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Preliminary data on the mineral chemistry of garnet from the skarn alteration associated with the Elatsite porphyry-copper gold deposit, Bulgaria

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Предварителни данни за химичния състав на гранат от скарнови промени, асоцииращи с медно-порфирно златно находище Елаците, България

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Abstract. The skarn alteration is poorly preserved at the Elatsite, restricted to the hornfelses from the East, Southeast and Southern part of the deposit. The rocks are defined as exoskarns, with a mineral composition including garnets, epidote, pyroxene, amphiboles, carbonates, prehnite, quartz, sulphides. The newly formed minerals occur in poorly preserved layers. The garnet grains are subhedral with inclusions of epidote and quartz, while some of them are corrode with carbonate and zeolites formed in the fractures. The garnets are grossular-andradite type, with higher values for HREE over LREE, and low values for Rb, Sr, Ba, Pb and U. The skarn formation is related with the intrusion of the magma which causes the heating of the metamorphic rocks (rich in carbonate material – chlorite-sericite-carbonite, sericite-carbonate schists, etc.) from the low-grade metamorphic rocks. The Fe^{+3}–Al^{+3} exchanges in the cores of the garnets indicate their formation from fluids with high oxygen fugacity.

Keywords: skarn formation, porphyry deposits, garnet.

Introduction

The Elatsite porphyry-copper gold deposit (PCGD) is one of the largest operating open pit mines in Bulgaria. It has been -in exploitation since 1983–1984 with more than 255 390 tons ore with Cu content 0.388% extracted until the end of 2008 (Georgiev, 2009).

During the years of exploitation, multiple researchers have worked at the deposit, but with the progressing exploitation and new prospecting drillings in deeper parts of the hydrothermal system a lot of new information is collected. Assumptions about the presence of skarn mineralization in the Elatsite deposit were expressed by Prof. Zhivko Ivanov in several industrial reports and oral communications. Before that, Kanazirski (in Popov et al., 2000) mentioned a limited skarn formation around the low-grade metamorphic schists and phyllites of the Berkovitsa Group of the Diabase-Phyllitoid complex – and Lazarova (2007) described a skarn formation in the halo around the Vezhen pluton outside

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the open pit, with mineral composition presented by epidote and garnets and multiple epidote and feldspar veins. During the last years a skarn alteration in the Elatsite deposit was defined based on detailed petrographic investigations and geochemical mineral analyses.

The current work is dedicated to the occurrence and characterization of garnet minerals from the skarn mineralization in the Elatsite PCGD, their redistribution and mineral chemistry.

Geology

The Elatsite PCGD is situated at the most northern part of the Panagyurishte ore region which is a part of the Apuseni-Banat-Timok-Srednogorie Late Cretaceous copper belt (e.g. Popov et al., 2002). The geology of the deposit consists of a Variscan basement, intruded by Upper Cretaceous magmatic subvolcanic to hypabyssal dykes and dyke-like intrusive porphyritic bodies. The main porphyritic rocks are presented by quartz-monzodiorites, granodiorites as well as quartz-diorites (e.g von Quadt et al., 2002). The basement comprises low-grade Paleozoic variegated schists intruded by the Upper Carboniferous Vezhen granitoid (mainly granodiorite) pluton (e.g. Lazarova, 2008; Georgiev et al., 2020). At the contact of the Vezhen pluton with the metamorphic rocks different hornfelses and mottled schists are formed (e.g. Kalaidziev et al., 1984, Lazarova, 2008).

The hydrothermal alteration products are represented by propylitic, K-silicate, K-silicate-sericitic, sericitic (e.g. Kanazirski et al., 2002), phyllic-argillic (Tarkian et al., 2003), argillic (Kehayov, 2005; Georgiev, 2019) and quartz-adularia-carbonate alterations (Ivanov et al., 2014) and calcic-potassic alteration (Georgiev, 2019). Our new investigation characterizes Na-Ca alteration (rare in the deposit), Na-Ca-K-silicate (transitional between Na-Ca and K-silicate alteration) and skarn alteration (Georgieva et al., 2019).

