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Geochronology of garnet-bearing skarns from the region of Babyak and Galabovo, Western Rhodopes (Bulgaria)

Геохронология на гранатови скарни от района на Бабяк и Гълъбово, Западни Родопи (България)

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Introduction

Intensive granitoid magmatism and subsequent formation of diverse deposits and ore occurrences are related to the Alpine evolution of the Rhodopes (e.g., Georgiev et al., 2007; Popov, Popov, 2019). The Rila-West Rhodopes batholith (RWRB) is the main pluton described in the western parts of the Rhodopes Massif. It is defined as a complex magmatic body consisting of two rock types: Upper Cretaceous hornblende-biotite and biotite granodiorites and Paleogene biotite- and two-mica leucocratic and aplitoid granites (Valkov et al., 1989; Kamenov et al., 1999; Peytcheva et al., 2007). According to the lithotectonic subdivision in this part of the Rhodopes, they intrude a variety of metamorphic lithotectonic units: the Sarnitsa, Mesta, Slashten, Obidim, Malyovitsa and Ograzhden (Sarov et al., 2008). Some of these units are marble bearing and the intrusion of the granitoids and their pegmatites result in the formation of skarns (e.g., Vassileva et al., 2018).

The present study is focused on the temporal relationships between the magmatic activity and the subsequent hydrothermal products near the villages of Babyak and Galabovo, Western Rhodopes, where garnet-bearing skarns were found. We apply the U-Pb high-resolution (HR) LA-ICP-MS dating on zircons of ore-hosting granite and garnets of the hydrothermal skarns with the aim to check the hypothesis if the hydrothermal activity at Babyak deposit is related only to the Paleogene magmatism (as considered in earlier studies) or also to the Late Cretaceous magmatism. The age dating is combined with mineralogical and geochemical studies on the skarn garnets to better constrain the temporal and geochemical evolution of the magmatic-hydrothermal system at this peripheral part of the RWRB. Grossular-andradites (grandites) may contain increased U concentrations than the other garnets because of the Fe^{3+} for Al^{3+}substitution which facilitates U^{4+} incorporation into the Ca^{2+} position (DeWolf et al., 1996). This makes the grandites a suitable "geochronometer" for U-Pb LA-ICP-MS dating (e.g., Seman et al., 2017).

Geological setting

Coarse to medium-grained biotite to rarely amphibole-biotite granites are the main magmatic rock type in the studied region. Pegmatites and aplitic veins are intruded in the granite and the hosting metamorphic rocks – various gneisses, marbles, schists and amphibolites of the Jurassic Sarnitsa lithotectonic unit (Sarov et al., 2008, 2010). The latest magmatic stage is represented by relatively rare dykes of mainly dioritic, quartz dioritic and spessartitic composition (e.g., Sarov et al., 2010).

The Babyak ore deposit is Mo-Ag-Au-W-base metal bearing (e.g., Deltchev, Dimitrov, 1964; Georgiev et al., 2007; Vidinli, Mladenova, 2016; Popov, Popov, 2019). The economic mineralization is hosted in the brittle contacts between granites and gneisses or cross-cut the different lithologies affected by moderate to strong wall-rock alterations. More than 17 bigger zones with many apophyses are distinguished, with width ranging from few cm to 5–10 m, length between 300 and 1500 m and depth about 350–400 m. The zones are represented mainly by quartz to quartz-pegmatite veins, which include the ore mineralization as sulfide and sulfosalt disseminations, veinlets, and nests. The most common hydrothermal alteration types related to the ore mineralization are phyllic, silicification, greisen-like and argillic. The skarn mineralization occurs only locally.

