СПИСАНИЕ НА БЪЛГАРСКОТО ГЕОЛОГИЧЕСКО ДРУЖЕСТВО, год. 80, кн. 3, 2019, с. 69–71
REVIEW OF THE BULGARIAN GEOLOGICAL SOCIETY, vol. 80, part 3, 2019, p. 69–71

Национална конференция с международно участие „ГЕОНАУКИ 2019“
National Conference with international participation “GEOSCIENCES 2019”

U-Pb dating and chemical composition of garnets from the southern parts of Srednogorie zone

U-Pb датиране и химичен състав на гранати от южната част на Средногорската зона

Valentin Grozdev[1], Rossitsa Vassileva[1], Irena Peytcheva[1,2], Albrecht von Quadt[2], Yulia Plotkina[3]
Валентин Гроздев[1], Росица Василева[1], Ирена Пейчева[1,2], Албрехт фон Квадт[2], Юлия Плоткина[3]

[1] Geological Institute, Bulgarian Academy of Sciences, 1113 Sofia, Bulgaria; E-mail: val.grozdev@gmail.com
[2] Institute of Geochemistry and Petrology, ETH-Zurich, Switzerland
[3] Institute of Precambrian Geology and Geochronology, RAS, St. Petersburg, Russian Federation

Keywords: U-Pb dating, garnets, trace elements, skarns, Late Cretaceous granites.

Introduction

Present study is focused on the garnet mineralizations along the Maritsa Shear Zone (MSZ; Bonchev, 1971; Naydenov et al., 2008) in the segment between Sofia and Kostenetz towns, known as Iskar-Yavoritsa Shear Zone (IYSZ; Georgiev et al., 2009). The MSZ separates two first-order units of the Balkan orogenic system – the Rhodopes and Srednogorie zones. It was an active dextral strike-slip shear zone from 130 Ma (Naydenov et al., 2008) to ~77 Ma (Georgiev et al., 2009). In the studied segment a series of composite plutons – Vitosha, Plana, Gutsal and Vurshilo are intruded along the IYSZ and their age spreads from 82 to 75 Ma (U-Pb zircon dating; e.g., von Quadt et al., 2005; Peytcheva et al., 2008). Calcium (or Ca-bearing) garnets are found in skarns and pegmatites and we would like to test whether they are related to the plutons and magmatic-hydrothermal fluids or to regional-metamorphic and deformational events. The study is part of systematic attempt to apply U-Pb geochronology on calcic garnets from skarn ore mineralizations in different tectonic zones of Bulgaria. Here we are focused on samples from the Srednogorie zone as part of the Late Cretaceous Apuseni-Banat-Timok-Srednogorie magmatic and metallogenic belt in SE Europe. Our investigation concerns LA-ICP-MS dating, compositional variations and trace-element distribution in calcium garnets to constrain the timing and the evolution of processes that may form ore mineralization.

Analytical methods

The chemical composition of garnets was determined by EPMA at the Institute of Precambrian Geology and Geochronology, RAS, St. Petersburg, Russian Federation. Trace element signatures (37 elements, including REE) of the skarn minerals (garnets, epidote, diopside) were defined using the LA-ICP-MS equipment at the Geological Institute, BAS, Sofia. The U-Pb isotope dating of the garnets is performed 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. Mali garnet (Seaman et al., 2017) and NIST 612 were used as primary external standard for dating and tracing, respectively.

Sampling

Here we describe two types of garnet mineralizations (Table 1):

(1) Skarn garnets from Gorni Okol village are sampled in the apical parts of the Plana pluton close to the NE contact with the metamorphic frame. Along with intensive hornfelse formation on the contacts, three linear skarns bodies are formed northwards of the village, resulting from grabbing of former Upper Turonian sediments during intrusion of the Plana pluton (Boyadzhiev, Ivanova-Panayotova, 1986). The magmatic activity turned the

