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DUSKY APATITE FROM THE VARISCAN GRANITOIDS OF THE WESTERN CARPATHIANS

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Abstract: The composition of the carbonaceous matter of dusky apatites was studied from the Variscan granitoids of the Tríbeč and Malá Fatra Mts. crystalline cores. Dark-coloured pigment in the apatite of the Tríbeč Mts. biotite tonalite contains 45.3 wt. % of graphite, 45.3 wt. % of hydrocarbons, and 9.4 wt. % of carbide. The apatite from the Malá Fatra granodiorite contains 24.1 wt. % of graphite, 61.6 wt. % of hydrocarbons, 8.7 wt. % of carbide and 5.6 wt. % of carbonates. Carbon-bearing dusky apatite originated by the assimilation of graphite-bearing crystalline schists by granitoid melts. The presence of dusky apatite indicates reducing conditions in these melts.

Key words: dusky apatite, granites, carbonaceous matter, Western Carpathians.

Introduction

Besides the coloration of apatites due to trace element contamination (McConnel 1979), the cases of dark-coloured pigmentation are sporadically reported, caused by the presence of other mineral phases. The pigmentation is localized predominantly to the cores of apatite crystals forming dark stick-like forms in their centers (Lyakhovich 1968) (Fig. 1).

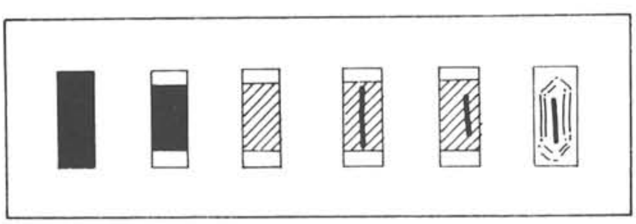

Fig. 1. Sketch of the most frequent shapes of the dark-coloured parts of apatites in the Tríbeč granitoids.

The apatite coloured by other mineral phases becomes more or less pleochroic in a similar way to the apatite coloured by trace element contamination. The dark colour of the apatites is generally considered to be caused by minute inclusions of silicates, e.g. chlorite (Simpson 1933; Baker 1941), amphibole or biotite (Baker 1941; Portnov et al. 1977). After Serdyuchenko (1960) the abundant dark inclusions in apatite may be caused also by the presence of organic matter or iron oxides. Hoppe (1970) also supposes inclusions of Fe-bearing minerals in pigmented apatites. In every case, owing to the more abundant occurrence of dusky apatites in hybrid (contaminated) granitoids, Lyakhovich (1968) could have stated that the pleochroic apatites are indicators of assimilation processes in granitoid melts.

The dusky apatite is present in minor amounts in granitoid (Mišík 1955; Hovorka & Hvožďara 1965; Hovorka 1968; Dyda 1976; Veselský & Gbelský 1978; Broska 1986 and other) as well as metamorphic rocks, e.g. the Veporic unit (Chovan 1971), Malé Karpaty Mts. (Veselský & Kovalská 1981), Tríbeč Mts., village of Krnča area (Broska unpubl.).

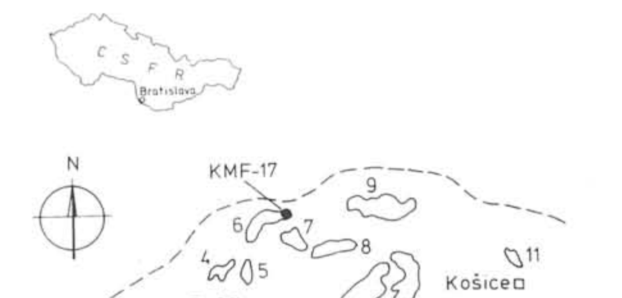

Fig. 2. Geological sketch of granitoid massifs of the Western Carpathians with sample locations of dusky apatite-bearing granitoids.
Legend: 1 - Malé Karpaty Mts.; 2 - Považský Inovec Mts.; 3 - Tríbeč Mts.; 4 - Suchý and Malý Magura Mts.; 5 - Žiar Mts.; 6 - Malá Fatra Mts.; 7 - Veľká Fatra Mts.; 8 - Nízke Tatry Mts.; 9 - Tatry Mts.; 10 - Veporic granitoid types; 10 - Čierna Hora Mts.
Broken line indicates the course of the Klippen belt.
Sample localization: T-87 biotite tonalite, the Tríbeč Mts., village of Krnča, 1 *km* SSE of elev. point Tábor, forest road cut. 3350/700 *m* of elev. point Tábor. KMF-17 biotite tonalite, the Malá Fatra Mts. The running quarry of Bystričky.

