and  $\text{Te}$  (Table 2, column 9).

#### Berthierite

Berthierite occurs as acicular grains, very similar in appearance to jamesonite. These occur either in gangue matrix or intergrown with the antimonian arsenopyrite. Electron probe microanalysis of berthierite,  $\text{FeSb}_2\text{S}_4$  indicates the incorporation of significant amounts of  $\text{Mn}$  (0.25–0.5 wt. %) in the structure,

**Table 3:** Electron probe microanalyses of sulphosalt minerals.

	Berthierite (H-210, HJ-11)		Zinkenite (GV-100)	Boulangerite (HJ-14)	Heteromorphite (GV-100, HJ-12)	Veenite (HJ-13)	
	① mean n=7	② mean n=5	③ mean n=11	④ mean n=16	⑤ mean n=5	⑥ mean n=3	⑦ mean n=2
<b>Cu</b>	0	0	0	0	0	0	0
<b>Fe</b>	11.81±0.15	12.74±0.08	0	0	0	0	0
<b>Mn</b>	0.25±0.04	0.26±0.05	0	0	0	0	0
<b>Zn</b>	0	0.04±0.02	0	0.02±0.02	0.25±0.12	0.04±0.03	0
<b>Ag</b>	0.02±0.03	0	0.16±0.05	0.10±0.12	0.03±0.05	0	0
<b>Pb</b>	0.15±0.17	2.02±0.64	31.70±0.44	54.31±0.55	46.87±0.56	47.69±0.90	50.35±0.03
<b>Sb</b>	56.17±0.26	54.68±0.50	44.72±0.47	26.33±0.32	30.74±0.64	31.42±1.10	29.71±0.32
<b>As</b>	0	0	0	0	0	0	0
<b>Bi</b>	0.13±0.04	0.13±0.07	0.19±0.09	0.17±0.08	0.28±0.09	0.09±0.03	0.05±0.05
<b>S</b>	29.39±0.34	28.89±0.09	22.58±0.17	18.58±0.26	20.08±0.26	19.89±0.16	19.47±0.17
<b>Te</b>	0	0	0	0	0	0	0
<b>Total</b>	97.92	98.76	99.35	99.51	98.25	99.13	99.58

**Formulae:**

① (Fe<sub>0.92</sub>Mn<sub>0.02</sub>(Cu,Ag,Pb)<sub>0.01</sub>)<sub>0.95</sub>Sb<sub>2.01</sub>S<sub>4</sub>  
 ② (Fe<sub>1.01</sub>Mn<sub>0.02</sub>(Cu,Ag,Pb)<sub>0.04</sub>)<sub>1.07</sub>Sb<sub>2.00</sub>S<sub>4</sub>  
 ③ (Ag<sub>0.09</sub>Pb<sub>9.12</sub>)<sub>9.21</sub>(Sb<sub>21.90</sub>Bi<sub>0.05</sub>)<sub>21.95</sub>S<sub>42</sub>  
 ④ (Ag<sub>0.02</sub>Pb<sub>4.98</sub>)<sub>5.00</sub>(Sb<sub>4.10</sub>Bi<sub>0.01</sub>)<sub>4.11</sub>S<sub>11</sub>  
 ⑤ (Zn<sub>0.11</sub>Ag<sub>0.01</sub>Pb<sub>6.86</sub>)<sub>6.98</sub>(Sb<sub>7.66</sub>Bi<sub>0.04</sub>)<sub>7.70</sub>S<sub>19</sub>  
 ⑥ (Zn<sub>0.02</sub>Ag<sub>0.00</sub>Pb<sub>7.04</sub>)<sub>7.06</sub>(Sb<sub>7.90</sub>Bi<sub>0.01</sub>)<sub>7.91</sub>S<sub>19</sub>  
 ⑦ Pb<sub>2.01</sub>Sb<sub>2.01</sub>S<sub>5</sub>

together with minor Cu, Zn, Ag, Pb, As and Bi at trace levels in a portion of the analyses (Table 3, columns 1, 2).

