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Titanite from Titanite-Spots Granodiorites of the Moldanubian Batholith (Central European Variscan Belt)

Miloš René

Abstract

Titanite-rich granodiorites occurring in the Austrian Mühlviertel are intimately associated with the I/S-granites of the Mauthausen/Freistadt granite suite. These rocks form small irregular bodies in granites of this granitic suite of the Moldanubian batholith that are represented by usually fine-grained and dark granodiorites, which contain a large amount of titanite hell “spots” formed by aggregates of plagioclases and quartz. Titanite as a relative plentiful accessory mineral exists in the center of these “spots” as idiomorphic and sphenoidal grains. The composition of titanite ranges from 89 to 92 mol.% titanite end-member. According to its Al concentration, the analyzed titanites could be considered as low-Al titanites (Al = 0.05–0.08 atoms per formula unit). Titanite contains low concentrations of both (Al + Fe³⁺)–OH (2–9 mol.%) and (Al + Fe³⁺)–F (0–8 mol.%). Titanite together with Na-enriched plagioclase and quartz is originated during late-magmatic evolution of titanite-spots granodiorites.

Keywords: titanite, petrology, geochemistry, mineralogy, Bohemian Massif, Moldanubian zone

1. Introduction

In the SW part of the Moldanubian batholith, titanite-rich granitic rocks occur, which were described in the past as titanite-spots granites and diorites. These rocks were described in detail at the Austrian Mühlviertel, SSW of Aigen [1], and at the southern part of the Fürstenstein pluton [2, 3]. For titanite-spots granitic rocks at the Fürstenstein pluton, a local name “engelburgite” was used [2, 4]. In these usually fine-grained and dark granitic rocks, a significant large amount of titanite clots mantled by hell aggregates of feldspars and quartz are found. Although many petrographic studies on these titanite-spots granitic rocks have been performed several decades ago, the origin of these clots remains uncertain [2–11]. The main aim of the present paper is the detailed significance of the petrology and mineralogy of these rocks, in addition to the chemical composition of titanite enclosed in hell “spots”.

2. Geological setting

The titanite-spots granodiorites at the northern Mühlviertel (Austria) occur as small irregular intrusive bodies, concentrated in a local SSW-NNE zone, W of Schlägl. According the most recent geological map 1:200,000 [11], a biggest body that was sampled in the Schlägl quarry forms N-S intrusion, W of Schlägl. These magmatic bodies are enclosed in bigger intrusions of the fine- to medium-grained Mauthausen granites (**Figure 1**). The Mauthausen granites are part of the youngest Freistadt/Mauthausen I/S-type suite (320–310 Ma) of the Moldanubian batholith [12–16]. The titanite-spots granodiorites form small irregular bodies enclosed in these granites.

The titanite-spots granodiorites and tonalites from the Fürstenstein pluton occur in the SSW part of the Bavarian Forest (Germany) forming smaller bodies and blocks enclosed in the medium-grained, porphyritic Saldenburg biotite granites, which form the main part of the Fürstenstein pluton [3, 10, 17]. This pluton represents the largest intrusive body in the Bavarian Forest (**Figure 2**). These granites are equivalent to the Weinsberg medium- to coarse-grained, porphyritic biotite granites at the southern part of the Moldanubian batholith [3, 11]. The titanite-spots granodiorites and tonalites occur predominantly in contact zones between the Saldenburg granites and the medium- to coarse-grained Tittling biotite granites and granodiorites. Their age as determined by Chen and Siebel [10] is 321 ± 4 Ma, by the U/Pb dating method in titanite.

