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From relative to absolute timing of ore mineralization using garnets: a case study of the Karavansalija Cu-Au skarn deposit in Rogozna Mountains, SW Serbia

От относително към абсолютно датиране на рудна минерализация с използване на гранати: примерно изследване на Cu-Au скарново находище Каравансалия в планините Рогозна, ЮЗ Сърбия

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Introduction

Skarn ore deposits are major sources for a variety of metals, including Fe, Cu, Au, W, Mo, and rare earth elements (Meinert et al., 2005). The availability of geochronological data of the skarn hydrothermal deposits is rare, compared to epithermal and porphyry Cu deposits, due to scarcity of dateable primary skarn minerals, or a lack of crosscutting relationships that directly constrain the duration of magmatic hydrothermal activity. Potential minerals for geochronological studies of skarns are the calcium garnets. They may contain uranium in a quantity that make them reliable as a U-Pb geochronometer. Earlier U-Pb skarn garnet dating implies ID-TIMS techniques but the real revival of the method is connected with the application of the LA-ICP-MS technique (Seman et al., 2017). The latter is fast and can be applied directly to thin/thick section or to separated mounted grains. An important advantage is the possibility to avoid inclusions (if visible), choosing the position of the LA-craters.

In present study we are testing the U-Pb garnet dating techniques on the skarns of Karavansalija Mineralized Centre (KMC) in the Rogozna Mountains, SW Serbia (Borojević-Šoštarić et al., 2013 and references therein). Precise CA-ID-TIMS U-Pb zircon dating (Hoerler, 2017) revealed 1.7 Ma magma evolution, skarn formation and about 140 Ka timespan of economic ore mineralization and these results provide a perfect opportunity to compare it with our new geochronological garnet data.

Geological setting and relative timing

The Karavansalija Mineralized Center in the Rogozna Mountains is related to a magmatic suite that is part of the NW-SE oriented Oligo-Miocene Serbo-Macedonian Magmatic and Metallogenic Belt (SMMMB), which can be traced from Serbia to Macedonia, Bulgaria and Greece. The belt is represented by Pb-Zn-Ag (±Sb±Cu±Au±W) veined hydrothermal and/or skarn replacement mineralization. A few of the empiric base metal deposits situated within the Rogozna Mts. and its surrounding areas are Trepca, Crnac, Belo Brdo and Leskova Glava (Borojević-Šoštarić et al., 2013).

Two main magmatic episodes are distinguished in the Cenozoic magmatic complex of Rogozna Mts.: i) an older succession (Ar/Ar ages of ~30 Ma) composed mostly of andesite-dacite ± quartz-latite volcanic rocks, in the eastern part of the complex, and ii) an younger succession (29 to 24 Ma) comprising quartz-latite and related pyroclastics (Borojević-Šoštarić et al., 2013). Borojević-Šoštarić et al. (2012) found numerous disequilibrium textures, which indicate that the younger rocks formed by crystallization of hybridized magmas. Thus, they concluded a petrogenetic link to the adjacent Pb-Zn-Ag Crnac deposit (~5 km north from KMC).

The KMC Cu-Au skarn deposit is a result of multiphase hydrothermal activity caused by discrete magmatic pulses. Zircon LA-ICP-MS and ID-TIMS dating together with zircon trace element and Hf isotope measurements suggest that the magmatism starts around 29.3 Ma with andesitic to trachy-andesitic extrusives and shallow intrusive volcanics. Shallow magmatic injection of more evolved trachyandesites into Cretaceous limestone at ca. 29.0 Ma leads to the formation of an extensive prograde exoskarn field. The fluids in excess show 550 °C and 55 wt% NaCl equivalent, indicating a magmatic fluid source. A retrograde hydrothermal phase in the exoskarns leads to incomplete reaction of garnet to hydrous phases like chlorite and epidote. After a period of quiescence of about 1.2 Ma, an increased heat and fluid pressure leads to the expulsion of a crowded porphyritic (CP) stock at ca. 27.76 Ma, strongly interacting with the skarns and establishing/reactivating the hydrothermal system which leads to the formation of endoskarn veins with garnets but also to an enrichment of valuable ore minerals (arsenian pyrite, chalcopyrite, sphalerite and galena). During the retrograde stage the gold bearing minerals precipitated. Soon after an unmineralized second pulse of porphyry dykes cut the previous crowded porphyries and skarns at ca. 27.62 Ma, thus bracketing the maximum timespan of economic ore mineralization to about 140 Ka (Hoerler, 2017).

Analytical techniques

EPMA analyses are performed at ETH-Zurich using JEOL JXA-8200 SuperProbe Electron Probe Microanalyzer. U-Pb isotope and trace element composition of the garnets are defined at ETH Zurich and the Geological Institute of the Bulgarian Academy of Sciences, using a Resonetics Resolution 155 laser ablation system coupled to a Thermo Element XR Sector-field ICP-MS and UP193FX New Wave LA system and Elan DRCe quadrupole ICP-MS, respectively. Mali (Seaman et al., 2017) and Dashkesan garnets are applied as primary external standards for dating, and NIST 612 for tracing. The results were calculated using Iolite combined with VizualAge to obtain ages and ratios corrected for instrumental drift and down-hole fractionation. Iolite or SILLS programs and the SiO_2 content of the garnets (as internal standard) are used for calculation of their trace element composition.

Samples and results of the U-Pb garnet age dating

The first group (i) of garnet (Gar) samples for dating are from the exoskarns related to the early trachyandesitic shallow intrusion. They form a main greenish mass of disseminated “atoll” garnets with chlorite and epidote, which are cross-cut by later Gar-Q-Ca veins with arsenopyrite. The second group (ii) of Gar samples are from the endoscarn veins in the CP, where they form aggregates to well-shaped muddy orange-greenish crystals.

EPMA analyses of the garnets reveal andradite-grossular to end-member andradite composition with changing chemistry in narrow and/or wide growth zones. Typical trace elements are Ti and Mn (0.1–2.6% TiO_2 and 0.1–0.8% MnO). Uranium content is also highly variable (<1% to >30 ppm) with generally higher quantity in grossular-andradites and lower in andradite-grossular and end-member andradite.

U-Pb garnet age dating with the quadrupole ICP-MS was possible only in the case of U>5 ppm and resulted in ages with ≥10% uncertainty. The LA-XR-ICP-MS dating yields lower intercept ages of 27.56±0.20 Ma for type (ii) grossular-andradites, whereas type (i) garnets are dated with higher uncertainties at 27.27±0.68 Ma (atoll garnets) and 26.98±0.75 Ma (vein grossular-andradites). ID-TIMS dating is in progress.

Conclusions

U-Pb age dating of grossular-andradites of KMC revealed ages that are in agreement with the high precision zircon data. The precision of the garnet LA-(XR-) ICP-MS ages (≥1–2% uncertainties) is similar to the one of zircons. In the case of KMC absolute timing of the skarn garnets outlines the progress of mineralizing events but is complicated by possible Pb-loss during the overprinting hydrothermal process.

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