#### Zinkenite

Zinkenite is an abundant mineral in the investigated samples, occurring embedded in sphalerite as elongate fibrous grains up to 1.0 mm in length, either as dense often radial aggregates (Fig. 3c) or as isolated blades. Compositional variation would appear to be extremely limited, without detectable Cu and close to ideal stoichiometry (Pb<sub>9</sub>Sb<sub>22</sub>S<sub>42</sub>), except for minor Ag and Bi (Table 3, column 3).

#### Boulangerite

Boulangerite (Pb<sub>5</sub>Sb<sub>4</sub>S<sub>11</sub>) is a widespread component, both as fine-grained aggregates and as blunt needles, associated with tetrahedrite, sphalerite and galena (Fig. 3d). Boulangerite was not seen in intimate association with zinkenite or jamesonite. Compositionally, the mineral is close to stoichiometric (Table 3, column 4). Some analyses of the needle-shaped grains did, however, show a deficiency in Pb and enrichment in Sb, towards the composition Pb<sub>4.65</sub>Sb<sub>4.35</sub>S<sub>11</sub>. Boulangerite has been shown to show significant variation in composition (Mozgova et al. 1983). These authors introduced the name plumosite for Pb-poor compositions comparable to those described here and falkmannite for Pb-rich, Sb-poor varieties. Plumosite *sensu* Mozgova et al. (1983) did not receive acceptance as a distinct mineral phase, and should be regarded as Pb-poor boulangerite. Furthermore, this should not be confused with the Herja „plumosite“ discussed in a later section of this paper.

#### Heteromorphite (?)

Compositions of a Pb-Sb-S phase, concordant with that of the mineral heteromorphite (Pb<sub>7</sub>Sb<sub>8</sub>S<sub>19</sub>) are reported from the Baia Mare area for the first time. The phase occurs as small elongate grains, intimately intergrown with zinkenite enclosed in a sphalerite matrix. Microprobe analyses indicate

close to ideal stoichiometry (Table 3, columns 5, 6). The minor Zn detected in some analyses may best be attributed to the surrounding sphalerite.

#### Veenite (?)

Similarly, compositions concordant with those of the mineral veenite (Pb<sub>2</sub>Sb<sub>2</sub>S<sub>5</sub>) are also reported for the first time from the Herja deposit. Only seen in a single sample, grains with this composition occur as a fine reaction rim, about 50 µm thick between galena and an aggregate of jamesonite. Electron probe microanalysis (Table 3, column 7) indicated the composition to be stoichiometric.

#### Twinnite (?)

In the sample from the upper part of the Clementina vein (GV-100) which also contains zinkenite, fülöppite and heteromorphite, a number of small grains were detected whose composition closely matches that of the rather rare sulphosalt twinnite, PbSb<sub>2</sub>S<sub>4</sub>, (Jambor 1967; Bracci et al. 1980). Similar in appearance and composition to the twinnite described by Moëlo et al. (1983), our grains contains no As. With the exception of minor Ag and Bi (Table 4), the analysed compositions fit very closely to the stoichiometry of twinnite. However, since twinnite has a dimorph, guettardite, only a tentative identity may be assigned to the PbSb<sub>2</sub>S<sub>4</sub> phase in the absence of supporting X-ray data. However, this represents the first reported occurrence of either of these rare minerals on Rumanian territory.

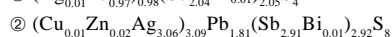
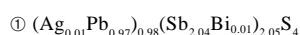
#### Diaphorite

Electron probe microanalyses of diaphorite are summarized in Table 4. Although generally stoichiometric with respect to (Ag+Pb):Sb:S ratios, the Herja diaphorite is characterized by a conspicuously high Ag/Pb ratio, which exceeds 1.5 in all analyses. Although the number of chemical or microprobe analyses of diaphorite reported in the literature is small (an overview was given by Hoffmann et al. 1977), con-



