

BARITE MINERALISATION IN THE AREA OF THE *OBICHNIK* ORE DEPOSIT, THE EASTERN RHODOPE, BULGARIA (PRELIMINARY DATA)

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ABSTRACT. The study presents the results of a mineralogical and geochemical analysis of barite containing samples from the area of the *Obichnik* Au-Ag deposit (Kardzhali region). The *Obichnik* epithermal deposit is in the Southeastern Rhodopes. It is part of the Zvezdel-Pcheloyad ore field, which includes hydrothermal Pb-Zn, Au-Ag, and Au-Pb-Zn deposits and mineral occurrences associated with the Oligocene Zvezdel volcano. The ore mineralisation is hosted by felsic, intermediate to mafic volcanics, volcano-sedimentary, and intrusive rocks. The aim of the present study is to determine the mineral composition in samples containing barite from the deposit associated with ore mineralisation, and barite raw material vein type mineralisation in the periphery parts of the deposit. Optical microscopy and XRD methods were used.

Key words: barite, ore deposits, critical raw materials, the Rhodope massive.

БАРИТНА МИНЕРАЛИЗАЦИЯ В РАЙОНА НА РУДНОТО НАХОДИЩЕ „ОБИЧНИК“, ИЗТОЧНИ РОДОПИ, БЪЛГАРИЯ (ПРЕДВАРИТЕЛНИ ДАННИ)

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РЕЗЮМЕ. Изследването представя резултати от минералогични и геохимични анализи на образци от барит-съдържаща минерализация в района на златно-сребърното находище „Обичник“ (Кърджалийско). Епитермалното находище, попада в югоизточните Родопи и е част от Звездел-Пчелоядското рудно поле, включващо Pb-Zn, Au-Ag и Au-Pb-Zn находища и рудопроявления. Те са свързани с магматата дейност на Олигоценския Звезделски вулкан. Рудните минерализации в района са поместени в кисели, средни до базични по състав вулкански, вулcano-сидиментни и интрузивни скали. Целта на настоящото изследване е да се определи минералния състав на баритната минерализация, както в пределите на епитермалното находище Обичник – асоциираща с орудяването, така и баритната жилната минерализация в периферните му части. За целта са проведени микроскопски изследвания, при ползване на отразена и проходяща светлина, както и XRD.

Ключови думи: барит, рудни находища, суровини от критично значение, Родопски масив.

Introduction

The *Obichnik* Au-Ag epithermal deposit is located about 220 km southeastern of Sofia and about 25 km of the regional town of Kardzhali. It is situated in the East Rhodope unit of the Morava-Rhodope zone. The unit is built up by high-grade metamorphic basement, Late Cretaceous intrusive bodies, Paleogene shallow marine sediments, associated with dominantly acid, and intermediate volcanic and volcano-sedimentary rocks (Fig. 1B) (Dabovski et al., 2002).

The *Obichnik* ore deposit is situated in the northern part of the Zvezdel-Pcheloyad ore field, which includes hydrothermal lead-zinc, gold-lead zinc, and gold-silver deposits and mineral occurrences associated with the Oligocene Zvezdel volcano-plutonic complex (Georgiev, 2012; Popov and Popov, 2022). The deposit is situated to the north of the village of Obichnik and to the east of the village of Drumche. The Obichnik gold-silver mineralisation is associated mainly with pyrite, sphalerite, galena, chalcopryite, tennantite-tetrahedrite, and enargite, with gold variably distributed within these sulphides and quartz, sericite, kaolinite, illite/smectite, and adularia (Petrova and Stanchev, 1994).

The ore bodies come in two types - isometric (unclearly tubular) and sub-horizontal stratiform according to their deposition format and conditions. The ore-forming process in the Obichnik area is in two-stages: gold-bearing quartz-sulphide and carbonate (Dragiev and Dragieva, 2010).

