## TITANITE-ILMENITE ASSEMBLAGE IN MICROGRANODIORITES FROM THE NORTHEASTERN MARGIN OF THE KLENOV GRANITE BODY (BOHEMIAN MASSIF, CZECH REPUBLIC)

## Miloš RENÉ

Institute of Rock Structure and Mechanics, Academy of Sciences of the Czech Republic, v.v.i., V Holešovičkách 41, 182 09 Prague, Czech Republic Corresponding author's e-mail: rene@irsm.cas.cz

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#### ABSTRACT

An assemblage of Al-low titanite and ilmenite is present in Ti-rich microgranodiorites intruded in the Moldanubian Zone of the Bohemian Massif. Titanite is characterized by coupled substitution (Al, Fe<sup>3+</sup>) + (F, OH)  $\Leftrightarrow$  Ti +O, with a slight excess of (Al, Fe<sup>3+</sup>)–OH component over of (Al, Fe<sup>3+</sup>)–F component. Ilmenites have FeTiO<sub>3</sub> amount between 86 and 95 mol. % and are partly enriched in the MnTiO<sub>3</sub> (pyrophanite) component (4–10 mol. %). The relatively low content of MnTiO<sub>3</sub> component in ilmenite, together with absence of magnetite suggests that first crystallization phase of microgranodiorites connected with origin of ilmenite started in conditions of low *f*O<sub>2</sub>. However, titanite together with ferroactinolite originated in late-magmatic stage most likely due to hydration reaction such as clinopyroxene + ilmenite + quartz + H<sub>2</sub>O = titanite + amphibole during some increasing of *f*O<sub>2</sub> and *f*H<sub>2</sub>O.

KEYWORDS: Bohemian Massif, Moldanubian Zone, microgranodiorite, titanite, ilmenite

#### INTRODUCTION

Titanite and ilmenite are common accessory minerals in igneous rocks, especially in calc-alkaline granites (s.l.) with I-type signature (e.g., Lee and Silver, 1964; Piccoli et al., 2000; Helmy et al., 2004; Broska et al., 2007). In the present study titaniteilmenite assemblage from microgranodiorites of the Moldanubian Zone (Bohemian massif) is described. The aim of this paper is to describe ad discuss association of titanite and ilmenite, their textural relationships, chemical composition and origin.

The examined microgranodiorites are parts of late Variscan intermediate to basic porphyries and lamprophyric dyke swarms which are common throughout whole Moldanubian Zone of the Bohemian Massif (Němec, 1970, 1974; Vrána et al., 1993; Košler et al., 2001; Krmíček, 2010). Occurrences geochemically specialized Ti-rich microgranodiorites from the northeastern margin of the Klenov granite body were described in detail in papers of Kratochvíl and Konta (1951) and René (2003).

### **GEOLOGICAL SETTING**

The examined microgranodiorite dykes outcrop at the NE and E margin of the Klenov granite body. This granite body forms independent intrusion western of Central Moldanubian Pluton. Microgranodiorites occur in en-echelon, NW-SW striking dykes filling faults oblique to younger, NNE-SSW striking shear zones filled by hydrothermal mineralization of the Okrouhlá Radouň uranium deposit (René et al., 1999, Fig. 1). Microgranodiorite dykes penetrate older dykes of the two-mica Deštná granite of the Klenov granite body in several cases. Higher age of microgranodiorite dykes than that mineralised shear zones is confirmed by horizontal displacement these dykes recorded in some places of the Okrouhlá Radouň uranium deposit. This displacement is accompanied by hydrothermal chloritization and albitization of microgranodiorites.

#### ANALYTICAL METHODS

Major element analyses on whole-rock samples were performed in the laboratory of Institute of Rock Structure and Mechanics of the AS CR, Prague by conventional wet chemical methods. Trace elements were determined by ICP MS at Activation Laboratories Ltd., Lancaster, Canada on a Perkin Elmer Sciex ELAN 6100 ICP mass spectrometer (Table 1).