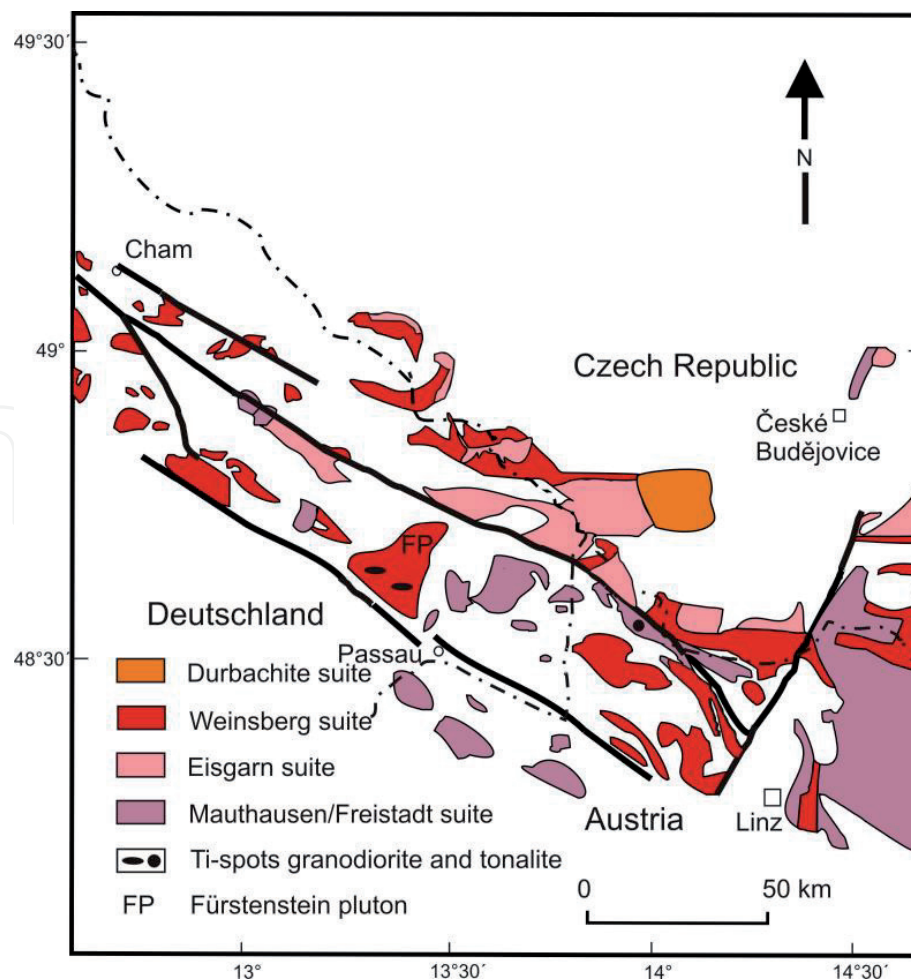


Figure 1.
Geological sketch map of the Šumava Moldanubian batholith branch after [1, 2], modified by the author.