Barite (barite) is naturally occurring BaSO_4 . Its solid solution series with celestine (celestite) $\text{SrSO}_4 - (\text{Ba},\text{Sr})\text{SO}_4$ occur in diverse geological environment and over a long period of geological time from the Archaen to present. Barium can be substituted isomorphously by strontium and calcium. Barite is inert and non-toxic. It has high density (4.5), low hardness 2.5-3.5 (on the Mohs scale), and low oil absorption. Barium occurs in the Earth's crust mainly as divalent cation Ba^{2+} . Because of its large size, barium is not easily accommodated in common rock-forming minerals except in minor content in feldspars and micas in some cases, where it substitutes K^+ .

The main part of barite deposits in Bulgaria are located in the Srednogorie zone - related mainly to Late Cretaceous magmatism and Moravo-Rhodipe zone – related mainly to Oligocene magmatism (tectonic zones are after Dabovski et al., 2002, Figure 1B). The biggest part of extracted barite in Bulgaria in the second half of the 20th century came from the Stara Zagora (open pit) and the Kashana (underground) deposits and later from the Kremikovtsi (open pit) mines. The largest part of mined barite in Bulgaria was exported. More than 75 barite deposits were in operation in Bulgaria during the previous century (Andreevich et al., 1989).

The aim of this investigation is to determine the mineral composition of the barite raw material from the area of the *Obichnik* Au-Ag epithermal deposit and to present our ideas about its genesis.

The present study reports new geological and mineralogical data on the mineral composition of barite raw material.

Barite production and application

Barite has been part of the list of critical raw materials according to the European Commission (European Commission, Study on the EU's list of Critical Raw Materials, 2020) since 2016. About 60% of barite consumption is for weighting agent in oil and gas drilling fluids (drilling-grade barite), about 30% is for fillers in rubber, plastic, paint, and paper production, and about 10% goes to the chemical industry. The leading world suppliers of barite are China (about 40% of the world production), followed by India, Morocco, United States, Iran, and Kazakhstan. In the EU, the only mining activities are in Germany (primary) and Bulgaria (reworking tailings) (European Commission, Study on the EU's list of Critical Raw Materials, 2020). The drilling grade barite is produced from commercial barium sulphate raw material. It can contain various minerals in addition to barite, and commercial products can vary in colour from white to red or brown. Barite application in oil and gas drilling fluids is to increase the density of these solutions in order to control wellbore pressure, stabilising the borehole, and preventing blowouts. Some of the properties of commercial drilling grade barite are: specific gravity of 4.2 or higher and, content of BaSO₄ of 90 % or higher.

Geological setting and mineralisation

The *Obichnik* Au-Ag epithermal deposit is situated in the Morava-Rhodope zone of the Balkan orogenic system and its East Rhodope tectonic unit according to the tectonic scheme of Dabovski et al. (2002, Figure 1B). The unit is built up by high-grade metamorphic basement, Late Cretaceous intrusive bodies, Paleogene shallow marine sediments, associated with dominantly acid and intermediate volcanic and volcano-sedimentary rocks (Dabovski et al., 2002). During the Late Cretaceous–Eocene, the region experienced subduction-collision events. The late Eocene-Oligocene magmatism is represented by volcano-plutonic rocks. Late Cretaceous–Palaeocene magmatism is represented exclusively by intrusions composed of amphibole-biotite, biotite- and two-mica granites, and granodiorite. In contrast, Late Eocene–Oligocene magmatism is represented by volcano-plutonic suites and intrusions with largely variable K and Si content (Marchev 2007). Epithermal deposits in the area are associated with magmatic rocks (Georgiev, 2012; Popov and Popov, 2022).

The *Obichnik* Au-Ag epithermal deposit is situated in the northern part of the Zvezdel-Pcheloyad ore field, which includes hydrothermal lead-zinc and gold-lead-zinc mineral deposits and occurrences associated with the Oligocene Zvezdel volcano-plutonic complex (Georgiev, 2012; Popov and Popov, 2022). The Zvezdel volcano is considered a stratovolcano (Nedialkov and Pe-Piper 1998, Yanev et al., 1998) with parasitic and satellite volcanic vents and domes. The volcano structure is composed of lava flows intercalated with epiclastic and rare pyroclastic rocks and cut by domes and dykes (Figure 1A). The Zvezdel volcanic rocks are predominately high-K calc-alkaline, ranging in composition from basalts to andesites and dacites (Raicheva and Marchev, 2014). The host rocks in the *Obichnik* area are presented by a suite over 300 m thick consisting of epiclastics (mud flow products) in alternation with autobrecciated to massive andesites, pillow-bearing flows-foot breccias, and probably some pumice (Kunov et al., 1994). The epiclastic rock contains mainly various crystalloclasts and

