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Mimetite and Sb-rich segnitite from the Zlatá Idka Ag-Au-Sb deposit, Spišsko-gemerské rudohorie Mts., Slovakia

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Abstract

A new occurrence of mimetite and Sb-rich segnitite was discovered at the dump of the Najvyšší Štefan adit at the Zlatá Idka Ag-Au-Sb deposit near Zlatá Idka, Spišsko-gemerské rudohorie Mts., Košice-okolie Co., Košice Region, Slovakia. Mimetite occurs as white to colourless prismatic crystals up 2.5 mm in size, developed on fractures or in cavities of quartz gangue. Its average (n = 15) empirical formula (based on sum of As+P+S = 3 *apfu*) is $Pb_{4.99}[(AsO_4)_{2.75}(PO_4)_{0.22}(SO_4)_{0.03}]_{\Sigma 3.00}Cl_{1.12}$. Sb-rich segnitite forms greenish-yellow botryoidal microcrystalline crusts, which are partly covering or replacing crystals of mimetite. Significant contents of Sb (ranging from 0.15 to 0.34 *apfu*) substituting for Fe^{3+} on *B*-site were observed in studied sample. The average (n = 12) empirical formula of segnitite from the Zlatá Idka-Ag-Au-Sb deposit (based on sum of As+P+Si+S = 2 *apfu*) is $Pb_{1.09}(Fe_{2.73}Sb_{0.22}Al_{0.02}Zn_{0.01})_{\Sigma 2.98}[(AsO_4)_{1.08}(AsO_3OH)_{0.56}(PO_4)_{0.27}(SO_4)_{0.07}(SiO_2)_{0.02}]_{\Sigma 2.00}(OH)_{6.17}$.

Key words: *mimetite, segnitite, chemical composition, Zlatá Idka, Gemeric Unit, Spišsko-gemerské rudohorie Mts., Slovak Republic*

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Introduction

Mimetite and segnitite are generally rare minerals in supergene zones of various types of ore mineralization in the Spišsko-gemerské rudohorie Mts. Ďuďa, Peterec (1992) and later Števko et al. (2013) and Števko (2020) described relatively abundant occurrence of mimetite in the hydrothermal quartz-carbonate veins with nickeline, krutovite and galena hosted in serpentinite breccia from abandoned asbestos quarry near Dobšiná. Mimetite associated with segnitite and oxyplumboroméite was identified at the carbonate hosted hydrothermal Au-Pb-Zn-Sb-As mineralization at the Dúbrava occurrence near Rochovce (Radková et al. 2019) as well as with oxyplumboroméite and members of the segnitite-beudantite series at the Kobylianka ore occurrence near Hýľov (Števko 2022, Števko unpublished data). Sb and Bi rich members of the segnitite-phillipsbornite series containing up to 0.4 *apfu* of Sb were recently described by Ondrejka et al. (2023) from the hydrothermal quartz vein with U-REE-Au-Pb-Sb-As mineralization at the Prakovce-Zimná Voda occurrence.

A new occurrence of mimetite associated with Sb-rich segnitite was recently discovered at the Zlatá Idka Ag-Au-Sb deposit in Slovakia and its description is presented in this short paper.

Geological setting

The Zlatá Idka Ag-Au-Sb deposit is situated around 3 km NW of the Zlatá Idka village, 19 km NW of the Košice town in the Spišsko-gemerské rudohorie Mts., Košice-okolie Co., Košice Region, Slovakia. Samples with mimetite and segnitite were collected at the dump of the Najvyšší Štefan adit, which exploited the subsurface parts of the Štefan vein. GPS coordinates (WGS84) of this dump are: 48.769129° N and 20.973672° E, 942 m a.s.l.