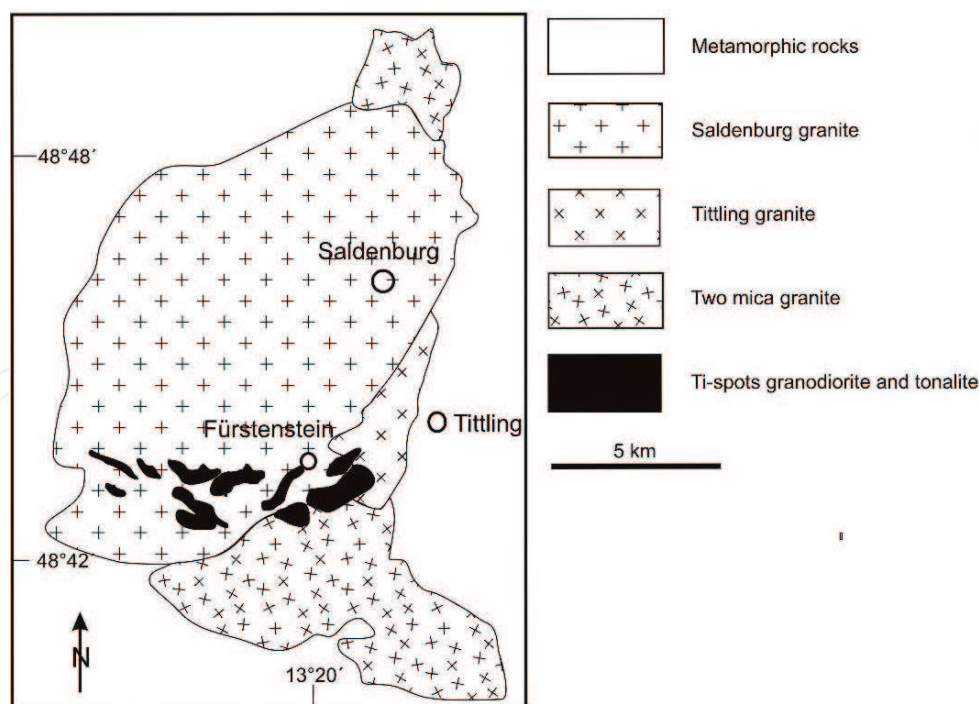


Figure 2.
Geological sketch map of the Fürstenstein pluton after [10], modified by the author.

3. Analytical methods

Approximately 30 quantitative electron probe microanalyses of titanite were performed in the three representative samples of titanite-spots granodiorites from the western Mühlviertel area (Austria). Minerals were analyzed in polished thin sections, and back-scattered electron images (BSE) were acquired to study the interaction of examined titanite with surrounding minerals and the internal structure of individual mineral grains. Element abundances of Al, Ca, Ce, F, Fe, La, Mg, Na, Nb, Nd, Pr, Si, Ta, Th, Ti, Y, and Zr in selected accessory titanite were determined using a CAMECA SX 100 electron probe microanalyzer (EPMA) operated in wavelength-dispersive mode. The contents of the abovementioned elements were determined using an accelerating voltage and beam current of 15 keV and 20 nA, respectively, with a beam diameter of 2–5 μm . The following standards, X-ray lines, and crystals (in parentheses) were used: AlK α , sanidine (TAP); CaK α , fluorapatite (PET); CeL α , CePO $_4$ (PET); FK α , topaz (PC1); FeK α , almandine (LIF); LaL α , LaPO $_4$ (PET); MgK α , Mg $_2$ SiO $_4$ (TAP); NbL α , columbite (PET); NdL β , NdPO $_4$ (LIF); PrL β , PrPO $_4$ (LIF); SiK α , sanidine (TAP); TaL α , CrTa $_2$ O $_6$ (LIF); TbL α , TbPO $_4$ (LIF); ThM α , CaTh(PO $_4$) $_2$ (PET); TiK α , anatase (PET); YL α , YPO $_4$ (PET); and ZrL α , zircon (TAP). Intra-REE overlaps were partially resolved using L α and L β lines. The raw data were converted into concentrations using appropriate PAP matrix corrections [18]. The detection limits were approximately 400 ppm for Y and 180–1700 ppm for REE.

4. Results

4.1 Petrography

The titanite-spots granodiorites from the northern Mühlviertel are dark, fine-grained rocks with many light spots formed by plagioclase and bigger, usually idiomorphic titanite crystals (**Figures 3 and 4**).



Figure 3.
Titanite-spots granodiorite from the Schlägl quarry (Mühlviertel, Austria) (photo by René).

