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U-Pb garnet geochronology of grossular-diopside skarns from the Central Pirin batholith

U-Pb геохронология по гранат на гросулар-диопсидови скарни от Централнопиринския батолит

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Introduction

Recent advances in the U-Pb geochronology reveal the potential of grossular-andradite (grandite) garnets for the in-situ LA-ICP-MS age determination (e.g., Seaman et al., 2017; Deng et al., 2017; Wafforn et al., 2018; Vassileva et al., 2019a,b; Peytcheva et al., 2019). This work represents new data for the geochemical features and age of the contact skarns occurring SE of the Vihren peak (Central Pirin).

Geological setting

The Central Pirin pluton (Machev, 1993) is presented by three temporally successive facies: coarse-grained (Spanchevo granites, 56.72±0.3 Ma), porphyritic (Bezbog type, 33.14±0.21) and equigranular (Pirin type, 32.61±0.34 Ma) granodiorites (Filipov, Marchev, 2012 and references therein). In the area SE of the Vihren peak, a large zone of reaction calcic bimetasomatic skarns (20–30 meters in width) is formed on the contact between the latest equigranular granodiorite with the marbles from the lower tectonic unit (LTU) in the sense of Burg et al. (1996) corresponding to the rocks of the Synanitsa metamorphic complex (various gneisses and schists, calc-silicates and marbles, Milovanov et al., 2009). Hydrothermal processes in the skarns led to the deposition of sulphide ore mineralization and minor oxides (magnetite – Tarassova, 1993).

Analytical procedures

The mineral relationships were studied by optical microscopy and 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. A Resonetics Resolution 155 laser ablation system coupled to a Thermo Element XR Sector-field ICP-MS was used, equipped with some improvements compared to similar systems previously described. Energy density on sample ca. 3 J/cm^{-2}, repetition rate of 5, and ablation craters of 40 μm were applied as standard conditions. Mali garnet (Seaman et al., 2017) was used as primary external standard for dating and NIST 612 for tracing. The results were calculated using Iolite combined with Vizual Age to obtain ages and ratios corrected for instrumental drift and down-hole fractionation. The plots were processed using ISOPLOT. Iolite or SILLS programs and the SiO_2 content in garnet (as internal standard from EPMA) were used for calculation of the chemical composition.

Results

Mineralogy

The studied calcic skarns have dominantly clinopyroxene-garnet composition. Both minerals form alternating bands with relatively sharp contacts and 0.5–2 cm in width (Fig. 1A). The mineral composition of the skarns reveals some plagioclase and carbonates as well (Fig. 1B, C), and accessories of apatite and titanite. Skarns suffered intensive hydrothermal alteration with deposition of secondary carbonates, sericite and ore minerals. The ore mineralization is generally presented as reduced sulphide type with prevailing sphalerite and some galena and pyrite. Oxidation processes led to the formation of lenses of magnetite (sometimes intimately associating with andradite garnet).

According to the chemical composition the clinopyroxene is member of the hedenbergite-diopside solid solution with MgO (10.23–14.24 wt%), FeO (6.4–10.96 wt%), Al_2O_3 (1.2–2.7 wt%), MnO (up to 0.5 wt%) and some TiO_2 (up to 0.27 wt%), defining it as a ferroan diopside. Garnet is determined as grossular-dominated member ($Gro_{70–83}And_{17–30}$) of the grandite solid solution. Iron incorporation is generally in the range of 5.84–9.30 wt% Fe_2O_3 and small amounts of FeO (up to 1.5 wt%). Minor TiO_2 (less than 1.9 wt%) are presented as well. The crystalochemical distribution of the elements shows that the tetrahedral site in the garnet structure is occupied by Si (2.94–2.96 apfu) and completed with Al^{3+} (0.04–0.06 apfu). Changing proportions of Fe^{3+} (0.3–0.4 apfu) and Al^{3+} (1.47–1.55 apfu), together with Ti^{4+} (0.04–0.07 apfu) and Fe^{2+} (up to 0.03 apfu) are assigned in the in the octahedral position. The largest dodecahedral site accommodates Ca (2.95 apfu), Mg (0.02 apfu) and Fe^{2+} (0.02 apfu).

Geochemical features

The geochemical patterns of the studied garnets suggest general trend of trace elements enrichment for the following elements in ppm: Mg (3933–4997), Ti (6210–13470), V (222–544), Mn (3494–8499), Y (14–178) and Zr (107–729). Minor incorporation show: P (26–35), Sc (4–21), Cr (up to 72), Sr (1–3), Nb (19–49). The rare earth elements (REE) are well measured and reveal an enrichment of some LREE and depletion of HREE: Ce (10–18), Pr