The Zlatá Idka Ag-Au-Sb deposit is consisting of system of hydrothermal quartz±carbonate veins with Ag-Au-Sb ore mineralization hosted predominantly in Early Paleozoic metarhyolites and metasandstones of the Bystrý potok Formation, belonging to the Gelnica Group and Gemeric tectonic unit (Bajaník et al. 1984; Grecula et al. 1995). The hydrothermal veins are dominantly NE - SW trending and are parallel arranged, forming around 6 km long and 1 km wide ore belt. The most important ore veins (from west to east) are Matej, Štefan, František, Bertalan (Bartolomej), Trojičná, Jozef, František-Jozef, Všechsvätých and Katalin (Katarína) (Rozlozsnik 1912; Grecula et al. 1995).

Hydrothermal ore mineralization at the Zlatá Idka deposit is representing a specific type of unusual Ag-Sb-Au-Pb-Zn ore assemblage, which is different from the typical siderite-sulfide or quartz-stibnite type veins widespread in the Gemeric unit and has no equivalent in the Western Carpathians (Pršek, Lauko 2009; Mikuš, Števko unpublished data). The dominant gangue mineral is quartz accompanied by minor amounts of minerals of the dolomite-ankerite series and at some veins siderite is also abundant (e.g., Jozef or Anton vein). Jamesonite, berthierite, stibnite, arsenopyrite, sphalerite, pyrite and Ag-rich members of the tetrahedrite group are the most common ore minerals accompanied by wide spectrum of other minerals including acanthite, antimony, aurostibite, bou-

Fig. 1 *Prismatic crystals of mimetite partly covered by Sb-rich segnitite (greenish-yellow) from the Zlatá Idka Ag-Au-Sb deposit. Field of view is 3.6 mm. Photo by L. Hrdlovič.*

Fig. 2 *Greenish-yellow botryoidal crusts of Sb-rich segnitite partly covering prismatic crystals of mimetite, Zlatá Idka Ag-Au-Sb deposit. Field of view is 3 mm. Photo by L. Hrdlovič.*

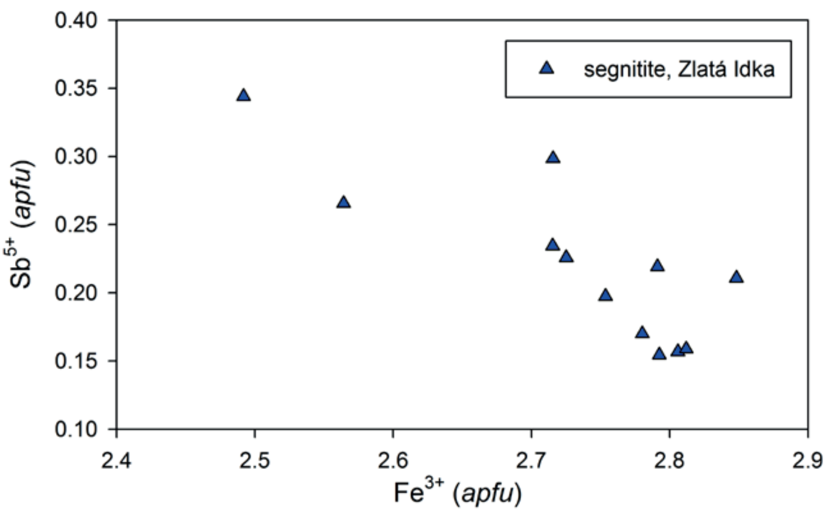

Fig. 3 *Sb^{5+} vs. Fe^{3+} plot (apfu) for segnitite from the Zlatá Idka Ag-Au-Sb deposit.*

langerite, bournonite, chalcopyrite, galena, gold, nisbite, pyrargyrite (?), pyrrhotite, senandorite, stephanite (?) and ullmannite (Varček 1979; Grecula et al. 1995; Pršek, Lauko 2009). Only a little attention has been paid to the supergene minerals at this locality so far. Anglesite, cerussite, cervantite, goethite, oxyplumboroméite and valentinite were briefly mentioned (Zepharovich 1873; Pršek, Lauko 2009). Števko, Sejkora (2024) additionally recently described occurrence of scorodite, sulphur and stibioclaudetite from the Štefan vein.

