CONSIDERATIONS ON THE PRESENCE OF PLATINUM AND PLATINUM GROUP ELEMENTS IN MINERALIZATIONS FROM ROMANIA

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Abstract: Platinum Group Elements (PGEs) are among the rarest metals in the world and are also considered as critical metals/minerals. Their economically important occurrences are limited to orthomagmatic deposits, porphyry-type hydrothermal deposits, alluvial accumulations (placers), and residual-type deposits. In Romania, Pt was firstly mentioned in 1853 by Karl Zerrenner in the alluvial deposits from Pianu, Sebeș Mts., and later, in 1855, by Michael Johann Ackner. Other occurrences in which platinum and PGEs were reported are Vâlsan Valley (Făgăraș Mts.), associated with metamorphosed basic rocks, and Southern Banat (Tișovița-Iuți area), associated with serpentinised ultrabasic rocks. Moreover, a platinum mineral, namely sperrylite, was mentioned in 1966 by Rădulescu and Dimtrescu in Holbav area (Făgăraș Mts.), associated with ultrabasic rocks bodies within the metamorphic sequences. The presence of Pt and PGEs in the mineralizations from Romania has been mostly qualitatively highlighted until now. Further investigations will allow to enlarge the knowledge about the presence of PGEs at a qualitative level and eventually in other occurrences. Further investigations will allow us to expand the knowledge about the qualitative presence of PGEs and eventually in other occurrences in Romania.

Key-words: platinum and platinum group elements in Romania, alluvial deposits (placers), orthomagmatic deposits, Sebeș Mts., Făgăraș Mts., Southern Banat, Romania.

Résumé: Les éléments du groupe du platine (EGP) sont parmi les métaux les plus rares au monde et sont également considérés comme des métaux/minéraux critiques. Leurs occurrences économiquement importantes sont limitées aux dépôts orthomagmatiques, aux dépôts hydrothermaux de type porphyrique, aux accumulations alluviales (placers) et aux dépôts de type résiduel. En Roumanie, le platine a été mentionné pour la première fois en 1853 par Karl Zerrenner dans les dépôts alluviaux de Pianu, Monts Sebeș, et plus tard, en 1855, par Michael Johann Ackner. D'autres occurrences dans lesquelles le platine et les EGP ont été signalés sont la vallée de Vâlsan (Monts Făgăraș), associée à des roches basiques métamorphosées, et le sud du Banat (région de Tișovița-Iuți), associé à des roches ultrabasiques serpentinisées. De plus, un minéral de platine, à savoir la sperrylite, a été mentionné en 1966 par Rădulescu et Dimtrescu dans la région de Holbav (Monts Făgăraș), associé à des corps de roches ultrabasiques dans les séquences métamorphiques. La présence de Pt et d'EGP dans les minéralisations de Roumanie a été principalement mise en évidence qualitativement jusqu'à présent. Des enquêtes supplémentaires permettront d'élargir les connaissances sur la présence d'EGP à un niveau qualitatif et éventuellement dans d'autres occurrences.

Mots-clés: platine et éléments du groupe du platine, dépôts alluviaux (placers), dépôts orthomagmatiques, Monts Sebeș, Monts Făgăraș, Banat Méridional, Roumanie.

INTRODUCTION

Platinum, palladium, iridium, osmium, rhodium, and ruthenium are part of the so-called **platinum group elements (PGEs)**. They are metals with similar chemical properties but quite different physical properties. Platinum, iridium, and osmium are the densest known metals; platinum and palladium are ductile, malleable, and resistant to high temperatures and corrosion; rhodium and iridium are very difficult to process due to their hardness and brittleness. These elements occur together in natural deposits, and their properties make them indispensable for many industrial applications. In addition to being among the rarest metals, they fall into the category of so-called critical metals/minerals. The platinum group elements can be divided into heavy platinum group elements – Pt, Ir, Os, and light platinum group elements – Pd, Rh, Ru (Zientek *et al*., 2017).

Economically important occurrences of Pt and PGEs are considered mainly the magmatic deposits group associated with ultrabasic-basic rocks, as well as alluvial accumulations (placers), which have the former as their protolith.

In magmatic deposits associated with ultrabasic and basic rocks, platinum group elements can occur in association with Ni-Cu deposits, sometimes exceeding Ni and Cu in importance. They can also occur in association with Cr deposits.

