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Ore-bearing potential of target 185 in the Chelopech deposit: a LA-ICP-MS study

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Потенциална рудоносност на таргет 185 в находище „Челопеч“: LA-ICP-MS изследване

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Abstract. The concentrations of trace elements in pyrite and enargite-luzonite from target 185 of the copper-gold high sulphidation Chelopech deposit were determined by LA-ICP-MS. Their average contents in ppm based on 12 analyses of pyrite and 10 analyses of enargite-luzonite are respectively: Ti (6548) > Cu (3449) > V (580) > Mn (299) > Pb (173) > As (157) > Se (149) > Te (122) > Zn (80) > Co (79) > Bi (41) > Cr (29) > W (25) > Sn (22) > Ni (17) > Au, Ga (15) > Ag (14) > Mo (9) > Sb (5) > Tl (4) > Hg (1) > In (0.2) for the first one and Fe (26531) > Zn (22140) > Sb (11014) > Bi (7956) > Se (1730) > Sn (1016) > Pb (995) > Te (326) > Mn (205) > Mo (170) > Hg (100) > Ge (88) > Ag (46) > Ti (42) > W (25) > Cd (24) > V (19) > Au (16) > In (4) > Tl (3) > Ga (1) for the second.

Keywords: high sulphidation Cu-Au deposits, Chelopech, pyrite, enargite-luzonite, trace elements, invisible gold, LA-ICP-MS.

Introduction

The present LA-ICP-MS study reports 22 analyses of 33 elements (including 'invisible gold') in pyrite and enargite-luzonite from target 185 (that is a potential zone) of the epithermal copper-gold high sulphidation Chelopech deposit, which is a part of the Panagyurishte ore region in the Central Srednogorie Zone. Target 185 is located in the northwestern flank of the deposit, north of the block 147 (Fig. 1) and is intersected by drilling at a depth of 164–169 m (EXT147_200_13 and EXT147_200_14 boreholes). The target is distinguished by a less pronounced quartz-sericite alteration in narrow halos around the ore bodies. The sampling density is not yet sufficient to accurately define the shape and dimensions of the bodies. Given its spatial position, it can be assumed to be similar to block 147, which is characterized by a predominant structural control and more fractured mineralization compared to the other blocks in the deposits. The predominant ore minerals in target 185 are pyrite (recrystallized collomorphic or subhedral to euhedral, with a grain size of tens and hundreds micrometer) and later massive enargite-luzonite, spotty replaced by chalcopyrite. Pyrites and enargite-luzonites are the significant gold-bearing ore minerals in the deposit with higher frequency of occurrence and mean contents in comparison to other ore minerals. Thus, the main objective of this research is to evaluate their metal potential (especially the 'invisible gold' content) as well as the concentration of In, Ga and Ge,