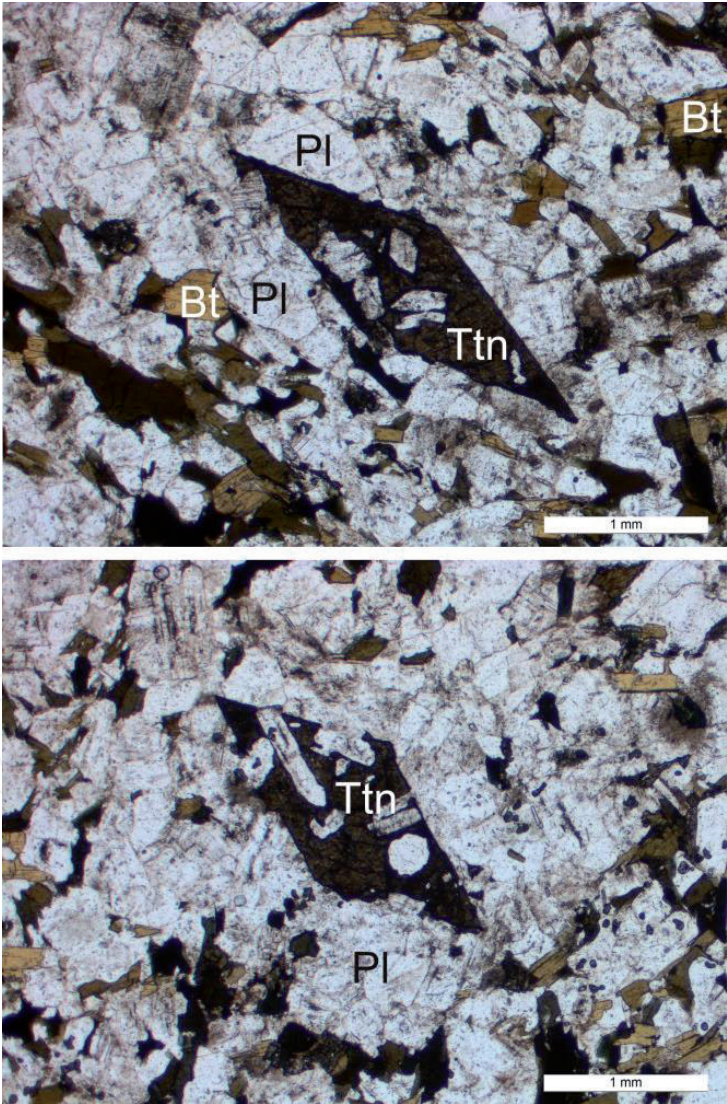


Figure 4.
Microphotography of titanite-spots granodiorite (Ttn, titanite; Pl, plagioclase; Bt, biotite) (photo by René).

The titanite-spots granodiorites contain plagioclase (An_{30-55}) (36–46 vol.%), biotite (15–32 vol.%), quartz (21–28 vol.%), K-feldspar (6–16 vol.%), rare amphibole (0–1 vol.%), and pyroxene (0–1 vol.%). Plagioclase grains in light “spots,”

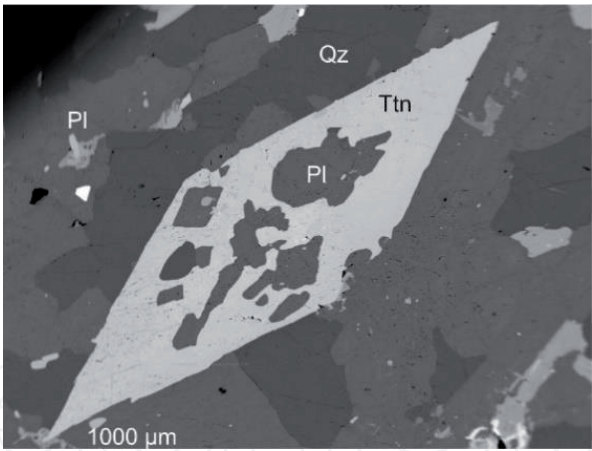


Figure 5.
BSE image of titanite from titanite-spots granodiorite in Mühlviertel area, Austria. Ttn, titanite; Pl, plagioclase; Qz, quartz.

