

# THE Pb-Zn-Ag HYDROTHERMAL-REPLACEMENT AND SKARN DEPOSIT TREPÇA, KOSOVO

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## INTRODUCTION

The Pb-Zn-Ag Trepça mineral deposit (42.9°N, 20.9°E) is situated near the town of Kosovska Mitrovica, 40 km NW from Pristina, Kosovo (Fig. 1). The deposit is related to Tertiary postcollisional magmatism (Cvetkovic et al., 2004) within the Kopaonik block of the Western Vardar zone in the easternmost part of Dinarides (Dimitrijevic, 1997). Numerous lead-zinc-silver, antimony, bismuth and molybdenum, copper, iron, tin, tungsten and gold deposits are present within the Vardar zone. The Pb-Zn-Ag mineral deposits extend northward from Kosovo and southern Serbia (Trepça mineral belt) through western Serbia to easternmost Bosnia. The Trepça mineral belt hosts several skarn, hydrothermal replacement and vein type Pb-Zn-Ag deposits (Fig. 1). The most important are Trepça, Crnac, Belo Brdo, Kisnica, Avajlija and Novo Brdo.

Mining works in this area have begun during the Illyrian time and industrial production started in 1927. In the past 70 years the total ore production reached 32 million tones with average annual production of 580,000 t. According to ITT/UNMIK, 2001 report, the potential ore reserves were estimated as 29 million tones with grades varying from 3.40 to 3.45 % Pb, 2.23 to 2.36% Zn and 74 to 81 g/t Ag.

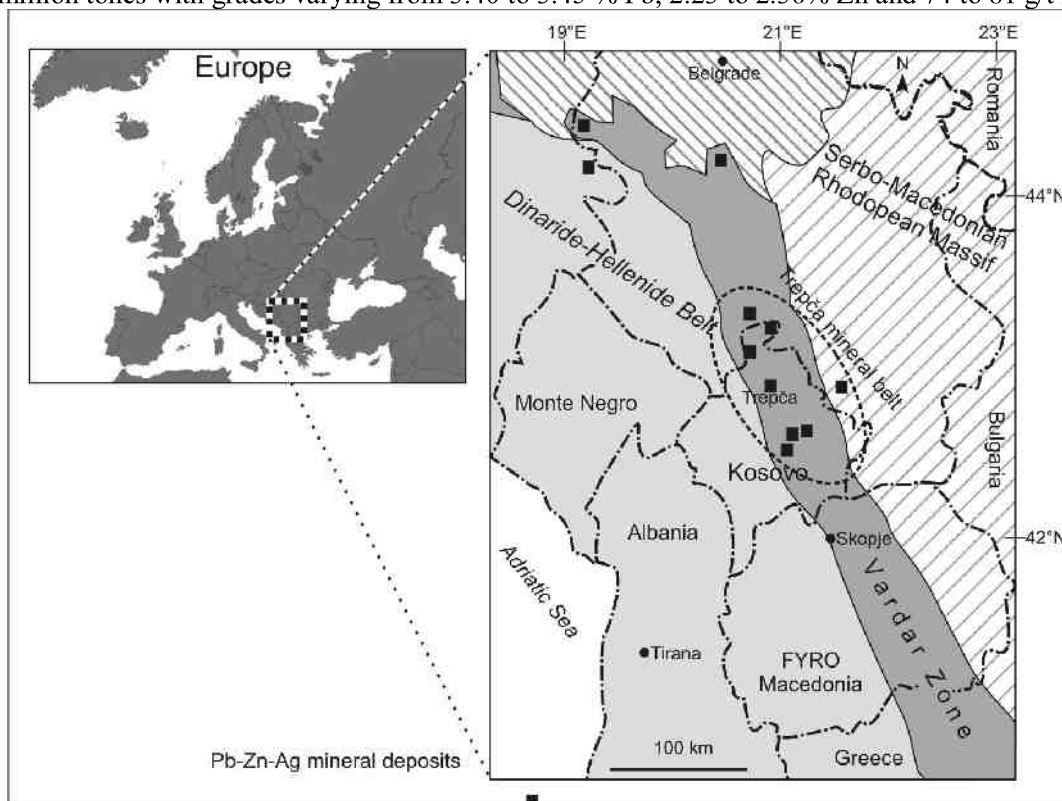


Figure 1. Geographical and geological setting of the Pb-Zn-Ag Trepça mineral deposit within the Western Vardar zone in the easternmost part of Dinarides.

