

EPMA and TEM study of monazite hydrothermal alteration in Igralishte granite pluton, Southwestern Bulgaria

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The Igralishte pluton (Ograzhden block, Serbo-Macedonian massif) is built-up of two-mica S-type granite with age of 243.28 ± 0.84 Ma, embedded among high-metamorphic rocks (gneisses, gneiss-schists and amphibolites). The most significant alterations of the plutonic rocks are caused by postmagmatic high-temperature alkaline (K and Na) metasomatism. Besides, a tectonic and hydrothermal overprint at 36.36 ± 0.56 Ma is recently recognized using Rb-Sr analysis of whole rock and biotite. Monazite brings clear signs of hydrothermal alteration being presented by randomly shaped relics of the mineral surrounded by pseudomorphic dispersed aggregates of secondary products. In backscattered electron (BSE) images these aggregates appear as much darker areas than those of the monazite relics and contain very small lighter spots with increased content of Th, REE, Si and Y. According to EPMA data, the major part of the aggregates corresponds to apatite containing variable quantity of britholite molecule. Beside the pseudomorphic replacement of monazite, in the internal parts of the monazite relics in fissures there are a lot of inclusions of thorite and xenotime. The performed EPMA dating of the thorite and xenotime, although giving wide variation in the age (180-250 Ma), evidences their formation due to the postmagmatic high-temperature hydrothermal process and alteration of monazite. Pseudomorphic replacement of monazite + inclusions of thorite and xenotime is proposed to be realized at lower temperatures due to the later hydrothermal overprint.

Two types of monazite particles were found during transmission electron microscopy (TEM) examination: the first one represents intact mineral grains related to the relic forms of monazite and giving selected area electron diffraction (SAED) patterns typical for monocrystal material; the second one is altered monazite presented by polycrystalline aggregates whose SAED patterns show spot reflections grouped in rings. The performed EPMA in TEM evidences that the altered monazite contains much more Si, slightly more Y, Th and Ca than that in the intact monazite, while the ratio between (P+Si) and other elements (REE+Th+Ca+etc) in both varieties of monazite is almost the same. These data indicate that at least on the early stage of the monazite breakdown, mainly the PO_4 sublattice of the mineral is affected by hydrothermal alteration - through the substitution of P by Si. This process can be considered as britholitization of monazite. The inspection of series of particles of the polycrystalline monazite allows establishing that they are not composed of randomly oriented domains. This fact is illustrated by a case particle whose polycrystalline SAED pattern is superposition and derivative of series of slightly rotated and inclined SAED patterns originated from one and the same [211] zone. The domains (with prevailing size 10-20 nm) of this particle demonstrate characteristic Moiré fringes with spacings of ~ 2.0 and 4.5 nm originated from (120) and (011) atomic planes of monazite. The obtained results allow one to suggest that the observed microstructure of the polycrystalline monazite is a manifestation of original mosaic microstructure of the mineral but influenced by the later alteration processes. Most probably the established altered monazite represents an intermediate state of the monazite microstructure before their collapse into the pseudomorphic aggregates.