In the last decades, the presence of PGEs has been highlighted in porphyry-type hydrothermal deposits (e.g., Macdonald, 1987; Economou-Eliopoulos, 2005; Zientek *et al*., 2017), although not always with economic importance.

Additionally, besides the concentration of EGP in alluvial accumulations (placers), they can also be present in residual-type deposits, associated with nickel laterites (Zientek *et al*., 2017).

THE PRESENCE OF PLATINUM AND PLATINUM GROUP ELEMENTS IN ROMANIA

PIANU VALLEY, SEBEŞ MTS. (SOUTHERN CARPATHIANS) – THE HISTORICAL OCCURRENCE

In Romania, a first occurrence, with historical value, in which native platinum was mentioned, is represented by alluvial accumulations from Pianu Valley, Sebeş Mountains (Udubaşa *et al*., 2002; Udubaşa *et al*., 2004; Udubaşa and Udubaşa, 2015). It is known that Michael Johann Ackner mentioned in his treatise from 1855, "Mineralogie Siebenbürgens" (Mineralogy of Transylvania), the very rare presence of platinum in the gold-bearing placers from Pianu – Oláhpian, Siebenbürgen (Ackner, 1855). The author mentions the identification of several Pt granules (with iron content – "Eisenplatin") alongside some granules of "lead and copper, but also titanium, nigrin, etc.".

A few years later, however, Victor Leopold von Zepharovich in "Mineralogisches Lexikon" (Lexicon of Mineralogy) published in 1959 (von Zepharovich, 1859), mentions a work by Karl Zerrenner from 1853, published in "Sitzungsberichte der Keiserlichen Akademie der Wissenschaften mathematisch-naturwissenschaftliche Klasse" from Vienna (Communications of the Imperial Academy of Vienna – Class of mathematics–natural sciences), which announced the identification of several granules of native platinum in the placers from Pianu – „Goldsande von Oláhpian, Siebenbürgen" (Zerrenner, 1853). Therefore, it seems that this would be the first mention of native platinum in Pianu and, therefore, on the current territory of Romania. These pieces of information were afterward taken over by Antal Koch (1885), Eduard Albert Bielz (1889), and later by Petru Poni (1900).

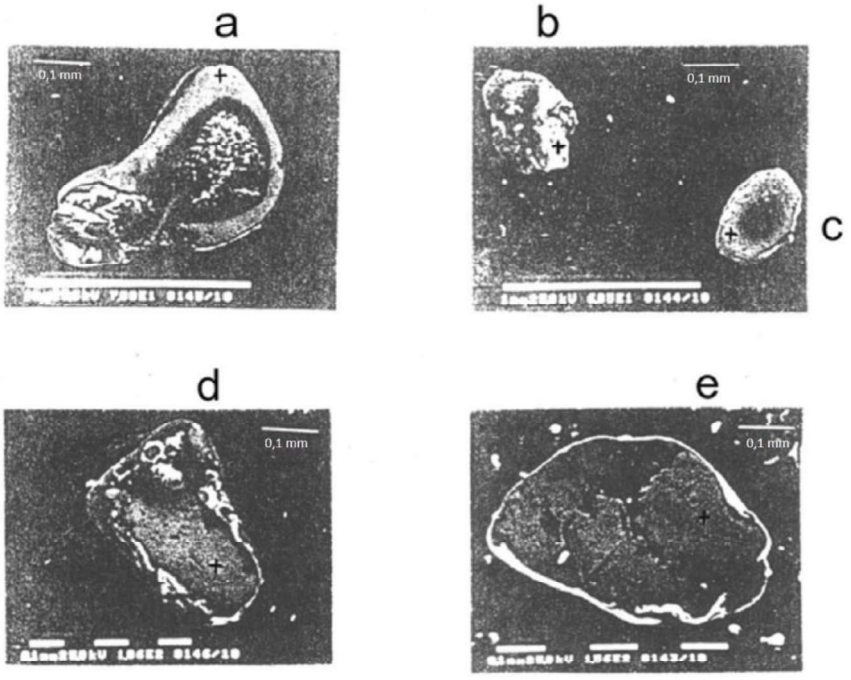
A sample from these placers from Pianu Valley, which is very old and quantitatively small, called "Platina" ("Platinum"), is found in the mineralogical collection of Babeş-Bolyai University in Cluj-Napoca. It was studied by a group of researchers from the Geological Institute of Romania (IGR),

Bucharest and the Babeş-Bolyai University of Cluj-Napoca (Udubaşa *et al*., 2004), and the research revealed the presence of several grains of native Pt, rounded and zoned (Fig. 1.A).