Trepca has been classified as Pb-Zn-Ag high-temperature hydrothermal-replacement and skarn deposit with strict structural control (e.g. Forgan, 1948; Schumacher, 1950, 1954).

A geochemical study of the Trepca deposit, as a part of the ongoing doctoral thesis, comprises host rocks, ore and gangue minerals and associated igneous rocks. Besides, fluid inclusion study on ore and gangue minerals from different stages of mineralization, together with stable isotope data provides P-T-X conditions of the mineralizing processes.

## GEOLOGICAL SETTING

The Trepca mineral deposit is located within metamorphosed and folded sedimentary complex, composed of schists and recrystallized limestones, named “the metamorphic Trepca series” within Kopaonik block of the Western Vardar Zone (Fig. 2). The Western Vardar zone is dominated by ophiolites; remains of the Tethys ocean. The strict structural control on the mineralization processes is evident on the cross-section through the deposit (Fig. 2). The major host rock, principle bearer of the mineralization is recrystallized limestone with paleokarst features. It is placed within the core of an anticline and covered by schists. A nearly circular volcanic pipe transects the limestone-schist contact along the crest of the anticline. The volcanic pipe with trachytic core, surrounded by breccia mantle, is a product of phreatomagmatic volcanism, which pre-dated ore formation. Trachyte core with the form of steeply dipping inverted cone is hydrothermally altered. Breccia mantle is composed of angular to subrounded fragments of country rocks (limestone, schist), fragments of pyrite and pyrrhotite and rounded clasts of trachyte. The contact between breccia and the wall rocks is sharp and at places branches into lateral fractures, filled with rock flour (“milled matrix, fluidized breccia”) or with angular fragments (“jigsaw-fit breccia”).

During the Oligocene-Miocene time, the Trepca area was the location of considerable volcanic activity characterized by numerous lava flows and large masses of volcanoclastic rocks. The volcanic rocks are trachytes, quartz-latites and andesites (Schumacher, 1950; Cvetkovic et al., 2004). Travertine occurrences on the top of the deposit suggest existence of thermal springs at the time of mineralization.

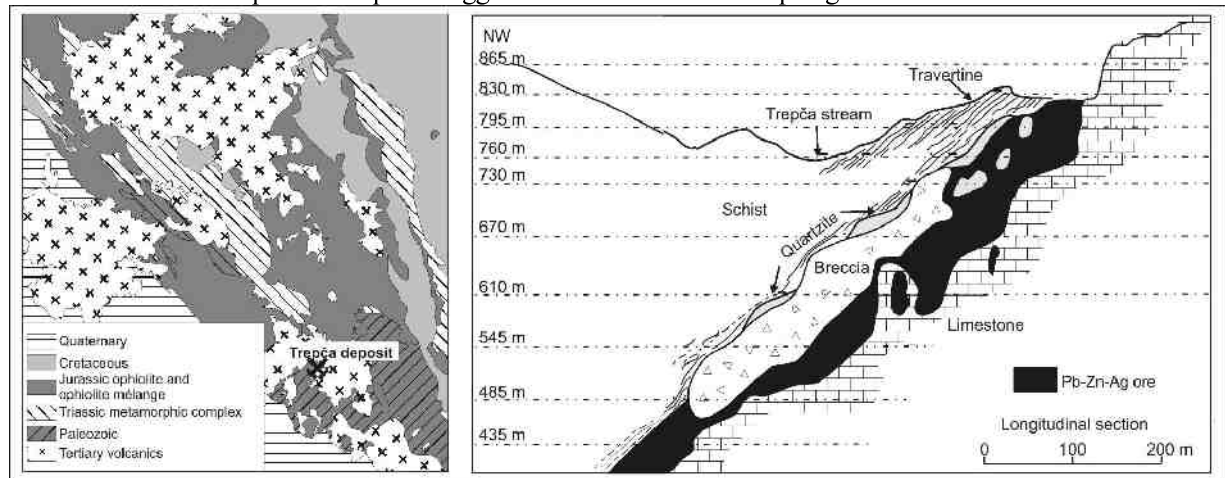


Figure 2. Geological map of the Kopaonik block and longitudinal section through the Trepca deposit.