Sampling and analytical techniques

The samples for the present study are from the host coarse-grained undeformed granite and skarn lenses formed in marbles and carbonate-bearing schists of the Sarnitsa lithotectonic unit, close to granite and pegmatite contacts. The mineral relationships were studied by optical and scanning-electron microscopy (SEM-BSE regime). Major elements were determined by EPMA in the Institute of Precambrian Geology and Geochronology, Russian Federation. The garnet composition is recalculated using the Locock (2008) procedure. U-Pb isotope and trace element composition of the minerals were defined at the Institute of Geochemistry and Petrology of ETH Zurich, Switzerland using Resonetics Resolution 155 laser ablation system coupled to a Thermo Element XR Sector-field ICP-MS. Mali garnet (Seaman et al. 2017) was applied as primary external standard for dating and NIST 612 for tracing. The trace element composition was defined complimentary at ETHZ and the Geological Institute of the BAS (see also Peytcheva et al., 2018, for details).

Results

The skarn mineralization in the range of Babyak deposit appears as layers and lenses, in spots and irregular bodies with thickness from about few cm to 60–70 cm. They are formed mainly in the marbles (as exoskarns) near to the contacts with granites and pegmatites. Main skarn minerals are garnet, epidote and pyroxene (diopside). Amphibole (actinolite), vesuvianite, plagioclase (andesine), calcite, quartz, ±magnetite, ±chlorite, ±zircon are less common. Retrograde hydrothermal minerals include pyrite, molybdenite, chlorite, sericite, and zeolites deposited in microcracks or quartz veinlets.

The lateral zonation in the studied samples 1307, 17143 and 16119 is not very clear, rather a transition from the granite to a proximal zone of epidote-garnet-diopside±vesuvianite is observed. Chlorite (±epidote) alters the primary skarn minerals.

Garnet is a main skarn mineral. It is medium-grain and dark red-brown in sample 1307 and coarse-grain, orange-light brown in samples 17143 and 16119. EPMA analyses define them as calcium garnets of the grossular-andradites (grandites; $Ca_3Al_2Si_3O_{12}$–$Ca_3Fe_2Si_3O_{12}$) series. In the sample 1307 (exoskarn in the calk-schists) the garnets are determined as andradites with Fe_2O_3 in the range 20.77–23.95 wt% and 5.4–7.15 wt% Al_2O_3. Minor elements are Mn, Ti, and rarely Mg. The general formula is $(Ca_{2.67–2.83}Mn_{0.04–0.12}Fe^{2+}_{0.08–0.25})_{3.00}(Al^{3+}_{0.56–0.70}Fe^{3+}_{1.30–1.50}Ti^{4+}_{0.01–0.03})_{2.00}(Si_{2.94–2.96}Al_{0.03})_{3.00}O_{12}$. The other two garnets (from exoskarns in the marbles) vary in composition as follows: $(Ca_{2.70–2.98}Mn_{0.01–0.25}Fe^{2+}_{0.03–0.12}Mg_{0.00–0.20})_{3.00}(Al^{3+}_{1.11–1.67}Fe^{3+}_{0.29–0.89}Ti^{4+}_{0.01–0.06})_{2.00}(Si_{2.96–3.00}Al_{0.00–0.03})_{3.00}O_{12}$. Trace elements in the andradites and grossulars are similar but reveal some differences. Typical values in the andradite in ppm are: V (57–107), Y (72–102), Zr (100–148), Nb (29–193), Nd (~0.1–11), Sm (0.2–6), Dy (9–11), Er (7–15), Yb (9–31), Hf (6–8), Ta (6–42). The grossulars are richer in V (362–758 ppm), but with decreased content of heavy rare earth elements (HREE) and Ta (ppm): Er (1–7), Yb (1–7), Hf (1–5), Ta (~0.1–1).

Uranium content in the garnets is of special importance for the U-Pb dating. It is higher in the andradite (6–47 ppm) than in the grossular (4–8 ppm). The latter are measured with bigger uncertainties but all garnets lay on a discordia line with a lower intercept age of 68.55±0.74 Ma (Fig. 1a, b).

The U-Pb LA-ICP-MS zircon dating of granite sample 18-3 defines an upper intercept age of 71.12±0.72 Ma (Fig. 1c). Most of analyzed zircon grains are long- to medium prismatic, inherited cores are missing or rare (Fig. 1d).