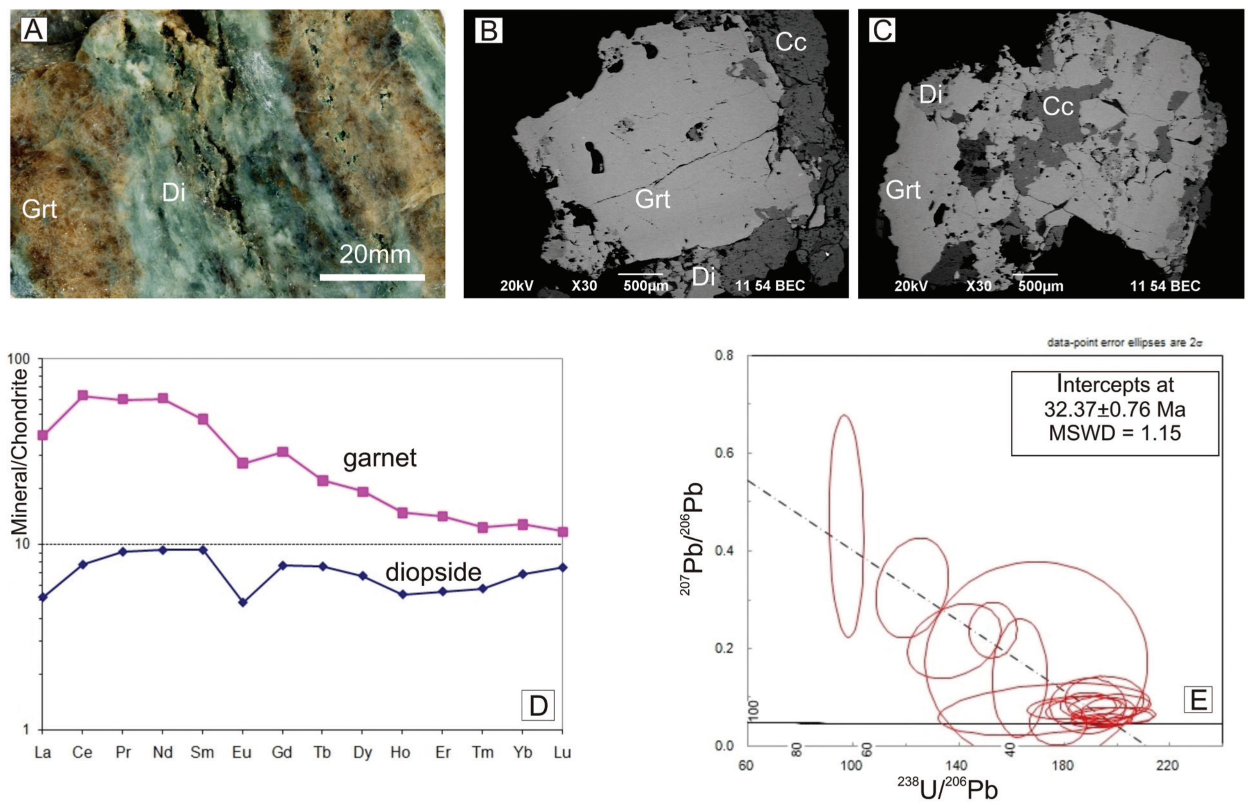

Fig. 1. *A*, macrophotograph of the studied garnet-dioside samples; *B–C*, BSE images of the garnet grains, associating with diopside and carbonates; *D*, average chondrite-normalised patterns of garnet and diopside; *E*, Terra-Wasserburg plot of the garnet. Abbreviations refer to: Grt, garnet, Di, diopside, Cc, calcite

(3.54–5.96), Nd (26.98–43.33), Sm (7.41–20.39), Eu (1.26–5.34), Gd (3.26–15.61), Tb (0.72–3.19), Dy (3.28–29.80), Ho (0.74–6.30), Er (1.05–12.94), Tm (0.14–2.87), Yb (1.26–19.80), Lu (0.15–2.78). The garnets show flat time-resolved signals obtained from depth profile LA-ICP-MS analyses for the measured elements, indicating that elements are structurally attached. Uranium content in the studied garnets is generally high (10.45–20.11 ppm), being positively correlated with the REE-content, thus suggesting that the U-incorporation into the garnet is largely controlled by substitution mechanisms. The amount of Pb (0.23–0.44) is low, while Th-incorporation varies within 3.1–12.1 ppm. The measured amounts of Hf reach 16.48 ppm. The chondrite-normalized patterns of the garnet and diopside show similar characteristics, with higher LREE and comparatively well-expressed Eu-anomaly (Fig. 1D).

U-Pb geochronology

The HR-LA-ICP-MS dating results strongly depend on the U-content in the garnet structure, but also on inclusions of other (Pb-bearing) phases and probably on overprinting processes leading to possible garnet alteration and new garnet growth. The dating record of the studied skarn garnets reveals an age of 32.37±0.76 Ma, defined by the lower intercept in the Terra-Wasserburg plot (Fig. 1E).

Discussion and concluding remarks

The zircon ages for the Central Pirin batholoith and its phases reveal successive intrusion from ~34 to 32.6 Ma (Filipov, Marchev, 2012). In the studied area, the materials of latest magmatic impulse have intruded onto the marbles from the host metamorphic complex (LTU) causing bimetasomatic reactions within the carbonate layers and skarnification.

The consistency between the garnet and zircon U-Pb dates confirms the reliability and accuracy of garnet U-Pb dating. Given the occurrence of Ca-garnet in contacts rocks and hydrothermal ore deposits, our results highlight the potential utilization of garnet as a powerful U-Pb geochronometer for dating magmatism and skarn-related mineralization.

Recently, the geochronological data acquired on the grossular-andradite (grandite) samples states that the andradite-rich garnets are more reliable for dating, giving better results (Deng et al., 2017; Wafforn et al., 2018). Here we prove the ability of grossular to yield precise ages.

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