Table 1: Chemical (major elements) and spectral (trace elements) analyses of dusky apatite parent rocks.

a)

Sample	SiO_2	TiO_2	Al_2O_3	Fe_2O_3	FeO	MnO	MgO	CaO	Na_2O	K_2O	H_2O^+	H_2O^-	P_2O_5	Total
T-87	70.01	0.37	15.61	1.41	1.31	0.04	0.95	2.29	3.22	2.88	0.22	1.60	0.31	100.22
KMF-17	68.67	0.41	16.01	0.17	2.18	0.04	0.92	2.92	4.93	1.77	1.44	0.08	0.32	99.76

b)

Sample	Ba	Be	B	Pb	Mo	Sn	V	Cu	Ag	Ni	Zr	Co	Y	Sc	Cr	Sr
	810	3	9.6	19	~1	~1.2	46	3	1	7.9	126	14.8	15.1	5.2	9	530
KMF-17	400	~2	18.6	22.6	n.d.	~2.5	35	3.1	n.d.	~2.3	198	4.1	18	5.9	5.2	~650

Note: Major elements analyzed by E. Walzel, trace elements by J. Medveď. The analysis of biotite granodiorite is taken from Kamenický et al. 1985.

Parent rocks and the characterization of their apatites

We tried to analyze and to identify the dark-colouring components of dusky apatite from two samples of the Western Carpathian granitoids (the Malá Fatra and Tríbeč Mts.) where its content reaches 80 - 90 vol. % of bulk apatite content (Fig. 2). The first sample (KMF-17, the Malá Fatra Mts.) is biotite tonalite with composition (vol. %): plagioclase 55, quartz 22, biotite 11, K-feldspar 8 (Kamenický et al. 1985), the second sample (T-87, the Tríbeč Mts.) is biotite tonalite containing (vol. %): plagioclase 54.6, quartz 30, biotite 15, K-feldspar 0.4. Both granitoids are medium-grained with hypidiomorphic texture. According to chemical composition (low SiO_2 content, higher CaO, P_2O_5, Zr, Sr contents, etc.) the granitoids belong to earlier differentiates (Tab. 1a,b).

The apatite content in biotite tonalite KMF-17 is 0.03 vol. %, in biotite tonalite T-87 is 0.05 vol. %. In both cases the apatite is subhedral, located mainly in biotites, with less in the intergranular spaces. The maximum size of apatite is about 0.2 *mm*. The dark colouration is of variable intensity and it is usually concentrated in the centers of grains, the rims often being colourless (Fig. 3 a,b). The oscillation zonality of dark pigments is sometimes also observed in apatites (Fig. 3b), and more rarely an irregular distribution in the whole crystal volume is encountered.

The composition of dark-colouring matter in apatites

Because the pyrolysis and subsequent IR spectrometry of dusky (to black) apatites from the sample T-87 determined 0.1 wt. % of C_{org} we analyzed the apatites for carbonaceous matter, since the determined carbon could not have been a part of normal apatite structure.

Dark-colouring matter was analyzed in pure apatite separates by the photoelectric spectroscopy (an ES-2401 instrument with 50 *eV* of exciting voltage, vacuum 1.3×10^{-9} *Pa*, and margin of error of $\pm$ 0.1 *eV*). Based on the energetical levels of dark-colouring components in apatite (Fig. 4) the composition of the carbonaceous matter was determined as follows (%): graphite 45.3, hydrocarbons 45.3 and carbide 9.4 (Fig. 4, Tab. 2). Besi-

