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Occurrence of Native Platinum and PGE-bearing Pyrite in the Porphyry-Skarn-Epithermal Ore Complex at Recsk, Hungary

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Termésplatina és platinafém-tartalmú pirit első észlelése a recski rézporfíros-szkarn-epitermás érces komplexum területéről

Összefoglalás

Ezen rövid közleményben bemutatjuk egy platinafém-csoport-elem ásvány általunk elsőként felismert előfordulását a recski ércesedés egy közepes szulfidációs fokú hidrotermás breccsatelérében. Az ércesedés piritjének nyomelemtartalmára vonatkozó adatok további információval szolgálnak a platinafémek megjelenéséről az ércesedésben. A Cu-tartalmú termésplatinával együtt jelenik meg az ércesedésben talált egyik legmagasabb platinatartalmú pirit, valamint a termésplatina paragenezisbe tartozó ércásványként megfigyeltünk Sn- és Pt-tartalmú termésrezet, tiszta termésrezet, valamint Ag-tartalmú tenoritot. További új ásványként krokoitot és vanadinitet is azonosítottunk kizárólag SEM-EDS módszerrel, ugyanezen paragenezisből. Új eredményeink további adalékul szolgálnak a platinafémek potenciális gazdasági jelentőségének továbbkutatásához a recski ércesedési rendszerben.

Kulcsszavak: platina, platinafém-elemek, porfír, ércesedés, termésplatina, nyomelem, pirit

Abstract

In this short report we present the first detection of a platinum group element (PGE) mineral and Cu-bearing native platinum in a hydrothermal breccia pipe in the intermediate sulfidation mineralization of the Recsk ore complex in Hungary. Trace element analyses of pyrite provide further insights into the enrichment of PGE in the mineralized complex. The occurrence of native platinum is associated with one of the highest observed Pt contents in pyrite, as well as with other ore minerals such as Sn- and Pt-bearing native copper, pure native copper, and Ag-bearing tenorite. Crocoite and vanadinite were identified by SEM-EDS as secondary minerals possibly from the same paragenesis. Our new results suggest that the Recsk complex might contain economic PGE resources.

Keywords: platinum, PGE, porphyry, mineralization, native platinum, trace element, pyrite

Introduction

Platinum group elements (PGE) in the form of various minerals occur in many Cu-porphyry ore deposits in the Carpathians and Dinarides (ECONOMOU-ELIOPOULOS 2005). Most of these are Pd dominated sulfides and tellurides that occur in the potassic alteration zone associated with Cu-bearing sulfide veins usually coupled with enrichment in Te and Bi (MCFALL 2018).

The form in which platinum group elements occur in the porphyry-skarn-epithermal ore complex of Oligocene epoch at Recsk is a long-debated question which goes back to the reporting of 0.12-0.16 ppm Pt contents in the enargite-luzonite-pyrite concentrate from the high-sulfidation type (HS) epithermal ore of the Lahóca Hill (NAGY & ZENTAI, 1967). More recently, modern nickel sulfide fire assay methods were used for analysis of Pt and platinum group elements (PGE) not only from the epithermal zones but also in representative samples of the porphyry-copper type mineralization. BERTALAN et al. (2004) reported 0.32-35.4 ppb Pt, <1 to 5.37 ppb Pd, <1 to 0.55 ppb Ir, <2 to 39.1 ppb Ru, <100 ppb Rh and < 1 ppb Os in ore samples selected both from epithermal and porphyry type ores. Molnár (2008) reported 0.07-0.41 ppm Pt and 0.05-0.1 ppm Pd contents for samples with high Cu, As, Sb and Sn concentrations from the massive and disseminated-breccia ores of the Lahóca Hill.

This paper reports the occurrence of Pt in nanoscale inclusions or as trace elements as solid solution in pyrite and as native metal alloys with various compositions in the Oligocene Recsk porphyry – skarn – carbonate-replacement – high-sulfidation (HS) and intermediate-sulfidation (IS) epithermal mineralization (Molnár 2007, Takács et al. 2017).

Methodology

Petrography and Scanning Electron Microscopy–Energy Dispersive Spectroscopy (SEM-EDS) based mineralogical mapping and analyses were performed on 100-µm-thick polished thin sections from 50 samples collected from the vertical RM series drill cores of the exploration program completed in the 1960-70s. Microscopy was performed with a Zeiss Axioplan polarized light microscope and SEM imaging was implemented by Hitachi SU3900 scanning electron microscope equipped with Oxford X-Max 51-XMX1234 energy dispersive detector with a resolution of 127eV at 5.9 keV for the semi-cquisition times of 20 s.