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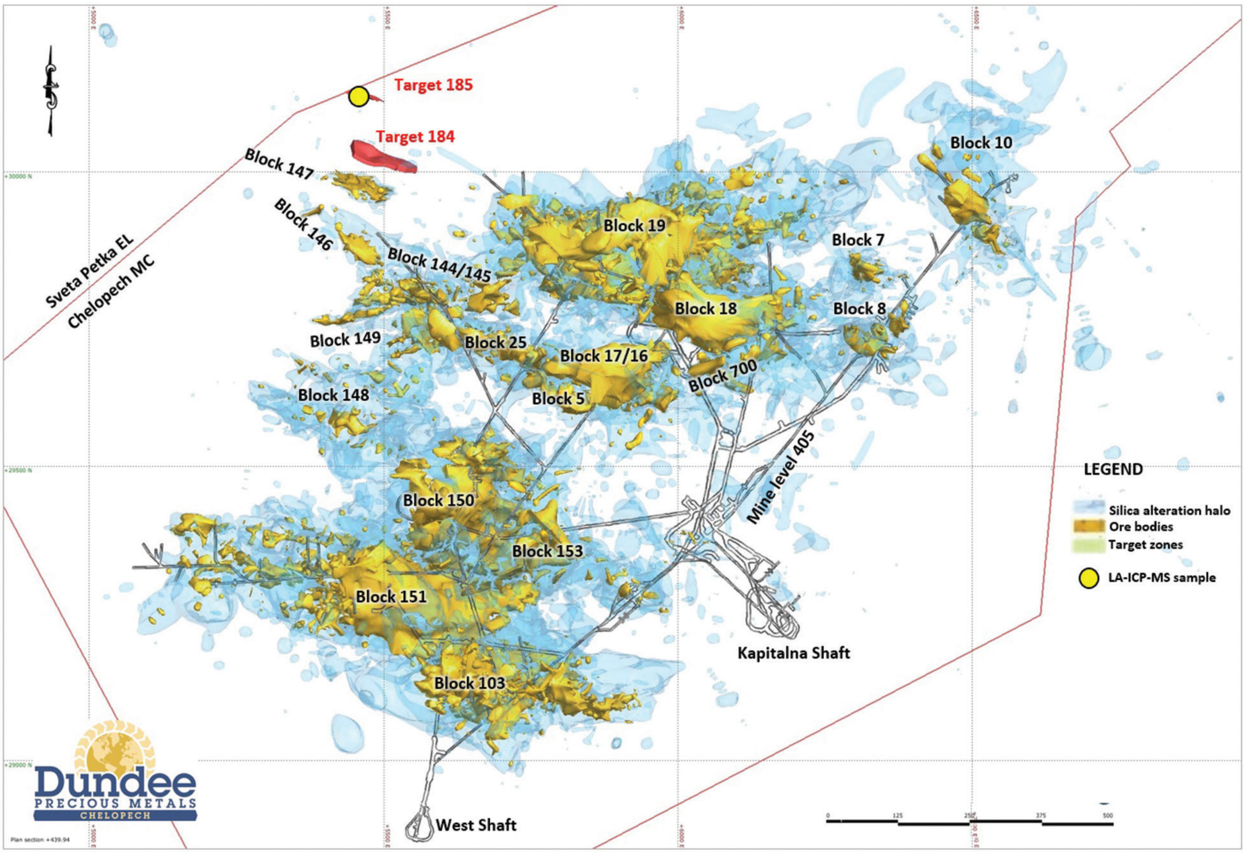

Fig. 1. Location of target 185 relative to the other blocks in the Chelopech deposit

using modern micro-analytical techniques, because the northwestern zones are subjects of a new exploration drilling in the Chelopech deposit.

Analytical procedures

Minor and trace elements in pyrite and enargite-luzonite are determined by laser ablation inductively coupled plasma mass spectrometry (LA-ICP-MS) on polished sections at the Geological Institute (Bulgarian Academy of Sciences), Sofia, Bulgaria (analyst: Dimitrina Dimitrova). The analyses were performed using a NW UP193-FX excimer laser ablation system combined with PE ELAN DRC-e ICP-MS at the following operating conditions: 35 μm laser beam size with 4–6 Hz repetition rate and 5.6 J/cm^2 energy density on the sample. The NIST SRM 610 and MASS 1 sulfide standard are used as external standards and were measured recurrently during the course of the analyses.

Results

The concentrations of trace elements in pyrite from target 185 of the Chelopech deposit are summarized in Table 1. Ubiquitous are Mn, Ti, Cr, Co, Cu, Ag, Se, Te and Pb. Also common are Au, As and Bi (determinated in 92% of the analyses); V and Ni (in 83% of the analyses) as well as Sb, Sn and Tl (in 75% of the analyses). Their average contents in ppm based on 12 analyses of pyrite are: Ti (6548) > Cu (3449) > V (580) > Mn (299) > Pb (173) > As (157) > Se (149) > Te (122) > Zn (80) > Co (79) > Bi (41) > Cr (29) > W (25) > Sn (22) > Ni (17) > Au, Ga (15) > Ag (14) > Mo (9) > Sb (5) > Tl (4) > Hg (1) > In (0.2).

The relatively flat depth profiles of Mn, Cr, Hg, Se and Tl, rarely Ti and V indicate their occurrence mostly as structurally bound. Predominant irregular signals for As, Cu, Zn, Pb, Bi, Sb, W, Sn, In and Ga, as well as positive correlations Pb vs. Bi ($R = 0.83$), Pb vs. Tl ($R = 0.72$), Sn vs. In ($R = 0.39$) and Cu vs. Sb ($R = 0.22$) imply the presence of aikinite, Bi- and Tl-bearing galena, In-bearing Sn minerals, enargite, chalcopyrite and Cu-Sb-bearing minerals (as tetrahedrite and bournonite) described in the Chelopech deposit (Arizanov, Terziyski, 2003). Irregular fluctuated signals of Co and Ni, as well as their positive correlation ($R = 0.69$) suggest the presence of Co-Ni minerals.