**Table 4:** Electron probe microanalyses of twinnite and diaphorite.

	Twinnite (GV-100)			Diaphorite (GV-10)		
	① mean n=7	max.	min.	② mean n=6	max.	min.
<b>Cu</b>	0	0	0	0.02±0.05	0.12	0
<b>Fe</b>	0	0	0	0	0	0
<b>Mn</b>	0	0	0	0	0	0
<b>Zn</b>	0	0	0	0.10±0.09	0.19	0
<b>Ag</b>	0.12±0.01	0.14	0	24.73±0.23	24.92	24.34
<b>Pb</b>	34.60±1.14	37.45	34.29	28.03±0.35	28.34	27.44
<b>Sb</b>	42.68±1.01	43.52	40.16	26.50±0.25	26.85	26.17
<b>As</b>	0	0	0	0	0	0
<b>Bi</b>	0.20±0.11	0.27	0	0.11±0.11	0.27	0
<b>S</b>	22.02±0.36	22.47	21.40	19.18±0.29	19.46	19.23
<b>Te</b>	0	0	0	0.02±0.05	0	0
<b>Total</b>	99.62			98.69		

**Formulae:**

siderable variation in the Ag/Pb ratio would appear to be characteristic. Mozgova et al. (1989) addressed compositional variation in diaphorite, citing microanalytical and crystal structural data from various deposits. They argued that a continuous solid solution series exists between diaphorite ( $\text{Ag}_3\text{Pb}_2\text{Sb}_3\text{S}_8$ ) and a phase with the formula  $\text{Ag}_2\text{PbSb}_2\text{S}_5$ , for which they proposed revival of the name „brongniardite“ (*sic.*). Mozgova et al. (1989) considered that this latter phase, with Ag/Pb ratios between 1.75 and 2.00 may be considered as an Ag-rich diaphorite. Our data would appear to strongly support such an argument, in that the Herja diaphorite exhibits a wide range of Ag/Pb ratios, from 1.53 to 1.69. Furthermore, we note anomalously high Ag/Pb ratios in diaphorite reported from other localities, e.g. the recently described diaphorite from the Apuan Alps, Italy which has a Ag/Pb ratio of 1.67 (Frizzo & Simone 1995).

**Chalcostibite**

Also confirmed for the first time from Herja is chalcostibite. This mineral is present as coarse blastic grains and needle-like crystals, associated with a range of other Sb-sulphosalts (Fig. 3e). Microanalysis of 9 grains gave a mean formula of  $\text{Cu}_{0.99}\text{Sb}_{1.02}\text{S}_2$ .

**Jamesonite**

Extremely abundant in all of the sulphosalt-rich samples, jamesonite,  $\text{Pb}_4(\text{Fe} > \text{Mn})\text{Sb}_6\text{S}_{14}$ , occurs as fibrous crystals up to 1 cm in length growing within gangue and overgrowing earlier formed minerals, notably arsenopyrite and tetrahedrite (Figs. 3a–b). Less commonly, jamesonite also occurs in thick dense aggregates, particularly as a reaction rim between galena and tetrahedrite (Fig. 3f). The felted „plumosite“ masses were also identified as being exclusively jamesonite. Microanalysis of jamesonite from all textural types revealed extensive homogeneity in composition (Table 5). Noteworthy is the consistent Mn content, which ranges from 0.09 to a maximum of about 0.25 wt. %, corresponding to about 4–8 mol. % of the ideal Fe-free

Mn-rich end-member b navid site. This is discussed further, with reference to X-ray diffraction data, in a later section. Almost all analysed jamesonite grains contained detectable Ag and Bi. Particularly the coarse fibrous „plumosite“ was found to be Ag-rich, commonly exceeding 0.20 wt. %.

**Other minerals**

Two small grains of *electrum* were observed (12 and 8 µm in diameter). Both gave compositions close to  $\text{Au}_{0.5}\text{Ag}_{0.5}$  (65 wt. % Au, 35 wt. % Ag). The presence of Hg, Cu or other metals was not detected. *Stibnite* ( $\text{Sb}_2\text{S}_3$ ) is abundant. All microanalyses gave perfect stoichiometry — no other elements were present. *Manganite*,  $\text{Mn}(\text{OOH})$  was recognized; the mean composition was determined to be (in wt. %) 0.30  $\text{SiO}_2$ , 0.08  $\text{MgO}$ , 0.42  $\text{CaO}$ , 78.38  $\text{MnO}$ , 0.39  $\text{BaO}$ , giving a calculated formula of  $(\text{Mn}_{0.98}\text{Ca}_{0.01}(\text{Mg},\text{Si},\text{Ba})_{0.01})_{1.00}\text{OOH}$ , assuming ideal stoichiometry.