LA-ICP-MS measurements were completed on a single-collector Nu Instruments AttoM High Resolution LA-ICP-MS equipped with a =193 nm nanosecond excimer laser (model Excite). Diameter of the laser ablation pits were 40 µm, with 5 s pre-ablation and 30 s ablation time with 440 measurement cycles in total. Trace element data from 34 elements (Si, S, Ti, V, Cr, Mn, Fe, Co, Ni, Cu, Zn, Ga, Ge, As, Se, Nb, Mo, Ru, Rh, Pd, Ag, Cd, In, Sn, Sb, Te, Ba, W, Re, Os, Ir, Pt, Au, Hg, Tl, Pb, Bi, U given in UQAC FeS-1 reference material) were evaluated using the Glitter software (Griffin et al. 2008). *Table I* shows the eight elements that showed the strongest correlations with Pt. Detection limits for PGE and Au are typically 0.01 ppm, and 0.08 and 0.13 ppm for Ge and Zn, respectively. Values around the detection limit have significantly higher uncertainties. Mass 106 and 108 were both used to quantify Pd concentrations, which, due to the formation of $Zn^{66}Ar^{40}$ and $Zn^{68}Ar^{40}$ in the plasma, may yield erroneously high Pd concentrations in Zn-rich minerals. However, this was not the case for these analyses since there is no Zn-Pd correlation (*Table I*).

Polarized light microscopy and petrography was completed at the Department of Mineralogy, Eötvös Loránd University, whereas SEM-EDS and LA-ICP-MS measurements were performed in Espoo, at the Finnish Geosciences Research Laboratory of the Geological Survey of Finland.

Results

Copper bearing native Pt was found in a single sample from the intermediate sulfidation (IS) epithermal mineralization, and PGE-bearing pyrite was detected in several samples (*Table I*).

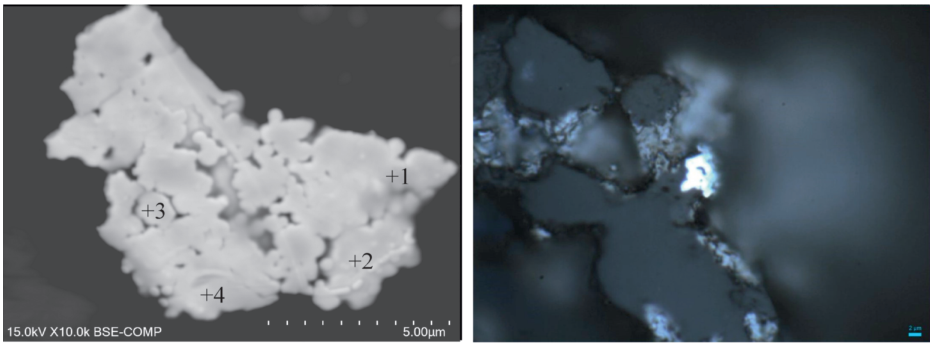
Occurrence of the native platinum mineral

Cu-bearing native platinum occurs in a pit on the surface of a silicified breccia clast together with illite (*Figure 1*), while native copper and Sn-Pt-bearing native copper occur close to the oxidation rim of disseminated pyrite and chalcocite grains in the breccia matrix. The native platinum grain shows irregular, cellular-dendritic texture and contains vugs between the individual sub-micrometer to micrometer-sized skeletal crystals forming the dendritic aggregate (*Figure 1*). The native platinum grain shows slightly higher copper contents towards the rim. Sn- and Pt-bearing native copper grains are embedded in illite masses close to the oxidation rim of pyrite, while native copper occurs mostly as encrusting layers on mineralized breccia clasts together with chalcocite. All of these mineral phases are difficult to detect in reflected light, mostly due to their small sizes (1–2

Table I. Trace element compositions (in ppm) of the platinum-bearing pyrite crystals from porphyry (PO), skarn (SK), high sulfidation epithermal (HS), and intermediate sulfidation epithermal (IS) mineralization. Only elements with correlation values with Pt above |0.65| are shown in the table, except for Zn values, which are shown to verify the validity of the Pd values. Values of PGE reaching 0.1 ppm are highlighted with bold font style

I. táblázat. *Nyomelem-koncentráció értékek (ppm-ben) a rézporfíros (PO), szkarn (SK), magas szulfidációs fokú epitermás (HS) és közepes szulfidációs fokú epitermás (IS) ércesedések platinafém-tartalmú piritjéből. A táblázatban kizárólag a platinával |0.65|-t meghaladó korrelációs együtthatóval rendelkező elemek vannak feltüntetve, kivéve a Zn-értékeket, melyek a Pd-koncentrációk validálása végett vannak feltüntetve. A 0.1 ppm-t meghaladó platinafém-koncentrációk félkövérrel vannak kiemelve*

