

Biotite from Čierna hora Mountains granitoids (Western Carpathians, Slovakia) and estimation of water contents in granitoid melts

KATARÍNA BÓNOVÁ¹, IGOR BROSKA² and IGOR PETRÍK²

¹Institute of Geography, Faculty of Sciences, Pavol Jozef Šafárik University, Jesenná 5, 040 01 Košice, Slovak Republic; katarina.bonova@upjs.sk

²Geological Institute of the Slovak Academy of Sciences, Dúbravská cesta 9, 840 05 Bratislava, Slovak Republic; igor.broska@savba.sk; igor.petrík@savba.sk

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Abstract: Biotite is the dominant ferromagnesian mineral in different granites from the Čierna hora Mountains, in the Western Carpathians (Slovakia). A higher content of Fe³⁺ (up to 20 %) is characteristic for the biotites from I-type Sokol and Sopotnica granitoid bodies in contrast to the biotites from S-type Ťahanovce granitoids showing decreased Fe³⁺ amount (around 5 %). The Fe/(Fe + Mg) ratio in biotites from the Sokol and Sopotnica massifs between 0.47 and 0.54 is rather low with respect to that in biotite from the Ťahanovce [Fe/(Fe + Mg) = 0.55–0.63] and Miklušovce [Fe/(Fe + Mg) = 0.73–0.81] granite body. Water fugacities and contents calculated using Wones' (1981) calibration of biotite stability equation and Burnham's (1994) water dissolution model yield relatively similar values of 4–5 wt. % in remaining melts at 400 MPa and various levels of f_{O_2} and activities of annite for magnetite-bearing assemblages. This suggests an effective buffering role of biotite in both oxygen and water fugacities. Comparison of the peraluminosity index (A/CNK) of biotite with the same index in whole-rock shows distinctly higher A/CNK values for biotite indicating its aluminous character and important role as a significant aluminium carrier. The biotite composition indicates that granitoids in the Čierna hora Mts can be primarily derived from the lower crust; their protolith was influenced by mixing and/or assimilation process.

Key words: Variscan orogeny, Western Carpathians, water content, granitoids, biotite, oxygen fugacity, Mössbauer spectroscopy.

Introduction

Biotite, which is defined as a member of quadrilateral isomorphous system annite–flogophite–siderophyllite–eastonite according to nomenclature of micas (Rieder et al. 1998), has an important role in detection of the magma evolution. Despite the biotite tendency to re-equilibrate significantly during granite solidification, biotite-bearing assemblages still can actually reflect the physico-chemical conditions of the primary melt. Besides muscovite, cordierite, garnet and Al₂SiO₅ polymorphs or feldspars, biotite is the most important aluminium concentrator and in biotite-dominated granitoids it directly determines the peraluminosity of magma (Zen 1988; Shabani et al. 2003). Biotite is also a very useful and suitable indicator of the oxidation-reduction state in a melt (Wones & Eugster 1965; Burkhard 1991, 1993). In this sense it can play an important role as discriminative tool in identification of some tectono-magmatic events unravelling the granitoid petrogenesis (Barrière & Cotton 1979; El Sheshtawi et al. 1993; Lalonde & Bernard 1993; Abdel-Rahman 1994; Hecht 1994; and others). Generally, biotite in the association with K-feldspar and magnetite — through its annite activity — may be used to calculate the temperature, oxygen fugacity and water fugacity in the parental magma.

Geochemistry of biotite in the Western Carpathian granitoids studied in numerous contributions pointed to differences among various Variscan granitoid massifs (Ďurkovičová 1966; Petřík 1980; Fejdi & Fejdiová 1981). Petřík (1980) and Buda et al.

(2004) determined the genetic relations between biotite compositions using its Fe/Mg ratio and crystallizing magma. The evaluation of water content in magma of granitoid rocks based on biotite composition was carried out by Petřík & Broska (1994) in Tribeč Mts. The first data on biotites from the Čierna hora granitoids were introduced by Jacko (1984) who assumed the presence of Fe-biotite in these granitoid rocks. From the correlation between biotite composition and morphology of zircon (sensu Pupin 1985) Jablonská et al. (1995) inferred that granitoids from the Miklušovce Complex and the Ťahanovce area are derived from crustal melting due to regional anatexis and/or melting induced by rising of granitic or more basic melts. Biotite composition from the Sokol and Sopotnica granitoids corresponds to that of biotites from hybrid granites (l.c.).

In this paper, new mineralogical, petrological and geochemical data on biotite from the Čierna hora granitoids are presented. The purpose of this study is to discuss new and existing biotite data in terms of oxygen and water fugacity in parental magmas. These have been used to calculate their water contents and derive information on melting processes relevant to the origin and evolution of the Čierna hora granitoids.

I- and S-type granitoids in the Western Carpathians

The Variscan granitic cores of the Tatric Unit and the Vepor pluton of the Veporic Unit represent separate intrusions with

independent histories. Geochemical and petrological studies revealed criteria, which enabled their subdivision into S-, I- and A-type groups (Fig. 1a) (Cambel & Petřík 1982; Petřík et al. 1994; Petřík & Kohút 1997; Kohút et al. 1999; Broska & Uher 2001). These include mineralogical criteria — character of rock-forming minerals (Petřík & Broska 1994), accessory mineral assemblage including zircon typology and allanite-monazite dichotomy (Broska & Uher 1991), magnetite-ilmenite (Broska & Gregor 1992), the presence or absence of dark microgranular enclaves (Broska & Petřík 1993a). The S-type granite group is generally characterized by ferruginous, Al- and Ti-rich biotite containing 0–8 % (typically 3–5 %) of fer-

ric iron component, which, together with lacking magnetite, indicate reducing conditions during magma crystallization (Petřík & Broska 1994). The suite of S-type granitoids is dated to the period 360–340 Ma (Finger et al. 2003).

The biotite from I-type granitoids, in amount typically 10–15 vol. %, is Mg-dominant [$Fe/(Fe+Mg)=0.4-0.5$] and oxidized (15 % of ferric iron). It associates with magnetite, allanite and titanite indicating the oxidized character of this group (Petřík & Broska 1994; Petřík & Kohút 1997). The suite of I-type granitoids seems to have originated in two separate events: the first, coeval with S-type granitoids, emplaced in the Late Devonian–Mississippian period (360–340 Ma) as