Strong positive correlation Au vs. Ag ($R = 0.89$), Au vs. Te ($R = 0.98$) and their intensity profiles

Table 1. Trace-element concentration in pyrite (in ppm) from target 185 of Chelopech deposit (according LA-ICP-MS)

	169.3 m (borehole)											
Ti49	51.59	3.54	90.64	441.83	8.60	16950	6.82	4.70	19553	25315	16146	7.87
V51	1.46	1.28	2.75	2.71	4.47	1108.50	<0.25	<0.50	1410.37	2789.16	477.43	3.23
Cr53	22.57	15.28	18.37	16.21	12.66	55.03	16.46	20.58	69.32	57.54	25.95	17.63
Mn55	18.77	23.15	29.24	20.55	16.29	952.17	35.13	16.69	782.39	1300.57	371.34	20.36
Fe57	465500	465500	465500	465500	465500	465500	465500	465500	465500	465500	465500	465500
Co59	249.37	52.39	187.38	30.27	3.02	77.65	6.90	0.38	124.91	107.78	86.59	24.38
Ni60	36.80	3.13	38.68	18.09	<1.62	25.49	1.15	<1.13	18.47	8.33	18.62	2.75
Cu65	2803.09	1756.58	2454.84	5902.92	2412.83	4024.42	433.43	52.46	1890.92	3453.95	8357.58	7844.68
Zn66	<6.27	<5.05	<4.96	<5.00	<4.27	119.99	11.66	<5.58	47.19	194.67	28.04	<4.31
Ga71	<0.26	<0.24	<0.22	<0.25	<0.26	13.26	<0.22	<0.16	19.09	20.90	6.61	<0.29
As75	42.39	65.88	30.80	346.47	7.88	406.39	<4.85	25.46	238.46	317.90	59.09	186.18
Se82	372.78	26.15	285.72	130.73	7.03	141.76	337.34	74.72	59.98	11.55	220.39	117.87
Y89	<0.07	<0.07	<0.06	0.35	<0.06	4.42	<0.07	<0.07	2.44	5.95	4.85	<0.06
Zr90	<0.29	<0.15	1.09	2.92	0.22	8.31	<0.15	<0.17	31.00	10.02	9.90	<0.15
Nb93	<0.16	<0.10	<0.11	0.63	<0.14	2.53	<0.11	<0.17	5.05	4.57	5.99	<0.11
Mo95	14.59	<0.91	<2.88	3.10	<0.78	<1.21	<1.75	<0.90	<1.22	<2.23	<2.71	<0.77
Ag107	63.09	10.10	22.13	3.58	2.81	25.74	0.84	1.18	10.46	7.94	12.14	2.06
Cd110	<0.90	<1.17	<0.79	<1.03	<1.16	<0.85	<1.49	<0.97	<1.14	<1.48	<1.15	<1.23
In115	<0.03	<0.05	<0.04	0.20	<0.05	0.44	<0.03	<0.04	0.28	<0.10	<0.05	0.04
Sn118	2.49	1.23	1.06	64.73	<0.30	47.74	<0.36	<0.21	51.43	29.28	3.26	1.15
Sb121	1.27	<0.32	0.69	12.81	1.73	7.97	<0.24	<0.32	2.69	4.51	7.65	1.93
Te125	719.98	72.79	187.76	78.91	51.50	66.65	52.82	40.47	23.31	2.55	158.82	4.25
La139	<0.06	<0.05	<0.04	0.33	<0.05	7.51	<0.05	<0.12	2.90	3.78	20.83	<0.05
Hf178	<0.12	<0.11	<0.10	<0.13	<0.11	<0.23	<0.19	<0.12	0.81	<0.31	<0.45	<0.11
Ta181	<0.04	<0.04	<0.05	<0.05	<0.04	<0.04	<0.04	<0.04	<0.05	<0.09	<0.04	<0.04
W182	<0.21	<0.27	<0.26	3.90	<0.19	49.95	<0.28	<0.22	9.99	7.81	51.50	<0.20
Re185	<0.05	<0.04	<0.04	<0.05	<0.06	<0.06	<0.05	<0.05	<0.04	<0.08	<0.04	<0.04
Pt195	<0.43	<0.28	<0.26	<0.34	<0.27	<0.28	<0.63	<0.31	<0.26	<0.33	<0.25	<0.26
Au197	107.96	3.51	19.34	3.47	1.40	8.46	0.78	<0.13	3.70	1.89	11.85	0.89
Hg202	<0.40	<0.35	<0.38	0.33	<0.31	1.46	<0.29	<0.35	0.82	0.89	1.47	<0.31
Tl205	0.13	0.19	<0.09	0.42	0.30	26.67	<0.07	<0.06	2.85	6.66	1.61	1.55
Pb208	34.61	5.26	29.93	124.54	6.74	748.29	1.04	7.66	487.07	239.29	133.46	257.79
Bi209	1.34	1.03	9.25	30.22	2.58	143.79	0.33	<0.07	132.23	63.00	61.95	5.97