**„Plumosite“**

Fibrous aggregates known as „plumosite“ are known from many of the mines in the vicinity of Baia Mare and in other Miocene vein type deposits elsewhere in northern Rumania (Uduba a et al. 1993). These authors remarked upon the morphology of these felt-like masses which may reach several cm in width and thickness, and incorporate small (1–2 mm) sized crystals of sphalerite, galena, tetrahedrite, quartz and siderite. Earlier, Mo iu et al. (1972), Ghiurca & Mo iu, (1986) had described plumosite from Herja (of jamesonite composition, like in the present study) which, in some cases, forms as curved crystals and concentric rings. Uduba a et al. (1993) note that most „plumosite“ is of jamesonite composition, although boulang rite dominates in some deposits, and robinsonite in the S sar vein system.

The term „plumosite“ has been used to describe fibrous varieties of a number of Pb-sulphosalts over the past 150 years

**Table 5:** Electron probe microanalyses of jamesonite.

	G V-10	606b	HJ-12	HJ-13	HJ-15
	①	②	③	④	⑤
	mean n=3	mean n=8	mean n=13	mean n=25	mean n=5
Cu	0	0	0	0	0
Fe	2.28±0.15	2.49±0.16	2.65±0.240	2.48±0.11	2.47±0.06
Mn	0.22±0.09	0.16±0.07	0.09±0.04	0.11±0.03	0.11±0.01
Zn	0.05±0.07	0.06±0.15	0.04±0.06	0	0
Ag	0.61±0.86	0.04±0.07	0.20±0.05	0.01±0.01	0.22±0.16
Pb	38.16±0.52	39.63±0.45	39.00±0.28	39.10±0.45	38.54±0.84
Sb	34.47±0.27	34.43±0.34	35.91±0.41	35.36±0.42	35.70±0.47
As	0	0	0	0	0
Bi	0.09±0.13	0.15±0.13	0.15±0.11	0.30±0.23	0.16±0.08
S	21.77±0.23	21.46±0.30	21.63±0.28	21.28±0.22	21.50±0.19
Te	0	0	0.02±0.05	0	0
Total	97.65	98.42	98.67	98.63	98.70

**Formulae:**

① (Fe<sub>0.84</sub>Zn<sub>0.02</sub>Mn<sub>0.08</sub>)<sub>0.94</sub> (Ag<sub>0.11</sub>Pb<sub>3.80</sub>)<sub>3.91</sub> (Sb<sub>5.84</sub>Bi<sub>0.01</sub>)<sub>5.85</sub>S<sub>14</sub>

② (Fe<sub>0.93</sub>Zn<sub>0.02</sub>Mn<sub>0.06</sub>)<sub>1.01</sub> (Ag<sub>0.03</sub>Pb<sub>3.97</sub>)<sub>4.00</sub> (Sb<sub>5.87</sub>Bi<sub>0.03</sub>)<sub>5.90</sub>S<sub>14</sub>

③ (Fe<sub>0.99</sub>Zn<sub>0.01</sub>Mn<sub>0.04</sub>)<sub>1.03</sub> (Ag<sub>0.04</sub>Pb<sub>3.91</sub>)<sub>3.95</sub> (Sb<sub>6.12</sub>Bi<sub>0.02</sub>)<sub>6.14</sub>S<sub>14</sub>

④ (Fe<sub>0.94</sub>Zn<sub>0.00</sub>Mn<sub>0.04</sub>)<sub>0.98</sub> (Ag<sub>0.00</sub>Pb<sub>3.98</sub>)<sub>3.98</sub> (Sb<sub>6.12</sub>Bi<sub>0.03</sub>)<sub>6.15</sub>S<sub>14</sub>

⑤ (Fe<sub>0.93</sub>Zn<sub>0.00</sub>Mn<sub>0.04</sub>)<sub>0.97</sub> (Ag<sub>0.04</sub>Pb<sub>3.89</sub>)<sub>3.93</sub> (Sb<sub>6.12</sub>Bi<sub>0.02</sub>)<sub>6.14</sub>S<sub>14</sub>

but is presently considered as being synonymous with boulangerite, Pb<sub>5</sub>Sb<sub>4</sub>S<sub>11</sub> (Mumme 1989; Clark 1993). We would suggest usage of the term plumosite in the sense of Chace (1948) „as a descriptive term which may be applied to jamesonite, boulangerite, zinkenite, any other lead sulphosalt, or as mixture thereof, that has a plumose texture or that occurs in a fibrous aggregate“.