Analyses of titanite and ilmenite were performed using a CAMECA SX 100 electron microprobe working in WDX mode employing the PAP matrix correction program (Pouchou and Pichoir, 1985) at the Institute of Geology of the Academy of Sciences of the Czech Republic. The operating conditions were 15 kV acceleration voltage, 15 nA beam current, and 2  $\mu$ m beam diameter. Counting times on the peaks were 10–30 seconds depending on the element. Background counts were measured in each case in half the time for peak measurement on both sides of the peak. Calibrations were done using standard sets



Fig. 1 Geological sketch map of the southeastern part of the Central Moldanubian Pluton (after Breiter and Sokol 1997, modified of author).

from SPI. Standards included jadeite (Na, Al), diopside (Si, Ca, Mg), rutile (Ti), hematite (Fe), spinel (Mn), crockoite (Cr), willemite (Zn) and apatite (F). Detection limits for these elements are as follows: F 0.09–0.15 wt.%, other elements 0.03–0.20 wt.%. Mineral formulae were recalculated using the Minpet 2.0 software.

# PETROGRAPHY AND ROCK-FORMING MINERALS COMPOSITION

The examined microgranodiorites are porphyric rocks with aphanitic to fine-grained texture of the groundmass. Plagioclase phenocrysts, several millimetres, up to 1 cm in size are sometimes oscillatory zoned, with basic core (An31-54) and acid rim (An<sub>14-22</sub>). Some phenocrysts display partial remelting of their grain margins and/or their refraction during groundmass crystallization. I some cases plagioklase evolved in rim zone of are phenocrysts reactions zones with small grains of quartz (Fig. 2a, b). The groundmass is formed by plagioclase (An<sub>25-54</sub>), biotite (Mg-siderophyllite),

Fig. 2 Microphotography of microgranodiorites, performed by author, a – partly remelted plagioclase phenocrysts in aphanitic to fine-grained groundmass, b – plagioclase phenocryst in groundmass enriched in plagioclase and ilmenite.



Sample	1/23-32	No-8049	Re-532	Re-637
SiO <sub>2</sub>	56.16	55.67	55.23	54.21
TiO <sub>2</sub>	1.94	1.93	1.95	1.85
$Al_2O_3$	15.05	15.73	15.11	15.64
Fe <sub>2</sub> O <sub>3</sub>	1.11	1.99	1.53	0.31
FeO	8.11	7.94	8.24	7.87
MnO	0.15	0.14	0.16	0.14
MgO	2.92	3.10	3.10	2.78
CaO	6.48	5.77	5.70	8.00
Na <sub>2</sub> O	3.19	3.14	3.29	3.92
K <sub>2</sub> Õ	2.49	2.43	2.46	2.55
$\tilde{H_2O^+}$	0.57	1.85	1.64	2.28
$H_2O^-$	0.25	0.23	0.32	0.02
$P_2O_5$	0.56	0.54	0.76	0.54
$\overline{CO_2}$	n.d.	n.d.	0.10	0.25
Total	98.98	100.46	99.59	100.36
ppm				
Cr	72	42	65	38
Ni	5	10	35	10
V	176	102	200	96
Pb	5	5	4	4
Rb	84	97	97	103
Ba	699	627	612	618
Sr	212	215	292	215
Nb	11	14	15	15
Zr	250	260	280	258
Y	n.d.	46	50	45
Th	15.4	12.6	12.1	11.8
U	1.2	4.6	4.1	4.5
La		51.24	48.54	
Ce		94.90	98.43	
Pr		9.98	11.75	
Nd		41.58	45.59	
Sm		10.18	10.96	
Eu		2.34	1.32	
Gd		8.02	11.51	
Tb		1.36	1.99	
Dy		8.45	11.65	
Но		1.61	2.44	
Er		4.06	6.91	
Tm		0.60	0.98	
Yb		3.91	6.17	
Lu		0.71	0.97	
$La_N/Yb_N$		8.86	5.32	
En/En*		0.79	0.36	

 
 Table 1 Major and trace element concentrations for microgranodiorites from the eastern margin of the Klenov granite body (wt.%).