lithoclasts of hydrothermal altered and nonaltered andesites and are of up to 10 cm in size. They are cut by several volcanic bodies and dykes of pyroxene andesites to basaltic andesites. The autobreccias consist of andesitic fragments of up to 15 cm, and some cement (Fig. 2A). The *Obichnik* deposit is in the outward part of an eroded Paleo-Zvezdel volcano of probably Priabonian age (Kunov et al., 1994). The rock fractures are filled by quartz and adularia ($\pm$ clay minerals, carbonates, sericite, or barite). The quartz is represented by 2 generations: 1. coarse-grained crystallised at about 260–300 °C, and fine-grained – 230–250 °C – according to the homogenisation of the gas-fluid inclusions (Kunov et al., 1994).

According to the hydrothermal alteration products the *Obichnik* epithermal deposit is referred to adularia-sericite or low-sulphatisation Au-Ag type by Kunov et al. (1994).

Over 60 rock-forming, ore, and secondary minerals occur in the deposit (Kunov and Mandova, 1997). The gold mineralisation is associated mainly with pyrite, sphalerite, galena, chalcopyrite, tetrahedrite-tennantite, and enargite, with gold being unevenly distributed within these sulphides, quartz, sericite, kaolinite, illite/smectite, and adularia (Petrova, Stanchev, 1994).

The *Obichnik* deposit can be considered as epithermal adularia-sericite type Au-Ag mineralisation with quartz-sulphide gold-bearing and carbonate phases in the hypogene stage (Kunov and Mandova, 1997).

Materials and analytical techniques

The ore samples were collected from exploration drill holes in the *Obichnik* Au-Ag epithermal deposit. More than 30 polished sections have been prepared for examination in reflected light. They were investigated under reflected light with a *Leica DM2500P* microscope. The microphotographs illustrating mineral composition, relationships, and textures were taken with a *Leica DFC295* integrated digital camera, CMOS type sensor, and lens magnification from $\times 4$ to $\times 50$. The same also served to more precisely identify interesting mineral grains subject to microprobe analysis. The electron microprobe analyses were done with a JEOL JSM-6010 PLUS LA X-ray spectral micro analyser, with an EDS spectrometer at the University of Mining and Geology “St. Ivan Rilski”, Sofia, Bulgaria. The mode of operation is determined by the following analytical conditions: 20 kV accelerating voltage, 30 Pa pressure, and high vacuum. No standards were used.

The samples from hydrothermal barite vein type mineralisation were collected from exploration trenches located in the periphery of the *Obichnik* Au-Ag epithermal deposit. The prepared thin sections were analysed using a *Meiji* polarising microscope and an *Olympus 5060* digital camera in the Optical Laboratory for Minerals and Rocks at the University of Mining and Geology “St. Ivan Rilski”.

The measurements of one powdered sample of barite were performed on a *Bruker D2-Phaser X-Ray* powder diffractometer. The conditions which were applied during the measurements were the following: Cu radiation with wavelength $\lambda = 1,54184$, current - 10 mA, voltage - 30 kV, increment 0.02° in the interval of 2 θ 5–90° for 30 min of gathering diffraction data. The measurements were performed at the Laboratory of Powder Diffraction at the University of Mining and Geology “St. Ivan Rilski”.