Detailed sampling at the dump of the Najvyšší Štefan adit is indicating that ore exploitation locally reached the base of the supergene zone of the Štefan vein. Large blocks of quartz gangue with abundant nests of slightly to strongly altered stibnite, berthierite, arsenopyrite and pyrite were discovered here. Thin fractures and cavities in such ore blocks are occasionally filled by crystals and aggregates of supergene minerals, especially valentinite, oxyplumboroméite, scorodite, anglesite, sulphur and rare stibioclaudetite. One fist size ore fragment with weathered jamesonite, pyrite and arsenopyrite contained cavity with mimetite and Sb-rich segnitite.

Analytical methods

The quantitative (WDS) chemical analyses of mimetite and segnitite were performed using a Cameca SX100 electron microprobe (Department of Mineralogy and Petrology, National Museum, Prague, Czech Republic). The following conditions, standards and X-ray lines were used for mimetite: 15 kV, 10 nA, 5 µm wide beam, albite (Na*K*α), almandine (Fe*K*α), apatite (Ca*K*α, P*K*α), baryte (Ba*L*α), Bi (Bi*M*α), celestine (S*K*α, Sr*L*β), clinoclase (As*L*α), Co (Co*K*α), Cr_2O_3 (Cr*K*α), $CuFeS_2$ (Cu*K*α), diopside (Mg*K*α), halite (Cl*K*α), LiF (F*K*α), Ni (Ni*K*α), rhodonite (Mn*K*α), sanidine (Al*K*α, K*K*α, Si*K*α), vanadinite (Pb*M*α, V*K*α) and ZnO (Zn*K*α), and for segnitite: 15 kV, 8 nA, 5 μm wide beam, albite (Na*K*α), apatite (Ca*K*α, P*K*α), baryte (Ba*L*α), Bi (Bi*M*α), celestine (S*K*α, Sr*L*β), clinoclase (As*L*α, Cu*K*α), Cr_2O_3 (Cr*K*α), diopside (Mg*K*α), halite (Cl*K*α), hematite (Fe*K*α), LIF (F*K*α), rhodonite (Mn*K*α), sanidine (Al*K*α, K*K*α, Si*K*α), Sb_2S_3 (Sb*L*α), vanadinite (Pb*M*α, V*K*α) and ZnO (Zn*K*α). Contents of the above-listed elements, which are not included in the tables, were analysed quantitatively, but their contents were consistently below the detection limit (ca. 0.03 - 0.05 wt. % for individual elements). Raw intensities were converted to the concentrations of elements using automatic "PAP" matrix-correction algorithm (Pouchou, Pichoir 1985).

Results

Mimetite is a rare mineral at the studied locality. It forms colourless to white, prismatic crystals up 2.5 mm long (Fig. 1), locally covered or replaced by crusts of younger segnitite. Crystals of mimetite are developed on fractures or in cavities of quartz gangue with coatings of amorphous Fe oxides and abundant altered nests and aggregates of jamesonite, pyrite and arsenopyrite. Quantitative WDS chemical analyses of mimetite from the Zlatá Idka depo-

Table 1 *Quantitative WDS analyses (wt.%) and calculated empirical formulae of mimetite from the Zlatá Idka Ag-Au-Sb deposit*

