



## Application of EBSD and micro-Raman spectroscopy for identification of microphases formed due to partial fluid-mediated alteration of monazite

### Използване на EBSD и микро-Раманова спектроскопия за идентификация на микрофази, формирани при частично изменение на монацит в хидротермални условия

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#### Introduction

Partial fluid mediated alteration of monazite (Ce,La,Nd,Th)PO<sub>4</sub> causing local changes in the chemical composition of the mineral and preserving the integrity of its crystals seems to be common phenomena for magmatic and metamorphic rocks, repeatedly reported in the literature (Poitrasson et al., 2000; Harlov et al., 2010; Hetherington et al., 2010). During this process, a redistribution of chemical elements occurs in the monazite crystals giving rise to development of metasomatic zonality with patchy or curved areas and sharp compositional boundaries, overprinting and disturbing the growth zonality, and, occasionally, to crystallization of micrometric to sub-micrometric neo-formed minerals. In the present communication, we report results on identification of neo-formed phases in metasomatically altered monazite from the Igralishte granite pluton (243 Ma) (Southwestern Bulgaria) using two different local methods – electron backscatter diffraction (EBSD) in SEM and micro-Raman spectroscopy recognized today as very effective tools for phase identification and characterization with spatial resolution of about 1 μm – for micro-Raman spectroscopy and 100–25 nm – for EBSD.

#### Material and methods

Grains of monazite manually picked from the heavy fractions of several granite samples of the Igralishte pluton, incorporated into epoxy resin tablet and polished according to preparation protocol for EBSD were used for the present study. A camera with Peltier-cooled CCD, a part of the EDAX Trident System attached to the scanning electron microscope ZEISS SEM EVO 25LS (Institute of Mineralogy

and Crystallography – BAS) was used for collection of EBSD patterns at 20 kV acceleration voltage. A single Raman spectrometer LabRAM HR Visible equipped with an optical microscope and Peltier-cooled CCD detector (Sofia University, Faculty of Physics) was applied for collection of Raman spectra using a 633 nm He-Ne laser with power on spot of 6 mW and 100X objective.

#### Results and discussion

The partial alteration of the study monazite including redistribution of REE, Th and U and crystallization of new phases is related to the early stage of high-temperature postmagmatic alkaline (potassium) metasomatism in the Igralishte pluton (Tarassov et al., 2011). On the first step of our work, the new phases were analyzed by EDS. The obtained results allowed us to tentatively identify the phases and to infer that xenotime, YPO<sub>4</sub>, and Th-enriched phases (mainly thorite, ThSiO<sub>4</sub>) occasionally accompanied by zircon, ZrSiO<sub>4</sub> and apatite, Ca<sub>5</sub>(PO<sub>4</sub>)<sub>3</sub>(F,OH), are the most typical neo-formed minerals for this stage of monazite alteration. The second step was to examine these phases by EBSD and micro-Raman spectroscopy techniques. In what follows, we consider two examples demonstrating advantages and shortcomings of the two methods applied. The first example shows results of combined use of the two methods on the example of three provisionally identified as monazite-related neo-formed phases – *Th-Si-*, *Th-*, and *La-Nd-Ca-enriched monazites*. The second example considers *xenotime-zircon-thorite* intergrowths as studied by EBSD.

##### (1) Monazite-related phases

These phases are grouped as veinlets crosscutting the initial monazite grain or occur as randomly

shaped inclusions in the mineral. Provisionally identified as *Th-Si-enriched (huttonitic) and Th-enriched monazites* they are unambiguously confirmed by micro-Raman spectroscopy: the positions of the Raman peaks in the range 450–1100 cm<sup>-1</sup> related to the internal modes of PO<sub>4</sub> group as well as the spectral region below 450 cm<sup>-1</sup> related to the lattice vibrations well correspond to the published Raman spectra of monazite-type rare-earth orthophosphate. The spectrum of the *Th-enriched monazite* shows lower intensity and pronounced broadening of the Raman peaks indicating for a much greater disorder or imperfection of the structure of the phase than that of the *Th-Si-enriched (huttonitic) monazite*. EBSD study of the identified minerals displaying no Kukichi bands in the EBSD patterns evidences that the two phases are with defect structure or low crystallinity ones and that the EBSD method cannot be used in this case for phase identification. On the other hand, the presence of *La-Nd-Ca enriched monazite* was explicitly proved by EBSD technique only: the obtained EBSD patterns of the neo-formed phase are in a good match to the monazite standard. Moreover, the neo-formed monazite and the neighbor matrix monazite have the same EBSD pattern, thus indicating that the secondary monazite forms via oriented (epitaxial) crystallization over the initial monazite matrix. In contrast to EBSD, the Raman spectroscopy cannot be used for the phase identification of the latter mineral as its Raman spectrum is characterized by extremely high fluorescence background with weakly pronounced Raman peaks hampering the phase identification.