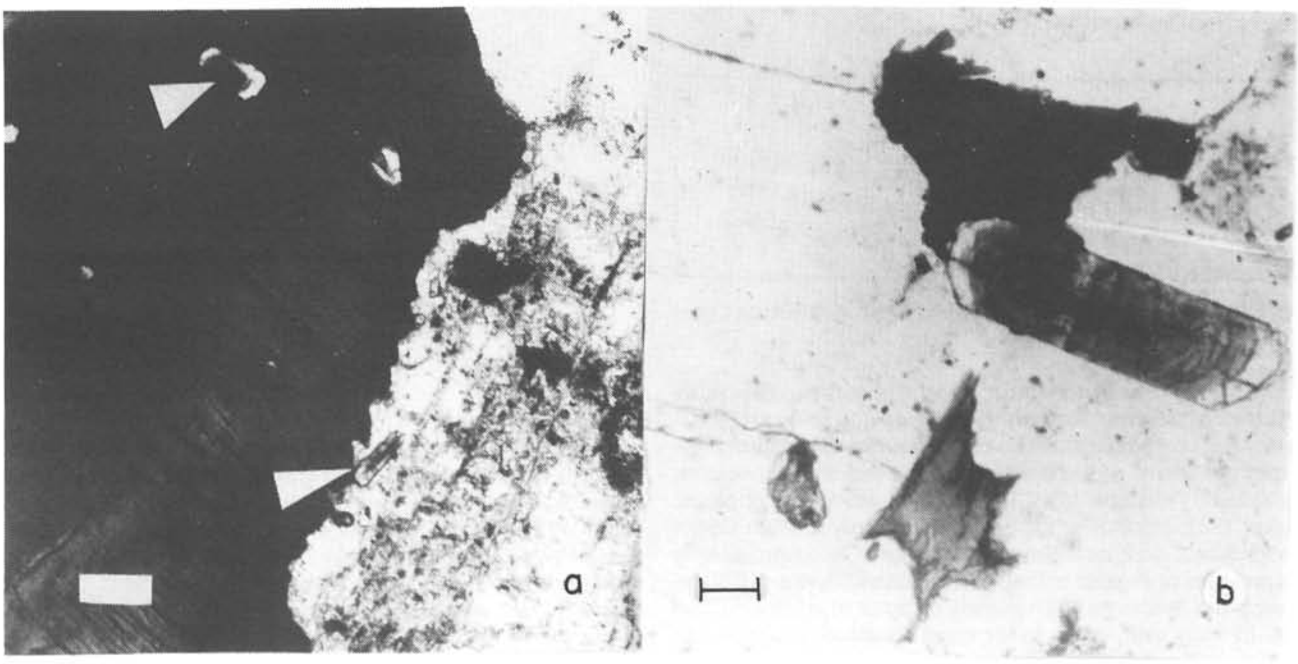

Fig. 3. Dusky apatites in biotite tonalite (Tríbeč Mts.). **a** - the most frequent site of apatite is biotite, interstitial apatite is less frequent; **b** - oscillatory zoning of dark matter in apatite. Note the intense dark coloured stick-like form in the center of the apatite. Bar corresponds to 10 *m*.

des the above components, the Malá Fatra Mts. sample contains also a carbonate. We do not know whether it lies in the structural position Z, or it has formed as a secondary product of the reaction:

$$2C + 2H_2O = CO_2 + CH_4$$

formely described for progressive metamorphosis by Ohmoto & Kerrick (1977). The carbide content (8.7 %) in apatite from the Malá Fatra granodiorite is comparable to that of the Tríbeč a-

Table 2: The content of the carbonaceous phases in dusky apatite from Tríbeč biotite tonalite.

Component	intensity imp/sec	1/2 width e.v.	position e.v.	integrated area in %
carbide	142	0.92	283.25	9.4
graphite	683	1.00	284.71	45.3
hydrocarbons	586	1.15	285.20	45.3

Note: The proportions of carbonaceous matter in the sample are given by the integration of sinusoide areas.

Table 3: The content of carbonaceous phases in dusky apatite from Malá Fatra biotite granodiorite.

Component	intensity imp/sec	1/2 width e.v.	position e.v.	integrated area in %
carbide	588	1.25	283.72	8.7
graphite	2504	0.82	284.61	24.1
hydrocarbons	5672	0.94	285.29	61.6
carbonates	394	1.21	288.65	5.6

Note: The proportions of carbonaceous matter in the sample are given by the integration of sinusoide areas.

