Clinozoisite from the Petrovitsa Pb-Zn deposit, Madan region, Central Rhodopes
Клиноцоизит от Pb-Zn находище Петровица, Мадански район, Централни Родопи

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**Introduction**

The ongoing underground mining activities in the Madan Pb-Zn deposits, Central Rhodopes, revealed the presence of large pegmatite bodies embedded in the host high-grade metamorphic complex. These concordant (rarely crosscutting) veins suffered intense hydrothermal alteration during the ore deposition processes. In attempt to evaluate the formation processes of pegmatite, their relationship with the sulphide mineralization and their possible metallogeny we have studied a well exposed concordant pegmatite body from the 820 mine level in the Pb-Zn Petrovitsa deposit. The pegmatite body contacts with skarnified marble, including scarce sulphide mineralization. Although pegmatite characteristics are still poorly described in this area, the field observation and preliminary investigations determined the epidote group minerals as one of the major constituents of the altered pegmatites. Here we present mineralogical and geochemical data obtained about clinozoisite as one of the wide spread products on the pegmatite-marble contact.

**Geological background**

The Tertiary (~30 Ma) Pb-Zn (±Ag) mineralization in the Madan region is attached to six subparallel NNW-SSE regional fault zones, cutting through the Rhodopean metamorphic complex (various gneisses, amphibolites and certain marble packages) (Vassileva et al., 2009 and references therein). The hydrothermal processes led to the formation of sulphide ores of economic importance. Although their mineral composition is uniform (galena-sphalerite-chalcopyrite) the mechanisms and style of mineralization differs according to the host rocks. Subvertical pollymetallic veins are formed by open-space filling in aluminosilicate rocks, while metamorphic replacement in carbonate environment led to formation of rich skarn-ore bodies at the intersections with the marbles. The source of the metals and the genetic link with possible magmatic body is still controversial (Vassileva et al., 2009 and references therein), although pegmatite bodies (more than 2 m wide) are becoming major lithology in depth (Fig. 1a). The age of pegmatite formation is determined by in-situ LA-ICP-MS on pegmatite-hosted titanite crystals as 49.63±0.94 Ma (Milenkov et al., 2020, this volume).

**Analytical procedures**

Materials used in this study represent highly hydrothermally altered samples from the contact between pegmatite bodies and marble lenses of the Petrovitsa Pb-Zn deposit. Thin-sections of representative samples were studied by optical microscopy in transmitted and reflected light, powder X-Ray Diffraction, BSE-EDS and LA-ICP-MS. The clinozoisite is determined by XRD method as monoclinic, using Malvern Panalytical Multipurpose X-ray diffractometer Empyrean in the Laboratory of X-ray Diffraction Methods and Computed Tomography, Institute of Physical Chemistry, BAS. The positive optical sign determined using microscopic exami-
nation also complements the characteristic features of the mineral. The relationships in clinozoisite association and chemical composition were studied using JEOL JSM-6010PLUS/LA in the University of Mining and Geology. The minor and trace element signature of clinozoisite was 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.

Results

Mineral relationships

The clinozoisite mineralization occurs in the altered pegmatite along the contact with skarnified marble, forming thin 2–3 mm veinlets and nests in well-de-

Fig. 1. Occurrence and mineral relationships in the clinozoisite association: a, pegmatite-marble contact and position of the pegmatite alteration zone; b, close view of a on the hydrothermal products after marble and pegmatite; c, CPL image of clinozoisite prismatic crystals and their aggregates formed after anorthite. Note the adularization in the plagioclase and late carbonate veinlets; d, BSE image of altered anorthite crystal and aggregates of zonal clinozoisite; e, the chemical variation of Al³⁺/Fe³⁺ in the clinozoisite crystals defines the zoning. BSEI, Abb.: Czo, clinozoisite; An, anorthite; Ad, adularia; Qz, quartz; Cal, calcite; Chl, chlorite; Bst, bustamite; Ep, epidote; Sph, sphalerite; Gal – galena.
veloped (up to 5 cm thick) hydrothermal alteration zone (Fig. 1b). It is characterized by generally pale to deep pink or red color and is presented mainly as single sub- to euhedral prismatic crystals or fine-crystalline clusters, often representing radiating aggregates. Within the zone of hydrothermal alteration the mineral assembles with fine-grained green clinochlore, fine-grained calcite, minor galena, sphalerite, accessory sub- to euhedralapatite and euhedral titanite subjected to hydrothermal dissolution and replacement by fine crystalline TiO$_2$ (anatase/rutile). The clinozoisite mineralization regularly penetrates through the pegmatite bodies and replaces coarse-grained pegmatitefeldspars (anorthite, orthoclase) and intersects quartz (Fig. 1c–d). Within the pegmatite cavities the studied mineral appears as medium-grained, usually 600 µm, rarely larger prismatic crystals showing clear zonation based on the Al/Fe chemical heterogeneity (Fig. 1e). The interstitial spaces between the crystals are filled by calcite and quartz. Late carbonate mineralization is represented as thin veins generally intersectingfeldspars and clinozoisite aggregates. Beside calcite alteration, feldspars are subject to intensive adularization with formation of fine network of adularia veins and nests. The formation of clinozoisite in the pegmatite corresponds to the skarnification of the graphite-bearing marble and deposition of fine-fibrous radiating aggregates of bastnamate in association with later quartz and secondary manganese carbonate such as Mn-calcite.

