



## Two geochemical types of rutile in granulites from Chepelare mélange, Rhodope massif, Bulgaria – application of Zr-in-rutile thermometry

### Два различни геохимични типа рутил в гранулити от Чепеларски меланж, Родопски масив, България и приложение на термометрия по съдържание на Zr в рутил

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#### Introduction

Rutile is a common accessory phase in variety of metamorphic lithologies, and the number of studies on its geochemistry and role as controller of Nb and Ta behaviour in subduction zone processes, increase significantly during the last two decades. Rutile in metamorphic rocks is formed during medium- to high-grade metamorphic processes, but it can be also produced through low-grade reactions (Meinhold, 2010). In high-pressure rocks it appears after the breakdown of Ti-bearing phases (e.g. titanite, ilmenite, titanomagnetite, and Ti-rich biotite). Rutile is important carrier of HFSE, generally immobile during metamorphism, and behaves as refractory phase at low degree of melting. In some rocks, rutile can carry almost the total content of Ti, Nb, Ta, Sb and W, but also significant amounts of V, Cr, Mo, Sn, Zr and Hf. Relatively low closure temperature for Pb diffusion (~500 °C; Bracciali et al., 2012), could be used for reconstruction of cooling history of high-grade metamorphic rocks.

#### Sample description and textural position

Leucocratic garnet-bearing granulite crops out close to the garnet-kyanite gneisses in Chepelare mélange to the E of the town of Chepelare. It is composed of feldspars, quartz, biotite, resorbed kyanite and garnet, and late muscovite and chlorite. The accessory minerals are represented by abundant zircon and monazite, apatite, titanite and rutile. Petrological observations, preliminary thermobarometry estimates and U-Th-Pb geochronology suggest granulite facies metamorphism (650–850 °C, >1 GPa) at 120–140 Ma (Georgieva et al., 2011). During the mineral separation, two types of rutiles were observed in 0.125–0.250 µm fraction:

bright-red rutile with elongated bean-like shapes, and green rutile with square sections. Both rutile types are not well-distinguished in thin sections. Well-visible non-pleochroic red rutile associates mainly with biotite, which forms a mantle around resorbed garnet grains. Close to the garnet, big apatite grains were also observed. The green pleochroic rutile grains associate with red-brown biotite in the matrix. Both types of biotite are later partly chloritized. Although being difficultly recognizable in thin sections, it appears that the red rutile type is formed through reaction of garnet consumption or was present as inclusion in garnet. The green rutile could be formed during the low temperature recrystallization of high-Ti biotite in the matrix.

#### Trace elements geochemistry

Trace elements analyses were performed in mineral separates by LA-ICP-MS, at 8Hz, with 50µm laser spot size and standard NIST 610. All analyzed trace elements show some variation from grain to grain and it is stronger for the green rutiles. No systematic record for core to rim change in trace elements contents were received. The presence of small mineral inclusions also hampers the use of some data.

The two groups of rutiles show significant differences in Fe, Al, V, Sn, Zr, Hf, U contents and Nb/Ta ratio. Fe and Al are incorporated in rutile structure by coupled substitution with HFSE. Fe content is supposed to increase with metamorphic grade (Meinhold, 2010), and it is higher in red rutiles, while Al is enriched in green grains (Table 1). V has positive correlation with Fe, and together with Sn shows higher contents in red rutiles. Cr is another element usually reported in rutiles and used in several discrimination plots as provenance indicator. The contents for both

Table 1. Trace elements contents in rutiles

ppm	Red rutiles	Green rutiles
Fe	5000–5500	2000–3000
Al	200–400	300–1400
V	400–780	250–450
Sn	450–600	40–60
Cr	12–29	6–15
Nb	1700–2900	1400–3200
Ta	120–230	90–150
Zr	370–470	6–12

groups overlap and are much lower than published for rutiles from metapelitic rocks (>250 ppm, Zack et al., 2002). Nb and Ta values show significant spread and can not be used to distinguish two rutile groups (Table 1), whereas the Nb/Ta ratios differ with lower values for red rutiles (10–18), and higher for the green ones (17–28). Nb/Ta ratios reflect probably a different mechanism of formation: different mineral precursors and presence of melt or fluid during crystallization. Zr and Hf contents are much higher in red rutiles (Table 1). Both groups show different Zr/Hf values of 15–22 and 11–16 for the red and green rutiles, respectively. REE contents are very low and often below the detection limit and  $\Sigma_{\text{REE}}$  from 1 to 3 ppm. The few chondrite normalized patterns are flat with weak negative Eu anomaly. U content in both groups is very different. It is higher in red rutiles and often <0.5 ppm in the green ones (Table 1).

### Zr in rutile thermometry

In metamorphic assemblages that contain zircon, quartz and rutile, the Zr content in rutile is a useful thermometer. There is no pressure influence found (Zack et al., 2004), although more recent calibration requires a pressure estimate (Tomkins et al., 2007). Having higher Zr contents, the red rutiles give higher temperatures, using different calibrations: 745–775 °C (Zack et al., 2004), 660–680 °C (Watson et al., 2006) and 690–715 °C (10 kbar,  $\beta$ -quartz equation, Tomkins et al., 2007). For the green grains the calculated temperatures are lower and the spread is significant: very low using Zack et al. (2004) calibration (225–400 °C) and higher for Watson et al. (2006) equation (410–

530 °C). The results indicate clearly that the rutiles are formed at different temperatures during retrogression. They could be useful for the revelation of the cooling history reconstruction.

### Discussion

The presence of two different rutile types in the same sample is an intriguing fact, yet poorly considered in metamorphic rocks studies. The geochemical features clearly distinguish the two groups of rutiles. Green rutile is depleted in all trace elements, except for Al and Nb, comparing to the red one. The application of Zr-in-rutile thermometry shows also crystallization at different temperatures, which should be used for cooling P-T-t path reconstruction. Further petrological observations and data on geochemistry of main and accessory minerals could reveal the mechanism of formation of the two rutile types, while the U-Pb geochronology could link the rutile formation to distinct metamorphic events or different stages of metamorphic evolution.

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