Trace elements in titanites from different metamorphic rocks, Chepelare shear zone, Rhodope massif, Bulgaria

Елементи следи в титанити от различни метаморфни скали от Чепеларската зона на срязване, Родопски масив, България

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Introduction

The accessory minerals are commonly used for P-T-t reconstruction of metamorphic complexes and were reported as controlling factor of trace elements distribution in various magmatic and metamorphic rocks. Apart from zircon and monazite, the data from titanite are also valuable geochronometer, geothermometer and tracer for magmatic and metamorphic processes are increasingly used in the last years (e.g. Aleinikoff et al., 2002; Frost et al., 2000). Titanites are often zoned and can record several magmatic and metamorphic events, due to its refractory behavior and long growth history. The titanite is widespread accessory phase in different lithologies from the Chepelare shear zone (Arda lithotectonic unit, Central Rhodope massif), which have a complex metamorphic history.

Samples and methods

We present new data on trace elements contents in titanite grain profiles, from different lithologies in the Chepelare shear zone: retrogressed ultrabasics, garnet-bearing metabasics, amphibole-bearing leucosomes, Grt-cPx-Kfs granulites and impure marbles. The rocks from the shear zone have undergone similar metamorphic conditions, but the titanites associate with different main and accessory minerals, and formed by different metamorphic reactions respectively. The *in situ* profiles in big titanite grains ware performed using LA-ICP-MS equipment at Geological institute, (Bulgarian Academy of Sciences), at 8Hz, with 35–50 µm laser spot size and standard NIST 610. For each sample 4 to 5 profiles were made.

Geochemistry

Trace element patterns of fluid-mobile and immobile elements (Zr, Hf, Nb, Ta, REE, Y, U, Sr and P) in titanites can help in deciphering the evolution of complex metamorphic terrains, but still little is known about the influence of the protolith geochemistry in metamorphic rocks. The titanites in *retrogressed ultrabasics* (clinopyroxene, plagioclase ± amphibole) show significant HREE enrichment. The La/Lu ratio ranges from 0.001 to 0.155, with peak for Ho, Er and Tm on chondrite-normalized plots. ΣREE depends on LREE, which vary significantly: lower contents (La/Lu 0.001–0.005) and week positive Eu anomaly (1.17–1.27), when included in clinopyroxene and much higher (La/Lu 0.04–0.155), with negative Eu anomaly (0.58–0.73), when the grain is close to plagioclase. In some grains a transition form low to higher LREE contents and positive to negative Eu anomaly, from the core to the rim were observed. The Zr, Hf, Nb and Ta enrichment towards rim, followed by depletion, suggest a complex growing history of titanites. The P contents (200–840 ppm) have positive correlations with Zr, Hf, Nb, Ta, Sr and negative with Y and U. The U contents are generally below 10 ppm (1–10 ppm) with higher values in grains and zones of higher LREE and negative Eu anomaly. In *garnet-bearing metabasics* (garnet, clinopyroxene, amphibole, plagioclase, quartz and accessory zircon, apatite, rutile and sulfides), the titanites are abundant and present in different structural positions (Georgieva et al., 2010). LREE contents are higher (La/Lu 161–380) than HREE. The ΣREE is up to 0.7–1 wt.% and on chondrite-normalized plots REE have deep negative Eu anomaly (0.57–0.63). The P contents (1200–2000 ppm) decrease from the core to the rim and correlate positively with Zr, U, Th; Sr and Hf. The U (150–300 ppm) is lower than Th (130–490 ppm) and both elements correlate positively with ΣREE. In *amphibole-bearing leucosome* (Cherneva, Georgieva, 2007), the titanites have two contrast REE patterns. Grains included in leucosome show HREE enrichment (La/Lu 0.07–0.34), week negative to absent Eu anomaly (0.81–1.08) and low ΣREE (350–770 ppm). Titanites close to the amphibole have higher contents for LREE (La/Lu 37–102), negative Eu anomaly (0.51–0.63) and ΣREE from 0.08 to 3 wt.%. In some grains both patterns are present with higher REE in inner parts and lower to the rim. The P (177–690 ppm) correlates positively with Y (up to 0.4 wt.%), Zr, Hf, Nb (up to 0.3 wt.%), Ta and Sr. The Th contents are very high when titanite is included in amphibole (470–870 ppm) and lower when the grains are in leucosome (1–25 ppm). The U (1–100 ppm) also shows higher values when ΣREE are higher. The Zr values split in two groups (100–180 and 460–740 ppm), with lower contents in leucosome and rims. In *garnet-clinopyroxene-K-feldspar granulites* (± amphibole, plagioclase, quartz, epidote and accessory zircon, pyrite, apatite) (Vladinova, Georgieva, 2013, this volume), the geochemistry of the titanites again shows significant variation. The LREE enrichment is the most common feature, especially close to garnet, clinopyroxene and amphibole. Titanites in leucocratic matrix or inner parts of the grains display flat or bell shaped REE distribution on chondrite-normalized plots (La/Lu 7–11), however, with no evident Eu anomaly. When plagioclase is present, the Eu anomaly is weekly negative (0.88–0.98). The P (160–560 ppm) shows positive correlation with Nb, Hf, Sr and U. The U content is in the range 15–85 ppm, with higher values in grains close to feldspars and quartz. In this sample is more difficult to outline core to rim changes as variations within every single grain are more pronounced. In *impure marbles* (calcite, diopside, scapolite, K-feldspar, plagioclase, quartz and accessory apatite, zircon and graphite), titanites often associate with apatites (Georgieva et al., 2009). On chondrite-normalized plots, REE show LREE enrichment (La/Lu 20–30), with higher values for Pr, Nd and Sm and negative Eu anomaly (0.55–0.73). In some grains LREE vary significantly (La/Lu 3–12). The P has positive correlation only with Nb, Ta and Th, and negative with ΣREE. In profiles P, Nb and Th decrease towards rims, whereas Y and Ta show enrichment, but in some cases the trends are more complicated. The U (23–460 ppm) contents vary significantly and have positive correlation with ΣREE.

Thermobarometry

Zr-in-sphene thermometer (Hayden et al., 2008) was applied for the studied titanites. In retrogressed ultrabasics, the Zr contents and respectively temperatures vary from 770–780 °C in core to 790–840 °C to the rim, and lower values again in the outermost parts (780–800 °C) associate with the outermost parts. Titanites from garnet-bearing metabasics show again a complex variation, which gives temperatures from 760 to 800 °C. Temperatures for titanite grains in amphibole-bearing leucosome give lower temperature (740–775 °C), than the grains included in amphibole (830–860 °C). For titanites in garnet-clinopyroxene-K-feldspar granulites temperatures range from 730 to 820 °C, similar to that in impure marbles (715–835 °C).

Conclusions

Studied titanites have complex zonation. REE patterns are very different from one sample to another and even in a single grain. This variation should be explained by specific metamorphic reactions of formation for each sample and supposes a detail geochemical study of titanites before using them for geochronology. The influence of neighbor minerals and other accessories is evident, but needs to be confirmed by more data. The application of Zr-in-sphene thermometer is consistent and for all studied samples gives similar temperatures, close to the already published for the area.

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