demonstrate their presence as discrete inclusions of native gold/electrum and Au tellurides (e.g., calaverite). The incorporation of ‘invisible gold’ in solid solution and/or adsorption in recrystallized collomorphic pyrite aggregates are also possible.

The concentrations of trace elements in enargite-luzonite from target 185 of the Chelopech deposit are summarized in Table 2. Ubiquitous are Fe, Ge, Se, Au, Ag, In, Sn, Sb, Te and Bi. Also common are Hg and Tl (determinated in 90% of the analyses); Ti, Mn, Zn and W (in 80% of the analyses) as well as V and Ga (in 70% of the analyses). Their average contents in ppm based on 10 analyses of enargite-luzonite are: Fe (26531) > Zn (22140) > Sb (11014) > Bi (7956) > Se (1730) > Sn (1016) > Pb (995) > Te (326) > Mn (205) > Mo (170) > Hg (100) > Ge (88) > Ag (46) > Ti (42) > W (25) > Cd (24) > V (19) > Au (16) > In (4) > Tl (3) > Ga (1).

In most cases, the LA-ICP-MS profiles of Fe, Mn, Ge, Ga, Se, Sb, Hg, Sn, In, Pb, Ag, Bi, Tl and Te are smooth thus suggesting their occurrence in a solid solution. The strong positive correlations Sn vs. In (R = 0.998) and Ag vs. Se (R = 0.82) imply the presence of Sn-bearing minerals containing indium (as stannite, kesterite etc.) and eucarite. The occurrence of Sb-containing galena/bournonite and Ag-bearing tetrahedrite as inclusions or crosscutting veinlets in enargite-luzonites is emphasized by the rounded profiles of Pb, Sb and Ag and the positive correlation of Pb vs. Sb and Ag vs. Sb (R = 0.61 and 0.64 respectively). Regardless of the weaker correlations Pb vs. Se (R = 0.37), V vs. Ge (R = 0.32), Te vs. Bi (R = 0.29) and Pb vs. Ag (R = 0.28), the presence of clausthalite, germanocolusite, tetradymite/tellurobismuthite and Ag-bearing galena can be assumed due to the distinct peaks of these elements in some spectra.

Strong positive correlation Au vs. Ag (R = 0.92) and their depth spectra suggest discrete native gold/electrum inclusions. The presence of Ag- and Au-bearing tellurides (as sylvanite, petzite, etc.) despite the negligible correlations Ag vs. Te and Au vs. Te (R = 0.20 and 0.17 respectively) as well as their

Table 2. Trace-element concentration in enargite-luzonite (in ppm) from target 185 of the Chelopech deposit (according LA-ICP-MS)