Discussion and conclusions

The new U-Pb zircon data suggest the development of ore-forming processes related to Upper Cretaceous granites in the western parts of the Rila-West Rhodope batholith. So far, the rocks in the studied area have been described as Paleogene granites (e.g., Valkov et al., 1989). The main granitic magmatism in the region of Babyak and Galabovo villages is defined at 71.12±0.72 Ma. Skarn formation marks the beginning of hydrothermal processes at Babyak Mo-Ag-Au-W-base metal deposit. They are dated at 68.55±0.74 Ma – a bit younger than the granite, possibly due to alteration during retrograde hydrothermal overprinting. However, Paleogene skarns are described at the eastern contact of the RWRB (Vassileva et al., 2018). Further analyses of the Babyak vein-hosted ores and alteration products are needed to better constrain the timing of the hydrothermal economic mineralization.

The studied skarns are small in size and in agreement with the deeper level of formation at a contact to granites. The close relationships to the granites, as well as the type of mineralization show some specific characteristics of the intrusion-related gold

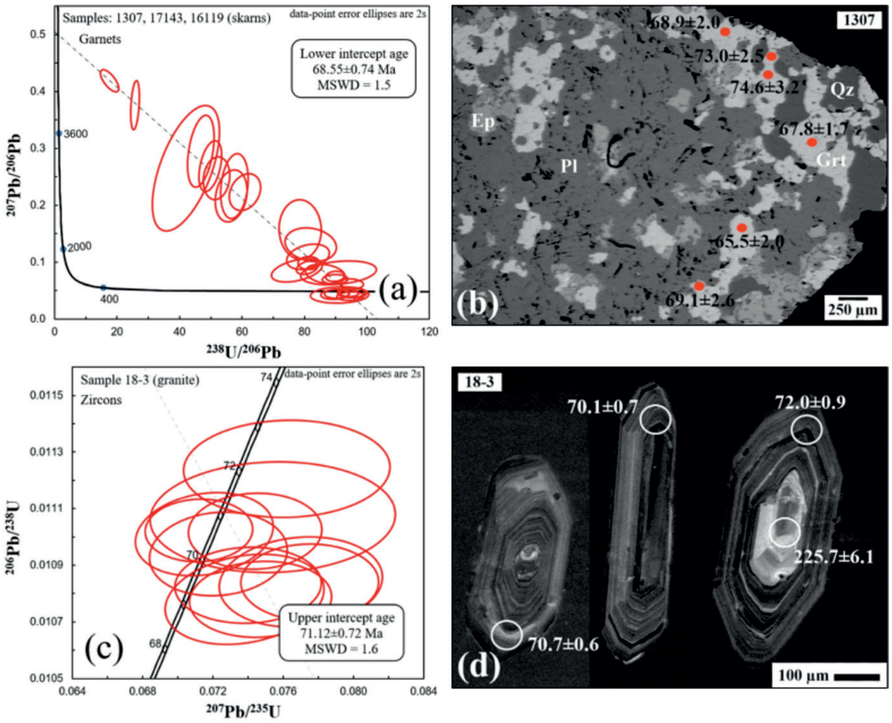

Fig. 1. *a*, HR-LA-ICP-MS U-Pb dating results for all analyzed garnets from Babyak deposit (plotted on Tera-Wasserburg concordia diagram); *b*, BSE image of part of sample 1307; ^{206}Pb/^{238}U age of the individual garnet analyses are shown; *c*, concordia diagram with LA-ICP-MS U-Pb zircon data for Babyak deposit host granite (sample 18-3); *d*, cathodoluminescence (CL) images of selected zircons from sample 18-3; white circles show the position of the laser ablation craters with the corresponding ^{206}Pb/^{238}U age. *Abbreviations*: *Grt*, garnet; *Ep*, epidote; *Qz*, quartz; *Pl*, plagioclase.

systems (IRGS), as it was shown at Pisani Skali ore occurrence (Vidinli, Mladenova, 2016).

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