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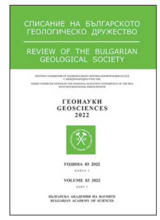

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Assessing the potential of Assarel porphyry copper deposit for critical raw materials: mineral-geochemical data for combination with agile exploration methods and better geo-modeling

Оценка на потенциала на медно-порфирно находище Асарел за критични суровини: минералого-геохимични данни за комбиниране с гъвкави проучвателни методи и по-добро геомоделиране

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Abstract. The supply of European critical raw materials (CRMs) does not currently meet the European demand. This gap is predicted to increase, making Europe even more dependent on outside suppliers. AGEMERA is a project to help tackle this strategic problem by studying several CRM sites in Finland, Poland, Spain, the Balkans, and Zambia in different deposit types. To check the potential of the porphyry systems in Europe as a source of CRMs, the Assarel porphyry-Cu deposit was chosen as a test site. Here we present preliminary geochemical and mineral chemistry data for hydrothermal ore and alteration minerals in Assarel that reveal the potential of the deposit to source some CRMs as by-products. Further studies will combine the geochemical data with innovative geophysical methods for an improved deposit model and provide enhanced knowledge about effective exploration techniques for CRMs.

Keywords: critical raw materials, AGEMERA, porphyry systems, Assarel, geochemistry.

Introduction

The worldwide demand for critical raw materials (CRMs) is rapidly increasing due to the transition to greener tech and energy production and a more digital world. In order for the European Union (EU) to become more resilient and develop strategic autonomy, it is essential to mobilize Europe's domestic CRM potential. Europe has a long tradition in mining and extracting base metals (e.g., Cu, Zn and Pb), but less so to source CRMs. This is partly because many of the CRMs were not considered valuable earlier. Nevertheless, Europe has significant CRM-potential locked in many ore districts.

It is paramount that raw material supply bottlenecks are corrected in the near future to achieve strategic autonomy for the supply chains of European industries. This is especially important for CRMs, which have an essential role in transitioning to a low-carbon and digital economy. In many cases, the same raw materials are required by multiple technologies and sectors critical for the clean energy transition, which are, therefore, effectively competing with one another.

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A new Horizon Europe project called 'AGEMERA: Agile Exploration and Geo-modelling for European Critical Raw Materials' is going to contribute to the unlocking of Europe's CRM potential by conducting local state-of-the-art geological and geophysical surveys in six EU countries and one African country (Zambia). AGEMERA is a three-year research and development project that will tackle some of the critical problems of European CRM sourcing. Its main goal is to increase the geologic understanding of the studied ore districts and to improve their genetic models, including information for CRMs as either main ore or by-products. The project will also aim at enhancing public awareness of the crucial role of CRMs in both the green transition and the EU's strategic autonomy and resilience. AGEMERA combines the resources, expertise, innovation power, and novel technologies of 20 consortium partners from 11 countries and includes two Bulgarian partners, one academic – GI-BAS, and one from the industry – Assarel Medet JSC.

Mineral exploration targeting, sampling, modeling, and geophysical field trialing are planned in different exploration sites to ensure a variety of locations and mineral systems. The pre-selected areas are located in Bosnia-Herzegovina, Bulgaria, Finland, Poland, Spain, and Zambia. The targets represent orogenic Au, karst bauxite, volcanic-hosted massive sulfide, porphyry-copper-Au-Mo systems, stratabound Cu-Ag, and sediment-hosted stratiform Cu. The deposits to be studied are located in the Peräpohja Schist Belt (Finland), the Iberian Pyrite Belt (Spain), the Kupferschiefer district (Poland), the Panagyurishte & Rossen districts (Bulgaria), the Jajce and Posušje areas (Bosnia-Herzegovina) and the Zambian Copperbelt (Zambia).

Porphyry-type deposits are the main source for global Cu and Mo production and may contain economic grades of Au, Ag, and even platinum-group elements (PGE). Several strategic and high-tech elements such as Re, W, Bi, In, Te and Se may reach economic concentrations and be extracted as by-products. To check the CRMs potential of the porphyry systems in Europe , the Assarel porphyry-Cu deposit was chosen as a test site. Here we present preliminary geochemical and mineral chemistry data for hydrothermal ore and alteration minerals of the deposit. They will make a basis for further combination with agile exploration methods and better geo-modeling of the deposit.

Regional position and geological setting of Assarel porphyry copper deposit

Most of the world's economically important magmatic-hydrothermal porphyry Cu (±Au±Mo) and epithermal Au±Ag±Cu deposits are genetically related to magmatic arcs (Sillitoe, 2010). In Southeastern Europe, the Late Cretaceous Apuseni-Banat-Timok-Srednogorie (ABTS) belt represents the westernmost arc in the Alpine-Himalayan orogenic system related to the subduction of Neotethys (Popov et al., 2002; von Quadt et al., 2005). This magmatic arc extends over 1000 km length from the Apuseni Mountains in Romania, through Serbia and Bulgaria to the Black Sea, and further east to Iran.