	169.3 m (borehole)									
	En	En	En	En-Luz	En-Luz	En-Luz	En-Luz	En-Luz	En	En
Ti49	9.24	<8.10	36.09	75.95	107.70	10.15	8.69	6.54	<5.48	77.63
V51	1.47	0.84	2.32	2.82	3.65	10.36	110.95	<0.52	<0.74	<0.65
Cr53	<13.63	<14.68	<11.22	<15.40	<14.67	<15.75	<13.33	<16.88	<16.06	<24.01
Mn55	87.63	87.17	6.05	9.58	7.89	<1.49	<1.49	773.56	659.51	9.84
Fe57	69249	97711	6465.71	8278.35	7662.36	613.07	4703.67	24226	21381	25019
Co59	<0.42	<0.40	0.42	<0.43	<0.29	<0.60	<0.31	<0.28	<0.46	<0.39
Ni60	<3.15	<2.12	<1.58	<2.77	<1.52	<3.68	<1.67	<1.49	<1.74	<2.08
Cu65	484100	484100	484100	484100	484100	484100	484100	484100	484100	484100
Zn66	6628.34	14262.24	1599.41	347.37	41.01	<7.12	<6.66	25520	33876	94849
Ga71	1.15	1.01	1.49	1.10	2.14	<0.70	0.73	0.85	<0.31	<0.42
Ge74	37.16	41.97	158.68	130.16	156.29	114.08	192.94	14.67	12.80	16.92
As75	261335	260238	246825	204392	199967	232669	250304	237338	272396	315735
Se82	938.40	723.88	866.24	5093.72	6856.19	1440.30	101.82	378.52	356.69	546.13
Y89	<0.15	<0.14	<0.10	<0.10	<0.16	<0.18	<0.10	<0.20	<0.18	1.18
Zr90	<0.34	<0.70	<0.52	<0.33	<1.60	<0.34	<0.24	<0.36	<0.25	8.58
Nb93	<0.24	<0.31	<0.33	<0.24	<0.56	<0.17	<0.17	<0.15	<0.18	0.32
Mo95	<1.72	<1.61	<1.19	<1.22	<1.14	<1.73	4.58	444.89	43.54	188.42
Ag107	26.21	34.95	5.44	69.77	193.40	31.00	15.37	39.29	15.40	25.46
Cd110	7.19	38.79	<1.88	<3.07	<2.19	<1.96	<1.96	23.59	20.66	29.27
In115	1.17	0.97	0.97	11.42	19.56	2.96	0.97	0.97	1.39	1.72
Sn118	99.27	105.84	116.42	3106.60	5731.40	679.77	42.86	18.64	166.79	90.16
Sb121	3755.11	2463.08	4346.07	22273	29901	14651	103.06	21066	3976.85	7608.80
Te125	1070.95	325.19	69.72	390.59	689.87	73.48	23.28	434.68	60.76	126.38
Hf178	<0.25	<0.32	<0.17	<0.17	<0.16	<0.17	<0.17	<0.22	<0.25	<0.21
Ta181	<0.09	<0.08	<0.06	<0.06	<0.06	<0.06	<0.06	<0.06	<0.09	<0.08
W182	11.53	14.40	14.55	29.75	41.07	27.94	62.37	0.34	<0.33	<0.39
Re185	<0.10	<0.09	<0.10	<0.10	<0.09	<0.10	<0.07	<0.19	<0.13	<0.09
Pt195	<0.62	<1.11	<0.41	<0.59	<0.39	<0.72	<0.93	<0.37	<0.43	<0.51
Au197	9.39	8.55	1.19	34.24	71.09	21.60	2.51	3.91	0.85	4.28
Hg202	141.23	134.78	24.31	18.31	14.32	1.02	<0.41	266.88	251.61	47.58
Tl205	4.05	5.26	0.62	2.60	2.81	<0.14	0.15	7.48	1.64	3.81
Pb208	394.23	507.02	803.63	2599.54	1883.83	19.04	34.60	2230.66	176.43	1298.26
Bi209	10046	11733	3911.60	17037	22355	8470.37	4199.67	1146.85	623.50	37.00

isomorphic incorporation in the lattice of enargite-luzonite because of relatively flat depth profiles in rare cases are also possible.

Discussion and conclusions

The results obtained indicate that pyrites from target 185 are significantly enriched with Ti, V, Co, Ni, Cr and Ga, whereas enargite-luzonites contain more Zn, Sb, Bi, Se, Sn, Pb, Hg, Ge, In, Cd, Ag and Te. Thallium, Mn and W show almost same contents in both minerals. The average gold content is comparable in both minerals, but it reaches its highest values in pyrite (up to 108 ppm). In both cases, the presence of 'invisible gold' is mainly due to micro inclusions of auriferous phases, which would favor its extraction. Thus, target 185 may become an industrially significant area in the deposit especially in terms of its gold bearing with the highest 'invisible gold' contents in pyrite compared to all other blocks in the mine Chelopech (Vangelova et al., 2023) and some of highest in enargite-luzonite (Vangelova, 2023). In most cases enargite-luzonites are more enriched in gold and critical raw materials (especially germanium and indium) than pure enargites.

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