Table 4: The summary table of the content of carbonaceous phases in the studied granitoid apatites.

Sample	carbide	graphite	hydrocarbons	carbonates
T-87	9.4	45.3	45.3	-
KMF-17A	8.7	24.1	61.6	5.6

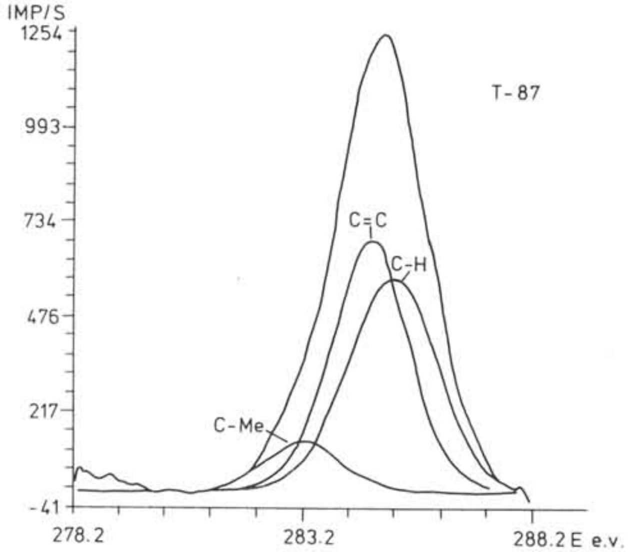

Fig. 4. X-ray electron spectrum of 1s carbon electrons in apatites from the Tríbeč Mts. biotite tonalite.
The carbon spectrum is represented by the superposition of three independent phases (graphite C=C, heavy hydrocarbons C-H, and carbide C-Me). Since 2p electrons of Fe were detected in apatite spectrum (E 707.0 *eV*) Fe-carbide (cohenite) is a probable phase present.

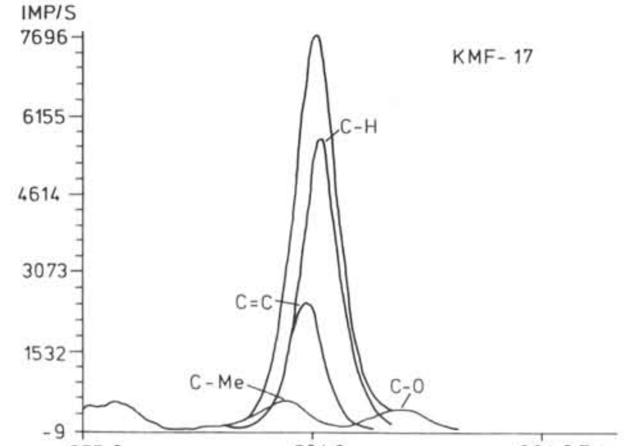

Fig. 5. X-ray electron spectrum 1s of carbon electrons in apatite from the Malá Fatra Mts. granodiorite is represented by the superposition of four phases: graphite, heavy hydrocarbons, carbide and carbonate.