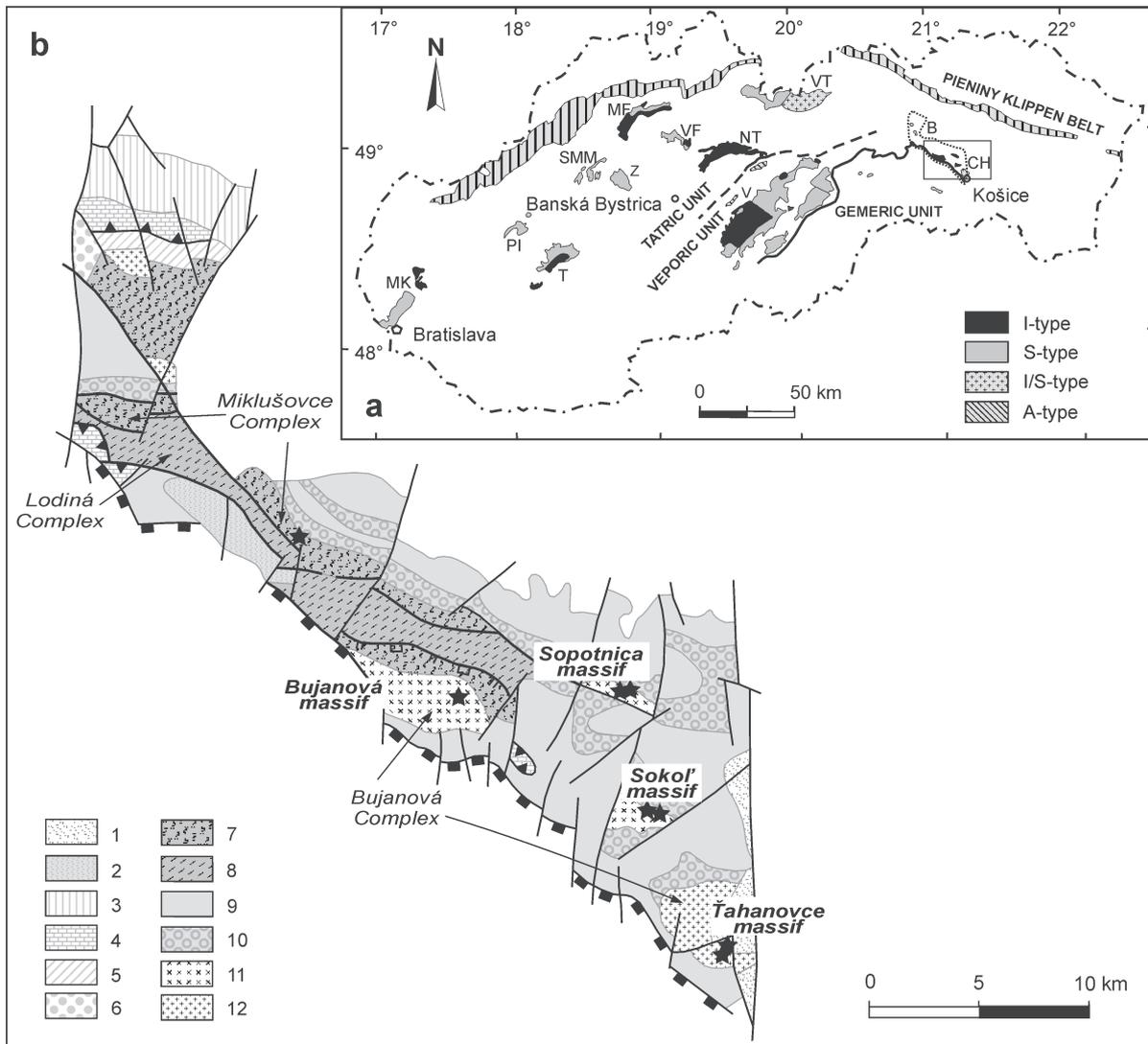


Fig. 1. a — Schematized map of the distribution of Variscan West-Carpathian granitoids. *Explanations:* MK — Malé Karpaty Mts, T — Tribeč Mts, PI — Považský Inovec Mts, SMM — Suchý and Malá Magura Mts, Z — Žiar Mts, MF — Malá Fatra Mts, VF — Veľká Fatra Mts, NT — Nízke Tatry Mts, VT — Vysoké Tatry Mts, V — Vepor Mts, B — Branisko Mts, CH — Čierna hora Mts. b — Schematic geological map of the Čierna hora Mts (Bezák et al. 2004a) partly modified. Stars show sample location. *Explanations:* 1 — sedimentary filling (Neogene–Quaternary), 2 — sedimentary filling (Paleogene–Upper Cretaceous). **Hronicum:** 3 — Čierny Váh development, 4 — clastic and volcanic sequences. **Tatricum:** 5 — Mesozoic formations with $J-C_1$ shallow water sediments, 6 — clastic sediments (Upper Paleozoic). **Variscan tectonic units in crystalline basement:** 7 — Upper lithotectonic unit, 8 — Middle lithotectonic unit. **Veporicum:** 9 — sequence of Veľký Bok ($T-C_1$), 10 — cover sequence (Upper Paleozoic), 11 — Suite of I-type granitoids, 12 — Suite of S-type granitoids. Lodiná, Miklušovce and Bujanová Complexes are retired according to Jacko (1985).

the result of partial melting in the thickened Variscan collisional-accretionary wedge (Broska & Uher 2001; Finger et al. 2003). The intrusion of the second group between ca. 320–300 Ma (the middle/Late Carboniferous; Broska et al. 1990; Bibikova et al. 1990) was probably associated with crustal collapse and following a thermal event was contributed by infracrustal or mantle material (Kohút et al. 1999; Petrik 2000; Broska & Uher 2001; Gawęda et al. 2005; Poller et al. 2005). The Variscan S- and I-type magmatism was followed by a Permian event producing distinct A-type and specialized S-type granite magmas of the Veporic and Gemeric Units, respectively (Petrik et al. 1994, 1995; Uher & Broska 1996; Finger et al. 2003).

The above S/I-type subdivision is supported by isotope data, which indicate different source material and different melting conditions for the I- and S-type granitoids (Kráľ 1994; Kohút & Nabelek 1996; Kohút et al. 1999; Petrik 2000; Poller et al. 2001, 2005; Kohút & Recio 2002).

Geological setting

The Čierna hora Mts is the easternmost morphostructural elevation of the Veporic Unit in the Central Western Carpathians (Fig. 1b). This unit is composed of the basement rocks and Upper Paleozoic-Mesozoic cover sequences. The characteristic basement rocks are medium- to high-grade metamorphosed schists and gneisses intruded by granitoids. Granitoid rocks are represented by several types involving biotite granodiorites to tonalites, biotite-muscovite granites and leucogranites. Jacko (1985) distinguished three lithostructural complexes within the Čierna hora crystalline basement: 1 — the Lodiná, 2 — the Miklušovce and 3 — the Bujanová Complex. The selected complexes as well as contacts between the crystalline basement and cover envelope sequences are tectonic (i.c.). According to the Variscan structure of the Central Western Carpathians (sensu Bezák 1994; Bezák et al. 1997), the granite-free Lodiná Complex belongs to the Middle lithotectonic unit, whereas the Miklušovce and Bujanová Complexes with presence of granitoids belong to the Upper lithotectonic unit (Jacko et al. 1995).

The Miklušovce Complex is built by strongly diaphorized migmatites, gneisses, amphibolites and intrafolial leucogranite bodies. The best exposed aplitic granites are known in the Vyšná dolina Valley and Predná dolina Valley. The K/Ar muscovite dating of aplitic granite from the Predná dolina Valley locality shows the age of 259 Ma (cf. Cambel et al. 1990).

On the basis of existing datings, the Bujanová Complex is characterized by the presence of Neo-Variscan (Bujanová, Sopotnica, Veľká Lodina, Sokol) and Meso-Variscan granitoids (Ťahanovce). The Rb/Sr biotite dating from the Sokol area (borehole SGR-V-10; Grecula et al. 1977) shows age of 310 ± 21 Ma (Kovach et al. 1986). The age 309 Ma (K/Ar dating) for these granitoids was reported by Jacko & Petrik (1987). The age of around 350 Ma was obtained by CHIME monazite dating from granitoids in the Ťahanovce area (Bónová 2006). Detailed petrographic characteristics of the crystalline basement of the Bujanová Complex were given by

Jacko (1975, 1978), and the granitoid rocks were described by Jacko & Petrik (1987).

Investigated samples

The investigated samples cover all main granitoid massifs in the Bujanová Complex. Samples ČH-SK1 and ČH-SK2 (Sokol massif) have been taken from the Uhrinče Valley approximately 1.5 km NW from the village of Sokol. Samples ČH-SP and ČH-150 (Sopotnica massif) are from the Sopotnica Valley approximately 1.75 km NE of the village of Veľká Lodina. The ČH-BJN sample (Bujanová massif) was collected from the road cut of Košické Hámre-Ružin, ca. 950 m NE of elevation point 780.8. The samples ČH-TH1 and ČH-TH2 are the biotite granodiorites (Ťahanovce massif) taken from a large quarry situated ca. 2 km NW from Košice. The sample ČH-HAG (Miklušovce Complex) comes from the Predná dolina Valley locality, approximately 800 m E of elevation point 689 (Fig. 1b).

Analytical methods

The chemical composition of biotite was obtained by the electron microprobe (CAMECA SX-100 housed in the laboratories of the State Geological Institute of Dionýz Štúr in Bratislava) and the analyses were supplemented from the literature (Jacko & Petrik 1987; Jablonská 1992). Operating conditions included an accelerating voltage of 15 kV and beam current of 20 nA. Analyses of individual elements in biotite were carried out using the following standards: K — orthoclase, Na — albite, Si and Ca — wollastonite, Al-Al₂O₃, Mg-MgO, Fe — hematite, Ti-TiO₂, Cr — chromite, and Mn — rhodonite. Calculation of biotite structural formula was based on 22 (O) or 24 (O, OH).

The concentrates of biotite were obtained using standard mineral separation procedures: rock crushing, sieving, preliminary concentration on a Wilfley table, heavy liquid and finally magnetic separation.