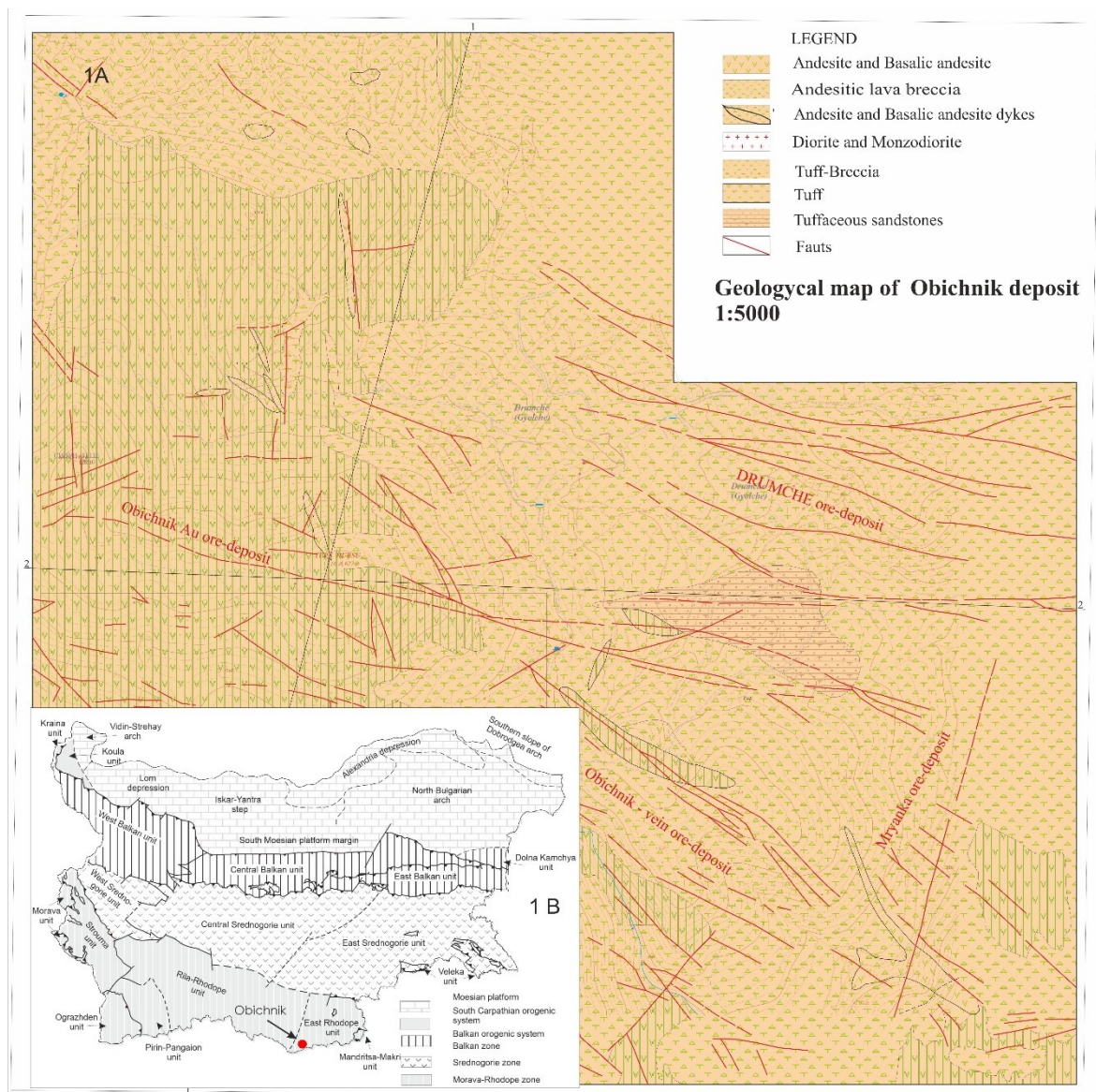
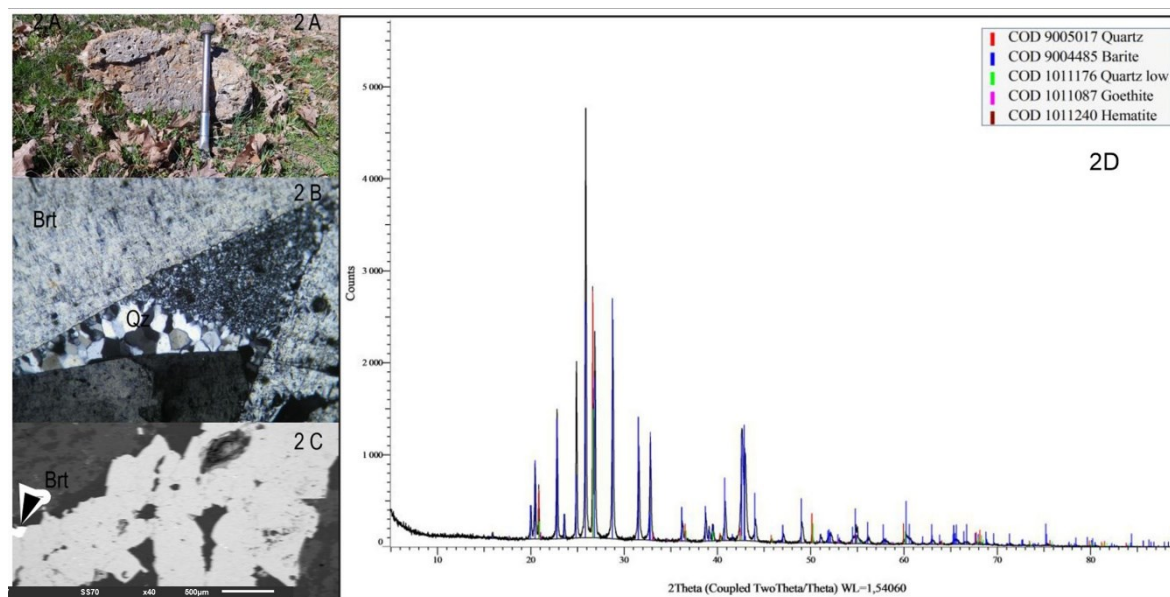