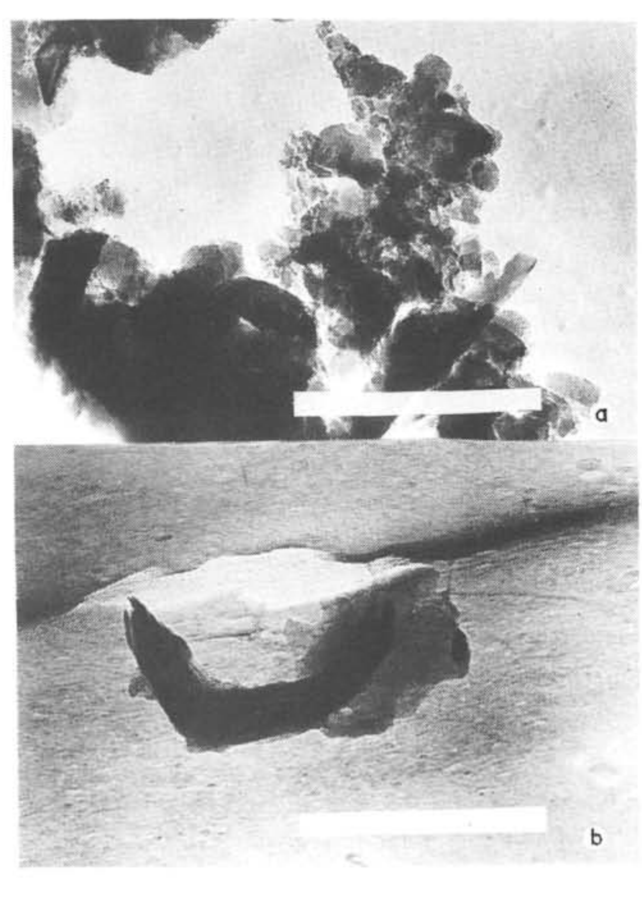

Fig. 6. The suspension of black apatites contains a fine dispersion of layered silicates. **a** - biotites and **b** - fine graphite flakes, which were confirmed by microdiffraction.

patites the difference being in graphite (24.1 %) and hydrocarbons (61.6 %) contents, (Fig. 5, Tabs. 3, 4).

The suspension of black apatites (the Tríbeč sample T-87) was studied also by means of electron microscopy (JEOL, JEM 100) in combination with an energy dispersive spectrometer KEVEX 5100. A finely dispersed mixture of layered silicates of sub-micrometer size together with finely dispersed graphite (Fig. 6a,b) was identified in the suspension. Subsequently, the graphite was confirmed independently by means of the X-ray microdiffraction method. A layered silicate was identified as biotite by the energy dispersive spectrometer. Owing to the very small size of biotite in apatites (0.0X m) and the relatively high, pyrolytically determined, content of C_{org} (0.1 %) with high light absorption we suppose that the colouring of apatite was caused predominantly by carbonaceous matter in non-structural positions, and only to a lesser degree by inclusions of layered silicates of biotite type.

Discussion

The samples of dusky apatites with carbonaceous substance come from the monazite-ilmenite granitoid series of the Western Carpathians (Broska & Uher 1991; Broska & Gregor; 1992 Petrík & Broska in prep.). This granitoid series, characterized by the association of monazite, (-) magnetite, (±) and ilmenite, indicates a decreased oxygen fugacity in magma (Ishihara 1977) and reducing conditions. Besides the magnetite absence the reducing conditions during crystallization are unequivocally confirmed by the absence of titanite and by the increased iron and titanium contents of the biotites. The FeO_{Tot} content of the biotites from the monazite-ilmenite series granitoids in the Tríbeč Mts. is generally higher than 20 wt. %, the TiO_2 content attains up to 4.5 wt. % The reducing conditions in the monazite-ilmenite series also indicate a lower water content in the magma (Petrík & Broska in prep.). By contrast, the dusky apatite is rare in the allanite-magnetite granitic series (Dyda 1976; Broska 1986; Broska & Gregor 1992) originated in oxidation conditions. In these granitoids (the Tríbeč Mts.) biotite shows decreased iron and titanium contents (FeO_{Tot} 17 - 18 wt. %, TiO_2 2 - 3.5 wt.%, Broska & Gregor 1992; Petrík & Broska in prep.).

We think that, in this sense, the presence of dusky apatite may be considered as the indicator of reducing conditions in monazite-, ilmenite-bearing magmas of the Western Carpathian granitoids.

The presence of dusky (pigmented by carbonaceous matter) apatite itself, we explain by the contamination of granitoid magma by graphite shales. In the Tríbeč case it is confirmed by the presence of graphite shales (containing 2.86 wt. % of graphite) in the vicinity of biotite tonalite. In the Malá Fatra Mts. crystalline graphite is wide-spread both in shales and in granitoid, pegmatite and aplite rocks (Pulec 1989). The presence of dusky apatite thus indicates the assimilation of carbonaceous shales in granitic melts.

Conclusions

Dusky apatite in monazite-, ilmenite-bearing granitoids indicates reducing conditions in a magma. It is due to the fact that graphite along with heavy hydrocarbons, the very presence of which is conditioned by reducing environment, predominate among black-colouring components. We suppose that the carbonaceous matter was incorporated into apatite in a magmatic stage when magmatic intrusion came into contact with carbon-bearing shale formations.

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