Mineralization consists of skarn and hydrothermal paragenesis (Fig. 3). The skarn paragenesis with characteristic zonal structure contains calc-silicate minerals (pyroxene, Mn-ilvaite, minor garnet), magnetite, pyrite and pyrrhotite. The zoning pattern is symmetrical about paleokarst system which must have served as the main fluid conduit in the deposit.

The hydrothermal mineral assemblages comprise galena, sphalerite, pyrrhotite, pyrite, marcasite, arsenopyrite and chalcopyrite. The major gangue minerals are carbonates and minor quartz.

Hydrothermal mineralization commonly overprints the skarn mineralization and exhibits open space filling textures with well developed euhedral crystals. Skarn mineralization free of hydrothermal assemblage and hydrothermal mineralization without skarn precursor are found as well.

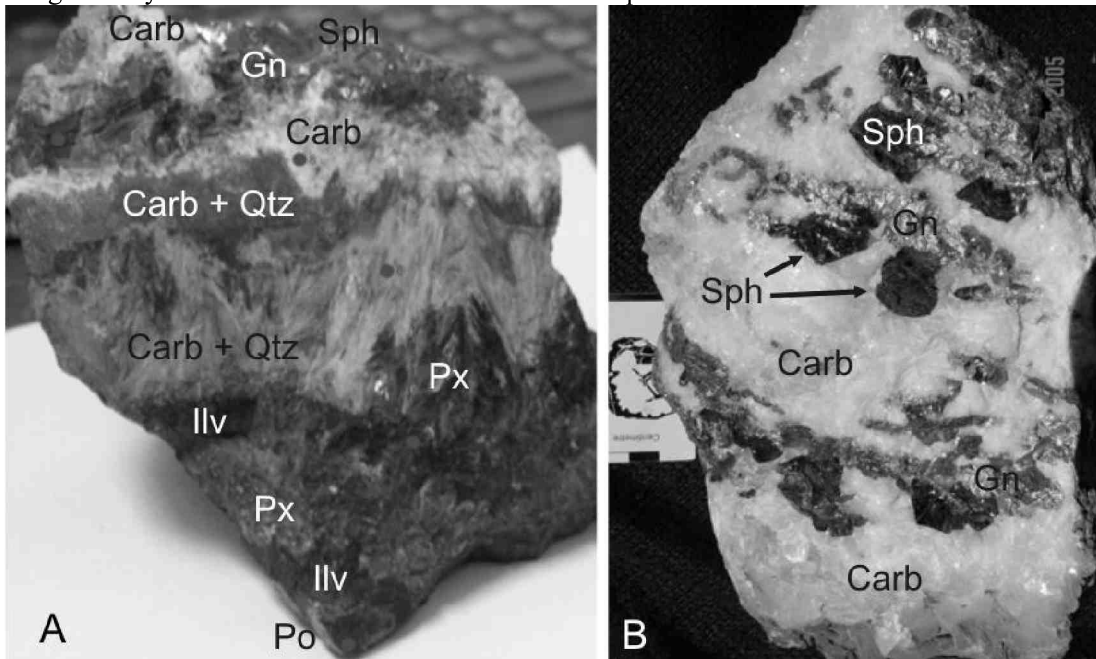


Figure 3. A) Skarn and B) hydrothermal paragenesis from the Trepča mineral deposit. Po-pyrrhotite, Ilv-ilvaite, Px-pyroxene, Carb-carbonates, Qtz-quartz, Gn-galena, Sph-sphalerite.