Mössbauer spectroscopy technique (Department of Nuclear Physics and Technics, Slovak Technical University, Bratislava) was used on six biotite concentrates with purity better than 99.9 %. All spectra were obtained at room temperature using a ⁵⁷Co rhodium matrix source. Data were collected on 512 channels. To minimize possible oxidation of iron the minerals were not pulverized. The adverse effects of preferred orientation on relative intensities of peaks in spectrograms were eliminated according to Dyar & Burns (1986). The biotites, in which the oxidation state of iron was determined namely two biotite separates (ČH-TH1, ČH-TH2) from the Ťahanovce area, two biotite separates (ČH-SK1, ČH-SK2) from the Sokol massif and the same number of samples (ČH-SP, ČH-150) from the Sopotnica massif, were analysed in the course of this study by electron microprobe (see above). On the basis of Mössbauer spectroscopy results the total FeO content was divided into Fe₂O₃ and FeO values.

Major and trace element analyses of whole rocks were determined by ICP-MS spectrometry at the ACME Analytical Laboratories (Vancouver) Ltd., Canada.

Results

Petrographical and geochemical characteristics of granitoids

Sokoľ, Sopotnica and Bujanová granite bodies. The main rock types in the Sokoľ, Sopotnica and Bujanová granite massifs are represented by medium-grained undeformed biotite granodiorite to tonalite. Dominant are plagioclase, quartz, biotite and K-feldspar and accessories such as zircon, apatite, titanite, allanite and magnetite (Table 1). *Plagioclase* forms euhedral to subhedral prismatic crystals and occasionally encloses biotite flakes or accessories. It is commonly zoned: rim An₂₇, core An₃₃ (Bónová 2006). Some plagioclases exhibit a reversed zoning indicating mixing processes (Słaby et al. 2007). *Alkali feldspar* occurs as a minor interstitial phase with An-content usually <1. *Biotite* forms subhedral sporadically euhedral dark brown flakes which vary in size from 0.3 to 2 mm. It commonly encloses scattered primary accessories — apatite and zircon. The presence of numerous minute inclusions of primary accessories trapped during biotite growth, suggests, along with biotite interstitial grain position, its primary magmatic origin. The magmatic origin is also supported by their chemical composition (Fig. 2). An incipient chloritization alters biotite crystals from their margins or along cleavage. Secondary Ca-rich mineral phases, such as epidote and titanite, crystallize at the expense of biotite resulting in the loss of TiO₂ (the B field in

Table 1: Modal analyses of representative Čierna hora granitoids.

Sample	Pl	Qtz	Kfs	Bt	Ms	Ep	Ttn	Ap	Mt
ČH-TH2	51.8	25.3	8	9.4	2.7	0.7	0.1	2.3	0.1
ČH-SP	52.4	26.8	2.1	14.6	0.2	1.3	0.9	1.6	0.7
ČH-SK2	65.9	17.7	1.7	10.3	0.13	1.1	1.4	1.8	1.1
ČH-HAG	22.8	39.2	23.8	3.4	10.1	—	—	0.4	0.1

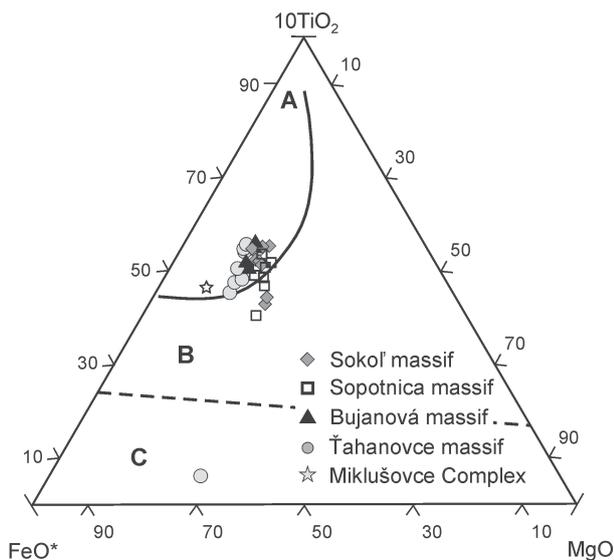


Fig. 2. Composition of biotites in the 10 TiO₂-FeO*-MgO ternary diagram (Nachit et al. 2005). **A** — domain of primary magmatic biotites, **B** — domain of reequilibrated biotites, **C** — domain of neoformed biotites.

Fig. 2). However, primary euhedral titanite also occurs in the tonalites. Early-crystallized *apatite* is abundant in biotite, the apatite crystals located inside and on rims of the primary titanite probably represent a younger generation (Broška et al. 2004, 2006). Late-magmatic *magnetite* occurs in characteristic aggregates with titanite and apatite (Fig. 3a). It is almost

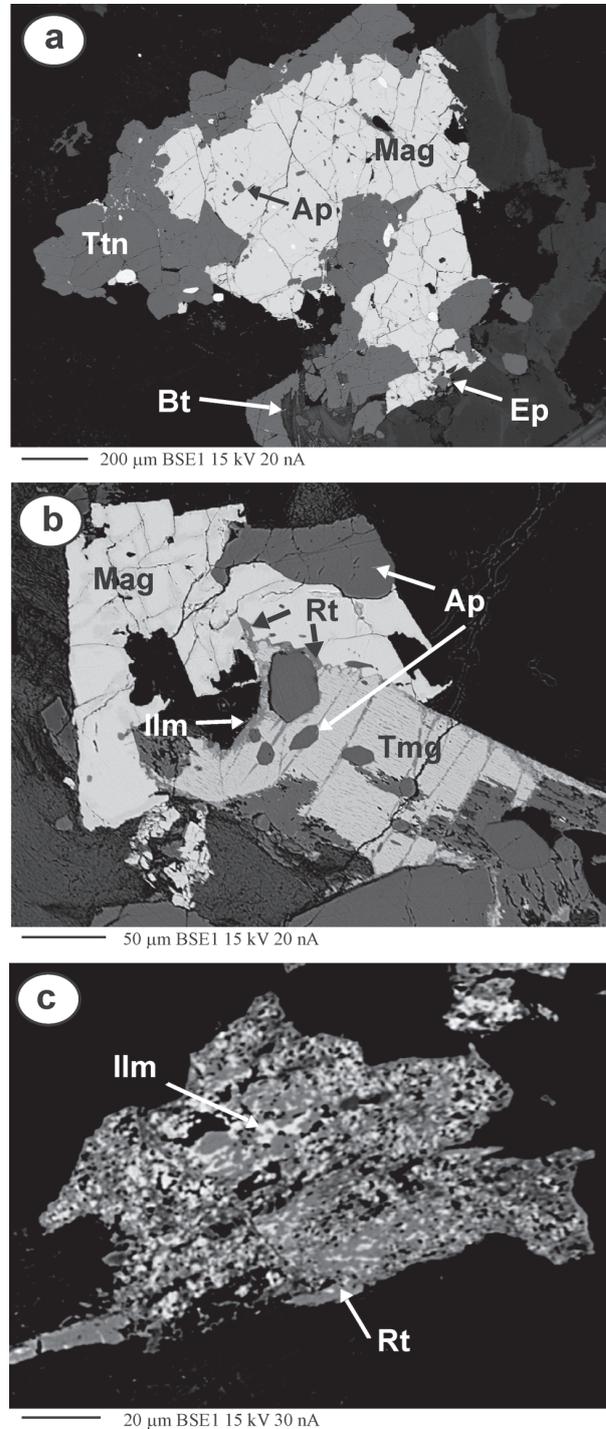


Fig. 3. **a** — BSE image of magnetite overgrown by titanite and enclosing apatite (Sokoľ, ČH-SK2). **b** — BSE image of titanomagnetite overgrown by magnetite and enclosing apatite (Sokoľ, ČH-SK2). **c** — BSE image of strongly altered ilmenite to rutile (Ťahanovce, ČH-TH2).

pure, typically unzoned and shows a maximum TiO₂ content of 0.17 wt. % (i.e. 0.5 % Usp). Early *titanomagnetite* is extensively oxy-exolved (fine exsolution lamellae of ilmenite within titanomagnetite as a breakdown product are typical features) (Fig. 3b). The predominating morphological *zircon* types from tonalites according to Pupin (1980) are S₁₂ and S₁₇; S₂₂₋₂₄ types (Jablonská 1993). Zircon grains display oscillatory zoning, typical of the magmatic growth.