Table 1. Characteristics of the studied garnets

Characteristics/ sample	GO	MFZ
Locality	**Plana pluton**, N of Gorni Okol village	**Gutsal pluton**, near Kostenets town
Occurrence	massive garnet-epidote skarns	spherulite-like aggregate
Mineral association	hedenbergite, epidote, scheelite	quartz, K-feldspar, magnetite
Average chemical composition	$(Ca_{2.94}Mn_{0.03}Fe^{2+}_{0.03})_{3.00}$ $(Al^{3+}_{0.78}Fe^{3+}_{1.17}Ti^{4+}_{0.03}V_{0.01})_{2.00}(Si_{2.97}Al_{0.03})_{3.00}O_{12}$	$(Mn_{2.1}Mg_{0.06}Ca_{0.49}Y_{0.03}Fe^{2+}_{0.30})_{2.98}$ $(Al^{3+}_{1.55}Fe^{3+}_{0.43}Ti^{4+}_{0.04})_{2.02}(Si_{2.90}Al_{0.10})_{3.00}O_{12}$
	$And_{55–65}Gross_{30–38}Alm_{0.4–1.7}Spess_{0.8–1.4}$	$Spess_{70}And_{14}Pyr_{2}Alm_{1–6}$
Selected traces elements, ppm	Sc (8.44), V (504), Cr (20), Co (2.25), Ni (2.44), Cu (9.61), Zn (9.19), Ga (25.93), Ge (7.1), As (7.6), Y (116.6), Zr (248), Sn (16.56), La (1.82), Ce (16.92), Pr (4.81), Nd (34.25), Sm (12.95), Eu (2.87), Gd (15.30), Tb (2.69), Dy (18.17), Ho (3.88), Er (11.95), Tm (1.76), Yb (12.39), Lu (1.96), W (34.23), U (8.33)	Sc (245.69), V (59.72), Cr (13.65), Zn (88.06), Ga (48.13), Ge (58.05), Y (6005), Zr (13.55), Nb (19.91), Sn (68.42), La (0.14), Ce (0.99), Pr (0.58), Nd (10.84), Sm (31.46), Eu (2.40), Gd (144.24), Tb (45.99), Dy (513.11), Ho (167.65), Er (789.59), Tm (163.64), Yb (1640.91), Lu (320.61), W (1.76), U (1.58)
Genetic remarks	contact skarns in the apical parts of the Plana pluton	pegmatite veins in the vicinity of the Gutsal pluton
U-Pb age, Ma	81.02±0.80 Ma	76.98±1.47 Ma

sand sediments into andalusite-cordierite hornfelses, while the limestones-marls are altered to calcic-skarns with scheelite mineralization.

(2) Garnets from pegmatite veins in the metamorphic rocks of the Thracian Lithotectonic Unit (Naydenov et al., 2008) and the periphery of the Gutsal pluton were obtained NE of Kostenets village. The host rocks are tectonically reworked as part of the MSZ. The sample is a garnet-quartz spherulite-like aggregate (3 cm in diameter).

Mineralogy and geochemistry

The skarn mineralization from the Gorni Okol locality is presented by hedenbergite-garnet±epidote±quartz assemblage. Garnets from the studied samples closely associate with epidote. Both minerals are characterized with varying Fe^{3+}/Al^{3+} ratios (generally 2–2.6 for garnet and 0.4–0.7 for epidote). According to their chemical composition garnets are determined as andradite with Fe_2O_3 content in the range of 16.82–22.28 and Al_2O_3 – 5.91–9.57 wt%. BSE images reveal that garnet grains are generally homogeneous, although some well-shaped crystals on the contacts with quartz show slightly Fe-enriched rims. Ti-content up to 0.71 wt% TiO_2 is characteristic in the andradite and lacks in the epidote. Manganese incorporation is typical for both minerals, although its values are preferably higher in the garnet (average 0.5 wt% MnO).

The garnet from Kostenets locality is formed in a very peculiar spherulite-like aggregate, where elongated, irregular crystals alternate with quartz. According to the chemical composition, it is determined as spessartine, although showing significant Mn-Ca and Al^{3+}-Fe^{3+} substitutions. Almost constant amounts of Fe_2O_3 (10.06–11.12 wt%) and CaO (4.8–5.66 wt%) are typical for all analyzed points (n=55). Apart from the main elements, MgO (0.52–0.67 wt%), TiO_2 (0.57–0.79 wt%) and Y_2O_3 (0.53–0.98 wt%) are detected by EPMA as well. The average chemical formula are shown in Table 1, where elements are distributed along the structural positions for both garnet types.