The analyses carried out by the authors of that study with the electron microprobe highlighted the presence of Fe, in addition to Pt, in the studied granules. The contents vary between approx. 91–94% Pt and approx. 4–9% Fe (Fig. 1.B). Therefore, it represents a platinum with iron contents that brings it closer to what was called "polyxene" (platinum with 6–11% Fe), a name that is no longer accepted by International Mineralogical Association (IMA) today (Udubaşa and Udubaşa, 2015).

These analyses represent the first analytical evidence of the presence of native platinum in Pianu, and therefore in Romania, approximately 150 years after the first mention. Additionally, this confirms the iron content of native platinum grains mentioned by the first researchers.

A.



B.

	Pt (%)	Fe (%)
a	93,92	6,08
b	91,15	8,85
c	91,41	8,59
d	90,87	9,13
e	90,63	9,37

Fig. 1. A) SEM images of Pt granules from Pianu, some with zonal aspect. B) The contents measured at the points marked with "+" in the images (after Udubaşa *et al*., 2004).

VÂLSAN VALLEY, FĂGĂRAŞ MTS. (SOUTHERN CARPATHIANS)

Another occurrence where platinum was mentioned is on Valea Vâlsanului, Făgăraş Mountains. Here, in metamorphosed basic rocks, a Cu-Ni(±Co) mineralization occurs with main metallic minerals as: chalcopyrite, pyrrhotite, pentlandite, pyrite, rutile, etc. Udubaşa *et al*. (1988) mention platinum as being present in association with cobalt-pentlandite, pentlandite and pyrrhotite. The presence of cobalt-pentlandite has also been reported in our country in the Cu mineralizations from Baia de Aramă by Gheorghe C. Popescu (1990), in the form of inclusions in chalcopyrite, a presence also confirmed by the author through quantitative analyses with the electron microprobe.

Subsequent studies (Cristea-Stan *et al*., in Ţarigradschi, 2013) on samples from the mineralization at Valea Vâlsanului also showed, analytically, through the micro-PIXE method (Proton-Induced X-ray Emission), the presence of platinum in association with cobalt-pentlandite, besides pyrrhotite, pentlandite, and chalcopyrite.

The investigation of these mineralizations from Valea Vâlsanului was continued through SEM-EDS (Scanning Electron Microscope – Energy Dispersive Spectroscopy) analyses, in the laboratories of the National Institute for Nonferrous and Rare Metals Research and Development – IMNR, Pantelimon. In the collected samples, in a few analysis points from the investigated polished sections, on pentlandite and pyrrhotite aggregates, the presence of platinum was highlighted through SEM-EDS analyses (Ghiță *et al*., 2017).

Fig. 2 shows the analysis points and spectra obtained by EDS. These highlight the presence of platinum, in association with pentlandite, pyrrhotite (presence of Ni, Fe, S).