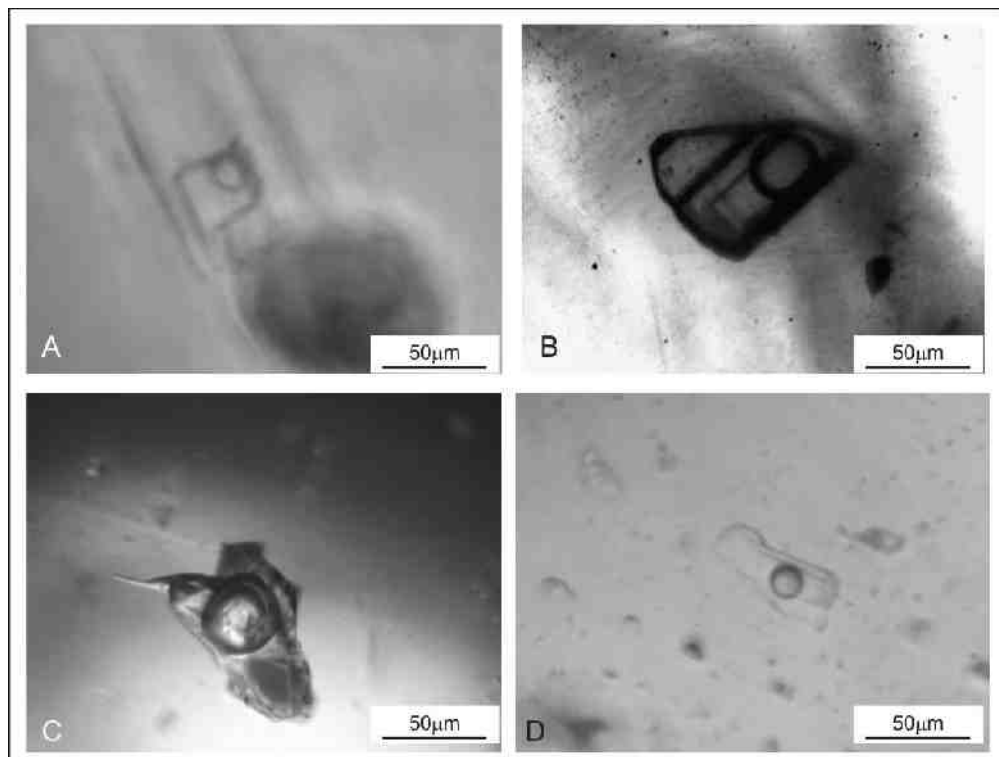


Figure 4. Primary fluid inclusion within A) hedenbergite, B) sphalerite, C) quartz and D) carbonate

## SAMPLES AND METHODS

The host and gangue carbonates were analyzed at ACTLABS (Activation Laboratories Inc., Ontario, Canada) after lithium metaborate or tetraborate fusion using ICP for major elements and ICP-MS for trace elements.

The chemical compositions of ore and gangue minerals were determined using the SEM/EDS method for major and SEM/WDS method for trace elements.

Microthermometric measurements were performed on primary fluid inclusions within transparent (hedenbergite, carbonate and quartz) and opaque (sphalerite) minerals (Fig. 4). Measurements within transparent minerals were carried out at Linkam THMS 600 stage mounted on an Olympus BX 51 microscope using 10x and 50x Olympus long-working distance objective lenses for visible light. Fluid inclusions studies within sphalerite were conducted at Olympus BHSM-IR equipped with an infrared sensitive TV camera (Hamamatsu C-2400) and the USGS heating/freezing system. Long working distance IR objectives with magnifications of 10x, 20x, 50x and 80x were available.

## RESULTS AND DISCUSSION

### HOST AND GANGUE CARBONATES

Mineralization is hosted exclusively by recrystallized limestone. ( $\text{CaCO}_3$  content up to 99.3 wt.%). The REE content in the limestone is low, especially Ce and Eu (Fig. 5). The negative chondrite-normalized Ce anomaly suggests marine origin of the limestones (Hu et al., 1988). The lack of positive  $\text{Eu}_{\text{CN}}$  anomaly gives the evidence that during recrystallization REE were not added to sedimentary precursor.

The major gangue minerals are carbonates with variable composition (mostly kutnohorite,  $\text{Ca}(\text{Mn,Mg,Fe}^{2+})(\text{CO}_3)_2$ ). The presence of positive  $\text{Eu}_{\text{CN}}$  anomaly is common feature of all gangue carbonates. The total amount of REE varies in carbonates from different stages of mineralization (Fig. 5).