Materials and methods

Garnet from drillhole GP-10 was studied in two samples. Standard petrographic observations were combined with optical cathodoluminescence (Cold-CL) imaging. Cold-CL images were obtained using a CATHODYNE optical cathodoluminescence system (NewTec Scientific, France) at the Geological Institute of the Bulgarian Academy of Sciences. JEOL JSM 35 CF at "Eurotest-Control" EAD, Sofia, Bulgaria was used for determination of a major element composition of minerals with EDS (100 seconds for spectra acquisition, at 15 KEV acceleration voltage, using natural and synthetic standards, EDX-TRACOR NORTHERN TN-2000). LA-ICP-MS technique was applied to determine minor and trace elements in garnets. The used LA-ICP-MS system at the Geological Institute of the Bulgarian Academy of Sciences consists of a Perkin Elmer-ELAN DRC-e spectrometer (Perkin Elmer, Canada) with 193 nm ArF excimer laser (ATLEX-LR, Germany). The internal standard (SiO_2) is from the microprobe analyses of the respective minerals. The laser system operated at constant 8 Hz pulse rate and laser energy 1.80–2.60 J/cm^2 on the sample surface for 25 to 35 μm spot size.

Results

Petrography

The formation of the skarn alteration is revealed in drillholes from the East, Southeast and Southern part of the deposit, where it occurs in the hornfelses. The rocks are knotted schists with partial preservation of the schistosity, and the skarn alteration is developed with different intensity. Metamorphic minerals (biotite, chlorite, andalusite, amphibole, quartz and feldspar) are preserved in some places, and newly formed minerals are usually in layers. With the increasing intensity of the skarn alteration the hydrothermal minerals replace metamorphic ones. Metamorphic amphibole is replaced by epidote, while the andalusite porphyroblasts are completely replaced by the newly formed minerals.

The knotted schists and the skarns are cross-cut by a multiple diversity of veins: amphibole-epidote; fine epidote veins with sulphides; thicker – monomineral epidote veins (up to 6–8 mm); pyroxene veins; zeolites or carbonate veins.

The mineral composition of the skarn alteration is established as garnet, epidote, pyroxene, carbonate, prehnite, quartz, amphiboles and a few sulphides. These minerals occur in layers with partial preservation of the schistosity. With the increasing intensity of the process, they are forming parallel stripes, as their occurrence is related to certain layers of the metamorphic rock (containing more carbonate) (Fig. 1A).

The garnets predominate in the intensely skarn areas and with the decreasing intensity the grains move apart, and the participation of the other skarn minerals predominate. The garnet grains are subhedral with inclusions of epidote and quartz (Fig. 1B.). Few of the grains are fractured and corroded and carbonate minerals and zeolites are formed in the fractures.

Cathodoluminescence images reveal slight zonation in the garnet grains (Fig. 1C) with darker cores and lighter rims.