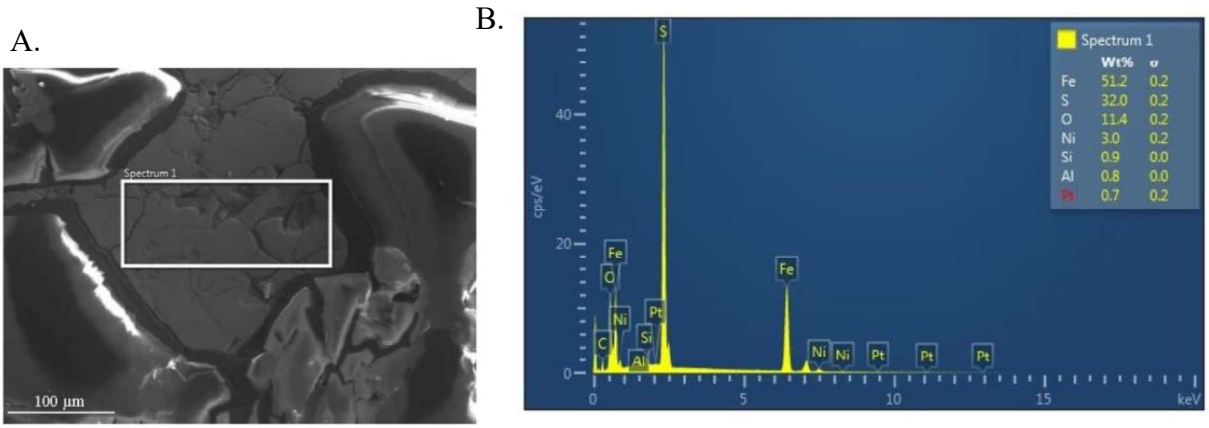


Fig. 2. A) SEM-BSE (backscattered electrons) image of the sulfide association from a Valea Vâlsanului sample. B) EDS analysis of the area marked with a rectangle in the left image, which highlights the presence of Pt (from Ghiță *et al*., 2017).

SOUTHERN BANAT (SOUTHERN CARPATHIANS)

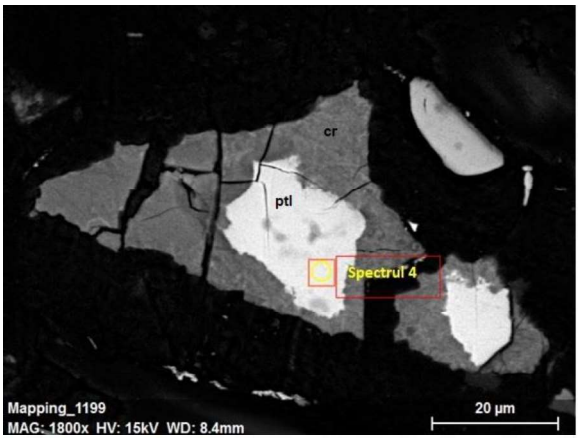
The chromium accumulations in southern Banat, associated with the serpentinites from the Tișovița-Iuți area (serpentinized ultrabasic rocks), are another category of mineralizations where platinum group elements have been reported over time.

In the serpentinite complex of southern Banat (Tișovița-Iuți-Eibenthal area), chromium mineralizations were identified even before World War I. These were mostly exploited by German companies, from 1914 to 1918, but also later until the depletion of known reserves (Mârza, 1982). Hîrtopanu *et al*. (1991) mention platinum contents of 1.4–5.4 g/t in the serpentinized ultramafic bodies from the Eibenthal-Tișovița-Plavișevița-Ciucaru Mare area, in southern Banat.

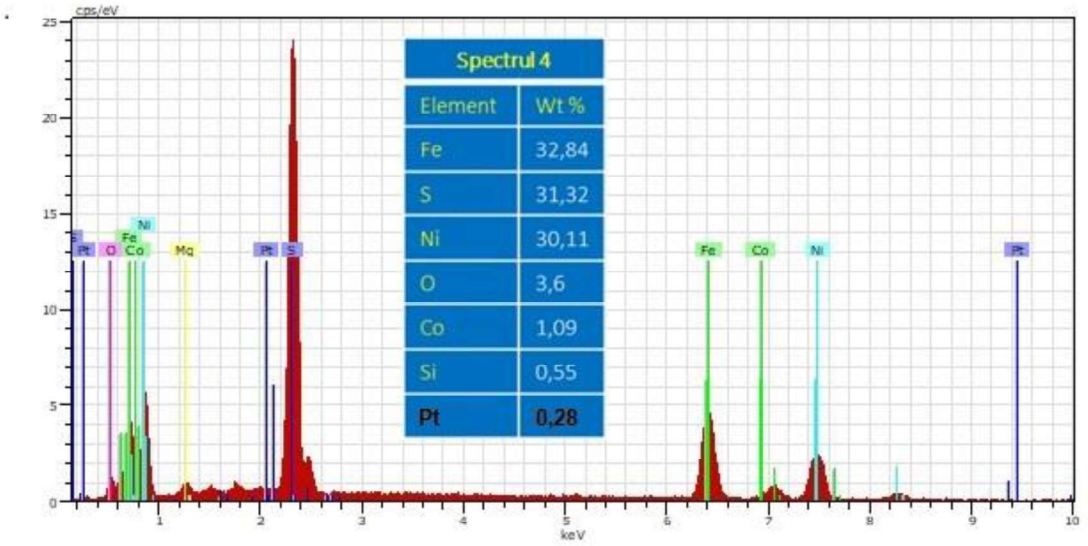
A series of analyses carried out on samples from the Tişoviţa-Ciucaru Mare area (Lupu, 2017; Ghiță *et al*., 2017) highlighted the presence of platinum and cobalt-pentlandite in some of the samples. Optical microscopy revealed pentlandite associated with chromite and magnetite, while SEM-EDS analyses revealed the presence of Co in accordance with Ni and Fe in sulfide-bearing zones (Lupu, 2017; Ghiță *et al*., 2017). Therefore, it can be considered that it is a cobalt-pentlandite (Fig. 3). Additionally, the obtained X-ray spectra and compositional maps highlighted the presence of platinum in association with pentlandite/cobalt-pentlandite, magnetite, and chromite.

