

Two types of titanite in I-type tonalites from Tatric and Veporic units: Magmatic vs. post-magmatic oxidation

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Abstract: Titanite, a characteristic mineral of Tatric (Tribeč) and Veporic (Sihla) I-type tonalites crystallizes in two generations: magmatic titanite I originated by slightly different ways, at the expense of Ti-biotite in Tribeč tonalite, and at the expense of Fe–Ti oxides in Sihla tonalite. Both rocks were oxidised in late stages, producing postmagmatic/metamorphic titanite II+magnetite, the Sihla type oxidised more intensely due to oxidising effect of the Alpine overprint.

Introduction

I-type tonalites and granodiorites represent important rock types building the Variscan basement of the Tatric and Veporic units (Petrík & Broska 1994; Broska et al. 2013; Broska & Petrík 2015). A characteristic accessory mineral assemblage of this granitoid rock, magnetite+titanite+allanite, indicates oxidation conditions during late- to post-magmatic stages (Broska et al. 2007). However, titanite population is not uniform, and at least two types of this mineral can be distinguished in different textural positions. In this contribution I present new interpretation of both titanite types and discuss their petrogenetic significance on the example of Tribeč tonalite (Tatric unit) and Sihla tonalite (Veporic unit).

Occurrence and petrography of the tonalites

Titanite-bearing tonalites typically occur in Tatric unit (Tribeč. Mts., Nízke Tatry Mts.) and NW part of the Veporic unit (the Sihla type tonalite). By contrast, titanite is not found in more common peraluminous S-type granitoids occurring in both tectonic units.

Medium-grained granitoids are composed of strongly retrogressed plagioclase (saussurite), if preserved with An_{28-30} abundant biotite [$Fe/(Fe+Mg)=0.40-0.42$, TiO_2 1.5–2 wt. %], both extensively replaced by epidote/clinozoisite or rare secondary muscovite. The assemblage is completed by a rich accessory assemblage (magnetite, allanite, titanite, apatite, zircon). The presence of accessory amphibole (hornbende) is significant in the Tribeč tonalite, while it is missing in Sihla tonalite. Plagioclase is less altered in Tatric tonalite, and it is replaced by tiny white mica and fine-grained clinozoisite. In contrast, Veporic plagioclase is heavily

replaced by abundant large epidote. Titanite is also different: in the Tatric Tribeč tonalite a euhedral titanite I is associated mostly with plagioclase always containing resorbed grains of Ti magnetite (Fig. 1a). Titanite I in Veporic Sihla tonalite is up to several millimeters in size, sub- to euhedral also associated with plagioclase but without enclosed Ti magnetite (Fig. 1c). Titanite II in both rock types is small anhedral, typically associated with biotite and epidote (Fig. 1d). Titanite II commonly merges with large grains of titanite I (Fig. 1b).

P-T-X conditions of titanite formation

Magmatic titanite commonly crystallizes from magmas with increased Ca/Al ratio, not necessarily oxidised. High Ca content stabilises titanite at the expense of ilmenite (e.g. Frost et al. 2000). It is stable over wide P–T range including magmatic, postmagmatic and metamorphic conditions.

Pseudosections

P–T evolution was modelled by pseudosections calculated from whole rock analyses of Tribeč and Sihla tonalites using the Perplex software packet (Connolly 2005). P–T window used were at $T=500-850$ °C and $P=1-7$ kbar. Chosen water contents were 1.25 wt. H_2O for Sihla tonalite and 1.45 for Tribeč tonalite. These contents were estimated from isobaric T- H_2O pseudosections at the H_2O values, which best correspond to the observed modal mineralogy, especially the presence/absence of amphibole and presence of titanite or ilmenite. Reduced conditions (FeO) were used because an oxidated system in Perplex produces hematite, phlogopite and no Fe–Ti oxide. However, oxidation