Sample, wt. %	1719–66	1725–15	1725–16	1725–21	1725–23	1725–27
SiO ₂	30.43	30.55	30.68	30.18	29.99	30.44
TiO ₂	37.20	37.13	36.70	36.91	36.25	37.06
Nb ₂ O ₅	0.30	0.28	0.19	0.28	0.41	0.38
Al ₂ O ₃	1.61	1.30	1.57	1.37	1.55	1.39
Fe ₂ O ₃	1.08	1.33	1.52	1.37	1.57	1.43
CaO	28.51	27.49	28.08	27.28	26.85	27.21
Na ₂ O	0.01	b.d.l.	0.01	0.02	0.02	0.01
La ₂ O ₃	b.d.l.	0.08	0.02	0.10	0.12	0.15
Ce ₂ O ₃	0.02	0.54	0.36	0.81	0.84	0.86
Pr ₂ O ₃	0.14	0.02	0.16	0.27	0.34	0.11
Nd ₂ O ₃	b.d.l.	0.50	0.28	0.78	0.99	0.90
Y ₂ O ₃	b.d.l.	0.32	0.19	0.37	0.64	0.48
F	0.61	0.33	0.44	0.28	0.25	0.23
O=F	0.26	0.14	0.19	0.12	0.11	0.10
Total	99.65	99.70	100.02	99.90	99.71	100.55
Si	1.00	1.00	1.00	1.00	1.00	1.00
Ti	0.92	0.91	0.90	0.92	0.91	0.92
Nb	0.00	0.00	0.00	0.00	0.06	0.01
Al	0.06	0.05	0.06	0.05	0.06	0.05
Fe ³⁺	0.03	0.03	0.04	0.03	0.04	0.04
Ca	1.04	0.96	0.98	0.97	0.96	0.96
Na	0.00	0.00	0.00	0.00	0.00	0.00
La	0.00	0.00	0.00	0.00	0.00	0.00
Ce	0.00	0.01	0.00	0.01	0.01	0.01
Pr	0.00	0.00	0.00	0.00	0.00	0.00
Nd	0.00	0.01	0.00	0.01	0.01	0.01
Y	0.00	0.01	0.00	0.01	0.01	0.01
F	0.06	0.03	0.05	0.03	0.03	0.02

Sample, wt. %	1719–66	1725–15	1725–16	1725–21	1725–23	1725–27
OH	0.03	0.05	0.05	0.06	0.07	0.07
X(Ttn)	0.91	0.92	0.91	0.91	0.90	0.91
X(Al,Fe ³⁺ –F)	0.06	0.03	0.05	0.03	0.03	0.02
X(Al,Fe ³⁺ –OH)	0.03	0.05	0.05	0.06	0.07	0.06

b.d.l., below detection limit.

Table 1.
Representative analyses of titanite in titanite-spots granodiorites and tonalites in Mühlviertel area, Austria. Concentration of OH was calculated based on $OH^- = (Al + Fe^{3+}) - F$, according to [19].

which are enriched in albite component (An_{33–39}), contain bigger titanite crystals in their cores (**Figures 4** and **5**). Biotite is annite with $Fe/(Fe + Mg) = 0.51–0.54$ and 0.24–0.54 apfu (atoms per formula unit). Amphibole is cummingtonite with $Mg/(Mg + Fe) 0.44–0.45$ apfu. The accessory minerals are titanite, apatite, zircon, magnetite, ilmenite, allanite, and pyrite.

4.2 Mineralogy and mineral chemistry of titanite

Titanite as a relatively plentiful accessory mineral usually has up to 1–2 mm long. The idiomorphic, sphenoidal crystals are enclosed in light “spots” of fine-grained aggregates of plagioclase and quartz (**Figures 3** and **4**). In some cases, larger titanite crystals contain irregular inclusions of plagioclase (**Figures 4** and **5**). Titanite in thin sections is usually dark brown and indistinctly pleochroic. It is compositionally homogeneous, that is, without obvious zoning. The electron microprobe data show that the chemical composition of titanite in these titanite-spots granodiorites and tonalites varies over a wide range. The formula of titanite is calculated on the basis of 1 Si as suggested by Harlov et al. [19] (**Table 1**).

The composition of titanite ranges from 89 to 92 mol.% titanite end-member. The Al and Fe³⁺ contents range from 0.05 to 0.08 atoms per formula unit (apfu) and 0.02–0.05 apfu, respectively. Titanite shows some Al + Fe³⁺ excess over F, which indicates the coupled substitution of (Al + Fe³⁺) below the line (Al + Fe³⁺) + F[–] = Ti⁴⁺ + O^{2–} (**Figure 6**). The presence of this substitution in analyzed

