Geochemistry of rutiles from metamorphic rocks of Asenitsa and Arda Units, Central Rhodope, Bulgaria – preliminary results

Milena Georgieva¹, Tzvetomila Vladinova²

¹ Sofia University St. Kliment Ohridski, 15 Tsar Osvoboditel Blvd., 1504 Sofia, Bulgaria; milena@gea.uni-sofia.bg
² Geological Institute, Bulgarian Academy of Sciences, Acad. G. Bonchev Str., 1113 Sofia Bulgaria; E-mail: tz.vladinova@gmail.com

Abstract. We present new data on the geochemistry of rutiles from metamorphic rock of the Asenitsa and Arda Units, Central Rhodope Massif, Bulgaria. Trace elements in studied rutiles show large variations that depend on protolith type (metapelites and metabasites), metamorphic grade, the rock geochemistry and mineral association. Zr-in-rutile thermometry distinguishes the rutiles from both units with higher temperatures (650–750 °C) for the Arda Unit and lower temperatures (520–630 °C) for the Asenitsa Unit. The uranium content of most rutiles is too low (<0.5 ppm) for U-Pb dating.

Keywords: rutile geochemistry, Arda Unit, Asenitsa Unit, Central Rhodope, Bulgaria.

Introduction

Rutile is a common mineral in metamorphic rocks mainly in moderate- to high pressure metapelitic and high pressure metabasic rocks (Zack, Kooijman, 2017). Its geochemistry, Zr-in-rutile thermometry and the low closure temperature of the U-Pb system makes the rutile a useful mineral in petrochronology, and a powerful tool for constraining the P-T-t path of metamorphic terrains. Moreover, rutile could include and preserve minerals from prograde and peak stages. The mineral is a principal carrier for Ti, Nb, Ta, Mo, Sn, Sb and W in rutile-bearing metamorphic rocks (Zack et al., 2002). In contrast to zircon, rutile is not stable during metamorphic processes exceeding subgreenschist facies conditions (Zack et al., 2004) and is used to date the last significant metamorphism or the cooling history of high-grade metamorphic rocks.

Methodology and samples description

Trace elements analyses were performed in mineral separates and in thin sections by LA-ICP-MS, at 5–8 Hz, with 35 μm laser spot size and standard NIST 610 and TiO₂ as internal standard. All analyzed trace elements show variation from grain to grain and the presence of small mineral inclusions also hampers the use of some data. Analyses that show contamination with Al and Fe (more than 10 000 ppm) are typical for analyzed in thin sections rutiles included in garnet and kyanite, but usually the other trace elements are not affected.

We studied rutiles from 8 different metamorphic rocks from the Asenitsa and Arda Units. Metapelites (samples V-9, PCh-21), metabasites (V-18, PCh-23, PCh-44), and garnet-bearing gneiss (PCh-25) from the Asenitsa Unit and garnet-kyanite gneiss (ZA-346a) and metabasite (HP-38) from the Chepelare
shear zone, the Arda Unit. Only in sample ZA-346a rutiles were analyzed in a thin section.

In two metapelitic samples of Asenitsa Unit (staurolite-muscovite and garnet-muscovite schist; Georgieva, 2021), opaque minerals are abundant and rutile is observed only in garnet porphyroblasts of the second sample. In amphibolites porphyroblasts the same unit the rutile is the main accessory mineral and is present in the matrix and in epidote and garnet porphyroblasts. The garnet-bearing gneiss contains also calcite and tourmaline and we suggest a sediment protolith. Rutile is included in K-feldspar but is present also in the matrix. For the samples from Arda Unit, rutile is a common mineral in matrix and also as inclusion in kyanite and garnet porphyroblasts.

