First data on monazite with a negative Ce anomaly from the Igralishte pluton, Southwestern Bulgaria

Първи данни за монацит с отрицателна цериева аномалия от Игралищенския плутон, Югозападна България

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Introduction

Recently, during a systematic investigation of REE-Th-U minerals in the Igralishte granite pluton (243 Ma), Southwestern Bulgaria, we found unusual Ce-depleted forms of monazite (LREEPO₄). First data on the occurrence and chemical composition of the mineral, its relationships with other minerals and possible genesis are discussed in the current report.

Material and methods

Polished sections as well as crystals of monazite manually picked from the heavy fractions of granite samples of the Igralishte pluton, incorporated into epoxy resin pellet and then polished were used for the present study. Imaging in backscattered electrons (BSE) and X-ray mapping at 20 kV and electron probe micro-analysis (EPMA) with energy dispersive (EDS) and wave dispersive (WDS) spectrometers at 14 kV on a scanning electron microscope ZEISS SEM EVO 25LS (IMC–BAS) equipped with an EDAX Trident analytical system were employed for characterization of the material.

Results and discussion

The Ce-depleted monazite is distinguished from the magmatic accessory monazite only in BSE images with strongly enhanced contrast. The mineral is found only as microcrystals sized between 0.3 to 3.0 µm (some aggregates of its crystals are with size to 7 µm). The Ce-depleted monazite occurs as (i) fine veinlets crosscutting the magmatic accessory monazite-(Ce) (the most common case) and other minerals as plagioclase (more rare case); (ii) aggregate replacing the peripheral parts of the primary monazite-(Ce) crystals (common case shown in Fig. 1); (iii) outer zone

Fig. 1. BSE image of magmatic accessory monazite-(Ce) partially replaced by Ce-depleted monazite (indicated by arrow). The outlined rectangle shows an area scanned for X-ray mapping of P K, LaL and CeL.
of a complex texture of replacement of the magmatic monazite consisting of the central relic monazite surrounded by apatite zone and then by zone of secondary monazite (common case); (iv) individual crystals or their aggregates replacing apatite crystals.

The obtained EPMA data show that a part of the analyses of the secondary mineral are with totals 89–92 wt%. The possible reason for this is the small size of the mineral crystals analyzed (although crystals with size >1.5 µm have been selected for analysis). Another reason for the low totals could be the presence of Ce-depleted rhabdophane (LREEPO₄·H₂O) at least in a part of the analyzed areas, and this problem requires additional investigation with diffraction and spectroscopic methods. Therefore in the further considerations we will use only the analyses with appropriate totals (close to 100%).

Chemical composition of the neoformed secondary monazite is characterized by the following features:

- very low content of Ce 1.5–6.0 wt% especially in comparison with the content of Ce in the unaltered magmatic monazite-(Ce) 22–27 wt%;
- chondrite normalized LREE patterns (Fig. 2) of the secondary monazite show strong Ce anomaly; the distribution of other LREE (La, Pr, Nd, Sm) is close to that of the unaltered monazite although slight fractionation of the elements – decrease in the content of La (from 12–13 to 10–12 wt% in unaltered and secondary monazites, respectively) and increase in the content of Nd (from 8–9 to 9–11 wt%) and Sm (from 1.3–1.4 to 1.2–2.3 wt%) can be seen in Fig. 2;
- Ce-depletion in the composition of secondary monazite is accompanied by essential increase in the content (in wt%) of Th (to 16), U (to 2), Y (to 3), Ca (to 4), and Si (to 2), as compared with the composition of unaltered monazite (Th to 7, U to 1.0, Y to 2.0, Ca to 0.6, and Si to 0.7);

- according to the current nomenclature of monazite solid solutions, the neoformed Ce-depleted monazite can be classified as monazite-(La) or monazite-(Nd) (the contents of La and Nd are very close) enriched by cheralite (CaTh(PO₄)ₓ) component. Similar Th-enriched monazite-(La) was recently described by Mayer et al. (2014) from metadiorite from the SW Slavonian Mountains, Croatia.

Cerium occurs in nature as Ce³⁺ like the majority of lanthanides, or as Ce⁴⁺ in oxidizing conditions. It is generally accepted that Ce anomalies (positive or negative) in minerals, rocks and waters is indication for oxidizing comparatively low-temperature conditions. In compilation of Mayer et al. (2014), negative Ce anomalies in REE minerals from metamorphic rocks can serve as evidence for a later metamorphic event developed in highly oxidized and fluid-rich environments.

The chemical alteration of the magmatic monazite into Ce-depleted monazite in the Igralishte pluton could be connected with the tectonic and hydrothermal overprint (to 300±50 °C) at 36.36±0.56 Ma according to Rb-Sr analysis of whole rock and biotite (Peytcheva et al., 2009). This thermal overprint can be related to the Paleogene volcanism in the region (Zagorchev, Dinkova, 1991) and well corresponds to our recent data on the alteration of zircon (Anastasova et al., 2014).

Conclusions

The obtained first data on monazite with a negative Ce anomaly from the Igralishte pluton allow us to suggest that the mineral is formed at the expense mainly of magmatic monazite-(Ce) at highly oxidized media activated by hydrothermal overprint at temperature <300 °C about 36 Ma ago.

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References