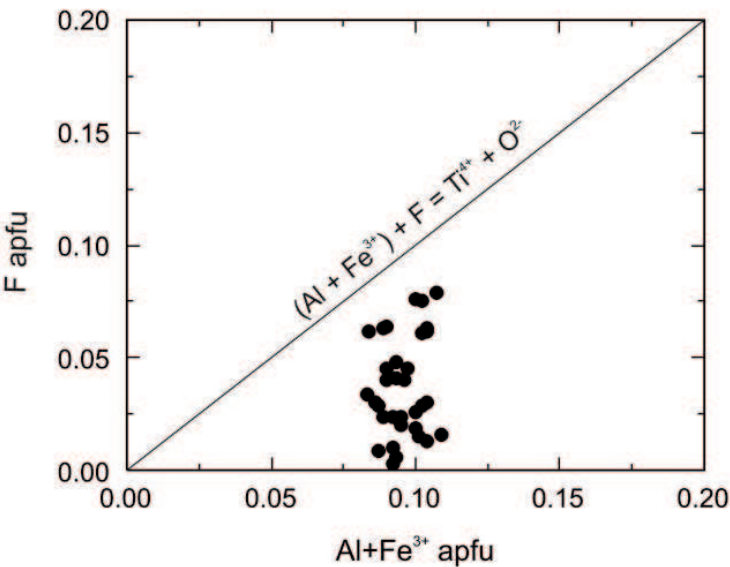


Figure 6.
(Al + Fe³⁺) vs. F plot indicating additional (Al + Fe³⁺)–OH component in analyzed titanites.

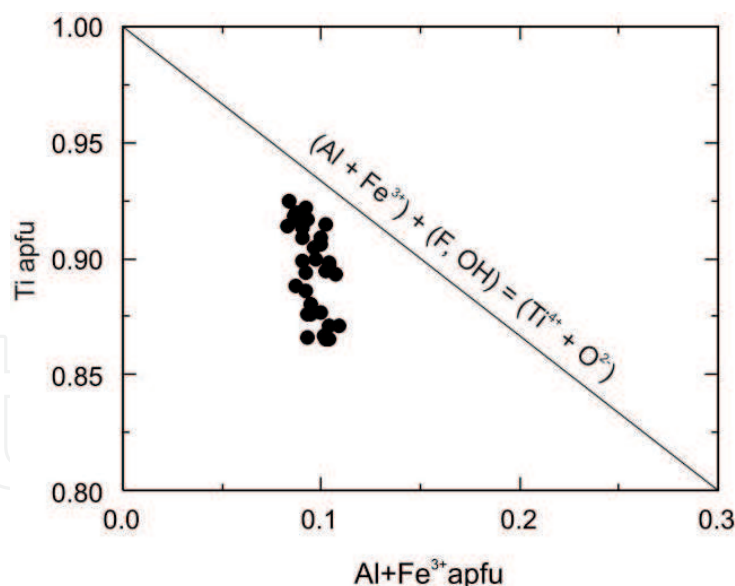


Figure 7.
(Al + Fe³⁺) vs. Ti plot indicating additional (Al + Fe³⁺) + (F, OH) = (Ti⁴⁺ + O²⁻) substitutions in analyzed titanites.

titanites is shown also in the plot of Ti vs. (Al + Fe³⁺) (**Figure 7**). Calculation of OH content allows the estimation of (Al + Fe³⁺)–OH component from 2 to 9 mol.%. The content of (Al + Fe³⁺)–F component is lower than the amount of (Al + Fe³⁺)–OH component and ranges from 0 to 8 mol.%. The content of REE in analyzed titanite is usually below the microprobe detection limits. However, the contents of La, Ce, Pr, and Nd in some cases could be up to 0.99 wt.% (La₂O₃ up to 0.15 wt.%, Ce₂O₃ up to 0.86 wt.%, Pr₂O₃ up to 0.34 wt.%, Nd₂O₃ up to 0.99 wt.%).

