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Epidote metasomatic zone in pegmatites from the vicinity of Strashimir Pb-Zn vein deposit, Central Rhodopes: mineralogy, geochemistry and *in-situ* U/Pb age determination

Епидотова метасоматична зона по пегматити в района на Pb-Zn жилно находище Страшимир, Централни Родопи: минералогия, геохимия и „*in-situ*“ U/Pb възрастови определения

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Abstract. The epidote-group minerals are the major hydrothermal constituent, along with titanite, chlorite, quartz, and carbonates, developed in pegmatite on the contact with marble in the vicinity of Strashimir Pb-Zn vein deposit, Central Rhodopes. The U-Pb age of titanite (39.7 ± 1.3 Ma) fixes the time of the hydrothermal mineralization. Trace element signatures of epidotes reveal minor REE-amounts, probably due to the concurrent growth of other REE-concentrating minerals (e.g. hydrothermal titanite).

Keywords: Madan region, hydrothermal alteration, epidote-group minerals, titanite, REE.

Introduction

The Tertiary (~30 Ma) vein and metasomatic base metal deposits in the Madan ore district are hosted by the high-grade metamorphic complex in the Central Rhodopes, composed of gneisses, amphibolites and marbles (Vassileva et al., 2009 and references therein). Numerous concordant or crosscutting pegmatite bodies represent an important constituent of the ore-hosting rocks. Their formation age is determined by U-Pb geochronology on pegmatite-hosted titanite as 49.63 ± 0.94 Ma (Milenkov et al., 2020). These pegmatites suffered intense hydrothermal alteration prior to and during the ore deposition. In attempt to elucidate their mineral composition and potential minerals-concentrators of critical elements, as well as their relationship with the ore mineralization, we have studied a well exposed pegmatite body outcropping on the upper part of the Strashimir vein deposit. It represents a large dyke, more than 6 m thick, emplaced along the contact between marbles and gneisses with amphibolite lenses from the Madan unit. The outcrop is situated above

the plane of a subhorizontal fault assigned as Madan detachment (Sarov et al., 2006) that had been intercepting and screening the ore-bearing fluids. The field observation determined the epidote-group minerals as one of the major constituent of the altered pegmatites. In this study, we present mineralogical and geochemical data on epidote, titanite and allanite. The age of this hydrothermal alteration is determined by *in-situ* U/Pb dating of titanite.

Analytical procedures

Thin-sections of representative samples were studied by optical microscopy, SEM-EDS and LA-ICP-MS. The mineral relationships were studied by optical microscopy in GI-BAS and then using JEOL JSM-6010PLUS/LA in the University of Mining and Geology. U-Pb isotope characteristics for titanite geochronology, and major, minor and trace element signatures of the minerals were analyzed by the LA-ICP-MS system in Geological Institute, BAS, consisting of New Wave Research (NWR) 193 nm Excimer laser UP-193FX attached

to a Perkin-Elmer ELAN DRC-e quadrupole inductively coupled plasma mass spectrometer with 6 Hz and 25–50 μm laser ablation craters. NIST 610 and MKED1 standard reference materials (SRMs) were used as external standards for element concentration and dating analyses, respectively. Theoretical SiO_2 content is applied as internal standard for data recalculation of the chemical composition.

Results

Mineral relationships. The hydrothermal alteration mineralization in the pegmatite is observed along the contact with marble, forming well-developed zone of replacement, veins and nests. The main alteration products after pegmatite are epidote, less titanite, followed temporally and quantitatively by chlorite, hematite, quartz and carbonates (Fig. 1A). The occurrence, association and morphology of the studied members of the epidote solid solution (Ep_{ss}) do not differ significantly from similar ones found in other deposits in the region e.g. Petrovitsa (Georgieva et al., 2021) except for the crystal size. The length of the studied epidote crystals here exceeds 5 cm. The color is deep pink to red or yellow to pistachio green. Elongated prismatic crystals, clusters or radiating aggregates are typical. Single crystals show color variation from red to green (see Fig. 1A). Fine-grained dark-green chlorite, sub- to euhedral calcite and later quartz generally fill the voids between epidote crystals. In the studied contact zone, the pegmatite miner-

als are preserved only as relics. Accessory sub- to euhedral allanite (up to 1 mm, Fig. 1A, B), apatite and K-feldspar with irregular shapes are observed among epidotes. Allanite is fragmented and wrapped by later epidote mineralization. Titanite is established both as anhedral crystals enclosed in epidote matrix (Fig. 1C) and as euhedral crystals (up to 3 mm long) in the cavities between the prismatic epidote crystals filled also with chlorite and carbonate (Fig. 1D). Sulphide mineralization was not observed in the studied samples, although the altered pegmatite body is located spatially above the Strashimir Pb-Zn vein deposit.