	1	2	3	4	5	6	7	8	9	10	11	12	13	14	15
PbO	75.26	75.39	75.28	75.41	76.28	75.43	75.02	75.23	74.74	75.14	75.27	74.90	75.01	74.69	75.52
As_2O_5	21.49	21.70	21.97	21.13	21.23	21.09	20.45	21.33	22.30	22.06	21.86	20.63	21.01	22.56	19.25
P_2O_5	0.98	1.04	0.69	0.88	1.17	0.98	1.18	0.89	0.56	0.90	1.08	1.42	0.89	0.57	2.38
SO_3	0.15	0.14	0.30	0.18	0.26	0.05	0.17	0.25	0.20	0.06	0.17	0.14	0.15	0.16	0.19
Cl	2.67	2.66	2.71	2.66	2.64	2.70	2.63	2.69	2.64	2.65	2.72	2.66	2.73	2.64	2.69
total	100.55	100.93	100.95	100.26	101.58	100.25	99.45	100.39	100.44	100.81	101.10	99.75	99.79	100.62	100.03
Pb^{2+}	4.991	4.937	4.944	5.106	5.014	5.122	5.126	5.024	4.914	4.917	4.874	5.002	5.112	4.865	4.990
As^{5+}	2.768	2.760	2.803	2.779	2.710	2.781	2.714	2.767	2.848	2.804	2.749	2.676	2.781	2.854	2.470
P^{5+}	0.204	0.214	0.143	0.187	0.242	0.209	0.254	0.187	0.116	0.185	0.220	0.298	0.191	0.117	0.495
S^{6+}	0.028	0.026	0.055	0.034	0.048	0.009	0.032	0.047	0.037	0.011	0.031	0.026	0.028	0.029	0.035
Σ	3.000	3.000	3.000	3.000	3.000	3.000	3.000	3.000	3.000	3.000	3.000	3.000	3.000	3.000	3.000
Cl^-	1.115	1.097	1.121	1.134	1.093	1.154	1.131	1.131	1.093	1.092	1.109	1.118	1.171	1.083	1.119

Calculated empirical formalae are based on sum (As+P+S) = 3 *apfu*.

Table 2 *Quantitative WDS analyses (wt.%) and calculated empirical formulae of Sb-rich segnitite from the Zlatá Idka Ag-Au-Sb deposit*

	1	2	3	4	5	6	7	8	9	10	11	12
PbO	29.06	29.40	29.56	29.12	28.30	29.12	29.30	28.45	29.14	28.44	29.09	29.32
ZnO	0.00	0.00	0.00	0.00	0.00	0.00	0.39	0.00	0.32	0.00	0.00	0.00
Fe_2O_3	26.44	25.98	26.71	26.73	25.95	25.35	26.35	26.48	24.53	25.92	25.68	25.13
Al_2O_3	0.34	0.29	0.00	0.00	0.00	0.00	0.00	0.00	0.90	0.24	0.00	0.00
Sb_2O_5	3.84	4.36	3.02	3.31	3.89	5.64	2.95	3.03	6.86	4.12	4.49	5.27
SiO_2	0.27	0.00	0.00	0.00	0.00	0.53	0.31	0.00	0.73	0.27	0.00	0.00
As_2O_5	22.34	22.31	22.72	22.28	22.08	21.96	20.66	24.05	21.88	21.22	23.43	23.81
P_2O_5	2.28	2.56	2.49	2.64	2.25	2.07	1.77	1.66	2.60	2.25	2.07	2.37
SO_3	0.76	0.69	0.45	0.78	0.35	0.38	2.12	0.26	0.59	0.94	0.31	0.39
H_2O*	7.40	7.34	7.35	7.33	7.21	6.99	7.47	7.21	7.10	7.30	7.06	6.79
total	92.73	92.93	92.29	92.19	90.03	92.04	91.32	91.14	94.65	90.70	92.13	93.07
Pb^{2+}	1.083	1.103	1.111	1.084	1.111	1.116	1.111	1.081	1.059	1.096	1.100	1.070
Zn^{2+}	0.000	0.000	0.000	0.000	0.000	0.000	0.041	0.000	0.032	0.000	0.000	0.000
Fe^{3+}	2.754	2.725	2.806	2.780	2.848	2.716	2.792	2.812	2.492	2.791	2.715	2.564
Al^{3+}	0.055	0.048	0.000	0.000	0.000	0.000	0.000	0.000	0.143	0.040	0.000	0.000
Sb^{5+}	0.197	0.226	0.157	0.170	0.211	0.298	0.154	0.159	0.344	0.219	0.234	0.265
Σ *B*-site	3.006	2.999	2.962	2.950	3.059	3.014	2.987	2.971	3.011	3.051	2.950	2.830
$(SiO_4)^{4-}$	0.037	0.000	0.000	0.000	0.000	0.075	0.044	0.000	0.099	0.039	0.000	0.000
$(AsO_4)^{3-}$	1.011	1.077	0.972	0.950	1.105	1.231	0.830	1.092	1.233	1.026	1.190	1.219
$(AsO_3OH)^{2-}$	0.605	0.549	0.687	0.660	0.578	0.403	0.691	0.682	0.312	0.562	0.531	0.469
$(PO_4)^{3-}$	0.267	0.302	0.294	0.309	0.278	0.249	0.211	0.198	0.297	0.273	0.246	0.272
$(SO_4)^{2-}$	0.079	0.072	0.047	0.081	0.038	0.041	0.224	0.028	0.060	0.101	0.033	0.040
Σ *T*-site	2.000	2.000	2.000	2.000	2.000	2.000	2.000	2.000	2.000	2.000	2.000	2.000
OH	6.226	6.274	6.157	6.098	6.438	6.239	6.324	6.101	6.081	6.405	6.082	5.670