Major and trace elements in the investigated rocks are listed in Table 2. The content of SiO₂ in tonalite ranges from 61.6 to 63.4 wt. %. Their main feature is a metaluminous to

Table 2: Chemical composition of the investigated granitoids. Oxides in wt. %, trace elements in ppm.

Granite type	S	I/S	I	I	I
	ČH-HAG	ČH-TH2	ČH-BJN	ČH-SK2	ČH-SP
SiO ₂	75.22	65.08	65.68	61.62	63.42
Al ₂ O ₃	13.59	16.8	15.84	17.19	17.11
Fe ₂ O ₃	1.14	4.09	3.87	5.1	4.36
MgO	0.27	1.55	1.41	2.22	1.86
CaO	0.33	2.66	2.7	3.54	3.5
Na ₂ O	2.99	4.42	4.08	4.34	4.45
K ₂ O	4.92	2.35	3.01	2.43	2.18
TiO ₂	0.10	0.60	0.58	0.92	0.76
P ₂ O ₅	0.19	0.30	0.25	0.33	0.28
MnO	0.01	0.07	0.06	0.07	0.07
LOI	1.0	1.8	2.2	1.9	1.6
Total	98.76	97.93	97.48	97.76	97.99
Ba	1605	1117	1323	1073	1247
Be	1	3	2	2	2
Sc	5	8	7	6	6
Co	0.6	9.1	8	11.3	9.9
Cs	4.6	1.6	3.1	1.6	1.8
Ga	17.4	22.2	21.9	19.5	23.6
Hf	5.4	7.2	7	5.9	6.9
Nb	7	10.1	7.1	6.6	9.5
Rb	267.8	65.7	74.5	66.5	54.2
Sn	6	2	3	2	2
Sr	58.6	707.6	674.7	924.4	1030
Ta	1.2	0.6	0.4	0.4	0.5
Th	6.8	18.1	13	14.6	10.9
U	9.9	2.8	2	1.3	1.6
V	9	65	72	113	92
W	4.1	14.7	<0.5	<0.5	<0.5
Zr	160.7	248.4	239	224.4	244.7
Y	26.7	22	12.5	8.8	20
Mo	0.3	0.4	0.2	<0.1	0.2
Cu	8.4	11.2	7.8	9.5	6.2
Pb	6.3	10	11	10.2	8
Zn	8	78	84	100	99
Ni	1.3	5.1	6.9	8.9	7.9
As	81.5	2.6	1.1	1.1	1.7
Sb	2.8	0.3	1.2	<0.1	0.2
La	9.4	70	48	82.5	54.7
Ce	20.9	137.9	91.5	157.9	108.2
Pr	2.61	15.93	10.08	17.49	12.37
Nd	8.2	58.4	36.3	61.7	43.9
Sm	2.4	9.07	5.08	7.96	6.35
Eu	0.21	1.78	1.36	1.86	1.85
Gd	2.29	5.9	2.79	3.29	3.48
Dy	3.18	4.43	1.82	2.35	2.92
Tb	0.56	0.91	0.39	0.56	0.61
Ho	0.67	0.83	0.3	0.33	0.59
Er	1.84	1.86	0.64	0.73	1.6
Tm	0.34	0.3	0.11	0.17	0.25
Yb	2.14	1.79	0.68	2.37	1.46
Lu	0.31	0.25	0.11	0.35	0.2

subaluminous character (A/CNK=0.93 to 1.07), predominance of Na₂O over K₂O as well as elevated CaO, MgO and TiO₂ contents. High concentrations of Zn (ca. 100 ppm) reflect significant modal abundance of opaque oxides. The REE patterns do not show negative Eu anomaly (Eu/Eu*~1) reflecting the higher temperature and fugacity O₂ in magma (Drake 1975) or a cumulate character of the studied rocks caused by accumulation of plagioclase crystals (Cambel & Vilišovič 1987; Jacko & Petrik 1987). Geochemistry features as well as rock-forming and accessory mineral assemblage confirm the I-type affinity of these rocks.

Tahanovce granitoid massif. Medium- to coarse-grained biotite granodiorite is characteristic of this massif. The primary magmatic minerals are plagioclase, quartz, K-feldspar, biotite and accessory minerals — apatite, zircon, monazite, ilmenite, magnetite ± titanite ± allanite. Epidote, sericite, calcite and chlorite present in small quantities are the secondary phases.

Plagioclase forms euhedral to subhedral prismatic crystals twinned according to albite law. It locally encloses quartz and biotite. It is commonly zoned with anorthite component between An₆ in rim and An₁₇ in core. *Alkali feldspar* occurs as a minor interstitial phase enclosing quartz, plagioclase occasionally biotite. *Biotite* (maximum 1.7 mm in size) forms subhedral dark brown flakes which are often pressure-kinked. The biotite is locally fully replaced by chlorite forming pseudomorphs. Biotite commonly encloses primary accessories — apatite, zircon and monazite indicating its primary magmatic origin. *Magnetite* is rare, a single grain was found in the matrix. *Ilmenite* grains are altered to rutile (leucogenization). The dissolution-reprecipitation mechanism seems to be responsible for such breakdown being documented by the formation of numerous pores (Fig. 3c). *Zircons* are mainly represented by low morphological S subtypes (S_{1,2,7}) less by S_{12,17} and L_{2,3} types with the mean point represented by subtype S₇ (Jablonská 1993).

The biotite granodiorite in comparison to Sokol and Sopotnica granitoids is more peraluminous (A/CNK ratio from 1.15 to 1.3), with low Th, U, Nb and Sr. The peraluminous character of these granitoids is rather due to secondary alteration than to primary peraluminous character of the protolith. The SiO₂ content throughout the rocks ranges widely between 65.1 and 71.1 wt. %. Chondrite-normalized REE patterns of rocks are not significantly different from the pattern of tonalites (Fig. 4) with negligible Eu anomaly (Eu/Eu*~0.7). The granite shows S-type affinity.

Granites of the Miklušovce Complex. The Miklušovce Complex contains abundant aplitic granite dykes exposed mainly in the Predná dolina Valley locality, in thickness reaching several tens of centimeters to several meters.

The leucogranite is fine-grained, massive-textured rock sporadically with features of cataclastic brittle deformation. It consists of K-feldspar, plagioclase (An₆), quartz, biotite and muscovite. The muscovite I is primary magmatic, muscovite II clearly grows at the expense of feldspar and biotite. It is commonly intergrown with vermicular quartz. Biotite is frequently baueritized. Apatite, zircon (S₇, S_{2,3-7}, S₁₂ and L₁₋₄ morphological types; Jablonská 1993) garnet and negligible opaque minerals occur as accessories. The representative mi-

Table 3: Representative microprobe analyses of rock-forming minerals (in wt. %) from the Čierna hora granitoids. **n.a.** — not analysed. Ferrous and ferric ratio in Fe-Ti oxides calculated according to Droop (1987).