1/23-32 - Dívčí Kopy, abandoned quarry, No-8049 - Dívčí Kopy, abandoned quarry, Re-532 - Nová Včelnice, borehole, 108.0 m, Re-637 - Okrouhlá Radouň, uranium mine, 12. level.

during late-magmatic stage. Consequently its composition is not usable for determination of crystallization temperature of studied microgranodiorites. Ilmenite, apatite, zircon, titanite, rutile and allanite are common accessories.

# WHOLE-ROCK GEOCHEMISTRY

These dyke rocks have a metaluminous character (A/CNK = 0.66-0.87), significant high content of TiO<sub>2</sub> (1.9–2.0 wt. %), relatively high content of  $K_2O$ (2.4-2.6 wt.%). They displays relatively low content of SiO<sub>2</sub> (54.2-56.3 wt. %) and low mg-values  $(MgO/(MgO + FeO) \times 100 \text{ mol.}) = 30-40$ . A typical feature of these microgranodiorites is the high content of normative apatite (0.2-1.3 %) and ilmenite (0.4-3.8 %) (CIPW-norm) (Fig. 3a). The contents of Rb, Ba, Th and U are significantly enriched compared to those in primitive upper mantle. Depletion in Nb, Ta, V, Cr and Ni was observed compared to their amounts in primitive upper mantle (Fig. 3b). The examined microgranodiorites are characterised by relatively high LREE/HREE ratio ( $La_N/Yb_N = 4.9-8.9$ ) and negative Eu anomaly  $(Eu/Eu^* = 0.36-0.79)$  (René, 2003). Melting temperatures calculated using the Zr concentrations (Watson, 1979) are for examined microgranodiorites in range 718-793 °C.

#### MINERAL CHEMISTRY

Titanite belongs to not very common accessory minerals of the studied microgranodiorites. Its subhedral to anhedral grains achieve the size of about 200 µm and have irregular or elongated habitus (Fig. 4a). Titanite is distinctly younger as ilmenite, very probably crystallized in late magmatic stage of microgranodiorite. However, the chloritization of Tienriched biotite is not accompanied by origin of postmagmatic titanite. Titanite is in thin section usually pale brown and indistinctly pleochroic. In some cases it encloses corroded tabular grains of ilmenite, not more than 20 µm long (Fig. 4b). Titanite is compositionally homogenous, without obvious zoning. The formula of titanite was calculated on the basis of 1 Si as suggested by Harlov et al. (2006). The composition of titanite ranges from 80 to 93 mol. % titanite end-member (Table 3). The Al and Fe contents range from 0.05 to 0.17 atoms per formula (apfu) and 0.01 to 0.03 apfu respectively. Titanite shows some  $Al+Fe^{3+}$  excess over F, which indicates the presence coupled substitution of (Al,  $Fe^{3+}$ ) + (F, OH)  $\Leftrightarrow$  Ti + O (Fig. 5). Calculation of OH content allows the estimation of the  $(Al + Fe^{3+})$ -OH titanite component, which ranges from 3 to 12 mol. %. The content of  $(Al + Fe^{3+})$ -F component is partly lower than the amount of  $(A1 + Fe^{3+})$ -OH component, and ranges from 1 to 11 mol. %. The contents of REE in analysed titanite are under detection limit of microprobe.