Calculated empirical formalae are based on sum (As+P+S+Si) = 2 *apfu*; H_2O* content calculated on the base of charge balance.

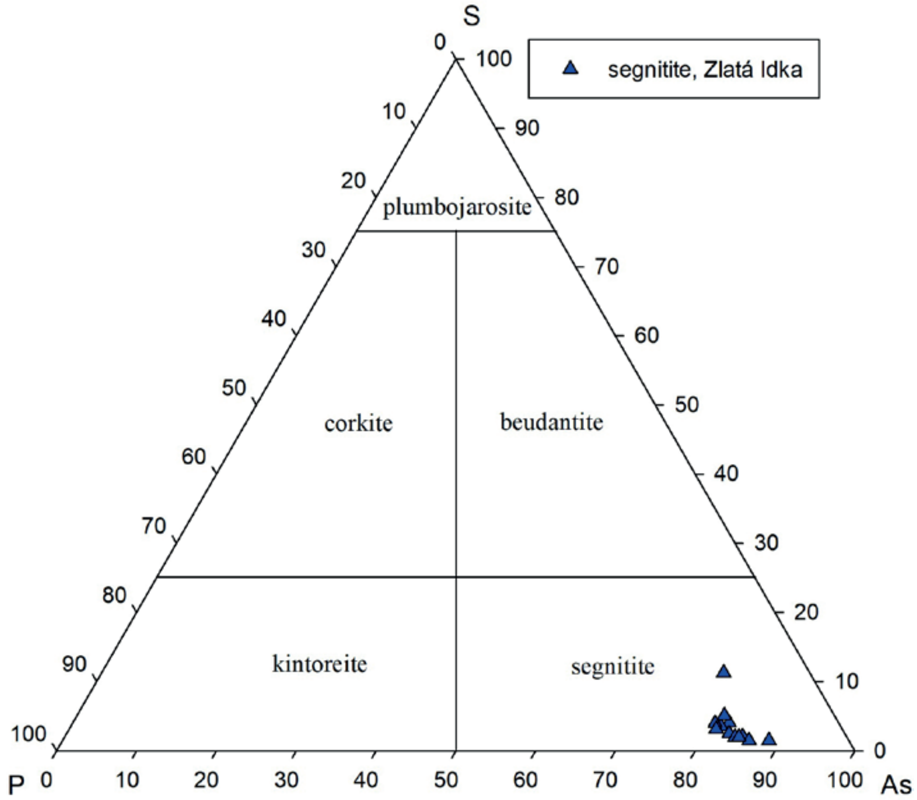

Fig. 4 *Projection of chemical composition of segnitite from the Zlatá Idka Ag-Au-Sb deposit in ternary As-S-P diagram.*