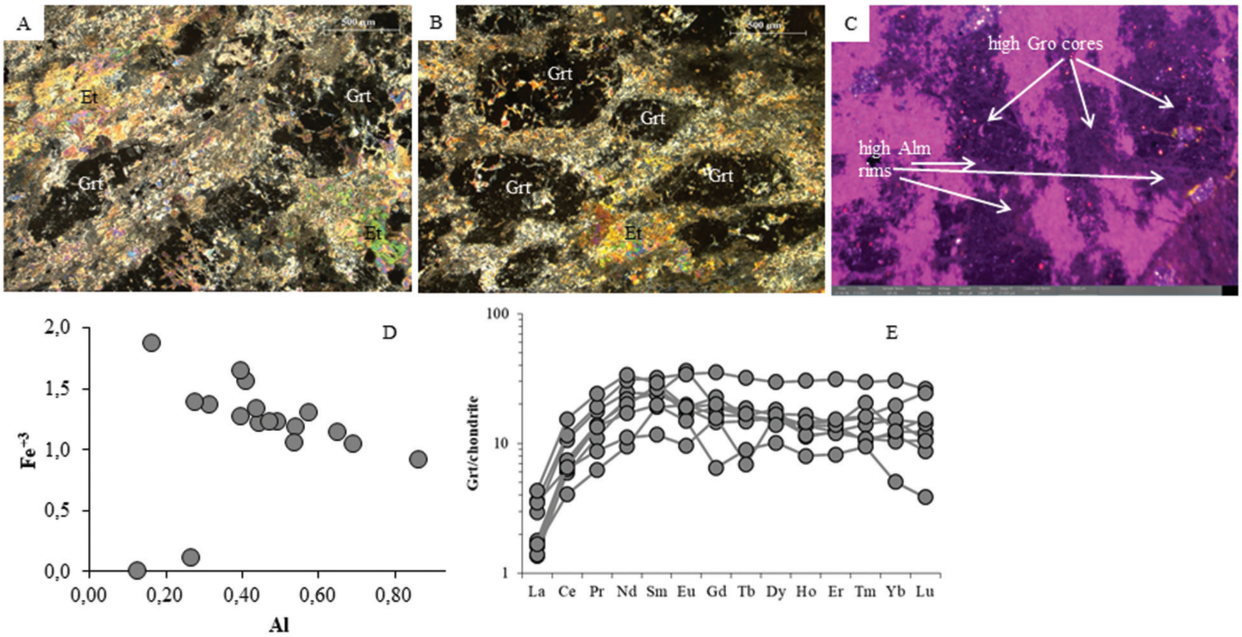

Fig. 1. *A* and *B*, microphotography of layered-formed garnet grains with epidote in the skarns; *C*, cold-CL image of garnets; *D*, graphic construction of Fe^{+3}–Al^{+3} exchange in garnets; *E*, chondrite-normalized REE-distribution pattern in garnets (norm. after Boynton, 1984)

Mineral chemistry of garnets

The garnets are defined as grossular-andradite with Gro component (15.66–43.26), andradite (45.97–76.89) and an Alm component (3.76–8.02). The positive Fe^{+3}–Al^{+3} exchange is present (Fig. 1D) which is typical for the garnets from grossular-andradite varieties. In the core, higher values for the andradite component are established, while the rims show slightly higher Alm component.

The REE-distribution pattern (Fig. 1E) shows higher concentration of HREE over LREE, and La_N/Yb_N ratio between 0.11–0.20 for all the grains, but slightly higher values for REE in the cores over the rims of the garnets. All garnets have low values for Rb, Sr and Ba, and very low values for Pb and U (that does not allow the age determinations).

Discussions and conclusions

At this stage of the deposit exploitation, skarns are revealed at limited places. As already been mentioned they are observed in drillholes from the East, Southeast and Southern part, in the hornfelses. The occurrence of the skarn alteration is probably related to the circulation of water from the metamorphic basement (rich in carbonates) during the emplacement of the magma. Such formation mechanism has been proposed by several authors (e.g. Mollo et al., 2009). Inhomogeneity of metamorphic rocks and the variable content of the carbonate material caused layered occurrence of skarn alteration. The formation of the garnet minerals is related with carbonate rich layers.

The Fe^{+3}–Al^{+3} exchange present at the cores of the garnet grains shows a formation from fluids with high oxygen fugacity during the early stage. The presence of a slightly higher almandine component (Alm up to 8.02) in the rims, probably indicates changes in the redoxy conditions in the later stage of skarn formation.

The petrography of the garnets reveals that the grains are fractured and corroded, and the fractures are filled with later materials (zeolites and carbonates). This is probably related to later hydrothermal activity affecting the rocks, leading to the formation of multiple veins with diverse mineral composition.

The time formation of the skarn alteration in the Elatsite deposit is a problem that cannot be solved by the available data. The low content of U in the analyzed garnets makes these minerals inappropriate for age dating. The studied skarn alteration is associated with the rocks of the Upper Carboniferous Vezhen granodiorite pluton and no direct connection to the Upper Cretaceous rocks is observed. In general, the skarn alteration stays as a halo around the pluton and according to data from Lazarova (2007, 2008) the skarn formation outside the open pit is related to the emplacement of the Vezhen pluton. We can assume that the time of formation of the skarn mineralization associated with the Elatsite deposit will be similar to the described by Lazarova (2007, 2008), but to be excluded a genetic relation with the Late Cretaceous magmatism requires reliable isotope dating techniques in the future.

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References

Boynton, W. 1984. Cosmochemistry of the rare earth elements: Meteorite studies. – In: Henderson, P (Ed.), *Rare Earth Element Geochemistry.* Amsterdam, Elsevier, 63–114; https://doi.org/10.1016/B978-0-444-42148-7.50008-3.

Georgiev, G. 2009. Ore mineral association in porphyry copper deposit Elatsite and their relationships whit wallrock alterations (part 2). – *Geol. Miner. Resour*., *4*, 24–31 (in Bulgarian with English abstract).