## M. René

Mineral	Fe-augite	Fe-augite	biotite	biotite	plagioclase matrix	plagioclase phenocryst
Analysis	Re637-15	Re637-16	Re637-21	Re637-45	No8049-2	Re637-5
SiO <sub>2</sub>	47.71	48.65	36.46	35.71	58.83	54.79
TiO <sub>2</sub>	0.86	0.30	3.76	3.58	0.17	0.00
$Al_2O_3$	5.64	5.01	12.24	13.76	25.95	28.79
FeO	25.58	25.48	25.72	25.73	0.55	0.90
MnO	0.47	0.53	0.18	0.15	0.18	0.13
MgO	7.24	7.86	7.25	6.84	0.71	0.87
CaO	11.69	11.42	0.03	0.08	7.25	9.72
Na <sub>2</sub> O	0.56	0.48	0.03	0.06	5.38	4.38
K <sub>2</sub> O	0.26	0.26	9.76	9.73	0.99	0.24
Total	100.01	99.99	95.43	95.64	100.01	99.82
Formulae based on	(O=6)	(O=6)	(O=24)	(O=24)	(O=8)	(O=8)
Si	1.880	1.913	2.883	2.819	2.628	2.470
Ti	0.025	0.009	0.224	0.213	0.006	0.000
Al	0.261	0.231	1.141	1.281	1.365	1.528
Fe <sup>2+</sup>	0.843	0.838	1.561	1.582	0.021	0.034
Mn	0.016	0.018	0.012	0.010	0.007	0.005
Mg	0.425	0.461	0.855	0.805	0.047	0.058
Ca	0.493	0.481	0.003	0.007	0.347	0.469
Na	0.043	0.037	0.005	0.009	0.466	0.383
Κ	0.013	0.013	0.985	0.980	0.056	0.014

Table 2 Chemical compositions of rock-forming minerals of microgranodiorites (wt.%).



- microgranodiorites from the eastern margin of the Klenov granite body
- intermediate to basic dyke rocks
   from the Moldanubian Zone (Němec 1970, 1972, 1974, Vrána et al. 1993)

Fig. 3 Chemical composition of microgranodiorites.
a – distribution of normative ilmenite and apatite (CIPW norm),
b – normalised incompatible trace elements patterns. Normalising value of the primitive mantle from Sun and McDonough (1989).



Fig. 4 BSE image of titanite-ilmenite assemblage, a – anhedral to subhedral titanite (Ttn) aggregate, b – ilmenite (Ilm) enclosed in younger titanite grain, Bt – biotite, Pl – plagioclase. Mineral abbreviations according to Whitney and Evans (2010).

Sample	Re532-16	Re532-19	Re637-15	Re637-40	No8050-18	No8050-19
SiO <sub>2</sub>	30.80	30.67	30.42	30.02	30.77	30.89
TiO <sub>2</sub>	37.58	37.02	35.55	36.75	38.26	34.89
Al <sub>2</sub> O <sub>3</sub>	1.90	2.03	3.80	2.46	1.99	3.49
Fe <sub>2</sub> O <sub>3</sub>	0.30	0.59	0.67	1.17	0.81	1.20
MnO	0.01	0.03	0.00	0.00	0.00	0.01
CaO	28.91	28.82	29.11	28.98	28.77	28.74
Na <sub>2</sub> O	0.01	0.00	0.00	0.01	0.00	0.00
F	0.18	0.48	0.74	0.56	0.42	0.47
O=F	0.05	0.14	0.22	0.17	0.13	0.14
Total	99.46	99.50	100.07	99.78	100.89	99.55
Formulae calculated on						
the basis of 1 Si						
Si	1.000	1.000	1.000	1.000	1.000	1.000
Ti	0.918	0.908	0.879	0.921	0.935	0.849
Al	0.073	0.078	0.147	0.097	0.076	0.133
Fe <sup>3+</sup>	0.007	0.014	0.017	0.029	0.020	0.029
Mn	0.000	0.001	0.000	0.000	0.000	0.000
Ca	1.006	1.007	1.025	1.034	1.002	0.997
Na	0.001	0.000	0.000	0.001	0.000	0.000
F	0.018	0.049	0.077	0.059	0.043	0.048
ОН	0.062	0.043	0.087	0.067	0.053	0.114
$\Sigma$ cations	3.005	3.008	3.068	3.082	3.033	3.008
X(Ttn)	0.920	0.908	0.843	0.880	0.907	0.840
$X(Al,Fe^{3+}-F)$	0.018	0.049	0.074	0.056	0.042	0.047
$X(Al,Fe^{3+}-OH)$	0.062	0.043	0.083	0.064	0.051	0.113

 Table 3 Representative analyses of titanite (wt. %).