Sample point	ČH-SK2			ČH-TH2		ČH-HAG	
	Ilm	Mag	Pl	Kfs	Pl	Pl	Kfs
SiO ₂	0.00	0.00	61.12	64.39	61.56	67.77	65.40
TiO ₂	47.57	8.40	0.03	0.00	0.01	0.00	0.00
Al ₂ O ₃	0.02	0.03	24.50	18.51	24.39	20.29	18.36
Fe ₂ O ₃	10.15	49.89	—	—	—	—	—
FeO	34.14	38.13	0.09	0.18	0.20	0.08	0.06
MnO	8.34	0.40	0.00	0.00	0.01	0.00	0.01
MgO	0.09	0.02	0.00	0.00	0.02	0.00	0.00
CaO	0.04	0.02	5.77	0.00	5.37	1.32	0.04
BaO	n.a.	n.a.	0.13	0.62	0.05	0.00	0.00
Na ₂ O	n.a.	n.a.	7.98	0.35	8.15	10.61	0.58
K ₂ O	n.a.	n.a.	0.27	16.06	0.40	0.11	16.30
P ₂ O ₅	n.a.	n.a.	0.08	0.00	0.07	n.a.	n.a.
Cr ₂ O ₃	0.00	0.06	n.a.	n.a.	n.a.	n.a.	n.a.
ZnO	0.15	0.00	n.a.	n.a.	n.a.	n.a.	n.a.
V ₂ O ₅	0.10	0.36	n.a.	n.a.	n.a.	n.a.	n.a.
Total	100.6	97.30	99.9	100.1	100.2	100.2	100.8
	3 O	4 O		8 O			
Si	0.000	0.000	2.717	2.986	2.728	2.959	3.001
Ti	0.901	0.248	0.001	0.000	0.000	0.000	0.000
Al	0.001	0.001	1.284	1.012	1.274	1.044	0.993
Fe ³⁺	0.192	1.474					
Fe ²⁺	0.719	1.251	Fe _{tot} 0.003	0.007	0.007	0.003	0.002
Mn	0.178	0.013	0.000	0.000	0.000	0.000	0.000
Mg	0.003	0.001	0.000	0.000	0.002	0.000	0.001
Ca	0.001	0.001	0.275	0.000	0.255	0.062	0.002
Ba			0.002	0.011	0.001	0.000	
Na			0.688	0.032	0.701	0.898	0.051
K			0.015	0.950	0.023	0.006	0.955
P			0.003	0.000	0.003	0.000	
Cr	0.000	0.002					
Zn	0.003	0.000					
V	0.002	0.009					
Total	2.000	3.000	4.988	4.998	4.994	4.972	5.005
X _{ilm}	0.893	X _{Ab}	0.700	0.030	0.720	0.930	0.050
X _{hem}	0.107	X _{An}	0.280	0.000	0.260	0.060	0.000
X _{usp}		0.251	X _{Or}	0.020	0.960	0.020	0.010
X _{mt}		0.749	X _{Cs}	0.000	0.010	0.000	0.000

croprobe analyses of some rock-forming minerals (wt. %) are listed in Table 3.

Geochemistry of leucogranite from the Miklušovec Complex indicates more a fractionated magma with higher SiO₂ ~75.2 wt. %, Rb, Y and lower MgO, CaO, TiO₂ contents. The more pronounced Eu-negative anomaly (ca. 0.3) and the lowest value of the LREE (La_N/Yb_N=2.96) are characteristic. A slight tetrad effect observable in the REE chondrite normalized pattern indicates the presence of strong fluid activity during cooling of the magma system. Granites from the Miklušovec Complex are probably the derivatives of an S-type granite suite.

Biotite chemistry

Čierna hora biotite chemistry corresponds to other granitoid massifs of the Western Carpathians: while I-type tonalites contain Mg-biotite (Fe-phlogopite to Mg-siderophyllite after Rieder et al. 1998) with Fe/(Fe+Mg)=0.44–0.54 and low alumina (total Al=2.7–3.1, Al^{IV}=2.5), the S-type granodiorites contain Fe-biotite [Fe/(Fe+Mg)=0.55–0.62 (Ťahanovce)], and

leucogranite (Miklušovec) with Fe-rich biotite Fe/(Fe+Mg) ~0.74. Proportions of octahedral cations are shown in diagram (Fig. 5) after Foster (1960). Compared to the Tribeč I-type tonalite, the primary biotites from the Sokol and Sopotnica massifs are relatively rich in TiO₂: 2.4–3.6, 2.1–3.6 wt. %, respectively (Jablonská 1992; Table 4). This is consistent with the less abundant titanite than in the Tribeč tonalite. The lower TiO₂ content (2.7 wt. %) in biotite from the Miklušovec Complex corresponds to more evolved granite. A slightly elevated TiO₂ is found in biotite from the Ťahanovce massif (to 2.6–3.7 wt. %). The increasing biotite Fe/Mg ratio correlates well with total alumina concentration (Figs. 5, 6) reflecting the increased activity of alumina from biotite tonalite to two mica leucogranite.

The composition of biotites from the Sokol, Sopotnica and Bujanová granitoid massifs implies high Mg values and a relatively low Al^{VI} content (Fig. 7). The centres of grains are slightly more Mg-rich compared to crystal margins in Sokol biotite. The trend of iron enrichment in rims indicates a decrease in temperature and/or an increase in the water content. The compositions of biotite in leucogranite from the Miklušovec Complex are the most Fe-rich and show low Mg and high Al^{VI} amounts.

Comparison of the peraluminosity index (A/CNK) of biotite with the same index in whole rock (Fig. 8) shows distinctly higher A/CNK values for biotites indicating their aluminous character and important role as a significant aluminium carrier in Čierna hora granitoids, since cordierite, garnet or the Al₂SiO₅ polymorphs are missing in these rocks. The subordinate amount of muscovite in granodiorites and tonalites, which occasionally forms symplectitic intergrowths with quartz, is a product of secondary alterations. An exception is

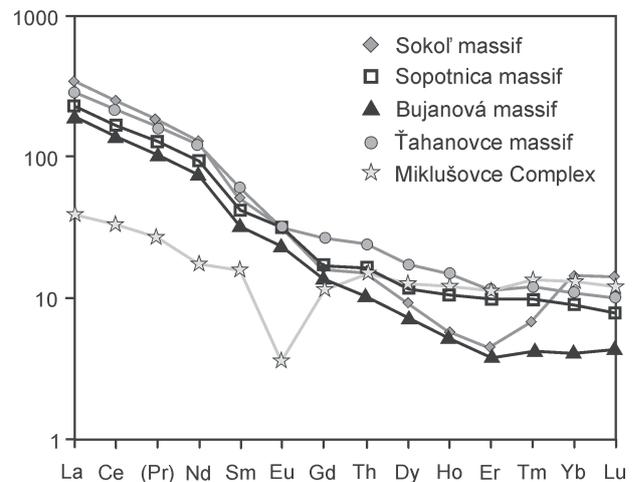
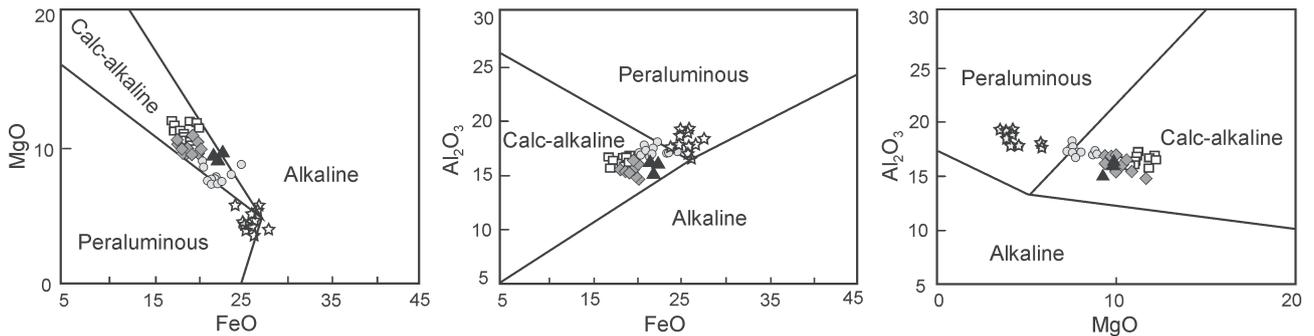


Fig. 4. Plot of REE patterns for the investigated granitoids normalized according to Evensen et al. (1978).

Table 4: Chemical composition of biotites from selected Čierna hora granitoids. c — core, c/r — transitional zone, r — rim.

