Timing of pegmatite emplacement and skarn formation in the Malyovitsa Unit, NW Rila: evidence from zonal grossular crystals

Възраст на внедряване на пегматити и скарнообразуване в Мальовишката единица, СЗ Рила по данни от зонални гросулатови кристали

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Abstract. Contact Ca-skarns are formed in the marbles of the Malyovitsa Lithotectonic Unit as a result of emplacement of crosscutting pegmatite injections in the area of the Dzhendemski Ezera, NW Rila Mt. Large (up to 4 cm), well-shaped garnet crystals dominate the mineral association with additional vesuvianite, diopside, scapolite and zoisite. Garnets were selected for mineralogical, geochemical and U-Pb geochronological study. Their crystals show clear zonal pattern due to variation in the octahedral position (Fe³⁺/Al³⁺), although the overall composition defines grossular predominance (72–95 mol.% grossular; 4–24% andradite). Trace-element signatures reveal constant isomorphic incorporation of P, V, Zn, Ga, Ge and Y, REE, HFSE, U. Results from the in-situ U-Pb dating of the studied skarn materials suggest the timing of pegmatite intrusion onto the metamorphic rocks and marble-hosted skarn formation at 58.37±0.70 Ma.

Keywords: Ca-garnets, skarn mineralization, trace elements, U-Pb geochronology, Rila.

Introduction
Calcic-garnets with composition within the grossular-andradite (known as grandites) solid solution tend to be used as natural geochronometers due to the elevated incorporation of elements such as U, Th, Hf, and REE into the dodecahedral position of their crystal structure. Their deposition is above all attributed to skarn formation and results from active metasomatic processes in carbonate environment. In this way, the skarns formed on the contact with magmatic and/or pegmatitic body record directly the timing of their intrusion onto the host marble.

The present study reports new mineralogical, geochemical and geochronological data on skarn garnets formed on the contact with pegmatite body from the region of the Dzhendemski Ezera in the northwest Rila Mountain.

Methods and materials
The studied materials have been collected in 1997 and 2003 by Assoc. Prof. Svetoslav Petrusenko. Optical microscopy and back-scattered electron images (BSEI) on scanning electron microscope (SEM) were applied for investigation on the mineral relationships, mineral inclusions in garnet and zonality. Major elements in the mineral compound were determined by electronprobe microanalyzer (EPMA) in the Institute of Precambrian Geology.
and Geochronology, Russian Federation. The garnet composition is recalculated using the Locock (2008) procedure. Trace element signatures and U-Pb isotopes were defined using LA-ICP-MS at the Geological institute, BAS (for preliminary trace element studies) and lately in the Institute of Geochemistry and Petrology of ETH Zurich, applying high-resolution (HR)-LA-ICP-MS (Element XR ICP sector field MS connected to a 193 nm Resonetics ArF excimer laser system). Primary external standard for dating was Mali garnet (Seman et al., 2017) and NIST 612 for tracing. The content of SiO₂ in garnet from EPMA was used as internal standard for calculation of the chemical composition with Io-lite and/or SILLs programs.

Geological setting

The region of the Dzhendemski Ezera in the NW Rila Mountain comprises an area with extremely variegated lithological compound (Sarov et al., 2011). The outcropping rocks are metamorphites (Malyovitsa Unit), magmatic rocks (Rila-West Rhodope Batholith and Kalin pluton to NE) and certain serpentinitized ultrabasic bodies. Lithologically, the Malyovitsa Unit consists of biotite and amphibole-biotite paragneisses, mica schists, marbles as well as lenses of metaultrabasites. The lower parts of the unit are built by orthogneisses (Gorinova et al., 2019). The metamorphic sequence is intruded by the granodiorites to granites of the Rila-West Rhodope Batholith (RWRB) with different time of formation (von Quadt, Peytcheva 2005; Peytcheva et al., 2007; Gorinova et al., 2019), forming characteristic intrusive contacts. Marble lenses and layers form a NW-SE elongated strip cropping out in the studied area. Certain pegmatite dykes (mainly microcline-albite in composition) crosscut the metamorphic sequences and skarnificate the marbles (Arnaudov et al., 2011; Petrusenko, Karov, 2021 and references therein). The skarn mineralogy in most of the localities includes diopside, wollastonite, grossular, andradite, scapolite, vesuvianite, zoisite, epidote and sometimes phlogopite, amphiboles, clinzoisite, allanite, Be-minerals (helvine, beryl), scheelie and others (Petrussenko, 2002 and references therein).

