U/Pb dating and trace element compositions in pegmatite-hosted titanite from the Petrovitsa Pb-Zn deposit, Madan district, South Bulgaria

U/Pb датиране и елементи-следи на титанит от пегматити в находище Петровица, Мадански район, Южна България

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Introduction
The Petrovitsa Pb-Zn deposit is located in the Madan district, Central Rhodopes. The region was one of the most important base metal producers in Europe in the past with present intensive underground activities in several mines. Rich skarn-ore metasomatic bodies and quartz-sulphide veins hosted by high-grade metamorphic rocks are the main base metal source in the deposits of the area. Host gneisses and marbles belong to the Madan Lithotectonic Unit (Ivanov et al., 2000), part of the Middle Allochthon of the Rhodope Metamorphic Complex (Jahn-Awe et al. 2010). Abundant massive pegmatite bodies (up to 2 m thick) are commonly observed as concordant or crosscutting injections relative to the main metamorphic foliation in the host gneisses and marbles. Using modern analytical techniques, our study is taking place in attempt to clarify their age, origin, and potential for strategic metals.

Titanite is an important accessory mineral that has a high closure temperature (up to 700 °C) and does not get affected easily by diffusion. It also incorporates significant U-contents in its structure (Frost et al., 2000), which makes it useful for dating. Last but not least, titanite is a repository mineral for REE and HFSE in metamorphic and magmatic environments.

Here we present U/Pb in-situ LA-ICP-MS dating and trace element signature of pegmatite-hosted titanite crystals, formed near the lithological contacts with skarnified and mineralized marbles in the Petrovitsa deposit (Fig. 1A).

Analytical procedures
The mineral relationships in titanite association were studied by optical and scanning-electron microscopy (SEM-BSE regime). The chemical composition of the studied minerals was performed by JEOL JSM-6390 in the Institute of Physical Chemistry, Bulgarian Academy of Sciences, using natural and synthetic standards for the measured elements. U-Pb isotope characteristics and trace-element composition of titanite crystals were defined at the Geological Institute of BAS, using the LA-ICP-MS system consisting of New Wave Research 193 nm Excimer laser UP-193FX attached to a Perkin-Elmer ELAN DRC-e quadrupole inductively coupled plasma mass spectrometer. Ablation craters for dating were 30 µm and 25–50 µm for tracing. MKED1 standard was the primary external standard for age determination and NIST 610 for compositional characteristics. Isoplot and SILLS programs and the SiO₂ content in titanite (as internal standard from EPMA) were used for data reduction and calculation of the chemical composition.

Results
We have studied a single pegmatite body (Fig. 1A), which is composed mainly of K-feldspar and some plagioclase and quartz. Titanite crystals occur near the contact with skarnified marble. Field relationships show that the pegmatite predates the skarn formation. It is elongated parallel to the skarn but also deformed by the main metamorphic foliation in the
host rocks. The prograde skarns, presented mainly by clinopyroxene from hedenbergite-johannsenite series and minor rhodonite, are developed along the pegmatite-marble contact and do not result from the pegmatite emplacement, considering the localized skarnification of both alumosilicate and carbonate rocks. The hydrothermal activity and base metal deposition affected both skarn and pegmatite. Infiltration-driven reactions and intensive hydrothermal alteration along the lithological contacts in the studied body are characteristic with formation of epidote, clinozoisite, chlorite (clinohlore), later carbonates and quartz as seen from the optical microscopy in thin sections. Minor apatite and some pyrite complement the association on places. The same fluid pathways were used by the lower-temperature ore-precipitating fluids which deposited the economic galena-sphalerite mineralization.

Fig. 1. A, the studied outcrop in the Petrovitsa deposit, mine level 856; B, BSE image of titanite crystals; C, U/Pb Concordia diagram; D, trace element contents in titanites; E, chondrite-normalized REE diagram. Abbreviations: Tit, titanite; KFs, K-feldspar; Ep, epidote; Py, pyrite.
The studied euhedral titanite crystals do not display any obvious chemical inhomogeneity in BSE images (Fig. 1B). Most of the crystals were clear of inclusions. After applying correction for common Pb the calculated U-Pb age of formation is 49.63±0.94 Ma (Fig. 1C).

The chemical composition shows Al₂O₃ incorporation in the range 1.06–2.51 wt%. Minor quantities of FeO (0.62 wt%) were detected as well. Trace element signature reveals significant amounts of Y (1167–1804 ppm), Zr (449–818 ppm), Nb (500–683 ppm), although all measured elements in titanite structure generally reveal variation in close ranges as seen from Fig. 1D. A possible substitution mechanism in the octahedral site is Al³⁺+Nb⁵⁺=2Ti. The average metals incorporation in ppm is presented by: Mn (726), V (487), Cr (629), Ni (268), Ga (73), Ge (93), Mo (44), W (47). The ΣREE ranges from 3169–7576 ppm with average of 6053 ppm (Fig. 1D). Uranium content is <288 ppm and Th is up to 739 ppm. The Th/U ratio reaches 2.76 with mean values of 1.91, while Lu/Hf averages ~0.55, and Dy/Yb ratio of 2.05. The LREE are prevailing over the HREE. The titanite is showing negative Eu-anomaly in the chondrite-normalised pattern (Fig. 1E).

Discussion

The combination of the morphological (euhedral crystals) and geochemical features, like Th/U ratio above 1.5 (indicating magmatic origin, Scibiorski et al., 2019, and references therein), Dy/Yb ratio above 2.00 (suggesting HREE depletions), Lu/Hf ratio above 0.3 (characteristic for magmatic origin, Li et al., 2009), high ΣREE concentrations (3169–7576 ppm), negative Eu anomaly (Pan et al., 2019, and references therein) and the geological environment suggest magmatic origin of the studied titanites.

The obtained U/Pb age suggests pegmatite intrusions ~50 Ma in the Madan Unit that should be linked to magmatic events in the Middle Allochthon of the Central Rhodopes. Similar in tectonic position are zircon and alanite-rich bedded migmatic pegmatites, hosted by the gneisses of the same unit along the Vacha River with U-Pb ages in the range 58–49 Ma (Arnaudov et al., 1990a; Cherneva et al., 1995). Rare-metal pegmatites crosscutting the metamorphic sequence near the village of Dolen, Zlatostran, and Drangovo pluton 49.9±0.42 Ma (Marchev et al., 2013, and references therein). These events coincide with the wider range of 56–40 Ma granitoids and pegmatites in the units of the same allochthon in Central (Dolno Dryanovo granite – 56 Ma; Jahn-Awe et al., 2010), Eastern (Topolovo – 52.5 Ma; Marchev et al., 2013) and Western Rhodopes (Vishtertitsa pegmatite – 50±5 Ma; Arnaudov et al., 1969). It should be mentioned that the wide 62–32 Ma Paleogene age range of melt production in the metamorphic complexes of the Rhodopes was suggested by Arnaudov et al. (1990b) using model Pb-Pb ages in K-feldspars and the U-Pb ages of zircons from migmatites in the Central Rhodopes.

Considering field relationships and the obtained ages, the studied pegmatite body is clearly pre-ore. Although, the source of the metals in the Madan hydrothermal system is still controversial, the new data on the pegmatites in depth could bring insight onto the crustal magmatism in the region.

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References