**Results and discussion**

Contents of trace elements in rutile show large variations for Cr (150–3900 ppm), Nb (10–7300 ppm), Sb (<3–85 ppm), W (3–4000 ppm), Pb (<1–6 ppm), U (<0.1–12 ppm), Ta (<0.3–450 ppm), V (550–3200 ppm), Zr (26–480 ppm), Sn (10–200 ppm), and Hf (2–28 ppm). Some trace elements differ with respect to their source rocks – Sn, Nb, and Ta are enriched in metapelitic samples compared to rutile in metabasic rocks. Other elements (Cr, V) are in higher concentrations in metabasic rocks than in metapelites, but at lower values, the data overlap. Chromium and Nb contents distinguish the rutiles from metapelites and garnet-bearing gneiss from the metabasic samples (Meinhold et al., 2008) (Fig. 1a). Lead, Th, Y, and REE contents are low in rutiles from all lithologies.

Trace elements also reflect the different metamorphic grade in the Arda and Asenitsa Units. The content of Zr and Hf is higher in the Arda Unit and lower in the Asenitsa Unit (Fig. 1b). We applied three Zr-in-rutile thermometers for the zircon-bearing samples. In three samples (V-18, PCh-23 and ZA-346a) we didn’t find zircon, although the peak of Zr in some rutile grains suggest the presence of Zr-bearing phases. The three thermometers give similar temperatures at ~550 °C but show some discrepancy at higher temperatures with lower temperatures for Watson et al. (2006) and Tompkins et al. (2007) and higher for Zack et al. (2004) and Watson et al. (2006).

![Fig. 1](image.png)

Fig. 1. a, plot of Nb vs. Cr contents in studied rutiles, after Meinhold et al. (2008); b, plot of Zr vs. Hf contents, that distinguish the rutiles with lower content from the metamorphic rocks of the Asenitsa Unit and higher content of rutiles in Arda Unit; c, calculated temperatures of the Zr in rutile thermometer using various calibrations at 10 kbar: Zack et al. (2004), Watson et al. (2006), and Tompkins et al. (2007); d, plot of Zr/Hf vs. Nb/Ta ratios, dashed lines represent chondritic values, after Meyer et al. (2011).
al. (2004) (Fig. 1c). For metamorphic rocks of the Asenitsa Unit, the temperatures range from 450 to 700 °C, average 520–630 °C. Lower temperatures were obtained for amphibolite (PCh-44) and garnet-bearing gneiss (PCh-25), while for schist they were higher. The large spread of temperatures recorded in garnet-bearing gneiss (400–640 °C), could be explained with presence of two rutile generations or significant recrystallization at lower temperatures. Higher temperatures were calculated for Arda Unit with average values from 650 to 750 °C.

The Zr/Hf and Nb/Ta ratios are predominantly subchondritic and do not differ for rutiles from both units (Fig. 1d).

Conclusions

Trace elements in the studied rutiles show large variations, that depend on protolith type (Nb, Ta, Sn) and metamorphic grade (Zr, Hf). They also differ from sample to sample, reflecting the rock geochemistry and mineral association (e.g., the Nb content of metapelites, Cr content in metabasites, etc.). Since we analyzed mainly separated rutiles, we cannot properly estimate the difference in the composition of matrix grains from those included in porphyroblasts or the presence of two rutile generations. Analyzed in situ rutiles in metapelitic sample (ZA-346a) did not show systematic variations in composition for inclusions in garnet and kyanite and matrix grains.

Zirconium-in-rutile thermometry distinguishes both units. The higher temperatures (650–750 °C) for the Arda Unit are consistent with previous Zr-in-rutile data from the same unit (Georgieva, Cherneva, 2012). Higher variation and lower temperatures (520–630 °C) for the Asenitsa Unit reflect the lower metamorphic grade.

Rutile records the last significant metamorphism or cooling, because of the relatively low closure temperature for Pb diffusion of ~600 °C (Cherniak, 2000). Unfortunately, the U content in most of rutiles from both units is too low (<0.5 ppm) to be dated (Zack, Kooiijman, 2017). Only rutiles from the garnet-kyanite gneiss of the Arda Unit show higher U content (average 8.5 ppm) and together with rutiles from granulitic gneiss from the same unit (average U content of 22 ppm; Georgieva, Cherneva, 2012) are suitable for U-Pb dating.

Acknowledgements: This study is financially supported by the Sofia University Scientific Research Grant 80-10-38/2023.

References