Usage of the name plumosite is further complicated following the proposal of Mozgova et al. (1983). On the basis of analysis of compositional and structural investigations of falkmanite and boulangerite, these authors suggested that the name plumosite be revived for Pb-poor boulangerite (Pb<sub><4.7</sub>Sb<sub>>4.2</sub>S<sub>11</sub>). Falkmanite, boulangerite and „plumosite“ were proposed to belong to the „boulangerite homologous series“, with the general formula Me<sub>9</sub>S<sub>11</sub>. According to these authors, there is a compositional gap between boulangerite and their „plumosite“ (see also discussion in *Am. Mineral.*, 69, 411). Mumme (1989) addressed the crystal structure of near ideal composition boulangerite, and noted that there are considerable difficulties related to a series of minerals extending from falkmannite through boulangerite to plumosite (*sensu* Mozgova et al. 1989). Furthermore, Mumme (1989) noted the apparent structural identity of „plumosite“ (*sensu* Mozgova et al.) to jaskolskiite and suggested that this mineral, with the composition Pb<sub>4.8</sub>Sb<sub>4.2</sub>S<sub>11</sub> to Pb<sub>4.4</sub>Sb<sub>4.4</sub>S<sub>11</sub> (general formula Pb<sub>2</sub>Sb<sub>2</sub>S<sub>5</sub>) analysed by Mozgova & Bortnikov (1980) and Mozgova et al. (1983), may in fact be a discrete phase within the meneghinite homologous series.

### X-ray diffraction

A previous X-ray diffraction study of „plumosite“ from Herja (Udubaša 1992) showed the phase to correspond to jamesonite, although a slight peak shift and divergence in the unit cell parameters was noted when the diffraction pattern was compared with literature data for jamesonite. Incorpora-

tion of Ag, Mn and Tl at concentrations of 6000, 400 and 250 ppm respectively, were reported in the investigated sample. It was concluded that the relatively high Mn content of the Herja „plumosite“ causes this shift towards the Mn-analogue of jamesonite, benavidesite, Pb<sub>4</sub>(Mn,Fe)Sb<sub>6</sub>S<sub>14</sub> (Oudin et al. 1982; Chang et al. 1987).

Subsequently, Udubaša et al. (1993) showed, using a number of „plumosite“ samples from different occurrences in northern Rumania, that the cell parameters can be positively correlated with Mn content. It is not entirely clear which role, if any, the substitution of Ag (which has been confirmed in the present study) and Tl play in modification of unit cell dimensions. These authors interpret „plumosite“ to have been one of the latest minerals to have crystallized from hydrothermal solution and argue, for this reason, that they have collected the relatively incompatible elements Tl and Mn.

X-ray diffraction studies carried out in the present study confirm the earlier results. Diffraction patterns for Herja „plumosite“ from vein 90, level-5, together with those of jamesonite (JCPDS-ICDD Card 13-461, after Garavelli 1958) and of benavidesite from Uchucchacua, Peru (Oudin et al. 1982), which had a Mn/(Fe+Mn) ratio of 0.61, are given in Table 6. Four other samples of „plumosite“ from Herja gave identical X-ray diffraction spectra to that quoted in the table. Comparison of the diffraction spectra with published data for jamesonite (Berry 1940; Garavelli 1958) would appear to show a relatively strong shift in the positions of all major peaks towards those of benavidesite, as determined by Oudin et al. (1982). This is commensurate with the microanalytical data described above showing 4–8 mol. % of the Mn end member present within the Herja „plumosite“. However, the reader will note that there are considerable discrepancies in the peak patterns between those given by Berry (1940) and Garavelli (1958) for end-member jamesonite. These differences are sufficiently large that the shift in peak positions cannot be readily correlated with Mn substitution. Indeed, the peak positions for Herja „plumosite“ given in Table 6 are

