Elementi u tragovima i fluidne inkluzije distalnih skarnova Rudnika

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ELEMENTI U TRAGOVIMA I FLUIDNE INKLUZIJE DISTALNIH SKARNOVA RUDNIKA

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Skarnovi u Rudničkoj vulkanskoj oblasti (centralna Srbija) formirani su na kontaktu silova i dajkova kiselih vulkanita kasnomiocenske do ranooligocenske starosti, i gornjokrednih klastično-karbonatnih sedimenata (Cvetković et al., 2016; Kostić et al., 2021). Klasifikovani su kao epidotski, granat-vezuvijanski i granat-piroksenski skarnovi. Prema podeli kontaktno metamorfnih stena, skarnovi su definisani po facijama na one iz albit-epidotske hornfels facije, hornblenda hornfels facije i piroksenske hornfels facije. Sva ispitivanja granata izvršena su na uzorcima dobijenim iz bušotina. Distalni skarnovi Rudnika izgrađeni su od kvarca, kalcita, epidota, hlorita i granata. Obično se smenjuju sa manje ili više kontaktno metamorfisanim i izmenjenim metaklastitima. Struktura im je granoblastična, a tekstura masivna. U vrlo retkim slučajevima pokazuju blago ubiranje koje je nastalo kao rezultat blizine manjih pukotina ili raseda. Granati u distalnim skarnovima Rudnika su podređeni, dominantno kalcijskog grosular-andraditskog sastava ($Grs_{2.9-53.9}Adr_{39.3-88.9}Alm_{0.5-10.0}$) sa izraženom hemijskom zonalnošću, koja se najbolje zapaža ispitivanjem na mikrosondi i BSE slikama.
Fluidne inkluzije se u granatima pojavljuju u blago izduženim i elipsastim oblicima. Nepravilne forme fluidnih inkluzija su retke. Generalno, populacije ispitivanih fluidnih inkluzija pripadaju tečno-gasovitim i veličine su oko 3-5 mikrona. Temperature homogenizacije (Th) se kreću između 373-392 ºC, dok je procenat saliniteta oko 15 % NaCl. Preračunata gustina prema Bodnar (1993) je 0.77 g/cm^3.
Rezultati dobijeni metodom LA-ICP-MS na granatima normalizovani na primitivni omotač ukazuju na obogaćenje LREE i osiromašenje HREE elemenata i stroncijuma. Neutralna korelacija između aluminijuma i ukupnog sadržaja REE ukazuje na to da se skarnovi Rudnika razlikuju u odnosu na svetska skarnovska ležišta u kojima dominira YAG tip substitucije. U odnosu na skarnove iz proksimalne zone bliže kontaktu sa vulkanskim stenama kod kojih granati pokazuju jedva primetnu negativnu europijumovu anomaliju (Kostić et al., 2021), granati iz distalne zone imaju izraženu pozitivnu europijumovu anomaliju i obogaćenje uranijumom i olovom. U blago kiselim sredinama, ponašanje REE u velikoj meri kontrolisano je prisustvom kompleksih jona poput hlora, koji povećavaju stabilnost rastvorenog Eu^{2+} u hidrotermalnim fluidima, što uzrokuje ugradnju europijuma u granat.
Odsustvo linearne veze između kalcijuma, uranijuma, itrijuma i koncentracije REE^{3+} u granatima distalnih skarnova Rudnika ukazuje da je inkorporacija elemenata u tragovima i retkih zemalja u granate distalnih skarnova Rudnika bila direktno povezana sa hemizmom i fizičko-hemijskim osobinama hidrotermalnih fluida (pH, fO_2).
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TRACE ELEMENTS AND FLUID INCLUSIONS IN DISTAL SKARN ZONE FROM RUDNIK

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Key words: skarn, garnet, grossularite, andradite, REE, fluid inclusion

Skarns on Rudnik Mts. Volcano-intrusive complex (central Serbia) were formed along the contact between the (Cvetković et al., 2016; Kostić et al., 2021) Late Miocene-Early Oligocene volcanic rocks that appear as sills and dikes, intruding into the Upper Cretaceous clastic-carbonate sediments (Cvetković et al., 2016; Kostić et al., 2021). Skarns are classified as epidote, garnet-vesuvianite and garnet-pyroxene bearing. According to metamorphic mineral assemblages, the skarns belong to the albite-epidote hornfels facies, hornblende hornfels facies and pyroxene hornfels facies. All investigations were applied on drill core samples. The main constituents in distal skarns on Rudnik are quartz, calcite, epidote, chlorite and garnet. Skarns commonly alternate with low-grade contact metamorphosed clastic rocks, i.e., metaclastites. The texture is granoblastic and the structure is generally massive excluding rare cases of skarns derived adjacent to cracks and faults that demonstrate slightly folded structure. Garnets are subordinated constituents in distal skarns in Rudnik. They are dominantly calcium grossularite-andradite in composition ($Grs_{2.9\text{-}53.9}Adr_{39.3\text{-}88.9}Alm_{0.5\text{-}10.0}$). Chemical zonation in garnets is particularly evident at the BSE images and by results obtained by microprobe analysis. Fluid inclusions in garnets are either gently elongated or ellipsoidal, rarely irregular in shape. In general, the analyzed population of fluid inclusions are liquid-vapour and about 3-5 microns in size. The homogenization temperature (Th) ranges between 373-392 ºC, and the estimated salinity is about 15 % NaCl. The calculated density according to Bodnar (1993) is 0.77 g/cm^3.

Results obtained by the LA-ICP-MS method on garnets normalized to primitive mantle display enrichment in LREE and depletion in HREE elements and strontium. Neutral correlation between alumina and total REE points to differences of skarns from Rudnik from skarns within worldwide deposits in which prevail YAG substitution. In relation to skarns from the proximal zone closer to contact with volcanic rocks where garnets show a barely noticeable negative europium anomaly (Kostić et al., 2021), garnets from the distal zone have a pronounced positive europium anomaly and enrichment with uranium and lead.

In slightly acidic systems, the behaviour of REE is strongly controlled by the presence of complex ions, such as chloride ions. Their presence increases the stability of dissolved Eu^{2+} in hydrothermal fluids and leads to its incorporation in garnet. Lack of linear correlation between calcium, uranium, yttrium and REE^{3+} concentrations in garnets suggests that the incorporation of trace elements and rare earth elements in garnets in distal skarns on Rudnik might be directly linked to chemistry and physical-chemical properties of hydrothermal fluids (pH, fO_2).

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