



Alteration of monazite in the Igralishte granite pluton, Southwestern Bulgaria

Изменение на монацит в Игралищенския гранитен плутон, Югозападна България

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In the last decade significant efforts have been done by a number of researchers for investigation of stability of monazite, $(\text{Ce,La,Th})\text{PO}_4$ during fluid-rock interactions (Poitrasson et al., 2000; Broska et al., 2005). The reason for these studies lies in the exclusive importance of the mineral as a repository of REE and Th in the continental crust, as a unique object for Th-U-Pb geochronology, geothermometry and geochemistry, as a potential structural form for nuclear wastes. Two principle alteration processes and products have been established for the monazite so far: (i) monazite-fluid ion exchange (REE, Ca, Y, Th, U) along fissures and periphery of the mineral carried out without essential disturbance of the $[\text{PO}_4]$ sub-lattice, and (ii) complete breakdown of the mineral giving rise mainly to apatite + allanite mineral assemblage. Such methods as SEM, EPMA and LA-ICP-MS are commonly used for the study of monazite and other REE-Th-U minerals alteration giving, however mainly chemical information of the processes. The present report gives more detailed insight into the structural characteristics of the alteration process as well as into the phase identification of the secondary products which almost uniformly are dispersive. For this purpose, monazite from the Igralishte granite pluton (Ograzhden block of Serbo-Macedonian Massif) with pronounced signs of alteration (Tarassov, Tarassova, 2005) as well as complex of electron microscopy methods TEM, SEM and EPMA were applied. Both polished massive and thin sections of granite as well as polished resin tablet with incorporated monazite grains from heavy fractions of the granite were used for the study. Specimens for TEM investigation were prepared by grinding the monazite grains in an agate mortar under alcohol and dispersing the particles onto holey carbon film supported by Cu grids.

Igralishte pluton (~245 Ma) is embedded among high-metamorphic rocks (gneisses, gneiss-schists and amphibolites) and built-up of two-mica (muscovite-biotite) granite. The most significant postmagmatic alterations of the rocks are caused by high-temperature alkaline (K and Na) metasomatism (Tarassova, Tarassov, 2007).

Typical texture of monazite replacement

The mineral occurs as anhedral to hemihedral inclusions to 0.5 mm in plagioclase and biotite. The anhedral (relic) outlook of the mineral is due to its replacement by aggregates/masses of dispersive ($< 1 \mu\text{m}$) alteration products whose phase composition is complicated and needs of further detail identification. In the backscattered electron (BSE) images these aggregates appear as much darker areas surrounding the monazite relics and containing very small lighter spots. According to EPMA data the major parts of the aggregates may correspond to apatite containing variable quantity of britholite molecule while the lighter spots are with increased content of Th, REE, Si, Y and sometimes Al and could be attributed to dispersive monazite, thorite, allanite and xenotime. Inclusions of thorite and xenotime with size to 10 mm are commonly encountered in fissures of the monazite relics. Typical microtexture of the monazite replacement includes central relic monazite core followed by zone of pseudomorphic aggregate of apatite (\pm monazite, allanite, thorite) and then by outer mantle of epidote. The well preserved contours of pseudomorphs indicate that the primary monazite crystals were euhedral. The epidote zone in all cases overgrows the pseudomorphs "capturing" the volume of the matrix (biotite or plagioclase) minerals and most probably is of magmatic origin.

Intact and altered monazite

Two types of monazite particles were found during TEM examination: the first one represents intact mineral grains related to relic forms of monazite and giving selected area electron diffraction (SAED) patterns typical for monocrystal material; the second one are clearly polycrystalline aggregates whose SAED patterns show spot reflections grouped in rings. The obtained SAED patterns of several [uvw] zones of the intact monazite demonstrate sharp reflections thus indicating that despite the respective age (~245 Ma) and the significant content of Th (ThO₂ – up to 10 wt.%) the mineral is without any signs of metamictization. The performed EPMA in TEM evidences that the content of principle elements as LREE and P (all analysis are normalized to the content of P) in both varieties of monazite are almost the same. More significant differences are observed in the content of Si, Y, Th, U and Ca which are significantly higher in the polycrystalline 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 the case particle whose polycrystalline SAED pattern in fact 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 related to (120) and (011) atomic planes of monazite. The observed Moiré patterns indicate that the overlapping one and the same atomic planes ((120) or (011)) in the domains are with angular rotation of 4–9°. The obtained results allows 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 interme-

diate state of the monazite microstructure before their collapse.

Thorite and other secondary products

Thorite, ThSiO₄, is distinctly later mineral included in monazite and formed during postmagmatic hydrothermal processes. It contains significant quantities of REE, U, Ca, Y. The mineral is known to have a zircon type of structure and a space group I4₁/amd. The obtained SAED patterns of the mineral are with sharp reflections indicating absence of metamictization. At the same time, the SAED patterns contain extra reflections serving as an argument that the real structure of the studied mineral is more ordered than that of the ideal zircon. Besides the well crystallized forms of thorite, several low crystallized (or amorphous) particles with increased content of Th and variable quantities of other components were also found. In additions to the thorite, all examined in TEM grains of apatite containing and not containing REE demonstrate high degree of crystallinity. It is noticeable that all inspected particles with composition which can be tentatively related to allanite turn out to be amorphous material.

Concluding remarks

The obtained results show that during the monazite alteration under postmagmatic conditions two principle types of secondary products are formed - well crystallized form (as thorite and apatite) and low-crystallized (amorphous) material forming pseudomorph aggregate with apatite. It is most probably, that the pseudomorph aggregates are formed after collapse of the “altered monazite” described in the present study. In this respect, the pseudomorph after monazite can be considered rather as a residue after the alteration while the well crystalline mineral forms (thorite) as a remobilized and reprecipitated components of the monazite.

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