During more recent investigations (Ghiță *et al*., 2021) on serpentinite samples from the Tișovița area the analyses revealed not only the presence of platinum. Microscopically, in reflected light, the authors of the study (Ghiță *et al*., 2021) identified platinum granules in association with chromite, magnetite, and pentlandite (Fig. 4). EDS analyses carried out on some of these granules revealed the

presence of Pt, but also Pd in some cases (Fig. 5). This time, the association of PGE with oxide minerals (chromite, magnetite) is noteworthy, as well as the presence of small amounts of sulfides (pentlandite).



A



B

Fig. 3. Electron microprobe investigations on one of the sulfide samples from the serpentinites in the Tişoviţa-Ciucaru Mare area (after Lupu, 2017). A) BSE image on a supposed pentlandite grain (ptl), included in chromite (cr), with the localization of the EDS analysis point. B) EDS analysis at the marked point, which confirms the presence of Co, so the host mineral is cobalt-pentlandite, as well as it confirms the presence of Pt, related to it.

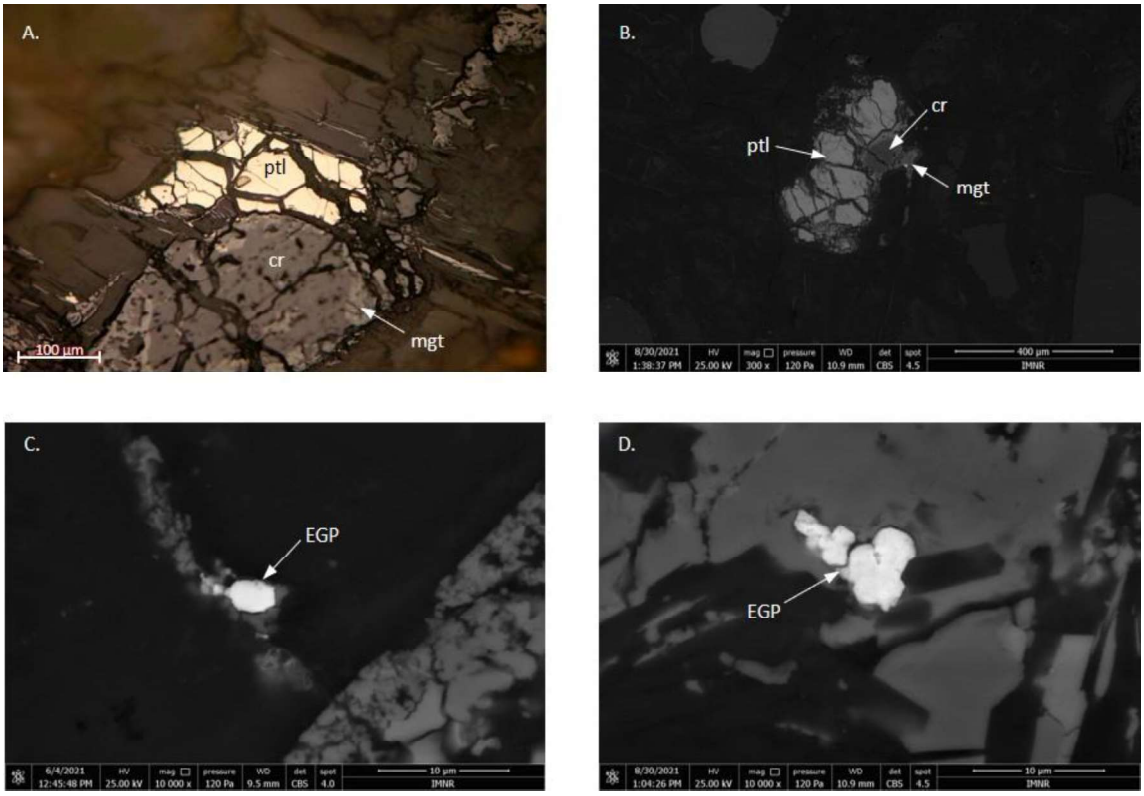


Fig. 4. A) Reflected light microscopic image, immersion in cedar oil, showing the presence of the chromite (cr), magnetite (mgt), pentlandite (ptl) association; B) SEM-BSE image, with the chromite (cr), magnetite (mgt), pentlandite (ptl) association; C-D) SEM-BSE images with magnetite and chromite aggregates and grains of PGEs on which EDS analyses were performed (after Ghiță *et al*., 2021).