**Table 6:** X-ray diffraction spectra.

h k l	Plumosite, Herja (present study)		Jamesonite (JCPDS-ICCD 13-461)		Jamesonite (Berry 1940)		Benavidesite (Oudin et al. 1982)	
	dcalc	I	dcalc	I	I	dcalc	I	
020	9.552	1	9.47	8		9.57	5	
120	8.161	9	8.09	14		8.17	10	
220	6.065	6	6.01	12	6.05	5	6.08	5
130	5.901	1	5.87	8		5.91		
310	5.048	1	5.03	6	5.05	5	5.06	5
240	4.080	28	4.06	25	4.07	30	4.09	30
400	3.926	2	3.90	16	3.92	40	3.93	5
410	3.845	7	3.82	30			3.85	20
150	3.712	2	3.70	35	3.70	20	3.72	10
121	3.587	4			3.59	30		
340	3.528	10	3.51	12			3.53	5
250	3.436	100	3.43	100	3.43	100	3.44	100
430	3.342	3	3.33	10	3.34	10	3.35	10
311	3.196		3.20	12				
060	3.184				3.17	50		
231	3.153	6	3.14	12			3.166	20
160	3.120	2	3.11	14				
510	3.099	3			3.10	50	3.103	
350	3.086	13					3.091	20
041	3.078		3.08	30				
141	3.035		3.01	10				20
260	2.951	12	2.94	16	2.93	20	2.956	40
411	2.825	6			2.83	90	2.831	
331/530	2.819	7	2.813	35			2.821	30
421	2.658	3	2.656	12			2.742	
360	2.720	30	2.714	35			2.725	
341	2.682	2	2.675	16				
421	2.658		2.656	12			2.677	5
261/180	2.367	1	2.361	8	2.36	10	2.356	5
640	2.295	8	2.290	12	2.29	30		
280	2.285	2					2.289	5
171	2.242	5	2.236	12	2.23	40	2.249	
470	2.241	5					2.245	20
560	2.236	3						
720	2.184						2.187	5
380	2.173	2						
730	2.116	1	2.109	6				
541							2.185	
090							2.127	10
461	2.126	1					2.130	
631							2.104	
551							2.104	
631							2.060	5
371	2.061	2						
081	2.054	2	2.047	12			2.061	
181	2.032	1	2.026	12				
740	2.030	3					2.034	
660	2.022	3						
002	2.013	1					2.030	
471	1.943	3						
721			1.942	8				
0100	1.910	4	1.909	25(132)				
580			1.894	10				
490	1.867							
191			1.857	10				
481			1.826	12				
751			1.756	8				
831			1.716	10				
5101			1.516	6				
572			1.452	6				

appreciably closer to those of benavidesite (Oudin et al. 1982) than to either of the patterns for jamesonite. These discrepancies are best attributed to the fact that the spectra reported in the cited studies (Berry 1940; Garavelli 1958;

Oudin et al. 1982) lack the absolute precision of the present investigation.

Cell parameters for our sample are calculated as  $a$  15.71,  $b$  19.10,  $c$  4.03, also showing an apparent strong shift towards benavidesite. Cell dimensions for jamesonite have been variously given as  $a$  15.71,  $b$  19.05,  $c$  4.04 (Berry 1940);  $a$  15.67,  $b$  19.06,  $c$  4.02 (Hiller 1955);  $a$  15.57,  $b$  18.98,  $c$  4.03 (Niizeki & Buerger 1957); and  $a$  15.65,  $b$  19.03,  $c$  4.03 (Garavelli 1958). Oudin et al. (1982) gave the cell parameters for benavidesite as  $a$  15.65,  $b$  19.03,  $c$  4.03 and  $a$  15.74,  $b$  19.14,  $c$  4.06. These data contrast somewhat with those of Chang et al. (1987) who gave a much narrower range in cell parameters on synthetic jamesonite and benavidesite, Mn/(Mn+Fe) = 0.7;  $a$  15.74–15.75,  $b$  19.17–19.14,  $c$  3.99–4.04. The uncertainties about the cell parameters of jamesonite, the differing investigative methods and experimental conditions, as well as possible errors in the various analyses, clearly do not readily permit correlation between cell parameters and degree of Mn substitution.