Fig. 1. A. Geological map of the area of the *Obichnik* Au-Ag epithermal deposit, 5 000 scale, after Dragiev and Dragieva (2010). B. Tectonic scheme of Bulgaria, after Dabovski et al., 2002.



Results and discussion

The main ore minerals in the Obichnik Au-Ag epithermal deposit are: pyrite, marcasite, galena, sphalerite, and chalcopyrite. The gold mineralisation is represented by grains from several μm to about 100 μm (Apostolova et al., 2024), associated with minerals of quartz-sulphide stage, and included or in fractures in coarse-grained pyrite. It is classified as high-grade native gold (between 870 and 915 ‰). Barite is presented as fine grain crystals (about 100 μm – Fig. 2C) in sulphide ore mineralisation associated with pyrite, marcasite, galena, sphalerite, and chalcopyrite, and as coarse crystals (2 to 5 cm in size) associated with quartz, carbonates, and Fe-oxide minerals in the hydrothermal veins located in the periphery of the deposit.

Barite from the vein-type mineralisation from the periphery of the deposit commonly occurs as well-formed crystals and aggregates showing polysynthetic twinning. In thin sections, barite is colourless and non-pleochroic under plane-polarised light (PPL). It exhibits moderate relief and low to moderate first-order interference colours under crossed polars (XPL). The mineral shows perfect cleavage and exhibits straight extinction that is often parallel to the cleavage traces. Under the microscope, barite occurs in association with quartz and chalcedony (?), together with impregnations of iron hydroxides (Figure 2B).

The XRD-analysis from the vein-type mineralisation from the periphery of the deposit shows that the main detected minerals are quartz (two generations high- and low-temperature ones) and barite; ore minerals are also presented by goethite and Fe-oxides (Figure 2D).

Concluding remarks

Barite as small xenomorph crystals (about 100 μm) is present in the ore mineralisation in the Obichnik Au-Ag epithermal deposit. It associates with: pyrite, marcasite, galena, sphalerite, chalcopyrite, quartz, and Fe oxides.

Barite is also presented as well-formed crystals (up to several cm in size) and aggregates showing polysynthetic twinning in association with quartz and chalcedony (?), together with impregnations of iron hydroxides in massive hydrothermal veins in the periphery of the deposit. It could be considered as a potential source of barite raw material after additional exploration activities. To characterise the geological position of barite mineralisation in the area, we plan additional field work and sampling, along with laboratory performing of geochemical and mineralogical investigations.