sit and the corresponding empirical formulae are shown in Table 1. Studied mimetite is chemically homogenous and compositionally close to the end member composition with only minor amounts of P (up to 0.49 *apfu*) and S (up to 0.05 *apfu*) detected. Its average (n = 15) empirical formula (based on sum of As+P+S = 3 *apfu*) is $Pb_{4.99}[(AsO_4)_{2.75}(PO_4)_{0.22}(SO_4)_{0.03}]_{\Sigma 3.00}Cl_{1.12}$.

Segnitite is rare and it was observed as greenish-yellow botryoidal microcrystalline crusts, which are partly covering (Fig. 2) or replacing crystals of mimetite. Quantitative WDS chemical analyses of segnitite from the studied locality and the corresponding empirical formulae are shown in Table 2. The *A*-site in the studied segnitite is exclusively occupied by Pb (ranging between 1.06 to 1.12 *apfu*). Iron is the dominant element on the *B*-site (ranging between 2.50 to 2.92 *apfu*) and it is substituted by minor amounts of Al (up to 0.14 *apfu*), Zn (up to 0.04 *apfu*) as well as significant amounts of Sb (from 0.15 to 0.34 *apfu*). The substitution of Sb^{5+} for Fe^{3+} on *B*-site has obvious negative trend (Fig. 3) and it is in line with data published by Kolitsch et al. (1999) for Sb-rich dussertite, Mills et al. (2014) for Sb-rich segnitite or more recently by Ondrejka et al. (2023) for Sb-rich members of phillipsbornite-segnitite series, which are fully supporting this type of substitution rather than Sb^{5+} for As^{5+} on the *T*-site. The *T*-site is predominantly filled by As (ranging between 1.52 to 1.77 *apfu*, Fig. 4) accompanied by P (0.20 - 0.31 *apfu*) as well as S (0.04 to 0.22 *apfu*) and locally also minor amounts of Si (up to 0.10 *apfu*). The substantial content of pentavalent cations on the *B*-site and the exchange of $(Al,Fe)^{3+}$ for Sb^{5+} requires compensation by the deprotonation of oxygen atoms in the $(AsO_3OH)^{2-}$ tetrahedra *via* the $0.5Sb^{5+} + (AsO_4)^{3-} \leftrightarrow 0.5Fe^{3+} + (AsO_3OH)^{2-}$ substitution mechanism (Kolitsch et al. 1999; Ondrejka et al. 2023). The average (n = 12) empirical formula of studied segnitite (based on sum of As+P+Si+S = 2 *apfu*) is $Pb_{1.09}(Fe_{2.73}Sb_{0.22}Al_{0.02}Zn_{0.01})_{\Sigma 2.98}[(AsO_4)_{1.08}(AsO_3OH)_{0.56}(PO_4)_{0.27}(SO_4)_{0.07}(SiO_4)_{0.02}]_{\Sigma 2.00}(OH)_{6.17}$.

Conclusions

A new occurrence of mimetite and Sb-rich segnitite was discovered at the Štefan vein, Zlatá Idka Ag-Au-Sb deposit, Spišsko-gemerské rudohorie Mts., Slovakia. The studied assemblage of supergene Pb/Pb-Fe arsenates resulted from weathering of primary ore minerals such as jamesonite, arsenopyrite and pyrite in oxide zone *in-situ*. Moreover, elevated contents of Sb observed in segnitite confirm previous assumptions about at least partial mobility of Sb during weathering of complex Pb-Sb sulfosalts, especially under slightly acidic conditions.

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