Ttn: titanite, Al,Fe<sup>3+</sup>–F: Al,Fe<sup>3+</sup>–F titanite; Al,Fe<sup>3+</sup>–OH: Al,Fe<sup>3+</sup>–OH titanite.

Ilmenite in examined microgranodiorites forms very thin and long laths, underlined texture of their groundmass (Fig. 6). The analysed ilmenite typically has FeTiO<sub>3</sub> amount between 86 and 95 mol. % and is partly enriched in the  $MnTiO_3$  (pyrophanite)

component (4–10 mol. %) (Table 4). The content of geikielite component (MgTiO<sub>3</sub>) is negligible (0–0.2 mol.%). The amount of the hematite component is very low (0–3 mol. %) (Fig. 7).



Fig. 5  $(Al + Fe^{3+})$  vs. F plot indicating additional (Al + Fe<sup>3+</sup>)-OH component in analysed titanites.



Fig. 6 BSE image of ilmenite (Ilm) laths in silicate matrix of investigated microgranodiorite. Mineral abbreviations according to Whitney and Evans (2010).

Table 4 Representative analyses of ilmenite (wt. %).

Sample	Re532-21	Re532-23	Re532-24	No8050-1	No8050-3	No8050-7
SiO <sub>2</sub>	0.03	0.06	0.00	0.06	0.05	0.03
TiO <sub>2</sub>	51.74	51.59	51.89	51.01	51.20	52.17
$Al_2O_3$	0.00	0.00	0.01	0.01	0.02	0.02
$Cr_2O_3$	0.01	0.07	0.07	0.02	0.05	0.01
$Fe_2O_3$	1.60	1.90	1.50	3.10	2.20	0.60
FeO	43.60	43.60	43.70	43.40	43.70	44.50
MnO	2.75	2.64	2.71	2.28	2.24	2.05
MgO	0.04	0.02	0.02	0.03	0.01	0.01
CaO	0.06	0.11	0.10	0.13	0.12	0.09
ZnO	0.00	0.00	0.07	0.03	0.01	0.00
Nb <sub>2</sub> O <sub>5</sub>	0.00	0.01	0.01	0.00	0.02	0.00
Total	99.83	100.00	100.10	100.08	99.62	99.48
Formulae based on	(O=6)	(O=6)	(O=6)	(O=6)	(O=6)	(O=6)
Si	0.001	0.001	0.000	0.002	0.001	0.001
Al	0.000	0.000	0.000	0.000	0.001	0.001
Ti	0.984	0.980	0.985	0.969	0.976	0.995
Cr	0.000	0.001	0.001	0.000	0.001	0.000
Fe <sup>3+</sup>	0.030	0.036	0.028	0.059	0.042	0.011
Fe <sup>2+</sup>	0.922	0.921	0.922	0.916	0.927	0.943
Mn	0.059	0.056	0.058	0.049	0.048	0.044
Mg	0.002	0.001	0.001	0.004	0.000	0.000
Ca	0.002	0.003	0.003	0.001	0.003	0.002
Zn	0.000	0.000	0.001	0.001	0.000	0.000
Nb	0.000	0.000	0.000	0.000	0.000	0.000
∑cations	2.000	1.999	1.999	2.001	1.999	1.997
X(Hem)	0.015	0.018	0.014	0.030	0.021	0.006
X(Ilm)	0.922	0.921	0.922	0.916	0.927	0.943
X(Gk)	0.002	0.001	0.001	0.001	0.000	0.000
X(XPph)	0.059	0.056	0.058	0.049	0.048	0.044

Hem – hematite, Ilm – ilmenite, Gk – geikielite, Pph – pyrophanite. Recalculations of  $FeO_t$  using the method of Carmichael (1967).



Fig. 7 Composition of ilmenite (IIm – ilmenite, Pph – pyrophanite, Hem – hematite). Mineral abbreviations according to Whitney and Evans (2010).