The Mn, Fe, Ba, Y, Mo and As concentrations are significantly higher in all analyzed syn- and post-ore carbonates in comparison with those recorded in the host limestone, indicating distant source of mineralizing fluid. Particularly, enrichment in Mn, Fe, Zn and Pb and depletion in Mg, Al and Cu are positively correlated with distance between inferred fluid source and depositional site (Einaudi et al., 1981; Yun & Einaudi, 1982; Meinert et al., 2005).

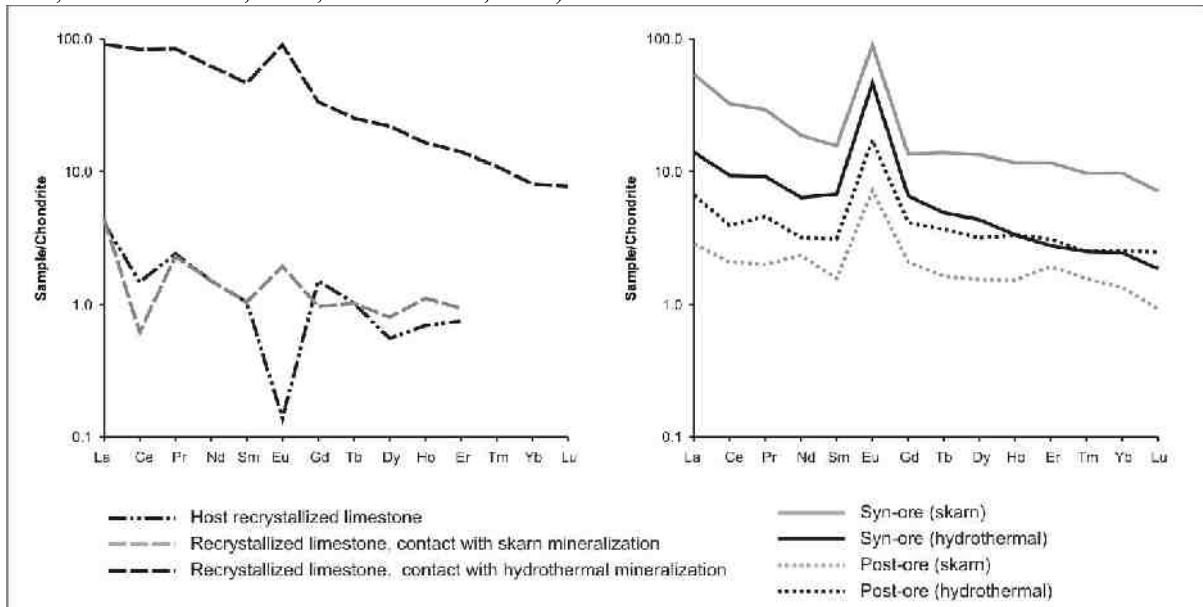


Figure 5. Chondrite-normalized REE abundances in the host and gangue carbonates from the Trepca deposit.

### SKARN AND HYDROTHERMAL MINERALIZATION

In the Trepca mineral deposit pyroxene is more abundant than garnet. Electron microprobe analysis of pyroxenes determined predominance of Fe over Mg and Mn ( $\text{Hd}_{54-93}\text{Jo}_{2-7}$ ).

Ore microscopy observations suggest that galena precedes sphalerite deposition occasionally.

Electron microprobe analysis of galena found Bi and Ag as the most important minor elements. Galena from the skarn paragenesis is slightly enriched in the elements ( $0.69 \pm 0.03$  wt. % Bi, 720-980 ppm Ag) in comparison with galena from the hydrothermal paragenesis ( $0.48 \pm 0.17$  wt. % Bi, 60-760 ppm Ag).

Sphalerite is enriched in iron ( $11.2 \pm 0.8$  wt. %), manganese ( $0.65 \pm 0.19$  wt. %), and cadmium ( $0.23 \pm 0.08$  wt. %). The copper content of sphalerite associated with pyrite and pyrrhotite (Hutchison & Scott, 1981, in the range between 0.02 and 0.05 mol. %), corresponds to a formation temperature comprised between 360 and 405°C. Significant differences between sphalerite separated from skarn and hydrothermal paragenesis are not observed.

### FLUID INCLUSION STUDY

According to the microthermometric study pyroxene was precipitated from high-temperature and moderate saline fluid (homogenization into liquid phase between 385 and 450°C; salinity=14.8-18.5 wt.% NaCl equ.).