Chemical composition and tracing signatures. According to the major elements the studied epidotes represent members of the clinozoisite-epidote solid solution, predominantly Fe^{3+} -rich clinozoisite (Armbruster et al., 2006). The red-rose parts of the studied minerals are relatively Al-rich, while in the green Fe augment. The content of CaO is between 18.12–22.13 wt%, Al_2O_3 is 19.38–23.48 wt%, whereas Fe_2O_3 is in range 5.84–11.77 wt%. The minerals are characterized by constant incorporations of MnO (up to 0.7 wt%), TiO_2 (0.2 wt%), MgO (1.4 wt%), P_2O_5 (0.1 wt%), B (49.4 ppm), Zn (224 ppm), Ga (88 ppm), Sr (1117 ppm), Y (28 ppm), Pb (65 ppm), and Bi (31 ppm). The ΣREE reaches up to 57 ppm. Close to allanite, the content of REE in epidote (e.g. Ce 1961 ppm, La 545 ppm), Th and U increases significantly. According to the chemical composition the dominant REE in allanite is Ce_2O_3 (up to 3.5 wt%), followed by La_2O_3 (1.8 wt%), Nd_2O_3

Fig. 1. A, macrophotograph of alteration assemblage in pegmatite; B, BSE image of allanite intersected by late epidote and quartz; C, BSE image of anhedral titanite grain enclosed in epidote; D, BSE image of euhedral titanite on the contact between chlorite, epidote, and quartz; E, chondrite-normalized REE diagram for titanite; F, U-Pb age diagram for euhedral titanite in association with chlorite; G, U-Pb age diagram for anhedral titanite enclosed in epidote. Abbr.: Czo, clinozoisite, Qz, quartz, Cal, calcite, Chl, chlorite, Aln, allanite, Ttn, titanite.

(0.9 wt%), Pr_2O_3 (0.3 wt%), Sm_2O_3 (0.1 wt%) and ΣREE reaches up to 57 448 ppm. High contents of ThO_2 (up to 1.5 wt%), U (884 ppm), Y (1064 ppm), Ga (652 ppm), and Ge (494 ppm) are established.

The chemical composition of titanite reveals incorporation of Al_2O_3 up to 3.84 wt% and Fe_2O_3 (1.56 wt%) with minor amounts of MnO and MgO. Trace element signature indicates considerable incorporation of Nb. In certain titanite crystal zones the Nb_2O_5 content reaches up to 5.22 wt%. The ΣREE ranges from 2835 to 12 719 ppm. Uranium is up to 941, whereas Th is 513 ppm. Significant incorporation of Y_2O_3 (up to 2.83 wt%), Ta (3544 ppm), Sn (3403 ppm), Zr (2632 ppm), and V (853 ppm) is established as well. Chondrite-normalized pattern shows relative depletion of LREE relative to HREE (Fig. 1E).

U-Pb age of titanite. The titanites from the altered pegmatite in the vicinity of Strashimir deposit reveal discordant U-Pb ages. After the application of the common ^{204}Pb correction (Andersen, 2002) they yield a U-Pb age of 39.7 ± 1.3 Ma with Mean Square Weighted Deviation (MSWD) of 1.3 for chlorite associated euhedral titanite (Fig. 1F), and 38.6 ± 1.7 Ma with MSWD 0.62 for epidote-enclosed anhedral titanite (Fig. 1G).

Concluding remarks

According to the mineral relationships epidote and titanite are formed at the beginning of the hydrothermal process. An oscillatory zoning is observed in the epidote crystals determined by the fluctuation of Al and Fe in the fluid. Aluminum enrichment is due to the feldspar replacement, while Fe is introduced by the dissolution of biotite from gneisses. REE enrichment in epidote is detected in crystals formed next to allanite.