#### (2) *Xenotime-zircon-thorite intergrowths*

The minerals are known to be with one and the same structure – tetragonal system, S.G. *I41/amd*, and close cell parameters and their presence in the studied samples was preliminarily proved by TEM. The minerals form vein-like aggregates of euhedral crystals of zircon and anhedral crystals of xenotime and thorite. Rarely, some of the zircon crystals are overgrown by thorite giving zonal outlook of the zircon-thorite intergrowth. It is found that, unlike the xenotime and

zircon, the studied thorite gives no any diffraction in the EBSD patterns – indication of partially disturbed structure of the mineral due to metamictization. It is found also that the zircon and xenotime crystals in the aggregates give almost equivalent EBSD patterns evidencing their similar crystallographic orientation. Besides, the mutual orientation of xenotime and zircon crystals is observed even in cases when they are separated by the metamict thorite. The obtained EBSD data allow us to conclude that the thorite-xenotime-zircon intergrowths are formed via simultaneous oriented growth (syntactic growth) of the three minerals facilitated by equivalent structure and uniform oxygen sublattice. Although the studied thorite gives no Kukichi bands in the EBSD pattern, the mineral can be indirectly identified on the base of EBSD data of the neighboring xenotime and zircon building oriented intergrowths with thorite.

The sensitivity to the degree of structure perfection is an intrinsic feature of the EBSD method that could be used for evaluation and comparison of the structural state of minerals. During the current study of monazite and mineral inclusions in its crystals we found that the quality of the obtained EBSD patterns worsens essentially in the following mineral sequence: xenotime > zircon > initial monazite > La-Nd-Ca enriched monazite >> thorite, Th-Si- and Th enriched monazite, thus indicating that in this sequence the mineral structures become more and more defect.

## Conclusion

The obtained results show high efficiency of the combined application of EBSD and micro-Raman spectroscopy technique for identification and characterization of micrometric and submicrometric minerals on the example of mineral inclusions in monazite. It is noteworthy, that according to the EBSD data of the studied minerals, the structure of xenotime seems to be most robust – the fact that should be taken into account in using the REE phosphate ceramics for immobilization of dangerous radioactive wastes.

## References

- Harlov, D. E., R. Wirth, C. J. Hetherington. 2010. Fluid-mediated partial alteration in monazite: the role of coupled dissolution-reprecipitation in element redistribution and mass transfer. – *Contr. to Mineral. and Petrol.* (published online: 09 December 2010, DOI 10.1007/s00410-010-0599-7).
- Hetherington, C. J., D. E. Harlov, B. Budzyń. 2010. Experimental metasomatism of monazite and xenotime: mineral stability, REE mobility and fluid composition. – *Mineral. and Petrol.*, 99, 165–184.
- Poitrasson, F., S. Chenery, Th. J. Shepherd. 2000. Electron microprobe and LA-ICP-MS study of monazite hydrothermal alteration: Implication for U-Th-Pb geochronology and nuclear ceramics. – *Geochim. et Cosmochim. Acta*, 64, 19, 3283–3297.
- Tarassov, M., E. Tarassova, M. Abrashev, L. Lialina, D. Zozulya, E. Savchenko. 2011. Fluid-mediated alteration of monazite in Igralishte granite pluton (SW Bulgaria) as factor for REE, Th and U redistribution in weathering rocks and soils. – In: *Proceedings of International Scientific Technical Conference “Ecology Problems in Mineral Raw-Material Branch”*. Varna, Bulgaria, 28 August–1 September, 52–58.