**Chemical composition and tracing signatures**

According to the major elements, the studied mineral is member of the clinozoisite-epidote-group minerals, Fe$^{3+}$-rich clinozoisite (Armbruster et al., 2006). The content of CaO is between 22.06–24.18 wt%, Al$_2$O$_3$ is 21.73–24.2 wt%, whereas Fe$_2$O$_3$ is in range 7.85–9.98 wt%. The detected minor and trace elements in clinozoisite using LA-ICP-MS analytical technique are Ti, Mn, Mg, Na, K, P, B, Sc, V, Zn, Ga, Ge, As, Rb, Sr, Y, Zr, Nb, Sb, Cs, Ba, REE, Hf, Ta, Pb, and U. The mineral is characterized by constant incorporations of MnO (1.13–1.78 wt%), TiO$_2$ (0.01–0.09 wt%), MgO (0.03–0.1 wt%), P$_2$O$_5$ (0.01–0.03 wt%), B (38.84–96.83 ppm), Sr (1137.95–2187.03 ppm), Zn (10.11–29.25 ppm), Ga (25.02–78.17 ppm), Sb (4.87–48.56 ppm), and Pb (18.83–54.09 ppm). A negative correlation between Al$^{3+}$ and Fe$^{3+}$Mn is observed in the composition of the analyzed crystal zones. Generally, the central parts of the studied mineral are enriched in Al, while in the peripheries Fe and Mn augment. Wide variety of elements are detected in the predominant number of the studied points with different magnitude of concentration (in ppm) as: V (2.44–5.32), Y (0.51–8.40), Nb (0.57–1.77), Cs (0.34–1.85), Ba (2.76–12.72), Eu (0.63–6.96) and U (0.38–1.74). Elements as As (11.22–17.16), Rb (1.56–3.86), Zr (1.06–2.12), La (0.44–1.52), and Ce (0.38–1.27) are random constituent and do not show characteristic patterns. The last group of established elements such as Sc, Cr, Ge, Tb, Dy, Ho, Yb, Lu, Hf, Ta, and Th are sparsely scattered in the studied samples.

**Concluding remarks**

Both the pegmatite and post-pegmatite mineralization occurring along the contact with skarnified marble are formed in Ca-rich environment. Apart from clinozoisite, the mineral assemblage includes anorthite, titanite, apatite, epidote, carbonates. This assemblage is closely associated with Ca-rich bastnamate skarns and secondary manganese carbonate.

As a part of the epidote group minerals clinozoisite is one of the major minerals developed as an alteration product on the studied pegmatite. According to the mineral relationships, it is formed in the initial part of the hydrothermal process, corresponding to the skarnification of the marbles, and prior to the sulphide deposition. Initially, the clinozoisite formation is developed at the expense of the feldspar (anorthite) replacement, confirmed by the Al-dominated crystal cores. Lately the hydrothermal fluid is enriched in Fe and Mn (by biotite from gneisses and Mn-rich skarns in the marbles) resulting in more Fe- and Mn-enriched zones in the rims of the clinozoisite crystals.

Trace element signatures of clinozoisite reveal minor REE-amounts, although the crystal structures of the epidote group minerals utilizes significant incorporation of such elements. A possible explanation is the concurrent growth of other REE-concentrator mineral (e.g., titanite, epidote etc.).

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**References**