Locality Sample Point	Sokol' massif ČH-SK2			Sopotnica massif ČH-SP		Ťahanovce massif ČH-TH2		Bujanová massif ČH-BJN		Miklušovce Complex ČH-HAG	
	Bt c	Bt c/r	Bt r	Bt 1	Bt 2	Bt 1	Bt 2	Bt c	Bt r	Bt c	Bt r
SiO ₂	37.06	36.78	37.01	36.63	36.33	36.25	35.44	36.24	36.12	35.83	36.30
TiO ₂	3.55	3.53	3.58	3.10	3.01	2.80	2.61	3.28	2.78	2.74	2.70
Al ₂ O ₃	16.13	15.97	15.73	16.17	15.59	16.82	16.95	16.48	16.04	16.33	16.98
FeO _{tot}	—	—	—	—	—	—	—	21.61	22.58	26.31	26.00
Fe ₂ O ₃	3.47	3.55	3.63	4.38	4.39	1.13	1.23	—	—	—	—
FeO	16.06	16.42	16.79	14.76	14.79	19.82	21.45	—	—	—	—
MnO	0.35	0.33	0.46	0.28	0.33	0.30	0.27	0.20	0.25	0.00	0.05
MgO	10.65	10.39	9.89	11.07	10.65	9.01	8.56	9.50	9.67	5.39	5.20
CaO	0.00	0.02	0.02	0.07	0.05	0.01	0.03	0.03	0.08	0.02	0.01
Na ₂ O	0.08	0.10	0.07	0.00	0.01	0.12	0.13	0.13	0.07	0.08	0.02
K ₂ O	9.80	9.68	9.86	9.14	9.54	9.38	8.78	9.50	9.33	9.55	9.48
Cr ₂ O ₃	0.00	0.00	0.02	0.03	0.00	0.01	0.00	0.00	0.00	0.00	0.00
NiO	0.00	0.11	0.01	0.00	0.00	0.00	0.02	0.00	0.00	0.05	0.02
F	0.26	0.59	0.61	0.46	0.43	0.69	0.23	0.00	0.25	0.57	0.48
Cl	0.05	0.05	0.05	0.04	0.04	0.03	0.05	0.07	0.06	0.03	0.04
Total	97.11	97.17	97.36	95.69	94.72	96.27	95.61	97.04	97.22	96.91	97.28
calculated on the basis 24 O											
Si	2.758	2.752	2.771	2.751	2.768	2.767	2.729	2.746	2.752	2.797	2.806
Al ^{IV}	1.242	1.248	1.229	1.249	1.232	1.233	1.271	1.254	1.248	1.203	1.194
Al ^{VI}	0.173	0.161	0.160	0.182	0.168	0.280	0.267	0.218	0.192	0.299	0.353
Ti	0.199	0.199	0.201	0.175	0.172	0.161	0.151	0.187	0.159	0.161	0.157
Fe ³⁺	0.194	0.200	0.204	0.248	0.252	0.065	0.071	0.000	0.000	0.000	0.000
Fe ²⁺	0.999	1.027	1.051	0.927	0.943	1.265	1.381	1.369	1.438	1.718	1.681
Mn	0.022	0.021	0.029	0.018	0.021	0.019	0.017	0.013	0.016	0.000	0.003
Mg	1.181	1.159	1.104	1.240	1.209	1.025	0.983	1.073	1.098	0.627	0.600
Cr	0.000	0.000	0.001	0.002	0.000	0.001	0.000	0.000	0.000	0.000	0.000
Ni	0.000	0.007	0.001	0.000	0.000	0.000	0.001	0.000	0.000	0.003	0.001
Ca	0.000	0.002	0.002	0.005	0.004	0.001	0.002	0.003	0.006	0.002	0.001
Na	0.012	0.015	0.011	0.000	0.001	0.018	0.019	0.019	0.010	0.012	0.004
K	0.931	0.924	0.942	0.876	0.927	0.913	0.862	0.918	0.907	0.951	0.935
Total cat.	7.710	7.714	7.707	7.672	7.697	7.748	7.756	7.800	7.828	7.773	7.733
F	0.061	0.140	0.144	0.109	0.103	0.167	0.056	0.000	0.060	0.141	0.118
Cl	0.006	0.006	0.006	0.005	0.005	0.004	0.007	0.009	0.008	0.004	0.005
OH	3.933	3.854	3.850	3.886	3.892	3.830	3.937	3.991	3.933	3.855	3.876
X _{Fe²⁺}	0.333	0.342	0.350	0.309	0.314	0.422	0.460	—	—	—	—
Fe/Fe+Mg	0.503	0.514	0.532	0.487	0.497	0.565	0.596	0.560	0.570	0.733	0.737

**Fig. 9.** The plot of biotites from Čierna hora granitoids on the Abdel-Rahman (1994) discrimination diagrams. Oxides are in wt. %. Symbols are the same as in Fig. 2.

the magma is buffered, a_{ann} in biotite increases through reaction of K-feldspar with magnetite, with resulting growth of the $\text{Fe}^{2+}/(\text{Fe}^{2+} + \text{Mg})$ ratio. When f_{O_2} is allowed to decrease, at the same temperature and $f_{\text{H}_2\text{O}}$, biotite also reacts by increase of a_{ann} , either by decrease of $\text{Fe}^{3+}/\text{Fe}_{\text{tot}}$ or by increase of $\text{Fe}^{2+}/(\text{Fe}^{2+} + \text{Mg})$ ratios. Therefore, less oxidized, more leucocratic S-type granitoid melts always contain more iron-rich

biotites (coexisting with ilmenite rather than magnetite). For buffered biotite compositions the relative content of Fe^{3+} (i.e. $\text{Fe}^{3+}/\text{Fe}_{\text{tot}}$) is approximately constant its percentage depending on the f_{O_2} (buffer). If we are able to estimate the f_{O_2} in the magma (best through coexisting Fe-Ti oxides, which may provide precise estimates of both oxygen fugacity and temperature) and activities of magnetite and K-feldspar with

Discussion

Estimation of oxygen fugacity

In Figure 11, the most reducing biotites from the Ťaha-novce granitoid body plot on the QFM buffer, while the more oxidized biotite analyses from the Sokol and Sopotnica tonalites are shifted between the NNO and HM buffers. The oxidizing conditions of the tonalite magma are also supported by the presence of titanomagnetite and euhedral titanite (Ishihara 1977; Wones 1989) in Sokol tonalite. The f_{O_2} vs. T relationship was estimated for two samples: Sokol and Sopotnica tonalites. The conditions for the Sokol magma were calculated for a magnetite-ilmenite pair using the conversion of atomic proportions to molar fractions according to Stormer (1983) and calibrations of Andersen & Lindsley (1985) as presented in the ILMAT program (Lepage 2003). The pair indicates an increased $\log f_{O_2} = -13.94$ to -14.07 at temperatures $T = 768-784$ °C. The fugacity is above the NN buffer (Δ_{NN} ranges between 0.27 and 0.52), which is in accord with the oxidized character of the Sokol biotite (16.3 % Fe^{3+}). This fugacity was used for calculations of the Sokol biotite stability curve (Table 6). The f_{O_2} in another tonalite from Sopotnica could not be calculated by oxybarometry because of the re-equilibrated nature of magnetite. This re-equilibration involved oxidation of the ulvöspinel component in Ti-magnetite producing titanite and magnetite (cf. Broska et al. 2006). The f_{O_2} was therefore approximated by the buffer TMQA (titanite-magnetite-quartz-amphibole; Noyes et al. 1983) which is ca. 1.45 log unit above the NNO buffer. The high oxidation conditions of this buffer are consistent with the highest Fe^{3+} in this biotite (0.211 %).

The derivation of water content in magma

The water content is calculated for the above two samples which contain the required assemblage biotite + K-feldspar + magnetite: ČH-SK2 (Sokol) and ČH-SP (Sopotnica), both representing I-type tonalites. The other two granites (ČH-TH, ČH-HAG) either do not contain magnetite or K-feldspar in sufficient amounts (Table 1). The pressure estimate, 400 MPa, for both samples is obtained from the mineral assemblage of surrounding metamorphic rocks which were formed during the periplutonic tectonothermal event (cf. Jacko et al. 1990). This value is similar to other pressure estimates from similar metamorphic rocks intruded by granite (Strážovské vrchy Mts, Vilinovičová 1990; or Velká Fatra Mts, Janák & Kohút 1996). The derivation of T and H_2O is based on the concept of minimum water content in the melt of haplogranite composition (Clemens & Vielzeuf 1987; Johannes & Holtz 1996), which allows us to obtain both parameters from intersection of the minimum water content curve with the biotite stability curve in the T - H_2O space calculated by the above procedure (Fig. 12). Comparison of three biotite activity — composition models: Czamanske & Wones (1973), Bohlen et al. (1980) and Patiño Douce (1993) shows that they result in the maximum of 10–23 % difference in final water contents depending mostly on F concentrations. Fabbrizio et al. (2006) recently experimentally tested several annite activity models and con-

cluded that the partly ionic model of Czamanske & Wones [$a_{ann} = (X_{Fe^{2+}})^3(X_{OH})^2$] most closely follows experimental data. This activity model was used in the calculations. For the K-feldspar activity the value 0.6 was used following Czamanske & Wones (1973). Using the higher value $a_{Kfs} = 0.8$ would change the intersection to a lower water content by ca. 0.35 % and higher T by 10 °C.