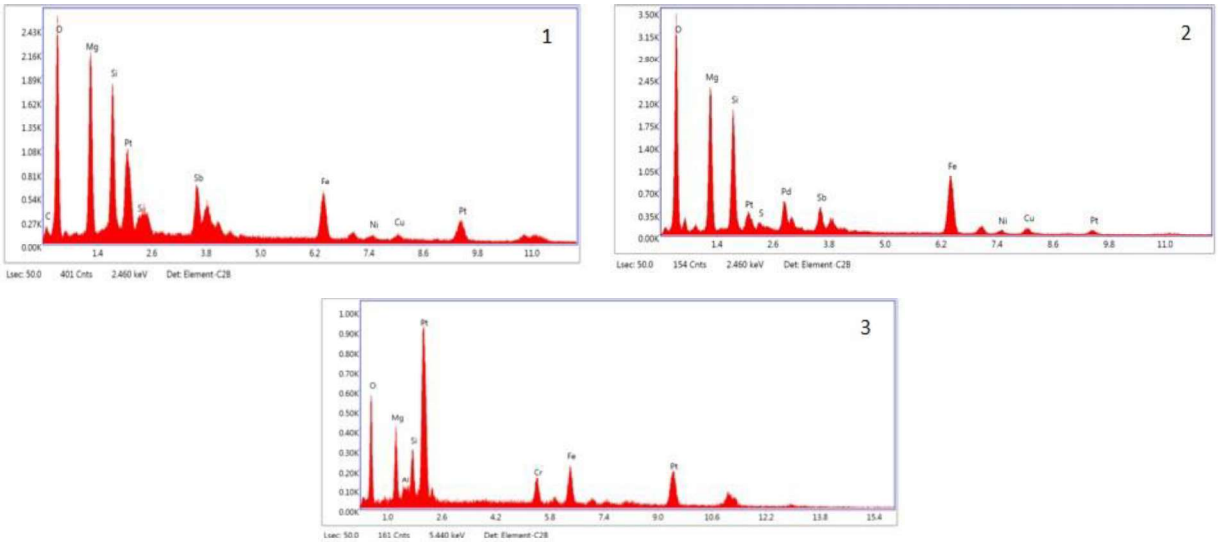


Fig. 5. EDS spectra (after Ghiță *et al*., 2021) performed on the PGEs granules illustrated in Fig. 4C (spectra 1 and 2) and 4D (spectrum 3). These show the presence of Pt, as well as Pd (spectrum 2).

OTHER OCCURRENCES

In addition to the presence of PGEs as native metals, some minerals with platinum group elements have also been identified in several mineralizations in Romania. One such mineral is sperrylite – PtAs2 (cubic system), mentioned by Rădulescu and Dimitrescu (1966) as being present, quite rarely, in the Holbav area (Făgăraș Mountains). In that area, in the ultrabasic rock bodies with nickeliferous mineralizations from metamorphites, sperrylite was observed microscopically as inclusions in pyrrhotite, associated with chalcopyrite (Codarcea *et al*., 1952; Udubaşa *et al*., 2002).

CONCLUSIONS

The research conducted so far has highlighted mainly the qualitative presence of platinum and/or other platinum group elements in Romania. Further investigation into the occurrences presented, as well as expanding the area of investigation to other similar or even genetically different types, can clarify the overall picture of the presence of platinum and platinum group elements in mineralizations in Romania, as well as the possible outlining of quantitative information in these accumulations.

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