The Bulgarian part of the ABTS belt is known as the Srednogorie magmatic/metallogenic zone, and it is an 80- to 100-km wide, east-west oriented tectono-magmatic unit situated between the Balkan Zone to the north and the Rhodope Massif to the south. The most mineralized Central Srednogorie segment of the zone, called also the Panagyurishte Ore District (Popov et al., 2002), consists of an NNW-SSE trending alignment of porphyry and epithermal Cu-Au deposits situated 60 to 90 km east of Sofia. The basement of the Central Srednogorie is Cadomian to Variscan in age. It is built up by metamorphic rocks (mainly gneisses, gneiss-schists and amphibolites) with Paleozoic and older protoliths and 330–340 Ma high-grade metamorphic overprint (Carrigan et al., 2005, 2006; Lazarova et al., 2015). They are intruded by Variscan granitoids and gabbros at 314–305 and at ≈290 Ma (Carrigan et al., 2006; Peytcheva, von Quadt, 2004) and intruded and overlain by calk-alkaline magmatic rocks with Late Cretaceous age (intrusives/shallow intrusives, volcanics, and volcaniclastics/epiclastics) in shallow marine sedimentary basin. The main late Alpine compressional event in the Sredna Gora Zone was related to the closure of the intra-arc/back-arc basins at the end of Maastrichtian–middle Eocene and formation of mostly NW-SE trending regional fold and fault structures. The post-magmatic/metalogenic tectonics is crucial for understanding the displacement of the ore system and has significant exploration importance.

More than 150 ore deposits and occurrences are known in the Panagyurishte district, mostly consisting of porphyry copper and coeval high-sulfidation Cu-Au epithermal types (e.g., Popov et al., 2012). The Assarel porphyry copper deposit is one of the biggest operating mines in the area, with resources of 467 Mt ore at an average grade of 0.32% Cu and 0.12 ppm Au (Milev et al., 2007). The ore formation is related to the successive intrusion of pre- and syn- to post-ore shallow magma bodies and dykes of mainly intermediate composition. Several hydrothermal mineral assemblages have been identified: early quartz-magnetite-hematite; quartz-pyrite-chalcopyrite main Cu-bearing mineral association, related to propylitic, sericitic and transitional sericitic-propylitic alterations, which occur as veinlets, small nests and disseminations in the host rocks; quartz-molybdenite association mainly related to the propylitic alteration; quartz-pyrite association, locally occurring in veins and veinlets; quartz-sphalerite-galena (pyrite, chalcopyrite) association, occuring as veins in the upper and marginal parts of the deposit; a supergene alteration assemblage, containing variable amounts of chalcocite, covellite, and Fe-hydroxide. Specific rare (Cu-Au-Te and Cu-Ag-Bi-Te with Se, Pb, and Zn) associations are described by Petrunov et al. (1991).

The Assarel porphyry copper deposit is challenging in terms of mineralogical and geochemical predictability. This is due to the fact that there are secondary enrichment zones, extensive alteration zones with significant argillic to advanced argillic alteration, and complicated structures, such as pre-, syn- and post-ore normal faults. One of the latter (the Mialski fault) displaced the eastern part of the deposit and resulted in the exhumation of basement rocks with cross-cutting subvolcanic dikes, exposing these on the same level as the volcanics in the western part. Other important post-mineralization structure is the so called Raslatitsa fault.

Sampling and analytical methods

Samples for the present study were collected from the Assarel open pit and exploration drillcores as well as from the flotation plant. For SEM-EDS definition of the major elements in minerals, the JEOL JSM-6610 LV scanning electron microscope at the University of Belgrade (Faculty of Mining and Geology) was applied. The LA-ICP-MS analyses of trace elements were performed at the Geological Institute of BAS using an NW excimer laser connected to DRC-e PE system. SILLS software (Signal Integration for Laboratory Laser Systems) was applied for data reduction.

Results and conclusions

Our preliminary studies on the CRMs potential of the Assarel deposit (Fig. 1) reveal high concentrations of several trace elements (some of them CRMs) in some ore and alteration minerals. In the studied pyrite, Co contents are up to 1000–1630 ppm, whereas galena features Se concentrations of 2–3 wt%. Molybdenite is not evenly distributed and is the main carrier of Mo and Re, but the content of the latter varies from