ČH-SK2: Biotite analyses from this tonalite show slightly more Fe-rich compositions for rim compared to centre (Table 4, ČH-SK2, Bt-c and Bt-r) probably recording an effect of cooling. The oxygen fugacity derived for this sample is $\log f_{O_2} = -14.07$ at $T = 768$ °C. This temperature is lower than zircon saturation ($T = 799$ °C for Sokol), which is in accord with textural relations with zircon being enclosed in biotite. The calculated water contents of the intercepts are 3.99 and 4.05 wt. % at $T = 772$ and 769 °C for biotite core and rim, respectively (Fig. 12, Table 6), close to the Fe-Ti oxide temperature. Although the difference is negligible and certainly within the error of the estimate, the biotite rim seems to record an increase in the water content of crystallizing melt at a slight decrease in T . The derived H_2O amounts refer to the remaining melt coexisting with biotite, K-feldspar and magnetite. The growth of the biotite rim may record the build-up of H_2O resulting from concomitant feldspar + quartz crystallization.

ČH-SP: This tonalite has high magnetite and titanite contents (0.7, 0.9 %, respectively) but only 0.1 % of K-feldspar (Table 1). It contains the most Mg-rich and most oxidized biotite from the Čierna hora Mts. The magnetite is mostly pure and commonly overgrown by titanite. Assuming equilibrium among biotite, K-feldspar and magnetite the intersection of the curves (Fig. 12, Table 6) gives 4.76 % H_2O at 744 °C (with $a_{mag} = 1$). The highest H_2O estimate at the lowest T corresponds to the high degree of crystallization necessary for the precipitation of K-feldspar.

Table 6: Calculated melt and magma water contents for Čierna hora granitoid biotite compositions using $a_{K-f} = 0.6$, $a_{mag} = 1$ (except in Sokol with $a_{mag} = 0.853$ (sensu model of Woodland & Wood 1994) and $f_{O_2} = NNO + 0.52$ according to mag-ilm oxybarometry), $P = 400$ MPa (Jacko et al. 1990), Mössbauer based Fe^{3+} contents and biotite stability curve (3) after Wones (1981). See text for details on a_{ann} and buffers.

Sample	ČH-SK2 core	ČH-SK2 rim	ČH-SP	T88
Locality	Sokol ¹	Sokol ¹	Sopotnica	Tribeč
a_{ann}^1	0.0345	0.0368	0.0262	0.0295
Fe^{3+}/Fe_{tot}	0.163	0.163	0.211	0.157
X_{mag}	0.75	0.75	1	1
a_{mag}^2	0.852	0.853	1	1
a_{san}	0.6	0.6	0.6	0.6
T_{zir} °C	799.8	799.8	811	796
T °C by intersection	772	769	744	739
Buffer	NN+0.52	NN+0.52	TMQA ³	TMQA ³
P (MPa)	400	400	400	400
H_2O (T) wt. %	3.99	4.05	4.76	4.94

Notes: ¹ — Annite activity after Czamanske & Wones (1973), cf. Fabbrizio et al. (2006). ² — After Woodland & Wood (1994). The calculations assume constant H_2O in biotite 3.6 %. ³ — TMQA ~ NN+1.45. Tribeč tonalite also shown for comparison. The annite activity in T88 recalculated with 0.3 % F in biotite analysis.

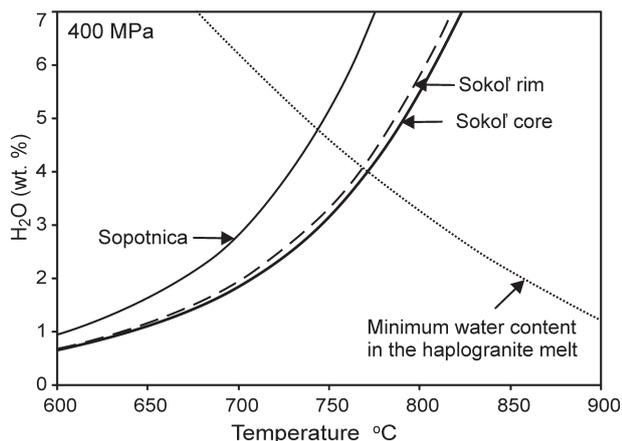


Fig. 12. Intersections of the calculated biotite stability curves with the curve of minimum water content in the haplogranite system (after Johannes & Holtz 1996: fig. 2.24, 2.25).

A procedure similar to that described above was used by Petrik & Broska (1994) to derive melt water contents for two types of biotite tonalite from the Tribeč Mts. Contrasting biotite compositions along with accessory assemblages (magnetite vs. ilmenite) indicated different f_{O_2} in individual magmas and higher water contents estimated for the I-type tonalite (ca. 5.2 %, TMQA buffer, 350 MPa) compared with the peraluminous S-type biotite tonalite with only 2.3 % H_2O (FMQ buffer, 250 MPa) both at 700 °C and using earlier calibration by Wones (1972). The recalculation of Tribeč I-type tonalite using the present procedure (Table 6) results in a slightly lower water content of 4.94 % at a higher temperature of 739 °C.

Generally small differences in the water contents of all tonalites (Sokol, Sopotnica and Tribeč) indicate the buffering role of biotite in the system annite-K-feldspar-magnetite- H_2O . Biotite effectively reacts to different oxygen fugacities by changing its annite activity and buffers water content in the melt.

Total water in the system

The above estimates refer to the remaining melt, the total water content in the system crystals+melt is lower than that indicated by biotite composition. From the modal compositions (Table 1) it follows that because of low content of K-feldspar the assemblage biotite-magnetite-K-feldspar may have equilibrated only at high degrees of crystallinity, namely when much of plagioclase, quartz and biotite had crystallized. If we estimate that after 80–85 % crystallization ca. 20–15 % of melt remains and the K-feldspar joined the assemblage, the total water in magma would be in the range 1–1.5 wt. % H_2O .

Biotite and parental magma

Biotite composition may be a reliable indicator of the origin of the parental magma (Burkhard 1993; Lalonde & Bernard 1993; Aydin et al. 2003; Machev et al. 2004; and others). The composition of biotite from the Sokol and Sopotnica massifs — relatively high Mg and low Al^{VI} contents — reflects a slightly fractionated magma (Hecht 1994). This is typical of the I-type granitoids, where a contribution of mantle material

to melt and mixing process is assumed. The inverse zoning of some feldspars in the Sokol tonalite confirms this presumption. The higher Al^{VI} content in cores combined with higher Mg concentration in rims of some investigated biotites probably resulted from later transformation by fluids during late-magmatic events. It may be interpreted by the increasing partial water pressure from separated fluids, which evolved during magma crystallization, emphasizing a more oxidizing regime (Czamanske & Wones 1973; Chivas 1981; Burkhard 1993; Johannes & Holtz 1996). A subsequent increase of the f_{O_2} in melt is suggested by the almost pure magnetite growing during later stages of magma evolution (Fig. 3b). The biotite in granodiorite from the Bujanová massif reflects almost identical features.

The higher Al^{IV} content in biotite from the Ťahanovce granitoids (cf. Jablonská 1992; Table 4) compared to the Sokol and Sopotnica biotites supposes its precipitation from more Al-rich magma. It would be consistent with melt which was generated from a metapelitic source with important crustal material contamination (Batchelor 2003).

The Fe content increases in primary biotites from all investigated granitoids with magma crystallization which can be seen related to the solidification index of rock (cf. Speer 1984; Fig. 13). While in Sokol and Sopotnica the host rock $FeO_{tot}/(MgO+FeO_{tot})$ ratio is higher compared to the same ratio in biotite, both ratios are similar in Ťahanovce, and biotite ratio is significantly higher in the Miklušovce Complex. The differences are explained by the iron bound in magnetite (0.66–1.1 vol. %) at increased f_{O_2} and f_{H_2O} (e.g. Broska et al. 2006) in the first case, the lack of the abundant magnetite in the second case, and the presence of Mg-rich chlorite in the last case.