### Jamesonite and parajamesonite

Zsivny & Náray-Szabó (1947) described a mineral from Herja, found in the upper levels of the Šálan vein. Compositionally indistinguishable from „normal“ jamesonite, this phase was distinguished by a significantly different X-ray powder diffraction pattern. The mineral is reported to occur as columnar crystals up to  $8 \times 2$  mm in size, with rounded faces and lacking good terminations. An orthorhombic or lower symmetry was inferred. They named the mineral parajamesonite, due to the apparent paramorphous relationship with jamesonite. Koch et al. (1960) investigated jamesonite and „plumosite“ from Herja. Their study included a number of samples from the same part of the mine as the parajamesonite-bearing samples of Zsivny & Náray-Szabó (1947), and which had a strong morphological resemblance to the crystals in the original description. X-ray diffraction patterns of these crystals, however, proved to be identical to those of „normal“ jamesonite from elsewhere at Herja and from other localities. Since that time, the discrete identity of parajamesonite has been questioned in most standard mineralogical reference texts. No further samples of parajamesonite have been reported and it is particularly unfortunate that the original small crystal of parajamesonite, which was the subject of the 1947 description, was lost during the near total destruction by fire of the *Magyar Nemzeti Museum*, Budapest (Náray-Szabó 1961). Furthermore, the parts of the mine which yielded the original sample, which was collected during the period 1915–1920, are no longer accessible, thus preventing further clarification. In the absence of unambiguous evidence that parajamesonite does not exist, many mineralogists are prepared to believe that a dimorph of jamesonite does exist at Herja, but that this is exceptionally rare and restricted to a small part of the vein system. The crystallographic studies reported here have not been able to confirm the existence of parajamesonite in the sample suite.

**Table 7:** Sulphur isotope data on sulphides from the Herja deposit ( $\delta^{34}\text{S}$  ‰).

Sample	Pyrite	Galena	Sphalerite	Pyrrhotite
GV-101			- 4.90	
F-32				- 5.10
F-90-4	-8.01	-10.15		
F-50-4	-8.23	-11.13		
583-F-30	-7.36			

### Sulphur isotope geothermometry

S-isotope compositions of pyrite, galena, sphalerite and pyrrhotite within the Herja vein system are given in Table 7. The data confirm the strong volcanic identity of the ores, with all values lying within a relatively narrow field from -11.3 to +3.1 ‰  $\delta^{34}\text{S}$ . Such values suggest that the sulphur in the ore-forming fluids was derived from igneous sources at conditions in which  $\text{H}_2\text{S}$  was the dominant sulphur species (Rye & Ohmoto 1974). Some equilibration with the sedimentary host rocks may have taken place, resulting in the shift towards lower values shown by some samples.

S-isotopic concentrations within coexisting pairs may be used to determine temperatures of crystallization, assuming that the minerals are pure, formed contemporaneously and in equilibrium and that they did not re-equilibrate after crystallization. Given the more-or-less single stage of mineralization as documented by relationships between the main sulphides in the Herja deposit and the proven purity of the coarse-grained sulphides used for analysis, these assumptions may be considered valid. Using the geothermometric calibration of Ohmoto & Rye (1979), the following temperatures are obtained from two coexisting pyrite-galena pairs:  $417 \pm 75$  °C (Vein 90, level 4) and  $320 \pm 70$  °C (Vein 50, level 4). These results are significantly different to those of Pomáreanu (1971) who determined the following temperatures on the basis of fluid inclusion data; 215–275 °C for quartz, 190–200 °C for calcite and 220–225 °C for fluorite. Borcoş et al. (1975) used the data to argue in support of temperatures of about 300 °C for pyrrhotite and arsenopyrite crystallization, 250–280 °C for sphalerite and galena and temperatures below 215 °C for the stibnite and sulphosalt parageneses. An explanation of this discrepancy may be sought either in some disequilibrium between sulphides in the present study or that the fluid-inclusion based temperatures of Borcoş et al. (1975) are too low; i.e. they represent temperatures on the cooling path and do not reflect the true temperature maxima.

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