Min.t.	Sample nr.	Zn - 67	Ge - 73	Ru - 101	Pd - 106	Pd - 108	Os - 190	Ir - 193	Pt - 194	Pt - 195
PO	7042py6-81	7,46	0,15	0,05	**0,28**	**0,12**	0,02	0,00	**0,09**	**0,10**
IS	7084py7	0,12	0,48	0,03	**0,18**	**0,27**	0,03	0,00	**0,31**	**0,29**
HS	L97py2-14	29,75	0,89	0,08	0,15	0,01	0,01	0,01	**0,12**	**0,15**
HS	L97py2-17	73,38	1,78	0,03	0,14	0,07	0,10	0,02	**0,11**	**0,07**
HS	R377py3-35	85,56	1,43	0,02	0,13	0,02	0,01	0,00	**0,17**	**0,07**
HS	R377py4-36	65,03	0,93	0,10	**0,17**	**0,13**	0,02	0,00	0,13	0,02
PO	7042py3-74	2,82	1,29	**0,12**	0,02	0,02	**0,38**	0,08	0,10	0,03
IS	JUV44py11	290,63	12,02	**0,14**	0,48	0,11	**0,29**	0,00	0,00	0,00
SK	7001py1-9	12,65	0,35	0,02	0,02	0,01	**0,26**	0,00	0,01	0,01
HS	R377py7-49	3,36	0,10	0,03	0,02	0,02	**0,19**	0,04	0,01	0,02



Measurement point	Cu wt%	Pt wt%	Total
1	2.6	97.4	100
2	1.3	98.7	100
3	8.1	91.9	100
4	8.8	91.2	100

Figure 1. Cu-bearing native platinum grain showing cellular-dendritic texture in BSE image (a) and the same native platinum grain in plane-polarized reflected light (rotated 90° left), after removing carbon coating by repolishing the thin section (b). Semi-quantitative SEM-EDS measurements (c) of the mineral show compositions 91.2–98.7 w% Pt with 1,3–8.8 w% Cu at multiple spots

***1. ábra.** Sejtes-dendrites szövetű, réztartalmú termésplatina-szemcse elektronmikroszkópos (BSE) képen (a) ugyanaz a termésplatina-szemcse polarizált fényben reflexiós mikroszkópi fotón (90°-al balra forgatva) a gőzölt szénréteg lepolírozása után (b). Félkvantitatív SEM-EDS mérési eredmények (c) változó 91,2–98,7 w% Pt- és 1,3–8,8 w% Cu-összetételt mutatnak több mérési pontról*

µm) and the presence of thin oxidized layers covering them. Additional minerals in similar textural position (i.e., in vugs between breccia clasts, in oxidized rims of ore minerals, or as isolated grains embedded in illite) are tenorite, vanadinite and crocoite. Tenorite forms microcrystalline aggregates 5-10 µm in size and contains up to 0.5 wt% silver. Vanadinite and crocoite both occur in illite-filled vugs of the breccia. Crocoite shows elongated idiomorphic shapes, while the shape of vanadinite is isometric-xenomorphic. Both minerals were identified with SEM-EDS. Vanadinite contains Pb, V, O, and Cl, while crocoite contains Pb, Cr, O, and minor Fe.

Mineralogy and petrography of the PGE-bearing pyrite

Pyrite is the most abundant ore mineral in every ore type of the Recsk ore complex. Seven hundred and eleven LA-ICP-MS analyses were completed on 633 grains but only around 3% of them showed a detectable (>0.1ppm) enrichment of PGE in pyrite (*Table I*). PGE-bearing pyrites were found in samples from all deposit types (*Table I*). PGE-bearing pyrite cannot be texturally discriminated from the barren variety. Pyrite with the highest platinum concentrations (from 0.07 to 0.31 ppm, *Table I*) from the HS and IS mineralization types is hosted by vuggy silica and pyrite in hydrothermal breccia matrix. Pyrite grains in this sample are usually idiomorphic, ranging from 20 to 500 µm in size and mostly occur disseminated in the silica matrix. Pyrite is associated with galena and enargite in those samples. Platinum-bearing pyrite in the IS-type mineralization occurs in a clast supported hydrothermal breccia consisting of silicified diorite porphyry, andesitic volcanic and sedimentary rock fragments in quartz-illite matrix crosscut by quartz-sulfide veins. Pyrite with the highest platinum contents occurs in the quartz dominated matrix. The highest Pt concentration in this type of pyrite is 0.31 ppm (*Table I*). Besides quartz, illite is the most abundant gangue mineral in these breccias. Part of the pyrite formed together with sphalerite, galena, fahlore and minor chalcopyrite and native gold in the IS-type ore. In addition to the above-mentioned minerals, pyrite occasionally also contains inclusions of pyrrhotite. Besides epithermal pyrite grains, breccia clasts in the pipe contain pyrite crystals of two additional distinct origins: pyrite that originated from the deep-seated porphyry, and another generation of pyrite that is related to carbonate replacement mineralization.