## DISCUSSION AND CONCLUSIONS TIME CONSTRAINTS ON MICROGRANODIORITE DYKE EMPLACEMENT

The emplacement of microgranodiorite dykes occurred after the solidification of granites of the Klenov granite body, including the youngest dykes of two-mica granites and aplites. In view of the fact that the boundary of microgranodiorite dykes with the surrounding metamorphic and granitic rocks is always sharp, it is possible to suppose that a longer time interval elapsed between the emplacement of the Klenov granite body and basic dyke rocks. The radiometric dating of two-mica granites of the Klenov granite body yielded its emplacement age of 327 Ma (U/Pb, monazite) (Verner et al., 2011). The upper limit of the time interval for emplacement of microgranodiorite dykes is defined by the origin of uranium hydrothermal mineralization, which caused chloritization and albitization of microgranodiorites.

The crystallization of microgranodiorites has not running in one magmatic stage. The relatively longer crystallization history of microgranodiorite dykes can be documented by remelting of marginal parts of some plagioclase phenocrysts (Fig. 2 a, b). Plagioclase phenocrysts formed in the early phase of crystallization were later broken and/or partialremelted on their margins during crystallization of groundmass melt. In the groundmass have firstly crystallized plagioclase, pyroxene and ilmenite. Amphibole has originated by alteration of pyroxene during a later magmatic stage. Titanite is distinctly younger as ilmenite, it crystallized very probably also in a later magmatic stage. In some cases titanite encloses corroded tabular grains of ilmenite, not more than 20 µm long.

A few radiometric dating of basic dyke rocks from area of the Moldanubian Zone have been available. The isotopic age of related basic dykes on margin of the Ševětín granite body has been broadly constrained by K-Ar dating of bulk-rock samples, which yielded ages of 263 and 222 Ma, respectively (Vrána et al., 1993). A more precise Ar/Ar dating of primary titanian pargasite of 270 Ma of the same rocks was interpreted as the minimum emplacement age of these dyke rocks by Košler et al. (2001).

This time constraint is also supported by the determination of the age of lateral movements on the most significant NNE-SSW-striking shear zone (Rodl Zone, 281 Ma; Brandmayr et al., 1995). The other constraint for the age of the emplacement of microgranodiorites on the northeastern margin of the Klenov granite body is the age of uranium mineralization (U/Pb, pitchblende 255 Ma; Anderson et al., 1989) of the Okrouhlá Radouň uranium deposit. it was mentioned above, some As of microgranodiorite dykes were altered by this uranium mineralization. The above-mentioned ages give probably time constraint for the emplacement of investigated microgranodiorite dykes - 250-280 Ma.

## POTENTIAL MAGMA SOURCES

Based on a detailed study of modal and major element compositions in microsyenites, microdiorites, lamprophyres of the microgranodiorites and Moldanubian Zone, Němec (1970, 1972, 1975, 1977) preferred the origin of these dyke rocks from contaminated tholeiitic magma. According to Gerdes et al. (2000), lamprophyre magma in the Moldanubian Zone was separated from a hydrated lithospheric mantle as a result of thickening of the crust and of intensive melting of subducted deeper parts of lithospheric crust and rocks at the crust/mantle boundary. The examined microgranodiorites show significantly low mg-number, together with relatively high content of titanium. Other significant feature of geochemical composition of these mafic dyke rocks is their enrichment in Rb, Ba, Th and U compared with primitive mantle composition.