Sphalerite contains fluid inclusions with a salinity of 8.0 to 14.6 wt.% NaCl equ. and homogenization into liquid phase between 240 and 305°C. The pressure in the range from 0.8 to 1.25 kbars was determined by combination of fluid inclusion data and sphalerite geothermometer.

Syn-ore calcite and quartz host moderate saline (8-13.5 wt. % NaCl equ.) and moderate-temperature ( $T_h=270-355^\circ\text{C}$ ) fluids. Post-ore gangue minerals were precipitated at lower temperature (homogenization into liquid phase,  $T_h=220-280^\circ\text{C}$ ) from fluid with variable salinity (4.7-12.5 wt. % NaCl equ.).

### CONCLUSION

The Trepca deposit is a calcic Pb-Zn-Ag skarn deposit according to the classification proposed by Einaudi et al. (1981). It is confirmed by structural control, absence of significant metamorphic aureoles centered on the skarn, pyroxene as dominant calc-silicate mineral, association of sulfide mineralization with pyroxene rather than with garnet and the Mn-rich ilvaite formed during the retrograde stage.

The presence of phreatomagmatic breccia, geological and lithological setting of the deposit point to phreatomagmatic volcanism, which pre-dated ore formation.

The structural control and trace element geochemistry of ore and gangue minerals suggest that mineralizing fluid was not locally derived from the small trachyte body within breccia pipe. The mineralization was formed in the carbonate unit encountered by ore-forming solution that had risen through non-reactive rocks from a magmatic body situated at deeper level. Equivalent situation was recorded by Yun & Einaudi (1982) in the Yeonhwa deposit, Korea.

The fluid inclusion studies recognized three major stages of mineralization (Fig. 6): 1. Metasomatic formation of skarn minerals (pyroxenes,  $\text{Hd}_{54-93}\text{Jo}_{2-7}$ ) during the prograde stage of mineralization from saline and high-temperature fluid of distal magmatic origin; 2. Precipitation of the ore minerals (sphalerite, galena) and syn-ore gangue minerals formed by mixing of magmatic and meteoric fluids during the retrograde stage; 3. Deposition of post-ore gangue carbonates and quartz from more diluted fluids. Alternatively, the high and low-temperature fluids can be modeled as originating from 6 to 8 wt percent solutions, most likely exsolved from an underlying pluton, which followed different cooling paths on ascent (Meinert et al., 1997).

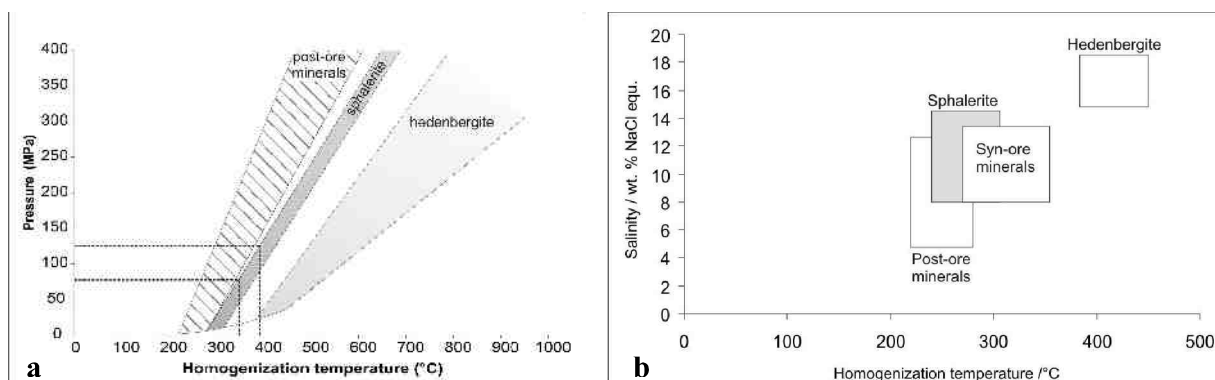


Figure 6. a) PT diagram with fluid inclusions isochores for pyroxenes, sphalerite and post-ore minerals. b) Homogenization temperature-salinity characteristics of fluid inclusions associated with major stages of mineralization

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