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Geochemistry and geochronology of Ca-garnets from Musomishte village, SW Bulgaria

Геохимия и геохронология на калциеви гранати от с. Мусомище, ЮЗ България

Valentin Grozdev[1], Rossitsa Vassileva[1], Irena Peytcheva[1, 2], Marcel Guillong[2], Albrecht von Quadt[2]
Валентин Гроздев[1], Росица Василева[1], Ирена Пейчева[1, 2], Марсел Гуилонг[2], Албрехт фон Квадт[2]

[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

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Introduction

The present study is based on the application of a relatively new method of U-Pb geochronology of grossular-andradite garnets (grandites; Seaman et al., 2017; Salnikova et al., 2017). It can be applied for dating of different geological processes (regional metamorphic events, tectonic deformation and ore-formation) but its main target are skarns. Here we present a pilot study on the dating of garnets from infiltration and contact skarns in the area of Gotse Delchev town, SW Bulgaria. The U-Pb age data are combined with EPMA analyses of the chemical composition and LA-ICP-MS studies of the distribution of trace element in grandites.

Analytical methods

U-Pb isotope and trace element composition of the garnets are 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 are applied as standard conditions. We used Mali garnet (Seaman et al., 2017) as primary external standard for dating, and NIST 612 for tracing. Analytical protocols include the two SRM in the beginning, every 10–15 analyses and at the end. 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 3.0 or ISOPLOT 4.15. Iolite or SILLS programs and the SiO_2 content in garnet (as internal standard from EPMA) are used for calculation of the chemical composition (44 major and trace elements).

Geological setting

The investigated skarn mineralizations are located 2 km southward of Musomishte village. The outcrops are in the NE part of the Teshevo granite, embedded in the marbles of the Dobrostan Formation (Kozhuokharov, Marinova, 1994). The contact between granite and marbles is cold, without any interaction and skarnification, and often marked by tectonic reworking. Close to this contact passes the Mesta fault zone (Zagorchev et al., 1974).

Two types of garnet-bearing skarn assemblages were outlined based on field observation: 1) infiltration skarns (skarnoids) and 2) contact skarns. Infiltration skarns are formed by the metasomatic processes in the metamorphic sequence, framing the pluton, being presented as levels of diopside-dominated rocks (up to 5 m thick) with garnet and wollastonite alternating levels. Thin garnet bands (1–5 mm) associated with clinopyroxene are separated by pure wollastonite levels. Garnet zone (up to 2 cm) always mark the sharp boundary with the marble stratum. This variegated lithology is mostly developed next to the quartz-amphibole gneisses with cataclastically deformed fish-like quartz lenses (up to 10 cm). The formation of mineral layers and banding in infiltration skarns is strongly tectonic influenced.

Contact skarns result from the intrusion of granite dykes (later than the Teshevo pluton) in the marbles. They are occurring as lenses and pockets (up to 1 m wide) with massive garnet-epidote mineralization.

Mineralogy, geochemistry and geochronology of grandite

The mineral assemblage in the infiltration skarns is more diverse, compared to contact ones. Major minerals are clinopyroxenes from diopside-hedenbergite series (7.17–12.48 wt% FeO), andradite-grossular garnets and pure wollastonite. According to the chemical composition garnets are determined as ferroan grossular with various Fe_2O_3 (5.5–10 wt%). Those closely associated and intergrown with diopside reveal the highest Fe-content (up to 11 wt% Fe_2O_3). Phlogopite and anorthite are among the minor minerals in the assemblage, while apatite, zircon and pyrite are observed as accessories. The contact skarns are composed by garnet, epidote, secondary carbonates and quartz. The garnet composition is defined as andradite with Fe_2O_3 reaching ~18 wt% and Al_2O_3 within close range of 8–9 wt%.

Trace elements signatures of garnet are distinct in the two skarn types. The grossular from the infiltration zones is depleted in trace elements compared with the andradite from the contact zone. A trend of increasing of the average values from infiltration to contact garnets is observed for: Mn (5189–14 620 ppm), V (136–722 ppm), Zr (59.27–135.06 ppm), Nb (15.93–41.24 ppm), Ta (0.34–1.62 ppm), Hf (0.70–1.42 ppm) and U (1.41–9.87 ppm), as well as all LREE (La–Gd). The opposite behaviour is characteristic for the M-HREE (Dy–Lu) elements, showing enrichment in the grossular together with Cr, Y, Th and Pb.

The obtained LA-ICP-MS U-Pb isotope ages of the Ca-garnets are defined by the lower intercept with Concordia, using Tera-Wasserburg plots. The grossular from the infiltration zone is dated at 43±16 Ma and the high uncertainty is explained by the low uranium content of the garnet (U ≤1 ppm). On the other hand the contact skarn andradite was dated precisely and the obtained age is 30.27±0.78 Ma, in accordance with the U content (9.87 ppm) in the analysed grains.

Discussion and conclusions

According to the Fe-content in the garnet we assume that grossular is formed in more acid environment, while contact andradite garnet is typical for more alkaline environment, which on the other hand is characteristic for bimetasomatic skarns (Bojadjiev, Ivanova-Panajotova, 1986).

Considering trace element composition in the studied garnets we may suggest mineralogical control on their behaviour. The lower trace element content in the infiltration grossular (e.g. LREE; U, Zr; V, Nb, Ta) may be due to the co-existing apatite, zircon and iron oxides and sulphides scavenging these trace elements from the fluids. The elevated contents of the same elements in andradite we explain with the lack of accessory minerals in the contact skarns and with their proximal position to the granitic source.

The age of the andradite from the contact skarn is close to the U-Pb zircon age of the Teshevo granite 32±0.2 Ma (Jahn-Awe et al., 2010) and interpreted to date the time of skarnification/interaction of granitic melt with marbles. The poorly defined age of the infiltration skarns cannot be used for geological interpretations due to the high uncertainty. Generally, the U-Pb isotope ages are better defined in the Fe-rich and Al-poor contact andradite with higher U-content (9.87 ppm) compared to the Fe-poor infiltration grossular.

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