Results

Occurrence and mineral association. The studied mineral association is formed at the intersection of pegmatite dyke with gneiss-enclosed marble layer and crops out eastwards from the Teodosievi Karauli peak in the NW Rila Mt. The contact skarn body resembles lens-like morphology with thickness of 1.5–2 m, controlled by the size of the host marble. Garnet is presented as massive pale orange aggregates, forming nests among other minerals and as rhombododecahedral crystals (Fig. 1A). In some cases the crystals are large (reaching 3–4 cm; Fig. 1B) with visible zonal pattern and intense orange color. The mineral association includes also diopside, vesuvianite, amphiboles, scapolite, pink zoisite (thulite). Diopside and vesuvianite are observed as massive and/or radiating aggregates or prismatic crystals (1–3 cm long), while scapolite occurs as white masses and small colorless crystals (Fig. 1A). Amphiboles are generally presented by tremolite. Epidote is characteristic on places, forming veinlets or mm-sized elongated crystals in carbonate nests.

Chemical composition of garnet. According to the EPM analyses (more than 30), made along a profile normal to the zonality of a selected crystal (Fig. 1C), the composition of the garnet is determined as member of the andradite-grossular, (Table 1). Chemical variations in the dodecahedral, octahedral and tetrahedral sites are responsible for the changing color and zonal distribution (Fig. 1C; Table 1). The dodecahedral position is larger compared to others and accommodates mainly Ca²⁺, but also Mn²⁺, Fe³⁺ and Mg. The detected amounts of REE, U, Th and Hf preferably substitute for calcium by means of heterovalent isomorphism. The biggest substitutions are attributed to the octahedral site, where Al³⁺ is mainly replaced by Fe³⁺ but certain amounts of Ti⁴⁺, Mn³⁺ and Fe²⁺ are presented as well. Vanadium, Zn, Ga, Ge positively correlate with Fe-content. The tetrahedral site accommodates only Si and negligible Al³⁺. The grossular component is significant, ranging from 72–95 mol.%. The higher values correspond to compound with the smallest Fe-content (grossular end member), corresponding to the white zones in the studied crystal). Trace-element signatures in most LA-ICP-MS analyses (above 60) reveal constant isomorphic incorporation of Y, Zr, Nb, REE, Ta, U (Table 1), despite their low concentrations as seen also from the REE chondrite-normalized patterns (Fig. 1D). HFSE ratios are indicative for the conditions of formation: Zr/Hf (generally 21–33 but reaching over 40 at some points); Zr/Nb (0.84–6.7), Nb/Ta (0.9–2.08 with extreme values to 5–6). The higher values of the ratios correspond to the lowest Fe-incorporation. These ratios are sensitive to crystal/fluid interaction (Bau, 1996), and their variation (due to zonal pattern) supports the bimetasomatic skarn formation of garnet by diffusion-involved processes. On the other hand, U-content is relatively stable (1.8–2.65 ppm), without clear dependence of the major elements in the garnet composition.

U-Pb dating. A large set of in-situ garnet U-Pb isotope data (n=51) is acquired. The insignificant content of common Pb enables the measurement of
the radiogenic Pb and the isotope U/Pb ratios with a precision that allows to define a lower intercept age of 58.37 ± 0.70 Ma (Fig. 1E), despite the low U-content.

Discussion and concluding remarks

The studied materials belong to the northwestern parts of the Alpine Rhodope Metamorphic Complex, namely NW Rila Mt. Magmatism related with the RWRB produced Upper Cretaceous plutons (72–70 Ma) hosted in the Malyovitsa Unit (von Quadt, Peytcheva 2005; Peytcheva et al., 2007) and activities continued to Late Eocene. Garnet formation resulted from pegmatite injection into the marbles of the variegated part of Malyovitsa Unit suggests time of pegmatite intrusion of ~ 58 Ma. Although similar ages are received for the Kalin pluton (~ 60 Ma, Gorinova et al., 2019), field relations and tectonic position reject their possible genetic link, considering the active at that time (ca. 58–48 Ma, Gorinova et al., 2019) Dodov Vruh shear zone, which separates the materials of the Malyovitsa Unit from the overthrust rocks of the Kabul Unit (including the Kalin pluton). Consequently, the studied mineralization resulted from the magmatic and post-magmatic activity of the RWRB, suggesting generation of granitic-pegmatitic magma at ~ 58 Ma in the lower parts of the Malyovitsa Unit, similarly to other granitic intrusions in the Middle Allochthon of the Rhodope Metamorphic Complex (e.g. Marchev et al., 2013).

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Table 1. Representative microprobe and LA-ICP-MS analyses of calcic garnet

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<tr>
<th>EPMA data</th>
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<td></td>
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* The FeO/Fe₂O₃ and MnO/Mn₂O₃ are recalculated according to the Locock (2008) procedure.

References