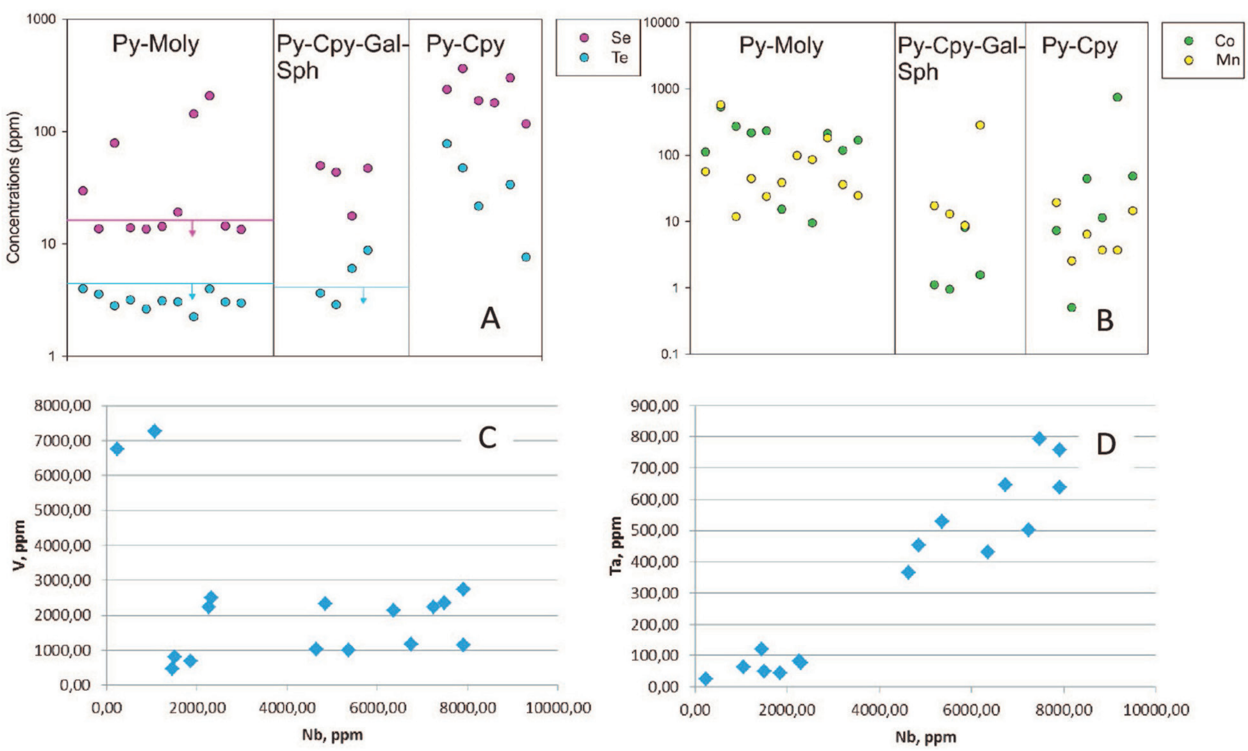

Fig. 1. Distribution of selected elements in pyrite (*A–B*) and hydrothermal rutile (*C–D*) of the Assarel porphyry-copper deposit. Abbreviation of hydrothermal mineral assemblages used on A–B: Py-Moly, pyrite-molybdenite association; Py-Cpy, pyrite-chalcopyrite association; Py-Cpy-Gal-Sph, pyrite-chalcopyrite-galena-sphalerite association. The lines with an arrow in Fig. 1A show the limit of detection during the LA-ICP-MS analyses.

600 to 45 790 ppm. From the alteration minerals, hydrothermal rutile concentrates trace elements like V (110–6700 ppm), Nb (2300–4600 ppm), Ta, W, and Sc; epidotes and APS (aluminium-phosphate-sulphate) minerals have elevated contents of REE, whereas hydrothermal chlorite (the Ti/Sr ratio) could potentially be used as an exploration fingerprinting tool.

Recent studies by Cioacă et al. (2020) indicate the occurrence of Au-, Ag-, Bi-, Te-, and Se-bearing minerals as minute inclusions in pyrite and chalcopyrite from the main chalcopyrite-pyrite ore assemblages and in the upper epithermal and supergene alteration zones. Platinum-group elements are scarce and reported as rare Pd-bearing tellurides occurring in pyrite. Our studies confirm the presence of the associations Cu-Au-Te and Cu-Ag-Bi-Te with Se, Pb, and Zn but there is no data yet available about their distribution in the deposit.

Along with the geochemical studies of the hydrothermal ore and alteration minerals, we also followed the behavior of the CRMs during the crushing and flotation at the conditions of the applied technology at Assarel-Medet JSC. Some elements follow Cu and Au to the final concentrate, whereas others are concentrated preferentially in the waste (e.g., cobalt), or in the intermediate products.

In the frame of the AGEMERA project new data on the spatial distribution of CRMs in ore and alteration minerals of Assarel deposit will be acquired. They will be linked with additional structural studies and innovative geophysical methods to result in an improved deposit model and enhanced knowledge about fast and effective exploration techniques of CRMs in the porphyry systems.

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