5. Discussion

Titanite, with its considerable variation on chemical composition, is a highly sensitive indicator of oxygen fugacity (f_{O_2}) and water fugacity (f_{H_2O}) during the evolution of geological environment (e.g., [19–25]). The chemical composition of the analyzed titanite shows that the substitution (Al, Fe³⁺) + F = Ti⁴⁺ + O²⁻ and the substitution (Al, Fe³⁺) + OH = Ti⁴⁺ + O²⁻ were the most significant substitutions in these titanites (**Figures 6 and 7**). In both substitutions, it could be up to 30% of Ti replaced by aluminum and ferric iron [21]. According to their F, Al, and Fe³⁺ concentrations, the titanites considered as low-Al titanites could be analyzed [26]. Their low F and Al content could be well compared with contents of both elements in similar magmatic titanites [27, 28]. The partial Al + Fe³⁺ excess over F indicates the presence of Al-involving substitution reaction such as (Al, Fe³⁺) + OH = Ti + O (**Figure 4**).

The origin of titanite that is usually concentrated in light spots is thought to be formed with albite-enriched component plagioclases (oligoclase) and quartz on the expense of andesine and Ti-annite as expressed by the following reaction:



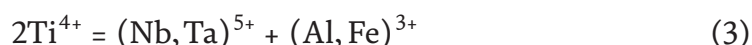
Similar late-magmatic reaction is supposed for titanite origin from I-type granites occurred in the Třibec Mountains (Western Carpathians, Slovakia) [28]. This suggestion for the origin of titanite-spots granodiorites in the Austrian Mühlviertel by late-magmatic crystallization was presented in the past by Rupp et al. [11]. Late-magmatic origin of titanite in titanite-spots granodiorites and tonalites from

the Fürstenstein pluton is supposed by Chen and Siebel [10]. In the past, the origin of these titanite-spots granitic rocks in the Fürstenstein pluton was given in detailed discussion of older papers [6–8] and also supposed by Troll [3]. Especially according to old detailed studies of titanite-spots granodiorites and tonalites from the Fürstenstein pluton, Drescher [6], Fischer [7], and Troll [3] supposed that titanite in the light spots originated by late-magmatic and/or younger hydrothermal crystallization. In all these cases, biotite served as a source of Ti for titanite, and titanite is most likely originated from a reaction involving biotite and probably anorthite component in plagioclase, during its deaorthization.

Incorporation of the REE in titanite is realized by the coupled substitution:



Partial enrichment of REE, especially Ce and La, is significant for magmatic titanite, especially for titanite occurred in alkalic magmatic rocks and lamprophyres [29, 30]. Incorporation of Nb and Ta is realized by the following reaction:



Both the exchange reactions (2 and 3) are significant for primary magmatic titanite [21]. The Nb and Ta enriched titanite was described from some granitic pegmatites [31].

6. Conclusions

Titanite-rich granodiorites occur in the Austrian Mühlviertel as small irregular bodies enclosed in I/S-type granites of the Freistadt/Mauthausen suite, which are usually fine-grained and dark granitic rocks having significant large amount of titanite spots mantled by hell aggregates of plagioclase and quartz.

Titanite as a relative plentiful accessory mineral usually forms idiomorphic, sphenoidal grains enclosed in light “spots” of fine-grained aggregates of plagioclases and quartz. The composition of titanite ranges from 89 to 92 mol.% titanite end-member. According to its Al concentration, the analyzed titanites could be considered as low-Al titanite with an aluminum of 0.05–0.08 apfu. The Fe^{3+} contents range from 0.02 to 0.05 apfu. Titanite shows some $\text{Al} + \text{Fe}^{3+}$ excess over F, which indicates the presence of coupled substitution of $(\text{Al} + \text{Fe}^{3+}) + (\text{F, OH}) = \text{Ti}^{4+} + \text{O}^{2-}$. Calculation of OH content allows the estimation of $(\text{Al} + \text{Fe}^{3+})\text{--OH}$ component from 2 to 9 mol.%. The content of $(\text{Al} + \text{Fe}^{3+})\text{--F}$ component is lower than the amount of $(\text{Al} + \text{Fe}^{3+})\text{--OH}$ component and ranges from 0 to 8 mol.%. Titanite of these titanite-spots granodiorites together with plagioclase and quartz was originated during late-magmatic evolution. The origin of titanite can be described by the following reaction:



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Conflict of interest

The author declares no conflict of interests.

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