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References

- Andreevich M., Bozhinov, K., Velinov, I., Grigorov, A., Zhelyazkova-Panayotova, M., Ivanov, I., Kanazirski, M., Katskov, N., Popov, S., Angelov, T., & Trashliev, S. (1989). *Non-metallic mineral deposits in Bulgaria. Vol. 2. Endogenic industrial minerals and rocks*. Technika, Sofia. 260 p. (in Bulgarian with English abstract).
- Apostolova, R., Mladenova, V. & Stoykov, S. (2024). Gold occurrence at the Obichnik ore deposit, Eastern Rhodopes, Bulgaria. *Rev. Bulg. Geol. Soc.*, 85(3). 101-104. <https://doi.org/10.52215/rev.bgs.2024.85.3.101>
- Dabovski, C., Boyanov, I., Khrishev, K., Nikolov, T., Sapounov, I., Yanev, Y. & Zagorchev, I. (2002). Structure and Alpine evolution of Bulgaria. *Geologica Balcanica*, 32, 9-15.
- Dragiev, H. & Dragieva, B. (2010). "The Zvezdel-Pcheloyad ore region". The Momchilgrad and Asara prospect area – Geological report of gold-silver ore with calculation reserves and resources as of 01.12.2010 on the Obichnik, Rudarka and Plovka area. Gorubso Kardjali.
- European Commission, Study on the EU's list of Critical Raw Materials. (2020). Factsheets on Critical Raw Materials. (<http://www.europa.eu>).
- Georgiev, V. (2012). *Metallogeny of the Eastern Rhodope*. "Prof. Marin Drinov" Academic Publishing House (in Bulgarian with extended English summary).
- Kunov, A., Velinov, I., Yanev, Y., Nakov, R. & Stephanov, N. (1994). Adularia-sericite type of wall-rock alternation of the Epithermal Au-Ag mineral occurrence of Obichnik (Eastern Rhodopes, Bulgaria). *Comptes rendus de l'Academie bulgare des Sciences*, 47(8). 61-64.
- Kunov, A. & Mandova, E. (1997). Supergene minerals from Au Ag deposit Obichnik (Eastern Rhodopes). – *Rev. Bulg. Geol. Soc.*, 58(1), 19–24.
- Marchev, P. (2007). Magmatic influence on the zonation of the Paleogene epithermal mineralization in the Central-Eastern Rhodopes, Bulgaria and Greece. – In: *Proceedings 9th Biennial SGA Meeting*, 857–860.
- Nedialkov, R., & Pe-Piper. (1998). Petrology of the volcanism in the southeastern part of Momchilgrad-Arda volcanic region, Southeastern Bulgaria. *Acta Vulcanologica*, 10, 243-253.
- Popov, P. & K. Popov. (2022). *Metallogeny of Bulgaria*. Publ. BMGK Commerce EOOD, Sofia, (in Bulgarian with extended English summary). 426 p.
- Petrova, K. & Stanchev, C., (1994). Mineralogy of the adularia-sericite type epithermal mineral occurrence Obichnik (East Rhodopes, Bulgaria) – *C.R. Acad. Bulg. Sci.*, 47, 61-64.
- Raicheva, R. & Marchev, P. (2014). Mineral diversity, melt inclusions, and gabbroitic xenoliths of the Upper series of the Zvezdel volcano (Eastern Rhodopes): Evidence for mush chamber recharge and magma differentiation. *Bul. Shk. Gjeol. Proceedings of XX CBGA Congress*, 1, 441-444.
- USGS, Department of the Interior. (2022). Final list of critical minerals. Fed. Reg.-list.
- Yanev, Y., Innocenti, F., Maretti, P., & Serri, G. (1998). Upper Eocene-Oligocene Collision-related Volcanism in the Eastern Rhodopes (Bulgaria) – Western Thrace (Greece): Petrologic Affinity and Geodynamic significance. *Acta Vulcanologica*, 10 (2), 279-291.