Besides the IS hydrothermal breccia, Pt-bearing pyrite occurs in the high sulfidation epithermal orebody and shallow porphyry diorite as well. The highest platinum contents typically occur together with the highest Pd concentrations. In addition to elevated Pd and Pt concentrations, Os shows also elevated levels in some of the pyrite grains. Additionally, the highest Os levels (0.29–0.38 ppm) are accompanied by the highest Ru (0.1–0.15 ppm) levels in pyrite in the shallow porphyry and epithermal samples (*Table I*).

Discussion

Pyrite in the porphyry, skarn and epithermal type ores at Recsk occasionally contains trace amounts of PGE. The heterogeneity of the time-resolved LA-ICP-MS profile of platinum during the ablation without correlation with other trace elements of pyrite suggests that platinum occurs as native metal nano-inclusions.

The mineral assemblage of sulfur-bearing native copper, tenorite, vanadinite, crocoite and further native metals can be related to the oxidation of primary sulfide ore in the lithocap zone of the porphyry system. The observed mineral assemblage suggests a low-temperature oxidative environment with near-neutral pH (stability field of illite). At low temperatures native platinum is stable over a wide range of pH with intermediate to high oxygen fugacity, while native copper and tenorite are stable within the pH range of 7–14 with intermediate Eh values at the same temperature in a sulfurous environment (Schlesinger et al. 2011, Southwood & Viljoen 1986). The stability of native platinum extends to low oxygen fugacity over a wide range of pH at 300 °C, too. Thus, native platinum can be a product of the hydrothermal syn-ore stage, related to the primary sulfide mineral assemblage as well (MOUNTAIN &WOOD 1988). However, PGE enrichment in porphyry copper ores is usually related to Te-Bi element association and the PGE are usually Pd-dominated (MCFALL et al. 2021). Thus, the occurrence of copper-bearing native platinum at Recsk is rather uncommon.

A possible explanation for the presence of PGE without significant amounts of Bi-Te in the porphyry-skarn epithermal ore complex at Recsk can be related to the potential sources of these metals. Among the dominantly carbonate and siliceous shale country rock of the porphyry-intrusion, the occurrence of an incomplete ophiolite-like sequence (submarine pillow basalt with gabbro intrusions) has also been recognized (KOVÁCS et al. 2013). These mafic rocks may have been a potential source of Pt-metals and semimetals mobilized by the hydrothermal fluids driven by the cooling diorite porphyry of the Paleogene period. Similar mafic rocks exposed NE and E of the mineralized Paleogene volcanic rocks contain 1–2 ppb Pd (MOLNÁR 2008). Hydrothermal remobilization of the PGE from the basaltic units is therefore possible. However, considering the dendritic morphology (*Figure 1.*) of the Cu-bearing native platinum grain and the composition of the observed ore mineral paragenesis, low temperature oxidation-cementation appears to be a more probable formation process instead of a hydrothermal origin. According to this model the source of platinum could be the PGE-bearing pyrite grains where the primary source of platinum remains unresolved.

Conclusions

This study presents the first description of a platinum group mineral in the porphyry-skarn-epithermal ore complex of Oligocene age at Recsk, NE-Hungary. Pyrite grains from the porphyry-Cu ore, and from the shallow high- and intermediate sulfidation type mineralization locally also contain over 0.1 ppm of PGE. The distribution of platinum in pyrite grains is heterogenous, indicating that Pt together with other PGE elements most probably occur as nano-scale inclusions in pyrite.

The copper bearing native platinum together with native copper, tenorite, crocoite and vanadinite was most probably precipitated during low temperature epigenetic oxidation-cementation processes. The metal source for the oxidation products were the sulfide minerals precipitated during the earlier hydrothermal stage. Our new results warrant interest in the potential of PGE enrichment in the Recsk ore complex.

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