Lower Mg and higher Al^{VI} contents in biotites from the Ťahanovce granites and especially from aplitic granites in the Miklušovce Complex suggest a more advanced degree of magmatic fractionation (cf. Hecht 1994). High total Al and Fe concentrations indicate a crustal source for the parental magma. The Fe, Al-rich, Si-poor biotite crystallized from a peraluminous melt originating mostly from the partially melted Al-rich continental crust (Buda et al. 2004). The presence of

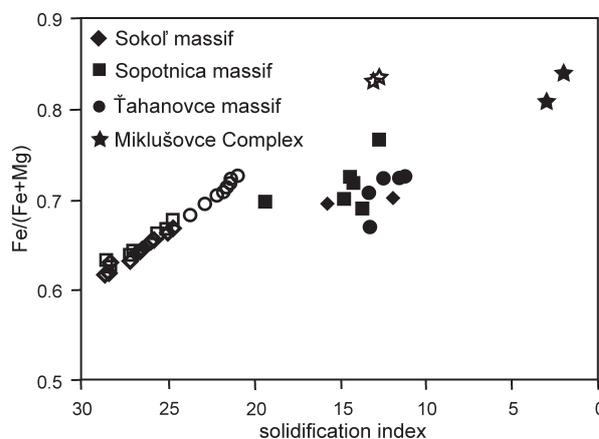


Fig. 13. Relationship between $Fe/(Fe+Mg)$ ratio in biotites (empty symbols) and their host rocks (full symbols) and the solidification index of rock $100 \cdot MgO/(MgO+FeO+Fe_2O_3+Na_2O+K_2O)$ (cf. Speer 1984).

subsolidus (autometamorphosed) biotite, in which Al^{VI} content increases markedly and TiO_2 amount partly decreases, is also characteristic for these rocks.

Tectono-magmatic implication of biotite compositions

Consequently the biotite chemistry, granitoid rocks from the Čierna hora Mts could belong to two different granitoid suites: (1) Granodiorites to tonalites from the Sokol, Sopotnica (and Bujanová) massifs (the Bujanová Complex) with the affinity to the I-type granitoid suite with Mg-rich biotites, as was assumed by Broska & Petřík (1993b), or to the magnetite series of magmatic rocks (Ishihara 1977) suggested by Gregor (1990). The I-type character of these granitoids is also documented in the discrimination diagrams of Abdel-Rahman (1994). (2) Granitoid rocks from Ťahanovce massif (the Bujanová Complex) and mainly granitoids from the Miklušovce Complex display affinity to the S-type granitoid suite as shown by their Fe-rich biotites. The Al-rich biotites coexisting with primary muscovites in the Miklušovce granites indicate their S-type character. A progressive increase of Fe and total Al values in biotites is interpreted as reflecting conditions of low oxygen fugacity caused by significant contributions of metasedimentary material to the magma, either by assimilation or anatexis (Neiva 1981; Shabani et al. 2003).

However, the chondrite-normalized REE patterns of the Ťahanovce granitoids are not significantly different from the pattern of tonalites from the Sokol and Sopotnica massifs. The major element composition of these rocks, the chemistry of apatite namely its low Mn and Fe content (cf. Jablonská 1992) and monazite/allanite antagonism point to mixed I/S-type character of granitoids. Such (rather metaluminous) granitoids with affinity to I/S-type were proposed by Kohút & Janák (1994) in the Tatra Mountains (Western Carpathians) as a result of contamination of originally acid melts of I-type originating by dehydration melting of basic protolith by the material of middle crust. A similar granitoid suite (I/S-type)

was also described in the Vepor pluton. Its age allocation is Late Devonian–middle Carboniferous (cf. Broska in Bezák et al. 2004b). According to tectonic setting discrimination (Batchelor & Bowden 1985), the Ťahanovce granitoids represent a pre-plate collision environment (Fig. 14a). A volcanic arc setting is suggested by the plot of Pearce et al. (1984), (Fig. 14b). The tectonic environment cannot be identified with certainty on the basis of the present data set and more detailed study is necessary. On the other hand, the granite composition of the Miklušovce Complex on the diagram of Batchelor & Bowden (l.c.) indicates its post-orogenic character (Fig. 14a). The S-type granite magma could have formed by heating of the protolith due to the thermal effect of an earlier hot I-type melt. This was suggested by Hraško et al. (2000) in the Veporic Unit and an analogous process could have participated in the formation of the Miklušovce Complex granites.

Summarizing data on the origin of the granite in the Čierna hora Mts it is concluded that they are primarily derived from the lower crust, their protolith being influenced by a mixing and/or assimilation process (I- or I/S-type characteristics). More than one magmatic event occurred in the Čierna hora area. The different character of the Western Carpathian granitoids can be related to various source rocks (Petřík et al. 1994; Petřík 2000; Kohút & Nabelek 2008). The Nd isotopes indicate a variable proportion of crustal material during the derivation of host rocks of S-type granitoid suite (l.c.).

Conclusions

The biotites from various granitoids of the Čierna hora Mts show contrasting compositions: biotite from the I-type Sokol, Sopotnica and Bujanová massifs are Mg-rich. In contrast, biotite compositions from the S-type Ťahanovce massif and especially from the Miklušovce Complex show a remarkable increase in Fe. The various oxygen fugacity values indicated by variable Fe^{3+} contents suggest the primary differences in

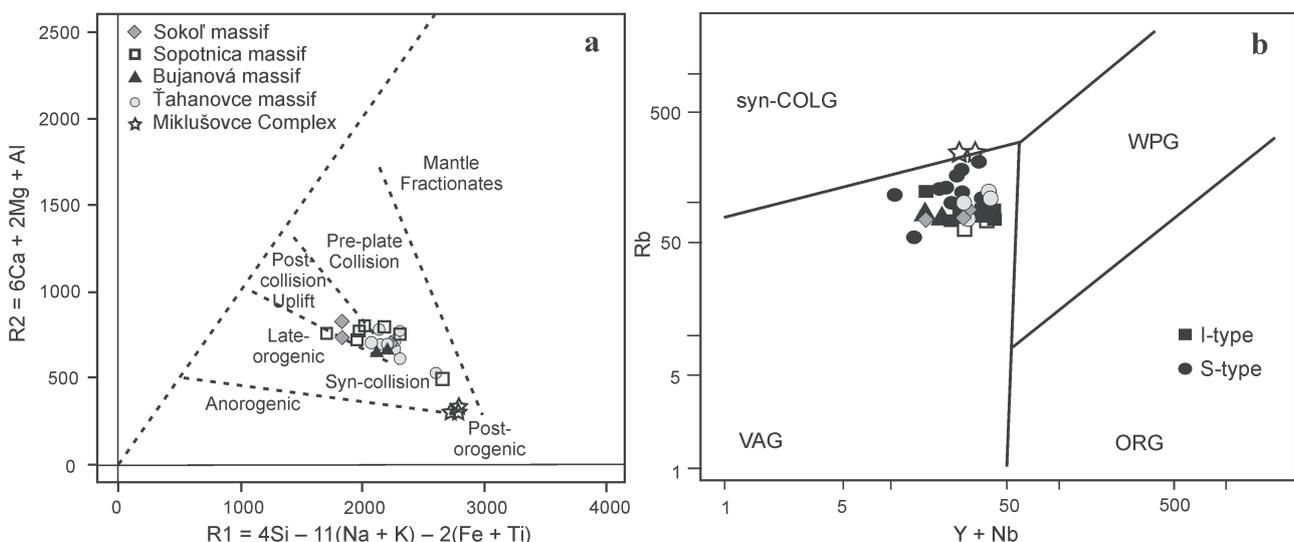


Fig. 14. **a** — Multicationic discrimination diagram for investigated granitoids sensu Batchelor & Bowden (1985). **b** — Rb-(Y+Nb) discrimination diagram for investigated granitoids sensu Pearce et al. (1984) compared with granitoids from adjacent regions of the Veporic Unit.

redox state of the host magmas. Water fugacities and contents calculated using Wones' (1981) calibration of the biotite stability equation and Burnham's (1994) water dissolution model, yield relatively uniform values of 4–5 wt. % in residual melt at 400 MPa and various levels of f_{O_2} and activities of annite for magnetite-bearing assemblages. This suggests an effective buffering role of biotite in both oxygen and water fugacities. In magnetite-lacking assemblages (S-type) the procedure used in the present paper cannot be applied. However, if this phase is considered as consumed, the values of water fugacities and percentages would represent lower limits. The melt water contents provided by biotite differ from those in the magma (crystals+melt), and depending on the melt proportion they range from 1–1.5 wt. % H_2O .

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