## TITANITE

Titanite, with its considerable variation on crystal chemistry, is a highly sensitive indicator of oxygen fugacity ( $fO_2$ ) and water fugacity ( $fH_2O$ ) during the evolution of geological environment (e.g., Wones, 1989; Piccoli et al., 2000; Xirouchakis et al., 2001a,b; Troitzsch and Ellis, 2002; Tropper et al., 2002; Harlov et al., 2006). The chemical composition of the examined titanite shows that the substitution (Al, Fe<sup>3+</sup>) + F  $\Leftrightarrow$  Ti + O as well as the substitution (Al, Fe<sup>3+</sup>) + OH  $\Leftrightarrow$  Ti + O were the most significant substitutions in this titanite (Fig. 4). According to its F, Al and Fe<sup>3+</sup> content, could be analysed titanite considered as low-Al titanite (Oberti et al., 1991). Their low F and Al content could be well compared

with contents of both elements in other magmatic titanites (Enami et al., 1993). The minor  $Al+Fe^{3+}$  excess over F indicates the presence of Al-involving substitution reaction such as (Al, Fe<sup>3+</sup>) + OH  $\Leftrightarrow$  Ti + O. The (Al+Fe<sup>3+</sup>) content in range from 0.05 to 0.20 apfu could be also well compared with contents of both elements in magmatic titanite (Enami et al., 1993). Both, the (Al+Fe<sup>3+</sup>)–F and (Al+Fe<sup>3+</sup>)–OH component together, are below 20 mol.%. On average, the (Al+Fe<sup>3+</sup>)–OH component slightly exceeds the (Al+Fe<sup>3+</sup>)–F component in the examined titanites (Table 3).

#### ILMENITE

As show results of compositional variations of ilmenite in igneous rocks (Snetsinger, 1969: Czamanske and Mihálik, 1972; Tsusue, 1973; Neumann, 1974; Haggerty, 1976; Sasaki et al., 2003), these ilmenites have a considerable variability of FeTiO<sub>3</sub> and MnTiO<sub>3</sub> contents. The variability of FeTiO<sub>3</sub> and MgTiO<sub>3</sub> contents in magmatic rocks is distinctly lower and a higher MgTiO<sub>3</sub> values occurred in some Mg-enriched rocks as kimberlites (Haggerty, 1976). Ilmenites from typical basic magmatic rocks (gabbros) have usually only small contents of MnTiO<sub>3</sub> and MgTiO<sub>3</sub> component (Haggerty, 1976). However, distinctly higher concentrations of MnTiO<sub>3</sub> occur in diorites and/or granodiorites (up to 32 mol. % MnTiO<sub>3</sub>, Czamanske and Mihálik, 1972). The reasons for high concentrations of MnTiO<sub>3</sub> are thought to be following: enrichment of Mn in the S-granite melt (Tsusue, 1973), low crystallization temperature (Buddington and Lindsley, 1964; Anderson, 1968) and high oxygen fugacity, which leads to oxidation of  $Fe^{+2}$  to  $Fe^{+3}$  and thus lowering of the  $Fe^{+2}/Mn$  ratio (Anderson, 1968; Czamanske and Mihálik, 1972; Neumann, 1974). Accordingly, if ilmenite from analysed microgranodiorites shows rather lower amount of MnTiO<sub>3</sub> (4–10 mol. %), in can be assumed that ilmenite in these rocks crystallised in conditions of higher temperature and/or lower  $fO_2$ .

#### **ORIGIN OF TITANITE**

Subhedral to anhedral titanite, in which are older ilmenite laths sometimes enclosed (Fig. 3 b) could be crystallized later as a product of late-stage oxidation. Origin of titanite in examined microgranodiorites could be described by following reaction:

> Fe-augite + ilmenite + quartz +  $H_2O =$ = titanite + ferroactinolite

The absence of magnetite in this assemblage suggests that this oxidised environment not reached stability of magnetite. Occurrence of titanite as product of late-stage oxidation was found in Finmarka igneous complex, Norway (Czamanske and Wones, 1979). However, in this case titanite occurs together with magnetite. Origin of ferroactinolite together with titanite is commonly explained by higher  $fH_2O$ 

(Harlov et al., 2006). Consequently, textural evidence suggests that titanite + ferroactinolite assemblage in examined microgranodiorites originated most likely due to hydration reaction such as clinopyroxene + ilmenite + quartz +  $H_2O$  = titanite + amphibole. Overstepping of this reaction requires  $fO_2$  and  $fH_2O$  to be high for titanite formation, which is also in accordance with equilibrium involving Al–OH titanite.

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