The trace elements signature (Table 1) differs in both garnets. The andradite garnet from Gorni Okol locality is enriched in V, Zr and U compared to the spessartine garnets from Kostenets. The elevated contents of elements that are typical for granitoids, suggest Plana granodiorite as source for these elements in the andradite. Cobalt, Ni, Cu are detected in small quantities. Tungsten reaching 65 ppm in the garnets from Plana pluton is in good agreement with the scheelite mineralization connected with the skarns.

In the Ca-bearing spessartine of Kostenets (MSZ) Sc, Zn, Sn, Ge are detected in higher values (compared with the group 1 Plana garnets). Cobalt, Ni, Cu remain below detection limits. Yttrium content above 6000 ppm corresponds to the extremely

high incorporation of the MREE and HREE (average sum of REE from Sm to Lu is 3820 ppm). The enrichment of Y and HREE elements is typical for the Fe-series garnets that are carriers of these elements in magmatic and metamorphic processes (as well as zircon).

Geochronology

The precision of the U-Pb age dating strongly depends on the U-content (Table 1) in the structure of the analyzed garnets. The U-Pb age of the andradite from the Plana pluton (high U content of 8.3 ppm) is well defined at 81.02±0.80 Ma. The acquired age of spessartine is 76.98±1.47 Ma (lower intercept age with the Concordia). We interpret it as the time of pegmatite formation and link it to the intrusion of Gutsal pluton. Higher uncertainties in age dating should be related to the low U-content (average of 1.6 ppm).

Conclusions

Our U-Pb garnet dating proves the ability of the Ca-garnets (grandites) to record the time of skarn-formation and magmatic-hydrothermal process. Both studied garnets from plutons along the IYSZ yield Late Cretaceous ages and infer a relation to the magmatic activity in the Srednogorie zone. However, studied garnets result from two different geological processes: i) skarn-formation with scheelite ore mineralization in Plana pluton (81.02 Ma); and ii) pegmatite emplacement in the frame of Gutsal pluton (76–77 Ma). These differences result in distinct occurrence and composition. The data prove also how important is the link between tectonics and magmatism for magmatic-hydrothermal mineralization.

Acknowledgements: The study is supported by the DNTS 02/15 bilateral project, financed by the Bulgarian National Science Fund.

Reference

Bonchev, E. 1971. *Problems of Tectonic of Bulgaria*. Sofia, Technika, 203 p. (in Bulgarian).

Boyadjiev, S., V. Ivanova-Panajotova. 1986. Sheelite mineralization in metasomatites related to Plana pluton. – *Geochem., Mineral. and Petrol*., *20–21*, 58–68.

Georgiev, N., B. Henry, N. Jordanova, N. Froitzheim, D. Jordanova, Z. Ivanov, D. Dimov. 2009. The emplacement mode of Upper Cretaceous plutons from the southwestern part of the Sredna Gora Zone (Bulgaria): structural and AMS study. – *Geologica Carpathica*, *60,* 1, 15–33.

Naydenov, K., S. Sarov, E. Voynova, T. Jelezarsky, I. Georgieva, D. Nikolov, N. Petrov, N. Markov, R. Marinova. 2008. *Explanatory Note to the Geological Map of the Republic of Bulgaria. Scale 1:50 000. Map Sheet K-34-72-B (Kostenets)*. Sofia, Ministry of Environment and Water, Bulgarian Geological Survey, 42 p.

Peytcheva I., A. von Quadt, N. Georgiev, Zh. Ivanov, C.A. Heinrich, M. Frank. 2008. Combining trace-element compositions, U–Pb geochronology and Hf isotopes in zircons to unravel complex calcalkaline magma chambers in the Upper Cretaceous Srednogorie zone (Bulgaria). – *Lithos*, *104*, 405–427.

Seaman, S., D. F. Stockli, N. M. McLean. 2017. U-Pb geochronology of grossular-andradite garnet. – *Chemical Geol.*, *460*, 106–116.

von Quadt, A., R. Moritz, I. Peytcheva, C. Heinrich. 2005. Geochronology and Cu-Au mineralization in the Panagyurishte region of the Apuseni-Banat-Timok-Srednogorie belt, Bulgaria. – *Ore Geol. Rev*., *27*, 95–126.