The geochemical features of titanite such as Th/U ratio 0.11–1.22, $(\text{Dy}/\text{Yb})_{\text{N}}$ 0.49–1.47, depletion of LREE relative to HREE suggest hydrothermal origin of the mineral (Li et al., 2010; Pan et al., 2018; Scibiorski et al., 2019 and references therein). The U-Pb ages of the studied mineral show significant similarities to those from Petrovitsa deposit, defined as hydrothermal by Milenkov (39.2 ± 1.5 Ma, unpublished data). However, the enhanced values for ΣREE (up to 12 719 ppm) and relatively high Lu/Hf ratio (0.43–1.69), are probably controlled by complex factors such as crystallization sequence, dissolution-precipitation, and/or whole-rock composition. The formation age of titanite most likely refers to post-magmatic hydrothermal events and thus fixes the time of the alteration.

Trace element signatures of Ep_{ss} minerals reveal minor REE-amounts, although the crystal structure of the epidote-group minerals utilizes significant incorporation of such elements. An appropriate explanation is the concurrent growth of other REE-concentrating minerals (e.g. hydrothermal titanite).

The pegmatites from Madan region contain a number of accessory minerals (e.g. allanite, titanite, apatite, rutile, zircon) that are significantly enriched in REE and therefore represent a potential source for critical elements.

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References

- Andersen, T. 2002. Correction of common lead in U-Pb analyses that do not report ^{204}Pb . – *Chem. Geol.*, 192, 59–79; [https://doi.org/10.1016/S0009-2541\(02\)00195-X](https://doi.org/10.1016/S0009-2541(02)00195-X).
- Armbruster, T., P. Bonazzi, M. Akasaka, V. Bermanec, C. Chopin, R. Gieré, S. Heuss-Assbichler, A. Liebscher, S. Menchetti, Y. Pan, M. Pasero. 2006. Recommended nomenclature of epidote-group minerals. – *Eur. J. Mineral.*, 18, 551–567.
- Georgieva, S., R. Vassileva, G. Milenkov, E. Stefanova. 2021. Epidote-group minerals in altered pegmatites from Madan ore region, Central Rhodopes, Bulgaria: occurrence and chemistry. – *9th Intern. Confer. Mineralogy and Museums. Extended Abstracts*. Sofia, August 24–26, 2021, 39–40.
- Li, J.-W., D. X. Deng, F. M. Zhou, S. Y. Liu, F. X. Zhao, L. J. Guo. 2010. Laser ablation ICP-MS titanite U-Th-Pb dating of hydrothermal ore deposits: A case study of the Tonglushan Cu-Fe-Au skarn deposit, SE Hubei Province, China. – *Chem. Geol.*, 270, 56–67; <https://doi.org/10.1016/j.chemgeo.2009.11.005>.
- Milenkov, G., R. D. Vassileva, I. Peytcheva, V. Grozdev. 2020. U/Pb dating and trace element compositions in pegmatite-hosted titanite from the Petrovitsa Pb-Zn deposit, Madan district, South Bulgaria. – *Rev. Bulg. Geol. Soc.*, 81, 3, 90–92.
- Pan, L.-C., R.-Z. Hu, X.-W. Bi, C. Li, C.-L. Wang, X.-S. Wang, J.-J. Zhu. 2018. Titanite major and trace element compositions as petrogenetic and metallogenic indicators of Mo ore deposits: Examples from four granite plutons in the southern Yidun arc, SW China. – *Amer. Mineral.*, 103, 1417–1434; <https://doi.org/10.2138/am-2018-6224>.
- Sarov, S., E. Voynova, S. Moskovski, T. Jelezarski, K. Naydenov, D. Nikolov, I. Georgieva, N. Petrov, N. Markov. 2006. *Geological Map of the Republic of Bulgaria, Scale 1:50 000, Map Sheet K-35-86-F (Madan)*. Sofia, Ministry of Environment and Water, Bulgarian National Geological Survey.
- Scibiorski, E., C. Kirkland, N. Evans. 2019. Trace elements in titanite: A potential tool to constrain polygenetic growth processes and timing. – *Chem. Geol.*, 509, 1–19; <https://doi.org/10.1016/j.chemgeo.2019.01.006>.
- Vassileva, R. D., R. Atanassova, I. K. Bonev. 2009. A review of the morphological varieties of ore bodies in the Madan Pb-Zn deposits, Central Rhodopes, Bulgaria. – *Geochem., Mineral. and Petrol.*, 47, 31–49.