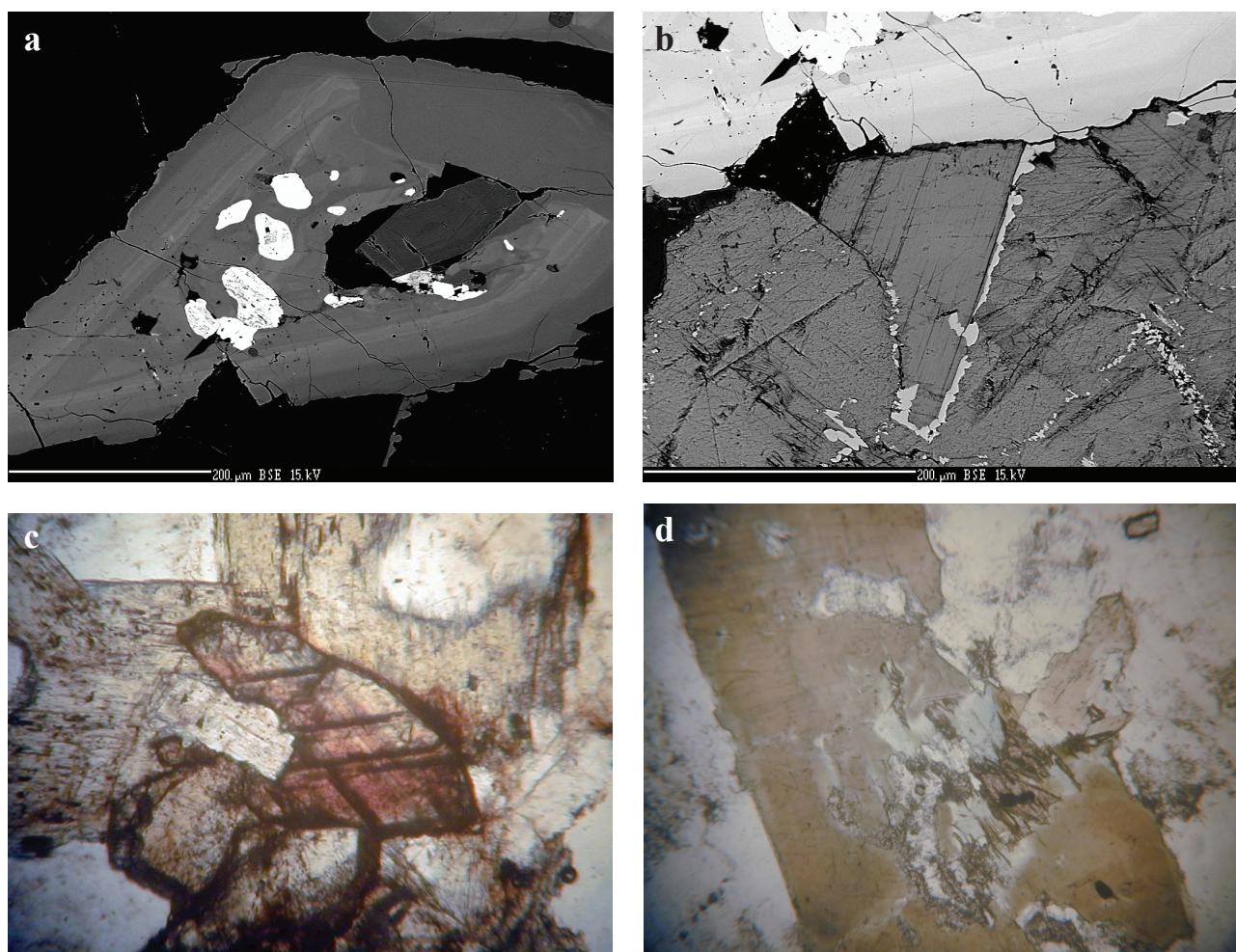


Fig. 1. BSE (a–b) and optical microphotos (c–d) images of titanite generations. **a** — Primary titanite with inclusions of early Ti-magnetite and late rims; **b** — secondary titanite “chains” evolved along biotite cleavage coalescing with primary titanite from (a), Tribeč tonalite; **c** — anhedral titanite associated with plagioclase; **d** — secondary titanite associated with biotite, Sihla tonalite.

conditions (Fe_2O_3) were used for calculation of post-magmatic assemblages involving epidote.

Sihla tonalite: At the used value 1.25 % H_2O titanite starts to crystallize <760 °C at 4 kbar, and <740 °C at 3 kbar. Amphibole is not stable and ilmenite is stable over the whole window except >6 kbar, where it is replaced by titanite. The most important feature is that at the beginning of titanite I crystallization the content of ilmenite drops from ca. 0.3 wt. % to 0.05 vol. % indicating that titanite forms at the expense of ilmenite (in real rock ulvöspinel+titanohematite). This can explain the absence of Fe–Ti oxides enclosed in titanite.

Tribeč tonalite shows slightly different relations, the system requires higher H_2O (1.45 wt.) to stabilise amphibole, and the beginning of titanite crystallization is accompanied by much lower decrease in ilmenite from 0.2 to 0.15 vol. %. Titanite I, therefore, seems to form at the expense of biotite, enabling ilmenite

(ulvöspinel–titanohematite) to be preserved within titanite crystals.

Crystallization of titanite I does not require oxidation conditions, which is confirmed by compositions of Fe–Ti oxides (Broska & Petřík 2015, fig. 8d).

Late oxidation

Tribeč I-type tonalite: the occurrence of resorbed Ti-magnetite in titanite enabled calculation of late oxidation reactions (Broska & Petřík 2015) involving biotite (annite), ilmenite, actinolite, celadonite and producing magnetite, epidote and titanite II. Intersections of the reactions are at 610, 477 and 471 °C.

Sihla tonalite: titanite II originated by reactions involving removal of Ti from biotite, which shows low TiO_2 contents <2 wt. %. Pseudosections (solution model of Tajčmanová et al. 2009) indicate subsolidus

temperatures for such biotite compositions: Sihla 540 °C (1.83 wt. % TiO₂), Tribeč 550 °C (1.93 wt. % TiO₂).

A low temperature alteration was observed in Tribeč tonalite leading to backward replacement of titanite by ilmenite (Broska et al. 2007).

Discussion and conclusions

I-type tonalites from Tatric and Veporic basement show very similar mineralogy indicating late oxidation conditions (titanite, magnetite, epidote). While the early titanite I associated with plagioclase is magmatic in both rock types, the late secondary titanite II probably originated by differing ways in Tatric Tribeč tonalite as opposed to the Veporic Sihla tonalite. In the first case the Variscan thrusting of altered tonalite (Broska & Petřík 2015) documents that titanite II is product of ulvöspinel oxidation and Ti-rich biotite decomposition during retrogression. On the other hand, titanite II in Sihla tonalite, probably formed during Alpine overprint, both at similar temperature (below 600 °C) but different pressures: much higher in the Sihla tonalite. The Alpine overprint was accompanied by oxidation producing a large amount of new epidote, increasing the Fe³⁺/Fe²⁺ ratios in biotite and allanite. Titanite intergrown with epidote in Sihla tonalite indicates formation of titanite below 500 °C.

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