Georgiev, G. 2019. *Hydrothermal Metasomatites in Elatsite Porphyry Copper Deposit*. Sofia, Scientific and Technical Union of Mining, Geology and Metallurdy, 100 p.

Georgiev, S., I. Gerdjikov, I. Peytcheva, P. Makaveev, 2020. Time frame of the Carboniferous tectonic and magmatic activity in the area of Vezhen pluton, Bulgaria. – *Rev. Bulg. Geol. Soc*., *81*, 3 (Geosciences 2020), 72–74.

Georgieva, H., R. Nedialkov, I. Krumov. 2019. Hydrothermal amphiboles from Na-Ca and Na-Ca-K-silicate alterations: An example from Elatsite porphyry copper-gold deposit, Bulgaria. – In: *Proceedings of Geologica Carpathica*, *70*, Smolenice, October 2019, 65–68.

Ivanov, Zh., R. Nedialkov, K. Bogdanov. 2014. Magmatic and ore-related breccias in the Elatsite porphyry-copper deposit (PCD), Bulgaria. – In: *Proceedings of XX CBGA Congress.* Tirana, Special Issue, 158–161.

Kalaidziev, S., G. Hadziiski, K. Angelkov. 1984. Structural conditions for localization of porphyry copper deposit Elatsite – *Rev. Bul. Geol. Soc*., *45*, 2, 189–196 (in Bulgarian with English abstract).

Kanazirski, M., S. Chipchakova, M. Gorova, R. Arnaudova. 2002. Wallrock alterations in the porphyry copper deposits of the Panagyurishte ore district and formation–facial belonging of the metasomatites. – *Geologica Balc*., *32*, 77–80. https://doi.org/10.52321/GeolBalc.32.2-4.77.

Kehayov, R. M. 2005. *Mineral Association of Gold and Conditions of Their Formation in Copper-porphyry Deposit Elatsite.* PhD Thesis, Sofia University, 208 p. (in Bulgarian).

Lazarova, A. 2007. *Structure, Emplacement Settings and Tectonic Position of the Vezhen Pluton*. PhD Thesis, Sofia University, 180 p. (in Bulgarian).

Lazarova, A. 2008. Shallow-crustal post-tectonic emplacement of Vezhen pluton, Central Stara planina Mountains. – *C. R. Acad. Bulg. Sci.*, *61*, 10, 1315–1322.

Mollo, S., M. Gaeta, C. Freda, T. Di Rocco, V. Misiti, P. Scarlato. 2010. Carbonate assimilation in magmas: A reappraisal based on experimental petrology. – *Lithos*, *114*, 503–514; https://doi.org/10.1016/j.lithos.2009.10.013.

Popov, P., R. Petrunov, V. Kovachev, S. Strashimirov, M. Kanazirski. 2000. Elatsite-Chelopech Ore field. – In: Strashimirov S., Popov P. (Eds.), *Geology and Metallogeny Features of the Panagyurishte Ore Region (Srednogorie Zone, Bulgaria)*. ABCD-Geode 2000, Workshop, Borovets, Bulgaria, 8–18.

Popov, P., T. Berza, A. Grubic, I. Dimitru. 2002. Late Cretaceous Apuseni-Banat-Timok-Srednogorie (ABTS) magmatic and metallogenic belt in the Carpathian-Balkan Orogen. – *Geologica Balc*., *32*, 2–4, 145–163; https://doi.org/10.52321/GeolBalc.32.2-4.145.

Tarkian, M., U. Hünken, M. Tokmakchieva, K. Bogdanov. 2003. Precious-metal distribution and fluid-inclusion petrography of the Elatsite porphyry copper deposit, Bulgaria. – *Miner. Deposita*, *38*, 261–281; https://doi.org/10.1007/s00126-002-0336-x.

von Quadt, A., I. Peytcheva, B. Kamenov, L. Fanger, A. Heinrich, M. Frank. 2002. The Elatsite porphyry copper deposit in the Panagyurishte ore district, Srednogorie zone, Bulgaria: U-Pb zircon geochronology and isotope-geochemical investigation of the magmatism and ore genesis. – In: Blundell, D. J., F. Neubauer, A. von Quadt (Eds.). *The Timing and Location of Major Ore Deposits in an Evolving Orogeny.* London, Geol. Soc. Spec. Publ., 204, 119–135; https://doi.org/10.1144/GSL.SP.2002.204.01.08.